

Taming XeO₃: Insights from Computational Investigations of Sigma Hole-Mediated Aerogen Bonding

by

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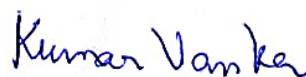
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गुरुर्ब्रह्मा गुरुर्विष्णुः गुरुर्देवो महेश्वरः ।
गुरुर्साक्षात् परब्रह्म तस्मै श्री गुरवे नमः ॥

Dedicated to All My Teachers

ध्यानमूलं गुरोर्मूर्तिः पूजामूलं गुरोः पदम् ।
मंत्रमूलं गुरोर्वाक्यं मोक्षमूलं गुरोः कृपा ॥

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Abbreviations and Notations

NCI	Noncovalent Interactions
vdW	Van der Walls
DFT	Density Functional Theory
AO	Atomic Orbital
MO	Molecular Orbital
HB	Hydrogen Bond
Ng	Noble Gas
au	atomic units
HF	Hartree-Fock
MD	Molecular Dynamics
NBO	Natural Bond Orbital
NPA	Natural Population Analysis
EDA	Energy Decomposition Analysis
ETS-NOCV	Extended Transition State-Natural Orbital for Chemical Valence
LP	Lone Pair
KS	Kohn-Sham
BSSE	Basis Set Superposition Error
MEP/MESP	Molecular Electrostatic Potential Surface
WBI	Wiberg Bond Indices
ΔE_{oi}	Energy term for Orbital Contribution

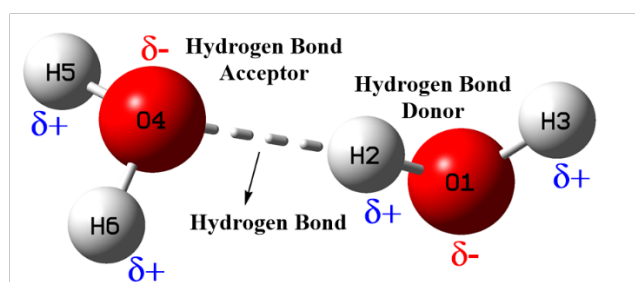
Chapter-1

Introduction

Abstract: This chapter provides a brief overview of noncovalent interactions and their development with a special focus on the advancements in sigma (σ) holes and their potential applications. Additionally, the chapter delves into the concept of aerogen bonding (also called as noble gas bonding) and includes a brief historical perspective on noble gas chemistry. The chapter also addresses the explosive nature of xenon trioxide (XeO_3) and its significance. An overview of the thesis's objectives, and outline is also included.

1.1. A Brief Overview of Noncovalent Interactions

Noncovalent interactions (NCIs) are fundamental forces that play a critical role in shaping the structure, stability, and function of complex molecular systems across chemistry, biology, and materials science. Unlike covalent bonds, where atoms share electrons, NCIs arise from weaker forces such as hydrogen bonds (HBs, **Scheme 1.1**), van der Waals (vdW) forces, electrostatic interactions, and π - π stacking. These interactions, though subtle, are crucial for dictating the behavior of molecules, influencing processes like molecular recognition, self-assembly, and the functioning of biological structures.^[1,2] The significance of NCIs was first recognized in the early 20th century, leading to a deeper understanding of their role in biological processes and material design. As the field of chemistry advanced, these interactions have become essential to the development of new materials, drug design, and the detailed understanding of biomolecular architecture. Today, the study of NCIs remains a dynamic and expanding area of research, offering profound insights into the delicate balance of forces that govern molecular behavior.^[3-5]



Scheme 1.1. A schematic diagram of water dimer showing hydrogen bonding between them.

Notably, the energy associated with the formation of NCIs typically falls within 1-5 kcal/mol/bond.^[6] Many molecules have sufficient energy (owing to their average kinetic energy at the room temperature) to break these interactions, rendering them dynamic. Therefore, the term ‘interactions’ is more commonly used than ‘bond’ for describing such phenomenon. Despite considered weak, multiple NCIs can stabilize peculiar shapes, conformations and associations of large molecules. For instance, various types of NCIs are crucial in stabilizing the three-dimensional supramolecular assemblies, nucleic acids, and proteins.^[1-5,7] Additionally, these interactions enable large molecules to transiently bind in various accessible conformations, forming the basis of numerous dynamic biological systems. Molecular recognition, which is essential for the reactivity and selectivity of different biomolecules, is also facilitated by NCIs.^[8] The flexibility of enzymes permits a variety of

molecules to access their active sites. However, catalysis is only initiated when specific NCIs align with the particular substrates involved.^[9] Similarly, specific cell surface receptors identify distinctive NCI patterns with ligands, enabling them to distinguish between foreign and endogenous molecules that must traverse a membrane.^[10] NCIs are also crucial in determining several physical properties of chemical compounds, including their solubility in different solvents (for solutes), their viscosity (for liquids), their boiling and melting points, and the aggregation behaviors (for molecular clusters and oligopeptides).^[1-6] It is noteworthy that certain strong NCIs have been documented, such as HBs featuring ions^[11] and cation- π interactions^[12] amongst easily polarizable π -systems and small cations. These instances exhibit substantial covalent contributions within NCIs. Nevertheless, weak NCIs are widespread and play a more critical role due to their fundamental influence on molecular behavior. A key feature of NCIs is that when two molecules engaged in noncovalent bonding come close to each other, one with higher electrostatic potential can induce a polarization in the electron density of the other molecule. This interaction causes a slight transfer of electron density from the second molecule to the first, which can be described as a donor-acceptor interaction or a covalent-like contribution to the NCI. Consequently, the NCIs often involves a minimal but measurable charge transfer between the interacting partners. Additionally, the polarization effect alters the atomic charges compared to their isolated state, impacting the bond strength through what is known as the induction or polarization effect in NCIs.^[13]

The concept of NCIs was first introduced in the 1870s by van der Waals, who attributed the inconsistencies in state functions of real and ideal gases to the presence of attractive forces amongst the molecules of polyatomic gases or the atoms of noble gases.^[14] These forces are now known as vdW interactions. Later, in 1930, Fritz London utilized emerging quantum mechanics to elucidate the underlying principles of vdW interactions, a description that was subsequently expanded upon by Hans Hellmann.^[15,16] Subsequently, a variety of natural interactions were identified and thoroughly investigated, leading to a greater understanding of their roles in chemistry.^[1,2] These interactions can be categorized based on the structures of the interacting entities into several categories: classical HBs and non-classical HBs, π - π stacking, σ -hole mediated bonds, anion- π , lone pair (LP) interactions, cation- π , LP-cation- π , and hydrophobic interactions. While the strength and characteristics of these interactions can vary significantly, they all share a common origin. They fundamentally arise from the attraction amongst an electron deficient center/region (whether permanent or transient) and an electron

rich center/region, which may involve an easily polarizable electron cloud, or a π -electron cloud, or a permanent negative charge, or a lone pair of electrons.^[13]

1.2. Different categories of NCIs

The NCIs are influenced by several well-defined physical factors (**Figure 1.1**): electrostatic interactions, polarization (inductive forces), London dispersion, Fermi repulsion, and covalent orbital contribution, which is basically the donor-acceptor charge transfer. While these factors are clearly defined in theory, none of these contributions are physical observables.

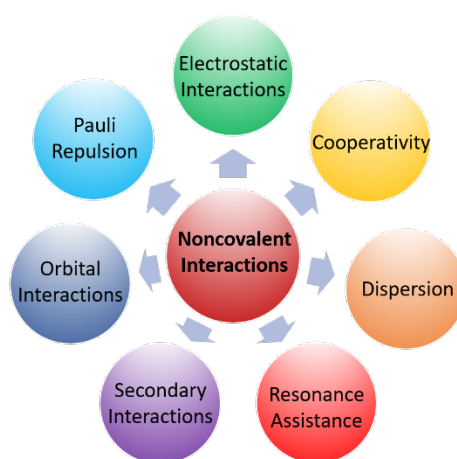


Figure 1.1. Important components of NCIs.

The range of their effects varies depending on their nature; for instance, short-range interactions stem from the overlapping of MOs or charge transfer between partners, limiting their influence to close distances. In MD simulations, forces which diminish more rapidly with distance than r^{-d} (where d represents the system's dimensionality) are categorized as short-range forces. In contrast, electrostatic forces, or the NCIs dominated by electrostatic interactions, are classified as long-range forces since they diminish with distance (as r^{-2}). The impact of electrostatic interactions are non-negligible even at distances greater than 15 Å.^[17] The dispersion and polarization interactions are also recognized as long-range but are effective over shorter distances compared to electrostatic forces, generally impacting up to around 5 Å.^[18] However, interactions *via* London dispersion can extend their influence up to approximately 8 Å.^[19] Donor-acceptor charge transfer and exchange-repulsion interactions are typically considered short-range interactions.^[19] Noncovalent interactions can be categorized into two primary types based on the predominant attractive energy components: (1)

electrostatic-dominated interactions, which include the classical hydrogen bonds, the σ -hole mediated bonding, dipole-dipole interactions, and ion-pair interactions in solutions *etc.*, and (2) dispersion-governed interactions, which encompass π - π , anion- π , and CH- π interactions, among others. It is important to recognize that the long-range effects of electrostatic contributions are significant, and since they are inherently directional, their long-range influences also exhibit directional characteristic.

1.3. Cooperativity in NCIs

The strength of NCIs is significantly influenced by the local atomic arrangement within the interacting partners and the surrounding chemical environment.^[17,20,21] Moreover, the interactions among different NCI units are often non-additive.^[19] For instance, in water clusters, the average strength of HBs surges as the bond lengths decrease, nearly doubling in strength within a decamer.^[22] This nonadditivity in NCIs arises from phenomena such as cooperativity, noncooperativity, and anticooperativity.^[19,23] When two NCIs enhance themselves, they are considered cooperative; however, when they weaken themselves, they are considered anticooperative. Notably, cooperativity occurs when the combined interaction energy exceeds the sum of the individual interaction energies.

The nonadditivity of NCIs is primarily due to long-range interactions amongst the atoms within bonded partners and their surrounding molecules.^[19,23] These interactions can be categorized into three main effects: (i) electrostatic, (ii) dispersion, and (iii) polarization. Long-range electrostatic interactions, which can be either attractive or repulsive, play a significant role in this nonadditivity by introducing directionality into the interactions between atom pairs within the bonded partners or between the bonded partners and nearby atoms.^[20] Dispersion, an attractive component of the vdW equation, results from the effect of electron correlation.^[24] In the context of multi-body interactions, the contribution of dispersion is generally considered to be minimal.^[19] Polarization, which is also attractive, occurs when the electron density cloud of bonded partners is influenced by the electrostatic field of surrounding molecules, including solvents. Because the electrostatic fields from neighbouring molecules can either reinforce or negate each other depending on their orientation, polarization effects are similarly nonadditive.^[25] In some systems, the establishment of an initial NCI has been observed to promote the formation of subsequent NCIs.^[26] This phenomenon is primarily attributed to the

reduced entropic cost associated with forming subsequent NCIs after the first one has been established.^[19,27] This effect, often referred to as the chelate effect, is thought to be a driving force behind the cooperative nature of helix propagation.^[26]

1.4. Directionality in NCIs

It was long assumed that electrostatic (Coulombic) interactions within NCIs lacked significant directionality, meaning their energy was thought to be largely independent of the bond angle. This misconception likely stemmed from two primary errors in understanding: (i) the belief that atoms involved in such interactions possess isotropic charge distributions, and (ii) the assumption that secondary long-range electrostatic interactions have minimal impact or that their spatial arrangements negate any directional influence. The slight directionality observed in NCIs is often linked to covalent contributions. Although, MEP distribution reveals that the potential surrounding atoms within a molecule is not symmetrical. This is because of anisotropic electron density around an atom, influenced by electronegativity or polarising effect of covalently bonded atoms, which diminishes with distance. When the electron density distribution around an atom is significantly uneven, it introduces pronounced directionality to NCIs, rooted in Coulombic forces. The MEP describes how an isolated molecule interacts electrostatically with its environment. MEP is the result of the combined contributions from both nuclei and electron density. MEP is typically visualized using a colored isodensity surface.^[27] This provides valuable insights into the electrostatic potential across a molecule's surface. One notable aspect of MEP is that regions where the electron density is sparse will display a positive potential.^[27] For heavier atoms in groups 14-17, this positive region often appears as an extension along the covalent bond with more electronegative atoms.^[28,29]

This positive region, known as the σ -hole, results from the uneven distribution of electron density around heavier atoms in groups 14-17.^[28,29] Notably, σ -holes often coexist with areas of negative potential, on the opposite side of the heavy atoms. These σ -holes attract atoms or groups from the negatively charged regions, facilitating the formation of noncovalent bonds, known as σ -hole bonds. Thus, σ -hole bonds are NCIs that occur amongst a covalently bonded heavier atom from Groups 14-17 and a negatively charged site, such as an anion, a Lewis base or a lone pair. Simultaneously, the negative potential on the opposite side of the same heavy atom can attract positive groups or σ -holes, leading to the formation of multiple

noncovalent bonds involving heavy atoms from groups 14-17.^[28,29] These σ -hole bonds are highly directional, with their angular positions being nearly fixed.

The classical hydrogen bond, often cited as a prime example of electrostatic-dominated interactions, is commonly referred to simply as the hydrogen bond.^[13] While these bonds are primarily electrostatic in nature, their observed tendency toward a linear X-H...Y angle is often attributed to covalent contributions. This covalent aspect is thought to arise from the donation of electron density from the lone pair of Y to the antibonding orbital of X-H ($\sigma^*_{\text{X-H}}$), with maximum orbital overlap occurring in a collinear arrangement.^[13] However, discussions on hydrogen bonding directionality frequently overlook that the power of a covalent interaction is governed by 2 factors: the symmetry or degree of overlap amongst the interacting orbitals & energy gap between them.^[30] Given that X-H bonds are typically strong, the bonding orbital ($\sigma_{\text{X-H}}$) is significantly low in energy, while the corresponding antibonding orbital ($\sigma^*_{\text{X-H}}$) is high in energy.^[13] Due to the elevated energy of these antibonding orbitals, they are generally poor electron acceptors, making covalent interactions in classical HBs unlikely, when X-H bond is powerful. Thus, the covalent contributions to NCIs stem from the redistribution of electron density from Y to the X-H bond, driven *via* the polarization of Y due to electrostatic potential field of X-H bond, rather than from the mixing of Y's lone pair with $\sigma^*_{\text{X-H}}$.^[31]

Thus, the directionality observed in NCIs is primarily rooted in electrostatic factors, which can be explained by 2 key aspects: (i) the uneven distribution of electron density around atomic nuclei and (ii) the influence of long-range secondary electrostatic interactions. Anisotropic nature of electron density drives these interactions to favor specific directions, impacting all components of the interaction energy since they all rely on electron density & are inherently anisotropic.^[32] Additionally, electrostatic interactions are inherently directional. When considering multi-point long-range electrostatic interactions, this inherent directionality naturally emerges in the overall noncovalent interaction due to the characteristics of electrostatic forces.

1.5. Sigma (σ) Holes

Classification of σ -Hole Interactions				IUPAC Recommended			Noble Gas (Aerogen) Bond
Coinage (Region) Bond	Spodium Bond	Triel Bond	Tetrel Bond	Psictogen Bond	Chalcogen Bond	Halogen Bond	NgB
		TrB	TtB	PnB	ChB	HaB	Group 18
		Group 13	Group 14	Group 15	Group 16	Group 17	He
		B	C	N	O	F	Ne
CiB	SpB	Al	Si	P	S	Cl	Ar
Group 11	Group 12						
Cu	Zn	Ga	Ge	As	Se	Br	Kr
Ag	Cd	In	Sn	Sb	Te	I	Xe
Au	Hg	Tl	Pb	Bi	Po	At	Rn

Figure 1.2. Classifications of σ -hole interactions.

The concept of the σ -hole, which describes a localized region of positive electrostatic potential on the extension of a covalent bond, was formally introduced by Timothy Clark at a conference in Prague in 2005,^[33] specifically for atoms from groups 14-17, such as halogens.^[34] This idea marked a significant shift in understanding how certain electronegative atoms could still participate in interactions with nucleophilic sites. Before Clark's clarification, Mulliken had investigated halogen bonds, particularly the dimer of I₂ and its interaction with benzene, but he believed these interactions were purely driven by charge transfer from the π -system of benzene to the halogen,^[35-37] without recognizing the directional positive potential - the sigma hole - that actually facilitates these interactions. Clark's work provided the correct electrostatic basis for these bonds, explaining how even atoms like iodine could have regions of positive potential due to the anisotropic distribution of electron density, thus allowing them to form bonds with electron-rich sites.^[34] The source of positive potentials on electronegative atoms can be traced to a phenomenon known as "polar flattening",^[38-46] where atoms in covalent bonds exhibit shorter radii and reduced electron density along the extensions of these covalent bonds compared to their lateral sides. Clark identified this localized region of lesser electron density as the σ -hole.^[34] Often, this σ -hole is associated with a positive electrostatic potential, which can engage in favorable interactions with a negatively charged site, forming the basis of

halogen bonding.^[47,48] This corrected a significant misunderstanding in the field and paved the way for a more accurate and comprehensive understanding of halogen bonding. It also triggered a paradigm shift in the development of σ -hole-mediated interactions. This phenomenon is not limited to halogens; covalently bonded atoms in other groups of the periodic table also exhibit similar lower electron densities, or σ -holes, on the extensions of their bonds. In recent years, σ -holes have been observed for atoms across various groups, and the bonds mediated by these σ -holes have been named according to the generic name of the respective group,^[49-51] as illustrated in **Figure 1.2**.

A crucial aspect of σ -hole interactions is that it refers specifically to a region along the extension of a covalent bond where the electron density is reduced, rather than the electrostatic potential itself, as is sometimes mistakenly inferred. While this reduced electron density (the σ -hole) often corresponds to a region of positive potential, this is not always the case. The magnitude and location of this positive potential can be influenced by other parts of the molecule, which can significantly alter its characteristics.^[52-54] A common criterion for identifying such NCIs is that the distance amongst interacting atoms should be approximately equal to or less than or the combined vdW radii of those atoms. When such proximity is observed within a crystal lattice for a specific pair of atoms, it is referred to as a 'close contact' and is typically taken as evidence of an attractive NCI. However, this approach has some limitations.^[55-57] One issue is that vdWs radii are often based on the assumption that covalently bonded atoms are spherical, which is not accurate.^[38,41-46] The σ -hole interactions, for instance, highlights the asymmetry, uneven distribution of electron density, in covalently bound atoms. Additionally, NCIs in crystal lattices, amongst a pair of atoms, occur over a range of distances, with van der Waals radii being assigned based on an intermediate value.^[58] As Dance^[55] and Alvarez^[56] have noted, relying on the sum of vdW radii as a strict criterion may overlook numerous NCIs, which can have separations slightly greater than their sum. Thus, an internuclear distance shorter than the sum of the vdW radii should be considered a sufficient but not essential condition for identifying an attractive NCI, provided that the interaction is indeed attributable to those exact atoms.^[38,59] In this thesis, the term 'bond' is used interchangeably with 'interaction'. A chemical bond is defined as the scenario in which the forces between two atoms or groups of atoms are strong enough to produce a stable aggregate or a host-guest complex, in the context of this research. This stability renders the aggregate significant enough for chemists to regard it as a distinct, independent molecular species.^[51]

Within the scope of this thesis, the chemistry of noble gases mediated by σ -holes, known as aerogen bonds or noble gas bonds, is investigated, with a particular emphasis on xenon trioxide (XeO_3).

1.6. Aerogen (Noble Gas) Bonding (NgB)

The term "aerogen," derived from the Greek word "aeros" meaning air, is used in chemistry to refer to noble gas (Ng) atoms (Group 18). In 2015, the group of Bauza and Frontera presented theoretical evidence from *ab initio* calculations demonstrating an attractive interaction amongst a covalently bonded atom of Group 18 and an electron-rich species.^[60] This interaction was further substantiated by various X-ray solid-state structures of Xe(VI) derivatives, where it plays a significant role in determining the crystal packing.^[61,62] These interactions which are mediated by novel σ -holes are termed as "aerogen bonding".^[60] It was shown that the strength of aerogen bonding is comparable to hydrogen bonding (HB) and other σ -hole interactions like chalcogen bonding and halogen bonding. However, it was also noted that this interaction might be less directional due to the less pronounced anisotropy around the Ng-atoms compared to chalcogen or halogen atoms.^[63] The initial exploration of this topic was motivated by the solid-state structure of XeO_3 ,^[61] as depicted in **Figure 1.3**. This figure reveals that in solid state, every XeO_3 molecule engages in three $\text{Xe}\cdots\text{O}$ interactions with neighbouring XeO_3 units. These $\text{Xe}\cdots\text{O}$ distances (2.80-2.90 Å) are notably longer than the sum of the covalent radii ($\Sigma(\text{Xe-O})_{\text{cov}} = 2.06$ Å) but remarkably lesser than the sum of the vdWs radii ($\Sigma(\text{Xe-O})_{\text{vdW}} = 3.68$ Å), indicating the presence of strong NCIs. Additionally, these NCIs exhibit a high degree of directionality, aligning opposite to the $\text{O}=\text{Xe}$ bonds, which is characteristic of σ -hole mediated interactions.

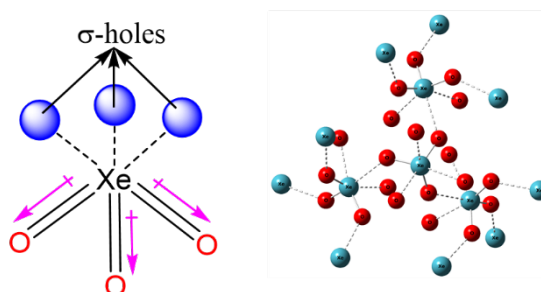


Figure 1.3. Left: Pictorial representation of σ -holes present at the extension of the covalent $\text{Xe}=\text{O}$ double bond, in the pyramidal XeO_3 , created due to withdrawal of electron density from xenon by more electronegative oxygen atoms (dipole moment vector is shown by pink arrow).

Right: Network-like crystal structure of XeO_3 in the solid state. Dotted lines represent the σ -hole mediated NCIs.

It is important to note that these NgB interactions share several common characteristics with other σ -hole interactions as mentioned in section 1.5. The binding strength is influenced by polarizability of the σ -hole containing atom (D) & the electron-withdrawing capacity of the group attached to the D, as well as basicity of electron rich centre. For Ng atoms, polarizability values calculated at the MP2/aug-cc-pVQZ level (with aug-cc-pVQZ-PP basis set for Xe), in atomic units, are as follows: Xe = 27.06, Kr = 16.70, Ar = 11.10, Ne = 2.62, He = 1.36. Consequently, more pronounced σ -holes are observed for krypton and xenon (**Figure 1.4**).^[63-65] The findings of Bauza and Frontera created a paradigm shift in the field of directional noncovalent interactions associated with the noble gas compounds, prompting further theoretical and experimental investigations into the aerogen bonding interactions.^[66-71]

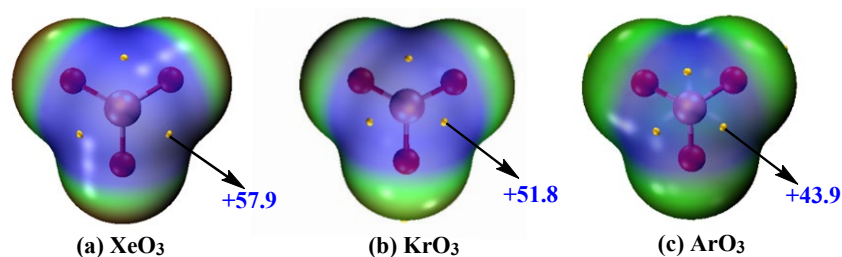


Figure 1.4. MEP of noble gas trioxides with their respective maxima ($V_{s,\text{max}}$ in kcal/mol) around their σ -holes, computed at the APFD/def2-TZVPD level of theory. Blue and red represent the positive and negative regions, respectively, while green denotes the intermediate zone between them. The isovalue of the isodensity surface is set at 0.001 a.u..

1.7. Origin of Noble Gas Chemistry & The Story of XeO_3

For many years, noble gases were considered chemically nonreactive, earning them the title of “loners” on the Periodic Table due to their stable electron configurations. This view was widely accepted and taught globally. However, a few scientists, including Walter Kossel and Linus Pauling, challenged this belief, suggesting that highly reactive atoms like fluorine could potentially form compounds with xenon, the heaviest noble gas, due to its less tightly bound electrons.^[72,73]

"I think I identified at times with the inert gases, and at other times anthropomorphized them, imagining them lonely, cut off, yearning to bond. Was bonding, bonding with other elements, absolutely impossible for them?"

— Oliver Sacks, *Uncle Tungsten*
(New York: Alfred A. Knopf, 2001), p. 202, fn. 8.

The Prelude:

In 1961, Neil Bartlett was a chemistry professor at the University of British Columbia in Vancouver, Canada. Years earlier, he had unintentionally synthesized a deep-red solid during experiments involving fluorine and platinum, but its precise chemical nature remained elusive. With the help of his graduate student Derek Lohmann, Bartlett diligently investigated the red solid's composition. After extensive research, they determined that platinum hexafluoride (PtF_6), a known gaseous fluoride, could oxidize oxygen to form the red compound identified as $\text{O}_2^+\text{PtF}_6^-$. What set this compound apart was its incorporation of positively charged oxygen ions, which is unusual since oxygen typically carries a negative charge. Oxygen usually acts as an oxidizing agent by attracting electrons from other substances. Bartlett posited that PtF_6 , a more potent oxidizing agent than oxygen itself, was capable of stripping electrons from oxygen, thus rendering the oxygen positively charged. Although PtF_6 had been synthesized earlier by researchers at Argonne National Laboratory, its oxidizing capability had not been fully acknowledged until Bartlett's work. This discovery prompted Bartlett to hypothesize that if PtF_6 could oxidize oxygen, it might also be able to oxidize xenon, a feat previously considered unattainable due to xenon's high ionization potential (I.P), which is similar to that of O_2 (1st I.P.: Xe = 12.13 eV, O_2 = 12.2 eV).^[72,73]

The Act:

In March 1962, Bartlett designed a straightforward experiment to test his theory. He arranged a glass setup with platinum hexafluoride (PtF_6), a red gas, in one chamber and xenon, a colorless gas, in a separate chamber, separated by a seal. Bartlett, working alone in his lab, recounted that the reaction occurred almost instantaneously at room temperature and was "extraordinarily exhilarating." He was confident that the resulting orange-yellow solid was the first noble gas compound ever created. However, persuading others of this achievement proved challenging. The scientific community at the time was skeptical, clinging to the belief that noble gases were inherently inert. Bartlett's claim, met with both amusement and disbelief, was

substantiated by the new compound he had synthesized. This orange-yellow solid was later identified as xenon hexafluoroplatinate (XePtF_6), marking it as the first compound involving a noble gas.^[74] In the following months, other chemists replicated Bartlett's experiment successfully, and the composition of the complex was later revised to $[\text{XeF}]^+[\text{PtF}_5]^-$. This experiment's groundbreaking significance on noble gas chemistry was unmistakable.

The Revelation:

By the start of 1963, Bartlett hypothesized that it should be feasible to synthesize a xenon oxide, a compound combining the inert gas xenon with oxygen. His graduate student P. R. Rao managed to produce crystals from the hydrolysis of xenon tetrafluoride (XeF_4) that seemed to be either $\text{XeO}_2 \cdot 2\text{H}_2\text{O}$ or $\text{Xe}(\text{OH})_4$, prompting Bartlett to visit the lab to examine them. This solid was later confirmed to be the first oxide of xenon- XeO_3 .^[75] Suspecting that Rao's impressive, elongated crystals might contain water, which could cause them to disintegrate upon drying, Bartlett suggested Rao use a vacuum pump to dry the crystals. Both researchers were wearing plastic face shields, although Bartlett's was somewhat scratched. As Bartlett approached to inspect the results, he momentarily raised his visor to get a clearer view. At that precise moment, the sample in its quartz tube exploded, as Pitzer had predicted.^[76] Both Bartlett and Rao were injured. Bartlett suffered severe damage to his right eye, resulting in complete loss of vision in that eye.^[72,73,75] They were hospitalized for over four weeks, and upon recovery, Bartlett learned that different group of researchers had already synthesized the XeO_3 .^[77] A fragment of glass remained embedded in Bartlett's eye until it was finally removed 27 years later.^[72,73,75] The colorless solid XeO_3 is highly hygroscopic, readily absorbing moisture from the air to convert into an aqueous solution.^[78] At room temperature, the solid does not exhibit volatility but is highly sensitive to mechanical and thermal disturbances. It can detonate with minimal friction, upon heating, when in contact with cellulose, or even if left undisturbed. The explosion of XeO_3 releases xenon and oxygen gases and generates 97 kcal/mol of energy.^[79] This explosive behavior makes the storage and handling of XeO_3 in its solid form extremely challenging and has impeded further research into its solid-state properties. Despite the setback, Bartlett's groundbreaking work shattered existing notions about the inert gases and sparked extensive research, leading to the discovery of numerous noble gas compounds.

1.8. Objectives of the Thesis

XeO_3 , which is a clean & strong oxidant,^[80] and whose byproduct xenon is being used as a space fuel in ion thrusters propel spacecraft like NASA's Dawn for space missions,^[81] has immense potential to transform the utilization and understanding of noble gas chemistry, if it can be stabilized for practical purposes. The curse of σ -holes which is responsible for the explosiveness of XeO_3 , could also act as a boon to stabilize it, if XeO_3 were to be provided with an appropriate host. The host could be a Lewis base or an anion willing to share its electrons to quench the electron thirst of the σ -hole regions, as the aerogen bonding is predominantly electrostatic. Our goal is to find the "chosen one", that is, the best among the pool of potential hosts, explore the leading causes for stabilization, and determine guidelines to minimize the risk associated with an experimental exploration. Thus, the objectives of this thesis are as follows:

- To gain an in-depth understanding of sigma (σ) holes, with a particular focus on aerogen bonding.
- To identify an appropriate host capable of stabilizing the highly explosive and shock-sensitive guest xenon trioxide (XeO_3).
- To analyse the features which influences the stabilization of these host-guest complexes through the use of various computational tools.
- To explore novel complexes involving XeO_3 and investigate their chemistry.

1.9. Outline of Thesis

The thesis is distributed among 7 chapters. Chapter 1 provides the introduction to noncovalent interactions, sigma (σ) holes, aerogen bonding, and the significance of xenon trioxide (XeO_3). Chapter 2 covers the computational methods used for understanding the NCIs. Chapters 3, 4, 5, and 6 each focus on different aspects of employing sigma (σ) hole interactions to stabilize xenon trioxide (XeO_3) and uncover new chemistry related to XeO_3 . Together, these chapters offer a detailed examination of the factors that govern the stabilization of these σ -hole mediated host-guest complexes. Chapter 7 provides a summary of this thesis and future outlook of σ -Holes.

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Chapter-2

Computational Methods for Understanding Noncovalent Interactions

Abstract: In this chapter, we explore the computational methods that are essential for understanding and analyzing noncovalent interactions. These interactions, which play a critical role in various molecular systems, require sophisticated tools for accurate modelling and interpretation. The chapter provides an overview of the key computational approaches, ranging from quantum chemical methods to more approximate techniques, highlighting their strengths and limitations. Additionally, a summary of the specific tools utilized in this thesis is presented, offering insight into how these methods contribute to the investigation of noncovalent interactions within the studied systems. This foundational knowledge sets the stage for the detailed analyses that follow in subsequent chapterschapter provides a brief discussion on different computational methods to understand and analyze a noncovalent interaction. A brief summary about different tools which are employed in this thesis have been discussed.

2.1. Introduction

Accurately describing noncovalent interactions (NCIs) is crucial for understanding various properties of molecular systems. Like covalent interactions, NCIs can be analyzed using standard quantum chemistry methods. Two primary quantum chemical approaches widely used in this context are (i) wave function (*ab initio*) approach and (ii) DFT. Additionally, there are MO based semiempirical approaches and classical methods, such as continuum mechanics, coarse-grained force fields, atomistic molecular dynamics. However, classical methods, which are founded on classical mechanics and do not explicitly account for electrons, are less sophisticated than quantum chemical methods. Unfortunately, there is a trade-off between the accuracy and efficacy of these methods, requiring careful selection based on system magnitude and availability of computational power.

High-level methods, such as CCSD(T), which are based on wave function approaches that include the electron correlation, are among the most accurate for describing NCIs, as they account for all energy contributions.^[1] However, these approaches are computationally costly & are typically limited to systems with up to 100 atoms,^[2] making them impractical for larger molecular systems. Consequently, CCSD(T) methods are often used for benchmarking DFT methods. Another recommended approach is the second-order Møller-Plesset perturbation (MP2) theory, which also computes NCIs with great accuracy but remains costly and challenging to apply to large molecular systems.^[3] Recent advancements, such as the resolution of identity (RI) approximations, have extended the applicability of MP2 to systems with up to 1000 atoms, though a full-scale geometry optimization of modest-sized systems remains difficult.^[4]

DFT, by contrast, is a more cost-effective option that can be applied to moderate-sized systems.^[1] Full scale geometry optimizations using DFT are feasible due to the efficiency and speed of modern supercomputers. However, DFT's local framework struggles to accurately capture dispersion interactions, a key component of NCIs, due to the long-range electron correlation (nonlocal nature) associated with these dispersion interactions.^[5] The Hartree-Fock (HF) method faces similar challenges, as it lacks electron-electron correlation. This failure to account for London dispersion arises from the origin of dispersion energy which are based on wave functions. In response, various approximations have been developed to incorporate London dispersion into DFT, leading to the emergence of dispersion-corrected DFT-D

methods, which now offer high accuracy and have become widely adopted in the investigations of NCIs.^[6]

Semiempirical MO methods provide an affordable option for electronic structure computations, even for large systems containing up to 10^3 – 10^4 atoms.^[7] These methods generally fall into two categories: those approximating either DFT or HF method.^[1] In both approaches, nominal AO basis sets are employed to inflate the MOs. However, the approximations in integrals and basis sets introduce faults in electrostatic term, polarization term, & exchange-repulsion terms, as well as in dispersion interactions. While the repulsion term is slightly corrected using empirical potentials specific to the element pair, the poor representation of induction & electrostatic interactions leads to inaccurate descriptions of electrostatic-governed interactions.^[8] To address these issues, geometry-dependent corrections for NCIs have been proposed.^[9] Recently, both semiempirical methods mentioned above have been enhanced with D3 dispersion corrections, resulting in improved performance across various systems.^[10] The errors from neglecting 3- and 4-centered 2-electron integrals in HF have been mitigated through 1-electron corrections and potentials specific to the element-pair.^[11] Despite these improvements, semiempirical approaches still lack sufficient accuracy for a wide range of systems, making them relatively crude and approximate for applications involving moderately sized molecular systems.

2.2. Counterpoise Correction Method

One significant issue with DFT methods when applied to noncovalent molecular complexes is their inconsistency in handling basis sets. This inconsistency is rooted in the Kohn-Sham formalism due to the use of the variational principle. In variational calculations, the total system is represented as summation of the basis sets of its subsystems, resulting in a more comprehensive basis set description for the subsystems within the complex than when they are isolated. This discrepancy artificially lowers the energy of the entire system. Essentially, this error occurs because the subsystems are incompletely treated and attempt to correct this *via* borrowing the orbitals of nearby subsystems. As a result, this error lacks any physical significance and is purely mathematical. Boys and Bernardi addressed this issue by introducing the counterpoise correction method, which they identified as a solution to what is now known as BSSE.

BSSE can get resolved either by defining the basis sets of components in relation to the whole supersystem or by employing an infinite atomic orbital basis set. The counterpoise correction, in DFT methods, is achieved through the introduction of ghost orbitals. These ghost orbital based components have basis set functions positioned at atomic locations, but they lack actual electrons & nuclei. This implies that, similar to interaction energy, the BSSE is reliant on geometry, resulting in varying BSSE values for different atomic orientations of ghost subsystems, within the same complex. It is worth noting that the properties corrected for BSSE converge more rapidly to their limiting values compared to those uncorrected for BSSE. Another approach to eliminate BSSE involves extrapolating to the limit of complete basis set (CBS), where BSSE naturally disappears by definition. To determine whether a specific variational method is free from the BSSE, the obtained interaction energy can be compared with that derived from perturbation methods, as they are inherently free from this BSSE. It's important to note that the BSSE is not exclusive to clusters of molecules; this can also occur, when one fragment of the molecule borrow functions from another fragment of the isolated molecule to enhance its description of basis sets.^[12] Various methods have been proposed to address this error.^[13] The intramolecular BSSE can be corrected by treating one molecule as distinct fragments, hypothetically equivalent to the total number of atoms, as suggested by Asturial. One of the most well-known solutions to this issue was proposed by Jensen.^[13,14]

In this thesis, the counterpoise correction method is employed to address the BSSE. In summary, when computing the interaction energy amongst the molecular fragments (two or more), an artificial additional stabilization term can arise. This term is due to electrons of molecule 1 potentially occupying the basis functions defining the atomic orbitals associated with atoms in molecule 2. Essentially, the interaction energy (E_{int}), for the case of a dimer is derived from the energy difference amongst the dimer and the individual (separately calculated) fragments (**Equation 2.1**).

$$E_{\text{int}} = E_{\text{AB}} - E_{\text{A}} - E_{\text{B}} \quad (2.1)$$

$$E_{\text{int}}^{\text{CP}} = E_{\text{AB}}^{\text{AB}} - E_{\text{A}}^{\text{AB}} - E_{\text{B}}^{\text{AB}} \quad (2.2)$$

To correct for this BSSE, the Counterpoise method provides an adjustment to **Equation 2.1**. In this method, the energies of fragments A and B are computed using their respective basis sets, while for the combined system EAB, a basis set encompassing both A and B is

employed. The Counterpoise method (**Equation 2.2**) involves calculating the energy of each fragment with the basis set for both fragments.

2.3. The Choice of Functional

Functional - a higher order mathematical construct, defined as a function that takes another function as its input. In other words, a functional operates on a function as its argument. Typically, a functional is denoted with the function inside square brackets: $F[f]$. For instance, integrating $|f|^2$ over all space for each square-integrable function $f(x)$ represents a functional.

$$F(f) = \int_{-\infty}^{+\infty} f^*(x)f(x) dx \quad (2.3)$$

The key difference between a function and a functional lie in their inputs and outputs: a function grabs a number as an input and produces a number as an output, while a functional grabs a function as input and returns a number as output. Despite this distinction, the properties of functionals closely resemble those of functions. For example, functionals can also have derivatives, much like functions. The process of differentiating a functional $F[g]$ follows a similar formulation to the differentiation of functions (**Equation 2.4**), with analogous rules applying to their differentiation (**Equation 2.5 and 2.6**).

$$\partial F[g] = F[g + \partial x] - F[g] = \int \frac{\partial F}{\partial g(x)} \partial g(x). dx \quad (2.4)$$

$$\frac{\partial}{\partial f(x)} (c_1 F_1 + c_2 F_2) = c_1 \frac{\partial F_1}{\partial f(x)} + c_2 \frac{\partial F_2}{\partial f(x)} \quad (2.5)$$

$$\frac{\partial}{\partial f(x)} (F_1 \cdot F_2) = \frac{\partial F_1}{\partial f(x)} F_2 + \frac{\partial F_2}{\partial f(x)} F_1 \quad (2.6)$$

For the research discussed in this thesis, the Austin-Frisch-Petersson (APF) functional is employed with dispersion (D).^[15] The APF functional effectively eliminates the erroneous long-range attractive or repulsive forces that are common in many DFT models, establishing a reliable foundation for incorporating a correction term, derived from a spherical atom model (SAM), to account for the empirical dispersion. The APFD dispersion model employs nine adaptable parameters, alongside effective atomic polarizability and ionization potential (two calculated atomic properties) for each element. APFD provides accurate descriptions of a wide range of potential energy surfaces, including noble gas complexes with many diatomic

molecules. The accuracy of APFD method in modelling of these NCIs are comparable to that calculated from employing the CCSD(T)/aug-cc-pVTZ. The APFD functional has also been benchmarked for reproducing the geometric parameters of the experimentally obtained crystal structure of the σ -hole-mediated host-guest complex of 15-crown-5 and XeO_3 .^[16]

2.4. Conformer–Rotamer Exploration and Sampling Tool (CREST):

The CREST is an open-source software designed for the efficient and automated exploration of molecular chemical space.^[17] Initially introduced as an automated tool for extended tight-binding (xTB) calculations, CREST now offers a wide range of capabilities, including geometry optimization, metadynamics (MTD) and molecular simulations, and analysis of molecular structures. The program features automated algorithms for tasks such as: finding deprotonations and protonation sites, studying explicit solvation models, sampling of different conformations, and computing absolute molecular entropy. CREST is user-friendly, requiring minimal input, and includes the GFNn-xTB Hamiltonians and GFN-FF force field.

One specialized function of CREST is sampling of molecular aggregates, also known as NCI mode, which focuses on identifying various conformations of the complexes which are non-covalently bound, by examining the arrangement of fragments. CREST offers a physics-based approach to conformational sampling with the ability to define a sequence of geometric restraint, particularly useful for sampling the complexes, which are bound non-covalently. CREST employs an ellipsoidal potential to the complex under study to prevent issues related to MTD bias, which, by expanding the distance/separation amongst the fragments that are non-covalently bound, could otherwise minimize energy and generate dissociated aggregates. CREST includes a dedicated NCI-MTD, which automatically sets up the ellipsoid potential and adjusts the bias potential parameters, for sampling the NCIs in a host-guest complex. In this research, CREST is used to ensure that all low-lying conformers are accounted for.

2.5. MEP/MESP (Molecular Electrostatic Potential):

The importance of MEP in understanding NCIs has already been discussed in Chapter-1. The electrostatic potential $V(r)$ generated by a system of electrons and nuclei, is derived from

Coulomb's law and serves as a measurable physical quantity, accessible through both experimental and computational methods.^[18] When $V(r)$ is assessed in a molecule's outer areas, it provides insight into how the molecule interacts with an approaching entity, offering valuable guidance on its reactivity, particularly in NCIs. Beyond its reactivity implications, $V(r)$ is a fundamental characteristic of a system. For instance, the energy associated with an atom or molecule can be accurately described using the electrostatic potentials at its nuclei.

$$V_{(r)} = \frac{1}{4\pi\epsilon_0} \left[\sum_A \frac{Z_A e}{|R_A - r|} - e \int \frac{\rho(r') dr'}{|r' - r|} \right] \quad (2.7)$$

Equation 2.7 provides the expression for the electrostatic potential at a specific point r . Here, $Z_A e$ denotes the charge of nucleus A , which is positioned at R_A , with $|R_A - r|$ representing the distance between nucleus A and point r . Similarly, $|r' - r|$ is the distance from r to each infinitesimal electronic charge $-e\rho(r')dr'$. For atoms, the sum in **Equation 2.7** contains only a single term. The potential $V(r)$ is termed 'electrostatic' despite the electrons not being truly stationary, as $\rho(r)$, the average electron density per unit volume, is considered static. It is to be noted that the potential $V(r)$ can be either negative or positive in a specified region, depending on whether the influence of the electrons or the nuclei is more pronounced in that area.

2.6. NCI (Noncovalent Interaction) Plot

NCIs exhibit distinct characteristics that can be identified exclusively through electron density ($\rho(r)$). **Equation 2.8** represents the electron density, $\rho(r)$, where ϕ represents orbital wavefunction, η_i represents i^{th} orbital's occupation number.

$$\rho(r) = \sum_i \eta_i |\phi_i(r)|^2 \quad (2.8)$$

These NCIs are nonlocal and appear in real space as low-density regions with minimal gradient isosurfaces. The nature of these interactions is determined by second Hessian eigenvalue's sign, while their strength is assessed based on the density observed on the NCI surface. This technique offers a quick and detailed depiction of HBs, vdW forces, & steric clashes, needing only atomic coordinates for analysis. The NCI approach, also referred to as the reduced density gradient (RDG) method, is widely used for examining weak interactions.

$$RDG(r) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla\rho(r)|}{\rho(r)^{4/3}} \quad (2.9)$$

$$\text{where, } \nabla^2\rho(r) = \frac{\partial^2\rho(r)}{\partial x^2} + \frac{\partial^2\rho(r)}{\partial y^2} + \frac{\partial^2\rho(r)}{\partial z^2} \quad (2.10)$$

It is to be noted that the positive and negative values of this function indicate regions where electron density is either locally reduced or locally increased, respectively. This function's relationship with the $\nabla^2\rho$ (Laplacian of electron density) is connected to the VSEPR model, electron localization, the type of chemical bond, and chemical reactivity.

$$\Omega(r) = \text{sign}[\lambda_2(r)\rho(r)] \quad (2.11)$$

In **Equation 2.11**, $\text{sign}[\lambda_2(r)]$ refers to the sign of the Hessian Matrix's second largest eigenvalue of electron density at the position r .

To visualize the NCIs, the regions of weak interactions have to be separated from other areas. The table (**Table 2.1**) below indicates that by retaining only those regions having RDG function's values within the 0 to medium range, the 'Boundary of molecule' and 'Around nuclei' regions will be excluded. Further isolating areas with low $\rho(r)$ values for the remaining regions, the weak interaction areas is distinctly revealed.

Table 2.1. Employing RDG isosurface to isolate the NCIs

	Around nuclei	Around chemical bond	Weak interaction region	Boundary of molecule
$ \nabla^2\rho(r) $	Large	0 ~ Minor	0 ~ Small	Very small ~ Small
$\rho(r)$	Large	Medium	Small	0 ~ Small
$RDG(r)$	Medium	0 ~ Minor	0 ~ Medium	Medium ~ Very Large

The intensity of weak interactions is positively correlated with the $\rho(r)$ in the corresponding region. vdW interactions regions typically exhibit very low ρ values, whereas areas related to robust steric influences or perceptible attractive weak interactions tend to have higher ρ values. To quantify this, a real-space function, $\text{sign}(\lambda_2)\rho$, can be defined, which is the product of the sign of λ_2 and ρ , where, $\text{sign}[\lambda_2(r)]$ refers to the sign of the Hessian Matrix's second largest eigenvalue of electron density at the position r (**Equation 2.10**).

$$\Omega(r) = \text{sign}[\lambda_2(r)\rho(r)] \quad (2.12)$$

By using diverse colours to represent this function's value and mapping them onto RDG isosurfaces, the location of the NCIs can be observed and the type of NCIs can be identified

visually. In this research MultiWFN program module has been used to generate the NCI plots,^[20] which are then visualized with VMD software.^[21]

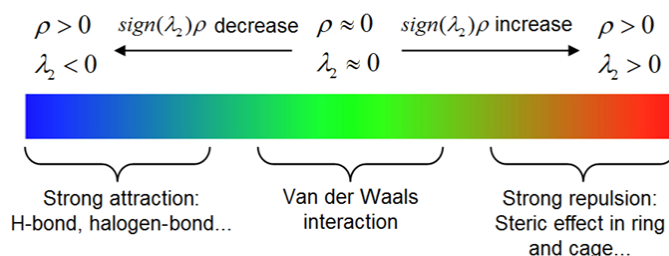


Figure 2.1. Colour bar representing different types of NCIs, in the RGB colour scale.

2.7. AIM (Atoms-in-Molecules) Analysis of Bond Critical Points (BCP)

Bader's topology analysis technique was initially developed for examining electron density within the AIM framework, also referred to as 'quantum theory of AIM' (QTAIM).^[22] This approach has since been adapted to other real-space functions. In the language of topology, critical points (CPs) are locations where the gradient of a function becomes zero, excluding points at infinity. CPs are categorized into four distinct types based on number of -ve eigenvalues in Hessian matrix of the real-space function.

A **(3,-3)** CP occurs when all three eigenvalues are negative, representing a local maximum. In electron density analysis, these points are often found near the nuclei of heavy atoms and are therefore termed nuclear critical points (NCPs). Typically, the number of (3,-3) CPs corresponds to the number of atoms in a system, with rare exceptions such as Li_2 or KrH^+ , where the count differs.

A **(3,-1)** CP has two negative eigenvalues and corresponds to a second-order saddle point. In electron density analysis, these points usually appear between atoms that are bonded and are hence referred to as bond critical points (BCPs). The value of the real-space function at a BCP, particularly the ρ and the sign of $\nabla^2\rho$, provides crucial insights into bond strength and type.

A **(3,+1)** CP, with one negative eigenvalue, represents a first-order saddle point, similar to a transition state on a potential energy surface. These points generally occur at the center of ring systems in electron density analyses and are known as ring critical points (RCPs).

Finally, a **(3,+3)** CP, where all eigenvalues are positive, indicates a local minimum. In electron density analysis, these points are typically found at the center of cage-like structures, such as in the P₄ molecule, and are termed cage critical points (CCPs).

The locations of CPs are usually determined using Newton's method, where the iterations converge to the nearest CP from a chosen starting point. By selecting appropriate starting positions and performing iterations from each, all CPs can be identified. After finding the CPs, one can verify completeness using the Poincaré-Hopf relationship:

$$\text{Isolated Systems: } n_{(3,-3)} - n_{(3,-1)} + n_{(3,+1)} - n_{(3,+3)} = 1 \quad (2.13)$$

$$\text{and Periodic systems: } n_{(3,-3)} - n_{(3,-1)} + n_{(3,+1)} - n_{(3,+3)} = 0 \quad (2.14)$$

If the relationship/connection is not satisfied, some CPs might be missing, necessitating further searches from different starting points. However, for complex real-space functions the satisfaction of this relationship does not guarantee in obtaining all the CPs. In these cases, especially for large and medium systems, the search for CPs may be considered complete once all points of interest have been located. It is worth mentioning that maximum gradient path connecting a BCP to its associated local maxima (two) is known as a ‘bond path,’ which illustrates the atomic interaction pathway for various types of bonding. The assembly of bond paths forms a ‘molecular graph,’ providing a clear definition of the structure of the molecule. Bond paths can be either curves or straight lines; in the case of curves, the bond path length exceeds the addition of distances amongst the BCP and its associated (3,-3) CPs.

2.8. NBO (Natural Bond Orbital) Analysis

NBO refers to a series of naturally localized orbitals that are essential for calculating charge transfer and electron density distribution within molecules. The idea of ‘natural’ localized orbitals, which Per-Olov Löwdin introduced in 1955 by defining a distinct group of orthonormal *I*-electron functions, which are intrinsic to many-electron wave function $\Psi(1, 2, \dots, n)$. NBO analysis is a technique that transforms a given wave function, Ψ , into a localized representation, corresponding to the lone pairs and bond components of the Lewis structure. The NBO method relies on 2nd-order perturbation theory, considering all interactions amongst acceptor and donor NBOs.^[23] The energy associated with donor-acceptor interactions, $E^{(2)}$, can be expressed as follows:

$$E^2 = \nabla E_{ij} = q_i \frac{F_{[ij]}}{\epsilon_i - \epsilon_j} \quad (2.15)$$

Where q_i denotes the occupancy of donor orbital, and $F(i,j)$ denotes the Fock matrix element of NBO.

As a part of the NBO program, Wiberg bond orders (or WBI: Wiberg bond indices) are computed based on natural atomic orbitals (NAOs), which are produced using the occupancy-weighted symmetric orthogonalization (OWSO).^[24] WBI is defined as:

$$I_{AB} = \sum_{a \in A} \sum_{b \in B} P_{ab}^2 \quad (2.16)$$

2.9. EDA (Energy Decomposition Analysis)

Within the context of KS-MO theory and utilizing the fragmentation method, the bond energy (ΔE) amongst fragments/components of a molecular system can be broken down into components corresponding to different electrostatic and orbital interactions.^[25] In this research we have used the ADF program, which uses a Morokuma-type EDA. The ΔE is divided into 2 primary components. The 1st is ΔE_{deform} or ΔE_{prep} : the preparation/deformation energy, which represents the energy needed to deform the individual fragments from their equilibrium structures to the orientation they adopt in the combined molecule. The 2nd component is ΔE_{int} : the interaction energy, which represents the energy of interaction between the prepared fragments.

$$\Delta E = \Delta E_{\text{prep}} + \Delta E_{\text{int}} \quad (2.17)$$

$$\Delta E_{\text{int}} = \Delta V_{\text{elst}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{oi}} + \Delta E_{\text{disp}} \quad (2.18)$$

The interaction energy, ΔE_{int} , can be further broken down into four physically significant terms. The initial term, ΔV_{elst} , represents the classical electrostatic interaction occurring between the unaltered charge distributions of the fragments when they are brought into proximity. ΔV_{elst} is typically attractive for neutral fragments. The 2nd term, ΔE_{Pauli} , stems from the energy variation linked to enforcing the wave function $\Psi^0 = N_A[\Psi_A \Psi_B]$ to comply with the Pauli exclusion principle by renormalizing and antisymmetrizing the product of the

fragment wave functions. ΔE_{Pauli} encompasses the repulsive interactions amongst occupied orbitals & is responsible for steric repulsion.

Finally, once the wave function is permitted to relax from Ψ^0 to a completely converged Ψ . The resulting ΔE_{oi} , encompasses bonding of electron pairs, charge transfer, and polarization (mixing of empty and occupied orbitals within one portion). Among symmetric molecules, this energy can be additionally divided into the contributions from separate irreducible representations Γ using the extended transition state (ETS) approach. This symmetry partitioning provides valuable insights in molecular systems with distinct σ/π separation.

$$\Delta E_{\text{oi}} = \sum_{\Gamma} \Delta E_{\text{oi},\Gamma} \quad (2.19)$$

For asymmetric molecules, ETS-NOCV approach can be applied, which breaks down bonding interactions using the framework of natural orbitals for chemical valence.^[26]

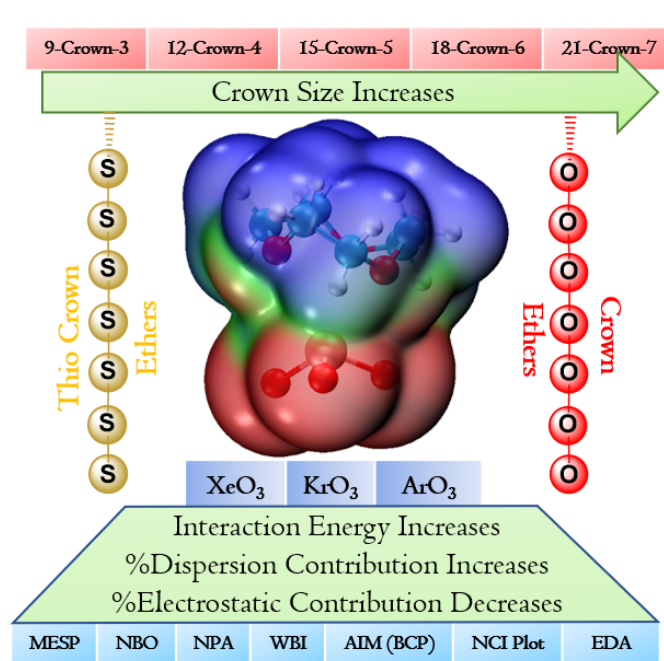
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Chapter-3

Computational Insights into the Crowning of Noble Gas Trioxides



Abstract: In pursuit of enhancing the stability of the highly explosive and shock-sensitive compound XeO_3 , we performed quantum chemical calculations to investigate its possible complexation with electron-rich crown ethers, including 9-Crown-3, 12-Crown-4, 15-Crown-5, 18-Crown-6, and 21-Crown-7, as well as their thio analogues. Furthermore, we expanded our study to other noble gas trioxides (NgO_3), namely KrO_3 and ArO_3 . The basis set superposition error (BSSE) corrected interaction energies for these adducts range from -13.0 kcal/mol to -48.2 kcal/mol, which is notably high for σ -hole mediated non-covalent interactions. The formation of these adducts was observed to be more favorable with the increase in the ring size of the crowns and less favorable while going from XeO_3 to ArO_3 . A comprehensive analysis by various computational tools revealed that the C-H...O interactions, as well as dispersion interactions, play a pivotal role in stabilizing adducts involving larger crowns. A noteworthy outcome of our study is the revelation of a coordination number of 9 for xenon in the complex formed between XeO_3 and the thio analogue of 18-Crown-6, which is higher than the largest number reported to date.

3.1. Introduction

The reluctance of noble gases to share their filled outer shell electrons makes their chemistry challenging. However, since the discovery of xenon fluorides of platinum by Neil Bartlett in 1962, researchers have been trying to coerce noble gases into participating in chemical reactions.^[1-3] This received a boost in 2015, when Bauza and Frontera provided theoretical evidence for the presence of an attractive interaction between an electron rich atom and the covalently bonded noble gas compounds XeO₃ and XeOF₂.^[4] The directionality & strength of the interaction was shown to be arising due to the presence of a localized positive region, located at the extension to the Xe=O bonds. The positive region was created at the location of lone pair, resulting in the formation of unconventional σ -holes (**Figure 3.1**).

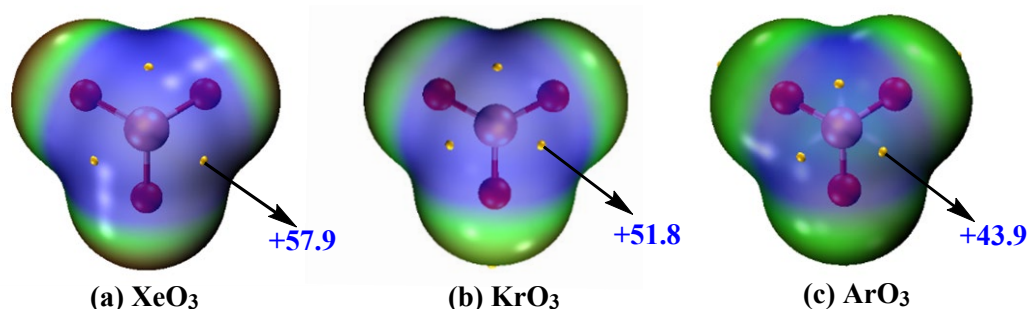


Figure 3.1. Molecular electrostatic potential (MEP) of noble gas trioxides with their respective maxima ($V_{s,max}$ in kcal/mol) around their σ -holes, computed at the APFD/def2-TZVPD level of theory. Blue and red represent the positive and negative regions, respectively, while green denotes the intermediate zone between them. The isovalue of the isodensity surface is set at 0.001 a.u..

Prior to the work of Bauza and Frontera, even though σ -hole interactions, originally coined by Clark for halogen bonding,^[5] had been investigated enthusiastically^[6-8], they were not associated with Group 18 elements. Bauza and Frontera thus introduced the term “aerogen bond” for such interactions. Their findings created a paradigm shift in the field of directional noncovalent interactions associated with the noble gas compounds, prompting further theoretical and experimental investigations into aerogen-bond related interactions.^[9-15] One of the major beneficiaries of aerogen bonding stabilization is the xenon trioxide (XeO₃) molecule, which, being a capable oxidizing agent in solution,^[16-18] is also known to be unstable in the solid state, because of its high shock sensitivity and explosiveness.^[19] Schrobilgen and coworkers employed the σ -hole strategy to synthesize adducts of XeO₃ with nitrogen-based

compounds (acetonitrile: CH_3CN and pyridine: $\text{C}_5\text{H}_5\text{N}$), which were found to be shock insensitive and stable at room temperature.^[20,21] In the pursuit of making improved XeO_3 complexes with higher stability and shock resistance, the group of Schrobilgen eventually focused on crown ethers. Ever since they had been reported by Pederson in 1967, crown ethers have been at the forefront of host-guest and supramolecular chemistry,^[22] because of their highly selective recognition of specific cationic and molecular species.^[23,24] Crown ethers are the cyclic oligomers of ethylene oxide, which provide a unique electron rich cavity, allowing their interaction with a plethora of guest species, depending on their size, shape and donor properties.^[25] Their host-guest interactions with AB_3 type main group compounds ($\text{A} = \text{As}, \text{Sb}, \text{Bi}$, and $\text{B} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) are well known in literature,^[26,27,28] and later attributed to the presence of weak σ -hole interactions.^[29] Furthermore, the resistance of crown ethers towards a strongly oxidizing environment^[30] have made them suitable candidates for investigating the aerogen bonding with XeO_3 . Encouraged by these characteristics, the group of Schrobilgen synthesized an adduct of 15-Crown-5 with XeO_3 , and obtained a crystal, which was so stable at room temperature that it did not explode even after substantial mechanical stress (hitting with a hammer).^[31] The only other report of a crown ether adduct with noble gas trioxides is a computational investigation by the group of Gao, reporting a very strong noncovalent interaction between the 18-Crown-6 and XeO_3 ,^[32] which is comparable to the strongest of cation- π noncovalent interactions.^[33] It should be noted that their work focused solely on the 18-Crown-6: XeO_3 complex, and no comparative study has been conducted subsequently to elucidate how changes in the size of crown ethers affected their complexation with XeO_3 .

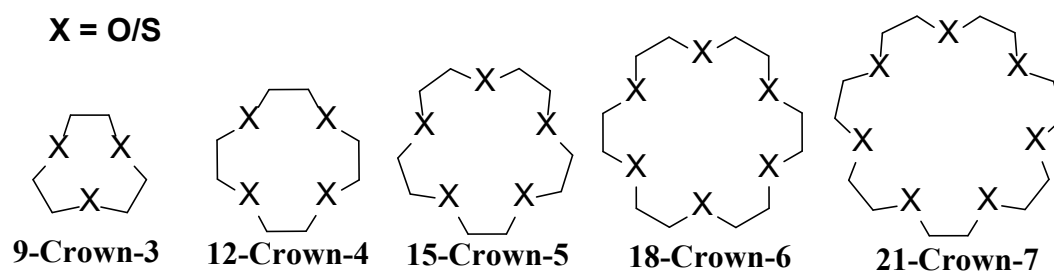


Figure 3.2. Different crown ethers with increasing size used in this study. X donates the donor atom as oxygen (O) or sulfur (S).

Aerogen bonding interactions arising due to σ -hole interactions have elicited much interest in recent years, and have been seen to be useful in crystal engineering, due to their directional nature. This has provided us with the motivation to develop an improved understanding of such interactions.^[9,34] Drawing inspiration from the aforementioned reports,

we have selected various crown ethers (9-Crown-3, 12-Crown-4, 15-Crown-5, 18-Crown-6, and 21-Crown-7) and their thio analogs^[35,36] as hosts for this work (see **Figure 3.2**). We are aware that thio crown ethers are less robust towards oxidation; nevertheless, we have included them in order to investigate how efficiently the less electronegative sulfur, in comparison to oxygen, shares its lone pair of electrons with the σ -holes, resulting in the formation of aerogen-bonded adducts. The set of guests has also been extended to include other noble gas trioxides (NgO_3 , Ng = Kr and Ar), as they too possess a σ -hole at the location of the lone pair, and at the extension of their respective Ng=O bonds (**Figure 3.1**).^[37] By means of quantum chemical calculations, deeper understanding is obtained of how the change in electron rich cavity and the increase in crown size alters their host-guest complexation with NgO_3 . The interaction energies of the adduct formation have been compared and different computational tools such as MEP, WBIs, AIM, NBO, NCI plots, and EDA have been employed to elucidate the physical nature of interactions between the crown ethers and NgO_3 .

3.2. Computational Methodology

All the DFT calculations have been performed utilizing the Gaussian 09 program.^[38] Each model was optimized in the gas phase by employing the APFD^[39] functionals along with def2-TZVPD basis set.^[40] This level of theory was selected because it had been benchmarked as the most reliable combination when compared to the experimentally obtained adduct of 15-Crown-5 with XeO_3 by Schrobilgen's research group.^[31] Furthermore, harmonic frequency calculations were performed to confirm all the stationary points as minima. Conformational search analysis has been carried out with Grimme's semi-empirical Conformer–Rotamer Ensemble Sampling Tool (CREST)^[41] at the xTB-GFN2 levels of theory.^[42-44] The counterpoise correction method was employed to obtain more accurate interaction energy (ΔE_{int}) values by correcting the basis set superimposition error (BSSE).^[45] The ΔE_{int} is calculated as the disparity amongst the energy of the adduct/complex & the energy of the isolated monomers in the configuration of the complex. Deformation energies corresponding to each case have also been evaluated. MEP, NCI plot and AIM analysis were executed in the MultiWFN program^[46] & visualized using the Visual Molecular Dynamics (VMD) program.^[47] NBO analysis were carried out as incorporated in Gaussian 09 software module. For EDA^[48], the BP86^[49] functional with D3(BJ) correction was used together with the TZ2P basis set^[50] as

implemented in ADF 2022. The frozen core approximation was used and the numerical quality was set to good. A strictly closed-shell fragmentation scheme was chosen. To enhance the robustness of the study, the interaction energy has been additionally assessed through single-point calculations at the EDA/MP2/ZORA/TZ2P and APFD/aug-cc-pVTZ (-PP for Xe) levels of theory, which incorporate the electron correlation and relativistic effects.^[51,52] The robustness of the WBI, NPA, and NBO calculations has been further confirmed by utilizing the NBO 6 program.^[53]

3.3. Results and Discussion:

3.3.1. Molecular Electrostatic Potentials of Isolated Molecules (MEP)

The MEP provides an effective way of examining noncovalent interactions (NCI), as NCIs are mostly columbic in nature.^[54] However, it must be noted that MEP not only reflects the effects of electrons but also the effects of the nuclei.^[55] Here, MEP plots were computed for the noble gas trioxides, which confirmed the presence of three σ -holes opposite to their respective Ng-O bond. As shown in **Figure 3.1**, the blue color represents the electron deficient region with the orange dots indicating the location of the σ -holes. The MEP maxima ($V_{s,max}$) values for the XeO_3 , KrO_3 and ArO_3 obtained at the APFD/def2-TZVPD level of theory was found to be close with the earlier reported values at the MP2/aug-cc-pVTZ level of theory.^[4] A decrease in $V_{s,max}$ from Xe to Ar was observed due to their decreasing atomic polarizabilities and electronegativity difference, in accordance with the literature.^[9] The presence of such strong positive potential regions (σ -holes) makes these noble gas trioxides attractive for electron rich crown ethers.

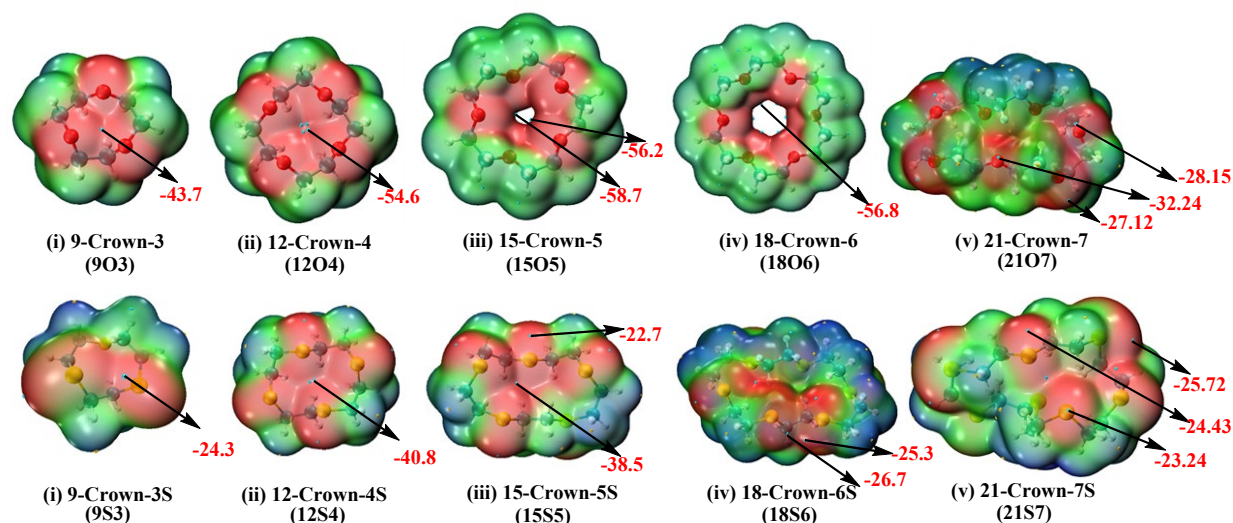


Figure 3.3. Selected MEPs of the crown ethers and their thio analogues with their respective energy values of minima ($V_{s,min}$ in kcal/mol). Blue and red represent the positive and negative regions, respectively, while green denotes the intermediate zone between them. The isovalue of the isodensity surface is set at 0.001 a.u..

The MEPs have also been computed for the crown ethers as depicted in **Figure 3.3** (See **Table S3.1** for the complete list of MEPs: $V_{s,min}$), where the red color represents the electron rich region of the crown ethers. All the crown ethers from 9-Crown-3 to 21-Crown-7 were found to have an intense region of negative potential at the center. As shown in **Figure 3.3**, a shared negative potential was found to be increasing with increase in the size of the crown ethers from 9-Crown-3 to 15-Crown-5. However, a decrease in the cumulated negative potential was observed upon further increase in size from 15-Crown-5 to 21-Crown-7, but it was distributed among the individual oxygen centers, as listed in **Table S3.1**. The MEPs of the thio analogues were found to be more dispersed around the molecule, owing to the lower electronegativity and exodentate orientation of sulfur atoms, in contrast to the endodentate conformation found in their oxygen counterparts.^[35,36]

3.3.2. Interaction Energies

The interaction energies for all the adduct formation were evaluated (**Table 3.1**) and it was observed that increase in the size of the crown ethers favored its complexation with the

noble gas trioxides. A similar trend was observed for all three noble gas trioxides, i.e., XeO₃, KrO₃ and ArO₃.

Table 3.1. Interaction energy (ΔE in kcal/mol) with BSSE corrections computed at the APFD/def2-TZVPD level of theory. Donor atoms of the crowns are denoted by their atomic symbol (O/S) for comparison.

Crown ethers		Thio-crown ethers	
Complex	ΔE_{BSSE}	ΔE_{BSSE}	Complex
XeO ₃ :9O3	-25.0	-24.2	XeO ₃ :9S3
XeO ₃ :12O4	-30.6	-27.6	XeO ₃ :12S4
XeO ₃ :15O5	-38.3	-35.4	XeO ₃ :15S5
XeO ₃ :18O6	-40.2	-42.8	XeO ₃ :18S6
XeO ₃ :21O7	-41.2	-48.2	XeO ₃ :21S7
KrO ₃ :9O3	-20.1	-18.7	KrO ₃ :9S3
KrO ₃ :12O4	-22.6	-19.3	KrO ₃ :12S4
KrO ₃ :15O5	-25.7	-23.0	KrO ₃ :15S5
KrO ₃ :18O6	-26.0	-27.6	KrO ₃ :18S6
KrO ₃ :21O7	-26.4	-36.4	KrO ₃ :21S7
ArO ₃ :9O3	-15.4	-13.5	ArO ₃ :9S3
ArO ₃ :12O4	-16.1	-13.0	ArO ₃ :12S4
ArO ₃ :15O5	-17.2	-14.8	ArO ₃ :15S5
ArO ₃ :18O6	-17.6	-18.0	ArO ₃ :18S6
ArO ₃ :21O7	-17.9	-23.8	ArO ₃ :21S7

The thio-analogues of the crown ethers exhibit a similar trend for the adduct formation with XeO₃, KrO₃ and ArO₃. The only exception is the formation of the ArO₃ adduct with 12S4, which could be attributed to the lowest polarizability of Ar compared to Kr and Xe. Interestingly, it was also observed that the complexation of smaller thio-analogues (9S3, 12S4 and 15S5) of crown ethers with NgO₃ show less favorable binding as compared to their oxygen

counterparts, whereas the larger thio-analogues (18S6, 21S7) show more favorable binding with NgO_3 , as compared to their oxygen peers. It should be noted that we also obtained a different mode of binding for XeO_3 with 21-Crown-7, through CREST, which was found to be unfavorable by +1 kcal/mol (ΔE) than the one reported above. However, the similar binding modes for KrO_3 and ArO_3 were favorable by -3.5 kcal/mol and -2.9 kcal/mol, respectively. These alternative modes are referred to as $\text{NgO}_3(21\text{-Crown-7})'$ in the discussion. The deformation energies by different crowns for complexation with the NgO_3 have also been computed (details in **Table S3.2**) and it was observed to decrease from Xe to Ar. This can be explained by the overall interaction energy, which increases from Ar to Xe: a larger interaction energy allows the crown ether to compensate more energy for its deformation to maximize the bonding interaction. As stated earlier, MEPs cannot be the sole indicator of such non-covalent interactions, which is also reflected in the trend of interaction energies. Hence, other computational tools were employed to obtain insights into the factors influencing the interaction energy for the host-guest complex of crown ethers (as well as their thio-analogues) and noble gas trioxides. A consistent trend in interaction energies was observed in the data obtained from both the EDA/MP2/ZORA/TZ2P level of theory and the APFD/aug-cc-pVTZ (-PP for Xe) level of theory (see **Table S3.3**).

3.3.3. Structural Characteristics, WBI, and Charge Analysis

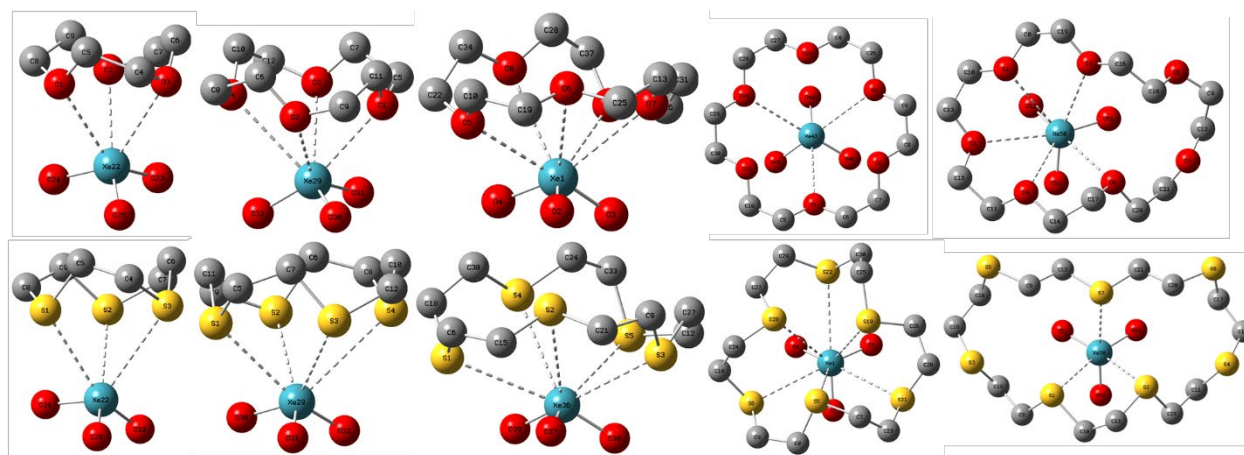


Figure 3.4. Optimized geometries of the complexes involving XeO_3 with crown ethers (top) and their thio analogues (bottom) are presented with an increasing crown size, arranged from left to right. Hydrogen atoms have been omitted for clarity.

The optimized geometries of all the complexes are depicted in **Figures 3.4 and S3.1** (for XeO₃), **Figure S3.2** (for KrO₃), and **Figure S3.3** (for ArO₃). The **Figures S3.1-S3.3** include their respective primary Ng-O bond lengths, secondary Ng...X (X=O/S) bond distances, Wiberg bond indexes and the charge analysis values obtained from natural population analysis and Mulliken charge analysis. **Figure S3.4** illustrates an alternative binding mode of NgO₃ with 21-Crown-7, in which Ng is seen to be interacting with only three oxygen atoms of 21-Crown-7, as opposed to the five oxygen atoms observed in the previous cases. In all cases, an increase in the Ng-O bond lengths was observed upon complex formation. The only exception was found in one of the Xe-O bond lengths in the XeO₃:21O7 complex. It is to be noted that the elongation of Ng-O bonds in ArO₃ was relatively smaller compared to their analogues in KrO₃ and XeO₃. Furthermore, we observed that the elongation of Ng-O bonds was more pronounced when forming complexes with thio-crown ethers, as opposed to their oxygen-based analogs. The intermolecular distances of secondary Ng...X (X=O/S) interactions, specifically the one interacting with the noble gases as shown in **Figures S3.1-S3.4**, were observed to be lower than the summation of their corresponding vdWs radii ($\Sigma(\text{Xe-O})_{\text{vdW}} = 3.68 \text{ \AA}$, $\Sigma(\text{Kr-O})_{\text{vdW}} = 3.54 \text{ \AA}$, $\Sigma(\text{Ar-O})_{\text{vdW}} = 3.4 \text{ \AA}$, $\Sigma(\text{Xe-S})_{\text{vdW}} = 3.96 \text{ \AA}$, $\Sigma(\text{Kr-S})_{\text{vdW}} = 3.82 \text{ \AA}$, $\Sigma(\text{Ar-S})_{\text{vdW}} = 3.68 \text{ \AA}$, according to Bondi)^[56] for all cases. A comparative summary of the changes in bond lengths for the case of XeO₃ is presented in **Table 3.2**.

Table 3.2. Bond lengths of Xe-O upon complexation and the secondary bond distances between xenon and donor atom of the crown. All the values are in Å.

	Isolated	9O3	12O4	15O5	18O6	21O7
Xe-O	1.7597	1.7652	1.7651	1.7673	1.7605	1.7585
	1.7597	1.7651	1.7649	1.7640	1.7605	1.7620
	1.7597	1.7658	1.7651	1.7623	1.7605	1.7670
Xe....O	-	2.8184	2.8049	2.9088	3.1493	2.9733
		2.9265	2.9474	2.9616	3.1493	3.0428
		2.9494	2.9691	2.9627	3.1493	3.1338
			3.1220	3.0745	3.4010	3.1427
				3.2590	3.4010	3.1668

					3.4010	
	Isolated	9S3	12S4	15S5	18S6	21S7
Xe-O	1.7597	1.7675	1.7702	1.7727	1.7710	1.7760
	1.7597	1.7699	1.7666	1.7683	1.7710	1.7792
	1.7597	1.7675	1.7666	1.7634	1.7710	1.7757
Xe....S	-	3.1846	3.2080	3.2648	3.3223	3.1155
		3.2151	3.2391	3.3618	3.3230	3.1323
		3.4580	3.4843	3.4863	3.3240	3.1834
			3.5669	3.5038	3.4717	
				3.5607	3.4719	
					3.4722	

In concurrence with the observed bond elongation, a reduction in the Wiberg bond indices (WBI) of Ng and O was noted during complexation with both crown ethers and their thio analogues in all cases, except for the complexes involving XeO₃ with 9S3, 12S4, and 21S7, where the changes were marginal. The bond orders of Ng...O and Ng...S secondary interactions were evaluated using WBI analysis, employing NBO 6, and the results are presented in **Table S3.4**. The analysis reveals a noticeable trend wherein, for individual crowns, the bond orders of the secondary interactions follow the sequence Xe > Kr > Ar. Notably, the bond orders associated with Ng...S interactions were observed to be greater than those of their oxygen analogs. The <O-Ng-O bond angles in NgO₃ followed the order Xe < Kr < Ar before and after complexation in all cases. Additionally, the average <O-Ng-O bond angles decreased with increasing crown size for both oxygen and thio analogues, with a few exceptions (complexes of NgO₃:21O7, XeO₃:21O7', and ArO₃:12S4). The magnitude of the decrease in bond angle with increase in the size of the crowns was most significant in XeO₃ complexes, followed by KrO₃ and ArO₃ (Xe > Kr > Ar). Concerning XeO₃ complexes, the decrease in average bond angles was more pronounced in thio analogues, except for XeO₃:18S6. There were no such discernible patterns in the average bond angles between crown ethers and their thio analogues for the complexes of KrO₃ and ArO₃. The values corresponding to the NgO₃ bond angles mentioned above are listed in **Table S3.19**. Additionally, natural population analysis revealed that, upon complex formation, the charges on Ng and O within NgO₃ were elevated. In other

words, Xe, Kr, and Ar exhibited a more positive charge, while oxygen displayed a higher negative charge. These findings suggest an enhanced polar-covalent nature in the primary Ng-O bonds of NgO_3 upon complex formation. Interestingly, the charge derived from the Merz-Kollman (MK) model indicates a decrease in charge on Ng and O upon complexation, with a few exceptions. There is no consistent trend in the charges on Ng and O with the increasing crown size in the MK analysis. Conversely, charges on Ng obtained from NPA analysis (utilizing NBO 6) were observed to increase with the growth in the crown size. A comparative summary of the MK and NPA charge analyses is presented in **Tables S3.5-S3.7**. Each method for charge analysis has its merits and drawbacks. While electrostatic fitting models (MK) offer better charge estimation for surface atoms, they are notably limited in accurately estimating charges for buried atoms. This could be the reason for discrepancy between the MK and NPA charges.

3.3.4. NCI and BCP (from AIM Analysis)

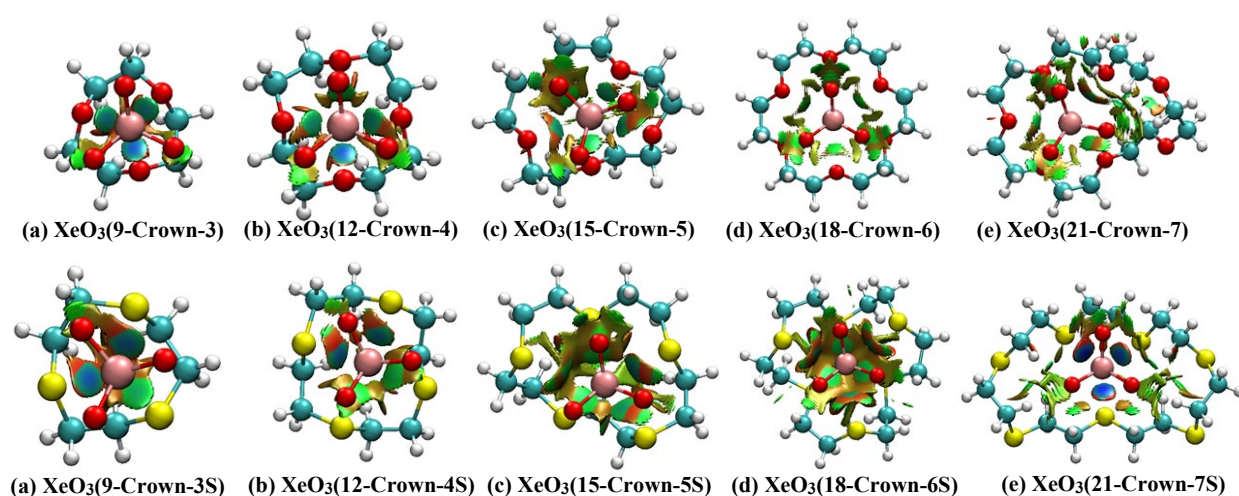


Figure 3.5. NCI plots (isovalue 0.5 a.u.) of the complexes of XeO_3 with crown ethers (top) and their thio analogues (bottom). Blue regions represent strong attractive forces, green region indicates intermediate attraction, while red regions signify repulsive forces.

In order to gain deeper insights into the binding of Ng with different crown ethers, NCI plots analyses were conducted (**Figures 3.5, S3.5, and S3.7**). This revealed that, apart from the conventional aerogen bonds, i.e., the interaction between the donor atom of the crowns and the

Ng, attractive regions depicting the hydrogen bonding interactions between the C-H...O exist, which become more prominent in larger crowns. It is to be noted that the attractive nature of the aerogen bonding also decreases as the size of the crown increases, which is represented *via* a change in intensity of the region from blue-green to green. The exception to this trend was observed in adducts of 21S7 with NgO₃, which were found to be more attractive in nature as compared to other crowns. Also, the NCI plot analysis for the alternative binding mode of NgO₃ with 21-Crown-7 revealed a more attractive aerogen bonding region (**Figure S3.9**). Interestingly, a faded region of greenish surface was observed between the three oxygen atoms which are farther away from the NgO₃ in their complex with 18-Crown-6, indicating a very weak attractive interaction. Whereas, the **Figure 3.5(e)** indicates stronger attractive interactions of all six donor atoms of 18S6 as compared to the 18O6.

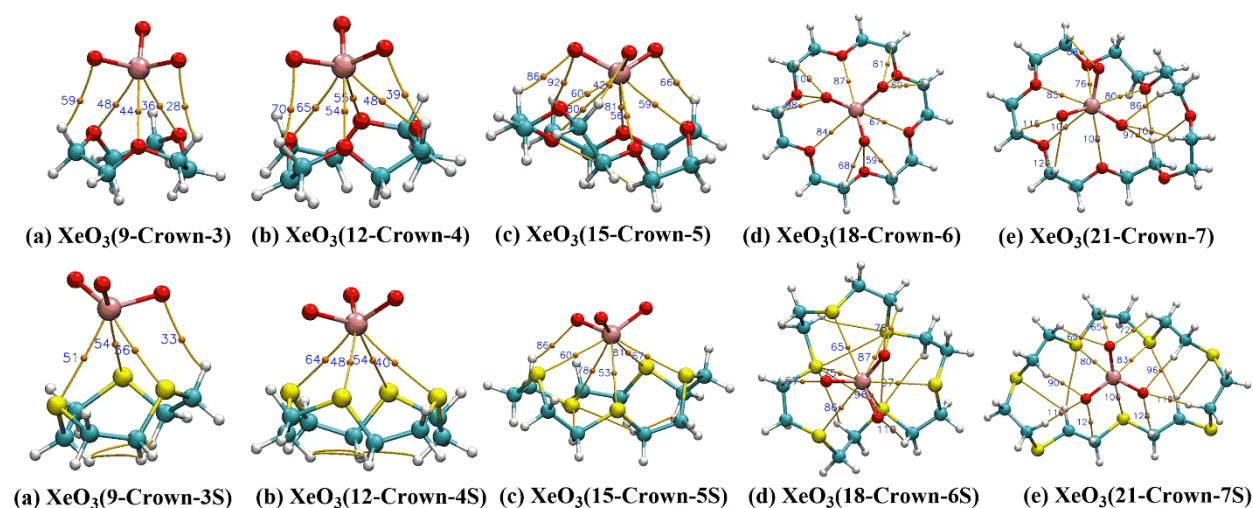


Figure 3.6. Bond critical points (BCPs) obtained from AIM analysis for the complexes of XeO₃ with crown ethers (top) and their thio analogues (bottom). Please refer to **Table S3.8** for enlarged images of bond critical points along with their respective electron density (ρ , in a.u.) and the Laplacian of the electron density ($\nabla^2\rho$, in a.u.).

Similarly, bond critical points (BCPs) obtained from the AIM analysis concurred with the earlier observation that the C-H...O hydrogen bonding interactions are more prominent in larger crowns (**Figures 3.6, S3.6, and S3.8**). The values corresponding to the bond critical points, along with their respective electron density (ρ , in a.u.) and Laplacian of the electron density ($\nabla^2\rho$, in a.u.) are deposited in the ESI (**Tables S3.8-S3.10**). The C-H...O interactions

were observed to be highest (up to 9) in the complexes of 21S7. The more attractive aerogen bonding interactions, as indicated from the NCI plots along with the highest number $C-H\cdots O$ hydrogen bonding interactions agrees well with the interaction energy trend, which suggests that 21S7 binds to NgO_3 the strongest, as compared to the other crown ethers in the present study. It also revealed the existence of six BCPs between the 18S6 and XeO_3 , indicating that all six sulfur atoms are interacting with the Xe, as compared to the three BCPs in its oxygen analogues. This further validates the coordination number of 9 (3 oxygen atoms of parent XeO_3 and 6 sulfur atoms of 18S6) for Xe in the complex of 18S6 and XeO_3 . The same is also true for KrO_3 , whereas for the case of ArO_3 , only three BCPs were observed, owing to its lowest polarizability and thus lowest σ -hole strength. As evident from the BCPs, the exodentate nature of thio-crown ethers restricts proper $C-H\cdots O$ interactions compared to their oxygen analogues, with the exception of thio-21-Crown-7 (21S7). The smaller thio-crown ethers are more significantly affected, while thio-18-Crown-6 (18S6) compensates for the loss of additional support from $C-H\cdots O$ interactions by binding to NgO_3 via all six sulfur atoms. Notably, 21S7 exhibits strong binding with NgO_3 , and its binding mode allows for the maximum $C-H\cdots O$ interactions among the crown ethers studied. This explains why the smaller thio-crown ethers with NgO_3 show less favorable binding as compared to their oxygen counterparts, whereas the larger thio-analogues show more favorable binding with NgO_3 .

3.3.5. NBO Analysis

To elucidate the orbital effects within the context of aerogen crown-ether/thio-crown-ether complexes, NBO calculations were conducted. These calculations aimed to shed light on the donor-acceptor interactions between the crown-ether/thio-crown-ether molecules and aerogen species, quantified as second-order perturbation energy (E^2). For the lighter aerogens, such as ArO_3 and KrO_3 , we observed relatively lower orbital interactions between the donor orbitals (lone pairs, LPs) originating from the oxygen atoms of the crown ether/the sulfur atoms of the thio-crown-ether and the antibonding orbitals (BD^*) associated with Ae-O bonds. Specifically, these interactions fell within the range of 0.06-0.38 kcal/mol for ArO_3 and 0.06-0.88 kcal/mol for KrO_3 . A similar trend emerged in the case of thio-crown-ether complexes with lighter aerogens, with interactions in the range of 0.10-2.07 kcal/mol for ArO_3 and 0.23-5.92 kcal/mol for KrO_3 . These findings align reasonably well with the lower total interaction energies observed in these complex types compared to XeO_3 complexes. The significance of

orbital contributions becomes more pronounced in xenon complexes (XeO_3), where second-order perturbation interaction energies spanned from 0.05 to 1.65 kcal/mol for crown ether complexes and from 0.34 to 8.96 kcal/mol for thio-crown-ether complexes. In all XeO_3 complexes (both crown ether and thio-crown ether), the total interaction energies were markedly higher compared to their counterparts involving argon or krypton (ArO_3 and KrO_3). These results are concisely summarized in **Table S3.11**. It is also worth noting that across all cases involving NgO_3 , the aerogens paired with thio-crown-ether consistently exhibited more pronounced orbital interactions compared to their oxygen analogues in crown-ether complexes as shown in **Tables S3.12-S3.14**. This contributes to the enhanced nine (9) coordination number for Xe in $\text{XeO}_3\cdot 18\text{S}6$ host-guest complex. In this complex, the lone pairs of all six sulfur atoms exhibit increased orbital interactions with the antibonding (σ^*) Xe-O orbital, in contrast to the $\text{XeO}_3\cdot 18\text{O}6$ complex (as shown in **Table 3.3**). It is worth mentioning that the highest coordination number for Xe previously reported in literature was 8, for the adduct of XeO_3 with 15-Crown-5.^[31] **Table S3.15** summarizes the NBO data for the alternative binding modes of 21-Crown-7 with the noble gas trioxides ($\text{NgO}_3\cdot 21\text{O}7'$). A comparison between the data obtained from NBO 3.1 and NBO 6 was conducted. It was noted that the absolute values corresponding to E^2 values slightly improved with the use of NBO 6. However, the overall trends described above remained the same.

Table 3.3. Second order perturbation energies (E^2) obtained from NBO analysis at the APFD/def2-TZVPD level of theory for the complexes of XeO_3 . The E^2 values are in kcal/mol. The bracketed E^2 values are from the NBO 6 output.

$\text{XeO}_3\cdot 18\text{-Crown-6 (-O)}$			$\text{XeO}_3\cdot \text{Thio-18-Crown-6 (-S)}$		
Donor	Acceptor	E^2	Donor	Acceptor	E^2
LP (1) O1	BD*(1) Xe 43 - O44	0.61 (0.75)	LP (2) S5	BD*(1)Xe1 - O3	0.76 (0.83)
LP (1) O3	BD*(1) Xe 43 - O45	0.61 (0.75)	LP (2) S5	BD*(1)Xe1 - O4	0.81 (0.88)
LP (1) O24	BD*(1) Xe 43 - O46	0.61 (0.75)	LP (2) S6	BD*(1)Xe1 - O3	2.65 (2.93)
LP (2) O2	BD*(1) Xe 43 - O44	0.14 (0.16)	LP(2) S19	BD*(1)Xe1 - O2	0.81 (0.88)
LP (2) O2	BD*(1) Xe 43 - O45	0.14 (0.16)	LP(2) S19	BD*(1)Xe1 - O4	0.76 (0.83)
LP (2) O23	BD*(1) Xe 43 - O45	0.14 (0.16)	LP(2) S20	BD*(1)Xe1 - O2	0.76 (0.83)
LP (2) O23	BD*(1) Xe 43 - O46	0.14 (0.16)	LP(2) S20	BD*(1)Xe1 - O3	0.81 (0.88)

LP (2) O25	BD*(1) Xe 43 - O46	0.14 (0.16)	LP(2) S21	BD*(1)Xe1 - O4	2.66 (2.94)
LP (2) O25	BD*(1) Xe 43 - O44	0.14 (0.16)	LP(2) S22	BD*(1)Xe1 - O2	2.67 (2.95)

3.3.6. EDA

All the density functional theory (DFT) calculations have been carried out using the All the above findings were further supported by Ziegler-Rauk energy decomposition analysis. Although the absolute interaction energies differ from the higher level computations due to the varying functional/basis set (cf. **Tables 3.4, S3.16-S3.18**), the relative trends are conserved and allow additional interpretations. Overall, the attractive interaction is around 50-60 % electrostatic and 50-40 % orbital/London-dispersive in nature. As expected, the thio-crown ethers show larger orbital and London-dispersive contributions compared to the oxygen analogs. Along the line $\text{Ar} > \text{Kr} > \text{Xe}$, all three attractive contributions (electrostatic, orbital, dispersion) increase irrespective of the type and size of the crown ethers. Thus, a more efficient σ -hole (electrostatic) *and* orbital overlap-based interaction is accountable for the strongest binding of the XeO_3 , emphasizing that this type of “special interaction” behaves similar to the conventional Lewis acid-base type of interaction. The percentage contribution changes along the elements: while the relative amount of orbital interaction increases from $\text{Ar} < \text{Kr} < \text{Xe}$, the relative importance of electrostatic and dispersive attraction decreases, $\text{Ar} > \text{Kr} > \text{Xe}$. Considering the effect of ring size, it was interesting to observe that the percentage of electrostatic contribution gradually decreases with increasing crown ether’s size (from 55 to 52% for XeO_3 , from 55 to 51% for KrO_3 , from 58 to 51% for ArO_3). A similar observation was also made for the complexes of thio analogues of XeO_3 and KrO_3 , with the exception of 18S6, which could be due to its unusually high coordination number of nine in the $\text{NgO}_3\text{:18S6}$ complexes. No particular trend was observed in the thio complexes of ArO_3 , except for an initial decrease in the percentage contribution (of electrostatic interaction) from 9S3 to 15S5. Additionally, we also found that the percentage of orbital contribution decreases with increasing crown ether’s size (from 9-Crown-3 to 18-Crown-6) and their thio analogues, with the exception of 21O7 and 21S7. Lastly, we also observed that the percentage contribution from dispersion interactions increases progressively with increasing crown ether’s size, for all three noble gas trioxides (from 16 to 22% for XeO_3 , from 18 to 28% for KrO_3 , and from 21 to

32% for ArO_3). With the exception of 21S7, the percentage contribution for the complexes of thio analogues was also found to increase with increasing crown ether's size from 9-Crown-3S (9S3) to 18-Crown-6S (18S6). All the relevant EDA data discussed above are presented in **Table 3.4** (for XeO_3), **Table S3.16** (for KrO_3) and **Table S3.17** (For ArO_3). It is worth noting that the alternative binding modes of 21O7 with NgO_3 (**Table S3.18**) show increased contribution from orbital interactions and decreased contribution from electrostatic as well as dispersion interactions.

Table 3.4. The energy decomposition analysis (EDA) of all the complexes of XeO_3 at the BP86-D3BJ/TZ2P level of theory. The energy values are in kcal/mol. Contribution to the sum of all attractive energy terms are shown as percentages. E_{Pauli} represents Pauli repulsion, E_{elstat} represents electrostatic interactions, E_{oi} represents orbital interaction and the E_{disp} represents the dispersion interaction.

	ΔE	E_{Pauli}	E_{elstat}	%	E_{oi}	%	E_{disp}	%
$\text{XeO}_3:9\text{O}3$	-21.31	37.81	-32.46	55	-17.08	29	-9.58	16
$\text{XeO}_3:12\text{O}4$	-25.96	41.48	-36.94	55	-18.68	28	-11.82	18
$\text{XeO}_3:15\text{O}5$	-32.24	49.16	-43.92	54	-22.35	27	-15.13	19
$\text{XeO}_3:18\text{O}6$	-33.99	40.62	-40.13	54	-17.81	24	-16.67	22
$\text{XeO}_3:21\text{O}7$	-34.58	53.09	-45.36	52	-22.97	26	-19.34	22
$\text{XeO}_3:9\text{S}3$	-23.57	44.94	-34.24	50	-23.05	34	-11.22	16
$\text{XeO}_3:12\text{S}4$	-26.69	48.01	-36.62	49	-24.13	32	-13.95	19
$\text{XeO}_3:15\text{S}5$	-33.89	53.67	-42.36	48	-26.84	31	-18.36	21
$\text{XeO}_3:18\text{S}6$	-40.86	69.79	-54.22	49	-33.72	30	-22.71	21
$\text{XeO}_3:21\text{S}7$	-48.09	96.05	-68.43	47	-51.51	36	-24.2	17

3.4. Conclusions

Our investigation into the formation of adducts between various crown ethers and noble gas trioxides has revealed key insights into the factors governing their stability. Notably, the formation of complexes between various crown ethers and noble gas trioxides became increasingly favorable with larger crown ring sizes and less favorable as the trioxide shifted from XeO_3 to ArO_3 . The pivotal role of $C-H\cdots O$ interactions in stabilizing the complexes of larger crown ethers has also been revealed. Furthermore, our analysis demonstrated that thio-crown ethers exhibit larger orbital/London-dispersive contributions compared to their oxygen analogs. One significant finding of our research is the discovery of a 9-coordination number for Xe in the complex of XeO_3 and the 18-thio-crown-6. This surpasses the previously recorded highest coordination number of Xe, 8, as observed in the synthetically reported complex of XeO_3 with 15-Crown-5.^[31] Lastly, our investigation revealed that, with few exceptions, the percentage contribution from electrostatic interactions tended to decrease as the size of the crown ethers increased. In contrast, the percentage contribution from dispersion interactions increased with larger crown size. This distinction in interaction types provides valuable insights into the nature of bonding within these complexes. We are aware of the high thermodynamic and kinetic difficulties regarding any potential synthesis or handling of compounds ArO_3 or KrO_3 , and that this challenge most likely will prevent any synthetic realization. However, we believe that the strong thermodynamic and kinetic stabilization under described conditions might guide the way for future strategies to at least temporarily get a glimpse on such elusive species. In summary, our study provides insights into the intricate factors that influence the stability of crown ether-noble gas trioxide host-guest complexes, particularly as the crown size varies.^[57] These findings contribute to the broader understanding of sigma hole-mediated noble gas complexes, as well as supramolecular chemistry.

3.5. References

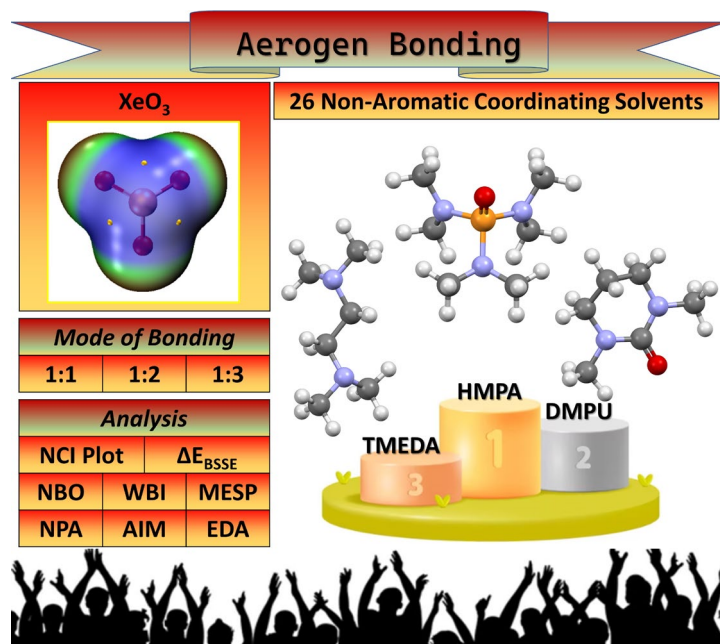
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Chapter-4

Unconventional σ -Hole Interactions of XeO_3 with Non-Aromatic Coordinating Solvents



Abstract: In order to control the explosiveness and shock sensitivity of XeO_3 , we have investigated its plausible interaction with various non-aromatic coordinating solvents, serving as potential Lewis base donors, through density functional theory (DFT) calculations. Out of twenty six such solvents, the top ten were thus identified and then thoroughly examined by employing various computational tools. The amphoteric nature of XeO_3 was also explored by investigating the extent of back donation from the lone pair of Xe to the antibonding orbital of the donating atom/group of the solvent molecules. The C-H...O interactions were also found to be a contributing factor in the stabilization of these adducts. Although these aerogen-bonding interactions were found to be predominantly electrostatic, significant contributions from the orbital contributions, as well as dispersion interactions, were observed. The top three non-aromatic solvents (among the twenty six studied) which form the strongest adducts with XeO_3 are proposed to be hexamethylphosphoramide (HMPA), N,N'-dimethylpropyleneurea (DMPU) and tetramethylethylenediamine (TMEDA).

4.1. Introduction

Noncovalent interactions (NCIs) such as HB, π - π stacking, & vdWs forces, which are primarily driven by electrostatic forces, Pauli repulsion, dispersion, polarization, and charge transfer, serve as the backbone of supramolecular chemistry.^[1-6] While NCIs may be weaker than covalent interactions, the growing interest in NCIs extends beyond theoretical considerations, given their pivotal role in developing functional materials, crystal engineering, ion recognition, protein folding, and drug (guest)-receptor (host) interactions.^[7-11] Besides the extensively studied hydrogen bond,^[12] 21st-century supramolecular chemistry is renewing interest in different kinds of unconventional NCIs and challenging the established perspectives by introducing novel interaction types named after the involved groups of elements.^[13,14] The localized area of positive electrostatic potential, which is positioned on a σ^* orbital on the extension of a covalent bond between the recipient atom bound to an electron-withdrawing atom/group, also known as a sigma hole, gives rise to the NCIs (**Figure 4.1**, left).^[15] These include halogen, chalcogen, pnictogen, tetrel, icosagen (or triel), and, more recently, spondium, regium, and aerogen bonds.^[16-25]

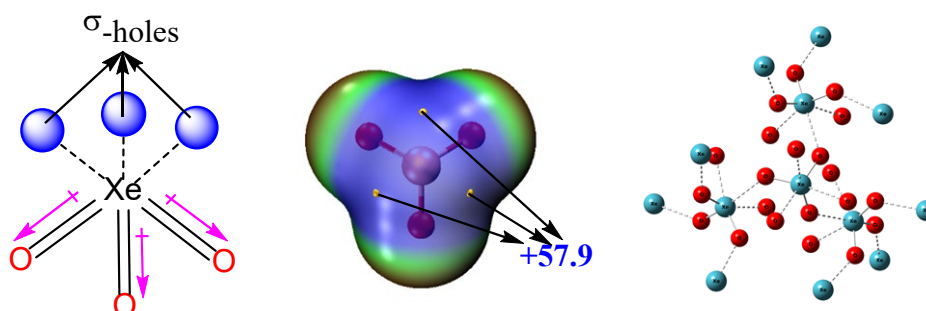
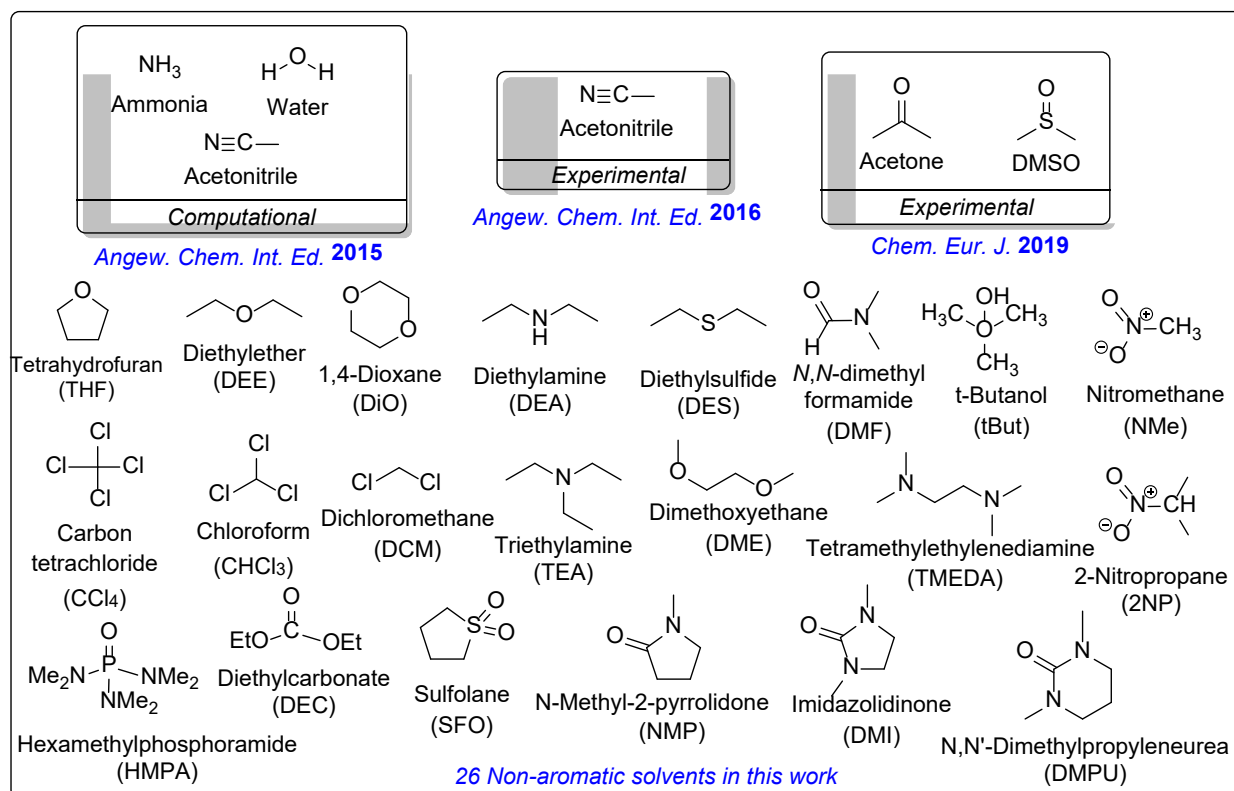


Figure 4.1. Left: Pictorial representation of σ -holes present at the extension of the covalent Xe-O double bond, in the pyramidal XeO_3 , created due to withdrawal of electron density from xenon by more electronegative oxygen atoms (dipole moment vector is shown by pink arrow). Middle: the molecular electrostatic surface potential (MEP) plot of XeO_3 with the maxima ($V_{s,\text{max}}$ in kcal/mol) around the σ -holes, obtained at the APFD/def2-TZVPD level of theory. Right: Network-like crystal structure of XeO_3 in the solid state.^[26,27] Dotted lines represent the σ -hole mediated NCIs.

In the case of aerogen bonding or noble gas bonding, the existence of unconventional σ -holes was revealed by Bauza and Frontera,^[18] and provided key insights into the unique crystal structure of XeO_3 .^[26,27] In the crystal structure, the three σ -holes present at the extension

of each Xe=O bond provide three binding sites that direct the interaction with the nucleophilic oxygens of neighboring XeO₃ molecules, leading to a network-like structure (**Figure 4.1**), which is highly shock-sensitive and explosive in nature.^[28] However, interestingly, the σ -holes that are responsible for the explosive nature of XeO₃ also enable/direct other nucleophiles such as anions and Lewis bases to interact with XeO₃, thus disrupting the Xe...O secondary interactions present in the parent XeO₃ crystal, making the newly obtained adduct of XeO₃ stable and shock-insensitive. Considering the hospitalization of Bartlett and Rao due to the detonation of XeO₃, who were the first to experimentally verify its explosive nature,^[29] brave efforts by the group of Schrobilgen in utilizing this principle led to the successful experimentally obtained stable adducts of XeO₃ with different nucleophilic molecules.^[30-33] On the computational front, while there have been many studies on aerogen bonding with different types of anions, nucleophiles, crown ethers, and aromatic molecules such as benzene and its derivatives (aerogen- π interactions),^[34-41] we observed a paucity in the number of detailed studies on non-aromatic coordinating solvents.

Although the pioneering work by Bauza and Frontera shows the interaction between ammonia, water and acetonitrile with XeO₃, only a 1:1 binding mode between them has been discussed.^[18] Experimentally, only three non-aromatic solvents have been explored for stabilizing XeO₃, the first among them being acetonitrile,^[30] inspired by the computational prediction (**Scheme 4.1**).^[18] The other two were acetone and DMSO,^[33] among which acetone was lost from the XeO₃ crystal, due to adduct dissociation at room temperature, which could be attributed to the evaporation of acetone, which is a low boiling point solvent. Lastly, the 1:3 adduct of DMSO was successfully characterized, and the obtained crystalline moiety was found to be less shock-sensitive as compared to the parent solid XeO₃. However, over the course of multiple days, DMSO decomposed to yield the redox product Me₂SO₂ due to the oxidant nature of XeO₃.^[42-44] The risk associated with the explosiveness of XeO₃, although it has a promising future to lead the noble gas chemistry, hinders a vast experimental exploration, which in turn makes pre-computational analysis of possible hosts or suitable candidates for stabilizing XeO₃ very important.^[45-49] There are undoubtedly other factors, such as the possibility of unwanted side reactions leading to the decomposition of the adduct, which would influence the choice of optimal solvent(s) for XeO₃. Nevertheless, among the numerous factors influencing the stability of XeO₃ in the solid state, a computationally screenable aspect is the binding capability of potential hosts.



Scheme 4.1. Previous computational and experimental reports on XeO₃:solvent adducts and different non-aromatic coordinating solvents used in this study.

In this study, we aim to gain a deeper understanding of such unconventional aerogen bonding interactions. Inspired and motivated by the previous reports, we have selected twenty six different non-aromatic coordinating solvents (**Scheme 4.1**), considering them as Lewis base donors, to investigate their interactions with XeO₃. Considering the presence of three σ -holes associated with XeO₃, three plausible binding modes 1:1, 1:2, and 1:3 have been investigated. Beginning with the molecular electrostatic potential surface analysis (MEP),^[50,51] we have conducted a comparative analysis of the interaction energies for all the adduct formations. To further our understanding and to unveil the underlying physical properties governing the interactions between XeO₃ and different non-aromatic coordinating solvents, a comprehensive analysis of geometrical characteristics,^[52,53] natural population charge (NPA), Wiberg bond indices (WBIs), NCI plot, bond critical points (BCP), NBO^[54] and EDA have been conducted.

4.2. Computational Methodology

The Gaussian 09 suite of programs was utilized for conducting all the density functional theory (DFT) calculations.^[55] Optimization of each model in the gas phase was carried out by employing the APFD^[56] functionals along with the def2-TZVPD basis set.^[57] This specific theoretical approach was chosen based on its established reputation for reliability, as demonstrated in benchmarks against experimentally obtained adducts of XeO₃, by Schrobilgen's research group.^[32,33] Additionally, all the stationary points were confirmed to be minima by performing harmonic frequency calculations. Furthermore, Grimme's semi-empirical Conformer–Rotamer Ensemble Sampling Tool (CREST)^[58] was employed for conformational search analysis at the xTB-GFN2 levels of theory.^[59-61] The models or conformers obtained from CREST underwent additional optimization through DFT. With a few exceptions, a consensus between the CREST and DFT models was observed concerning the orientation and binding mode of the solvents. Only the most stable geometry for all the adducts was considered. It is to be noted that CREST was employed solely to ensure that no lower energy conformer (or a more stable binding mode) was omitted from our study.^[58] In order to enhance the accuracy of interaction energy (ΔE) values *via* rectifying the basis set superimposition error (BSSE), the counterpoise correction method was utilized.^[62] The MultiWFN program^[63] was used to generate and evaluate ESP, NCI plot, and AIM analysis, and the Visual Molecular Dynamics (VMD) software^[64] was used for visualization. NBO analysis was performed using the incorporated module in the Gaussian 09 software. For EDA^[65], the BP86/TZ2P^[66,67] level of theory was applied, accompanying the Grimme's DFT-D3 correction with BJ (Becke-Johnson) damping, as implemented in ADF 2023. The frozen core approximation with scalar relativistic effect was used and the numerical quality was set to good. A strictly closed-shell fragmentation scheme was chosen. The APFD functional, as well as the def2TZVPD basis set are not implemented in ADF 2023 and the EDA has not been checked for consistency and robustness with this method, whereas it is well established for BP86/TZ2P level of theory. Additionally, a recent publication has shown that the selection of the functional is not a determining factor in deriving meaningful conclusions from the EDA analysis.^[68]

4.3. Results and Discussions

4.3.1. MEP/MESP Analysis

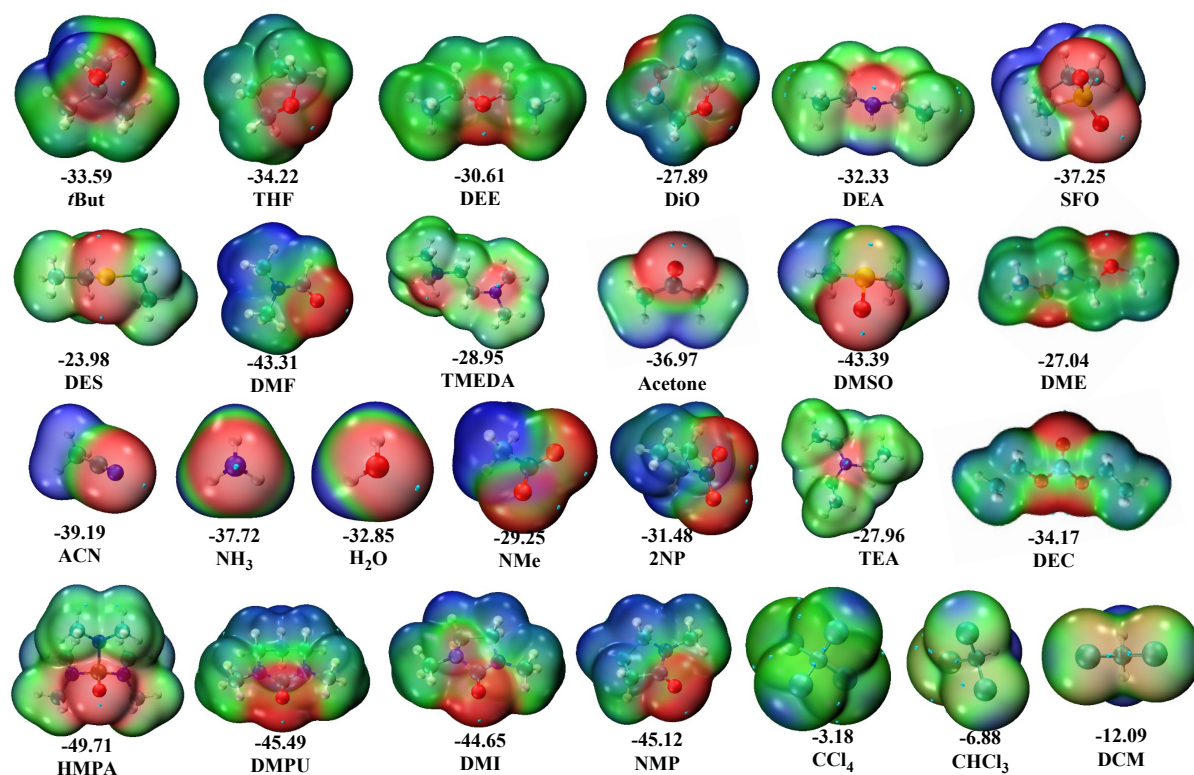


Figure 4.2. MESPs for different solvents with their corresponding minima ($V_{s,min}$ in kcal/mol) generated using the RGB color scale (isovalue 0.001 a.u.), where red represents negative regions, blue denotes positive regions, and green signifies the intermediate zone between them.

MEP, being a real physically observable property, has found extensive utility in σ -hole mediated non-covalent interactions, which are majorly driven by electrostatic interactions.^[50] Nevertheless, it is essential to highlight that MEP involves not just the influences of electrons but also those of the nuclei.^[51] **Figure 4.1** (Middle) depicts the MEP plot for XeO₃, which shows the presence of three σ -holes (orange dots) in the positively charged zone (blue color), opposite to each Xe-O double bond, and associated with a $V_{s,max}$ (MEP maxima) value corresponding to +57.9 kcal/mol, which also correlates well with the previously reported value at the MP2/aug-cc-pVTZ level of theory.^[18,47] The MESPs have also

been evaluated for isolated non-aromatic solvent molecules to examine their negative potential sites (red-colored regions) for possible binding with XeO_3 , as shown in **Figure 4.2**.

The $V_{s,\min}$ (MEP minima) for each isolated solvent are shown as blue dots, and the corresponding values are listed below. Compared to the well-explored DMSO,^[33] a higher negative potential was observed for the case of HMPA, DMPU, DMI, and NMP, suggesting a possibility of stronger electrostatic interaction with XeO_3 . Among the twenty six non-aromatic solvents, in this study, TMEDA and DME provide a bidentate binding site, each of which has a MEP minima of -28.95 and -27.04 respectively. SFO which is widely proposed as a possible alternative to DMSO,^[52] has a lower $V_{s,\min}$ value as compared to DMSO, due to the presence of an additional electronegative oxygen atom bound to sulfur, although two $V_{s,\min}$ corresponding to both the oxygen atoms were observed to be at -37.25 kcal/mol, which increases its overall nucleophilicity. It is also observed that, in accordance with the electronegativity trends, nitrogen donor solvents have higher negative potential, when there is a one-to-one comparison with oxygen donor solvents, such as DEA vs DEE, TMEDA vs DME, NH_3 vs H_2O . Halogen donor solvents such as DCM, CHCl_3 , and CCl_4 were found to be having the lowest $V_{s,\min}$ values, and are probably the worst possible candidates for the current cause, as they have their own σ -holes along the extension of C-Cl bond (corresponding to the halogen bonds), with a $V_{s,\max}$ of +9.05, +14.95, +19.10 kcal/mol respectively.

4.3.2. Interaction Energies

The solvents are ordered as per their decreasing MEP ($V_{s,\min}$) values, and their interaction energies (BSSE corrected) with XeO_3 were evaluated considering three binding modes, such as $\text{XeO}_3\text{:Solvent}$ (1:1), $\text{XeO}_3\text{:}(\text{Solvent})_2$ (1:2), and $\text{XeO}_3\text{:}(\text{Solvent})_3$ (1:3), as shown in **Table 4.1**. It is to be noted that the correlation of MEP values with the interaction energies is not always straightforward, as there are many factors other than electrostatic interactions, such as orbital contribution, dispersion interactions, and intramolecular interactions. Apart from DMSO, the top three solvents in terms of interaction energy values were revealed as HMPA, DMPU, and TMEDA across the different modes of binding. As expected from MEP values, the halogen donor solvents (DCM, CHCl_3 , and CCl_4) were found to be associated with the lowest interaction energies. Furthermore, consistent with the MEP trend, nitrogen donor solvents demonstrate stronger interaction energies in one-to-one

comparisons with oxygen donor solvents. For example, DEA > DEE, TMEDA > DME, and NH_3 > H_2O across the three binding modes.

Table 4.1. Comparative interaction energies (with counterpoise correction) of XeO_3 with various solvents across three binding modes (1:1, 1:2, and 1:3) evaluated at the APFD/def2-TZVPD level of theory.

Solvent	$V_{s,\min}$ (in kcal/mol)	ΔE_{BSSE} (in kcal/mol)		
		1:3	1:2	1:1
HMPA	-49.71	-70.6	-48.0	-25.9
DMPU	-45.49	-62.1	-41.6	-22.1
NMP	-45.12	-55.8	-37.6	-19.7
DMI	-44.65	-57.8	-38.2	-19.9
DMSO	-43.39	-58.4	-41.2	-21.9
DMF	-43.31	-44.6	-32.3	-17.8
ACN	-39.19	-32.4	-20.9	-11.1
NH_3	-37.72	-36.5	-25.6	-13.6
SFO	-37.25	-56.3	-37.2	-19.2
Acetone	-36.97	-42.0	-29.7	-15.8
THF	-34.22	-48.4	-32.7	-16.5
DEC	-34.17	-52.9	-33.2	-17.4
<i>t</i> But	-33.59	-44.1	-29.8	-15.2
H_2O	-32.85	-32.7	-22.1	-11.3
DEA	-32.33	-54.3	-37.0	-19.3
2NP	-31.48	-35.9	-24.0	-12.0
DEE	-30.61	-47.1	-30.6	-15.2
NMe	-29.25	-36.8	-24.9	-12.7
TMEDA	-28.95	-58.1	-52.1	-33.5
TEA	-27.96	-52.0	-39.1	-20.9
DiO	-27.89	-41.9	-27.7	-13.7
DME	-27.04	-46.7	-36.0	-20.1
DES	-23.98	-52.6	-33.9	-16.5
DCM	-12.09	-24.2	-16.0	-8.2
CHCl_3	-6.88	-23.2	-15.6	-7.6
CCl_4	-3.18	-18.5	-11.2	-5.3

Among other solvents, considering 1:3 binding mode, $\text{HMPA} > \text{DMPU} > \text{DMSO} > \text{TMEDA} > \text{DMI} > \text{SFO} > \text{NMP} > \text{DEA} > \text{DEC} > \text{TEA}$, makes the list of top ten candidates for stabilizing XeO_3 . It is to be noted that, although DES has slightly better interaction energy as compared to TEA, there is a high chance that its adduct with XeO_3 will be short-lived, leading to a redox decomposition of DES, as observed experimentally for the case of DMSO.^[29] Considering the same, among the sulfur-containing solvents, SFO might be a good candidate

for stabilizing XeO_3 , as it has a higher chance to resist oxidation, and trails only by 2.1 kcal/mol ($\Delta\Delta E_{\text{BSSE}}$) with respect to DMSO for the case of the 1:3 binding mode. It should be noted that SFO also has the highest boiling point (287.3°C) among all the 26 solvents in this study. The interaction energy order for 1:2 binding mode was observed to be slightly changed, where $\text{TMEDA} > \text{HMPA} > \text{DMPU} > \text{DMSO} > \text{TEA} > \text{DMI} > \text{NMP} > \text{SFO} > \text{DEA} > \text{DME}$, makes the list of top ten candidates. TMEDA being a bidentate ligand tops the chart among the top three. Similarly, DME which is also another bidentate ligand makes the top ten list. Significant improvement in ranking for TEA was observed in the 1:2 binding case due to its bulky nature, which has more accommodative space in 1:2, thus lesser steric repulsion as compared to its 1:3 adduct. The top ten non-aromatic solvents (in this study) for 1:1 binding mode constitutes the same group of solvents, with slight change in their order; $\text{TMEDA} > \text{HMPA} > \text{DMPU} > \text{DMSO} > \text{TEA} > \text{DME} > \text{DMI} > \text{NMP} > \text{DEA} > \text{SFO}$. Again, the improvement in the ranking of DME can be attributed to its bidentate nature, which allows it to interact with two out of the three σ -holes present in XeO_3 , leading to a higher stabilization. As, evident from **Table 4.1**, MEPs alone cannot serve as the exclusive indicator for the strength of these non-covalent interactions, thus prompting us to employ different computational tools to obtain further insights into the factors influencing the stability of these aerogen bond adducts.

4.3.3. Geometrical Characteristics, WBI, and Charge Analysis

The optimized geometries corresponding to the adducts of the top ten solvents (1:3, 1:2, and 1:1) along with their bonding parameters, such as primary Xe-O bond length, secondary $\text{Xe}\cdots\text{X}$ (X = donating atom of the solvent) bond distances, bond angles associated with the aerogen bonds, NPA charge analysis (obtained from NBO), and WBI are shown in **Figure S4.2-S4.10**. A comparative summary of the above-mentioned parameters for the top three solvents is listed in **Table 4.2**. In general, elongation of Xe-O bond upon adduct formation was observed for all cases, and follows the order $1:1 > 1:2 > 1:3$, with a couple of exceptions. The increase in Xe-O bond distances is observed to be highest in TMEDA for 1:1 and 1:2 adducts, where TMEDA is bound to XeO_3 in a bidentate fashion. For the 1:3 adduct of TMEDA, a monodentate binding mode had to be considered, which showed lesser elongation of the Xe-O bond as compared to its 1:2 and 1:1 adducts. Similar observations were also made for DME,

which is another bidentate solvent in this study. However, no bidentate mode of binding could be observed for its cyclic analogue DiO, due to the rigid backbone of the latter.

Table 4.2. Geometrical parameters. X denotes the donating atom of different solvents. WBI values are listed along with the atomic charges (in a.u.) obtained from the natural population analysis at the APFD/def2-TZVPD level of theory.

Solvent	Ratio	Xe-O (in Å)	Xe...X (in Å)	<O-Xe...X (in °)	WBI (XeO ₃)	WBI (Xe...X)	NPA (XeO ₃)
HMPA	1:3	1.7701	2.6420	166.74	Xe1 = 3.3125	0.0458	Xe1 = +3.016
		1.7720	2.6414	166.28	O2 = 1.4259	0.0481	O2 = -1.021
		1.7734	2.6391	167.37	O3 = 1.4153	0.0500	O3 = -1.031
					O4 = 1.4094		O4 = -1.038
	1:2	1.7666	2.6169	165.36	Xe1 = 3.3212	0.0509	Xe1 = +2.957
		1.7675	2.6011	163.37	O2 = 1.4367	0.0585	O2 = -0.997
		1.7675			O3 = 1.4541		O3 = -0.999
	1:1	1.7644	2.5688	161.79	O4 = 1.4405		O4 = -1.016
		1.7645			Xe1 = 3.3436	0.0699	Xe1 = +2.868
		1.7641			O2 = 1.4723		O2 = -0.969
DMPU	1:3	1.7712	2.7353	170.86	O3 = 1.5006		O3 = -0.965
		1.7711	2.7366	170.71	O4 = 1.4711		O4 = -0.972
		1.7711	2.7318	170.85	Xe1 = 3.3278	0.0420	Xe1 = +2.945
					O2 = 1.4345	0.0419	O2 = -1.009
	1:2	1.7677	2.6445	165.43	O3 = 1.4346	0.0425	O3 = -1.009
		1.7731	2.7076	167.42	O4 = 1.4343		O4 = -1.010
		1.7638			Xe1 = 3.3343	0.0576	Xe1 = +2.905
	1:1	1.7616	2.6115	162.07	O2 = 1.4432	0.0466	O2 = -0.992
		1.7668			O3 = 1.4438		O3 = -1.009
		1.7647			O4 = 1.4816		O4 = -0.970
TMEDA	1:3	1.7702	2.9278	177.96	Xe1 = 3.3508	0.0659	Xe1 = +2.844
		1.7707	2.9220	177.33	O2 = 1.4918		O2 = -0.955
		1.7708	2.9275	177.30	O3 = 1.4655		O3 = -0.975
					O4 = 1.5041		O4 = -0.960
	1:2	1.7759	2.8110	158.90	Xe19 = 3.3458	0.0596	Xe19 = +2.897
		1.7754	2.7986	162.22	O20 = 1.4366	0.0604	O20 = -1.005
		1.7720	2.8875	176.64	O21 = 1.4361	0.0594	O21 = -1.006
					O22 = 1.4359		O22 = -1.006
	1:1	1.7684	2.7591	160.51	Xe12 = 3.3521	0.0644	Xe12 = +2.888
		1.7729	2.7156	159.39	O13 = 1.4400	0.0707	O13 = -1.009
		1.7728			O14 = 1.4412	0.0597	O14 = -1.009
					O15 = 1.4246		O15 = -1.009
					Xe1 = 3.3601	0.0776	Xe1 = +2.850
					O2 = 1.4314	0.0862	O2 = -0.990
					O3 = 1.4708		O3 = -0.990
					O4 = 1.4698		O4 = -0.990

The secondary bond distances corresponding to the σ -hole interactions and their associated bond angles were also found to be increasing from the 1:1 to the 1:3 adducts, which could be attributed to an increase in steric crowding. It is also interesting to note that adducts of HMPA have the shortest secondary bond distance among the top three, enabling it to have

a stronger interaction with the σ -hole of XeO_3 . It must be noted that the intermolecular secondary bond distances ($\text{Xe}\cdots\text{X}$) were observed to be shorter than the sum of their respective vdWs radii ($\Sigma(\text{Xe-O})_{\text{vdW}} = 3.68 \text{ \AA}$, $\Sigma(\text{Xe-N})_{\text{vdW}} = 3.71 \text{ \AA}$, according to Bondi)^[53] and larger than the sum of their corresponding covalent radii ($(\Sigma(\text{Xe-O})_{\text{cov}} = 2.03 \text{ \AA}$, $\Sigma(\text{Xe-N})_{\text{cov}} = 2.11 \text{ \AA}$). Consistent with the observed bond elongation, there was a gradual decrease in the Wiberg bond indices of both Xe and O upon the formation of adducts, following the order of 1:1 > 1:2 > 1:3. A similar trend was also noted for the aerogen bonds ($\text{Xe}\cdots\text{X}$), with an overall reduction in WBI values following the order of 1:1 > 1:2 > 1:3. Furthermore, natural population analysis revealed that, upon the formation of the adducts, the charges on Xe and O within XeO_3 were enhanced. In particular, Xe demonstrated an increase in positive charge, whereas oxygen exhibited an increase in negative charge, while both follow the trend 1:3 > 1:2 > 1:1, more $\pm$ to less $\pm$). These results indicate an increased polar-covalent nature in the primary $\text{Xe}=\text{O}$ bonds of XeO_3 upon complexation. It is interesting to note that the adducts of HMPA show the maximum enhancement in the charges of Xe and O, suggesting a stronger charge transfer from HMPA to XeO_3 among the top three.

4.3.4. NCI Plot and BCP Analysis

To obtain more insights into the binding between XeO_3 and the various non-aromatic coordinating solvents, NCI plots were carried out, which unveiled that beyond the aerogen bonds involving the donor atom of the solvents and Xe, there exist attractive regions indicative of $\text{C-H}\cdots\text{O}$ interactions. NCI plots for the adducts of XeO_3 with the top three solvents are illustrated in **Figure 4.3** and **Figure S4.12**. The σ -hole mediated aerogen bonds are depicted by an intense blue-colored region, suggesting very strong stabilizing interactions, whereas, the $\text{C-H}\cdots\text{O}$ interactions are revealed as weakly stabilizing interactions, which are indicated by the greenish surface associated with them. Some intermolecular stabilizing weak interactions between the solvent molecules were also observed, as indicated by the greenish surface between them. Owing to the greater number of neighboring atoms, the number of $\text{C-H}\cdots\text{O}$ interactions increase in the order 1:1 < 1:2 < 1:3. These observations are further corroborated by bond critical point (BCP) analyses.

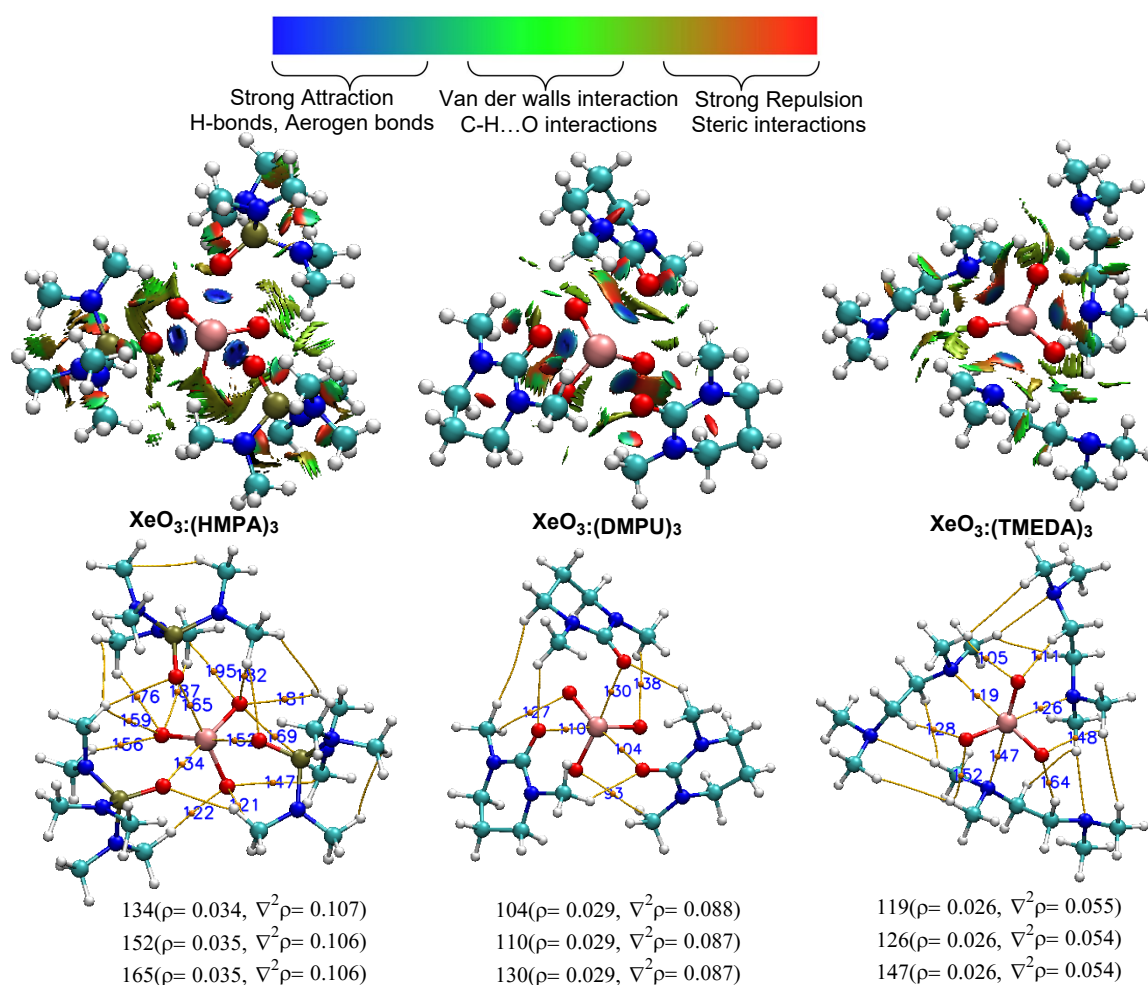


Figure 4.3. NCI plots (isovalue 0.5 a.u.) and bond critical points (of aerogen bonds) obtained from the AIM analysis of the adducts of XeO₃ with the top three solvents, for the 1:3 binding mode and their respective electron density (ρ , in a.u.) and Laplacian of the electron density ($\nabla^2\rho$, in a.u.).

As revealed by NCI plots, bond critical points were observed corresponding to aerogen bonds as well as $C-H\cdots O$ interactions. A consistent trend in ρ and $\nabla^2\rho$ associated with the BCPs of aerogen bonds was observed to follow the order $1:3 < 1:2 < 1:1$, consistent with the shorter secondary (Xe...X) bond distances in the same order. From BCP analysis, it is evident that the number of $C-H\cdots O$ interactions are highest for HMPA adducts, the best among the top three. Some intermolecular $C-H\cdots N$ and $C-H\cdots O$ interactions were also observed from the AIM/BCP analysis. The Laplacian values were found to be positive for all the cases, which suggests a close-shell system as per Bader's AIM theory. These BCPs are shown in **Figure 4.3** and **Figure S4.13** along with their respective ρ and $\nabla^2\rho$. The largest value of ρ at the BCPs corresponding to the aerogen bonds was observed for the adducts of HMPA, which provides a

clear indication that the interactions between HMPA and XeO_3 are the strongest. In general, by comparing the absolute value of ρ , it can also be implied that the 1:1 adducts show stronger aerogen bonding interactions as compared to 1:2 and 1:3 adducts. The NCI plots and BCPs related to the remaining top ten solvents are shown in **Figure S4.14-S4.20**.

4.3.5. NBO Analysis

NBO calculations were carried out to enhance our understanding of the donor-acceptor nature of these adducts by investigating the orbital interactions between the solvent molecules and XeO_3 quantified through second-order perturbation energy (E^2).^[54] Some interesting results from NBO analysis were observed, and are summarized in **Table 4.3** (for the top three solvents), and **Tables S4.1-S4.3** (for the remaining solvents among the top ten candidates). It was observed that the E^2 values corresponding to the interaction amongst the LP on the donating atom and the acceptor $\sigma^*(\text{Xe-O})$ orbital (corresponding to the σ -hole) increase while moving from 1:3 to 1:1 adducts, in accordance with the decrease in their secondary bond distances ($\text{Xe}\cdots\text{X}$). Considering the amphoteric Lewis acid/base nature of XeO_3 , the strength of back donation of Xe's LP to the donating group/atom's antibonding orbital was also examined for individual solvent molecules, which although smaller, but not negligible, follows the order 1:1 > 1:2 > 1:3. This provides another explanation for the trend in secondary bond distances, which follows the same order. It should be noted that the cumulative strength of back-donation was found to be highest for the adducts of HMPA for the 1:3 binding mode, and TMEDA for the 1:2 and the 1:1 binding mode (due to its bidentate nature), among the top three solvents, which correlates with the interaction energy trends. A very interesting observation from NBO analysis was the revelation of a stronger donation from the bonding O=C orbital of DMPU to the σ -hole of XeO_3 ($\pi \rightarrow \sigma^*$), as compared to the donation from the lone pair of oxygen to the same ($n \rightarrow \sigma^*$), for each binding mode, in the order of 1:1 > 1:2 > 1:3. The absence of such interaction, in case of HMPA, can be attributed to the enhanced polar character of the O=P orbital, due to larger electronegativity difference between O and P. It should be noted that two bonding NBOs corresponding to O=C in DMPU (one σ and one π) were observed, whereas only one bonding NBO related to O=P in HMPA (only σ) was observed. However, this leads to the accumulation of charge on the donor oxygen atom of HMPA leading to a stronger $n \rightarrow \sigma^*$ (lone pair of oxygen to the σ -hole) interactions in its aerogen bond

complexes, as compared to that of DMPU, which overcompensates the absence of earlier mentioned $\pi \rightarrow \sigma^*$ interactions in HMPA adducts. The NBO analysis also confirms the presence of C-H...O hydrogen bonds. However, they are significantly weaker than the aerogen bonds, with the associated E^2 values ranging only 0.07-1.43 kcal/mol for HMPA, 0.05-0.18 kcal/mol for DMPU, and 0.05-1.86 kcal/mol for TMEDA (**Table S4.4**), in the order of 1:3 > 1:2 > 1:1.

Table 4.3. Second-order perturbation energy values (E^2 , in kcal/mol) obtained from natural bond orbital (NBO) analysis of selected adducts of XeO_3 at the APFD/def2-TZVPD level of theory.

Solvent	Ratio	Donor	Acceptor	E^2
HMPA	1:3	LP (1)Xe1	BD*(1)O5 - P9	0.92
		LP (1)Xe1	BD*(1)O6 - P10	0.81
		LP (1)Xe1	BD*(1)O7 - P8	0.79
		LP (1)O5	BD*(1)Xe1 - O3	2.33
		LP (3)O5	BD*(1)Xe1 - O3	4.30
		LP (1)O6	BD*(1)Xe1 - O2	1.94
		LP (3)O6	BD*(1)Xe1 - O2	5.26
		LP (1)O7	BD*(1)Xe1 - O4	1.92
		LP (3)O7	BD*(1)Xe1 - O4	5.53
	1:2	LP (1)Xe1	BD*(1)O5 - P8	1.14
		LP (1)Xe1	BD*(1)O6 - P7	1.01
		LP (1)O5	BD*(1)Xe1 - O3	2.54
		LP (3)O5	BD*(1)Xe1 - O3	4.23
		LP (1)O6	BD*(1)Xe1 - O4	2.00
		LP (3)O6	BD*(1)Xe1 - O4	6.49
	1:1	LP (1)Xe1	BD*(1)O5 - P6	1.23
		LP (1)O5	BD*(1)Xe1 - O3	2.04
		LP (3)O5	BD*(1)Xe1 - O3	6.90
DMPU	1:3	LP (1)Xe1	BD*(1)O5 - C27	0.25
		LP (1)Xe1	BD*(2)O5 - C27	0.30
		LP (1)Xe1	BD*(1)O6 - C8	0.25
		LP (1)Xe1	BD*(2)O6 - C8	0.30
		LP (1)Xe1	BD*(1)O7 - C18	0.25
		LP (1)Xe1	BD*(2)O7 - C18	0.31
		BD (2) O5 - C27	BD*(1)Xe1 - O3	2.84
		LP (1) O5	BD*(1)Xe1 - O3	0.92
		BD (2) O6 - C8	BD*(1)Xe1 - O2	2.84
		LP (1) O6	BD*(1)Xe1 - O2	0.92
		BD (2) O7 - C18	BD*(1)Xe1 - O4	2.87
		LP (1)O7	BD*(1)Xe1 - O4	0.95
	1:2	LP (1)Xe1	BD*(2) O5 - C16	0.57
		LP (1)Xe1	BD*(2) O6 - C7	0.39
		LP (1)Xe1	BD*(1) O6 - C7	0.29
		BD (2) O5 - C16	BD*(1)Xe1 - O3	3.55
		LP (1)O5	BD*(1)Xe1 - O3	1.37
		BD (2) O6 - C7	BD*(1)Xe1 - O4	3.08
		LP (1) O6	BD*(1)Xe1 - O4	0.92
	1:1	LP (1)Xe1	BD*(1) O5 - C6	0.49
		LP (1)Xe1	BD*(2) O5 - C6	0.70

		BD (2) O5 - C6	BD*(1)Xe1 - O4	4.00
		LP (1)O5	BD*(1)Xe1 - O4	1.41
TMEDA	1:3	LP (1)Xe19	BD*(1) C1 - N25	0.36
		LP (1)Xe19	BD*(1) N25 - C41	0.28
		LP (1)Xe19	BD*(1) C3 - N23	0.36
		LP (1)Xe19	BD*(1) N23 - C73	0.28
		LP (1)Xe19	BD*(1) C14 - N27	0.36
		LP (1)Xe19	BD*(1) N27 - C57	0.27
		LP (1)N25	BD*(1)Xe19 - O20	4.92
		LP (1)N23	BD*(1)Xe19 - O21	4.86
		LP (1)N27	BD*(1)Xe19 - O22	4.83
	1:2	LP (1)Xe12	BD*(1) C1 - N33	0.41
		LP (1)Xe12	BD*(1) C2 - N33	0.25
		LP (1)Xe12	BD*(1) C3 - N34	0.29
		LP (1)Xe12	BD*(1) C24 - N34	0.34
		LP (1)Xe12	BD*(1) N33 - C49	0.38
		LP (1)Xe12	BD*(1) N34 - C45	0.45
		LP (1)Xe12	BD*(1) C7 - N35	0.35
		LP (1)Xe12	BD*(1) C16 - N35	0.29
		LP (1)Xe12	BD*(1) N35 - C37	0.20
		LP (1) N 35	BD*(1)Xe12 - O15	5.41
		LP (1) N 33	BD*(1)Xe12 - O13	6.08
		LP (1) N 34	BD*(1)Xe12 - O14	6.68
	1:1	LP (1)Xe 1	BD*(1) C5 - N12	0.36
		LP (1)Xe 1	BD*(1) C6 - N11	0.33
		LP (1)Xe 1	BD*(1) N11 - C21	0.58
		LP (1)Xe 1	BD*(1) N11 - C25	0.32
		LP (1)Xe 1	BD*(1) N12 - C13	0.61
		LP (1)Xe 1	BD*(1) N12 - C17	0.35
		LP (1) N 11	BD*(1)Xe1 - O4	7.20
		LP (1) N 12	BD*(1)Xe1 - O3	8.15

4.3.6. EDA

The aforementioned observations were additionally corroborated through the Ziegler-Rauk energy decomposition analysis.^[61] The energy decomposition analysis was carried out for all the adducts across the three binding modes (1:1, 1:2, and 1:3). While the absolute interaction energies may vary with different functional/basis set combinations (**Tables S4.5-S4.7**), the same group of solvents were found to constitute the top ten (except DES), with variation in their order, enabling further interpretations. In summary, ignoring the halogen-containing solvents, the attractive interaction consists of approximately 47-64% electrostatic, 26-34% orbital, and 8-24 % dispersion components. For halogenated solvents (DCM, CHCl₃, and CCl₄), the electrostatic nature of NCIs reduces to 35-55%, whereas an increased contribution from dispersion factors (18-43%) was observed. Overall, apart from a few exceptions (highlighted in **Table S4.8**), going from 1:1 to 1:3 mode of binding, the percentage contributions from electrostatic and orbital interactions were found to be decreasing, with

increased contribution from the dispersion interaction. In general, electrostatic interactions remain the dominant contributor for all the cases except for CCl_4 , where the contribution from dispersion interactions overcomes that of the electrostatic (**Table S4.8**). A comparative summary of the energy decomposition analysis for the top three solvents is listed in **Table 4.4**. Notably, the order of interaction energy obtained from EDA varies from the BSSE corrected interaction energy. This difference in the interaction energy from EDA as compared to earlier trends also could be attributed to the BSSE correction, and the variation in the level of theory. Consistent with the interaction energy, BCP and the NBO analysis trend, HMPA shows the highest orbital interaction, as well as electrostatic and dispersion interaction among the top three, for 1:3 adducts, whereas TMEDA was observed to be the highest for 1:2 and 1:1 adducts. Although TEA breaks into the top three adducts for 1:2, and 1:1 binding mode, considering the interaction energy obtained from EDA, it could be attributed to its higher contribution from dispersion as well as orbital interaction. It is also observed that in agreement with the MEP and interaction energy trends, nitrogen donor solvents have a higher percentage contribution from orbital interactions, as compared to oxygen donor solvents when there is a one-on-one comparison, such as DEA vs DEE, TMEDA vs DME, NH_3 vs H_2O (for all three binding modes).

Table 4.4. The energy decomposition analysis (EDA) of selected adducts of XeO_3 with different solvents at the BP86-D3BJ/TZ2P level of theory. Percentage contribution to the total attractive energy is shown below, where electrostatic interactions are denoted as E_{elstat} , orbital interactions as E_{oi} , and dispersion interactions as E_{disp} .

Solvent	Ratio	ΔE	E_{Pauli}	E_{elstat}	%	E_{oi}	%	E_{disp}	%
HMPA	1:3	-64.1	118.3	-91.8	50	-52.4	29	-38.15	21
	1:2	-43.2	81.0	-66.6	54	-36.9	30	-20.59	17
	1:1	-23.2	44.4	-37.7	56	-20.7	31	-9.18	14
DMPU	1:3	-53.7	99.0	-78.3	51	-43.8	29	-30.72	20
	1:2	-36.0	69.0	-55.5	53	-31.3	30	-18.2	17
	1:1	-19.3	37.9	-31.6	55	-18.2	32	-7.48	13
TMEDA	1:3	-55.4	109.0	-80.3	49	-48.1	29	-36.06	22
	1:2	-48.6	102.6	-79.1	52	-46.3	31	-25.76	17
	1:1	-31.6	75.7	-58.8	55	-35.8	33	-12.72	12

4.4. Conclusions

Our probe into the adduct formation between diverse non-aromatic coordinating solvents and XeO_3 has provided crucial insights into the factors dictating their strength. Nitrogen donor solvents were found to have a stronger affinity towards the σ -holes of XeO_3 , as compared to their analogous oxygen donor solvents. The top three solvents which form the strongest adducts with XeO_3 , among the twenty six non-aromatic solvents in the current study, were found to be hexamethylphosphoramide (HMPA with a $\text{O}=\text{P}$ donating site), $\text{N,N}'$ -dimethylpropyleneurea (DMPU with an $\text{O}=\text{C}$ donating site) and tetramethylethylenediamine (TMEDA, a bidentate solvent with two nitrogen donating sites). Other solvents that constitute the top ten list, apart from the experimentally well-explored DMSO ,^[33] are imidazolidinone (DMI), sulfolane (SFO), $\text{N-Methyl-2-pyrrolidone}$ (NMP), diethylamine (DEA), diethylcarbonate (DEC), triethylamine (TEA) and dimethoxyethane (DME). In a happy coincidence, seven out of the top ten solvents identified possess high boiling points ($>100^\circ\text{C}$), with SFO (285°C) being the highest among them. This feature is expected to inhibit solvent evaporation and prevent adduct dissociation – a phenomenon observed experimentally with the low-boiling-point solvent acetone (56°C).^[33] The important role of the $\text{C-H}\cdots\text{O}$ interaction, as well as that of back donation from Xe's LP to the donating group/atom's antibonding orbital, in stabilizing these adducts has also been revealed. Lastly, it was also confirmed from the energy decomposition analysis that these σ hole-mediated interactions are predominantly electrostatic in nature. However substantial contributions from ΔE_{oi} (up to 34%) & ΔE_{disp} (up to 24%) were also noted. In conclusion, our investigation sheds light on the key factors influencing the strength of the aerogen-bonded adducts, highlighting variations in their stability when bound in 1:1, 1:2, and 1:3 configurations. Our findings not only contribute to the broader understanding of sigma hole-mediated non-covalent interactions but also offer insights into the nucleophilicity (coordinating ability) of non-aromatic solvents as Lewis base donors. We note here that there are other factors, such as the possibility of unwanted side reactions,³³ that can influence the choice of the optimal solvent for XeO_3 . Nevertheless, the current work can serve as a guide for experimentalists and aid them in screening for the best solvent(s) for preparing XeO_3 adducts.

4.5. References

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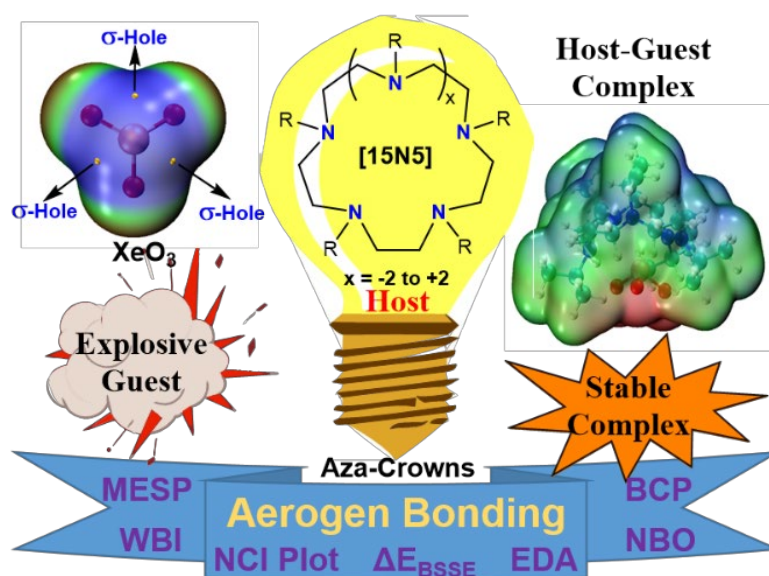
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Chapter-5

Taming XeO_3 with Aza-Crowns



Abstract: Various aza-crowns with different sizes and substituents have been explored computationally as potential hosts for stabilizing the explosive guest xenon trioxide (XeO_3) through σ -hole-mediated aerogen bonding interactions. Interestingly, aza-crowns demonstrate superior binding towards XeO_3 compared to their oxygen and thio counterparts. However, unlike the latter cases, where the binding was found to be increasingly favorable with the increase in the size of the crowns, aza-crowns exhibit a variable size preference for XeO_3 , peaking with aza-15-crown-5, and reducing thereafter with increase in crown size.

5.1. Introduction

Great science often demands sacrifices and encourages people to take risks, as was the case for the discovery of the explosive nature of XeO₃, leading to the hospitalization of Bartlett and Rao.^[1] However, ironically, the curse of σ -holes (a positively charged localized region present at the extension of the Xe=O bond),^[2-4] which is responsible for the explosiveness of XeO₃, could also act as a boon to stabilize it, if XeO₃ were to be provided with an appropriate host.^[5,6] The host could be a Lewis base or an anion willing to share its electrons to quench the electron thirst of the σ -hole, as the aerogen bonding is predominantly electrostatic, similar to the halogen bonds as well as the pnictogen bonds as defined by IUPAC recently.^[7-13] Among the few experimental attempts to stabilize XeO₃ by utilizing this principle, its adduct with 15-crown-5 stands out, achieving high stability and shock insensitivity in comparison to the others.^[14-16] In a continuous effort to further improve the stability of the XeO₃ adducts, different crown ethers, along with their thio analogues, have been investigated computationally.^[17,18] While experimental and computational studies have explored the aerogen bonding interactions of nitrogen based donors with XeO₃,^[2,13,19-21] there have been no reports thus far on macrocyclic nitrogen based donors in this context.

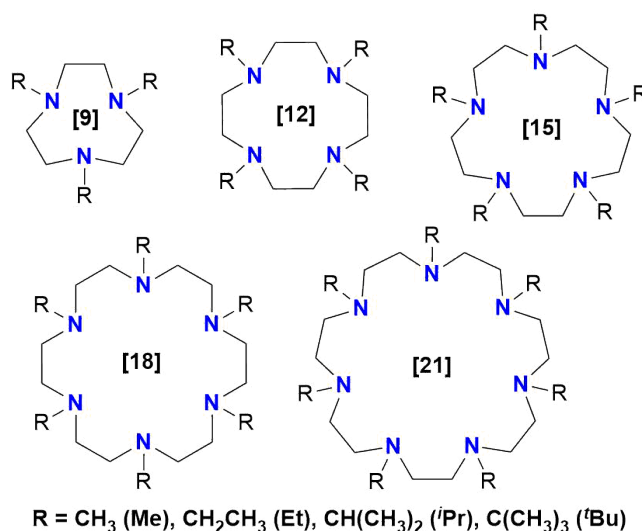


Figure 5.1. Different aza-crowns (with increasing crown size) having different substituents (with increasing steric bulk) used as potential hosts for XeO₃ in this study.

Hence, herein, we have investigated the aza-crowns, which are nitrogen analogues of the crown ethers, as a potential macrocyclic host to stabilize XeO₃ by means of different computational techniques. Our goal is to find the “chosen one”, that is, the best among the pool

of potential aza-crown hosts, explore the leading causes for stabilization, and determine guidelines to minimize the risk associated with an experimental exploration. In addition to their role as polydentate ligands, aza-crowns offer the advantage of having substituents bound to the nitrogen atoms,^[22] whose effect on the strength of host-guest complexes is also investigated in this study, along with the ongoing exploration on the impact of increasing crown sizes. Different alkyl groups (**Figure 5.1**) were considered as the substituents, as they exhibit +I effects that can enhance the nucleophilicity of the nitrogen atoms towards the σ -holes of XeO₃. These groups can also potentially facilitate C-H...O interactions when properly aligned, which could further strengthen the binding of XeO₃.

5.2. Computational Methodology

All the DFT calculations have been performed utilizing the Gaussian 09 program.^[23] Each model was optimized in the gas phase by employing the APFD^[24] functionals along with def2-TZVP basis set, tailed by single point computation at def2-TZVPD basis set.^[25] This specific level of theory was chosen due to its benchmarking as the most reliable combination, as demonstrated through comparison with the experimentally obtained adduct of 15-Crown-5 with XeO₃ by Schrobilgen's research group.^[14] Furthermore, harmonic frequency calculations were performed to confirm all the stationary points as minima. Conformational search analysis has been carried out with Grimme's semi-empirical Conformer–Rotamer Ensemble Sampling Tool (CREST)^[26] at the xTB-GFN2 levels of theory.^[27-29] The counterpoise correction method was employed to obtain more accurate interaction energy (ΔE_{int}) values by correcting the basis set superimposition error (BSSE).^[30] The ΔE_{int} is calculated as the disparity amongst the energy of the adduct/complex & the energy of the isolated monomers in the configuration of the complex. Deformation energies corresponding to each case have also been evaluated. ESP, NCI plot and AIM analysis were executed in the MultiWFN program^[31] & visualized using the Visual Molecular Dynamics (VMD) program.^[32] NBO analysis were carried out as incorporated in Gaussian 09 software module. To enhance the robustness of the study, the second-order perturbation energy ($E^{(2)}$) values were re-evaluated using the NBO 7.0 software package.^[33] For EDA, the BP86 functional with D3(BJ) correction was used together with the TZ2P basis set as implemented in ADF 2022.^[34-37] The frozen core approximation was used and the numerical quality was set to good. A strictly closed-shell fragmentation scheme was chosen. The BSSE corrected interaction energies were also evaluated at the APFD/aug-cc-pVTZ (-PP for Xe) level of theory to take relativistic effect into the consideration.^[38]

5.3. Results and Discussion

5.3.1. MEP Analysis

While the negative potential obtained from the molecular electrostatic potential surface (MEP) analysis does not increase with the size of the substituent from Me to ^tBu (Figures S5.1-S5.5, Table S5.1), natural population analysis (Table S5.2) reveals the expected rise in charge on the nitrogen atoms (Me < Et < ⁱPr < ^tBu). Among the different sizes of aza-crowns (Figure 5.2, Table S5.1), the shared negative potential was found to be highest for aza-18-crown-6 (18N6) with Me, Et, and ⁱPr substituents. Except for ^tBu substituents, a decrease in shared negative potential was observed in the order Me > Et > ⁱPr.

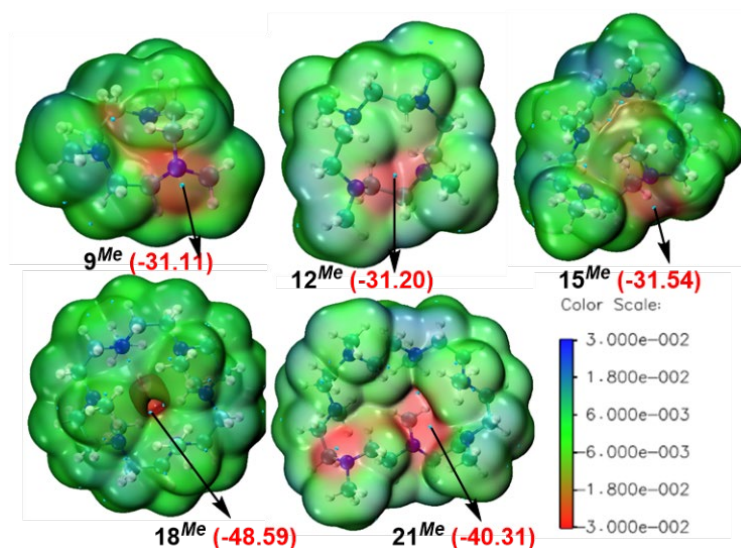


Figure 5.2. The MEP (color scale: RGB, isovalue = 0.001 a.u.) of different aza-crowns with their corresponding highest $V_{s,min}$ in kcal/mol. See Table S1 for details.

5.3.2. Interaction Energies

The interaction energies, accounting for the basis set superposition error (Table 5.1), indicate higher values for the host-guest complexation between aza-crowns and XeO₃ as compared to their thio and oxygen analogues.^[17] Nevertheless, interestingly, in contrast to crown ethers and thio-crown ethers, the interaction energies do not tend to increase with the

increasing aza-crown's size. Instead, they show an increase from aza-9-crown-3 (9N3) to aza-15-crown-5 (15N5), followed by a decrease up to aza-21-crown-7 (21N7), for Me, Et, and ⁱPr substitutions. Among the ^tBu substituted complexes, aza-12-Crown-4 (12N4) shows the highest interaction energy.

Table 5.1. BSSE corrected interaction energies (in kcal/mol) for the complexation of XeO₃ with various aza-crowns, computed at the APFD/def2-TZVPD level of theory. Bracketed values at the APFD/aug-cc-pVTZ (-PP for Xe) level of theory.

ΔE_{BSSE}	Me	Et	ⁱ Pr	^t Bu
9N3	-42.3 (-41.8)	-43.4 (-43.0)	-46.3 (-45.9)	-46.6 (-46.3)
12N4	-52.7 (-52.5)	-53.8 (-53.6)	-52.0 (-52.0)	-53.6 (-53.5)
15N5	-58.2 (-58.2)	-59.4 (-59.4)	-54.9 (-55.0)	-42.5 (-42.5)
18N6	-55.6 (-55.8)	-54.9 (-55.1)	-52.9 (-53.0)	-40.5 (-40.5)
21N7	-50.6 (-50.7)	-51.5 (51.6)	-53.0 (-53.1)	-42.3 (-42.3)

The deformation energies associated with the complexation of aza-crowns with XeO₃ (listed in **Table S5.3**) were observed to be higher (except for 9N3^{Me}) in comparison to their oxygen and thio analogues, which could be attributed to the loss of intramolecular C-H...N interactions present in the parent aza-crowns. Additionally, deformation energies were found to rise with increasing steric bulk of the substituents. With a few exceptions, they were found to increase as the size of the aza-crowns expanded up to 18N6, followed by a decrease for 21N7.

5.3.3. Geometrical Characteristics, WBI and NPA Charge Analysis

The optimized geometries of the host-guest complexes formed by aza-crowns and XeO₃ are depicted in **Figures 5.3, S5.6-S5.10**. An alternative mode of binding was observed for the Me ($\Delta E_{\text{BSSE}} = -50.5$ kcal/mol) and Et ($\Delta E_{\text{BSSE}} = -51.2$ kcal/mol) substituted 21N7 (21N7') cases, where Xe binds to three of nitrogen donor atoms instead of four (**Figure S5.11**). In all

cases, the Xe=O bond lengths were observed to elongate upon complexation. This elongation can be attributed to the allocation of electron density from the LP of nitrogen atoms to the σ -holes located at the antibonding (σ^*) Xe-O orbital.

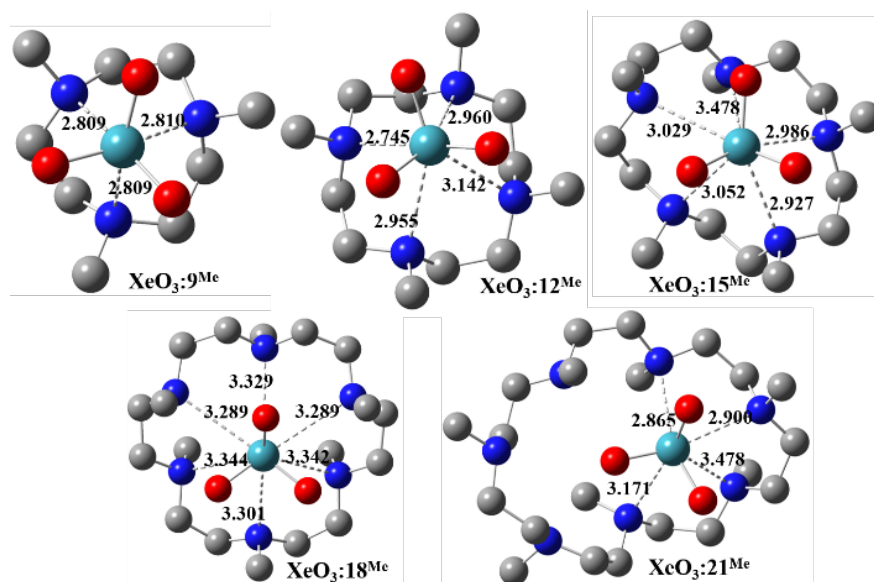


Figure 5.3. Optimized models of host-guest complexes of aza-crowns (Me) and XeO₃ with increasing crown size. Bond distances corresponding to Xe...N interactions are shown in Å. Hydrogen atoms have been omitted for clarity.

Consequently, an increase in the polar covalent nature of the primary Xe=O bonds was observed, which is also reflected by the enhanced charges (natural population analysis), and reduced Wiberg bond indices (WBI) corresponding to Xe and O atoms (**Tables 5.2, S5.4-S5.7**). The secondary bond distances associated with the interacting nitrogen atoms and Xe were found to fall within the range of the sum of their corresponding covalent radii ($\Sigma(\text{Xe-N})_{\text{cov}} = 2.11 \text{ \AA}$) and van der Waals radii ($\Sigma(\text{Xe-N})_{\text{vdW}} = 3.71 \text{ \AA}$, as per Bondi).^[39] It was observed that the Xe...N secondary bond distances increased with the increase in the crown size from 9N3 to 18N6, followed by a decrease for 21N7 and 21N7'. The longer Xe...N distance in the 18N6 complexes can also be attributed to the steric factors, which prevent XeO₃ from approaching the nitrogen donor sites more closely. With a few exceptions, the Xe...N distances generally increased with the increase in the substituent size. The bond orders associated with the secondary Xe...N interactions, as determined from the WBI analysis, align with the trends observed in bond distances (**Tables 5.2, S5.4-S5.7**).

Table 5.2. Bond parameters host-guest complexes of aza-crowns (Me) and XeO₃. The electron density (ρ) and the Laplacian of electron density ($\nabla^2\rho$) values of the BCPs corresponding to the aerogen bonds are listed.

Me	Xe-O (in Å)	Xe...N (in Å)	WBI (Xe...N)	ρ (in a.u.)	$\nabla^2\rho$ (in a.u.)
9N3	1.776	2.809	0.0555	0.038	0.073
	1.776	2.809	0.0554	0.033	0.073
	1.776	2.810	0.0552	0.033	0.073
12N4	1.774	2.745	0.0767	0.036	0.074
	1.773	2.960	0.0393	0.024	0.056
	1.772	2.955	0.0374	0.024	0.057
		3.142	0.0185	0.017	0.044
15N5	1.775	3.029	0.0431	0.020	0.050
	1.772	3.052	0.0250	0.020	0.047
	1.772	2.927	0.0483	0.025	0.058
		2.986	0.0435	0.025	0.052
		3.478	0.0071	0.008	0.024
18N6	1.766	3.289	0.0221	0.012	0.031
	1.766	3.342	0.0122	-	-
	1.766	3.301	0.0213	0.011	0.035
		3.344	0.0121	-	-
		3.290	0.0221	0.012	0.031
		3.329	0.0127	0.011	0.030
21N7	1.760	2.900	0.0578	0.027	0.058
	1.769	2.865	0.0569	0.029	0.063
	1.775	3.773	0.0026	-	-
		3.478	0.0072	0.008	0.024
		3.171	0.0288	0.016	0.038
		4.439	0.0011	-	-
		5.235	0.0004	-	-

5.3.4. NCI and BCP Analysis

The NCI plot analysis reveals a gradual decrease in aerogen bonding strength, indicated by a colour shift on the surface between nitrogen atoms and Xe, transitioning from bluish to greenish from 9N3 to 18N6, followed by an increase for 21N7 and 21N7', albeit with less coordination with the donor atoms. Similar to observations in crown ethers, *C-H...O* interactions were found to increase with the increase in the crown size.^[17] A gradual decrease in aerogen bond strength and an increase in *C-H...O* interactions were also noted with the increase in the substituent size, except for ^tBu substituted aza-crowns, as illustrated in the NCI plot analysis (Figures 5.4, S5.6-S5.11).

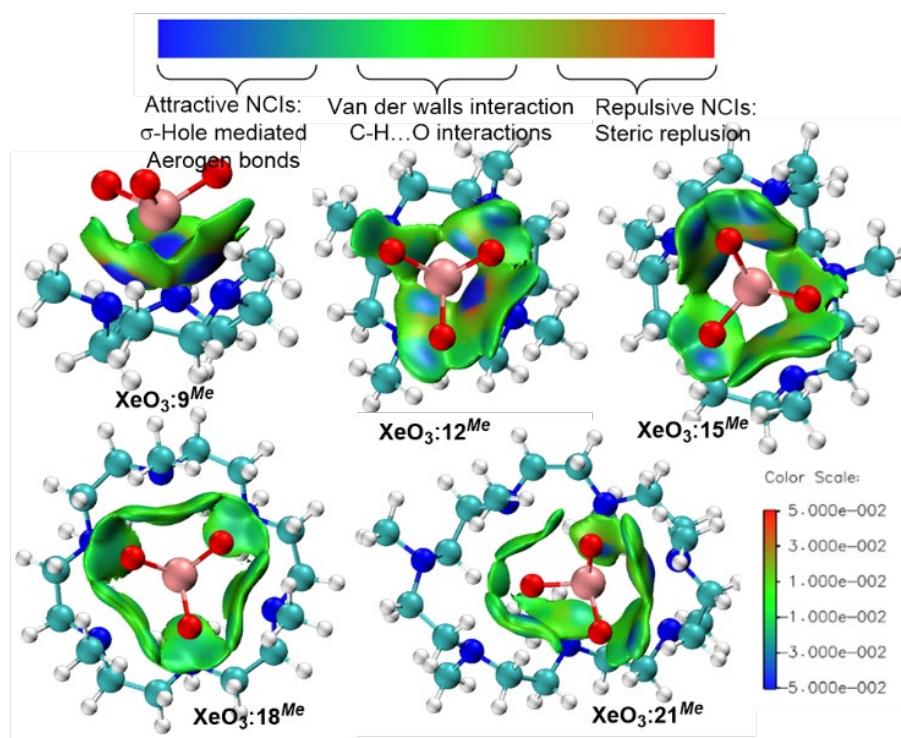


Figure 5.4. NCI plots (IGM method: intramolecular interactions are excluded for clarity) of the host-guest complexes of aza-crowns (Me) and XeO_3 with increasing crown size (isovalue = 0.01 a.u.).

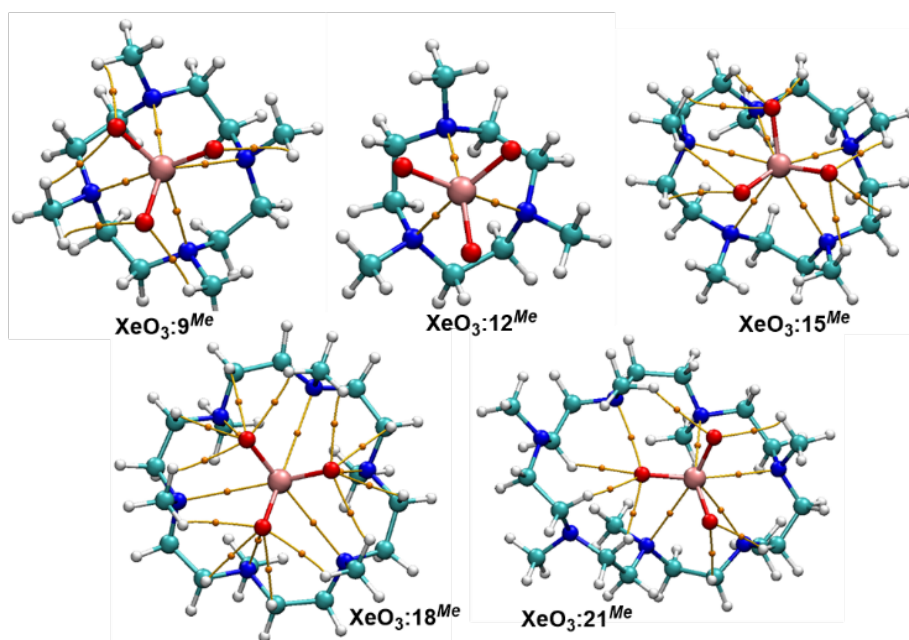


Figure 5.5. Bond critical points (intramolecular interactions are excluded for clarity) corresponding to the interactions between the XeO_3 with various aza-crowns (Me) in their host-guest complexes. Please see the **Figures S5.6-S5.11** for associated values.

The bond critical points (BCPs) obtained from the AIM analysis (**Figures 5.5, S5.6-S5.11**) align with the NCI plot analysis. In the case of 9N3 (for all substituents), three BCPs corresponding to aerogen bonds between the three nitrogen donor atoms and xenon were observed. Similar observations were made for 12N4 (four BCPs). However, for the ^tBu substituted aza-crowns, as the crown size increases to 15N5, 18N6, and 21N7, only two BCPs were obtained for aerogen bonding, indicating the binding of xenon with only two of the nitrogen donor atoms *via* two σ -holes of XeO₃, leaving the third σ -hole unquenched. This explains why, among ^tBu substituted aza-crowns, 12N4, and not 15N5, exhibits the strongest binding with XeO₃, even though the supporting strength from C-H...O interactions were observed to be increased for larger crowns. Among different substituents in 18N6, six BCPs were observed only for ⁱPr (**Figure S5.9**). In general, ρ and $\nabla^2\rho$ values associated with BCPs for aerogen bonds were found to decrease with increase in the size of aza-crowns from 9N3 to 18N6, followed by an increase for 21N7 and 21N7'. With the exception of ^tBu substituted aza-crowns, these values were also seen to decrease with the increasing size of the substituents. It is to be noted that these changes were observed to be marginal for 21N7'.

5.3.5. NBO Analysis

The NBO analysis further reveals that among the various orbital interactions between the aza-crowns and XeO₃, the aerogen bonding interaction, which involves the transfer of electron density from the LP of the nitrogen atom to the antibonding Xe-O orbital, is the dominant interaction (**Tables 5.3 and S5.8-S5.10**). Additionally, a weak interaction corresponding to back-donation from Xe's LP to the antibonding C-N orbital was also observed. Both of these interactions were found to be weakest in the case of 18N6 due to the longer Xe...N distance. It is noteworthy that the orbital interactions for the complexes of aza-crowns were also found to be stronger, as indicated by higher E^2 energy values compared to their oxygen analogues.^[17] When compared to thio analogues, smaller aza-crowns (9N3, 12N4, 15N5) exhibit better orbital interactions, whereas 18N6, 21N7, and 21N7' show weaker orbital interactions due to the steric hindrance of additional substituents, leading to their distorted binding nature. Additionally, it was observed that an increase in the size of the substituents led to lower orbital interaction, with a few exceptions. With the exception of the ^tBu substituted complex and 21N7^{Et}, the second order perturbation energy of C-H...O interactions was observed to increase from 9N3 to 15N5, followed by a decrease for 18N6, and then an increase again for 21N7 and 21N7'.

Table 5.3. Natural bond orbital (from NBO 7.0) analysis of complexes of different aza-crowns with XeO₃ at the APFD/def2-TZVPD level of theory. E² (in kcal/mol) represents sums of second-order perturbation energy values (Threshold = 0.10 kcal/mol).

<i>Me</i>	Donor	Acceptor	E ²
9N3	LP N	BD* Xe – O	18.32
	LP Xe	BD* C – N	2.22
	LP O	BD* C - H	1.58
12N4	LP N	BD* Xe – O	20.21
	LP Xe	BD* C – N	3.05
	LP O	BD* C - H	4.48
15N5	LP N	BD* Xe – O	17.29
	LP Xe	BD* C – N	3.34
	LP O	BD* C - H	7.22
18N6	LP N	BD* Xe – O	9.17
	LP Xe	BD* C – N	-
	LP O	BD* C - H	6.77
21N7	LP N	BD* Xe – O	16.37
	LP Xe	BD* C – N	1.9
	LP O	BD* C - H	8.65
21N7'	LP N	BD* Xe – O	18.27
	LP Xe	BD* C – N	2.07
	LP O	BD* C - H	14.76

5.3.6. EDA

The EDA analysis reveals that aza-crowns exhibit enhanced electrostatic, orbital, and dispersive interactions compared to crown ethers (**Tables S5.11-S5.14**) in all cases.^[17] As illustrated in **Figure 5.6** (Me substituted aza-crowns), despite a decrease in the Pauli repulsion, a reduction in interaction energy was observed for the 18N6 complex due to lower contributions from stabilizing orbitals and electrostatic interactions. This could be the consequence of the inimical steric interactions, which is reflected in the EDA, resulting in one favourable effect - the reduction of the Pauli repulsion, and two unfavourable effects: the decrease in the orbital and electrostatic interactions. This eventually leads to the overall reduction in the interaction energy for 18N6 complexes. Although both factors slightly improved for 21N7, an increase in Pauli repulsion led to an overall decrease in interaction energy for the related complex compared to 15N5. Similar trends were observed for Et and ⁱPr substituted complexes. This also explains why 15N5 (Me, Et, and ⁱPr) exhibits the highest binding affinity towards XeO₃. It is noteworthy that while the interactions between aza-crowns and XeO₃ are primarily electrostatic (47-54%), there is also a substantial contribution from orbital (27-33%) and dispersion (14-24%) interactions.

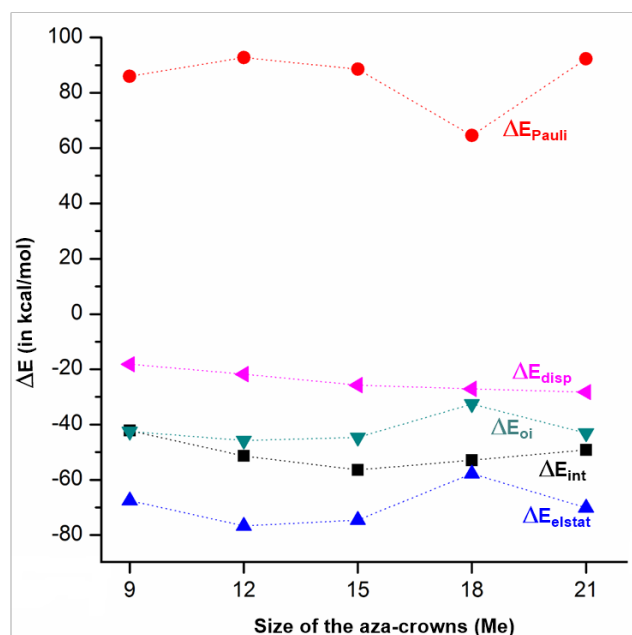


Figure 5.6. The EDA evaluated at the at the BP86-D3BJ/TZ2P level of theory for the host-guest complexes of aza-crowns (Me) and XeO₃. ΔE_{int} = Interaction energy, ΔE_{Pauli} = Pauli repulsion, ΔE_{elstat} = electrostatic interactions, ΔE_{Oi} = orbital interactions, and ΔE_{disp} = dispersion interactions.

5.4. Conclusions

In summary, aza-crowns exhibit a remarkably high binding affinity towards the σ -holes of XeO₃, positioning them as promising hosts for stabilizing the highly explosive and shock-sensitive XeO₃. Smaller aza-crowns (9N3, 12N4, and 15N5) outperform their oxygen and thio analogues not only in terms of interaction energy but also in their individual components (electrostatic, orbital, and dispersion) during complexation with XeO₃. Similar to crown ethers, aza-crowns demonstrate an increase in the secondary bond distances and $C-H\cdots O$ interactions with increasing crown sizes. However, unlike crown ethers, the increased number of $C-H\cdots O$ interactions fails to compensate for the diminished strength of the primary binding force – the σ -hole mediated aerogen bonds associated with larger aza-crowns (18N6 and 21N7). This leads to size selectivity of aza-crowns towards XeO₃, as evidenced by the case of aza-15-crown-5 (Me, Et, and ⁱPr substituted 15N5). Overall, our findings provide new insights, not only into the σ -hole mediated host-guest complexes of aza-crowns, but also into the broader aspects of molecular recognition and supramolecular chemistry.

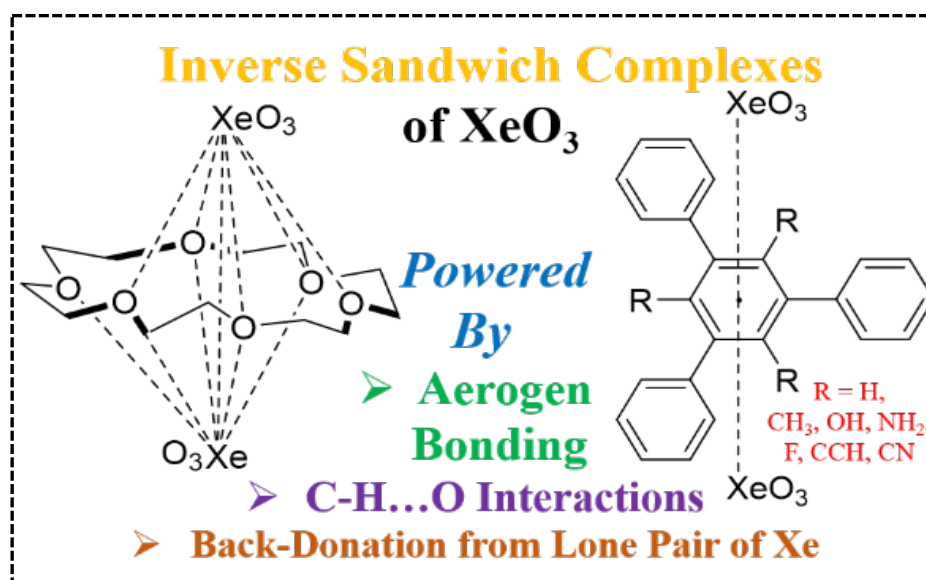
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Chapter-6

Unveiling the Inverse Sandwich Complexes of XeO₃



Abstract: This chapter introduces the design of inverse sandwich (iSw) complexes incorporating a noble gas compound: xenon trioxide (XeO₃). Through comprehensive computational analyses, we have investigated the critical factors influencing their stability by employing a variety of state-of-the-art computational tools. We demonstrated that the coordination number of xenon in the iSw complex of XeO₃ with 18-crown-6 is influenced by the presence of a rare, weakly stabilizing Xe...Xe interaction between the XeO₃ molecules. Furthermore, we observed that the stability of iSw complexes of 1,3,5-triphenylbenzene (TPB) and its derivatives is not solely attributed to aerogen bonding, but also involves contributions from C-H...O interactions and back donation from the lone pair of Xe to the antibonding C-C orbitals of TPB. Additionally, the significant contributions from orbital interactions and dispersion interactions in the TPB derivatives highlight the multifaceted amphoteric properties of XeO₃ and reveal that the iSw complexes of TPB and derivatives are not predominantly governed by electrostatic interactions, contrary to conventional belief.

6.1. Introduction

The allure of novel sandwich and inverse sandwich complexes continues to captivate researchers, expanding the horizons of organometallic chemistry.^[1] Sandwich complexes made their debut with the serendipitous discovery of ferrocene in 1951,^[2] whereas the terminology of “inverse sandwich” was devised by Professor Hoffmann much later in 1976,^[3,4] to label complexes featuring a planar ring coordinated by Lewis conjugates, both above and below the plane of the ring. The initial experimental proof for such kind of inverse sandwich (iSw) complexes was provided by Schmidbaur.^[5,6,7] Intriguingly, the stability of the first experimentally obtained inverse sandwich complex, $[\text{C}_6(\text{CH}_3)_6][\text{BiCl}_3]_2$, and the subsequent discovery of iSw complexes of group 15 halides, can be attributed to pnictogen bonding *via* σ -hole interactions, a concept yet to be recognized at that time.^[8] A σ -hole denotes a confined area of positive electrostatic potential situated on a σ^* orbital along the extension of a covalently bound parent atom with an atom/group of electron-withdrawing nature. Initially introduced for halogen bonds,^[9] this idea was later extended to chalcogen, pnictogen, tetrel, triel, spondium, regium, and aerogen bonds.^[10-18]

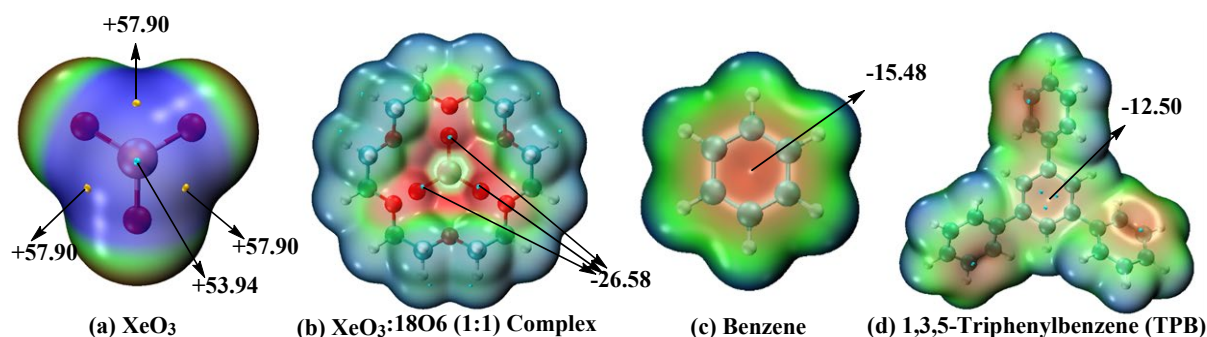
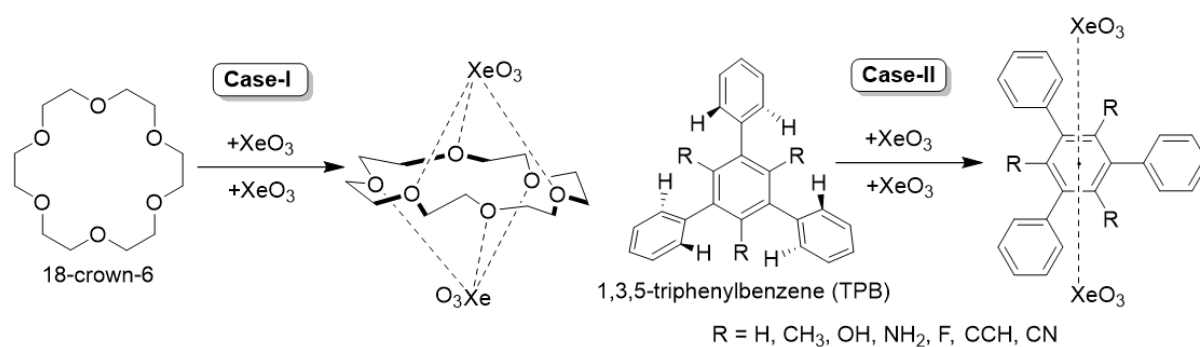


Figure 6.1. Molecular electrostatic potential (MEP) plots of (a) XeO_3 , (b) 1:1 complex of XeO_3 and 18-crown-6, (c) benzene, (d) 1,3,5-triphenylbenzene, produced at the APFD/def2-TZVPD level of theory. The plots were generated utilizing the RGB color scale (isovalue 0.001 a.u.), where blue and red depict the positive and negative regions, respectively, while green signifies the intermediate zone between them.

The term ‘aerogen bonding’ was introduced by the group of Bauza and Frontera to delineate the σ -hole interactions of noble gas compounds.^[12] Among the recipients of aerogen bonding stabilization is the xenon trioxide (XeO_3) molecule, notorious for its instability in the solid state due to its high shock sensitivity and explosiveness,^[19,20] attributable to the presence

of sigma holes (depicted as orange spheres in **Figure 6.1a**).^[21,22] The hazardous nature of XeO_3 makes computational studies an ideal means of exploring new chemistry with this important compound, prior to experimental investigations. While investigating different crown ethers for stabilizing the explosive XeO_3 ,^[23-25] we realized that 18-crown-6 (18O6) provides a distinctive binding site, where three alternating oxygen donor atoms are bound to XeO_3 *via* three σ -holes (in a 1:1 complex), and the remaining three free oxygen atoms face the opposite side (**Figure 6.1b**), making them available for further binding. The availability of these free oxygen donor atoms, in principle, should allow another XeO_3 to approach them to quench its electron-deficient σ -holes, which could lead to an inverse sandwich complex of XeO_3 . Remarkably, in the rapidly evolving field of inverse sandwich complexes,^[26-31] no reports of such complexes involving noble gas compounds have surfaced, to the best of our knowledge.

This further motivated us to search for potential hosts capable of providing a uniform nucleophilic donating center, preferably binding with three σ -holes at the top and three σ -holes at the bottom to allow complexation with XeO_3 . One of the usual suspects for such a role is arenes; however, the question arises: which arene to choose? Simple benzene (**Figure 6.1c**) could potentially host two pyramidal AB_3 -type molecules with electron-deficient σ -hole centers. The 1:1 complexes of XeO_3 with benzene and its derivatives have been previously explored;^[32,33] however, they lacked secondary support *via* C-H...O interactions, which has proven to be crucial in enhancing the stability of such aerogen bonding complexes.^[25,34,35] In our quest for such a host, we came across a highly intriguing benzene derivative, 1,3,5-triphenylbenzene (TPB-H), which was utilized to synthesize an inverse sandwich complex of $\text{Ca}(\text{THF})_3$.^[36] It is noteworthy that the binding nature of calcium to the π -center was entirely different from the context of this study, leading to a debate over the true oxidation states of calcium and the existence of Ca-Ca interactions through the π -center.^[37-39]



Scheme 6.1. Proposed inverse sandwich complexes of XeO_3 and the ligands/hosts used in this study.

However, the TPB-H ligand in its unperturbed state (**Figure 6.1d**) satisfies both criteria for hosting two XeO₃ molecules to form an inverse sandwich complex: (1) the central π -ring provides the binding site for the sigma holes of XeO₃, and (2) the substituent phenyl groups can provide secondary C-H...O interactions. Keeping these parameters in mind, we investigated the σ -hole mediated complexation between 1,3,5-triphenylbenzene (TPB) and XeO₃, leading to the formation of an inverse sandwich complex between them. Furthermore, different electron withdrawing and donating groups were carefully chosen, satisfying the criterion that they are planar to the central ring, as any large deviation from planarity might lead to distortion in the formation of the desired inverse sandwich complex (**Scheme 6.1**). The factors governing the stability of these inverse sandwich complexes of XeO₃ have been investigated using various computational tools.

6.2. Computational Methodology

Gaussian 09 suite of programs was employed to carry out all the density functional theory (DFT) calculations.^[40] All the models were optimized by utilizing the APFD^[41] functionals in combination with the def2-TZVPD basis set in gas phase.^[42] This choice of theory was made based on its benchmarking as the most reliable combination, particularly in comparison to the experimentally derived adduct of 15-Crown-5 with XeO₃ by Schrobilgen's research group.^[23] Additionally, all the stationary points were confirmed to be minima by conducting harmonic frequency calculations. Grimme's semi-empirical Conformer–Rotamer Ensemble Sampling Tool (CREST)^[43] at the xTB-GFN2 levels of theory was also employed to carry out Conformational search analyses.^[44-46] In order to obtain more accurate interaction energy (ΔE_{int}) values, the counterpoise correction method was applied to correct for basis set superimposition error (BSSE).^[47] For each complexation the deformation energies required by the hosts were also computed. The typical accuracy level of the reported energy values is ± 0.5 kcal/mol. *Ab initio* molecular dynamics (AIMD) simulations were conducted using the GPU-based TeraChem software package for a duration of 50 picoseconds at 298.15 K with a time step of 0.5 femtoseconds to assess the stability of the proposed iSw complexes.^[48] The simulations employed the ω B97X functional along with 6-31+G(d) basis set, except Xe, for which the crenbl_ecp basis set was utilized. This specific combination of functional and basis set was chosen based on recommendations from TeraChem support, given the limited availability of suitable level of theory. MultiWFN program^[49] was utilized to generate and evaluate ESP, NCI plot and AIM analysis along with the Visual Molecular Dynamics (VMD)

software for visualization.^[50] NBO analysis were performed using the Gaussian 09 module. The BP86-D3BJ/TZ2P^[51,52] level of theory was employed to carry out energy decomposition analysis (EDA) as implemented in ADF 2023.101.^[53] A strictly closed-shell fragmentation scheme (three fragments: the host and 2 XeO₃ units for iSw complexes) was chosen along with the ZORA relativistic effect, frozen core approximation, and good numerical quality for the EDA.

6.3. Results and Discussion

6.3.1. MEP Analysis

Analysis of noncovalent interactions (NCIs) can be effectively conducted through the examination of the molecular electrostatic potential (MEP), given that NCIs are predominantly columbic in nature.^[54] It's important to highlight that MEP reflects not only the influence of electrons but also that of nuclei.^[55] **Figure 6.1a** shows the computed MEP plot of XeO₃ confirming the presence of three σ -holes at the extension of Xe-O bond. These σ -holes are represented by the orange dots residing in the electron deficient region, as indicated by the blue color. The $V_{s,max}$ value associated with the σ -holes of XeO₃ computed at the APFD/def2-TZVPD level of theory closely matched earlier reported values at the MP2/aug-cc-pVTZ.^[12] Furthermore, it should be noted that an area of accumulated positive charge was observed at the position of the Xe's LP, previously assumed to be the site of the σ -hole, as indicated by the blue dot in **Figure 6.1a**.^[12, 22]

Figure 6.1b confirms the presence of three unbound oxygen atoms serving as electron-rich donors (blue dots) in the 1:1 complex (mono) of XeO₃ with 18-crown-6 (18O6). As anticipated, the electron density was observed to be withdrawn from central π -ring of TPB-H as compared to the benzene ring (**Figure 6.1c,d**), due to the presence of three electron-withdrawing phenyl groups. The $V_{s,min}$ corresponding to the central π -ring of the substituted TPB ligands follow the trend: CN < F < CCH < OH $\approx$ H < CH₃ < NH₂, as depicted by **Figure 6.2**.

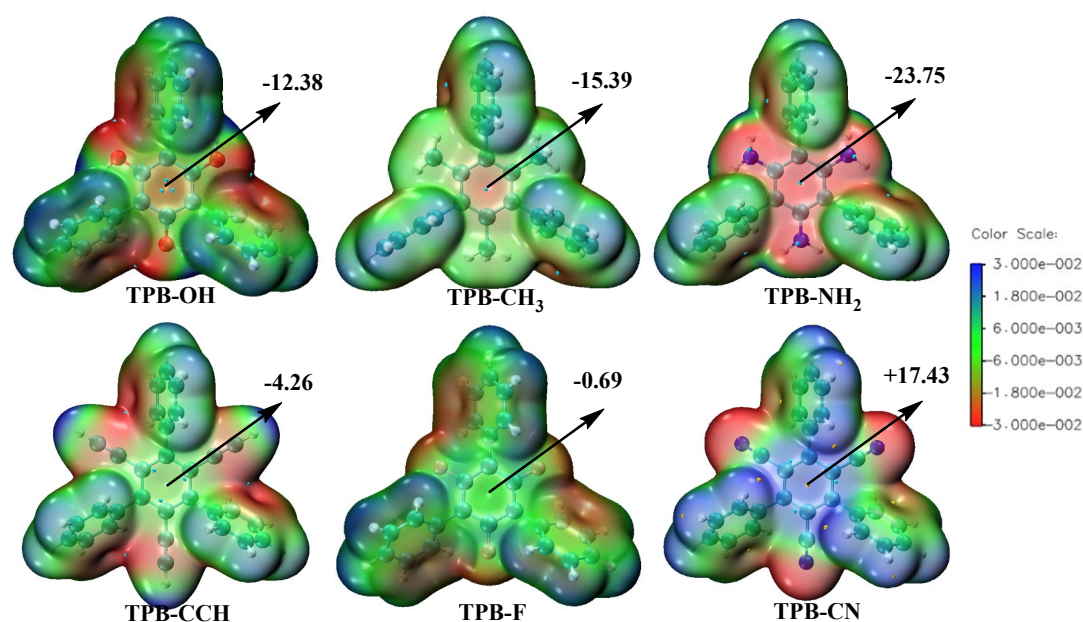


Figure 6.2. Chosen MEPs of the central arene ring along with their corresponding energy values at minima ($V_{s,min}$ in kcal/mol). The plots were generated utilizing the RGB color scale (isovalue 0.001 a.u.), where blue and red depict the positive and negative regions, respectively, while green signifies the intermediate zone between them.

6.3.2. Interaction Energies

Table 6.1. Interaction energies (ΔE in kcal/mol), incorporating the counterpoise (BSSE) corrections calculated at the APFD/def2-TZVPD level of theory, along with the deformation energies (ΔE_{deform}) associated with the hosts upon complexation. (*values obtained from chapter 3)^[25]

Hosts	1:1 (Mono)		1:2 (iSw)	
	ΔE_{BSSE}	ΔE_{deform}	ΔE_{BSSE}	ΔE_{deform}
18O6	-40.2*	1.5*	-72.0	4.5
TPB-NH ₂	-29.6	0.7	-49.7	1.9
TPB-CH ₃	-23.6	0.7	-40.8	1.2
TPB-OH	-22.1	0.5	-37.8	0.9
TPB-H	-18.3	0.3	-32.1	0.7
TPB-CCH	-16.5	0.1	-29.8	0.3
TPB-F	-14.7	0.3	-25.6	0.7
TPB-CN	-10.3	0.1	-18.5	0.2

The evaluation of BSSE corrected interaction energies for all adduct formations was conducted as shown in **Table 6.1**. The 1:1 complexes are denoted as Mono, while the 1:2

inverse sandwich complexes are labeled as iSw. The interaction energies exhibited a similar trend in both the Mono and iSw complexes: $\text{CN} < \text{F} < \text{CCH} < \text{H} < \text{OH} < \text{CH}_3 < \text{NH}_2$. It is noteworthy that TPB-OH, which had a negligible difference in MEP compared to TPB-H, demonstrated favorability by 3.8 kcal/mol ($\Delta\Delta E_{\text{BSSE}}$) for Mono and 5.7 kcal/mol ($\Delta\Delta E_{\text{BSSE}}$) for the iSw complexes of XeO_3 . Interestingly, the interaction energy of XeO_3 was observed to be more favorable for 1:1 complexes of TPB (-H, -F, -CCH) compared to benzene ($\Delta E_{\text{BSSE}} = -13.0$ kcal/mol), despite the withdrawal of electron density from the central ring. It was observed that very less deformation energy was consumed by the TPB ligands for complexation with XeO_3 , which is <1.0 kcal/mol for Mono and <2.0 kcal/mol for iSw complexes. For 18-crown-6, a notably strong interaction with XeO_3 was observed for both the Mono and the iSw cases. This high interaction energy enables 18O6 to offset the necessary deformation energy for complexation. These patterns discussed above imply that MEPs alone cannot serve as the exclusive indicator of such noncovalent interactions. Consequently, additional computational tools were utilized to gain insights into the factors influencing the interaction energy for the iSw complexes of XeO_3 .

6.3.3. Structural Characteristics, WBI, and NPA Charge Analysis

For all the complexes, the optimized geometries, along with their respective primary Xe-O bond lengths, secondary $\text{Xe}\dots\text{X}$ ($\text{X}=\text{O}/\text{C}$) bond distances, Wiberg bond indexes, and charge analysis values obtained from natural population analysis, are illustrated in **Figures S6.1-S6.7** (for Mono) and **Figures S6.8-S6.15** (for iSw). A comparative analysis of the aforementioned parameters is also presented in **Table 6.2** for the TPB derivatives. AIMD simulations confirmed the stability of the iSw complex of 18-crown-6 and XeO_3 , which remained intact throughout the 50 ps simulation at 298.15 K (i.e., XeO_3 did not dissociate). In the case of the iSw complex of TPB-H, XeO_3 was observed to hover around the central arene ring for up to 21 ps before relocating (one of the XeO_3) to a neighboring phenyl group for the remainder of the simulations. The optimized shifted complex (**Figure S6.16**) was found to be 1.7 kcal/mol more favorable ($\Delta\Delta E_{\text{BSSE}}$) than the proposed inverse sandwich structure. Nevertheless, the stability of the inverse sandwich complex of TPB-H for up to 21 ps was encouraging, prompting further investigation into iSw complexes. Although, upon lowering the temperature to 273.15 K (0°C), both XeO_3 remained with the central arene ring throughout the entire 50 ps simulation. **Figure 6.3** depicts the optimized geometry for the iSw complexes of 18-crown-6 (18O6) and TPB-H.

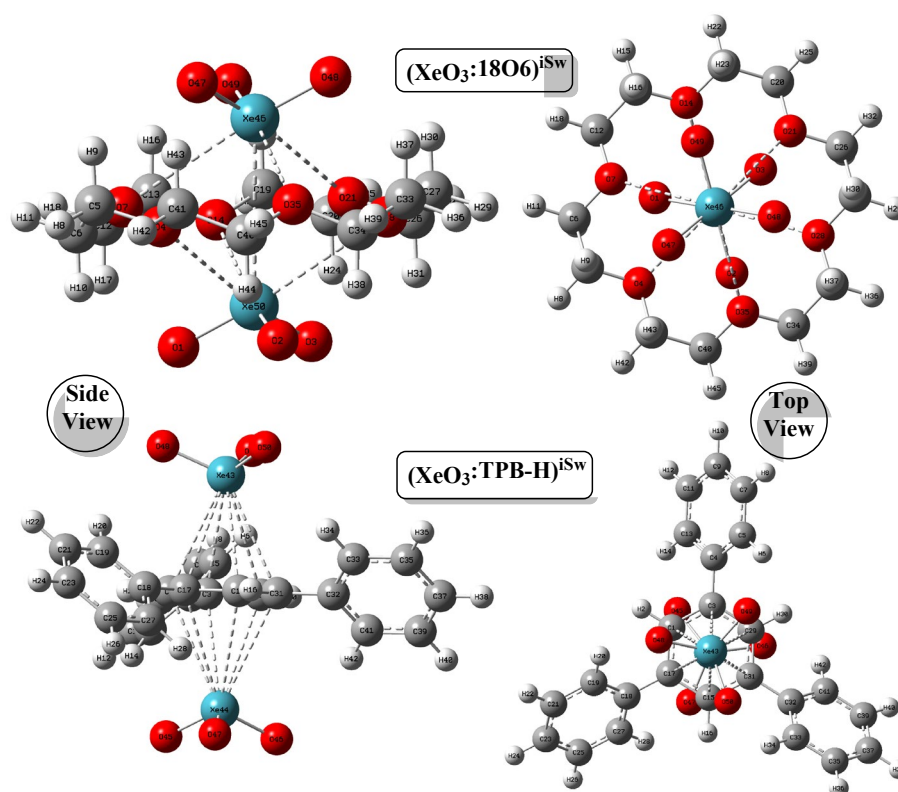


Figure 6.3. Optimized geometries of the inverse sandwich complexes involving XeO_3 with 18-crown-6 (top) and with TPB-H (bottom).

Upon complex formation, Xe-O bonds were observed to be elongated for both the cases (Mono and iSw). The intermolecular distances of secondary $\text{Xe}\dots\text{X}$ ($\text{X}=\text{O}/\text{C}$) interactions, illustrated in **Figures S1-S16**, were found to be lower than sum of their respective vdWs radii ($\Sigma(\text{Xe}-\text{O})_{\text{vdW}} = 3.68 \text{ \AA}$, $\Sigma(\text{Xe}-\text{C})_{\text{vdW}} = 3.86 \text{ \AA}$, as per Bondi)^[56] across all scenarios. Intriguingly, in the iSw complex of 18O6 (**Figure S15**), the $\text{Xe}\dots\text{Xe}$ distance measured $3.82 \text{ \AA}$, falling lower than the sum of their corresponding vdWs radii ($\Sigma(\text{Xe}-\text{Xe})_{\text{vdW}} = 4.32 \text{ \AA}$).^[56] This suggests the potential existence of a rare $\text{Xe}\dots\text{Xe}$ interaction, which could be one of the reasons for the slight tilt of XeO_3 away from the central axis of 18O6, unlike its 1:1 counterpart.^[24,25]

The $\text{Xe}\dots\text{Xe}$ distance for the iSw complexes of TPB derivatives was observed to be much longer, following the reverse pattern compared to the interaction energies: $\text{CN} > \text{F} > \text{CCH} > \text{H} > \text{OH} > \text{CH}_3 > \text{NH}_2$. This further supports the notion that the primary force driving the formation of the iSw complexes is the σ -hole-mediated aerogen bonding, where stronger interactions lead to shorter $\text{Xe}\dots\text{Xe}$ distances. The distance of Xe from the center of the central arene ring also follows a similar trend as mentioned above. Interestingly, the $\angle\text{O}-\text{Xe}-\text{Xe}-\text{O}$

dihedral angle around the C1 atom was also observed to follow a similar trend, except for TPB-NH₂ and TPB-F.

Table 6.2. Geometrical parameters of different inverse sandwich complexes of XeO₃. Xe... π represents the distance (in Å) of Xe from the centre of the central π -ring. C $^{\pi}$ represents the carbon atoms of central π ring and avg. represents the average values.

Hosts	Xe-O (avg.)	Xe...Xe	Xe... π	<O-Xe- Xe-O	NPA (avg.)		WBI (avg.) Xe...C $^{\pi}$
					Xe	O	
Only XeO ₃	1.760	-	-	-	2.765	-0.922	
TPB-NH ₂	1.767	5.750	2.857	32.12	2.835	-0.955	0.016
TPB-CH ₃	1.765	5.840	2.928	29.41	2.844	-0.946	0.012
TPB-OH	1.764	5.879	2.942	33.84	2.826	-0.946	0.012
TPB-H	1.763	5.967	2.984	40.54	2.828	-0.941	0.010
TPB-CCH	1.762	6.052	3.026	43.53	2.831	-0.936	0.008
TPB-F	1.763	6.059	3.030	37.15	2.811	-0.935	0.009
TPB-CN	1.762	6.202	3.101	49.00	2.811	-0.926	0.007

Consistent with the observed bond elongation, a decrease in the Wiberg bond indices (WBI)^[57] of Xe and O was observed during complexation. For comparative purposes, **Table 6.2** presents the WBI values as averages for the Xe...C $^{\pi}$ interaction, as XeO₃ binds to the central arene (π) ring in an η^6 fashion. However, individual WBI values are detailed in the ESI (**Figures S6.1-S6.15**). The average bond orders of Xe...C secondary interactions were found to mirror the same order as the interaction energies, except for the case of TPB-F. It was also observed that the bond orders corresponding to the carbon atoms with phenyl substituents are slightly higher than those relate to the carbon atoms with the varying functional groups. Interestingly, the WBI value corresponding to the Xe...Xe interaction in (XeO₃:18O6)^{iSw} complex was found to be 0.77, which further indicates the presence of a rare Xe...Xe interaction. Moreover, natural population analysis indicated that, upon complex formation, the charges on Xe and O within XeO₃ increased, suggesting enhanced polar-covalent character in the primary Xe-O bonds of XeO₃.

6.3.4. NCI and AIM Analysis

To obtain further insights into the nature of interaction between XeO₃ with 18O6 and TPB derivatives, analyses of noncovalent interaction (NCI) plots were conducted (refer to

Figures 6.4, S6.17, and S6.18).^[58] These analyses revealed that, in addition to conventional aerogen bonds (such as the interaction between the host's donor atom – oxygen for 18O6, carbon atoms of the central arene ring for TPBs – and Xe), there are attractive regions indicating $C-H\cdots O$ interactions. Furthermore, a green region suggesting a weak noncovalent interaction between $Xe\cdots Xe$ in the $(XeO_3:18O6)^{iSw}$ complex was also observed, confirming previous observations. For TPB derivatives, the intensity of the red region indicating repulsive interactions at the center of the arene ring linking both XeO_3 molecules followed similar trends with the interaction energies (refer to **Figures S6.17-S6.18**), intensifying with the increase in interaction energy and shorter $Xe\cdots Xe$ distance, and diminishing with the decrease in interaction energy and longer $Xe\cdots Xe$ distance. It is also to be noted that additional regions of greenish surface indicative of weak attractive interactions were uniformly observed between XeO_3 and the substituted phenyl ring, both at the top and at the bottom.

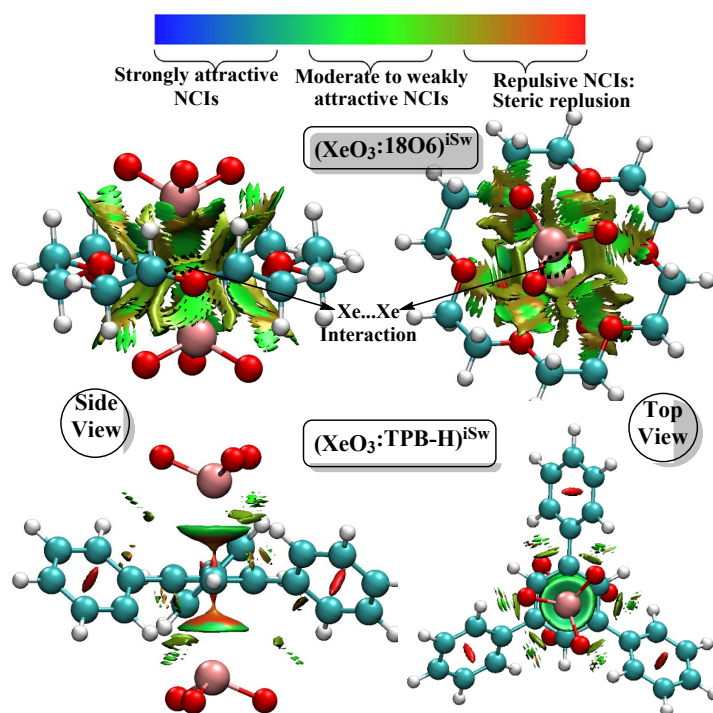


Figure 6.4. Noncovalent interaction (NCI) plots (isovalue 0.5 a.u.) for the inverse sandwich complexes involving XeO_3 with 18-crown-6 (top) and with TPB-H (bottom).

The examination of bond critical points (BCPs, indicated by orange sphere) derived from the AIM analysis of the $(XeO_3:18O6)^{iSw}$ complex reveals the intriguing binding nature of the inverse sandwich complex. The slight distortion of XeO_3 , as discussed in section 3.3, enables Xe to bind with five of the oxygen atoms (resulting in 5 BCPs between each Xe and

the 18O6) both at the top and bottom (**Figure 6.5**), elevating its coordination number to 8 at each xenon center, unlike the 6 coordination number observed in the 1:1 complex. Additionally, one BCP corresponding to Xe...Xe interaction was also observed. In the case of TPB-H (**Figures 6.5**) three BCPs were noted between each Xe and the three carbon atoms (which are subjected to substitution by different groups) of the central arene ring. Each oxygen atom was found to be associated with one BCP corresponding to $C-H\cdots O$ interaction with the C-H of the substituent phenyl group. Additionally, three ring critical points (RCP, indicated by yellow spheres) were obtained between each Xe and the C-C bond of the central arene ring.

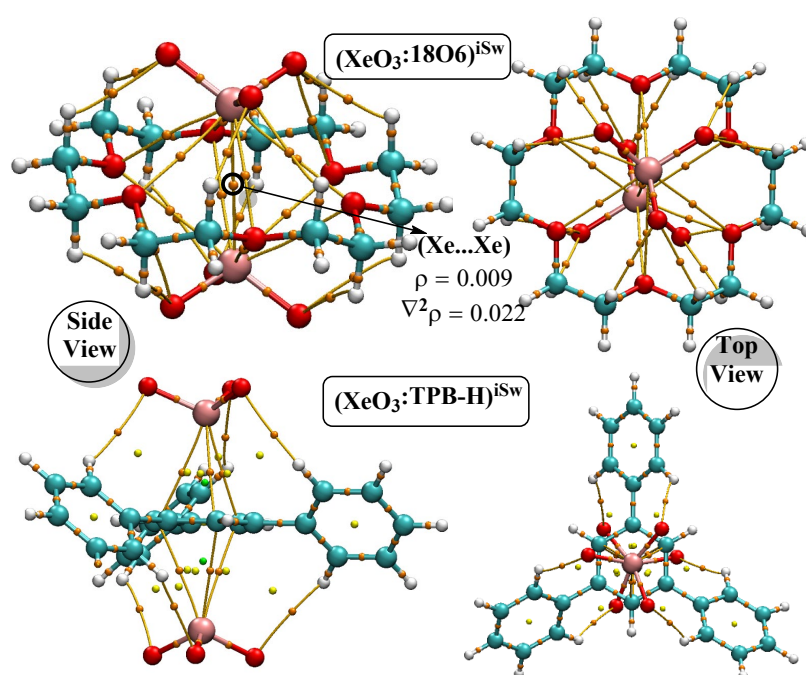


Figure 6.5. AIM analysis for the inverse sandwich complexes involving XeO_3 with 18-crown-6 (top) and with TPB-H (bottom). The associated values (ρ , $\nabla^2\rho$, H) are shown in **Table S6.1**.

For TPB derivatives, except for the case of TPB-CN, three RCPs, as mentioned above, were observed between Xe and the central carbon atoms with varying substitutions, whereas three BCPs were observed between Xe and the central carbon atoms with phenyl substituent (**Figures S6.19, S6.20**). The combination of these three RCPs and three BCPs corresponds to the aerogen bonding interactions, with their ρ and $\nabla^2\rho$ values mirroring the interaction energy trend, except for the case of TPB-F (**Table S6.1**). Three additional RCPs were observed between each XeO_3 and the C-C linker bond connecting the central arene ring and the phenyl substituents, for all cases. Alongside these, a cage critical point (green sphere) was also

observed between each Xe and the central π -ring, whose ρ and $\nabla^2\rho$ values also followed the abovementioned trend. The energy density values (H) were determined to be positive across all cases, which is typical for closed shell calculations.

6.3.5. NBO Analysis

Table 6.3. E^2 values in kcal/mol derived from NBO analysis at the APFD/def2-TZVPD level of theory for the iSw complexes of XeO_3 . (C-C)^{arene} indicates the carbon atoms of the central arene ring, C^{Ph} indicates the carbon attached to the phenyl substituents.

iSw	Donor	Acceptor	ΔE^2
18O6	LP O	σ^* (Xe-O)	-5.74
	LP Xe	σ^* (Xe-O)	-0.36
	LP O	σ^* (C-H)	-7.28
NH ₂	π (C-C) ^{arene}	σ^* (Xe-O)	-8.54
	LP Xe	σ^* (C-C ^{Ph})	-1.83
	LP Xe	σ^* (C-NH ₂)	-1.50
	LP O	σ^* (C-H)	-6.67
	LP O	π^* (C-C) ^{arene}	-0.24
CH ₃	π (C-C) ^{arene}	σ^* (Xe-O)	-6.79
	LP Xe	σ^* (C-C ^{Ph})	-2.10
	LP Xe	σ^* (C-CH ₃)	-2.13
	LP O	σ^* (C-H)	-6.01
OH	π (C-C) ^{arene}	σ^* (Xe-O)	-6.39
	LP Xe	σ^* (C-C ^{Ph})	-1.62
	LP Xe	σ^* (C-OH)	-0.66
	LP O	σ^* (C-H)	-5.18
H	π (C-C) ^{arene}	σ^* (Xe-O)	-5.40
	LP Xe	σ^* (C-C ^{Ph})	-1.68
	LP O	σ^* (C-H)	-1.44
CCH	π (C-C) ^{arene}	σ^* (Xe-O)	-4.10
	LP Xe	σ^* (C-C ^{Ph})	-1.58
	LP Xe	σ^* (C-CCH)	-1.38
	LP O	σ^* (C-H)	-6.03
F	π (C-C) ^{arene}	σ^* (Xe-O)	-4.52
	LP Xe	σ^* (C-C ^{Ph})	-1.29
	LP O	σ^* (C-H)	-2.78
CN	π (C-C) ^{arene}	σ^* (Xe-O)	-2.85
	LP Xe	σ^* (C-C ^{Ph})	-1.38
	LP Xe	σ^* (C-CN)	-0.72
	LP O	σ^* (C-H)	-3.76

To explore the orbital interactions, NBO calculations were conducted for the Mono (Table S6.2) and iSw (Tables 6.3, S6.3) complexes of XeO_3 . Consistent with previous observations, second-order perturbation energies (E^2) corresponding to orbital interactions ($n \rightarrow \sigma^*$) between lone pairs of five oxygen donor atoms and the σ^* antibonding Xe-O orbital

were obtained for the $(\text{XeO}_3:18\text{O}_6)^{\text{iSw}}$ complex (see **Table 6.3**). Additionally, $n \rightarrow \sigma^*$ orbital interactions were observed amongst Xe's LP and σ^* antibonding orbital of $\text{Xe}=\text{O}$ ($E^2 = 0.18$ kcal/mol, for each Xe), providing further evidence of the existence of a weakly attractive noncovalent $\text{Xe} \cdots \text{Xe}$ interaction amongst the two XeO_3 moieties. Significant orbital interactions from C-H...O interactions were also noted. For TPB derivatives, $\pi \rightarrow \sigma^*$ orbital interactions amongst C-C bonding orbital corresponding to central arene ring & the antibonding Xe-O orbital corresponding to the aerogen bonds were observed. The summed E^2 values corresponding to the above interactions followed the interaction energy trend, except for the case of TPB-F: $\text{CN} (-2.9) < \text{CCH} (-4.1) < \text{F} (-4.5) < \text{H} (-5.4) < \text{OH} (-6.4) < \text{CH}_3 (-6.8) < \text{NH}_2 (-8.5)$. In concurrence with the NCI plot analysis and the RCPs, $n \rightarrow \sigma^*$ orbital interactions were noted originating from Xe's LP to the antibonding C(arene)-C(phenyl) orbital. In complexes where carbon-containing substituents (CH_3 , CCH, CN) had replaced H of the C(arene), $n \rightarrow \sigma^*$ orbital interactions were also observed between the Xe's LP and the antibonding C(arene)-C(substituent) orbital. These observations provide testament to the amphoteric nature of XeO_3 . Additionally, non-negligible orbital interactions corresponding to the C-H...O interactions were also observed.

6.3.6. EDA

The conclusions drawn above were additionally substantiated by the Ziegler-Rauk energy decomposition analysis. It was found that while the absolute interaction energies varied from those obtained through higher-level computations, due to differences in functional and basis set (**Table 6.4**, refer **Table S6.4** for Mono), the relative trends remained consistent, enabling further insights. In all cases, the percentage contribution from electrostatic interactions decreased upon the formation of 1:2 iSw complexes, as compared to the 1:1 Mono complexes. This reduction occurs due to the sharing of electron-rich sources between the two XeO_3 molecules. At the same time, the percentage contribution from dispersion interactions increased for the same. No clear trend was detected in the percentage contribution from orbital interactions. Regarding the TPB derivatives, electrostatic interactions were found to increase with higher interaction energies and decrease with lower interaction energies, aligning with the electron donating and withdrawing abilities of the substituents. Conversely, a reverse trend was noted for dispersion interactions. Interestingly, for the most electron-deficient TPB-CN case, interactions were predominantly due to dispersive interactions (50% for iSw, 46% for Mono), with electrostatic interactions contributing only about 14% for iSw and 19% for Mono. With

the exception of the TPB-NH₂ case, significant contributions from orbital and dispersion interactions were observed for all TPB derivatives, even those with electron-donating groups attached.

Table 6.4. Energy decomposition analysis of iSw (three fragments were considered: the host and 2 XeO₃ units) complexes of XeO₃ at the BP86-D3BJ/ZORA/TZ2P level of theory. The energy values are in kcal/mol. Contribution to the sum of all attractive energy terms are shown as percentages. E_{Pauli} indicates Pauli repulsion, E_{elstat} denotes electrostatic interactions, E_{oi} signifies orbital interaction and the E_{disp} indicates the dispersion interaction.

iSw	ΔE_{int}	ΔE_{Pauli}	ΔE_{elstat}	%	ΔE_{oi}	%	ΔE_{disp}	%
18O6	-63.0	70.3	-64.1	48	-34.9	26	-34.3	26
TPB-NH ₂	-49.0	70.1	-46.2	39	-42.0	35	-30.8	26
TPB-CH ₃	-39.8	63.2	-36.7	36	-34.4	33	-32.0	31
TPB-OH	-36.8	57.5	-32.4	34	-33.0	35	-28.8	31
TPB-H	-31.3	45.2	-25.2	33	-25.3	33	-25.9	34
TPB-CCH	-30.2	46.8	-20.7	27	-26.2	34	-30.1	39
TPB-F	-25.3	42.5	-17.7	26	-24.0	35	-26.1	39
TPB-CN	-19.8	37.3	-8.1	14	-20.4	36	-28.5	50

Furthermore, the natural orbitals for chemical valence (NOCV), combined with EDA, also known as ETS-NOCV analysis,^[59] confirmed the existence of a weak, attractive *Xe...Xe* interaction in (XeO₃:18O6)^{iSw} complex. For TPB derivatives, the orbital interaction energies corresponding to the aerogen bonds were identified using ETS-NOCV analysis, and were observed to follow the trend: CN (-9.1) < F (-12.9) $\approx$ CCH (-12.9) < H (-14.6) < OH (-18.5) $\approx$ CH₃ (-18.4) < NH₂ (-24.2). **Figure 6.6** depicts NOCVs associated with the Xe...Xe interaction in the (XeO₃:18O6)^{iSw} complex along with the corresponding NBOs, and the aerogen bonding NOCVs for the iSw complex of TPB-H.

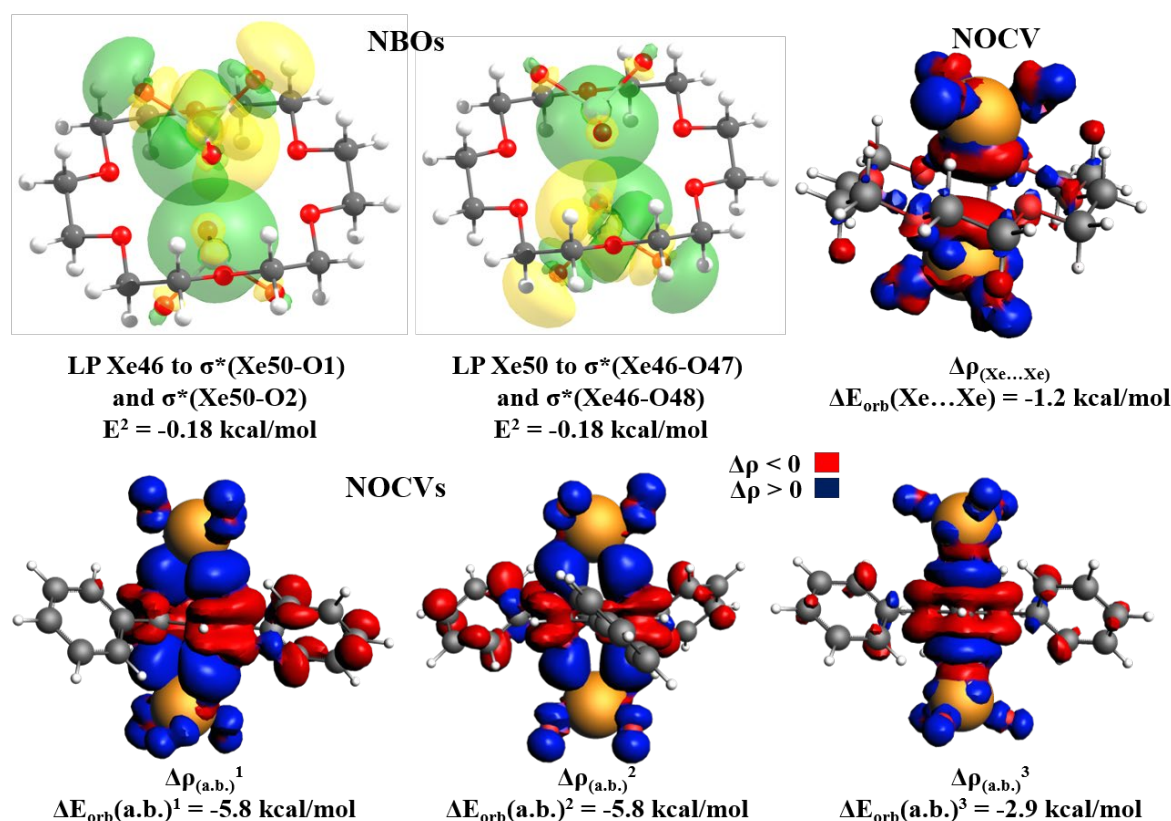


Figure 6.6. Top: NBOs and NOCV associated with the Xe...Xe interaction in the $(\text{XeO}_3:18\text{O6})^{\text{iSw}}$ complex; Bottom: aerogen bonding (a.b.) NOCVs for the iSw complex of TPB-H. Red region represents outflow of electron density (charge depletion) and blue region represents inflow of electron density (charge accumulation). $\Delta\rho$ were plotted with isovalues ± 0.0001 a.u. for clarity.

6.4. Conclusions

In this chapter, we have offered insights into the rational design of inverse sandwich complexes involving XeO_3 , along with a thorough computational investigation into the key factors governing their stability. The NCI plot, BCP, NBO, and ETS-NOCV analysis all confirmed the occurrence of a rare, weak, attractive $\text{Xe}\cdots\text{Xe}$ interaction in the inverse sandwich complex of XeO_3 with 18-crown-6. This interaction caused XeO_3 to tilt away from the central axis of the crown, enabling its interaction with five oxygen atoms and increasing its coordination number to 8. This stands in contrast to the monomeric 1:1 complex, where Xe was bound to only three oxygen atoms, resulting in a coordination number of 6.^[24,25] For the inverse sandwich complexes of TPB and its derivatives, besides $\text{C-H}\cdots\text{O}$ interactions and aerogen bonding, interactions between Xe's LP and the C-C antibonding orbitals were found

to contribute to the overall orbital interactions, showcasing the non-negligible amphoteric prowess of the XeO₃ molecule. It is noteworthy that the inverse sandwich complexes of TPB and derivatives exhibit substantial contributions from ΔE_{oi} (33-36%) and ΔE_{disp} (26-50%) as compared to conventional electrostatic interactions (14-39%). This study presents the first report of inverse sandwich complexes of XeO₃, stabilized by aerogen bonding, alongside C-H...O interactions, & back donation from Xe's LP. Overall, we believe this study has the potential to initiate the development of novel inverse sandwich complexes of noble gas compounds, thereby impacting our broader understanding of supramolecular chemistry and σ -hole mediated non covalent interactions.

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Chapter-7

Summary and Future Outlook

7.1. Summary

Work presented in this thesis is primarily covered in Chapters 3 through 6. While the overarching objective, as outlined in Chapter 1, remained consistent - namely, the pursuit of a host capable of stabilizing XeO_3 through σ -hole mediated host-guest complexation - we also explored various facets of NCIs along the way. A chapter-wise summary is provided below.

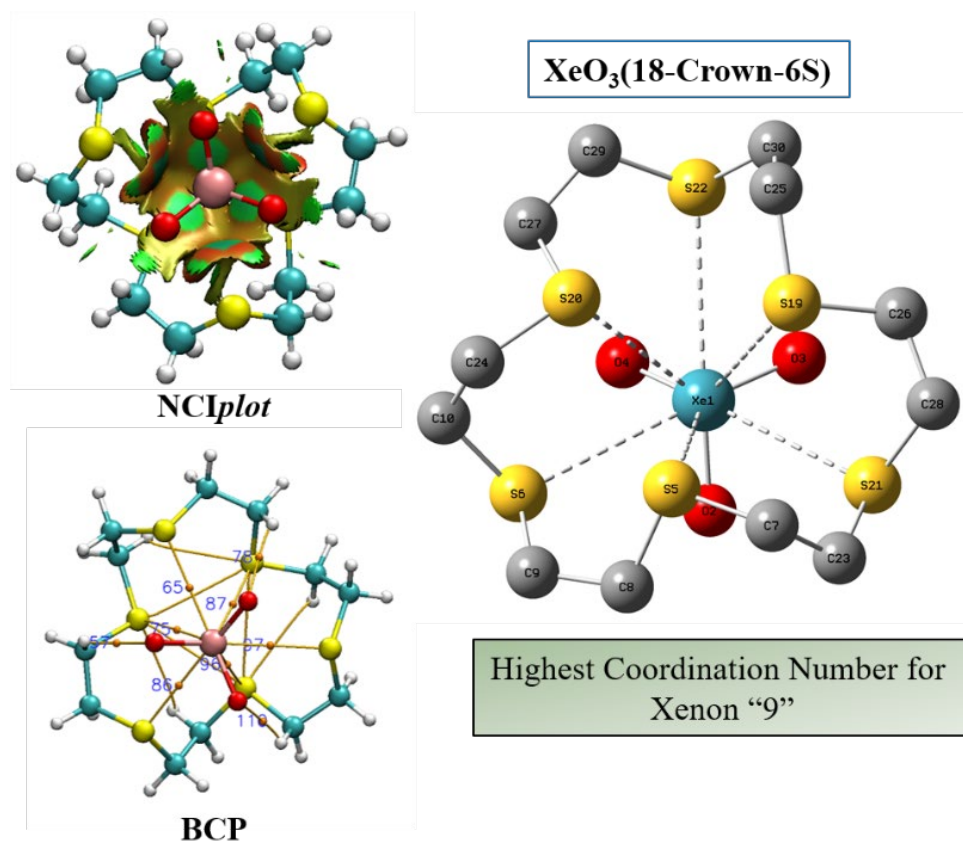


Figure 7.1. Highlight of the host-guest complex of 18-thio-crown-6 with XeO_3 .

In Chapter 3, the focus is on the stabilization of xenon trioxide (XeO_3), a highly explosive and shock-sensitive compound, through its complexation with electron-rich crown ethers and their thio analogues. Quantum chemical calculations reveal that the interaction energies, corrected for BSSE, range significantly, highlighting the effectiveness of σ -hole-mediated NCIs. The stability of these complexes increases with the crown ether ring size and decreases from XeO_3 to ArO_3 . The research uncovers the crucial role of $\text{C-H}\cdots\text{O}$ interactions and dispersion forces in stabilizing larger crown complexes. The enhanced orbital interaction in thio crowns led to an unprecedented 9-coordination number for Xe in a complex with the thio analogue of 18-Crown-6 (**Figure 7.1**). This finding surpasses previously known coordination numbers and offers new insights into the stabilization mechanisms of such

complexes. While acknowledging the challenges in synthesizing compounds like ArO_3 and KrO_3 , the study suggests that the strong thermodynamic stabilization observed could guide future experimental strategies to explore these elusive species.

Chapter 4 explores different non-aromatic coordinating solvents as readily available off-the-shelves candidates to stabilize XeO_3 . DFT calculations identified the top ten solvents out of 26 examined, with hexamethylphosphoramide (HMPA), N,N' -dimethylpropyleneurea (DMPU), and tetramethylethylenediamine (TMEDA) forming the strongest adducts with XeO_3 . The study reveals that nitrogen donor solvents have a stronger affinity for XeO_3 's σ -holes compared to oxygen donor solvents. Additionally, $C-H\cdots O$ interactions & back donation from Xe's LP to the solvent donor site's antibonding orbitals significantly stabilize these complexes. In a happy coincidence, seven out of the top ten solvents identified possess high boiling points ($>100^\circ\text{C}$), with sulfolane (285°C) being the highest among them. This feature is expected to inhibit solvent evaporation and prevent adduct dissociation – a phenomenon observed experimentally with the low-boiling-point solvent acetone (56°C). The investigation shows that σ -hole-mediated interactions are predominantly electrostatic but also have substantial contributions from orbital and dispersion interactions. The research provides a deeper understanding of the nucleophilicity of non-aromatic solvents as Lewis base donors and thereby offering practical insights for experimentalists in selecting solvents for XeO_3 stabilization.

In Chapter 5, the thesis delves into the potential of aza-crowns (nitrogen analogues of the crown ethers) to stabilize XeO_3 through σ -hole-mediated aerogen bonding. Computational studies reveal that aza-crowns showcase superior binding to XeO_3 compared to their thio & oxygen counterparts. In contrast to the crown ethers, aza-crowns show a unique size selectivity for xenon trioxide, with binding peaking at aza-15-crown-5 & decreasing with larger crowns. Smaller aza-crowns, such as 9N3, 12N4, and 15N5, outperform their analogues in terms of interaction energy and the individual contributions of electrostatic, orbital, and dispersion forces. However, the increased number of $C-H\cdots O$ interactions in larger aza-crowns does not compensate for the reduced strength of the primary σ -hole-mediated aerogen bonds, leading to size selectivity. This chapter provides valuable insights into the molecular recognition processes within σ -hole-mediated host-guest complexes, contributing to the broader field of supramolecular chemistry.

Chapter 6 presents the rational design of inverse sandwich (iSw) complexes incorporating XeO_3 , investigated through comprehensive computational analyses. The research

highlights the critical factors influencing the stability of these complexes, such as a rare $\text{Xe}\cdots\text{Xe}$ interaction observed in the iSw complex of XeO_3 with 18-crown-6. This interaction increases xenon's coordination number as compared to its mono adduct. Additionally, the study explores the iSw complexes of derivatives of 1,3,5-triphenylbenzene, revealing that their stability is not entirely dependent on aerogen bonding but also on substantial donations from $\text{C-H}\cdots\text{O}$ interactions & back donation from xenon's LP to the TPB's antibonding orbitals. This chapter emphasizes the, often ignored, multifaceted amphoteric properties of XeO_3 , showing that contrary to conventional belief, these complexes are not predominantly ruled by electrostatic interactions. The findings suggest that the iSw complexes of XeO_3 (**Figure 7.2**) represent a novel class of noble gas compounds stabilized by multiple interactions, potentially influencing the future development of supramolecular chemistry and σ -hole-mediated non-covalent interactions.

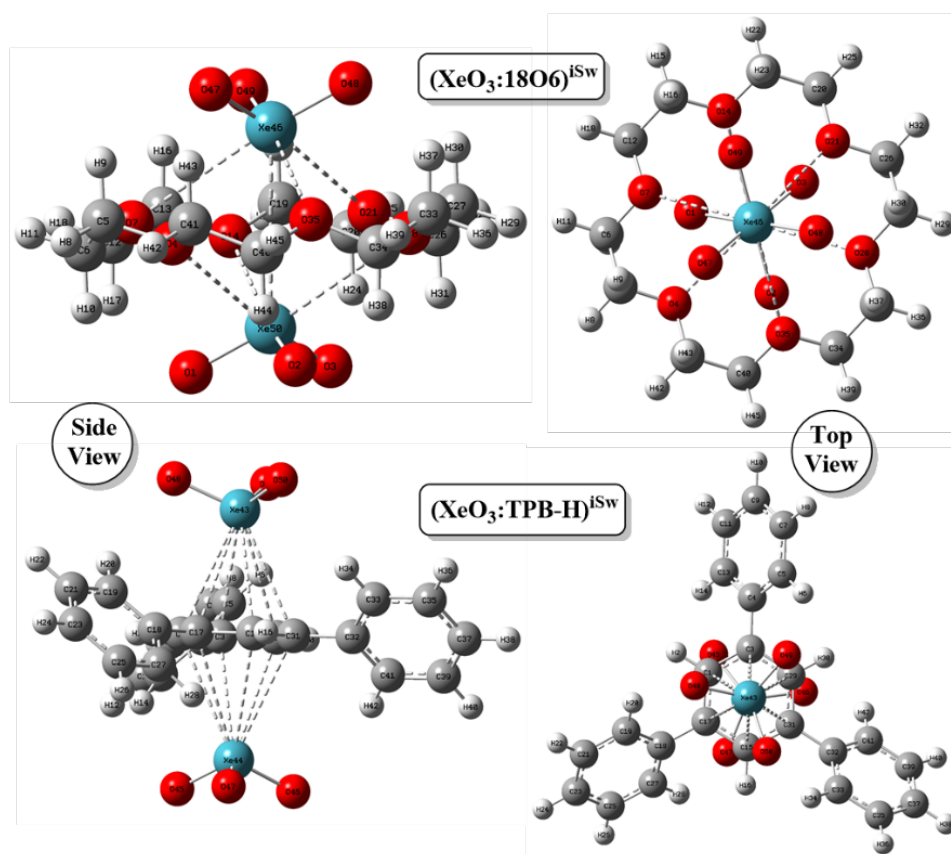


Figure 7.2. The first inverse sandwich complex of a noble gas compound (XeO_3).

7.2. Future Outlook

Exploring supramolecular assemblies like calixarenes, cryptands, molecular bowls, and scorpionate ligands as hosts for stabilizing XeO_3 presents an exciting opportunity in the field of supramolecular chemistry. With their customizable cavities and selective binding abilities, calixarenes and cryptands are particularly well-suited for encapsulating XeO_3 through various σ -hole-mediated NCIs. These hosts have demonstrated their capacity to stabilize different guest molecules, making them potential candidates for interacting with reactive species like XeO_3 . Similarly, molecular bowls, with their unique concave structures, could potentially stabilize XeO_3 by leveraging a combination of π -interactions and σ -hole-mediated NCIs. Scorpionate ligands, known for their multi-dentate binding modes, could also offer stabilization by coordinating with XeO_3 in a tridentate fashion. Investigating these supramolecular hosts not only provides new strategies for stabilizing XeO_3 but also expands our understanding of host-guest interactions, leading to novel applications in areas such as materials science and catalysis, as σ -holes also offer several promising applications in the realm of catalysis:

- **Transition State Stabilization:** σ -hole interactions can be employed to stabilize transition states within catalytic reactions, thereby reducing activation energy and accelerating the reaction rate.
- **Catalytic Selectivity:** The directional nature of σ -hole interactions can be exploited to control the spatial arrangement of reactants at the catalytic active site. This precision can enhance the selectivity of catalytic reactions, leading to the preferential formation of desired products with high efficiency.
- **Substrate Activation:** By inducing polarization or facilitating electron transfer, σ -hole interactions can activate substrates, rendering them more reactive under milder conditions. This is particularly valuable in catalytic processes where traditional activation methods are less effective or overly harsh.
- **Novel Catalyst Design:** Understanding σ -hole interactions opens up avenues for designing innovative catalysts that leverage these interactions to achieve specific catalytic effects. Incorporating atoms that exhibit pronounced σ -holes into catalytic structures can create active sites that utilize NCIs to drive catalytic activity.
- **Supramolecular Catalysis:** In the context of supramolecular chemistry, σ -hole interactions can be harnessed to assemble intricate catalytic systems. These interactions

facilitate the self-assembly of catalytic frameworks or organize reactants near catalytic sites, enhancing overall reaction efficiency.

- **Milder Reaction Conditions:** Catalysts based on σ -hole-mediated NCIs often operate under gentler conditions compared to traditional catalysts, which is advantageous for reactions involving sensitive substrates or functional groups.

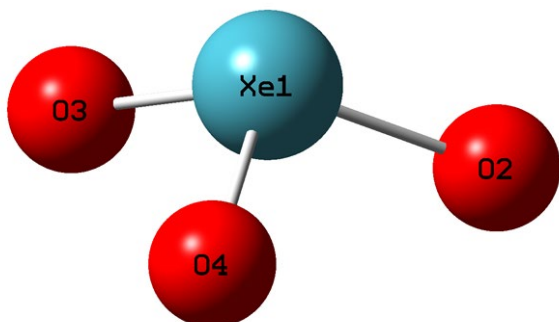
σ -holes offer a versatile toolset for catalysis, providing opportunities to develop catalysts that are more efficient, selective, and environmentally friendly. The exploration of σ -hole interactions in catalytic processes is a rapidly growing frontier, with significant potential to advance both chemical synthesis and industrial applications. The use of noble gas compounds as σ -hole-mediated catalysts could transition from science fiction to reality within the next decade.

Appendix

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28. **Table S3.19.** Change in the bond angles of NgO_3 ($\angle\text{O-Ng-O}$, in degree) upon complexation.
29. Optimized Cartesian coordinates

XeO₃**Bond Lengths (in Å)**

Xe1-O2 = 1.7597
 Xe1-O3 = 1.7597
 Xe1-O4 = 1.7597

NPA

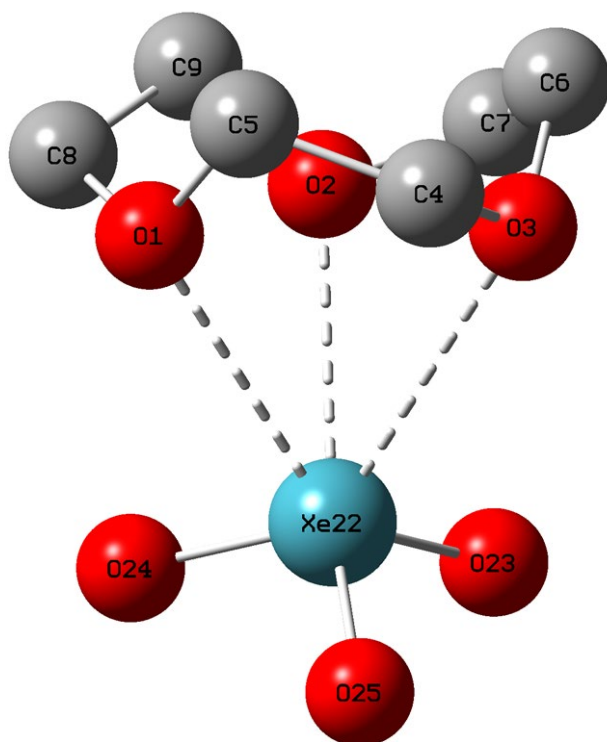
Xe1 = +2.765
 O2 = -0.922
 O3 = -0.922
 O4 = -0.922

WBI

Xe1 = 3.3618
 O2 = 1.5318
 O3 = 1.5318
 O4 = 1.5318

Mulliken

Xe1 = +1.542
 O2 = -0.514
 O3 = -0.514
 O4 = -0.514

**XeO₃(9-Crown-3)****Bond Lengths (in Å)**

Xe22-O23 = 1.7652
 Xe22-O24 = 1.7651
 Xe22-O25 = 1.7658
 Xe22-O1 = 2.9265
 Xe22-O2 = 2.8184
 Xe22-O3 = 2.9494

NPA

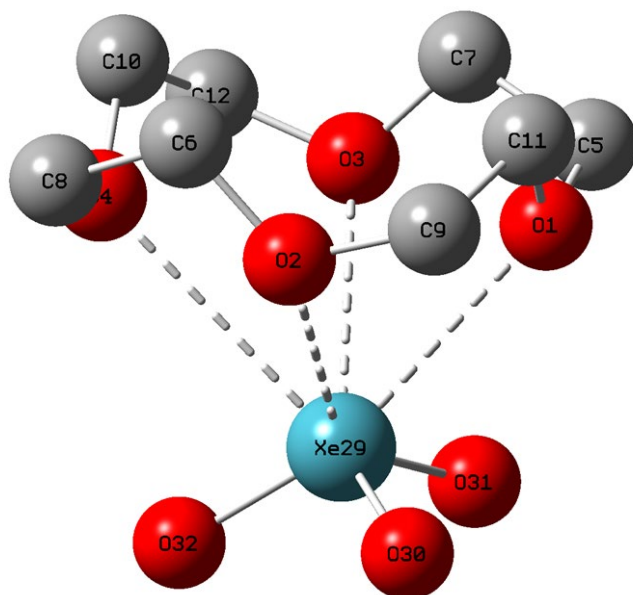
Xe22 = +2.875
 O23 = -0.965
 O24 = -0.965
 O25 = -0.962
 O1 = -0.550
 O2 = -0.551
 O3 = -0.550

Mulliken

Xe22 = +1.669
 O23 = -0.612
 O24 = -0.604
 O25 = -0.582
 O1 = -0.328
 O2 = -0.323
 O3 = -0.352

WBI

Xe22 = 3.3364
 O23 = 1.4879
 O24 = 1.4869
 O25 = 1.4981

XeO₃(12-Crown-4)**Bond Lengths (in Å)**

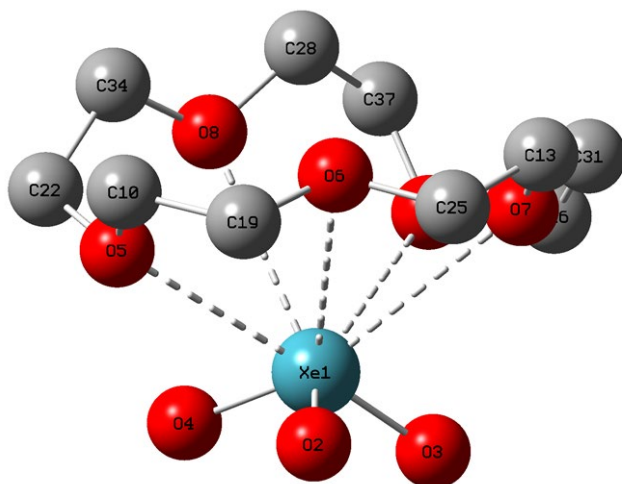
Xe29-O30 = 1.7651
 Xe29-O31 = 1.7649
 Xe29-O32 = 1.7651
 Xe29-O1 = 2.8046
 Xe29-O2 = 2.9474
 Xe29-O3 = 2.9691
 Xe29-O4 = 3.1220

NPA

Xe29 = +2.890
 O30 = -0.971
 O31 = -0.971
 O32 = -0.967
 O1 = -0.552
 O2 = -0.544
 O3 = -0.541
 O4 = -0.533

Mulliken

Xe29 = +1.689
 O30 = -0.612
 O31 = -0.597
 O32 = -0.483
 O1 = -0.250
 O2 = -0.218
 O3 = -0.219
 O4 = -0.242

XeO₃(15-Crown-5)**Bond Lengths (in Å)**

Xe1-O2 = 1.7673
 Xe1-O3 = 1.7636
 Xe1-O4 = 1.7623
 Xe1-O5 = 2.9088
 Xe1-O6 = 3.2590
 Xe1-O7 = 2.9627
 Xe1-O8 = 3.0745
 Xe1-O9 = 2.9616

NPA

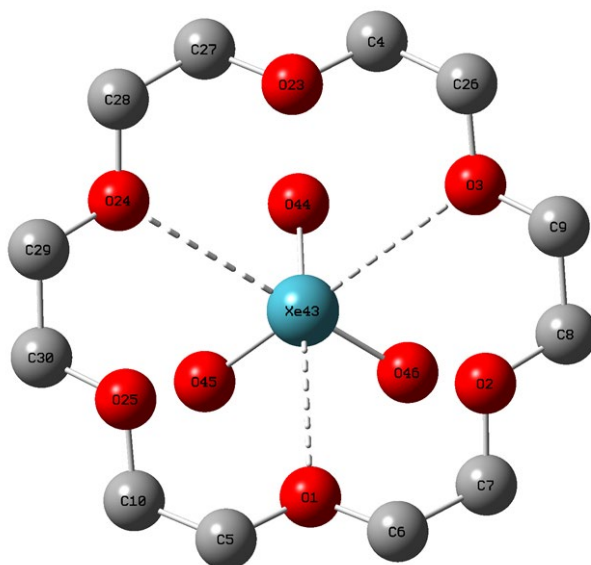
Xe1 = +2.913
 O2 = -0.991
 O3 = -0.975
 O4 = -0.965
 O5 = -0.539
 O6 = -0.545
 O7 = -0.553
 O8 = -0.547
 O9 = -0.535

Mulliken

Xe1 = +1.750
 O2 = -0.645
 O3 = -0.646
 O4 = -0.600
 O5 = -0.280
 O6 = -0.030
 O7 = -0.084
 O8 = -0.143
 O9 = -0.374

WBI

Xe1 = 3.3214
 O2 = 1.4578
 O3 = 1.4717
 O4 = 1.4866

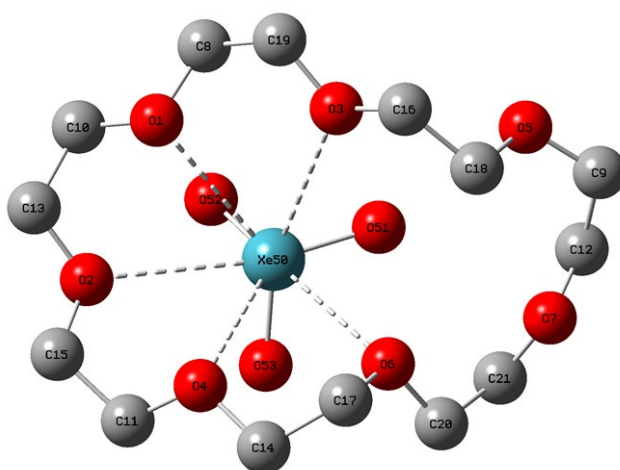
XeO₃(18-Crown-6)**Bond Lengths (in Å)**

Xe43-O44 = 1.7605
 Xe43-O45 = 1.7605
 Xe43-O46 = 1.7605
 Xe43-O1 = 3.1493
 Xe43-O2 = 3.4010
 Xe43-O3 = 3.1493
 Xe43-O23 = 3.4010
 Xe43-O24 = 3.1493
 Xe43-O25 = 3.4010

NPA	Mulliken
Xe43 = +2.913	Xe43 = +2.085
O44 = -0.974	O44 = -0.686
O45 = -0.974	O45 = -0.686
O46 = -0.974	O46 = -0.686
O1 = -0.538	O1 = -0.126
O2 = -0.533	O2 = -0.151
O3 = -0.538	O3 = -0.126
O23 = -0.533	O23 = -0.151
O24 = -0.538	O24 = -0.126
O25 = -0.533	O25 = -0.151

WBI

Xe43 = 3.3249
 O44 = 1.4753
 O45 = 1.4753
 O46 = 1.4753

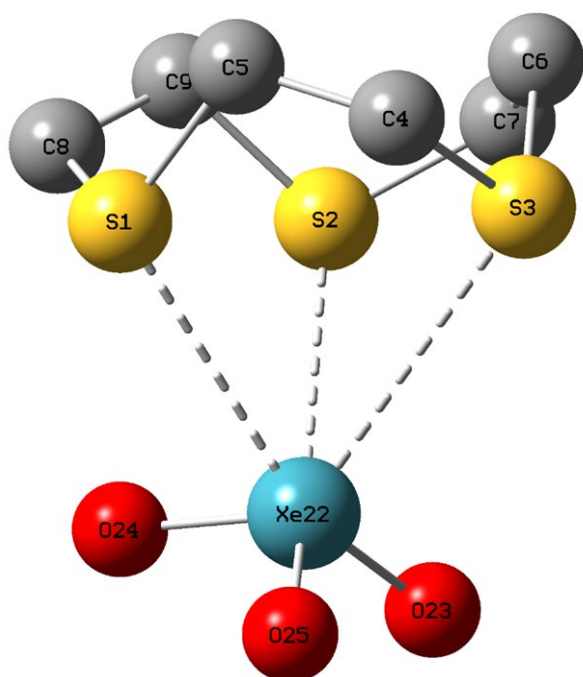
XeO₃(21-Crown-7)**Bond Lengths (in Å)**

Xe50-O51 = 1.7585
 Xe50-O52 = 1.7620
 Xe50-O53 = 1.7670
 Xe50-O1 = 3.1668
 Xe50-O2 = 3.0428
 Xe50-O3 = 3.1338
 Xe50-O4 = 3.1427
 Xe50-O5 = 4.6028
 Xe50-O6 = 2.9733
 Xe50-O7 = 4.4410

NPA	Mulliken
Xe50 = +2.911	Xe50 = +1.883
O51 = -0.969	O51 = -0.620
O52 = -0.974	O52 = -0.627
O53 = -0.986	O53 = -0.650
O1 = -0.543	O1 = -0.113
O2 = -0.540	O2 = -0.217
O3 = -0.542	O3 = -0.184
O4 = -0.546	O4 = -0.071
O5 = -0.516	O5 = -0.331
O6 = -0.549	O6 = -0.285
O7 = -0.535	O7 = -0.296

WBI

Xe50 = 3.3288
 O51 = 1.4876
 O52 = 1.4712
 O53 = 1.4573

**XeO₃(9S-Crown-3)****Bond Lengths (in Å)**

Xe22-O23 = 1.7675
 Xe22-O24 = 1.7699
 Xe22-O25 = 1.7675
 Xe22-S1 = 3.2151
 Xe22-S2 = 3.1846
 Xe22-S3 = 3.4580

NPA

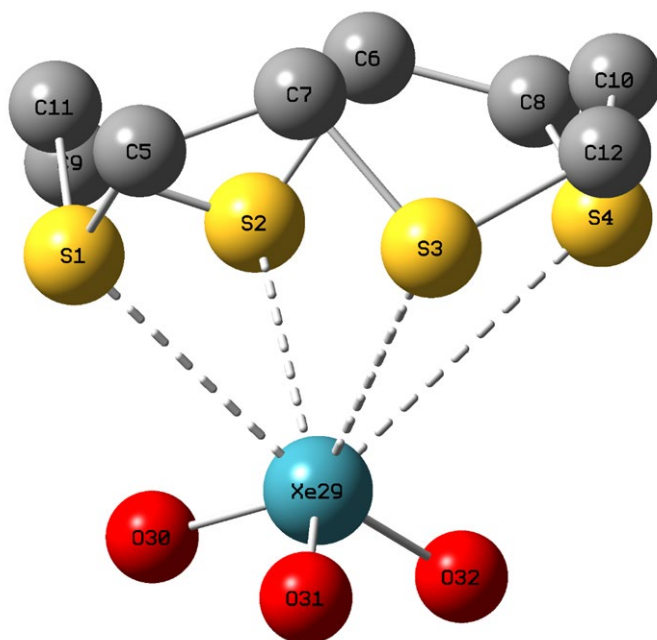
Xe22 = +2.826
 O23 = -0.967
 O24 = -0.983
 O25 = -0.965
 S1 = +0.200
 S2 = +0.208
 S3 = +0.183

Mulliken

Xe22 = +1.513
 O23 = -0.580
 O24 = -0.606
 O25 = -0.590
 S1 = -0.357
 S2 = -0.340
 S3 = -0.363

WBI

Xe22 = 3.3631
 O23 = 1.4920
 O24 = 1.4678
 O25 = 1.4962

**XeO₃(12S-Crown-4)****Bond Lengths (in Å)**

Xe29-O30 = 1.7702
 Xe29-O31 = 1.7666
 Xe29-O32 = 1.7666
 Xe29-S1 = 3.2391
 Xe29-S2 = 3.2080
 Xe29-S3 = 3.4843
 Xe29-S4 = 3.5669

NPA

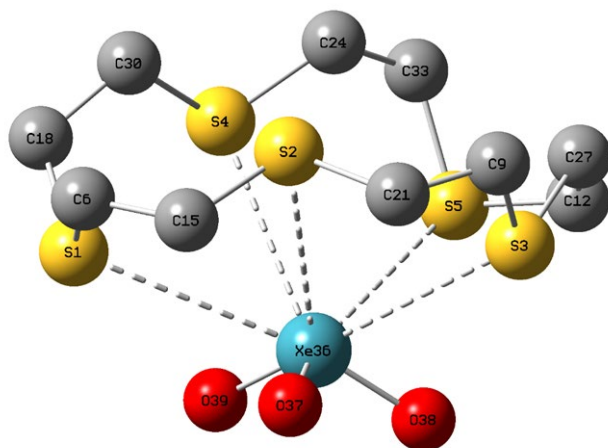
Xe29 = +2.837
 O30 = -0.985
 O31 = -0.969
 O32 = -0.967
 S1 = +0.212
 S2 = +0.214
 S3 = +0.209
 S4 = +0.208

Mulliken

Xe29 = +1.481
 O30 = -0.609
 O31 = -0.577
 O32 = -0.585
 S1 = -0.263
 S2 = -0.340
 S3 = -0.283
 S4 = -0.253

WBI

Xe29 = 3.3604
 O30 = 1.4641
 O31 = 1.4879
 O32 = 1.4904

XeO₃(15S-Crown-5)**Bond Lengths (in Å)**

Xe36-O37 = 1.7727
 Xe36-O38 = 1.7683
 Xe36-O39 = 1.7634
 Xe36-S1 = 3.4863
 Xe36-S2 = 3.5607
 Xe36-S3 = 3.2648
 Xe36-S4 = 3.5038
 Xe36-S5 = 3.3618

NPA

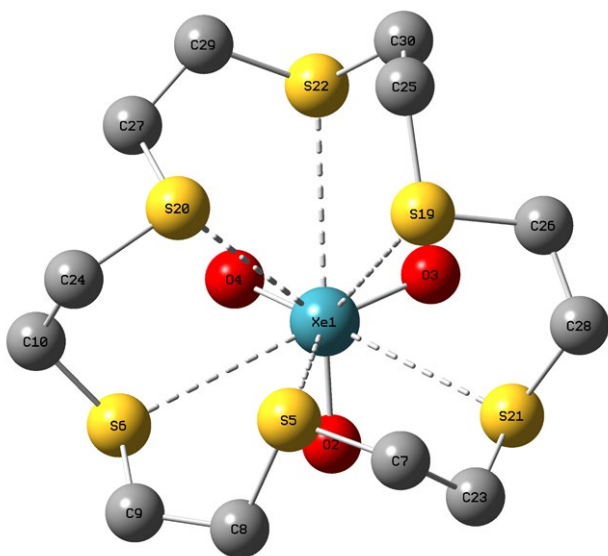
Xe36 = +2.858
 O37 = -1.002
 O38 = -0.978
 O39 = -0.959
 S1 = +0.219
 S2 = +0.148
 S3 = +0.202
 S4 = +0.182
 S5 = +0.211

Mulliken

Xe36 = +1.457
 O37 = -0.626
 O38 = -0.541
 O39 = -0.570
 S1 = -0.279
 S2 = -0.314
 S3 = -0.331
 S4 = -0.444
 S5 = -0.304

WBI

Xe36 = 3.3498
 O37 = 1.4514
 O38 = 1.4712
 O39 = 1.4967

XeO₃(18S-Crown-6)**Bond Lengths (in Å)**

Xe1-O2 = 1.7710
 Xe1-O3 = 1.7710
 Xe1-O4 = 1.7710
 Xe1-S5 = 3.4719
 Xe1-S6 = 3.3240
 Xe1-S19 = 3.4717
 Xe1-S20 = 3.4722
 Xe1-S21 = 3.3230
 Xe1-S22 = 3.3223

NPA

Xe1 = +2.878
 O2 = -0.992
 O3 = -0.992
 O4 = -0.992
 S5 = +0.185
 S6 = +0.225
 S19 = +0.185
 S20 = +0.185
 S21 = +0.225
 S22 = +0.225

Mulliken

Xe1 = +1.316
 O2 = -0.539
 O3 = -0.539
 O4 = -0.539
 S5 = -0.230
 S6 = -0.312
 S19 = -0.229
 S20 = -0.229
 S21 = -0.313
 S22 = -0.312

WBI

Xe1 = 3.3436
 O2 = 1.4631
 O3 = 1.4632
 O4 = 1.4632

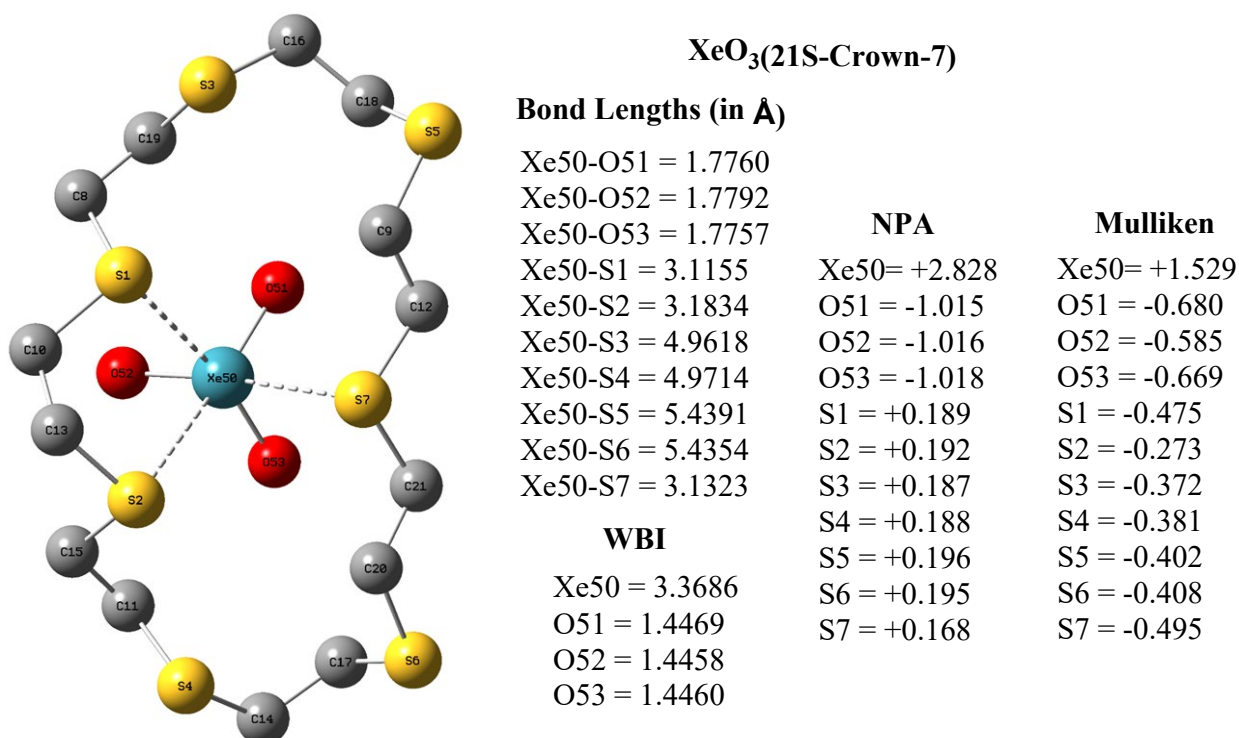
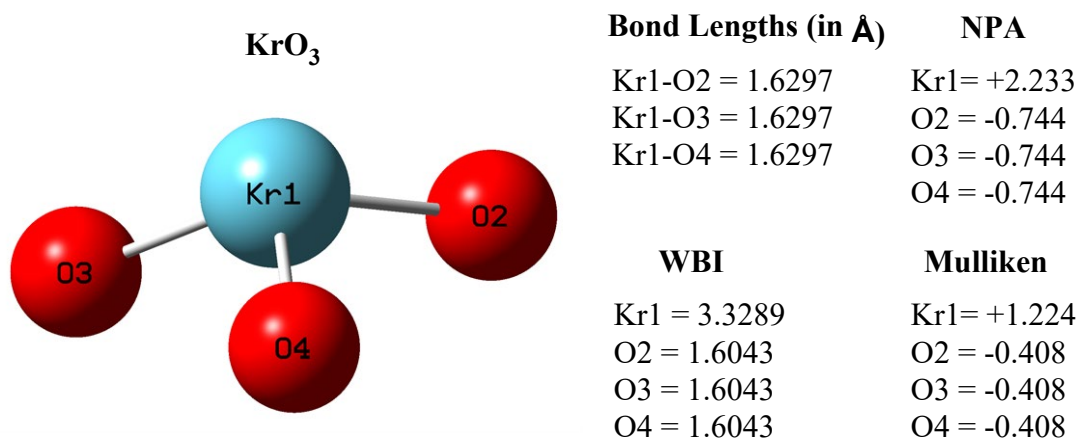
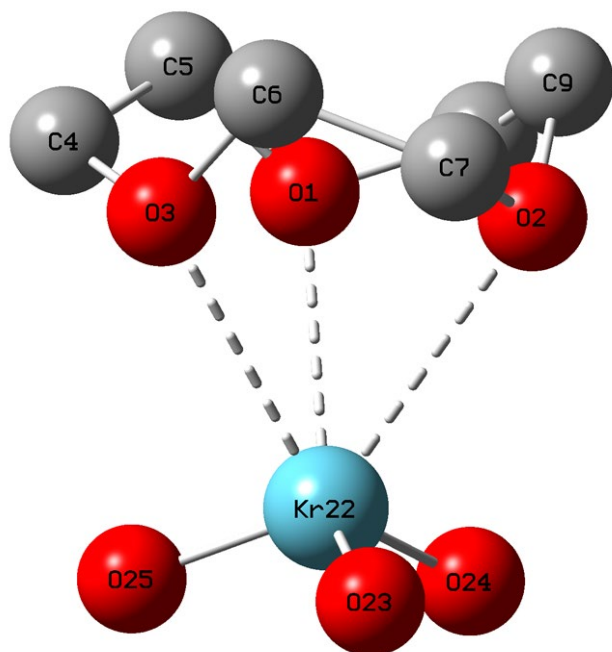


Figure S3.1. Optimized geometries of XeO₃ and its adducts with different crown ethers, along with their thio analogues. The bond distances, WBI values and charge analysis (NPA and Mulliken) data are shown. Hydrogen atoms have been omitted for clarity.



**KrO₃(9-Crown-3)****Bond Lengths (in Å)**

Kr22-O23 = 1.6351
 Kr22-O24 = 1.6352
 Kr22-O25 = 1.6352
 Kr22-O1 = 2.8204
 Kr22-O2 = 2.8222
 Kr22-O3 = 2.8205

NPA

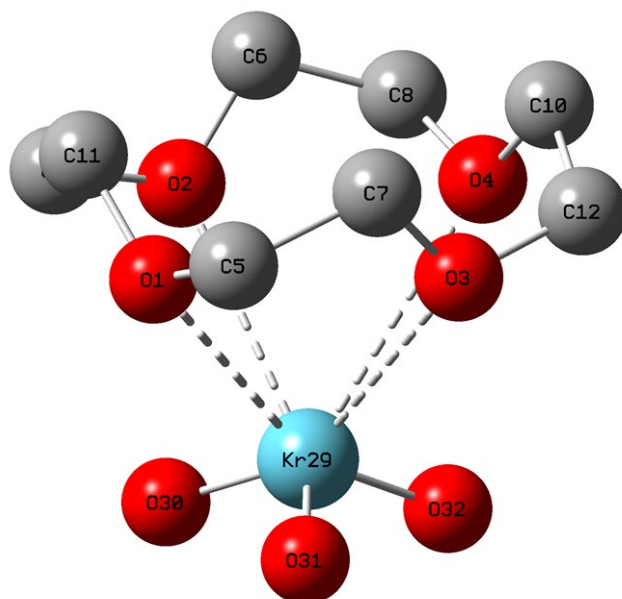
Kr22 = +2.316
 O23 = -0.774
 O24 = -0.774
 O25 = -0.774
 O1 = -0.545
 O2 = -0.545
 O3 = -0.545

Mulliken

Kr22 = +1.647
 O23 = -0.548
 O24 = -0.548
 O25 = -0.548
 O1 = -0.378
 O2 = -0.378
 O3 = -0.378

WBI

Kr22 = 3.3057
 O23 = 1.5742
 O24 = 1.5741
 O25 = 1.5741

**KrO₃(12-Crown-4)****Bond Lengths (in Å)**

Kr29-O30 = 1.6345
 Kr29-O31 = 1.6346
 Kr29-O32 = 1.6332
 Kr29-O1 = 2.8056
 Kr29-O2 = 2.9977
 Kr29-O3 = 2.8628
 Kr29-O4 = 3.1974

NPA

Kr29 = +2.322
 O30 = -0.776
 O31 = -0.778
 O32 = -0.771
 O1 = -0.543
 O2 = -0.532
 O3 = -0.539
 O4 = -0.523

Mulliken

Kr29 = +1.658
 O30 = -0.569
 O31 = -0.552
 O32 = -0.545
 O1 = -0.273
 O2 = -0.232
 O3 = -0.236
 O4 = -0.273

WBI

Kr29 = 3.3060
 O30 = 1.5705
 O31 = 1.5642
 O32 = 1.5802

KrO₃(15-Crown-5)**Bond Lengths (in Å)**

Kr1-O2 = 1.6358
 Kr1-O3 = 1.6339
 Kr1-O4 = 1.6293
 Kr1-O5 = 3.0794
 Kr1-O6 = 3.4168
 Kr1-O7 = 2.9685
 Kr1-O8 = 3.0929
 Kr1-O9 = 2.9578

NPA

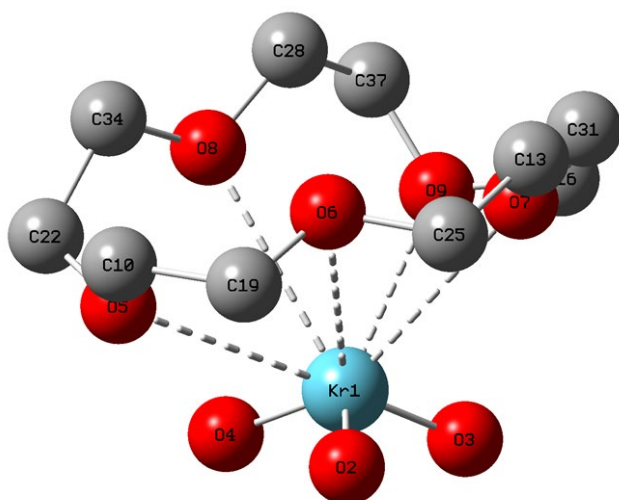
Kr1 = +2.330
 O2 = -0.789
 O3 = -0.777
 O4 = -0.762
 O5 = -0.526
 O6 = -0.536
 O7 = -0.546
 O8 = -0.539
 O9 = -0.526

Mulliken

Kr1 = +1.734
 O2 = -0.584
 O3 = -0.580
 O4 = -0.565
 O5 = -0.315
 O6 = -0.057
 O7 = -0.127
 O8 = -0.152
 O9 = -0.389

WBI

Kr1 = 3.3074
 O2 = 1.5581
 O3 = 1.5621
 O4 = 1.5892

**KrO₃(18-Crown-6)****Bond Lengths (in Å)**

Kr1-O2 = 1.6300
 Kr1-O3 = 1.6300
 Kr1-O4 = 1.6300
 Kr1-O5 = 3.2353
 Kr1-O8 = 3.4924
 Kr1-O15 = 3.2353
 Kr1-O22 = 3.4924
 Kr1-O29 = 3.2353
 Kr1-O36 = 3.4924

NPA

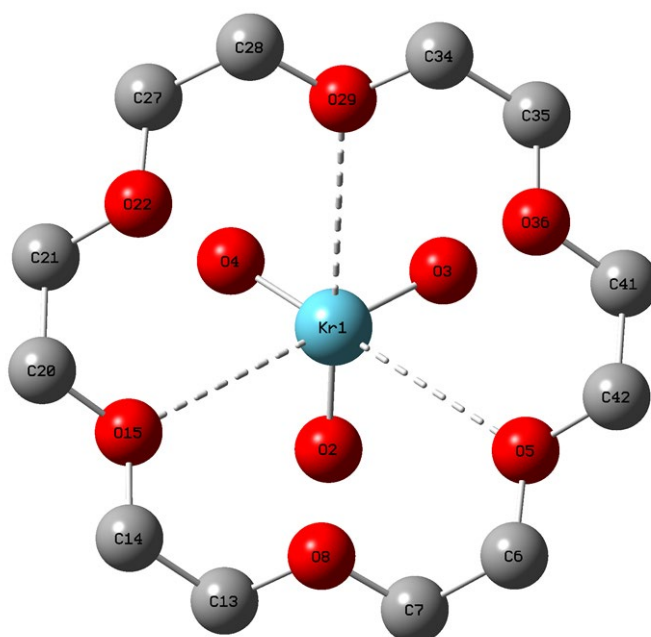
Kr1 = +2.331
 O2 = -0.776
 O3 = -0.776
 O4 = -0.776
 O5 = -0.529
 O8 = -0.525
 O15 = -0.529
 O22 = -0.525
 O29 = -0.529
 O36 = -0.525

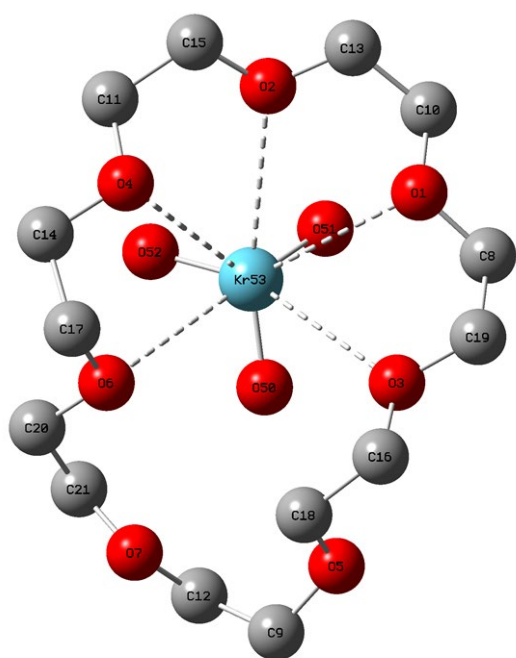
Mulliken

Kr1 = +1.880
 O2 = -0.601
 O3 = -0.601
 O4 = -0.601
 O5 = -0.095
 O8 = -0.181
 O15 = -0.095
 O22 = -0.181
 O29 = -0.095
 O36 = -0.181

WBI

Kr1 = 3.3154
 O2 = 1.5722
 O3 = 1.5722
 O4 = 1.5722



**KrO₃(21-Crown-7)****Bond Lengths (in Å)**

Kr53-O50 = 1.6272
 Kr53-O51 = 1.6317
 Kr53-O52 = 1.6363
 Kr53-O1 = 3.2563
 Kr53-O2 = 3.0698
 Kr53-O3 = 3.2739
 Kr53-O4 = 3.2123
 Kr53-O5 = 4.5664
 Kr53-O6 = 3.1663
 Kr53-O7 = 4.4250

WBI

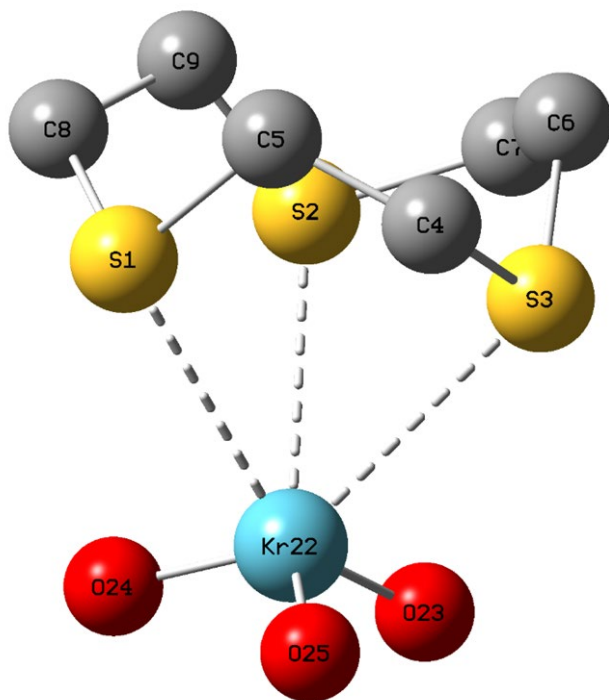
Kr53 = 3.3148
 O50 = 1.5944
 O51 = 1.5654
 O52 = 1.5565

NPA

Kr53 = +2.324
 O50 = -0.760
 O51 = -0.776
 O52 = -0.785
 O1 = -0.533
 O2 = -0.534
 O3 = -0.529
 O4 = -0.536
 O5 = -0.517
 O6 = -0.534
 O7 = -0.531

Mulliken

Kr53 = +1.802
 O50 = -0.522
 O51 = -0.589
 O52 = -0.630
 O1 = -0.129
 O2 = -0.166
 O3 = -0.156
 O4 = -0.109
 O5 = -0.327
 O6 = -0.304
 O7 = -0.263

**KrO₃(9S-Crown-3)****Bond Lengths (in Å)**

Kr22-O23 = 1.63805
 Kr22-O24 = 1.63808
 Kr22-O25 = 1.63804
 Kr22-S1 = 3.18906
 Kr22-S2 = 3.18902
 Kr22-S3 = 3.19056

NPA

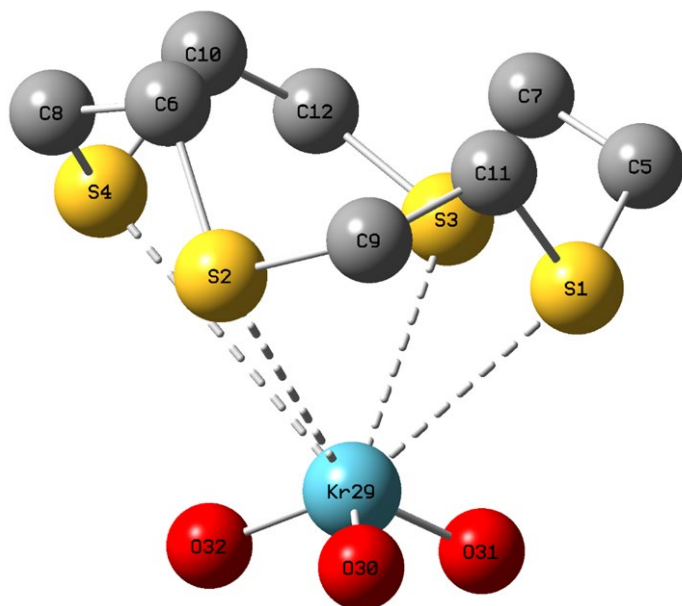
Kr22 = +2.277
 O23 = -0.778
 O24 = -0.778
 O25 = -0.778
 S1 = +0.197
 S2 = +0.197
 S3 = +0.197

Mulliken

Kr22 = +1.395
 O23 = -0.522
 O24 = -0.522
 O25 = -0.522
 S1 = -0.348
 S2 = -0.348
 S3 = -0.348

WBI

Kr22 = 3.3239
 O23 = 1.5712
 O24 = 1.5710
 O25 = 1.5712

KrO₃(12S-Crown-4)**Bond Lengths (in Å)**

Kr29-O30 = 1.6394
 Kr29-O31 = 1.6361
 Kr29-O32 = 1.6340
 Kr29-S1 = 3.1977
 Kr29-S2 = 3.2279
 Kr29-S3 = 3.3529
 Kr29-S4 = 3.8963

NPA

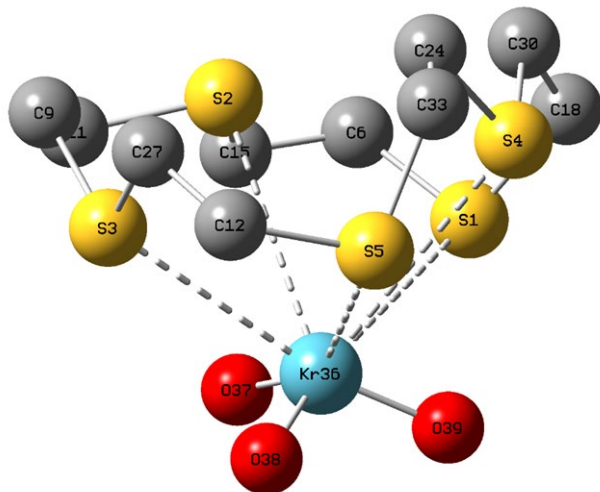
Kr29 = +2.287
 O30 = -0.782
 O31 = -0.772
 O32 = -0.768
 S1 = +0.203
 S2 = +0.204
 S3 = +0.203
 S4 = +0.214

Mulliken

Kr29 = +1.418
 O30 = -0.542
 O31 = -0.525
 O32 = -0.536
 S1 = -0.277
 S2 = -0.341
 S3 = -0.291
 S4 = -0.275

WBI

Kr29 = 3.3201
 O30 = 1.5587
 O31 = 1.5715
 O32 = 1.5863

KrO₃(15S-Crown-5)**Bond Lengths (in Å)**

Kr36-O37 = 1.6398
 Kr36-O38 = 1.6365
 Kr36-O39 = 1.6300
 Kr36-S1 = 3.7987
 Kr36-S2 = 3.6649
 Kr36-S3 = 3.2515
 Kr36-S4 = 3.5034
 Kr36-S5 = 3.3932

NPA

Kr36 = +2.301
 O37 = -0.795
 O38 = -0.773
 O39 = -0.755
 S1 = +0.212
 S2 = +0.158
 S3 = +0.190
 S4 = +0.183
 S5 = +0.205

Mulliken

Kr36 = +1.433
 O37 = -0.546
 O38 = -0.527
 O39 = -0.535
 S1 = -0.282
 S2 = -0.290
 S3 = -0.330
 S4 = -0.431
 S5 = -0.308

WBI

Kr36 = 3.3172
 O37 = 1.5530
 O38 = 1.5667
 O39 = 1.5950

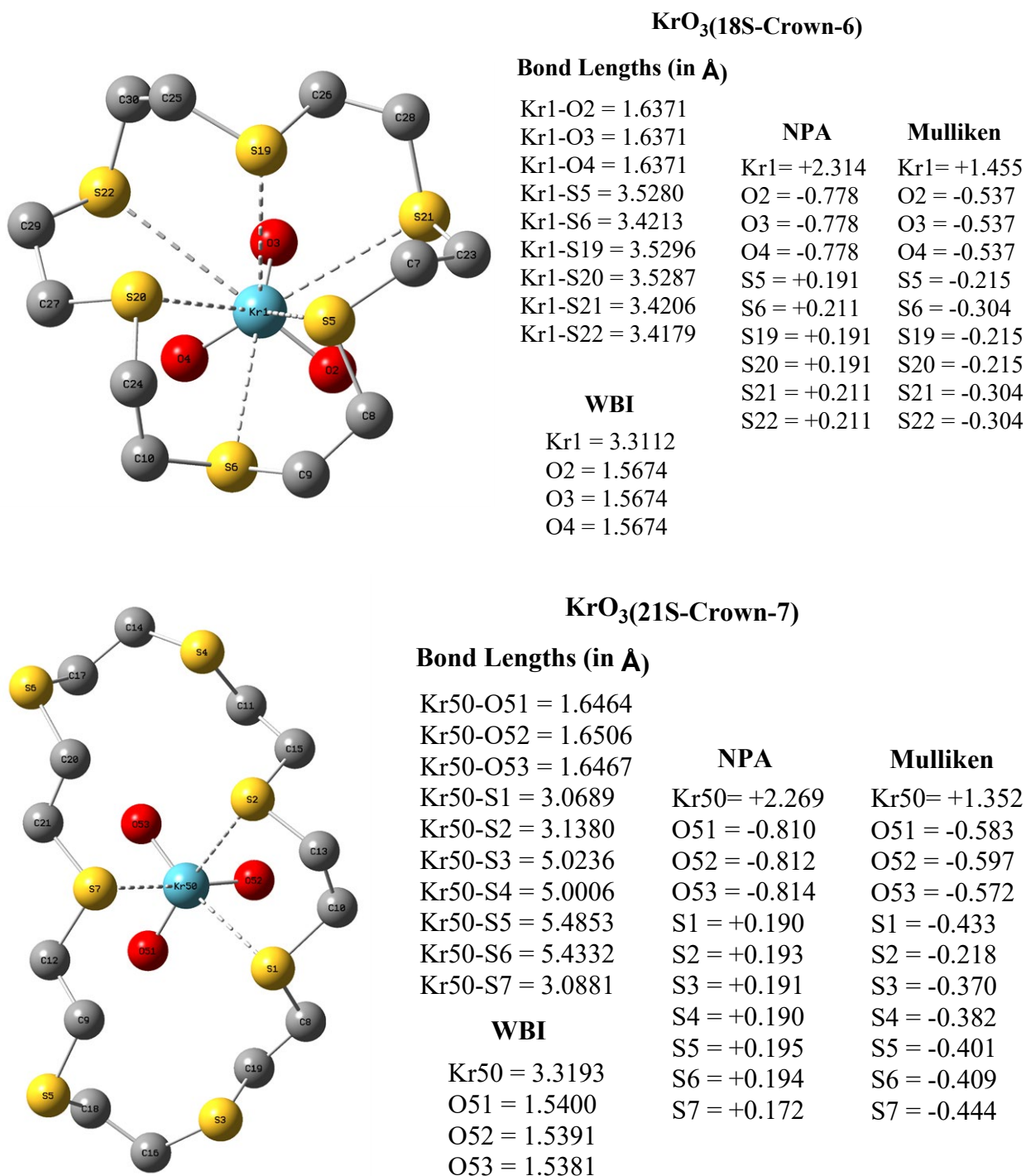
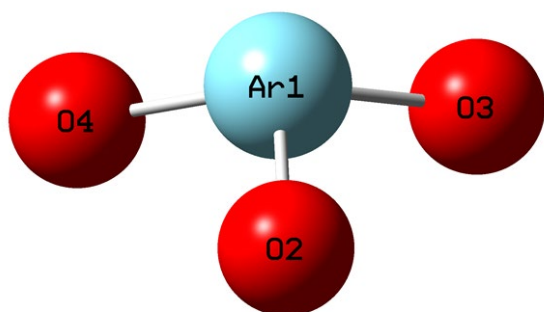


Figure S3.2. Optimized geometries of KrO₃ and its adducts with different crown ethers, along with their thio analogues. The bond distances, WBI values and charge analysis (NPA and Mulliken) data are shown. Hydrogen atoms have been omitted for clarity.

ArO₃**Bond Lengths (in Å)**

Ar1-O2 = 1.4808

Ar1-O3 = 1.4808

Ar1-O4 = 1.4808

NPA

Ar1 = +1.875

O2 = -0.625

O3 = -0.625

O4 = -0.625

WBI

Ar1 = 3.4951

O2 = 1.6906

O3 = 1.6906

O4 = 1.6906

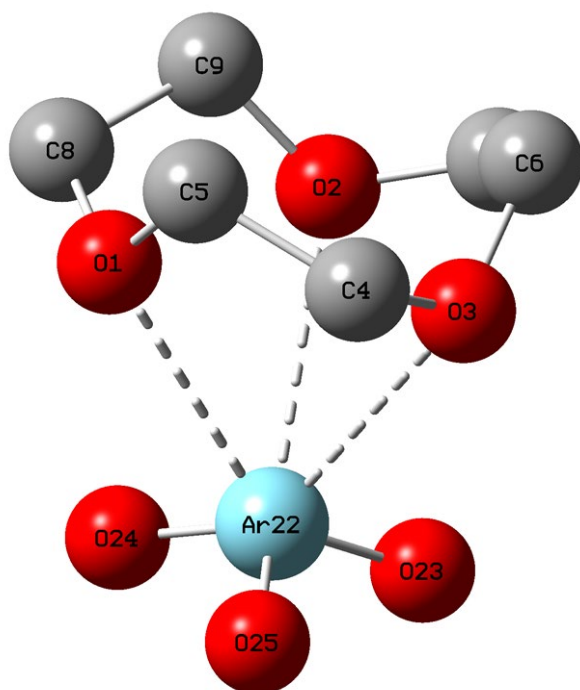
Mulliken

Ar1 = +1.055

O2 = -0.352

O3 = -0.352

O4 = -0.352

ArO₃(9-Crown-3)**Bond Lengths (in Å)**

Ar22-O23 = 1.4861

Ar22-O24 = 1.4861

Ar22-O25 = 1.4861

Ar22-O1 = 2.8129

Ar22-O2 = 2.8134

Ar22-O3 = 2.8130

NPA

Ar22 = +1.929

O23 = -0.642

O24 = -0.642

O25 = -0.642

O1 = -0.538

O2 = -0.538

O3 = -0.538

Mulliken

Ar22 = +1.408

O23 = -0.505

O24 = -0.505

O25 = -0.505

O1 = -0.327

O2 = -0.327

O3 = -0.327

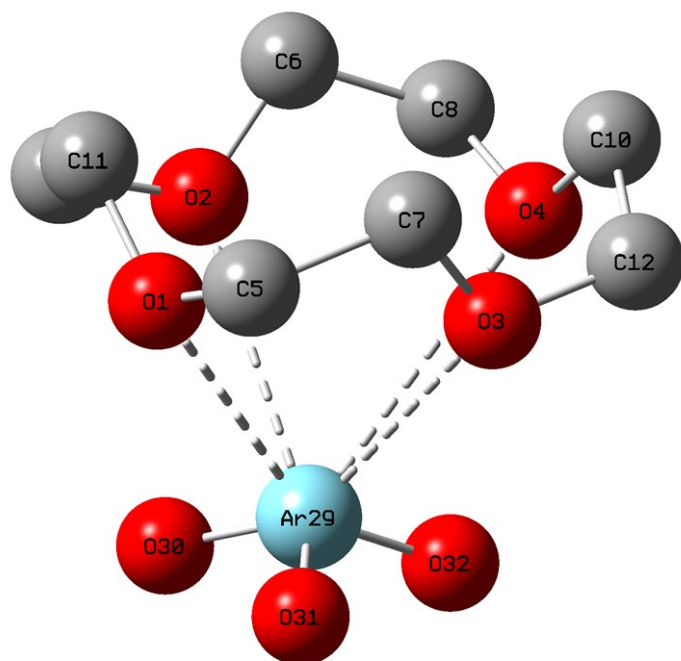
WBI

Ar22 = 3.4510

O23 = 1.6626

O24 = 1.6625

O25 = 1.6626

**ArO₃(12-Crown-4)****Bond Lengths (in Å)**

Ar29-O30 = 1.4858
 Ar29-O31 = 1.4856
 Ar29-O32 = 1.4832
 Ar29-O1 = 2.8143
 Ar29-O2 = 3.0457
 Ar29-O3 = 2.8433
 Ar29-O4 = 3.3753

NPA

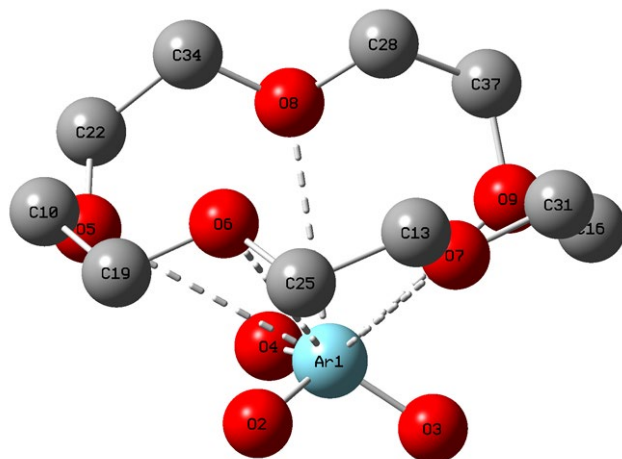
Ar29 = +1.930
 O30 = -0.643
 O31 = -0.645
 O32 = -0.636
 O1 = -0.536
 O2 = -0.525
 O3 = -0.534
 O4 = -0.515

Mulliken

Ar29 = +1.473
 O30 = -0.544
 O31 = -0.522
 O32 = -0.524
 O1 = -0.238
 O2 = -0.206
 O3 = -0.188
 O4 = -0.293

WBI

Ar29 = 3.4583
 O30 = 1.6605
 O31 = 1.6579
 O32 = 1.6725

**ArO₃(15-Crown-5)****Bond Lengths (in Å)**

Ar1-O2 = 1.4858
 Ar1-O3 = 1.4863
 Ar1-O4 = 1.4782
 Ar1-O5 = 3.3520
 Ar1-O6 = 3.5889
 Ar1-O7 = 2.9804
 Ar1-O8 = 3.1342
 Ar1-O9 = 2.9008

NPA

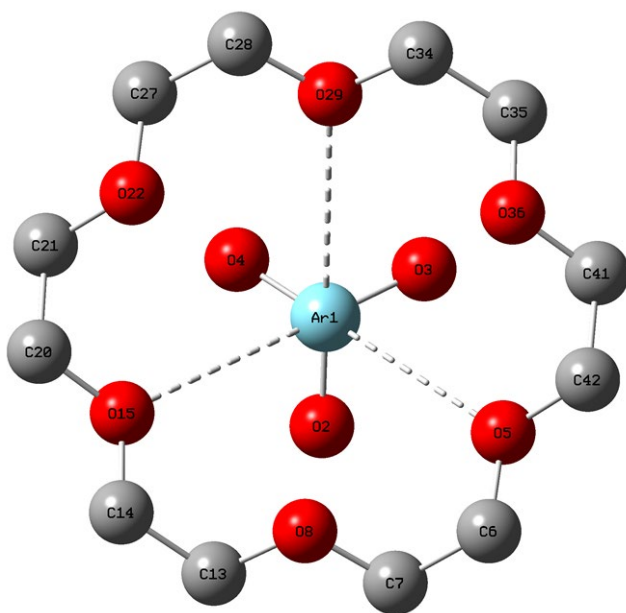
Ar1 = +1.932
 O2 = -0.653
 O3 = -0.647
 O4 = -0.625
 O5 = -0.517
 O6 = -0.530
 O7 = -0.540
 O8 = -0.531
 O9 = -0.522

Mulliken

Ar1 = +1.531
 O2 = -0.538
 O3 = -0.596
 O4 = -0.532
 O5 = -0.312
 O6 = -0.049
 O7 = -0.087
 O8 = -0.154
 O9 = -0.349

WBI

Ar1 = 3.4644
 O2 = 1.6561
 O3 = 1.6530
 O4 = 1.6883

ArO₃(18-Crown-6)**Bond Lengths (in Å)**

Ar1-O2 = 1.4811
 Ar1-O3 = 1.4811
 Ar1-O4 = 1.4811
 Ar1-O5 = 3.2942
 Ar1-O8 = 3.5572
 Ar1-O15 = 3.2942
 Ar1-O22 = 3.5572
 Ar1-O29 = 3.2942
 Ar1-O36 = 3.5572

NPA

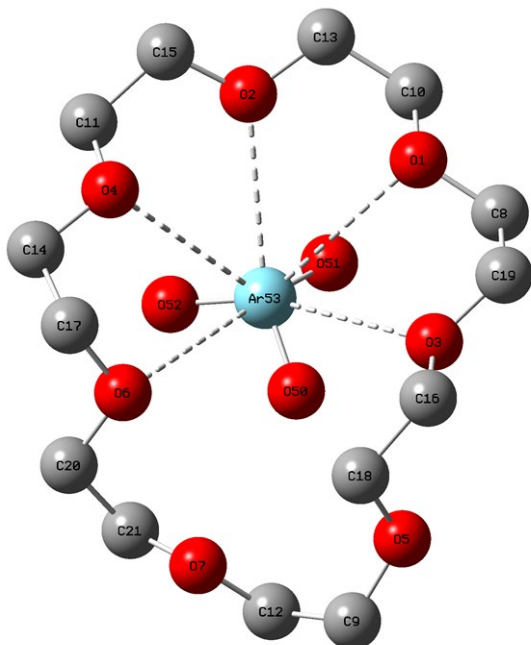
Ar1 = +1.933
 O2 = -0.643
 O3 = -0.643
 O4 = -0.643
 O5 = -0.522
 O8 = -0.519
 O15 = -0.522
 O22 = -0.519
 O29 = -0.522
 O36 = -0.519

Mulliken

Ar1 = +1.714
 O2 = -0.601
 O3 = -0.601
 O4 = -0.601
 O5 = -0.074
 O8 = -0.154
 O15 = -0.074
 O22 = -0.154
 O29 = -0.074
 O36 = -0.154

WBI

Ar1 = 3.4772
 O2 = 1.6689
 O3 = 1.6689
 O4 = 1.6689

ArO₃(21-Crown-7)**Bond Lengths (in Å)**

Ar53-O50 = 1.4757
 Ar53-O51 = 1.4843
 Ar53-O52 = 1.4880
 Ar53-O1 = 3.2840
 Ar53-O2 = 2.9889
 Ar53-O3 = 3.4979
 Ar53-O4 = 3.2646
 Ar53-O5 = 4.6824
 Ar53-O6 = 3.3840
 Ar53-O7 = 4.4180

NPA

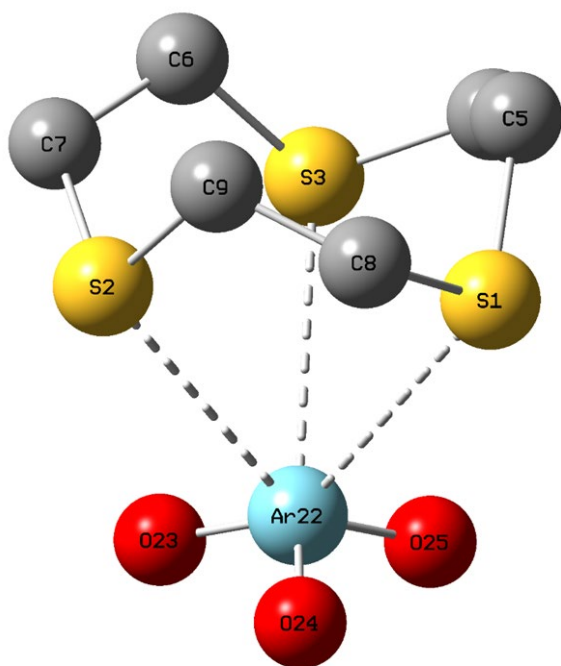
Ar53 = +1.928
 O50 = -0.622
 O51 = -0.645
 O52 = -0.654
 O1 = -0.527
 O2 = -0.532
 O3 = -0.517
 O4 = -0.529
 O5 = -0.518
 O6 = -0.522
 O7 = -0.528

Mulliken

Ar53 = +1.617
 O50 = -0.490
 O51 = -0.604
 O52 = -0.620
 O1 = -0.102
 O2 = -0.134
 O3 = -0.129
 O4 = -0.116
 O5 = -0.324
 O6 = -0.268
 O7 = -0.249

WBI

Ar53 = 3.4715
 O50 = 1.7085
 O51 = 1.6571
 O52 = 1.6489

**ArO₃(9S-Crown-3)****Bond Lengths (in Å)**

Ar22-O23 = 1.4874
 Ar22-O24 = 1.4874
 Ar22-O25 = 1.4874
 Ar22-S1 = 3.2118
 Ar22-S2 = 3.2131
 Ar22-S3 = 3.2101

NPA

Ar22 = +1.907
 O23 = -0.641
 O24 = -0.641
 O25 = -0.641
 S1 = +0.194
 S2 = +0.194
 S3 = +0.194

Mulliken

Ar22 = +1.221

WBI

Ar22 = 3.4653
 O23 = 1.6632
 O24 = 1.6632
 O25 = 1.6632

O23 = -0.466

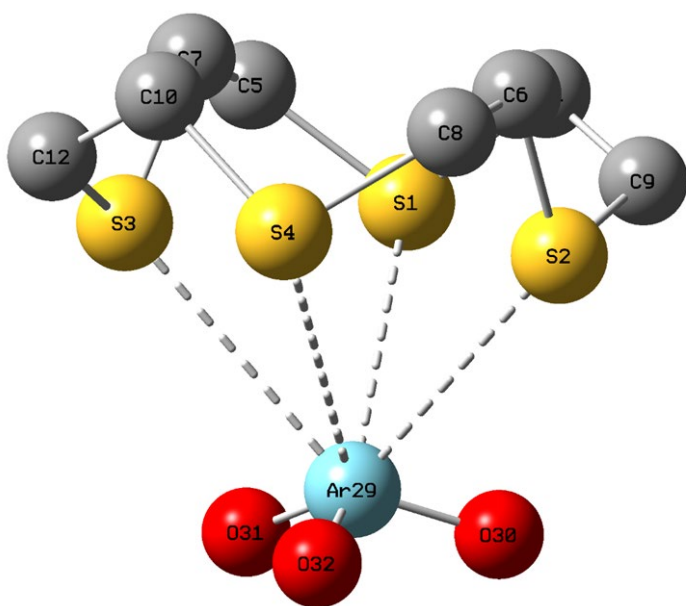
O24 = -0.466

O25 = -0.465

S1 = -0.306

S2 = -0.306

S3 = -0.306

**ArO₃(12S-Crown-4)****Bond Lengths (in Å)**

Ar29-O30 = 1.4898
 Ar29-O31 = 1.4859
 Ar29-O32 = 1.4824
 Ar29-S1 = 3.2577
 Ar29-S2 = 3.2119
 Ar29-S3 = 3.2892
 Ar29-S4 = 4.3789

NPA

Ar29 = +1.910
 O30 = -0.647
 O31 = -0.637
 O32 = -0.629
 S1 = +0.194
 S2 = +0.204
 S3 = +0.201
 S4 = +0.212

Mulliken

Ar29 = +1.247

WBI

Ar29 = 3.4673
 O30 = 1.6552
 O31 = 1.6675
 O32 = 1.6803

O30 = -0.487

O31 = -0.483

O32 = -0.470

S1 = -0.275

S2 = -0.267

S3 = -0.235

S4 = -0.307

ArO₃(15S-Crown-5)**Bond Lengths (in Å)**

Ar36-O37 = 1.4882
 Ar36-O38 = 1.4847
 Ar36-O39 = 1.4793
 Ar36-S1 = 3.8595
 Ar36-S2 = 3.9514
 Ar36-S3 = 3.2862
 Ar36-S4 = 3.4476
 Ar36-S5 = 3.5963

WBI

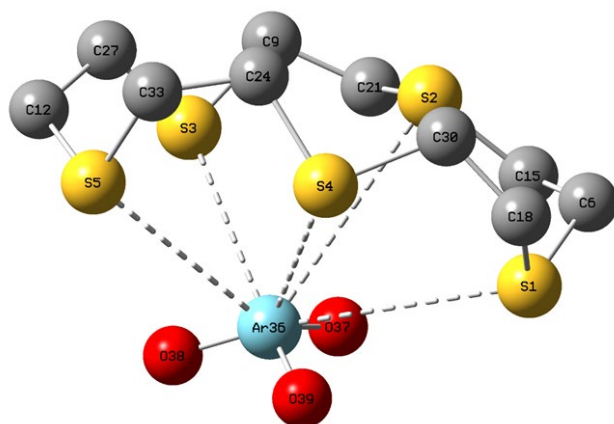
Ar36 = 3.4724
 O37 = 1.6527
 O38 = 1.6691
 O39 = 1.6873

NPA

Ar36 = +1.917
 O37 = -0.656
 O38 = -0.635
 O39 = -0.622
 S1 = +0.207
 S2 = +0.169
 S3 = +0.186
 S4 = +0.178
 S5 = +0.206

Mulliken

Ar36 = +1.308
 O37 = -0.467
 O38 = -0.493
 O39 = -0.513
 S1 = -0.281
 S2 = -0.313
 S3 = -0.253
 S4 = -0.403
 S5 = -0.298

**ArO₃(18S-Crown-6)****Bond Lengths (in Å)**

Ar1-O2 = 1.48468
 Ar1-O3 = 1.48471
 Ar1-O4 = 1.48465
 Ar1-S5 = 3.5923
 Ar1-S6 = 3.5163
 Ar1-S19 = 3.5935
 Ar1-S20 = 3.5957
 Ar1-S21 = 3.5270
 Ar1-S22 = 3.5229

WBI

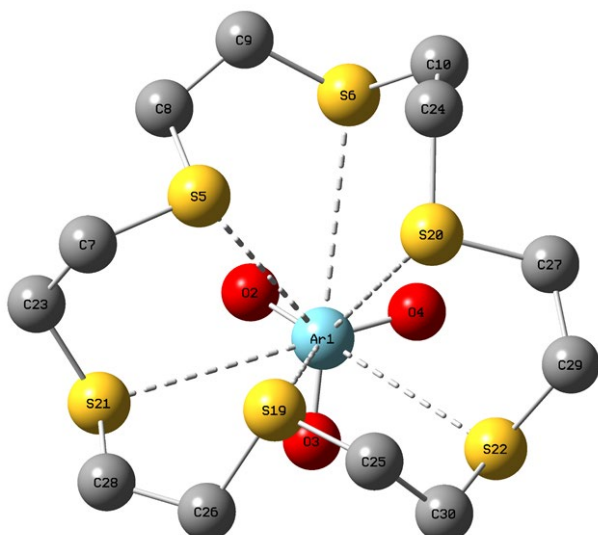
Ar1 = 3.4654
 O2 = 1.6669
 O3 = 1.6668
 O4 = 1.6671

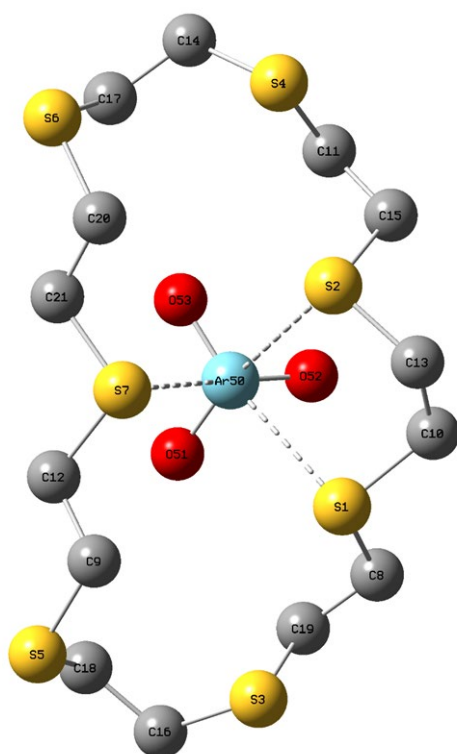
NPA

Ar1 = +1.926
 O2 = -0.639
 O3 = -0.639
 O4 = -0.639
 S5 = +0.198
 S6 = +0.205
 S19 = +0.198
 S20 = +0.199
 S21 = +0.205
 S22 = +0.205

Mulliken

Ar1 = +1.464
 O2 = -0.541
 O3 = -0.541
 O4 = -0.541
 S5 = -0.196
 S6 = -0.297
 S19 = -0.196
 S20 = -0.196
 S21 = -0.297
 S22 = -0.297





ArO₃(21S-Crown-7)

Bond Lengths (in Å)

Ar50-O51 = 1.4915
 Ar50-O52 = 1.4950
 Ar50-O53 = 1.4928
 Ar50-S1 = 3.1328
 Ar50-S2 = 3.2103
 Ar50-S3 = 5.0906
 Ar50-S4 = 5.0440
 Ar50-S5 = 5.5476
 Ar50-S6 = 5.4536
 Ar50-S7 = 3.1734

WBI

Ar50 = 3.4455
 O51 = 1.6460
 O52 = 1.6418
 O53 = 1.6415

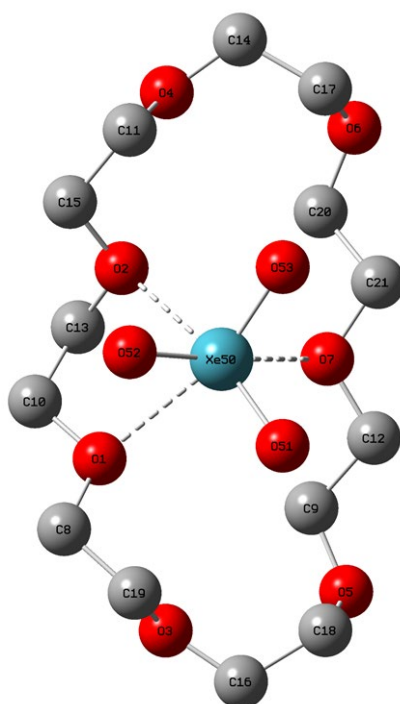
NPA

Ar50 = +1.911
 O51 = -0.654
 O52 = -0.656
 O53 = -0.659
 S1 = +0.179
 S2 = +0.186
 S3 = +0.195
 S4 = +0.194
 S5 = +0.194
 S6 = +0.193
 S7 = +0.163

Mulliken

Ar50 = +1.509
 O51 = -0.589
 O52 = -0.602
 O53 = -0.597
 S1 = -0.404
 S2 = -0.202
 S3 = -0.364
 S4 = -0.376
 S5 = -0.396
 S6 = -0.406
 S7 = -0.443

Figure S3.3. Optimized geometries of ArO₃ and its adducts with different crown ethers, along with their thio analogues. The bond distances, WBI values and charge analysis (NPA and Mulliken) data are shown. Hydrogen atoms have been omitted for clarity.



XeO₃(21O-Crown-7)'

Bond Lengths (in Å)

Xe50-O51 = 1.7686
 Xe50-O52 = 1.7670
 Xe50-O53 = 1.7661
 Xe50-O1 = 2.8115
 Xe50-O2 = 2.7410
 Xe50-O3 = 4.5493
 Xe50-O4 = 4.6187
 Xe50-O5 = 4.8030
 Xe50-O6 = 4.9100
 Xe50-O7 = 2.8207

WBI

Xe50 = 3.3238
 O51 = 1.4656
 O52 = 1.4656
 O53 = 1.4609

NPA

Xe50 = +2.919
 O51 = -0.993
 O52 = -0.984
 O53 = -0.990
 O1 = -0.565
 O2 = -0.568
 O3 = -0.525
 O4 = -0.527
 O5 = -0.515
 O6 = -0.515
 O7 = -0.576

Mulliken

Xe50 = +1.725
 O51 = -0.607
 O52 = -0.675
 O53 = -0.601
 O1 = -0.056
 O2 = -0.173
 O3 = -0.401
 O4 = -0.383
 O5 = -0.450
 O6 = -0.456
 O7 = -0.332

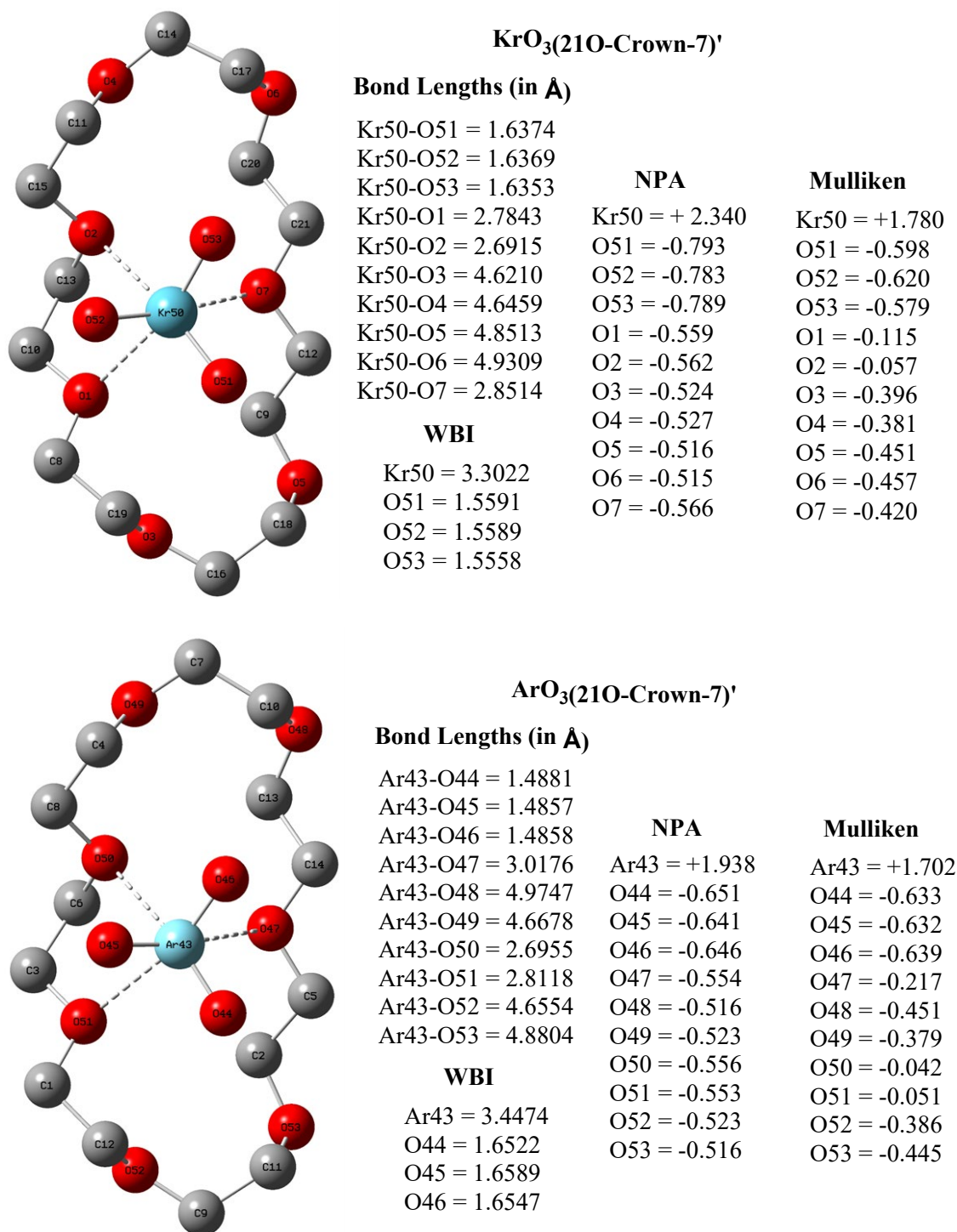


Figure S3.4. Optimized geometries of NgO₃ complex with 21-Crown-7 with different mode of binding. The bond distances, WBI values and charge analysis (NPA and Mulliken) data are shown. Hydrogen atoms have been omitted for clarity.

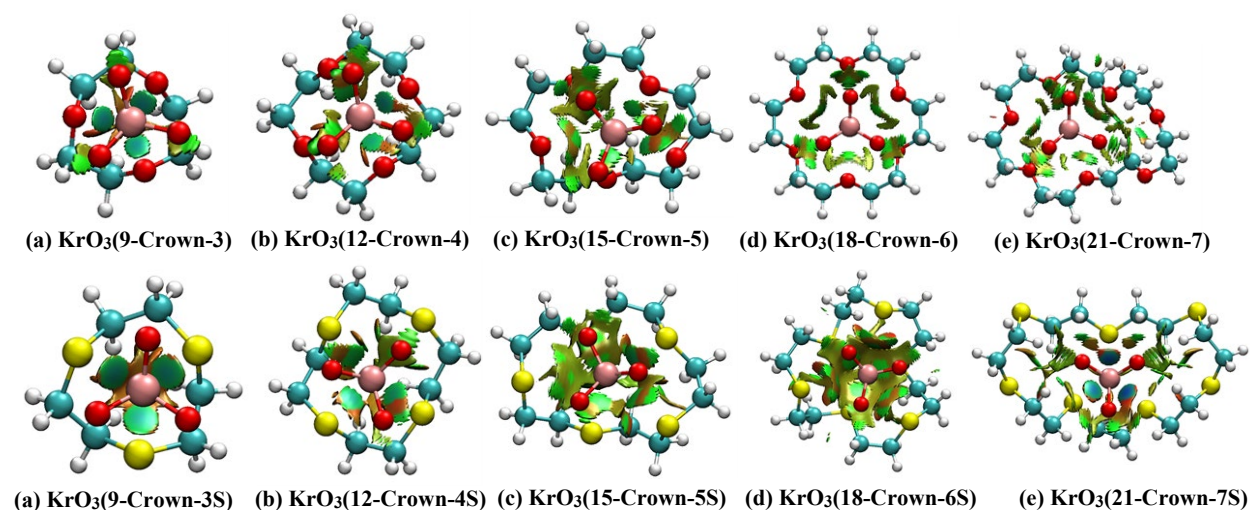


Figure S3.5. NCI plots of the complexes of KrO_3 with crown ethers (top) and their thio analogues (bottom).

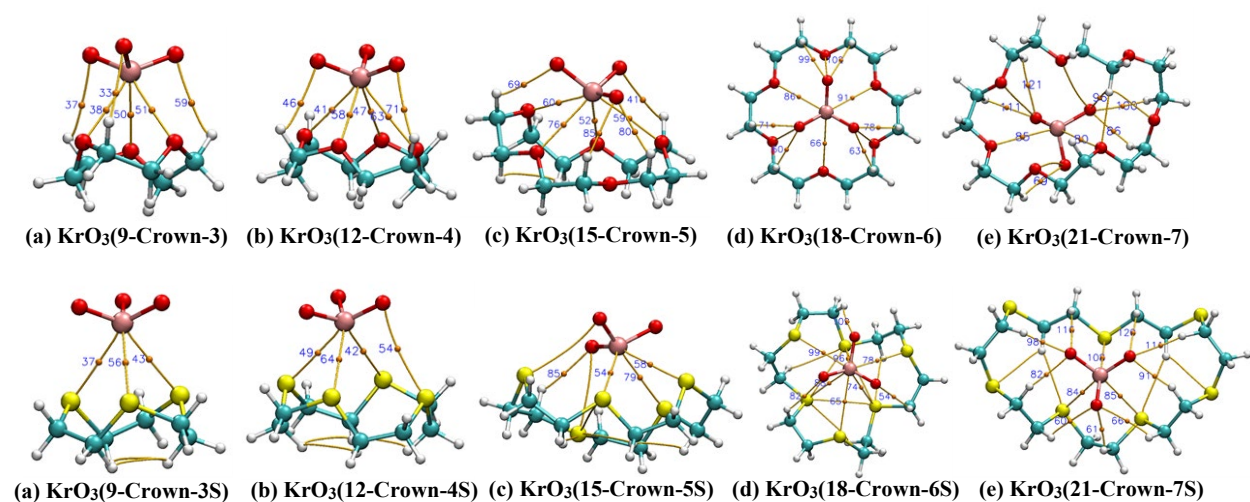


Figure S3.6. Bond critical points obtained from AIM analysis for the complexes of KrO_3 with crown ethers (top) and their thio analogues (bottom).

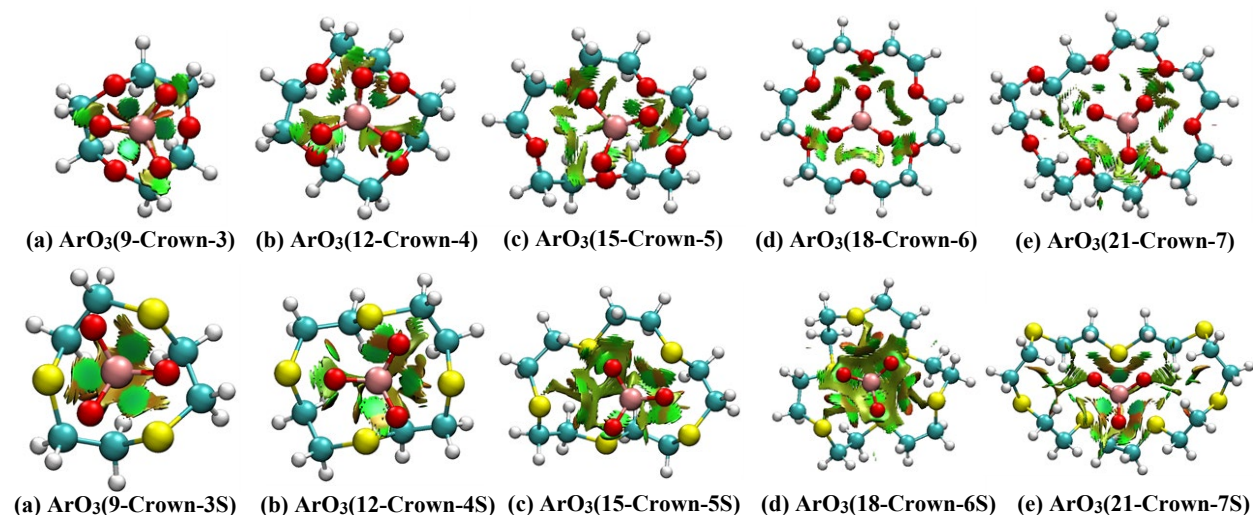


Figure S3.7. NCI plots of the complexes of ArO_3 with crown ethers (top) and their thio analogues (bottom).

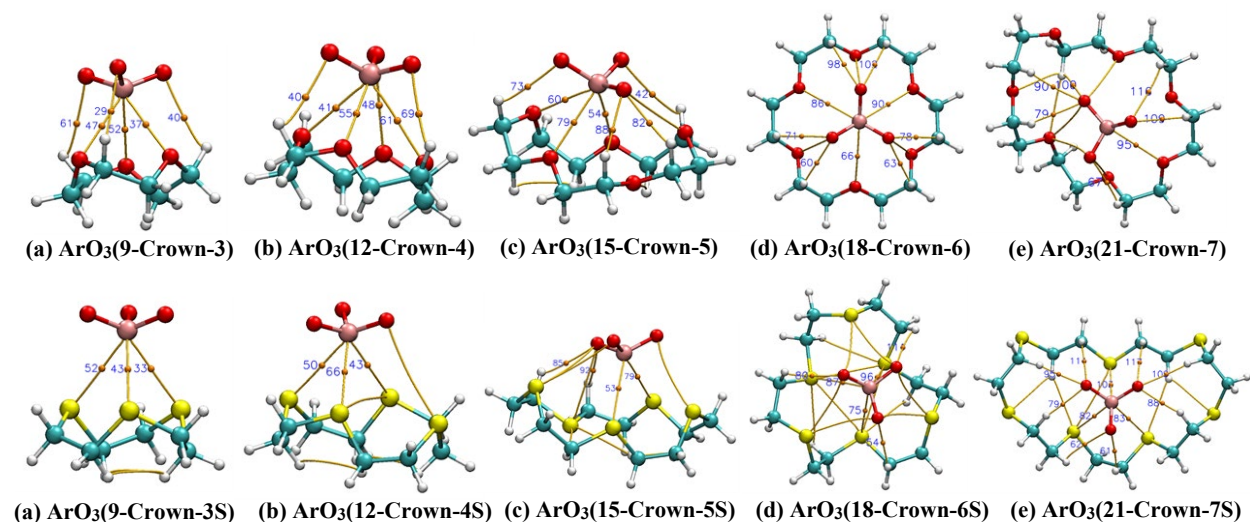


Figure S3.8. Bond critical points obtained from AIM analysis for the complexes of ArO_3 with crown ethers (top) and their thio analogues (bottom).

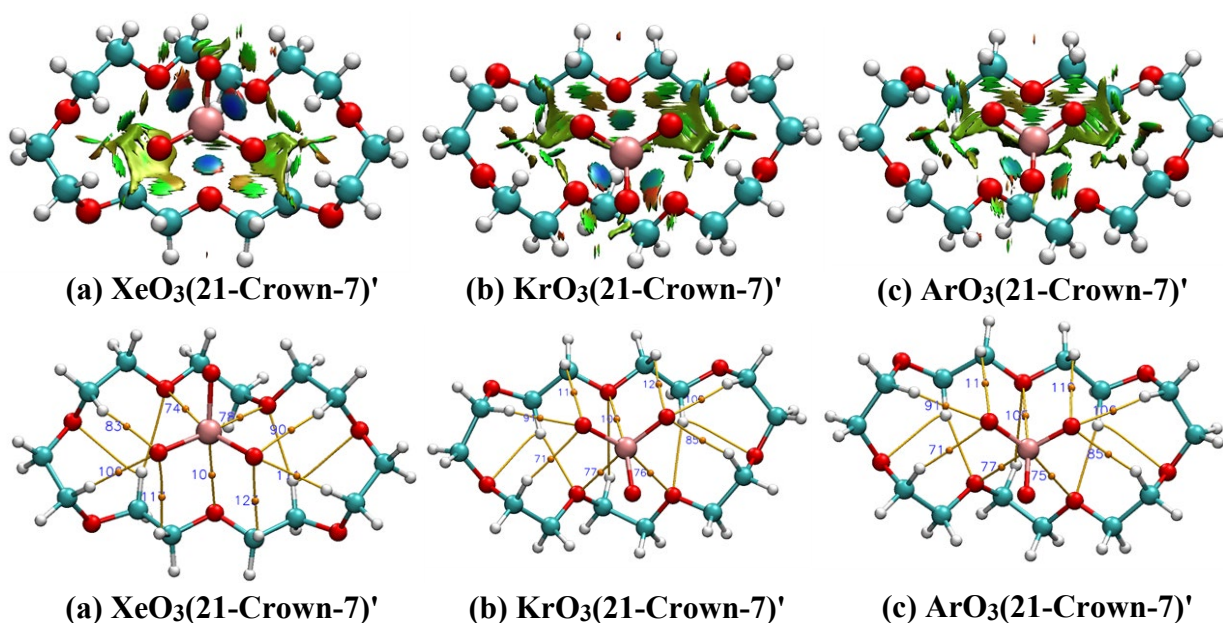


Figure S3.9. NCI plot (top) and bond critical points (bottom) obtained from AIM analysis for the complexes of NgO_3 with 21-Crown-7 (21O7) having different mode of binding.

Table S3.1. All the MEPs (minima: $V_{s,\text{min}}$) of the crown ethers and their thio analogues with their respective energy values in kcal/mol.

	9-Crown-3	12-Crown-4	15-Crown-5	18-Crown-6	21-Crown-7
$V_{s,\text{min}}$ In kcal/mol	-43.7	-54.59	-56.22	-56.76	-32.24
		-54.59	-58.69	-56.76	-25.64
		-54.59		-56.76	-27.12
		-54.59		-56.76	-30.73
				-56.76	-32.26
				-56.76	-28.15
	9-Crown-3S	12-Crown-4S	15-Crown-5S	18-Crown-6S	21-Crown-7S
	-18.81	-21.53	-22.26	-19.66	-19.17
	-20.18	-23.35	-22.92	-20.35	-20.24
	-12.29	-40.86	-38.45	-20.10	-14.28
	-24.25	-40.83	-22.69	-25.28	-24.53
	-22.12	-23.35	-12.27	-26.66	-18.20
		-21.53	-20.44	-26.66	-23.24
			-20.82	-25.28	-22.76
				-20.10	-23.64
				-20.35	-25.72
				-19.65	-22.57

Table S3.2. Deformation energy (at APFD/def2TZVPD) required by the crown ethers in complex formation with NgO₃. Donor atoms of the crowns are denoted by their atomic symbol (O/S).

	9O3	12O4	15O5	18O6	21O7	21O7'
XeO ₃	5.33	0.74	2.55	1.53	4.88	4.37
KrO ₃	5.13	0.46	1.57	0.83	3.41	3.62
ArO ₃	5.04	0.29	0.79	0.43	2.52	2.60
	9S3	12S4	15S5	18S6	21S7	
XeO ₃	3.99	1.51	4.97	4.83	9.2	
KrO ₃	3.82	1.03	4.21	4.78	8.8	
ArO ₃	3.73	0.37	3.32	4.78	8.5	

Table S3.3. Interaction Energy (ΔE , in kcal/mol) at different level of theory. BE = Bonding Energy

	EDA/MP2/ZORA/TZ2P		APFD (ΔE_{BSSE})	
	Only MP2	Total BE	def2-TZVPD	aug-cc-pVTZ (-PP for Xe)
XeO ₃ :9O3	-17.1	-28.1	-25	-24.8
XeO ₃ :12O4	-18.3	-34.3	-30.6	-30.5
XeO ₃ :15O5	-21.5	-40.8	-38.3	-38.2
XeO ₃ :18O6	-22.2	-46.2	-40.2	-40.3
XeO ₃ :21O7	-26.7	-46.0	-41.2	-41.2
XeO ₃ :21O7'	-30.8	-45.6	-40.2	-40.0
XeO ₃ :9S3	-15.5	-23.0	-24.2	-23.9
XeO ₃ :12S4	-16.9	-25.3	-27.6	-27.4
XeO ₃ :15S5	-21.0	-31.4	-35.4	-35.1
XeO ₃ :18S6	-28.3	-40.5	-42.8	-42.4
XeO ₃ :21S7	-40.5	-50.1	-48.2	-47.9
KrO ₃ :9O3	-17.6	-27.9	-20.1	
KrO ₃ :12O4	-17.7	-30.4	-22.6	
KrO ₃ :15O5	-20.7	-34.3	-25.7	
KrO ₃ :18O6	-20.8	-34.8	-26.0	
KrO ₃ :21O7	-25.7	-36.2	-26.4	
KrO ₃ :21O7'	-30.6	-41.7	-29.9	
KrO ₃ :9S3	-16.1	-22.4	-18.7	
KrO ₃ :12S4	-16.4	-22.4	-19.3	
KrO ₃ :15S5	-19.4	-26.5	-23.0	
KrO ₃ :18S6	-24.4	-31.4	-27.6	
KrO ₃ :21S7	-39.5	-44.8	-36.4	
ArO ₃ :9O3	-11.0	-18.7	-15.4	
ArO ₃ :12O4	-11.0	-19.8	-16.1	
ArO ₃ :15O5	-13.8	-22.0	-17.2	

ArO ₃ :18O6	-15.3	-23.4	-17.6
ArO ₃ :21O7	-18.8	-24.3	-17.9
ArO ₃ :21O7'	-20.2	-26.5	-20.7
ArO ₃ :9S3	-9.4	-13.5	-13.5
ArO ₃ :12S4	-10.8	-13.3	-13.0
ArO ₃ :15S5	-12.5	-15.9	-14.8
ArO ₃ :18S6	-16.4	-19.5	-18.0
ArO ₃ :21S7	-25.1	-26.8	-23.8

Table S3.4. Bond orders of Ng...O and Ng....S from Wiberg bond index (WBI) analysis, obtained from NBO 6 calculations, for all the complexes under study.

	Ng....O Bond Order (WBI)		
	XeO ₃	KrO ₃	ArO ₃
9-Crown-3	Xe22-O1 = 0.0154 Xe22-O2 = 0.0241 Xe22-O3 = 0.0137	Kr22-O1 = 0.0115 Kr22-O2 = 0.0114 Kr22-O3 = 0.0115	Ar22-O1 = 0.0067 Ar22-O2 = 0.0067 Ar22-O3 = 0.0067
12-Crown-4	Xe29-O1 = 0.0233 Xe29-O2 = 0.0131 Xe29-O3 = 0.0128 Xe29-O4 = 0.0076	Kr29-O1 = 0.0119 Kr29-O2 = 0.0063 Kr29-O3 = 0.0099 Kr29-O4 = 0.0041	Ar29-O1 = 0.0064 Ar29-O2 = 0.0037 Ar29-O3 = 0.0060 Ar29-O4 = 0.0021
15-Crown-5	Xe1-O5 = 0.0188 Xe1-O6 = 0.0057 Xe1-O7 = 0.0130 Xe1-O8 = 0.0091 Xe1-O9 = 0.0150	Kr1-O5 = 0.0064 Kr1-O6 = 0.0028 Kr1-O7 = 0.0073 Kr1-O8 = 0.0053 Kr1-O9 = 0.0082	Ar1-O5 = 0.0021 Ar1-O6 = 0.0017 Ar1-O7 = 0.0044 Ar1-O8 = 0.0036 Ar1-O9 = 0.0053
18-Crown-6	Xe43-O1 = 0.0101 Xe43-O2 = 0.0047 Xe43-O3 = 0.0101 Xe43-O23 = 0.0047 Xe43-O24 = 0.0101 Xe43-O25 = 0.0047	Kr1-O5 = 0.0051 Kr1-O8 = 0.0029 Kr1-O15 = 0.0051 Kr1-O22 = 0.0029 Kr1-O29 = 0.0051 Kr1-O36 = 0.0029	Ar1-O5 = 0.0031 Ar1-O8 = 0.0022 Ar1-O15 = 0.0031 Ar1-O22 = 0.0022 Ar1-O29 = 0.0031 Ar1-O36 = 0.0022
21-Crown-7	Xe50-O1 = 0.0088 Xe50-O2 = 0.0124 Xe50-O3 = 0.0101 Xe50-O4 = 0.0088 Xe50-O6 = 0.0180	Kr53-O1 = 0.0046 Kr53-O2 = 0.0065 Kr53-O3 = 0.0045 Kr53-O4 = 0.0046 Kr53-O6 = 0.0058	Ar53-O1 = 0.0034 Ar53-O2 = 0.0047 Ar53-O3 = 0.0024 Ar53-O4 = 0.0030 Ar53-O6 = 0.0023
21-Crown-7'	Xe50-O1 = 0.0285 Xe50-O2 = 0.0351 Xe50-O7 = 0.0332	Kr50-O1 = 0.0170 Kr50-O2 = 0.0219 Kr50-O7 = 0.0185	Ar43-O47 = 0.0073 Ar43-O50 = 0.0118 Ar43-O51 = 0.0085
9-Crown-3S	Xe22-S1 = 0.0504 Xe22-S2 = 0.0577 Xe22-S3 = 0.0220	Kr22-S1 = 0.0279 Kr22-S2 = 0.0279 Kr22-S3 = 0.0277	Ar22-S1 = 0.0130 Ar22-S2 = 0.0129 Ar22-S3 = 0.0130
12-Crown-4S	Xe29-S1 = 0.0470 Xe29-S2 = 0.0478 Xe29-S3 = 0.0201 Xe29-S4 = 0.0149	Kr29-S1 = 0.0278 Kr29-S2 = 0.0217 Kr29-S3 = 0.0159 Kr29-S4 = 0.0028	Ar29-S1 = 0.0113 Ar29-S2 = 0.0108 Ar29-S3 = 0.0087 Ar29-S4 = 0.0006
15-Crown-5S	Xe36-S1 = 0.0231 Xe36-S2 = 0.0150	Kr36-S1 = 0.0034 Kr36-S2 = 0.0055	Ar36-S1 = 0.0014 Ar36-S2 = 0.0015

	Xe36-S3 = 0.0423 Xe36-S4 = 0.0188 Xe36-S5 = 0.0327	Kr36-S3 = 0.0220 Kr36-S4 = 0.0095 Kr36-S5 = 0.0153	Ar36-S3 = 0.0082 Ar36-S4 = 0.0060 Ar36-S5 = 0.0043
18-Crown-6S	Xe1-S5 = 0.0200 Xe1-S6 = 0.0335 Xe1-S19 = 0.0200 Xe1-S20 = 0.0200 Xe1-S21 = 0.0336 Xe1-S22 = 0.0337	Kr1-S5 = 0.0079 Kr1-S6 = 0.0110 Kr1-S19 = 0.0079 Kr1-S20 = 0.0079 Kr1-S21 = 0.0111 Kr1-S22 = 0.0112	Ar1-S5 = 0.0032 Ar1-S6 = 0.0032 Ar1-S19 = 0.0032 Ar1-S20 = 0.0032 Ar1-S21 = 0.0031 Ar1-S22 = 0.0031
21-Crown-7S	Xe50-S1 = 0.0944 Xe50-S2 = 0.0781 Xe50-S7 = 0.1016	Kr50-S1 = 0.0625 Kr50-S2 = 0.0501 Kr50-S7 = 0.0696	Ar50-S1 = 0.0263 Ar50-S2 = 0.0207 Ar50-S7 = 0.0295

Table S3.5. Change in the charge of XeO₃ upon complexation with different crown ethers and their thio analogues. Comparative analysis from Merz-Kollman (MK) electrostatic model and natural population analysis (NPA) obtained from NBO 6.

	MK Charges		NPA Charges from NBO 6	
Parent XeO ₃	Xe 1.127740 O -0.376430 O -0.375526 O -0.375784		Xe 2.75726 O -0.91909 O -0.91909 O -0.91909	
In Complexes	Crown Ethers (O)	Thio-Crown Ethers (S)	Crown Ethers (O)	Thio-Crown Ethers (S)
9-Crown-3	Xe 0.796698 O -0.349985 O -0.348498 O -0.351100	Xe 1.076929 O -0.423263 O -0.414856 O -0.425836	Xe 2.86118 O -0.96188 O -0.96196 O -0.95871	Xe 2.81385 O -0.96394 O -0.97787 O -0.96204
12-Crown-4	Xe 0.781336 O -0.362867 O -0.362840 O -0.354376	Xe 1.221776 O -0.456419 O -0.456205 O -0.455978	Xe 2.87588 O -0.96784 O -0.96735 O -0.96248	Xe 2.82408 O -0.97959 O -0.96518 O -0.96389
15-Crown-5	Xe 0.611699 O -0.324279 O -0.328838 O -0.312627	Xe 1.023653 O -0.423908 O -0.407179 O -0.387839	Xe 2.89593 O -0.98586 O -0.97013 O -0.96051	Xe 2.84263 O -0.99697 O -0.97282 O -0.95542
18-Crown-6	Xe 0.437429 O -0.264996 O -0.267240 O -0.267240	Xe 0.766498 O -0.345419 O -0.342303 O -0.345230	Xe 2.89571 O -0.96782 O -0.96782 O -0.96782	Xe 2.86146 O -0.98665 O -0.98660 O -0.98660
21-Crown-7	Xe 0.542662 O -0.257961 O -0.303070 O -0.309058	Xe 0.819814 O -0.352021 O -0.400472 O -0.358566	Xe 2.89929 O -0.96408 O -0.96927 O -0.98101	Xe 2.81577 O -1.01002 O -1.01170 O -1.01335

21-Crown-7' (Alternative Mode of Binding)	Xe 0.628663 O -0.298183 O -0.335373 O -0.299328	-	Xe 2.90184 O -0.98679 O -0.97909 O -0.98450	-
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Table S3.6. Change in the charge of KrO_3 upon complexation with different crown ethers and their thio analogues. Comparative analysis from Merz-Kollman (MK) electrostatic model and natural population analysis (NPA) obtained from NBO 6.

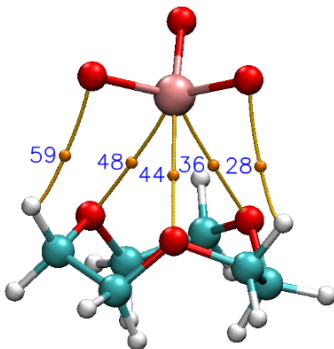
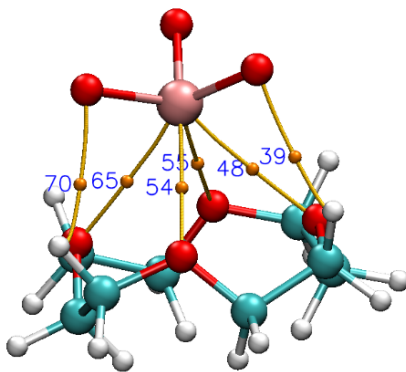
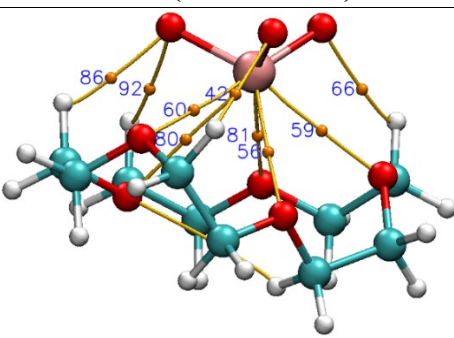
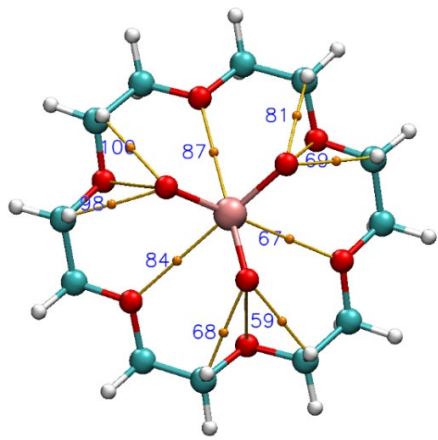
	MK Charges		NPA Charges from NBO 6	
Parent KrO_3	Kr 0.895775 O -0.299347 O -0.298203 O -0.298225		Kr 2.23467 O -0.74489 O -0.74489 O -0.74489	
In Complexes	Crown Ethers (O)	Thio-Crown Ethers (S)	Crown Ethers (O)	Thio-Crown Ethers (S)
9-Crown-3	Kr 0.370784 O -0.208583 O -0.206825 O -0.207479	Kr 0.662027 O -0.283208 O -0.282133 O -0.280973	Kr 2.31228 O -0.77401 O -0.77402 O -0.77402	Kr 2.27604 O -0.77798 O -0.77807 O -0.77797
12-Crown-4	Kr 0.419546 O -0.227611 O -0.235917 O -0.219584	Kr 0.801489 O -0.322222 O -0.303858 O -0.302861	Kr 2.31661 O -0.77528 O -0.77650 O -0.76928	Kr 2.28381 O -0.78203 O -0.77222 O -0.76612
15-Crown-5	Kr 0.272859 O -0.190587 O -0.198792 O -0.170856	Kr 0.603072 O -0.276758 O -0.255734 O -0.229378	Kr 2.32430 O -0.78738 O -0.77559 O -0.76064	Kr 2.29585 O -0.79352 O -0.77212 O -0.75430
18-Crown-6	Kr 0.338191 O -0.193431 O -0.195470 O -0.192978	Kr 0.228450 O -0.150942 O -0.151651 O -0.152110	Kr 2.32443 O -0.77375 O -0.77375 O -0.77375	Kr 2.30928 O -0.77625 O -0.77628 O -0.77625
21-Crown-7	Kr 0.344875 O -0.161443 O -0.205334 O -0.197461	Kr 0.423810 O -0.218910 O -0.261559 O -0.208944	Kr 2.32160 O -0.75908 O -0.77433 O -0.78376	Kr 2.26878 O -0.80824 O -0.81117 O -0.81298
21-Crown-7' (Alternative Mode of Binding)	Kr 0.273024 O -0.178780 O -0.202382 O -0.172362	-	Kr 2.33441 O -0.79046 O -0.78178 O -0.78697	-

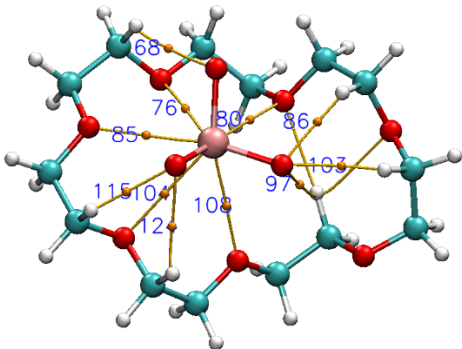
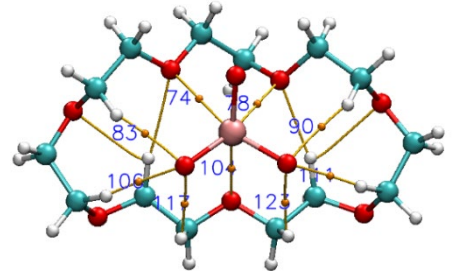
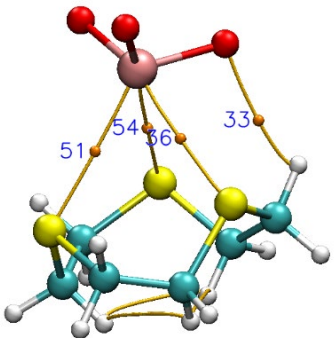
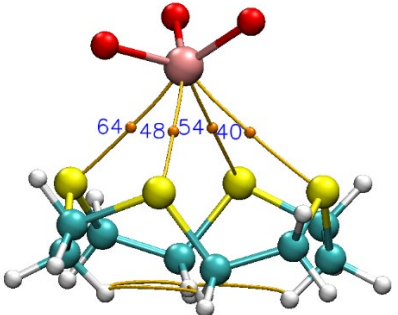
Table S3.7. Change in the charge of ArO₃ upon complexation with different crown ethers and their thio analogues. Comparative analysis from Merz-Kollman (MK) electrostatic model and natural population analysis (NPA) obtained from NBO 6.

	MK Charges		NPA Charges from NBO 6	
Parent ArO ₃	Ar 0.710825 O -0.237472 O -0.236551 O -0.236803		Ar 1.87519 O -0.62506 O -0.62506 O -0.62506	
In Complexes	Crown Ethers (O)	Thio-Crown Ethers (S)	Crown Ethers (O)	Thio-Crown Ethers (S)
9-Crown-3	Ar 0.207035 O -0.136169 O -0.135155 O -0.131602	Ar 0.501029 O -0.204167 O -0.202773 O -0.202972	Ar 1.92656 O -0.64164 O -0.64164 O -0.64163	Ar 1.90596 O -0.64080 O -0.64079 O -0.64088
12-Crown-4	Ar 0.318768 O -0.171539 O -0.181245 O -0.158786	Ar 0.574268 O -0.235211 O -0.215021 O -0.207015	Ar 1.92773 O -0.64315 O -0.64433 O -0.63530	Ar 1.90806 O -0.64728 O -0.63681 O -0.62855
15-Crown-5	Ar 0.119444 O -0.114051 O -0.130392 O -0.086073	Ar 0.393372 O -0.186690 O -0.167096 O -0.139301	Ar 1.93078 O -0.65186 O -0.64697 O -0.62529	Ar 1.91472 O -0.65460 O -0.63507 O -0.62212
18-Crown-6	Ar 0.235993 O -0.135830 O -0.137577 O -0.136558	Ar -0.005905 O -0.047183 O -0.048411 O -0.050368	Ar 1.93067 O -0.64211 O -0.64211 O -0.64211	Ar 1.92364 O -0.63839 O -0.63844 O -0.63833
21-Crown-7	Ar 0.269528 O -0.093589 O -0.164027 O -0.135251	Ar 0.183498 O -0.101376 O -0.142340 O -0.096705	Ar 1.92586 O -0.61957 O -0.64553 O -0.65393	Ar 1.90874 O -0.65279 O -0.65571 O -0.65741
21-Crown-7' (Alternative Mode of Binding)	Ar 0.083428 O -0.086785 O -0.115937 O -0.088974	-	Ar 1.93617 O -0.64988 O -0.64066 O -0.64532	-

Table S3.8. Bond critical points along with their respective electron density (ρ , in a.u.) and Laplacian of the electron density ($\nabla^2\rho$, in a.u.) for the complexes of XeO₃ with different crown ethers and their thio analogues.

XeO ₃ (9-Crown-3)	Xe....O			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$

	36	0.020	0.066	28	0.008	0.028
	44	0.025	0.079	59	0.008	0.029
	48	0.021	0.068			
XeO₃(12-Crown-4)	Xe....O			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$
	48	0.019	0.064	39	0.008	0.029
	54	0.025	0.081	70	0.007	0.028
	55	0.013	0.046			
	65	0.018	0.061			
XeO₃(15-Crown-5)	Xe....O			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$
	56	0.015	0.050	42	0.008	0.032
	59	0.018	0.061	66	0.012	0.048
	60	0.019	0.065	86	0.013	0.051
	80	0.010	0.036	92	0.008	0.032
	81	0.017	0.061			
XeO₃(18-Crown-6)	Xe....O			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$
	67	0.011	0.040	59	0.011	0.044
	84	0.011	0.040	68	0.011	0.044
	87	0.011	0.040	69	0.011	0.044
				81	0.011	0.044
				98	0.011	0.044
XeO₃(21-Crown-7)	Xe....O			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$

	76	0.013	0.044	68	0.010	0.041
	80	0.017	0.057	86	0.015	0.059
	85	0.014	0.050	97	0.007	0.026
	104	0.012	0.043	103	0.009	0.039
	108	0.012	0.043	115	0.015	0.057
				124	0.008	0.031
XeO₃(21-Crown-7)'	Xe....O			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$
	74	0.026	0.080	83	0.012	0.044
	78	0.030	0.090	90	0.011	0.040
	104	0.026	0.077	106	0.008	0.030
				111	0.010	0.038
				117	0.008	0.032
				123	0.010	0.039
XeO₃(9-Crown-3S)	Xe....S			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$
	36	0.022	0.048	33	0.007	0.026
	51	0.015	0.036			
	54	0.023	0.050			
XeO₃(12-Crown-4s)	Xe....S			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$
	40	0.011	0.029	-	-	-
	48	0.022	0.049			
	54	0.013	0.033			
	64	0.021	0.046			
XeO₃(15-Crown-5S)	Xe....S			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$

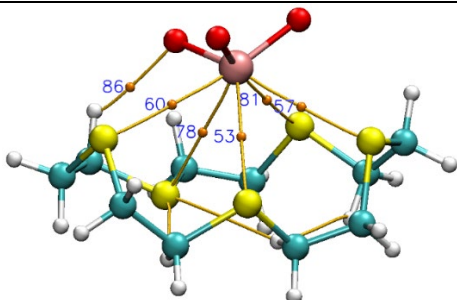
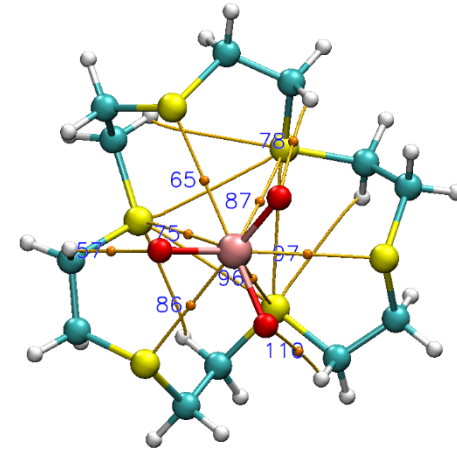
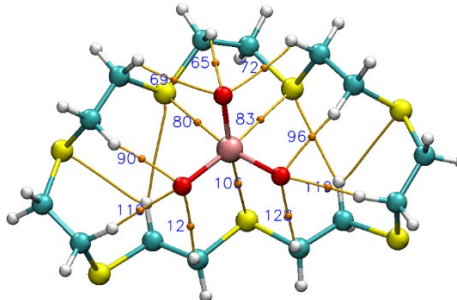
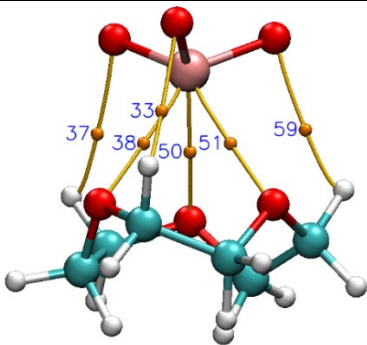
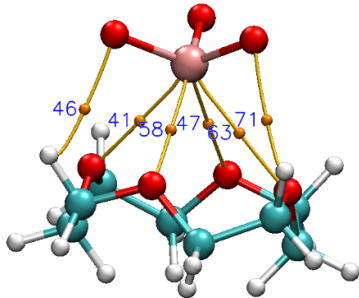
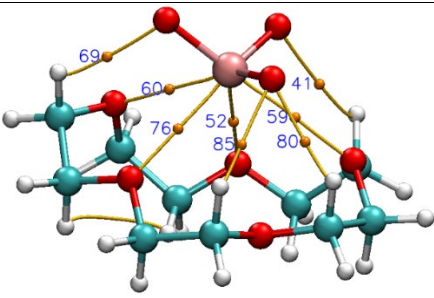
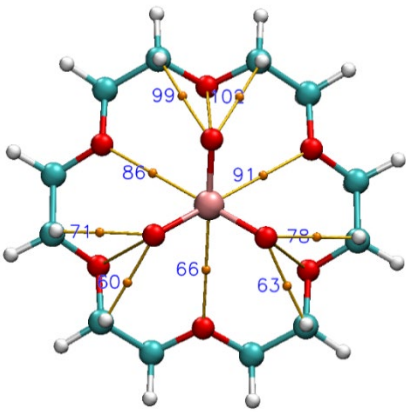
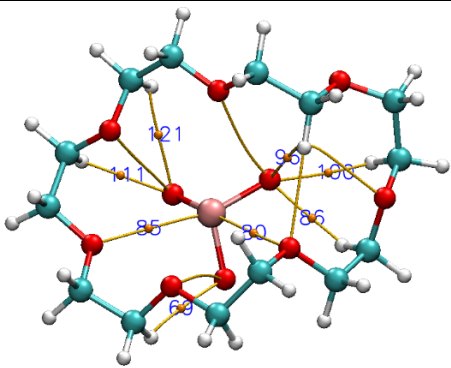
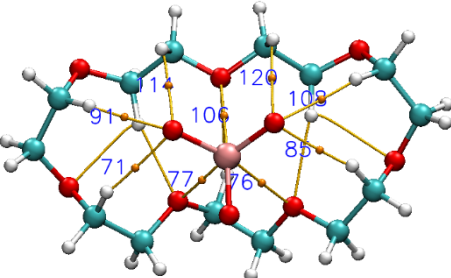
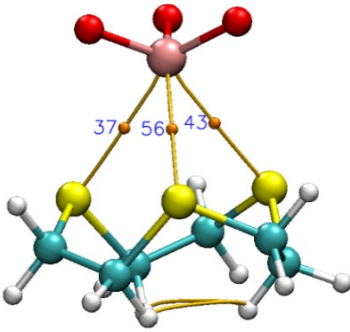
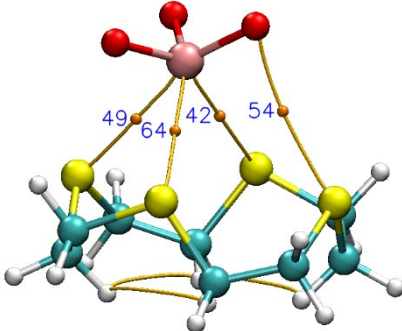
	53	0.013	0.032	86	0.011	0.043
	57	0.016	0.039			
	60	0.012	0.031			
	78	0.012	0.029			
	81	0.019	0.044			
XeO₃(18-Crown-6S)	Xe....S			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$
	65	0.017	0.041	57	0.008	0.030
	75	0.014	0.033	78	0.008	0.029
	86	0.017	0.041	110	0.008	0.029
	87	0.014	0.034			
	96	0.014	0.034			
	97	0.017	0.041			
XeO₃(21-Crown-7S)	Xe....S			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$
	80	0.029	0.051	65	0.010	0.038
	83	0.025	0.047	69	0.007	0.026
	106	0.028	0.048	72	0.007	0.028
				90	0.014	0.053
				96	0.014	0.050
				110	0.010	0.037
				119	0.012	0.047
				121	0.011	0.039
				128	0.012	0.046

Table S3.9. Bond critical points along with their respective electron density (ρ , in a.u.) and Laplacian of the electron density ($\nabla^2\rho$, in a.u.) for the complexes of KrO₃ with different crown ethers and their thio analogues.

KrO₃(9-Crown-3)	Kr....O			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$

	38	0.019	0.073	33	0.006	0.024
	50	0.019	0.073	37	0.006	0.024
	51	0.019	0.073	59	0.006	0.024
KrO₃(12-Crown-4)	Kr....O			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$
	41	0.017	0.066	46	0.007	0.030
	47	0.008	0.034	71	0.006	0.024
	58	0.019	0.073			
	63	0.013	0.051			
KrO₃(15-Crown-5)	Kr....O			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$
	52	0.010	0.042	41	0.006	0.025
	59	0.010	0.041	69	0.011	0.043
	60	0.014	0.054	80	0.011	0.045
	76	0.013	0.052	85	0.008	0.030
KrO₃(18-Crown-6)	Kr....O			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$
	66	0.007	0.029	60	0.009	0.039
	86	0.007	0.029	63	0.009	0.039
	91	0.007	0.029	71	0.009	0.039
				78	0.009	0.039
				99	0.009	0.039
KrO₃(21-Crown-7)	Kr....O			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$

	80	0.009	0.035	69	0.009	0.036
	85	0.010	0.042	86	0.012	0.048
				96	0.007	0.028
				100	0.008	0.033
				111	0.012	0.050
				121	0.006	0.025
KrO₃(21-Crown-7)'	Kr....O			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$
	76	0.021	0.076	71	0.010	0.035
	77	0.026	0.091	85	0.011	0.042
	106	0.019	0.065	91	0.009	0.034
				108	0.007	0.026
				114	0.010	0.040
				120	0.009	0.033
KrO₃(9-Crown-3S)	Kr....S			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$
	37	0.018	0.048	-		
	43	0.018	0.048			
	56	0.018	0.048			
KrO₃(12-Crown-4S)	Kr....S			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$
	42	0.013	0.037	-		
	49	0.017	0.046			
	54	0.005	0.017			
	64	0.016	0.045			
KrO₃(15-Crown-5S)	Kr....S			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$

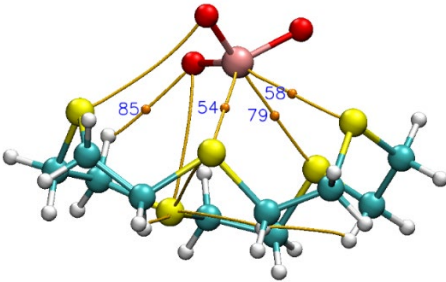
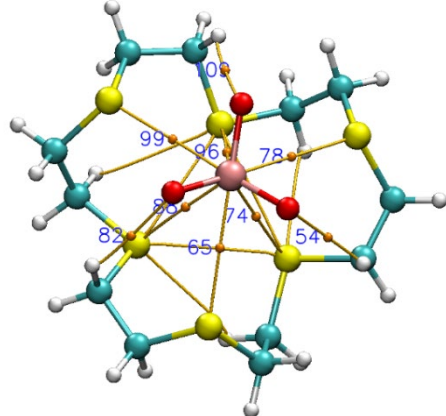
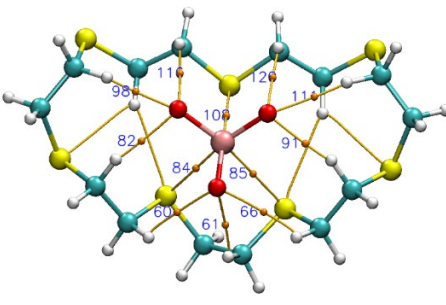
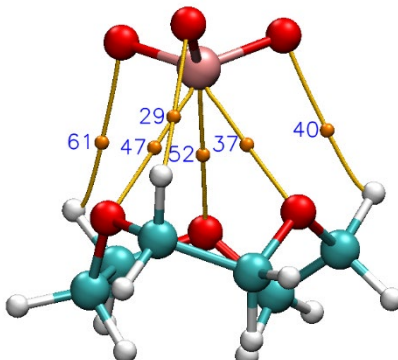
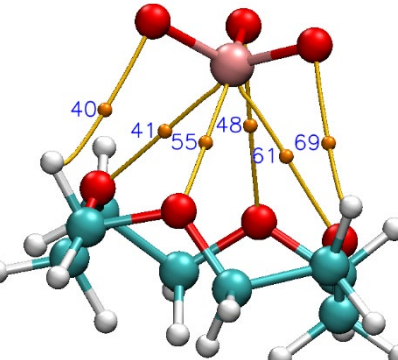
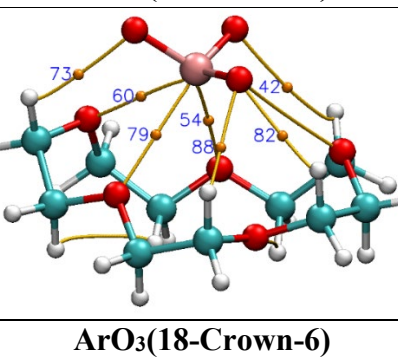
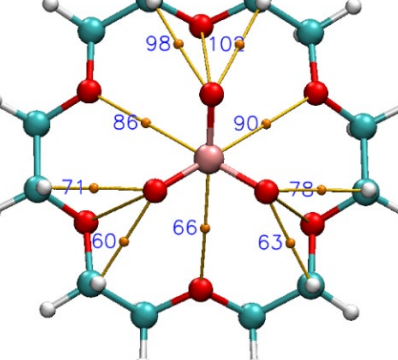
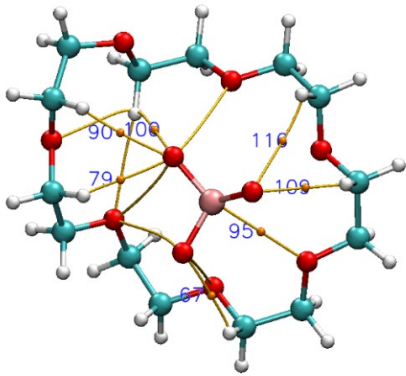
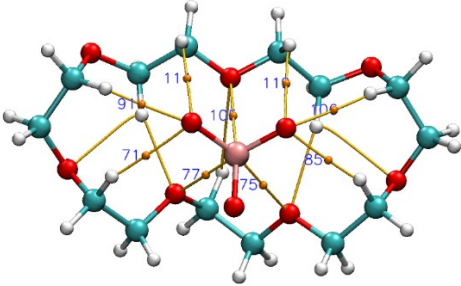
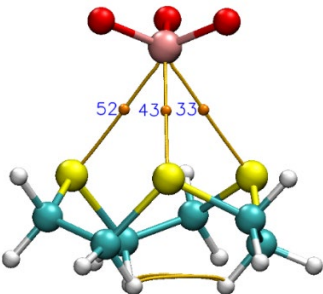
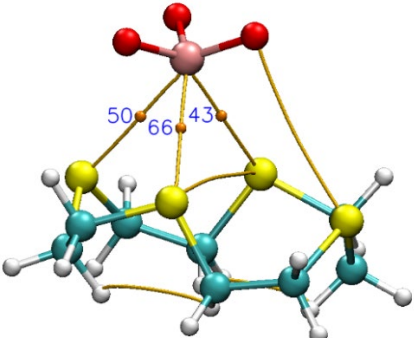
	54	0.010	0.029	85	0.009	0.035
	58	0.012	0.034			
	79	0.015	0.042			
KrO₃(18-Crown-6S)	Kr....S			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$
	65	0.011	0.033	54	0.006	0.023
	74	0.009	0.028	82	0.006	0.023
	78	0.011	0.033	109	0.006	0.023
	88	0.009	0.028			
	96	0.009	0.028			
	99	0.011	0.033			
KrO₃(21-Crown-7S)	Kr....S			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$
	84	0.021	0.049	60	0.007	0.025
	85	0.024	0.053	61	0.009	0.035
	108	0.024	0.050	66	0.006	0.026
				82	0.013	0.047
				91	0.013	0.049
				98	0.010	0.041
				111	0.007	0.027
				116	0.012	0.046
				120	0.010	0.039

Table S3.10. Bond critical points along with their respective electron density (ρ , in a.u.) and Laplacian of the electron density ($\nabla^2\rho$, in a.u.) for the complexes of ArO₃ with different crown ethers and their thio analogues.

ArO₃(9-Crown-3)	Ar....O			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$

	37	0.015	0.069	29	0.006	0.025
	47	0.015	0.069	40	0.006	0.025
	52	0.015	0.069	61	0.006	0.025
ArO₃(12-Crown-4)	Ar....O			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$
	41	0.014	0.063	40	0.006	0.030
	55	0.015	0.068	69	0.006	0.024
	61	0.009	0.042			
ArO₃(15-Crown-5)	Ar....O			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$
	54	0.007	0.034	42	0.004	0.016
	60	0.012	0.057	73	0.009	0.038
	79	0.009	0.046	82	0.009	0.039
				88	0.007	0.029
ArO₃(18-Crown-6)	Ar....O			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$
	66	0.005	0.022	60	0.008	0.033
	86	0.005	0.022	63	0.008	0.033
	90	0.005	0.022	71	0.008	0.033
				78	0.008	0.033
				98	0.008	0.033
				102	0.008	0.033
ArO₃(21-Crown-7)	Ar....O			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$

	95	0.009	0.045	67	0.008	0.033
				79	0.010	0.040
				90	0.005	0.025
				100	0.006	0.026
				109	0.011	0.043
				116	0.004	0.019
	ArO₃(21-Crown-7)'			Ar....O		C-H....O
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$
	75	0.015	0.068	71	0.008	0.031
	77	0.020	0.087	85	0.010	0.038
	105	0.010	0.043	91	0.008	0.029
				106	0.007	0.024
				114	0.009	0.037
				119	0.008	0.031
ArO₃(9-Crown-3S)			Ar....S		C-H....O	
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$
	33	0.014	0.045	-		
	43	0.013	0.045			
	52	0.014	0.045			
ArO₃(12-Crown-4S)			Ar....S		C-H....O	
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$
	43	0.011	0.038	-		
	50	0.012	0.041			
	66	0.012	0.044			
ArO₃(15-Crown-5S)			Ar....S		C-H....O	
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$

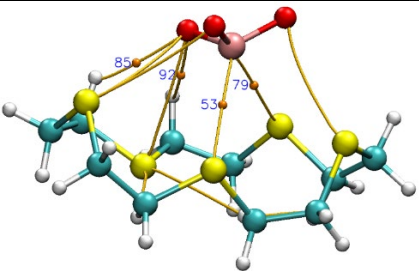
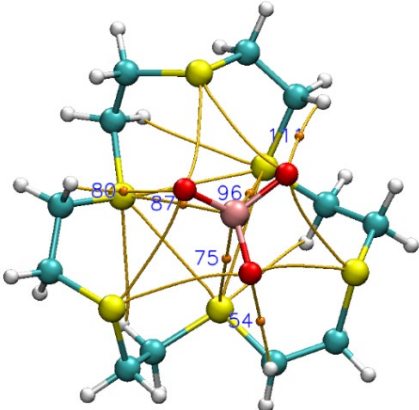
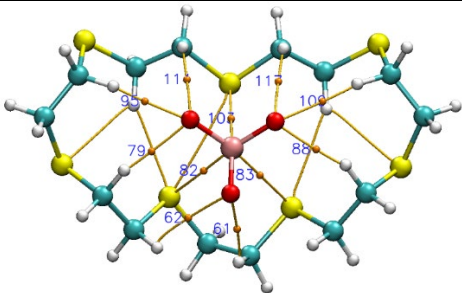
	53 79	0.008 0.010	0.029 0.038	85 92	0.007 0.004	0.028 0.018
ArO₃(18-Crown-6S)	Ar....S			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$
	75	0.006	0.023	54	0.004	0.018
	87	0.006	0.023	80	0.004	0.018
	96	0.006	0.023	111	0.004	0.018
ArO₃(21-Crown-7S)	Ar....S			C-H....O		
	Index	ρ	$\nabla^2\rho$	Index	ρ	$\nabla^2\rho$
	82	0.014	0.044	61	0.008	0.030
	83	0.017	0.050	62	0.005	0.021
	103	0.016	0.045	79	0.011	0.041
				95	0.008	0.033
				109	0.005	0.020
				114	0.010	0.041
				117	0.009	0.034

Table S3.11. ^aTotal interaction energy. ^b Second-order perturbation energy (E^2 , in kcal/mol) range from NBO analysis. ^c Second-order perturbation energy (E^2 , in kcal/mol) range from NBO 6 analysis.

	Crown Ethers (O)			Thio-Crown Ethers (S)		
	ArO ₃	KrO ₃	XeO ₃	ArO ₃	KrO ₃	XeO ₃
9-Crown-3	-15.4 ^a (0.32-0.34) ^b (0.35-0.37) ^c	-20.1 ^a (0.68-0.69) ^b (0.74-0.76) ^c	-25.0 ^a (0.5-1.62) ^b (0.5-1.71) ^c	-13.5 ^a (0.17-0.81) ^b (0.19-0.87) ^c	-18.7 ^a (0.45-2.32) ^b (0.49-2.50) ^c	-24.2 ^a (0.72-4.73) ^b (0.85-5.41) ^c
12-Crown-4	-16.1 ^a (0.06-0.38) ^b (0.09-0.41) ^c	-22.6 ^a (0.07-0.88) ^b (0.21-0.96) ^c	-30.6 ^a (0.18-1.65) ^b (0.23-2.02) ^c	-13.0 ^a (0.13-0.72) ^b (0.15-0.77) ^c	-19.3 ^a (0.23-2.41) ^b (0.26-2.60) ^c	-27.6 ^a (0.61-3.88) ^b (0.72-4.49) ^c
15-Crown-5	-17.2 ^a (0.07-0.22) ^b (0.08-0.24) ^c	-25.7 ^a (0.07-0.57) ^b (0.29-0.62) ^c	-38.3 ^a (0.18-1.21) ^b (0.26-1.44) ^c	-14.8 ^a (0.14-0.44) ^b (0.15-0.46) ^c	-23.0 ^a (0.24-1.89) ^b (0.27-1.93) ^c	-35.4 ^a (0.55-3.47) ^b (0.62-3.93) ^c

18-Crown-6	-17.6 ^a - ^b - ^c	-26.0 ^a (0.06-0.18) ^b (0.07-0.21) ^c	-40.2 ^a (0.14-0.61) ^b (0.16-0.75) ^c	-18.0 ^a (0.10-0.26) ^b (0.11-0.27) ^c	-27.6 ^a (0.32-0.99) ^b (0.35-1.06) ^c	-42.8 ^a (0.76-2.67) ^b (0.83-2.95) ^c
21-Crown-7	-17.9 ^a (0.06-0.20) ^b (0.07-0.23) ^c	-26.4 ^a (0.10-0.37) ^b (0.25-0.41) ^c	-41.2 ^a (0.56-1.08) ^b (0.62-1.19) ^c	-23.8 ^a (1.44-2.07) ^b (1.43-2.04) ^c	-36.4 ^a (4.47-5.92) ^b (4.71-6.46) ^c	-48.2 ^a (0.34-8.96) ^b (0.39-9.79) ^c

Table S3.12. Second order perturbation energies (E²) obtained from NBO analysis at the APFD/def2-TZVPD level of theory for the complexes of XeO₃. The E² values are in kcal/mol. The bracketed E² values are from NBO 6 output.

Complex	Oxygen(O) Containing Crown Ether			Sulfur(S) Containing Thio Crown Ether		
	Donor	Acceptor	E ²	Donor	Acceptor	E ²
XeO ₃ (9-Crown-3)	LP (1) O1	BD*(1) Xe22 - O23	0.77 (0.99)	LP (1) S1	BD*(1) Xe22 - O23	0.72 (0.85)
	LP (2) O1	BD*(1) Xe22 - O23	0.60 (0.65)	LP (2) S1	BD*(1) Xe22 - O23	3.78 (4.36)
	LP (1) O2	BD*(1) Xe22 - O25	1.36 (1.69)	LP (1) S2	BD*(1) Xe22 - O25	0.84 (0.98)
	LP (2) O2	BD*(1) Xe22 - O25	1.62 (1.71)	LP (2) S2	BD*(1) Xe22 - O25	4.73 (5.41)
	LP (2) O3	BD*(1) Xe22 - O24	0.51 (0.54)	LP (2) S3	BD*(1) Xe22 - O24	1.07 (1.25)
XeO ₃ (12-Crown-4)	LP (1) O1	BD*(1) Xe29 - O32	1.65 (2.02)	LP (1) S1	BD*(1) Xe29 - O32	0.72 (0.83)
	LP (2) O1	BD*(1) Xe29 - O32	1.30 (1.31)	LP (2) S1	BD*(1) Xe29 - O32	3.84 (4.45)
	LP (1) O2	BD*(1) Xe29 - O31	0.71 (0.87)	LP (2) S2	BD*(1) Xe29 - O31	3.88 (4.49)
	LP (1) O3	BD*(1) Xe29 - O30	0.71 (0.86)	LP (2) S3	BD*(1) Xe29 - O30	1.10 (1.29)
	LP (1) O4	BD*(1) Xe29 - O31	0.18 (0.23)	LP (2) S4	BD*(1) Xe29 - O30	0.61 (0.72)
XeO ₃ (15-Crown-5)	LP (1) O9	BD*(1) Xe1 - O2	0.81 (1.00)	LP (2) S1	BD*(1)Xe36 - O38	1.66 (1.92)
	LP (1) O5	BD*(1) Xe1 - O3	1.10 (1.34)	LP (2) S2	BD*(1)Xe36 - O38	0.74 (0.84)
	LP (2) O5	BD*(1) Xe1 - O3	0.94 (0.99)	LP (2) S2	BD*(1)Xe36 - O39	0.55 (0.62)
	LP (1) O7	BD*(1) Xe1 - O4	1.21 (1.44)	LP (2) S3	BD*(1)Xe36 - O39	3.47 (3.93)
	LP (2) O6	BD*(1) Xe1 - O3	0.27 (0.30)	LP (2) S4	BD*(1)Xe36 - O37	0.79 (0.91)
	LP (2) O6	BD*(1) Xe1 - O4	0.23 (0.26)	LP (2) S4	BD*(1)Xe36 - O38	0.75 (0.85)
	LP (2) O8	BD*(1) Xe1 - O3	0.25 (0.27)	LP (2) S5	BD*(1)Xe36 - O37	2.20 (2.53)
XeO ₃	LP (1) O1	BD*(1) Xe 43 - O44	0.61 (0.75)	LP (2) S5	BD*(1)Xe1 - O3	0.76 (0.83)

(18-Crown-6)	LP (1) O3	BD*(1) Xe 43 - O45	0.61 (0.75)	LP (2) S5	BD*(1)Xe1 - O4	0.81 (0.88)
	LP(1)O24	BD*(1) Xe 43 - O46	0.61 (0.75)	LP (2) S6	BD*(1)Xe1 - O3	2.65 (2.93)
	LP (2) O2	BD*(1) Xe 43 - O44	0.14 (0.16)	LP(2) S19	BD*(1)Xe1 - O2	0.81 (0.88)
	LP (2) O2	BD*(1) Xe 43 - O45	0.14 (0.16)	LP(2) S19	BD*(1)Xe1 - O4	0.76 (0.83)
	LP(2)O23	BD*(1) Xe 43 - O45	0.14 (0.16)	LP(2) S20	BD*(1)Xe1 - O2	0.76 (0.83)
	LP(2)O23	BD*(1) Xe 43 - O46	0.14 (0.16)	LP(2) S20	BD*(1)Xe1 - O3	0.81 (0.88)
	LP(2)O25	BD*(1) Xe 43 - O46	0.14 (0.16)	LP(2) S21	BD*(1)Xe1 - O4	2.66 (2.94)
	LP(2)O25	BD*(1) Xe 43 - O44	0.14 (0.16)	LP(2) S22	BD*(1)Xe1 - O2	2.67 (2.95)
XeO ₃ (21-Crown-7)	LP (1) O2	BD*(1) Xe50 - O51	0.87 (1.04)	LP (2) S1	BD*(1)Xe50 - O53	8.46 (9.54)
	LP (2) O6	BD*(1) Xe50 - O52	1.08 (1.19)	LP (2) S2	BD*(1)Xe50 - O51	6.77 (7.66)
	LP (1) O6	BD*(1) Xe50 - O52	0.82 (0.95)	LP (1) S2	BD*(1)Xe50 - O51	0.43 (0.50)
	LP (1) O3	BD*(1) Xe50 - O53	0.58 (0.67)	LP (2) S7	BD*(1)Xe50 - O52	8.96 (9.79)
	LP(2) O1	BD*(1) Xe50 - O53	0.56 (0.62)	LP (1) S7	BD*(1)Xe50 - O52	0.34 (0.39)

Table S3.13. Second order perturbation energies (E^2) obtained from NBO analysis at the APFD/def2-TZVPD level of theory for the complexes of KrO₃. The E^2 values are in kcal/mol. The bracketed E^2 values are from NBO 6 output.

Complex	Oxygen(O) Containing Crown Ether			Sulfur(S) Containing Thio Crown Ether		
	Donor	Acceptor	E^2	Donor	Acceptor	E^2
KrO ₃ (9-Crown-3)	LP (1) O1	BD*(1) Kr 22 -O 23	0.68 (0.75)	LP (1) S1	BD*(1) Kr22 – O23	0.45 (0.49)
	LP (2) O1	BD*(1) Kr 22 -O 23	0.69 (0.76)	LP (2) S1	BD*(1) Kr22 – O23	2.32 (2.50)
	LP (1) O3	BD*(1) Kr 22 -O 24	0.68 (0.74)	LP (1) S2	BD*(1) Kr22 – O25	0.45 (0.49)
	LP (2) O3	BD*(1) Kr 22 -O 24	0.69 (0.75)	LP (2) S2	BD*(1) Kr22 – O25	2.32 (2.50)
	LP (1) O2	BD*(1) Kr 22 -O 25	0.68 (0.75)	LP (1) S3	BD*(1) Kr22 – O24	0.45 (0.49)
	LP (2) O2	BD*(1) Kr 22 -O 25	0.69 (0.76)	LP (2) S3	BD*(1) Kr22 – O24	2.32 (2.50)
KrO ₃ (12-Crown-4)	LP (1) O3	BD*(1) Kr 29 - O30	0.68 (0.75)	LP (1) S1	BD*(1) Kr29 – O32	0.45 (0.49)
	LP (2) O3	BD*(1) Kr 29 - O30	0.42 (0.45)	LP (2) S1	BD*(1) Kr29 – O32	2.41 (2.60)
	LP (1) O2	BD*(1) Kr 29 - O31	0.26 (0.28)	LP (1) S2	BD*(1) Kr29 – O31	0.38 (0.43)

	LP (2) O2	BD*(1) Kr 29 - O31	0.19 (0.21)	LP (2) S2	BD*(1) Kr29 – O31	1.67 (1.82)
	LP (1) O1	BD*(1) Kr 29 - O32	0.88 (0.96)	LP (1) S3	BD*(1) Kr29 – O30	0.23 (0.26)
	LP (2) O1	BD*(1) Kr 29 - O32	0.60 (0.65)	LP (2) S3	BD*(1) Kr29 – O30	1.05 (1.14)
KrO ₃ (15-Crown-5)	LP (2) O9	BD*(1) Kr 1 – O2	0.41 (0.45)	LP (2) S1	BD*(1) Kr36 – O38	0.24 (0.27)
	LP (1) O9	BD*(1) Kr 1 – O2	0.39 (0.43)	LP (2) S2	BD*(1) Kr36 – O38	0.32 (0.35)
	LP (2) O5	BD*(1) Kr 1 – O3	0.30 (0.33)	LP (2) S3	BD*(1) Kr36 – O39	1.79 (1.93)
	LP (1) O5	BD*(1) Kr 1 – O3	0.25 (0.29)	LP (2) S4	BD*(1) Kr36 – O37	0.25 (0.28)
	LP (1) O7	BD*(1) Kr 1 – O4	0.57 (0.62)	LP (2) S4	BD*(1) Kr36 – O38	0.48 (0.52)
	LP (2) O9	BD*(1) Kr 1 – O2	0.41 (0.45)	LP (2) S5	BD*(1) Kr36 – O37	1.06 (1.15)
KrO ₃ (18-Crown-6)	LP (1) O29	BD*(1) Kr 1 – O2	0.18 (0.21)	LP (2) S6	BD*(1) Kr1 – O3	0.97 (1.06)
	LP (1) O15	BD*(1) Kr 1 – O3	0.18 (0.21)	LP(2) S21	BD*(1) Kr1 – O4	0.98 (1.06)
	LP (1) O5	BD*(1) Kr 1 – O4	0.18 (0.21)	LP(2) S22	BD*(1) Kr1 – O2	0.99 (1.07)
	*	*	*	LP (2) S5	BD*(1) Kr1 – O3	0.32 (0.35)
	*	*	*	LP (2) S5	BD*(1) Kr1 – O4	0.32 (0.35)
	*	*	*	LP(2) S20	BD*(1) Kr1 – O2	0.32 (0.35)
	*	*	*	LP(2) S20	BD*(1) Kr1 – O3	0.32 (0.35)
	*	*	*	LP(2) S19	BD*(1) Kr1 – O2	0.32 (0.35)
	*	*	*	LP(2) S19	BD*(1) Kr1 – O4	0.32 (0.35)
KrO ₃ (21-Crown-7)	LP (1) O2	BD*(1) O 50 - Kr 53	0.37 (0.41)	LP (2) S1	BD*(1) Kr50 – O53	5.92 (6.21)
	LP (2) O6	BD*(1) O 51 - Kr 53	0.28 (0.30)	LP (2) S2	BD*(1) Kr50 – O51	4.47 (4.71)
	LP (2) O1	BD*(1) O 52 - Kr 53	0.23 (0.25)	LP (2) S7	BD*(1) Kr50 – O52	6.12 (6.46)

Table S3.14. Second order perturbation energies (E^2) obtained from NBO analysis at the APFD/def2-TZVPD level of theory for the complexes of ArO₃. The E^2 values are in kcal/mol. The bracketed E^2 values are from NBO 6 output.

Complex	Oxygen(O) Containing Crown Ether			Sulfur(S) Containing Thio Crown Ether		
	Donor	Acceptor	E^2	Donor	Acceptor	E^2
ArO ₃ (9-Crown-3)	LP (2) O1	BD*(1) Ar 22 – O23	0.34 (0.37)	LP (1) S1	BD*(1) Ar22 - O23	0.17 (0.19)
	LP (1) O1	BD*(1) Ar 22 – O23	0.32 (0.35)	LP (2) S1	BD*(1) Ar22 - O23	0.81 (0.87)

	LP (2) O3	BD*(1) Ar 22 – O24	0.34 (0.37)	LP (1) S2	BD*(1) Ar22 - O25	0.17 (0.19)
	LP (1) O3	BD*(1) Ar 22 – O24	0.33 (0.35)	LP (2) S2	BD*(1) Ar22 - O25	0.81 (0.87)
	LP (2) O2	BD*(1) Ar 22 – O25	0.34 (0.37)	LP (1) S3	BD*(1) Ar22 - O24	0.17 (0.19)
	LP (1) O2	BD*(1) Ar 22 – O25	0.32 (0.35)	LP (2) S3	BD*(1) Ar22 - O24	0.81 (0.87)
ArO ₃ (12- Crown-4)	LP (1) O3	BD*(1) Ar 29 - O30	0.37 (0.40)	LP (1) S1	BD*(1) Ar29 – O32	0.13 (0.15)
	LP (2) O2	BD*(1) Ar 29 - O31	0.09 (0.10)	LP (2) S1	BD*(1) Ar29 – O32	0.72 (0.77)
	LP (1) O2	BD*(1) Ar 29 - O31	0.08 (0.09)	LP (1) S2	BD*(1) Ar29 – O31	0.19 (0.21)
	LP (1) O1	BD*(1) Ar 29 - O32	0.38 (0.41)	LP (2) S2	BD*(1) Ar29 – O32	0.59 (0.61)
	LP (2) O1	BD*(1) Ar 29 - O32	0.24 (0.26)	LP (1) S3	BD*(1) Ar29 – O30	0.15 (0.17)
	*	*	*	LP (2) S3	BD*(1) Ar29 – O30	0.36 (0.38)
ArO ₃ (15- Crown-5)	LP (2) O9	BD*(1) Ar1– O 2	0.22 (0.24)	LP (1) S3	BD*(1) Ar36 – O39	0.14 (0.15)
	LP (1) O9	BD*(1) Ar1– O 2	0.21 (0.25)	LP (2) S3	BD*(1) Ar36 – O39	0.44 (0.46)
	LP (2) O8	BD*(1) Ar1– O 3	0.07 (0.08)	LP (2) S4	BD*(1) Ar36 – O38	0.24 (0.26)
	LP (1) O7	BD*(1) Ar1– O 4	0.21 (0.24)	LP (2) S5	BD*(1) Ar36 – O37	0.18 (0.20)
ArO ₃ (18- Crown-6)	*	*	*	LP(2) S6	BD*(1) Ar1 – O3	0.26 (0.27)
	*	*	*	LP(2) S21	BD*(1) Ar1 – O4	0.24 (0.26)
	*	*	*	LP(2) S22	BD*(1) Ar1 – O2	0.25 (0.26)
	*	*	*	LP(2) S5	BD*(1) Ar1 – O3	0.10 (0.11)
	*	*	*	LP(2) S19	BD*(1) Ar1 – O4	0.10 (0.11)
	*	*	*	LP(2) S20	BD*(1) Ar1 – O2	0.10 (0.11)
ArO ₃ (21- Crown-7)	LP (1) O2	BD*(1) O 50 -Ar 53	0.20 (0.23)	LP (2) S1	BD*(1) Ar50 – O53	2.07 (2.04)
	LP (2) O4	BD*(1) O 51 -Ar 53	0.06 (0.07)	LP (2) S2	BD*(1) Ar50 – O51	1.44 (1.43)
	LP (2) O1	BD*(1) O 52 -Ar 53	0.11 (0.12)	LP (2) S7	BD*(1) Ar50 – O52	1.99 (2.01)

Table S3.15. Second order perturbation energies (E^2) obtained from NBO analysis at the APFD/def2-TZVPD level of theory for the complexes of NgO_3 with 21-Crown-7 for different mode of binding. The E^2 values are in kcal/mol. The bracketed E^2 values are from NBO 6 output.

Complex	Oxygen(O) Containing Crown Ether		
	Donor	Acceptor	E^2
XeO_3 (21-Crown-7)'	LP (1) O1	BD*(1) Xe50 - O53	0.99 (1.18)
	LP(2) O1	BD*(1) Xe50 - O53	2.60 (2.85)
	LP (1) O2	BD*(1) Xe50 - O51	1.50 (1.74)
	LP(2) O2	BD*(1) Xe50 - O51	3.20 (3.50)
	LP (1) O7	BD*(1) Xe50 - O52	0.70 (0.81)
KrO_3 (21-Crown-7)'	LP (1) O1	BD*(1) Kr50 – O53	0.67 (0.74)
	LP (2) O1	BD*(1) Kr50 – O53	1.59 (1.73)
	LP (1) O2	BD*(1) Kr50 – O51	1.09 (1.21)
	LP (2) O2	BD*(1) Kr50 – O51	1.96 (2.10)
	LP (2) O7	BD*(1) Kr50 – O52	1.89 (2.34)
ArO_3 (21-Crown-7)'	LP (2) O47	BD*(1) Ar43 – O45	0.49 (0.53)
	LP (1) O50	BD*(1) Ar43 – O44	0.57 (0.61)
	LP (2) O50	BD*(1) Ar43 – O44	0.74 (0.79)
	LP (1) O51	BD*(1) Ar43 – O46	0.32 (0.33)
	LP (2) O51	BD*(1) Ar43 – O46	0.57 (0.63)

Table S3.16. The energy decomposition analysis (EDA) of all the complexes of KrO_3 at the BP86-D3BJ/TZ2P level of theory. The energy values are in kcal/mol. Contribution to the sum of all attractive energy terms are shown in percent. E_{Pauli} represents Pauli repulsion, E_{elstat} represents electrostatic interactions, E_{oi} represents orbital interaction and the E_{disp} represents the dispersion interaction.

	ΔE	E_{Pauli}	E_{elstat}	%	E_{oi}	%	E_{disp}	%
$\text{KrO}_3:9\text{O}3$	-16.87	27.9	-24.83	55	-11.9	27	-8.04	18
$\text{KrO}_3:12\text{O}4$	-18.46	26.93	-25.09	55	-10.97	24	-9.33	21
$\text{KrO}_3:15\text{O}5$	-20.75	29.09	-26.87	54	-11.54	23	-11.43	23
$\text{KrO}_3:18\text{O}6$	-20.87	25.54	-24.56	53	-9.44	20	-12.41	27
$\text{KrO}_3:21\text{O}7$	-20.83	31.92	-26.76	51	-11.42	22	-14.57	28
$\text{KrO}_3:9\text{S}3$	-18.5	33.09	-26.36	51	-15.74	31	-9.49	18
$\text{KrO}_3:12\text{S}4$	-18.38	30.56	-24.39	50	-13.83	28	-10.72	22
$\text{KrO}_3:15\text{S}5$	-21.65	30.58	-25.42	49	-13.16	25	-13.65	26

KrO ₃ :18S6	-18.33	45.8	-31.83	50	-15.22	24	-17.08	27
KrO ₃ :21S7	-36.15	70.67	-50.99	48	-36.46	34	-19.37	18

Table S3.17. The energy decomposition analysis (EDA) of all the complexes of ArO₃ at the BP86-D3BJ/TZ2P level of theory. The energy values are in kcal/mol. Contribution to the sum of all attractive energy terms are shown in percent. E_{Pauli} represents Pauli repulsion, E_{elstat} represents electrostatic interactions, E_{oi} represents orbital interaction and the E_{disp} represents the dispersion interaction.

	ΔE	E_{Pauli}	E_{elstat}	%	E_{oi}	%	E_{disp}	%
ArO ₃ :9O3	-11.41	21.24	-18.89	58	-6.86	21	-6.9	21
ArO ₃ :12O4	-12.22	19.15	-17.95	57	-5.83	19	-7.59	24
ArO ₃ :15O5	-13.11	20.2	-18.3	55	-5.95	18	-9.06	27
ArO ₃ :18O6	-13.39	18.95	-17.24	53	-5.15	16	-9.95	31
ArO ₃ :21O7	-13.12	23.29	-18.53	51	-6.24	17	-11.64	32
ArO ₃ :9S3	-11.71	22.76	-18.7	54	-7.81	23	-7.96	23
ArO ₃ :12S4	-11.33	20.13	-16.09	51	-6.91	22	-8.46	27
ArO ₃ :15S5	-12.94	18.99	-15.73	49	-5.66	18	-10.54	33
ArO ₃ :18S6	-15.56	24.81	-20.61	51	-6.32	16	-13.44	33
ArO ₃ :21S7	-21.13	45.27	-33.44	50	-17.21	26	-15.75	24

Table S3.18. The energy decomposition analysis (EDA) of all the complexes of NgO₃:21O7' at the BP86-D3BJ/TZ2P level of theory. The energy values are in kcal/mol. Contribution to the sum of all attractive energy terms are shown in percent. E_{Pauli} represents Pauli repulsion, E_{elstat} represents electrostatic interactions, E_{oi} represents orbital interaction and the E_{disp} represents the dispersion interaction.

	ΔE	E_{Pauli}	E_{elstat}	%	E_{oi}	%	E_{disp}	%
XeO ₃ :21O7'	-35.59	71.59	-54.83	51	-32.88	31	-19.47	18
KrO ₃ :21O7'	-25.81	48.92	-38.3	51	-21.08	28	-15.35	21
ArO ₃ :21O7'	-16.06	33.5	-25.99	52	-11.02	22	-12.55	25

Table S3.19. Change in the bond angles of NgO₃ (<O-Ng-O, in degree) upon complexation.

	Isolated	9O3	12O4	15O5	18O6	21O7	21O7'
<O-Xe-O	106.48	105.031	103.629	101.258	102.353	101.093	103.997
	106.48	104.809	104.320	105.094	102.353	103.658	103.101
	106.48	104.845	104.325	103.197	102.353	102.744	102.850
Average	106.48	104.895	104.091	103.183	102.353	102.498	103.316
<O-Kr-O	108.47	107.169	106.281	104.505	105.993	105.291	106.532
	108.47	107.169	107.046	107.712	105.993	106.911	105.774
	108.47	107.165	106.464	106.336	105.993	106.011	105.575
Average	108.47	107.168	106.597	106.184	105.993	106.071	105.960
<O-Ar-O	109.90	109.084	108.661	107.777	108.687	108.621	108.948
	109.90	109.084	109.158	109.514	108.687	109.372	108.271
	109.90	109.084	108.885	109.034	108.687	108.361	108.466
Average	109.90	109.084	108.901	108.775	108.687	108.785	108.562
	Isolated	9S3	12S4	15S5	18S6	21S7	
<O-Xe-O	106.48	104.542	103.584	102.460	102.842	103.128	
	106.48	104.830	104.527	104.917	102.829	101.837	
	106.48	104.305	103.726	102.155	102.841	101.743	
Average	106.48	104.559	103.946	103.177	102.837	102.236	
<O-Kr-O	108.47	106.928	106.242	105.736	105.985	105.459	
	108.47	106.924	106.738	107.217	105.973	104.444	
	108.47	106.929	106.871	105.879	105.986	104.168	
Average	108.47	106.927	106.617	106.277	105.981	104.690	
<O-Ar-O	109.90	109.040	108.814	108.593	108.753	108.387	
	109.90	109.044	109.159	109.345	108.774	107.726	
	109.90	109.044	109.273	108.929	108.758	107.557	
Average	109.90	109.043	109.082	108.956	108.762	107.890	

Optimized Cartesian Coordinates

XeO ₃				KrO ₃				ArO ₃			
Xe	0.00000000	0.00000900	-0.20562300	Kr	-0.00000200	-0.00000100	-0.22779700	Ar	-0.00000200	0.00000000	0.27605400
O	1.42363500	0.78945900	0.46265900	O	-1.52699100	0.00103100	0.34169700	O	0.95797600	1.02054800	-0.20704000
O	-0.02808900	-1.62762700	0.46263600	O	0.76439100	1.32189800	0.34169300	O	-1.36281100	0.31935100	-0.20704100
O	-1.39554500	0.83810900	0.46266100	O	0.76260800	-1.32292300	0.34169500	O	0.40484000	-1.33989900	-0.20704000

9-Crown-3 (9O3)				12-Crown-4 (12O4)				15-Crown-5 (15O5)			
O	1.82949200	0.54448900	-0.22007900	O	-0.98836100	1.78414100	-0.53375500	O	2.70104500	-0.77900000	-0.90662600
O	-0.38819400	-1.49935600	0.54874800	C	0.08147600	2.57976200	-0.08809000	O	1.30485200	1.50358000	0.32024500
O	-1.05990300	1.02864100	-0.72875500	H	-0.25527300	3.31261200	0.66212800	O	-1.51861600	1.49150200	-0.21256500
C	-0.15997900	1.92803200	-0.12357700	H	0.42843500	3.13051900	-0.96535500	O	0.12623700	-1.96665500	0.09795100
C	0.97982900	1.27323200	0.64109300	C	1.24022000	1.78414000	0.48241900	O	-2.45692300	-1.07057900	-1.02121900
C	-1.92234700	0.34153100	0.15200000	H	1.99515900	2.48304400	0.87873600	C	3.29437500	0.31284900	-0.24305600
C	-1.67775000	-1.15685100	0.10264700	H	0.89915600	1.17267600	1.32855800	H	3.40527600	0.11595800	0.83061700
C	1.87367100	-0.84928300	-0.03038200	O	1.78414100	0.98836100	-0.53375500	H	4.30058600	0.47532500	-0.65380800
C	0.61826800	-1.59479400	-0.44628900	C	2.57976200	-0.08147600	-0.08809000	C	-0.88313700	2.34855800	0.69421200
H	0.25701500	2.51921000	-0.94235800	H	3.31261200	0.25527300	0.66212700	H	-1.44462300	3.29013800	0.80368800
H	-0.69251400	2.61603300	0.55150200	H	3.13051900	-0.42843400	-0.96535600	H	-0.81591700	1.88296200	1.69005700
H	1.57139900	2.07162500	1.10912900	C	1.78414100	-1.24022000	0.48241900	C	-3.29328500	0.03252000	-0.79441400

H	0.59218300	0.63144300	1.43847700	H	2.48304500	-1.99515900	0.87873500	H	-3.40325100	0.51581700	-1.76797600
H	-2.96073900	0.54793900	-0.14005200	H	1.17267600	-0.89915600	1.32855800	H	-4.29219700	-0.29690100	-0.46388700
H	-1.79147600	0.69407700	1.18244300	O	0.98836100	-1.78414100	-0.53375500	C	2.49181300	1.57964600	-0.42601400
H	-1.85058200	-1.52771300	-0.91565400	C	-0.08147600	-2.57976200	-0.08809000	H	2.26213200	1.71491600	-1.49268800
H	-2.39519600	-1.65689100	0.76256900	H	0.25527300	-3.12612000	0.66212800	C	3.10079300	2.43841000	-0.09853300
H	2.70641100	-1.19962000	-0.64679600	H	-0.42843500	-3.13051900	-0.96535500	H	2.50088300	-1.92635300	-0.11547900
H	2.10686400	-1.09337200	1.01633700	C	-1.24022000	-1.78414000	0.48241900	H	3.40623000	-2.15654100	0.46568200
H	0.26553400	-1.18858800	-1.39885300	H	-1.99515900	-2.48304400	0.87873600	H	2.33394300	-2.75045900	-0.81317000
H	0.86978800	-2.65533000	-0.58901000	H	-0.89915600	-1.17267600	1.32855800	C	0.49965400	2.64402700	0.17739900
				O	-1.78414100	-0.98836100	-0.53375500	H	0.42588200	2.93326500	-0.88060900
				C	-2.57976200	0.08147600	-0.08809000	H	0.93166000	3.49318500	0.73029000
				H	-3.12612000	-0.25527300	0.66212700	C	-1.00122500	-1.66572300	0.87276500
				H	-3.13051900	0.42843400	-0.96535600	H	-1.02932700	-2.30272400	1.77459000
				C	-1.78414100	1.24022000	0.48241900	H	-0.95389500	-0.62051200	1.20240300
				H	-2.48304500	1.99515900	0.87873500	C	-2.77640100	1.04930800	0.20644800
				H	-1.17267600	0.89915600	1.32855800	H	-2.71712600	0.61170900	1.21546300
								H	-3.49579000	1.88341800	0.26285500
								C	1.31811600	-1.82939600	0.82529900
								H	1.39321100	-2.62630000	1.58493300
								H	1.33611800	-0.86341600	1.34943400
								C	-2.26244900	-1.93257400	0.07306700
								H	-2.19968900	-2.94556700	-0.33632600
								H	-3.12685000	-1.90063600	0.75334200

18-Crown-6 (18O6)				21-Crown-7 (21O7)				9-Crown-3S (9S3)			
O	1.42982500	0.25541100	2.47670500	O	1.699922433	1.692037152	0.183181786	S	2.293022198	0.217185815	-0.179331507
O	-1.42982500	-0.25541100	2.47670700	O	-1.175496359	1.249428253	0.072441569	S	-0.922227725	-1.770441905	0.576456193
O	-2.85965700	0.25553000	0.00000000	O	4.302046069	0.520712143	0.139757264	S	-0.883854517	1.621809727	-0.775633790
C	-2.71492900	0.29167100	-2.36888000	O	-3.997493978	1.140678693	0.036667104	C	0.333906721	2.102663468	0.470364543
C	2.71492800	-0.29167100	2.36887900	O	3.246682417	-2.340352716	0.143949921	C	1.215156956	1.003004595	1.050816723
C	0.69400000	-0.29164400	3.53580300	O	-3.907273337	-1.933281905	0.272101777	C	-2.149956456	0.762544082	0.206033082
C	-0.69400000	0.29164400	3.53580500	O	-0.295743255	-1.790424633	0.653606072	C	-2.268081577	-0.737228703	-0.050614482
C	-2.71492900	0.29167100	2.36888000	C	2.886126445	2.407321647	-0.035126558	C	1.723153214	-1.499894396	-0.256381209
C	-3.40887900	-0.29159100	1.16680200	C	2.078858635	-1.766836695	0.704170720	C	0.309111005	-1.751771701	-0.770967230
C	3.40888000	0.29159200	1.16680200	C	0.796383544	2.347823074	1.031197598	H	0.949387483	2.845444203	-0.044105189
H	2.66347200	-1.38583600	2.26414800	C	-3.228024611	1.756788418	-0.965548043	H	-0.185259448	2.629209642	1.278223909
H	3.30615700	-0.06807700	3.27244700	C	0.839662110	-2.129247137	-0.101168084	H	1.862053933	1.440854201	1.817213178
H	0.62899000	-1.38581200	3.43890700	C	-0.411791524	1.460562963	1.234164908	H	0.613169389	0.227250617	1.524828492
H	1.18095800	-0.06803700	4.49957500	C	-4.931546497	0.195118488	-0.437749448	H	-3.106285824	1.237018935	-0.035164099
H	-0.62899100	1.38581300	3.43890900	C	-1.988644223	2.323991323	-0.323608722	H	-1.951772872	0.953090734	1.263219554
H	-1.18095800	0.06803700	4.49957700	C	4.857867456	-0.613625582	-0.489598660	H	-2.406702970	-0.942674393	-1.114895791
H	-2.66347300	1.38583600	2.26414900	C	-4.331673687	-1.151847460	-0.819904139	H	-3.159519267	-1.115146123	0.459874055
H	-3.30615900	0.06807600	3.27244700	C	3.822449219	-1.637494334	-0.932370937	H	2.442465213	-1.949379022	-0.947839248
H	-4.48702200	-0.06805200	1.22697400	C	3.852139085	1.506523844	-0.755487022	H	1.879240272	-1.984697915	0.711809182
H	-3.29240500	-1.38575200	1.17459600	C	-2.651107372	-1.597399289	0.837239959	H	0.023359333	-0.985502126	-1.491305775
H	4.48702300	0.06805200	1.22697600	C	-1.489308708	-1.996508146	-0.058528554	H	0.269086274	-2.728230966	-1.261221132
H	3.29240600	1.38575200	1.17459600	H	3.328242406	2.728001462	0.919847973				
O	-1.42982500	-0.25541100	-2.47670700	H	2.692902569	3.308473529	-0.638044080				
O	1.42982500	0.25541100	-2.47670500	H	2.172819692	-0.681977106	0.798502909				
O	2.85965900	-0.25553000	0.00000000	H	1.981237361	-2.192961744	1.705529505				
C	-3.40887900	-0.29159100	-1.16680200	H	0.504895936	3.322164397	0.606764402				
C	-0.69400000	0.29164400	-3.53580500	H	1.260077421	2.544326627	2.010926554				
C	0.69400000	-0.29164400	-3.53580300	H	-3.805004622	2.555864273	-1.456090347				
C	2.71492800	-0.29167100	-2.36887900	H	-2.925942345	1.038325377	-1.738556553				
C	3.40888000	0.29159200	-1.16680200	H	-1.040046489	1.888981827	2.029166315				
H	-2.66347300	1.38583600	-2.26414900	H	-0.084008799	0.469281117	1.551156468				
H	-3.30615900	0.06807600	-3.27244700	H	-1.465902224	2.978180458	-1.036012920				
H	-0.62899100	1.38581300	-3.43890900	H	-2.280878490	2.933141235	0.543174141				
H	-1.18095800	0.06803700	4.49957700	H	0.851884913	-3.207335056	-0.320805967				
H	0.62899000	-1.38581200	-3.43890700	H	0.825127912	-1.591748813	-1.061221729				
H	1.18095800	-0.06803700	4.49957500	H	-5.647024365	0.045515503	0.374538037				
H	2.66347200	-1.38583600	-2.26414800	H	-5.481198260	0.598652290	-1.303234434				
H	3.30615700	-0.06807700	-3.27244700	H	-2.589986389	-0.532411998	1.068374379				
H	4.48702300	0.06805200	-1.22697600	H	-2.588462047	-2.163009984	1.769336835				
H	3.29240600	1.38575200	-1.17459600	H	-5.112537303	-1.736505382	-1.316576554				
H	-4.48702200	-0.06805200	-1.22697400	H	-3.523160236	-1.016058996	-1.549587865				
H	-3.29240500	-1.38575200	-1.17459600	H	4.702667976	2.092601559	-1.136021070				
				H	3.338589858	1.061509966	-1.618211798				
				H	5.518260776	-1.080385687	0.245483878				
				H	5.470979953	-0.314292603	-1.354062269				
				H	4.323515403	-2.383737032	-1.558379595				
				H	3.052423063	-1.159967680	-1.552073966				
				H	-1.591866693	-3.053608706	-0.347214588				
				H	-1.477098128	-1.392421434	-0.976449687				

12-Crown-4S (12S4)				15-Crown-5S (15S5)			
S	2.828666565	-0.441113519	-0.430383950	S	2.933025245	-1.177661324	-1.133629898
C	2.191322110	-1.816751143	0.561170279	S	2.331885531	1.784868828	0.896853491
H	2.728316100	-1.853110134	1.513930627	S	-1.734300761	2.118638815	-0.613710425
H	2.482597889	-2.704834167	-0.005889046	S	-0.292267804	-1.616728673	-0.048014510
C	0.692676191	-1.831530450	0.823228574	S	-3.407467209	-0.920048319	-0.877430225
H	0.451270491	-2.711389324	1.430622385	C	4.104498513	-0.106946824	-0.244420425
H	0.403988384	-0.948353841	1.400254818	H	4.231894205	-0.510597896	0.762204319
S	-0.243288216	-1.902489700	-0.721786671	H	5.066749115	-0.201584236	-0.757343323
C	-1.906011518	-2.165971164	-0.066899721	C	-0.325436941	1.945132243	0.511197850
H	-1.907032301	-3.039851722	0.594575307	H	-0.299206142	2.778084332	1.220105160
H	-2.504703856	-2.433071370	-0.941695828	H	-0.447410713	1.013782856	1.066330051
C	-2.540574458	-0.982040254	0.659830281	C	-4.063318818	0.624043653	-0.207686489
H	-3.497317304	-1.298592714	1.086951596	H	-4.520308855	1.104147481	-1.077740436
H	-1.911671767	-0.660102172	1.492012703	H	-4.878852863	0.391882498	0.486089649
S	-2.828666083	0.441110820	-0.430382396	C	3.730996416	1.370798108	-0.174600688

C	-2.191322374	1.816752466	0.561165035	H	3.529120867	1.772384573	-1.170413078
H	-2.728320456	1.853117670	1.513922520	H	4.584225069	1.928425498	0.223239706
C	-2.482595926	2.704831981	-0.005900653	C	2.344261664	-2.304013289	0.161605149
C	-0.692677911	1.831533948	0.823228690	H	3.193729110	-2.551060820	0.804150125
H	-0.451274865	2.711394785	1.430620326	H	2.071370682	-3.217149432	-0.373590061
H	-0.403991385	0.948359800	1.400259491	C	0.957866564	1.868407881	-0.289752451
S	0.243286721	1.902489335	-0.721784184	H	0.957455632	0.970148138	-0.908334251
C	1.906011497	2.165969873	-0.066901948	H	1.084367105	2.750659678	-0.923785946
H	1.907036672	3.039853500	0.594568925	C	-1.586474652	-1.583409716	1.218898525
H	2.504700316	2.433065337	-0.941702046	H	-1.373260677	-2.360830436	1.960322879
C	2.540578120	0.982042006	0.659829450	H	-1.579080299	-0.624668125	1.744078708
H	3.497323824	1.298594645	1.086943950	C	-3.090228406	1.585785324	0.469123723
H	1.911680477	0.660105077	1.492016275	H	-2.649504595	1.122258747	1.352578170
				H	-3.650098719	2.461014686	0.814190872
				C	1.171140696	-1.827617708	1.003993442
				H	0.955384940	-2.586085194	1.764794801
				H	1.416260371	-0.885748971	1.504149066
				C	-2.953519068	-1.862174988	0.601618265
				H	-2.989548820	-2.901638546	0.266529937
				H	-3.736001184	-1.738562188	1.357487411

18-Crown-6S (18S6)				21-Crown-7S (21S7)			
S	4.094358673	0.964485058	0.608254576	S	-0.135216132	1.018994871	0.638163044
S	2.569875204	-2.080153257	-0.585225438	S	1.765559383	0.813824792	-2.165760070
S	-0.766428302	-2.367907145	-0.514203738	S	-3.522054817	1.793791174	0.680040079
C	-3.170473691	-1.661736992	0.787368565	S	4.517318612	0.602423752	-0.126160843
C	3.170474098	1.661737437	-0.787367094	S	-4.625638872	-1.282755540	-0.940889981
C	4.886136205	-0.471059062	-0.169620846	S	3.238062231	-2.411916086	1.338062076
C	4.227084264	-1.819946437	0.094650839	S	-0.315534470	-2.126783584	-1.236189836
C	1.506023718	-1.321169987	0.682591300	C	-1.064180094	1.889590508	1.931347329
C	0.263957424	-2.142431265	0.965739706	C	-2.853435415	-1.157718533	-1.313243806
C	2.318164452	2.828689848	-0.300133014	C	-0.258279081	2.208843068	-0.725004862
H	2.556159496	0.883074478	-1.246965409	C	3.368994838	2.005082125	-0.225112494
H	3.888877771	2.015906837	-1.533473423	C	-1.958315985	-2.054458701	-0.473300255
H	4.951814330	-0.277571810	-1.242799715	C	0.134683564	1.592204620	-2.055246487
H	5.910241256	-0.496452964	0.215685351	C	4.359892169	0.157587268	1.620416208
H	4.196035488	-2.030548108	1.167114922	C	2.872771499	2.156872078	-1.655798951
H	4.836194922	-2.604750784	-0.365898586	C	-4.955333099	0.743309024	1.017628636
H	1.234322878	-0.304206604	0.395240441	C	3.158991968	-0.714683445	1.979710695
H	2.097334298	-1.240559343	1.596493279	C	-4.765172297	-0.752454106	0.784823582
H	-0.331939747	-1.609777972	1.713621826	C	-2.492851471	1.397083781	2.115186130
H	0.530328299	-3.125502557	1.364436524	C	2.173918110	-2.313411958	-0.122451817
H	2.068030166	3.486036356	-1.137245412	C	0.703377981	-2.421776198	0.235866375
H	2.873087788	3.437500415	0.418278733	H	-1.035402583	2.964069084	1.729551231
S	-4.094358815	-0.964485381	-0.608253137	H	-0.515031493	1.729416693	2.862618519
S	-2.569874966	2.080154474	0.585223248	H	-2.526969909	-0.120588212	-1.233875120
S	0.766427661	2.367906092	0.514204146	H	-2.809387029	-1.450313790	-2.366718052
C	-2.318164679	-2.828689965	0.300134737	H	0.368435656	3.075154348	-0.492635122
C	-4.886135871	0.471059322	0.169621595	H	-1.295241868	2.547610336	-0.791417030
C	-4.227084296	1.819946522	-0.094651902	H	3.881786970	2.917658504	0.097861579
C	-1.506023845	1.321170109	-0.682593015	H	2.524804336	1.818455671	0.442721912
C	-0.263956858	2.142430635	-0.965740293	H	0.041382713	2.353476984	-2.836157793
H	-2.556158612	-0.883073885	1.246966007	H	-0.542853052	0.772872760	-2.304770282
H	-3.888877030	-2.015905688	1.533475555	H	2.354428000	3.111116503	-1.785571861
H	-4.951813134	0.277573090	1.242800705	H	3.712261366	2.161016737	-2.355814280
H	-5.910241256	0.496452756	-0.215683818	H	-2.385811709	-3.055465007	-0.377581885
H	-4.196036112	2.030547002	-1.167116240	H	-1.830027867	-1.628393105	0.524880358
H	-4.836194874	2.604751260	0.365896973	H	5.287130669	-0.364095670	1.867013631
H	-1.234323999	0.304206441	-0.395242199	H	4.344738422	1.081406205	2.208822488
H	-2.097333938	1.240560274	-1.596495385	H	2.389012427	-1.381516519	-0.646110652
H	0.331940763	1.609777078	-1.713621869	H	2.484116294	-3.137616271	-0.768841144
H	-0.530326850	3.125502086	-1.364437313	H	3.101590080	-0.805928298	3.068709731
H	-2.068030071	-3.486036023	1.137247386	H	2.225376999	-0.254984895	1.645829818
H	-2.873088629	-3.437500817	-0.418276291	H	-2.929192054	1.855278163	3.009633753
				H	-2.483390168	0.313617507	2.259741362
				H	-5.741889547	1.123877431	0.362738864
				H	-5.275258096	0.924316060	2.049895966
				H	-5.652323810	-1.276170966	1.154502326
				H	-3.921709256	-1.146351409	1.356226112
				H	0.480154118	-3.404352112	0.659238100
				H	0.438959298	-1.661254128	0.974354299

XeO ₃ (9-Crown-3)				KrO ₃ (9-Crown-3)				ArO ₃ (9-Crown-3)			
O	1.14423100	1.47939400	0.72384000	O	-0.87313500	1.00961600	1.28529200	O	0.62304000	-1.52547400	-0.58996300
O	1.00618900	-0.12903900	-1.58280800	O	-0.87546000	-1.61850000	0.23178500	O	0.62409800	0.25171900	1.61562000
O	1.18089500	-1.35789200	0.94135500	O	-0.87352900	0.60843900	-1.51662000	O	0.62351000	1.27328400	-1.02597200
C	1.68537400	-0.51993600	1.96115000	C	-1.32351300	1.81648400	-0.93951900	C	1.07648400	0.36862600	-2.00811200
C	2.15963100	0.84336900	1.47239700	C	-1.83575100	1.66598400	0.48803000	C	1.58581800	-0.95425500	-1.44687600
C	2.08791000	-1.73933500	-0.07441400	C	-1.83731500	-0.40928800	-1.68561200	C	1.58612900	1.73039000	-0.10294200
C	1.48521600	-1.45323700	-1.44428800	C	-1.32578400	-1.72145500	-1.10296700	C	1.07698500	1.55462600	1.32337900
C	1.51447600	1.98496700	-0.54538800	C	-1.32430500	-0.09414300	2.04234800	C	1.07604300	-1.92369800	0.68460200
C	1.96835300	0.90561200	-1.52027000	C	-1.83817800	-1.25429000	1.19801200	C	1.58644000	-0.77637600	1.54926200
H	0.85214000	-0.38998000	2.65594600	H	-0.44865700	2.46904600	-0.94609900	H	0.20578300	0.18393700	-2.63927100
H	2.50290100	-1.00979300	2.50839300	H	-2.10495400	2.28449300	-1.55522000	H	1.86263200	0.81773300	-2.63329500
H	2.40862100	1.45683000	2.34712600	H	-2.02918300	2.66661600	0.89469400	H	1.78287400	-1.63356500	-2.28655900
H	3.07465000	0.74987800	0.87893500	H	-2.78788600	1.12557400	0.50892800	H	2.53804800	-0.81586200	-0.92349600
H	2.29108800	-2.81425300	0.00155200	H	-2.03199200	-0.55704800	-2.75534400	H	1.78231800	2.79739400	-0.27137400
H	3.04501900	-1.22312800	0.05217800	H	-2.78875300	-0.12027700	-1.22692100	H	2.53884100	1.20884100	-0.24491200
H	0.61173000	2.46595100	-0.92556300	H	-0.44956400	-0.41616500	2.61014400	H	0.20509400	-2.37709900	1.16045800
H	2.30134100	2.74622100	-0.45451800	H	-2.10509100	0.20565000	2.75598300	H	1.86160400	-2.69027300	0.60819200
H	2.94513800	0.50119000	-1.23561000	H	-2.78947700	-1.00049300	0.71872300	H	2.53883400	-0.39300300	1.16740300

H	2.08391700	1.35701600	-2.51282800	H	-2.03368400	-2.10630400	1.86127200	H	1.78361100	-1.16390200	2.55738400
H	0.60577700	-2.08080400	-1.59984000	H	-0.45126200	-2.05366700	-1.66519900	H	0.20613700	2.19333900	1.47904800
H	2.22045300	-1.69009300	-2.22500300	H	-2.10778900	-2.48806300	-1.20078700	H	1.86314000	1.87150900	2.02489600
Xe	-1.28574900	-0.00698500	0.05286300	Kr	1.42521200	-0.00046400	0.00000600	Ar	-1.66540600	0.00013300	0.00009200
O	-1.84517700	-1.36567100	-0.92540700	O	2.02908400	-1.05671800	-1.09240200	O	-2.16963300	1.25483700	0.61659900
O	-1.79486100	1.43363600	-0.83081400	O	2.03016200	-0.41800100	1.46064300	O	-2.17021600	-1.16077700	0.77859600
O	-2.30603700	-0.03798900	1.49377300	O	2.02909600	1.47361300	-0.36896500	O	-2.17067400	-0.09325500	-1.39438400

XeO ₃ (12-Crown-4)				KrO ₃ (12-Crown-4)				ArO ₃ (12-Crown-4)			
O	0.21745700	0.29133000	-2.01395400	O	-0.28087400	1.49110800	1.35383200	O	-1.13649400	1.09727800	1.27498000
O	0.76015700	-1.95549200	-0.36962200	O	0.81477200	1.43745200	-1.26372300	O	0.57062800	1.66244100	-0.93738100
O	0.82796600	1.97277200	0.19021700	O	0.37772600	-1.27221500	1.50411800	O	0.15644500	-1.43553100	1.22936900
O	1.34488900	-0.27192700	1.80064000	O	1.48166900	-1.29009300	-1.10084400	O	1.89577200	-0.84078300	-0.95495000
C	0.60261900	1.64642900	-2.14223500	C	-0.05966800	0.79873900	2.56379800	C	-0.99604400	0.26490300	2.40333500
C	2.00542000	-2.04383300	0.27375700	C	2.14909700	1.02707900	-1.39785300	C	1.95101000	1.58129900	-0.71018800
C	1.52193100	2.09849200	-1.02665300	C	0.92034700	-0.34668100	2.41100900	C	0.24961100	-0.59682500	2.34944400
C	1.80487700	-1.60167000	1.70902900	C	2.13872900	-0.38261700	-1.95273400	C	2.47181100	0.35162400	-1.42631300
C	0.78885600	-1.99416400	-1.78104400	C	0.61931400	2.61800000	-0.51976600	C	-0.09802100	2.64564300	-0.18370600
C	2.33195300	0.71176400	1.62536900	C	2.23667000	-1.73143100	-0.00418600	C	2.39815400	-1.30868100	0.26753500
C	1.18235300	-0.66331300	-2.39033500	C	0.73021900	2.39184900	0.97455300	C	-0.31683500	2.23857400	1.25981600
C	1.62844500	2.02392700	1.35106100	C	1.27395100	-2.25738600	1.04010700	C	1.32719400	-2.15708100	0.92302400
H	-0.32746700	2.21517400	-2.09756300	H	-1.03339600	0.40363100	2.85692500	H	-1.87745200	-0.37852600	2.40647400
H	1.08024500	1.82263400	-3.11480300	H	0.29121500	1.48339700	3.34804100	H	-0.99451000	0.85432800	3.33127800
H	2.75599900	-1.41466100	-0.22283700	H	2.67364200	1.05521200	-0.43263600	H	2.17555700	1.52132400	0.36423300
H	2.37951600	-3.07780700	0.25309400	H	2.69518600	1.69175400	-2.08468600	H	2.46485300	2.47525000	-1.09795300
H	1.02949200	-2.21680200	2.17082600	H	1.57818200	-0.39367700	-2.89008600	H	2.20290100	0.41480400	-2.48308000
H	2.73502700	-1.73909900	2.27741700	H	3.16748000	-0.70712700	-2.16523200	H	3.56935900	0.32279900	-1.35466900
H	2.95100500	0.80684400	2.52975300	H	2.92667600	-2.53530500	-0.30287000	H	3.30029800	-1.92008500	0.11036400
H	3.00465800	0.45508800	0.79593600	H	2.84892300	-0.91942900	0.41082000	H	2.68555500	-0.47841900	0.92606400
H	2.36284400	2.83819200	1.28720700	H	1.83437200	-2.70097400	1.87518500	H	1.73593900	-2.63874900	1.82355400
H	0.94448000	2.24482700	2.17331600	H	0.65031000	-3.03410800	0.59296700	H	1.01684600	-2.93843100	0.22640700
H	1.81220000	3.14542800	-1.19690100	H	1.08508600	-0.81831500	3.39154500	H	0.32087800	-1.18946400	3.27497700
H	2.44366300	1.50148000	-1.01709400	H	1.89301700	0.02451200	2.06085300	H	1.14864200	0.03297900	2.29909200
H	2.18264900	-0.36012900	-2.05592600	H	1.72271500	2.00080900	1.23298200	H	0.64359300	2.04147300	1.75270900
H	1.21609800	-0.75705800	3.48493600	H	0.60888200	3.34903300	1.50238500	H	-0.79725500	3.06459200	1.80521100
H	-0.22974200	-2.24326300	-2.08351000	H	-0.39233300	2.95085700	-0.75941700	H	-1.06709600	2.78024600	-0.66797600
H	1.46569000	-2.78157000	-2.13860600	H	1.32600100	3.40122200	-0.82925400	H	0.44169200	3.60376400	-0.21770000
Xe	-1.36890600	-0.02271300	0.27744700	Kr	-1.48547100	-0.29907600	-0.43938400	Ar	-1.47075500	-0.59779900	-0.94655100
O	-2.86776600	-1.35300300	-0.54523300	O	-2.12364300	0.89539100	-1.35457600	O	-2.03343100	0.47843800	-1.80257600
O	-2.17217100	1.41510200	-0.35673700	O	-2.48907100	-0.48402500	0.83745700	O	-2.55763000	-1.14374900	-0.09346000
O	-1.92704200	-0.13360200	1.94828800	O	-1.58694700	-1.67637800	-1.31117200	O	-0.94747500	-1.68364600	-1.81082600

XeO ₃ (15-Crown-5)				KrO ₃ (15-Crown-5)				ArO ₃ (15-Crown-5)			
Xe	0.04226580	-1.92793063	-1.72747140	Kr	0.12388900	-0.16444000	1.51043500	Ar	0.32505200	-0.20067500	1.75258000
O	-0.43646283	-3.01315148	-0.41734020	O	-0.89427700	1.00923700	2.02184800	O	-0.68472100	0.82517400	1.21069000
O	1.55022455	-2.67284422	-2.25794838	O	1.51166300	0.11343600	2.32674600	O	1.58090700	0.11681800	2.48125700
O	-1.06897225	-2.28454646	-3.04796970	O	-0.44970500	-1.58946800	2.05341500	O	-0.15150500	-1.53549000	2.17226600
O	-2.50066446	-0.79509292	-0.88409932	O	-2.54631300	-0.64991700	0.05544300	O	-2.64784100	-0.77057000	0.31287200
O	-0.55974683	-0.25016816	1.00083085	O	-1.33118800	1.61948000	-1.01445400	O	-1.46842500	1.54352500	-0.82062600
O	1.96178299	-0.32672732	-0.13717173	O	1.43308900	1.54344800	-0.53429300	O	1.36157200	1.53391500	-0.43822500
O	-0.85753873	0.90798747	-2.50237404	O	-0.14412300	-1.82972500	-1.08201700	O	-0.13580000	-1.78766800	-0.91058000
O	1.78711578	0.16004342	-2.89665995	O	2.39169300	-1.07490400	-0.15581200	O	2.46222700	-1.02144900	-0.02885200
C	-2.83130194	-0.40248341	0.42911937	C	-3.26072400	0.31395400	-0.68116800	C	-3.37975100	0.22906800	-0.35523100
H	-2.90497866	0.68968021	0.50270801	H	-3.25309400	0.07775500	-1.75269700	H	-3.45995800	0.01580500	-1.42841600
H	-3.80321710	-0.82773912	0.71369569	H	-4.30904900	0.33889800	-0.35183900	H	-4.40082300	0.27352900	0.04925000
C	1.76643145	0.01723076	1.21242646	C	0.81082600	2.56761100	-1.26888300	C	0.66401200	2.50937300	-1.17002200
H	2.64716716	-0.25546199	1.81123256	H	1.38203900	3.50395100	-1.18379000	H	1.20584300	3.46715800	-1.14667900
H	1.61346023	1.10272615	1.30503640	H	0.76588100	2.29463200	-2.33409700	H	0.57213100	2.20175700	-2.22305300
C	3.02276754	0.02602469	-2.22887948	C	3.24770500	0.04001800	-0.23128400	C	3.25845800	0.12785400	-0.17619300
H	3.27427588	-1.03084197	-2.31200929	H	3.39401400	0.35713300	0.80100500	H	3.44419200	0.47812500	0.83960300
C	3.79952848	0.61729293	-2.73327672	H	4.22328400	-0.24865400	-0.64935200	C	4.22567900	-0.12639300	-0.63589600
C	-1.76200956	-0.88702374	1.36859895	C	-2.62992500	1.66446300	-0.47616000	C	-2.71391100	1.56794800	-1.17043800
H	-1.65233753	-1.97342552	1.28882306	H	-2.58988900	1.89966800	0.59321000	H	-2.58107600	1.76879700	0.89952800
H	-2.03654944	-0.62931004	2.40263886	H	-3.23427900	2.43418400	-0.98134400	H	-3.35681800	2.35807100	-0.59088700
C	-2.98140451	0.06905215	-1.89193488	C	-2.45542900	-1.90919700	-0.56857700	C	-2.46031200	-1.95585300	-0.42001000
H	-4.02381225	0.35391175	-1.69694159	H	-3.42972800	-2.22028900	-0.97143100	H	-3.40617000	-2.29222400	-0.86975600
H	-2.94297689	-0.50522678	-2.81902927	H	-2.16664400	-2.61401300	0.21334300	H	-2.14232300	-2.71152100	0.30160000
C	0.55458650	-0.71204541	1.72236659	C	-0.58138300	2.77318700	-0.74052600	C	-0.70498200	2.69420200	-0.57601500
H	0.67325033	-1.79442333	1.58303444	H	-0.54781500	2.95860900	0.34112300	H	-0.61514100	2.87230200	0.50380900
H	0.43614216	-0.51144635	2.79788543	H	-1.02617200	3.65550200	-1.22692100	H	-1.17836200	3.57959600	-1.02962700
C	0.16098237	1.84601752	-2.26371519	C	0.86575500	-1.51337300	-2.00281800	C	0.87198800	-1.47769500	-1.83333800
H	-0.16982197	2.86124217	-2.53030923	H	0.78201400	-2.13774400	-2.90661800	H	0.78098200	-2.10572000	-2.73528300
O	0.42749797	1.83946150	-1.19760560	H	0.77394900	-0.46175300	-2.30630600	H	0.78035600	-0.42908400	-2.14478700
C	2.96653903	0.42373262	-0.76942149	C	2.69256800	1.19208000	-1.04257700	C	2.61778800	1.23821100	-0.98453500
H	2.75538746	1.49872317	-0.65724282	H	2.60692200	0.92174600	-2.10676500	H	2.51397900	0.94743300	-0.04164300
H	3.94729439	0.23342019	-0.30821905	H	3.39280700	2.03968800	-0.98036300	H	3.27819100	1.21973900	-0.95864500
C	-2.11986934	1.30533633	-2.02467433	C	-1.41678800	-1.92971900	-1.66868600	C	-1.40889800	-1.83289600	-1.50232600
H	-2.58464143	2.01889173	-2.72083798	H	-1.49827100	-2.86421700	-2.24534400	H	-1.47847300	-2.69904900	-2.18037700
H	-2.01506910	1.80563283	-1.05207854	H	-1.58077500	-1.09283600	-2.36228600	H	-1.58045600	-0.92582200	-2.09903700
C	1.33968000	1.47625022	-3.13632191	C	2.20087000	-1.79804800	-1.34992400	C	2.21653800	-1.76523100	-1.19878900
H	1.02851219	1.52079000	-4.18466391	H	2.23704400	-2.85853200	-1.08236000	H	2.23923500	-2.81859600	-0.90394300
H	2.14828857	2.20379205	-2.99142467	H	3.01019000	-1.60245000	-2.06620300	H	3.01118300	-1.60568800	-0.90122200

C	-1.16477000	3.42041400	-0.40582300	O	-1.30174000	-0.75156000	1.86354300	O	-1.20343500	-0.69480400	1.95017000
C	1.16005300	-3.38894000	-0.96551800	C	2.43243700	1.40436800	-0.37265200	O	2.44804900	1.41338200	-0.25380600
C	-1.16005300	-3.38894000	-0.96551800	C	2.35860400	2.70218100	-0.90520000	C	2.36173800	2.70564200	-0.79374700
C	-2.37978000	-2.71892800	-0.40582300	C	1.16595100	3.41996400	-0.34108000	C	1.16642300	3.41740300	-0.22431000
C	-3.54455100	-0.70148700	-0.40582300	O	0.00000000	2.81553600	-0.83339200	O	0.00000000	2.82367100	-0.72587400
C	-3.51493500	0.68983500	-0.96551800	H	3.27088900	3.26777500	-0.65789300	H	3.27129000	3.28110500	-0.55721400
C	2.37978000	-2.71892800	-0.40582300	H	2.27675200	2.65841400	-2.00155000	H	2.27075800	2.65701600	-1.88928600
H	1.16533600	-3.31408900	-2.06297200	H	1.18727700	3.37852900	0.75549500	H	1.18800900	3.36226900	0.87247400
H	1.17943400	-4.45674200	-0.69909500	H	1.20948000	4.47799400	-0.64614200	H	1.21248400	4.48032500	-0.51256300
H	-1.16533600	-3.31408900	-2.06297200	C	-1.16595100	3.41996400	-0.34108000	C	-1.16642300	3.41740300	-0.22431000
H	-1.17943400	-4.45674200	-0.69909500	C	-2.35860400	2.70218100	-0.90520000	C	-2.36173800	2.70564200	-0.79374700
H	-2.34094100	-2.71582500	0.68993800	O	-2.43243700	1.40436800	-0.37265200	O	-2.44804900	1.41338200	-0.25380600
H	-3.27220300	-3.28136000	-0.72287100	H	-3.27088900	3.26777500	-0.65789300	H	-3.27129000	3.28110500	-0.55721400
H	-3.52244400	-0.66940200	0.68993800	H	-2.27675200	2.65841400	-2.00155000	H	-2.27075800	2.65701600	-1.88928600
H	-4.47784300	-1.19313100	-0.72287100	H	-1.18727700	3.37852900	0.75549500	H	-1.18800900	3.36226900	0.87247400
H	-4.44936900	1.20695200	-0.69909500	H	-1.20948000	4.47799400	-0.64614200	H	-1.21248400	4.48032500	-0.51256300
H	-3.45275300	0.64783400	-2.06297200	C	-3.51946000	0.69152100	-0.90520000	C	-3.52402400	0.69250400	-0.79374700
H	3.27220300	-3.28136000	-0.72287100	C	-3.54475100	-0.70023900	-0.34108000	C	-3.54277000	-0.69854900	-0.22431000
H	2.34094100	-2.71582500	0.68993800	O	-2.43832600	-1.40776800	-0.83339200	O	-2.44537100	-1.41183600	-0.72587400
O	0.00000000	2.80715900	-0.89525500	H	-4.46542100	1.19878600	-0.65789300	H	-4.47716600	1.19246800	-0.55721400
O	2.41073300	1.39183700	-0.44811600	H	-3.44063000	0.64251800	-2.00155000	H	-3.43642300	0.63802600	-1.88928600
O	2.43107100	-1.40357900	-0.89525500	H	-3.51953000	-0.66105200	0.75549500	H	-3.50581500	-0.65228900	0.87247400
C	-2.35488200	2.69910600	-0.96551800	H	-4.48279600	-1.19155700	-0.64614200	H	-4.48631700	-1.19012100	-0.51256300
C	1.16477000	3.42041400	-0.40582300	C	-2.37880000	-2.71972500	-0.34108000	C	-2.37634700	-2.71885400	-0.22431000
C	2.35488200	2.69910600	-0.96551800	C	-1.16085500	-3.39370200	-0.90520000	C	-1.16228600	-3.39814600	-0.79374700
C	3.51493500	0.68983500	-0.96551800	O	0.00000000	-2.80873700	-0.37265200	O	0.00000000	-2.82676400	-0.25380600
C	3.54455100	-0.70148700	-0.40582300	H	-1.19453100	-4.46656100	-0.65789300	H	-1.20587500	-4.47357300	-0.55721400
H	-1.18150300	3.38522700	0.68993800	H	-1.16387800	-3.30093200	-2.00155000	H	-1.16566500	-3.29504200	-1.88928600
H	-1.20564000	4.47449100	-0.72287100	H	-2.33225300	-2.71747600	0.75549500	H	-2.31780600	-2.70998100	0.87247400
H	1.18150300	3.38522700	0.68993800	H	-3.27331600	-3.28643700	-0.64614200	H	-3.27383300	-3.29020400	-0.51256300
H	1.20564000	4.47449100	-0.72287100	C	1.16085500	-3.39370200	-0.90520000	C	1.16228600	-3.39814600	-0.79374700
H	2.28741800	2.66625500	-2.06297200	C	2.37880000	-2.71972500	-0.34108000	C	2.37634700	-2.71885400	-0.22431000
H	3.26993500	3.24979100	-0.69909500	O	2.43832600	-1.40776800	-0.83339200	O	2.44537100	-1.41183600	-0.72587400
H	3.45275300	0.64783400	-2.06297200	H	1.19453100	-4.46656100	-0.65789300	H	1.20587500	-4.47357300	-0.55721400
H	4.44936900	1.20695200	-0.69909500	H	1.16387800	-3.30093200	-2.00155000	H	1.16566500	-3.29504200	-1.88928600
H	4.47784300	-1.19313100	-0.72287100	H	2.33225300	-2.71747600	0.75549500	H	2.31780600	-2.70998100	0.87247400
H	3.52244400	-0.66940200	0.68993800	H	3.27331600	-3.28643700	-0.64614200	H	3.27383300	-3.29020400	-0.51256300
H	-3.26993500	3.24979100	-0.69909500	C	3.54475100	-0.70023900	-0.34108000	C	3.54277000	-0.69854900	-0.22431000
H	-2.28741800	2.66625500	-2.06297200	C	3.51946000	0.69152100	-0.90520000	C	3.52402400	0.69250400	-0.79374700
Xe	0.00000000	0.00000000	1.02471900	H	4.46542100	1.19878600	-0.65789300	H	4.47716600	1.19246800	-0.55721400
O	0.00000000	1.58373300	1.79351300	H	3.44063000	0.64251800	-2.00155000	H	3.43642300	0.63802600	-1.88928600
O	1.37155300	-0.79186600	1.79351300	H	3.51953000	-0.66105200	0.75549500	H	3.50581500	-0.65228900	0.87247400
O	-1.37155300	-0.79186600	1.79351300	H	4.48279600	-1.19155700	-0.64614200	H	4.48631700	-1.19012100	-0.51256300

XeO ₃ (21-Crown-7)				KrO ₃ (21-Crown-7)				ArO ₃ (21-Crown-7)			
O	-2.24221400	2.11059600	0.47954800	O	-2.29781300	2.12435600	0.43423100	O	2.24022700	2.20596300	-0.34159700
O	-3.35618100	-0.35837900	-0.02679500	O	-3.38796800	-0.36807000	-0.11503200	O	3.38644800	-0.29660300	0.18890900
O	0.53917100	2.26179500	0.86926600	O	0.49317300	2.34434600	0.83574800	O	-0.56015100	2.46876700	-0.74939500
O	-1.62157600	-2.01300400	1.26789700	O	-1.65234900	-2.10578600	1.13923200	O	1.72538700	-2.19209000	-0.10425800
O	3.45785200	1.92576000	0.37465500	O	3.34793900	1.96316700	0.25406100	O	-3.33892300	1.95484900	-0.14428800
O	1.28568300	-1.71839700	0.83613300	O	1.30544800	-1.83776000	0.86008800	O	-1.25391000	-2.02051500	-0.85103900
C	3.79602600	-1.04931200	-0.12382100	C	3.74036100	-0.99547100	-0.14455600	O	-3.59661100	-1.02377500	0.21216400
C	-1.49240800	3.25212300	0.13879300	O	-1.56138000	3.27668700	0.10950900	C	1.50367500	3.35548400	-0.00785800
C	4.59314600	1.20248800	-0.03222000	C	4.49848700	1.26307100	-0.14589300	C	-4.44738000	1.19909200	0.27107500
C	-3.45004100	-1.02177800	-0.23573000	C	-3.48606800	-2.00258000	-0.30306600	C	3.42673300	2.07689800	0.39465200
C	-2.75071300	-2.55332100	0.62092500	C	-2.79249200	-2.58560100	0.47170200	C	2.89344600	-2.56125800	-0.32944500
C	4.30295300	0.00304600	-0.91328900	C	4.22756700	0.02688600	-0.97922200	C	-4.09873700	-0.03561400	1.07648900
C	-4.15667000	0.77064900	0.23098000	C	-4.18919500	0.75512100	0.15459300	C	4.15031600	0.84972400	-0.08830700
C	-0.65535000	-2.98170000	1.58844500	C	-0.70421700	-3.10933500	1.39526700	C	0.82280000	-3.25513000	-1.17394300
C	-3.82692500	-1.50576500	0.63268300	C	-3.85247000	-1.52222600	0.53337400	C	3.88948500	-1.44101200	-0.44758100
C	1.59663900	2.24837200	1.80893500	C	1.55792000	2.34532300	1.75950700	C	-1.61135100	2.45774700	-1.68051300
C	0.62108500	-2.25984000	1.95417700	C	0.56333800	-2.44710300	1.88933300	C	-0.45399500	-2.71120600	-0.177960900
C	2.69810900	1.31166300	1.39065300	C	2.64120500	1.39046500	1.33364900	C	-2.64706200	1.44756800	-1.26668700
C	-0.32683900	3.34604100	1.08195700	C	-0.40682800	3.39134000	1.06589900	C	0.35866700	3.49727700	-0.97442400
C	2.09748100	-2.66767000	0.16263600	C	2.18420700	-2.73224000	0.21303900	C	-2.16046200	-2.85645800	-0.17457700
C	3.01398400	-1.98312900	-0.82005000	C	3.01228800	-1.99461300	-0.80584800	C	-2.90591100	-2.05680400	0.85999200
H	-2.10719000	4.15912400	0.23898000	H	-2.19248500	4.17431700	0.20064200	H	2.14141900	4.25103700	-0.07329600
H	-1.14751600	3.18413400	-0.90141900	H	-1.19649400	3.21911900	-0.92511100	H	1.12273500	3.28251200	1.02048300
H	5.17607600	0.87591400	0.84343000	H	5.10474900	0.98238900	0.72949400	H	-5.06331000	0.90467900	-0.59265400
H	5.20655300	1.90825100	-0.59947200	H	5.08264100	1.96589100	-0.74724900	H	-5.04629200	1.86527900	0.89916400
H	-3.25380700	1.96600500	-1.31133700	H	-3.27234800	1.95352100	-1.37673400	H	3.21402500	2.00022300	1.46801100
H	-4.09058500	2.88286900	-0.02914900	H	-4.14453100	2.86681900	-0.12144500	H	4.07706200	2.95271800	0.23863400
H	-3.11616900	-3.44266900	1.15452600	H	-3.17659900	-3.49411000	0.95998400	H	3.33343300	-3.46922400	-0.77094400
H	-2.48755800	-2.84061600	-0.40397200	H	-2.54430100	-2.83174500	-0.56867500	H	2.66847300	-2.77022300	0.72508800
H	-5.12700300	0.68209500	-0.27926600	H	-5.16194000	0.67029800	-0.35339800	H	5.13546400	0.78705400	0.39963500
H	-4.34558800	0.84371200	1.31169900	H	-4.37667700	0.82359300	1.23610100	H	4.31501800	0.93516000	-1.17238800
H	-4.73375500	-1.89340700	0.14520300	H	-4.77754900	-1.89118300	0.06402600	H	4.84642700	-1.74961700	0.00204200
H	-4.07972500	-1.25655400	1.67332800	H	-4.07443500	-1.29523300	1.58639000	H	4.06884000	-1.23150000	-1.51236700
H	5.23183000	-0.30908600	-1.41731000	H	5.15846400	-0.29067300	-1.47698000	H	-4.99847200	-0.40012600	1.59952600
H	3.57311400	0.29035900	-1.67824100	H	3.49169700	0.27128500	-1.75514700	H	-3.34967800	3.20323800	1.83415

Xe	-0.46446000	-0.09477800	-0.93619500	O	1.04710700	0.37835000	-1.30708000	O	-0.80027800	0.31064200	1.20337400
O	1.16822000	0.37806300	-1.38696300	O	-1.37415800	0.78317100	-2.13419900	O	1.33087500	0.70174900	2.24495400
O	-1.41753700	0.83595200	-2.08942700	O	-0.57795500	-1.65238700	-1.63739600	O	0.64458000	-1.55286400	1.74042200
O	-0.60679400	-1.74411500	-1.55413200	Kr	-0.49000300	-0.11129600	-1.09460300	Ar	0.60252900	-0.14318700	1.26580600

XeO ₃ (21-Crown-7)'				KrO ₃ (21-Crown-7)'				ArO ₃ (21-Crown-7)'			
O	-1.546923003	-1.610148059	0.931299984	O	1.553294020	-1.552888962	-0.812839965	C	2.686290793	-2.344457273	-0.299625962
O	1.415930980	-1.289017899	1.044724984	O	-1.395989976	-1.223990925	-0.921105965	C	2.168679134	1.802614769	-0.979010962
O	-4.168637062	-0.504984200	0.816771984	O	4.210514033	-0.534822996	-0.720508965	C	0.704607799	-2.267668110	-1.554371962
O	4.149129948	-0.696282752	0.834895984	O	-4.158463970	-0.727085891	-0.779173965	C	-3.478202155	-1.707537766	0.187891038
O	-3.449744220	2.422419839	0.837103984	O	3.444921069	2.375838014	-0.745005965	C	1.044341192	-2.507696862	-0.236610962
O	3.712991787	2.300571224	0.636230984	O	-3.713296932	2.268114104	-0.514730965	C	-0.489452129	-1.390121012	-1.856251962
O	0.119431807	1.926575031	0.560384984	O	-0.123263938	1.830670059	-0.492085965	C	-4.967114003	0.132569356	0.039772038
C	-2.684485965	-2.319463120	0.466119984	C	2.674604011	-2.306658977	-0.396217965	C	-2.309639201	-0.275737862	-0.575919962
C	-2.165110193	1.927963908	1.138504984	C	2.169414063	1.855270030	-1.056793965	C	4.947144028	0.511834541	-0.041762541
C	-0.665247959	-2.431520011	1.667832984	C	0.687920011	-2.285868952	-1.648611965	C	-4.215586904	1.339229294	0.590040038
C	3.499432996	-1.585203787	-0.040122016	C	-3.501097981	-1.638789899	0.066669035	C	4.079354123	1.671140612	0.430447038
C	-1.082758232	2.644622966	0.342414984	C	1.072559071	2.549216044	-0.263107965	C	3.694346866	-1.449821356	0.369989038
C	0.532248997	-1.613937947	2.099816984	C	-0.505976978	-1.425500937	-1.997300965	C	-2.471161862	1.848593151	-0.940040962
C	4.978980897	0.251034292	0.191201984	C	-4.978573958	0.207620119	-0.106955965	C	-1.327635809	2.493816057	-0.168879962
C	2.388714033	-2.268202847	0.713980984	C	-2.347728989	0.540190914	-0.690888965	H	3.140200755	-2.801427311	-1.189954962
C	-4.936457120	0.562892759	0.299411984	C	4.956880046	0.240179995	-0.189758965	H	2.388525727	-3.149327249	0.387818038
C	4.243583832	1.461566253	-0.370394016	C	-4.233089943	1.403888110	0.472826035	H	2.120695046	0.727916773	-0.794632962
C	-4.113937183	1.759621803	-0.207451016	C	4.111933061	-1.370726005	0.303497035	H	2.043952146	1.952623780	-0.2054849962
C	-3.658213016	-1.365318173	-0.171503016	C	3.680238022	-1.707108989	0.255904035	H	0.383965721	-3.223959084	-1.114289962
C	2.422933806	1.937656155	1.077953984	C	-2.434645937	1.903031088	-0.995355965	H	1.234159781	-2.493762154	-2.491926962
C	1.324014769	2.623834096	0.275496984	C	-1.312457929	2.537707073	-0.184031965	H	-4.150274222	-2.523599711	0.494049038
H	-3.161566937	-2.826900146	1.314627984	H	3.131351004	-2.795094982	1.267475965	H	-3.107643115	-1.219686797	1.095956038
H	-2.372774924	-3.072509103	-0.269135016	H	2.359109001	-3.082144973	0.314965035	H	-1.026771161	-1.789266968	-2.726572962
H	-2.104743135	0.849254911	0.969471984	H	2.126298049	0.777013030	-0.891154965	H	-0.141461046	-0.382707041	-2.097106962
H	-1.998721202	2.089901917	2.206950984	H	2.008289065	2.022758032	-1.215178965	H	-1.867526270	-3.107763899	-0.011743962
H	-0.352245912	-3.290603995	1.058973984	H	0.367778999	-3.211198948	-1.148495965	H	-2.655766233	-2.656940834	-1.545737962
H	-1.180249938	-2.814457039	2.559926984	H	1.214211007	-2.566812958	-2.572291965	H	0.969597278	3.552744868	-0.565784962
H	4.201854037	-2.347599749	-0.410220016	H	-4.189282991	-2.437969890	0.381463035	H	1.238798192	2.512460846	0.844699038
H	3.083138968	-1.064968810	-0.909539016	H	-3.120123975	-1.149268904	0.969167035	H	-5.704287975	0.481095417	-0.687810962
H	1.077817026	-2.148435918	2.886282984	H	-1.041851984	-1.866710930	-2.846885965	H	-5.509549044	-0.359040599	0.862366038
H	0.188436946	-0.660886965	2.510363984	H	-0.158861966	-0.430834941	-2.288599965	H	-2.332658951	0.767853139	-0.940951962
H	1.946567075	-3.056382871	0.093319984	H	-1.908599999	-3.063337919	-0.108119965	H	-2.455628834	2.187476150	-1.979047962
H	2.781511057	-2.711904826	1.636832984	H	-2.702447994	-2.641114909	-1.650418965	H	-4.916088856	1.923541352	1.157898038
H	-0.973951287	3.678847972	0.688118984	H	0.959941084	3.588178045	-0.596241965	H	-3.401411930	1.019849227	1.251865038
H	-1.333702233	2.676416953	-0.725160016	H	1.317630072	2.562542040	0.806477035	H	4.494929815	-2.069980422	0.802109038
H	5.687457879	0.990071331	0.950965984	H	-5.693816953	0.566360128	-0.851211965	H	3.211198911	-0.900909316	1.190236038
H	5.551911923	-0.227359677	-0.618141016	H	-5.545435964	-0.286034873	0.697663035	H	5.602856057	0.869409487	-0.839492962
H	2.278933864	0.857172147	1.034559984	H	-2.306080950	0.820989086	-0.995675965	H	5.580952000	0.169881489	0.791678038
H	2.351118790	2.231956151	2.128526984	H	-2.379038932	2.2241890087	-2.033207965	H	4.731108184	2.407332559	0.912754038
H	4.967963799	2.065244292	-0.926490016	H	-4.947862936	1.995317119	1.056097035	H	3.353810096	1.337933672	1.182746038
H	3.461735848	1.154960211	-0.174167016	H	-3.443459947	1.075893100	1.158918035	H	-1.242004722	3.559560050	-0.41861962
H	-4.470346984	-1.425136216	-0.628095016	H	4.478717014	-2.011503999	0.699836035	H	-1.503050815	2.418828071	0.911853038
H	-3.161621046	-0.809617146	-0.974265016	H	3.197960029	-0.841185983	1.066227035	Ar	0.021331945	-0.494328054	1.413551038
H	-5.567283138	0.904458725	1.123664984	H	5.596936051	0.890399987	-1.003204965	O	1.216989900	0.167874848	2.001964038
H	-5.594483101	0.207174723	-0.508681016	H	5.606419042	0.192321987	0.628940035	O	0.014281827	-1.924210054	1.817012038
H	-4.798778222	2.459842766	-0.666325016	H	4.782088070	2.438338997	0.767524035	O	-1.192779001	0.157415046	1.969165038
H	-3.403659166	1.423102841	-0.980277016	H	3.401391057	1.381972014	1.072969035	O	-0.145043865	1.809994960	-0.527612962
H	1.222919713	3.675666090	0.565432984	H	-1.193834915	3.597806072	-0.441027965	O	-3.736418833	2.204802255	-0.414400962
H	1.543953772	2.88774107	-0.796661016	H	-1.528407930	2.472825076	0.888562035	O	-4.156568800	-0.799883711	-0.645684962
Xe	-0.038292070	-0.359284978	-1.084619016	Kr	0.021511034	-0.438939943	1.227978035	O	-1.373202116	-1.240012939	-0.769339962
O	-1.384272109	0.361104950	-1.977584016	O	1.301029043	0.251100041	1.981552035	O	1.560014855	-1.583712181	-0.672617962
O	-0.018183980	-2.041315977	-1.625442016	O	0.013687014	-0.164556943	1.671896035	O	4.222861939	-0.568759400	-0.590056962
O	1.382031893	0.325975099	-1.879766016	O	-1.307838958	0.218132073	1.917497035	O	3.432310178	2.334372665	-0.631393962

XeO ₃ (9-Crown-3S)				KrO ₃ (9-Crown-3S)				ArO ₃ (9-Crown-3S)			
S	0.805917095	-1.849381144	0.837643076	S	-0.705067782	-1.801145007	-0.907398109	S	0.465924775	1.928643130	0.552899928
S	0.756952214	1.691529131	1.102907095	S	-0.704958229	1.686835993	-1.105692109	S	0.471211111	-0.485588869	-1.945758072
S	1.320616203	0.146220993	-1.962625138	S	-0.709996027	0.114238992	2.012623891	S	0.462402244	-1.443104870	1.393426928
C	2.066776201	-1.471419156	-1.636781115	C	-1.475240819	-1.509800106	1.776272891	C	1.235449057	-0.100501763	2.328992928
C	3.206592208	-1.853570195	-0.180203002	C	-1.981588774	-1.860241171	0.381032891	C	1.741932889	1.107548308	1.546198928
C	2.474998332	1.286350039	-1.147070074	C	-1.983244175	1.262171829	1.417153891	C	1.744719307	-1.891043692	0.191860928
C	1.808970317	2.309056142	-0.234150006	C	-1.473287307	2.294699894	0.417235891	C	1.245433317	-1.965278761	-1.248278072
C	1.249130162	-0.827774079	2.266568183	C	-1.467227912	-0.784824105	-2.197779109	C	1.246326756	2.065366239	-1.074310072
C	1.844567261	0.551028004	2.006981167	C	-1.977148089	0.597761830	-1.804859109	C	1.750295935	0.781662309	-1.727816072
H	1.364061126	-2.168421186	-2.101186148	H	-0.679948731	-2.197976004	2.075187891	H	0.444028015	0.202326127	0.310935928
H	3.007971274	-1.555376196	-2.189213153	H	-2.292772803	-1.635311211	2.493316891	H	2.054078113	-0.498494649	2.937323928
H	2.736391208	-2.858855285	-0.153896000	H	-2.398387645	-2.871053224	0.411565891	H	2.155897789	1.828613365	2.257208928
H	3.039085288	-1.191568171	0.283771033	H	-2.796843859	-1.198758275	0.083993891	H	2.560307929	0.824380422	0.882328928
H	3.035371395	1.825742060	-1.915976137	H	-2.400915243	1.794543776	2.276528891	H	2.158434443	-2.866918634	0.462680928
H	3.202007369	0.688869967	-0.595087032	H	-2.798601099	0.675570725	0.991102891	H	2.561919207	-1.173719578	0.282778928
H	0.295505094	-0.738592038	2.793406225	H	-0.669357923	-0.697978002	-2.940258109	H	0.459601693	2.516235129	-1.685220072
H	1.931446195	-1.390803146	2.910503233	H	-2.282298841	-1.343974029	-0.668169109	H	0.206759655	2.787579353	-1.029873072
H	2.788275328	0.480030966	1.464011125	H	-2.794191080	0.522655725	-1.085760109	H	2.565898295	0.345950423	-1.148589072
H	2.076037290	1.006606033	2.973618241	H	-2.392437151	1.075983777	-2.696616109	H	2.167661899	1.035576367	-2.706683072
H	1.126376286	2.944490214	-0.804984050	H	-0.678467384	2.896793996	0.865743891	H	0.456588842	-2.717767871	-1.336023072
H	2.577244399	2.966049165	0.185535026	H	-2.289522395	2.979301790	0.165542891	H	2.068268362	-2.290025647	-1.893348072
Xe	-1.627184025	0.000402087	-0.160669001	Kr	1.764521987	0.00123310	0.001797891	Ar	-0.241663957	0.000400781	-0.003339072
O	-2.425073036	1.520910231	-0.578357035	O	-2.76489807	1.407023388	0.575677891	O	-2.547795774	0.311659290	-0.487775072
O	-2.013139065	-0.249507919	1.548551127	O	2.374935014	-0.206412612	-1.504210109	O	-2.546769106	1.075754711	-0.898268072
O	-2.556014141	-1.244698974	-1.004350065	O	2.375791141	-1.200826612	0.933058891	O	-2.549013990	0.237547710	1.374616928

XeO ₃ (12-Crown-4S)				KrO ₃ (12-Crown-4S)				ArO ₃ (12-Crown-4S)			
S	0.644868048	2.412964185	-0.183789014	S	-1.583809795	0.415021223	1.893327989	S	-2.115496864	0.158275738	1.493812065
S	0.288895022	-0.040188003	2.407564185	S	-0.040979536	2.169353995	-0.749458011	S	-0.017207254	1.950124024	-0.671982935
S	-1.406432105	0.378040029	-2.111825161	S	0.810089854	-1.962262130	1.047469989	S	0.513927428	-1.922755157	0.731460065
S	-1.730864130	-1.962462152	0.388685030	S	2.389468125	-0.124624363	-1.423925011	S	2.767650098	0.047242076	-1.090605935
C	-0.757279060	2.888433219	-1.225748095	C	-0.525577939	-0.560806933	2.991503989	C	-1.145540209	-0.855639592	2.638821065
C	-1.507046115	-0.165679013	2.555641193	C	1.678884487	2.329966742	-0.221461011	C	1.510473829	2.194082503	0.260352065
C	-1.911793145	1.897750146	-1.272345099	C	0.876046017	-0.858042140	2.477176989	C	0.325793728	-1.039933093	2.296352065
C	-1.945517150	-1.567322119	2.143017165	C	2.593533389	1.665610607	-1.244369011	C	2.713334690	1.783752094	-0.578618935
C	0.589322043	1.739565133	2.517530192	C	-0.928776440	2.822536126	0.682392989	C	-1.237070032	2.600732439	0.489177065
C	-3.104377235	-1.024091081	-0.327919025	C	3.171030039	-0.705881479	0.103456989	C	3.102726817	-0.780764039	0.487920065
C	-0.072560005	2.623668198	1.469173111	C	-0.787475555	2.041309106	1.983292989	C	-1.428088300	1.813471504	1.781945065
C	-2.838851216	-0.678131051	-1.787329137	C	2.556591846	-0.201489838	0.583768989	C	2.311332376	-2.074591769	0.646148065
H	-0.325398025	3.025483231	-2.220371168	H	-1.081163076	-1.488522851	3.150616989	H	-1.658750537	-1.820759418	2.640641065
H	-1.118732087	3.867201295	-0.898014067	H	-0.464887865	-0.055573942	3.959541989	H	-1.239365068	-0.441086560	3.646624065
H	-1.989609151	0.584794042	1.924782149	H	1.814466420	1.872802722	0.762289989	H	1.485082634	1.620330512	1.190802065
H	-1.807451139	0.024266002	3.591263274	H	1.938949644	3.390331703	-0.133943011	H	1.603769189	3.252491472	0.527568065
H	-1.361505105	-2.322994178	2.674615204	H	2.401572449	2.068378635	-2.242261011	H	2.725202880	2.342169090	-1.518215935
H	-2.992085230	-1.726796133	2.416994182	H	3.637893422	1.889225453	-1.008334011	H	3.635762775	2.033962780	-0.046263935
H	-4.023051308	-1.615899124	-0.264884020	H	4.242151017	-0.858201637	-0.063885011	H	4.170629738	-1.011548402	0.551509065
H	-3.264258251	-0.115392009	0.256850019	H	3.071346153	0.064919536	0.870787989	H	2.874559052	-0.089901961	1.301807065
H	-3.731069283	-0.215978017	-2.220906171	H	3.137109789	-2.403575474	1.426475989	H	2.665250194	-2.611083890	1.532920065
H	-2.638968200	-1.584001119	-2.365886180	H	2.600523735	-2.770398394	-0.205268011	H	2.483756152	-2.732332828	-0.209833935
H	-2.754061209	2.346273178	-1.809624136	H	1.458437947	-1.334126226	3.273395989	H	0.807862532	-1.616251257	3.093801065
H	-2.250208171	1.666305125	-0.259106020	H	1.384075154	0.107127278	2.206325989	H	0.824816059	-0.068762263	2.243209065
H	-1.145209085	2.26029185	1.417358107	H	0.265594425	1.904478950	2.237180989	H	-0.480808335	1.710676181	2.314604065
H	0.049396004	3.669732280	1.766084136	H	-1.245055470	2.615221173	2.794926989	H	-2.106684112	2.367050735	-0.347970065
H	1.678223128	1.812705139	2.456111187	H	-1.971825437	2.842002280	0.356188989	H	-2.166251026	2.618023755	-0.086099935
H	0.295662023	2.083942161	3.513383268	H	-0.625211287	3.860770082	0.849102989	H	-0.991265679	3.640254355	0.730822065
Xe	1.485798114	-0.699510055	-0.494894038	Kr	-1.447684962	-0.715305797	-1.094824011	Ar	-1.511423171	-0.745083468	-1.577236935
O	2.809287215	-0.008289001	0.455984035	O	-0.626341798	0.394983777	-1.350902011	O	-2.475954808	0.322467860	-1.963704935
O	1.992101153	-0.432497033	-2.166134167	O	-2.191471158	-2.040882687	-0.489448011	O	-2.268887593	-1.983564210	-1.260687935
O	1.659909129	-2.440586184	-0.251931019	O	-0.863385023	-1.128671883	-2.563737011	O	-0.596120261	-1.008225779	-2.713195935

XeO ₃ (15-Crown-5S)				KrO ₃ (15-Crown-5S)				ArO ₃ (15-Crown-5S)			
S	-3.150809242	-0.413282032	0.420104032	S	-3.299228200	-0.468849537	0.544941009	S	-3.307531993	-0.688921175	0.538178901
S	-1.075585081	1.458899111	-1.550737116	S	-1.140027017	1.433933255	-1.382655991	S	-1.253281994	1.596310922	-1.199357099
S	2.140256161	1.768905138	-0.420993032	S	2.124415013	1.738773941	-0.366747991	S	1.964929809	1.736419072	0.005100901
S	-0.575572044	-0.490306184	-0.770895060	S	-0.587238374	-2.278602798	-0.597280991	S	-0.374716925	-2.135013037	-0.632887099
S	2.515807190	-1.727045132	0.118047009	S	2.591809683	-1.688572104	0.177735009	S	2.853958048	-1.558794886	0.186005901
C	-3.630758275	0.930287068	-0.708676056	C	-3.711509066	0.920822502	-0.555140991	C	-3.764652062	0.788529804	-0.421284099
C	-3.817947292	0.507660039	-1.699353128	C	-3.899056104	0.529057520	-1.558487991	C	-3.905959048	0.498578797	-1.466283099
H	-4.574062347	1.347771103	-0.348488027	H	-4.648775024	1.354377592	-0.197725991	H	-4.736323077	1.122214759	-0.090401099
C	1.358933102	2.656402203	-1.794571139	C	1.281482101	2.655381022	-1.683762991	C	1.164321841	2.863285035	-1.165074099
H	1.900390147	3.587035172	-1.981773153	H	1.809596191	3.593192972	-1.874010991	H	1.683047796	3.825724059	-1.172144099
H	1.421772107	2.048220156	-2.701874209	C	1.310432044	2.066531020	-2.605477991	H	1.233994861	2.442425038	-2.173201099
C	3.727017283	-0.470159036	-0.358802027	C	3.769644802	-0.451323217	-0.419876991	C	3.906123983	-0.167949837	-0.302372099
H	4.063483313	-0.058498004	0.596380845	H	4.202860842	-0.033613258	0.492881009	H	4.342577967	0.177807183	0.638495901
H	4.582053352	-0.979149073	-0.812567060	H	4.574160752	-0.971842294	-0.947715991	H	4.727069001	-0.551542799	-0.915916099
C	-2.597762199	2.039961155	-0.777660057	C	-2.654245961	2.012758401	-0.588287991	C	-2.780893116	1.945497850	-0.305449099
H	-2.342755181	2.390974182	0.225102017	H	-2.402105931	2.390300976	0.426540009	H	-2.532030124	2.123078862	0.743920901
H	-2.994463231	2.875443219	-1.362674105	H	-3.039848878	2.874804438	-1.142204991	H	-3.240289158	2.852064829	-1.172844099
C	-3.239874250	-1.850080139	-0.676912054	C	-3.289935334	-1.865444538	-0.606293991	C	-3.110710934	-1.945301165	-0.749394099
H	-4.193661319	-1.820595137	-1.210800092	H	-4.215920332	-1.851147449	-1.188501991	C	-4.001660934	-1.942691207	-1.384275099
H	-3.280656253	-2.710570205	-0.003422000	H	-3.338944419	-2.747292534	0.037904009	H	-3.119670889	-2.892305166	-0.202116099
C	-0.089439007	2.961276224	-1.449693112	C	-0.155088872	2.944803160	-1.278790991	C	-0.291882168	3.065456967	-0.771912099
H	-0.172234013	3.352169255	-0.431014033	H	-0.199375836	3.314331165	-0.249751991	H	-0.378431176	3.236338962	0.305471901
H	-0.488232037	3.708981282	-2.141248162	H	-0.578758739	3.709304201	-1.936913991	H	-0.696857209	3.940243498	-1.289195099
C	0.679908054	-1.966943151	-1.995810151	C	0.658317659	-1.935767918	-1.861898991	C	0.873427051	-1.611346979	-1.832607099
H	0.454341035	-2.462143188	-2.945920225	H	0.391114609	-2.460055892	-2.785562991	H	0.613238070	-2.022009991	-2.813987099
H	0.656163051	-0.884700688	-2.147932163	H	0.668494763	-0.860760919	-2.059445991	H	0.858049000	-0.520643980	-1.893102099
C	3.250659247	0.636309051	-1.288478099	C	3.220611908	0.654946836	-1.309348991	C	3.236253929	0.986646132	-1.033814099
H	2.733896211	0.191590187	-2.157121167	H	2.671589868	0.232706889	-2.155592991	H	2.782620945	0.638745110	-1.966746099
H	4.119840314	1.191549809	-1.654651129	H	4.056069064	1.235513756	-1.712049991	H	3.997716894	1.729818167	-1.292657099
C	-2.091402158	-2.000074155	-1.665525129	C	-2.093854343	-1.958790653	-1.542631991	C	-1.864728938	-1.845591107	-1.615260099
H	-2.321497178	-2.797650216	-2.379423179	H	-2.254916421	-2.77359638	-2.257018991	H	-1.921373903	-2.593605110	-2.413733099
H	-1.934793146	-0.175062084	-2.226011171	H	-1.969051254	-0.181864665	-2.108260991	H	-1.793947985	-0.859413104	-2.080337099
C	2.039899156	-2.428811186	-1.490360114	C	2.014743612	-2.429726048	-1.378280991	C	2.243156075	-2.134799915	-1.423516099
H	2.037840154	-3.513574270	-1.361746103	H	1.971200508	-3.506639044	-1.200364991	H	2.213784126	-3.224818916	-1.356771099
H	2.820356217	-2.192042166	-2.218648172	H	2.778713628	-2.259385122	-2.142243991	H	2.990041063	-1.878399880	-2.180923099
Xe	0.104821008	0.134844010	1.540081116	Kr	0.239956862	0.169558122	1.768346009	Ar	0.177971979	-0.080404011	2.079918901
O	-0.723416055	1.677310128	1.817889139	O	-0.591409003	1.572884202	1.937436009	O	-0.653292079	1.148973950	2.191366901
O	1.640629128	0.66929028	2.384689181	O	1.666014884	0.403210985	2.536383009	O	1.440006699	0.131648048	2.832677901
O	-0.722023054	-1.019207076	2.586097196	O	-0.550045247	-0.966106802	2.630379009	O	-0.551128968	-1.220736046	2.676989901

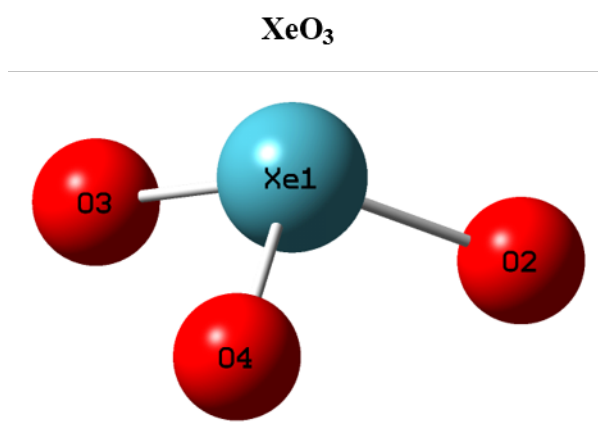
XeO ₃ (18-Crown-6S)				KrO ₃ (18-Crown-6S)				ArO ₃ (18-Crown-6S)	
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H	4.257053186	-2.404017105	-0.023004172	H	3.897015416	-3.011212162	-0.001358972	H	0.526567946	4.926246613	0.057394094
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H	3.760141916	1.866074580	0.080009836	H	4.022466941	1.294396248	0.133784028	H	-3.215184382	2.775340245	0.229372094
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S	-1.883344634	-2.591703538	0.524180870	S	-2.279445511	-2.329567060	0.589261028	S	3.237943496	-0.737292744	0.688881094
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XeO ₃ (21-Crown-7S)				KrO ₃ (21-Crown-7S)				ArO ₃ (21-Crown-7S)			
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S	-4.764847366	-0.726562056	0.414915031	S	4.800998998	-0.757270912	-0.337710901	S	4.813256918	-0.786255343	-0.267683079
S	4.754603363	-0.790021061	0.396231030	S	-4.788989002	-0.789554975	-0.339364901	S	-4.804719083	-0.802914891	-0.282575079
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S	4.247428325	2.759314208	0.322838025	S	-4.209670025	2.747286029	-0.276883901	S	-4.193811917	2.726776081	-0.227444079
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C	-2.615118202	2.128694162	1.197510091	C	2.632830980	2.051990073	-1.164717901	C	2.637536049	2.004093759	-1.129828079
C	-0.558734042	-3.293894251	1.144328089	C	0.558291014	-3.243248940	-1.123214901	C	0.557500801	-3.266913143	-1.021280079
C	3.612859278	-1.742044132	-0.647673048	C	-3.650153996	-1.764445967	0.687914099	C	-3.676685129	-1.792940944	0.742396921
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C	0.618510047	-2.907579222	2.024688152	C	-0.620554989	-2.821408948	-1.985273901	C	-0.617561179	-2.844751088	-1.889906079
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C	-3.778539287	-1.620925123	-0.817214061	C	3.785558004	-1.634176919	0.883499099	C	3.798676877	-1.656184295	0.959483921
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H	-0.236474018	-3.523335267	1.26087010	H	0.231086016	-3.532900942	-0.121907901	H	0.220603787	-3.564964127	-0.024818079
H	-1.053187082	-4.176342320	1.562310117	H	1.063036020	-4.097708937	-1.585326901	H	1.064337761	-4.120732167	-1.482828079
H	4.186491321	-2.374096180	-1.332350100	H	-4.226837991	-2.417143971	1.350198099	H	-4.262134160	-2.442409916	1.400224921
H	3.015249229	-1.051247081	-1.243756097	H	-3.059811000	-1.087406964	1.305610099	H	-3.083225098	-1.123595972	1.365491921
H	1.220448094	-3.792774288	2.248081169	H	-1.223464983	-3.695342952	-2.247210901	H	-1.218636220	-3.718292059	-2.157525079
H	0.274564021	-2.508940190	2.982238226	H	-0.274606992	-2.382379945	-2.924309901	H	-0.262454158	-2.406630104	-2.825987079
H	2.014341155	-3.149067238	-0.486040037	H	-2.059293986	-3.178368957	0.499946099	H	-2.113684197	-3.237350017	0.548696921
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H	-1.294506100	3.794394290	0.784890058	H	1.275230969	3.687036065	-0.762073901	H	1.273334126	3.629174824	-0.723032079
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H	2.813939212	2.104344183	2.161350166	H	-2.788042022	2.376603038	-2.120958901	H	-2.779038934	2.354062014	-2.075766079
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H	3.448630261	1.307492099	-1.412010109	H	-3.424998015	1.282865034	1.451843099	H	-3.411834986	1.255331044	1.496373921
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H	-4.915706375	2.4290206185	-1.647487127	H	4.9101122977	2.421248088	1.689942099	H	4.910678068	2.43456653	1.725009921
H	-3.505429269	1.438684109	-1.307051099	H	3.512003984	1.414893709	1.352775099	H	3.517309021	1.399073718	1.398701921
H	1.385637106	3.795300289	0.709314053	H	-1.390337031	3.701815048	-0.684693901	H	-1.382495873	3.651315944	-0.641758079
H	1.449123109	2.573752194	-0.583841047	H	-1.432600023	2.512207047	0.628006099	H	-1.425520929	2.472503950	0.672575921
Xe	-0.010160001	-0.367415028	-0.957660471	Kr	-0.007443004	-0.419360944	1.076969099	Ar	-0.023310066	-0.445875115	1.283560921
O	-1.392545108	0.440090034	-1.726361134	O	1.294123991	0.343131065	1.736747099	O	1.180643967	0.58981828	1.810918921
O	0.039534003	-1.947785151	-1.77346133	O	-0.057439995	-1.905016944	1.794582099	O	-0.069240130	-1.81428213	1.78374921
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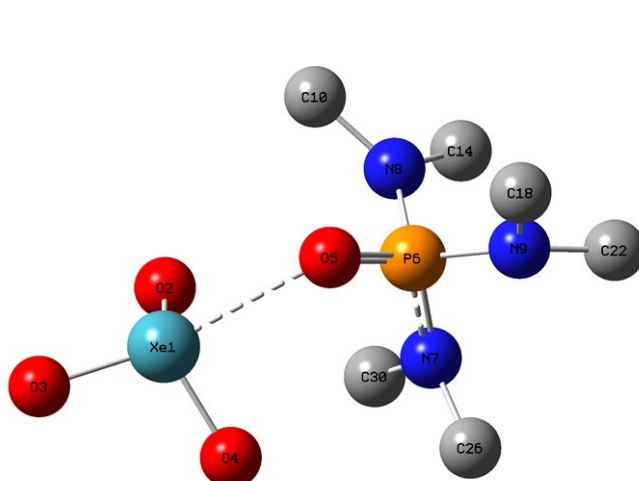
Table of Contents (Chapter-4):

1. **Figure S4.1-S4.11.** Optimized geometries of XeO_3 and its adducts with the top ten solvents along with their bond parameters, WBI values, and charge analysis (NPA).
2. **Figure S4.12-S4.20.** NCI plot and bond critical points (of aerogen bonds) of the adducts of remaining top ten solvents with XeO_3 , for the three binding modes, 1:3, 1:2 and 1:1, and their respective electron density (ρ , in a.u.) and laplacian of electron density ($\nabla^2\rho$, in a.u.).
3. **Table S4.1-S4.3.** Natural bond orbital (NBO) analysis of adducts of remaining top ten solvents with XeO_3 at the APFD/def2-TZVPD level of theory. (E^2 = Second order perturbation energy in kcal/mol).
4. **Table S4.4** Range of second-order perturbation energy (E^2 , in kcal/mol) values corresponding to the C-H...O (hydrogen bonding) interactions, obtained from the natural bond orbital (NBO) analysis of all the adducts of XeO_3 at the APFD/def2-TZVPD level of theory.
5. **Table S4.5-S4.7.** The energy decomposition analysis (EDA) of 1:3, 1:2, and 1:1 adducts of XeO_3 with all the 26 solvents at the BP86-D3BJ/TZ2P level of theory. Percentage contribution to total attractive energy is shown below, where electrostatic interactions are denoted as E_{elstat} , orbital interactions as E_{oi} , and dispersion interactions as E_{disp} .
6. **Table S4.8.** The energy decomposition analysis (EDA) of 1:3, 1:2, and 1:1 adducts of XeO_3 with all the 26 solvents at the BP86-D3BJ/TZ2P level of theory for comparing the trends in percentage contribution to total attractive energy. Electrostatic interactions are denoted as E_{elstat} , orbital interactions as E_{oi} , and dispersion interactions as E_{disp} . The exceptions to the trends discussed in the manuscript are highlighted in red.
7. Optimized Cartesian Coordinates

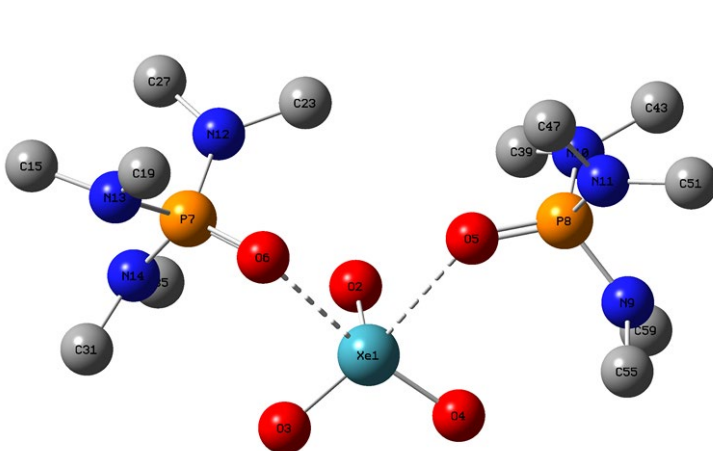


Bond Lengths (in Å)	NPA
Xe1-O2 = 1.7597	Xe1 = +2.765
Xe1-O3 = 1.7597	O2 = -0.922
Xe1-O4 = 1.7597	O3 = -0.922
	O4 = -0.922
WBI	
Xe1 = 3.3618	
O2 = 1.5318	
O3 = 1.5318	
O4 = 1.5318	

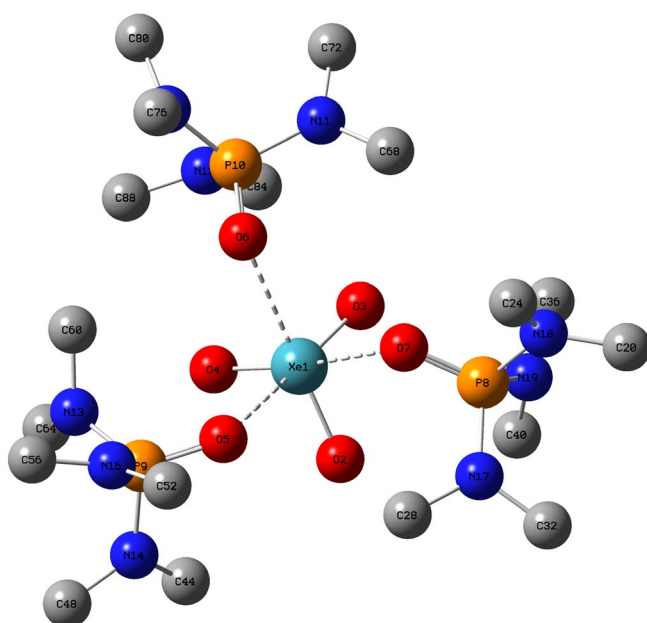
Figure S4.1. The optimized geometry of XeO₃ along with its bonding parameters, natural population charges, and Wiberg bond indexes.



Bond Parameters (in Å and °)	NPA
Xe1-O2 = 1.7644	Xe1 = +2.868
Xe1-O3 = 1.7645	O2 = -0.969
Xe1-O4 = 1.7641	O3 = -0.965
Xe1...O5 = 2.5688	O4 = -0.972
∠O3-Xe1-O5 = 161.79	O5 = -1.177
WBI	
Xe1 = 3.3436	Xe1...O5 = 0.0699
O2 = 1.4723	
O3 = 1.5006	
O4 = 1.4711	

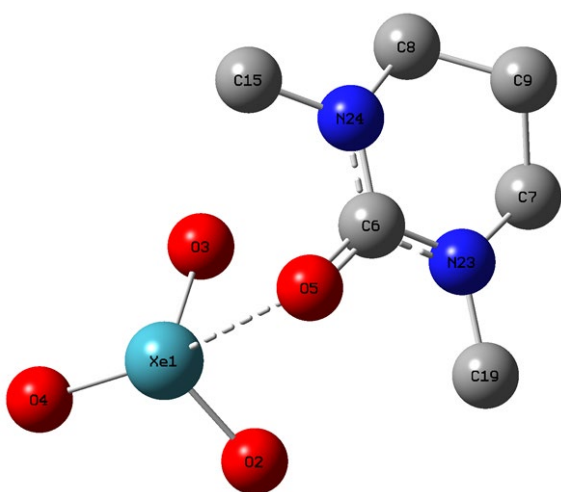


Bond Parameters (in Å and °)	NPA
Xe1-O2 = 1.7666	Xe1 = +2.957
Xe1-O3 = 1.7675	O2 = -0.997
Xe1-O4 = 1.7706	O3 = -0.999
Xe1...O5 = 2.6169	O4 = -1.016
Xe1...O6 = 2.6011	O5 = -1.172
∠O3-Xe1-O5 = 165.36	O6 = -1.159
∠O4-Xe1-O6 = 163.37	
WBI	
Xe1...O5 = 0.0509	Xe1 = 3.3212
Xe1...O6 = 0.0585	O2 = 1.4367
	O3 = 1.4541
	O4 = 1.4405

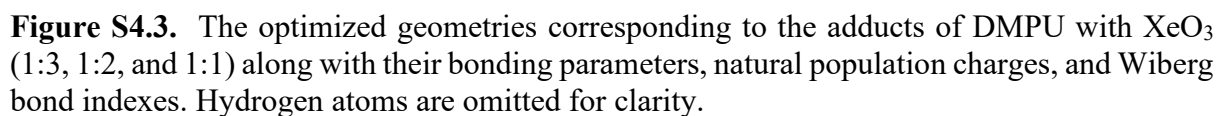


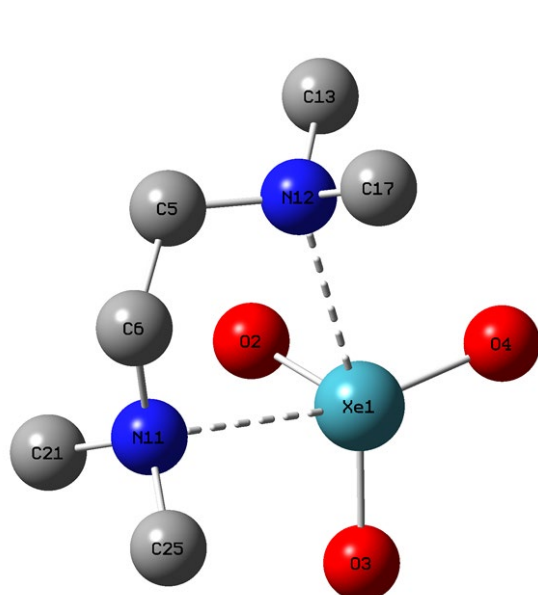
XeO₃:(HMPA)₃	
Bond Parameters (in Å and °)	NPA
Xe1-O2 = 1.7701	Xe1 = +3.016
Xe1-O3 = 1.7720	O2 = -1.021
Xe1-O4 = 1.7734	O3 = -1.031
Xe1...O5 = 2.6420	O4 = -1.038
Xe1...O6 = 2.6414	O5 = -1.158
Xe1...O7 = 2.6391	O6 = -1.154
∠O3-Xe1-O5 = 166.74	O7 = -1.154
∠O4-Xe1-O7 = 166.28	
∠O2-Xe1-O6 = 167.37	
WBI	WBI
Xe1...O5 = 0.0458	Xe1 = 3.3125
Xe1...O6 = 0.0481	O2 = 1.4259
Xe1...O7 = 0.0500	O3 = 1.4153
	O4 = 1.4094

Figure S4.2. The optimized geometries corresponding to the adducts of HMPA with XeO₃ (1:3, 1:2, and 1:1) along with their bonding parameters, natural population charges, and Wiberg bond indexes. Hydrogen atoms are omitted for clarity.



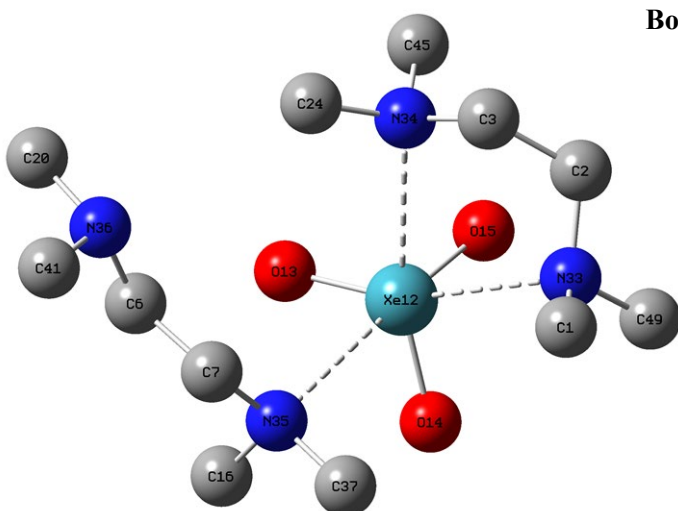
XeO₃:(DMPU)₁	
Bond Parameters (in Å and °)	NPA
Xe1-O2 = 1.7616	Xe1 = +2.844
Xe1-O3 = 1.7668	O2 = -0.955
Xe1-O4 = 1.7647	O3 = -0.975
Xe1...O5 = 2.6115	O4 = -0.960
∠O3-Xe1-O5 = 162.07	O5 = -0.760
WBI	WBI
Xe1...O5 = 0.0659	Xe1 = 3.3508
	O2 = 1.4918
	O3 = 1.4655
	O4 = 1.5041





XeO₃:(TMEDA)₁		
Bond Parameters (in Å and °)		NPA
Xe1-O2 = 1.7684		Xe1 = +2.850
Xe1-O3 = 1.7729		O2 = -0.990
Xe1-O4 = 1.7728		O3 = -0.990
Xe1...N12 = 2.7591		O4 = -0.990
Xe1...N11 = 2.7156		N11 = -0.460
∠O3-Xe1-N12 = 160.51		N12 = -0.455
∠O4-Xe1-N11 = 159.39		

WBI	WBI
Xe1...N11 = 0.0776	Xe1 = 3.3601
Xe1...N12 = 0.0862	O2 = 1.4314
	O3 = 1.4708
	O4 = 1.4698



XeO₃:(TMEDA)₂		
Bond Parameters (in Å and °)		NPA
Xe12-O13 = 1.7759		Xe12 = +2.888
Xe12-O14 = 1.7754		O13 = -1.009
Xe12-O15 = 1.7720		O14 = -1.009
Xe12...N33 = 2.8110		O15 = -1.009
Xe12...N34 = 2.7986		N33 = -0.453
Xe12...N35 = 2.8875		N34 = -0.457
∠O13-Xe12-N33 = 158.90		N35 = -0.445
∠O14-Xe12-N34 = 162.22		
∠O15-Xe12-N35 = 176.64		

WBI	WBI
Xe12...N33 = 0.0644	Xe12 = 3.3521
Xe12...N34 = 0.0707	O13 = 1.4400
Xe12...N35 = 0.0597	O14 = 1.4412
	O15 = 1.4246

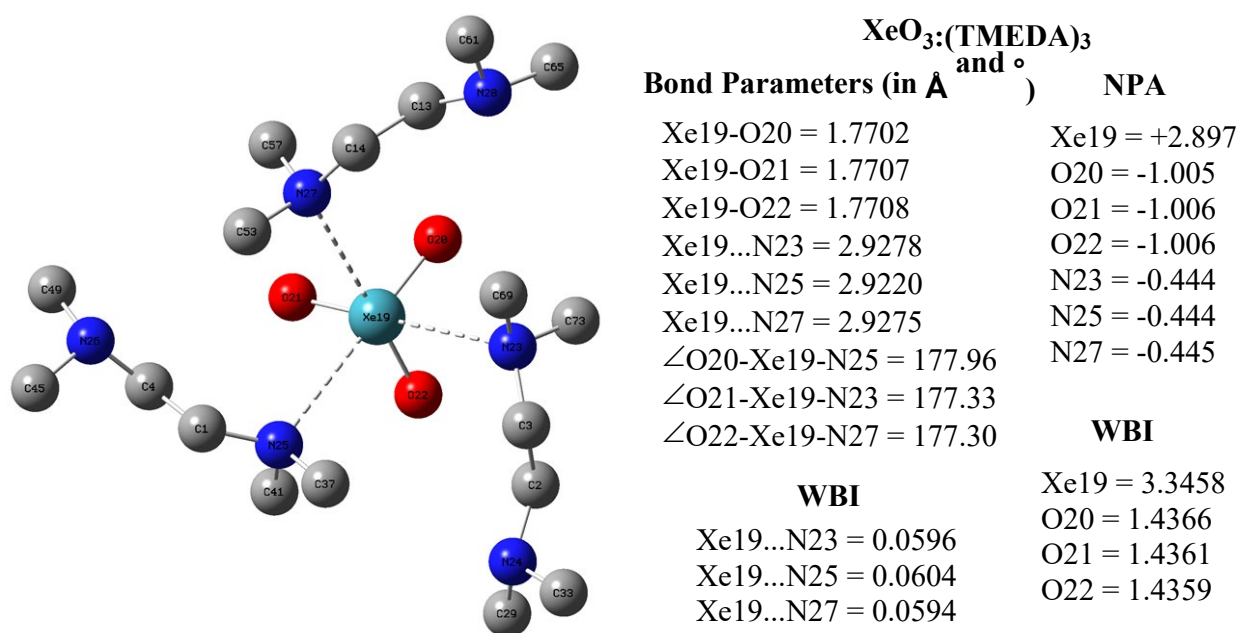
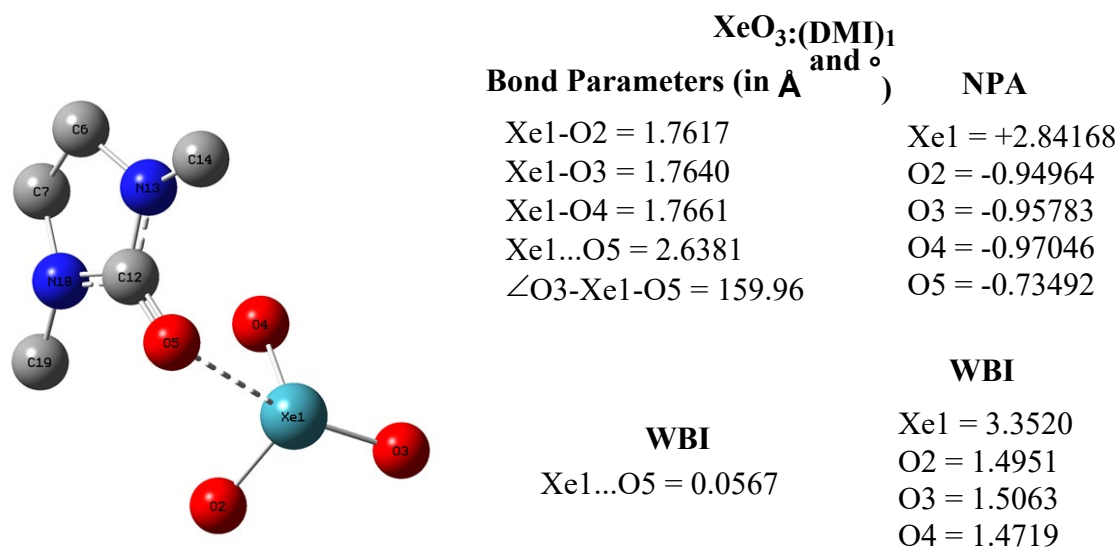


Figure S4.4 The optimized geometries corresponding to the adducts of TMEDA with XeO₃ (1:3, 1:2, and 1:1) along with their bonding parameters, natural population charges, and Wiberg bond indexes. Hydrogen atoms are omitted for clarity.



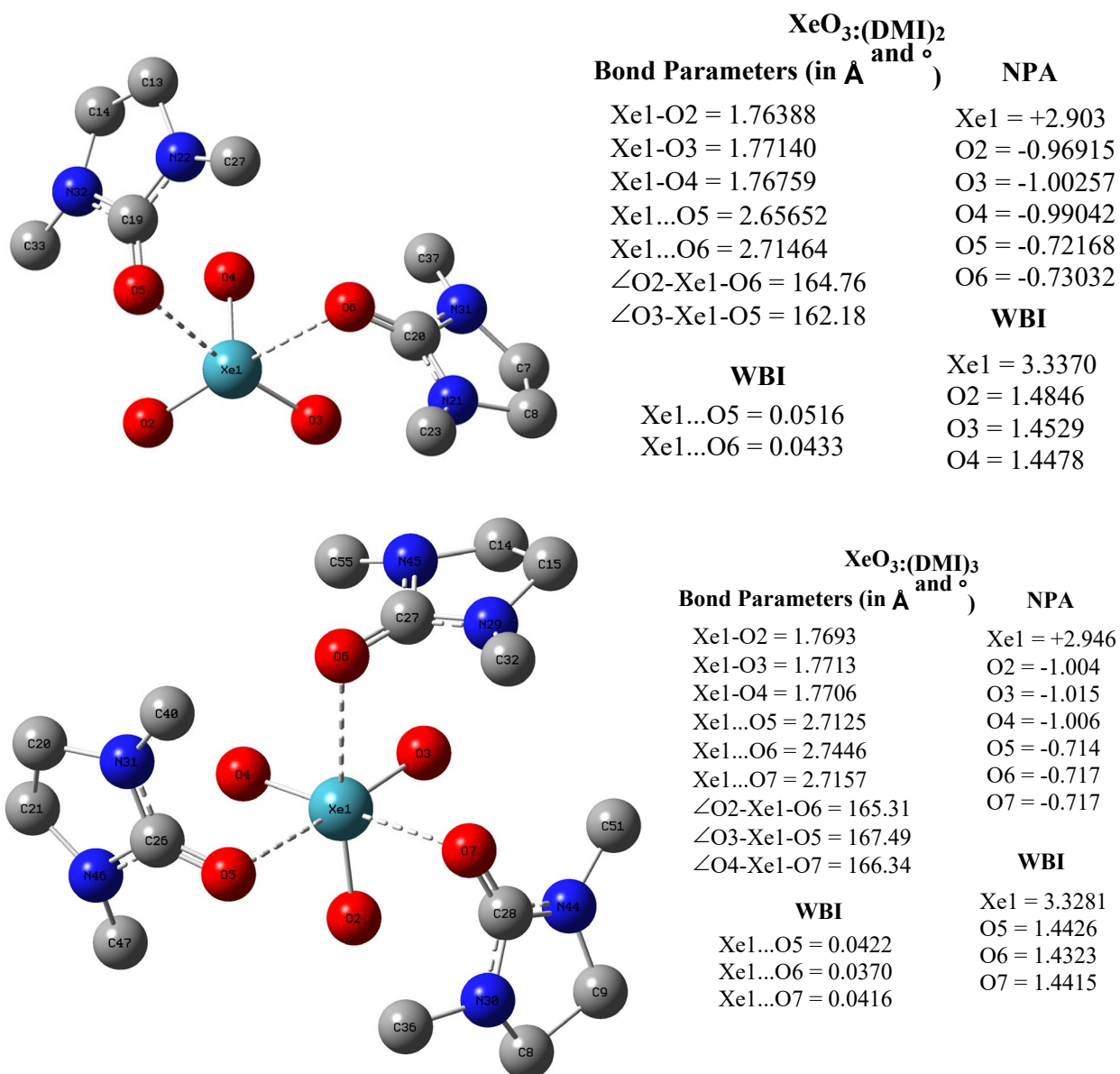


Figure S4.5. The optimized geometries corresponding to the adducts of DMI with XeO₃ (1:3, 1:2, and 1:1) along with their bonding parameters, natural population charges, and Wiberg bond indexes. Hydrogen atoms are omitted for clarity.

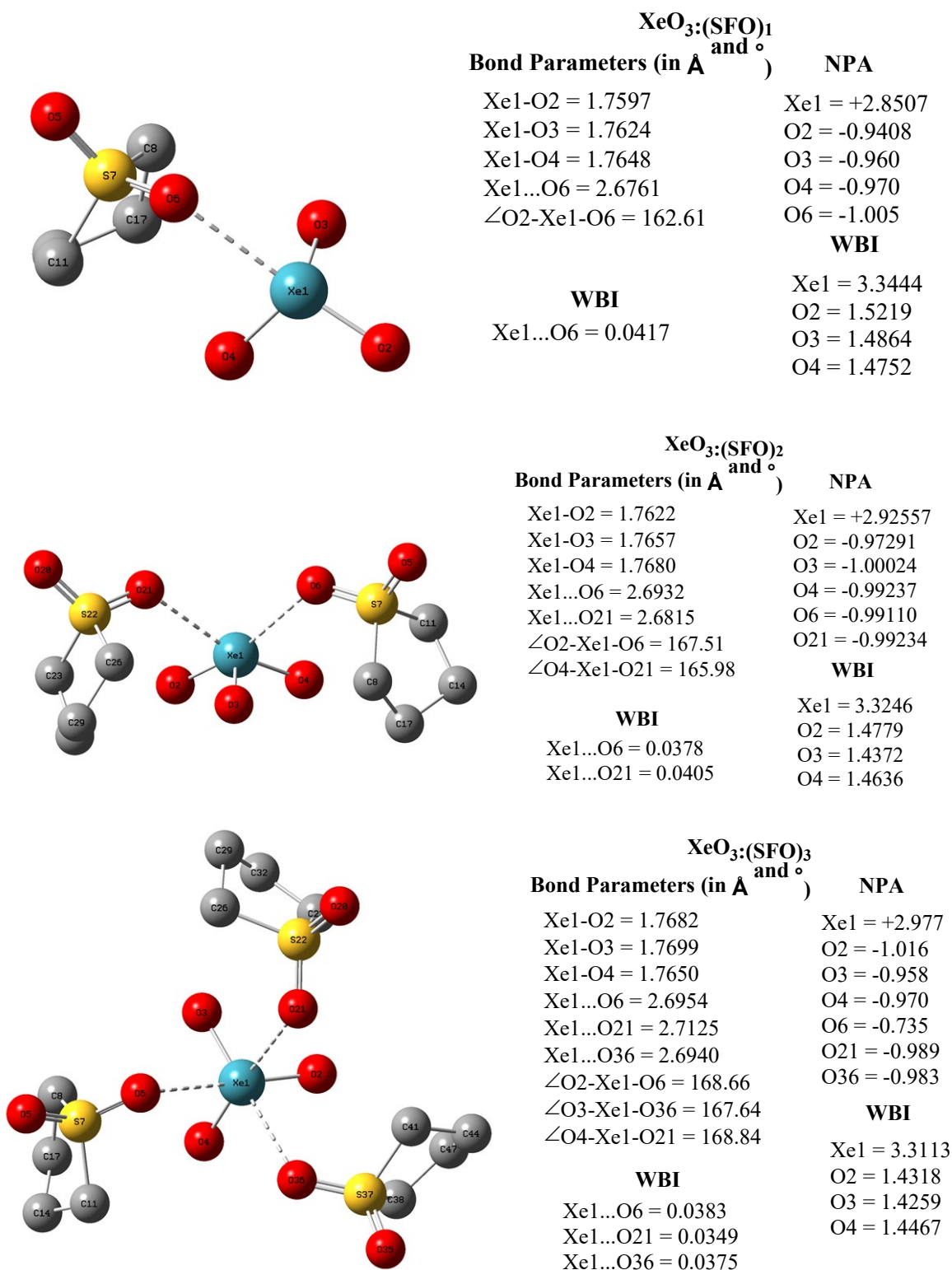


Figure S4.6. The optimized geometries corresponding to the adducts of SFO with XeO₃ (1:3, 1:2, and 1:1) along with their bonding parameters, natural population charges, and Wiberg bond indexes. Hydrogen atoms are omitted for clarity.

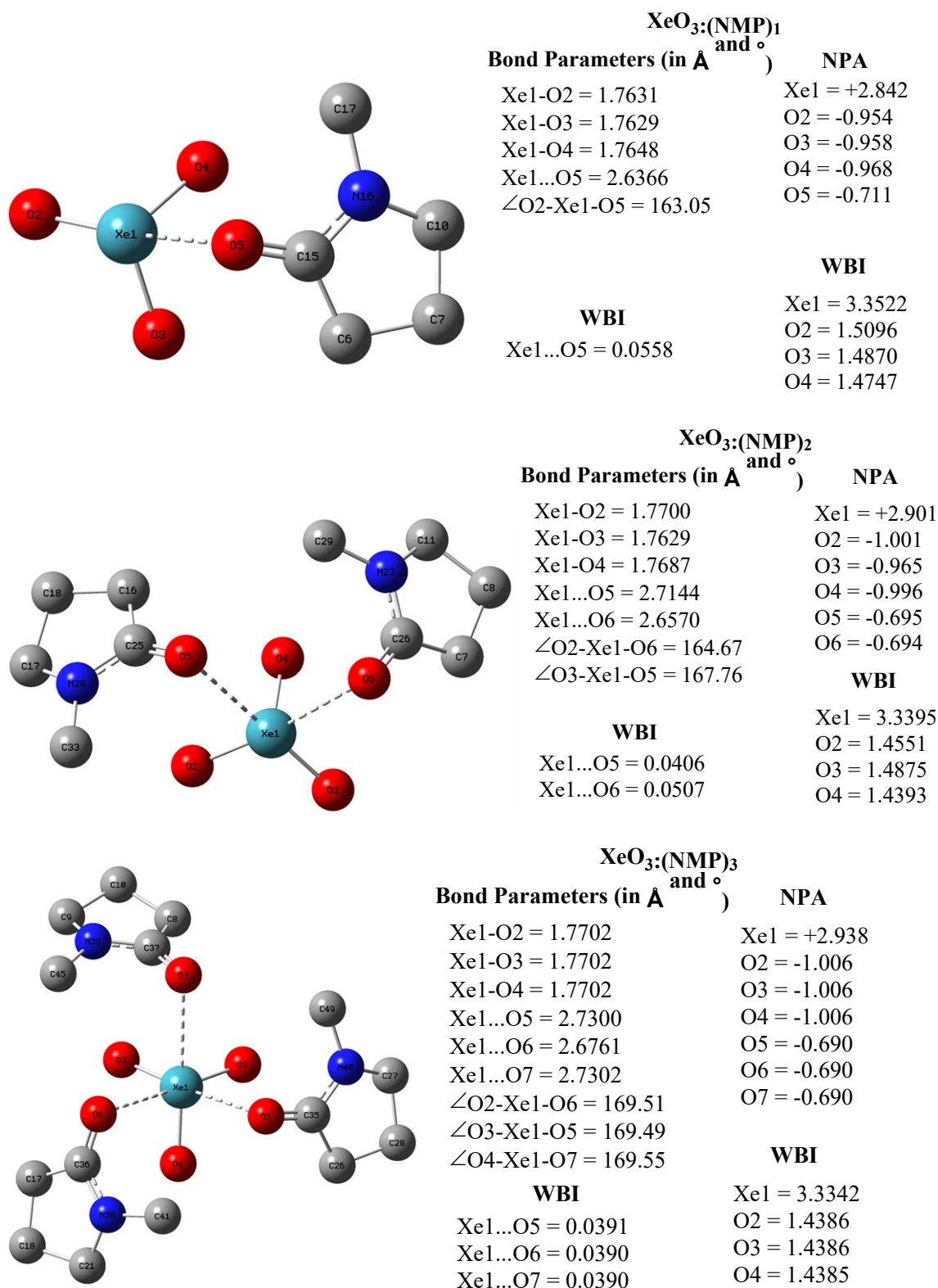
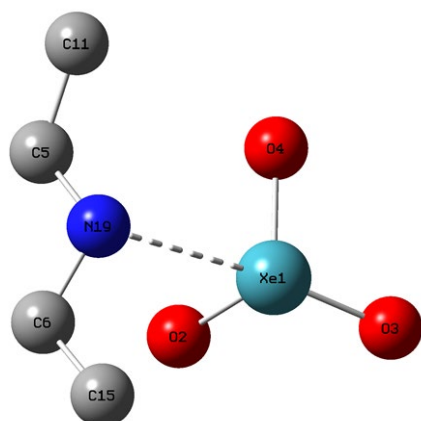
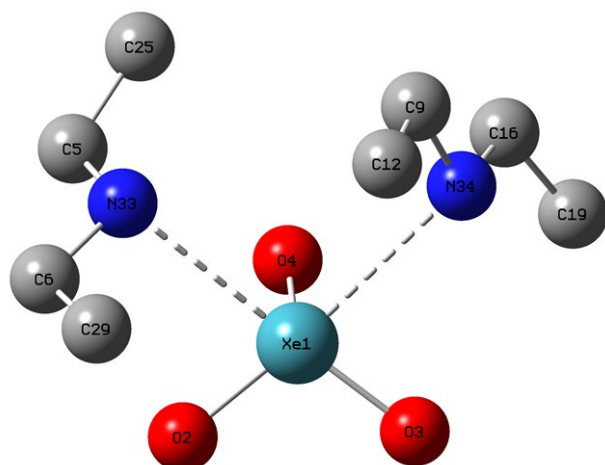


Figure S4.7. The optimized geometries corresponding to the adducts of NMP with XeO₃ (1:3, 1:2, and 1:1) along with their bonding parameters, natural population charges, and Wiberg bond indexes. Hydrogen atoms are omitted for clarity.



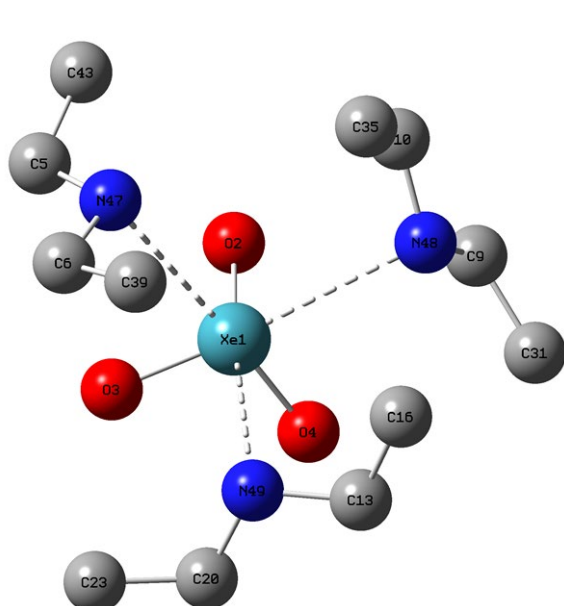
XeO₃:(DEA)₁ Bond Parameters (in Å and °)		NPA
Xe1-O2 = 1.765		Xe1 = +2.815
Xe1-O3 = 1.767		O2 = -0.963
Xe1-O4 = 1.764		O3 = -0.961
Xe1...N19 = 2.754		O4 = -0.961
∠O3-Xe1-N19 = 168.07		N19 = -0.643

WBI	WBI
Xe1...N19 = 0.0945	Xe1 = 3.3615
	O2 = 1.4754
	O3 = 1.5060
	O4 = 1.4816



XeO₃:(DEA)₂ Bond Parameters (in Å and °)		NPA
Xe1-O2 = 1.7704		Xe1 = +2.857
Xe1-O3 = 1.7705		O2 = -0.993
Xe1-O4 = 1.7677		O3 = -0.986
Xe1...N33 = 2.8418		O4 = -0.987
Xe1...N34 = 2.7837		N33 = -0.643
∠O3-Xe1-N33 = 168.92		N34 = -0.638
∠O2-Xe1-N34 = 170.47		

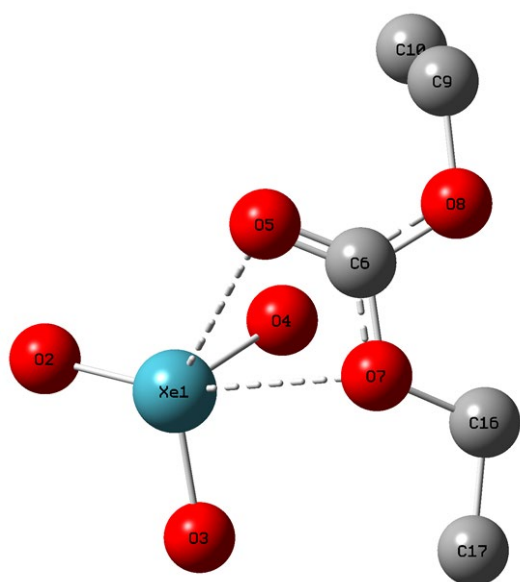
WBI	WBI
Xe1...N33 = 0.0701	Xe1 = 3.3527
Xe1...N34 = 0.0814	O2 = 1.4627
	O3 = 1.4625
	O4 = 1.4468



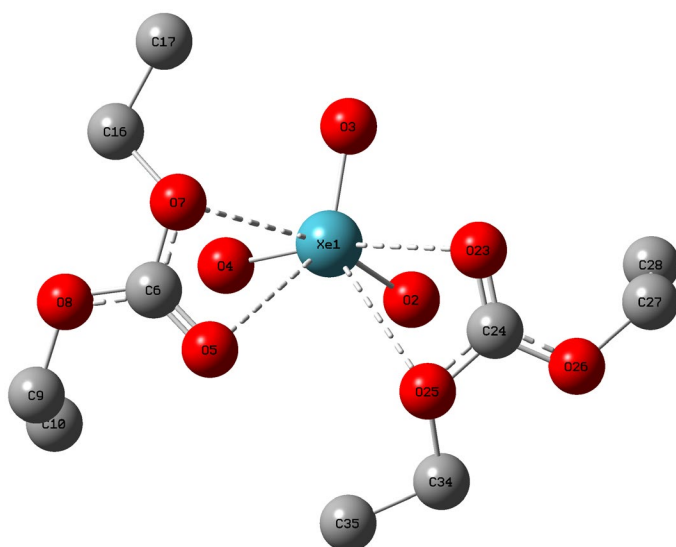
XeO₃:(DEA)₃ Bond Parameters (in Å and °)		NPA
Xe1-O2 = 2.8947		Xe1 = +2.891
Xe1-O3 = 2.8841		O2 = -1.009
Xe1-O4 = 2.8918		O3 = -1.009
Xe1...N47 = 2.8947		O4 = -1.009
Xe1...N48 = 2.8841		N47 = -0.640
Xe1...N49 = 2.8918		N48 = -0.641
∠O2-Xe1-N49 = 174.86		N49 = -0.641
∠O3-Xe1-N48 = 175.02		
∠O4-Xe1-N47 = 174.74		

WBI	WBI
Xe1...N47 = 0.0615	Xe1 = 3.3498
Xe1...N48 = 0.0631	O2 = 1.4358
Xe1...N49 = 0.0619	O3 = 1.4359
	O4 = 1.4358

Figure S4.8. The optimized geometries corresponding to the adducts of DEA with XeO₃ (1:3, 1:2, and 1:1) along with their bonding parameters, natural population charges, and Wiberg bond indexes. Hydrogen atoms are omitted for clarity.



XeO₃:(DEC)₁ Bond Parameters (in Å and °)		NPA
Xe1-O2 = 1.7606		Xe1 = +2.841
Xe1-O3 = 1.7629		O2 = -0.936
Xe1-O4 = 1.7646		O3 = -0.953
Xe1...O5 = 2.9489		O4 = -0.962
Xe1...O7 = 2.9381		O5 = -0.652
∠O2-Xe1-O7 = 162.08		O7 = -0.526
∠O3-Xe1-O5 = 134.35		
WBI		WBI
Xe1...O5 = 0.0152		Xe1 = 3.3409
Xe1...O7 = 0.0163		O2 = 1.5194
		O3 = 1.5048
		O4 = 1.4816



XeO₃:(DEC)₂ Bond Parameters (in Å and °)		NPA
Xe1-O2 = 1.7667		Xe1 = +2.890
Xe1-O3 = 1.7611		O2 = -0.977
Xe1-O4 = 1.7681		O3 = -0.955
Xe1...O5 = 3.0365		O4 = -0.985
Xe1...O7 = 2.9563		O5 = -0.644
Xe1...O23 = 2.8217		O7 = -0.521
Xe1...O25 = 3.0515		O23 = -0.656
∠O2-Xe1-O7 = 164.40		O25 = -0.502
∠O3-Xe1-O5 = 133.51		
∠O3-Xe1-O25 = 134.00		
∠O4-Xe1-O23 = 164.53		
WBI		WBI
Xe1...O5 = 0.0104		Xe1 = 3.3291
Xe1...O7 = 0.0141		O2 = 1.4681
Xe1...O23 = 0.0287		O3 = 1.4955
Xe1...O25 = 0.0077		O4 = 1.4649

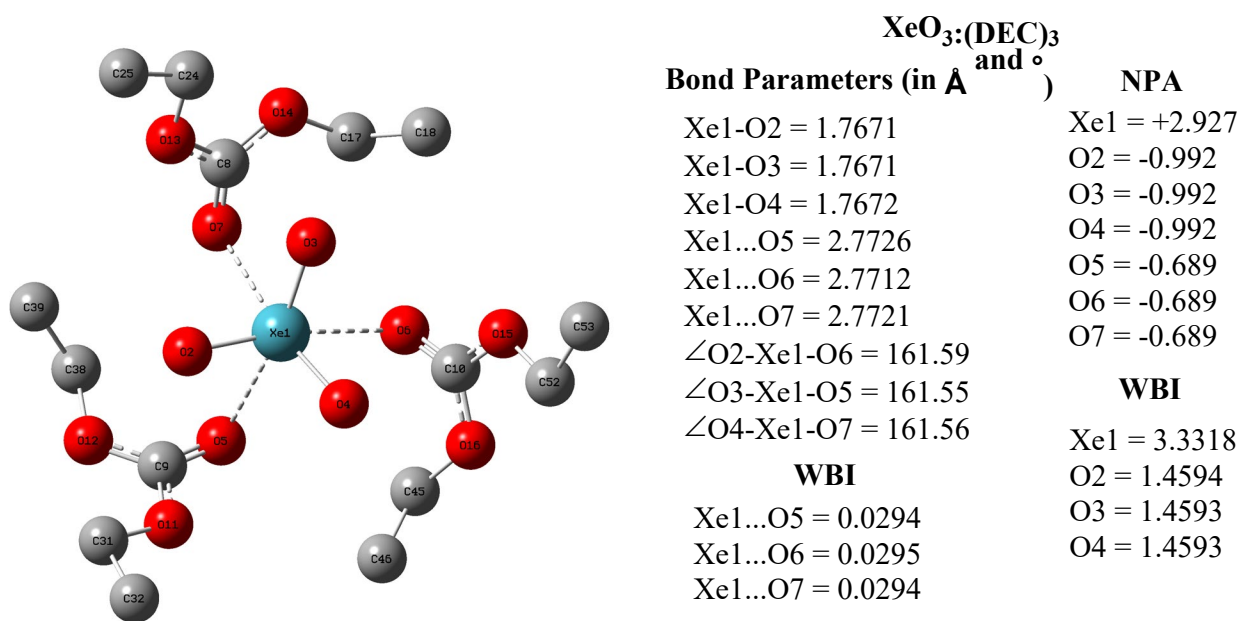
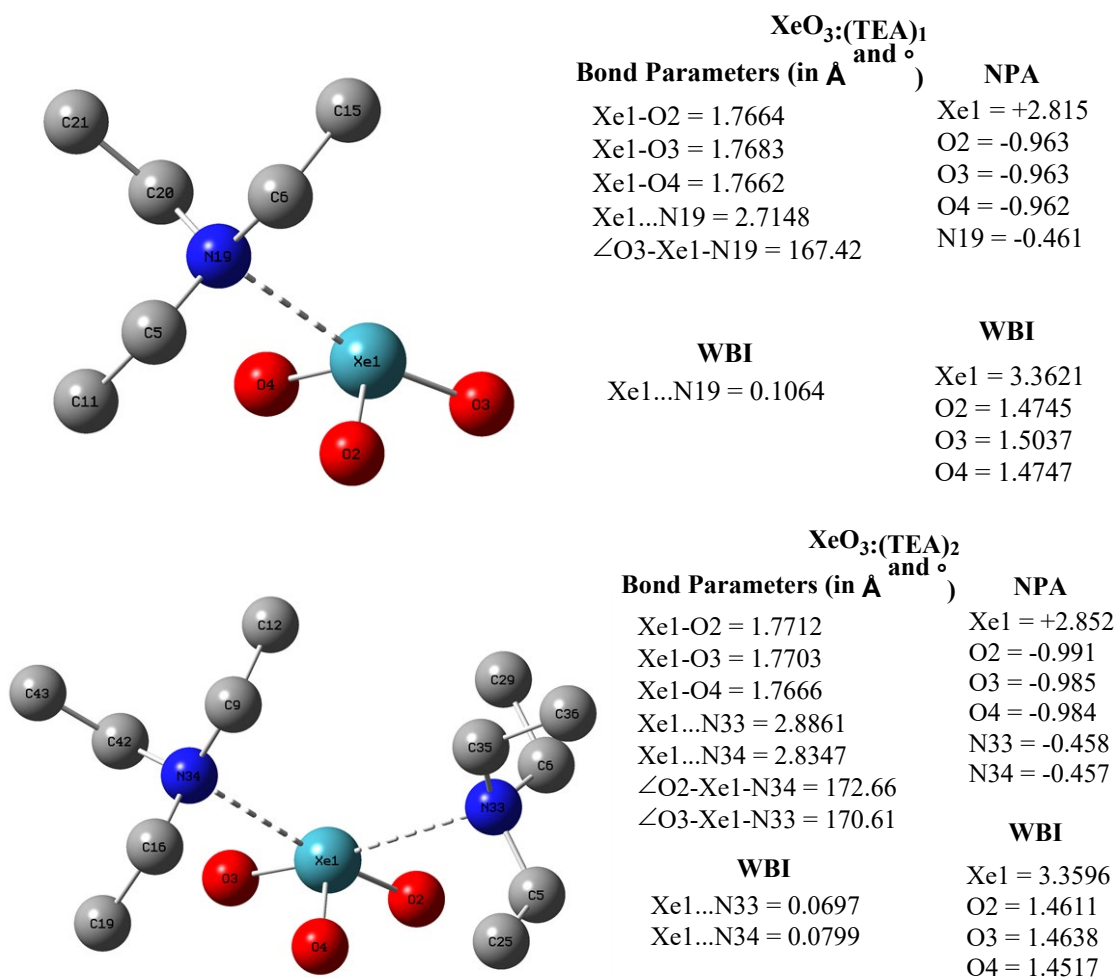


Figure S4.9. The optimized geometries corresponding to the adducts of DEC with XeO₃ (1:3, 1:2, and 1:1) along with their bonding parameters, natural population charges, and Wiberg bond indexes. Hydrogen atoms are omitted for clarity.



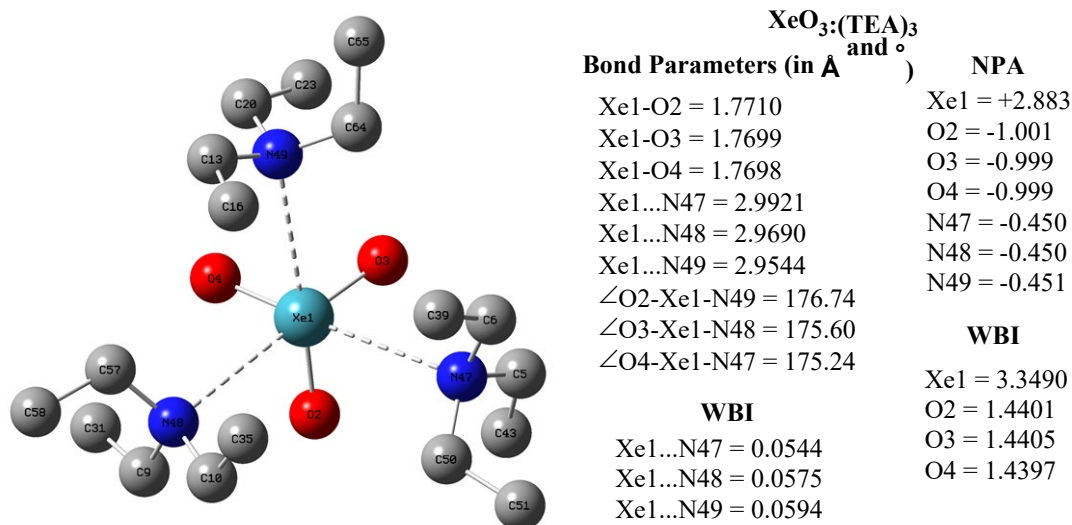
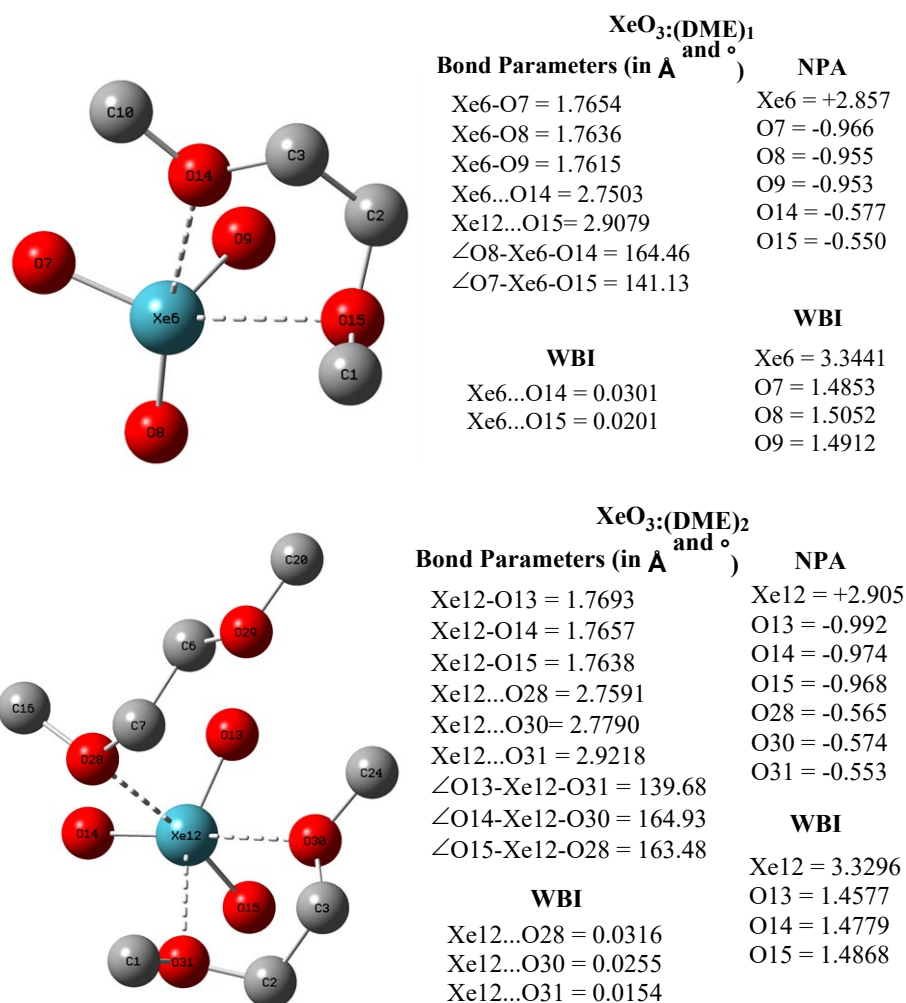


Figure S4.10. The optimized geometries corresponding to the adducts of TEA with XeO₃ (1:3, 1:2, and 1:1) along with their bonding parameters, natural population charges, and Wiberg bond indexes. Hydrogen atoms are omitted for clarity.



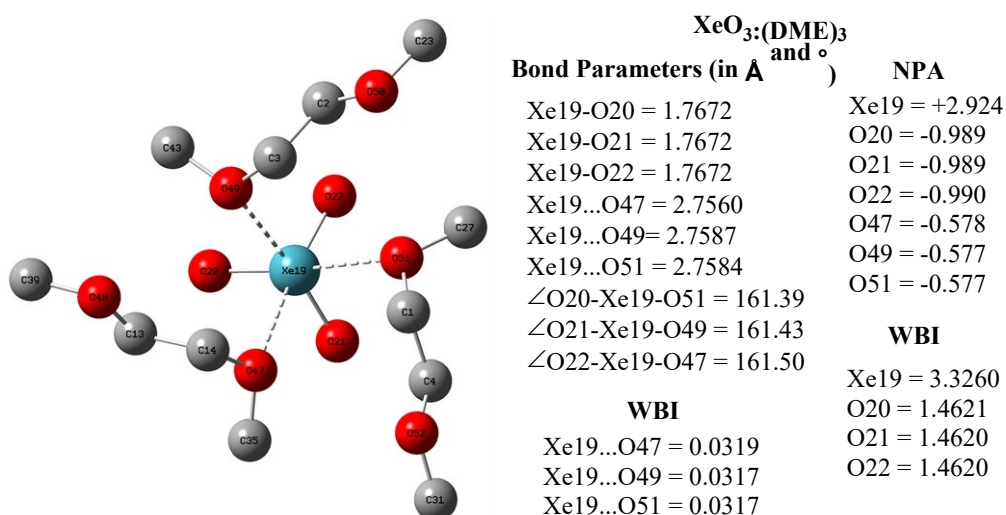


Figure S4.11. The optimized geometries corresponding to the adducts of DME with XeO₃ (1:3, 1:2, and 1:1) along with their bonding parameters, natural population charges, and Wiberg bond indexes. Hydrogen atoms are omitted for clarity.

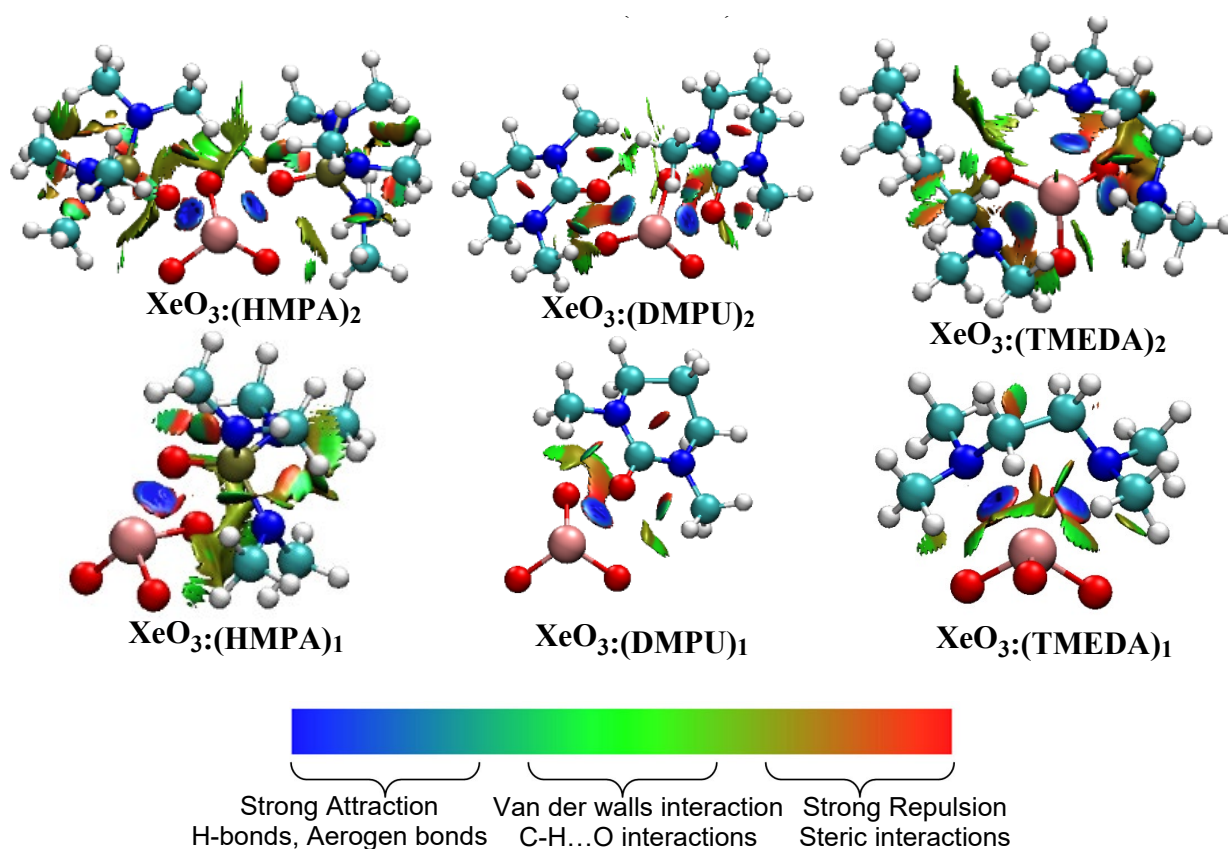


Figure S4.12. NCI plots for the adducts of XeO₃ with top three solvents, for the binding modes 1:2 (top) and 1:1 (bottom).

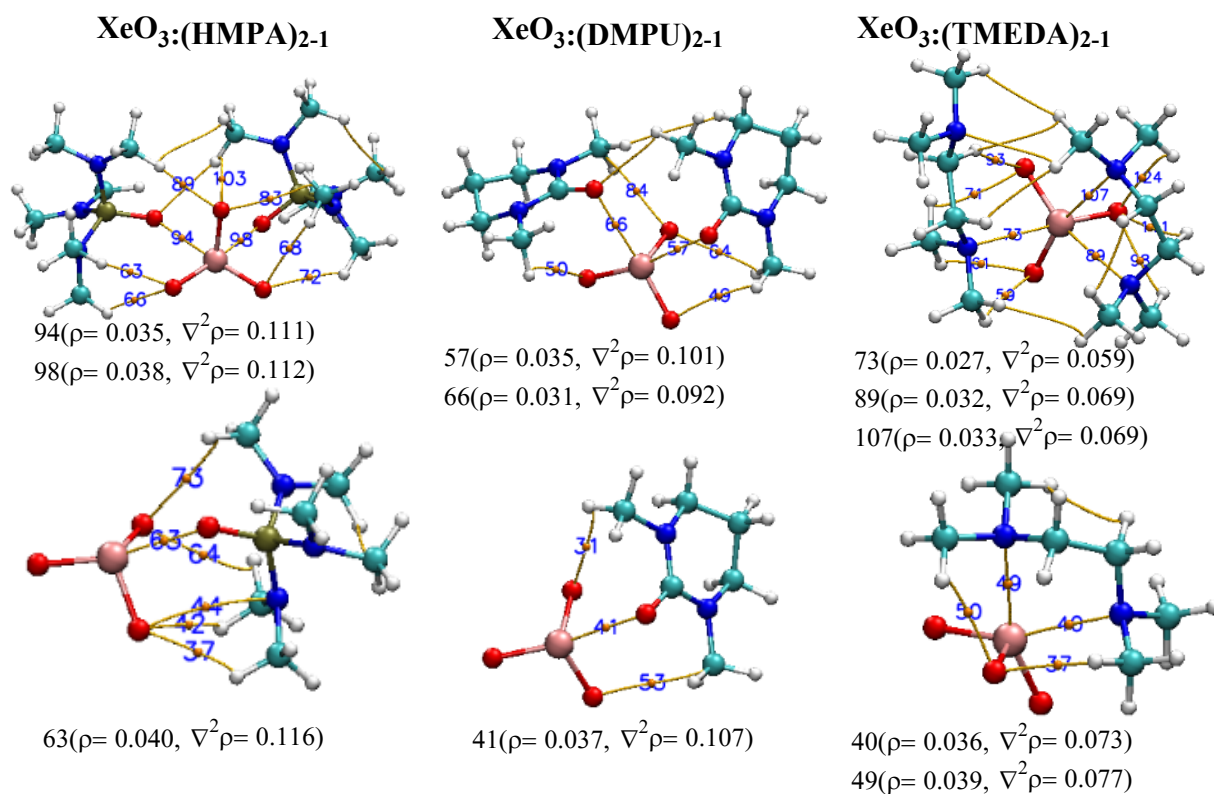


Figure S4.13. Bond critical points for the adducts of XeO₃ with top three solvents, for the binding modes 1:2 (top) and 1:1 (bottom), and their respective electron density (ρ , in a.u.) and laplacian of electron density ($\nabla^2\rho$, in a.u.).

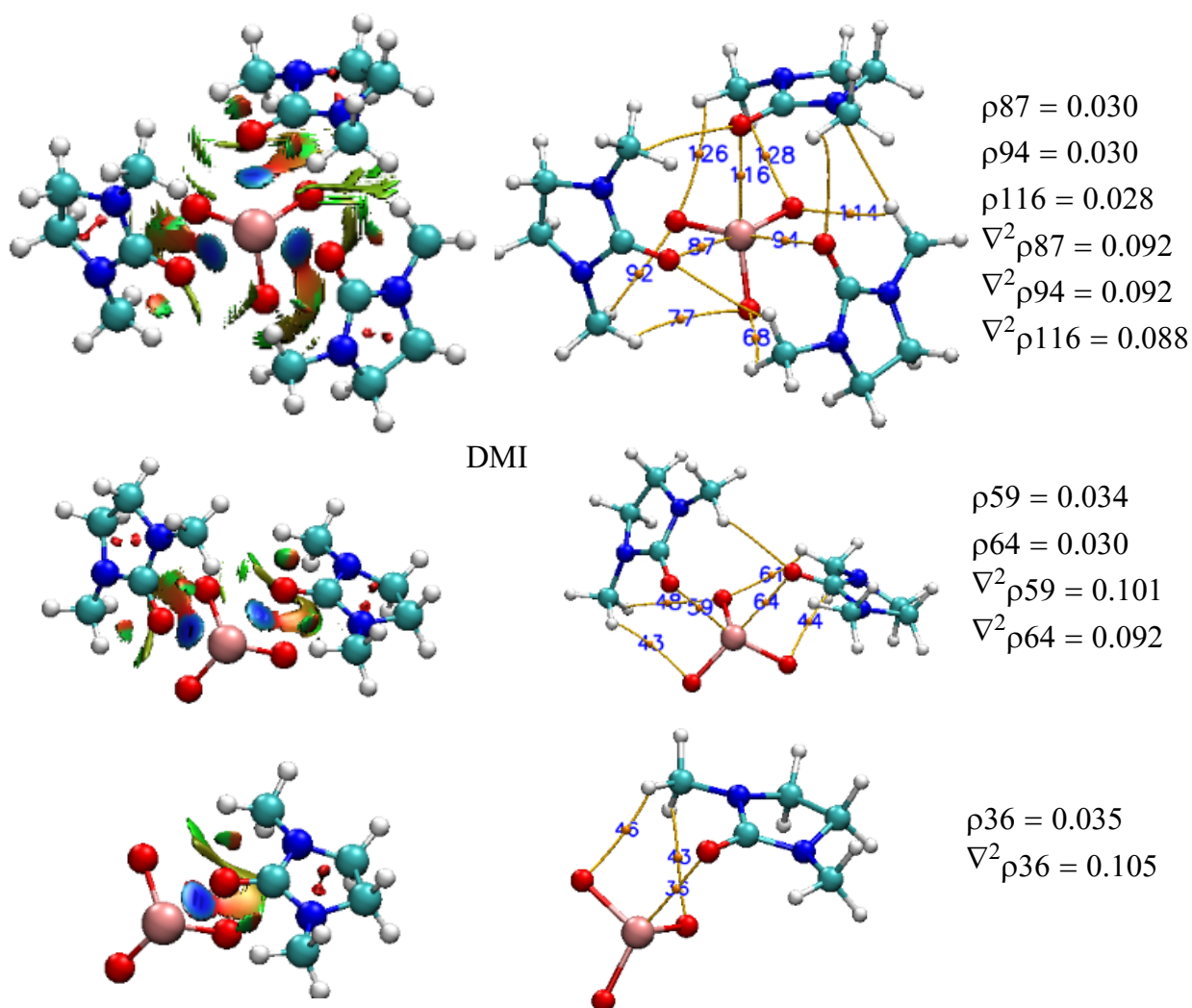


Figure S4.14. NCI plot and bond critical points (of aerogen bonds) of the adducts of DMI with XeO_3 , for the three binding modes, 1:3 (top), 1:2 (middle) and 1:1 (bottom), and their respective electron density (ρ , in a.u.) and laplacian of electron density ($\nabla^2\rho$, in a.u.).

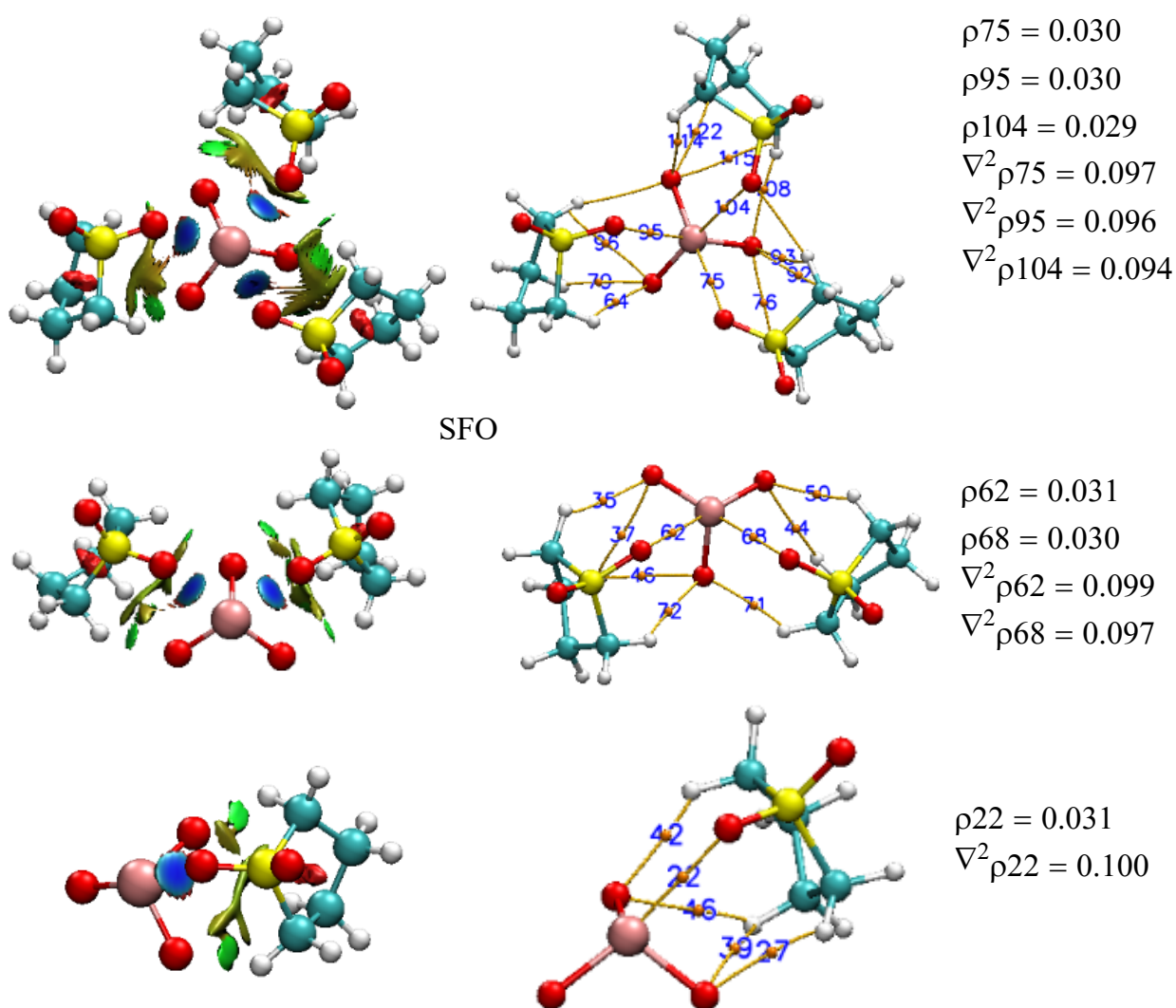


Figure S4.15. NCI plot and bond critical points (of aerogen bonds) of the adducts of SFO with XeO_3 , for the three binding modes, 1:3 (top), 1:2 (middle) and 1:1 (bottom), and their respective electron density (ρ , in a.u.) and laplacian of electron density ($\nabla^2\rho$, in a.u.).

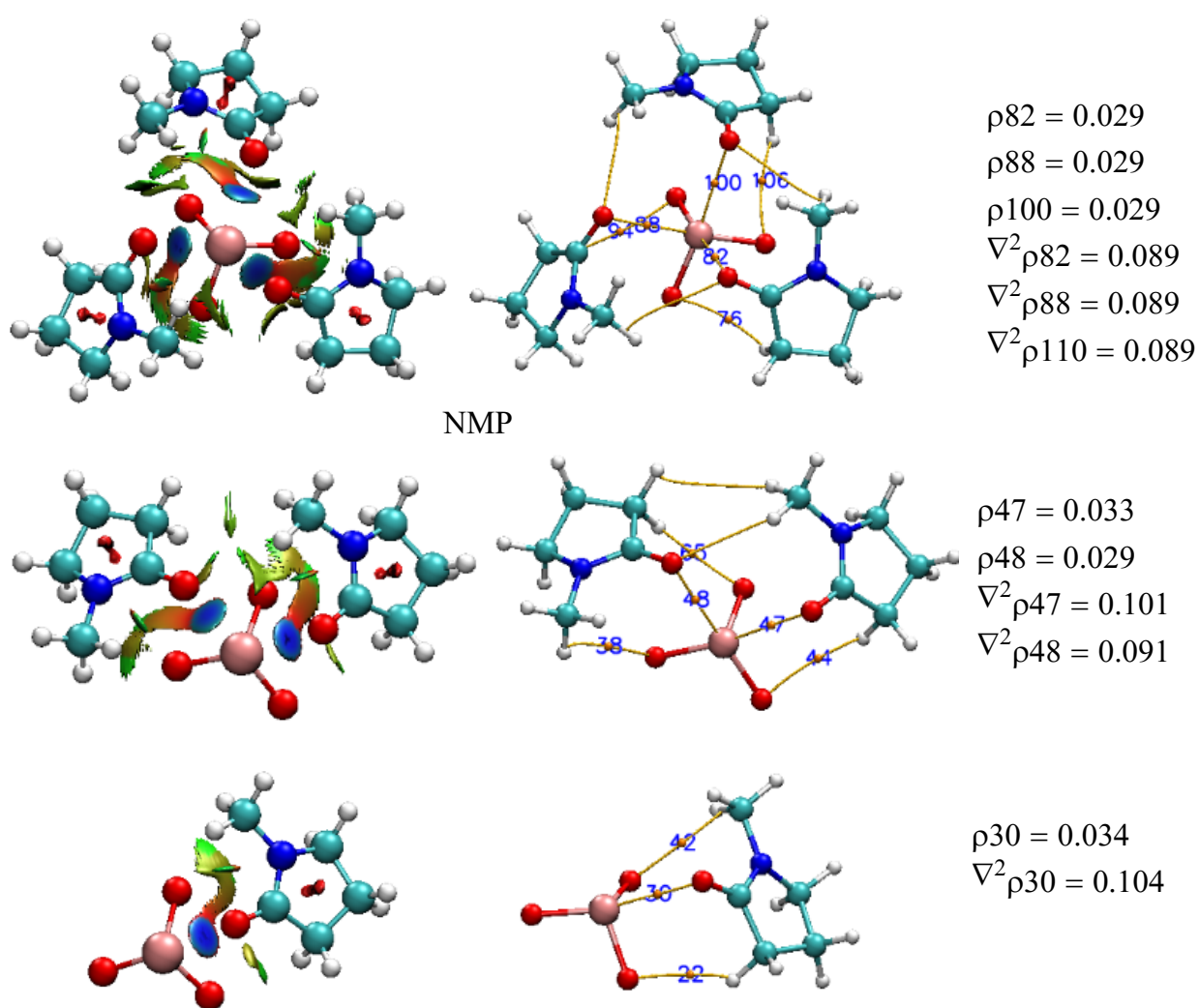


Figure S4.16. NCI plot and bond critical points (of aerogen bonds) of the adducts of NMP with XeO_3 , for the three binding modes, 1:3 (top), 1:2 (middle) and 1:1 (bottom), and their respective electron density (ρ , in a.u.) and laplacian of electron density ($\nabla^2 \rho$, in a.u.).

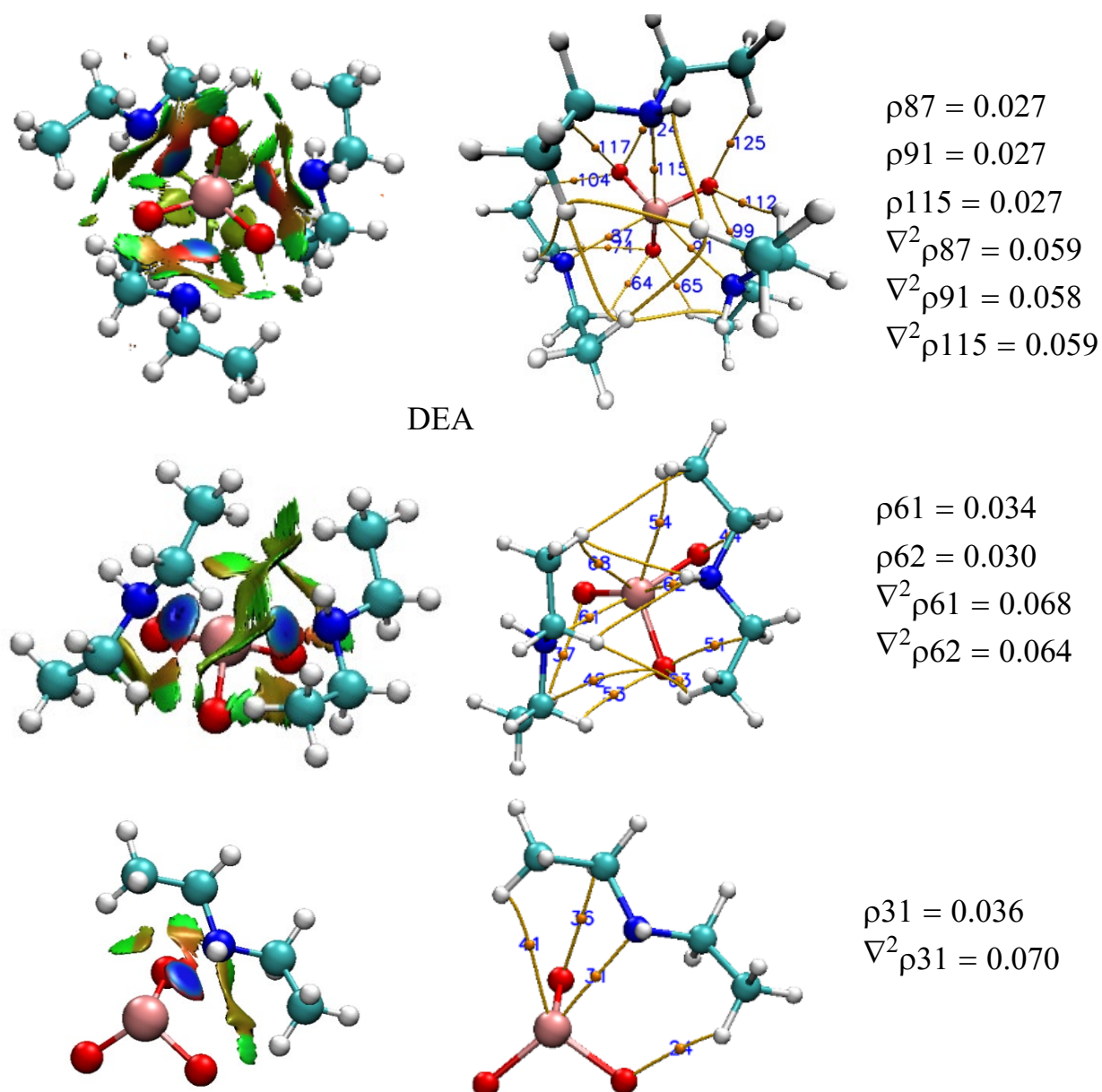


Figure S4.17. NCI plot and bond critical points (of aerogen bonds) of the adducts of DEA with XeO_3 , for the three binding modes, 1:3 (top), 1:2 (middle) and 1:1 (bottom), and their respective electron density (ρ , in a.u.) and laplacian of electron density ($\nabla^2 \rho$, in a.u.).

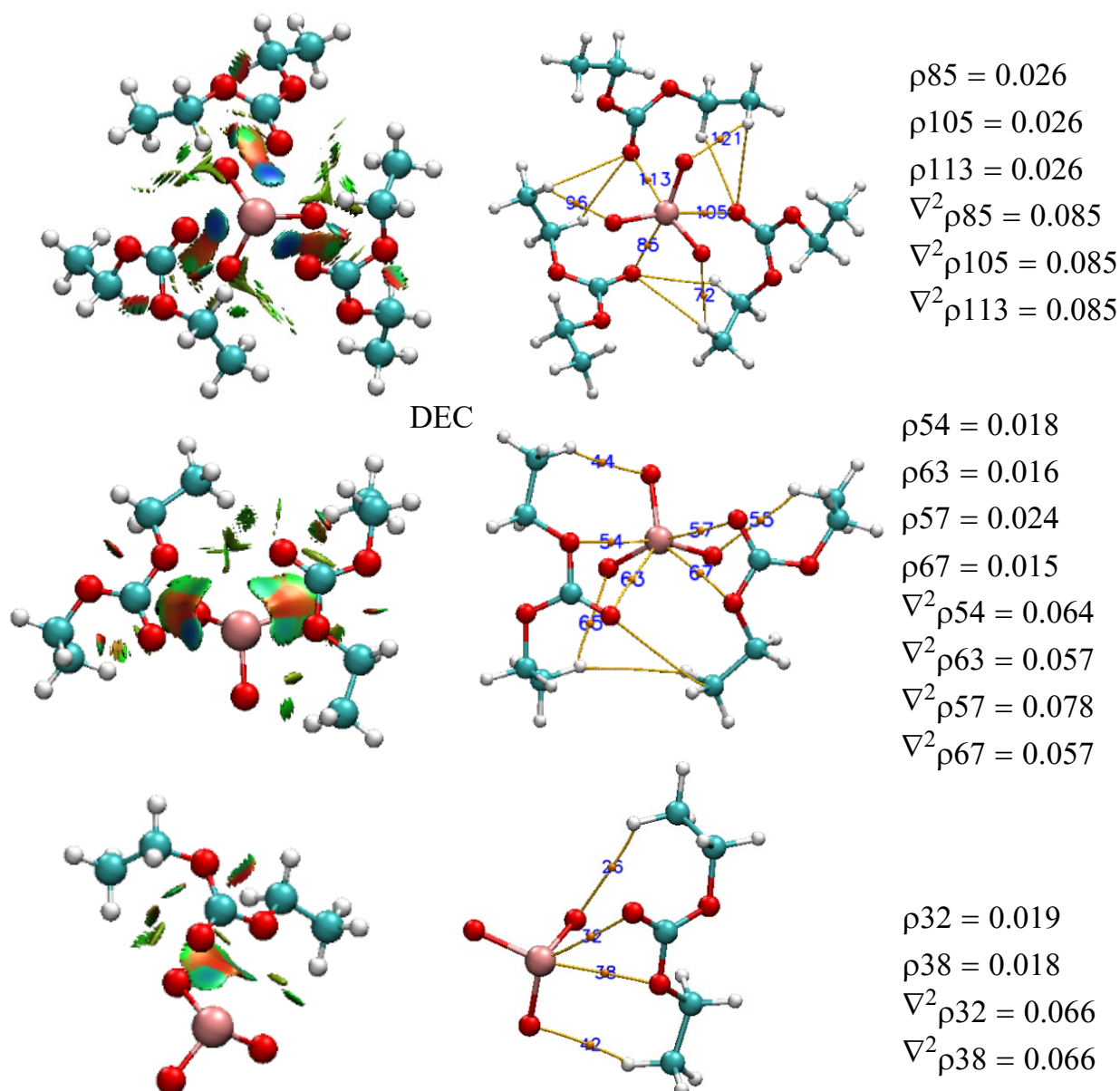


Figure S4.18. NCI plot and bond critical points (of aerogen bonds) of the adducts of DEC with XeO_3 , for the three binding modes, 1:3 (top), 1:2 (middle) and 1:1 (bottom), and their respective electron density (ρ , in a.u.) and laplacian of electron density ($\nabla^2 \rho$, in a.u.).

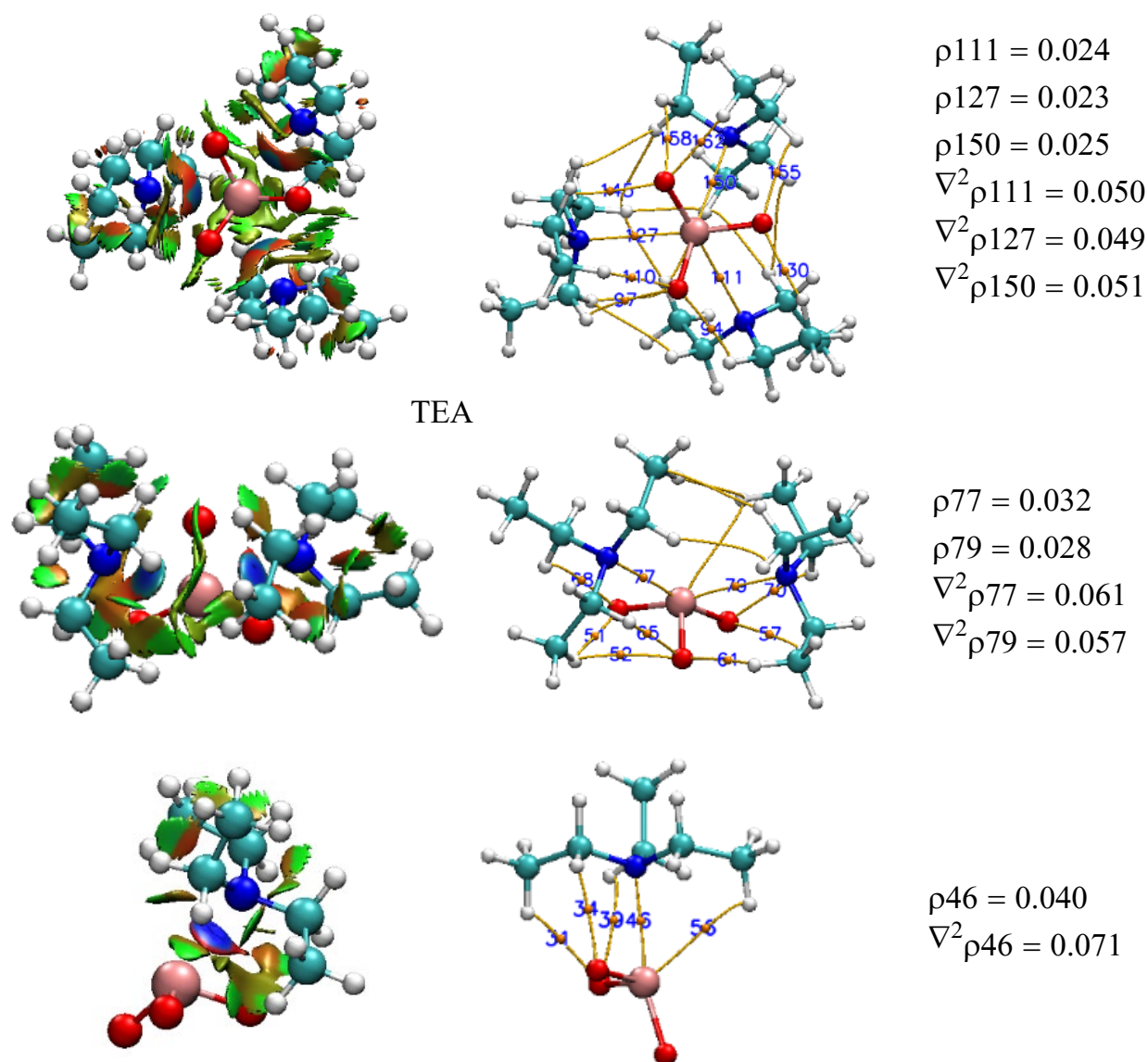


Figure S4.19. NCI plot and bond critical points (of aerogen bonds) of the adducts of TEA with XeO_3 , for the three binding modes, 1:3 (top), 1:2 (middle) and 1:1 (bottom), and their respective electron density (ρ , in a.u.) and laplacian of electron density ($\nabla^2 \rho$, in a.u.).

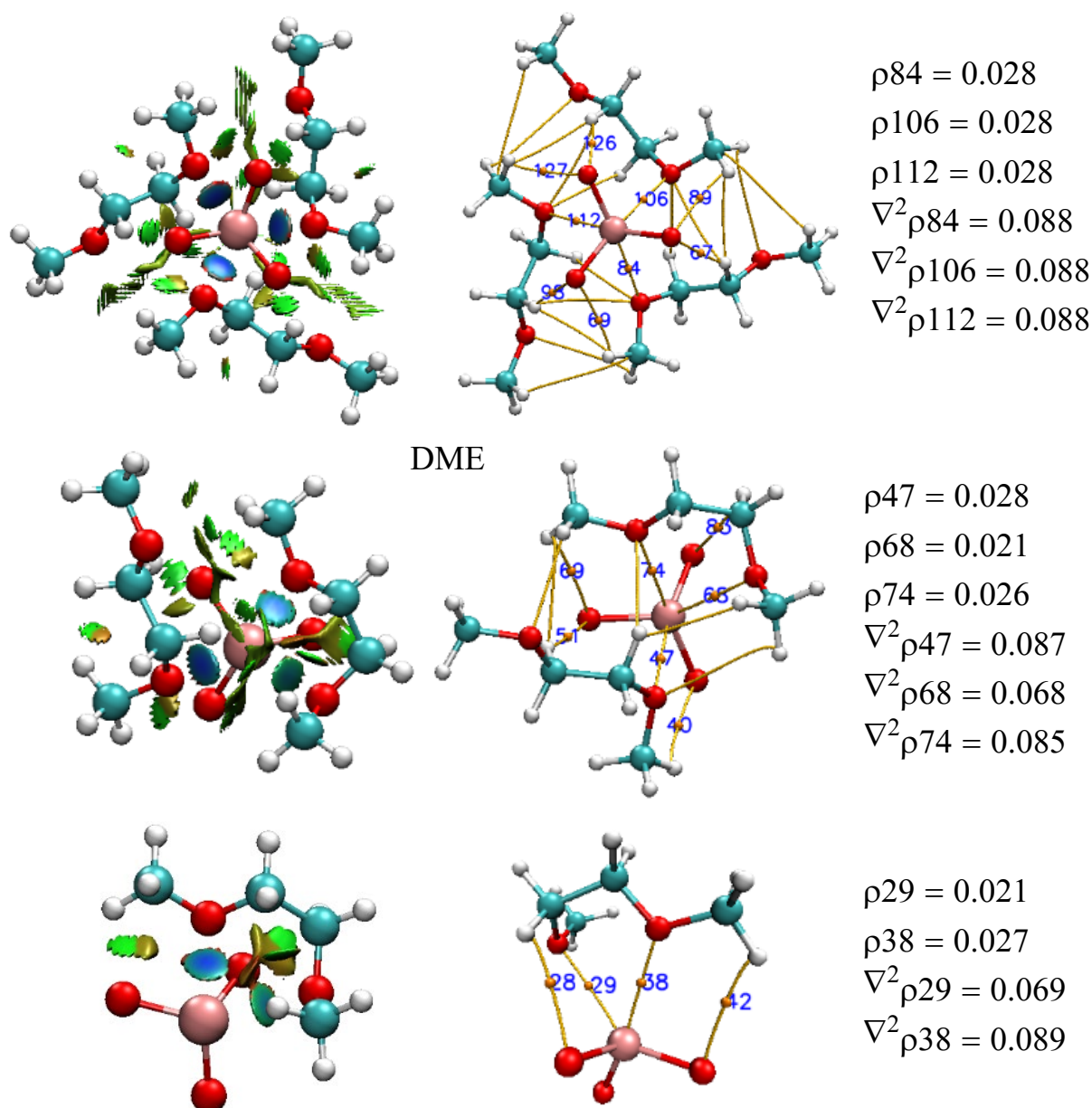


Figure S4.20. NCI plot and bond critical points (of aerogen bonds) of the adducts of DME with XeO_3 , for the three binding modes, 1:3 (top), 1:2 (middle) and 1:1 (bottom), and their respective electron density (ρ , in a.u.) and laplacian of electron density ($\nabla^2\rho$, in a.u.).

Table S4.1. Natural bond orbital (NBO) analysis of 1:3 adducts of remaining top ten solvents with XeO_3 at the APFD/def2-TZVPD level of theory. (E^2 = Second order perturbation energy in kcal/mol)

1:3	Donor	Acceptor	E^2
DMI	LP (1)Xe 1	BD*(1) O 5 - C 26	0.27
	LP (1)Xe 1	BD*(2) O 5 - C 26	0.28
	LP (1)Xe 1	BD*(1) O 6 - C 27	0.26

	LP (1)Xe 1	BD*(2)O 6 - C 27	0.29
	LP (1)Xe 1	BD*(1)O 7 - C 28	0.29
	LP (1)Xe 1	BD*(2)O 7 - C 28	0.31
	BD (2)O 5 - C 26	BD*(1)Xe 1 - O 3	3.23
	LP (1)O 5	BD*(1)Xe 1 - O 3	0.92
	BD (2)O 6 - C 27	BD*(1)Xe 1 - O 2	2.64
	LP (1)O 6	BD*(1)Xe 1 - O 2	0.82
	BD (2)O 7 - C 28	BD*(1)Xe 1 - O 4	3.25
	LP (1)O 7	BD*(1)Xe 1 - O 4	0.81
SFO	LP (1)Xe 1	BD*(1)O 6 - S 7	0.30
	LP (1)Xe 1	BD*(1)O 21 - S 22	0.28
	LP (1)Xe 1	BD*(1)O 36 - S 37	0.31
	LP (1)O 6	BD*(1)Xe 1 - O 2	1.41
	LP (3)O 6	BD*(1)Xe 1 - O 2	4.86
	LP (1)O 21	BD*(1)Xe 1 - O 4	1.31
	LP (3)O 21	BD*(1)Xe 1 - O 4	4.48
NMP	LP (1)Xe 1	BD*(1)O 5 - C 35	0.32
	LP (1)Xe 1	BD*(2)O 5 - C 35	0.29
	LP (1)Xe 1	BD*(1)O 6 - C 36	0.32
	LP (1)Xe 1	BD*(2)O 6 - C 36	0.29
	LP (1)Xe 1	BD*(1)O 7 - C 37	0.32
	LP (1)Xe 1	BD*(2)O 7 - C 37	0.29
	BD (2)O 5 - C 35	BD*(1)Xe 1 - O 3	3.12
	LP (1)O 5	BD*(1)Xe 1 - O 3	0.83
	BD (2)O 6 - C 36	BD*(1)Xe 1 - O 2	3.12
	LP (1)O 6	BD*(1)Xe 1 - O 2	0.83
	BD (2)O 7 - C 37	BD*(1)Xe 1 - O 4	3.12
	LP (1)O 7	BD*(1)Xe 1 - O 4	0.83
DEA	LP (1)Xe 1	BD*(1)C 5 - N 47	0.24
	LP (1)Xe 1	BD*(1)C 6 - N 47	0.14
	LP (1)Xe 1	BD*(1)C 9 - N 48	0.25
	LP (1)Xe 1	BD*(1)C 10 - N 48	0.14
	LP (1)Xe 1	BD*(1)C 13 - N 49	0.14
	LP (1)Xe 1	BD*(1)C 20 - N 49	0.24
	LP (1)N 47	BD*(1)Xe 1 - O 4	5.77
	LP (1)N 48	BD*(1)Xe 1 - O 3	5.96
	LP (1)N 49	BD*(1)Xe 1 - O 2	5.84
DEC	LP (1)Xe 1	BD*(1)O 5 - C 9	0.11
	LP (1)Xe 1	BD*(2)O 5 - C 9	0.37
	LP (1)Xe 1	BD*(1)O 6 - C 10	0.11
	LP (1)Xe 1	BD*(2)O 6 - C 10	0.37
	LP (1)Xe 1	BD*(1)O 7 - C 8	0.11
	LP (1)Xe 1	BD*(2)O 7 - C 8	0.37
	BD (2)O 5 - C 9	BD*(1)Xe 1 - O 3	2.14
	LP (1)O 5	BD*(1)Xe 1 - O 3	0.66
	LP (2)O 5	BD*(1)Xe 1 - O 3	0.20
	BD (2)O 6 - C 10	BD*(1)Xe 1 - O 2	2.15
	LP (1)O 6	BD*(1)Xe 1 - O 2	0.67
	LP (2)O 6	BD*(1)Xe 1 - O 2	0.20

	BD (2) O 7 - C 8	BD*(1)Xe 1 - O 4	2.15
	LP (1) O 7	BD*(1)Xe 1 - O 4	0.67
	LP (2) O 7	BD*(1)Xe 1 - O 4	0.20
TEA	LP (1)Xe 1	BD*(1) C 5 - N 47	0.26
	LP (1)Xe 1	BD*(1) C 6 - N 47	0.16
	LP (1)Xe 1	BD*(1) N 47 - C 50	0.15
	LP (1)Xe 1	BD*(1) C 9 - N 48	0.29
	LP (1)Xe 1	BD*(1) C 10 - N 48	0.16
	LP (1)Xe 1	BD*(1) N 48 - C 57	0.17
	LP (1)Xe 1	BD*(1) C 13 - N 49	0.18
	LP (1)Xe 1	BD*(1) C 20 - N 49	0.30
	LP (1)Xe 1	BD*(1) N 49 - C 64	0.18
	LP (1) N 47	BD*(1)Xe 1 - O 4	4.33
	LP (1) N 48	BD*(1)Xe 1 - O 3	4.64
	LP (1) N 49	BD*(1)Xe 1 - O 2	4.86
DME	LP (1)Xe 19	BD*(1) C 1 - O 51	0.31
	LP (1)Xe 19	BD*(1) C 27 - O 51	0.44
	LP (1)Xe 19	BD*(1) C 3 - O 49	0.31
	LP (1)Xe 19	BD*(1) C 43 - O 49	0.43
	LP (1)Xe 19	BD*(1) C 14 - O 47	0.31
	LP (1)Xe 19	BD*(1) C 35 - O 47	0.44
	LP (1) O 51	BD*(1)Xe 19 - O 20	1.94
	LP (2) O 51	BD*(1)Xe 19 - O 20	1.97
	LP (1) O 49	BD*(1)Xe 19 - O 21	1.92
	LP (2) O 49	BD*(1)Xe 19 - O 21	2.00
	LP (1) O 47	BD*(1)Xe 19 - O 22	1.96
	LP (2) O 47	BD*(1)Xe 19 - O 22	1.98

Table S4.2. Natural bond orbital (NBO) analysis of 1:2 adducts of remaining top ten solvents with XeO₃ at the APFD/def2-TZVPD level of theory. (E² = Second order perturbation energy in kcal/mol)

1:2	Donor	Acceptor	E ²
DMI	LP (1)Xe 1	BD*(1) O 5 - C 19	0.38
	LP (1)Xe 1	BD*(2) O 5 - C 19	0.57
	LP (1)Xe 1	BD*(1) O 6 - C 20	0.32
	LP (1)Xe 1	BD*(2) O 6 - C 20	0.49
	BD (2) O 5 - C 19	BD*(1)Xe 1 - O 3	3.25
	LP (1) O 5	BD*(1)Xe 1 - O 3	1.22
	LP (2) O 5	BD*(1)Xe 1 - O 3	0.19
	BD (2) O 6 - C 20	BD*(1)Xe 1 - O 2	2.61
	LP (1) O 6	BD*(1)Xe 1 - O 2	0.96
	LP (2) O 6	BD*(1)Xe 1 - O 2	0.22
SFO	LP (1)Xe 1	BD*(1) O 6 - S 7	0.42
	LP (1)Xe 1	BD*(1) O 21 - S 22	0.45
	LP (1) O 6	BD*(1)Xe 1 - O 2	1.43
	LP (3) O 6	BD*(1)Xe 1 - O 2	4.27
	LP (1) O 21	BD*(1)Xe 1 - O 4	1.49

	LP (3) O 21	BD*(1)Xe 1 - O 4	4.50
NMP	LP (1)Xe 1	BD*(1) O 5 - C 25	0.36
	LP (1)Xe 1	BD*(2) O 5 - C 25	0.41
	LP (1)Xe 1	BD*(1) O 6 - C 26	0.44
	LP (1)Xe 1	BD*(2) O 6 - C 26	0.57
	BD (2) O 5 - C 25	BD*(1)Xe 1 - O 3	2.97
	LP (1) O 5	BD*(1)Xe 1 - O 3	0.87
	BD (2) O 6 - C 26	BD*(1)Xe 1 - O 2	3.47
	LP (1) O 6	BD*(1)Xe 1 - O 2	1.17
DEA	LP (1)Xe 1	BD*(1) C 5 - N 33	0.33
	LP (1)Xe 1	BD*(1) C 6 - N 33	0.20
	LP (1)Xe 1	BD*(1) C 9 - N 34	0.20
	LP (1)Xe 1	BD*(1) C 16 - N 34	0.48
	LP (1) N 33	BD*(1)Xe 1 - O 3	6.43
	LP (1) N 34	BD*(1)Xe 1 - O 2	7.84
DEC	LP (1)Xe 1	BD*(1) C 6 - O 8	0.17
	LP (1)Xe 1	BD*(1) O 7 - C 16	0.13
	LP (1)Xe 1	BD*(1) C 24 - O 26	0.19
	LP (1)Xe 1	BD*(1) O 25 - C 34	0.10
	BD (2) O 5 - C 6	BD*(1)Xe 1 - O 3	0.14
	LP (2) O 5	BD*(1)Xe 1 - O 3	0.38
	LP (1) O 7	BD*(1)Xe 1 - O 2	0.54
	LP (2) O 7	BD*(1)Xe 1 - O 2	1.21
	BD (2) O 23 - C 24	BD*(1)Xe 1 - O 4	0.80
	LP (1) O 23	BD*(1)Xe 1 - O 4	0.39
	LP (2) O 23	BD*(1)Xe 1 - O 4	1.97
	LP (1) O 25	BD*(1)Xe 1 - O 3	0.22
	LP (2) O 25	BD*(1)Xe 1 - O 3	0.38
TEA	LP (1)Xe 1	BD*(1) C 5 - N 33	0.37
	LP (1)Xe 1	BD*(1) C 6 - N 33	0.18
	LP (1)Xe 1	BD*(1) N 33 - C 35	0.32
	LP (1)Xe 1	BD*(1) C 9 - N 34	0.22
	LP (1)Xe 1	BD*(1) C 16 - N 34	0.45
	LP (1)Xe 1	BD*(1) N 34 - C 42	0.33
	LP (1) N 33	BD*(1)Xe 1 - O 3	5.67
	LP (1) N 34	BD*(1)Xe 1 - O 2	6.71
DME	LP (1)Xe 12	BD*(1) C 1 - O 31	0.31
	LP (1)Xe 12	BD*(1) C 2 - O 31	0.21
	LP (1)Xe 12	BD*(1) C 3 - O 30	0.23
	LP (1)Xe 12	BD*(1) C 24 - O 30	0.33
	LP (1)Xe 12	BD*(1) C 7 - O 28	0.31
	LP (1)Xe 12	BD*(1) C 16 - O 28	0.40
	LP (1) O 30	BD*(1)Xe 12 - O 14	2.67
	LP (1) O 31	BD*(1)Xe 12 - O 13	0.88
	LP (2) O 31	BD*(1)Xe 12 - O 13	0.30
	LP (1) O 28	BD*(1)Xe 12 - O 15	1.69
	LP (2) O 28	BD*(1)Xe 12 - O 15	2.31

Table S4.3. Natural bond orbital (NBO) analysis of 1:1 adducts of remaining top ten solvents with XeO₃ at the APFD/def2-TZVPD level of theory. (E² = Second order perturbation energy in kcal/mol)

1:1	Donor	Acceptor	E ²
DMI	LP (1)Xe 1	BD*(1)O 5 - C 12	0.50
	LP (1)Xe 1	BD*(2)O 5 - C 12	0.80
	BD (2)O 5 - C 12	BD*(1)Xe 1 - O 3	2.70
	LP (1)O 5	BD*(1)Xe 1 - O 3	1.35
	LP (2)O 5	BD*(1)Xe 1 - O 3	0.67
SFO	LP (1)Xe 1	BD*(1)O 6 - S 7	0.52
	LP (1)O 6	BD*(1)Xe 1 - O 2	1.39
	LP (3)O 6	BD*(1)Xe 1 - O 2	4.27
NMP	LP (1)Xe 1	BD*(1)O 5 - C 15	0.55
	LP (1)Xe 1	BD*(2)O 5 - C 15	0.73
	BD (2)O 5 - C 15	BD*(1)Xe 1 - O 2	3.37
	LP (1)O 5	BD*(1)Xe 1 - O 2	1.24
DEA	LP (1)Xe 1	BD*(1)C 5 - N 19	0.48
	LP (1)Xe 1	BD*(1)C 6 - N 19	0.23
	LP (1)N 19	BD*(1)Xe 1 - O 3	8.14
DEC	LP (1)Xe 1	BD*(1)C 6 - O 8	0.20
	LP (1)Xe 1	BD*(1)O 7 - C 16	0.16
	BD (2)O 5 - C 6	BD*(1)Xe 1 - O 3	0.24
	LP (1)O 5	BD*(1)Xe 1 - O 3	0.12
	LP (2)O 5	BD*(1)Xe 1 - O 3	0.59
	LP (1)O 7	BD*(1)Xe 1 - O 2	0.59
	LP (2)O 7	BD*(1)Xe 1 - O 2	1.14
TEA	LP (1)Xe 1	BD*(1)C 5 - N 19	0.81
	LP (1)Xe 1	BD*(1)C 6 - N 19	0.26
	LP (1)Xe 1	BD*(1)N 19 - C 20	0.43
	LP (1)N 19	BD*(1)Xe 1 - O 3	9.05
DME	LP (1)Xe 6	BD*(1)C 1 - O 15	0.27
	LP (1)Xe 6	BD*(1)C 2 - O 15	0.19
	LP (1)Xe 6	BD*(1)C 3 - O 14	0.30
	LP (1)Xe 6	BD*(1)C 10 - O 14	0.39
	LP (1)O 14	BD*(1)Xe 6 - O 8	2.95
	LP (1)O 15	BD*(1)Xe 6 - O 7	0.72
	LP (2)O 15	BD*(1)Xe 6 - O 7	0.89

Table S4.4. Range of second-order perturbation energy (E², in kcal/mol) values corresponding to the C-H...O (hydrogen bonding) interactions, obtained from the natural bond orbital (NBO) analysis of all the adducts of XeO₃ at the APFD/def2-TZVPD level of theory.

Solvent	Range of E ² (in kcal/mol)		
	1:3	1:2	1:1
HMPA	0.07 – 1.43	0.06 – 1.14	0.07 – 0.27

DMPU	0.05 – 0.18	0.07 – 0.24	0.07 – 0.15
TMEDA	0.05 – 1.86	0.05 – 1.23	0.05 – 0.37
DMI	0.06 – 0.23	0.07 – 0.22	0.08 – 0.21
SFO	0.05 – 0.93	0.05 – 0.84	0.07 – 0.78
NMP	0.06 – 0.18	0.07 – 0.54	0.06 – 0.39
DEA	0.05 – 0.62	0.05 – 0.63	0.05 – 0.58
DEC	0.06 – 0.30	0.05 – 0.48	0.05 – 0.43
TEA	0.05 – 1.12	0.05 – 0.49	0.05 – 0.63
DME	0.07 – 0.96	0.05 – 0.97	0.05 – 0.39

Table S4.5. The energy decomposition analysis (EDA) of all the 1:3 adducts of XeO₃ with different solvents at the BP86-D3BJ/TZ2P level of theory. Percentage contribution to total attractive energy is shown below, where electrostatic interactions are denoted as E_{elstat} , orbital interactions as E_{oi} , and dispersion interactions as E_{disp} .

1:3	ΔE	E_{Pauli}	E_{elstat}	%	E_{oi}	%	E_{disp}	%
HMPA	-64.09	118.32	-91.83	50	-52.44	29	-38.15	21
DMPU	-53.74	98.99	-78.26	51	-43.75	29	-30.72	20
NMP	-47.24	84.42	-68.1	52	-38.91	30	-24.65	19
DMI	-49.13	90.32	-70.77	51	-40.08	29	-28.6	21
DMSO	-50.89	104.92	-83.35	53	-50.83	33	-21.64	14
DMF	-37.22	73.02	-62.41	57	-35.86	33	-11.98	11
ACN	-29.5	41.99	-37.93	53	-18.37	26	-15.19	21
NH ₃	-32.2	73.54	-64.94	61	-32.42	31	-8.38	8
SFO	-48.21	90.24	-72.84	53	-40.49	29	-25.12	18
Acetone	-35.16	73.88	-61.41	56	-33.23	30	-14.4	13
THF	-41.69	83.31	-66.01	53	-36.33	29	-22.66	18
DEC	-44.32	79.22	-62.52	51	-34.37	28	-26.65	22
<i>t</i> But	-38	80.33	-65.28	55	-32.6	28	-20.45	17
H ₂ O	-25.56	68.48	-58.93	63	-28.28	30	-6.83	7

DEA	-50.65	103.44	-77.24	50	-45.81	30	-31.03	20
2NP	-29.31	58.12	-43.37	50	-24.35	28	-19.7	23
DEE	-40.76	81.55	-59.72	49	-33.38	27	-29.22	24
NMe	-30.24	65.15	-52.3	55	-29.87	31	-13.22	14
TMEDA	-55.43	109.02	-80.32	49	-48.07	29	-36.06	22
TEA	-49.78	106.53	-74.12	47	-45.58	29	-36.61	23
DiO	-36.15	73.08	-57.81	53	-31.12	28	-20.3	19
DME	-39.6	79.75	-60.48	51	-31.8	27	-27.06	23
DES	-51.15	96.45	-69.06	47	-46.36	31	-32.17	22
DCM	-23.91	43.42	-30.68	46	-18.83	28	-17.82	26
CHCl ₃	-22.9	43.91	-28.61	43	-19.32	29	-18.88	28
CCl ₄	-19.19	37.19	-19.65	35	-12.71	23	-24.01	43

Table S4.6. The energy decomposition analysis (EDA) of all the 1:2 adducts of XeO₃ with different solvents at the BP86-D3BJ/TZ2P level of theory. Percentage contribution to total attractive energy is shown below, where electrostatic interactions are denoted as E_{elstat} , orbital interactions as E_{oi} , and dispersion interactions as E_{disp} .

1:2	ΔE	E_{Pauli}	E_{elstat}	%	E_{oi}	%	E_{disp}	%
HMPA	-43.24	80.95	-66.65	54	-36.94	30	-20.59	17
DMPU	-35.96	69.04	-55.48	53	-31.32	30	-18.2	17
NMP	-31.95	59.67	-48.92	53	-28.04	31	-14.65	16
DMI	-31.11	67.47	-53.51	54	-27.87	28	-17.21	17
DMSO	-36.35	72.34	-59.95	55	-34.79	32	-13.94	13
DMF	-27.27	53.9	-47.06	58	-26.47	33	-7.64	9
ACN	-17.95	30.07	-25.79	54	-13.7	29	-8.53	18
NH ₃	-22.53	53.22	-47.02	62	-23.29	31	-5.45	7
SFO	-32.13	60.66	-49.82	54	-27.55	30	-15.42	17
Acetone	-25.04	52.27	-44.44	57	-23.61	31	-9.26	12
THF	-27.74	57.81	-45.74	53	-25.2	29	-14.6	17

DEC	-27.08	48.52	-39.3	52	-20.36	27	-15.94	21
<i>t</i> But	-25.33	57.01	-46.62	57	-23.86	29	-11.86	14
H ₂ O	-17.3	45.39	-39.69	63	-18.6	30	-4.4	7
DEA	-34.33	78.1	-59.12	53	-34.42	31	-18.88	17
2NP	-19.61	38.39	-29.46	51	-16.54	29	-12.01	21
DEE	-26.26	54.72	-40.86	50	-23.45	29	-16.67	21
NMe	-20.25	44.14	-35.89	56	-19.96	31	-8.54	13
TMEDA	-48.6	102.57	-79.09	52	-46.32	31	-25.76	17
TEA	-36.93	78.91	-57.82	50	-35.93	31	-22.09	19
DiO	-24.4	39.24	-33.54	53	-18.74	29	-11.37	18
DME	-30.53	57.7	-46.83	53	-23.93	27	-17.47	20
DES	-32.7	65.49	-47.62	48	-32.21	33	-18.37	19
DCM	-14.26	28.22	-19.84	47	-12.4	29	-10.25	24
CHCl ₃	-13.94	28.79	-18.19	43	-12.31	29	-12.24	29
CCl ₄	-11.07	23.12	-12.32	36	-8.44	25	-13.43	39

Table S4.7. The energy decomposition analysis (EDA) of all the 1:1 adducts of XeO₃ with different solvents at the BP86-D3BJ/TZ2P level of theory. Percentage contribution to total attractive energy is shown below, where electrostatic interactions are denoted as E_{elstat} , orbital interactions as E_{oi} , and dispersion interactions as E_{disp} .

1:1	ΔE	E_{Pauli}	E_{elstat}	%	E_{oi}	%	E_{disp}	%
HMPA	-23.16	44.4	-37.71	56	-20.67	31	-9.18	14
DMPU	-19.34	37.85	-31.56	55	-18.15	32	-7.48	13
NMP	-16.97	31.95	-27.29	56	-15.61	32	-6.01	12
DMI	-17.15	33.31	-28.28	56	-15.77	31	-6.41	13
DMSO	-19.19	39.94	-33.56	57	-19.37	33	-6.21	11
DMF	-15.27	30.51	-27.01	59	-15.11	33	-3.67	8
ACN	-9.69	15.32	-14.06	56	-7.12	28	-3.83	15
NH ₃	-11.99	29.4	-25.86	62	-12.89	31	-2.65	6

SFO	-16.63	30.65	-26.2	55	-13.86	29	-7.23	15
Acetone	-13.45	27.79	-24.06	58	-12.75	31	-4.43	11
THF	-14.49	22.17	-19.17	52	-11.35	31	-6.14	17
DEC	-14.5	23.81	-21.08	55	-10.26	27	-6.96	18
<i>t</i> But	-13.04	29.18	-24.34	58	-12.53	30	-5.35	13
H ₂ O	-8.85	23.06	-20.38	64	-9.39	29	-2.13	7
DEA	-17.95	42.98	-33.06	54	-20.17	33	-7.7	13
2NP	-9.66	19.89	-15.25	52	-8.85	30	-5.45	18
DEE	-13.07	27.73	-21.59	53	-12.27	30	-6.94	17
NMe	-10.37	22.01	-18.35	57	-9.91	31	-4.13	13
TMEDA	-31.59	75.72	-58.82	55	-35.77	33	-12.72	12
TEA	-19.84	50.28	-36.89	53	-23.66	34	-9.57	14
DiO	-11.68	26.76	-21.01	55	-12.13	32	-5.3	14
DME	-16.99	32.37	-27.8	56	-14.45	29	-7.11	14
DES	-15.54	33.18	-24.5	50	-16.54	34	-7.68	16
DCM	-14.5	23.81	-21.08	55	-10.26	27	-6.96	18
CHCl ₃	-6.82	13.96	-9.11	44	-6.23	30	-5.45	26
CCl ₄	-4.88	11.53	-6.01	37	-4.77	29	-5.63	34

Table S4.8. The energy decomposition analysis (EDA) of the adducts of XeO₃ with all the 26 solvents at the BP86-D3BJ/TZ2P level of theory for comparing the trends in percentage contribution to total attractive energy. Electrostatic interactions are denoted as E_{elstat} , orbital interactions as E_{oi} , and dispersion interactions as E_{disp} . The exceptions to the trends discussed in the manuscript are highlighted in red.

Solvent	1:3			1:2			1:1		
	% E_{elstat}	% E_{oi}	% E_{disp}	% E_{elstat}	% E_{oi}	% E_{disp}	% E_{elstat}	% E_{oi}	% E_{disp}
HMPA	50	29	21	54	30	17	56	31	14
DMPU	51	29	20	53	30	17	55	32	13
NMP	52	30	19	53	31	16	56	32	12

DMI	51	29	21	54	28	17	56	31	13
DMSO	53	33	14	55	32	13	57	33	11
DMF	57	33	11	58	33	9	59	33	8
CAN	53	26	21	54	29	18	56	28	15
NH ₃	61	31	8	62	31	7	62	31	6
SFO	53	29	18	54	30	17	55	29	15
Acetone	56	30	13	57	31	12	58	31	11
THF	53	29	18	53	29	17	52	31	17
DEC	51	28	22	52	27	21	55	27	18
<i>t</i> But	55	28	17	57	29	14	58	30	13
H ₂ O	63	30	7	63	30	7	64	29	7
DEA	50	30	20	53	31	17	54	33	13
2NP	50	28	23	51	29	21	52	30	18
DEE	49	27	24	50	29	21	53	30	17
NMe	55	31	14	56	31	13	57	31	13
TMEDA	49	29	22	52	31	17	55	33	12
TEA	47	29	23	50	31	19	53	34	14
DiO	53	28	19	53	29	18	55	32	14
DME	51	27	23	53	27	20	56	29	14
DES	47	31	22	48	33	19	50	34	16
DCM	46	28	26	47	29	24	55	27	18
CHCl ₃	43	29	28	43	29	29	44	30	26
CCl ₄	35	23	43	36	25	39	37	29	34

Optimized Cartesian Coordinates

XeO ₃ :(HMPA) ₃				XeO ₃ :(HMPA) ₂				XeO ₃ :(HMPA) ₁			
Xe	0.151598000	-0.050274000	-1.027218000	Xe	0.119428000	-1.622910000	-0.282399000	Xe	2.185526000	-0.042969000	-0.305876000
O	0.828210000	-1.440956000	-1.888293000	O	0.383987000	-1.102196000	1.384856000	O	1.691417000	1.267473000	0.767221000
O	1.187986000	1.255268000	-1.628543000	O	1.441445000	-2.768931000	-0.533047000	O	3.948164000	0.032574000	-0.278461000
O	-1.338463000	0.239653000	-1.944035000	O	-1.284671000	-2.692294000	-0.140643000	O	1.811484000	-1.518190000	0.586301000
O	-1.121413000	-1.872379000	0.400915000	O	-1.530062000	0.405170000	-0.401630000	O	-0.245901000	-0.006687000	-1.133977000

O	-0.767352000	1.696309000	0.728279000	O	1.734731000	0.289082000	-0.990023000	P	-1.414866000	-0.001079000	-0.197807000
O	1.990826000	-0.394945000	0.833817000	P	2.944006000	0.623364000	-0.183856000	N	-1.314633000	-0.832498000	1.216614000
P	3.335363000	-0.915432000	0.465719000	P	-2.974242000	0.596172000	-0.091681000	N	-1.736030000	1.552636000	0.253864000
P	-2.534611000	-2.328776000	0.353715000	N	-3.964407000	-0.717688000	-0.248466000	N	-2.684673000	-0.744478000	-0.968737000
P	-0.895352000	3.136809000	0.381273000	N	-3.132861000	1.155495000	1.455369000	C	-1.045639000	2.690357000	-0.313373000
N	0.572465000	3.875630000	0.521566000	N	-3.633801000	1.682676000	-1.148622000	H	-1.754737000	3.354893000	-0.820904000
N	-1.456886000	3.567167000	-1.109046000	N	2.505011000	1.567347000	1.096426000	H	-0.535047000	3.258256000	0.471324000
N	-3.684419000	-1.199084000	-0.009669000	N	4.042994000	1.366813000	-1.189404000	H	-0.301417000	2.357259000	-1.030131000
N	-2.681487000	-3.563539000	-0.734973000	N	3.837885000	-0.595933000	0.469199000	C	-2.796071000	1.892942000	1.173537000
N	-2.052058000	3.799627000	1.383951000	C	5.375769000	1.719648000	-0.758614000	H	-3.609862000	2.425338000	0.666787000
N	-3.002258000	-2.852729000	1.853793000	H	6.060852000	1.669037000	-1.611244000	H	-3.206014000	0.999692000	1.641843000
N	3.263219000	-2.551517000	0.266976000	H	5.426682000	2.738162000	-0.349469000	H	-2.414266000	2.541921000	1.969956000
N	4.404520000	-0.460438000	1.662049000	H	5.728654000	1.021758000	-0.000833000	C	-2.783243000	-0.641651000	-2.411282000
N	4.081699000	-0.343447000	-0.889402000	C	3.539925000	2.194166000	-2.266293000	H	-3.393513000	0.217669000	-2.720615000
C	5.825945000	-0.694626000	1.569763000	H	3.461198000	3.249782000	-1.970744000	H	-1.791380000	-0.543824000	-2.846030000
H	6.362673000	0.092108000	2.110649000	H	4.220708000	2.134181000	-3.121412000	H	-3.250965000	-1.547825000	-2.807858000
H	6.121107000	-1.659126000	2.006472000	H	2.559190000	1.841104000	-2.577738000	C	-3.958155000	-0.948121000	-0.314155000
H	6.148812000	-0.669577000	0.529944000	C	1.147440000	2.026787000	1.262985000	H	-4.440214000	-1.839711000	-0.726680000
C	3.913113000	-0.385539000	0.302201000	H	0.792820000	1.732426000	2.286389000	H	-3.819187000	-1.105589000	0.754342000
H	4.072426000	-1.325373000	3.569296000	H	1.096782000	3.120679000	1.218681000	H	-4.641080000	-0.100267000	-0.458505000
H	4.441930000	0.409214000	3.558440000	H	0.482094000	1.589055000	0.553817000	C	-1.323279000	-2.285427000	1.221743000
H	2.849561000	-0.156351000	3.018459000	C	3.464534000	2.091865000	2.036398000	H	-0.303852000	-2.674895000	1.292487000
C	2.032177000	-3.298560000	0.418238000	H	4.439298000	1.625964000	1.898646000	H	-1.899632000	-2.644650000	2.080498000
H	1.761368000	-3.785113000	-0.524804000	H	3.580611000	3.177898000	1.930424000	H	-1.779564000	-2.667967000	0.311000000
H	2.152966000	-4.069717000	1.189429000	H	3.141296000	1.888481000	3.064238000	C	-0.689365000	-0.267109000	2.399881000
H	1.213875000	-2.641298000	0.697475000	C	4.547472000	-1.507579000	-0.413577000	H	-0.566537000	0.807771000	2.297163000
C	4.418746000	-3.347603000	-0.062614000	H	5.492368000	-1.805234000	0.052753000	H	-1.309206000	-0.477265000	3.277931000
H	5.280208000	-2.716364000	-0.276259000	H	3.947305000	-2.401826000	-0.605445000	H	0.301608000	-0.701185000	2.552843000
H	4.682249000	-0.428211000	0.756722000	H	4.766131000	-1.024436000	-1.364263000				
H	4.224606000	-3.956932000	-0.953777000	C	3.509718000	-1.197238000	1.749594000				
C	4.460125000	1.056996000	-0.948597000	H	4.432994000	-1.387237000	2.307767000				
H	5.396699000	1.160806000	-1.507089000	H	2.867651000	-0.541034000	2.330582000				
H	3.681372000	1.642129000	-1.447402000	H	2.976395000	-2.140525000	1.608538000				
H	4.608850000	1.453878000	0.054444000	C	-2.204070000	0.764620000	2.495976000				
C	3.850653000	-0.914832000	-2.203711000	H	-1.884136000	1.649486000	3.057072000				
H	4.798958000	-0.957677000	-2.751276000	H	-2.668128000	0.065898000	3.204286000				
H	3.435906000	-1.915355000	-2.122668000	H	-1.327489000	0.284875000	2.065923000				
C	3.134571000	-0.311984000	-2.767117000	C	-4.360601000	1.744377000	1.929544000				
C	-1.829023000	-3.632962000	-1.904868000	H	-4.135507000	2.601815000	2.572363000				
H	-1.482386000	-4.663041000	-2.042444000	H	-4.968092000	2.099482000	1.099037000				
H	-2.365061000	-3.330552000	-2.813863000	H	-4.963085000	1.036691000	2.515643000				
H	-0.961257000	-2.986913000	-1.785936000	C	-2.818480000	2.784911000	-1.613517000				
C	-3.834296000	-4.427010000	-0.766736000	H	-3.116475000	3.729847000	-1.141657000				
H	-3.518280000	-5.467346000	-0.901208000	H	-1.770145000	2.592400000	-1.393359000				
H	-4.392922000	-4.364106000	0.165798000	H	-2.926136000	2.897410000	-2.697596000				
H	-4.518550000	-4.179223000	-1.590198000	C	-5.031812000	1.785267000	-1.488632000				
C	-2.033049000	-3.530094000	2.686937000	H	-5.159837000	1.775557000	-2.577437000				
H	-2.231051000	-4.608703000	2.738120000	H	-5.586329000	0.947863000	-1.069808000				
H	-1.030171000	-3.370760000	2.295407000	H	-5.468596000	2.720470000	-1.113753000				
H	-2.069900000	-3.129164000	3.705805000	C	-4.000124000	-1.388206000	-1.538220000				
C	-4.355987000	-2.903891000	2.344440000	H	-3.272834000	-2.204865000	-1.575445000				
H	-4.426199000	-2.408308000	3.320306000	H	-5.001613000	-1.794453000	-1.712123000				
H	-5.027068000	-2.397449000	1.653290000	H	-3.773837000	-0.682081000	-2.337460000				
H	-4.699725000	-3.939128000	2.475852000	C	-4.198835000	-1.614799000	0.868124000				
C	-3.694504000	0.016407000	0.787753000	H	-4.214345000	-1.062813000	1.805680000				
H	-3.061684000	0.788763000	0.344658000	H	-5.175376000	-2.091879000	0.741233000				
H	-4.720914000	0.388876000	0.873780000	H	-3.429400000	-2.390359000	0.928703000				
H	-3.315634000	-0.186521000	1.789595000								
C	-4.190539000	-1.011868000	-1.353656000								
H	-4.156430000	-1.946047000	-1.910049000								
H	-5.234646000	-0.684939000	-1.301538000								
H	-3.605913000	-0.267513000	-1.900652000								
C	1.763246000	3.159837000	0.927482000								
H	2.536935000	3.251431000	0.158114000								
H	2.155548000	3.572312000	1.865677000								
H	1.551363000	2.103119000	1.064713000								
C	0.757309000	5.287996000	0.302083000								
H	-0.143849000	5.739967000	-0.110179000								
H	1.012228000	5.809568000	1.233309000								
H	1.571774000	5.461445000	-0.411759000								
C	-2.179495000	3.269771000	2.725229000								
H	-1.849461000	2.233298000	2.745296000								
H	-1.588470000	3.844170000	3.452279000								
H	-3.228407000	3.311761000	3.037375000								
C	-2.521611000	5.157833000	1.247607000								
H	-3.566087000	5.219003000	1.571624000								
H	-1.942118000	5.864640000	1.857876000								
H	-2.472537000	5.474560000	0.206768000								
C	-0.582431000	3.686451000	-2.261977000								
H	0.450584000	3.812015000	-1.950564000								
H	-0.629089000	2.786248000	-2.879226000								
H	-0.889434000	4.552265000	-2.859393000								
C	-2.819742000	3.225748000	-1.477110000								
H	-3.227490000	4.004314000	-2.130471000								
H	-2.846461000	2.268227000	-2.006487000								
H	-3.448383000	3.154816000	-0.590880000								

XeO ₃ :(DMPU) ₃				XeO ₃ :(DMPU) ₂				XeO ₃ :(DMPU) ₁			
Xe	0.001041000	0.006999000	-0.461732000	Xe	-0.062781000	-1.398969000	-0.059711000	Xe	1.776258000	-0.070816000	0.019059000
O	0.683759000	1.441899000	-1.244056000	O	0.667020000	-0.327184000	-1.261063000	O	1.705037000	1.674617000	-0.207996000
O	-1.573599000	-0.123326000	-1.261932000	O	-1.709948000	-1.612395000	-0.680213000	O	0.667115000	-0.725749000	-1.190271000
O	0.909925000	-1.295584000	-1.245380000	O	0.669627000	-2.968272000	-0.394148000	O	3.371790000	-0.526988000	-0.581250000
O	2.212084000	0.391186000	1.102135000	O	2.076759000	-0.738353000	1.347129000	O	-0.390720000	0.050789000	1.471392000
O	-0.789112000	-2.111410000	1.079932000	O	-1.202585000	0.810759000	1.012283000	C	-1.397336000	0.026110000	0.727978000
O	-1.451287000	1.730845000	1.081564000	C	-2.298760000	0.908408000	0.428000000	C	-2.977597000	1.198964000	-0.762791000
C	-0.145146000	-3.070151000	0.615446000	C	-3.593439000	1.565703000	-1.569050000	C	-2.975907000	-1.759075000	-0.648755000

C	0.210840000	-4.696671000	-1.194460000	C	-4.614381000	0.137024000	0.152176000	C	-3.854802000	-0.028964000	-0.666954000
C	1.979374000	-4.298668000	0.466504000	C	-4.841247000	1.329764000	-0.748537000	H	-2.522540000	1.274205000	-1.759732000
C	1.239274000	-5.364233000	-0.310089000	H	-3.465540000	0.770048000	-2.315910000	H	-3.566955000	2.107556000	-0.611131000
H	0.701488000	-4.127308000	-1.996826000	H	-3.661644000	2.511769000	-2.114152000	H	-2.471881000	-1.392605000	-1.616299000
H	-0.432473000	-5.441854000	-1.671483000	H	-4.520404000	-0.784743000	-0.439245000	H	-3.570964000	-2.157786000	-0.467028000
H	2.607675000	-3.697122000	-0.206384000	H	-5.456274000	0.002066000	0.836597000	H	-4.450460000	0.009976000	0.250000000
H	2.641503000	-4.750129000	1.210725000	H	-5.060886000	2.213217000	-0.141407000	C	-1.335107000	-2.388162000	0.774975000
H	0.743299000	-6.049317000	0.384267000	C	2.710237000	0.142847000	0.732487000	H	-0.692064000	-2.749645000	-0.034798000
H	1.937568000	-5.947129000	-0.915450000	C	3.104828000	2.535722000	0.260068000	H	-0.733057000	-2.230011000	1.665216000
C	-2.603698000	1.652617000	0.617192000	C	4.123402000	0.808013000	-1.164237000	H	-2.092201000	-3.144915000	0.990526000
C	-4.194421000	2.167060000	-1.186036000	C	4.377007000	2.109544000	-0.437673000	C	-1.313478000	2.444437000	0.532084000
C	-4.732320000	0.429656000	0.468096000	H	3.292577000	3.386534000	0.921639000	H	-2.074983000	3.153417000	0.868558000
C	-5.285008000	1.608721000	-0.300361000	H	2.353585000	2.861451000	-0.474267000	H	-0.566505000	2.318473000	1.308145000
H	-3.950071000	1.459927000	-1.991635000	H	5.052506000	0.409908000	-1.581111000	H	-0.820689000	2.844984000	-0.357866000
H	-4.517998000	3.098941000	-1.658838000	H	3.430464000	0.958979000	-2.004577000	N	-1.937690000	1.172385000	0.244956000
H	-4.532213000	-0.413002000	-0.209612000	H	4.700979000	2.881626000	-1.139393000	N	-1.992485000	-1.155881000	0.408452000
H	-5.451732000	0.080908000	1.214434000	H	5.173730000	1.969789000	0.299173000	H	-4.544636000	-0.066352000	-1.512853000
H	-5.625497000	2.378381000	0.399042000	C	1.621736000	1.843317000	2.079071000				
C	2.735837000	1.416170000	0.628076000	H	1.300201000	0.962951000	2.625689000				
C	2.757115000	3.866390000	0.434684000	H	2.094655000	2.548146000	2.769154000				
C	4.006875000	2.496881000	-1.179731000	H	0.736497000	2.309101000	1.638465000				
C	4.063141000	3.736309000	-0.316005000	C	3.651888000	-1.548723000	-0.722068000				
H	2.807864000	4.679706000	1.164052000	H	4.695453000	-1.809758000	-0.915905000				
H	1.935501000	4.100151000	-0.257917000	H	3.245799000	-2.214295000	0.032635000				
H	4.981599000	2.296567000	-1.634217000	H	3.071900000	-1.678533000	-1.640314000				
H	3.285699000	2.628751000	-1.999006000	C	-3.262917000	-0.589438000	2.049573000				
H	4.235866000	6.208215000	-0.934205000	H	-3.132064000	-1.616704000	1.689589000				
H	4.890993000	3.656310000	0.395140000	H	-2.397371000	-0.305960000	2.641581000				
C	1.431161000	2.751269000	2.159617000	H	-4.154274000	-0.549022000	2.679227000				
H	1.356571000	1.813468000	2.701932000	N	2.571905000	1.457509000	1.062189000				
H	1.700636000	3.949473000	2.855614000	N	3.585227000	-0.181217000	-0.257943000				
H	0.453909000	2.567473000	1.719513000	C	-1.244939000	2.192923000	-1.336820000				
C	3.828873000	-0.071593000	-1.057079000	H	-1.447311000	3.229698000	-1.621415000				
H	4.883110000	-0.034355000	-1.326557000	H	-0.417328000	2.158717000	-0.636553000				
H	3.539033000	-0.735683000	-0.392632000	H	-0.958979000	1.624980000	-2.226650000				
H	3.215529000	0.002676000	-1.960495000	N	-2.421583000	1.625500000	-0.721286000				
C	1.621994000	-2.607447000	2.195833000	N	-3.420905000	0.330204000	0.948046000				
H	0.830047000	-2.077617000	2.716672000	H	-5.696062000	1.153321000	-1.405357000				
H	2.156751000	-3.243881000	2.905285000								
H	2.311204000	-1.866693000	1.781375000								
C	-1.812979000	-3.345529000	-1.111545000								
H	-2.389991000	-2.702117000	-0.455547000								
H	-1.546731000	-2.768719000	-2.002268000								
H	-2.417356000	-4.207676000	-1.405799000								
C	-3.082811000	-0.121635000	2.185866000								
H	-2.805738000	-1.091840000	1.764910000								
H	-2.213993000	0.285911000	2.693865000								
H	-3.892672000	-0.256313000	2.907364000								
N	-0.632573000	-3.811592000	-0.421149000								
N	1.047310000	-3.439981000	1.162598000								
N	2.460840000	2.645113000	1.149886000								
N	3.637373000	1.340268000	-0.393282000								
C	-2.011326000	3.243051000	-1.102936000								
H	-2.456626000	4.198353000	-1.393123000								
H	-1.165126000	3.419224000	-0.447084000								
H	-1.645447000	2.727681000	-1.996019000								
N	-3.003961000	2.450464000	-0.414652000								
N	-3.517708000	0.799516000	1.159704000								
H	-6.142161000	1.300657000	-0.903852000								

XeO ₃ :(NMP) ₃				XeO ₃ :(NMP) ₂				XeO ₃ :(NMP) ₁			
Xe	-0.000021000	0.000191000	-0.427498000	Xe	0.017713000	-1.213126000	-0.083701000	Xe	-1.546103000	0.001997000	0.089544000
O	0.619728000	1.460681000	-1.212731000	O	-1.575251000	-1.616023000	-0.741773000	O	-3.225695000	0.224932000	-0.397930000
O	-1.574955000	-0.194047000	-1.212086000	O	1.031238000	-2.550684000	-0.623491000	O	-1.148390000	-1.638255000	-0.419673000
O	0.954905000	-1.266760000	-1.212804000	O	0.536513000	0.121781000	-1.121576000	O	-0.630599000	1.036654000	-1.008503000
O	2.162978000	0.329296000	1.205275000	O	-1.401960000	0.658385000	1.276390000	O	0.699830000	-0.002696000	1.470722000
O	-0.796207000	-2.038143000	1.205124000	O	2.021141000	-0.391919000	1.456331000	C	2.146341000	-1.548636000	0.239597000
O	-1.366555000	1.710648000	1.203968000	C	3.933690000	-0.396431000	-0.067702000	C	3.475747000	-1.239733000	-0.444693000
C	-2.650379000	2.942097000	-0.473117000	C	4.714194000	0.805365000	-0.593236000	H	2.209288000	-2.251428000	1.070489000
C	-4.505431000	1.429412000	-0.325610000	H	4.510998000	-1.090441000	0.543041000	H	1.386065000	-1.932424000	-0.449439000
C	-4.145617000	2.851115000	-0.765444000	H	3.461925000	-0.981484000	-0.865394000	C	3.347011000	0.237019000	-0.830799000
H	-2.305946000	3.921304000	-0.139247000	C	3.679868000	1.934677000	-0.580426000	H	3.677176000	-1.873725000	-1.307857000
H	-2.032363000	2.648612000	-1.328620000	H	5.139264000	0.648969000	-1.584651000	H	4.301240000	-1.365174000	0.259990000
H	-5.517737000	1.345264000	0.078139000	H	5.534691000	1.048900000	0.086216000	H	2.955157000	0.369320000	-1.846856000
H	-4.402135000	0.707412000	-1.145675000	H	3.145328000	2.015969000	-1.535711000	H	4.289917000	0.785023000	-0.760970000
H	-4.695268000	3.575469000	-0.159010000	H	4.111080000	2.912435000	-0.350431000	C	1.656524000	-0.203288000	0.712481000
H	-4.396544000	3.033247000	-1.810535000	C	-2.204510000	1.995731000	-0.609989000	N	2.391713000	0.751503000	0.129388000
C	-1.223941000	-3.765342000	-0.471461000	C	-4.325920000	0.873901000	-0.652411000	C	2.095279000	2.154398000	0.221400000
C	-0.398821000	-5.015391000	-0.764603000	C	-3.642946000	2.173038000	-1.088869000	H	1.666542000	2.518475000	-0.715457000
H	-2.244008000	-3.955845000	-0.136620000	H	-1.721201000	2.909941000	-0.264115000	H	1.369971000	2.302834000	1.018464000
H	-1.279064000	-3.083254000	-1.326835000	H	-1.552069000	1.547926000	-1.367254000	H	3.005651000	2.715102000	0.445668000
C	1.013219000	-4.616949000	-0.326867000	H	-5.372274000	1.010993000	-0.368064000				
H	-0.432725000	-5.323961000	-1.809578000	H	-4.283373000	0.102597000	-1.431639000				
H	-0.751031000	-5.853216000	-0.157504000	H	-4.108951000	3.022175000	-0.582883000				
H	1.585934000	-4.166981000	-1.147834000	H	-3.725921000	2.339346000	-2.162866000				
H	1.592268000	-5.451882000	0.076168000	C	-2.308967000	0.987319000	0.508349000				
C	3.872803000	0.822256000	-0.471179000	C	2.807892000	0.216497000	0.726994000				
C	3.492928000	3.185665000	-0.325647000	N	2.754878000	1.529562000	0.455969000				
C	4.543377000	2.161638000	-0.764025000	N	-3.540354000	0.453582000	0.488516000				
H	4.547544000	0.033773000	-0.136548000	C	1.655179000	2.367590000	0.846705000				
H	3.309445000	0.433831000	-1.326590000	H	1.058394000	2.631232000	-0.030656000				
H	3.927090000	4.104102000	0.077879000	H	1.020005000	1.818457000	1.538835000				
H	2.817038000	3.457636000	-1.146415000	H	2.022705000	3.280740000	1.321670000				
H	5.445262000	2.274804000	-0.157086000	C	-3.908994000	-0.692368000	1.271714000				
H	4.827396000	2.286795000	-1.809010000	H	-4.906291000	-0.552998000	1.694842000				
C	2.848046000	1.146766000	0.588403000	H	-3.896601000	-1.596131000	0.656301000				

C	-0.430622000	-3.039955000	0.588056000	H	-3.185928000	-0.806089000	2.077399000
C	-2.417464000	1.893539000	0.587367000				
N	0.775828000	-3.621075000	0.695154000				
N	-3.523558000	1.139035000	0.696256000				
N	2.748765000	2.482085000	0.696054000				
C	1.865410000	-3.012008000	1.408135000				
H	2.531307000	-2.493081000	0.713704000				
H	1.464221000	-2.275289000	2.100623000				
H	2.425059000	-3.771764000	1.958274000				
C	-3.540986000	-0.107627000	1.411769000				
H	-2.703042000	-0.127011000	2.105128000				
H	-4.479226000	-0.211349000	1.961408000				
H	-3.424279000	-0.945209000	0.719136000				
C	1.676839000	3.121622000	1.409143000				
H	2.055283000	3.986713000	1.958250000				
H	0.894183000	3.438245000	0.714812000				
H	1.239882000	2.406570000	2.102696000				

XeO ₃ :(DMI) ₃				XeO ₃ :(DMI) ₂				XeO ₃ :(DMI) ₁			
Xe	-0.189904000	-0.214008000	-0.646560000	Xe	0.060538000	-1.300381000	-0.160459000	Xe	1.641158000	-0.211864000	-0.014574000
O	0.045889000	-1.873511000	-1.212860000	O	0.889358000	-2.836503000	-0.414755000	O	1.996260000	1.352197000	-0.743453000
O	1.123890000	0.631781000	-1.480824000	O	-1.506582000	-1.793244000	0.502172000	O	3.161308000	-0.711636000	0.727754000
O	-1.611471000	0.312768000	-1.561173000	O	0.887978000	-0.613427000	1.242325000	O	0.591232000	0.148157000	1.359168000
O	-2.008645000	-1.209198000	1.102494000	O	1.939357000	0.020997000	-1.495028000	O	-0.670728000	-0.368994000	-1.275539000
O	-0.268875000	2.105142000	0.819173000	O	-1.235687000	1.062072000	-0.488919000	C	-3.600853000	-0.282389000	0.632906000
O	1.631419000	-0.8049881000	1.264893000	C	-4.132155000	0.490101000	1.364709000	C	-3.038277000	1.128286000	0.809524000
C	2.591716000	-3.970270000	-0.089692000	C	-4.683299000	0.656797000	-0.052039000	H	-3.874573000	-0.750940000	1.580123000
C	3.740879000	-2.992245000	-0.522291000	H	-4.700459000	1.049510000	2.110172000	H	-4.482140000	-0.290035000	-0.024067000
H	1.897343000	-4.090358000	-0.920012000	H	-4.104313000	-0.566566000	1.661526000	H	-2.575473000	1.257128000	1.796851000
H	2.937241000	-4.866335000	0.300492000	H	-5.215790000	1.611112000	-0.173754000	H	-3.791277000	1.906615000	0.673754000
H	3.938022000	-3.046243000	-1.595362000	H	-5.358570000	-0.151779000	-0.339580000	C	-1.639519000	-0.071988000	-0.564865000
H	4.673619000	-3.224269000	0.011689000	C	3.413889000	2.429195000	0.569431000	N	-2.493695000	-0.965309000	0.006427000
C	2.257625000	3.791820000	-0.878260000	C	4.013762000	1.117836000	1.081063000	C	-2.584293000	-2.330631000	-0.418510000
C	2.915540000	3.503539000	0.471429000	H	2.995199000	3.042322000	1.370624000	H	-1.670722000	-2.587319000	-0.952111000
H	2.425860000	4.813615000	-1.224095000	H	4.154669000	3.033036000	0.025912000	H	-2.692849000	-2.992111000	0.443971000
H	2.608496000	3.093559000	-1.650093000	H	3.539082000	0.800093000	2.019316000	H	-3.438429000	-2.487140000	-1.089123000
H	3.018133000	4.414908000	1.078758000	H	5.092589000	1.176458000	1.237633000	N	-2.029454000	1.182995000	-0.224316000
H	3.903705000	3.048271000	0.371013000	C	2.605545000	0.664214000	-0.677312000	C	-1.172713000	2.328771000	-0.365014000
C	-4.837856000	0.787882000	0.564841000	C	-2.387733000	0.916658000	-0.070121000	H	-0.620758000	2.527386000	0.558794000
C	-4.871122000	-0.208025000	-0.604814000	N	-3.475835000	0.640906000	-0.839943000	H	-0.453869000	2.138683000	-1.158980000
H	-4.908924000	1.818987000	0.238062000	N	2.385202000	1.954694000	-0.320958000	H	-1.771018000	3.204495000	-0.624688000
H	-5.646238000	0.589416000	1.285608000	C	-3.480083000	0.790983000	-2.263136000				
H	-4.511127000	0.260616000	-1.530267000	H	-2.447406000	0.830386000	-2.606741000				
H	-5.865847000	-0.621499000	-0.782940000	H	-3.981478000	-0.056646000	-2.736739000				
C	-3.067298000	-0.694202000	0.733073000	H	-3.989192000	1.713363000	-2.570262000				
C	0.755442000	2.692863000	0.467922000	C	1.499949000	2.828159000	-1.030183000				
C	2.218746000	-1.798330000	0.738156000	H	0.823679000	2.220850000	-1.627220000				
N	1.973198000	2.591540000	1.068056000	H	0.902776000	3.412216000	-0.326572000				
N	1.936684000	-3.120682000	0.933005000	H	2.051759000	3.515102000	-1.684199000				
N	-3.552491000	0.500749000	1.150454000	N	-2.786623000	1.001371000	1.229694000				
C	2.147106000	2.054781000	2.384850000	N	3.679751000	0.194870000	0.020217000				
H	1.292615000	1.422681000	2.613492000	C	3.912419000	-1.215572000	0.177558000				
H	3.044893000	1.435478000	2.425757000	H	3.451162000	-1.592103000	1.096247000				
H	2.227717000	2.852903000	3.134478000	H	3.467431000	-1.740073000	-0.665827000				
C	0.655304000	-3.526711000	1.447811000	H	4.985923000	-1.415075000	0.201167000				
H	0.255411000	-2.722682000	2.063334000	C	-1.852007000	0.897771000	2.317421000				
H	-0.052637000	-3.712967000	0.634213000	H	-1.771031000	-0.134320000	2.671789000				
H	0.765356000	-4.427487000	2.054756000	H	-0.870781000	1.211145000	1.967251000				
C	-3.015483000	1.234145000	2.256110000	H	-2.168905000	1.542618000	3.140237000				
H	-2.059488000	0.791597000	2.527609000								
H	-2.839189000	2.274546000	1.976090000								
H	-3.691027000	1.200669000	3.119929000								
N	3.241482000	-1.695067000	-0.146231000								
N	0.862394000	3.548479000	-0.591930000								
N	-3.939404000	-1.227347000	-0.175821000								
C	-3.508040000	-2.245337000	-1.095815000								
H	-3.153053000	-1.805137000	-2.033152000								
H	-2.682077000	-2.791824000	-0.644218000								
H	-4.329615000	-2.934953000	-1.302600000								
C	3.932958000	-0.470863000	-0.410028000								
H	4.064183000	-0.334879000	-1.485832000								
H	3.321446000	0.348847000	-0.037055000								
H	4.917850000	-0.452721000	0.074815000								
C	-0.107646000	3.537984000	-1.653803000								
H	0.208709000	2.880928000	-2.469542000								
H	-1.048552000	3.157836000	-1.259933000								
H	-0.255928000	4.551392000	-2.034023000								

XeO ₃ :(DMSO) ₃				XeO ₃ :(DMSO) ₂				XeO ₃ :(DMSO) ₁			
Xe	-0.137617000	-0.233761000	-0.372323000	Xe	0.014627000	-1.109229000	-0.103994000	Xe	1.151278000	-0.070823000	-0.147746000
O	1.328862000	0.327491000	-1.215213000	O	0.379794000	-0.247002000	1.399842000	O	0.356614000	-0.986923000	1.139539000
O	-1.370349000	0.690090000	-1.251930000	O	1.036780000	-2.539382000	0.003335000	O	0.915278000	1.616001000	0.303748000
O	-0.346436000	-1.835144000	-1.086875000	O	-1.602971000	-1.758715000	0.226858000	O	2.867386000	-0.364088000	0.130778000
O	1.602806000	-1.421821000	1.254547000	O	-1.220574000	1.170267000	-0.720420000	O	-1.204262000	0.054761000	-1.217838000
O	-2.081414000	-0.930787000	1.259353000	O	2.018529000	0.197116000	-1.178546000	S	-2.517759000	0.198547000	-0.489936000
O	0.029849000	2.023831000	1.061366000	S	-2.556074000	1.595005000	-0.171807000	C	-2.220091000	1.188628000	0.974852000
C	3.998283000	-0.790232000	0.316279000	S	2.875938000	1.251002000	-0.534358000	H	-3.175112000	1.307375000	1.489328000
H	4.905251000	-1.245211000	-0.084911000	C	-2.625156000	1.084821000	1.547063000	H	-1.478803000	0.711563000	1.614548000
H	3.492064000	-0.174849000	-0.426833000	H	-3.596087000	1.387438000	1.943044000	H	-1.853478000	2.155568000	0.633473000
H	4.237712000	-0.209326000	1.206474000	H	-2.474199000	0.009190000	1.626838000	C	-2.816428000	-1.368372000	0.327630000
C	2.609264000	-2.811215000	-0.793871000	H	-1.827946000	1.615076000	2.065925000	H	-1.933489000	-1.636176000	0.907540000
H	2.296001000	-2.042793000	-1.499064000	C	-3.767657000	0.440638000	-0.815774000	H	-3.698937000	-1.266197000	0.961001000
H	3.541872000	-3.289165000	-1.099356000	H	-3.431842000	-0.574189000	-0.601571000	H	-3.006070000	-2.103997000	-0.453329000
H	1.819619000	-3.552935000	-0.685940000	H	-4.731942000	0.653030000	-0.351468000				

C	0.232490000	3.469328000	-1.171239000	H	-3.829552000	0.613146000	-1.889865000
H	0.696030000	4.388339000	-1.534420000	C	3.534458000	0.526216000	0.967853000
H	0.582178000	2.592981000	-1.715476000	H	4.100161000	1.290303000	1.503472000
H	-0.851795000	3.540080000	-1.240843000	H	2.711285000	0.137581000	1.566876000
C	2.389946000	3.001841000	0.374712000	H	4.198733000	-0.280598000	0.659848000
H	2.512821000	2.116866000	-0.249087000	C	1.763483000	2.437616000	0.218637000
H	2.854882000	3.881508000	-0.073078000	H	1.095280000	1.915268000	0.901915000
H	2.794160000	2.834421000	1.372605000	H	2.361817000	3.195036000	0.727558000
C	-4.045927000	0.697026000	0.547104000	H	1.193396000	2.886951000	-0.593475000
H	-3.353908000	1.123403000	-0.178871000				
H	-5.071564000	0.682869000	0.174596000				
H	-3.999353000	1.240037000	1.490564000				
C	-3.652035000	-1.630703000	-0.775917000				
H	-4.708454000	-1.669135000	-1.047448000				
H	-3.080335000	-1.002507000	-1.457714000				
H	-3.231700000	-2.635244000	-0.752585000				
S	0.631496000	3.306720000	0.571183000				
S	2.874180000	-2.093697000	0.829722000				
S	-3.537103000	-0.988136000	0.896246000				

XeO ₃ :(DMF) ₃				XeO ₃ :(DMF) ₂				XeO ₃ :(DMF) ₁			
Xe	-0.000556000	-0.002061000	0.573071000	Xe	0.000688000	-1.121706000	-0.215002000	Xe	-1.408244000	-0.148629000	-0.014436000
O	-0.085312000	-1.585254000	-1.361655000	O	1.390730000	-2.213029000	-0.143808000	O	-3.168748000	-0.044820000	-0.013267000
O	1.413817000	0.715137000	-1.362006000	O	-1.379145000	-2.225377000	-0.150574000	O	-0.901123000	0.956455000	-1.292441000
O	-1.328725000	0.861168000	-1.364601000	O	-0.008316000	-0.383003000	1.388460000	O	-0.916339000	0.649935000	1.478747000
O	-2.041761000	-1.036039000	0.904250000	O	1.906393000	0.706943000	-0.714458000	O	1.125270000	-0.899486000	-0.092850000
O	0.121971000	2.283060000	0.902988000	O	-1.915376000	0.690004000	-0.721828000	C	1.856045000	0.088828000	-0.029093000
O	1.917972000	-1.247216000	0.908349000	C	-2.821003000	0.528317000	0.090278000	H	1.438296000	1.104117000	0.008484000
C	0.214819000	3.207138000	0.105350000	H	-2.798867000	-0.298778000	0.813711000	C	3.910650000	-1.193553000	-0.041506000
H	0.278985000	3.027281000	-0.977142000	C	2.844831000	0.509687000	0.051265000	C	3.963930000	1.270900000	0.072717000
C	2.690115000	-1.759527000	0.108260000	H	2.873782000	-0.376391000	0.700983000	H	3.196357000	-2.011672000	-0.093847000
H	2.534197000	-1.672924000	-0.976346000	C	-4.104219000	2.434059000	-0.679447000	H	4.563971000	-1.223783000	-0.917544000
C	-2.875855000	-1.435438000	0.101927000	C	-4.926137000	1.033007000	1.176429000	H	4.525184000	-1.303743000	0.855925000
H	-2.729372000	-1.323709000	-0.981683000	H	-3.252582000	2.509833000	-1.351670000	H	3.296812000	2.131850000	0.099283000
C	0.176652000	4.931991000	1.808996000	H	-5.019702000	2.309239000	-1.264776000	H	4.582010000	1.277456000	0.974710000
C	0.363367000	5.527742000	-0.576516000	H	-4.188717000	3.353909000	-0.093920000	H	4.619238000	1.361003000	-0.798030000
H	0.091374000	4.050620000	2.441010000	H	-4.648113000	0.157439000	1.762499000	N	3.189579000	0.056718000	-0.000524000
H	1.074943000	5.491955000	2.085671000	H	-5.043718000	1.884563000	1.853056000				
H	-0.694543000	5.575598000	1.963361000	H	-5.888640000	0.839954000	0.693493000				
H	0.407846000	5.062345000	-1.561386000	C	4.037647000	2.518297000	-0.592575000				
H	-0.498861000	6.201116000	-0.546118000	C	4.970275000	0.992730000	1.106445000				
H	1.270206000	6.122439000	-0.428873000	H	3.158454000	2.623392000	-1.224185000				
C	4.145220000	-2.681930000	1.814191000	H	4.116994000	3.386281000	0.068020000				
C	4.635116000	-3.032045000	-0.577193000	H	4.932936000	2.475573000	-1.219502000				
H	3.406721000	-2.195751000	2.448010000	H	4.741920000	0.060179000	1.621723000				
H	4.169399000	-3.752298000	2.039427000	H	5.920898000	0.877057000	0.577422000				
H	5.134142000	-2.261632000	2.020178000	H	5.083832000	1.785661000	1.851594000				
H	4.240662000	-2.789255000	-1.563681000	N	-3.908586000	1.302310000	0.193459000				
H	5.650996000	-2.632451000	-0.498752000	N	3.910265000	1.309595000	0.184393000				
H	4.684733000	-4.120896000	-0.478596000								
C	-4.390274000	-2.267630000	1.802537000								
C	-4.953617000	-2.473224000	-0.589420000								
H	-3.594044000	-1.886528000	2.438329000								
H	-5.325942000	-1.754972000	2.044993000								
H	-4.522974000	-3.337695000	1.987867000								
H	-4.552015000	-2.235610000	-1.574275000								
H	-5.114672000	-3.554069000	-0.528794000								
H	-5.920989000	-1.973956000	-0.476397000								
N	0.251017000	4.508623000	0.433211000								
N	3.784014000	-2.465954000	0.435628000								
N	-4.031846000	-2.036741000	0.425685000								

XeO ₃ :(ACN) ₃				XeO ₃ :(ACN) ₂				XeO ₃ :(ACN) ₁			
Xe	-0.003218000	0.000514000	-0.859191000	Xe	0.054179000	0.699925000	-0.101443000	Xe	-0.707996000	-0.072968000	-0.113421000
O	-1.513436000	-0.572477000	-1.567381000	O	-1.081639000	1.984370000	0.288497000	O	-0.475254000	-0.791820000	1.475538000
O	1.244559000	-1.018832000	-1.576486000	O	1.640561000	1.403293000	0.211352000	O	-2.416981000	0.340840000	-0.202475000
O	0.252290000	1.592412000	-1.574106000	O	-0.143943000	-0.474605000	1.205384000	O	0.141269000	1.472538000	-0.044585000
C	-3.361617000	-0.741176000	1.207563000	C	-3.226274000	-1.735829000	0.825197000	C	3.384605000	0.605821000	0.393770000
H	-2.851018000	-1.633581000	1.573268000	H	-4.172745000	-1.269923000	1.103273000	H	3.804003000	0.182716000	1.307709000
H	-4.266601000	-0.560481000	1.789406000	H	-3.378108000	-2.807163000	0.685560000	H	4.194141000	0.967852000	-0.241819000
C	-3.618302000	-0.890069000	0.157209000	H	-2.494370000	-1.573461000	1.619905000	H	2.724078000	1.437904000	0.649276000
C	3.228530000	-2.542428000	1.196024000	C	3.182988000	-1.541084000	0.737194000	C	2.604064000	-0.391053000	-0.305450000
H	2.848398000	-1.667735000	1.590080000	H	3.645951000	-2.516635000	0.892754000	N	1.940751000	-1.158471000	-0.849740000
H	2.621267000	-3.435605000	1.749858000	H	3.956838000	-0.777036000	0.652819000				
H	2.586483000	-2.657453000	0.141690000	H	2.541237000	-1.299814000	1.587420000				
C	1.045018000	3.281849000	1.202893000	C	2.371386000	-1.548217000	-0.460640000				
H	0.022804000	3.286721000	1.584724000	C	-2.711729000	-1.138368000	-0.387516000				
H	1.663182000	3.976632000	1.773258000	N	1.688801000	-1.510631000	-1.386994000				
H	1.027925000	3.576009000	0.151935000	N	-2.266308000	-0.642995000	-1.326015000				
C	1.572073000	1.937990000	1.300747000								
C	-2.459884000	0.385409000	1.311432000								
C	0.902271000	-2.324946000	1.303801000								
N	1.960560000	0.855244000	1.347764000								
N	-0.229038000	-2.118747000	1.359102000								
N	-1.715242000	1.261898000	1.363691000								

XeO ₃ :(NH ₃) ₃				XeO ₃ :(NH ₃) ₂				XeO ₃ :(NH ₃) ₁			
Xe	-0.000134000	0.000747000	-0.199199000	Xe	-0.000080000	-0.259220000	-0.096569000	Xe	0.236219000	-0.000003000	-0.152317000
O	-0.282611000	1.573333000	-0.963038000	O	1.385627000	-1.356229000	-0.112830000	O	-0.138181000	1.406571000	0.844055000
O	-1.219933000	-1.030368000	-0.964770000	O	-1.386177000	-1.355659000	-0.113729000	O	1.994915000	0.000392000	-0.282090000
O	1.503468000	-0.540394000	-0.963344000	O	-0.000543000	0.407517000	1.540313000	O	-0.137579000	-1.406956000	0.843742000
N	-2.364047000	0.848024000	1.132949000	N	-2.126806000	1.579472000	-0.293637000	N	-2.548096000	-0.000020000	-0.334241000

H	-2.420191000	1.740658000	0.656020000	H	-2.871797000	0.895147000	-0.360835000	H	-2.752543000	-0.818086000	0.228754000
H	-2.968353000	0.200077000	0.640618000	H	-2.097649000	1.907915000	0.664885000	H	-2.752785000	0.819613000	0.226375000
N	0.445323000	-2.472478000	1.130304000	N	2.128031000	1.578578000	-0.293534000	H	-3.167072000	-0.001314000	-1.135961000
H	-0.301460000	-2.963671000	0.652491000	H	2.098180000	0.915115000	0.662128000				
H	1.307287000	-2.671455000	0.635519000	H	2.871269000	1.891681000	-0.353786000				
N	1.918606000	1.618752000	1.133330000	H	2.356385000	2.355027000	-0.901757000				
H	2.714133000	1.220331000	0.647707000	H	-2.351892000	2.361621000	-0.895728000				
H	1.660295000	2.470694000	0.648843000								
H	-2.709057000	0.961312000	2.077617000								
H	2.197360000	1.852887000	2.077637000								
H	0.520641000	-2.831822000	2.073412000								

XeO ₃ :(SFO) ₃			XeO ₃ :(SFO) ₂			XeO ₃ :(SFO) ₁					
Xe	-0.175594000	-0.103317000	-0.617698000	Xe	0.003497000	-1.109499000	-0.374374000	Xe	1.683377000	-0.158022000	-0.057935000
O	1.314978000	-0.301663000	-1.547939000	O	-1.262974000	-2.328932000	-0.254773000	O	3.411089000	0.169992000	-0.122046000
O	-0.756253000	1.462090900	-1.202717000	O	-0.151262000	-0.256332000	1.149032000	O	1.187827000	0.352079000	1.554645000
O	-1.279417000	-1.230486000	-1.409044000	O	1.478722000	-2.050957000	-0.139888000	O	0.963055000	1.038110000	-1.137222000
O	-4.488921000	0.317046000	1.929919000	O	3.588474000	2.445261000	-0.856706000	O	-3.132947000	-1.725219000	0.011934000
O	-2.119963000	0.230431000	1.218881000	O	1.695473000	0.860408000	-1.078452000	O	-0.689487000	-1.387543000	-0.197701000
S	-3.510093000	-0.126317000	0.970543000	S	2.953654000	1.224554000	-0.435825000	S	-2.023273000	-0.812356000	-0.038113000
C	-4.028324000	0.371080000	-0.681768000	C	2.763237000	1.205669000	1.354238000	C	-2.042362000	0.294959000	1.378358000
H	-4.845718000	1.073900000	-0.517874000	H	3.261931000	2.109622000	1.706603000	H	-2.994115000	0.109800000	1.878680000
H	-3.190270000	0.876586000	-1.160469000	H	1.698168000	1.241303000	1.576144000	H	-1.209360000	0.026557000	2.025777000
C	-3.682685000	-1.885283000	0.711572000	C	4.102411000	-0.15663000	-0.537363000	C	-2.279880000	0.447028000	-1.293888000
H	-2.731273000	-2.246407000	0.318344000	H	3.514720000	-1.022250000	-0.829734000	H	-1.307719000	0.621287000	-1.755841000
H	-3.900739000	-2.337283000	1.678483000	H	4.837826000	0.096653000	-1.301456000	H	-2.985737000	0.043059000	-2.018314000
C	-4.798930000	-1.964889000	-0.319243000	C	4.649886000	-0.290076000	0.877220000	C	-2.764101000	1.666711000	-0.519080000
H	-4.864678000	-2.965676000	-0.749749000	H	5.104803000	-1.271507000	1.022313000	H	-2.623821000	2.576866000	-1.104648000
H	-5.759488000	-1.744435000	0.155827000	H	5.422810000	0.463307000	1.058514000	H	-3.832439000	1.575787000	-0.299923000
C	-4.465124000	-0.914675000	-1.389070000	C	3.458586000	-0.070230000	1.816328000	C	-1.954818000	1.694478000	0.781843000
H	-5.317149000	-0.726843000	-2.044733000	H	3.770616000	0.014648000	2.858922000	H	-2.333717000	2.438693000	1.484527000
H	-3.639333000	-1.275968000	-2.003311000	H	2.768361000	-0.913051000	1.739502000	H	-0.912413000	1.940428000	0.567740000
O	2.805436000	3.312839000	1.580133000	O	-4.147476000	1.617506000	-1.371127000				
O	1.455979000	1.317117000	1.018726000	O	-1.943030000	0.491529000	-1.289953000				
S	1.750434000	2.726535000	0.793668000	S	-3.170990000	0.886044000	-0.609327000				
C	2.050622000	3.062285000	-0.949929000	C	-3.925901000	-0.546155000	0.174947000				
H	3.076425000	3.429728000	-0.990849000	H	-4.995840000	-0.451473000	-0.015977000				
H	1.966494000	2.121946000	-1.493887000	H	-3.525923000	-1.438217000	-0.304211000				
C	0.272467000	3.717470000	0.936611000	C	-2.756630000	1.760741000	0.904581000				
H	-0.569275000	3.075263000	0.673089000	H	-1.689677000	1.603711000	1.063851000				
H	0.199789000	4.048577000	1.971930000	H	-2.972742000	2.815204000	0.738567000				
C	0.506499000	4.814577000	-0.091304000	C	-3.596053000	1.081595000	1.979335000				
H	-0.411066000	5.373134000	-0.284364000	H	-3.192793000	1.285548000	2.972915000				
H	1.251833000	5.521859000	0.284293000	H	-4.621432000	1.463467000	1.954555000				
C	1.011766000	4.110349000	-1.359656000	C	-3.577563000	-0.415881000	1.652861000				
H	1.437383000	4.822154000	-2.068960000	H	-4.283281000	-0.977392000	2.267778000				
H	0.178034000	3.604106000	-1.847491000	H	-2.580273000	-0.823031000	1.832405000				
O	2.290120000	-3.968070000	1.523897000								
O	0.687835000	-2.230347000	0.792146000								
S	2.020160000	-2.811955000	0.708198000								
C	2.469230000	-3.174319000	-0.998891000								
H	2.625380000	-4.253016000	-1.025658000								
H	1.630047000	-2.896554000	-1.633758000								
C	3.282463000	-1.580122000	0.987941000								
H	2.870446000	-0.612027000	0.700391000								
H	3.514006000	-1.588590000	2.052450000								
C	4.404552000	-2.035238000	0.067345000								
H	5.161901000	-1.256933000	-0.042364000								
H	4.895611000	-2.918212000	0.486912000								
C	3.740439000	-2.367448000	-1.276837000								
H	4.415918000	-2.918980000	-1.933091000								
H	3.463576000	-1.440340000	-1.780676000								

XeO ₃ :(Acetone) ₃				XeO ₃ :(Acetone) ₂				XeO ₃ :(Acetone) ₁			
Xe	-0.066233000	-0.053771000	-0.559093000	Xe	-0.004344000	-0.830754000	-0.241969000	Xe	1.005250000	-0.179726000	-0.035933000
O	1.454801000	0.341000000	-1.370463000	O	-1.445249000	-1.850398000	-0.281856000	O	0.463660000	0.479973000	1.506949000
O	-1.206258000	1.067467000	-0.1315428000	O	0.112387000	-0.331005000	1.448181000	O	0.699401000	1.088871000	-1.221786000
O	-0.502665000	-1.598032000	-1.302236000	O	1.312686000	-0.1991166000	-0.429861000	O	2.760753000	-0.248698000	0.100104000
O	1.541658000	-1.561568000	1.080032000	O	1.899464000	1.071456000	-0.647244000	O	-1.593062000	-0.846246000	-0.309969000
O	-2.176700000	-0.501624000	1.150210000	O	-1.837564000	1.163281000	-0.540461000	C	-2.379082000	1.343770000	0.176364000
O	0.656067000	2.071281000	1.034695000	C	-3.165708000	0.393978000	1.276391000	H	-3.313570000	1.890016000	0.050093000
C	3.288460000	-3.038535000	1.671014000	H	-3.965032000	0.814634000	1.886937000	H	-2.038073000	1.466699000	1.209691000
H	3.155022000	-4.122070000	1.593847000	H	-3.471027000	-0.601855000	0.938121000	H	-1.597620000	1.753338000	-0.463602000
H	4.330850000	-2.835061000	1.406921000	H	-2.253543000	0.261690000	1.857269000	C	-3.930133000	-0.685834000	-0.011233000
H	3.087888000	-2.709195000	2.688886000	C	-3.994506000	2.120618000	-0.422881000	H	-4.406691000	-0.389507000	0.927640000
C	2.554461000	-2.673432000	-0.759904000	H	-4.923283000	1.551410000	-0.522847000	H	-4.531750000	-0.2053238000	-0.815300000
H	2.864063000	-1.762233000	-1.279035000	H	-4.182491000	2.893114000	0.329452000	H	-3.918232000	-1.769989000	-0.104944000
H	3.284494000	-3.464558000	-0.928119000	H	-3.732075000	2.585915000	-1.371119000	C	-2.544681000	-0.122320000	-0.076056000
H	1.586875000	-2.944205000	-1.187195000	C	3.838908000	2.357430000	-0.243179000				
C	1.029693000	3.490470000	-0.838416000	H	4.006970000	2.896116000	0.694323000				
H	1.121455000	4.566216000	-0.991578000	H	4.816202000	1.984546000	-0.565543000				
H	1.862544000	2.991126000	-1.344132000	H	3.430228000	0.320906000	-0.995861000				
H	0.115798000	3.102388000	-1.287246000	C	3.306203000	0.217895000	1.066846000				
C	1.748179000	4.104417000	1.541957000	H	4.320112000	0.377286000	1.432140000				
H	2.729678000	4.390523000	1.152800000	H	2.598633000	0.322036000	1.894544000				
H	1.148723000	5.019596000	1.578541000	H	3.184954000	-0.799471000	0.691021000				
H	1.844677000	3.687845000	2.542940000	C	2.922121000	1.196943000	-0.000329000				
C	-4.452102000	-0.603965000	1.779032000	C	-2.895158000	1.221290000	0.057788000				
H	-5.211038000	0.107614000	1.440735000								
H	-4.940758000	-1.582455000	1.823984000								
H	-4.088494000	-0.327760000	2.767113000								
C	-3.682722000	-0.891474000	-0.648358000								
H	-4.682609000	-1.310942000	-0.761403000								
H	-3.641277000	0.074910000	-1.161073000								

H	-2.932541000	-1.523266000	-1.124133000
C	-3.325787000	-0.658503000	0.788337000
C	2.379774000	-2.352182000	0.694079000
C	1.094375000	3.122699000	0.613029000

XeO ₃ :(THF) ₃				XeO ₃ :(THF) ₂				XeO ₃ :(THF) ₁			
Xe	-0.012447000	-0.099560000	-0.724497000	Xe	0.001375000	-1.011989000	-0.048440000	Xe	4.811998100	2.724073300	9.711429900
O	-0.083179000	-1.740030000	-1.376959000	O	1.202540000	-2.296730000	0.088682000	O	4.312030900	1.011405900	9.799359600
O	1.462396000	0.558686000	-1.447461000	O	-1.534802000	-1.829647000	0.255475000	O	4.900018400	3.225094300	11.423787000
O	-1.298858000	0.730293000	-1.607529000	O	0.255316000	-0.035836000	1.400183000	O	6.524988700	2.634196500	9.212890500
O	1.711254000	-1.182515000	1.121899000	O	2.051609000	0.429375000	-1.040766000	O	5.111852800	5.419808800	9.036866500
C	3.026433000	-1.337943000	0.595005000	C	1.883450000	1.829425000	-0.827213000	C	6.449239900	5.878363400	9.296601800
C	1.244160000	-2.493129000	1.453787000	C	3.310946000	0.089792000	-0.462298000	C	4.239148400	6.233034300	9.842724700
C	2.936769000	-2.577497000	-0.278429000	C	2.506722000	2.129775000	0.540681000	C	6.480127100	6.154569800	10.800151600
H	3.270685000	-0.426418000	0.050731000	H	2.399796000	2.368076000	-1.631322000	H	7.127618300	5.089864100	8.976725900
H	3.732612000	-1.471780000	1.426119000	H	0.817101000	2.045443000	-0.895529000	H	6.634073400	6.786770300	8.709454300
C	1.926511000	-3.460803000	0.474357000	C	3.376533000	0.889881000	0.833447000	C	5.017257400	6.539749400	11.135675100
H	1.519525000	-2.707956000	2.493093000	H	3.325651000	-0.990367000	-0.325060000	H	4.003353400	7.148240700	9.287673000
H	0.156816000	-2.479454000	1.374917000	H	4.106280000	0.379313000	-1.161346000	H	3.321775500	5.666389200	9.997021500
H	3.905476000	-3.060605000	-0.417433000	H	1.737776000	2.246135000	1.304081000	H	7.193306600	6.938389900	11.055725600
H	2.542434000	-2.302257000	-1.257344000	H	3.092742000	3.050065000	0.508828000	H	6.757252000	5.246463900	11.333482500
H	2.421717000	-4.270027000	1.015135000	H	2.946497000	0.310993000	1.650999000	H	4.920750300	7.591397200	11.406841700
H	1.205033000	-3.902605000	-0.212054000	H	4.403077000	1.146531000	1.100074000	H	4.647310100	5.937068500	11.962771500
O	-2.026580000	-0.998674000	0.860709000	O	-1.569615000	1.125350000	-0.737748000				
C	-2.618620000	0.106365000	1.547596000	C	-1.879387000	1.958860000	0.378455000				
C	-3.026224000	-1.649207000	0.055373000	C	-2.823572000	0.663179000	-1.247072000				
C	-3.767331000	0.454479000	0.660654000	C	-2.986941000	1.215259000	1.105074000				
H	-2.971301000	-0.227766000	2.532280000	H	-0.968685000	2.080846000	0.962285000				
H	-1.848678000	0.867644000	1.687580000	H	-2.214855000	2.937362000	0.009084000				
C	-4.295291000	-0.803563000	0.169114000	C	-3.767016000	0.545946000	-0.040857000				
H	-2.643067000	-1.698197000	-0.965393000	H	-3.189442000	1.389348000	-1.981965000				
H	-3.159664000	-2.668723000	0.426293000	H	-2.645687000	-0.286737000	-1.752072000				
H	-3.380040000	1.131292000	-0.173861000	H	-3.605834000	1.878574000	1.711433000				
H	-4.516126000	1.131324000	1.194505000	H	-2.547084000	0.461444000	1.759416000				
H	-4.824469000	-0.733027000	-0.782060000	H	-4.712394000	1.054151000	-0.240123000				
H	-4.981563000	-1.233793000	0.903980000	H	-3.983956000	-0.496588000	0.189080000				
O	0.053858000	2.216539000	0.721466000								
C	0.002854000	3.346567000	-0.168261000								
C	1.264943000	2.261503000	1.480314000								
C	1.314399000	4.106121000	0.021129000								
H	-0.115367000	2.962185000	-1.183035000								
H	-0.877559000	3.943634000	0.082193000								
C	2.236579000	3.045814000	0.621566000								
H	1.072472000	2.768237000	2.435168000								
H	1.568589000	1.233244000	1.685359000								
H	1.183497000	4.936114000	0.721419000								
H	1.687634000	4.516132000	-0.918273000								
H	3.063427000	3.468142000	1.195345000								
H	2.637843000	2.400269000	-0.162019000								

XeO ₃ :(DEC) ₃				XeO ₃ :(DEC) ₂				XeO ₃ :(DEC) ₁			
Xe	-0.000051000	-0.000403000	0.478317000	Xe	-0.090188000	0.709304000	0.623060000	Xe	-1.427522000	0.352796000	0.098870000
O	-1.569854000	-0.299038000	1.232855000	O	-1.437962000	0.149826000	1.618835000	O	-2.543718000	1.713016000	0.040192000
O	0.526103000	1.508415000	1.232911000	O	-0.172682000	2.466202000	0.711838000	O	-2.386453000	-1.064286000	-0.325417000
O	1.043590000	-1.210596000	1.232723000	O	1.321647000	0.306154000	1.608176000	O	-0.351305000	0.588463000	-1.279538000
O	-1.025128000	-1.802694000	-1.362439000	O	1.551405000	-1.224761000	-1.045801000	O	1.188776000	0.758012000	1.397647000
O	2.073372000	0.014609000	-1.360229000	C	2.466690000	-0.446872000	-0.930439000	C	1.643937000	-0.160070000	0.755374000
O	-1.048833000	1.788496000	-1.361398000	O	2.274841000	0.857187000	-1.144514000	O	0.948339000	-1.293111000	0.626746000
C	-0.906994000	2.850174000	-0.784134000	O	3.714826000	-0.746670000	-0.598751000	O	2.806190000	-0.179985000	0.128163000
C	-2.015573000	-2.210367000	-0.785093000	C	3.949563000	-2.116802000	-0.210343000	C	3.533352000	1.070913000	0.098090000
C	2.922136000	-0.639335000	-0.783604000	C	3.562493000	-2.350103000	1.232057000	C	3.019691000	1.970567000	-1.001775000
O	-1.922209000	-3.192204000	0.094334000	H	5.018111000	-2.256484000	-0.374083000	H	4.566192000	0.766775000	-0.069477000
O	-3.247776000	-1.766174000	-0.956605000	H	3.395095000	-2.767236000	-0.888198000	H	3.450799000	1.539958000	1.079111000
O	-1.803456000	3.259460000	0.096167000	H	3.771598000	-3.387873000	1.503081000	H	3.604111000	2.893494000	-0.1019426000
O	0.092771000	3.696210000	-0.956743000	H	4.129343000	-1.698193000	1.898972000	H	3.110236000	1.487628000	-1.976337000
O	3.725503000	-0.067843000	0.096199000	H	2.500930000	-2.155301000	1.385260000	H	1.972758000	2.228085000	-0.838384000
C	3.154338000	-1.928242000	-0.956362000	C	3.284960000	1.813746000	-0.750581000	C	1.340607000	-2.278436000	-0.358666000
C	1.223936000	3.263881000	-1.751208000	C	2.756302000	3.181658000	-1.094008000	C	0.323688000	-3.387756000	-0.305018000
C	2.479646000	3.331524000	-0.915886000	H	4.209525000	1.582266000	-1.282134000	H	2.346483000	-2.626044000	-0.117838000
H	1.260493000	3.945650000	-2.603421000	H	3.454922000	1.697026000	0.321740000	H	1.360159000	-1.786829000	-1.333206000
H	1.035315000	2.254234000	-2.110905000	H	3.490405000	3.936970000	-0.804560000	H	0.581764000	-4.150978000	-1.042351000
H	3.331711000	3.027948000	-1.528180000	H	2.575830000	3.273095000	-2.166872000	H	0.307261000	-3.857106000	0.680509000
H	2.658682000	4.345014000	-0.549951000	H	1.825446000	3.383878000	-0.562527000	H	-0.675871000	-3.014167000	-0.531936000
H	2.412326000	2.648897000	-0.069312000	O	-2.171299000	0.692386000	-1.282382000				
C	-1.480751000	4.337405000	0.993985000	C	-2.563736000	-0.421270000	-1.007050000				
C	-2.576041000	4.386188000	2.027451000	O	-1.698689000	-1.416137000	-0.862584000				
H	-1.410929000	5.266741000	0.423595000	O	-3.825405000	-0.775003000	-0.823207000				
H	-0.508359000	4.128335000	1.442899000	C	-4.787051000	0.304933000	-0.798929000				
H	-2.376537000	5.190516000	2.739077000	C	-4.806673000	0.988729000	0.548713000				
H	-3.546873000	4.571642000	1.563577000	H	-5.733835000	-0.185787000	-1.023757000				
H	-2.627446000	3.444246000	2.576029000	H	-4.542952000	1.000949000	-1.602313000				
C	-3.017002000	-3.451710000	0.992332000	H	-5.564273000	1.776119000	0.545837000				
C	-2.511693000	-4.425259000	2.025281000	H	-5.050018000	0.280311000	1.342728000				
H	-3.857043000	-3.855336000	0.421976000	H	-3.839663000	1.440666000	0.771170000				
H	-3.321687000	-2.505169000	1.441759000	C	-2.091856000	-2.638061000	-0.207992000				
H	-3.307870000	-4.654582000	2.737089000	C	-0.823324000	-3.381986000	0.119884000				
H	-2.187409000	-5.358714000	1.560967000	H	-2.740157000	3.200983000	-0.883346000				
H	-1.669899000	-3.999335000	2.573731000	H	-2.655984000	-2.382676000	0.690377000				
C	-3.437828000	-0.568940000	-1.749124000	H	-1.069579000	-4.341099000	0.580985000				
C	-4.126092000	0.482834000	-0.912969000	H	-0.231892000	-3.563560000	-0.778283000				
H	-4.044723000	-0.876516000	-2.603227000	H	-0.210377000	-2.811831000	0.819926000				
H	-2.468550000	-0.226330000	-2.106062000								
H	-4.288249000	1.373722000	-1.523788000								
H	-5.093018000	0.130250000	-0.540478000								

H	-3.502797000	0.764244000	-0.064706000
C	2.213347000	-2.691311000	-1.750047000
C	1.645626000	-3.813448000	-0.914803000
H	2.784269000	-3.062989000	-2.603459000
H	1.432498000	-2.023089000	-2.107943000
H	0.956251000	-4.399473000	-1.526699000
H	2.434532000	-4.475131000	-0.550208000
H	1.088889000	-3.414638000	-0.067339000
C	4.499021000	-0.886506000	0.992733000
C	5.089750000	0.037271000	2.026073000
H	5.268476000	-1.411042000	0.421171000
H	3.832598000	-1.624612000	1.441990000
H	5.687474000	-0.537886000	2.736760000
H	5.735069000	0.785755000	1.561940000
H	4.300154000	0.552237000	2.575786000

XeO ₃ :(tBut) ₃				XeO ₃ :(tBut) ₂				XeO ₃ :(tBut) ₁			
Xe	-0.000569000	0.004606000	-1.284586000	Xe	-0.008693000	-1.144291000	-0.092270000	Xe	1.243243000	-0.003169000	-0.154700000
O	-0.062108000	1.605307000	-2.032548000	O	-1.505670000	-2.075468000	-0.021658000	O	2.964004000	-0.321238000	-0.357551000
O	-1.354505000	-0.844614000	-2.040435000	O	0.326715000	-0.726198000	1.591080000	O	0.713377000	-1.157557000	1.067553000
O	1.413194000	-0.739328000	-2.041793000	O	1.206127000	-2.363385000	-0.492550000	O	1.166169000	1.583361000	0.613576000
O	-2.196157000	0.641697000	0.244063000	O	-1.524081000	1.082066000	0.302292000	O	-1.341448000	0.707869000	-0.504756000
H	-2.824166000	0.505748000	-0.475612000	H	-1.438561000	1.124646000	1.261849000	H	-1.297328000	1.547766000	-0.031641000
O	0.536129000	-2.227496000	0.229649000	O	2.158096000	0.312276000	-0.852410000	C	-2.514011000	-0.019627000	-0.059657000
H	0.957735000	-2.703746000	-0.495758000	H	2.693598000	-0.472690000	-1.022219000	C	-3.753961000	0.670648000	-0.613915000
O	1.660648000	1.579992000	0.243865000	C	2.922256000	1.229959000	-0.034963000	H	-3.712841000	0.718017000	-1.703830000
H	1.859087000	2.192029000	-0.475000000	C	-2.917415000	1.224543000	-0.060101000	H	-4.655550000	0.127282000	-0.223086000
C	-0.374111000	-3.099719000	0.932089000	C	3.984715000	1.890721000	-0.905291000	H	-3.838229000	1.689949000	-0.226741000
C	-2.498387000	1.869037000	0.940350000	H	3.521551000	2.411464000	-1.745776000	C	-2.541485000	-0.057844000	1.462415000
C	2.873768000	1.221188000	0.938156000	H	4.561917000	2.613266000	-0.323944000	H	-1.633098000	-0.519962000	1.850373000
C	0.421609000	-4.221239000	1.589793000	H	4.681015000	1.146951000	-1.302556000	H	-2.624570000	0.952098000	1.875884000
H	1.174582000	-3.811470000	2.266222000	C	3.556559000	0.472613000	1.124307000	H	-3.404052000	-0.629062000	1.812010000
H	-0.239355000	-4.876600000	2.161360000	H	2.791254000	-0.037850000	1.710227000	C	-2.358938000	-1.413064000	-0.639170000
H	0.928870000	-4.832710000	0.837771000	H	4.270825000	-0.272423000	0.759798000	H	-2.269671000	-1.368000000	-1.727118000
C	-1.406007000	-3.658750000	-0.038981000	H	4.100236000	1.160477000	1.775647000	H	-1.475822000	-1.904450000	-0.225959000
H	-1.928186000	-2.849395000	-0.550645000	C	1.918007000	2.251007000	0.466114000	H	-3.230396000	-2.022673000	-0.394682000
H	-0.927248000	-4.285317000	-0.797528000	H	1.397300000	2.720665000	-0.370832000				
H	-2.134424000	-4.275848000	0.491913000	H	1.180351000	1.774481000	1.112883000				
C	-1.031438000	-2.215773000	1.976948000	H	2.425664000	3.029686000	1.038429000				
H	-0.276991000	-1.781741000	2.637277000	C	-3.308031000	2.692315000	0.065093000				
H	-1.587763000	-1.404573000	1.504159000	H	-2.673309000	3.313610000	-0.569884000				
H	-1.723669000	-2.801400000	2.585009000	H	-4.348629000	2.838465000	-0.233109000				
C	-3.854162000	1.731339000	1.623251000	H	-3.202828000	3.035318000	1.098007000				
H	-3.854401000	0.879790000	2.306842000	C	-2.999369000	0.761558000	-1.503624000				
H	-4.090981000	2.633500000	2.191674000	H	-2.757624000	-0.300599000	-1.579801000				
H	-4.648877000	1.582986000	0.886281000	H	-4.009026000	0.906186000	-1.891654000				
C	-1.386887000	2.017628000	1.963677000	H	-2.309044000	1.333713000	-2.128053000				
H	-0.415787000	2.094931000	1.471723000	C	-3.776229000	0.349261000	0.842778000				
H	-1.543636000	2.915806000	2.564140000	H	-3.456417000	-0.691623000	0.780780000				
H	-1.369179000	1.155008000	2.633950000	H	-3.705528000	0.677014000	1.884860000				
C	-2.497233000	3.033380000	-0.041829000	H	-4.825780000	0.414747000	0.548009000				
H	-1.544075000	3.088899000	-0.569054000								
H	-3.290077000	2.914930000	-0.786600000								
H	-2.671451000	3.975255000	0.483203000								
C	2.443754000	0.182554000	1.958499000								
H	2.024496000	-0.695330000	1.463893000								
H	3.298814000	-0.133502000	2.559188000								
H	1.687724000	0.598228000	2.628822000								
C	3.878518000	0.637106000	-0.046614000								
H	3.445263000	-0.211541000	-0.577313000								
H	4.176156000	1.384571000	-0.788240000								
H	4.779775000	0.309959000	0.476773000								
C	3.437677000	2.459878000	1.624569000								
H	2.703010000	2.885799000	2.311075000								
H	4.337659000	2.208910000	2.190374000								
H	3.707609000	3.224123000	0.889880000								

XeO ₃ :(H ₂ O) ₃				XeO ₃ :(H ₂ O) ₂				XeO ₃ :(H ₂ O) ₁			
Xe	0.000105000	0.001159000	-0.152824000	Xe	0.000018000	-0.243268000	-0.093178000	Xe	0.234393000	0.000022000	-0.153010000
O	0.011513000	1.604063000	-0.900397000	O	1.389605000	-1.328651000	-0.034199000	O	-0.195901000	1.407958000	0.818186000
O	-1.393816000	-0.789976000	-0.901249000	O	-1.388734000	-1.329726000	-0.034754000	O	1.993404000	-0.000467000	-0.210023000
O	1.382227000	-0.808978000	-0.902789000	O	-0.000597000	0.567658000	1.477377000	O	-0.196631000	-1.407591000	0.818386000
O	-2.148262000	1.249478000	1.098140000	O	-2.111976000	1.523217000	-0.406458000	O	-2.509309000	-0.000108000	-0.426305000
H	-2.030399000	2.066594000	0.599677000	H	-2.791435000	0.841429000	-0.344179000	H	-2.694019000	-0.764979000	0.131072000
H	-2.791631000	0.743534000	0.587901000	H	-2.061201000	1.902815000	0.478266000	H	-2.695739000	0.765471000	0.129517000
O	-0.012119000	-2.487461000	1.094208000	O	2.111708000	1.523322000	-0.406590000				
H	-0.781883000	-2.787728000	0.596873000	H	2.061432000	1.905016000	0.477250000				
H	0.744453000	-2.793014000	0.579961000	H	2.790156000	0.840656000	-0.342700000				
O	2.160736000	1.227094000	1.099424000								
H	2.802035000	0.713043000	0.594875000								
H	2.049513000	2.041228000	0.594497000								

XeO ₃ :(DEA) ₃				XeO ₃ :(DEA) ₂				XeO ₃ :(DEA) ₁			
Xe	0.000911000	0.006887000	-0.805288000	Xe	-0.104508000	-1.002201000	-0.071065000	Xe	-0.989218000	-0.006402000	-0.107185000
O	0.060345000	1.596028000	-1.585032000	O	1.237228000	-2.139004000	0.133152000	O	-0.601318000	-0.461929000	1.553595000
O	-1.402480000	-0.731178000	-1.594438000	O	-1.410617000	-2.051920000	-0.642798000	O	-2.739292000	-0.227817000	-0.208631000
O	1.342161000	-0.833787000	-1.598994000	O	-0.554410000	-0.611059000	1.593080000	O	-0.774246000	1.742474000	-0.181363000
C	-2.988741000	1.838865000	-0.425986000	C	2.135424000	1.025149000	1.772266000	C	2.290290000	0.979180000	0.517710000
C	-2.924357000	-0.006709000	1.169877000	C	3.184174000	0.238773000	-0.276174000	C	2.112266000	-1.444857000	0.292583000
H	-2.866613000	1.266999000	-1.349533000	H	1.979301000	0.046979000	2.235587000	H	1.622043000	1.141885000	1.368331000
H	-2.927464000	-0.777920000	0.395106000	H	3.276967000	-0.763604000	0.147061000	H	1.678015000	-1.501070000	1.293465000
C	3.098782000	1.634291000	-0.439368000	C	-1.190351000	2.247487000	-0.979461000	H	3.273567000	0.710135000	0.930138000

C	1.480624000	2.537730000	1.149769000	H	-1.876043000	3.103620000	-1.080803000	H	3.203236000	-1.528476000	0.407981000
H	2.548238000	1.810965000	-1.367021000	H	-0.532863000	2.481423000	-0.135845000	C	2.408804000	2.234237000	-0.322705000
H	0.815934000	2.929314000	0.375157000	C	-0.386151000	2.080922000	-2.254091000	H	3.118137000	2.092374000	-1.144845000
C	1.462632000	-2.551644000	1.140863000	H	0.333100000	1.263025000	-2.176638000	H	1.441508000	2.520111000	-0.736033000
H	1.773416000	-3.587068000	1.353258000	H	-1.037613000	1.870898000	-3.107149000	H	2.774767000	3.064229000	0.284547000
H	2.130905000	-2.175605000	0.361701000	H	0.170381000	2.991970000	-2.484284000	C	1.595444000	-2.579069000	-0.571318000
C	1.579934000	-1.716064000	2.400327000	C	-2.843268000	1.198824000	0.470951000	H	0.503206000	-2.603793000	-0.610937000
H	1.252307000	-0.689946000	2.224316000	H	-2.249177000	1.302029000	1.382763000	H	1.968150000	-2.504551000	-1.597465000
H	0.967236000	-2.125470000	3.209498000	H	-3.418757000	2.130303000	0.348955000	H	1.920116000	-3.541917000	-0.172746000
H	2.612944000	-1.687227000	2.753993000	C	-3.780720000	0.015195000	0.595166000	N	1.756851000	-0.140894000	-0.260597000
C	-0.136189000	-3.495536000	-0.443486000	H	-4.396601000	-0.096112000	-0.302847000	H	2.095093000	-0.075736000	-1.216683000
H	0.291407000	-3.105234000	-1.370785000	H	-3.227672000	-0.911667000	0.742285000				
H	0.391882000	-4.434242000	-0.213510000	H	-4.455012000	0.155763000	1.442296000				
C	-1.617908000	-3.766143000	-0.609488000	H	3.156349000	1.347184000	2.029424000				
H	-2.049754000	-4.182845000	0.307262000	H	4.094832000	0.795294000	-0.004388000				
H	-2.147719000	-2.849660000	-0.868288000	C	1.129589000	2.024524000	2.304740000				
H	-1.785961000	-4.490986000	-1.408636000	H	1.282648000	3.015587000	1.863720000				
H	3.644618000	2.561820000	-0.205445000	H	0.111791000	1.694735000	2.096038000				
H	2.221680000	3.324843000	1.361468000	H	1.230726000	2.129444000	3.386694000				
H	-4.063352000	1.838293000	-0.184449000	C	3.058449000	0.154926000	-1.783913000				
H	-3.978305000	0.225130000	1.391784000	H	2.223612000	-0.484031000	-2.081155000				
C	4.078047000	0.490102000	-0.607100000	H	2.913917000	1.143328000	-2.231462000				
H	4.654224000	0.324541000	0.310057000	H	3.962427000	-0.274065000	-2.220509000				
H	3.553287000	-0.428494000	-0.868854000	N	2.007683000	0.856935000	0.326809000				
H	4.790127000	0.711627000	-1.404695000	N	-1.915410000	1.032868000	-0.643760000				
C	0.705108000	2.215647000	2.411838000	H	1.851540000	1.764507000	-0.102246000				
H	-0.026385000	1.425504000	2.234395000	H	-2.416794000	0.684679000	-1.455699000				
H	1.369712000	1.878961000	3.213613000								
H	0.171674000	3.096264000	2.776410000								
C	-2.236740000	-0.507375000	2.424433000								
H	-1.183905000	-0.723948000	2.235769000								
H	-2.284508000	0.233351000	3.228679000								
H	-2.711219000	-1.420288000	2.791150000								
C	-2.502923000	3.262680000	-0.609552000								
H	-3.060438000	3.756060000	-1.408361000								
H	-2.647908000	3.851175000	0.303242000								
H	-1.446487000	3.275363000	-0.877192000								
N	-2.237627000	1.156091000	0.625577000								
N	2.124898000	1.347263000	0.612427000								
N	0.107185000	-2.512367000	0.610463000								
H	-2.047677000	1.816238000	1.373048000								
H	2.592107000	0.849569000	1.363835000								
H	-0.554200000	-2.669434000	1.364262000								

XeO ₃ :(2NP) ₃				XeO ₃ :(2NP) ₂				XeO ₃ :(2NP) ₁			
Xe	-0.321440000	-0.559651000	-0.783915000	Xe	0.172668000	-1.356364000	-0.111905000	Xe	1.354233000	-0.045018000	-0.135593000
O	-1.366800000	0.698883000	-1.450337000	O	0.139853000	-0.395464000	1.368256000	O	0.717338000	-0.902954000	1.263572000
O	-1.209941000	-2.049156000	-1.099994000	O	1.812389000	-2.006141000	-0.153850000	O	0.797469000	1.616277000	0.060847000
O	1.022873000	-0.605675000	-1.923972000	O	-0.856608000	-2.737533000	0.245383000	O	3.097347000	0.015693000	0.100666000
O	2.843838000	-0.976716000	2.457782000	O	-3.477096000	1.467666000	-1.751561000	O	-2.529348000	-1.917556000	-0.153624000
O	1.402874000	-1.770576000	1.079147000	O	-2.055604000	0.008567000	-1.086326000	O	-1.150997000	-0.609996000	-1.152718000
O	2.925710000	2.690192000	0.837281000	O	1.220968000	2.732714000	0.340342000	N	-2.123089000	-0.822211000	-0.436871000
O	1.358868000	1.254378000	0.560000000	O	1.182539000	1.084063000	-1.033658000	C	-2.853288000	0.365254000	0.154317000
O	-3.473690000	1.544822000	1.187896000	N	-2.906062000	0.860947000	-0.881295000	H	-3.890691000	0.025914000	0.164241000
O	-0.020861000	-0.023716000	1.381756000	N	1.752104000	1.821983000	-0.243250000	C	-2.669853000	1.595564000	-0.702557000
N	1.804636000	2.388673000	0.508238000	C	3.216056000	1.573067000	0.052060000	H	-3.289884000	2.394490000	-0.290618000
N	-3.149901000	0.383659000	1.156647000	H	3.619985000	2.584891000	0.125584000	H	-1.631799000	1.927041000	-0.693586000
N	2.544458000	-1.486053000	1.408448000	C	-3.244576000	1.201077000	0.551635000	H	-2.978844000	1.421457000	-1.734293000
C	-4.222123000	-0.621497000	0.791591000	H	-4.192968000	1.730416000	0.455645000	C	-2.348567000	0.541230000	1.578776000
H	-5.096996000	-0.238723000	1.321386000	C	3.867347000	0.785077000	-1.059461000	H	-2.444620000	-0.381573000	2.151075000
C	0.908883000	3.480134000	-0.028548000	H	4.937263000	0.719614000	-0.850931000	H	-1.306796000	0.860846000	1.588091000
H	1.427375000	4.390067000	0.274638000	H	3.464672000	-0.226499000	-1.108543000	H	-2.948534000	1.314299000	2.062045000
C	3.670638000	-1.777808000	0.438455000	H	3.736613000	1.266584000	-2.029493000				
H	4.481897000	-2.079915000	1.103691000	C	3.291744000	0.881124000	1.404811000				
C	3.288932000	-2.882543000	-0.518538000	H	2.727878000	1.454373000	2.173044000				
H	2.490817000	-2.562755000	-1.187646000	H	2.862806000	-0.119414000	1.353127000				
H	4.164636000	-3.129650000	-1.122685000	H	4.342365000	0.791191000	1.686427000				
H	2.970709000	-3.783765000	0.007446000	C	-2.157382000	2.131654000	1.061985000				
C	4.027210000	-0.473149000	-0.256444000	H	-2.418578000	2.447298000	-3.373767000				
H	3.218341000	-0.162287000	-0.917855000	H	-1.196245000	1.620649000	1.100889000				
H	4.231480000	0.319408000	0.462969000	H	-2.065424000	3.021079000	0.437209000				
H	4.921623000	-0.638935000	-0.860113000	C	-3.394279000	-0.062878000	1.370471000				
C	-3.845779000	-2.008837000	1.254762000	H	-2.439473000	-0.568033000	1.506016000				
H	-4.688687000	-2.674994000	1.058620000	H	-3.771999000	0.212961000	2.357145000				
H	-2.979081000	-2.381777000	0.709367000	H	-4.103252000	-0.757642000	0.917105000				
H	-3.629367000	-2.035354000	2.323536000								
C	-4.440445000	-0.525720000	-0.710856000								
H	-4.662974000	0.497294000	-1.014107000								
H	-3.563567000	-0.877380000	-1.253947000								
H	-5.287816000	-1.160566000	-0.976029000								
C	-0.464203000	3.381805000	0.599933000								
H	-1.049380000	4.247636000	0.283829000								
H	-0.990925000	2.486479000	0.276394000								
H	-0.411584000	3.387028000	1.689777000								
C	0.895811000	3.348498000	-1.542727000								
H	0.415105000	2.419872000	-1.850424000								
H	0.320395000	4.178435000	-1.956704000								
H	1.904920000	3.392346000	-1.956288000								

XeO ₃ :(DEE) ₃				XeO ₃ :(DEE) ₂				XeO ₃ :(DEE) ₁			
Xe	0.005610000	-0.001454000	-0.833514000	Xe	0.147018000	-0.908638000	-0.227779000	Xe	-0.990719000	0.018945000	-0.113711000
O	1.229394000	-1.019517000	-1.595039000	O	1.614834000	-1.883873000	-0.271746000	O	-2.704187000	-0.037210000	-0.523253000
O	0.280204000	1.571505000	-1.585370000	O	0.139691000	-0.056870000	-1.772070000	O	-0.764987000	1.576293000	0.678905000
O	-1.488957000	-0.546346000	-1.597777000	O	-1.128707000	-2.117940000	-0.390153000	O	-0.792220000	-1.182788000	1.160095000

C	3.357006000	0.973086000	-0.292619000	C	3.233728000	0.747348000	-0.112379000	O	1.769879000	-0.065526000	-0.226370000
C	1.932333000	2.302452000	1.064183000	C	1.473372000	2.348817000	-0.066416000	C	2.241253000	-1.297374000	0.314479000
H	2.989942000	1.178638000	-1.304637000	H	3.074878000	0.217106000	-1.058163000	H	3.337759000	-1.260966000	0.337357000
H	1.554624000	2.893637000	0.221307000	H	1.167695000	2.220001000	-1.112059000	H	1.882857000	-1.405843000	1.344848000
C	-0.886047000	-3.377476000	-0.301551000	O	-2.187595000	0.550892000	0.360458000	C	1.772326000	-2.448959000	-0.544958000
C	1.019788000	-2.872030000	1.016350000	O	1.967372000	1.114252000	0.439717000	H	0.688705000	-2.570407000	-0.500345000
H	-0.541499000	-3.169024000	-1.320895000	C	-2.911723000	-0.205983000	1.321698000	H	2.077526000	-2.308466000	-1.584040000
H	1.700183000	-2.875944000	0.155990000	H	-3.859334000	0.310045000	1.525426000	H	2.213020000	-3.380097000	-0.182209000
O	-1.987859000	1.463057000	0.599709000	H	-3.142651000	-1.195228000	0.910250000	C	2.354281000	1.073671000	0.405154000
O	-0.271732000	-2.454371000	0.596699000	C	-2.099909000	-0.325614000	2.591692000	H	1.875911000	1.233268000	1.378677000
O	2.257867000	0.995174000	0.616311000	H	-1.215661000	-0.953617000	2.459348000	H	3.415408000	0.858560000	0.582055000
C	-2.974987000	0.543378000	1.042754000	H	-1.779672000	0.656716000	2.945016000	C	2.203367000	2.286519000	-0.483194000
H	-3.839900000	1.113094000	1.407973000	H	-2.703460000	-0.791426000	3.373473000	H	2.680376000	2.119225000	-1.451223000
H	-3.310953000	-0.067987000	0.196480000	C	-2.909559000	0.723089000	-0.858873000	H	1.152810000	2.533661000	-0.638167000
C	-2.403708000	-0.313260000	2.147585000	H	-2.790751000	-0.179282000	-1.470116000	H	2.679189000	3.148731000	-0.010460000
H	-1.580420000	-0.936955000	1.797484000	H	-3.975203000	0.826529000	-0.618976000				
H	-2.051387000	0.308386000	2.973813000	C	-2.412400000	1.952638000	-1.583697000				
H	-3.177056000	-0.983739000	2.529972000	H	-2.557880000	2.847747000	-0.975104000				
C	-2.499773000	2.431341000	-0.314160000	H	-1.355515000	1.855985000	-1.829850000				
H	-2.479862000	2.013338000	-1.327021000	H	-2.967155000	2.076998000	-2.516595000				
H	-3.547225000	2.630688000	-0.055202000	H	3.791060000	1.665646000	-0.333568000				
C	-1.687032000	-3.702714000	-0.226153000	H	2.288640000	3.083089000	-0.044387000				
H	-1.726499000	4.119222000	0.782982000	C	0.322541000	2.816436000	0.792435000				
H	-0.648771000	3.513472000	-0.494916000	H	-0.511599000	2.114421000	0.774319000				
H	-2.087095000	4.444691000	-0.921433000	H	0.646375000	2.948983000	-0.182182000				
H	-0.553131000	-4.388833000	-0.036667000	H	-0.047925000	3.775582000	0.422691000				
H	0.945489000	-3.902294000	1.389284000	C	3.997649000	-0.106314000	0.873283000				
H	4.048520000	1.779322000	-0.017391000	H	4.961863000	-0.389446000	0.444031000				
H	2.850110000	2.783918000	1.427386000	H	4.180779000	0.442388000	1.799831000				
C	-2.390748000	-3.278344000	-0.197846000	H	3.449568000	-1.019947000	1.101206000				
H	-2.725230000	-3.500519000	0.818071000								
H	-2.730522000	-2.282240000	-0.477468000								
H	-2.853885000	-3.997252000	-0.878038000								
C	1.516095000	-1.950804000	2.104879000								
H	1.659731000	-0.932256000	1.743253000								
H	0.816550000	-1.934014000	2.943783000								
H	2.482811000	-2.303047000	2.472582000								
C	0.910364000	2.206768000	2.171205000								
H	-0.028657000	1.777777000	1.820120000								
H	1.291717000	1.600082000	2.995596000								
H	0.686122000	3.204904000	2.554801000								
C	4.055517000	-0.365436000	-0.220559000								
H	4.897613000	-0.379932000	-0.916686000								
H	4.437346000	-0.550109000	0.786165000								
H	3.374236000	-1.168838000	-0.497634000								

XeO ₃ :(NMe) ₃				XeO ₃ :(NMe) ₂				XeO ₃ :(NMe) ₁			
Xe	0.000310000	-0.000375000	-0.519749000	Xe	0.000013000	-0.834766000	-0.220448000	Xe	-0.990285000	-0.174717000	-0.010686000
O	-1.498342000	0.543107000	-1.280245000	O	1.388208000	-1.920422000	-0.252016000	O	-2.749040000	-0.153823000	-0.002910000
O	0.279101000	-1.570172000	-1.279789000	O	-1.387884000	-1.920769000	-0.252489000	O	-0.522098000	0.876928000	-1.345746000
O	1.220529000	1.025865000	-1.279779000	O	-0.000347000	-0.188481000	1.423314000	O	-0.512477000	0.693058000	1.447948000
O	4.089311000	-1.480860000	1.533643000	O	-3.742434000	2.171676000	-0.313685000	O	3.791180000	-0.613977000	-0.015995000
O	2.106621000	-0.764841000	1.127602000	O	-1.903952000	1.126260000	-0.677941000	O	1.672320000	-0.947617000	-0.068723000
O	-0.761275000	4.281555000	1.532755000	O	3.743462000	2.170283000	-0.314715000	N	2.656077000	-0.217477000	0.013849000
O	-0.392341000	2.206081000	1.126629000	O	1.903872000	1.126347000	-0.677673000	C	2.408287000	1.241215000	0.057225000
O	-3.330524000	-2.796722000	1.533150000	N	2.941341000	1.312375000	-0.052958000	H	1.784661000	1.417626000	0.932229000
O	-1.715006000	-1.442569000	1.127003000	N	-2.941218000	1.312587000	-0.052992000	H	3.367558000	1.743146000	0.114141000
N	-0.597217000	3.360543000	0.774617000	C	3.209056000	0.413621000	1.094051000	H	1.841829000	1.512437000	-0.832317000
N	-2.613121000	-2.196310000	0.774997000	H	3.225654000	-0.603692000	0.705949000				
N	3.209350000	-1.163184000	0.775537000	H	4.151818000	0.709857000	1.540042000				
C	-2.816570000	-2.369168000	-0.682214000	C	2.368307000	0.508729000	1.772923000				
H	-1.877523000	-2.733844000	-1.095234000	C	-3.209960000	0.412633000	1.092842000				
H	-3.639039000	-3.060505000	-0.827449000	H	-2.368883000	0.505469000	1.777996000				
H	-3.013724000	-1.381961000	-1.096886000	H	-4.152158000	0.709667000	1.539496000				
C	-0.643146000	3.623435000	-0.682607000	H	-3.228264000	-0.604108000	0.703325000				
H	-1.427901000	2.992491000	-1.096678000								
H	-0.830574000	4.681367000	-0.828021000								
H	0.310934000	3.300594000	-1.095984000								
C	3.460257000	-1.254060000	-0.681698000								
H	3.305893000	-0.258848000	-1.095378000								
H	4.470341000	-1.620228000	-0.827095000								
H	2.703934000	-1.918945000	-1.095540000								

XeO ₃ :(TMEDA) ₃				XeO ₃ :(TMEDA) ₂				XeO ₃ :(TMEDA) ₁			
C	-2.927617000	-1.415980000	0.998334000	C	2.045604000	-0.251751000	2.646063000	Xe	-1.046571000	-0.179711000	-0.097144000
C	2.609676000	-3.001080000	0.046430000	C	2.699447000	1.587656000	1.215932000	O	-0.743029000	-0.070152000	1.641599000
C	2.691821000	-1.817521000	1.003032000	C	1.386562000	2.353253000	1.183360000	O	-1.841553000	-1.757012000	-0.249374000
C	-3.909155000	-0.736644000	0.050670000	H	1.600163000	3.424989000	1.332910000	O	-2.321500000	1.025506000	-0.351874000
H	-2.628269000	-0.695127000	1.763551000	H	0.757643000	2.053710000	2.025204000	C	2.091695000	1.050175000	0.468719000
H	-3.412740000	-2.256306000	1.525865000	C	-3.126949000	-0.235311000	-0.114454000	C	2.450249000	-0.241689000	-0.248772000
H	1.881219000	-2.762139000	-0.729685000	C	-2.405952000	-0.988985000	0.994698000	C	2.959682000	1.729713000	0.424564000
H	3.581511000	-3.157169000	-0.457254000	H	-2.388676000	0.078908000	-0.856302000	H	1.902745000	0.841639000	1.523494000
C	3.658443000	-1.814047000	1.537382000	H	-3.831473000	-0.910551000	-0.634117000	H	2.546667000	-0.057349000	-1.321106000
H	1.913987000	-1.929714000	1.762703000	H	-1.995447000	-0.259192000	1.701279000	H	3.446576000	-0.566232000	0.092577000
H	-4.529795000	-1.490996000	-0.467090000	H	-3.116185000	-1.616221000	1.561282000	N	1.471742000	-1.306398000	-0.058302000
H	-3.335982000	-0.214153000	-0.716885000	Xe	0.893532000	-0.515177000	-0.836252000	N	0.901745000	1.711480000	-0.054448000
C	1.314681000	3.752018000	0.033998000	O	-0.340009000	-0.320889000	-2.098972000	C	0.432629000	2.749129000	0.848018000
C	0.233778000	2.346265000	0.982033000	O	1.350768000	-2.230332000	-0.871915000	H	1.167976000	3.560517000	0.953962000
H	1.479799000	2.994549000	-0.733895000	O	2.305945000	0.206468000	-1.626361000	H	-0.501503000	3.162918000	0.466720000
H	0.974422000	4.667941000	-0.483605000	C	-1.722530000	-2.758652000	-0.509780000	H	0.231615000	2.310644000	1.824800000
H	0.706488000	2.631696000	1.752412000	H	-2.536542000	-3.407670000	-0.149052000	C	1.057786000	2.215296000	-1.403946000
H	-0.252201000	4.090038000	1.503229000	H	-2.049197000	-2.229675000	-1.403093000	H	1.122918000	2.677863000	-1.723214000
Xe	-0.000756000	-0.007945000	-1.074181000	H	-0.868211000	-3.734568000	-0.786846000	H	1.861930000	2.963160000	-1.478196000
O	1.076550000	1.143782000	-1.878305000	C	-4.356349000	1.705321000	-0.726376000	H	1.282838000	1.403429000	-2.097691000

O	-1.543798000	0.341512000	-1.869439000	H	-5.131186000	1.151561000	-1.286614000	C	1.596193000	-1.954945000	1.235484000
O	0.465269000	-1.529702000	-1.850583000	H	-4.803317000	2.630414000	-0.356123000	H	0.771456000	-2.655215000	1.369737000
N	2.502755000	-0.524846000	0.353183000	H	-3.561716000	1.964663000	-1.428149000	H	2.549289000	-2.499096000	1.319744000
N	2.175574000	-4.213330000	0.715571000	C	-0.782824000	2.460280000	0.144029000	H	1.527434000	-1.218286000	2.032968000
N	-1.720469000	-1.901316000	0.338629000	H	-1.223489000	1.827535000	0.914317000	C	1.501626000	-2.279332000	-1.134603000
N	-4.743352000	0.234701000	0.733746000	H	-0.945470000	3.512354000	0.426686000	H	2.468540000	-2.801015000	-1.198469000
N	-0.789415000	2.438384000	0.327249000	H	-1.314502000	2.270264000	-0.787517000	H	0.714351000	-3.017247000	-0.975828000
N	2.573148000	3.983649000	0.718579000	H	3.248908000	1.769612000	0.291160000	H	1.315491000	-1.785139000	-2.091261000
C	1.848451000	-5.239121000	-0.248398000	H	3.317481000	1.978623000	2.042862000				
H	2.719118000	-5.550648000	-0.853187000	H	1.064445000	0.183417000	2.839422000				
H	1.462549000	-6.121712000	0.266467000	H	1.946475000	-1.336785000	2.681413000				
H	1.078109000	-4.875253000	-0.931219000	H	2.724036000	0.059732000	3.456814000				
C	3.142099000	-4.693978000	1.676334000	N	2.541117000	0.143315000	1.344008000				
H	2.761436000	-5.593325000	2.164610000	N	0.622600000	2.154615000	-0.042013000				
H	4.113701000	-4.942130000	1.210385000	N	-1.305892000	-1.811796000	0.512510000				
H	3.320358000	-3.945548000	2.449957000	N	-3.816392000	0.943348000	0.377423000				
C	-0.844405000	-2.507456000	1.321935000	C	-0.689913000	-2.514984000	1.621046000				
H	0.049189000	-2.906390000	0.845248000	H	0.196414000	-3.041279000	1.265610000				
H	-0.549439000	-1.762189000	2.065714000	H	-0.394966000	-1.803301000	2.394089000				
H	-1.335910000	-3.337868000	1.854643000	H	-1.378729000	-3.243739000	2.078010000				
C	-2.035705000	-2.853295000	-0.714836000	C	-4.857975000	0.623383000	1.328588000				
H	-2.639749000	-3.690442000	-0.329566000	H	-5.350346000	1.541871000	1.653721000				
H	-2.581040000	-2.357421000	-1.516673000	H	-5.628710000	-0.045839000	0.903644000				
H	-1.111451000	-3.239778000	-1.138739000	H	-4.440307000	0.140700000	2.212986000				
C	-5.651656000	-0.379120000	1.675495000	C	1.161917000	2.916187000	-1.155573000				
H	-6.243391000	0.391425000	2.173700000	H	0.630408000	2.645549000	-2.068264000				
H	-6.349055000	-1.086226000	1.189476000	H	1.056843000	3.999029000	-0.983715000				
H	-5.099671000	-0.923013000	2.443462000	H	2.210084000	2.672332000	-1.310333000				
C	-5.459007000	1.052620000	-0.218838000	C	3.785911000	-0.543028000	1.039513000				
H	-6.158969000	0.469026000	-0.843538000	H	4.587940000	-0.263971000	1.740685000				
H	-6.034613000	1.816837000	0.308057000	H	3.629149000	-1.621002000	1.095718000				
H	-4.752311000	1.552815000	-0.884066000	H	4.090240000	-0.300496000	0.022148000				
C	-1.752786000	1.993518000	1.315410000								
H	-2.546735000	1.415475000	0.846344000								
H	-1.255880000	1.372163000	2.065442000								
H	-2.224697000	2.840151000	1.840321000								
C	-1.455151000	3.179386000	-0.732378000								
H	-1.877744000	4.124469000	-0.355001000								
H	-0.752487000	3.396370000	-1.535804000								
H	-2.252425000	2.569633000	-1.151623000								
C	2.495935000	5.065803000	1.673496000								
H	3.460158000	5.188195000	2.170909000								
H	2.229841000	6.028947000	1.200055000								
H	1.751294000	4.850160000	2.441290000								
C	3.638282000	4.207110000	-0.232174000								
H	3.483348000	5.115430000	-0.841740000								
H	4.588993000	4.312793000	0.294994000								
H	3.714973000	3.355581000	-0.911157000								
C	2.577671000	0.526212000	1.349263000								
H	2.485040000	1.505827000	0.883775000								
H	1.775632000	0.401677000	2.082096000								
H	3.535781000	0.508307000	1.894155000								
C	3.490951000	-0.304317000	-0.690778000								
H	4.516057000	-0.398756000	-0.297742000								
H	3.349660000	-1.022079000	-1.497714000								
H	3.355264000	0.690015000	-1.110518000								

XeO ₃ :(TEA) ₃				XeO ₃ :(TEA) ₂				XeO ₃ :(TEA) ₁			
Xe	-0.004502000	0.008949000	-0.892062000	Xe	-0.112635000	-1.094991000	-0.433955000	Xe	1.291129000	0.118054000	-0.097938000
O	0.170593000	-1.580694000	-1.652857000	O	1.134222000	-2.165967000	-1.093787000	O	1.292804000	-0.740376000	1.445884000
O	1.281707000	0.940969000	-1.672828000	O	-1.572653000	-1.885701000	-1.047881000	O	2.989942000	0.544236000	-0.341109000
O	-1.450528000	0.650618000	-1.685373000	O	-0.107011000	1.467007000	1.293043000	O	0.989212000	-1.094084000	-1.346475000
C	3.532658000	-0.915201000	-0.843643000	C	3.038446000	-0.572004000	1.061738000	C	-1.737587000	-1.125288000	1.070629000
C	3.045762000	-0.030056000	1.284094000	C	3.023827000	0.225103000	-1.177348000	C	-1.651032000	1.256429000	1.058653000
H	3.486695000	0.103642000	-1.233184000	H	2.844895000	-1.590278000	0.714389000	H	-1.109091000	-1.073261000	1.962171000
H	3.076761000	0.952045000	0.802289000	H	3.086511000	-0.836931000	-1.418047000	H	-0.997628000	1.188518000	1.935681000
C	-2.612291000	-0.2527129000	-0.873162000	C	-1.433053000	2.116618000	0.356848000	H	-2.781524000	-1.045701000	1.4141713000
C	-1.507809000	-2.623249000	1.206303000	H	-2.097365000	2.857321000	0.830835000	H	-2.679483000	1.243450000	1.450451000
H	-1.719998000	-2.963832000	-1.325934000	H	-0.572314000	2.019051000	1.024156000	C	-1.517034000	-2.459016000	0.383656000
H	-0.672522000	-3.089834000	0.675011000	C	-0.981842000	2.646248000	-0.991955000	H	-2.218057000	-2.627092000	-0.436825000
C	-1.500625000	2.604692000	1.283205000	H	-0.371569000	1.923153000	-1.536814000	H	-0.503812000	-2.546308000	-0.006450000
H	-1.837476000	3.615654000	1.568310000	H	-1.823697000	2.918762000	-1.630543000	H	-1.671357000	-3.259211000	1.110463000
H	-2.353650000	2.134023000	0.784591000	H	-0.378725000	3.545865000	-0.850492000	C	-1.410819000	2.573240000	0.338915000
C	-1.155670000	1.829599000	2.537298000	C	-2.488326000	0.441099000	1.674066000	H	-0.417176000	2.637947000	-0.111420000
H	-0.814464000	0.821981000	2.302570000	H	-1.572236000	0.375529000	2.265882000	H	-2.142990000	2.754680000	-0.449622000
H	-0.382915000	2.317851000	3.133978000	H	-3.089511000	1.255168000	2.111035000	H	-1.492235000	3.393619000	1.054513000
H	-2.043445000	1.735250000	3.166881000	C	-3.244675000	-0.869127000	1.784091000	N	-1.398916000	0.052981000	0.261780000
C	-0.944112000	3.511859000	-0.818606000	H	-4.252664000	-0.802860000	1.368756000	C	-2.004940000	0.062430000	-1.070630000
H	-1.794864000	2.969323000	-1.235395000	H	-2.715695000	-1.678409000	1.283607000	C	-3.527609000	0.103574000	-1.105527000
H	-1.339212000	4.456049000	-0.407301000	H	-3.344803000	-1.132944000	2.839150000	H	-1.631964000	-0.816923000	-1.595497000
C	0.033225000	3.827753000	-1.935700000	H	4.126264000	-0.413978000	0.982651000	H	-1.598008000	0.920270000	-1.612472000
H	0.859940000	4.460135000	-1.602977000	H	4.058148000	0.592932000	-1.089538000	H	-3.873227000	0.123084000	-2.141316000
H	0.445738000	2.922441000	-2.375291000	C	2.618576000	-0.440606000	2.514441000	H	-3.966120000	-0.775238000	-0.628521000
H	-0.499651000	4.378647000	-2.714528000	H	2.943588000	0.501541000	2.962048000	H	-3.927399000	0.989976000	-0.607257000
H	-3.213482000	-3.365307000	-0.482476000	H	1.539234000	-0.536174000	2.624958000				
H	-2.198698000	-3.442174000	1.468385000	H	3.082158000	-1.246318000	3.087843000				
H	4.552839000	-1.058868000	-0.448758000	C	2.322818000	0.948163000	-2.311831000				
H	4.086399000	-0.259432000	1.569903000	H	1.317721000	0.556185000	-2.487808000				
C	-3.406342000	-1.803965000	-1.944896000	H	2.244619000	2.024658000	-2.145747000				
H	-4.370703000	-1.442107000	-1.580043000	H	2.882781000	0.800925000	-3.237660000				
H	-2.850817000	-0.962247000	-2.352079000	N	2.343864000	0.316197000	0.116892000				
H	-3.612790000	-2.506744000	-2.755690000	N	-2.077424000	0.806791000	0.313132000				
C	-1.002544000	-1.982031000	2.482144000	C	2.193720000	1.688850000	0.595966000				
H	-0.310526000	-1.165842000	2.276525000	C	3.479691000	2.483235000	0.814244000				
H	-1.809511000	-1.590550000	3.104740000	H	1.629648000	1.644851000	1.529135000				
H	-0.463280000	-2.723529000	3.076713000	H	1.561500000	2.702870000	-0.116869000				

C	2.196714000	0.047739000	2.535399000	H	3.241624000	3.459468000	1.243314000
H	1.156278000	0.266824000	2.296753000	H	4.159540000	1.976138000	1.501965000
H	2.221923000	-0.874162000	3.119627000	H	4.017261000	2.658396000	-0.119891000
H	2.560786000	0.852081000	3.178887000	C	-3.154042000	0.708009000	-0.674857000
C	3.299230000	-1.887118000	-1.984938000	C	-4.382310000	1.645696000	-0.465103000
H	4.026641000	-1.676515000	-2.772725000	H	-3.482530000	-0.329859000	-0.685656000
H	3.441565000	-2.928701000	-1.686345000	H	-2.715813000	0.877031000	-1.661032000
H	2.300241000	-1.781390000	-2.401675000	H	-5.083261000	1.477133000	-1.246010000
N	2.574041000	-0.967535000	0.269979000	H	-4.826788000	1.474818000	0.496702000
N	-2.135613000	-1.711119000	0.254435000	H	-4.049206000	2.698817000	-0.509705000
N	-0.436203000	2.683550000	0.286440000				
C	2.324210000	-2.318984000	0.762668000				
C	3.523124000	-3.075054000	1.330649000				
H	1.881405000	-2.877013000	-0.063896000				
H	1.546264000	-2.253835000	1.525274000				
H	3.210206000	-4.066319000	1.667744000				
H	4.308485000	-3.214177000	0.584793000				
H	3.965144000	-2.560853000	2.187879000				
C	-3.164696000	-0.847966000	0.828278000				
C	-4.385263000	-1.545932000	1.423741000				
H	-3.470740000	-0.155747000	0.041844000				
H	-2.690076000	-0.234516000	1.595741000				
H	-5.087868000	-0.802995000	1.809075000				
H	-4.913663000	-2.145477000	0.679813000				
H	-4.116136000	-2.205216000	2.252635000				
C	0.852601000	3.132228000	0.807580000				
C	0.896922000	4.536386000	1.405480000				
H	1.567969000	3.045370000	-0.011708000				
H	1.175574000	2.410969000	1.560603000				
H	1.908829000	4.759417000	1.752464000				
H	0.623747000	5.299602000	0.673934000				
H	0.225855000	4.639971000	2.261975000				

XeO ₃ :(DiO) ₃				XeO ₃ :(DiO) ₂				XeO ₃ :(DiO) ₁			
Xe	0.011947000	-0.004341000	1.283218000	Xe	5.692360500	1.728188600	10.324797000	Xe	1.467281000	-0.066024000	-0.129080000
O	1.305926000	0.955901000	2.010749000	O	5.316450000	-0.001596800	10.088189600	O	0.986451000	-0.804553000	1.397814000
O	0.207862000	-1.603225000	2.011896000	O	5.573205700	1.971516600	12.090140300	O	1.268366000	1.670809000	0.092011000
O	-1.459637000	0.627578000	2.032195000	O	7.439186500	1.853627700	9.973108100	O	3.208655000	-0.318461000	-0.226539000
C	-1.027404000	-2.465832000	-0.946509000	C	2.319414600	1.466984200	9.186423400	C	-1.833233000	-1.206161000	-0.113421000
C	-2.880585000	-1.679614000	0.252189000	C	2.327817600	1.673135300	11.543900400	C	-1.794551000	1.114365000	0.231354000
C	-1.957378000	-3.235282000	-1.867145000	C	0.827456800	1.745757800	9.174175200	C	-3.331793000	-1.135557000	-0.354329000
H	-0.713899000	-3.093100000	-0.102957000	H	2.511618000	0.389926200	9.251423400	H	-1.618878000	-1.406468000	0.942652000
H	-0.138315000	-2.15877000	-1.474170000	H	2.814369500	1.861524500	8.298203700	H	-1.379970000	-1.991143000	-0.723444000
C	-3.797461000	-2.454215000	-0.676363000	C	0.836969500	1.953276200	11.516260600	C	-3.291199000	1.161069000	-0.014038000
H	-2.610892000	-2.287246000	1.124753000	H	2.517516800	0.600929600	11.666379700	H	-1.583256000	0.985711000	1.299754000
H	-3.341517000	-0.755400000	0.601296000	H	2.833137000	2.210936000	12.345347100	H	-1.299617000	2.019354000	-0.118804000
H	-1.484635000	-4.161124000	-2.200894000	H	0.338339400	1.191015600	8.372182600	H	-3.814633000	-2.047685000	0.001543000
H	-2.193317000	-2.623026000	-2.751256000	H	0.653145600	2.820286500	9.018023200	H	-3.529301000	-1.029681000	-1.431709000
H	-4.678249000	-2.806866000	-0.136659000	H	0.352195700	1.549694700	12.405912900	H	-3.748337000	1.945269000	0.592010000
H	-4.127583000	-1.802245000	-1.499731000	H	0.663931600	3.038608500	11.480532700	H	-3.486965000	1.377318000	-1.074927000
C	2.634444000	0.356966000	-0.957293000	C	6.076955800	3.048213000	7.035339600	O	-1.211990000	0.023451000	-1.489502000
C	2.911887000	-1.641078000	0.236030000	C	5.775359200	0.702744900	6.928058000	O	-3.909929000	-0.057456000	0.349445000
C	3.767932000	-0.046594000	-1.882715000	C	5.901075000	3.132066300	5.530317700				
H	3.015299000	0.945724000	-0.113739000	H	7.135257300	2.930643100	7.294523800				
H	1.876793000	0.942151000	-1.481451000	H	5.685683500	3.932555300	7.539825500				
C	4.043583000	-0.298999000	-0.697090000	C	5.599888200	0.803127100	5.424891800				
H	3.299459000	-1.100726000	1.108310000	H	6.825532600	0.524430100	7.184193700				
H	2.353487000	-2.510112000	0.584712000	H	5.170475800	-0.093228100	7.360848800				
H	4.320087000	0.833853000	-2.217363000	H	6.519787400	3.928770200	5.114889000				
H	3.359307000	-0.561571000	-2.765812000	H	4.848240900	3.341034400	5.291418500				
H	4.799300000	-2.606753000	-0.160784000	H	6.000565500	-0.083014000	4.931218200				
H	3.650351000	-2.645522000	-1.520579000	H	4.531682100	0.892171000	5.180297100				
C	-1.628740000	2.097184000	-0.942563000	O	5.342439300	1.925767900	7.547347600				
C	-0.037330000	3.336502000	0.250990000	O	6.310528600	1.922291900	4.904642200				
C	-1.848639000	3.281843000	-1.865835000	O	2.922250400	2.119173900	10.314499400				
H	-2.328184000	2.130073000	-0.098212000	O	0.224524800	1.328262400	10.392887300				
H	-1.754866000	1.148206000	-1.466699000								
C	-0.269595000	4.512416000	-0.679755000								
H	-0.697114000	3.400373000	1.125040000								
H	0.995505000	3.289343000	0.596912000								
H	-2.887476000	3.318822000	-2.199800000								
H	-1.198912000	3.188045000	-2.749700000								
H	-0.148884000	5.454493000	-0.141831000								
H	0.459384000	4.482795000	-1.504110000								
O	-3.150562000	-3.596972000	-1.202465000								
O	-1.687958000	-1.307218000	-0.439076000								
O	-0.294956000	2.111608000	-0.435939000								
O	-1.583651000	4.501616000	-1.203746000								
O	1.979231000	-0.804798000	-0.450064000								
O	4.691927000	-0.887521000	-1.222634000								

XeO ₃ :(DME) ₃				XeO ₃ :(DME) ₂				XeO ₃ :(DME) ₁			
C	-1.939398000	-1.144076000	-1.350118000	C	-0.989709000	-1.642728000	2.676875000	C	-2.039910000	-1.959674000	-1.124320000
C	-1.149504000	3.087285000	-2.765260000	C	-1.530973000	-2.636645000	0.586329000	C	-2.246684000	-0.772305000	0.926725000
C	-0.019724000	2.253765000	-1.349125000	C	-0.184290000	-2.848702000	-0.075230000	C	-2.587965000	0.580051000	0.330450000
C	-2.098249000	-2.538224000	-0.764587000	H	-0.247426000	-3.738379000	-0.717971000	H	-3.078172000	1.186602000	-1.104498000
H	-0.938868000	-1.075318000	-1.779162000	H	0.614913000	-3.030222000	0.658463000	H	-3.287615000	0.494963000	-0.513218000
H	-2.667285000	-0.962926000	-2.150028000	C	2.780678000	0.686886000	0.220443000	Xe	1.045773000	-0.071832000	-0.050750000
H	-1.502007000	2.617349000	0.162170000	C	1.862573000	0.354912000	1.386574000	O	1.656167000	1.541162000	-0.428003000
H	-0.814746000	4.105403000	-0.516055000	H	2.183769000	0.798641000	-0.694611000	O	2.403114000	-1.157683000	-0.348642000
H	0.502264000	2.794552000	-2.147622000	H	3.190010000	1.631079000	0.386889000	O	0.839458000	-0.083934000	1.698527000
H	-0.458940000	1.352925000	-1.779669000	H	1.511163000	-0.670426000	1.259655000	C	-1.543558000	2.543367000	-0.480401000
H	-3.147062000	-2.753772000	-0.5111045000	H	2.411438000	0.412614000	2.335762000	H	-2.237930000	2.638161000	-1.323829000
H	-1.511663000	-2.609438000	0.160667000	Xe	-1.210065000	0.708243000	-0.486448000	H	-1.913331000	3.144262000	0.357857000

C	3.248460000	-0.545494000	-0.764989000	O	-0.045747000	1.266785000	-1.695851000	H	-0.557417000	2.899994000	-0.772333000
C	1.961480000	-1.107508000	-1.347707000	O	-1.890680000	2.198370000	0.172244000	O	-1.396075000	1.192778000	-0.099622000
H	3.017244000	0.001675000	0.158195000	O	-2.526776000	0.015610000	-1.433751000	O	-1.438401000	-1.576632000	0.090994000
H	3.959644000	-1.345003000	-0.508588000	C	0.937059000	2.520108000	1.754045000	H	-1.660490000	-0.633966000	1.835743000
H	1.399695000	-0.277086000	-1.777514000	H	1.501598000	2.609519000	2.689427000	H	-3.177177000	-1.299347000	1.179251000
H	2.168477000	-1.829634000	-2.146554000	H	1.480577000	3.027180000	0.951344000	H	-2.161194000	-1.111321000	-1.808407000
Xe	0.000054000	-0.000446000	1.491003000	H	-0.039693000	2.986821000	1.861533000	H	-1.383330000	-2.695456000	-1.587751000
O	1.580048000	0.284174000	2.229612000	C	4.610843000	-0.190615000	-0.932469000	H	-3.020469000	-2.419121000	-0.951806000
O	-0.543490000	-1.511375000	2.229052000	H	5.212758000	0.715544000	-0.783407000				
O	-1.036486000	1.225416000	2.229837000	H	5.227280000	-1.056389000	-0.947511000				
C	-3.267397000	3.895371000	-1.313586000	H	4.100544000	-0.111055000	-1.901657000				
H	-2.987280000	4.941244000	-1.127774000	C	1.230108000	-1.858094000	-1.693315000				
H	-4.010704000	3.865132000	-2.110264000	H	2.145391000	-2.022813000	-1.114433000				
H	-3.709783000	3.488593000	-0.394236000	H	1.077573000	-2.692399000	-2.387594000				
C	-3.343529000	0.202941000	0.028647000	H	1.316836000	-0.931713000	-2.258852000				
H	-3.900776000	0.626523000	-0.814063000	O	0.703923000	1.158197000	1.449242000				
H	-3.878716000	-0.666386000	0.422690000	O	3.694796000	-0.376618000	0.115058000				
H	-3.251782000	0.943559000	0.821563000	O	0.114097000	-1.708804000	-0.843249000				
C	-1.745626000	-4.777773000	-1.311745000	O	-1.575708000	-1.487453000	1.406260000				
H	-2.790910000	-5.056060000	-1.119964000	H	-2.284027000	-2.472887000	-0.187622000				
H	-1.353169000	-5.408062000	-2.109764000	H	-1.805787000	-3.532354000	1.159666000				
H	-1.167532000	-4.957363000	-0.395264000	H	0.056284000	-1.964479000	2.618394000				
C	1.500189000	-2.996660000	0.032527000	H	-1.024678000	-0.670540000	3.165886000				
H	1.410156000	-3.690900000	-0.810109000	H	-1.548473000	-2.372277000	3.275672000				
H	2.521513000	-3.025525000	0.424289000								
H	0.814682000	-3.287973000	0.826851000								
C	5.010451000	0.878774000	-1.317494000								
H	5.774612000	0.114235000	-1.121546000								
H	5.360131000	1.530425000	-2.118231000								
H	4.875711000	1.473328000	-0.403844000								
C	1.840941000	2.799239000	0.038538000								
H	2.483024000	3.083505000	-0.802371000								
H	1.349284000	3.689697000	0.441993000								
H	2.441349000	2.346872000	0.826307000								
O	1.128256000	-1.694335000	-0.367296000								
O	3.802219000	0.303403000	-1.737651000								
O	0.905667000	1.823297000	-0.370246000								
O	-2.166533000	3.134178000	-1.733287000								
O	-2.030119000	-0.126660000	-0.372044000								
O	-1.636815000	-3.444515000	-1.733707000								

XeO ₃ :(DES) ₃				XeO ₃ :(DES) ₂				XeO ₃ :(DES) ₁			
Xe	-0.000169000	-0.000134000	-0.825306000	Xe	0.102525000	-1.014041000	-0.341919000	Xe	-1.212105000	-0.033894000	-0.134277000
O	-1.397625000	0.760490000	-1.610990000	O	0.208215000	0.159586000	-1.661262000	O	-0.718630000	-0.825480000	1.365159000
O	0.039591000	-1.590730000	-1.610932000	O	-1.255502000	-2.045466000	-0.826192000	O	-2.969331000	-0.208795000	-0.152107000
O	1.356971000	0.829615000	-1.611655000	O	1.501792000	-2.063445000	-0.609765000	O	-0.948186000	1.690207000	0.130826000
C	-3.353113000	-1.542717000	-0.530987000	C	-2.852373000	1.076637000	-1.075618000	C	2.200099000	1.289266000	0.599600000
C	-1.513942000	-3.168342000	0.766936000	C	-3.331356000	-0.570213000	1.117163000	C	2.242268000	-1.489980000	0.430691000
H	-2.752393000	-1.571886000	-1.442920000	H	-2.580294000	0.194780000	-1.660307000	H	1.431970000	1.236774000	1.374721000
H	-1.018499000	-3.240544000	-0.203236000	H	-3.248013000	-1.335407000	0.343220000	H	1.678601000	-1.385074000	1.359242000
C	0.341279000	3.673877000	-0.530809000	C	3.574711000	0.284333000	-0.034607000	S	1.890814000	-0.038548000	-0.592631000
C	-1.987451000	2.895123000	0.765060000	C	1.796992000	2.424927000	-0.011590000	H	3.171021000	1.085476000	1.058402000
H	0.016416000	3.168108000	-1.442937000	H	3.175736000	-0.037146000	-0.999276000	H	3.310608000	-1.481464000	0.660860000
H	-2.296903000	2.500630000	-0.204750000	H	1.446447000	2.091027000	-0.990134000	C	2.190623000	2.636881000	-0.097423000
S	2.424089000	-1.173779000	0.888049000	S	2.213605000	0.952610000	0.956127000	H	2.964986000	2.692893000	-0.865565000
S	-0.194798000	2.684701000	0.888416000	S	-2.280021000	0.817598000	0.621928000	H	1.221957000	2.830621000	-0.559514000
S	-2.228772000	-1.510946000	0.888479000	H	4.278239000	1.104007000	-0.202523000	H	2.375921000	3.430253000	0.630361000
C	3.501873000	0.273902000	0.764961000	H	2.719798000	2.995629000	-0.145212000	C	1.849063000	-2.758580000	-0.303523000
H	4.534502000	-0.084554000	0.788722000	H	-3.942416000	1.149164000	-1.040528000	H	0.771557000	-2.799031000	-0.478730000
H	3.315431000	0.738923000	-0.205003000	H	-4.363354000	-0.212254000	1.155017000	H	2.356982000	-2.842211000	-1.267064000
C	3.231609000	1.232949000	1.909095000	C	4.237603000	-0.869552000	0.694742000	H	2.113902000	-3.634158000	0.293239000
H	2.197180000	1.589923000	1.904253000	H	4.638190000	-0.552805000	1.660412000				
H	3.426714000	0.764615000	2.876469000	H	3.531880000	-1.685551000	0.854054000				
C	3.875895000	2.110973000	1.821844000	H	5.063452000	-1.259744000	0.095325000				
C	3.011990000	-2.132410000	-0.531579000	C	0.746316000	3.251645000	0.706246000				
H	2.735242000	-1.598484000	-1.443540000	H	-0.168855000	2.681054000	0.872597000				
H	4.102609000	-2.166455000	-0.463443000	H	1.107457000	3.600368000	1.676230000				
C	2.417659000	-3.528058000	-0.510571000	H	0.485928000	4.127048000	0.106511000				
H	2.678641000	-4.059613000	0.407447000	C	-2.886842000	-1.105833000	2.465843000				
H	1.332277000	-3.485731000	-0.598861000	H	-1.868406000	-1.499514000	2.423570000				
H	2.796263000	-4.104681000	-1.357923000	H	-2.918460000	-0.333621000	3.237899000				
H	-0.174064000	4.635580000	-0.461605000	H	-3.540312000	-1.922933000	2.779375000				
H	-2.192411000	3.968823000	0.787905000	C	-2.233419000	2.336141000	-1.652942000				
H	-3.928208000	-2.469875000	-0.461156000	H	-2.592781000	2.490619000	-2.673004000				
H	-2.340766000	-3.883266000	0.791864000	H	-2.496442000	3.217104000	-1.062972000				
C	1.847144000	3.856600000	-0.510775000	H	-1.147337000	2.249141000	-1.693184000				
H	2.177843000	4.346764000	0.407825000								
H	2.353158000	2.895656000	-0.601238000								
H	2.156527000	4.474318000	-1.357272000								
C	-2.683868000	2.183078000	1.909503000								
H	-2.470012000	1.112868000	1.904950000								
H	-2.375066000	2.585942000	2.876745000								
H	-3.766203000	2.303967000	1.822314000								
C	-0.547803000	-3.412813000	1.910880000								
H	0.271270000	-2.691564000	1.904552000								
H	-1.050372000	-3.345933000	2.878434000								
H	-0.110306000	-4.410226000	1.824772000								
C	-4.264209000	-0.329855000	-0.512129000								
H	-4.953098000	-0.370908000	-1.359231000								
H	-4.854829000	-0.288115000	0.405945000								
H	-3.684544000	0.588554000	-0.602427000								

XeO ₃ :(DCM) ₃				XeO ₃ :(DCM) ₂				XeO ₃ :(DCM) ₁			
Xe	-0.006039000	0.003971000	1.209629000	Xe	-0.318059000	0.830445000	-0.000186000	Xe	1.030343000	0.015071000	-0.090294000

O	1.287313000	-0.949367000	1.935980000	O	0.609681000	1.374417000	1.395820000	O	1.973912000	-1.467479000	-0.180192000
O	-1.484411000	-0.641538000	1.921483000	O	-1.769283000	1.831579000	-0.004430000	O	0.421483000	0.089793000	1.562665000
O	0.168299000	1.604886000	1.928078000	O	0.612183000	1.366228000	-1.397724000	O	2.183769000	1.337473000	-0.227221000
C	1.686204000	-3.084764000	-0.365264000	C	-3.574619000	-0.773887000	-0.002135000	C	-2.564888000	-0.016541000	0.572179000
C	-3.521178000	0.097962000	-0.379971000	Cl	-2.674623000	-1.187070000	-1.472351000	Cl	-2.143597000	1.461447000	-0.309317000
C	1.844805000	2.990922000	-0.369297000	Cl	-2.680566000	-1.180953000	1.473390000	Cl	-2.043929000	-1.482010000	-0.279008000
Cl	2.259214000	1.312596000	-0.783256000	H	-3.735544000	0.299481000	-0.004642000	H	-2.049891000	0.009706000	1.527132000
Cl	-2.270648000	1.286084000	-0.809311000	H	-4.500507000	-1.340035000	-0.002867000	H	-3.644681000	-0.053026000	0.675168000
Cl	0.027909000	-2.610004000	-0.794661000	Cl	2.033358000	-1.470486000	0.005899000				
Cl	-3.352043000	-1.419731000	-1.261047000	C	3.184634000	-0.104206000	-0.003765000				
Cl	2.907950000	-2.185239000	-1.263534000	H	2.989118000	0.467634000	-0.905291000				
Cl	0.456132000	3.594057000	-1.272931000	H	2.989232000	0.480209000	0.889710000				
H	1.815496000	-2.873763000	0.691630000	Cl	4.860191000	-0.635643000	0.000072000				
H	-3.415954000	-0.109346000	0.680390000								
H	1.597182000	3.007332000	0.687374000								
H	-4.482625000	0.536004000	-0.628520000								
H	1.792284000	-4.139346000	-0.598996000								
H	2.706389000	3.606167000	-0.608398000								

XeO ₃ :(CHCl ₃) ₃				XeO ₃ :(CHCl ₃) ₂				XeO ₃ :(CHCl ₃) ₁			
Xe	-0.006355000	-0.000763000	1.292778000	Xe	-0.000007000	1.293283000	-0.296139000	Xe	-1.560476000	0.013792000	-0.042882000
O	1.457191000	-0.670386000	2.011885000	O	-1.394954000	1.590105000	-1.333689000	O	-2.762511000	1.298166000	-0.012284000
O	-1.321413000	-0.932677000	2.005805000	O	1.394718000	1.589729000	-1.334095000	O	-0.746831000	0.092025000	1.520624000
O	-0.159569000	1.604380000	2.005216000	O	0.000321000	2.603839000	0.874852000	O	-2.456788000	-1.499769000	-0.036406000
C	2.312131000	-2.676969000	-0.240587000	C	-3.122891000	-0.667731000	-0.040260000	C	2.099771000	0.012862000	0.256163000
C	-3.487622000	-0.647506000	-0.238495000	C	3.122846000	-0.667831000	-0.040336000	Cl	1.501906000	-1.439343000	-0.576373000
C	1.181427000	3.333624000	-0.232607000	Cl	2.576033000	0.045383000	1.493519000	Cl	3.839564000	-0.036474000	0.465647000
Cl	1.956427000	1.790251000	-0.679773000	Cl	-1.888048000	-1.763626000	-0.684766000	Cl	1.586571000	1.476893000	-0.608420000
Cl	-2.536783000	0.793639000	-0.686753000	Cl	4.673053000	-1.469535000	0.141297000	H	1.619431000	0.036387000	1.228659000
Cl	0.585464000	-2.594176000	-0.681039000	Cl	-4.673063000	-1.469502000	0.141361000				
Cl	-5.205332000	-0.362173000	-0.472954000	Cl	1.887944000	-1.763893000	-0.684436000				
Cl	2.932027000	-4.308719000	-0.438871000	Cl	-2.575913000	0.045126000	1.493702000				
Cl	-2.927454000	-2.065016000	-1.126787000	H	-3.222170000	0.149904000	-0.746336000				
Cl	2.292454000	4.677571000	-0.446678000	H	3.222034000	0.149638000	-0.746615000				
Cl	3.248043000	-1.499317000	-1.162740000								
Cl	-0.315389000	3.564797000	-1.137449000								
H	2.373352000	-2.398369000	0.806183000								
H	-3.297396000	-0.823595000	0.815013000								
H	0.921183000	3.251185000	0.817444000								

XeO ₃ :(CCl ₄) ₃				XeO ₃ :(CCl ₄) ₂				XeO ₃ :(CCl ₄) ₁			
Xe	-0.001813000	-0.003914000	1.640254000	Xe	0.003362000	1.771091000	-0.060638000	Xe	1.879701000	-0.000928000	-0.118483000
O	-0.771729000	1.420145000	2.334279000	O	-0.870464000	3.070626000	-0.867710000	O	2.401966000	1.625281000	0.308760000
O	1.610916000	-0.058584000	2.345987000	O	1.639996000	2.381431000	0.159398000	O	3.343583000	-0.898120000	-0.510375000
O	-0.860957000	-1.382478000	2.320806000	O	-0.690504000	1.644926000	1.552644000	O	1.250595000	-0.717894000	1.360471000
C	0.450900000	3.386501000	-0.644148000	C	2.977379000	-1.030430000	-0.015742000	C	-2.138014000	-0.004958000	-0.025568000
C	2.716239000	-2.079168000	-0.646773000	Cl	-2.984299000	-1.029214000	-0.015504000	Cl	-1.169355000	1.494830000	-0.061772000
C	-3.163431000	-1.302186000	-0.648232000	Cl	-3.089414000	0.515934000	-0.894245000	Cl	-1.372575000	-1.209004000	-1.099351000
Cl	-3.254137000	0.189393000	0.309602000	Cl	1.851533000	-0.836578000	1.347105000	Cl	-2.200152000	-0.629773000	1.616029000
Cl	1.471587000	-2.905355000	0.312278000	Cl	-1.321881000	-1.654675000	-0.167292000	Cl	-3.766442000	0.344286000	-0.614869000
Cl	1.779945000	2.722505000	0.327848000	Cl	4.263015000	0.164334000	0.092310000				
Cl	-1.513587000	-1.451745000	-1.317351000	Cl	3.654038000	-2.664809000	0.011926000				
Cl	4.089073000	-1.668301000	0.378120000	Cl	-3.363307000	-0.769814000	1.685325000				
Cl	-0.484797000	2.030098000	-1.334229000	Cl	2.075352000	-0.804203000	-1.543687000				
Cl	-0.603282000	4.366723000	0.371522000	Cl	-4.114762000	-2.188831000	-0.725131000				
Cl	3.236177000	-3.128118000	-1.973573000								
Cl	-3.507931000	-2.694257000	0.374881000								
Cl	1.111622000	4.364605000	-1.962452000								
Cl	2.013754000	-0.583086000	-1.324829000								
Cl	-4.323728000	-1.222002000	-1.982249000								

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9. Optimized Cartesian Coordinates

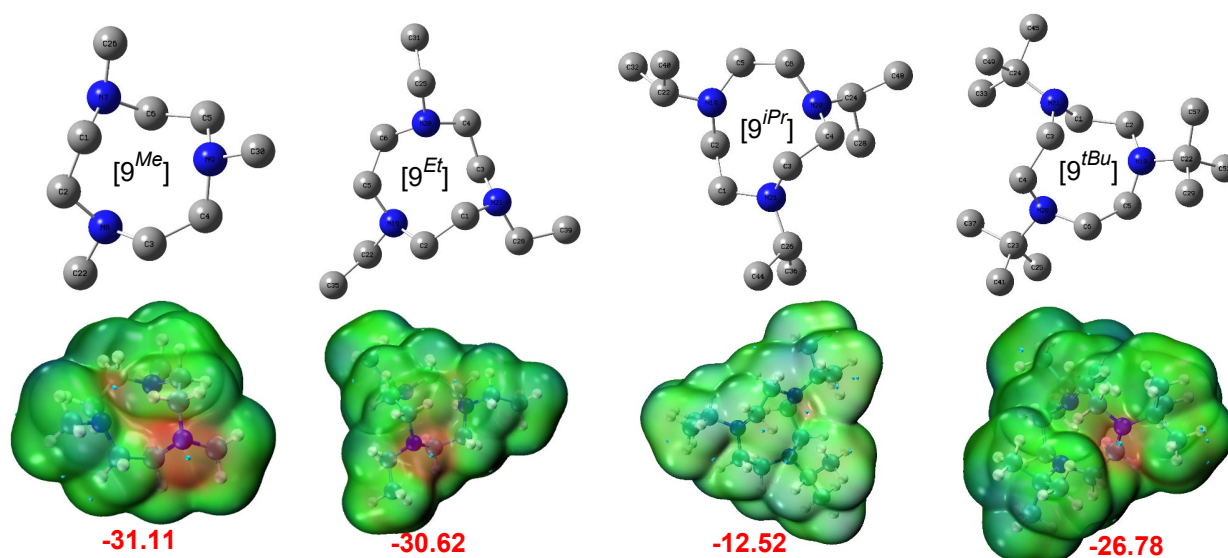


Figure S5.1. Optimized geometries of the Aza-9-Crown-3 with different substituents (Top) and their corresponding molecular electrostatic potential surfaces (Bottom: highest $V_{s,min}$ in kcal/mol; see Table S1 for details). Hydrogen atoms have been omitted for clarity.

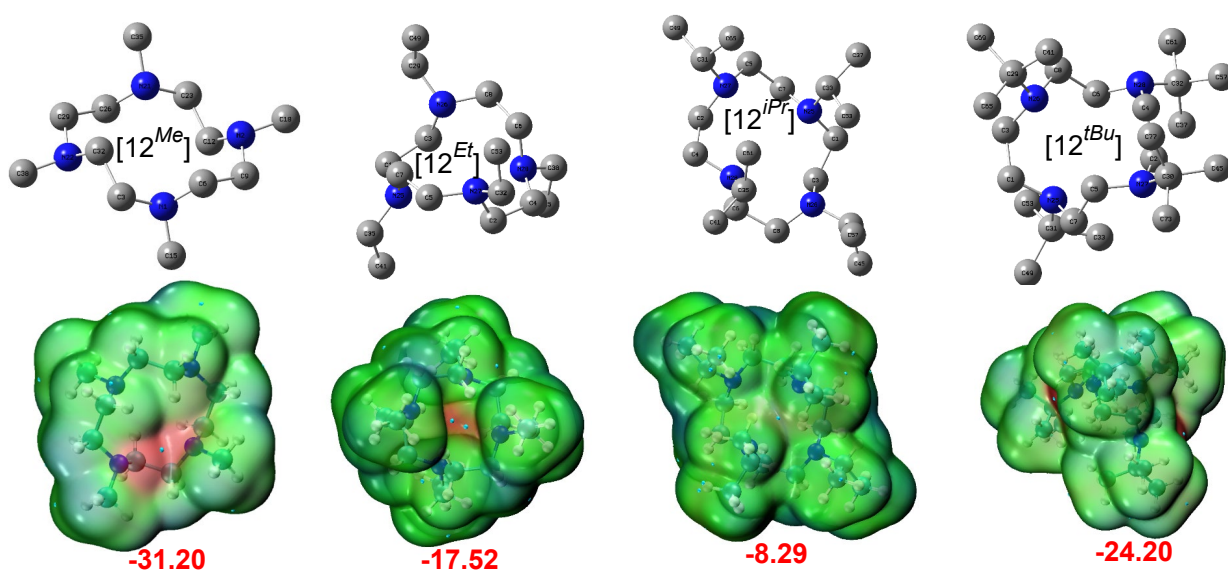


Figure S5.2. Optimized geometries of the Aza-12-Crown-4 with different substituents (Top) and their corresponding molecular electrostatic potential surfaces (Bottom: highest $V_{s,min}$ in kcal/mol; see Table S1 for details). Hydrogen atoms have been omitted for clarity.

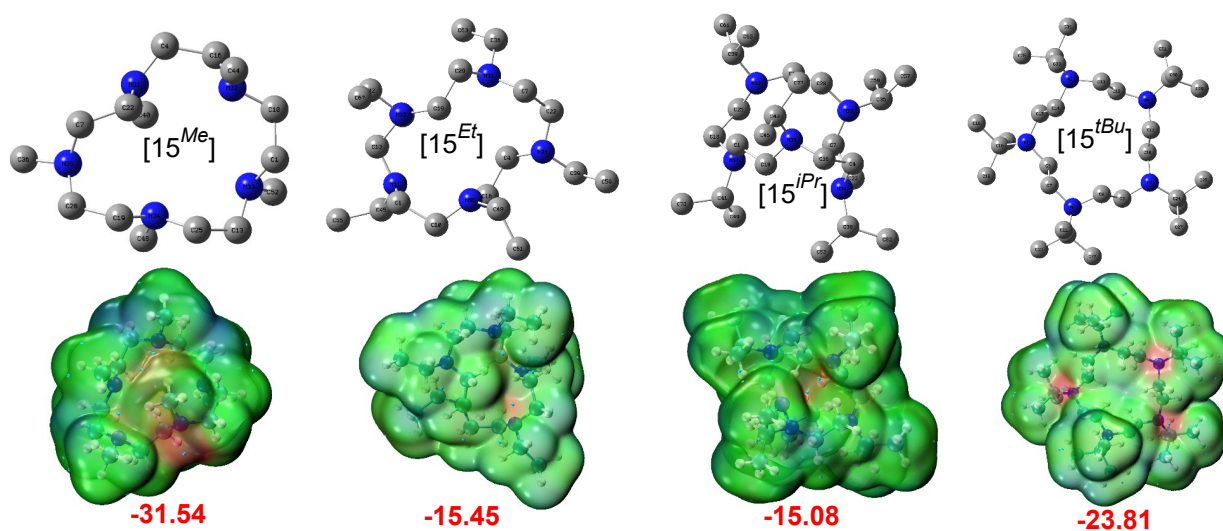


Figure S5.3. Optimized geometries of the Aza-15-Crown-5 with different substituents (Top) and their corresponding molecular electrostatic potential surfaces (Bottom: highest $V_{s,min}$ in kcal/mol; see Table S1 for details). Hydrogen atoms have been omitted for clarity.

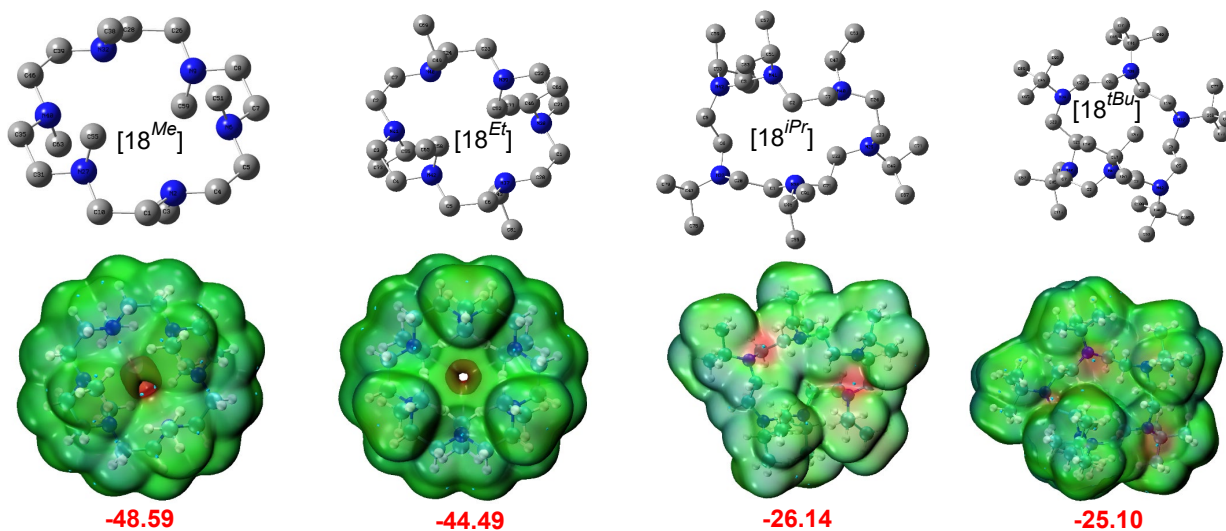


Figure S5.4. Optimized geometries of the Aza-18-Crown-6 with different substituents (Top) and their corresponding molecular electrostatic potential surfaces (Bottom: highest $V_{s,min}$ in kcal/mol; see Table S1 for details). Hydrogen atoms have been omitted for clarity.

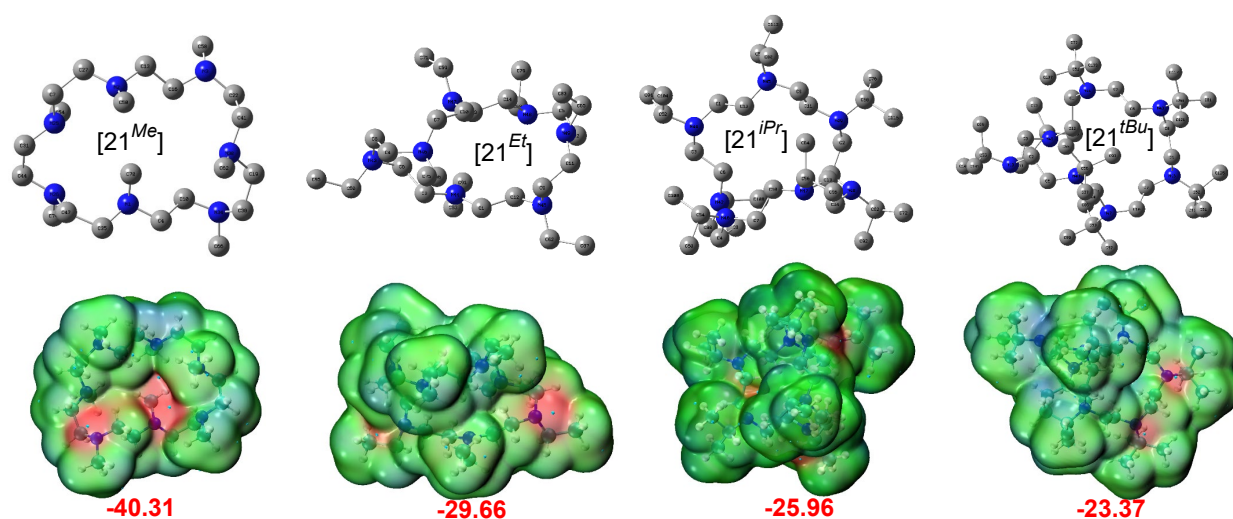


Figure S5.5 Optimized geometries of the Aza-21-Crown-7 with different substituents (Top) and their corresponding molecular electrostatic potential surfaces (Bottom: highest $V_{s,min}$ in kcal/mol; see Table S1 for details). Hydrogen atoms have been omitted for clarity.

Table S5.1. All the MEPs (minima: $V_{s,min}$ in kcal/mol) of the aza-crowns corresponding to the nitrogen centers computed at the APFD/def2-TZVPD level of theory.

-N(R)	9N3	12N4	15N5	18N6	21N7
Me	-31.11	-31.20	-31.54	-48.58	-40.31
	-14.98	-31.18	-12.77	-48.57	-25.08
	-13.88		-11.18	-48.56	-29.27
			-10.22	-48.55	-27.64
			-9.11	-48.54	
Et			-48.59		
	-30.62	-17.52	-15.45	-44.49	-29.66
	-10.17	-17.49	-13.89	-44.48	-17.14
	-9.42	-17.49	-14.63	-44.47	-17.10
		-17.47	-11.63	-44.46	
ⁱPr			-12.80		
	-12.52	-8.29	-15.08	-26.14	-25.96
			-14.46	-23.07	-23.71
			-13.14	-22.95	-22.26
			-10.07	-10.10	-17.13
^tBu					-14.25
					-11.36
	-26.78	-24.20	-23.81	-25.10	-23.07
		-24.19	-23.30	-23.71	-23.37
			-23.29	-22.20	-24.51
			-22.03	-15.61	-22.90
			-22.02		

Table S5.2. Natural population analysis (NPA) of the aza-crowns corresponding to the nitrogen centers computed at the APFD/def2-TZVPD level of theory.

NPA	Me	Et	ⁱ Pr	^t Bu
9N3	N 7 -0.42901	N 19 -0.45599	N 19 -0.46300	N 19 -0.46891
	N 8 -0.44421	N 20 -0.45608	N 20 -0.46076	N 20 -0.46842
	N 9 -0.44403	N 21 -0.43665	N 21 -0.45321	N 21 -0.46414

12N4	N 1	-0.42975	N 25	-0.44166	N 25	-0.43499	N 25	-0.46670
	N 2	-0.42488	N 26	-0.44167	N 26	-0.44158	N 26	-0.46670
	N 21	-0.42975	N 27	-0.44167	N 27	-0.44155	N 27	-0.45964
	N 22	-0.42488	N 28	-0.44166	N 28	-0.43490	N 28	-0.45964
15N5	N 31	-0.44276	N 31	-0.44938	N 31	-0.44298	N 1	-0.46529
	N 32	-0.43623	N 32	-0.44368	N 32	-0.46425	N 2	-0.46617
	N 33	-0.42326	N 33	-0.43794	N 33	-0.45385	N 3	-0.46926
	N 34	-0.42126	N 34	-0.43932	N 34	-0.45211	N 4	-0.46795
	N 35	-0.43860	N 35	-0.45084	N 35	-0.44047	N 5	-0.46350
18N6	N 2	-0.42183	N 37	-0.43486	N 37	-0.44725	N 37	-0.46638
	N 6	-0.42183	N 38	-0.43488	N 38	-0.44001	N 38	-0.47323
	N 9	-0.42184	N 39	-0.43488	N 39	-0.44772	N 39	-0.46203
	N 27	-0.42184	N 40	-0.43487	N 40	-0.44923	N 40	-0.47067
	N 32	-0.42183	N 41	-0.43488	N 41	-0.45651	N 41	-0.47156
	N 40	-0.42184	N 42	-0.43488	N 42	-0.44911	N 42	-0.46780
21N7	N 1	-0.42047	N 43	-0.43573	N 43	-0.44250	N 43	-0.47146
	N 2	-0.43170	N 44	-0.44641	N 44	-0.45312	N 44	-0.46729
	N 3	-0.41919	N 45	-0.45220	N 45	-0.45250	N 45	-0.47016
	N 25	-0.42311	N 46	-0.45766	N 46	-0.46372	N 46	-0.46813
	N 26	-0.42541	N 47	-0.44333	N 47	-0.45705	N 47	-0.46795
	N 30	-0.43345	N 48	-0.44073	N 48	-0.45260	N 48	-0.46537
	N 34	-0.42667	N 49	-0.44415	N 49	-0.44720	N 49	-0.46303

Table S5.3. Deformation energies (in kcal/mol) associated with the aza-crowns for the adduct formation with XeO₃ computed at the APFD/def2-TZVPD level of theory.

-N(R)	XeO ₃ :9N3	XeO ₃ :12N4	XeO ₃ :15N5	XeO ₃ :18N6	XeO ₃ :21N7	XeO ₃ :21N7'
<i>Me</i>	4.5	4.4	8.5	14.6	11.7	13.1
<i>Et</i>	5.5	11.4	15.5	20.2	16.4	15.8
<i>i</i> Pr	9.3	16.7	21.0	33.9	30.2	-
<i>Bu</i>	10.4	30.5	29.9	43.0	36.3	-

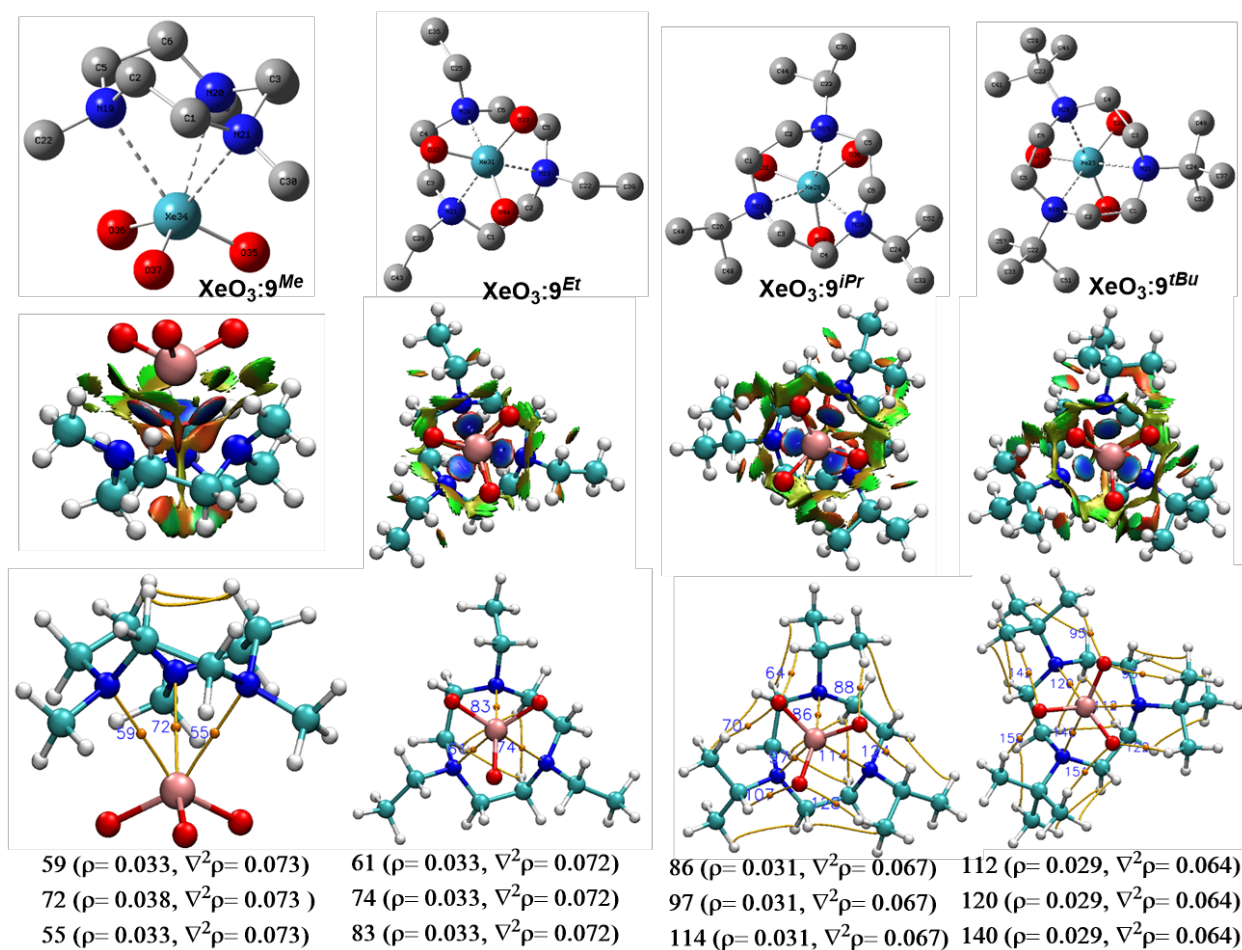


Figure S5.6. Optimized geometries of the complexes of XeO_3 and aza-9-crown-3 with different substituents (Top), their NCI plots (Middle), and their bond critical points (BCP) from AIM analysis (Bottom). The electron density (ρ , in a.u.) and the Laplacian of electron density ($\nabla^2\rho$, in a.u.) values of the BCPs corresponding to the aerogen bonds are shown.

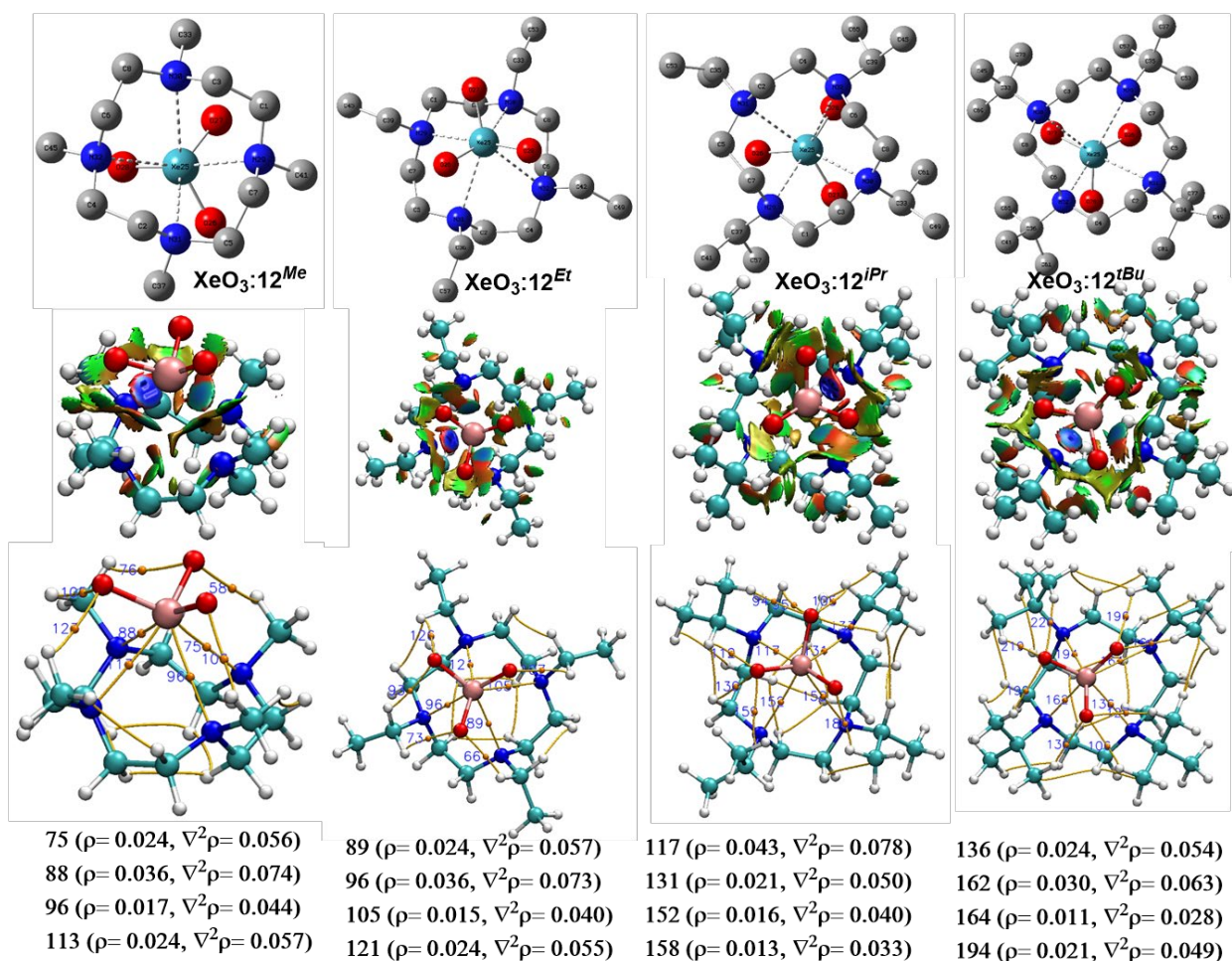


Figure S5.7. Optimized geometries of the complexes of XeO_3 and aza-12-crown-4 with different substituents (Top), their NCI plots (Middle), and their bond critical points (BCP) from AIM analysis (Bottom). The electron density (ρ , in a.u.) and the Laplacian of electron density ($\nabla^2\rho$, in a.u.) values of the BCPs corresponding to the aerogen bonds are shown.

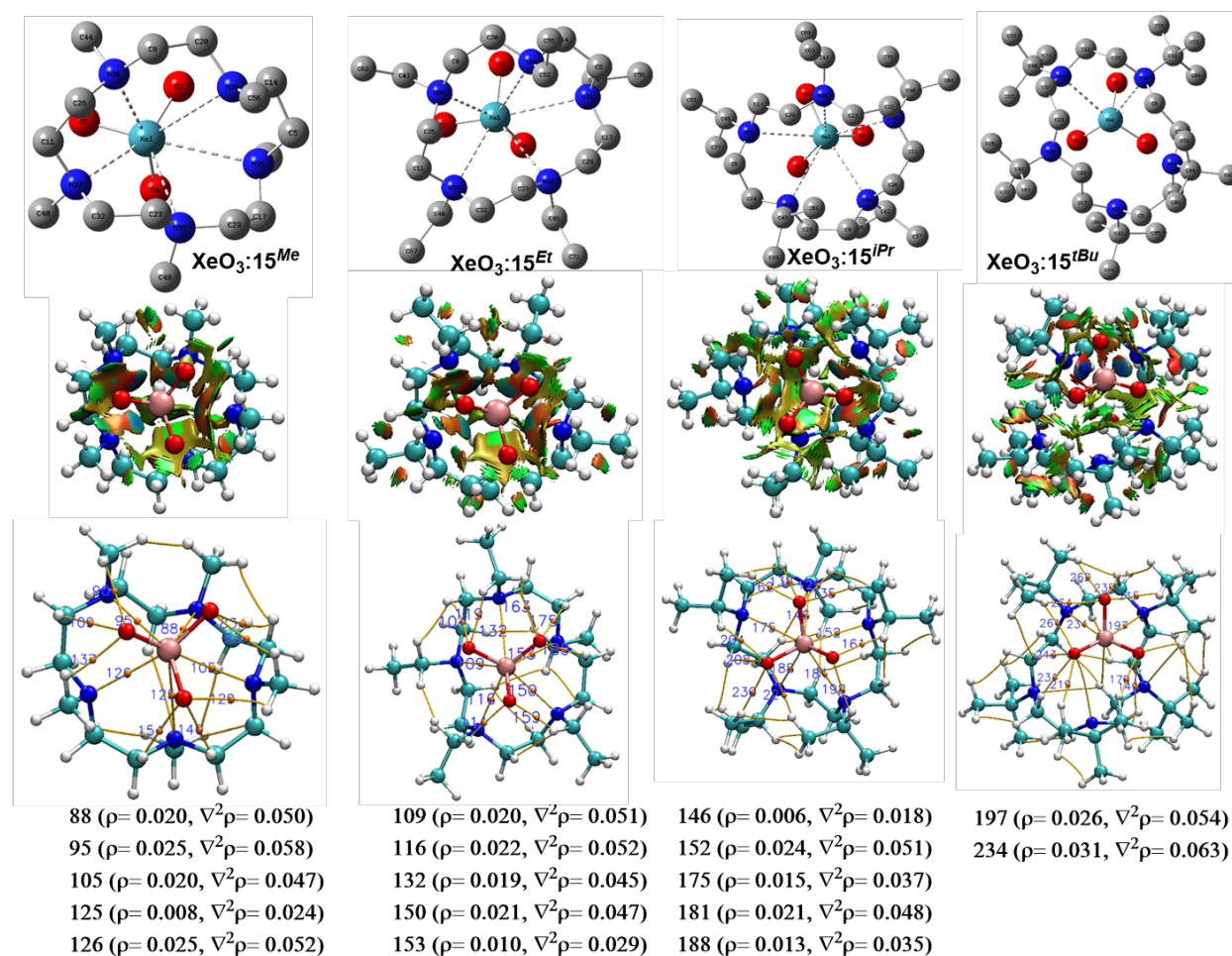


Figure S5.8. Optimized geometries of the complexes of XeO_3 and aza-15-crown-5 with different substituents (Top), their NCI plots (Middle), and their bond critical points (BCP) from AIM analysis (Bottom). The electron density (ρ , in a.u.) and the Laplacian of electron density ($\nabla^2\rho$, in a.u.) values of the BCPs corresponding to the aerogen bonds are shown.

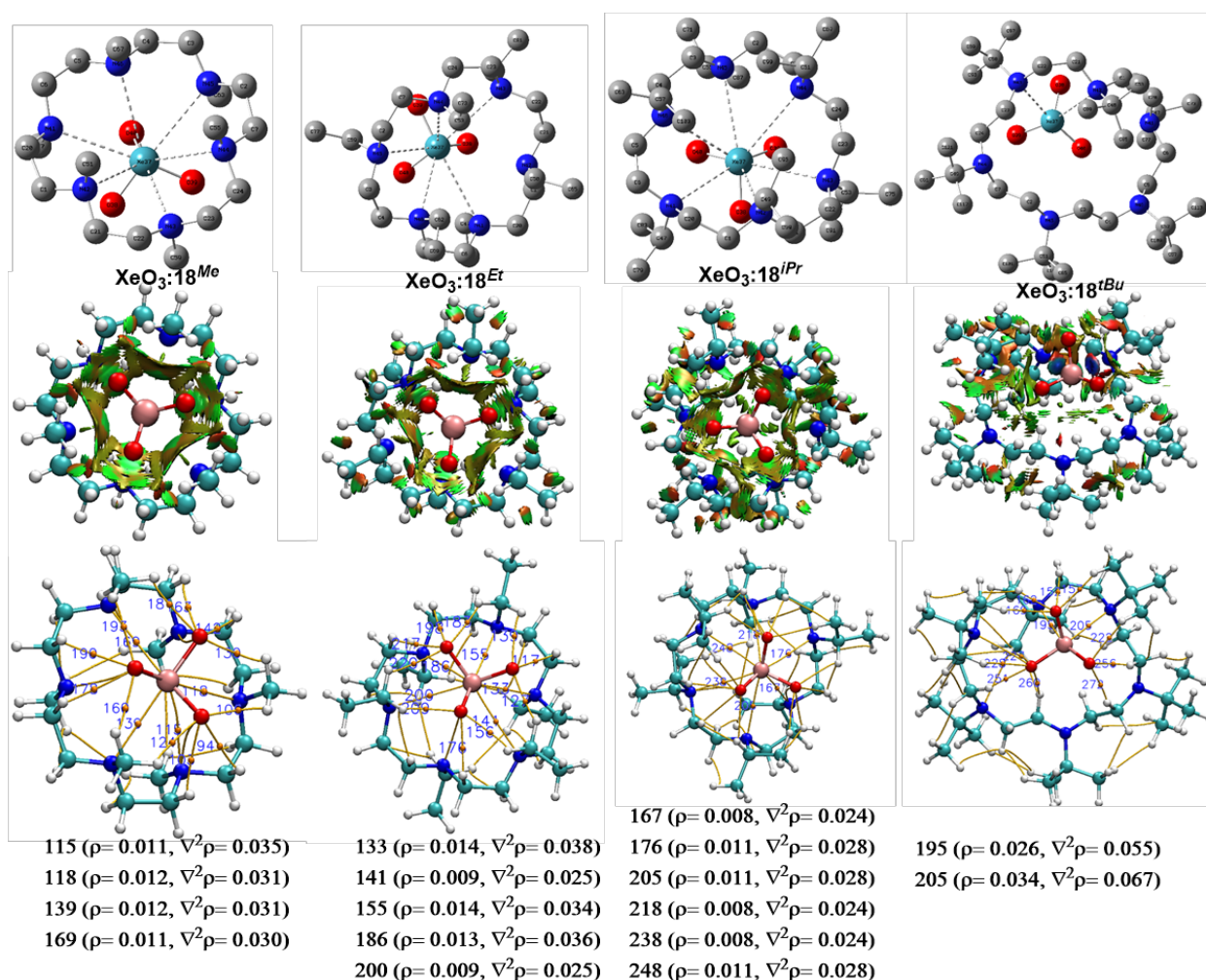


Figure S5.9. Optimized geometries of the complexes of XeO_3 and aza-18-crown-6 with different substituents (Top), their NCI plots (Middle), and their bond critical points (BCP) from AIM analysis (Bottom). The electron density (ρ , in a.u.) and the Laplacian of electron density ($\nabla^2\rho$, in a.u.) values of the BCPs corresponding to the aerogen bonds are shown.

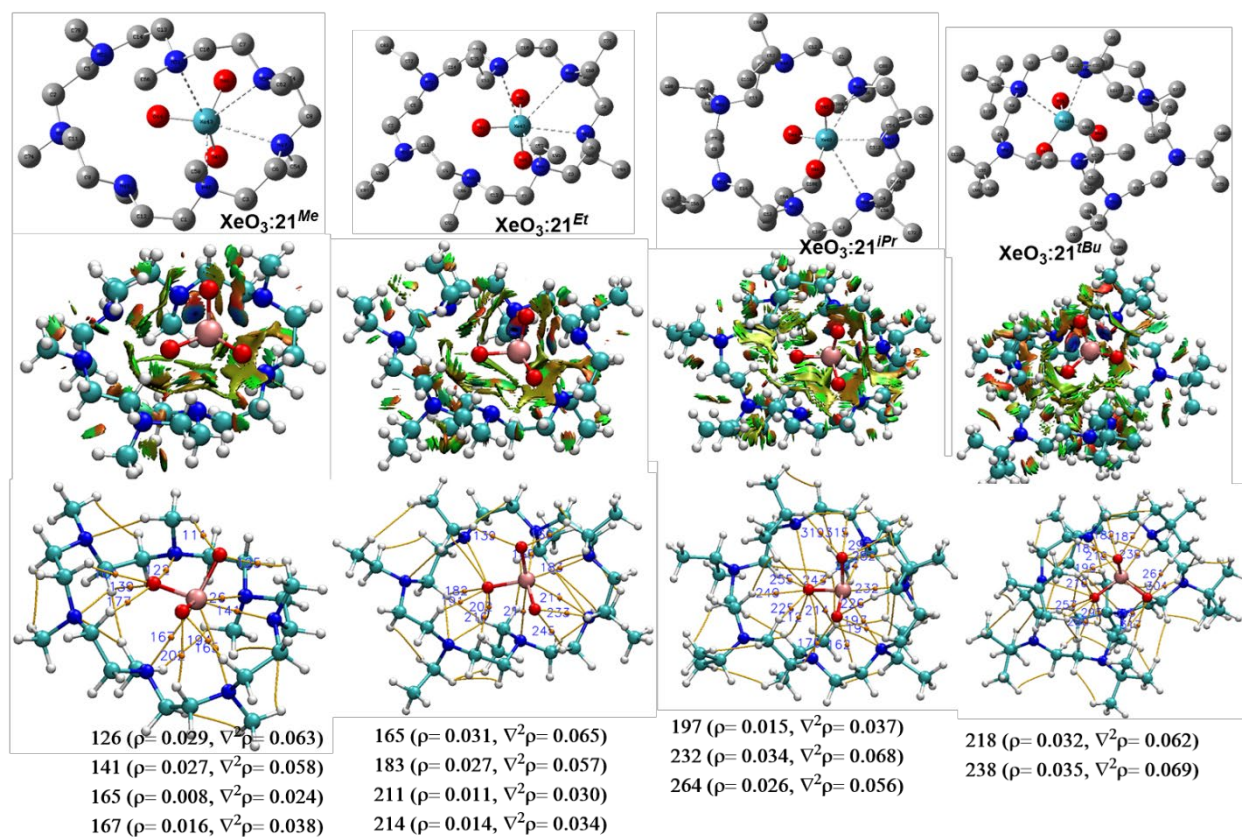


Figure S5.10. Optimized geometries of the complexes of XeO_3 and aza-21-crown-7 with different substituents (Top), their NCI plots (Middle), and their bond critical points (BCP) from AIM analysis (Bottom). The electron density (ρ , in a.u.) and the Laplacian of electron density ($\nabla^2\rho$, in a.u.) values of the BCPs corresponding to the aerogen bonds are shown.

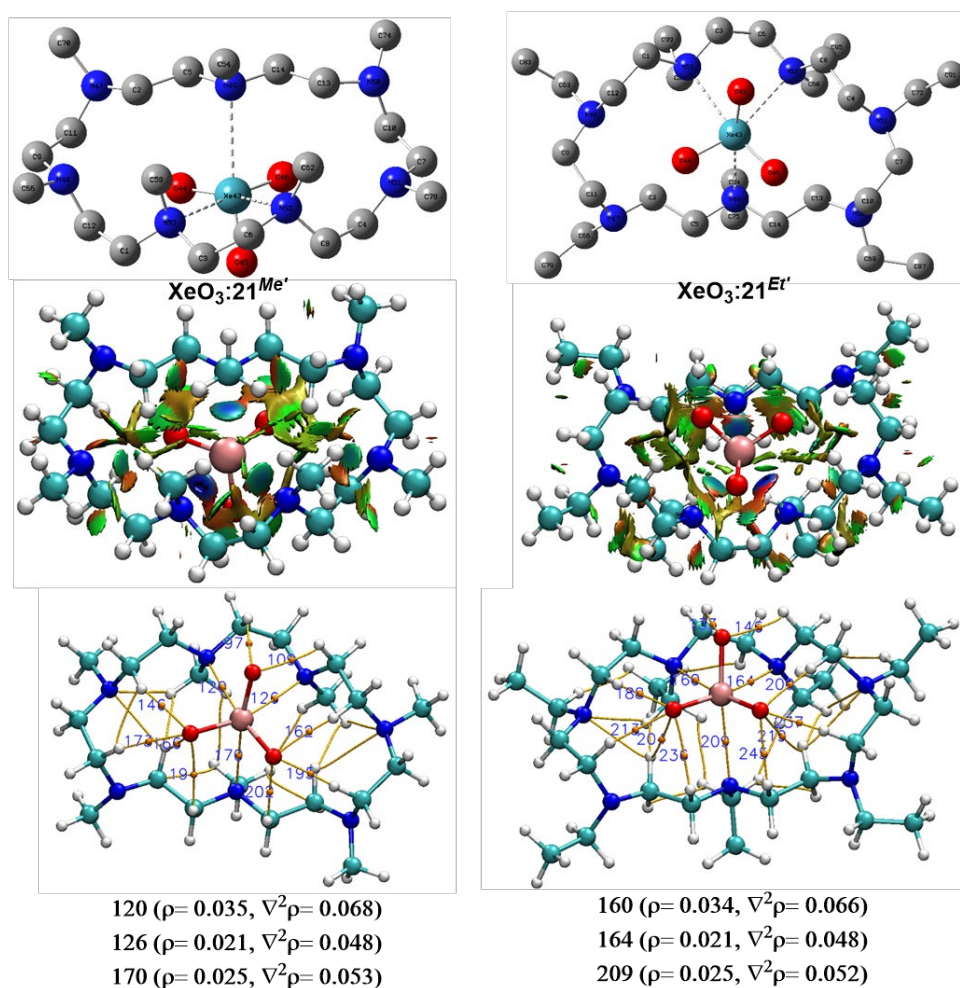


Figure S5.11. Optimized geometries of the alternative binding mode for the complexes of XeO_3 and aza-21-crown-7 with Me and Et substituents (Top), their NCI plots (Middle), and their bond critical points (BCP) from AIM analysis (Bottom). The electron density (ρ , in a.u.) and the Laplacian of electron density ($\nabla^2\rho$, in a.u.) values of the BCPs corresponding to the aerogen bonds are shown.

Table S5.4. Geometrical parameters of the complexes of different aza-crowns (Me) with XeO_3 . WBI values are listed along with the atomic charges (in a.u.) obtained from the natural population analysis at the APFD/def2-TZVPD level of theory.

Me	Xe-O (in Å)	Xe...N (in Å)	WBI (XeO ₃)	WBI (Xe...N)	NPA (XeO ₃)	NPA (N-Aza)
9N3	1.77591	2.80924	Xe ₃₄ = 3.3427	0.0555	Xe ₃₄ = 2.890	N ₁₉ = -0.468
	1.77594	2.80943	O ₃₅ = 1.4617	0.0554	O ₃₅ = -1.002	N ₂₀ = -0.468
	1.77593	2.81028	O ₃₆ = 1.4615	0.0552	O ₃₆ = -1.003	N ₂₁ = -0.468
			O ₃₇ = 1.4616		O ₃₇ = -1.003	
12N4	1.77358	2.74461	Xe ₂₅ = 3.3433	0.0767	Xe ₂₅ = 2.912	N ₂₉ = -0.456
	1.77338	2.96002	O ₂₆ = 1.4311	0.0393	O ₂₆ = -1.014	N ₃₀ = -0.450
	1.77199	2.95490	O ₂₇ = 1.4303	0.0374	O ₂₇ = -1.014	N ₃₁ = -0.451

		3.14217	O ₂₈ = 1.4651	0.0185	O ₂₈ = -1.001	N ₃₂ = -0.447
15N5	1.77521	3.02953	Xe ₁ = 3.3389	0.0431	Xe ₁ = 2.916	N ₃₅ = -0.448
	1.77163	3.05162	O ₂ = 1.4378	0.0250	O ₂ = -1.014	N ₃₆ = -0.446
	1.77160	2.92674	O ₃ = 1.4266	0.0483	O ₃ = -1.012	N ₃₇ = -0.461
		2.98590	O ₄ = 1.4518	0.0435	O ₄ = -0.999	N ₃₈ = -0.453
		3.47770		0.0071		N ₃₉ = -0.438
18N6	1.76640	3.28944	Xe ₃₇ = 3.3323	0.0221	Xe ₃₇ = 2.921	N ₄₁ = -0.443
	1.76635	3.34186	O ₃₈ = 1.4557	0.0122	O ₃₈ = -0.992	N ₄₂ = -0.429
	1.76655	3.30138	O ₃₉ = 1.4558	0.0213	O ₃₉ = -0.992	N ₄₃ = -0.443
		3.34399	O ₄₀ = 1.4549	0.0121	O ₄₀ = -0.992	N ₄₄ = -0.429
		3.28944		0.0221		N ₄₅ = -0.443
		3.32913		0.0127		N ₄₆ = -0.429
21N7	1.76051	2.89970	Xe ₄₃ = 3.3452	0.0578	Xe ₄₃ = 2.911	N ₄₇ = -0.455
	1.76903	2.86510	O ₄₄ = 1.4867	0.0569	O ₄₄ = -0.988	N ₄₈ = -0.449
	1.77502	3.77307	O ₄₅ = 1.4334	0.0026	O ₄₅ = -0.999	N ₄₉ = -0.429
		3.47852	O ₄₆ = 1.4343	0.0072	O ₄₆ = -1.012	N ₅₀ = -0.444
		3.17142		0.0288		N ₅₁ = -0.440
		4.43931		0.0011		N ₅₂ = -0.434
		5.23459		0.0004		N ₅₃ = -0.422
21N7'	1.76802	4.69516	Xe ₄₃ = 3.3463	0.0004	Xe ₄₃ = 2.910	N ₄₇ = -0.434
	1.77176	4.61706	O ₄₄ = 1.4472	0.0003	O ₄₄ = -1.006	N ₄₈ = -0.440
	1.76990	2.95098	O ₄₅ = 1.4417	0.0581	O ₄₅ = -1.006	N ₄₉ = -0.449
		4.78995	O ₄₆ = 1.4488	0.0008	O ₄₆ = -1.014	N ₅₀ = -0.443
		4.56833		0.0003		N ₅₁ = -0.440
		3.04293		0.0392		N ₅₂ = -0.462
		2.78149		0.0818		N ₅₃ = -0.454

Table S5.5. Geometrical parameters of the complexes of different aza-crowns (Et) with XeO₃. WBI values are listed along with the atomic charges (in a.u.) obtained from the natural population analysis at the APFD/def2-TZVPD level of theory.

Et	Xe-O (in Å)	Xe...N (in Å)	WBI (XeO ₃)	WBI (Xe...N)	NPA (XeO ₃)	NPA (N-Aza)
9N3	1.77628	2.80990	Xe ₃₁ = 3.3415	0.0567	Xe ₃₁ = 2.893	N ₁₉ = -0.475
	1.77628	2.81032	O ₃₂ = 1.4617	0.0563	O ₃₂ = -1.003	N ₂₀ = -0.475
	1.77634	2.80964	O ₃₃ = 1.4616	0.0566	O ₃₃ = -1.003	N ₂₁ = -0.475
			O ₃₄ = 1.4613		O ₃₄ = -1.004	
12N4	1.77359	2.74749	Xe ₂₅ = 3.3425	0.0795	Xe ₂₅ = 2.914	N ₂₉ = -0.463
	1.77330	2.96946	O ₂₆ = 1.4310	0.0403	O ₂₆ = -1.015	N ₃₀ = -0.457
	1.77213	2.95073	O ₂₇ = 1.4318	0.0397	O ₂₇ = -1.014	N ₃₁ = -0.458
		3.18319	O ₂₈ = 1.4655	0.0174	O ₂₈ = -1.002	N ₃₂ = -0.455
15N5	1.77377	3.05586	Xe ₁ = 3.3351	0.0422	Xe ₁ = 2.920	N ₃₅ = -0.454
	1.77164	3.03329	O ₂ = 1.4414	0.0280	O ₂ = -1.010	N ₃₆ = -0.456
	1.77196	2.98812	O ₃ = 1.4322	0.0417	O ₃ = -1.011	N ₃₇ = -0.465
		3.03300	O ₄ = 1.4505	0.0427	O ₄ = -1.000	N ₃₈ = -0.461
		3.38308		0.0102		N ₃₉ = -0.448
18N6	1.76547	3.41624	Xe ₃₇ = 3.3347	0.0160	Xe ₃₇ = 2.917	N ₄₁ = -0.451
	1.76714	3.50443	O ₃₈ = 1.4677	0.0079	O ₃₈ = -0.987	N ₄₂ = -0.434
	1.76718	3.42137	O ₃₉ = 1.4572	0.0163	O ₃₉ = -0.990	N ₄₃ = -0.451
		3.26757	O ₄₀ = 1.4566	0.0162	O ₄₀ = -0.989	N ₄₄ = -0.441
		3.22937		0.0287		N ₄₅ = -0.456
		3.22619		0.0185		N ₄₆ = -0.442
21N7	1.76057	2.90804	Xe ₄₃ = 3.3454	0.0579	Xe ₄₃ = 2.916	N ₄₇ = -0.462
	1.77023	2.83048	O ₄₄ = 1.4875	0.0647	O ₄₄ = -0.990	N ₄₈ = -0.456

	1.77483	3.87591 3.35550 3.24945 4.52572 5.45388	O ₄₅ = 1.4306 O ₄₆ = 1.4388	0.0027 0.0107 0.0235 0.0008 0.0002	O ₄₅ = -1.002 O ₄₆ = -1.010	N ₄₉ = -0.437 N ₅₀ = -0.453 N ₅₁ = -0.448 N ₅₂ = -0.445 N ₅₃ = -0.429
21N7'	1.76730 1.77206 1.76971	4.74666 4.58357 2.95669 4.77087 4.54980 3.03931 2.79309	Xe ₄₃ = 3.3445 O ₄₄ = 1.4443 O ₄₅ = 1.4411 O ₄₆ = 1.4469	0.0004 0.0003 0.0613 0.0008 0.0003 0.0418 0.0823	Xe ₄₃ = 2.912 O ₄₄ = -1.010 O ₄₅ = -1.006 O ₄₆ = -1.015	N ₄₇ = -0.440 N ₄₈ = -0.450 N ₄₉ = -0.455 N ₅₀ = -0.447 N ₅₁ = -0.450 N ₅₂ = -0.467 N ₅₃ = -0.461

Table S5.6. Geometrical parameters of the complexes of different aza-crowns (ⁱPr) with XeO₃. WBI values are listed along with the atomic charges (in a.u.) obtained from the natural population analysis at the APFD/def2-TZVPD level of theory.

ⁱ Pr	Xe-O (in Å)	Xe...N (in Å)	WBI (XeO ₃)	WBI (Xe...N)	NPA (XeO ₃)	NPA (N-Aza)
9N3	1.77548 1.77546 1.77550	2.84586 2.84571 2.84563	Xe ₂₈ = 3.3383 O ₂₉ = 1.4592 O ₃₀ = 1.4592 O ₃₁ = 1.4592	0.0561 0.0561 0.0562	Xe ₂₈ = 2.902 O ₂₉ = -1.002 O ₃₀ = -1.002 O ₃₁ = -1.002	N ₁₉ = -0.477 N ₂₀ = -0.477 N ₂₁ = -0.477
12N4	1.76922 1.77123 1.77172	2.67172 3.02190 3.16637 3.29331	Xe ₂₅ = 3.3424 O ₂₆ = 1.4384 O ₂₇ = 1.4264 O ₂₈ = 1.4610	0.1010 0.0371 0.0259 0.0132	Xe ₂₅ = 2.917 O ₂₆ = -1.007 O ₂₇ = -1.013 O ₂₈ = -1.006	N ₂₉ = -0.463 N ₃₀ = -0.466 N ₃₁ = -0.456 N ₃₂ = -0.453
15N5	1.76981 1.76798 1.76949	3.18373 3.26493 3.02789 2.96549 3.65431	Xe ₁ = 3.3374 O ₂ = 1.4411 O ₃ = 1.4437 O ₄ = 1.4623	0.0320 0.0145 0.0418 0.0563 0.0049	Xe ₁ = 2.916 O ₂ = -1.009 O ₃ = -0.995 O ₄ = -0.992	N ₃₅ = -0.453 N ₃₆ = -0.450 N ₃₇ = -0.461 N ₃₈ = -0.465 N ₃₉ = -0.454
18N6	1.76340 1.76341 1.76343	3.34863 3.51345 3.35642 3.52047 3.35426 3.51608	Xe ₃₇ = 3.3276 O ₃₈ = 1.4639 O ₃₉ = 1.4643 O ₄₀ = 1.4639	0.0220 0.0101 0.0214 0.0099 0.0216 0.0100	Xe ₃₇ = 2.929 O ₃₈ = -0.987 O ₃₉ = -0.987 O ₄₀ = -0.987	N ₄₁ = -0.454 N ₄₂ = -0.446 N ₄₃ = -0.454 N ₄₄ = -0.446 N ₄₅ = -0.454 N ₄₆ = -0.446
21N7	1.76515 1.77127 1.77128	2.78971 2.92300 2.92300 3.20741 3.52005 5.01896 5.71993	Xe ₄₃ = 3.3490 O ₄₄ = 1.4931 O ₄₅ = 1.4345 O ₄₆ = 1.4480	0.0773 0.0582 0.0032 0.0231 0.0075 0.0004 0.0003	Xe ₄₃ = 2.921 O ₄₄ = -1.009 O ₄₅ = -1.001 O ₄₆ = -0.998	N ₄₇ = -0.473 N ₄₈ = -0.454 N ₄₉ = -0.446 N ₅₀ = -0.455 N ₅₁ = -0.449 N ₅₂ = -0.461 N ₅₃ = -0.441

Table S5.7. Geometrical parameters of the complexes of different aza-crowns (^tBu) with XeO₃. WBI values are listed along with the atomic charges (in a.u.) obtained from the natural population analysis at the APFD/def2-TZVPD level of theory.

^t Bu	Xe-O	Xe...N	WBI	WBI	NPA	NPA
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	(in Å)	(in Å)	(XeO ₃)	(Xe...N)	(XeO ₃)	(N-Aza)
9N3	1.77248 1.77253 1.77250	2.87683 2.87684 2.87722	Xe ₂₅ = 3.3408 O ₂₆ = 1.4559 O ₂₇ = 1.4559 O ₂₈ = 1.4559	0.0556 0.0557 0.0556	Xe ₂₅ = 2.912 O ₂₆ = -1.003 O ₂₇ = -1.003 O ₂₈ = -1.003	N ₁₉ = -0.492 N ₂₀ = -0.492 N ₂₁ = -0.492
12N4	1.76658 1.76809 1.77033	3.03116 3.39178 2.84891 2.96274	Xe ₂₅ = 3.3370 O ₂₆ = 1.4391 O ₂₇ = 1.4625 O ₂₈ = 1.4277	0.0376 0.0108 0.0658 0.0458	Xe ₂₅ = 2.935 O ₂₆ = -1.009 O ₂₇ = -0.997 O ₂₈ = -1.014	N ₂₉ = -0.475 N ₃₀ = -0.462 N ₃₁ = -0.483 N ₃₂ = -0.473
15N5	1.77026 1.76343 1.76343	3.71043 3.74649 2.93764 2.84538 4.34884	Xe ₁ = 3.3513 O ₂ = 1.4696 O ₃ = 1.4516 O ₄ = 1.4780	0.0046 0.0021 0.0593 0.0692 0.0005	Xe ₁ = 2.896 O ₂ = -0.990 O ₃ = -0.986 O ₄ = -0.982	N ₃₅ = -0.459 N ₃₆ = -0.459 N ₃₇ = -0.481 N ₃₈ = -0.491 N ₃₉ = -0.466
18N6	1.76734 1.77077 1.76156	4.04861 2.92264 2.79112 4.30478 4.35671 5.03761	Xe ₃₇ = 3.3501 O ₃₈ = 1.4438 O ₃₉ = 1.4657 O ₄₀ = 1.4996	0.0035 0.0608 0.0818 0.0008 0.0004 0.0002	Xe ₃₇ = 2.890 O ₃₈ = -0.991 O ₃₉ = -0.991 O ₄₀ = -0.978	N ₄₁ = -0.461 N ₄₂ = -0.478 N ₄₃ = -0.493 N ₄₄ = -0.471 N ₄₅ = -0.458 N ₄₆ = -0.462
21N7	1.76071 1.76782 1.77477	2.77982 2.82869 4.12602 4.43324 4.43324 4.73796 5.81081	Xe ₄₃ = 3.3568 O ₄₄ = 1.4996 O ₄₅ = 1.4375 O ₄₆ = 1.4600	0.0818 0.0765 0.0065 0.0009 0.0009 0.0022 0.0001	Xe ₄₃ = 2.892 O ₄₄ = -0.983 O ₄₅ = -0.994 O ₄₆ = -1.000	N ₄₇ = -0.490 N ₄₈ = -0.482 N ₄₉ = -0.464 N ₅₀ = -0.457 N ₅₁ = -0.463 N ₅₂ = -0.464 N ₅₃ = -0.452

Table S5.8. Summed up second-order perturbation energy values (E^2 , in kcal/mol) obtained from natural bond orbital (NBO 7.0) analysis of complexes of different aza-crowns (Et) with XeO₃ at the APFD/def2-TZVPD level of theory.

Et	Donor	Acceptor	E^2
9N3	LP N LP Xe LP O	BD* Xe – O BD* C – N BD* C – H	18.33 2.23 2.63
12N4	LP N LP Xe LP O	BD* Xe – O BD* C – N BD* C – H	20.05 2.14 3.23
15N5	LP N LP Xe LP O	BD* Xe – O BD* C – N BD* C – H	16.28 1.61 7.26
18N6	LP N LP Xe LP O	BD* Xe – O BD* C – N BD* C – H	7.77 0.46 6.22
21N7	LP N LP Xe LP O	BD* Xe – O BD* C – N BD* C – H	16.93 2.12 7.72
21N7'	LP N LP Xe LP O	BD* Xe – O BD* C – N BD* C – H	18.53 0.22 16.9

Table S5.9. Summed up second-order perturbation energy values (E^2 , in kcal/mol) obtained from natural bond orbital (NBO 7.0) analysis of complexes of different aza-crowns (^iPr) with XeO_3 at the APFD/def2-TZVPD level of theory.

^iPr	Donor	Acceptor	E^2
9N3	LP N	BD* Xe – O	17.59
	LP Xe	BD* C – N	2.22
	LP O	BD* C – H	7.75
12N4	LP N	BD* Xe – O	20.5
	LP Xe	BD* C – N	1.97
	LP O	BD* C – H	8.25
15N5	LP N	BD* Xe – O	13.41
	LP Xe	BD* C – N	1.2
	LP O	BD* C – H	11.74
18N6	LP N	BD* Xe – O	6.01
	LP Xe	BD* C – N	-
	LP O	BD* C – H	12.15
21N7	LP N	BD* Xe – O	15.7
	LP Xe	BD* C – N	1.74
	LP O	BD* C – H	14.11

Table S5.10. Summed up second-order perturbation energy values (E^2 , in kcal/mol) obtained from natural bond orbital (NBO 7.0) analysis of complexes of different aza-crowns (^tBu) with XeO_3 at the APFD/def2-TZVPD level of theory.

^tBu	Donor	Acceptor	E^2
9N3	LP N	BD* Xe – O	17.49
	LP Xe	BD* C – N	2.44
	LP O	BD* C – H	11.96
12N4	LP N	BD* Xe – O	16.55
	LP Xe	BD* C – N	2.13
	LP O	BD* C – H	11.7
15N5	LP N	BD* Xe – O	13.0
	LP Xe	BD* C – N	1.6
	LP O	BD* C – H	10.66
18N6	LP N	BD* Xe – O	13.48
	LP Xe	BD* C – N	1.93
	LP O	BD* C – H	12.46
21N7	LP N	BD* Xe – O	17.44
	LP Xe	BD* C – N	2.28
	LP O	BD* C – H	12.95

Table S5.11. The energy decomposition analysis (EDA) of all the complexes aza-crowns (Me) with XeO_3 at the BP86-D3BJ/TZ2P level of theory. The energy values are in kcal/mol. Contribution to the sum of all attractive energy terms are shown in percent. E_{Pauli} represents Pauli repulsion, E_{elstat} represents electrostatic interactions, E_{oi} represents orbital interaction and the E_{disp} represents the dispersion interaction.

Me	ΔE	E_{Pauli}	E_{elstat}	%	E_{oi}	%	E_{disp}	%
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XeO ₃ :9N3	-40.98	83.27	-66.33	53	-40.80	33	-17.11	14
XeO ₃ :12N4	-49.53	89.42	-74.79	54	-43.57	31	-20.59	15
XeO ₃ :15N5	-54.34	88.97	-74.72	52	-44.00	31	-24.59	17
XeO ₃ :18N6	-52.05	63.62	-58.29	50	-31.44	27	-25.94	23
XeO ₃ :21N7	-47.82	88.28	-68.57	50	-40.53	30	-27.00	20
XeO ₃ :21N7'	-48.74	102.16	-76.54	51	-48.97	32	-25.38	17

Table S5.12. The energy decomposition analysis (EDA) of all the complexes aza-crowns (Et) with XeO₃ at the BP86-D3BJ/TZ2P level of theory. The energy values are in kcal/mol. Contribution to the sum of all attractive energy terms are shown in percent. E_{Pauli} represents Pauli repulsion, E_{elstat} represents electrostatic interactions, E_{oi} represents orbital interaction and the E_{disp} represents the dispersion interaction.

Et	ΔE	E _{Pauli}	E _{elstat}	%	E _{oi}	%	E _{disp}	%
XeO ₃ :9N3	-42.20	85.96	-67.49	53	-42.49	33	-18.18	14
XeO ₃ :12N4	-51.39	92.77	-76.63	53	-45.75	32	-21.79	15
XeO ₃ :15N5	-56.38	88.54	-74.55	51	-44.63	31	-25.73	18
XeO ₃ :18N6	-52.88	64.55	-57.74	49	-32.57	28	-27.13	23
XeO ₃ :21N7	-49.14	92.30	-70.06	50	-43.10	30	-28.28	20
XeO ₃ :21N7'	-49.89	106.85	-78.72	50	-51.56	33	-26.46	17

Table S5.13. The energy decomposition analysis (EDA) of all the complexes aza-crowns (ⁱPr) with XeO₃ at the BP86-D3BJ/TZ2P level of theory. The energy values are in kcal/mol. Contribution to the sum of all attractive energy terms are shown in percent. E_{Pauli} represents Pauli repulsion, E_{elstat} represents electrostatic interactions, E_{oi} represents orbital interaction and the E_{disp} represents the dispersion interaction.

ⁱ Pr	ΔE	E _{Pauli}	E _{elstat}	%	E _{oi}	%	E _{disp}	%
XeO ₃ :9N3	-47.11	93.98	-76.25	54	-43.74	31	-21.09	15
XeO ₃ :12N4	-49.22	104.64	-80.66	52	-47.71	31	-25.48	17
XeO ₃ :15N5	-52.29	88.19	-69.42	50	-42.66	30	-28.40	20
XeO ₃ :18N6	-51.46	69.73	-58.93	49	-32.54	27	-29.72	24
XeO ₃ :21N7	-51.10	108.90	-78.41	49	-48.94	31	-32.65	20

Table S5.14. The energy decomposition analysis (EDA) of all the complexes aza-crowns (^tBu) with XeO₃ at the BP86-D3BJ/TZ2P level of theory. The energy values are in kcal/mol.

Contribution to the sum of all attractive energy terms are shown in percent. E_{Pauli} represents Pauli repulsion, E_{elstat} represents electrostatic interactions, E_{oi} represents orbital interaction and the E_{disp} represents the dispersion interaction.

'Bu	ΔE	E_{Pauli}	E_{elstat}	%	E_{oi}	%	E_{disp}	%
XeO ₃ :9N3	-45.08	97.82	-74.42	52	-45.09	32	-23.39	16
XeO ₃ :12N4	-50.97	99.74	-77.61	52	-45.47	30	-27.64	18
XeO ₃ :15N5	-40.46	88.50	-61.39	47	-39.61	31	-27.95	22
XeO ₃ :18N6	-39.66	91.12	-61.90	47	-41.62	32	-27.26	21
XeO ₃ :21N7	-41.31	109.30	-71.63	47	-47.89	32	-31.09	21

Optimized Cartesian Coordinates

XeO ₃				Aza-9-Crown-3 ^{Me} (9N3 ^{Me})				Aza-12-Crown-4 ^{Me} (12N4 ^{Me})			
Xe	0.00000000	0.00000900	-0.20562300	C	-0.10545000	-1.43817500	-0.94341800	N	-0.09586200	-1.99707800	0.11472200
O	1.42363500	0.78945900	0.46265900	C	-1.56830400	-1.20074700	-0.61173500	N	-2.50587500	0.14034100	-0.18417800
O	-0.02808900	-1.62762700	0.46263600	C	-1.43796900	1.24365000	-0.48344000	C	1.17576800	-2.06186500	-0.58710600
O	-1.39554500	0.83810900	0.46266100	C	-0.22092600	1.90722800	0.16534400	H	1.08568900	-2.67224000	-1.50393400
				C	1.63719500	0.50386500	0.90816600	H	1.89440000	-2.57962900	0.05224500
				C	0.85204200	-0.76628300	1.23684900	C	-1.19254200	-1.86976000	-0.83117500
				N	0.73493400	-1.77298800	0.19308800	H	-1.40002100	-2.85294000	-1.29758200
				N	-1.86156600	0.00213500	0.14495600	H	-0.88094100	-1.19817100	-1.63425100
				N	1.06658600	1.30619100	-0.15648800	C	-2.49153400	-1.30599800	-0.27024200
				H	0.29797000	-0.58872400	-1.51408200	H	-3.29017100	-1.59484800	-0.96000000
				H	-0.08223100	-2.30428200	-1.61450400	H	-2.74374900	-1.77951200	0.69622100
				H	-1.92907700	-2.05305500	-0.02759600	C	-1.71881400	0.67575600	0.91665400
				H	-2.12992000	-1.20584800	-1.56754100	H	-0.88405400	-0.00322700	1.09766000
				H	-1.23361100	1.09681400	-1.55318500	H	-2.32095300	0.71079300	1.84348500
				H	-2.26462100	1.96093200	-0.42958300	C	-0.28367200	-3.12085500	1.00123600
				H	-0.37797100	1.93740700	1.25394100	H	-0.28879900	-4.09026900	0.46883900
				H	-0.20669000	2.95073300	-0.16808100	H	-1.23306700	-3.03031300	1.53158000
				H	2.65291100	0.23252100	0.60559700	C	-3.85624300	0.65084700	-0.15675200
				H	1.74332300	1.09213400	1.84255100	H	-3.84597400	1.74194100	-0.11955100
				H	1.34630400	-1.24132900	2.09284000	H	-4.43121200	0.29530400	0.71855200
				H	-0.15544600	-0.49956200	1.55563900	N	0.09586200	1.99707800	-0.11472200
				C	-3.23944400	0.02375000	0.57211600	N	2.50587500	-0.14034100	0.18417800
				H	-3.42035300	0.88623200	1.21665000	C	-1.17576800	2.06186500	0.58710600
				H	-3.95591800	0.06786700	-0.26908900	H	-1.08568900	2.67224000	-1.50393400
				H	-3.46215900	-0.87533100	1.15150300	H	-1.89440000	2.57962900	-0.05224500
				C	2.01097600	-2.28531800	-0.24310700	C	1.19254200	1.86976000	0.83117500
				H	1.86297200	-3.19430500	-0.83253800	H	1.40002100	2.85294000	1.29758200
				H	2.58908000	-1.58004900	-0.86545100	H	0.88094100	-1.19817100	-1.63425100
				H	2.62150300	-2.54473300	0.62553500	C	2.49153400	-1.30599800	-0.27024200
				C	2.01886800	2.26885800	-0.65941800	H	3.29017100	-1.59484800	-0.96000000
				H	2.31996300	3.02040200	0.09331000	H	2.74374900	-1.77951200	-0.69622100
				H	2.92181600	1.75502800	-0.99741600	C	1.71881400	-0.67575600	-0.91665400
				H	1.60054300	2.79881800	-1.51753200	H	0.88405400	-0.00322700	-1.09766000
								H	2.32095300	-0.71079300	-1.84348500
								C	0.28367200	3.12085500	-1.00123600
								H	0.28879900	4.09026900	-0.46883900
								H	1.23306700	3.03031300	-1.53158000
								C	3.85624300	-0.65084700	-0.15675200
								H	3.84597400	-1.74194100	-0.11955200
								H	4.43121200	-0.29530400	-0.71855100
								H	-4.39277800	0.35576500	-1.06130200
								H	-0.51277700	3.14068900	-1.74722400
								H	0.51277700	-3.14068900	1.74722400
								H	4.39277800	-0.35576500	1.06130300

Aza-15-Crown-5 ^{Me} (15N5 ^{Me})				Aza-18-Crown-6 ^{Me} (18N6 ^{Me})				Aza-21-Crown-7 ^{Me} (21N7 ^{Me})			
C	-2.87277200	-0.98431800	-0.54467700	C	0.27130900	-3.74905600	0.12499600	N	-0.50444600	-2.07096200	0.29495400
H	-2.35687400	-0.97714500	-1.50765500	N	1.09386700	-2.62949400	-0.26653100	N	-1.15243300	2.61077100	0.51439500
H	-3.79608500	-1.58045400	-0.68697500	C	0.94243800	-2.26762100	-1.65254900	N	2.30505000	3.02020600	-0.83710000
C	-0.60092200	3.03751000	0.55679400	C	2.46808100	-2.83568100	0.12353900	C	0.80172800	-2.69179700	0.27282700
H	-0.57819300	3.71672900	1.42039600	C	3.38300100	-1.63973500	-0.12581000	H	0.66431400	-3.75388900	0.04742700
H	-0.45686400	3.67223700	-0.32259300	N	2.82550600	-0.36759200	0.26658900	H	1.28755600	-2.64700400	1.26682400
C	2.48058300	1.42048300	-0.70121300	C	3.69047300	0.71947800	-0.12482300	C	-3.60945000	2.22757300	0.52576200
H	2.91175900	2.37136600	-0.37709600	C	3.11187000	2.10974100	0.12450400	H	-3.73195800	2.06021900	1.60135500
H	2.77185400	1.28991700	-1.75885900	N	1.73087800	2.26205000	-0.26647800	H	-4.53400600	2.74384200	0.19496300
C	-3.24225200	0.44975800	-0.18962000	C	-1.22194700	-3.55491200	-0.12419600	C	1.70279300	-2.06210700	-0.79677700
H	-3.49210200	0.50584700	0.87165300	H	0.44580300	-3.93032100	1.19068800	H	1.22706900	-2.21900200	-1.77032300
H	-4.16553600	0.72709400	-0.72763200	H	0.56813500	-4.68450500	-0.39183700	H	1.76505000	-0.98622500	-0.64073600

C	-1.32570000	-2.76998600	-0.12803300	H	-0.10149700	-2.03652200	-1.85631600	C	-0.05783300	3.31729600	-0.11822700
H	-2.01068600	-3.38032800	-0.74634200	H	1.27330300	-3.06580100	-2.34400700	H	0.34571700	4.12771200	0.51465900
H	-1.02317000	-3.42193300	0.69429100	H	1.51528300	-1.36517900	-1.85789800	H	-0.44456100	3.79107900	-1.02388800
C	-1.99969100	2.40699800	0.54064400	H	2.92166900	-3.70544500	-0.39418300	C	1.07045300	2.35471900	-0.47380700
H	-2.17170600	1.93800600	1.51233500	H	2.47460900	-3.08782300	1.18908000	H	1.27458800	1.72292100	0.39008100
H	-2.74707500	3.22102900	0.44984200	H	4.34184000	-1.85097300	0.39024500	H	0.72437700	1.67022500	-1.27000300
C	2.05543700	-1.52983600	-1.21138700	H	3.62651800	-1.57887100	-1.19163500	C	4.29712100	-0.70578900	0.27736300
H	2.39891600	-2.47953600	-1.67105500	H	3.91093400	0.59861700	-1.19055900	H	5.23493500	-0.61187500	0.86107000
H	1.66823200	-0.92213400	-2.03740400	H	4.67110800	0.67798100	0.39182200	H	4.52938100	-0.39043000	-0.74301500
C	0.96517400	1.56429600	-0.61474300	H	3.18199400	2.35156200	1.19015600	C	3.44058100	2.11284700	-0.80949500
H	0.46831500	0.60705400	-0.80701400	H	3.77322600	2.83465100	-0.39259800	H	4.30391500	2.66929100	-1.18457500
H	0.67486600	2.25242400	-1.41405400	H	-1.43691400	-3.68584900	-1.18986700	H	3.29012000	1.26075800	-1.49731200
C	-0.10636100	-2.44325900	-0.97482700	H	-1.74818400	-4.38316100	0.39287300	N	-3.46753500	0.93473100	-0.10614000
H	0.24776800	-3.40395600	-1.40383300	C	1.22196800	3.55485800	0.12443000	N	-3.32576500	-1.96290500	-0.42681800
H	-0.40001900	-1.82320800	-1.82965000	N	-1.73084600	-2.26208100	0.26668400	C	-2.45217600	3.18814800	0.27145500
C	3.29220700	-0.86700400	-0.62383100	C	-0.27126000	3.74905100	-0.12492200	H	-2.63170300	4.09336800	0.88395800
H	3.79348400	-1.56937600	0.04868900	H	1.43686800	3.68574400	1.19012000	H	-2.48317500	3.51757700	-0.76970000
H	3.99545200	-0.70119200	-1.46533900	H	1.74826500	4.38310200	-0.39258600	N	3.30431600	0.21418600	0.82075400
N	0.53152000	2.14103300	0.64769300	C	-3.11175500	-2.10965900	-0.12453600	C	-4.59557800	0.09312700	0.22920300
N	-2.17180900	1.38444300	-0.46572400	N	-1.09391500	2.62952800	0.26653700	H	-4.61530400	-0.01193200	1.31960600
N	-2.00714700	-1.61897000	0.43187000	H	-0.44561700	3.93028100	-1.19064400	H	-5.55837200	0.57322500	-0.04141900
N	0.96460400	-1.75443100	-0.28931900	H	-0.56811600	4.68452000	0.39185100	N	3.06452800	-2.56357000	-0.87139200
N	3.05399200	0.35364400	0.11076400	C	-3.69032100	-0.71940300	0.12484500	C	-1.48253500	-2.89532900	0.96384300
C	4.24350800	0.77297000	0.81348100	H	-3.18172800	-2.35138100	-1.19021900	H	-1.45157900	-3.89413100	0.51804900
H	5.07817600	1.04105700	0.13972100	H	-3.77321200	-2.83457600	0.39243500	H	-1.23666500	-3.03124100	2.03736100
H	4.01806400	1.63991800	1.43669100	C	-0.94269200	2.26761000	1.65256300	C	3.93405900	-2.18584200	0.22301900
H	4.59089200	-0.02999800	1.46893300	C	-2.46806500	2.83579800	-0.12367300	H	3.56349000	-2.53081100	1.20367700
C	0.40116900	1.16076600	1.70880600	N	-2.82542500	0.36765300	-0.26674100	H	4.87733600	-2.71977000	0.06975100
H	-0.35987400	0.39616800	1.49298200	H	-3.91064500	-0.59851000	1.19060500	C	3.73734500	1.58742600	0.59681600
H	1.35254900	0.64840800	1.83923500	H	-4.67100600	-0.67792000	-0.39171000	H	4.81454800	1.68687200	0.81977700
H	0.14647800	1.67131300	2.64282800	H	0.10119400	2.03640100	1.85643300	H	3.22471600	2.23972300	1.30781000
C	-2.25408400	1.90777000	-1.80491900	H	-1.27358500	3.06578900	2.34401300	C	-4.59614100	-1.27864100	-0.44093400
H	-1.37820800	2.51160600	-2.04058600	H	-1.51565000	1.36521200	1.85780700	H	-5.40259700	-1.87671100	0.02857400
H	-2.28773300	1.09040600	-2.52879900	C	-3.38302500	1.63983300	0.12545800	H	-4.88818100	-1.15875000	-1.48806000
H	-3.15214500	2.53458500	-1.96029400	H	-2.92168500	3.70552600	0.39408400	C	-2.89979200	-2.33705800	0.90018900
C	1.36385100	-2.36632300	0.95105400	H	-2.47444500	3.08806400	-1.18918300	H	-2.96389300	-1.45188100	1.53563700
H	2.14074500	-1.76251800	1.41746400	H	-4.34175600	1.85105200	-0.39080300	H	-3.57671600	-3.09403500	1.34630800
H	0.52163400	-2.38430200	1.64236000	H	-3.62678900	1.57899800	1.19122800	C	-0.91768500	2.36072100	1.91427600
H	1.74136800	-3.40002800	0.83228300	C	2.43846200	-0.31797000	1.65318000	H	-0.96141700	3.28511800	2.51917600
C	-2.72981800	-1.97980200	1.62920200	H	3.29602300	-0.43173100	2.34336500	H	-1.65334900	1.65708800	2.30493800
H	-3.51775900	-2.73382400	1.44481800	H	1.94454700	0.62970400	1.85982400	H	0.06432100	1.91055800	2.05956500
H	-2.03960800	-2.38178500	2.37357500	H	1.71586600	-1.10586900	1.85764400	C	-3.20245300	1.01780600	-1.52250100
H	-3.20701600	-1.10362000	2.06970400	C	-1.49296200	-1.95054900	1.65276900	H	-3.02548800	0.01800100	-1.91453100
				H	-1.81622500	-0.93157100	1.85745000	H	-4.02414800	1.49328900	-2.09012800
				H	-2.01739600	-2.63742600	2.34403700	H	-2.28904200	1.58821500	-1.68643100
				H	-0.42478500	-1.99382100	1.85741900	C	2.20619400	3.68135400	-2.11788500
				C	1.49272500	1.95051900	-1.65252800	H	1.99479500	2.97968900	-2.94560200
				H	2.01642000	2.63787300	-2.34387800	H	1.41282100	4.42969200	-2.10013900
				H	1.81668600	0.93182300	-1.85745900	H	3.14179300	4.19806300	-2.34212900
				H	0.42443700	1.99298000	-1.85678300	C	3.06146900	-0.02583900	2.22524500
				C	-2.43830800	0.31770500	-1.65329500	H	2.69485800	-1.03967000	2.38224000
				H	-1.94377300	-0.62974600	-1.85952000	H	3.96654500	0.11086900	2.84486900
				H	-3.29591400	0.43065400	-2.34356600	H	2.29258700	0.65898300	2.58840900
				H	-1.71622300	1.10598400	-1.85807800	C	3.13873100	-3.97757000	-1.15310200
								H	2.85751600	-4.62364400	-0.30357800
								H	2.47554600	-4.21733000	-1.98762000
								H	4.15745200	-4.24543000	-1.44631600
								C	-0.47030400	-0.73804400	0.85458500
								H	-0.33042700	-0.76077000	1.95312300
								H	0.35819700	-0.17780900	0.43159700
								H	-1.38475200	-0.19437700	0.61762800
								C	-3.28958500	-3.05780600	-1.36221600
								H	-2.26723800	-3.42016700	-1.47220600
								H	-3.93481100	-3.90633300	-1.06582200
								H	-3.62181500	-2.71153200	-2.34329100

Aza-9-Crown-3 ^{Et} (9N3 ^{Et})				Aza-12-Crown-4 ^{Et} (12N4 ^{Et})			
C	0.76894600	0.68368100	1.37408000	C	-2.33272400	0.48725800	-0.81853000
C	1.60151300	-0.54254600	0.99151100	C	1.30635200	-1.59689900	-0.63004500
C	-0.15739100	1.45104900	-0.78854800	C	-1.30635200	1.59688400	-0.63008400
C	-1.61647500	1.12077900	-0.51931400	C	2.33272300	-0.48727700	-0.81852200
C	-0.16894100	-1.98674800	0.09241600	C	-0.48720600	-2.33251800	0.81857300
C	-1.39777200	-1.33086200	-0.54486400	C	1.59687800	1.30619900	0.63001400
H	1.22278900	1.12255600	2.27102500	C	-1.59687700	-1.30617800	0.63005100
H	-0.23528400	0.36178000	1.64758500	C	0.48720700	2.33254800	0.81851500
H	2.61629600	-0.22377300	0.73247000	H	-3.18025400	0.60148500	-0.11767200
H	1.69998000	-1.17458300	1.89560500	H	-2.75661500	0.61579200	-1.81740800
H	0.29837500	0.65695000	-1.39802200	H	0.43794600	-1.34217600	-1.23682000
H	-0.16470800	2.35423600	-1.40501800	H	1.72665300	-2.54462300	-0.10940400
H	-0.08539600	-3.00208500	-0.31384200	H	3.18025500	-0.60148500	-0.11766300
H	-0.35787400	-2.10509700	1.16888100	H	2.75661200	-0.61583700	-1.81739800
H	-2.20414200	-2.07463300	-0.55781800	H	1.34212100	0.43774600	1.23671800
H	-1.17309800	-1.11125400	-1.59691800	H	2.54456200	1.72649900	1.01946900
H	-2.14105900	1.17440200	-1.49203400	H	0.60144200	3.18013800	0.11772900
H	-2.03775600	1.91008300	0.11202700	H	0.61573300	2.75634800	1.81742900
N	1.07696700	-1.27921100	-0.13790300	H	-1.72665300	2.54459800	-1.01947100
N	-1.85244300	-0.14174900	0.14790300	H	-0.43794800	1.34214200	-1.23685100
N	0.64324700	1.74783400	0.38894700	H	-2.54455800	-1.72647000	1.01952100
C	2.07361300	-2.03344200	-0.87051300	H	-1.34212200	-0.43770700	1.23673100
H	2.84011300	-1.32902000	-1.21338800	H	-0.61573200	-2.75629200	1.81749900
H	1.59926200	-2.42326900	-1.77733500	H	-0.60144300	-3.18012700	0.11780900
C	-3.15975800	-0.25345500	0.75927000	N	-1.76968500	-0.84867300	-0.74017700
H	-3.26710900	0.57097500	1.47340300	N	-0.84875600	1.76955700	0.74012800
H	-3.17150600	-1.17136000	1.35655000	N	0.84875800	-1.76953100	0.74017100

C	1.92055900	2.33751700	0.03305600	N	1.76968300	0.84865300	-0.74020400
H	2.55697100	2.30151000	0.92308300	C	-1.80892200	2.50432000	1.54324400
H	2.44403500	1.74796700	-0.74234100	H	-2.80930800	2.20599200	1.21929200
C	-4.35320600	-0.25039000	-0.19825100	H	-1.74005000	3.59168500	1.34843100
H	-4.28448800	-1.06212900	-0.92742000	C	1.80892700	-2.50427300	1.54330500
H	-5.28913900	-0.37687100	0.35235900	H	2.80931200	-2.20595000	1.21934200
H	-4.41860900	0.68953800	-0.75094100	H	1.74005700	-3.59164400	1.34851700
C	2.74281900	-3.17792100	-0.10787800	C	-2.50448200	-1.80888200	-1.54321900
H	2.01029000	-3.91285900	0.23638100	H	-3.59183300	-1.74004300	-1.34832300
H	3.46237800	-3.69916500	-0.74492000	H	-2.20609800	-2.80925300	-1.21927300
H	3.28079700	-2.80868200	0.76844700	C	2.50448000	1.80883500	-1.54327900
C	1.80813700	3.78542400	-0.42140100	H	3.59183200	1.73999800	-1.34838700
H	2.80101100	4.20949900	-0.59343300	H	2.20610300	2.80921700	-1.21936400
H	1.24918800	3.88552300	-1.35422000	C	-2.22589000	-1.68029600	-3.03172700
H	1.30201300	4.38313100	0.33983400	H	-1.16088700	-1.81509100	-3.23330300
				H	-2.78211000	-2.43467200	-3.59423800
				H	-2.51613900	-0.70271400	-3.42321000
				C	2.22587700	1.68019900	-3.03177900
				H	2.51612300	0.70260400	-3.42323300
				H	1.16087300	1.81498800	-3.23335200
				H	2.78209300	2.43455700	-3.59431900
				C	-1.68031400	2.22560900	3.03172700
				H	-0.70271300	2.51578800	3.42321000
				H	-2.43465600	2.78181600	3.59429800
				H	-1.81514700	1.16059500	3.23322200
				C	1.68032400	-2.22552900	3.03178200
				H	0.70272500	-2.51570100	3.42327600
				H	2.43466900	-2.78172300	3.59436300
				H	1.81515600	-1.16051100	3.23325400

Aza-15-Crown-5 ^{Et} (15N5 ^{Et})				Aza-18-Crown-6 ^{Et} (18N6 ^{Et})				Aza-21-Crown-7 ^{Et} (21N7 ^{Et})			
C	-2.09972600	-1.90100100	0.50292900	C	3.61001700	-1.05687100	-0.13767800	C	0.08376600	-1.95271100	-1.43668300
H	-2.13906900	-1.00719000	1.12576200	C	-3.61002800	1.05688100	0.13767900	C	4.19368100	0.35495900	-0.04935300
H	-2.94629200	-2.54310100	0.80523000	C	-3.51879200	-1.32784900	0.13855500	C	-2.18124500	-1.09543500	-1.42897900
C	1.63949700	-0.58566800	-1.13843200	C	-2.71990200	-2.59681300	-0.13416500	C	-3.90455500	-0.60987300	1.56656300
H	0.95219600	0.24791500	-1.00561900	C	-0.60900300	-3.70962000	-0.13584200	C	3.79576500	1.76294200	-0.48045100
H	1.84122600	-0.66119600	-2.22535200	C	0.88949400	-3.65273500	0.13626700	C	-2.94881500	0.22700900	-1.50725900
C	2.24717700	2.00316500	0.42842800	C	-2.90979400	2.38288100	-0.13477900	C	-1.85284900	0.20450800	2.62075400
H	2.80927300	2.87860500	0.80531900	H	-3.80427700	0.95965700	1.21211000	C	-4.22065200	0.53926400	0.59158200
H	1.99636700	1.39853100	1.30251800	H	-4.60963200	1.11468000	-0.33486800	C	2.41408200	-2.22089900	0.58535700
C	-0.79856900	-2.63134200	0.81252000	H	-3.71900600	-1.24539300	1.21314300	C	-0.59402300	0.79155300	1.99019900
H	-0.71910100	-3.55967500	0.22238500	H	-4.51148400	-1.46171500	-0.33314700	C	3.58524500	-1.55223800	1.29943100
H	-0.85538900	-2.95408500	1.85724800	H	-2.73413200	-2.81442700	-1.20843200	C	1.53654900	-1.48960500	-1.57330200
C	-2.84105500	-0.18754300	-1.08114600	H	-3.26845000	-3.43367800	0.33977000	C	0.05569800	1.79946500	-0.12347200
H	-3.82960200	-0.11372200	-0.59351400	H	-0.78100800	-3.84292800	-1.21022100	C	1.50942100	2.08949200	0.24554400
H	-3.02273300	-0.08262000	-2.15639500	H	-0.98963200	-4.63554300	0.33703600	H	-0.04248000	-2.95317300	-1.89294000
C	0.94105000	-1.85868400	-0.68750000	H	1.33922100	-4.54711300	-0.33668300	H	-0.14585000	-2.06795700	-0.37391200
H	0.10531200	-2.00330300	-1.37286400	H	1.07109000	-3.77267500	1.21062700	H	3.90242900	-0.34272700	-0.83460300
H	1.60237000	-2.73415800	-0.81150200	H	-3.52049600	3.17564800	0.33896200	H	5.29895000	0.31270800	0.02000900
C	-0.70874900	1.54559300	1.37837000	H	-2.94020500	2.59877500	-1.20906400	H	-2.08532100	-1.33796800	-0.37201500
H	-0.85365900	1.66018500	2.45487300	C	2.90979800	-2.38287200	0.13482800	H	-2.75745000	-1.90505800	-1.91414700
H	-0.08295100	0.65769200	1.24286100	C	3.51876400	1.32786100	-0.13867300	H	-4.44512400	-0.42600100	2.51239500
C	3.16340300	1.15658300	-0.45404500	C	2.71990200	2.59684100	0.13404600	H	-4.31408700	-1.54302100	1.16706700
H	4.18329800	1.28498400	-0.08517400	C	0.60900800	3.70964100	0.13583900	H	-3.11768100	0.49647100	-2.55867800
H	3.16500900	1.53928000	-1.49158100	C	-0.88949600	3.65275000	-0.13620800	H	-2.31834100	1.00922600	-1.07026400
C	-1.96321000	0.98035900	-0.63932600	H	3.80423700	-0.95969200	-1.21211700	H	-5.20405800	0.94138900	0.85751700
H	-0.93733100	0.75864900	-0.92788800	H	4.60963200	-1.11464200	0.33484000	H	-3.49811900	1.34217600	0.75946100
H	-2.25530400	1.87983400	-1.20652100	H	3.71889300	1.24535200	-1.21327200	H	4.42140800	2.00784600	-1.34474300
C	0.02065700	2.78170700	0.82216200	H	4.51149200	1.46173800	0.33293800	H	4.06515700	2.49932100	0.29632100
H	-0.71561100	3.45718000	0.38148500	H	2.73423300	2.81455500	1.20829100	H	-2.56475400	1.01030200	2.81850900
H	0.49651300	3.35274200	1.64022900	H	3.26841600	3.43365500	-0.34002100	H	-1.59784700	-0.20699800	3.60876600
N	-2.21437600	-1.47762200	-0.88107500	H	0.78107600	3.84300500	1.21020000	H	0.00143400	0.82767200	-0.61998500
N	-2.00239100	1.24057700	0.79187800	H	0.98961000	4.63554500	-0.33711100	H	-0.30590500	2.51993800	-0.86048900
N	1.00828300	2.44759700	-0.19599800	H	-1.33921400	4.54712100	0.33675000	H	0.05489500	1.19810100	2.78652100
N	2.85937100	-0.25982100	-0.41650900	H	-1.07111900	3.77269400	-1.21056000	H	-0.03223900	-0.02139300	1.52333300
N	0.37731300	-1.79173400	0.65062400	H	3.52050300	-3.17563400	-0.33892400	H	1.61302700	-0.45610600	-1.22514500
C	1.24470100	3.54950900	-1.11297900	H	2.94023000	-2.59876300	1.20911500	H	1.82659200	-1.47106300	-2.62948600
H	1.42190000	4.49059000	-0.55783100	N	1.52519100	-2.42250700	-0.27080300	H	2.29964200	-3.23464300	0.99398500
H	2.17102400	3.34165400	-1.65417100	N	2.86258500	0.10880400	0.26954400	H	1.50895000	-1.67553400	0.87256700
C	3.98134100	-1.07867500	-0.83651400	N	1.33613400	2.53113900	-0.27114600	H	4.53710300	-1.98297000	0.94451000
H	3.59499200	-2.07566700	-1.06120900	N	-1.52517600	2.42250800	0.27085000	C	3.50296700	-1.80993900	2.35902700
H	4.41445600	-0.70168200	-1.78266200	N	-2.86258700	-0.10877700	-0.26955500	H	1.61220000	3.10027700	0.67903100
C	-3.07732600	2.14039100	1.15140300	N	-1.33617200	-2.53114600	0.27117600	H	1.82170000	1.38209300	1.01351600
H	-3.95862000	1.82774800	0.58358400	C	1.26786700	-2.01449800	-1.63778600	N	-4.22838500	0.26429600	-0.83114500
H	-2.87188300	3.18026100	0.82913400	H	1.65431800	-1.00011200	-1.74651100	N	-0.84585000	-0.98651700	-1.97585900
C	-2.69120100	-2.51147000	-1.77839600	H	0.18616500	-1.92286100	-1.74554000	N	2.51720900	-2.28731000	-0.86314200
H	-2.09664200	-3.41177200	-1.59175800	C	2.38368900	0.09100000	1.63766000	N	-2.48614200	-0.80098900	1.78806500
H	-2.45606700	-2.20352600	-2.80426600	H	1.69774600	0.93219800	1.74709800	N	-0.88592600	1.79050200	0.98191300
C	1.33940400	-1.93653400	1.73501100	H	1.76489200	-0.80062900	1.74814200	N	2.40673700	1.89154400	-0.88137500
H	0.81359700	-1.69993300	2.66674800	C	-1.26782100	2.01448000	1.63782300	N	3.59329400	-0.10257800	1.19566500
H	2.10209500	-1.17020200	1.59498300	H	-0.18612800	1.92283000	1.74557400	C	-5.18854200	-0.70694600	-1.30121500
C	2.01580600	-3.30299300	1.86931900	H	-1.65426000	1.00009300	1.74654700	H	-4.97675500	-1.73369300	-0.95075500
H	2.68113000	-3.31054200	2.73700300	C	1.11033300	2.10454400	-1.63808000	H	-5.08830800	-0.74452500	-2.39171300
H	1.28854700	-4.10832000	2.00285600	H	0.03875100	1.93066700	-1.74568600	C	-0.79150300	-0.84744700	-3.42318100
H	2.62230800	-3.54407100	0.99311300	H	1.57298300	1.12258800	-1.74679900	H	-0.20581300	-1.67185000	-3.85373500
C	-4.17879400	-2.86127300	-1.68941500	C	-2.38355500	-0.09090300	-1.63762800	H	-1.80140900	-0.95892500	-3.83652400
H	-4.45994900	-3.19149300	-0.68677800	H	-1.69765400	-0.93213900	-1.74705200	C	-2.09858300	-2.15734000	2.12116500
H	-4.80575400	-2.00421500	-1.94666500	H	-1.76469000	0.80070200	-1.74798400	H	-2.37043200	-2.80479600	1.27895400
H	-4.42233500	-3.66996800	-2.38345500	C	-1.11052100	-2.10467100	1.63817300	H	-1.00427900	-2.18483600	1.27786900
C	5.06159800	-1.20648200	0.22495800	H	-1.57321000	-1.12274900	1.74694300	C	-1.16042300	3.08692600	1.57219300
H	4.64810000	-1.63954800	1.13827900	H	-0.03896300	-1.93075200	1.74591200	H	-1.88659000	2.92978800	2.37613900
H	5.87060300	-1.85217500	-0.12629300	C	3.45176000	0.13360100	2.73023100	H	-0.26564100	3.51501100	2.06063300
H	5.50526400	-0.24221800	0.48308900	H	2.98389300	0.15603300	3.71810000	C	2.71162000	-3.62207500	-1.38924300
C	0.12546700	7.37344500	-2.12290900	H	4.12873700	-0.72362300	2.67307030	H	1.92379900	-4.32041600	-0.105118200

H	-0.82643700	3.97570600	-1.64581000	H	4.06038300	1.03950500	2.67182700	H	2.61945700	-3.56102200	-2.47802900
H	0.36213800	4.54852000	-2.81150400	C	-1.60700400	-3.04830800	2.73329800	C	4.21175000	0.52319600	2.35293400
H	-0.01705800	2.81942900	-2.70304100	H	-1.12621500	-4.02867700	2.67682700	H	5.18320500	0.04780300	2.58509900
C	-3.42377900	2.12294200	2.63065100	H	-1.38754400	-2.63208400	3.72005300	H	4.44084300	1.55842100	2.09001400
H	-3.62177300	1.10186900	2.96494500	H	-2.68741500	-3.20656400	2.67724800	C	2.21194600	2.83500600	-1.97190800
H	-2.62234900	2.53131100	3.24984600	C	-1.83471400	2.91748800	2.73302300	H	1.18399900	2.73526800	-2.32730200
H	-4.31536900	2.72654500	2.81737400	H	-1.58406100	2.51914300	3.71972700	H	2.84437900	2.50592100	-2.80293700
				H	-1.43004400	3.93165600	2.67659800	C	-1.73867700	4.09077500	0.58969200
				H	-2.92404300	2.99294800	2.67711500	H	-1.00682000	4.40573200	-0.15714700
				C	-3.45152500	-0.13284000	-2.73030700	H	-2.59693900	3.66613600	0.06310200
				H	-4.12843500	0.72390100	-2.67319800	H	-2.06917200	4.98822500	1.11788900
				H	-2.98355300	-0.11539400	-3.71812400	C	-2.69181400	-2.73834900	3.40584300
				H	-4.06023100	-1.03923500	-2.67200000	H	-3.78187300	-2.78675500	3.35118300
				C	1.60673500	3.04807000	-2.73334100	H	-2.32204300	-3.75343900	3.57235500
				H	1.38711600	2.63178700	-3.72003400	H	-2.42842300	-2.14337000	4.28367100
				H	1.12602000	4.02847600	-2.67688100	C	2.49966600	4.30683200	-1.66657600
				H	2.68716100	3.20625700	-2.67744800	C	3.52670800	4.45425300	-1.32302300
				C	1.83479700	-2.91752400	-2.73295600	H	2.35973200	4.91305300	-2.56522900
				H	1.43009100	-3.93167900	-2.67655800	H	1.83065000	4.70109700	-0.89818200
				H	1.58421000	-2.51916400	-3.71967000	C	3.31789700	0.52578300	3.58165500
				H	2.92412100	-2.99302100	-2.67699600	H	3.82304500	1.00785500	4.42258400
								H	2.39201200	1.06836200	3.38052600
								H	3.04797800	-0.48393900	3.89920300
								C	4.07344700	-4.19849200	-1.03581600
								H	4.19522400	-4.31291900	0.04418200
								H	4.20225600	-5.18653600	-1.48558600
								H	4.87152800	-3.54439300	-1.39449400
								C	-0.20438500	0.48423900	-3.86808200
								H	-0.17143200	0.55822200	-4.95952600
								H	-0.80553400	1.31237400	-3.48588300
								H	0.80915400	0.60840000	-3.48283500
								C	-6.62625600	-0.35720200	-0.94844900
								H	-6.82039600	-0.44178500	0.12335900
								H	-6.86013900	0.66508500	-1.25549900
								H	-7.31499000	-1.03712900	-1.45581000

Aza-9-Crown-3 ^{iPr} (9N3 ^{iPr})				Aza-12-Crown-4 ^{iPr} (12N4 ^{iPr})			
C	-0.00261300	-1.82349200	0.52998100	C	1.10223900	2.24652800	-0.81498000
C	0.92539700	-0.79142100	1.17133100	C	-1.91741000	-1.12785400	-1.46184700
C	-0.81662300	-0.53280700	-1.38746200	C	1.91811700	1.13089800	-1.46126900
C	-1.21847400	0.93790900	-1.31262000	C	-1.10276900	-2.24460500	-0.81595100
C	1.89931400	1.29257100	0.30522400	C	-2.51772100	1.17940000	-1.02919900
C	0.89010800	1.95784000	-0.62800100	C	1.18048400	-1.82916400	-1.36895300
H	-0.39380700	-2.45642000	1.33083200	C	-1.18172300	1.83248400	-1.36764900
H	0.59160800	-2.48787400	-0.12356200	C	2.51686100	-1.17704600	-1.03037700
H	0.29618600	-0.02848700	1.62993600	H	1.67038300	2.66414800	0.01758800
H	1.48842100	-1.28404700	1.98219900	H	0.99421700	3.07232600	-1.54123400
H	-1.31823000	-0.99850000	-2.24921900	H	-1.27505500	-0.60554700	-2.17247200
H	0.25732700	-0.59641900	-1.57664000	H	-2.72960000	-1.57334800	-2.06403300
H	1.74571900	1.65677600	1.33308700	H	-1.67143000	-2.66224300	0.01622400
H	2.90078600	1.62478300	0.01587400	H	-0.99513100	-3.07004400	-1.54270800
H	1.10486200	1.62233600	-1.64820300	H	1.40918600	-2.86564100	-1.69233700
H	1.05331000	3.04727900	-0.62290000	H	0.75786900	-1.34708500	-2.25651600
H	-2.28278700	0.98881000	-1.07149900	H	3.13418800	-1.23304800	-1.94615200
H	-1.10190200	1.40122600	-2.30988900	H	3.03401800	-1.79215500	-0.29010500
N	1.82927200	-0.15072300	0.23474500	H	2.73095900	1.57758500	-2.06166900
N	-0.47725100	1.63446900	-0.29225000	H	1.27718900	0.60922500	-2.17364200
N	-1.12664200	-1.23017700	-0.15628300	H	-0.76015500	1.35266400	-2.25692700
C	3.08639300	-0.86158500	0.04808500	H	-1.41093400	2.86971100	-1.68827900
H	2.82154700	-1.92519800	0.07528900	H	-3.03485700	1.79361000	-0.28816100
C	-1.17686200	2.64166300	0.48661500	H	-3.13540500	1.23597800	-1.94469700
H	-0.42218600	3.05636900	1.16648300	N	-0.17829800	1.78153900	-0.33859000
C	-2.34693700	-2.02176800	-0.21221900	N	2.42065700	0.16657300	-0.50422800
H	-3.03694600	-1.43640300	-0.83240100	N	-2.42080200	-0.16462800	-0.50418700
C	-2.26270300	2.02016500	1.35629700	N	0.17792300	-1.78073600	-0.33888700
H	-2.68386200	2.76619800	2.03512800	C	3.62566600	0.62879000	0.18472100
H	-3.08602000	1.62735800	0.75422600	H	3.45406200	1.69256200	0.38212000
H	-1.85882600	1.19321600	1.94201000	C	-3.62577300	-0.62801200	0.18405500
C	4.11771500	-0.61235100	1.15282600	H	-3.45399800	-1.69198200	0.38017300
H	3.69616300	-0.80163400	2.14304800	C	-0.59527500	2.23159500	0.97905500
H	4.98672500	-1.26388500	1.02995800	H	-1.50603600	1.66701400	1.19552500
H	4.47621100	0.42033100	1.13283900	C	0.59579000	-2.23473400	0.97711000
C	-2.99589100	-2.15489900	1.16016000	H	1.50650700	-1.67051800	1.19483100
H	-2.39493400	-2.76894400	1.83623600	C	-0.92060400	3.72508000	1.06654200
H	-3.12473600	-1.17280900	1.61862600	H	-1.26511500	3.99053100	2.06968700
H	-3.97444000	-2.63468300	1.07668900	H	-0.03537400	4.33072300	0.84987800
C	3.67866400	-0.58511300	-1.32772200	H	-1.70361700	4.01309700	0.36015200
H	4.57337000	-1.19058800	-1.49322200	C	0.92171200	-3.72837100	1.05981700
H	2.95325500	-0.81294600	-2.11148200	H	1.26668900	-3.99681300	2.06200000
H	3.97238000	0.46271200	-1.43507800	H	0.03659200	-4.33361300	0.84159400
C	-2.17163900	-3.39281000	-0.87201900	H	1.70455300	-4.01392200	0.35224200
H	-3.13347100	-3.89786600	-0.99345700	C	4.91495800	0.51324200	-0.63619300
H	-1.71198700	-3.30342600	-1.85968800	H	5.73914600	1.01940900	-0.12783900
H	-1.53405700	-4.03919400	-0.26265600	H	5.20513000	-0.53215400	-0.77008100
C	-1.73676100	3.79248600	-0.35427400	H	4.81158000	0.96253800	-1.62666500
H	-2.52536100	3.43478800	-1.02208900	C	-4.91501500	-0.51180200	-0.63682900
H	-2.16775600	4.57257600	0.27883800	H	-5.73905800	-1.01899900	-0.12926700
H	-0.95874700	4.25125300	-0.97000500	H	-5.20560800	0.53364800	-0.76935000
				H	-4.81129200	-0.95973200	-1.62788700
				C	0.42512600	1.83186300	2.03701700
				H	0.77403900	0.81775900	1.84557500
				H	1.29458700	2.49537900	2.04416600
				H	-0.02111000	1.87925100	3.03328000
				C	3.79751900	-0.04863800	1.53858200

	H	4.64860000	0.38232900	2.07200400
	H	2.90679900	0.07654400	2.15473100
	H	3.99538400	-1.11897100	1.43540600
	C	-0.42419700	-1.83885100	2.03696800
	H	0.02279500	-1.88894000	3.03276000
	H	-0.77399400	-0.82437500	1.84907200
	H	-1.29316000	-2.50302300	2.04275300
	C	-3.79773600	0.04769100	1.53875000
	H	-2.90706600	-0.07842400	2.15480600
	H	-3.99540500	1.11819300	1.43694400
	H	-4.64892600	-0.38384700	2.07153300

Aza-15-Crown-5 ^{iPr} (15N5 ^{iPr})				Aza-18-Crown-6 ^{iPr} (18N6 ^{iPr})				Aza-21-Crown-7 ^{iPr} (21N7 ^{iPr})			
C	-0.61185000	-2.06795000	0.51166100	C	-0.64920100	-2.69674100	-0.07778000	C	-2.28979900	2.25797400	-0.96948300
H	-1.30109300	-1.26933800	0.78038200	C	0.48202400	1.33496000	1.81250900	C	3.06216500	0.39946100	-2.05792800
H	-0.99176300	-2.99784200	0.97457200	C	-1.67670300	2.09797000	0.99195300	C	-3.32735000	0.13533400	-1.55943100
C	2.43174900	1.01143500	1.08317600	C	-1.64183000	1.72313300	-0.48707600	C	-3.23681900	-3.40141900	0.31429600
H	3.32795400	1.56635300	1.41630800	C	-3.54701800	0.22489300	-0.72882000	C	2.54061000	-0.93854500	-1.54964000
H	1.61357500	1.72951900	1.02525700	C	-2.93593100	-1.01112300	-1.44112300	C	-2.10777300	-0.73339200	-1.27351300
C	0.60355900	1.36423600	-1.37554500	C	1.97012700	1.55946100	1.56144300	C	-0.81420600	-2.49172300	1.99708800
H	0.20175700	0.38062300	-1.11824100	H	0.17152500	0.46625400	1.22769200	C	-1.58506700	-3.08239500	-0.98560800
H	0.30128600	1.55728800	-2.42020700	H	0.35415200	1.04620600	2.87203900	C	1.14058100	2.84951300	0.03241000
C	0.77499700	-1.70808800	1.04772000	H	-2.12497400	1.28773400	1.59077500	C	-0.07124100	-1.16862500	1.85799200
H	1.38667600	-1.37449200	0.21107700	H	-2.34876600	2.95255300	1.08624000	C	1.58501300	2.08976300	-1.21186400
H	1.27452000	-2.59372800	1.48218100	H	-0.97633100	0.85846300	-0.64160700	C	-1.21820800	2.24829300	0.11779400
C	-1.99697700	-2.15307400	-1.46065200	H	-1.17036900	2.55315700	-1.01470300	C	2.29797300	-0.82067400	1.58032600
H	-2.68102300	-2.70737800	-0.79628100	H	-4.62004700	0.27995100	-0.93953300	C	2.63699300	-1.97300400	0.63942000
H	-2.01465300	-2.69250300	-2.41110900	H	-3.46190200	0.06842900	0.34971500	H	-2.68932600	3.27352100	-1.04931800
C	2.07801500	-0.01616800	2.15377600	H	-1.88834500	-0.78866500	-1.66535200	H	-1.81157800	2.06097900	-1.93775000
H	2.85467300	-0.79847500	2.21732600	H	-3.42439700	-1.16667600	-2.40834300	H	4.12536300	0.28947600	-2.28001100
H	2.10901600	0.50820400	3.11190100	H	2.49366400	0.72791500	2.04159300	H	2.57672500	0.64769800	-3.01724000
C	-2.35483900	1.47968400	-0.72520300	H	2.31507200	2.46625900	2.09172100	H	-3.38355600	0.39745100	-2.63113500
H	-2.09278700	1.66457100	-1.76798300	C	-2.04161300	-2.29847800	0.40062600	H	-4.21039700	-0.46913600	-1.33685600
H	-2.23396100	2.10830700	-0.53611800	C	1.71532800	-2.50768200	0.21867900	H	-3.39129800	-3.44208700	0.07526200
C	2.12907100	1.27531600	-1.32665600	C	1.97341800	-1.41572100	-0.83664600	H	-2.03363500	-4.41481100	0.64132100
H	2.55762300	2.29306000	-1.30864700	C	3.97070000	-0.33091000	0.04635400	H	-2.02253900	-0.81265800	-0.19170800
H	2.46407700	0.82333000	-2.26364600	C	3.74701700	1.17568300	-0.01102100	H	-1.18719200	-0.24240300	-1.63626600
C	-2.53744600	-0.75506700	-1.74436300	H	-0.45572100	-2.15661100	-1.00591900	H	-0.53722700	-2.81854000	-0.75647400
H	-1.82544800	-0.26877500	-2.41404100	H	-0.65794600	-3.76665700	-0.35434500	H	-1.54105200	-4.00660100	-1.56625400
H	-3.48301900	-0.85849600	-2.30933100	H	1.84230700	-3.50917800	-0.22749000	H	2.42740700	-1.63324100	-2.39703100
C	-1.17747000	1.93494900	0.18301700	H	2.47712600	-2.41613300	0.99409700	H	1.53097100	-0.79383700	-1.15414600
H	-1.50090800	2.74957100	0.83661900	H	1.55915400	-1.71260500	-1.80519400	H	-0.89250300	-2.76167100	3.06016200
H	-0.92430800	1.09185600	0.83212700	H	1.44157800	-0.51630400	-0.52135600	H	-0.20745600	-3.27987100	1.54033200
N	-0.64205600	-2.14747000	-0.94033000	H	3.64207000	-0.72190600	1.02205300	H	2.06399600	0.06958500	0.97878400
N	-2.68415400	0.07542800	-0.57131300	H	5.05055600	-0.49830100	0.02240600	H	3.19785500	-0.56681100	2.14456400
N	0.04613000	2.34990000	-0.46940100	H	4.40597800	1.66434500	0.73190800	H	0.04195600	-0.95842700	0.79076200
N	2.62313200	0.44994100	-0.24379500	H	4.07987400	1.50991600	-0.99483900	H	-0.70777700	-0.35919500	2.24283800
N	0.75618100	-0.59725700	1.98522200	H	-2.40698000	-3.01157100	1.14141000	H	-0.72818900	1.27303100	0.13135300
C	0.13433900	3.72556700	-0.93506600	H	-1.96699000	-1.33015400	0.92181200	H	-1.71112900	2.33998300	1.09717600
H	1.09344600	3.78849000	-1.46196500	N	-2.96458100	-2.25811100	-0.71103500	H	1.30712700	2.21862200	0.91912100
C	3.95860900	-0.10538500	-0.44776800	N	0.41455700	-2.36241400	0.84676500	H	1.76768500	3.73310400	0.16229000
C	-3.85106900	-0.22878300	0.24426300	N	3.35312600	-1.03911100	-1.05327200	H	1.52110900	2.77051800	-0.20764100
H	-3.89646900	-1.32283100	0.29895500	N	2.36136900	-1.56790600	0.16642600	H	0.85124000	1.30101300	-1.40624900
C	0.22671600	-3.18769100	-1.49142200	N	-0.36385700	2.46494600	1.47704000	C	3.22736200	-2.70917000	1.18815700
H	1.15065800	-3.13091300	-0.90829000	N	-2.96716300	1.51514900	-1.02707000	H	1.71320700	-2.49642800	0.34272800
C	0.06207900	-0.90296300	3.23697200	C	-4.25827700	-2.90391300	-0.54683500	N	-2.24314900	-2.07824700	-1.80038600
H	-0.85234600	-1.42711400	2.93763000	H	-4.81536300	-2.66153200	-1.46011800	N	-3.35755300	1.30783200	-0.71141900
C	0.82710800	-1.82735500	4.18896800	C	0.29573900	-3.01715100	2.15158200	N	-0.23179800	3.28766500	-0.09905100
H	0.20248300	-2.09797400	5.04390700	H	-0.74378300	-2.86562600	2.45864600	N	-2.11524700	-2.42787200	1.36398000
H	1.13366900	-2.75321700	3.69696500	C	1.97385300	2.77137900	-0.57497300	N	1.23139900	-1.18120100	2.49421400
H	1.72461900	-1.33986800	4.57888700	H	0.98381600	3.02193500	-0.19257400	N	3.37817700	-1.50015900	-0.50949800
C	0.59396100	-2.86909100	-2.93396900	C	4.18437600	-1.99013700	-1.77769800	N	2.87553600	1.45218800	-1.07916900
H	1.33222700	-3.58088700	-3.31184100	H	3.50337600	-2.48526900	-2.48030800	C	-1.96419000	-2.17318300	-3.23439700
H	-0.27564200	-2.92262300	-3.59501800	C	-0.33681300	3.53286600	2.47159700	H	-2.41828300	-1.27901900	-3.67360000
H	1.01111000	-1.86273100	-3.00372500	H	0.69775500	3.56924800	2.82952700	C	-4.68960700	1.87750600	-0.54110600
C	3.94867600	-1.21992400	-1.48690600	C	-3.21972200	2.05129800	-2.35865400	H	-5.33953400	1.02077300	-0.32568300
H	4.93291600	-1.69061600	-1.55297500	H	-4.21542300	1.68119100	-2.63244200	C	-3.22348200	-2.18402200	2.27759100
H	3.21612200	-1.98614000	-1.22904600	C	0.56429200	-4.52428300	2.14113100	H	-2.81336900	-1.52555900	3.05284300
H	3.70449400	-0.84379100	-2.48370300	H	-0.05807900	-5.04449300	1.40925800	C	1.24916600	-0.51538500	3.79205900
C	0.20604000	4.69793200	0.23627500	H	1.61035500	-4.73691100	1.90529200	H	0.31822200	-0.82271300	4.28472500
H	-0.73463200	4.72704400	0.79262600	H	0.35360100	-4.95689500	3.12225600	C	-0.56422000	4.54432600	0.56491400
H	0.99905300	4.40774800	0.92821800	C	-3.29633000	3.57447500	-2.30825100	H	-1.65150500	4.64409800	0.46563400
H	0.40342400	5.71345900	-0.11632300	H	-3.58309900	3.98313500	-3.28053900	C	4.00308900	2.36266400	-0.90556900
C	-5.17844800	0.26001400	-0.34607200	H	-4.02556300	3.89655100	-1.56286700	H	3.67589600	3.09796000	-0.16417000
H	-6.02027100	-0.09718000	0.25247200	H	-2.32883300	4.01189500	-2.04581500	C	4.42064000	-2.38287400	-1.01647400
H	-5.22835700	1.35198100	-0.36033900	C	2.88017400	3.98189900	-0.33963100	H	4.78284700	-1.90563600	-1.93564300
H	-5.32349900	-0.09671900	-1.36810000	C	3.87931400	3.83397200	-0.75846600	C	1.25436700	1.01386900	3.70826500
C	-3.67808600	0.28812500	1.66673700	H	2.45601200	4.87104800	-0.81338400	H	0.43003400	1.38540600	3.09500900
H	-4.52714200	-0.00692000	2.28782800	H	2.99177300	4.19987900	0.72596600	H	1.15866300	1.46051500	4.70122500
H	-2.76596500	-0.10062200	2.12140800	C	-0.63496600	4.88103900	1.82864800	C	2.18721400	1.37779100	3.26939500
H	-3.62211100	1.37999600	1.68775100	H	0.05548800	5.07521600	1.00554000	C	-3.74589300	-3.44716900	2.96565300
C	-0.95683700	4.15444300	-1.92156500	H	-1.65313100	4.92023200	1.43217300	H	-4.84422600	-3.19836900	3.73210000
H	-1.00822600	3.48852000	-2.78628700	C	-0.53986500	5.68797400	2.55963200	H	-4.22938500	-4.11394200	2.24665400
H	-1.93856900	4.16326700	-1.44035200	C	5.23643800	-1.25722100	-2.60502500	H	-2.93598700	-4.00198900	3.44665500
H	-0.76260300	5.16394900	-2.29368300	H	5.96089900	-0.74332300	-1.96645200	C	5.59771400	-2.4479	

C	5.03057000	0.93702900	-0.77893300	H	-5.30860300	-1.36283100	0.60204600	H	-0.67939300	3.71960500	2.58332700
H	4.87115800	1.36365200	-1.77272600	C	-1.23747200	3.28476800	3.68425600	H	0.84972400	4.52556100	2.22157600
H	5.03243000	1.75766600	-0.05751500	H	-1.07032800	4.04462600	4.45159700	C	-5.24665900	2.57982300	-1.78277000
H	6.02527900	0.48460900	-0.77099800	H	-2.29403500	3.32399300	3.40677500	H	-5.24502500	1.91531200	-2.64972800
				H	-1.04481700	2.30866300	4.13624400	H	-6.27642300	2.90490100	-1.61366600
				C	4.84461900	-3.08414400	-0.92834100	H	-4.66063500	3.46730100	-2.03701400
				H	5.40377200	-3.77617000	-1.56390300	C	-2.66318200	-3.37605000	-3.85446400
				H	5.55317000	-2.65807400	-0.21255600	H	-2.56768700	-3.35559400	-4.94300500
				H	4.10905100	-3.66341800	-0.36897600	H	-2.23053900	-4.32016600	-3.51266200
				C	1.16118900	-2.32110100	3.19455900	H	-3.72370600	-3.37617600	-3.59605200
				H	0.92584400	-2.69770700	4.19296100	C	3.93064300	-3.78726800	-1.38204000
				H	2.22696100	-2.49863600	3.02982200	H	4.72297400	-4.36361800	-1.86629000
				H	0.98721800	-1.24415100	3.17997800	H	3.62068400	-4.33727600	-0.48954800
				C	1.83451000	2.45756400	-2.05738000	H	3.07903900	-3.75200900	-2.06611300
				H	2.79069700	2.18840100	-2.51413700	C	2.39858700	-1.02002000	4.65358400
				H	1.15231400	1.61814800	-2.20460300	H	2.33282800	-0.60792600	5.66366700
				H	1.44604300	3.32499100	-2.59845000	H	2.37821400	-2.10955600	4.71673000
				C	-2.23922100	1.60846900	-3.45161700	H	3.36804500	-0.72206900	4.24552700
				H	-2.21764700	0.52457500	-3.56929200	C	-4.34501300	-1.41432000	1.59145000
				H	-2.51995000	2.04388500	-4.41441300	H	-3.96977300	-0.47497000	1.18010800
				H	-1.22276500	1.94271600	-3.22725900	H	-4.78333100	-1.99199300	0.77299600
								H	-5.14773100	-1.19320000	2.29990400
								C	-4.73325800	2.79376100	0.67415000
								H	-5.75462100	3.13377200	0.86116900
								H	-4.37130500	2.27160500	1.56209300
								H	-4.11667100	3.68533600	0.53003900
								C	-0.47596500	-2.15740700	-3.59395900
								H	0.03077700	-3.05428700	-3.22781500
								H	-0.34260600	-2.12323600	-4.67808000
								H	0.03285100	-1.28891100	-3.17117600
								C	0.06059500	5.73121600	-0.15595200
								H	1.15125900	5.72202500	-0.07831400
								H	-0.20213500	5.71576700	-1.21524400
								H	-0.28503300	6.67238200	0.27897000
								C	5.19572100	1.63427200	-0.30025100
								H	4.88657700	1.06587000	0.57773500
								H	5.64435800	0.93142200	-1.00681300
								H	5.97257800	2.34784900	-0.01391500

Aza-9-Crown-3 ^{tBu} (9N3 ^{tBu})				Aza-12-Crown-4 ^{tBu} (12N4 ^{tBu})			
C	-0.01698000	1.17866600	-1.10570100	C	2.70064800	0.75670000	-0.11065400
C	1.49143800	0.95959900	-1.13518100	C	-1.62532600	0.69730800	-0.33220700
C	-0.48560900	0.80405100	1.26778200	C	2.70076000	-0.75622500	0.11070500
C	-1.35335200	-0.46136200	1.23946100	C	-1.62523100	-0.69747600	0.33219300
C	1.44379400	-1.39412100	-0.56038200	C	0.03893300	1.92479700	0.90144700
C	0.39794300	-1.92411900	0.43199800	C	0.03924400	-1.92470500	-0.90143100
H	-0.53318400	0.25230000	-1.38345200	C	0.93647700	2.37233600	-0.25911000
H	-0.22178000	1.89788200	-1.89995400	C	0.93684500	-2.37213100	0.25912500
H	1.76861100	0.74762600	-2.18678400	H	2.65572900	1.24641000	0.86189000
H	1.95957100	1.90427500	-0.86421500	H	3.68036800	1.03821400	-0.52334600
H	-0.73860100	1.34961300	2.17757800	H	-0.83947000	0.70232800	-1.08732100
H	0.55627500	0.50441700	1.38039900	H	-2.56214400	0.86452100	-0.86703700
H	0.99830000	-1.39322900	-1.56210700	H	-0.83939200	-0.70237500	1.08732600
H	2.26194700	-2.11898700	-0.60678600	H	-2.56203600	-0.86482500	0.86700300
H	0.73840400	-1.69651300	1.44908200	H	0.13330000	-2.65495500	-1.70483600
H	0.39832900	-3.01534000	0.36662900	H	0.42215200	-0.97078600	-1.29193800
H	-2.39050300	-0.17878300	1.07138800	H	1.67190700	-3.10458100	-0.11467000
H	-1.31128500	-0.90109300	2.25642500	H	0.30289500	-2.90724800	0.96385200
N	1.96763500	-0.07676200	-0.24086700	H	3.68052400	-1.03760800	0.52338200
N	-0.95282500	-1.41946700	0.22450100	H	2.65590300	-1.24593100	-0.86184600
N	-0.52335500	1.72689200	0.14443900	H	0.30244800	2.90734700	-0.96384200
C	3.39109800	-0.02643400	0.13330300	H	1.67142100	3.10490700	0.11467900
C	-1.94766700	-2.44412500	-0.14583800	H	0.42198000	0.97094400	1.29198000
C	-1.68413500	2.62548300	-0.00486300	H	0.13286500	2.65507700	1.70483900
C	-1.46491800	-3.16919200	-1.40551600	N	1.61214700	1.26941600	-0.93585700
H	-0.53128900	-3.71200600	-1.25207400	N	1.61234000	-1.26912700	0.93590200
H	-2.21283900	-3.89784100	-1.72579300	N	-1.36270600	1.84082200	0.52577300
H	-1.31099300	-2.45352100	-2.21660300	N	-1.36241500	-1.84095000	-0.52578100
C	3.62774900	-0.98094700	1.30686300	C	1.96583300	-1.55199600	2.34656300
H	3.40570400	-2.01962800	1.05772900	C	-2.32990400	2.17684400	1.58263900
H	4.67437000	-0.93891900	1.61629600	C	1.96560600	1.55222200	-2.34654300
H	3.00529600	-0.69590700	2.15841900	C	-2.32953700	-2.17714000	-1.58266300
C	-2.84752500	2.01669600	-0.80495700	C	0.68681800	1.71104700	-3.17254300
H	-3.28213100	1.16204300	-0.28630700	H	0.06857900	2.54794100	-2.84633100
H	-3.63957900	2.75650100	-0.94926100	H	0.94502100	1.88920900	-4.21912800
H	-2.52616400	1.68266000	-1.79361100	H	0.08346700	0.80285800	-3.12333200
C	-3.27697400	-1.78274400	-0.51493200	C	-2.13027400	-1.38938600	-2.88877200
H	-3.93974800	-2.52501800	-0.96451200	H	-2.28575600	-0.32021400	-2.74183700
H	-3.80061400	-1.37240400	0.34992900	H	-1.12416500	-1.53250400	-3.28987700
H	-3.11874800	-0.98229900	-1.24004500	H	-2.83708200	-1.72873500	-3.65099200
C	-2.19617600	-3.45997100	0.97746500	C	0.68703200	-1.71171000	3.17236700
H	-2.56382400	-2.96156900	1.87781000	H	0.08324000	-0.80380200	3.12337700
H	-2.94337300	-4.19875800	0.67687700	H	0.06924300	-2.54880100	2.84579700
H	-1.28401900	-4.00134400	1.24006700	H	0.94519600	-1.89008800	4.21892400
C	-1.21628300	3.90612300	-0.70905700	C	-3.75204700	1.93824900	1.07870600
H	-0.39461300	4.35912400	-0.15081900	H	-4.46564400	2.30412800	1.81955400
H	-0.87171900	3.72184200	-1.72810800	H	-3.92973500	2.47527100	0.14398100
H	-2.03562400	4.62633200	-0.77406600	H	-3.96531400	0.87992800	0.91791600
C	-2.22014000	3.04851900	1.36171900	C	2.82577800	2.81553600	-2.49661200
H	-2.99384700	3.80634500	1.22370100	H	3.74732900	2.74600900	-1.91299300
H	-2.67203900	2.21861200	1.90857500	H	3.10865300	2.96555000	-3.54122200
H	-1.42974000	3.48285800	1.97884100	H	2.28615900	3.70659000	-2.16927400
C	4.32003200	-0.39583800	-1.03133100	C	2.72178100	0.36893900	-2.95249800
H	4.14228800	-1.41643500	-1.37940300	H	2.12635500	-0.54457900	-2.89860800

H	4.16985900	0.28063900	-1.87635900	H	2.92475600	0.57381100	-4.00562600
H	5.36888300	-0.32729900	-0.73154400	H	3.68253600	0.18803900	-2.46789700
C	3.75322800	1.37578100	0.63074100	C	-3.75173900	-1.93885500	-1.07874900
H	3.83048900	2.10305500	-0.17882900	H	-3.96523100	-0.88058300	-0.91793500
H	3.00965000	1.73334500	1.34686600	H	-4.46524700	-2.30486400	-1.81961900
H	4.72494700	1.34640600	1.12805900	H	-3.92933200	-2.47593900	-0.14404100
				C	-2.20960500	-3.67496000	-1.88915500
				H	-1.23663600	-3.93830100	-2.30816100
				H	-2.35292500	-4.25567400	-0.97580300
				H	-2.96531000	-3.97622200	-2.61871500
				C	2.72129600	-0.36843800	2.95288200
				H	2.92431500	-0.57348000	4.00596700
				H	3.68198100	-0.18684800	2.46840300
				H	2.12534600	0.54475000	2.89920900
				C	2.82666600	-2.81488000	2.49643100
				H	2.28755500	-3.70615400	2.16885500
				H	3.74822100	-2.74471900	1.91289100
				H	3.10954300	-2.96496700	3.54102900
				C	-2.21029000	3.67469700	1.88910200
				H	-2.35369700	4.25536100	0.97573100
				H	-2.96608500	3.97582000	2.61862700
				H	-1.23739300	3.93825000	2.30813800
				C	-2.13049800	1.38915500	2.88876400
				H	-1.12443100	1.53250500	3.28989300
				H	-2.83740200	1.72835700	3.65096100
				H	-2.28573600	0.31994600	2.74184100

Aza-15-Crown-5 ^{tBu} (15N5 ^{tBu})				Aza-18-Crown-6 ^{tBu} (18N6 ^{tBu})				Aza-21-Crown-7 ^{tBu} (21N7 ^{tBu})			
N	2.30357700	-1.97614900	0.75613200	C	1.08760600	2.47773100	-0.69476200	C	-1.26825600	1.70155500	-2.15799100
N	-1.09252600	-2.83772200	-0.58540300	C	-1.43405300	-3.27517100	1.31958700	C	-3.21833600	0.06576800	1.56233800
N	-3.14240100	0.17795100	0.31377000	C	0.73386500	-2.35161400	1.81924400	C	0.79931000	2.73716500	-1.47983100
N	-0.67390500	3.00773200	0.49238300	C	1.25152800	-2.04131500	0.41951900	C	3.88556400	0.01302400	0.03267000
N	2.70855200	1.57629000	-0.39583000	C	3.36195300	-0.90044300	0.48463600	C	-2.33733400	-0.71188300	2.55377800
C	0.86134300	-2.16967000	0.75522300	C	3.22884800	0.09056700	-0.69608400	C	1.65992700	2.32307300	-0.28713800
C	0.35350000	-2.73396200	-0.56755700	C	-2.39019300	-2.92828400	0.17529000	C	2.86368900	-2.08544300	-0.54568600
C	-1.71863600	-1.53155000	-0.72613800	H	-1.99857500	-3.82415100	2.08783100	C	3.56385700	1.04988200	-1.05432000
C	-2.65335000	-1.18205000	0.42859000	H	-0.70773800	-3.99181900	0.92422400	C	-3.37590600	-0.47212600	-1.51603300
C	-2.22896800	1.14874300	0.89189700	H	1.23835900	-1.68734000	2.51942100	C	2.41503700	-2.65923800	0.81773700
C	-1.61787800	2.10431700	-0.13300400	H	1.03907600	-3.37328200	2.09866600	C	-3.56431500	-1.39787500	-0.29295400
C	0.64813300	2.43468300	0.62130300	H	0.93154800	-1.02346700	0.16510900	C	-1.09748600	0.23615200	-1.72441500
C	1.54536600	2.41381500	-0.62412400	H	0.73990700	-2.06712300	-0.30515300	C	0.21198700	-1.73966900	1.11290900
C	2.37259100	0.16145100	-0.45460700	H	4.41436400	-1.06918800	0.71867200	C	-0.02806500	-1.35691100	2.56992800
C	2.66038500	-0.57513300	0.85074400	H	2.93993500	-0.42861500	1.37788500	H	-0.89486300	1.84160400	-3.18476100
C	3.07748000	-2.90377300	1.60047600	H	2.24104800	-0.05112700	-1.14384400	H	-2.33562500	1.91166200	-2.19714800
C	2.85325000	-2.65656700	3.09801400	H	3.93936800	-0.17208900	-1.48152800	H	-3.75784700	0.86371000	2.07007300
C	2.68916700	-4.34231300	1.25385900	H	-3.21632200	-2.31145700	0.55046400	H	-2.55141100	0.56863900	0.84928700
C	4.56916000	-2.76284600	1.28505600	H	-2.85288800	-3.86506200	-0.14507000	H	1.08894400	3.75004600	-1.78367400
C	-1.64082900	-3.91294900	-1.43343100	C	2.18698300	2.03889900	0.27714900	H	1.06978300	2.09857800	-2.32770400
C	-1.26992300	-3.73764300	-2.91210900	C	-1.11592000	2.35758600	0.33641000	H	4.78162000	0.31799000	0.57337500
C	-3.16333100	-3.94753200	-1.29667100	C	-2.17494000	2.09257200	-0.74762000	H	3.08196700	0.00776700	0.78352800
C	-1.12249800	-5.26558900	-0.93742900	C	-3.06936700	-0.12704200	-1.06137000	H	1.33117700	1.33216700	0.05225400
C	-4.57606600	0.38318500	0.57922300	C	-1.73291800	-0.84461600	-0.81725200	H	1.45939800	2.99287700	0.54869600
C	-4.95211700	1.83128900	0.26270400	H	0.69478400	1.61017000	-1.24037600	H	4.44809700	1.17006800	-1.68518800
C	-4.94801400	0.06710400	2.03382100	H	1.55025000	3.11038200	-1.45517300	H	2.80403200	0.61632900	-1.71258200
C	-5.39974700	-0.49976900	-0.36219100	H	-1.62232700	2.76231100	1.21630100	H	-2.31502100	-1.74312000	2.19872900
C	-0.82482500	4.43964700	0.20760200	H	-0.72400500	1.38916400	0.65472200	H	-2.83913500	-0.76683500	3.53158000
C	-2.19137900	4.89592700	0.73051900	H	-2.66398300	3.03065100	-1.01885400	H	2.06567800	-1.43545100	-0.92061700
C	-0.72948600	4.78145000	-1.28856200	H	-1.68130100	1.75231300	-1.66599600	H	2.94920300	-1.27998600	-1.27998600
C	0.23634300	5.23404700	0.96683200	H	-3.86304700	-0.79447300	-0.73060800	H	0.67552800	-0.88265600	0.60684700
C	3.93339300	1.97520200	-1.11569700	H	-3.22508900	0.04355600	-2.14295500	H	-0.74977100	-1.86621000	0.61797600
C	3.76410800	1.90848800	-2.63919300	H	-0.94541100	-0.03272200	-1.44625100	H	2.99210200	-3.55542100	1.05238600
C	4.32125200	3.40068900	-0.71227400	H	-1.43632700	-0.64903800	0.21303000	H	2.67946400	-1.93528800	1.59537400
C	5.09095600	1.06937100	-0.69330400	H	2.46081500	2.91633200	0.86069600	H	-1.12740600	0.22825500	-0.63091400
H	0.53249300	-2.83199800	1.56177200	H	1.75986600	1.32851900	1.00284500	H	-0.10329100	-0.13186300	-1.98964200
H	0.36666400	-1.21307900	0.95976000	N	3.35364100	1.50343900	-0.39475300	H	-4.20637100	-0.60654600	-2.21152000
H	0.79755700	-3.71792600	-0.70244900	N	0.02180400	3.17972500	-0.00847200	H	-3.44979400	0.56685500	-1.17704200
H	0.74186400	-2.11063900	-1.38965100	N	-3.16259000	1.10991400	-0.30990300	H	-2.56872900	-1.74736300	-0.01343100
H	-2.27416900	-1.43217400	-1.66596600	N	-1.73478100	-2.28894900	-0.94962400	H	-4.10885700	-2.29792200	-0.58623400
H	-0.93957000	-0.76476900	-0.78131000	N	-0.70172100	-2.15747000	1.90030700	H	-0.37528500	-2.24585800	3.11872500
H	-2.11795500	-1.34940400	1.37560200	N	2.69042800	-2.17349400	0.32851100	H	0.92669800	-1.08313900	3.02005400
H	-3.48386100	-1.88417100	0.43199100	C	4.65886600	2.02978700	0.03381700	N	3.06934000	2.33882600	-0.62312700
H	-1.411736500	0.61695700	1.40101500	C	-0.14678500	4.60197700	-0.31970600	N	-0.63078900	2.62212800	-1.23651600
H	-2.70687000	1.74961800	1.67269500	C	-1.93740700	-2.90018800	-2.26988900	N	-2.10798500	-0.69303500	-2.19056400
H	-2.42174900	2.66620500	-0.60657000	C	-4.53008800	1.63470100	-0.11829600	N	4.07950100	-1.29991400	-0.54673900
H	-1.16135000	1.51592500	-0.94201100	C	-1.21879500	-1.62671700	3.17436800	N	1.00427000	-2.94139500	0.97157100
H	1.20139100	2.92070000	1.42826300	C	3.20590800	-3.16420300	-0.62285100	N	-0.96227500	-0.24737300	2.66358700
H	0.50840400	-1.40399700	0.95843100	C	1.16517600	5.33439500	-0.01759900	N	-4.15518400	-0.81808200	0.89487800
H	1.87212900	3.42902400	-0.83796600	H	1.05208300	6.40536400	-0.20171900	C	3.93553100	3.22984200	0.15690200
H	0.96286600	2.08695500	-1.50206900	H	1.44765100	5.19087100	1.02767700	C	-1.36072400	3.88087900	-0.99428000
H	2.89720500	-0.35700800	-1.26458500	H	1.98457700	4.98228300	-0.64602300	C	5.37382900	-1.95092700	-0.30859200
H	1.31023900	0.06001000	-0.69844400	C	2.69643000	-4.54193800	-0.18806500	C	0.39370500	-4.04579300	0.21867000
H	2.13484900	-0.05829900	1.67139100	H	3.02212600	-4.59380000	0.83110100	C	-2.16717000	-1.06632300	-3.61017800
H	3.72141500	-0.47900300	1.06577200	H	1.60599300	-4.59633500	-0.21277300	C	-5.56947900	-0.42683100	0.89178300
H	3.44958800	-3.34519800	3.70188800	H	3.07817300	-5.32037700	-0.85305100	C	-0.67414100	0.74195800	3.71569400
H	3.14125400	-1.63841700	3.37118400	C	-3.41502100	-3.02064000	-2.67991500	C	1.35090900	-5.23415900	0.17322400
H	1.80522100	-2.79684400	3.37403600	H	-3.87718700	-2.03952500	-2.79435300	H	0.84489100	-6.09135800	-0.27514600
H	3.27977400	-5.03872400	1.85280200	H	-3.50659700	-3.54546100	-3.63466000	H	2.23706700	-5.02952500	-0.43192300
H	1.63766000	-4.55405900	1.45399100	H	-3.99132300	-3.58723200	-1.94129200	H	1.67231700	-5.51676700	1.17864200
H	2.88617300	-4.54539400	0.19868100	C	-1.01222300	-2.60285200	4.33934800	C	5.70714900	-2.14953400	1.71956900
H	5.12346300	-3.58123700	1.74953800	H	0.04920100	-2.82370400	4.47720500	H	5.00717200	-2.83496000	1.65851100
H	4.73245600	-2.80392100	0.20569600	H	-1.39073200	-2.18138600	5.27399800	H	6.71262000	-2.56305000	1.29547700
H	4.99721400	-1.83362000	1.66424300	H	-1.53456300	-3.54744300	4.16817200	H	5.67851400	-1.20334100	1.72515300

H	-1.68599700	-4.54718800	-3.51695300	C	-5.42813300	0.55237700	0.48669900	C	-1.74347000	1.83324000	3.70113800
H	-1.65438300	-2.79532500	-3.31043700	H	-4.94515400	0.08716400	1.34848100	H	-1.82789300	2.27538200	2.70620900
H	-0.18582200	-3.74453200	-3.04780100	H	-6.36415100	1.00318300	0.82278300	H	-2.72300600	1.45588500	4.00040100
H	-3.56643100	-4.76891700	-1.89265200	H	-5.69074900	-0.22832700	-0.22905800	H	-1.47185000	2.62297800	4.40048200
H	-3.45111100	-4.10890900	-0.25530900	C	4.93958300	1.84916500	1.53493200	C	-5.84388300	0.93491400	0.23043600
H	-3.63588700	-3.02934200	-1.64914300	H	5.88064300	2.33377000	1.80920500	H	-5.22735000	1.72456700	0.66598800
H	-1.65713100	-6.07489300	-1.43972800	H	4.15099000	2.29646300	2.14434600	H	-5.64471900	0.90451000	-0.84199300
H	-0.06034600	-5.41276900	-1.13897700	H	5.01668100	0.79538100	1.80475400	H	-6.89052900	1.22175900	0.36443900
H	-1.28504400	-5.35828100	0.13867600	C	5.77693900	1.35321800	-0.75692600	C	-2.90343600	-0.04712500	-4.49628500
H	-6.02422000	1.97460800	0.41278900	H	5.60646400	1.44594900	-1.83219700	H	-3.92381600	0.12772100	-4.14730400
H	-4.43709400	2.54668500	0.90520400	H	6.72876800	1.83350200	-0.52212200	H	-2.38490900	0.91217500	-4.51743600
H	-4.71817700	2.06840600	-0.77770300	H	5.87994700	0.29448800	-0.51027500	H	-2.96892600	-0.41333000	-5.52431500
H	-6.01667700	0.21594300	2.20845700	C	4.70980200	3.52481800	-0.29884900	C	-1.51256100	4.72239300	-2.26813100
H	-4.71096100	-0.97084800	2.28033500	H	3.98389500	4.09997700	0.27777000	H	-2.06597400	4.17559900	-3.03556800
H	-4.40484300	0.71150600	2.72961600	H	5.69773100	3.93234200	-0.07132200	H	-2.05547400	5.64854600	-2.06331400
H	-6.45770700	-0.23900600	-0.28570400	H	4.50337800	3.68077000	-1.35982300	H	-0.53841800	4.99349400	-2.68276600
H	-5.07964600	-0.34779700	-1.39552600	C	-1.21829400	5.20996000	0.58110300	C	5.36456800	3.16065000	-0.37704000
H	-5.31569200	-1.56247800	-0.12982400	H	-2.21283700	4.81703100	0.36715700	H	5.97918100	3.90821500	0.12822000
H	-2.31027400	5.97378600	0.59682400	H	-0.99336500	0.50225800	1.63399000	H	5.82884400	2.18842600	-0.20269100
H	-3.01635700	4.41289100	0.20388900	H	-1.25653900	6.28974300	0.42470900	H	5.38901700	3.36705200	-1.44951900
H	-2.28305700	4.66328600	1.79349500	C	-0.52152800	4.86392200	-1.78859100	C	0.00070600	-3.67211200	-1.21978000
H	-0.91599500	5.84613600	-1.45354000	H	-0.57059700	5.93741500	-1.99068700	H	-0.52668100	-4.50246100	-1.69818400
H	0.25734400	4.54886600	-1.69071300	H	0.21985900	4.43570700	-2.46718900	H	-0.66225900	-2.80401800	-1.25115800
H	-1.46790300	4.22450100	-1.87000700	H	-1.49166500	4.43165400	-2.03661200	H	0.88028000	-3.44840600	-1.82531700
H	0.04883900	6.30229800	0.84195400	C	-5.16634000	2.12825800	-1.42485300	C	-0.86284700	-4.49647900	0.97084200
H	0.20212700	5.00563500	2.03461800	H	-4.59083200	2.94236600	-1.87200100	H	-1.61880500	-3.71046200	1.01632000
H	1.24700400	5.03711800	0.60435700	H	-5.23368600	1.31985900	-2.15684100	H	-1.32023700	-5.35335700	0.47050700
H	4.67929000	2.22242900	-3.14729300	H	-6.17838000	2.49984200	-1.24645900	H	-0.60820400	-4.78192100	1.99350100
H	3.53220700	0.89383300	-2.97222100	C	-4.47886900	2.77918200	0.89361700	C	0.65792000	1.42473200	3.39979100
H	2.95699400	2.56582300	-2.97188800	H	-4.04668000	2.43342800	1.83509700	H	0.85444000	2.22259800	4.12003900
H	5.32459800	3.62906900	-1.07835800	H	-3.88857200	3.62356700	0.53711300	H	1.50620700	0.73947100	3.44064700
H	3.65334000	4.15687500	-1.12838600	H	-5.48668400	3.15142100	1.08973200	H	0.61949700	1.85564800	2.39856600
H	4.31892700	3.49783100	0.37562800	C	-0.52599000	-0.30059800	3.50150500	C	-0.62115500	0.11473700	5.11480100
H	6.00485600	1.37992900	-1.20395000	H	-1.03537100	0.18252000	4.33817900	H	0.17385000	-0.63107900	5.18592100
H	5.26063900	1.14222900	0.38331800	H	0.51721200	-0.42542600	3.79498300	H	-0.43181000	0.87587500	5.87591900
H	4.91824100	0.02197700	-0.94557300	H	-0.56644600	0.37334500	2.64408000	H	-1.56592600	-0.37522700	5.36397900
				C	-2.70730700	-1.30967500	3.02284500	C	-6.05164500	-0.38066300	2.34514900
				H	-2.86182600	-0.59472400	2.21102700	H	-5.87525700	-1.34373700	2.82836800
				H	-3.30695800	-2.19992200	2.82597700	H	-5.53589700	0.38754600	2.92503300
				C	-3.08422600	-0.86566600	3.94690200	H	-7.12005200	-0.15632100	2.38735300
				C	4.73110000	-3.19523700	-0.56818200	C	-6.39270400	-1.49040900	0.16875400
				H	5.10130600	-4.02583700	-1.17249500	H	-7.45573100	-1.26544300	0.27546100
				H	5.17726300	-2.28116500	-0.96693600	H	-6.17419900	-1.52381100	-0.90098800
				H	5.08190800	-3.33664400	0.45688700	H	-6.20836000	-2.48035800	0.59245400
				C	2.77264400	-2.91767600	-2.07756500	C	-0.75328700	-1.24766100	-4.15700100
				H	3.19228700	-1.99128000	-2.47091800	H	-0.18072100	-1.94355200	-3.54128600
				H	3.10460400	-3.73580000	-2.72254900	H	-0.80441000	-1.65296600	-5.16950200
				H	1.68631100	-2.85691400	-2.15896900	H	-0.20960700	-0.30196900	-4.21259200
				C	-1.20596200	-2.08489600	-3.33368500	C	-2.88381500	-2.41636400	-3.70828500
				H	-1.66130100	-1.10430200	-3.48607600	H	-2.93059500	-2.75244100	-4.74687000
				H	-0.15688200	-1.94020900	-3.06824200	H	-2.35384200	-3.16734100	-3.11997800
				H	-1.24322100	-2.61409800	-4.28786800	H	-3.90971000	-2.35917500	-3.33749400
				C	-1.31404200	-4.29985900	-2.25150600	C	3.44849500	4.66967700	-0.03387100
				H	-0.25091500	-4.24074000	-2.01091100	H	2.45159300	4.81904600	0.38370500
				H	-1.78932100	-4.95206400	-1.51602400	H	4.11777900	5.36911800	0.47263600
				H	-1.42039800	-4.77946400	-3.22742100	H	3.41817500	4.92132800	-1.09594900
								C	3.94863700	2.91768800	1.66339300
								H	4.37401000	1.93461300	1.86733800
								H	4.54401100	3.65854200	2.20411700
								H	2.94000200	2.93810500	2.08153400
								C	6.46454100	-1.08529400	-0.94755300
								H	7.44431400	-1.55483800	-0.83190800
								H	6.26251400	-0.95092400	-2.01199100
								H	6.52320900	-0.09675000	-0.48743400
								C	5.40510300	-3.31166400	-1.00036400
								H	6.40953300	-3.73332000	-0.92840100
								H	4.71990700	-4.02646200	-0.53945700
								H	5.15122100	-3.21739200	-2.05880700
								C	-0.62691000	4.70038000	0.06608600
								H	0.36106600	5.01739600	-0.26866800
								H	-1.19637500	5.60422100	0.29195400
								H	-0.51752200	4.12609600	0.98882100
								C	-2.74666400	3.56789700	-0.42221200
								H	-3.22284100	4.48944000	-0.07994400
								H	-3.42052400	3.11745200	-1.15252100
								H	-2.65848100	2.88755100	0.42673600

XeO ₃ :9N3 ^{Me}				XeO ₃ :12N4 ^{Me}			
C	-1.46166700	1.34245300	-1.61110500	C	1.70653300	1.47534100	1.70157400
C	-1.97307900	1.72130200	-0.22628900	C	-1.36796300	-2.03539800	1.48726100
C	-1.97695400	-1.05741400	-1.37243300	C	0.27558600	1.94967000	1.89559100
C	-1.46200200	-2.06710300	-0.35349000	C	-2.55665200	-1.51590500	0.69565500
C	-1.45569900	0.72687300	1.97036500	C	1.04711400	-2.22617700	1.48344100
C	-1.97117200	-0.66062700	1.60711000	C	-2.50831700	0.82185400	1.23381400
H	-0.60774100	1.98002800	-1.85925600	C	1.42746100	-0.90386100	2.13064100
H	-2.25206900	1.56096800	-2.35169600	C	-1.90385700	2.17041800	0.88894200
H	-2.27651000	2.77600200	-0.25471500	H	2.21503800	2.13511600	0.99697200
H	-2.88546800	1.16814900	0.00439600	H	2.23839500	1.56864300	2.66408100
H	-2.28268300	-1.60955600	-2.27074100	H	-1.15858400	-1.35531900	2.31446100
H	-2.88862400	-0.58174100	-1.00607700	H	-1.64426400	-2.99882300	1.95175600
H	-0.60064600	0.62101300	2.64485400	H	-2.73664400	-2.17104100	-0.15866100
H	-2.24371500	1.26083800	2.53148100	H	-3.46193900	-1.58479300	1.32619700
H	-2.88472400	-0.58161800	1.01482500	H	-3.57360400	0.97855800	1.48645200
H	-2.27374500	-1.16260300	2.53540800	H	-2.04499200	0.43480100	2.14320600

H	-0.60956800	-2.60089700	-0.78438700	H	-2.16274400	2.88579600	1.69046100
H	-2.25171400	-2.81777600	-0.16965800	H	-2.37150100	2.55502200	-0.01958400
N	-0.99081700	1.50130500	0.82922100	H	0.30371600	2.88683900	2.47971300
N	-0.99253200	-1.46721600	0.88659900	H	-0.26725500	1.23323800	2.51329100
N	-0.99629100	-0.03273400	-1.71247800	H	0.58610300	-0.52214400	2.70948000
C	-0.32281300	2.72396600	1.23629800	H	2.23395700	-1.09049300	2.85922800
H	0.10200300	3.21656100	0.36064500	H	1.85203800	-2.54556600	0.81952200
H	-1.00615500	3.42255400	1.74351300	H	0.96701800	-2.99288900	2.27502100
H	0.50265800	2.48376600	1.90855700	Xe	0.45355100	0.02562200	-1.18882300
C	-0.32533600	-2.43292100	1.74046600	O	1.53385300	-1.31455200	-1.61597400
H	0.10335600	-1.92198900	2.60364200	O	1.49141500	1.41081600	-1.57477300
H	-1.01023300	-3.21921600	2.09392000	O	-0.69865400	0.03037000	-2.53506200
H	0.49721500	-2.89792100	1.19437000	N	1.83941300	0.11950000	1.17833400
C	-0.33141200	-0.29124000	-2.97654400	N	-0.46660900	2.14708700	0.65899000
H	-1.01687100	-0.20138800	-3.83348000	N	-0.16769300	-2.17493100	0.68282800
H	0.49358500	0.41124500	-3.10670600	N	-2.36518600	-0.16971800	0.18588100
H	0.09364500	-1.29579100	-2.96649100	C	-0.05951100	3.37489100	-0.00433800
Xe	1.23302100	-0.00067800	-0.00169200	H	-0.54331300	3.44296200	-0.97870600
O	1.96850800	-1.47283700	-0.66927100	H	-0.32557000	4.26235000	0.59347900
O	1.97008100	0.15751000	1.60631500	H	1.01150400	3.36966100	-0.18676700
O	1.96805400	1.31342500	-0.94338200	C	-0.24431900	-3.34134700	-0.18038300
				H	0.62251500	-3.35942900	-0.83777700
				H	-0.29042100	-4.27650100	0.40183300
				H	-1.13041600	-3.28792900	-0.81229000
				C	3.20162800	-0.10212400	0.71583900
				H	3.42308600	0.59538300	-0.09156200
				H	3.92745300	0.03304700	1.53221000
				H	3.29895100	-1.10656300	0.30960800
				C	-3.26403100	0.09321800	-0.92198200
				H	-3.07382700	-0.61706500	-1.72447400
				H	-4.32274500	0.03096500	-0.61616900
				H	-3.07813200	1.08247000	-1.33661900

XeO ₃ :15N5 ^{Me}				XeO ₃ :18N6 ^{Me}				XeO ₃ :21N7 ^{Me}			
Xe	-0.19900600	-0.25314100	-1.16627700	C	3.30887200	1.58331400	0.42202500	C	0.32140900	-3.42075500	1.01043300
O	0.77153400	0.89622800	-2.10881400	C	-3.39817100	-1.62532400	0.72179200	C	-4.84283400	0.62372600	-0.81724400
O	-1.71607000	-0.10144700	-2.06859300	C	-1.73702400	-3.34217400	0.72094300	C	2.52854600	-2.63367400	0.81578400
O	0.29344500	-1.86172200	-1.72174100	C	-0.28684400	-3.65355600	0.42678700	C	3.92728200	1.59224300	-0.51786100
C	3.39440700	0.48529300	0.36542400	C	1.97873600	-3.08527900	0.43036200	C	-3.70579500	1.53740400	-1.26985200
H	3.51310400	0.27418800	1.43047100	C	3.10881900	-2.12488500	0.72536800	C	3.55966800	-1.54154300	0.58760600
H	4.41779600	0.54370500	-0.03385600	C	-3.66515900	-0.16679300	0.42460400	C	2.34709800	2.93779700	0.66754500
C	-0.76598500	2.96470800	0.94701000	H	-3.26101200	-1.76123100	1.79656700	C	4.51460500	0.21141500	-0.73597500
H	-1.22148900	3.96679200	0.89568100	H	-4.30829900	-2.19634700	0.46357500	C	-3.11540500	-1.96219700	1.38951400
H	-0.76800700	2.69147200	2.00338000	H	-1.87111700	-3.20298000	1.79575400	C	1.16031600	2.86239800	1.61321200
C	-3.28843800	0.19899000	0.54676000	H	-2.33522300	-4.23374700	0.45973200	C	-3.75077500	-0.66277400	0.89949500
H	-3.59551700	0.34282000	-0.48911600	H	-0.14631000	-3.76881700	-0.64982700	C	-1.12223000	-3.28519500	1.46875400
H	-4.20764100	0.01961900	1.13265900	H	-0.05612300	-4.63482600	0.88635100	C	-0.68783800	3.28844600	0.18242700
C	2.71504400	1.82745800	0.17791800	H	1.91183200	-3.25456400	-0.64623700	C	-1.76688000	2.83656000	-0.79584200
H	2.46331100	1.94418900	-0.87628700	H	2.23816000	-4.05854700	0.89158400	H	0.78283900	-4.19739100	1.64674300
C	3.42041900	2.63560000	0.44653700	H	4.05811300	-2.62828800	0.46755100	H	0.35581100	-3.79319100	-0.01616000
C	2.64675000	-1.80208500	0.56258600	C	3.15856600	-1.93636100	1.79987600	H	-5.47361100	1.12433700	-0.05780400
H	3.65587600	-2.05211400	0.93480900	H	-4.63965300	0.09435900	0.88240600	H	-5.48832600	0.48601000	-1.68948000
H	2.32745800	-2.63433300	-0.06590800	H	-3.77521700	-0.02528900	-0.65246900	H	2.51956400	-3.31705900	-0.03457600
C	0.66454800	3.03238000	0.44529600	C	3.76381300	0.17241100	0.72044400	H	2.87651200	-3.22655600	1.68105100
O	0.66855200	2.97825600	-0.64463800	C	1.68359900	3.26093300	0.41937900	H	4.75120000	2.32997600	-0.56186800
H	1.10216300	4.00878600	0.72467900	C	0.28701600	-3.76092900	0.71342800	H	3.25303900	1.80067500	-1.34826900
C	-0.59887000	-1.20073000	2.27346700	C	-2.03036100	3.18032000	0.71181900	H	4.55146300	-2.00354500	0.74282300
H	-0.44695400	-1.52824800	3.32073500	C	-3.02492000	2.07964700	0.41833900	H	3.45269100	-0.77202200	1.35055900
H	-0.34815700	-0.13582300	2.22896400	H	3.33722800	1.75852700	-0.65534400	H	4.98953700	0.22882200	-1.71960000
C	-2.64132800	1.46719300	1.06751500	H	4.04440100	2.27501200	0.87803300	H	5.32499500	-0.00221200	-0.02309100
H	-2.21471800	1.27711800	2.05564000	H	1.86188000	3.28190900	-0.65769200	H	-4.13769300	2.28037500	-1.96963500
C	-3.43570200	2.21970700	1.21821600	H	2.39726100	3.97506800	0.87554500	H	-2.99845200	0.92964500	-1.83624200
C	1.69024100	-1.64587000	1.73505600	H	0.09967600	3.71511000	1.78834000	H	2.96320400	3.82604900	0.89308300
H	1.98862900	-2.31803400	2.55945700	H	0.24836800	4.83355100	0.45030700	H	1.97924600	3.05530800	-0.35268300
H	1.76472700	-0.62785500	2.11950300	H	-1.84483000	3.22980900	1.78689400	H	-1.07485000	4.07703700	0.85420600
C	-2.07041300	-1.39347500	1.93611200	H	-2.50246500	4.14370900	0.44691600	H	0.07468700	3.77130100	-0.43359400
H	-2.34426800	-2.44252400	2.07789200	H	-3.99152100	2.37254100	0.87367800	H	1.42881100	2.25177200	2.47843400
H	-2.66032000	-0.84103100	2.67858000	H	-3.19145600	2.01261800	-0.65871700	H	0.91936400	3.86417500	2.01124100
N	2.67153100	-0.61290800	-0.26705000	H	4.83529800	0.09913200	0.46052500	H	-1.14646400	-2.99221800	2.52253100
N	0.30397500	-1.88009300	1.36600000	H	3.70909800	-0.01064600	1.79563300	H	-1.55577500	-4.30628200	1.43237600
N	-2.43112200	-0.97934200	0.58189600	Xe	0.00246500	-0.00780300	-1.04239300	H	-2.86179500	-1.79129700	2.44117300
N	-1.58394700	2.00051500	0.21883800	O	1.13043100	1.08342900	-1.85300500	H	-3.85174100	-2.78879800	1.39272500
N	1.48329300	1.93943900	0.94484600	O	-1.50672800	0.42305700	-1.85276300	H	-2.96167500	0.07818800	0.80189800
C	-3.05695900	-2.04965700	-0.17977300	O	0.38389100	-1.53097200	-1.85181400	H	-4.44264500	-0.31450200	1.69494800
H	-4.00635300	-2.37708600	0.27285000	N	2.99212400	-0.85108200	0.03983100	H	-2.04298800	3.73475000	-1.38467300
H	-3.24088900	-1.70321200	-1.19475500	N	1.96459400	1.90780100	0.86772400	H	-1.32253600	2.12805900	-1.48978300
H	-2.38861200	-2.90604600	-0.25182000	N	-0.75816000	3.01957100	0.03259200	Xe	0.72603100	-0.15969500	-0.90818500
C	-2.12688100	2.62680700	-0.97842800	N	-2.63357700	0.75491300	0.86857400	O	-1.02724000	-0.02526400	-0.82240400
H	-2.75234300	3.49657300	-0.72000500	N	-2.23580800	-2.16240500	0.03846700	O	0.88044900	-1.58553600	-1.94385100
H	-1.31260600	2.95514300	-1.62443300	N	0.66474800	-2.64971900	0.87197100	O	1.15954700	1.16320700	-2.00940400
H	-2.70889800	1.91247400	-1.55265700	C	3.41513700	-0.97465400	-1.34510300	C	3.52900600	-0.87583700	-0.71132000
C	0.05506200	-3.30124200	1.25717900	H	3.27857400	-0.02967800	-1.86584200	N	1.15036200	-2.21128200	1.04622600
H	0.76008800	-3.74363200	0.55587800	H	4.47439500	-1.27761400	-1.41018800	N	-1.89437200	-2.33899700	0.71050300
H	0.15813300	-3.81378500	2.22982100	H	2.79924600	-1.70650300	-1.86275000	N	3.15992100	1.72974700	0.70622200
H	-0.93866200	-3.49981600	0.86697200	C	1.80061900	1.75103800	2.29320100	N	-0.01657800	2.26764300	0.99298300
C	3.21418200	-0.88581600	-1.58594400	H	2.47503900	2.40227700	2.79992000	N	-2.95630600	2.22450000	-0.22739700
H	3.18907100	0.02473800	-2.18368500	H	0.77456600	1.97582700	2.58141900	N	-4.45273700	-0.70330500	-0.37360600
H	4.25341600	-1.24925000	-1.52958900	H	1.98833800	0.71777100	2.58218100	C	3.78595300	-1.80025900	-1.80596000
H	2.59655400	-1.62599000	-2.09124300	C	-2.41366000	0.69618400	2.29383400	H	3.69625200	-1.26601200	-2.75122700
C	1.77033200	2.11778800	2.35326100	H	-1.61272100	1.37680000	2.57957100	H	4.79245100	-2.24276500	-1.73301000
H	2.40987700	1.31769500	2.72421500	H	-3.31415800	0.95567700	2.88125000	H	3.04179300	-2.59024600	-1.82508000
H	2.28383500	3.07521300	2.55268200	C	-2.09397500	-0.30370600	2.58438300	C	1.00565100	-1.46206800	2.27614600
H	0.85690200	2.09613600	2.94819700	C	-0.86182400	3.43781400	-1.35521000	H	1.31072300	-0.23991400	3.16444400
				H	-1.61145900	2.84332200	-1.87237600	H	1.61017000	-0.55425900	2.23116800

	H	-1.12916600	4.50618700	-1.42823600	H	-0.03419400	-1.16125400	2.38755600
	H	0.08026100	3.26675300	-1.87102200	C	4.01723800	1.73737900	1.87386100
	C	-2.55233800	-2.46835000	-1.34660000	H	4.71296400	2.59450900	1.86769300
	H	-1.66470100	-2.82186200	-1.86626000	H	3.42256300	1.79585400	2.78678500
	H	-3.34333900	-3.23521300	-1.41213400	H	4.61443600	0.82700900	1.92886600
	H	-2.87860000	-1.56988000	-1.86535800	C	-0.90538100	1.76428200	2.02468500
	C	0.60558600	-2.42343800	2.29641700	H	-1.78527800	1.33271000	1.56051000
	H	-0.38420300	-2.06837900	2.58050900	H	-0.39295400	1.00460600	2.61482800
	H	0.83043600	-3.33066800	2.88765000	H	-1.22716700	2.56673500	2.71173300
	H	1.31215000	-1.64592200	2.58378500	C	-2.12381500	-2.79339600	-0.64599000
					H	-2.64629500	-3.76942000	-0.66061700
					H	-2.72813300	-2.06054600	-1.17275500
					H	-1.18108500	-2.88927200	-1.18264500
					C	-5.60367100	-1.57387600	-0.33319600
					H	-6.08748900	-1.59659100	-1.31180400
					H	-5.30296400	-2.59336000	-0.09172800
					H	-6.35496300	-1.25512900	0.41452500
					C	-3.76343500	3.18614800	0.48319200
					H	-3.18204200	3.65763700	1.27626000
					H	-4.14792600	3.98466000	-0.17939800
					H	-4.61629200	2.69826100	0.95516200

XeO ₃ :9N3 ^{Et}				XeO ₃ :12N4 ^{Et}			
C	-0.01073200	2.09832300	-1.32205100	C	-2.41025000	0.63036800	-1.29287100
C	-1.18504400	1.27045100	-1.83292900	C	1.72319100	-1.43214000	-1.68820500
C	1.69604600	0.38789300	-1.83193200	C	-1.30063500	1.58688900	-1.70397700
C	1.82550400	-1.04262300	-1.31962500	C	2.77006800	-0.48530100	-1.12455000
C	-1.81294000	-1.06205100	-1.32087400	C	-0.37855000	-2.54687800	-1.24615900
C	-0.50843600	-1.66591400	-1.82997200	C	1.76241500	1.64729300	-1.55132400
H	-0.34266500	2.69501100	-0.46625100	C	-1.34847000	-1.50696500	-1.79142200
H	0.26961600	2.80762600	-2.11885600	C	0.75722700	2.67879900	-1.07293800
H	-1.96941300	1.97327700	-2.13951300	H	-3.01988800	1.08920200	-0.51212400
H	-0.90559400	0.74522600	-2.74830900	H	-3.06621300	0.49435400	-2.16712400
H	2.69699800	0.71569300	-2.13824700	H	1.11216400	-0.89399900	-2.41414700
H	1.10198200	0.40726600	-2.74766200	H	2.23409700	-2.21908600	-2.26618800
H	-2.16560100	-1.64728900	-0.46546300	H	3.34970100	-0.99698300	-0.35316800
H	-2.56635900	-1.17387000	-2.11869500	H	3.48418000	-0.24759600	-1.93189500
H	-0.19337400	-1.16303000	-2.74629000	H	2.61191400	2.19096100	-1.99815000
H	-0.72465600	-2.69726800	-2.13451800	H	1.33096900	1.07703300	-2.37575600
H	2.50885000	-1.05341600	-0.46431600	H	0.60821400	3.39881800	-1.89516200
H	2.29888100	-1.64118100	-2.11604200	H	1.18634000	3.24910300	-0.24522800
N	-1.69686000	0.31355600	-0.86114300	H	-1.75959500	2.38942600	-2.30384900
N	0.57600800	-1.62834100	-0.85820100	H	-0.62087900	1.07535000	-2.38601900
N	1.12234500	1.31014800	-0.86140300	H	-0.83331800	-0.86602500	-2.50692900
C	-2.87865800	0.78516900	-0.13788200	H	-2.11762600	-2.03340000	-2.37572200
H	-2.63684600	1.77492500	0.25859700	H	-0.86897000	-3.11827900	-0.45573000
H	-3.00563000	0.13897000	0.73606500	H	-0.16228100	-3.25605600	-2.06314100
C	0.75822800	-2.88620500	-0.13245300	Xe	-0.26153700	-0.11701200	1.31246200
H	-0.22009500	-3.17121700	0.26373400	O	-0.67928100	-1.74070700	1.89102700
H	1.38071100	-2.67148400	0.74158500	O	-1.65752800	0.79407100	1.91722800
C	2.12104700	2.09809700	-0.13769700	O	1.01299100	0.36280800	2.44639600
H	1.62401800	2.53211900	0.73525100	N	-1.96294000	-0.66055200	-0.77524100
H	2.85673700	1.39397200	0.26020000	N	-0.51108800	2.13251400	-0.60978800
Xe	-0.00049500	0.00194400	1.35713800	N	0.84311500	-1.99235100	-0.67993800
O	1.56211300	-0.39637700	2.10196600	N	2.19541000	0.71042300	-0.53455200
O	-1.13114000	-1.14939900	2.09958200	C	-1.24346000	3.11919200	0.19340100
O	-0.43675500	1.55990600	2.09049000	H	-0.64942800	3.29515400	1.09396400
C	1.36622000	-4.03727400	-0.92775400	H	-2.15431900	2.64343600	0.55131900
H	2.38968200	-3.81949200	-1.24028400	C	1.51729300	-2.94432100	0.20943000
H	1.39872500	-4.93572200	-0.30747600	H	0.79242200	-3.21449200	0.97664700
H	0.78534500	-4.27856500	-1.82183200	H	2.30707700	-2.40453400	0.73797600
C	-4.17799100	0.83404200	-0.93561800	C	-3.03848700	-1.34563800	-0.04306000
H	-4.50043800	-0.16121600	-1.24878100	H	-3.26346100	-0.72818400	0.82945900
H	-4.97350700	1.25496000	-0.31675500	H	-2.61916400	-2.26917800	0.35617000
H	-4.09505000	1.45782600	-1.82948800	C	3.06365400	1.30633100	0.47999800
C	2.81438800	3.19790200	-0.93577600	H	3.19566600	0.55690600	1.26158300
H	2.11435400	3.97478700	-1.25039300	H	2.50954000	2.11157900	0.96527300
H	3.57628800	3.67658900	-0.31660800	C	-4.31493200	-1.63701300	-0.82698600
H	3.31379200	2.81307200	-1.82880800	H	-5.00989000	-2.18322500	-0.18548400

XeO ₃ :15N5 ^{Et}				XeO ₃ :18N6 ^{Et}				XeO ₃ :21N7 ^{Et}			
Xe	-0.09541500	-0.18210800	-1.24848200	C	3.65046700	-0.52948100	0.12096800	C	0.45068500	-3.25241100	1.27115200
O	0.78569200	1.06056500	-2.15715400	C	-3.62975200	0.53908500	0.84016300	C	-4.82591800	0.45514300	-0.73442700
O	-1.60429800	-0.16501900	-2.17674700	C	-3.30027500	-1.83393800	0.68385100	C	2.65183800	-2.56501000	0.80685700
O	0.55660300	-1.72105800	-1.83700300	C	-2.24405200	-2.86422200	0.34962300	C	4.00646100	1.54163500	-0.93585000
C	3.36315500	0.81852000	0.42560700	C	-0.03616800	-3.64466900	0.40900500	C	-3.66296700	1.19539900	-1.39447500

H	3.43237100	0.57800800	1.48856800	C	1.43593400	-3.44916900	0.69768400	C	3.70726500	-1.51641500	0.50493200
H	4.39928000	1.00454900	0.11047700	C	-3.09202900	1.90069500	0.46130300	C	2.39280400	3.03527000	-0.02637000
C	-1.01232600	3.04853700	0.76607500	H	-3.38995400	0.32844400	1.88468300	C	4.63824100	0.16233900	-0.93965500
H	-1.49803200	4.01189500	0.56562000	H	-4.72940900	0.58538700	0.79948600	C	-2.94871200	-1.72268000	1.75214100
H	-1.05751000	2.92690900	1.85046900	H	-3.32582800	-1.67382700	1.76405300	C	1.24350100	3.20377800	0.95317700
C	-3.23330000	-0.01471200	0.55504100	H	-4.27947600	-2.27038300	0.43563100	C	-3.64099000	-0.51249900	1.12864700
H	-3.63830100	0.16590400	-0.44201200	H	-2.21945900	-3.03391100	-0.72932600	C	-0.94491600	-3.03737600	1.83780000
H	-4.09030600	-0.24388600	1.20927500	H	-2.56198800	-3.81878600	0.80867900	C	-0.70009500	3.32301100	-0.41272200
C	2.57332600	2.09791100	0.22851300	H	-0.17709500	-3.83910100	-0.65754900	C	-1.78522200	2.66607000	-1.26135700
H	2.40532300	2.23743400	-0.84014600	H	-0.36391700	-4.56146300	0.93176000	H	0.94964800	-3.98187400	1.93172600
H	3.18454100	2.95107300	0.57058600	H	1.93349400	-4.42634500	0.58108000	H	0.38505900	-3.72618700	0.28813600
C	2.86750800	-1.54948300	0.47762700	H	1.57247800	-3.18149500	1.74832300	H	-5.39653500	1.13465800	-0.07364000
H	3.87365100	-1.71603900	0.89726200	H	-3.71534900	2.66219500	0.96427300	H	-5.51449700	0.17743400	-1.53444000
H	2.67434900	-2.37548400	-0.20865800	H	-3.22744000	2.06069500	-0.61129100	H	2.55423100	-3.25005500	-0.03769600
C	0.42905800	3.13110400	0.30808300	C	3.31405700	-1.97047600	0.44459000	H	3.02519500	-3.17270700	1.64727800
H	0.46207400	3.02588300	-0.77820200	C	3.23453800	1.77190100	0.27143800	H	4.81227200	2.28602200	-1.06852300
H	0.82544400	4.13384200	0.54305000	C	2.33019500	2.93767800	0.61256600	H	3.35960400	1.61516400	-1.81114300
C	-0.46934200	-1.36614600	2.12451200	C	0.10926900	3.84048100	0.46262700	H	4.69050600	-1.96968400	0.70875100
H	-0.29884900	-1.73700400	3.15237600	C	-1.32053000	3.41275300	0.20878800	H	3.60685100	-0.69371200	1.21079700
H	-0.31963400	-0.28329200	2.15720400	H	3.62871300	-0.38660100	-0.96180300	H	5.17948700	0.07654100	-1.88527400
C	-2.59669800	1.25934700	1.08072600	H	4.69618100	-0.35415800	0.43689000	H	5.40626200	0.07281400	-0.15909500
H	-1.98580400	1.02459500	1.95571900	H	3.36887800	1.72662100	-0.81199400	H	-4.05231600	1.69273800	-2.30053300
H	-3.40452600	1.91263100	1.44911700	H	4.23521600	1.98512300	0.69021400	H	-2.93641700	0.45539400	-1.73365600
C	1.85726900	-1.57362300	1.61432200	H	2.07443600	2.90681800	1.67453000	C	3.03090100	3.93319300	-0.02595400
H	2.20226700	-2.27081600	2.39523200	H	2.91342200	3.86465900	0.48306100	H	1.98145700	2.94457100	-1.03312000
H	1.83038900	-0.58971900	2.08411100	H	0.29659500	3.88327100	1.53815100	H	-1.10049100	4.21140200	0.10652400
C	-1.91612500	-1.66960500	1.76330700	H	0.21169900	4.88001000	0.11255500	H	0.02520800	3.711442900	-1.13159400
H	-2.07382900	-2.75019900	1.79745800	H	-1.97991600	4.32090400	0.61320500	H	1.53835000	2.82675000	1.93488200
H	-2.54851100	-1.26191200	2.56390600	H	-1.50808000	3.20740100	-0.86684800	H	1.03609500	4.27721600	1.09760100
N	2.80279200	-0.32029300	-0.28954700	H	4.15462000	-2.59243800	0.09732200	H	-0.87335100	-2.58268200	2.83070700
N	0.50495700	-1.88825900	1.18655900	H	3.28626500	-2.10953200	1.52799600	H	-1.36008200	-0.40808500	2.01657500
N	-2.34084800	-1.16351500	0.46140600	Xe	-0.15890300	-0.04392400	-1.19130400	H	-2.58981600	-1.19731000	-0.77711700
N	-1.74724000	1.95767400	0.12698200	O	1.40341600	0.16399400	-1.98679100	H	-3.67837700	-2.52417200	1.96973000
N	1.26577300	2.08085200	0.86609000	O	-1.10857200	1.20137300	-2.00992200	H	-2.86860000	0.18567800	0.81394900
C	-2.92452400	-2.19742600	-0.40052000	O	-0.74594100	-1.49313100	-2.01445900	H	-4.22973400	-0.01269400	1.92472100
H	-3.05565400	-1.74681100	-1.38425000	N	2.04876300	-2.41619100	-0.10998900	H	-2.07732000	3.41728900	-2.01922600
H	-2.17541800	-2.97891900	-0.53949600	N	2.75562400	0.46568500	0.68669400	H	-1.33611000	1.84060100	-1.80703700
C	-2.45982900	2.45115900	-1.06049700	N	1.09286800	2.96261200	-0.14269100	Xe	0.85891700	-0.25533200	-1.01544500
H	-1.72146400	2.99604400	-1.65437100	N	-1.68179100	2.10758100	0.73972000	O	-0.88016800	-0.11973100	-0.77711700
H	-2.73407400	1.59571300	-1.67402600	N	-3.10487300	-0.54798200	0.03181000	O	0.93570500	-1.79086400	-1.89291400
C	0.35051500	-3.30010700	0.85299900	N	-0.88936200	-2.51753900	0.74671900	O	1.18313500	0.91636500	-2.30851100
H	1.12411600	-3.54412100	0.12510800	C	2.17088200	-2.78055300	-1.52516600	N	3.67891300	-0.94276100	-0.83720300
H	-0.58217300	-3.42056600	0.30516200	H	2.65317800	-1.94148700	-2.02565500	N	1.30939200	-2.07284400	1.10713700
C	3.37888900	-0.45654100	-1.62931700	H	1.16994800	-2.82011100	-1.95496900	N	-1.79392700	-2.20776900	1.02737200
H	3.26711100	0.50903300	-2.12569800	C	2.53589000	0.33232100	2.11670300	N	3.17735200	1.83136800	0.22146500
H	2.74430400	-1.14902500	-2.18384800	H	1.77654100	1.06226600	2.40616100	N	0.05125400	2.48873500	0.52622000
C	1.34336600	2.12308100	2.32420600	H	2.07019700	-0.64103800	2.28480700	N	-2.94744400	2.14931500	-0.55566600
H	2.05731500	1.36104100	2.63923400	C	-1.29614400	1.89516800	2.12461200	N	-4.48062600	-0.76939400	-0.03064200
H	0.38179600	1.79961400	2.73329600	H	-0.20841400	1.97307800	2.16811400	C	3.88265200	-1.92725200	-1.90691300
C	1.73288100	3.45337600	2.97456700	H	-1.51307600	0.85535000	2.37435200	H	3.79487000	-1.37800000	-2.84729100
H	0.97295400	4.22330400	2.82577800	C	1.28162300	3.25863500	-1.56611600	H	3.03585300	-2.61017300	-1.90410000
H	1.85093500	3.31387500	4.05182900	H	0.29145500	3.25459300	-2.02259300	C	1.24010900	-1.11845400	2.20811600
H	2.67836700	3.83910000	2.58731700	H	1.79778200	2.41466000	-2.02178700	H	1.76420900	-0.20952100	1.89385800
C	4.83282400	-0.92156200	-1.69249800	C	-3.63397000	-0.55033900	-1.33926800	H	0.19007600	-0.83523400	2.29394600
H	4.95628400	-1.93065800	-1.29209100	H	-3.18266700	-1.40128700	-1.84923700	C	3.93198100	1.88958500	1.47324300
H	5.16304500	-0.94165100	-2.73376100	C	-3.23688000	0.32454900	-1.85355700	H	3.22545100	1.81260400	2.30512300
H	5.51361900	-0.26114900	-1.14880600	C	-0.75544800	-2.04886700	2.11525200	H	4.54666100	0.99004800	1.52940000
C	-3.68357500	3.32930100	-0.80614400	H	-1.37936500	-1.15915200	2.21278000	C	-0.73540600	2.00613500	1.65811500
H	-3.46981700	4.18508900	-0.16032400	H	0.26802300	-1.69016800	2.23959500	H	-1.58642500	1.47641200	1.24103000
H	-0.04831200	3.72179400	-1.75797400	C	3.75089200	0.47279600	3.03616100	H	-0.11899500	1.27025400	2.80732000
H	-4.50467800	2.76802400	-0.35366000	H	3.44984900	0.34156200	4.07802100	C	-2.07891900	-2.75767200	-0.29341400
C	-4.23426200	-2.81953400	0.07986100	H	4.52050200	-0.26624700	2.81564700	H	-2.66219000	-0.201178100	-0.82638600
H	-5.04519400	-2.08900400	0.11872100	H	4.21089200	1.46467000	2.95338100	H	-1.13699700	-2.84247500	-0.83718800
H	-4.53979500	-3.60746500	-0.61260100	C	-1.09532300	-3.03581400	3.23227400	C	-5.67619900	-1.52273800	0.30136600
H	-4.14349500	-3.27236100	1.07101800	H	-0.44152800	-3.91094200	3.21678900	H	-5.40793900	-2.26479200	1.05532800
C	0.39589900	-4.28874100	2.01794600	H	-0.97848700	-2.55510700	4.20679700	H	-6.43403800	-0.86880900	0.77637500
H	0.28774200	-5.30764900	1.63883800	H	-2.12579500	-3.39253900	3.16113000	C	-3.78494300	3.19287900	0.01710400
H	1.34019800	-4.24426700	2.56490600	C	-1.92399500	2.80885700	3.17799700	H	-3.12191900	3.89121800	0.53070600
H	-0.40997600	-4.11978500	2.73659700	H	-1.53568200	2.56076200	4.16899900	H	-4.40391600	2.74923600	0.80277900
				H	-1.70172800	3.86199100	2.99034200	C	-1.21493400	3.04731900	2.67139900
				H	-3.01073600	2.70222400	3.21488100	H	-1.80091000	2.55272500	3.45036800
				C	-5.15445100	-0.59221000	-1.49577300	H	-0.38568000	3.56419200	3.16164900
				H	-5.63707700	0.32176300	-1.14230800	H	-1.85733000	3.80405900	2.21916200
				H	-5.39860200	-0.69566300	-2.55545200	C	4.83635100	3.10343000	1.70134200
				H	-5.61289200	-1.43582700	-0.97360400	H	4.26684300	4.02611900	1.82676200
				C	2.01159600	4.55784900	-1.91183700	H	5.42198800	2.95493000	2.61173900
				H	1.97979600	4.70856200	-2.99341000	H	5.53962500	3.25191700	0.87890300
				H	1.55622400	5.43665200	-1.44793300	C	-4.67992900	3.97868000	-0.94540600
				H	3.06450600	4.53510400	-1.62116900	H	-5.17969900	4.78990700	-0.41005900
				C	2.91807700	-4.07718900	-1.84311600	H	-4.10921200	4.42512500	-1.76308200
				H	2.37491500	-4.96562400	-1.51244100	H	-5.45614100	3.34934400	-1.38629900
				H	3.04253700	-4.16145800	-2.92519900	C	-6.28177600	-2.24800500	-0.88987900

XeO ₃ :9N3 ^{iPr}				XeO ₃ :12N4 ^{iPr}			
C	-0.18621200	2.08326400	1.34432400	C	0.09107700	-2.57584900	1.27322700
C	1.06554200	1.37221300	1.84514800	C	-1.16434200	2.17215700	1.74303800
C	-1.72132300	0.23604400	1.84552800	C	1.28989000	-1.77492400	1.78161500
C	-1.71125400	-1.20344400	1.34463300	C	0.07624800	2.89068500	1.23558900
C	1.89786600	-0.88079900	1.34433200	C	-2.51803800	0.23265200	1.21838900
C	0.65607500	-1.60930600	1.84497700	C	1.72956100	1.29578500	1.84016400
H	0.08423200	2.72950400	0.50552900	C	-1.52299400	-0.81394500	1.73725000
H	-0.52166700	2.74360600	2.16076300	C	2.66973400	0.16797400	1.46047100
H	1.76029500	2.15477800	2.16943400	H	0.42042100	-3.21631700	0.45648000
H	0.84150600	0.81145300	2.75492300	H	-0.20925300	-3.23474100	2.10362400
H	-2.74638500	0.44653200	2.16986100	H	-0.90035800	1.49505200	2.55456400
H	-1.12351500	0.32243500	2.75523100	H	-1.81914800	2.92155300	2.21303800
H	2.32242700	-1.43822700	0.50567000	H	-0.22555700	3.55706700	0.42958400
H	2.63734400	-0.92032000	2.16091800	H	0.45172900	3.53778700	2.04992400
H	0.28263000	-1.13527700	2.75505400	H	2.28558200	1.98945900	2.49482800
H	0.98616600	-2.60250600	2.16876400	H	0.93805000	0.89413500	2.47436800
H	-2.40679700	-1.29261000	0.50639700	H	3.19282900	-0.14733600	2.37828500
H	-2.11447200	-1.82435800	2.16136300	H	3.44026800	0.54928600	0.79220300
N	1.69722400	0.48769400	0.87280300	H	1.95866000	-2.50939600	2.25234600
N	-0.42574900	-1.71351800	0.87245000	H	0.98077500	-1.12583800	2.60099500
N	-1.27123000	1.22525500	0.87302700	H	-0.64050300	-0.28692600	2.08519300
C	2.93659200	1.02025100	0.26098800	H	-1.94623500	-1.30308300	2.62529300
H	3.17831500	0.30368800	-0.53063500	H	-3.13138500	-0.18564400	0.42071200
C	-0.58428000	-3.05295600	0.26020900	H	-3.19881700	0.47352600	2.04965100
H	-1.32569900	-2.90371900	-0.53135700	Xe	-0.11340900	-0.34359500	-1.23775500
C	-2.35215200	2.03231400	0.26130800	O	-1.75007900	-0.57035900	-1.87022400
H	-1.85236800	2.60054900	-0.52980500	O	0.64839000	-1.85164900	-1.76945500
Xe	-0.00007700	0.00046800	-1.35894000	O	0.58282400	0.80170000	-2.39643400
O	-1.31713800	-0.91539400	-2.11977700	N	-1.06191600	-1.81646800	0.77943800
O	1.45138500	-0.68184200	-2.12050100	N	2.02320600	-0.96439200	0.80708900
O	-0.13520100	1.59925700	-2.11921600	N	-1.87437600	1.43787400	0.69905900
C	-1.10468500	-4.12400200	1.22096400	N	1.10411100	1.99649400	0.73392700
H	-2.07935500	-3.87423000	1.64290800	C	2.98418600	-1.77728700	0.02293900
H	-1.21518200	-5.06946600	0.68601100	H	2.38834400	-2.59136600	-0.39200300
H	-0.41081500	-4.30033400	2.04809600	C	-2.81071000	2.36539200	0.01544800
C	4.12414300	1.10479300	1.22198500	H	-2.25746800	3.30821900	-0.04742400
H	4.39596300	0.13539300	1.64240300	C	-2.16780100	-2.68390300	0.29337100
H	4.99791600	1.48344300	0.68776800	H	-2.81472000	-2.01029100	-0.27106700
H	3.92919300	1.79232400	2.05022200	C	2.08251900	2.64155300	-0.17021100
C	-3.01990500	3.01748200	1.22277100	H	2.58175800	1.81664900	-0.68647200
H	-2.31629600	3.73594200	1.64604300	C	-2.98840400	-3.32974300	1.41129400
H	-3.78296100	3.58677900	0.68808100	H	-3.75180900	-3.96942000	0.96405900
H	-3.52013700	2.50378800	2.04892800	H	-2.37388300	-3.96322400	2.05675000
C	2.70772900	2.36948500	-0.40402300	H	-3.50525900	-2.60163300	2.03921500
H	3.60765500	2.65442300	-0.95254800	C	3.14684500	3.48828000	0.53701300
H	1.88093600	2.34689700	-1.11379300	H	3.78164400	3.97055700	-0.20949200
H	2.51929800	3.15881300	0.32960200	H	2.68888400	4.28006400	1.13698500
C	-3.40565600	1.15945100	-0.40452600	H	3.80079300	2.90586200	1.18949000
H	-4.10235100	1.79640600	-0.95303000	C	4.13546600	-2.37096700	0.84133900
H	-2.97231600	0.45499500	-1.11433800	H	4.74036900	-3.01217100	0.19673300
H	-3.99511900	0.60128900	0.32877800	H	4.79390400	-1.59116700	1.23299900
C	0.69869500	-3.52915600	-0.40485600	H	3.80108500	-2.98412200	1.68060100
H	0.49568600	-4.45109000	-0.95325100	C	-4.09561800	2.63779300	0.80423300
H	1.09242800	-2.80180400	-1.11467200	H	-4.62606100	3.48401400	0.36307500
H	1.47645400	-3.76038500	0.32888500	H	-4.77075400	1.77917400	0.77134600
				H	-3.90649600	2.87971800	1.85305700
				C	-1.69847300	-3.74827900	-0.68799500
				H	-1.03842300	-3.33522300	-1.44803000
				H	-1.19130900	-4.57563800	-0.18388400
				H	-2.57429300	-4.16627300	-1.18840000
				C	3.55790000	-0.99852200	-1.15444500
				H	4.04297700	-1.69423600	-1.84218500
				H	2.79162300	-0.46973100	-1.71787900
				H	4.32236100	-0.28284600	-0.83803000
				C	1.41248800	3.48643900	-1.24649700
				H	2.12285600	3.65409100	-2.05825900
				H	0.54864100	2.98139000	-1.67394000
				H	1.11864900	4.46933900	-0.86720700
				C	-3.14919500	1.96664100	-1.40913600
				H	-2.26040300	1.88514800	-2.03193200
				H	-3.66759400	1.00869600	-1.45963800
				H	-3.80667100	2.72628500	-1.84104100

XeO ₃ :15N5 ^{iPr}				XeO ₃ :18N6 ^{iPr}				XeO ₃ :21N7 ^{iPr}			
Xe	0.28789700	0.09238500	-1.27415300	C	-0.51768000	-3.57799500	0.35040400	C	-1.13849500	3.67957500	0.27091900
O	-0.65957400	-1.12688800	-2.13895700	C	0.57210400	3.87591600	0.29404100	C	4.32251700	-0.28848000	0.37097900
O	1.82739200	-0.09291000	-2.12350000	C	-1.65829700	3.12680200	0.70511800	C	-3.19184200	2.57139400	0.43658000
O	-0.27133200	1.61699600	-1.97695000	C	-2.84104700	2.23927400	0.34537100	C	-3.87553100	-2.16632600	-0.34113600
C	-3.45260100	-0.47116200	0.29582200	C	-3.70241800	0.06166200	0.09607200	C	3.74694300	-0.75980000	-0.97152100
H	-3.50336000	-0.17527800	1.34745600	C	-3.64310000	-1.44254800	0.29728800	C	-4.03205800	1.30888600	0.58437500
H	-4.49944600	-0.54591600	-0.02332700	C	1.90421500	3.17425100	0.09316700	C	-2.01222700	-3.55715100	0.03372800
C	0.66004400	-3.11428900	0.87898400	C	0.39648300	4.05232800	1.35578500	C	-4.68041900	-0.89137400	-0.13911600
H	1.04136600	-4.13108000	0.73483300	H	0.66929900	4.87918000	-0.13991700	C	2.58742600	3.04092900	0.50976300
H	0.71421200	-2.94283300	1.95157000	H	-1.22077200	2.76249400	1.63030700	C	-0.64388200	-3.83734000	0.64596900
C	3.24866100	-0.33277700	0.69501800	C	-2.02874900	4.13999600	0.93066400	C	2.92878500	1.59045800	0.89300200
H	3.70450400	-0.61966800	-0.25262400	H	-2.94028800	2.18258700	-0.73602500	C	0.33099000	3.98647700	0.54954400
H	4.07328300	-0.22895400	1.41848500	H	-3.76698200	2.71672400	0.70936900	C	1.03224200	-3.30790900	-0.95804500
C	-2.81403300	-1.84876900	0.17182800	H	-3.51518100	0.26637300	-0.95565900	C	1.97689400	-2.31618900	-1.63099000

H	-2.52106200	-1.98461000	-0.86589700	H	-4.73639700	0.39097300	0.30055600	H	-1.70790000	4.56020100	0.61271200
H	-3.57387400	-2.61776200	0.39297700	H	-4.56025800	-1.86074500	-0.13647700	H	-1.28590400	3.62064600	-0.80808700
C	-2.48018100	1.75073700	0.33108500	H	-3.70791300	-1.68259600	1.35914800	H	3.78221700	-0.78975500	1.18985000
H	-3.40095700	2.18363600	0.75386700	H	2.70671700	3.90537200	0.29553600	H	5.36383400	-0.59551200	0.46516300
H	-2.06106500	2.48242100	-0.35224100	H	1.98683300	2.90755800	-0.95808900	H	-3.21302800	2.90496000	-0.60007100
C	-0.79098100	-3.08883200	0.42054600	C	-1.87738900	-2.99680900	0.70982400	H	-3.68204200	3.36839900	1.01640500
H	-0.79786900	-2.93598200	-0.65569800	H	1.79849500	-3.23516600	0.09820900	H	-4.58197400	-3.01306200	-0.31743300
H	-1.22563300	-4.08610300	0.59353400	C	3.07275300	-2.43288300	0.29796100	H	-3.45916100	-2.14531600	-1.34741200
C	0.77829500	1.41848600	2.15137400	C	3.54026500	-0.12606000	0.70581400	H	-5.06967700	1.61278000	0.78480000
H	0.66314300	1.72679400	3.20671800	C	3.36089400	1.34141300	0.34489800	H	-3.70962700	0.76777300	1.47061600
H	0.54063300	0.35657500	2.12531600	H	-0.41985100	-3.63894300	-0.73088100	H	-5.60111700	-0.99967500	-0.72108400
C	2.36751200	-1.46589400	1.20359000	H	-0.46758400	-4.61749000	0.71744300	H	-5.01118600	-0.80795700	0.89652100
H	1.69618200	-1.09091500	1.97498000	H	1.52702400	-3.17649000	-0.95348500	H	4.48421700	-0.54956200	-1.75988900
H	3.02163900	-2.1869700	1.71663700	H	2.02921500	-4.29526300	0.30415700	H	2.89632500	-0.11975900	-1.19293000
C	-1.48447500	1.46260700	1.45334700	H	3.31339700	-2.36781600	1.35964000	H	-2.62677700	-4.7041900	0.12409300
H	-1.91818500	1.71430600	2.43476300	H	3.89261100	-3.01986400	-0.13521200	H	-1.87394100	-3.37649100	-1.03216900
H	-1.32049200	0.38252200	1.46467600	H	3.00813400	-0.32262200	1.63222700	H	1.54933300	-4.27393100	-0.80439700
C	2.23543600	1.59110400	1.75639300	H	4.60355600	-3.10278000	0.92968500	H	0.23901400	-3.50715300	-1.68432400
H	2.47415200	2.65343300	1.70133000	H	4.23686400	1.90591200	0.70797700	H	-0.71242600	-3.88118900	1.73348800
H	2.85489900	1.19792300	2.57643500	H	3.36100100	1.45444600	-0.73662500	H	-0.36138500	-4.86019800	0.34227700
N	-2.75387000	0.56263800	-0.46011600	H	-2.56926700	-3.82373100	0.93810800	H	0.53319900	3.92121900	1.61624700
N	-0.17466300	2.07680300	1.27690900	H	-1.77991100	-2.43342700	1.63358600	H	0.44194900	5.06058800	0.30358400
N	2.59078700	0.95474500	0.49253200	Xe	-0.00264400	-0.00309700	-1.18026700	H	2.61204600	3.69181000	1.39032000
N	1.54440200	-2.15130500	0.20273200	O	0.08647700	-1.57068100	-1.98295500	H	3.38333400	3.40705100	-0.14770600
N	-1.62102900	-2.03675900	1.00109400	O	1.31196900	0.85671800	-1.98158900	H	2.19700400	0.96011000	0.39686200
C	3.41804000	1.80898300	-0.39045200	O	-1.40322000	0.70479700	-1.98461300	H	2.77657000	1.43174900	1.97570000
H	3.58836500	1.19108500	-1.27453500	N	-2.46069800	-2.08815500	-0.27261900	H	2.09211900	-2.65282300	-2.67391100
C	2.37552500	-2.79652200	-0.85122400	N	0.62115900	-2.80435900	0.84658500	H	1.47034800	-1.35728300	-1.67682700
C	-0.13280500	3.54388300	1.44221100	N	3.04177600	-3.00471300	-0.27351700	Xe	-1.22621900	0.08271300	-0.77717300
H	0.92708900	3.77286400	1.57087600	N	2.12267700	1.94119300	0.84370400	O	0.48971300	0.16428700	-0.37137600
C	-3.39349000	0.91783300	-1.74400900	N	-0.57836400	3.17518000	-0.27576200	O	-1.43102600	1.44083300	-1.89563600
H	-2.65361300	1.54573100	-2.25017700	N	-2.74212300	0.86720500	0.84474100	O	-1.30954800	-1.24288600	-1.94903500
C	-2.03104700	-2.25464200	2.40919900	H	-2.73477400	-2.76093800	-1.56344600	N	-3.99171800	0.35040200	-0.52649500
H	-2.90726000	-1.61213100	2.53578800	H	-1.75591000	-3.04142600	-1.95512700	N	-1.77522300	2.46854800	0.81979300
C	-2.47868900	-3.68130300	2.74323300	C	0.71886800	-2.93806500	2.31748500	N	1.29111700	3.16781800	-0.14457600
H	-1.63093300	1.95467400	2.79156600	H	-0.31862300	-2.98683300	2.65648900	N	-2.75047000	-2.39959100	0.56531500
H	-2.96222100	-3.69411100	3.72264600	C	2.19298900	2.09549500	2.31391500	N	0.36954700	-2.87621500	0.26640000
H	-3.19297300	-0.47565600	2.01735700	H	2.75501800	1.22217700	2.65327500	C	3.27226100	-2.13283900	-0.98931500
C	-4.68929000	1.72354500	-1.59336600	C	3.75849600	-0.99039800	-1.56607400	N	4.24987400	1.15970600	0.47586000
H	-4.53781700	2.67131100	-1.07415100	H	3.51229200	-0.00253400	-1.95830000	C	-4.47488900	0.91641700	-1.80859800
H	-5.09291000	1.95467400	-2.58165800	C	-1.02191400	3.74669600	-1.56822100	H	-3.79146600	1.73665100	-2.03291000
H	-5.45705700	1.16070400	-1.05377800	H	-1.75427500	0.03892600	-1.95937200	H	-1.61899000	2.27564100	2.27834400
C	3.46815800	-3.72633700	-0.31596500	C	-2.90999300	3.05929300	2.31533600	H	-2.35756000	1.50983000	2.52869400
H	3.05815600	-4.55193800	0.27270000	H	-2.43463500	1.77688300	2.65309200	C	-3.11936100	-2.63444400	1.98091900
H	4.00485600	-4.16616100	-1.15885600	C	1.39849200	-4.21335500	2.82412900	H	-2.28822500	-3.21280900	2.38471400
H	4.20512100	-3.20721100	0.29986100	H	1.27523600	-4.28673000	3.90733300	C	1.27124700	-2.47012600	1.34389400
C	4.77327200	2.19696100	0.20527100	H	0.97062100	-5.11594900	2.38201200	H	1.91646400	-1.71718700	0.89634300
H	5.37938200	1.32860100	0.47089500	H	2.47132300	-4.21289600	2.61772200	C	1.35223300	3.42118600	-1.58527200
H	5.34071900	2.77959600	-0.52380800	H	-4.35536300	0.90249300	2.81846800	C	0.31573400	3.41114600	-1.93404700
H	4.66041200	2.81759000	1.09889600	H	-4.89029900	-0.02782700	2.61356000	C	5.33371600	1.78247900	1.23275300
C	-0.85585700	4.06605200	2.68632000	H	-4.35989200	1.04914900	3.90122100	H	5.04844700	2.83612800	1.33365100
H	-0.62484200	5.12453000	2.82661700	H	-4.92254100	1.72267200	2.37257400	C	4.23969800	-3.16184800	-1.35107200
H	-1.94068300	3.98338400	2.58287200	C	2.95825100	3.32018000	2.81632400	H	3.69252900	-4.10960600	-1.27878600
H	-0.56048100	3.54081000	3.59784600	H	3.08604900	3.25536900	3.89937400	C	2.16323200	-3.58628900	1.88571300
C	-0.58671200	4.32202800	0.21068700	H	3.95274500	-3.04325200	2.37159000	H	2.84664500	-3.19321000	2.64332200
H	-0.23165900	3.85518300	-0.70713600	H	2.42052100	4.25120400	2.60917600	H	1.57312100	-4.38031500	2.35446900
H	-1.67413900	4.40683400	0.15894300	C	-1.69642400	5.11888100	-1.45726700	C	2.77011000	-0.42853900	1.09515700
H	-0.19296400	5.34080300	0.25987400	H	-1.02805300	5.86893500	-1.02409700	C	-4.38067800	-3.47242800	2.20539300
C	2.66759300	3.04465400	-0.85357800	H	-1.97346700	5.48662200	-2.45401000	H	-4.36177100	-4.40666700	1.64006300
H	1.69575600	2.78841600	-1.27082600	H	-2.60804400	5.04646700	-0.85718000	H	-4.46196500	-3.73074900	3.26371100
H	2.52310200	3.76955700	-0.04823000	C	5.28409500	-1.09287000	-1.45498400	H	-5.29013500	-2.93110200	1.93307200
H	3.24679400	3.54736100	-1.63147000	H	5.72550800	-1.02999100	-2.45186200	C	4.78179900	-3.05498600	-2.78192700
C	-3.64975200	-0.29087300	-2.63216700	H	5.71914600	-0.29022300	-0.85647700	H	5.38740500	-3.93149800	-3.02649500
H	-2.73549800	-0.85066100	-2.81422700	H	5.59895300	-0.04602400	-1.01993900	H	3.97808700	-2.99138000	-3.51841600
H	-4.40355300	-0.96050700	-2.20726600	C	-3.58471500	-2.03159300	-1.44899600	H	5.41900700	-2.17533800	-2.90187400
H	-4.03661900	0.05202200	-3.59445100	H	-4.56838100	3.82772000	-1.01566400	C	6.63515600	1.74525400	0.44324100
C	-1.02629000	-1.78152200	3.45680400	H	-3.74933800	-4.44877700	-2.44469800	H	7.41814700	2.30649500	0.95972300
H	-0.65085000	-0.78453800	3.23398400	C	-3.10663700	-4.80707400	-0.84747400	H	6.99961700	0.72196100	0.31755400
H	-1.51635700	-1.73972500	4.43340200	C	-3.34760900	-1.82413100	-2.59354100	H	6.49060600	2.17512700	-0.54963500
H	-0.17638400	-2.45728200	3.56362100	H	-4.36719700	-1.52930600	-2.32848000	C	1.96644500	4.77779900	-1.95159900
H	2.85359600	-1.97285100	-1.38133600	H	-2.74340300	-0.92999000	-2.72860500	H	1.87226500	4.95759500	-3.02525000
C	1.52814700	-3.52634800	-1.88264100	H	-3.40618500	-2.34246000	-3.55334700	H	1.47693400	5.60773100	-1.43587200
H	1.03758200	-4.41066600	-1.46586800	C	0.09698300	3.80619300	-2.59721200	C	3.03201400	4.81208800	-1.70852000
H	0.77385100	-2.87290100	-2.31611600	H	0.86240100	4.54162400	-2.33262600	C	-1.95065300	3.49728000	3.13928200
H	2.17735100	-3.87166300	-2.69004200	H	0.56850800	2.83519300	-2.73009800	H	-2.94832000	3.89595800	2.94248400
				H	-0.32132900	4.11471600	-3.55802900	H	-1.91330900	3.21393800	4.19368100
				C	3.25029300	-1.99004400	-2.59404900	H	-1.22989900	4.30412500	2.99294700
				H	3.50473700	-3.02039900	-2.32874900	C	-5.98824600	1.46991100	-1.74882700
				H	2.17357300	-1.91313900	-2.72649100	H	-6.17054300	1.87343600	-2.72612700
				H	3.72618700	-1.78277100	-3.55524300	H	-6.63015500	0.69559900	-1.50250100
				C	1.31530000	-1.71084400	2.99				

		H	-5.01810000	-0.92333900	-2.85168000
		H	-4.56774100	0.42064500	-3.89025300
		C	-3.31170800	-0.46143100	-3.02061100
		C	2.06694800	2.29910600	-2.32106400
		H	3.09916900	2.18423200	-1.97886900
		H	1.54644300	1.35594200	-2.17017100
		H	2.09305800	2.51359500	-3.39226700
		C	5.53162000	1.22093700	2.64404000
		H	5.89434400	0.19020100	2.61182500
		H	6.26781800	1.81235400	3.19425900
		H	4.60183500	1.23112100	3.21777700

XeO ₃ :9N3 ^{tBu}				XeO ₃ :12N4 ^{tBu}			
C	1.91916000	0.83576200	1.30143900	C	-1.15880400	2.49046300	1.26633600
C	1.61734000	-0.56744600	1.82243700	C	1.72397300	-1.24055500	1.83011300
C	-0.31690500	1.68476900	1.82144100	C	-2.00265000	1.29515800	1.70227600
C	-1.68298800	1.24480100	1.29992700	C	0.91115700	-2.44148800	1.34307100
C	-0.23592400	-2.07922900	1.30033400	C	2.35116200	1.03664500	1.40011100
C	-1.30046800	-1.11641400	1.82153700	C	-1.26758300	-1.64258200	1.78460600
H	2.59706300	0.73574900	0.45484200	C	1.06197600	1.79231400	1.73647800
H	2.47829600	1.34120300	2.10510500	C	-2.58611200	-0.98250600	1.40907600
H	2.57312700	-0.94595000	2.19226600	H	-1.72502200	3.08944200	0.56676000
H	0.98998800	-0.52253300	2.71317500	H	-1.06906500	3.09821000	2.18256600
H	-0.46695900	2.70180700	2.19109000	H	1.13626300	-0.65497000	2.53566600
H	-0.04271200	1.11877200	2.71225100	H	2.53909400	-1.65554300	2.43837200
H	-0.66148600	-2.61487500	0.45275100	H	1.50785100	-2.96746600	0.61542500
H	-0.07875800	-2.81711600	2.10331000	H	0.81319400	-3.11071300	2.21801200
H	-0.94790800	-0.59551100	2.71225600	H	-1.48820600	-2.40408800	2.54747100
H	-2.10601000	-1.75515300	2.19106300	H	-0.67244500	-0.89953300	2.31081500
H	-1.93403200	1.88137700	0.45252500	H	-3.14446100	-0.87688100	2.35638900
H	-2.40054400	1.47757700	2.10293300	H	-3.17842800	-1.65352100	0.79714300
N	1.04239500	-1.50892900	0.85708000	H	-2.85575300	1.73806800	2.23985500
N	-1.82857900	-0.14744800	0.85640500	H	-1.45636900	0.76230100	2.48078200
N	0.78631700	1.65710900	0.85658100	H	0.45606200	1.15704400	2.38375400
C	2.02277600	-2.56944200	0.43544400	H	1.37483900	2.62483100	2.38778200
C	-3.23761200	-0.46583100	0.43540000	H	2.95949100	1.63137600	0.73336600
C	1.21502400	3.03616600	0.43440600	H	2.89298900	0.99309800	2.35802000
Xe	-0.00008400	-0.00058000	-1.35973400	Xe	0.29001300	-0.07928500	-1.21158500
O	-0.85722500	1.34264500	-2.13609300	O	1.34839800	1.11886400	-1.96328300
O	-0.73552100	-1.41509600	-2.13441700	O	-1.15820800	0.09900100	-2.21009500
O	1.59178900	0.06888400	-2.13619200	O	1.00690400	-1.55829500	-1.86935800
C	-4.23033100	-0.36095900	1.60197900	N	0.17381400	2.28581400	0.68069800
H	-4.30926400	0.65753800	1.98680300	N	-2.46456900	0.30664300	0.72941800
H	-5.22354700	-0.65273900	1.25539500	N	2.26896200	-0.31617900	0.82408200
H	-3.97194800	-1.02084700	2.43353600	N	-0.40340700	-2.19570900	0.74232800
C	2.42734500	-3.48286400	1.60126100	C	-3.74336100	0.68983600	0.03964200
H	1.58477100	-4.06245600	1.98301200	C	3.64156700	-0.73355800	0.32485900
H	3.17864600	-4.19527600	1.25522900	C	0.61137200	3.59566000	0.05091200
H	2.86666700	-2.92973000	2.43474900	C	-0.95259800	-3.44503600	0.07108700
C	1.80268100	3.84431300	1.60017300	C	0.39585600	4.80565200	0.98000300
H	2.72516800	3.40456800	1.98395700	H	0.86552100	5.68144400	0.52869500
H	2.04509200	4.85061000	1.25323900	H	-0.65676500	5.04702600	1.13178200
H	1.10287000	3.94978100	2.43253000	H	0.85982500	4.66146100	1.95968000
C	-3.28709400	-1.88473900	-0.13194900	C	-1.75515400	-4.32163200	1.04239500
H	-3.07444600	-2.64625600	0.62139100	H	-2.01768900	-5.25445900	0.54005600
H	-4.29424100	-2.08278900	-0.50357900	H	-1.17488600	-4.58390100	1.93157000
H	-2.58712800	-1.99890900	-0.95912100	H	-2.68869300	-3.85673200	1.36528100
C	-3.69004500	0.48683600	-0.67007500	C	-4.93656600	0.79366700	1.00267200
H	-3.80558800	1.51300600	-0.31774300	H	-5.82445200	1.09589100	0.44334900
H	-3.00111300	0.49014000	-1.51356400	H	-5.16211900	-0.16346600	1.47797900
H	-4.66776600	0.16262000	-1.03153400	H	-4.78455900	1.53755600	1.78786200
C	0.01081500	3.78821600	-0.13306700	C	4.73073200	-0.52867300	1.39092300
H	0.34286100	4.75916600	-0.50543000	H	5.65613400	-0.98983700	1.04150300
H	-0.43844800	3.23881900	-0.95982600	H	4.94447800	0.52551900	1.57348700
H	-0.75461000	3.98545500	0.62051300	H	4.47829000	-0.99751900	2.34542600
C	2.26597700	2.95080600	-0.67122700	C	2.09416400	3.59676200	-0.31829900
H	3.21243600	2.53802000	-0.31861300	H	2.30119900	4.50122700	-0.89329100
H	1.92443600	2.35208500	-1.51440600	H	2.73569200	3.63372100	0.56521100
H	2.47417900	3.95942000	-1.03330800	H	2.34902100	2.74098800	-0.93766300
C	1.42485400	-3.43621300	-0.67147300	C	-0.18307500	3.81236400	-1.23758500
H	0.59223100	-4.04814700	-0.32117400	H	-0.01813800	2.99478500	-1.93673500
H	1.08012500	-2.84045600	-1.51544800	H	-1.25461200	3.91697800	-1.06354100
H	2.19417100	-4.12187000	-1.03168100	H	0.14936500	4.73989400	-1.70966600
C	3.27674100	-1.90211000	-0.13033700	C	0.15363900	-4.33025300	-0.51639100
H	3.02599100	-1.23719800	-0.95632200	H	0.73878700	-4.84814100	0.24644400
H	3.82998600	-1.33895400	0.62425200	H	-0.32621600	-5.09653700	-1.12827200
H	3.95158800	-2.67475500	-0.50350300	H	0.81525200	-3.75801200	-1.16532800
				C	-1.83281800	-3.04553700	-1.10887300
				H	-2.33982700	-3.93080900	-1.50200400
				H	-2.59309700	-2.32348100	-0.84176100
				H	-1.23433400	-2.61428700	-1.90962400
				C	-4.09920300	-0.33189400	-1.04119900
				H	-4.42340500	-1.29062100	-0.63204200
				H	-4.94134300	0.05065900	-1.62139500
				H	-3.25841600	-0.48612800	-1.71460400
				C	-3.57260700	2.02794100	-0.67633100
				H	-3.53390400	2.86805900	0.01858000
				H	-2.67731700	2.01483400	-1.29859700
				H	-4.43397400	2.20001200	-1.32435700
				C	4.02179200	0.06289200	-0.92159800
				H	3.34969200	-0.14889300	-1.74938500
				H	4.02781600	1.14097100	-0.76178200
				H	5.03534800	-0.22104900	-1.21465800
				C	3.66131800	-2.20590900	-0.08378000

	H	3.56516400	-2.88224300	0.76804200
	H	2.88486000	-2.41658600	-0.81744800
	H	4.62715500	-2.41753600	-0.54620900

XeO ₃ :15N ^{5tBu}				XeO ₃ :18N ^{6tBu}				XeO ₃ :21N ^{7tBu}			
Xe	-0.77700900	0.34239300	-1.41016500	C	-1.54468800	-3.09473400	1.03177100	C	-0.74303700	-3.62815700	0.92138300
O	0.68489100	0.77157700	-2.31153700	C	1.38786600	2.74144700	0.28843200	C	-3.69284700	1.96333600	-0.39656900
O	-1.93582000	1.45089600	-2.14368600	C	-0.97347600	2.53424400	0.19805200	C	1.55221200	-3.44783200	1.42464500
O	-1.24579700	-1.21269300	-2.10689400	C	-2.33784100	2.63215300	-0.48124300	C	4.08359800	0.47728200	-0.27269900
C	3.33191700	-1.16994100	-0.13492900	C	-3.80095400	0.70010700	-0.61806700	C	-2.79421400	1.74302100	-1.60520400
C	3.17701900	-1.41051800	0.91491100	C	-4.17004200	-0.60911100	0.12953200	C	2.90767500	-2.72731600	1.43418100
H	4.29160200	-1.63234700	-0.39643100	C	2.56314100	2.29554500	-0.59406200	C	2.49451800	2.19150300	0.20960900
C	0.63855200	2.18264800	1.15935900	H	1.12706300	1.87875200	0.90665600	C	3.68053900	-0.59682800	0.73335200
H	0.71664800	2.80703100	2.05685600	H	1.71142400	3.50675400	1.00739600	C	-3.96447100	-1.65419100	0.56717300
H	0.53347400	1.16201600	1.52183700	H	-0.75977800	1.46852800	0.25662500	C	1.91391700	2.89297500	1.43581700
C	-2.97317700	1.52949500	0.82594600	H	-1.08556300	2.88463400	1.23861700	C	-3.63357600	-0.14318400	0.67358600
H	-3.23815500	1.97642900	-0.12527700	H	-2.23916700	2.31754900	-1.52346200	C	-2.27996200	-3.39524700	0.92173600
H	-3.78392400	1.75804700	1.53606500	H	-2.67266300	3.67741600	-0.50763800	C	-0.18039500	3.37186000	0.30433100
C	3.45926400	0.36019100	-0.27228900	H	-2.98384300	0.45190300	-1.28574900	C	-0.66046600	2.28494700	-0.66229900
C	2.95956200	0.63782100	-1.19671900	H	-4.64427400	1.01105600	-1.25453600	H	-0.62570800	-4.55950300	1.49778000
H	4.51725700	0.62049800	-0.40673400	H	-5.24404500	-0.80533100	0.00784200	H	-0.43288100	-3.86183700	-0.09319300
C	1.34108800	-2.57318300	-0.15300900	H	-4.02738600	-0.42600500	1.18896800	H	-3.07449300	2.27256200	0.45729200
H	1.82557800	-3.48682400	0.23174000	H	2.98853800	3.14413600	-1.13195500	H	-4.34162800	2.81169000	-0.61029200
H	0.52544200	-2.87964600	-0.80444200	H	2.15093900	1.64422700	-1.36784600	H	1.51939300	-4.07293500	0.53406900
C	1.95556600	2.17677000	0.36992100	C	-3.00005300	-2.59613500	0.92224600	H	1.56226700	-4.14006800	2.28215900
H	1.72147000	1.97724000	-0.67176300	C	0.71834100	-3.17927400	1.60995800	H	5.13316000	0.35083300	-0.52559400
H	2.42389600	3.16939700	0.39695900	C	2.16255900	-2.67660000	1.61836200	C	3.51832800	0.37426400	-1.20269400
C	-1.15030400	-1.01854400	2.21344800	C	3.16840100	-0.72774200	0.74570900	H	3.64579600	-3.51355000	1.61302800
H	-1.08950800	-1.22800900	3.29220900	C	3.78499900	0.21186500	-0.29365300	H	2.99024500	-2.08365000	2.29981200
H	-0.49521000	-0.16332800	2.07347300	H	-1.24342200	-3.48659300	0.06489400	H	4.46263700	-0.66128400	1.50325600
C	-1.72597600	2.22690700	1.37754400	H	-1.58976600	-3.95906900	1.71386700	H	2.79509400	-0.22338100	1.25788300
H	-1.33605500	1.64834400	2.21411200	H	0.62666500	-3.87503800	0.77666400	H	-3.39419000	1.86434400	-2.50600300
H	-2.06014300	3.16490400	1.83248000	H	0.59329400	-3.78419400	2.52312700	H	-2.42596400	0.71262500	-1.62321900
C	0.73119700	-1.77367800	0.99627700	H	2.32405800	-1.97574500	2.42857500	H	2.30673700	2.76405500	-0.70799300
H	1.41518300	-1.74531600	1.85864500	H	2.76049600	-3.54819800	1.89337900	H	1.90843200	1.27941000	0.09509000
H	0.71175800	-0.73869800	0.65001700	H	2.27499700	-0.20855400	1.10737700	H	-1.05814600	3.95350000	0.58443800
C	-2.58786800	-0.58899100	1.92135900	H	3.83877300	-0.76930900	1.61645800	H	0.94969100	4.08314700	-0.18530600
H	-3.21742600	-1.46629900	2.00185000	H	4.84528100	-0.01048100	-0.41905800	H	2.34305500	2.39320200	2.30352800
H	-2.90140600	0.06938300	2.74518300	H	3.32647900	0.06062300	-1.26915200	H	2.24622700	3.93963700	1.47170900
N	2.24916100	-1.74913600	-0.92532400	H	-3.58796300	-3.52581800	0.96055300	H	-2.60615700	-3.11258600	1.92037700
N	-0.62915000	-2.11782100	1.41147500	H	-3.28521000	-2.06600200	1.82812900	H	-2.66100100	-4.42280800	0.79473800
N	-2.87057300	0.07612400	0.63331200	Xe	0.51732500	-1.15473600	-1.07979900	H	-4.22766700	-2.04263200	1.55801600
N	-0.61266500	2.49852300	0.43923400	O	0.28449700	-2.85285200	-1.51069800	H	-4.87174300	-1.74431400	-0.02378300
N	2.86999300	1.13371900	0.82266900	O	1.53297800	-0.58157900	-2.41230800	H	-2.63402300	-0.03470500	0.25894600
C	-4.12216100	-0.50774400	0.01107100	O	-1.03252000	-0.41684600	-1.47550900	H	-3.56256300	0.15297800	1.73201200
C	-0.67777800	3.89780300	-0.12439000	N	-3.38790500	-1.79333700	-0.22386900	H	0.18632800	1.82572700	-1.18314300
C	-0.77174800	-3.46962800	2.03111500	N	-0.40792100	-2.23311300	1.47419300	H	-1.06748600	1.49464500	-0.03243100
C	2.69474100	-2.35290100	-2.20460500	N	2.71040100	-2.08100900	0.37717100	Xe	0.89068000	-1.20814900	-0.92426300
C	3.83930400	1.54771700	1.86030700	N	3.60134700	1.58614900	0.14799100	O	-0.82411400	-0.85139600	-1.10400000
C	4.87937500	2.55044600	1.33571600	N	0.19268000	3.14456200	-0.45408200	O	0.99794200	-2.84206100	-1.59061200
H	4.40488100	3.45716500	0.95360900	N	-3.34117300	1.81512400	0.21228600	O	1.61800400	-0.24381300	-2.22459300
H	5.55789200	2.84910400	2.13815700	C	-3.94754400	-2.56947500	-1.35814000	N	3.30428500	-1.94061000	0.24424600
H	5.48694800	2.12470300	0.53496700	C	-0.73488000	-1.44369200	2.71540700	N	0.29502000	-2.66830800	1.42405300
C	3.60320800	-3.57467700	-1.99574600	C	4.83848400	2.32607600	0.44600000	N	-2.92220100	-2.49904200	-0.01897500
H	3.08575100	-4.36528800	-1.44691000	C	3.69882200	-2.99031500	-0.29530300	N	3.89866800	1.80029000	0.32269400
H	3.90210200	-3.98830500	-2.96167400	C	0.10087700	4.59545200	-0.76644100	N	0.46246400	2.79322600	1.49013500
H	4.51776800	-3.32650700	-1.45201000	C	-4.40837900	2.62414400	0.84526000	N	-1.69272300	2.70479800	-1.60477300
C	-0.23077800	4.93872700	0.90811700	C	-1.44220200	-2.29974200	3.78069700	N	-4.49612000	0.78928500	-0.53555900
H	0.82729300	4.83936100	1.15935600	H	-1.59201100	-1.05989500	4.67800100	C	4.31815800	-2.66108100	-0.60438300
H	-0.37347100	5.93995800	0.49719400	H	-2.41897600	-2.66491300	3.46978400	C	-0.05681100	-2.04190800	2.74603800
H	-0.80903900	4.88037700	1.83411200	H	-0.83739400	-3.16298200	4.07003100	C	4.89055700	2.78589900	-0.17231500
C	-5.35107100	-0.31867400	0.91342000	C	-5.20988600	3.46031700	-0.16635600	C	-0.12297700	3.24486300	2.77518800
H	-5.66119900	0.72703500	0.96932700	H	-5.68997700	2.82416700	-0.91336900	C	-3.33073900	-3.09390000	-1.31610800
H	-6.18838600	-0.88250900	0.49713200	H	-5.99718500	4.02164600	0.34230500	C	-5.75857300	1.16299900	0.63013800
H	-5.18715000	-0.68311800	1.92959700	H	-4.58266100	4.18244700	-0.69287100	C	-1.21823700	3.07507000	-2.95441400
C	0.33423300	-3.76185600	3.05375700	C	5.69971800	2.55094300	-0.80489300	C	0.03914100	4.75333800	3.00885200
H	0.15238000	-4.72469300	3.53588400	H	6.60782800	3.10755700	-0.56054800	H	-0.43154800	5.04630800	3.95060300
H	1.32003000	-3.81441500	2.58800100	H	6.00390700	1.60270700	-1.25467600	H	1.09193600	5.03907200	3.06474700
H	0.36757400	-3.00057400	3.83857700	H	5.15463800	3.12072700	-1.56111100	H	-0.42889000	5.33425500	2.21088100
C	-2.10289600	4.23803600	-0.56908200	C	-0.45087900	5.41509200	0.40570500	C	4.93222000	2.86998500	-1.70482700
H	-2.09424400	5.23595800	-1.01062500	H	0.15485700	5.27434800	1.30528400	H	3.95464900	3.12799900	-2.11879200
H	-2.45039900	3.53759900	-1.32652300	H	-0.44475000	6.48044800	0.16388200	H	5.63838600	3.64022000	-2.02337200
H	-2.81661800	4.26463000	0.25605100	H	-1.47773500	5.14228000	0.64826600	H	5.24752700	1.927857	

H	3.86193500	-0.39233300	2.83363400	H	1.10913000	-1.62811800	3.90206200	H	0.52307700	1.41911700	3.74494700
H	5.14843400	-0.19475800	1.63282300	H	1.11581100	-0.27288200	2.74488400	H	1.56191300	2.80607300	4.11369000
H	5.26744800	0.62279000	3.18569000	H	0.14158100	-0.19526600	4.20153700	H	-0.02410000	2.68277200	4.85524100
C	3.10741500	2.18983700	3.03781100	C	4.04203200	-2.50579400	-1.70325900	C	-1.61188500	2.89199400	2.80183900
H	3.81334000	2.38278900	3.84833200	H	3.14708600	-2.35030800	-2.30307900	H	-1.76270700	1.83765300	2.56790300
H	2.65701300	3.14709900	2.76909400	H	4.62268900	-1.58693800	-1.70929900	H	-2.02159300	3.08831200	3.79503500
H	2.32472200	1.52864100	3.41614600	H	4.65138600	-3.26953400	-2.19125700	H	-2.19679100	3.48157400	2.09586600
C	-3.89400600	-2.00228800	-0.23585800	C	3.06697100	-4.37409800	-0.47298000	C	-0.01821000	4.01435800	-2.84132800
H	-4.04158500	-2.60571600	0.66011600	H	2.87275000	-4.88840400	0.46944400	H	-0.26264300	4.88617900	-2.23019400
H	-4.61473400	-2.35915900	-0.97375700	H	2.13430500	-4.29580900	-1.03209500	H	0.85474800	3.51763000	-2.41374300
H	-2.88926000	-2.17857400	-0.62017100	H	3.75455300	-5.00409300	-1.03967800	H	0.26641800	4.36357200	-3.83593600
C	-2.11548200	-3.62007900	2.74921000	C	1.47415600	5.17034500	-1.12003200	C	-2.32487000	3.85583500	-3.66768500
H	-2.94974700	-3.51984800	2.05587900	H	2.17684300	5.12082400	-0.28809300	H	-1.96186000	4.22660400	-4.62926200
H	-2.16873100	-4.62240100	3.17726300	H	1.90490500	4.66211400	-1.98398400	H	-3.20488800	3.24415000	-3.87244400
H	-2.24883300	-2.91500400	3.57087500	H	1.35789800	6.22408400	-1.37919900	H	-2.63561700	4.70843900	-3.05965700
				C	-0.75334200	4.81095200	-2.02184900	C	-5.53526300	2.09477100	1.83220900
				H	-0.39946800	4.15807400	-2.82169700	H	-5.12056300	3.05803100	1.53029900
				H	-1.81094000	4.61439600	-1.86998800	H	-6.48143100	2.28832300	2.34298900
				H	-0.66498300	5.84809000	-2.35587300	H	-4.85329000	1.64852700	2.56055600
				C	-3.77872900	3.54973400	1.88577300	C	-6.49595900	-0.07726100	1.13039600
				H	-4.55712300	4.10330300	2.41615000	H	-6.70228400	-0.77265200	0.31480200
				H	-3.20830800	2.96757200	2.61268700	H	-5.93988800	-0.60501100	1.90697300
				H	-3.10894800	4.28436500	1.43867100	H	-7.45194500	0.22383200	1.56379800
				C	-5.39768200	1.73321400	1.59439700	C	-3.62684700	-1.96649100	-2.30610200
				H	-4.89139800	1.12616000	2.34715300	H	-4.36384800	-1.25454900	-1.92968700
				H	-6.13016900	2.36142600	2.10572000	H	-2.71163000	-1.41579900	-2.52248200
				H	-5.94963100	1.07148300	0.92578700	H	-4.01004500	-2.38701400	-3.23948200
				C	4.49351500	3.67989100	1.06239900	C	-2.21226500	-3.93631800	-1.92349000
				H	3.87299700	3.55137500	1.95155900	H	-1.29826800	-3.35923400	-2.04575600
				H	5.40996200	4.19721000	1.35403400	H	-1.99562900	-4.83210300	-1.33601900
				H	3.96638800	4.32715300	0.36091500	H	-2.52931000	-4.27782000	-2.91141900
				C	5.64656800	1.55520300	1.49199500	C	3.86977200	-4.10703700	-0.83996000
				H	5.04445200	1.39035700	2.38830800	H	3.84595900	-4.70896000	0.06955000
				H	5.99049400	0.58521900	1.12732600	H	2.88903700	-4.13240600	-1.31285800
				H	6.53454800	2.12581500	1.77273100	H	4.58440900	-4.58417400	-1.51250900
								C	4.42966900	-2.03223900	-1.99389200
								H	5.06476800	-2.67035100	-2.61228100
								H	3.45603600	-1.95753900	-2.47574900
								H	4.88571600	-1.04610900	-1.98584200
								C	6.27101500	2.39946600	0.36362900
								H	6.24199800	2.32524400	1.45265300
								H	6.63094500	1.44836700	-0.03302000
								H	7.00612300	3.15811000	0.08571600
								C	4.57688600	4.17537400	0.37626300
								H	3.64237700	4.57422300	-0.02116200
								H	4.51627200	4.16135700	1.46626800
								H	5.37279500	4.86505400	0.08851300
								C	-1.03643400	-0.91621900	2.45650900
								H	-1.48001500	-0.54153100	3.38219900
								H	-0.52471800	-0.08312700	1.96695300
								H	-1.82810600	-1.23367000	1.79636000
								C	1.12038100	-1.38710800	3.47169400
								H	0.71470600	-0.85070700	4.33122100
								H	1.83951700	-2.10902600	3.86102500
								H	1.63518900	-0.65235100	2.85301500

XeO ₃ :21N7 ^{Me}				XeO ₃ :21N7 ^{Et}			
C	-2.70189500	-2.55079600	-0.20555200	C	-2.69246800	-2.61776100	-0.50423300
C	-2.49662400	1.90265700	0.61823700	C	-2.54464700	1.86890900	0.46628800
C	-0.55319300	-3.22050000	0.54516700	C	-0.52112400	-3.28562400	0.22141600
C	3.51940000	-1.45633700	-0.66869400	C	3.52031100	-1.44522300	-1.01328200
C	-1.19832600	2.64173000	0.30245200	C	-1.25935900	2.60782400	0.10572900
C	0.68917600	-2.99074000	1.38947500	C	0.73307700	-3.06517400	1.05623100
C	5.01911500	0.43080100	-0.59795800	C	4.96280000	0.49833400	-0.94831600
C	2.62184300	-2.46743100	0.04877800	C	2.66484800	-2.49202300	-0.28945000
C	-5.13642600	0.39077900	-0.30175600	C	-5.12608700	0.32850900	-0.68001700
C	4.11451600	1.62966200	-0.87024500	C	4.02388300	1.69603800	-1.07131400
C	-4.32879800	1.51798200	-0.96478100	C	-4.29685800	1.51445800	-1.19740200
C	-3.70759000	-1.50187500	-0.68148900	C	-3.67728500	-1.55704300	-1.00225400
C	2.47281400	1.93813800	0.93004700	C	2.41001800	1.90606700	0.75377500
C	1.20838400	2.65414300	0.42578900	C	1.15873400	2.63985600	0.24436200
H	-3.19464700	-3.31023500	0.42505800	H	-3.21389300	-3.38878000	0.08488500
H	-2.37304800	-3.07070500	-1.10944600	H	-2.34028600	-3.12211000	-1.40800600
H	-2.37136400	0.85636000	0.35239900	H	-2.42487200	0.81614100	0.21759900
H	-2.70688100	1.91938800	1.69526700	H	-2.71928800	1.90385900	1.54792900
H	-0.28437400	-3.48558200	-0.47744700	H	-0.25871100	-3.49303700	-0.81583700
H	-1.07158200	-4.08866600	0.98934500	H	-1.00176000	-4.19324800	0.62236300
H	4.10473200	-2.03976000	-1.40653100	H	4.06995200	-1.99846400	-1.79608900
H	2.89860000	-0.77744400	-1.25066100	H	2.86372200	-0.76530200	-1.55189000
H	1.22611100	-3.95114600	1.44705500	H	1.25916100	-4.03143200	1.09322000
H	0.37878600	-2.77545100	2.41337900	H	0.42931300	-2.86551900	2.08343600
H	2.08358300	-2.99680900	-0.73980300	H	2.11483700	-3.00994000	-1.07787100
H	3.23301900	-3.21838500	0.57867500	H	3.30581800	-3.24953500	0.18972000
H	-1.23309200	3.66776800	0.70822400	H	-1.30777300	3.64817500	0.46460800
H	-1.11464200	2.72132300	-0.78287300	H	-1.18522300	2.64975800	-0.98255500
H	5.87089500	0.79201800	-0.01540100	H	5.85883300	0.83487200	-0.41906400
H	5.42220500	0.05677700	-1.55943500	H	5.28399500	0.19974900	-1.96310800
H	2.35203900	0.86912900	0.75847000	H	2.28142000	0.84393800	0.54775800
H	2.55588300	2.07653100	2.01456600	H	2.47274700	2.00864500	1.84358500
H	4.68374700	2.31499100	-1.50620900	H	4.53017400	2.43901300	-1.69696000
H	3.23986500	1.33591300	-1.45615900	H	3.11994900	1.41867700	-1.61618800
H	-4.46733000	-2.06053400	-1.26371900	H	-4.39375900	-2.10324100	-1.64313200
H	-3.19456500	-0.84564000	-1.37914800	H	-3.13486600	-0.88410700	-1.66049600
H	-5.77648800	0.82520600	0.47194900	H	-5.86489500	0.70170500	0.03629400

H	-5.82218300	-0.03049600	-1.06315400	H	-5.70625100	-0.06306400	-1.53568500
H	-5.03791700	2.09945500	-1.56460000	H	-4.95764100	2.10289800	-1.84119700
H	-3.60588200	1.10571400	-1.66953800	H	-3.49405300	1.16295000	-1.84428800
H	1.16937100	3.68167600	0.82567200	H	1.13329200	3.67156800	0.62776600
H	1.23589200	2.72200400	-0.66249000	H	1.18995700	2.70041500	-0.84408600
Xe	0.02283600	-0.34112000	-1.07841200	Xe	0.01002800	-0.35060200	-1.28223000
O	-1.43545200	0.32381900	-1.82482800	O	-1.44505200	0.34042200	-2.00927100
O	0.25809900	-1.84540200	-1.98446500	O	0.24294800	-1.82038400	-2.24435800
O	1.25554700	0.67979700	-1.83386500	O	1.23610000	0.69219600	-2.01788200
N	-3.62584500	2.44973800	-0.10746000	N	-3.70356700	2.40854600	-0.22060300
N	-4.36329200	-0.67723600	0.32379200	N	-4.37978400	-0.74002000	-0.02247400
N	-0.01471400	1.93747800	0.79639200	N	-0.06702100	1.92204900	0.60751900
N	3.73646600	2.32772700	0.34632000	N	3.69178100	2.28986000	0.21236300
N	4.40951100	-0.65484800	0.15783700	N	4.42204200	-0.63385700	-0.20771100
N	1.61519000	-1.92795700	0.97238200	N	1.66294600	-1.99804900	0.66487100
N	-1.48589500	-2.08851000	0.47304500	N	-1.48646100	-2.17730300	0.20942900
C	-0.08573500	1.74459500	2.23555000	C	-0.14536500	1.63043600	2.04143400
H	0.76774100	1.16952400	2.58576500	H	0.71342100	1.01364500	2.30408300
H	-0.09426400	2.70735700	2.77335800	H	-1.02136700	1.00510900	2.20700200
H	-0.98754400	1.20046500	2.50355600	C	-1.77156800	-1.63649800	1.54260300
C	-1.77664300	-1.53978200	1.78801800	H	-0.87812100	-1.10503500	1.87940700
C	-2.10369600	-2.32338800	2.49045200	H	-2.55343900	-0.88930100	1.40782500
H	-0.88858300	-1.06197300	2.19920400	C	2.27292600	-1.41653300	1.87296700
H	-2.56849900	-0.80033800	1.69582400	H	1.49167500	-0.85202000	2.39095800
C	2.24738100	-1.39083600	2.17333700	H	3.02329600	-0.70402000	1.53601000
H	1.49643400	-0.91394900	2.80540800	C	-5.21562400	-1.49607500	0.89968300
H	2.72633800	-2.19016200	2.76263100	H	-4.57454700	-2.18499900	1.45283600
H	3.00861800	-0.66538900	1.90016100	H	-5.59685900	-0.78621100	1.64130300
C	-5.21168300	-1.46267200	1.19111900	C	-4.62284100	3.08418300	0.67040600
H	-4.63258700	-2.22833400	1.70919400	H	-5.10146200	2.38753300	1.38635300
H	-5.66339800	-0.82059400	1.94986200	H	-4.02698400	3.77227500	1.27884300
H	-6.02520800	-1.96946700	0.64107700	C	4.02893700	3.68586300	0.36996400
C	-4.47022700	3.29845200	0.69071800	H	3.58491700	4.31809500	-0.42097600
H	-4.99361000	2.77392500	1.51071000	H	3.58512400	4.02464300	1.31262100
H	-3.87285300	4.09372700	1.14319700	C	5.46276500	-1.39232500	0.46935800
H	-5.22542400	3.77380900	0.05963300	H	4.98286100	-2.14044400	1.10351700
C	3.98519900	3.74543200	0.34788100	H	5.96815900	-0.70314300	1.15329400
H	3.38323400	4.31530600	-0.38076000	C	-0.20518300	2.83659900	2.97575800
H	3.77389100	4.15251100	1.34126200	H	-0.26681500	2.49739000	4.01269100
H	5.03864300	3.93969300	0.13171000	H	0.68238700	3.46660000	2.88733700
C	5.42397400	-1.46479200	0.79246300	H	-1.08003200	3.46041500	2.78004400
H	4.96667600	-2.24567000	1.40152500	C	-5.69607100	3.88115700	-0.05047500
H	6.09257800	-1.95663300	0.06265300	H	-6.41183200	3.23912500	-0.56889700
H	6.03413900	-0.84547900	1.45216900	H	-6.26081400	4.48434000	0.66432500
				H	-5.24616000	4.55020500	-0.78790300
				C	-6.38617600	-2.28130700	0.30280200
				H	-6.04900100	-3.05717100	-0.38817400
				H	-6.94803000	-2.77443200	1.09996200
				H	-7.07850900	-1.63097100	-0.23621100
				C	5.53069900	3.92126600	0.42233800
				H	6.02087200	3.60932900	-0.50315100
				H	5.75278000	4.98189700	0.56757600
				H	5.97610400	3.35479900	1.24344900
				C	6.50232700	-2.08578300	-0.41443600
				H	7.24383800	-2.59343000	0.20771900
				H	6.05085200	-2.83796600	-1.06519400
				H	7.03387000	-1.37176600	-1.04756300
				C	2.91147700	-2.38984100	2.86914200
				H	3.46466600	-1.82005000	3.61925100
				H	2.17793600	-3.00119300	3.39900600
				H	3.62051400	-3.06912000	2.39242000
				C	-2.19606700	-2.63585300	2.62061500
				H	-1.38918700	-3.30845500	2.91752100
				H	-2.51464800	-2.09073200	3.51199700
				H	-3.03489100	-3.25809700	2.30461600

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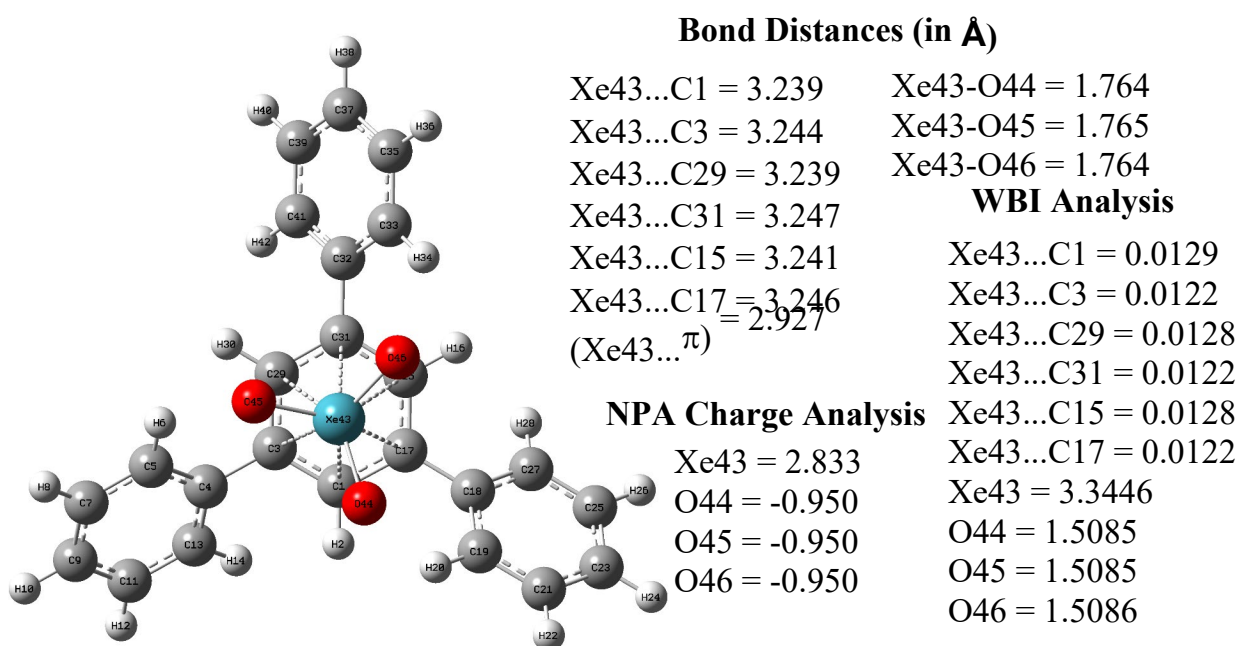


Figure S6.1. Optimized geometry of XeO₃ and its 1:1 (Mono) adduct with TPB-H. The bond parameters, WBI values and charge analysis (NPA) data are shown.

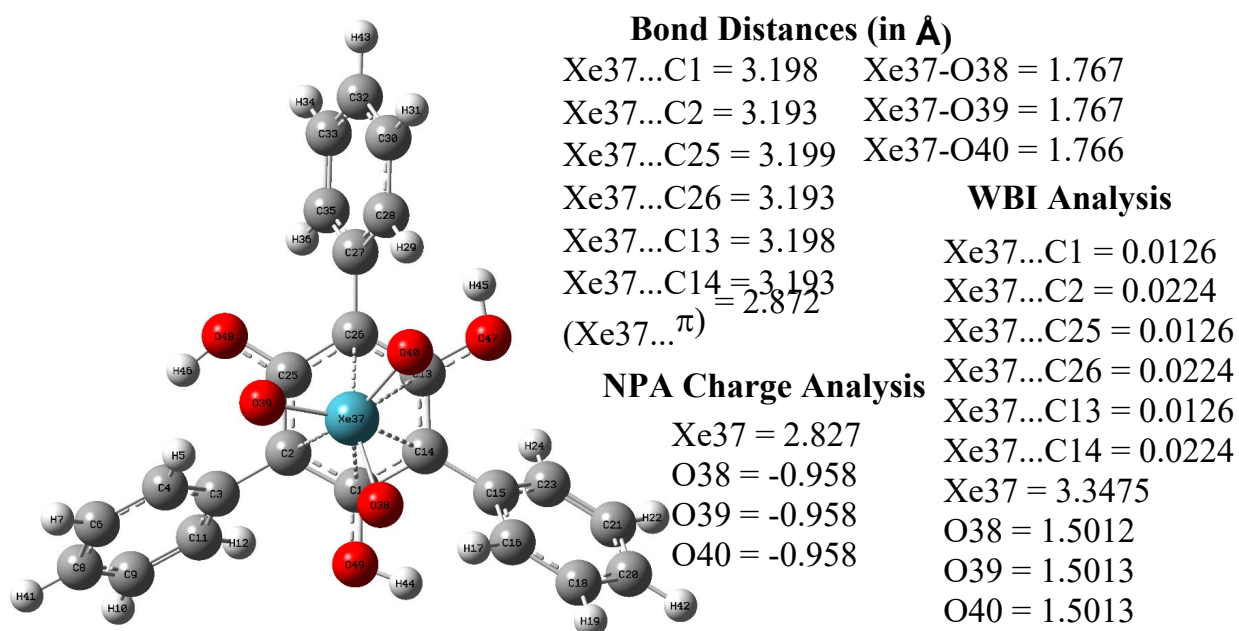


Figure S6.2. Optimized geometry of XeO₃ and its 1:1 (Mono) adduct with TPB-OH. The bond parameters, WBI values and charge analysis (NPA) data are shown.

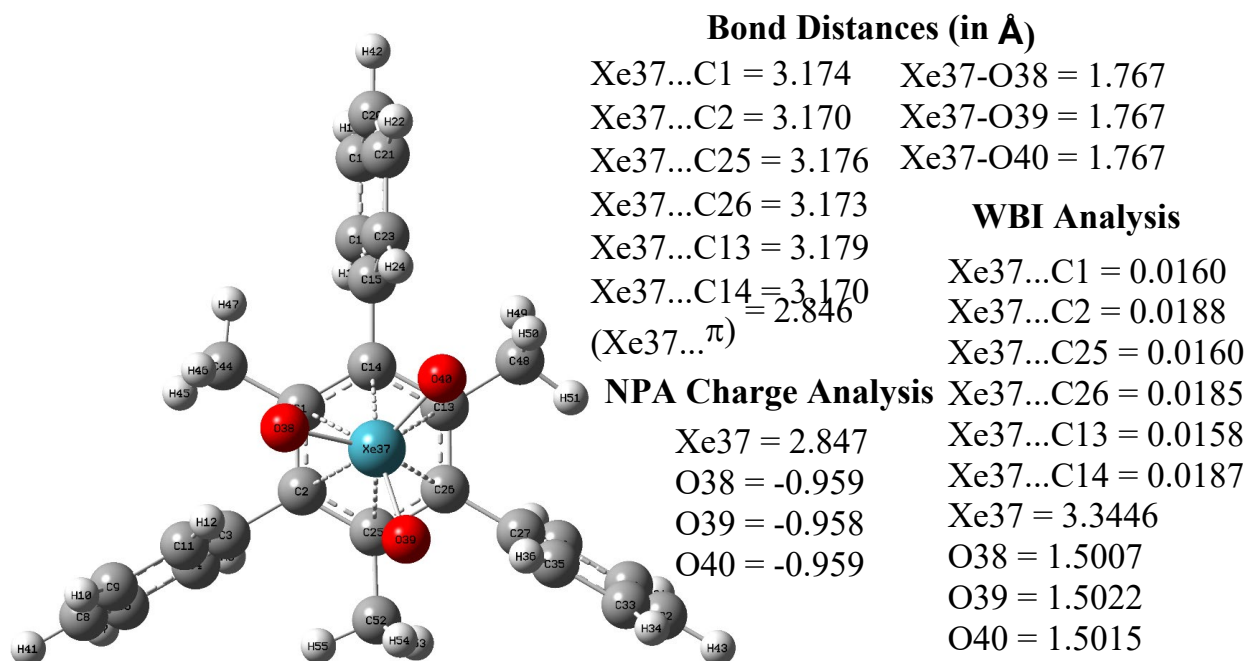


Figure S6.3. Optimized geometry of XeO₃ and its 1:1 (Mono) adduct with TPB-CH₃. The bond parameters, WBI values and charge analysis (NPA) data are shown.

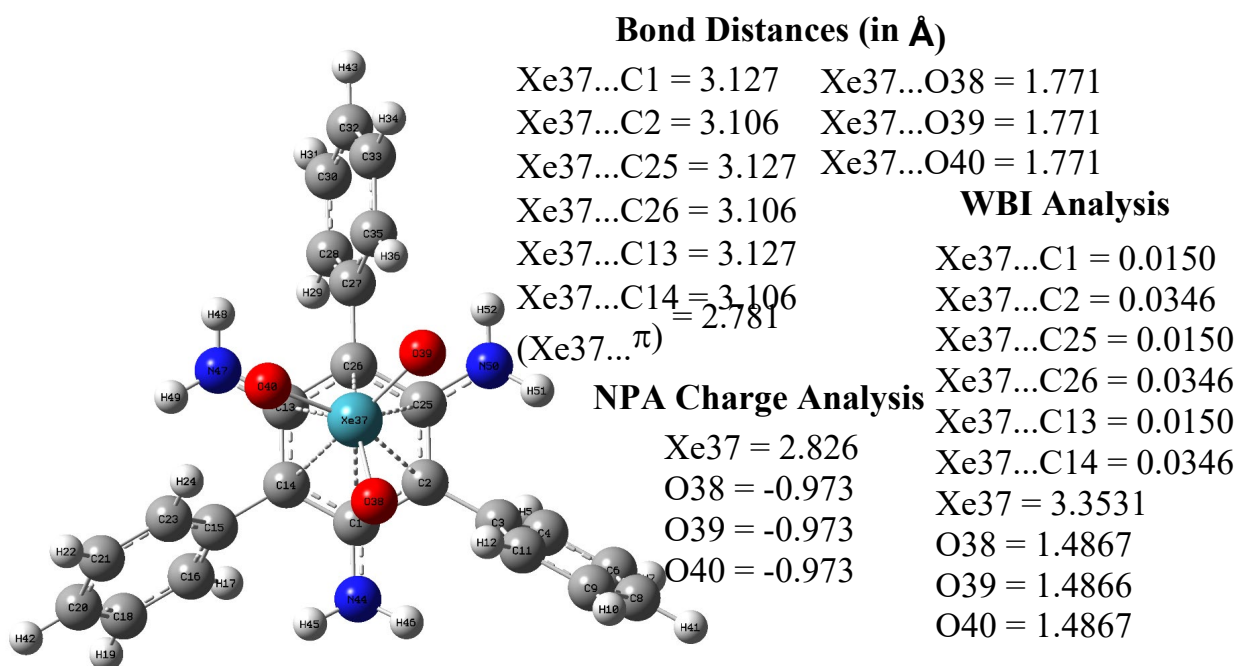


Figure S6.4. Optimized geometry of XeO₃ and its 1:1 (Mono) adduct with TPB-NH₂. The bond parameters, WBI values and charge analysis (NPA) data are shown.

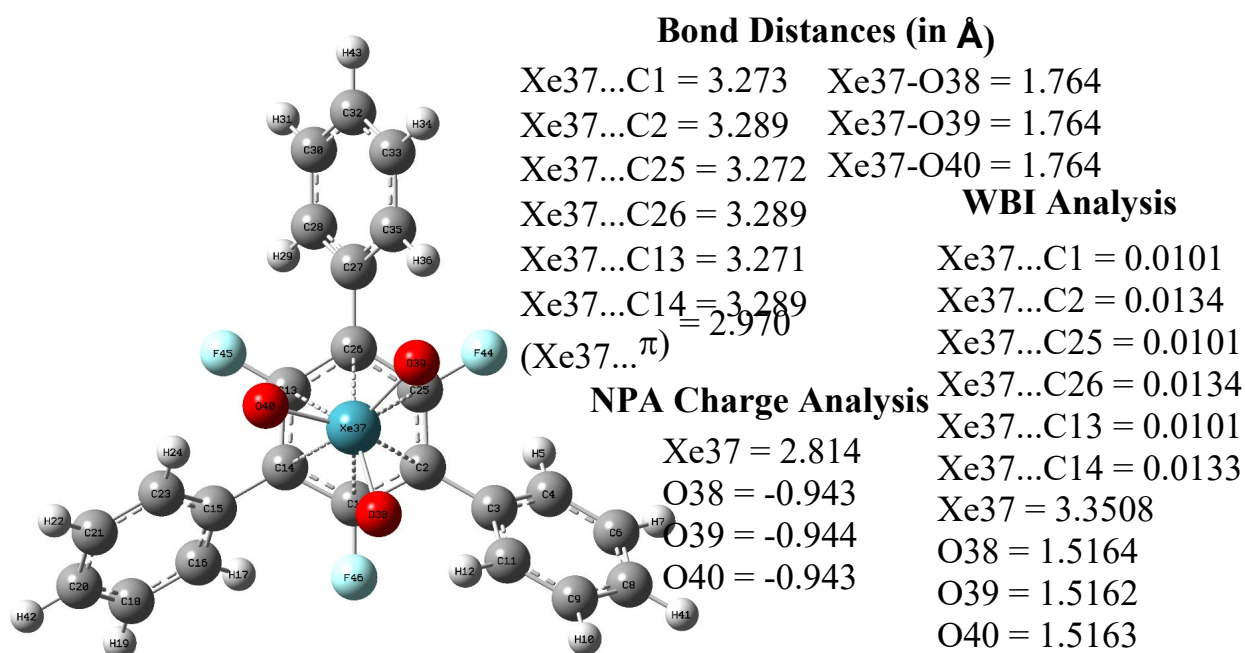


Figure S6.5. Optimized geometry of XeO₃ and its 1:1 (Mono) adduct with TPB-F. The bond parameters, WBI values and charge analysis (NPA) data are shown.

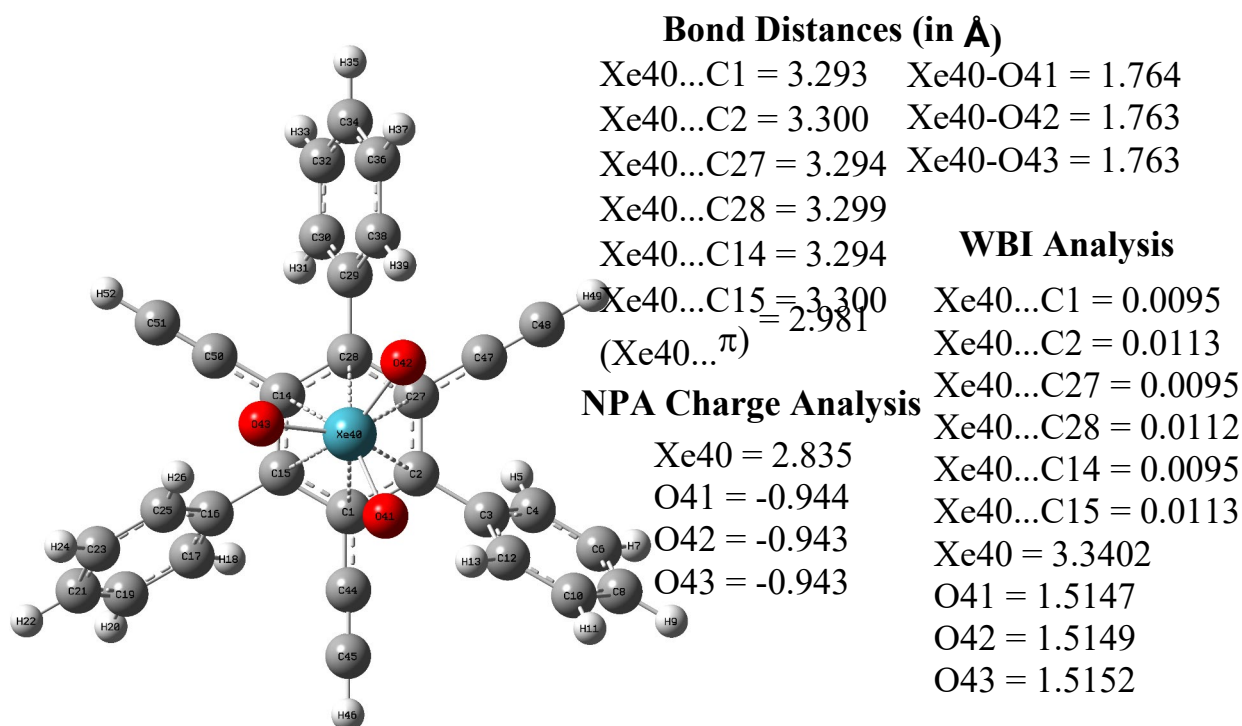


Figure S6.6. Optimized geometry of XeO₃ and its 1:1 (Mono) adduct with TPB-CCH. The bond parameters, WBI values and charge analysis (NPA) data are shown.

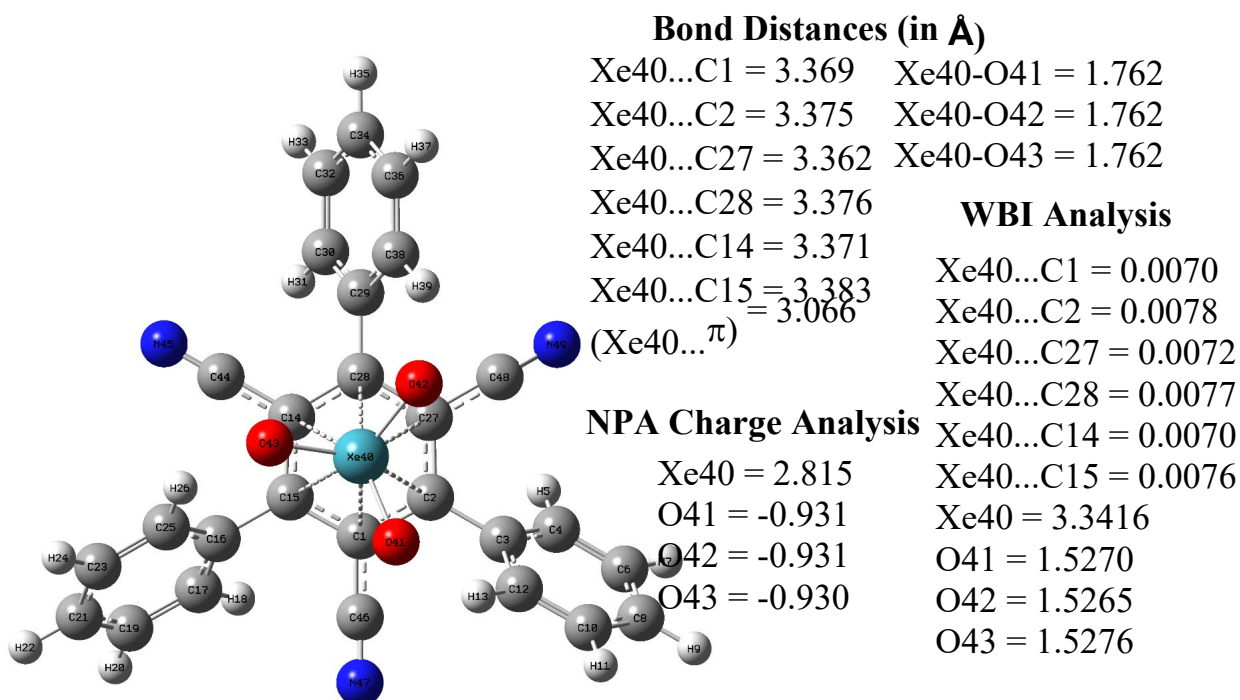


Figure S6.7. Optimized geometry of XeO₃ and its 1:1 (Mono) adduct with TPB-CN. The bond parameters, WBI values and charge analysis (NPA) data are shown.

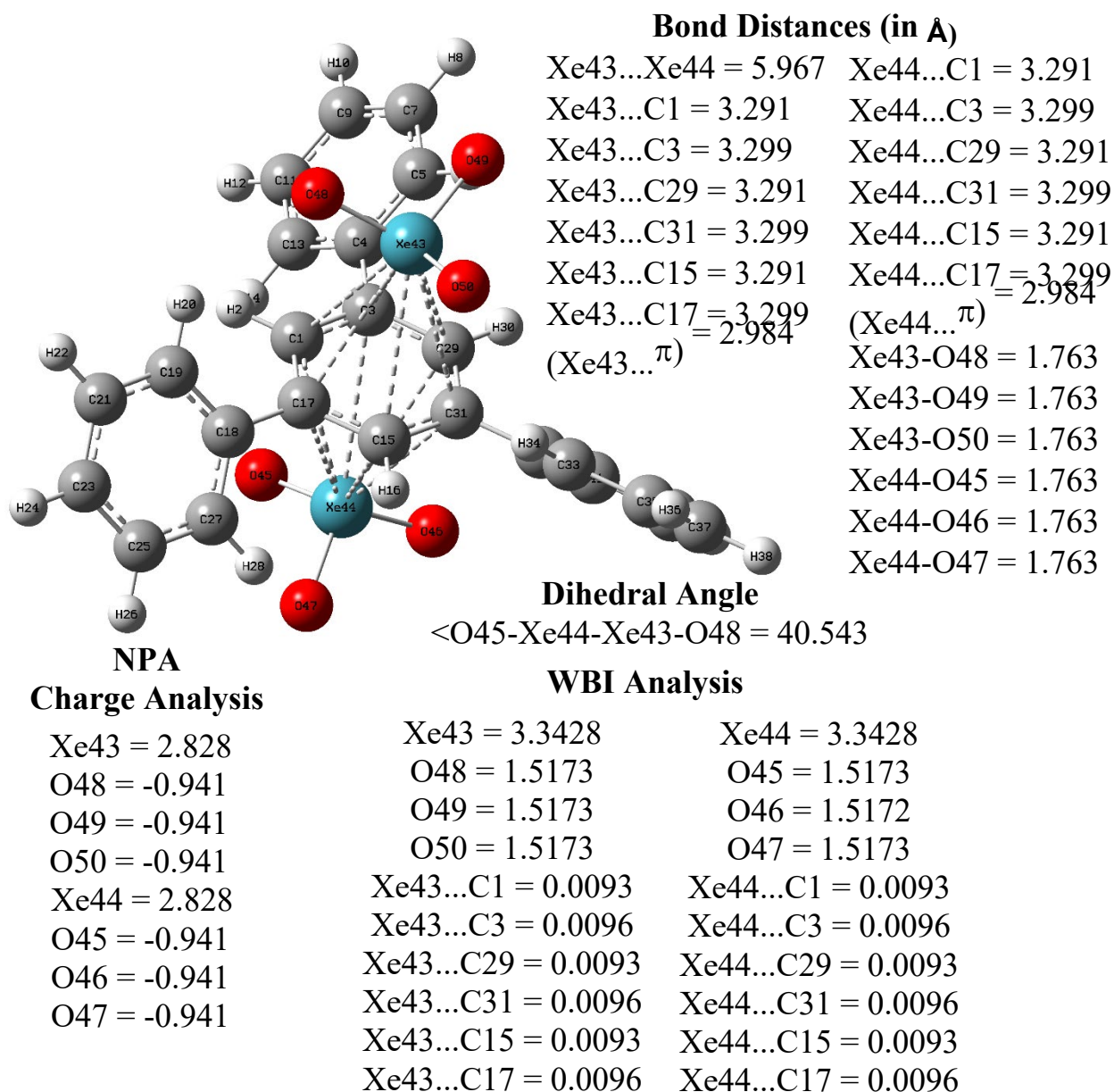


Figure S6.8. Optimized geometry of XeO₃ and its 1:2 (iSw) adduct with TPB-H. The bond parameters, WBI values and charge analysis (NPA) data are shown.

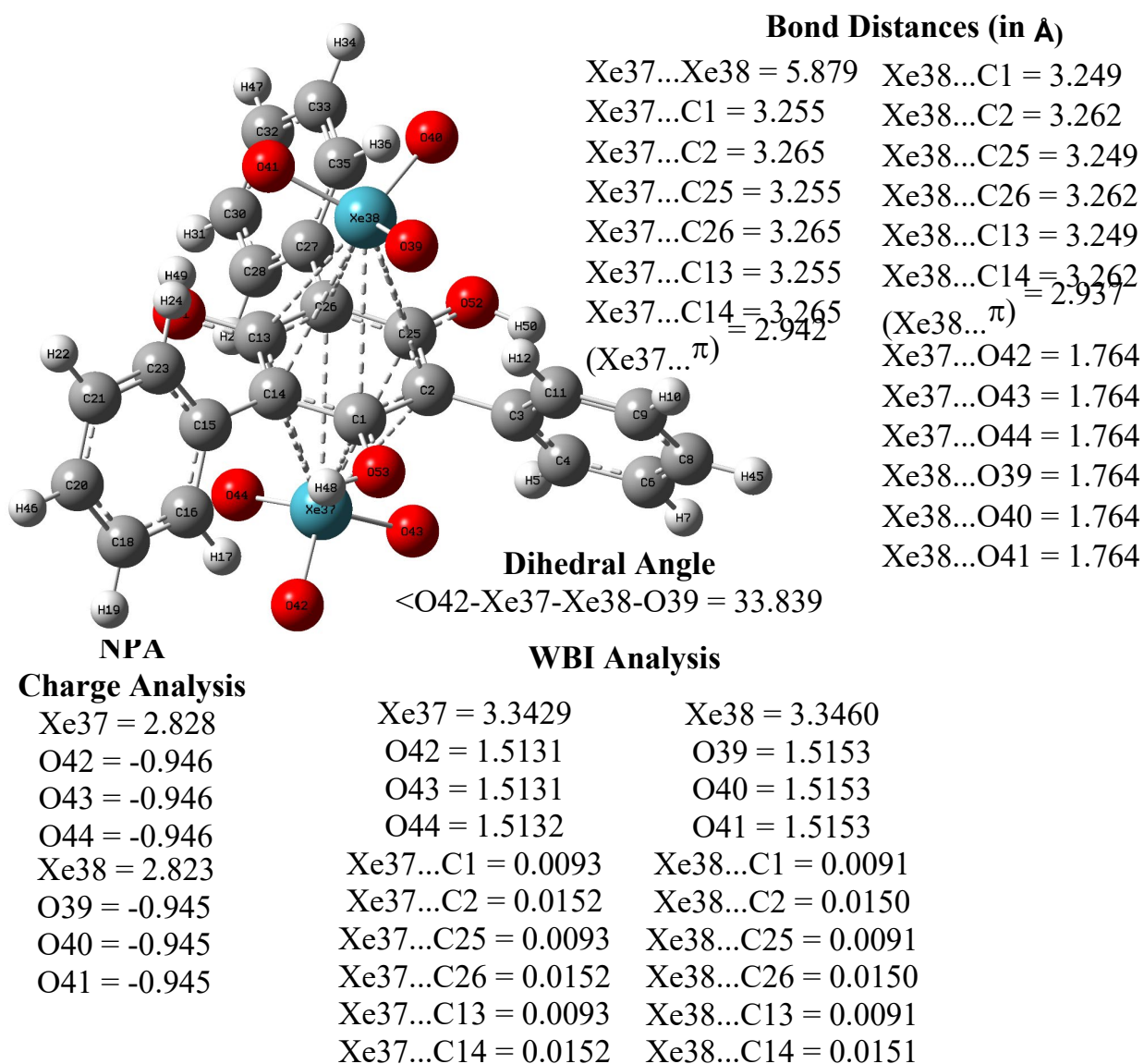


Figure S6.9. Optimized geometry of XeO₃ and its 1:2 (iSw) adduct with TPB-OH. The bond parameters, WBI values and charge analysis (NPA) data are shown.

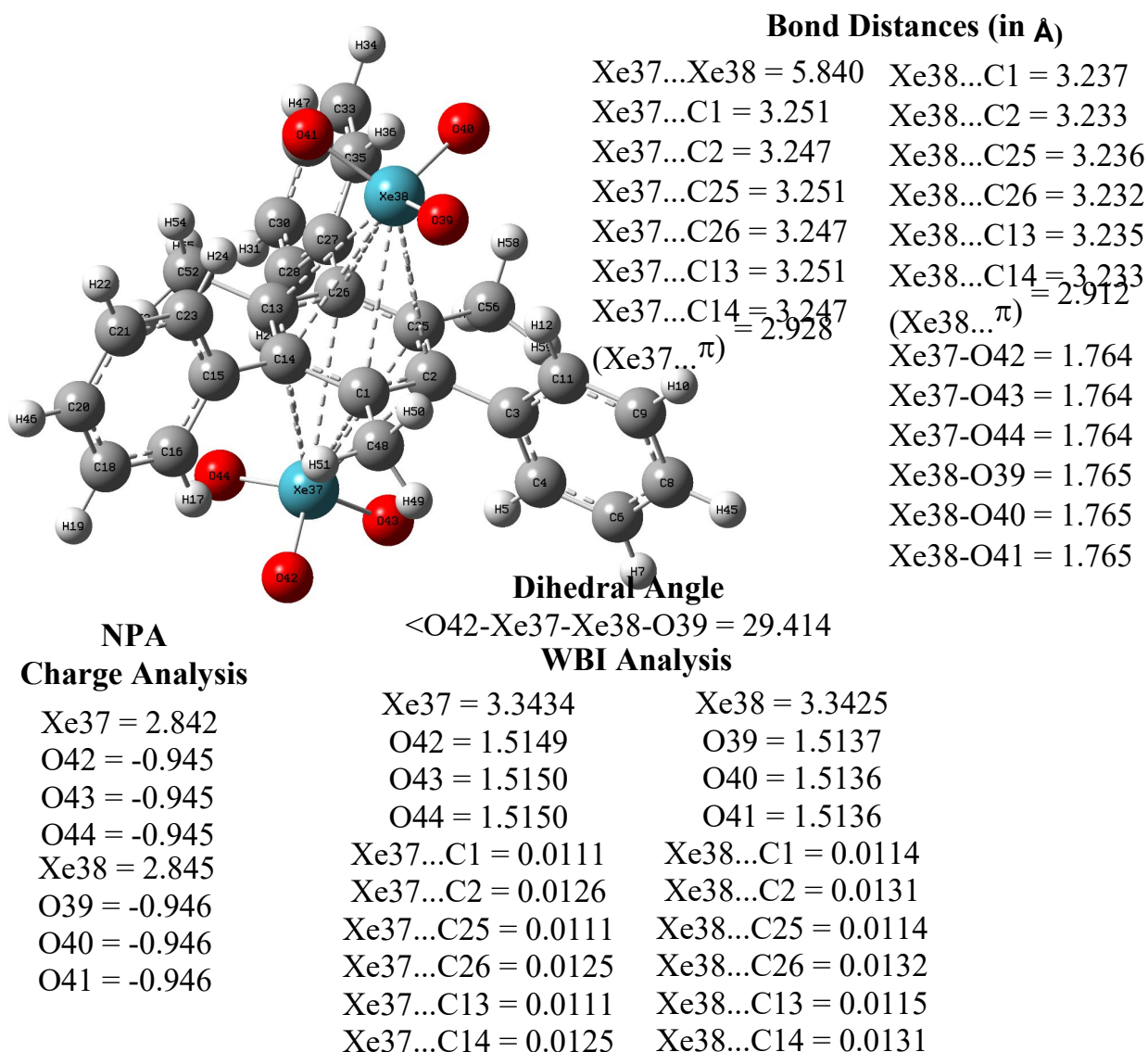


Figure S6.10. Optimized geometry of XeO₃ and its 1:2 (iSw) adduct with TPB-CH₃. The bond parameters, WBI values and charge analysis (NPA) data are shown.

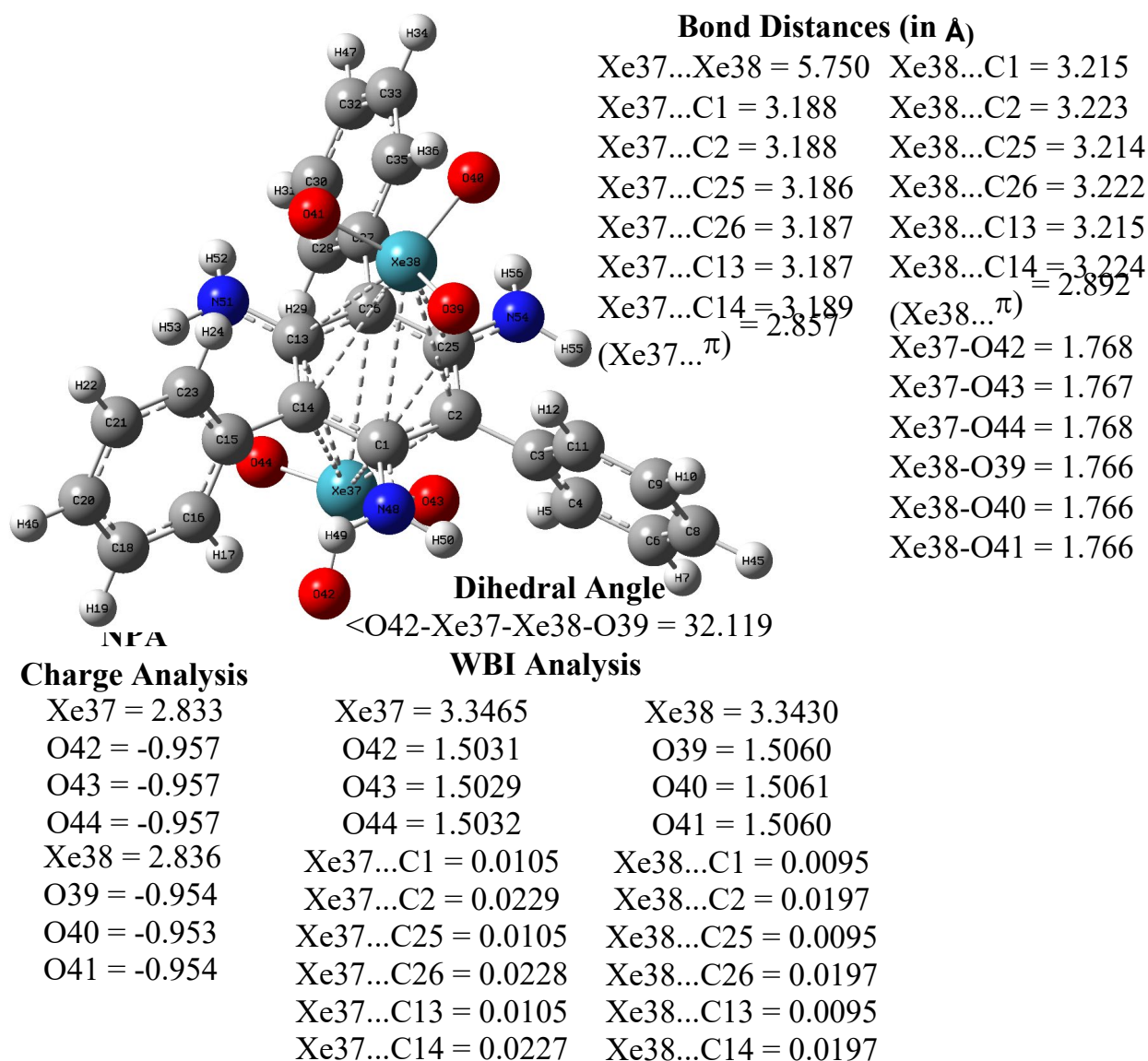


Figure S6.11. Optimized geometry of XeO₃ and its 1:2 (iSw) adduct with TPB-NH₂. The bond parameters, WBI values and charge analysis (NPA) data are shown.

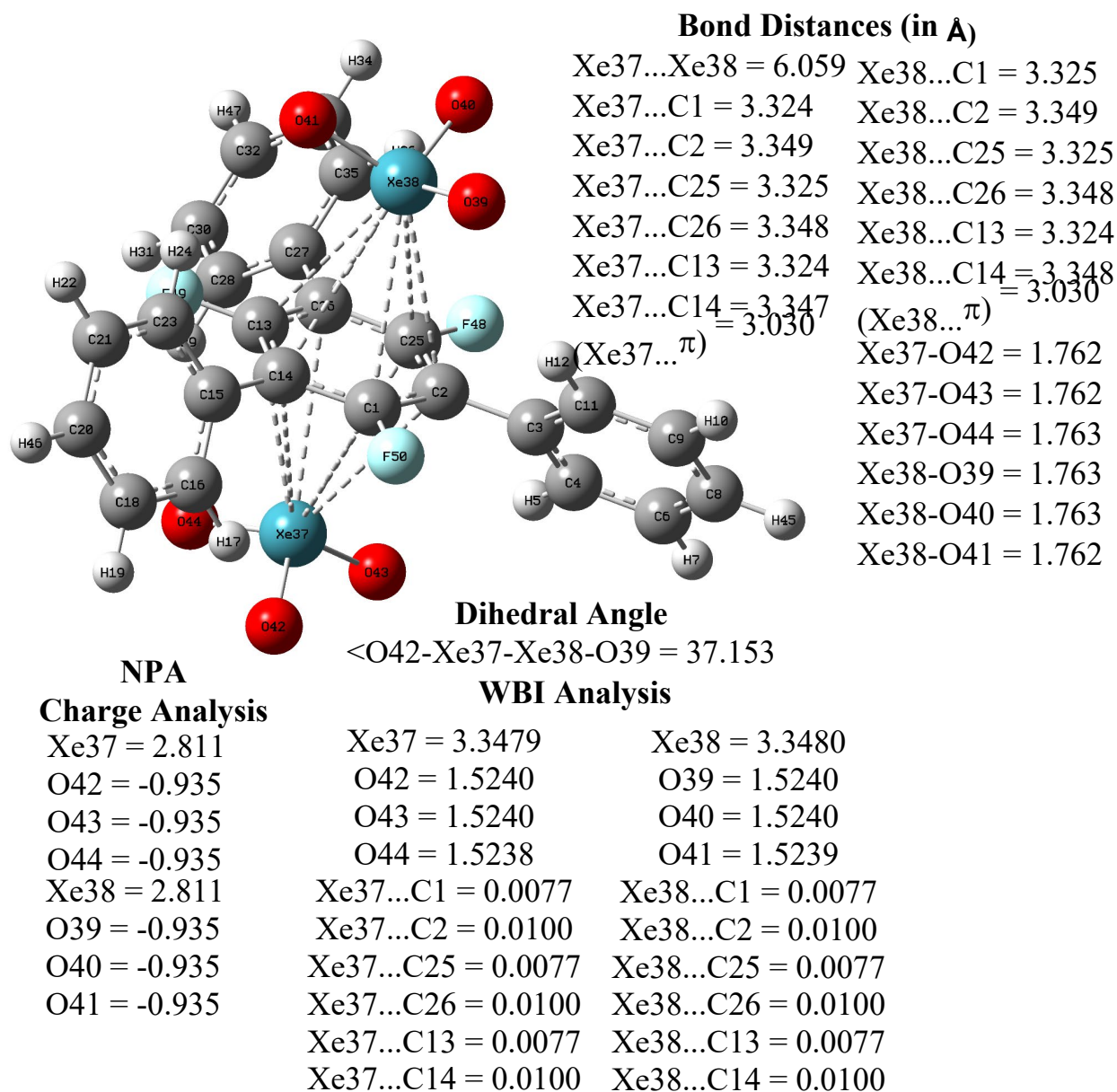


Figure S6.12. Optimized geometry of XeO₃ and its 1:2 (iSw) adduct with TPB-F. The bond parameters, WBI values and charge analysis (NPA) data are shown.

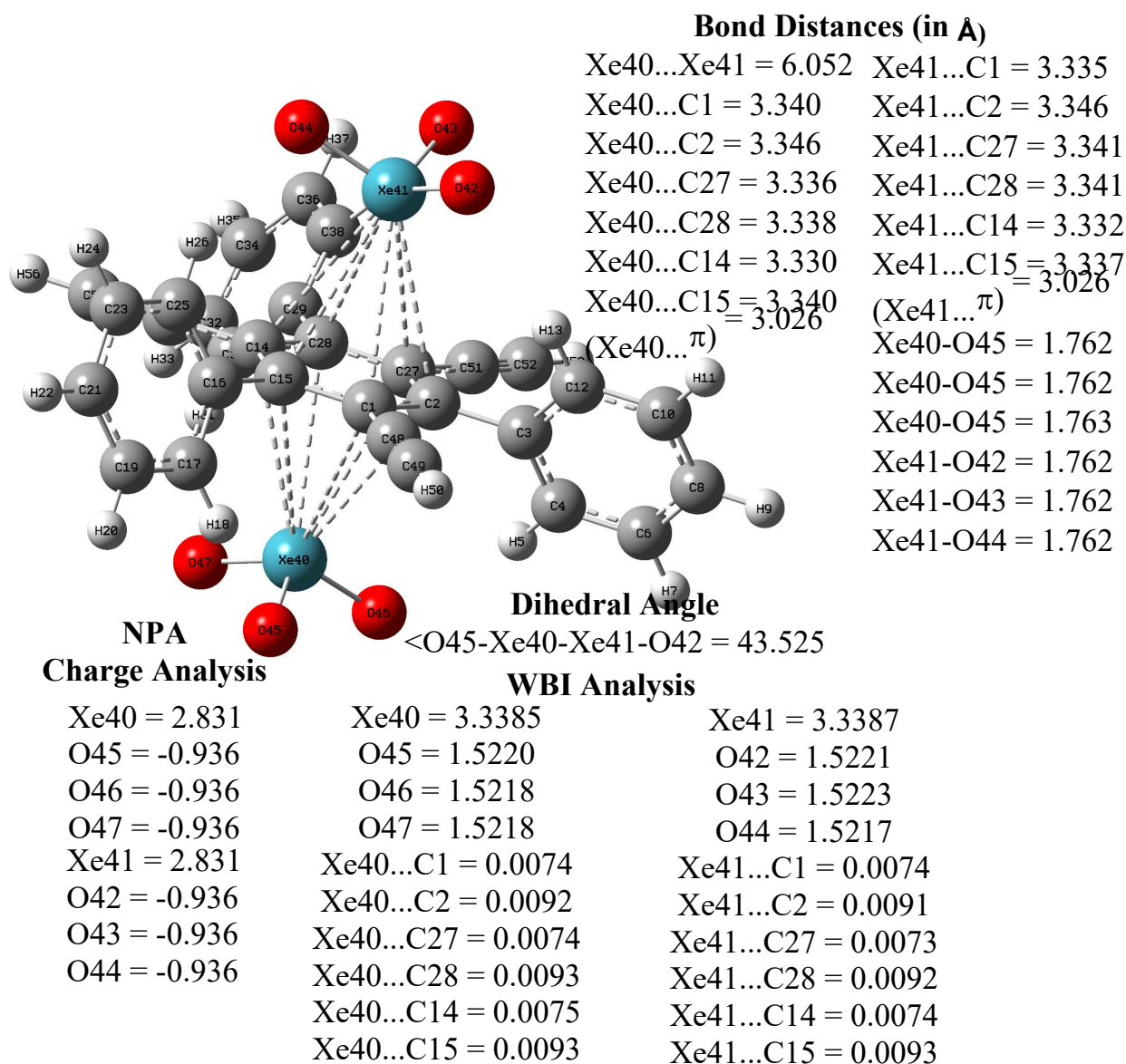


Figure S6.13. Optimized geometry of XeO₃ and its 1:2 (iSw) adduct with TPB-CCH. The bond parameters, WBI values and charge analysis (NPA) data are shown.

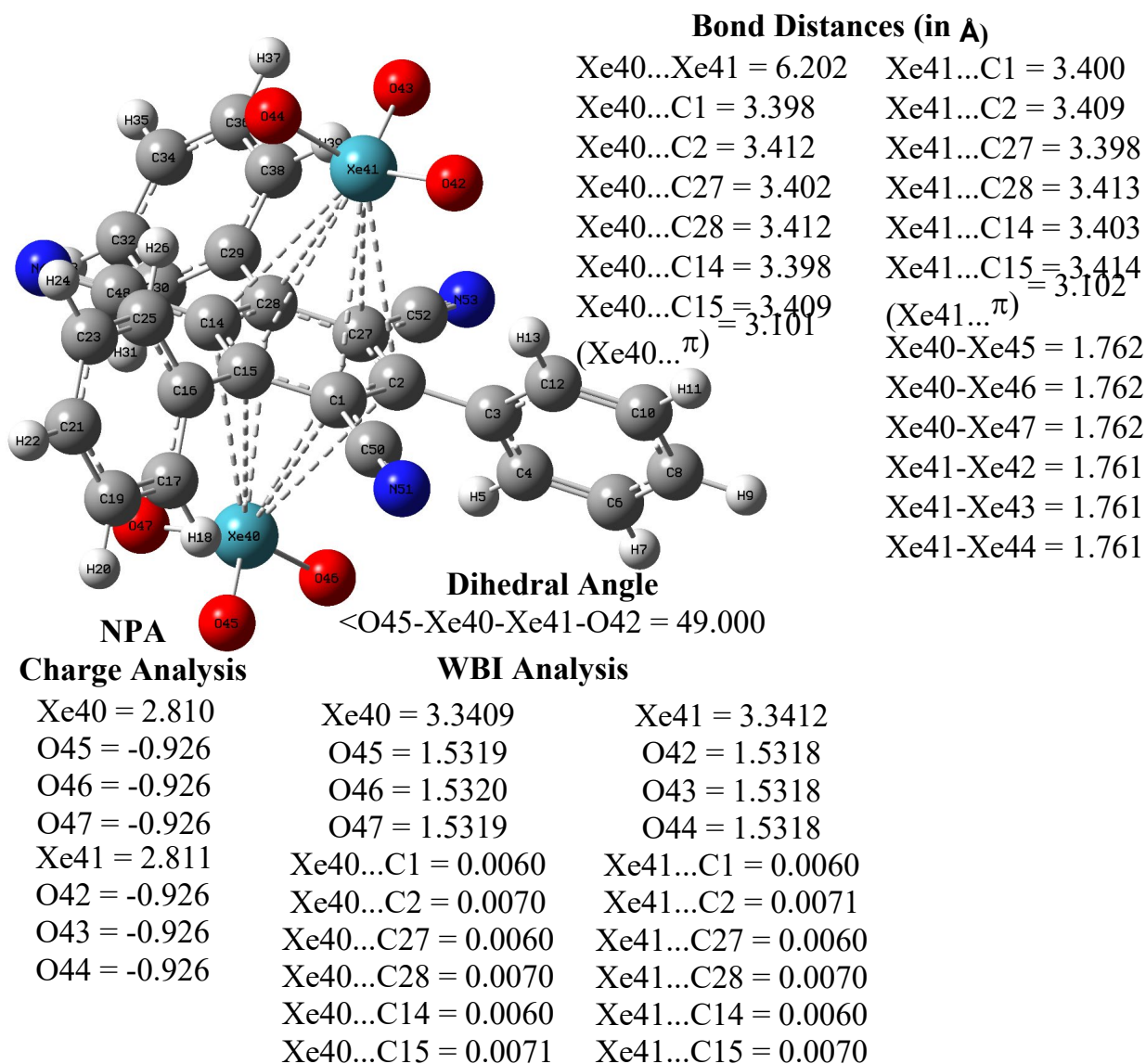


Figure S6.14. Optimized geometry of XeO₃ and its 1:2 (iSw) adduct with TPB-CN. The bond parameters, WBI values and charge analysis (NPA) data are shown.

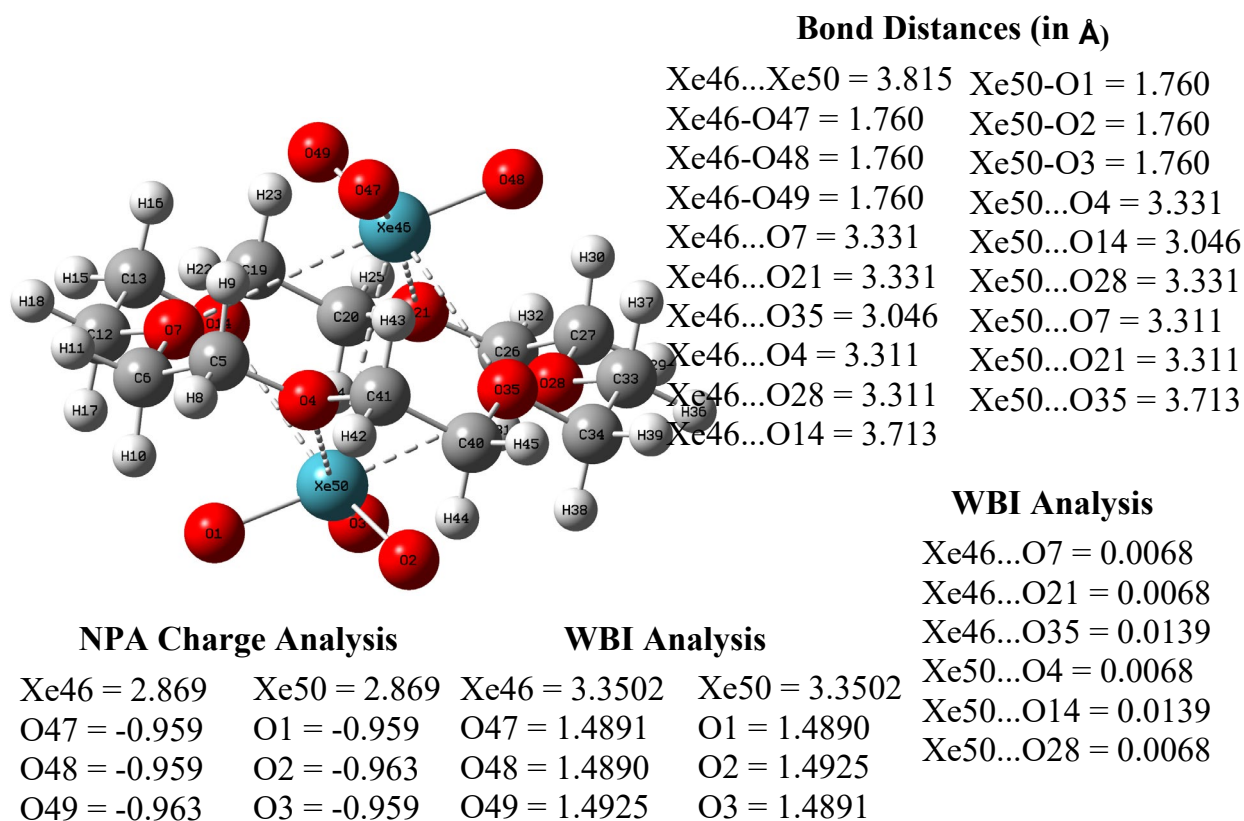


Figure S6.15. Optimized geometry of XeO₃ and its 1:2 (iSw) adduct with 18-crown-6. The bond parameters, WBI values and charge analysis (NPA) data are shown.

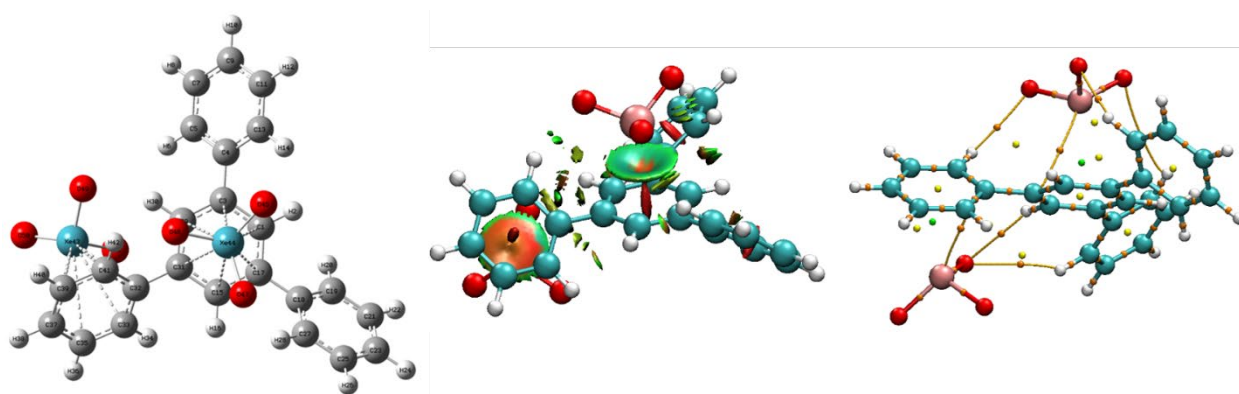


Figure S6.16. Optimized geometry, NCI plot, AIM analysis of XeO₃ and its 1:2 (shifted) adduct with TPB-H.

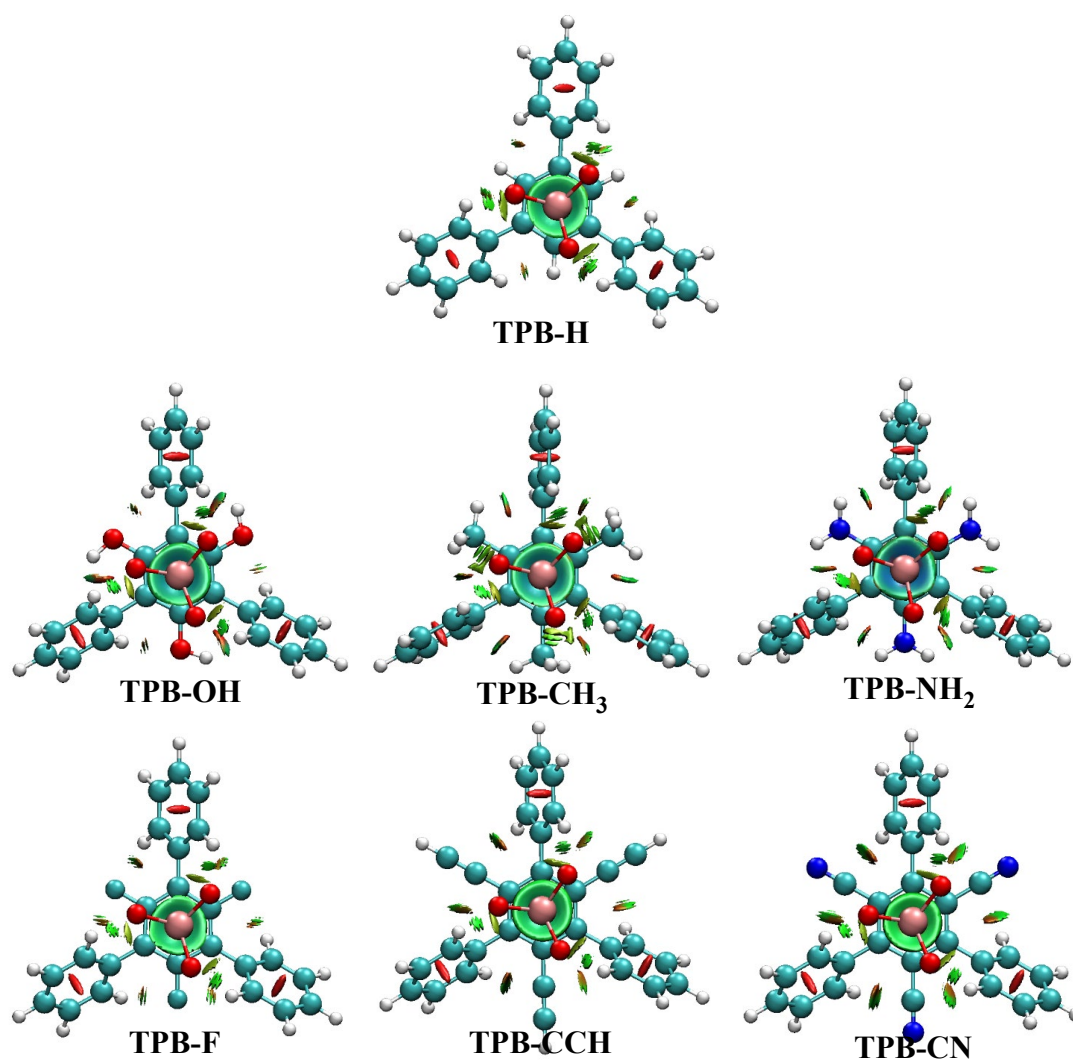
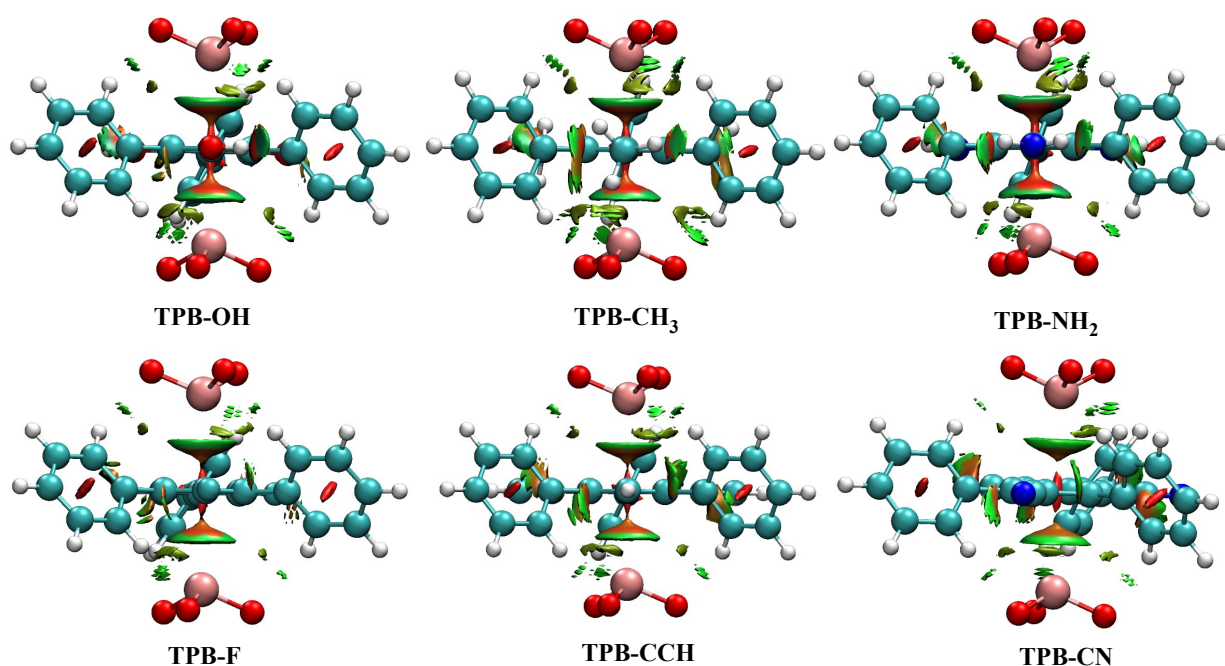


Figure S6.17. NCI plots (isovalue = 0.5 a.u.) of the Mono complexes of XeO₃ with TPB derivatives.



Figures S6.18. NCI plots (isovalue = 0.5 a.u.) of the iSw complexes of XeO₃ with TPB derivatives.

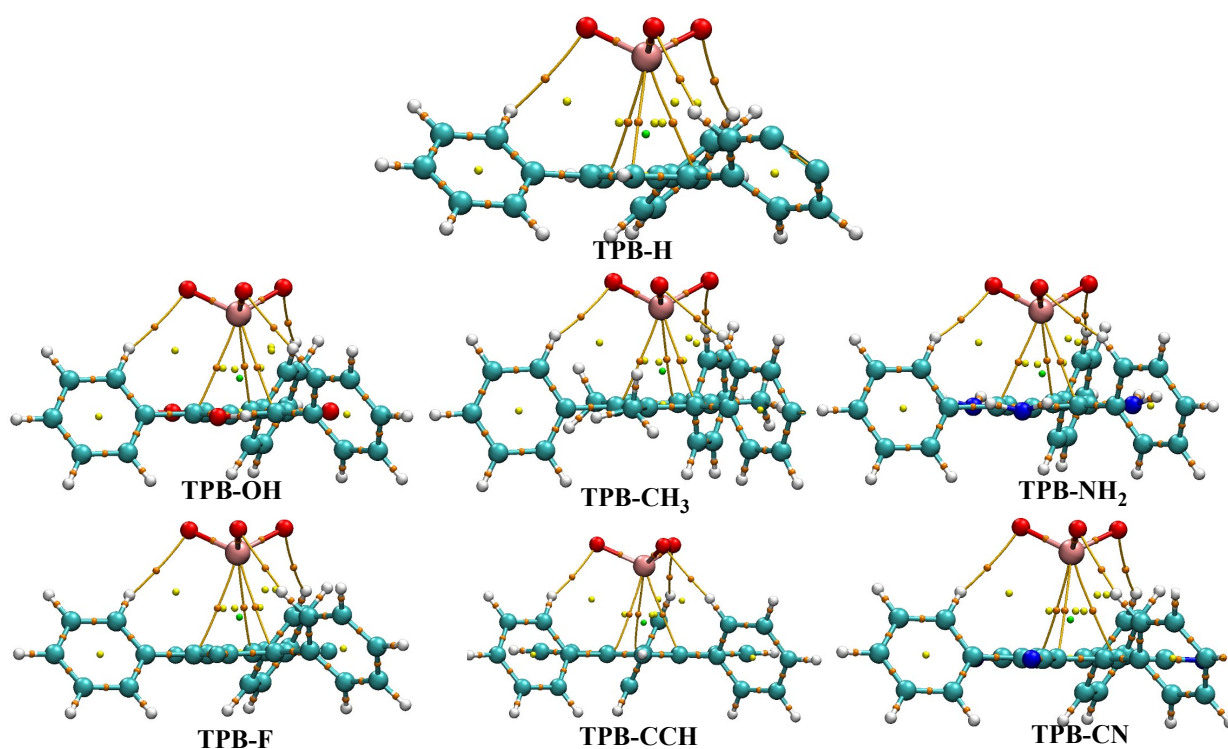


Figure S6.19. AIM analysis of the Mono complexes of XeO₃ with TPB derivatives.

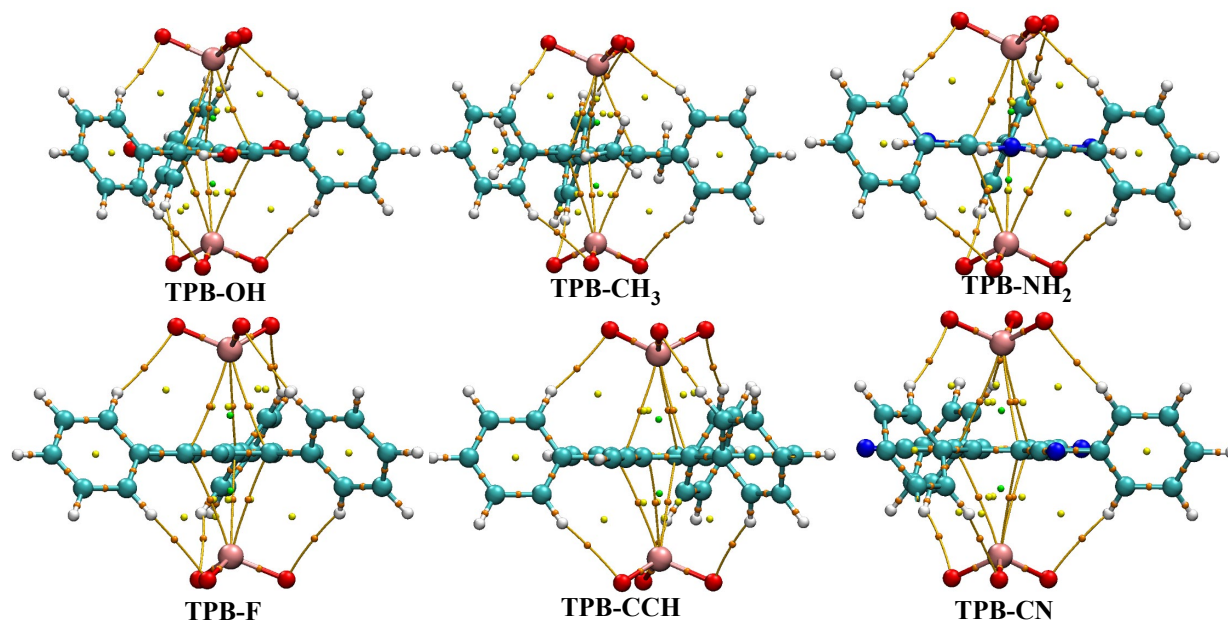


Figure S6.20. AIM analysis of the iSw complexes of XeO_3 with TPB derivatives.

Table S6.1. AIM analysis: The average values of $\rho(r)$: density of all electrons, $\nabla^2\rho(r)$: Laplacian of electron density, $G(r)$: Lagrangian kinetic energy, $V(r)$: Potential energy density, $H(r)$: Local energy density, corresponding to individual type of interactions are listed below in a.u.. π represents the carbon atoms of the central arene ring.

Type	$(\text{TPB-NH}_2)^{\text{iSw}}$	$\rho(r)$	$\nabla^2\rho(r)$	$H(r)$
(3,+1)	$\text{Xe}\dots\text{C}^\pi(\text{NH}_2)$	0.017	0.048	0.0004
(3,-1)	$\text{Xe}\dots\text{C}^\pi(\text{Ph})$	0.018	0.044	0.0002
(3,+1)	$\text{Xe}\dots(\text{C}^\pi\text{-C}^{\text{Ph}})$	0.005	0.017	0.0008
(3,+3)	$\text{Xe}\dots\pi(\text{arene})$	0.012	0.056	0.0014
(3,-1)	$\text{C-H}\dots\text{O}$	0.009	0.030	0.0016

Type	$(\text{TPB-CH}_3)^{\text{iSw}}$	$\rho(r)$	$\nabla^2\rho(r)$	$H(r)$
(3,+1)	$\text{Xe}\dots\text{C}^\pi(\text{CH}_3)$	0.016	0.044	0.0005
(3,-1)	$\text{Xe}\dots\text{C}^\pi(\text{Ph})$	0.016	0.043	0.0004
(3,+1)	$\text{Xe}\dots(\text{C}^\pi\text{-C}^{\text{Ph}})$	0.005	0.017	0.0009
(3,+3)	$\text{Xe}\dots\pi(\text{arene})$	0.011	0.054	0.0015
(3,-1)	$\text{C-H}\dots\text{O}$	0.008	0.029	0.0014

Type	$(\text{TPB-OH})^{\text{iSw}}$	$\rho(r)$	$\nabla^2\rho(r)$	$H(r)$
(3,+1)	$\text{Xe}\dots\text{C}^\pi(\text{OH})$	0.015	0.044	0.0006

(3,-1)	Xe...C ^π (Ph)	0.016	0.042	0.0003
(3,+1)	Xe...(C ^π -C ^{Ph})	0.004	0.015	0.0008
(3,+3)	Xe...π(arene)	0.011	0.052	0.0014
(3,-1)	C-H...O	0.008	0.027	0.0014

Type	(TPB-H) ^{iSw}	ρ(r)	∇ ² ρ(r)	H(r)
(3,-1)	Xe...C ^π (H)	0.014	0.040	0.0007
(3,+1)	Xe...C ^π (Ph)	0.014	0.040	0.0007
(3,+1)	Xe...(C ^π -C ^{Ph})	0.003	0.012	0.0008
(3,+3)	Xe...π(arene)	0.010	0.049	0.0015
(3,-1)	C-H...O	0.005	0.018	0.0010

Type	(TPB-CCH) ^{iSw}	ρ(r)	∇ ² ρ(r)	H(r)
(3,+1)	Xe...C ^π (CCH)	0.013	0.037	0.007
(3,-1)	Xe...C ^π (Ph)	0.013	0.037	0.0007
(3,+1)	Xe...(C ^π -C ^{Ph})	0.004	0.015	0.0008
(3,+3)	Xe...π(arene)	0.010	0.045	0.0015
(3,-1)	C-H...O	0.008	0.029	0.0015

Type	(TPB-F) ^{iSw}	ρ(r)	∇ ² ρ(r)	H(r)
(3,+1)	Xe...C ^π (F)	0.013	0.039	0.0007
(3,-1)	Xe...C ^π (Ph)	0.014	0.038	0.0006
(3,+1)	Xe...(C ^π -C ^{Ph})	0.003	0.013	0.0008
(3,+3)	Xe...π(arene)	0.010	0.046	0.0014
(3,-1)	C-H...O	0.006	0.021	0.0011

Type	(TPB-CN) ^{iSw}	ρ(r)	∇ ² ρ(r)	H(r)
(3,-1)	Xe...C ^π (CN)	0.012	0.034	0.0008
(3,+1)	Xe...C ^π (Ph)	0.011	0.034	0.0008
(3,+1)	Xe...(C ^π -C ^{Ph})	0.004	0.013	0.0008
(3,+3)	Xe...π(arene)	0.009	0.040	0.0014
(3,-1)	C-H...O	0.007	0.025	0.0013

Type	(18O6) ^{iSw}	ρ(r)	∇ ² ρ(r)	H(r)
(3,-1)	(Xe...O) ¹	0.009	0.033	0.0014
(3,-1)	(Xe...O) ²	0.008	0.028	0.0014
(3,-1)	(Xe...O) ³	0.014	0.050	0.0017
(3,-1)	(Xe...O) ⁴	0.008	0.028	0.0014
(3,-1)	(Xe...O) ⁵	0.009	0.033	0.0014
(3,-1)	Xe...Xe	0.009	0.022	0.0006
(3,-1)	(C-H...O) ^{avg}	0.010	0.038	0.0018

Table S6.2. NBO analyses of the Mono (1:1) complexes of XeO₃ with TPB derivatives. E² (in kcal/mol) denotes second-order perturbation energy values obtained from NBO analysis at the APFD/def2-TZVPD level of theory.

(XeO ₃ :TPB-H) ^{Mono}		
Donor	Acceptor	ΔE ²
BD (2) C 1 - C 17	BD*(1)Xe 43 - O 44	-0.18
BD (2) C 1 - C 17	BD*(1)Xe 43 - O 45	-0.77
BD (2) C 1 - C 17	BD*(1)Xe 43 - O 46	-0.34
BD (2) C 3 - C 29	BD*(1)Xe 43 - O 44	-0.34
BD (2) C 3 - C 29	BD*(1)Xe 43 - O 45	-0.18
BD (2) C 3 - C 29	BD*(1)Xe 43 - O 46	-0.77
BD (2) C 15 - C 31	BD*(1)Xe 43 - O 44	-0.77
BD (2) C 15 - C 31	BD*(1)Xe 43 - O 45	-0.34
BD (2) C 15 - C 31	BD*(1)Xe 43 - O 46	-0.18
LP Xe 43	BD*(1) C 3 - C 4	-0.26
LP Xe 43	BD*(1) C 17 - C 18	-0.26
LP Xe 43	BD*(1) C 31 - C 32	-0.26
LP O 44	BD*(1) C 19 - H 20	-0.26
LP O 45	BD*(1) C 5 - H 6	-0.26
LP O 46	BD*(1) C 33 - H 34	-0.26

(XeO ₃ :TPB-OH) ^{Mono}		
Donor	Acceptor	ΔE ²
BD (2) C 1 - C 2	BD*(1)Xe 37 - O 40	-1.87
BD (2) C 13 - C 14	BD*(1)Xe 37 - O 39	-1.87
BD (2) C 25 - C 26	BD*(1)Xe 37 - O 38	-1.87
LP Xe 37	BD*(1) C 1 - O 49	-0.11
LP Xe 37	BD*(1) C 2 - C 3	-0.30
LP Xe 37	BD*(1) C 13 - O 47	-0.11
LP Xe 37	BD*(1) C 14 - C 15	-0.30
LP Xe 37	BD*(1) C 25 - O 48	-0.11
LP Xe 37	BD*(1) C 26 - C 27	-0.30
LP O 38	BD*(1) C 16 - H 17	-1.12
LP O 39	BD*(1) C 4 - H 5	-1.12
LP O 40	BD*(1) C 28 - H 29	-1.12

(XeO ₃ :TPB-CH ₃) ^{Mono}		
Donor	Acceptor	ΔE ²
BD (2) C 1 - C 14	BD*(1)Xe 37 - O 38	-0.10
BD (2) C 1 - C 14	BD*(1)Xe 37 - O 39	-2.00
BD (2) C 2 - C 25	BD*(1)Xe 37 - O 39	-0.10
BD (2) C 2 - C 25	BD*(1)Xe 37 - O 40	-2.00
BD (2) C 13 - C 26	BD*(1)Xe 37 - O 38	-1.96
BD (2) C 13 - C 26	BD*(1)Xe 37 - O 40	-0.09
LP Xe 37	BD*(1) C 1 - C 44	-0.34

LP Xe 37	BD*(1) C 2 - C 3	-0.40
LP Xe 37	BD*(1) C 13 - C 48	-0.34
LP Xe 37	BD*(1) C 14 - C 15	-0.40
LP Xe 37	BD*(1) C 25 - C 52	-0.34
LP Xe 37	BD*(1) C 26 - C 27	-0.40
LP O 38	BD*(2) C 1 - C 14	-0.11
LP O 38	BD*(1) C 11 - H 12	-0.93
LP O 38	BD*(1) C 44 - H 46	-0.11
LP O 39	BD*(1) C 35 - H 36	-0.87
LP O 39	BD*(2) C 2 - C 25	-0.10
LP O 39	BD*(1) C 52 - H 54	-0.10
LP O 40	BD*(1) C 23 - H 24	-0.97
LP O 40	BD*(2) C 13 - C 26	-0.10
LP O 40	BD*(1) C 48 - H 50	-0.10

(XeO ₃ :TPB-NH ₂) ^{Mono}		
Donor	Acceptor	ΔE^2
BD (2) C 1 - C 14	BD*(1)Xe 37 - O 38	-0.10
BD (2) C 1 - C 14	BD*(1)Xe 37 - O 39	-2.60
BD (2) C 2 - C 25	BD*(1)Xe 37 - O 39	-0.10
BD (2) C 2 - C 25	BD*(1)Xe 37 - O 40	-2.60
BD (2) C 13 - C 26	BD*(1)Xe 37 - O 38	-2.60
BD (2) C 13 - C 26	BD*(1)Xe 37 - O 40	-0.10
LP Xe 37	BD*(1) C 1 - N 44	-0.28
LP Xe 37	BD*(1) C 2 - C 3	-0.35
LP Xe 37	BD*(1) C 13 - N 47	-0.28
LP Xe 37	BD*(1) C 14 - C 15	-0.35
LP Xe 37	BD*(1) C 25 - N 50	-0.28
LP Xe 37	BD*(1) C 26 - C 27	-0.35
LP O 38	BD*(2) C 1 - C 14	-0.12
LP O 38	BD*(1) C 11 - H 12	-1.10
LP O 39	BD*(1) C 35 - H 36	-1.10
LP O 39	BD*(2) C 2 - C 25	-0.12
LP O 40	BD*(1) C 23 - H 24	-1.10
LP O 40	BD*(2) C 13 - C 26	-0.12

(XeO ₃ :TPB-CCH) ^{Mono}		
Donor	Acceptor	ΔE^2
BD (2) C 1 - C 15	BD*(1)Xe 40 - O 42	-1.15
BD (2) C 2 - C 27	BD*(1)Xe 40 - O 43	-1.15
BD (2) C 14 - C 28	BD*(1)Xe 40 - O 41	-1.14
LP Xe 40	BD*(1) C 1 - C 44	-0.24
LP Xe 40	BD*(1) C 2 - C 3	-0.27
LP Xe 40	BD*(1) C 14 - C 50	-0.24
LP Xe 40	BD*(1) C 15 - C 16	-0.27
LP Xe 40	BD*(1) C 27 - C 47	-0.24
LP Xe 40	BD*(1) C 28 - C 29	-0.27
LP Xe 40	BD*(1) C 44 - C 45	-0.08
LP Xe 40	BD*(1) C 47 - C 48	-0.08
LP Xe 40	BD*(1) C 50 - C 51	-0.08

LP O 41	BD*(1) C 12 - H 13	-1.06
LP O 42	BD*(1) C 38 - H 39	-1.01
LP O 43	BD*(1) C 25 - H 26	-0.96

(XeO ₃ :TPB-F) ^{Mono}		
Donor	Acceptor	ΔE ²
BD (2) C 1 - C 14	BD*(1)Xe 37 - O 39	-1.21
BD (2) C 2 - C 25	BD*(1)Xe 37 - O 40	-1.23
BD (2) C 13 - C 26	BD*(1)Xe 37 - O 38	-1.24
LP Xe 37	BD*(1) C 14 - C 15	-0.21
LP Xe 37	BD*(1) C 2 - C 3	-0.21
LP Xe 37	BD*(1) C 26 - C 27	-0.21
LP O 38	BD*(1) C 11 - H 12	-0.56
LP O 39	BD*(1) C 35 - H 36	-0.56
LP O 40	BD*(1) C 23 - H 24	-0.57

(XeO ₃ :TPB-CN) ^{Mono}		
Donor	Acceptor	ΔE ²
BD (2) C 1 - C 15	BD*(1)Xe 40 - O 42	-0.74
BD (2) C 2 - C 27	BD*(1)Xe 40 - O 43	-0.79
BD (2) C 14 - C 28	BD*(1)Xe 40 - O 41	-0.76
LP Xe 40	BD*(1) C 1 - C 46	-0.13
LP Xe 40	BD*(1) C 2 - C 3	-0.22
LP Xe 40	BD*(1) C 14 - C 44	-0.14
LP Xe 40	BD*(1) C 15 - C 16	-0.21
LP Xe 40	BD*(1) C 27 - C 48	-0.14
LP Xe 40	BD*(1) C 28 - C 29	-0.22
LP O 41	BD*(1) C 12 - H 13	-0.80
LP O 42	BD*(1) C 38 - H 39	-0.86
LP O 43	BD*(1) C 25 - H 26	-0.73

Table S6.3. NBO analyses of the iSw (1:2) complexes of XeO₃ with TPB derivatives. E² (in kcal/mol) denotes second-order perturbation energy values obtained from NBO analysis at the APFD/def2-TZVPD level of theory.

(XeO ₃ :TPB-H) ^{iSw}		
Donor	Acceptor	ΔE ²
BD (2) C 1 - C 3	BD*(1)Xe 43 - O 50	-0.98
BD (2) C 15 - C 17	BD*(1)Xe 43 - O 49	-0.98
BD (2) C 29 - C 31	BD*(1)Xe 43 - O 48	-0.98
BD (2) C 1 - C 3	BD*(1)Xe 44 - O 45	-0.19
BD (2) C 1 - C 3	BD*(1)Xe 44 - O 46	-0.20
BD (2) C 1 - C 3	BD*(1)Xe 44 - O 47	-0.43
BD (2) C 15 - C 17	BD*(1)Xe 44 - O 45	-0.20
BD (2) C 15 - C 17	BD*(1)Xe 44 - O 46	-0.43

BD (2) C 15 - C 17	BD*(1)Xe 44 - O 47	-0.19
BD (2) C 29 - C 31	BD*(1)Xe 44 - O 45	-0.43
BD (2) C 29 - C 31	BD*(1)Xe 44 - O 46	-0.19
BD (2) C 29 - C 31	BD*(1)Xe 44 - O 47	-0.20
LP Xe 43	BD*(1) C 3 - C 4	-0.28
LP Xe 43	BD*(1) C 17 - C 18	-0.28
LP Xe 43	BD*(1) C 31 - C 32	-0.28
LP O 48	BD*(1) C 19 - H 20	-0.24
LP O 49	BD*(1) C 5 - H 6	-0.24
LP O 50	BD*(1) C 33 - H 34	-0.24
LP Xe 44	BD*(1) C 3 - C 4	-0.28
LP Xe 44	BD*(1) C 17 - C 18	-0.28
LP Xe 44	BD*(1) C 31 - C 32	-0.28
LP O 45	BD*(1) C 13 - H 14	-0.24
LP O 46	BD*(1) C 41 - H 42	-0.24
LP O 47	BD*(1) C 27 - H 28	-0.24

(XeO ₃ :TPB-OH) ^{iSw}		
Donor	Acceptor	ΔE ²
BD (2) C 1 - C 14	BD*(1)Xe 37 - O 42	-0.19
BD (2) C 1 - C 14	BD*(1)Xe 37 - O 43	-0.57
BD (2) C 1 - C 14	BD*(1)Xe 37 - O 44	-0.19
BD (2) C 2 - C 25	BD*(1)Xe 37 - O 42	-0.19
BD (2) C 2 - C 25	BD*(1)Xe 37 - O 43	-0.19
BD (2) C 2 - C 25	BD*(1)Xe 37 - O 44	-0.57
BD (2) C 13 - C 26	BD*(1)Xe 37 - O 42	-0.57
BD (2) C 13 - C 26	BD*(1)Xe 37 - O 43	-0.19
BD (2) C 13 - C 26	BD*(1)Xe 37 - O 44	-0.19
BD (2) C 1 - C 14	BD*(1)Xe 38 - O 39	-0.08
BD (2) C 1 - C 14	BD*(1)Xe 38 - O 40	-1.10
BD (2) C 2 - C 25	BD*(1)Xe 38 - O 40	-0.08
BD (2) C 2 - C 25	BD*(1)Xe 38 - O 41	-1.10
BD (2) C 13 - C 26	BD*(1)Xe 38 - O 39	-1.10
BD (2) C 13 - C 26	BD*(1)Xe 38 - O 41	-0.08
LP Xe 37	BD*(1) C 1 - O 53	-0.11
LP Xe 37	BD*(1) C 2 - C 3	-0.28
LP Xe 37	BD*(1) C 13 - O 51	-0.11
LP Xe 37	BD*(1) C 14 - C 15	-0.28
LP Xe 37	BD*(1) C 25 - O 52	-0.11
LP Xe 37	BD*(1) C 26 - C 27	-0.28
LP O 42	BD*(1) C 16 - H 17	-0.99
LP O 43	BD*(1) C 4 - H 5	-0.97
LP O 44	BD*(1) C 28 - H 29	-0.97
LP Xe 38	BD*(1) C 1 - O 53	-0.11
LP Xe 38	BD*(1) C 2 - C 3	-0.26
LP Xe 38	BD*(1) C 13 - O 51	-0.11
LP Xe 38	BD*(1) C 14 - C 15	-0.26
LP Xe 38	BD*(1) C 25 - O 52	-0.11
LP Xe 38	BD*(1) C 26 - C 27	-0.26
LP O 39	BD*(1) C 11 - H 12	-0.75
LP O 40	BD*(1) C 35 - H 36	-0.75
LP O 41	BD*(1) C 23 - H 24	-0.75

(XeO ₃ :TPB-CH ₃) ^{isw}		
Donor	Acceptor	ΔE ²
BD (2) C 1 - C 14	BD*(1)Xe 37 - O 42	-0.26
BD (2) C 1 - C 14	BD*(1)Xe 37 - O 43	-0.60
BD (2) C 1 - C 14	BD*(1)Xe 37 - O 44	-0.12
BD (2) C 2 - C 25	BD*(1)Xe 37 - O 42	-0.12
BD (2) C 2 - C 25	BD*(1)Xe 37 - O 43	-0.26
BD (2) C 2 - C 25	BD*(1)Xe 37 - O 44	-0.60
BD (2) C 13 - C 26	BD*(1)Xe 37 - O 42	-0.60
BD (2) C 13 - C 26	BD*(1)Xe 37 - O 43	-0.12
BD (2) C 13 - C 26	BD*(1)Xe 37 - O 44	-0.26
BD (2) C 1 - C 14	BD*(1)Xe 38 - O 39	-0.15
BD (2) C 1 - C 14	BD*(1)Xe 38 - O 40	-1.13
BD (2) C 2 - C 25	BD*(1)Xe 38 - O 40	-0.15
BD (2) C 2 - C 25	BD*(1)Xe 38 - O 41	-1.13
BD (2) C 13 - C 26	BD*(1)Xe 38 - O 39	-1.13
BD (2) C 13 - C 26	BD*(1)Xe 38 - O 41	-0.16
LP Xe 37	BD*(1) C 1 - C 48	-0.36
LP Xe 37	BD*(1) C 2 - C 3	-0.34
LP Xe 37	BD*(1) C 13 - C 52	-0.36
LP Xe 37	BD*(1) C 14 - C 15	-0.34
LP Xe 37	BD*(1) C 25 - C 56	-0.36
LP Xe 37	BD*(1) C 26 - C 27	-0.34
LP O 42	BD*(1) C 16 - H 17	-0.93
LP O 43	BD*(1) C 4 - H 5	-0.94
LP O 44	BD*(1) C 28 - H 29	-0.94
LP Xe 38	BD*(1) C 1 - C 48	-0.35
LP Xe 38	BD*(1) C 2 - C 3	-0.36
LP Xe 38	BD*(1) C 13 - C 52	-0.35
LP Xe 38	BD*(1) C 14 - C 15	-0.36
LP Xe 38	BD*(1) C 26 - C 27	-0.36
LP Xe 38	BD*(1) C 25 - C 56	-0.35
LP O 39	BD*(1) C 11 - H 12	-0.97
LP O 39	BD*(1) C 48 - H 50	-0.09
LP O 40	BD*(1) C 35 - H 36	-0.98
LP O 40	BD*(1) C 56 - H 58	-0.09
LP O 41	BD*(1) C 23 - H 24	-0.98
LP O 41	BD*(1) C 52 - H 54	-0.09

(XeO ₃ :TPB-NH ₂) ^{isw}		
Donor	Acceptor	ΔE ²
BD (2) C 1 - C 14	BD*(1)Xe 37 - O 42	-0.26
BD (2) C 1 - C 14	BD*(1)Xe 37 - O 43	-1.01
BD (2) C 1 - C 14	BD*(1)Xe 37 - O 44	-0.12
BD (2) C 2 - C 25	BD*(1)Xe 37 - O 42	-0.11
BD (2) C 2 - C 25	BD*(1)Xe 37 - O 43	-0.27
BD (2) C 2 - C 25	BD*(1)Xe 37 - O 44	-1.03
BD (2) C 13 - C 26	BD*(1)Xe 37 - O 42	-1.03
BD (2) C 13 - C 26	BD*(1)Xe 37 - O 43	-0.11
BD (2) C 13 - C 26	BD*(1)Xe 37 - O 44	-0.26
BD (2) C 1 - C 14	BD*(1)Xe 38 - O 39	-0.07
BD (2) C 1 - C 14	BD*(1)Xe 38 - O 40	-1.37

BD (2) C 2 - C 25	BD*(1)Xe 38 - O 40	-0.07
BD (2) C 2 - C 25	BD*(1)Xe 38 - O 41	-1.37
BD (2) C 13 - C 26	BD*(1)Xe 38 - O 39	-1.38
BD (2) C 13 - C 26	BD*(1)Xe 38 - O 41	-0.08
LP Xe 37	BD*(1) C 1 - N 48	-0.27
LP Xe 37	BD*(1) C 2 - C 3	-0.31
LP Xe 37	BD*(1) C 13 - N 51	-0.27
LP Xe 37	BD*(1) C 14 - C 15	-0.31
LP Xe 37	BD*(1) C 25 - N 54	-0.27
LP Xe 37	BD*(1) C 26 - C 27	-0.31
LP O 42	BD*(1) C 16 - H 17	-1.03
LP O 43	BD*(1) C 4 - H 5	-1.06
LP O 44	BD*(1) C 28 - H 29	-1.05
LP Xe 38	BD*(1) C 1 - N 48	-0.23
LP Xe 38	BD*(1) C 2 - C 3	-0.30
LP Xe 38	BD*(1) C 13 - N 51	-0.23
LP Xe 38	BD*(1) C 14 - C 15	-0.30
LP Xe 38	BD*(1) C 25 - N 54	-0.23
LP Xe 38	BD*(1) C 26 - C 27	-0.30
LP O 39	BD*(1) C 11 - H 12	-1.18
LP O 39	BD*(2) C 1 - C 14	-0.08
LP O 40	BD*(1) C 35 - H 36	-1.17
LP O 40	BD*(2) C 2 - C 25	-0.08
LP O 41	BD*(1) C 23 - H 24	-1.18
LP O 41	BD*(2) C 13 - C 26	-0.08

(XeO ₃ :TPB-CCH) ^{iSw}		
Donor	Acceptor	ΔE^2
BD (2) C 1 - C 2	BD*(1)Xe 40 - O 47	-0.75
BD (2) C 14 - C 15	BD*(1)Xe 40 - O 46	-0.75
BD (2) C 27 - C 28	BD*(1)Xe 40 - O 45	-0.76
BD (2) C 1 - C 2	BD*(1)Xe 41 - O 42	-0.14
BD (2) C 1 - C 2	BD*(1)Xe 41 - O 43	-0.15
BD (2) C 1 - C 2	BD*(1)Xe 41 - O 44	-0.32
BD (2) C 14 - C 15	BD*(1)Xe 41 - O 42	-0.14
BD (2) C 14 - C 15	BD*(1)Xe 41 - O 43	-0.34
BD (2) C 14 - C 15	BD*(1)Xe 41 - O 44	-0.15
BD (2) C 27 - C 28	BD*(1)Xe 41 - O 42	-0.33
BD (2) C 27 - C 28	BD*(1)Xe 41 - O 43	-0.13
BD (2) C 27 - C 28	BD*(1)Xe 41 - O 44	-0.14
LP Xe 40	BD*(1) C 1 - C 48	-0.23
LP Xe 40	BD*(1) C 2 - C 3	-0.26
LP Xe 40	BD*(1) C 14 - C 54	-0.23
LP Xe 40	BD*(1) C 15 - C 16	-0.27
LP Xe 40	BD*(1) C 27 - C 51	-0.23
LP Xe 40	BD*(1) C 28 - C 29	-0.27
LP O 45	BD*(1) C 17 - H 18	-1.03
LP O 46	BD*(1) C 4 - H 5	-1.05
LP O 47	BD*(1) C 30 - H 31	-1.08
LP Xe 41	BD*(1) C 1 - C 48	-0.23
LP Xe 41	BD*(1) C 2 - C 3	-0.26
LP Xe 41	BD*(1) C 14 - C 54	-0.23
LP Xe 41	BD*(1) C 15 - C 16	-0.26

LP Xe 41	BD*(1) C 27 - C 51	-0.23
LP Xe 41	BD*(1) C 28 - C 29	-0.26
LP O 42	BD*(1) C 12 - H 13	-0.93
LP O 43	BD*(1) C 38 - H 39	-0.92
LP O 44	BD*(1) C 25 - H 26	-1.02

(XeO ₃ :TPB-F) ^{iSw}		
Donor	Acceptor	ΔE^2
BD (2) C 1 - C 14	BD*(1)Xe 37 - O 42	-0.09
BD (2) C 1 - C 14	BD*(1)Xe 37 - O 43	-0.44
BD (2) C 1 - C 14	BD*(1)Xe 37 - O 44	-0.16
BD (2) C 2 - C 25	BD*(1)Xe 37 - O 42	-0.16
BD (2) C 2 - C 25	BD*(1)Xe 37 - O 43	-0.09
BD (2) C 2 - C 25	BD*(1)Xe 37 - O 44	-0.43
BD (2) C 13 - C 26	BD*(1)Xe 37 - O 42	-0.44
BD (2) C 13 - C 26	BD*(1)Xe 37 - O 43	-0.16
BD (2) C 13 - C 26	BD*(1)Xe 37 - O 44	-0.10
BD (2) C 1 - C 14	BD*(1)Xe 38 - O 40	-0.82
BD (2) C 2 - C 25	BD*(1)Xe 38 - O 41	-0.81
BD (2) C 13 - C 26	BD*(1)Xe 38 - O 39	-0.82
LP Xe 37	BD*(1) C 2 - C 3	-0.21
LP Xe 37	BD*(1) C 14 - C 15	-0.21
LP Xe 37	BD*(1) C 26 - C 27	-0.21
LP O 42	BD*(1) C 16 - H 17	-0.44
LP O 43	BD*(1) C 4 - H 5	-0.44
LP O 44	BD*(1) C 28 - H 29	-0.51
LP Xe 38	BD*(1) C 2 - C 3	-0.22
LP Xe 38	BD*(1) C 14 - C 15	-0.22
LP Xe 38	BD*(1) C 26 - C 27	-0.22
LP O 39	BD*(1) C 11 - H 12	-0.44
LP O 40	BD*(1) C 35 - H 36	-0.45
LP O 41	BD*(1) C 23 - H 24	-0.50

(XeO ₃ :TPB-CN) ^{iSw}		
Donor	Acceptor	ΔE^2
BD (2) C 1 - C 2	BD*(1)Xe 40 - O 47	-0.53
BD (2) C 14 - C 15	BD*(1)Xe 40 - O 46	-0.54
BD (2) C 27 - C 28	BD*(1)Xe 40 - O 45	-0.53
BD (2) C 1 - C 2	BD*(1)Xe 41 - O 42	-0.09
BD (2) C 1 - C 2	BD*(1)Xe 41 - O 43	-0.13
BD (2) C 1 - C 2	BD*(1)Xe 41 - O 44	-0.20
BD (2) C 14 - C 15	BD*(1)Xe 41 - O 42	-0.13
BD (2) C 14 - C 15	BD*(1)Xe 41 - O 43	-0.19
BD (2) C 14 - C 15	BD*(1)Xe 41 - O 44	-0.09
BD (2) C 27 - C 28	BD*(1)Xe 41 - O 42	-0.20
BD (2) C 27 - C 28	BD*(1)Xe 41 - O 43	-0.09
BD (2) C 27 - C 28	BD*(1)Xe 41 - O 44	-0.13
LP Xe 40	BD*(1) C 1 - C 50	-0.12
LP Xe 40	BD*(1) C 2 - C 3	-0.23
LP Xe 40	BD*(1) C 14 - C 48	-0.12

LP Xe 40	BD*(1) C 15 - C 16	-0.23
LP Xe 40	BD*(1) C 27 - C 52	-0.12
LP Xe 40	BD*(1) C 28 - C 29	-0.23
LP O 45	BD*(1) C 17 - H 18	-0.64
LP O 46	BD*(1) C 4 - H 5	-0.62
LP O 47	BD*(1) C 30 - H 31	-0.62
LP Xe 41	BD*(1) C 1 - C 50	-0.12
LP Xe 41	BD*(1) C 2 - C 3	-0.23
LP Xe 41	BD*(1) C 14 - C 48	-0.12
LP Xe 41	BD*(1) C 15 - C 16	-0.23
LP Xe 41	BD*(1) C 27 - C 52	-0.12
LP Xe 41	BD*(1) C 28 - C 29	-0.23
LP O 42	BD*(1) C 12 - H 13	-0.64
LP O 43	BD*(1) C 38 - H 39	-0.62
LP O 44	BD*(1) C 25 - H 26	-0.62

(XeO ₃ :18O6) ^{iSw}		
Donor	Acceptor	ΔE ²
LP (1) O 4	BD*(1) O 3 -Xe 50	-0.37
LP (2) O 7	BD*(1) O 2 -Xe 50	-0.17
LP (2) O 7	BD*(1) O 3 -Xe 50	-0.32
LP (1) O 14	BD*(1) O 2 -Xe 50	-1.04
LP (2) O 14	BD*(1) O 2 -Xe 50	-0.11
LP (2) O 21	BD*(1) O 1 -Xe 50	-0.32
LP (2) O 21	BD*(1) O 2 -Xe 50	-0.17
LP (1) O 28	BD*(1) O 1 -Xe 50	-0.37
LP (2) O 4	BD*(1)Xe 46 - O 48	-0.32
LP (2) O 4	BD*(1)Xe 46 - O 49	-0.17
LP (1) O 7	BD*(1)Xe 46 - O 48	-0.37
LP (1) O 21	BD*(1)Xe 46 - O 47	-0.37
LP (2) O 28	BD*(1)Xe 46 - O 47	-0.32
LP (2) O 28	BD*(1)Xe 46 - O 49	-0.17
LP (1) O 35	BD*(1)Xe 46 - O 49	-1.04
LP (2) O 35	BD*(1)Xe 46 - O 49	-0.11
LP (1)Xe 50	BD*(1)Xe 46 - O 47	-0.09
LP (1)Xe 50	BD*(1)Xe 46 - O 48	-0.09
LP (1)Xe 46	BD*(1) O 1 -Xe 50	-0.09
LP (1)Xe 46	BD*(1) O 3 -Xe 50	-0.09
LP O 1	BD* C - H	-1.26
LP O 2	BD* C - H	-1.12
LP O 3	BD* C - H	-1.26
LP O 47	BD* C - H	-1.26
LP O 48	BD* C - H	-1.26
LP O 49	BD* C - H	-1.12

Table S6.4. Energy decomposition analysis of the XeO₃ with 1:1 (Mono) adducts of TPB and derivatives at the BP86-D3BJ/ZORA/TZ2P level of theory. The energy values are in kcal/mol.

Contribution to the sum of all attractive energy terms are shown in percent. E_{Pauli} represents Pauli repulsion, E_{elstat} represents electrostatic interactions, E_{oi} represents orbital interaction and the E_{disp} represents the dispersion interaction. (* values obtained from previous study)

Mono	ΔE_{int}	ΔE_{Pauli}	ΔE_{elstat}	%	ΔE_{oi}	%	ΔE_{disp}	%
TPB-NH ₂	-28.9	45.2	-29.6	40	-28.4	38	-16.1	22
TPB-CH ₃	-22.4	37.9	-22.4	37	-21.6	36	-16.4	27
TPB-OH	-21.4	35.2	-20.8	37	-21.0	37	-14.8	26
TPB-H	-17.4	26.6	-15.1	34	-15.4	35	-13.5	31
TPB-CCH	-16.5	26.3	-12.8	30	-14.8	34	-15.3	36
TPB-F	-14.3	25.2	-11.4	29	-14.5	37	-13.6	34
TPB-CN	-10.9	21.0	-6.0	19	-11.2	35	-14.7	46
18O6*	-34.0	40.6	-40.1	54	-17.8	24	-16.7	22

Optimized Cartesian Coordinates

(XeO ₃ :TPB-H) ^{iSw}				(XeO ₃ :TPB-H) ^{Mono}			
C	0.00074500	-0.80573400	-1.13214400	C	-1.33494400	-0.37195700	-1.07744000
H	0.00140200	-1.43419500	-2.01517900	H	-2.37908100	-0.66222400	-1.05712800
C	-0.00102900	-1.40114200	0.13337200	C	-1.00035000	0.98266000	-1.07804600
C	-0.00213400	-2.86647700	0.27290800	C	-2.05211800	2.01415100	-1.03192700
C	0.86710600	-3.48694200	1.17051900	C	-1.93185500	3.10543000	-0.17046400
H	1.56981600	-2.88912700	1.74181700	H	-1.07357000	3.17692200	0.48927200
C	0.86792400	-4.86766800	1.29576900	C	-2.92875600	4.06797700	-0.11582800
H	1.55827200	-5.34411500	1.98284000	H	-2.83130600	4.90248800	0.56980100
C	-0.00489500	-5.63727500	0.53712100	C	-4.05317500	3.95635500	-0.92330100
H	-0.00595700	-6.71679800	0.64008600	H	-4.83149900	4.71028500	-0.87976300
C	-0.87636800	-5.02324800	-0.35344000	C	-4.18041500	2.87260500	-1.78295000
H	-1.56783800	-5.61959900	-0.93814900	C	-5.05406200	2.78234300	-2.41927000
C	-0.87276400	-3.64374500	-0.49141100	H	-3.18849800	1.90526800	-1.83383000
H	-1.57461200	-3.16332100	-1.16533700	H	-3.28213900	1.06806700	-2.51761800
C	0.00085900	1.38323800	-0.13175500	C	0.99089000	-0.97408500	-1.07531000
H	0.00158900	2.46219600	-0.23449600	H	1.76459200	-1.73300900	-1.05309500
C	0.00181400	0.58500100	-1.28015500	C	-0.34953800	-1.36170700	-1.07418700
C	0.00418900	1.19686700	-2.61891400	C	-0.71828800	-2.78787200	-1.02573100
C	0.87600600	0.72958000	-3.60271400	C	-1.72495000	-3.22666600	-0.16453100
H	1.57788300	-0.06425800	-3.36867500	H	-2.21458600	-2.51775400	0.49477900
C	0.88056000	1.31163600	-4.86099500	C	-2.06282300	-4.57055800	-0.10896700
H	1.57289900	0.95470000	-5.61525800	H	-2.83563700	-4.90129300	0.57613900
C	0.00891800	2.35379800	-5.15043000	C	-1.40468000	-5.49064200	-0.91464300
H	0.01076000	2.80454500	-6.13673200	H	-1.67057600	-6.54109000	-0.87045500
C	-0.86503500	2.81828000	-4.17568800	C	-0.40046500	-5.06177200	-1.77336100
H	-1.55545900	3.62323300	-4.40154700	H	0.11405200	-5.77486700	-2.40824100
C	-0.86514100	2.24787300	-2.91208400	C	-0.05638400	-3.71965500	-1.82561200
H	-1.56869800	2.59169700	-2.16083600	H	0.71683300	-3.38407000	-2.50877800
C	-0.00176900	-0.57755600	1.26375600	C	0.34963800	1.34128500	-1.07949200
H	-0.00309400	-1.02804500	2.24952800	H	0.62004700	2.39079700	-1.06126600
C	-0.00085900	0.81612000	1.14667500	C	1.35545500	0.37422600	-1.07627100
C	-0.00184900	1.66981800	2.34578900	C	2.77487600	0.76810000	-1.02837700

C	0.86928900	2.75585000	2.43491200	C	3.65714700	0.11820500	-0.16416200
H	1.57314400	2.95024600	1.63218600	H	3.28734900	-0.65842900	0.49700900
C	0.87051600	3.55496400	3.56781800	C	4.98988000	0.49739000	-0.10803000
H	1.56233000	4.38695600	3.63733700	H	5.66165400	-0.00445000	0.57962800
C	-0.00384700	3.28466600	4.61282800	C	5.45899500	1.52439400	-0.91662200
H	-0.00466400	3.91383700	5.49606800	H	6.50169700	1.81915400	-0.87215700
C	-0.87720000	2.20795200	4.52574600	C	4.58672900	2.17685900	-1.77879000
H	-1.56984200	2.00122800	5.33393100	H	4.94808400	2.97666400	-2.41600700
C	-0.87403600	1.39840300	3.40025500	C	3.25226000	1.80420000	-1.83137700
H	-1.57723300	0.57574400	3.32067100	H	2.57614900	2.30394500	-2.51719900
Xe	2.98367000	-0.00186400	0.00318400	Xe	-0.00213900	0.00462400	1.85005000
Xe	-2.98374800	0.00146000	-0.00320300	O	-1.35157400	-0.89041400	2.55082900
O	-3.67303500	-1.33980400	-0.91680400	O	-0.10445400	1.62181000	2.54853000
O	-3.67361400	-0.11788800	1.61501400	O	1.44674100	-0.71493800	2.55403200
O	-3.67073800	1.46381200	-0.70910400				
O	3.67456900	-0.42842600	-1.56190100				
O	3.66957100	-1.14574000	1.15637600				
O	3.67293600	1.56696200	0.41846800				

(XeO ₃ :TPB-OH) ^{iSw}				(XeO ₃ :TPB-OH) ^{Mono}			
C	-0.02135200	-1.06407200	0.89634900	C	0.24292900	1.36556900	-0.91753500
C	-0.02281300	-1.33399000	-0.48038200	C	1.32978200	0.48464700	-0.89732100
C	0.00165200	-2.71645800	-1.00630000	C	2.72813400	0.96700900	-0.90046400
C	-1.05497800	-3.18646000	-1.78916500	C	3.58254400	0.65401500	0.15943400
H	-1.92216700	-2.55576000	-1.96307000	H	3.20064400	0.10327800	1.01443900
C	-1.01399100	-4.47094100	-2.31698300	C	4.90693000	1.07470800	0.14043500
H	-1.84225300	-4.83028200	-2.91745600	H	5.55795200	0.83147800	-0.97291600
C	0.07614500	-5.29139700	-2.06532300	C	5.38736300	1.81474100	-0.92997300
C	1.12651000	-4.82846600	-1.28117700	C	4.53948100	2.13625000	-1.98394800
H	1.97911000	-5.46788500	-1.08117100	H	4.91003200	2.71855400	-2.82063400
C	1.09275700	-3.54776600	-0.75307700	C	3.21995700	1.71359300	-1.97121900
H	1.91283500	-3.18920600	-0.14038700	H	2.55697700	1.96454300	-2.79127800
C	-0.02105800	1.30828800	0.47312800	C	-1.30341800	-0.47372000	-0.91729000
C	-0.02280500	0.25095300	1.39524900	C	-1.08397600	0.90804400	-0.89827700
C	0.00160600	0.48667600	2.85545700	C	-2.20107500	1.87762900	-0.90210400
C	-1.05507400	0.04368700	3.65386000	C	-2.35660200	2.77592200	0.15628800
H	-1.92231700	-0.42210900	3.19455200	H	-1.68793400	2.72219300	1.01078600
C	-1.01408200	0.22863500	5.03019800	C	-3.38371900	3.71188200	0.13669500
H	-1.84237800	-0.11172900	5.64157900	H	-3.49813500	4.39867300	0.96810600
C	0.07609900	0.85664000	5.61498200	C	-4.26609900	3.75525900	-0.93276800
C	1.12648700	1.30431200	4.82206400	C	-4.12117500	2.85838300	-1.98525400
H	1.97911200	1.79712100	5.27588600	H	-4.81172300	2.88617000	-2.82119500
C	1.09274300	1.12148100	3.44886600	C	-3.09473700	1.92769600	-1.97197500
H	1.91284200	1.47278900	2.83202800	H	-2.98105300	1.22663700	-2.79085800
C	-0.02105500	-0.24446100	-1.36973500	C	1.06260500	-0.89321000	-0.91597800
C	-0.02247800	1.08280000	-0.91511700	C	-0.24373600	-1.39398000	-0.89668700
C	0.00243600	2.22947700	-1.84939300	C	-0.52506600	-2.84618500	-0.89972600
C	-1.05369000	3.14305400	-1.86468000	C	-1.22549400	-3.42920500	0.15897200
H	-1.92093000	2.97855500	-1.23152900	H	-1.51343200	-2.82267000	1.01303200
C	-1.01219800	4.24257600	-2.71290800	C	-1.52308400	-4.78658100	0.13996100
H	-1.84007200	4.94273100	-2.72361800	H	-2.06087300	-5.22846100	0.97154900
C	0.07795000	4.43442700	-3.54936100	C	-1.12004300	-5.57310500	-0.92924800
C	1.12775700	3.52323100	-3.54093200	C	-0.41563400	-4.99993300	-1.98206800
H	1.98033400	3.66936500	-4.19480000	H	-0.09489800	-5.61228900	-2.81788000
C	1.09350500	2.42536500	-2.69608200	C	-0.12213900	-3.64582400	-1.96931600
H	1.91313800	1.71495500	-2.69226200	H	0.42833100	-3.19741800	-2.78840400
Xe	-2.96383000	0.00055000	-0.00042100	Xe	-0.00110200	0.00150300	1.96500400
Xe	2.91526700	-0.00023300	0.00027000	O	-0.23605600	1.60092600	2.67730800
O	3.60994700	-1.43983200	0.74742800	O	1.49985500	-0.59517600	2.68029500
O	3.61188000	0.07276100	-1.61919400	O	-1.27004400	-1.00006100	2.67711400
O	3.61013000	1.36615900	0.87400700	H	6.41996100	2.14601400	-0.94280400
O	-3.66095000	-0.77861000	1.42093000	H	-5.06984700	4.48325400	-0.94598900
O	-3.66179200	-0.84085300	-1.38539800	H	-1.34921300	-6.63304900	-0.94206000

O	-3.66201000	1.62059800	-0.03615600	H	-0.30493300	3.17786900	-0.90575400
H	0.10743800	-6.29415800	-2.47702200	H	-2.59861500	-1.85460800	-0.90456900
H	0.10741200	1.00132300	6.68926800	H	2.90609200	-1.32501300	-0.90328400
H	0.10966800	5.29249800	-4.21171500	O	-2.58034100	-0.88690600	-0.93880900
H	-0.01098400	-1.80469700	2.63730800	O	2.05869500	-1.79273000	-0.93600300
H	-0.01009500	3.18633500	0.24405900	O	0.52386900	2.67795300	-0.93866900
H	-0.01045400	-1.38193600	-2.88154000				
O	-0.00792500	2.54717200	0.97315900				
O	-0.00802100	-0.43092100	-2.69265300				
O	-0.00854300	-2.11654400	1.71922700				

(XeO ₃ :TPB-CH ₃) ^{iSw}				(XeO ₃ :TPB-CH ₃) ^{Mono}			
C	0.00645700	-1.11998800	0.86056100	C	-1.40727800	0.03762000	-0.88779000
C	0.00581100	-1.29576100	-0.53904600	C	-0.72824900	-1.19549200	-0.88591100
C	0.00143600	-2.67603500	-1.09040500	C	-1.51884500	-2.45379600	-0.90602200
C	-1.17681300	-3.23097200	-1.58557000	C	-1.70800800	-3.13303900	-2.10778100
H	-2.09128400	-2.64656800	-1.59366300	H	-1.26731200	-2.73614400	-3.01669100
C	-1.18308500	-4.52541600	-2.08570900	C	-2.44831200	-4.30609000	-2.14489700
H	-2.10620600	-4.94809000	-2.46678100	H	-2.58855300	-4.82614100	-3.08649500
C	-0.01290500	-5.27294400	-2.10144900	C	-3.00639000	-4.81312800	-0.97830300
C	1.16404700	-4.72196700	-1.61273100	C	-2.82327100	-4.13956100	0.22186000
H	2.08234700	-5.29871600	-1.62382600	H	-3.25648600	-4.52900700	1.13674300
C	1.17161700	-3.43029400	-1.10495600	C	-2.08594700	-2.96359500	0.25857600
H	2.09310900	-3.01309100	-0.71207100	H	-1.95828200	-2.43569500	1.19771600
C	0.00699800	1.30466400	0.53971600	C	0.73835300	1.19917700	-0.88400600
C	0.00642300	0.18049800	1.39183300	C	-0.66894800	1.22701800	-0.88547700
C	0.00193200	0.39303000	2.86287600	C	-1.36236400	2.54164600	-0.90462800
C	-1.17598200	0.23878900	3.59102100	C	-1.83471700	3.05688500	-2.11001200
H	-2.08952500	-0.06284000	3.08873200	H	-1.69777500	2.48379900	-3.02146900
C	-1.18297500	0.45297300	4.96207300	C	-2.47660200	4.28652400	-2.14785500
H	-2.10587100	0.33211700	5.51855400	H	-2.84036900	4.67665100	-3.09240300
C	-0.01372700	0.81597800	5.61741200	C	-2.65352300	5.01416200	-0.97797700
C	1.16294100	0.96636300	4.89600700	C	-2.18283800	4.50743900	0.22575200
H	2.08057000	1.24716600	5.40113100	H	-2.31652700	5.07041700	1.14310400
C	1.17118000	0.76024600	3.52349100	C	-1.53759900	3.27852300	0.26337900
H	2.09262700	0.89382600	2.96619100	H	-1.16057000	2.89705100	1.20652500
C	0.00610800	-0.18547600	-1.39974500	C	0.67112300	-1.23950800	-0.88254500
C	0.00607900	1.11454700	-0.85223500	C	1.39877200	-0.03478700	-0.87970700
C	0.00097800	2.28232400	-1.77174600	C	2.88403700	-0.09146800	-0.89957800
C	-1.17728200	2.98967300	-2.00167200	C	3.56201900	0.04843200	-2.10879200
H	-2.09058000	2.70502200	-1.48911200	H	2.99397600	0.20675700	-3.01993300
C	-1.18499900	4.07002300	-2.87257600	C	4.94769500	-0.00987700	-2.15106800
H	-2.10814800	4.61207300	-3.04576600	H	5.46394300	0.10143400	-3.09860300
C	-0.01614400	4.45647600	-3.51507900	C	5.67083300	-0.20856400	-0.98187700
C	1.16083600	3.75682100	-3.28524500	C	5.00108900	-0.35069600	0.22591500
H	2.07810900	4.05413800	-3.78149000	H	5.55887900	-0.50661900	1.14292000
C	1.16985100	2.67118100	-2.42057000	C	3.61421100	-0.29549100	0.26804300
H	2.09145900	2.12185300	-2.25805800	H	3.09922600	-0.42187800	1.21469400
Xe	-2.92179100	0.00007000	0.00008500	Xe	-0.01145000	-0.00187600	1.96197800
Xe	2.91822300	0.00047100	-0.00033300	O	-1.57708000	-0.43101700	2.65899500
O	3.62021500	-1.49277800	0.62526800	O	1.12909900	-1.14273800	2.68153600
O	3.61558500	0.20610100	-1.60823500	O	0.39116600	1.55756200	2.68811800
O	3.61670700	1.29107700	0.97973600	H	-3.58351300	-5.73096300	-1.00541700
O	-3.62037100	-0.99414400	1.27931300	H	-3.15664500	5.97454400	-1.00510100
O	-3.61950400	-0.61225600	-1.50027300	H	6.75402900	-0.25254100	-1.01260700
O	-3.62238300	1.60431900	0.22022300	C	-2.90705100	0.05515800	-0.85098900
H	-0.01820000	-6.28342300	-2.49501800	H	-3.32242600	-0.68215300	-1.53977100
H	-0.01949300	0.98045900	6.68928200	H	-3.26512900	-0.21018600	0.14841500
H	-0.02246200	5.30259300	-4.19334200	H	-3.30412200	1.03735300	-1.09737800
C	0.02744400	-2.32310900	1.75351700	C	1.50102900	2.49034000	-0.84464200
H	-0.69507800	-3.06766100	1.41583200	H	1.10586800	3.19796700	-1.57575700
H	1.01153300	-2.79910700	1.72021700	H	1.39667000	2.96170700	0.13689900
H	-0.18685600	-2.06130600	2.78622900	H	2.56121100	2.33808300	-1.03342500

C	0.02917200	2.67963600	1.13491000	C	1.41145000	-2.54373000	-0.83961900
H	-0.69062000	2.75926000	1.95095300	H	2.20446000	-2.56477600	-1.58971000
H	1.01469000	2.88936200	1.56027900	H	1.89660100	-2.67147600	0.13226700
H	-0.18783400	3.44288700	0.39241700	H	0.74840400	-3.39064100	-0.99980000
C	0.02653000	-0.35784300	-2.88806900				
H	-0.69260400	0.31015300	-3.36447700				
H	1.01207300	-0.09618300	-3.28354100				
H	-0.19263500	-1.38222000	-3.17719600				

(XeO ₃ :TPB-NH ₂) ^{iSw}				(XeO ₃ :TPB-NH ₂) ^{Mono}			
C	0.01171500	-0.84257300	-1.12849900	C	-0.21828000	1.38555600	-0.91794200
C	0.00619400	0.55950100	-1.30232900	C	-1.31825600	0.50675900	-0.88929000
C	0.00303800	1.14547300	-2.66461300	C	-2.70161700	1.03900000	-0.87661100
C	-1.13354500	1.79539600	-3.15119500	C	-3.51013600	0.93416100	-2.00958100
H	-2.02077100	1.86647700	-2.52911100	H	-3.11146600	0.45738100	-2.89872000
C	-1.13438900	2.34796800	-4.42491200	C	-4.80600200	1.43065100	-2.00172700
H	-2.02411700	2.84782500	-4.79202100	H	-5.42297900	1.34194500	-2.88954500
C	-0.00499200	2.25264000	-5.22751000	C	-5.30974100	2.04493800	-0.86181800
C	1.12768000	1.60423600	-4.75227100	C	-4.51343800	2.15677800	0.27019400
H	2.01409000	1.52975100	-5.37273700	H	-4.90209700	2.62938400	1.16576400
C	1.13484100	1.05501500	-3.47734800	C	-3.21847400	1.65431800	0.26576100
H	2.02284300	0.55298000	-3.10622100	H	-2.60109800	1.73633400	1.15554300
C	-0.00252000	-0.55768600	1.29281500	C	1.30922100	-0.50306300	-0.91778200
C	0.00060400	-1.40926500	0.16564500	C	1.09813300	0.88891300	-0.88861700
C	-0.00990000	-2.88203600	0.33928600	C	2.25077600	1.82078600	-0.87563600
C	-1.14490000	-3.62476100	0.00562400	C	2.56457900	2.57310000	-2.00871500
H	-2.02582700	-3.11902900	-0.37826900	H	1.95255700	2.46606500	-2.89798400
C	-1.15282500	-5.00398800	0.16435000	C	3.64255300	3.44701500	-2.00081200
H	-2.04154300	-5.56852900	-0.09586800	H	3.87449400	4.02545200	-2.88871000
C	-0.03191900	-5.65531700	0.66255000	C	4.42614300	3.57633000	-0.86073900
C	1.09906200	-4.92328600	1.00051000	C	4.12452100	2.83110400	0.27138700
H	1.97890000	-5.42634700	1.38658300	H	4.72794100	2.93156100	1.16707100
C	1.11324300	-3.54461200	0.83852800	C	3.04182500	1.96093900	0.26690100
H	2.00024600	-2.97564600	1.09900200	H	2.80389200	1.38546400	1.15674000
C	0.00244300	1.39669300	-0.16445000	C	-1.09012900	-0.88161500	-0.91851300
C	-0.00803400	0.84645900	1.13680200	C	0.22090500	-1.39482100	-0.88927400
C	-0.02959500	1.73345400	2.32510900	C	0.45168600	-2.85896600	-0.87659800
C	-1.17288700	1.81744200	3.12320200	C	0.94739100	-3.50665500	-2.00932900
H	-2.05183300	1.23260200	2.86879300	H	1.16146400	-2.92294600	-2.89830700
C	-1.19163800	2.64559300	4.23746800	C	1.16531300	-4.87716700	-2.00144900
H	-2.08669900	2.70388700	4.84715700	H	1.55113400	-5.36707300	-2.88907600
C	-0.07341900	3.40186600	4.56347100	C	0.88450700	-5.62064200	-0.86176100
C	1.06603200	3.32645600	3.77283800	C	0.38886600	-4.98702700	0.27002200
H	1.94385800	3.91158900	4.02440100	H	0.17337200	-5.55999400	1.16541400
C	1.09108200	2.49588400	2.66073400	C	0.17656600	-3.61432000	0.26556300
H	1.98459600	2.43553100	2.04730000	H	-0.20370900	-3.12067000	1.15510800
Xe	-2.85564600	-0.00332600	-0.01576100	Xe	-0.00060000	-0.00049300	1.87711100
Xe	2.89387900	0.00462400	0.01671000	O	-0.55945800	1.51284300	2.60741600
O	3.61664400	-0.47934900	-1.52057900	O	-1.03254500	-1.24144300	2.60581600
O	3.60034900	1.58397400	0.37222300	O	1.58933200	-0.27405500	2.60723600
O	3.59962000	-1.08671800	1.21285300	H	-6.32205100	2.43426100	-0.85599900
O	-3.55982200	-1.23610500	-1.06866700	H	5.26952400	4.25827700	-0.85488700
O	-3.56140200	1.52022700	-0.56767800	H	1.05348900	-6.69199100	-0.85591600
O	-3.58267900	-0.29143700	1.56931900	N	-0.43149500	2.73354300	-0.96808900
H	-0.00773300	2.68290300	-6.22305500	H	0.33569400	3.33268700	-0.71290000
H	-0.04007800	-6.73253100	0.78805800	H	-1.34770900	3.06603900	-0.71817300
H	-0.09013900	4.05000000	5.43288400	N	2.58326300	-0.99233900	-0.96754200
N	0.04360600	-1.65027800	-2.21225700	H	2.71843600	-1.95639600	-0.71258500
H	-0.07140800	-2.64147000	-2.09903800	H	3.32913000	-0.36517900	-0.71690700
H	-0.04907900	-1.25561600	-3.13108300	N	-2.15086400	-1.74029400	-0.96901900
N	0.01329200	-1.09227400	2.53457500	H	-3.05337800	-1.37552800	-0.71389400
H	-0.10537300	-0.49796200	3.33526900	H	-1.98066700	-2.69999400	-0.71904900
H	-0.08426500	-2.08492000	2.65152500				

N	0.02475000	2.73948300	-0.32224200	
H	-0.09113900	3.13536400	-1.23789900	
H	-0.08455500	3.33645600	0.47796500	

(XeO ₃ :TPB-CCH) ^{iSw}				(XeO ₃ :TPB-CCH) ^{Mono}			
C	0.00847800	-1.26189600	-0.61376300	C	0.47134800	-1.31727000	-0.89669900
C	0.00132100	-1.17390800	0.79366400	C	1.38453900	-0.24630800	-0.90435600
C	-0.00799500	-2.39772500	1.62160300	C	2.84060600	-0.50279900	-0.91702000
C	1.07735900	-2.69420800	2.44244100	C	3.59883800	-0.13847800	-2.02662900
H	1.93191900	-2.02733700	2.47474700	H	3.11398900	0.33549100	-2.87295200
C	1.06770400	-3.84711800	3.21230900	C	4.96363800	-0.38048800	-2.04896200
H	1.92082300	-4.07916100	3.84013800	H	5.54606100	-0.10126900	-2.92025200
C	-0.03000200	-4.69725600	3.18136400	C	5.58230900	-0.97457700	-0.95637600
H	-0.03886600	-5.59464800	3.79047400	H	6.65129100	-1.15779500	-0.97091800
C	-1.11650600	-4.39752800	2.36996300	C	4.82991500	-1.33244700	0.15446300
H	-1.97815200	-5.05542500	2.34596600	H	5.30842300	-1.79217600	1.01221900
C	-1.10414400	-3.25622400	1.58308800	C	3.46174700	-1.10580100	0.17350800
H	-1.94958600	-3.02947200	0.94266600	H	2.87488000	-1.39192300	1.03925600
C	0.01149900	1.16365600	-0.78543800	C	-1.38666300	0.24376100	-0.89677200
C	0.01383300	-0.09982900	-1.41302700	C	-0.91550900	-1.08247500	-0.89575800
C	0.01887700	-0.20550000	-2.88678300	C	-1.86361800	-2.21696400	-0.90477800
C	1.10825100	-0.77431000	-3.54238000	C	-1.92154400	-3.05739200	-2.01345000
H	1.95468700	-1.14074000	-2.97195500	H	-1.26746300	-2.87280500	-2.85845500
C	1.11246900	-0.86510000	-4.92572900	C	-2.80881800	-4.12209400	-2.03676700
H	1.96878200	-1.29713100	-5.43157000	H	-2.85364300	-4.76734800	-2.90736700
C	0.02429300	-0.40875100	-5.65811600	C	-3.63357700	-4.36321600	-0.94541700
H	0.02630900	-0.48821100	-6.73981200	H	-4.32292500	-5.20052600	-0.96010300
C	-1.06663200	0.14916500	-5.00441300	C	-3.57310400	-3.53120100	0.16455900
H	-1.92120600	0.50197300	-5.57102900	H	-4.21121800	-3.71779800	1.02132400
C	-1.06773000	0.26107900	-3.62260200	C	-2.69724500	-2.45574600	0.18451200
H	-1.91658200	0.70497100	-3.11422900	H	-2.65612100	-1.80395100	1.05021800
C	-0.00118700	0.09945200	1.40048400	C	0.89422300	1.07200800	-0.90549200
C	0.00248100	1.27454900	0.62067800	C	-0.49012600	1.32784300	-0.90236000
C	-0.00539900	2.60318200	1.26754800	C	-0.99624600	2.71694300	-0.91094200
C	1.08248900	3.46006400	1.11877800	C	-1.71109400	3.18698900	-2.00956100
H	1.93830000	3.15309000	0.52767900	H	-1.89505900	2.52634900	-2.84955400
C	1.07340900	4.70251100	1.73393900	C	-2.18299100	4.49021200	-2.02918700
H	1.92857800	5.36024200	1.62485100	H	-2.73156600	4.85171600	-2.89212100
C	-0.02600000	5.10262600	2.48224100	C	-1.95689400	5.32780800	-0.94434500
H	-0.03401100	6.07824600	2.95601000	H	-2.33187200	6.34552400	-0.95669700
C	-1.11503500	4.25240600	2.62343800	C	-1.25110700	4.85958300	0.15597600
H	-1.97804700	4.56166500	3.20255300	H	-1.07618900	5.50747800	1.00784100
C	-1.10320900	3.00107900	2.02692100	C	-0.76405800	3.56110900	0.17184000
H	-1.95096900	2.33554600	2.14749400	H	-0.20723400	3.19943100	1.02912800
Xe	3.03175600	0.01114400	0.01334400	Xe	0.00126900	0.00799300	2.08087500
Xe	-3.02001000	0.00629300	-0.02707500	O	1.12417500	-1.16291800	2.77236600
O	-3.71031700	-1.60875200	-0.17362500	O	0.46218300	1.56077300	2.77771600
O	-3.73610800	0.69914500	1.42655500	O	-1.56605900	-0.37290500	2.79305500
O	-3.68634800	0.93025800	-1.37190800	C	0.95769200	-2.65372500	-0.87940400
O	3.73877000	-1.05952500	-1.19487800	C	1.36831000	-3.78199200	-0.85454700
O	3.70727200	-0.50352000	1.55765300	H	1.73266500	-4.78187300	-0.82745900
O	3.72138700	1.60257000	-0.30008900	C	1.80958700	2.16062500	-0.89915400
C	0.00855100	-2.53983500	-1.23431400	C	2.58385900	3.07852300	-0.88542100
C	0.00803100	-3.62046400	-1.75693000	H	3.26962100	3.89258300	-0.86828600
H	0.00642500	-4.57912300	-2.22053200	C	-2.78749200	0.48945200	-0.87872300
C	-0.00854300	0.19912300	2.81754000	C	-3.97026000	0.69589300	-0.85321400
C	-0.01432500	0.28275200	4.01498400	H	-5.01861500	0.87880500	-0.82545700
H	-0.01959100	0.35631400	5.07730200				
C	0.01829600	2.34049500	-1.58107000				
C	0.02553200	3.33457700	-2.25384900				
H	0.03162800	4.21658800	-2.85048300				

(XeO ₃ :TPB-F) ^{iSw}				(XeO ₃ :TPB-F) ^{Mono}			
C	-0.00442600	1.23358600	-0.59208300	C	0.14701600	-1.35718500	-0.98109700
C	-0.00223600	1.17761000	0.80431900	C	1.30309300	-0.57637200	-0.96922300
C	-0.00577800	2.39591800	1.63620400	C	2.65186500	-1.17492100	-0.93580900
C	-1.00355300	2.58475500	2.59064700	C	3.60250500	-0.82202500	-1.89144100
H	-1.78331400	1.84153500	2.71663400	H	3.34617500	-0.10922600	-2.66685100
C	-1.00760600	3.73363400	3.36634000	C	4.86931500	-1.38376900	-1.85504300
H	-1.79077600	3.88104000	4.10138700	H	5.60201100	-1.10694500	-2.60501700
C	-0.01410800	4.69004800	3.20147800	C	5.19853000	-2.29579300	-0.86061700
C	0.98359000	4.49961900	2.25423900	C	4.25565200	-2.64590800	0.09670400
H	1.76349700	5.24170100	2.12600400	H	4.50930400	-3.35163800	0.87981100
C	0.98791400	3.35833700	1.46737500	C	2.98514100	-2.09168100	0.06012200
H	1.77069500	3.20873000	0.73176400	H	2.25514200	-2.35991600	0.81584600
C	0.00245400	-1.12931300	-0.77077000	C	-1.24567000	0.55243900	-0.98233300
C	-0.00250300	0.10804600	-1.42049100	C	-1.14754500	-0.83913400	-0.97436900
C	-0.00548100	0.21934200	-2.89152800	C	-2.34078400	-1.70734500	-0.94232800
C	-1.00665700	0.94584700	-3.53346800	C	-2.51206300	-2.70654900	-1.89823500
H	-1.79027400	1.42165800	-2.95398200	H	-1.76709900	-2.84144600	-2.67405700
C	-1.00908100	1.04391600	-4.91622600	C	-3.63241500	-3.52216900	-1.86080200
H	-1.79485700	1.60236800	-5.41228200	H	-3.76031800	-4.29474800	-2.61093700
C	-0.01073600	0.42931400	-5.66087800	C	-4.58544400	-3.35142400	-0.86498300
C	0.99013100	-0.29036700	-5.02117400	C	-4.41534900	-2.36057200	0.09283000
H	1.77376800	-0.76758400	-5.59871900	H	-5.15208100	-2.22768900	0.87718500
C	0.99294100	-0.40190100	-3.63941300	C	-3.29986100	-1.53792300	0.05505400
H	1.77832600	-0.95973000	-3.14118800	C	-3.16523300	-0.77272200	0.81149800
C	0.00213900	-0.10257100	1.36486700	H	1.10463800	0.80378700	-0.97766800
C	0.00485200	-1.28393000	0.61822900	C	-0.14972900	1.41467300	-0.97103900
C	0.01105900	-2.61358500	1.25731400	C	-0.30556400	2.88208000	-0.93851200
C	-0.98368400	-3.53967500	0.94923000	C	-1.08754500	3.52865200	-1.89360400
H	-1.76965600	-3.28040900	0.24840500	H	-1.57774500	2.95002800	-2.66813400
C	-0.97700300	-4.78643200	1.55521200	C	-1.23448300	4.90660600	-1.85749600
H	-1.75785100	-5.50072400	1.31973200	H	-1.84147300	5.40244300	-2.60692200
C	0.02410900	-5.11725500	2.45924500	C	-0.60834500	5.64805300	-0.86390600
C	1.01848400	-4.19635900	2.76274900	C	0.16730100	5.00681000	0.09282700
H	1.80416600	-4.45252200	3.46450700	H	0.65239600	5.57953100	0.87534300
C	1.01210200	-2.94376400	2.16889500	C	0.32262800	3.62941300	0.05653300
H	1.79229900	-2.22779600	2.40312400	H	0.92010500	3.13137200	0.81203600
Xe	-3.02953100	-0.00932500	0.00341300	Xe	-0.00472100	-0.00097200	1.99361900
Xe	3.02979300	0.00887600	-0.00396500	O	0.60398400	-1.50111000	2.69309900
O	3.70676500	1.62332400	-0.20806300	O	0.99543800	1.28075000	2.67664600
O	3.71713000	-0.62110600	1.49174400	O	-1.60969400	0.22856600	2.68788800
O	3.70901100	-0.97103200	-1.30196200	H	6.19119700	-2.73152300	-0.83048200
O	-3.71971900	1.14998100	-1.13057700	H	-5.45945700	-3.99275900	-0.83420100
O	-3.71237100	0.38613500	1.57937200	H	-0.72742400	6.72558800	-0.83390600
O	-3.69978800	-1.57873900	-0.43729700	F	2.17947900	1.58834700	-0.97541400
H	-0.01734800	5.58585000	3.81265700	F	-2.46279700	1.09069500	-0.98426800
H	-0.01280700	0.51130200	-6.74221300	F	0.28934800	-2.68037100	-0.98154900
H	0.02925200	-6.09491900	2.92845800				
F	0.00398300	-0.20255600	2.68709600				
F	0.00520900	-2.22426400	-1.51852600				
F	-0.00908700	2.42863900	-1.16658000				

(XeO ₃ :TPB-CN) ^{iSw}				(XeO ₃ :TPB-CN) ^{Mono}			
C	0.00449900	-1.25152100	-0.61002500	C	0.32076200	-1.35861200	-0.94899700
C	-0.00550200	-1.17720100	0.79581100	C	1.35791300	-0.41006100	-0.94900200
C	-0.01158300	-2.39702100	1.62015300	C	2.77041400	-0.83127500	-0.92541400
C	1.02130500	-2.62724200	2.52855500	C	3.63256300	-0.44409000	-1.94995300
H	1.83500200	-1.91657500	2.62460900	H	3.26222900	0.16342200	-2.76797000
C	1.01697300	-3.78072800	3.29529000	C	4.95864500	-0.84312300	-1.92627000
H	1.82798000	-3.96382800	3.99061400	H	5.62332500	-0.54648300	-2.72955100
C	-0.02290600	-4.69337700	3.17506600	C	5.43396500	-1.61489400	-0.87388400
H	-0.02760500	-5.59113600	3.78316400	H	6.47431500	-1.92002000	-0.85314600
C	-1.05680600	-4.45922900	2.27782700	C	4.57931100	-1.99434600	0.15240800

H	-1.87234100	-5.16720300	2.18608400	H	4.94797400	-2.59152100	0.97844600
C	-1.04980500	-3.31923100	1.49119700	C	3.24755000	-1.61251500	0.12600900
H	-1.85916000	-3.13877300	0.79219900	H	2.58361000	-1.90744100	0.93106400
C	0.00841300	1.15565900	-0.77941300	C	-1.33493400	0.39176000	-0.95344700
C	0.01082300	-0.09892800	-1.41823400	C	-1.03213100	-0.98069200	-0.94920100
C	0.01904900	-0.20280000	-2.88682100	C	-2.10592400	-1.99050600	-0.91828600
C	1.06025400	-0.86990700	-3.53176600	C	-2.21089600	-2.93839300	-1.93470100
H	1.87066100	-1.30534700	-2.95742100	H	-1.50197000	-2.93265400	-2.75491500
C	1.06745800	-0.95725100	-4.91412600	C	-3.22684400	-3.87954000	-1.90054800
H	1.88477200	-1.46442300	-5.41362700	H	-3.30995700	-4.60872300	-2.69835300
C	0.03095200	-0.40167300	-5.65296900	C	-4.13044400	-3.89041200	-0.84574500
H	0.03563000	-0.47948800	-6.73448200	H	-4.92053500	-4.63256100	-0.81781400
C	-1.01166600	0.25290500	-5.01013300	C	-4.02203100	-2.95346200	0.17298900
H	-1.82470000	0.68221800	-5.58404500	H	-4.72158700	-2.96218400	1.00086000
C	-1.01645300	0.36403400	-3.62953900	C	-3.01863900	-1.99877300	0.13582400
H	-1.83294700	0.87494300	-3.13091700	C	-2.93814100	-1.26950100	0.93453900
C	-0.00908100	0.09904100	1.39008800	H	1.00862200	0.95079400	-0.95073700
C	-0.00172300	1.27925400	0.62306300	C	-0.33120200	1.37473800	-0.95188600
C	-0.00604800	2.60312800	1.26712200	C	-0.67177500	2.80899200	-0.92623500
C	1.03390600	3.49947000	1.02207400	C	-1.43828500	3.36581600	-1.94841700
H	1.85293000	3.22268000	0.36718100	H	-1.77982700	2.74433000	-2.76844000
C	1.02951100	4.74092000	1.63634500	C	-1.75504000	4.71391800	-1.92016500
H	1.84602500	5.43021700	1.45496200	H	-2.34413100	5.14401800	-2.72206600
C	-0.01728600	5.09935800	2.47573900	C	-1.32410100	5.50800300	-0.86517700
H	-0.02181900	6.07533900	2.94818700	H	-1.58005900	6.56143500	-0.84070100
C	-1.05820500	4.21080000	2.71166700	C	-0.56794500	4.95375700	0.15877200
H	-1.87912000	4.49022500	3.36186300	H	-0.23458900	5.56833900	0.98707200
C	-1.05161400	2.95893300	2.11890600	C	-0.23318400	3.60952900	0.12763500
H	-1.86688500	2.26803800	2.30473300	H	0.35504300	3.18006000	0.93114200
Xe	3.10175100	-0.00265100	0.01733200	Xe	0.00598300	0.00531100	2.11555300
Xe	-3.10035900	-0.00020600	-0.01690900	O	0.95495800	-1.31476800	2.79416000
O	-3.77179700	-1.62775600	-0.06238900	O	0.69759200	1.48896000	2.76783200
O	-3.78115000	0.77672100	1.40946200	O	-1.60129100	-0.13585200	2.82307000
O	-3.76515800	0.84992400	-1.40892000	C	-2.70597400	0.79913700	-0.96168900
O	3.77783600	-1.03997900	-1.23565200	N	-3.80882100	1.12881700	-0.97943600
O	3.76724800	-0.57121100	1.54593900	C	0.65309400	-2.74971200	-0.95045600
O	3.77476800	1.60315600	-0.25026600	N	0.91838100	-3.86986300	-0.96241400
C	0.01647400	2.34096200	-1.57949600	C	2.04675800	1.93472600	-0.95328200
N	0.02297800	3.29506400	-2.22301800	N	2.88325200	2.72553300	-0.96549100
C	0.00788700	-2.53741800	-1.23581700				
N	0.01072600	-3.57235000	-1.73921500				
C	-0.02137400	0.19967500	2.81656400				
N	-0.03117400	0.28111800	3.96450300				

(XeO ₃ :18O6) ^{iSw}				(XeO ₃ :TPB-H) ^{shifted}			
O	1.87004500	1.38262700	-2.16375700	C	1.88110700	0.74631500	-1.26059200
O	-0.42059300	0.00135400	-2.86121700	H	2.68620200	1.32435200	-1.69983300
O	1.86810000	-1.38356200	-2.16461100	C	0.79071500	1.41115700	-0.69479500
O	-1.21859900	2.34900500	-0.62374600	C	0.72114200	2.88192600	-0.67208300
C	-0.74487900	3.50237300	0.03204200	C	-0.49398400	3.53216900	-0.89483200
C	0.74952200	3.50139900	-0.02974400	H	-1.38587200	2.95176600	-1.10646600
O	1.22169900	2.34695000	0.62525700	C	-0.56127800	4.91650100	-0.86791300
H	-1.12528900	4.40547200	-0.46676800	H	-1.50890300	5.41064000	-1.05165700
H	-1.09127900	3.50608300	1.07278800	C	0.57898700	5.66695600	-0.60980000
H	1.09593100	3.50535700	-1.07048600	H	0.52326100	6.74972100	-0.58440300
H	1.13113500	4.40364800	0.46968300	C	1.78933600	5.02664000	-0.37719300
C	2.62786700	2.36453000	0.72196200	H	2.67911300	5.60618500	-0.15723600
C	3.06931900	1.15430200	1.47984500	C	1.86156800	3.64246300	-0.41023500
O	2.70519200	-0.00206400	0.75978300	H	2.80248400	3.14734900	-0.19367100
H	4.16056200	1.18668700	1.61246100	C	0.92476400	-1.38255800	-0.68973700
H	2.59564000	1.13478700	2.46843900	H	0.98255700	-2.46499800	-0.67955300
H	3.07025500	2.37881500	-0.28098300	C	1.96657000	-0.64625200	-1.25903600
H	2.95657300	3.26387700	1.26265500	C	3.14544700	-1.32850800	-1.82156300

C	3.06782800	-1.15938400	1.47906000	C	3.68839000	-0.91772600	-3.03924600
C	2.62474400	-2.36851400	0.72038000	H	3.21980200	-0.10749400	-3.58797300
O	1.21859900	-2.34900500	0.62374600	C	4.79999200	-1.55858500	-3.56449600
H	4.15903300	-1.19329300	1.61160700	H	5.20602600	-1.23798800	-4.51766800
H	2.59421600	-1.13990800	2.46768600	C	5.38756400	-2.61197800	-2.87525000
H	3.06707000	-2.38270100	-0.28259300	H	6.25964700	-3.11016400	-3.28430000
H	2.95228300	-3.26866200	1.26044900	C	4.85744800	-3.02184800	-1.65877100
C	0.74487900	-3.50237300	-0.03204200	H	5.32146800	-3.83267400	-1.10809100
C	-0.74952200	-3.50139900	0.02974400	C	3.74114000	-2.38731400	-1.13466700
O	-1.22169900	-2.34695000	-0.62525700	H	3.35306100	-2.68544500	-0.16629500
H	-1.13113500	-4.40364800	-0.46968300	C	-0.22999700	0.65212700	-0.12307400
H	-1.09593100	-3.50535700	1.07048600	H	-1.07875500	1.15512500	0.32464400
H	1.09127900	-3.50608300	-1.07278800	C	-0.17585100	-0.74173800	-0.12336700
H	1.12528900	-4.40547200	0.46676800	C	-1.28176300	-1.51489800	0.46956400
C	-2.62786700	-2.36453000	-0.72196200	C	-1.81141000	-2.62199900	-0.20115400
C	-3.06931900	-1.15430200	-1.47984500	H	-1.39239500	-2.91379700	-1.15745700
O	-2.70519200	0.00206400	-0.75978300	C	-2.90242800	-3.30588900	0.31784500
H	-2.95657300	-3.26387700	-1.26265500	H	-3.31448500	-4.15080900	-0.22254400
H	-3.07025500	-2.37881500	0.28098300	C	-3.47448100	-2.89907200	1.51946700
H	-2.59564000	-1.13478700	-2.46843900	H	-4.32935500	-3.43057100	1.92207800
H	-4.16056200	-1.18668700	-1.61246100	C	-2.94124000	-1.81272200	2.20425500
C	-3.06782800	1.15938400	-1.47906000	H	-3.37119400	-1.49995500	3.14908200
C	-2.62474400	2.36851400	-0.72038000	C	-1.85214700	-1.12393000	1.68542600
H	-2.95228300	3.26866200	-1.26044900	H	-1.42606500	-0.28920700	2.22975000
H	-3.06707000	2.38270100	0.28259300	Xe	-3.95432400	-0.20758100	-0.61973400
H	-2.59421600	1.13990800	-2.46768600	Xe	2.16714100	0.00762200	1.93755700
H	-4.15903300	1.19329300	-1.61160700	O	3.36211200	1.23848200	2.34215500
Xe	-0.89052400	-0.00007300	1.68702600	O	0.92211200	0.13479100	3.18272500
O	-1.86810000	1.38356200	2.16461100	O	2.96128700	-1.53758200	2.24555600
O	-1.87004500	-1.38262700	2.16375700	O	-3.18003200	-0.26611600	-2.20133800
O	0.42059300	-0.00135400	2.86121700	O	-3.52800500	1.37970400	0.02538900
Xe	0.89052400	0.00007300	-1.68702600	O	-5.68450700	-0.12823800	-0.94241000

ABSTRACT

Name of the Student: Soumya Ranjan Dash **Registration No.:** 10CC21A26058
Faculty of Study: Chemical Sciences **Year of Submission:** 2024
AcSIR academic centre/CSIR Lab: CSIR-NCL **Name of the Supervisor:** Dr. Kumar Vanka
Title of the thesis: Taming XeO₃: Insights from Computational Investigations of Sigma Hole-Mediated Aerogen Bonding

This thesis explores the fundamentals of non-covalent interactions (NCIs), with a particular focus on “aerogen bonding”. This interaction arises due to the presence of sigma (σ) holes, which are localized regions of positive electrostatic potential typically found along the extension of covalent bonds when highly electronegative atoms are bonded to a central atom. Additionally, the thesis provides a brief history of the development and understanding of sigma holes to date.

The presence of σ -holes, which contribute to the explosiveness of XeO₃, could also be leveraged to stabilize it, if XeO₃ was bound with an appropriate host. This host could be a Lewis base or an anion capable of donating electrons to mitigate the electron deficiency in the σ -hole regions, as aerogen bonding is predominantly electrostatic in nature. Although XeO₃ has been proposed as a clean and potent oxidant—producing xenon as a byproduct, which is utilized as fuel in ion thrusters for spacecraft like NASA's Dawn for space missions—its explosiveness and shock sensitivity present significant challenges to its storage and practical application. Our goal is to identify the most effective host to stabilize XeO₃ from a pool of potential candidates, investigate the primary factors contributing to stabilization, and establish guidelines to mitigate risks associated with experimental exploration.

In this thesis, we have explored various macrocyclic ligands, such as crown ethers (-O) of different sizes, along with their thio (-S) and aza (-NR) analogues, for stabilizing XeO₃. Additionally, we have also explored different non-aromatic co-ordinating solvents as readily available off the shelf hosts to stabilize XeO₃. Different trends in the strength of these host-guest complexes, along with the important factors contributing to their stabilization, have been thoroughly examined by employing various computational tools such as the mapping of the electrostatic potential surface (MESP), Wiberg bond indices (WBIs), non-covalent interaction (NCI) plots, Bader's theory of atoms-in-molecules (AIM), natural bond orbital (NBO) analysis, and the energy decomposition analysis (EDA). Overall, our findings contribute to the broader understanding of σ -hole-mediated noble gas complexes as well as supramolecular chemistry.

List of all publication(s) in SCI Journal(s) (published & accepted) with complete bibliographic details

- 1) **Dash, S. R.;** Vanka, K., Unveiling the Inverse Sandwich Complexes of XeO₃: A Computational Exploration. *Inorganic Chemistry* **2024**, 63 (29), 13585-13593.
- 2) **Dash, S. R.;** Vanka, K., Taming XeO₃ with Aza-Crowns: Computational Studies into σ -Hole Mediated Host-Guest Interactions. *ChemPhysChem* **2024**, e202400302.
- 3) **Dash, S. R.;** Sharma, H.; Tiwari, M. K.; Greb, L.; Vanka, K., Size Matters: Computational Insights into the Crowning of Noble Gas Trioxides. *Inorganic Chemistry* **2024**, 63 (9), 4099-4107.
- 4) **Dash, S. R.;** Vanka, K., Exploring Unconventional σ -Hole Interactions: Computational Insights into the Interaction of XeO₃ with Non-Aromatic Coordinating Solvents. *ChemPhysChem* **2024**, 25, e202300908.

Other Publications

- 1) Hossain, M. J.; Shah, B. K.; **Dash, S. R.;** Kashish; Vanka, K.; Khan, S., Ce[N(SiMe₃)₂]₃(THF)₃-Catalyzed Hydroboration of CO₂, Esters and Epoxides with Pinacolborane: Selective Synthesis of Methanol in Multigram Scale. *Chemistry-A European Journal* **2025**, e202403449.
- 2) Gour, K.; Pramanik, D.; **Dash, S. R.;** Shinde, D.; Venugopal, G.; Vanka, K.; Rath, A.; Sen, S.S., Germylene Mediated Reductive C–C and C–N Coupling of an Isocyanide and its Device Application. *Angewandte Chemie International Edition* **2024**, e202417052.
- 3) **Dash, S. R.;**[‡] Pandya, R.;[‡] Singh, G.;[‡] Sharma, H.;[‡] Das, T.;[‡] Halder, H.; Hotha, S.; Vanka, K., Unravelling the Prebiotic Origins of the Simplest α -Ketoacids in Cometary Ices: A Computational Investigation. *Chemical Communications* **2024**, 60, 11283-11286. ([‡]Equal Contribution)
- 4) Kundu, G.; Pramanik, D.; **Dash, S. R.;** Kumar, R.; Sangole, M. P.; Tothadi, S.; Ghosh, A.; Vanka, K.; Singh, K.; Sen, S. S., Unprecedented C–F bond cleavage from perfluoronaphthalene during cobaltocene reduction. *Dalton Transaction* **2024**, 53, 17789-17793.

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- 5) Shaikh, M. H.; Ramekar, R. V.; Jawoor, S.; **Dash, S. R.**; Birajadar, R. S.; Pawal, S. B.; Thenmani N.; Vanka K.; Chikkali, S. H., Designing of Imine Thiophene-Ligated Metal-Complexes and Implication in Ethylene Polymerization. *Journal of Macromolecular Science, Part A* **2024**, *61* (11), 874–884.
 - 6) Shaikh, S. R.; Gawade, R. L.; Dabke, N. B.; **Dash, S. R.**; Vanka, K.; Gonnade, R. G., Crystal Engineering for Intramolecular π - π Stacking: Effect of Substitution of Electron Donating and Withdrawing Group on Molecular Geometry in Conformationally Flexible Sulfoesters and Sulfonamides. *CrystEngComm* **2024**, *26*, 3557-3573.
 - 7) Gour, K.; Pramanik, D.; **Dash, S. R.**; Tothadi, S.; Vanka, K.; Sen, S. S., Activation of the Olefinic C–H Bond of NHC and NHO by Perimidine-Based Silicon and Germanium Compounds. *Organometallics* **2023**, *42* (15), 1909-1917.
 - 8) Kundu, G.; **Dash, S. R.**; Kumar, R.; Vanka, K.; Ghosh, A.; Sen, S. S., Enhancing Diradical Character of Chichibabin's Hydrocarbon through Fluoride Substitution. *ChemPlusChem* **2023**, *88* (8), e202300273.
 - 9) Mali, B. P.; **Dash, S. R.**; Annadhasan, M.; Biswas, A.; Manoj, K.; Vanka, K.; Gonnade, R. G., Cocrystal Approach to Modulate the Photoluminescent Properties of a GFP Chromophore Analogue: Role of Halogen/Hydrogen Bonding in Achieving a Wide Range of Solid-State Fluorescence Emissions. *Crystal Growth & Design* **2023**, *23* (7), 5052-5065.
 - 10) Nidhankar, A. D.; Goudappagouda; Kothavade, P.; Dongre, S. D.; Dnyaneshwar Veer, S.; **Dash, S. R.**; Rajeev, K.; Unni, K. N.; Shanmuganathan, K.; Santhosh Babu, S., Thermally Activated Delayed Fluorescent Solvent free Organic Liquid Hybrids for Tunable Emission Applications. *Chemistry–An Asian Journal* **2023**, *18* (13), e202300276.
 - 11) Gour, K.; Kundu, G.; **Dash, S. R.**; Vanka, K.; Tothadi, S.; Sen, S. S., Six-Membered NHC Stabilized Monomeric Zinc Complexes. *European Journal of Inorganic Chemistry* **2023**, *26* (21), e202300167.
 - 12) Agrawal, N. K.; **Dash, S. R.**; Vanka, K.; Jagirdar, B. R., Dual Routes toward Observation of a trans-H₂/Hydride Complex in an Iridium Pincer System and Hydrogenation Catalytic Activity. *Organometallics* **2023**, *42* (6), 441-456.
 - 13) Agrawal, N. K.; Gayathridevi, S.; **Dash, S. R.**; Vanka, K.; Jagirdar, B., H-atom site exchange in iridium trans-dihydrogen/hydride complex, trans-[Ir (H)(η^2 -H₂)(iPr) 4 (POCOP)(DMAP)]⁺. *Dalton Transactions* **2023**, *52*, 13858-13863.

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- 14) Kumar, R.; Pahar, S.; Chatterjee, J.; **Dash, S. R.**; Gonnade, R. G.; Vanka, K.; Sen, S. S., Luminescent magnesium complexes with intra-and inter-ligand charge transfer. *Chemical Communications* **2022**, 58 (84), 11843-11846.
 - 15) Kakde, N. R.; Bharathkumar, H.; Wavhal, B. A.; Nikam, A.; Patil, S.; **Dash, S. R.**; Vanka, K.; Krishnamoorthy, K.; Kulkarni, A.; Asha, S., Direct (hetero) arylation (DHAP) polymerization of conjugated polymers—new A–B–A monomer design for P (NDI2OD-T2) & the challenges of adopting DHAP for continuous flow processes. *Journal of Materials Chemistry C* **2022**, 10 (36), 13025-13039.
 - 16) Yadav, S.; Rajpurohit, D.; **Dash, S. R.**; Bhojani, G.; Chatterjee, S.; Paital, A. R., Hybrid material for ferric ion detection & remediation: Exceptional selectivity & adsorption capacity with biological applications. *Microporous and Mesoporous Materials* **2022**, 338, 111945.
 - 17) Ghule, S.; **Dash, S. R.**; Bagchi, S.; Joshi, K.; Vanka, K., Predicting the Redox Potentials of Phenazine Derivatives Using DFT-Assisted Machine Learning. *ACS omega* **2022**, 7 (14), 11742-11755.
 - 18) Agrawal, N. K.; **Dash, S. R.**; Vanka, K.; Nethaji, M.; Jagirdar, B. R., Reactivity of four coordinate iridium complex towards hydrogen: An experimental and computational study. *Journal of Organometallic Chemistry* **2022**, 965, 122317.
 - 19) Mali, B. P.; **Dash, S. R.**; Biswas, A.; Vanka, K.; Manoj, K.; Gonnade, R. G., Polymorphs of Green Fluorescence Protein Chromophore Analogue: Fluorescence Switching with Thermal Stimuli. *Crystal Growth & Design* **2022**, 22 (3), 1892-1905.
 - 20) Jadhav, S. B.; **Dash, S. R.**; Maurya, S.; Nanubolu, J. B.; Vanka, K.; Chegondi, R., Enantioselective Cu (I)-catalyzed borylative cyclization of enone-tethered cyclohexadienones and mechanistic insights. *Nature Communications* **2022**, 13 (1), 854.
 - 21) Alam, M. N.; **Dash, S. R.**; Mukherjee, A.; Pandole, S.; Marelli, U. K.; Vanka, K.; Maity, P., [1, 3]-Claisen Rearrangement via Removable Functional Group Mediated Radical Stabilization. *Organic Letters* **2021**, 23 (3), 890-895.
 - 22) Rani, S.; **Dash, S. R.**; Bera, A.; Alam, M. N.; Vanka, K.; Maity, P., Phosphite mediated asymmetric N to C migration for the synthesis of chiral heterocycles from primary amines. *Chemical Science* **2021**, 12 (26), 8996-9003.
 - 23) **Dash, S. R.**,[‡] Das, T.,[‡] Vanka, K., Insights into Chemical Reactions at the Beginning of the Universe: From HeH⁺ to H₃⁺. *Frontiers in Chemistry* **2021**, 9, 679750. ([‡]Equal Contribution)
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**List of papers with abstract presented (oral/poster) at
national/international conferences/seminars with complete details**

1. Received Best Oral presentation award at the 6th NCL-RF Annual Student's Conference, at CSIR-NCL, Pune, India (November 2024).
Title: Going where Experimentalists Fear to Tread: Computational Chemistry to the Rescue in Understanding XeO₃ Chemistry
2. Delivered an Oral Talk and presented a Poster at CRSI-ACS Early Career Researchers' Symposium at KIITS Bhubaneshwar, India (October 2024)
Title: Going where Experimentalists Fear to Tread: Computational Chemistry to the Rescue in Understanding XeO₃ Chemistry
3. Delivered an Oral Talk (Young Research Symposium) and presented a Poster on at CBOND2024, Vrije Universiteit Amsterdam, The Netherlands (September 2024).
Title: Going where Experimentalists Fear to Tread: Computational Chemistry to the Rescue in Understanding XeO₃ Chemistry
4. Presented Poster at 18th Theoretical Chemistry Symposium (TCS), IIT Madras, India (December 2023).
Title: *Size Matters: Computational Insights into the Crowning of Noble Gas Trioxides*
5. Presented Poster at the National Symposium On "Recent Trends in Inorganic Chemistry" (RTIC-2023), Maharaja Sayajirao University Baroda, India (October 2023).
Title: *Size Matters: Computational Insights into the Crowning of Noble Gas Trioxides*
6. Presented a poster on National Science Day Celebrations at CSIR-National Chemical Laboratory, Pune, India, February 2023.
Title: *Computational Insights into the Crowning of Noble Gas Trioxides*
7. Presented a research poster in International Conference on Main Group Synthesis And

Catalysis (ICMGSC), held in February 2023 at IISER Thiruvananthapuram, India.

Title: *Computational Insights into the Crowning of Noble Gas Trioxides*

8. Attended Virtual 20 h Chemistry Course “*Developments in Boron Chemistry: from Fundamental Studies to Applications*” corresponding to 3 ECTS Points within the European Credit Transfer and Accumulation System (Julius-Maximilians-Universität Würzburg, Oct, 2021).

About the Author



Mr. Soumya Ranjan Dash, son of Ganesh Chandra Dash and Kamalini Dash, was born in Balangir (Bolangir) district, Odisha, India, in 1992. He completed his B.Sc. (H) Chemistry from Kirori Mal College, Delhi University, New Delhi. He obtained his master's degree from The Maharaja Sayajirao University of Baroda. After qualifying GATE examination, he moved to Physical and Materials Chemistry Division, CSIR-National Chemical Laboratory, Pune, India as a project associate and later pursued his Ph.D. degree under the guidance of Dr. Kumar

Vanka. His research interest lies in “*Noncovalent Interactions*” & “*Origin of Life*”.

Education and Research Experience

Ph.D.: From August 2021 to till date, working under the supervision of Dr. Kumar Vanka at CSIR- National Chemical Laboratory.

Project Associate: CSIR-NCL (December 2018 to August 2021)
CSIR-CSMCRI (June 2017 to November 2018)

M.Sc.: (2014-2016) The Maharaja Sayajirao University of Baroda.

B.Sc.: (2011-2014) Kirori Mal College, Delhi University, India.

List of Scientific Contributions

34. **Dash, S. R.;** Vanka, K., Unveiling the Inverse Sandwich Complexes of XeO₃: A Computational Exploration. *Inorganic Chemistry* **2024**, 63 (29), 13585-13593.
33. **Dash, S. R.;** Vanka, K., Taming XeO₃ with Aza-Crowns: Computational Studies into σ -Hole Mediated Host-Guest Interactions. *ChemPhysChem* **2024**, e202400302.
32. Shaikh, S. R.; Gawade, R. L.; Dabke, N. B.; **Dash, S. R.;** Vanka, K.; Gonnade, R. G., Crystal Engineering for Intramolecular π - π Stacking: Effect of Substitution of Electron Donating and Withdrawing Group on Molecular Geometry in Conformationally Flexible Sulfoesters and Sulfonamides. *CrystEngComm* **2024**, 26, 3557-3573.

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31. **Dash, S. R.**; Sharma, H.; Tiwari, M. K.; Greb, L.; Vanka, K., Size Matters: Computational Insights into the Crowning of Noble Gas Trioxides. *Inorganic Chemistry* **2024**, 63 (9), 4099-4107.
30. **Dash, S. R.**; Vanka, K., Exploring Unconventional σ -Hole Interactions: Computational Insights into the Interaction of XeO₃ with Non-Aromatic Coordinating Solvents. *ChemPhysChem* **2024**, 25, e202300908.
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27. Mali, B. P.; **Dash, S. R.**; Annadhasan, M.; Biswas, A.; Manoj, K.; Vanka, K.; Gonnade, R. G., Cocystal Approach to Modulate the Photoluminescent Properties of a GFP Chromophore Analogue: Role of Halogen/Hydrogen Bonding in Achieving a Wide Range of Solid-State Fluorescence Emissions. *Crystal Growth & Design* **2023**, 23 (7), 5052-5065.
26. Nidhankar, A. D.; Goudappagouda; Kothavade, P.; Dongre, S. D.; Dnyaneshwar Veer, S.; **Dash, S. R.**; Rajeev, K.; Unni, K. N.; Shanmuganathan, K.; Santhosh Babu, S., Thermally Activated Delayed Fluorescent Solvent free Organic Liquid Hybrids for Tunable Emission Applications. *Chemistry–An Asian Journal* **2023**, 18 (13), e202300276.
25. Gour, K.; Kundu, G.; **Dash, S. R.**; Vanka, K.; Tothadi, S.; Sen, S. S., Six-Membered NHC Stabilized Monomeric Zinc Complexes. *European Journal of Inorganic Chemistry* **2023**, 26 (21), e202300167.
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23. Agrawal, N. K.; Gayathridevi, S.; **Dash, S. R.**; Vanka, K.; Jagirdar, B., H-atom site exchange in iridium trans-dihydrogen/hydride complex, trans-[Ir (H)(η^2 -H₂)(iPr)₄ (POCOP)(DMAP)]⁺. *Dalton Transactions* **2023**, 52, 13858-13863.
22. Kumar, R.; Pahar, S.; Chatterjee, J.; **Dash, S. R.**; Gonnade, R. G.; Vanka, K.; Sen, S. S., Luminescent magnesium complexes with intra-and inter-ligand charge transfer. *Chemical Communications* **2022**, 58 (84), 11843-11846.
21. Kakde, N. R.; Bharathkumar, H.; Wavhal, B. A.; Nikam, A.; Patil, S.; **Dash, S. R.**; Vanka, K.; Krishnamoorthy, K.; Kulkarni, A.; Asha, S., Direct (hetero) arylation (DHAP) polymerization of conjugated polymers—new A–B–A monomer design for P (NDI2OD-T2)
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- & the challenges of adopting DHAP for continuous flow processes. *Journal of Materials Chemistry C* **2022**, 10 (36), 13025-13039.
20. Yadav, S.; Rajpurohit, D.; **Dash, S. R.**; Bhojani, G.; Chatterjee, S.; Paital, A. R., Hybrid material for ferric ion detection & remediation: Exceptional selectivity & adsorption capacity with biological applications. *Microporous and Mesoporous Materials* **2022**, 338, 111945.
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 18. Babu, P.; **Dash, S. R.**; Parida, K., Mechanistic insight the visible light driven hydrogen generation by plasmonic Au-Cu alloy mounted on TiO₂@ B-doped g-C₃N₄ heterojunction photocatalyst. *Journal of Alloys and Compounds* **2022**, 909, 164754.
 17. Agrawal, N. K.; **Dash, S. R.**; Vanka, K.; Nethaji, M.; Jagirdar, B. R., Reactivity of four coordinate iridium complex towards hydrogen: An experimental and computational study. *Journal of Organometallic Chemistry* **2022**, 965, 122317.
 16. Mali, B. P.; **Dash, S. R.**; Biswas, A.; Vanka, K.; Manoj, K.; Gonnade, R. G., Polymorphs of Green Fluorescence Protein Chromophore Analogue: Fluorescence Switching with Thermal Stimuli. *Crystal Growth & Design* **2022**, 22 (3), 1892-1905.
 15. Jadhav, S. B.; **Dash, S. R.**; Maurya, S.; Nanubolu, J. B.; Vanka, K.; Chegondi, R., Enantioselective Cu (I)-catalyzed borylative cyclization of enone-tethered cyclohexadienones and mechanistic insights. *Nature Communications* **2022**, 13 (1), 854.
 14. Babu, P.; **Dash, S. R.**; Behera, A.; Vijayaraghavan, T.; Ashok, A.; Parida, K., Prominence of Cu in a plasmonic Cu–Ag alloy decorated SiO₂@S-doped C₃N₄ core–shell nanostructured photocatalyst towards enhanced visible light activity. *Nanoscale Advances* **2022**, 4 (1), 150-162.
 13. Verma, A.; Gahlyan, P.; Bawa, R.; **Dash, S. R.**; Prasad, A. K.; Kumar, R., Glycerol-Triazole Conjugated Rhodamine as Colorimetric and Fluorimetric Sensor for Cu₂⁺. *ChemistrySelect* **2021**, 6 (34), 9288-9292.
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 11. Khanvilkar, P.; **Dash, S. R.**; Banerjee, D.; Vohra, A.; Devkar, R.; Chakraborty, D., Organoruthenium (II) complexes featuring pyrazole-linked thiosemicarbazone ligands: Synthesis, DNA/BSA interactions, molecular docking, and cytotoxicity studies. *Applied Organometallic Chemistry* **2021**, 35 (10), e6343.

10. Rani, S.; **Dash, S. R.**; Bera, A.; Alam, M. N.; Vanka, K.; Maity, P., Phosphite mediated asymmetric N to C migration for the synthesis of chiral heterocycles from primary amines. *Chemical Science* **2021**, *12* (26), 8996-9003.
9. Khanvilkar, P.; **Dash, S. R.**; Pulipaka, R.; Shirsath, K.; Devkar, R.; Chakraborty, D., Imidazole/4, 4'-azopyridine bridging binuclear Ru (II) complexes: design, synthesis, bimolecular interactions and cytotoxicity against HeLa cell line. *Journal of the Iranian Chemical Society* **2021**, *18* (12), 3313-3326.
8. Kumar, G.; **Dash, S. R.**; Neogi, S., Dual-catalyst engineered porous organic framework for visible-light triggered, metal-free and aerobic sp^3 CH activation in highly synergistic and recyclable fashion. *Journal of Catalysis* **2021**, *394*, 40-49.
7. Alam, M. N.; **Dash, S. R.**; Mukherjee, A.; Pandole, S.; Marelli, U. K.; Vanka, K.; Maity, P., [1, 3]-Claisen Rearrangement via Removable Functional Group Mediated Radical Stabilization. *Organic Letters* **2021**, *23* (3), 890-895.
6. Khanvilkar, P.; **Dash, S. R.**; Vohra, A.; Devkar, R.; Chakraborty, D., Evaluation of biomolecular interactions and cytotoxic activity of organometallic binuclear Ru (II) complexes of ferrocenyl thiosemicarbazones. *Journal of Biomolecular Structure and Dynamics* **2021**, *39* (16), 6044-6055.
5. Mali, B. P.; **Dash, S. R.**; Nikam, S. B.; Puthuvakkal, A.; Vanka, K.; Manoj, K.; Gonnade, R. G., Five concomitant polymorphs of a green fluorescent protein chromophore (GFPc) analogue: understanding variations in photoluminescence with π -stacking interactions. *Acta Crystallographica Section B: Structural Science, Crystal Engineering and Materials* **2020**, *76* (5), 850-864.
4. Kumar, R.; Yadav, S.; Gour, K.; Sangtani, E.; **Dash, S. R.**; Raja, A.; Vanka, K.; Gonnade, R. G.; Sen, S. S., A Tale of Biphenyl and Terphenyl Substituents for Structurally Diverse Ketiminato Magnesium, Calcium and Germanium Complexes. *Chemistry-An Asian Journal* **2020**, *15* (6), 820-827.
3. Pulipaka, R.; **Dash, S. R.**; Khanvilkar, P.; Jana, S. S.; Devkar, R. V.; Chakraborty, D., Design, synthesis and in vitro bioactivity of mixed ligand Ru (II) complexes bearing the fluoroquinolone antibacterial agents. *Transition Metal Chemistry* **2019**, *44*, 721-735.
2. Goswami, R.; Seal, N.; **Dash, S. R.**; Tyagi, A.; Neogi, S., Devising chemically robust and cationic Ni (II)-MOF with nitrogen-rich micropores for moisture-tolerant CO₂ capture: highly regenerative and ultrafast colorimetric sensor for TNP and multiple oxo-anions in water with theoretical revelation. *ACS applied materials & interfaces* **2019**, *11* (43), 40134-40150.

1. Palmajumder, E.; **Dash, S. R.**; Mitra, J.; Mukherjea, K. K., A Multifunctional Biomimicking Oxidovanadium (V) Complex: Synthesis, DFT Calculations, Bromo peroxidation and DNA Nuclease Activities. *ChemistrySelect* **2018**, 3 (26), 7429-7438.

Symposia Attended

National conferences: 2 (Poster), 1 (Poster + Oral) , 1 (Oral)

International conferences: 2 (Poster), 1 (Poster + Oral)

Size Matters: Computational Insights into the Crowning of Noble Gas Trioxides

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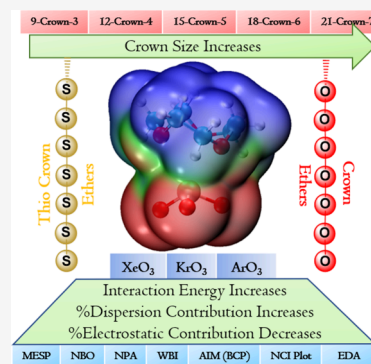


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ABSTRACT: In pursuit of enhancing the stability of the highly explosive and shock-sensitive compound XeO_3 , we performed quantum chemical calculations to investigate its possible complexation with electron-rich crown ethers, including 9-crown-3, 12-crown-4, 15-crown-5, 18-crown-6, and 21-crown-7, as well as their thio analogues. Furthermore, we expanded our study to other noble gas trioxides (NgO_3), namely, KrO_3 and ArO_3 . The basis set superposition error (BSSE) corrected interaction energies for these adducts range from -13.0 kcal/mol to -48.2 kcal/mol, which is notably high for σ -hole-mediated noncovalent interactions. The formation of these adducts was observed to be more favorable with the increase in the ring size of the crowns and less favorable while going from XeO_3 to ArO_3 . A comprehensive analysis by various computational tools such as the mapping of the electrostatic potential (ESP), Wiberg bond indices (WBIs), Bader's theory of atoms-in-molecules (AIM), natural bond orbital (NBO) analysis, noncovalent interaction (NCI) plots, and energy decomposition analysis (EDA) revealed that the $\text{C}-\text{H}\cdots\text{O}$ interactions, as well as dispersion interactions, play a pivotal role in stabilizing adducts involving larger crowns. A noteworthy outcome of our study is the revelation of a coordination number of 9 for xenon in the complex formed between XeO_3 and the thio analogue of 18-crown-6, which is higher than the largest number reported to date.



1. INTRODUCTION

The reluctance of noble gases to share their filled outer shell electrons makes their chemistry challenging. However, since the discovery of xenon fluorides of platinum by Neil Bartlett in 1962, researchers have been trying to coerce noble gases into participating in chemical reactions.^{1–3} This received a boost in 2015, when Bauza and Frontera provided theoretical evidence for the presence of an attractive interaction between an electron-rich atom and the covalently bonded noble gas compounds XeO_3 and XeOF_2 .⁴ The strength and directionality of the interaction were shown to arise due to the presence of a localized positive region, located at the extension to the $\text{Xe}-\text{O}$ bonds. The positive region was created at the location of a lone pair, resulting in the formation of unconventional σ -holes (Figure 1).

Prior to the work of Bauza and Frontera, even though σ -hole interactions, originally coined by Clark for halogen bonding,⁵ had been investigated enthusiastically,^{6–8} they were not associated with group 18 elements. Bauza and Frontera thus introduced the term “aerogen bond” for such interactions. Their findings created a paradigm shift in the field of directional noncovalent interactions associated with the noble gas compounds, prompting further theoretical and experimental investigations into aerogen-bond-related interactions.^{9–15}

One of the major beneficiaries of aerogen bonding stabilization is the xenon trioxide (XeO_3) molecule, which, being a capable oxidizing agent in solution,^{16–18} is also known

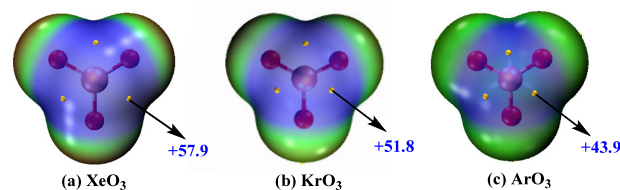


Figure 1. Molecular electrostatic potential (MEP) of noble gas trioxides with their respective maxima ($V_{s,\text{max}}$ in kcal/mol) around their σ -holes, computed at the APFD/def2-TZVPD level of theory. Blue and red represent the positive and negative regions, respectively, while green denotes the intermediate zone between them. The isovalue of the isodensity surface is set at 0.001 a.u.

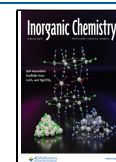
to be unstable in the solid state because of its high shock sensitivity and explosiveness.¹⁹ Schrobilgen and co-workers employed the σ -hole strategy to synthesize adducts of XeO_3 with nitrogen-based compounds (acetonitrile (CH_3CN) and pyridine ($\text{C}_5\text{H}_5\text{N}$)), which were found to be shock-insensitive and stable at room temperature.^{20,21} In the pursuit of making improved XeO_3 complexes with higher stability and shock

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resistance, the Schrobilgen group eventually focused on crown ethers. Ever since they had been reported by Pederson in 1967, crown ethers have been at the forefront of host–guest and supramolecular chemistry²² because of their highly selective recognition of specific cationic and molecular species.^{23,24} Crown ethers are the cyclic oligomers of ethylene oxide, which provide a unique electron-rich cavity, allowing their interaction with a plethora of guest species, depending on their size, shape, and donor properties.²⁵ Their host–guest interactions with AB₃-type main group compounds (A = As, Sb, Bi and B = F, Cl, Br, I) are well known in the literature^{26–28} and later are attributed to the presence of weak σ -hole interactions.²⁹ Furthermore, the resistance of crown ethers toward a strongly oxidizing environment³⁰ has made them suitable candidates for investigating the aerogen bonding with XeO₃. Encouraged by these characteristics, the Schrobilgen's group synthesized an adduct of 15-crown-5 with XeO₃ and obtained a crystal that was so stable at room temperature that it did not explode even after substantial mechanical stress (being hit with a hammer).³¹ The only other report of a crown ether adduct with noble gas trioxides is a computational investigation by Gao's group, reporting a very strong noncovalent interaction between the 18-crown-6 and XeO₃,³² which is comparable to the strongest of cation– π noncovalent interactions.³³ It should be noted that their work focused solely on the 18-crown-6:XeO₃ complex, and no comparative study has been conducted subsequently to elucidate how changes in the size of crown ethers affected their complexation with XeO₃.

Aerogen bonding interactions arising due to σ -hole interactions have elicited much interest in recent years and have been seen to be useful in crystal engineering due to their directional nature. This has provided us with the motivation to develop an improved understanding of such interactions.^{9,34} Drawing inspiration from the aforementioned reports, we have selected various crown ethers (9-crown-3, 12-crown-4, 15-crown-5, 18-crown-6, and 21-crown-7) and their thio analogs^{35,36} as hosts for this work (Figure 2). We are aware

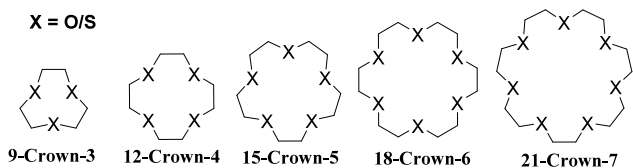


Figure 2. Different crown ethers with increasing size were used in this study. X donates the donor atom as oxygen (O) or sulfur (S).

that thio crown ethers are less robust toward oxidation; nevertheless, we have included them in order to investigate how efficiently the less electronegative sulfur, in comparison to oxygen, shares its lone pair of electrons with the σ -holes, resulting in the formation of aerogen-bonded adducts. The set of guests has also been extended to include other noble gas trioxides (NgO₃, Ng = Kr and Ar) as they too possess a σ -hole at the location of the lone pair and at the extension of their respective Ng=O bonds (Figure 1).³⁷ By means of quantum chemical calculations, a deeper understanding is obtained of how the change in the electron-rich cavity and the increase in the crown size alter their host–guest complexation with NgO₃. The interaction energies of adduct formation have been compared, and different computational tools such as the mapping of the electrostatic potential (ESP), Wiberg bond indices (WBIs), Bader's theory of atoms in molecules (AIM),

natural bond orbital (NBO) evaluation, noncovalent interaction (NCI) plots, and energy decomposition analyses (EDA) have been employed to elucidate the physical nature of interactions between the crown ethers and NgO₃.

2. METHODOLOGY

All of the density functional theory (DFT) calculations have been carried out using the Gaussian 09 suite of programs.³⁸ Each model was optimized in the gas phase by employing the APFD³⁹ functionals along with the def2-TZVPD basis set.⁴⁰ This level of theory was selected because it had been benchmarked as the most reliable combination when compared to the experimentally obtained adduct of 15-crown-5 with XeO₃ by Schrobilgen's research group.³¹ Furthermore, harmonic frequency calculations were performed to confirm all of the stationary points as minima. Conformational search analysis has been carried out with Grimme's semiempirical conformer–rotamer ensemble sampling tool (CREST)⁴¹ at the xTB-GFN2 level of theory.^{42–44} The counterpoise correction method was employed to obtain more accurate interaction energy (ΔE) values by correcting the basis set superimposition error (BSSE).⁴⁵ The interaction energy is calculated as the disparity between the energy of the complex and the energy of the isolated monomers in the configuration of the complex. Deformation energies corresponding to each case were also evaluated. ESP, NCI plot, and AIM analysis were performed with the MultiWFN program⁴⁶ and visualized using the visual molecular dynamics (VMD) software.⁴⁷ NBO analysis was carried out as incorporated in the Gaussian 09 software module. For EDA,⁴⁸ the BP86⁴⁹ functional with a D3(BJ) correction was used together with the TZ2P basis set⁵⁰ as implemented in ADF 2022. The frozen core approximation was used, and the numerical quality was set to good. A strictly closed-shell fragmentation scheme was chosen. To enhance the robustness of the study, the interaction energy has been additionally assessed through single-point calculations at the EDA/MP2/ZORA/TZ2P and APFD/aug-cc-pVTZ (-PP for Xe) levels of theory, which incorporate the electron correlation and relativistic effects.^{51,52} The robustness of the WBI, NPA, and NBO calculations has been further confirmed by utilizing the NBO 6 program package.⁵³

3. RESULTS AND DISCUSSION

3.1. Molecular Electrostatic Potentials of Isolated Molecules. The molecular electrostatic potential (MEP) provides an effective way of examining noncovalent interactions (NCI), as NCIs are mostly coulombic in nature.⁵⁴ However, it must be noted that MEP reflects not only the effects of electrons but also the effects of the nuclei.⁵⁵ Here, MEP plots were computed for the noble gas trioxides, which confirmed the presence of three σ -holes opposite their respective Ng–O bond. As shown in Figure 1, the blue color represents the electron-deficient region and the orange dots indicate the location of the σ -holes. The MEP maxima ($V_{s,max}$) values for the XeO₃, KrO₃, and ArO₃ obtained at the APFD/def2-TZVPD level of theory were found to be close to the earlier reported values at the MP2/aug-cc-pVTZ level of theory.⁴ A decrease in $V_{s,max}$ from Xe to Ar was observed due to their decreasing atomic polarizabilities and electronegativity difference, in accordance with the literature.⁹ The presence of such strong positive potential regions (σ -holes) makes these noble gas trioxides attractive for electron-rich crown ethers.

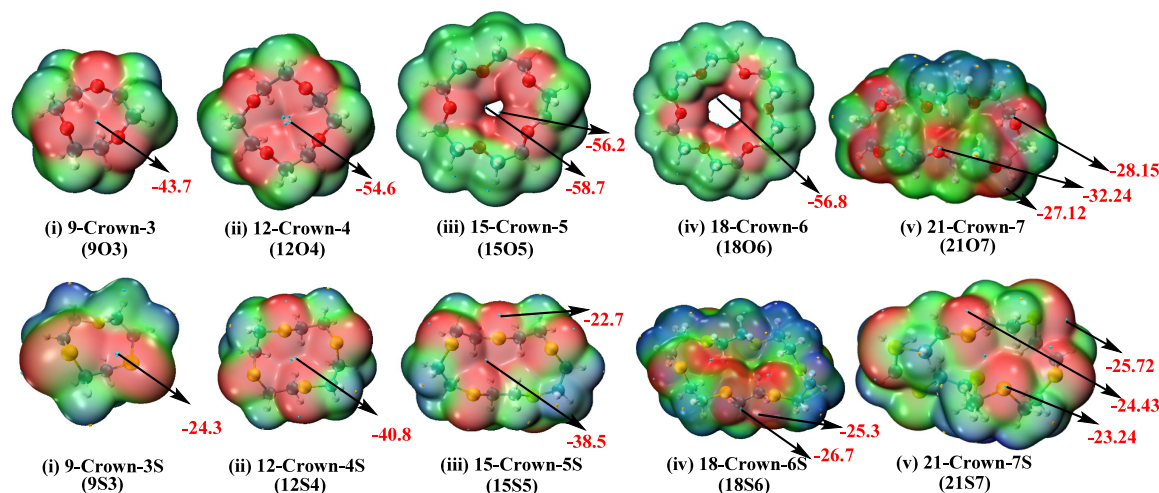


Figure 3. Selected MEPs of the crown ethers and their thio analogues with their respective energy values of minima ($V_{s,\min}$ in kcal/mol). Blue and red represent the positive and negative regions, respectively, while green denotes the intermediate zone between them. The isovalue of the isodensity surface is set at 0.001 a.u.

The MEPs have also been computed for the crown ethers as depicted in Figure 3 (see Table S1 for the complete list of MEPs: $V_{s,\min}$), where the red color represents the electron-rich region of the crown ethers. All of the crown ethers from 9-crown-3 to 21-crown-7 were found to have an intense region of negative potential in the center. As shown in Figure 3, a shared negative potential was found to be increasing with an increase in the size of the crown ethers from 9-crown-3 to 15-crown-5. However, a decrease in the cumulated negative potential was observed upon a further increase in size from 15-crown-5 to 21-crown-7, but it was distributed among the individual oxygen centers, as listed in Table S1. The MEPs of the thio analogues were found to be more dispersed around the molecule, owing to the lower electronegativity and exodentate orientation of sulfur atoms, in contrast to the endodentate conformation found in their oxygen counterparts.^{35,36}

3.2. Interaction Energies. The interaction energies for all of the adduct formations were evaluated (Table 1), and it was observed that an increase in the size of the crown ethers favored their complexation with the noble gas trioxides. A similar trend was observed for all three noble gas trioxides, i.e., XeO_3 , KrO_3 , and ArO_3 .

The thio-analogues of the crown ethers exhibit a similar trend for adduct formation with XeO_3 , KrO_3 , and ArO_3 . The only exception is the formation of the ArO_3 adduct with 12S4, which could be attributed to the lowest polarizability of Ar compared to that of Kr and Xe. Interestingly, it was also observed that the complexation of smaller thio-analogues (9S3, 12S4 and 15S5) of crown ethers with NgO_3 shows less favorable binding as compared to that of their oxygen counterparts, whereas the larger thio-analogues (18S6, 21S7) show more favorable binding with NgO_3 as compared to that of their oxygen peers. It should be noted that we also obtained a different mode of binding for XeO_3 with 21-crown-7, through CREST, which was found to be unfavorable by +1 kcal/mol (ΔE) compared to the one reported above. However, the similar binding modes for KrO_3 and ArO_3 were favorable by −3.5 and −2.9 kcal/mol, respectively. These alternative modes are termed $\text{NgO}_3(21\text{-crown-7})'$ in the discussion. The deformation energies by different crowns for complexation with the NgO_3 have also been computed (details in Table S2),

Table 1. Interaction Energy (ΔE in kcal/mol) with BSSE Corrections Computed at the APFD/def2-TZVPD Level of Theory^a

Crown ethers		Thio-crown ethers	
Complex	ΔE_{BSSE}	ΔE_{BSSE}	Complex
$\text{XeO}_3:9\text{O}3$	−25.0	−24.2	$\text{XeO}_3:9\text{S}3$
$\text{XeO}_3:12\text{O}4$	−30.6	−27.6	$\text{XeO}_3:12\text{S}4$
$\text{XeO}_3:15\text{O}5$	−38.3	−35.4	$\text{XeO}_3:15\text{S}5$
$\text{XeO}_3:18\text{O}6$	−40.2	−42.8	$\text{XeO}_3:18\text{S}6$
$\text{XeO}_3:21\text{O}7$	−41.2	−48.2	$\text{XeO}_3:21\text{S}7$
$\text{KrO}_3:9\text{O}3$	−20.1	−18.7	$\text{KrO}_3:9\text{S}3$
$\text{KrO}_3:12\text{O}4$	−22.6	−19.3	$\text{KrO}_3:12\text{S}4$
$\text{KrO}_3:15\text{O}5$	−25.7	−23.0	$\text{KrO}_3:15\text{S}5$
$\text{KrO}_3:18\text{O}6$	−26.0	−27.6	$\text{KrO}_3:18\text{S}6$
$\text{KrO}_3:21\text{O}7$	−26.4	−36.4	$\text{KrO}_3:21\text{S}7$
$\text{ArO}_3:9\text{O}3$	−15.4	−13.5	$\text{ArO}_3:9\text{S}3$
$\text{ArO}_3:12\text{O}4$	−16.1	−13.0	$\text{ArO}_3:12\text{S}4$
$\text{ArO}_3:15\text{O}5$	−17.2	−14.8	$\text{ArO}_3:15\text{S}5$
$\text{ArO}_3:18\text{O}6$	−17.6	−18.0	$\text{ArO}_3:18\text{S}6$
$\text{ArO}_3:21\text{O}7$	−17.9	−23.8	$\text{ArO}_3:21\text{S}7$

^aDonor atoms of the crowns are denoted by their atomic symbol (O/S) for comparison.

and they were observed to decrease from Xe to Ar. This can be explained by the overall interaction energy, which increases from Ar to Xe: a larger interaction energy allows the crown ether to compensate for more energy for its deformation to maximize the bonding interaction. As stated earlier, MEPs cannot be the sole indicator of such noncovalent interactions, which is also reflected in the trend in interaction energies. Hence, other computational tools were employed to obtain insights into the factors influencing the interaction energy for the host–guest complex of crown ethers (as well as their thio-analogues) and noble gas trioxides. A consistent trend in interaction energies was observed in the data obtained from both the EDA/MP2/ZORA/TZ2P level of theory and the APFD/aug-cc-pVTZ (−PP for Xe) level of theory (Table S3).

3.3. Structural Characteristics, WBI, and Charge Analysis. The optimized geometries of all of the complexes are depicted in Figures 4 and S1 (for XeO_3), Figure S2 (for

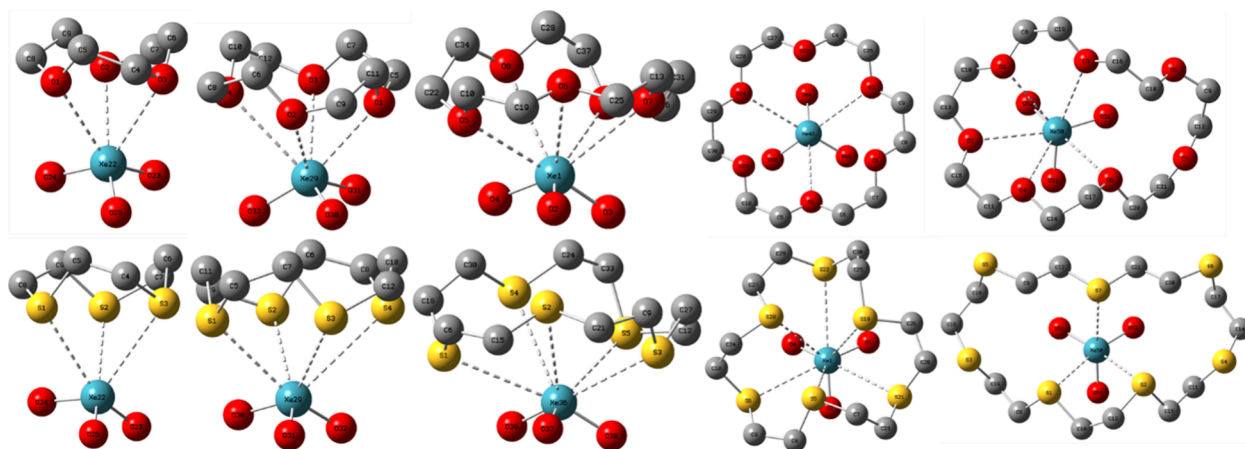


Figure 4. Optimized geometries of the complexes involving XeO_3 with crown ethers (top) and their thio analogues (bottom) are presented with an increasing crown size, arranged from left to right. Hydrogen atoms have been omitted for clarity.

KrO_3), and Figure S3 (for ArO_3). Figures S1–S3 include their respective primary $\text{Ng}-\text{O}$ bond lengths, secondary $\text{Ng}\cdots\text{X}$ ($\text{X}=\text{O}/\text{S}$) bond distances, Wiberg bond indexes, and the charge analysis values obtained from natural population analysis and Mulliken charge analysis. Figure S4 illustrates an alternative binding mode of NgO_3 with 21-crown-7, in which Ng is seen to be interacting with only three oxygen atoms of 21-crown-7 as opposed to the five oxygen atoms observed in previous cases. In all cases, an increase in the $\text{Ng}-\text{O}$ bond lengths was observed upon complex formation. The only exception was found in one of the $\text{Xe}-\text{O}$ bond lengths in the $\text{XeO}_3\cdot 21\text{O}7$ complex. It is to be noted that the elongation of $\text{Ng}-\text{O}$ bonds in ArO_3 was relatively smaller compared to their analogues in KrO_3 and XeO_3 . Furthermore, we observed that the elongation of $\text{Ng}-\text{O}$ bonds was more pronounced when forming complexes with thio-crown ethers, as opposed to their oxygen-based analogs. The intermolecular distances of secondary $\text{Ng}\cdots\text{X}$ ($\text{X}=\text{O}/\text{S}$) interactions, specifically the one interacting with the noble gases as shown in Figures S1–S4, were found to be lower than the sum of their corresponding van der Waals radii ($\Sigma(\text{Xe}-\text{O})_{\text{vdW}} = 3.68 \text{ \AA}$, $\Sigma(\text{Kr}-\text{O})_{\text{vdW}} = 3.54 \text{ \AA}$, $\Sigma(\text{Ar}-\text{O})_{\text{vdW}} = 3.4 \text{ \AA}$, $\Sigma(\text{Xe}-\text{S})_{\text{vdW}} = 3.96 \text{ \AA}$, $\Sigma(\text{Kr}-\text{S})_{\text{vdW}} = 3.82 \text{ \AA}$, and $\Sigma(\text{Ar}-\text{S})_{\text{vdW}} = 3.68 \text{ \AA}$, according to Bondi⁵⁶ for all cases. A comparative summary of the changes in bond lengths for the case of XeO_3 is presented in Table 2.

In concurrence with the observed bond elongation, a reduction in the Wiberg bond indices (WBI) of Ng and O was noted during complexation with both crown ethers and their thio analogues in all cases, except for the complexes involving XeO_3 with 9S3, 12S4, and 21S7, where the changes were marginal. The bond orders of $\text{Ng}\cdots\text{O}$ and $\text{Ng}\cdots\text{S}$ secondary interactions were evaluated using WBI analysis, employing NBO 6, and the results are presented in Table S4. The analysis reveals a noticeable trend wherein, for individual crowns, the bond orders of the secondary interactions follow the sequence $\text{Xe} > \text{Kr} > \text{Ar}$. Notably, the bond orders associated with $\text{Ng}\cdots\text{S}$ interactions were observed to be greater than those of their oxygen analogs. The $\angle\text{O}-\text{Ng}-\text{O}$ bond angles in NgO_3 followed the order $\text{Xe} < \text{Kr} < \text{Ar}$ before and after complexation in all cases. Additionally, the average $\angle\text{O}-\text{Ng}-\text{O}$ bond angles decreased with increasing crown size for both oxygen and thio analogues, with a few exceptions (complexes of $\text{NgO}_3\cdot 21\text{O}7$, $\text{XeO}_3\cdot 21\text{O}7'$, and $\text{ArO}_3\cdot 12\text{S}4$). The magnitude of the decrease in bond angle with an increase

Table 2. Bond Lengths of $\text{Xe}-\text{O}$ upon Complexation and the Secondary Bond Distances between the Xenon and Donor Atom of the Crown^a

	Isolated	9O3	12O4	15O5	18O6	21O7
$\text{Xe}-\text{O}$	1.7597	1.7652	1.7651	1.7673	1.7605	1.7585
	1.7597	1.7651	1.7649	1.7640	1.7605	1.7620
	1.7597	1.7658	1.7651	1.7623	1.7605	1.7670
$\text{Xe}\cdots\text{O}$	-	2.8184	2.8049	2.9088	3.1493	2.9733
		2.9265	2.9474	2.9616	3.1493	3.0428
		2.9494	2.9691	2.9627	3.1493	3.1338
			3.1220	3.0745	3.4010	3.1427
				3.2590	3.4010	3.1668
					3.4010	
	Isolated	9S3	12S4	15S5	18S6	21S7
$\text{Xe}-\text{O}$	1.7597	1.7675	1.7702	1.7727	1.7710	1.7760
	1.7597	1.7699	1.7666	1.7683	1.7710	1.7792
	1.7597	1.7675	1.7666	1.7634	1.7710	1.7757
$\text{Xe}\cdots\text{S}$	-	3.1846	3.2080	3.2648	3.3223	3.1155
		3.2151	3.2391	3.3618	3.3230	3.1323
		3.4580	3.4843	3.4863	3.3240	3.1834
			3.5669	3.5038	3.4717	
				3.5607	3.4719	
					3.4722	

^aAll values are in $\text{\AA}$.

in the size of the crowns was most significant in XeO_3 complexes, followed by KrO_3 and ArO_3 ($\text{Xe} > \text{Kr} > \text{Ar}$). Concerning XeO_3 complexes, the decrease in average bond angles was more pronounced in thio analogues, except for $\text{XeO}_3\cdot 18\text{S}6$. There were no such discernible patterns in the average bond angles between crown ethers and their thio analogues for the complexes of KrO_3 and ArO_3 . The values corresponding to the NgO_3 bond angles mentioned above are listed in Table S19. Additionally, natural population analysis revealed that upon complex formation the charges on Ng and O within NgO_3 were elevated. In other words, Xe, Kr, and Ar exhibited a more positive charge, while oxygen displayed a higher negative charge. These findings suggest enhanced polar-covalent character in the primary $\text{Ng}-\text{O}$ bonds of NgO_3 upon complex formation. Interestingly, the charge derived from the Merz–Kollman (MK) model indicates a decrease in charge on Ng and O upon complexation, with a few exceptions. There is no consistent trend in the charges on Ng and O with the

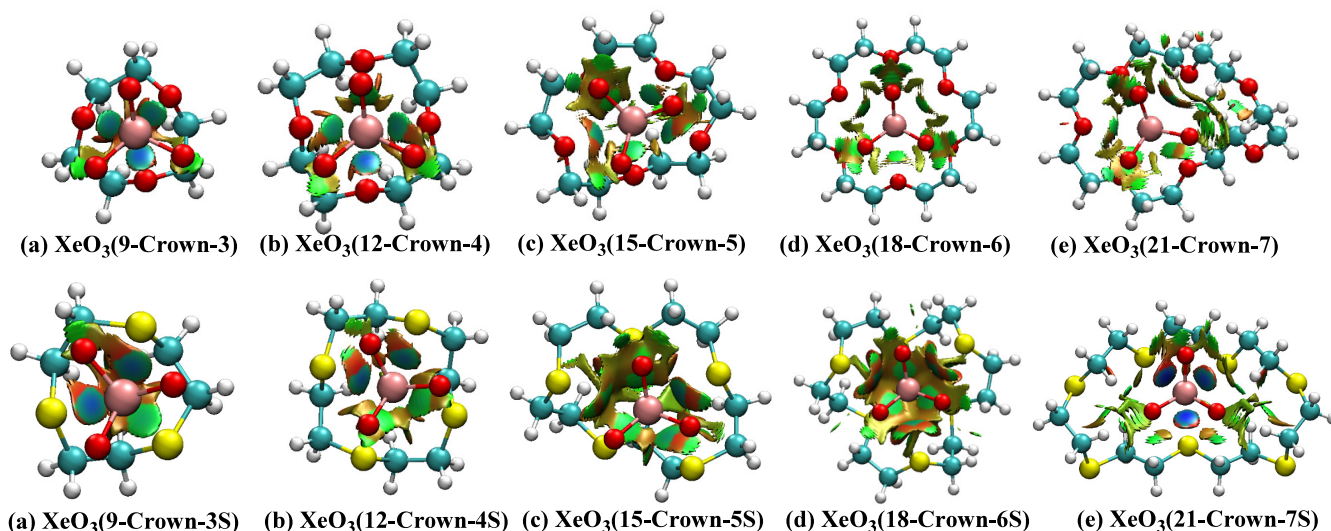


Figure 5. NCI plots (isovalue 0.5 a.u.) of the complexes of XeO_3 with crown ethers (top) and their thio analogues (bottom). Blue regions represent strong attractive forces; the green region indicates intermediate attraction, while red regions signify repulsive forces.

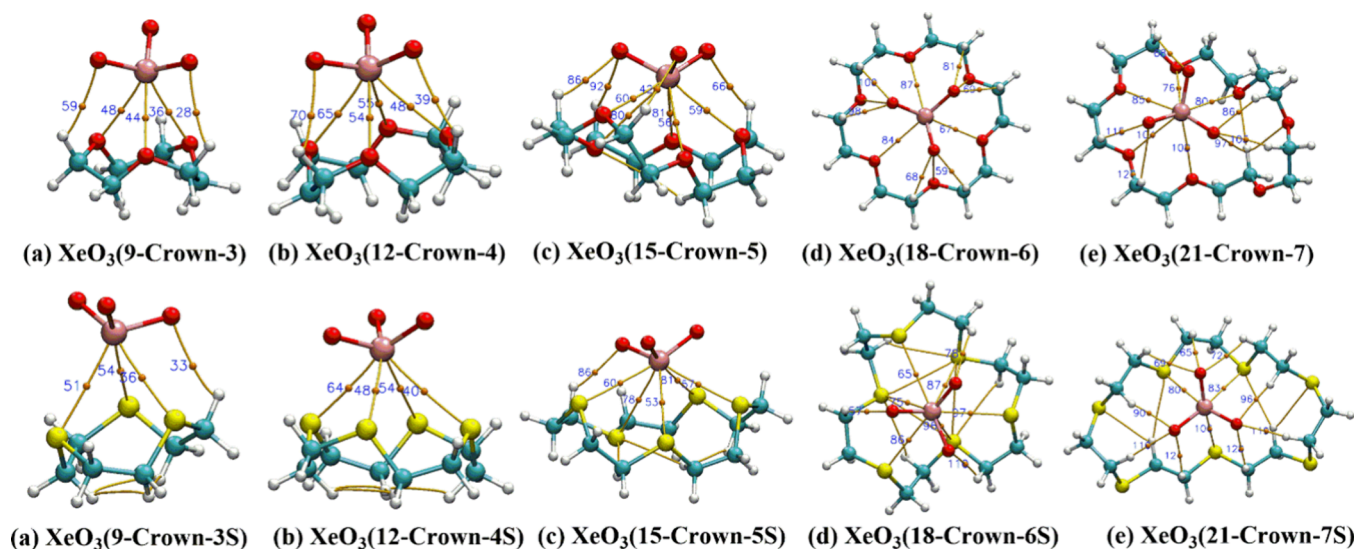


Figure 6. Bond critical points (BCPs) obtained from AIM analysis for complexes of XeO_3 with crown ethers (top) and their thio analogues (bottom). Please refer to Table S8 for enlarged images of bond critical points along with their respective electron densities (ρ , in a.u.) and the Laplacian of the electron density ($\nabla^2\rho$, in a.u.).

increasing crown size in the MK analysis. Conversely, charges on Ng obtained from NPA analysis (utilizing NBO 6) were observed to increase with the growth in the crown size. A comparative summary of the MK and NPA charge analyses is presented in Tables S5–S7. Each method for charge analysis has its merits and drawbacks. While electrostatic fitting models (MK) offer better charge estimation for surface atoms, they are notably limited in accurately estimating charges for buried atoms. This could be the reason for the discrepancy between the MK and NPA charges.

3.4. NCI and BCP (from AIM Analysis). In order to gain deeper insights into the binding of Ng with different crown ethers, NCI plot analyses were conducted (Figures 5, S5, and S7). This revealed that, apart from the conventional aerogen bonds, i.e., the interaction between the donor atom of the crowns and the Ng, attractive regions depicting the hydrogen bonding interactions between C–H...O exist, which become more prominent in larger crowns. It is to be noted that the

attractive nature of the aerogen bonding also decreases as the size of the crown increases, which is represented via a change in the intensity of the region from blue-green to green. The exception to this trend was observed in adducts of 21S7 with NgO_3 , which were found to be more attractive in nature compared to other crowns. Also, NCI plot analysis for the alternative binding mode of NgO_3 with 21-crown-7 revealed a more attractive aerogen bonding region (Figure S9). Interestingly, a faded region on the greenish surface was observed among the three oxygen atoms, which are farther away from the NgO_3 in their complex with 18-crown-6, indicating a very weak attractive interaction. Figure 5(e) indicates stronger attractive interactions of all six donor atoms of 18S6 as compared to those of 18O6.

Similarly, bond critical points (BCPs) obtained from the AIM analysis agreed with the earlier observation that the C–H...O hydrogen bonding interactions are more prominent in larger crowns (Figures 6, S6, and S8). The values

Table 3. Second-Order Perturbation Energies (E^2) Were Obtained from NBO Analysis at the APFD/def2-TZVPD Level of Theory for the Complexes of XeO_3 ^a

XeO_3 :18-Crown-6 (-O)			XeO_3 :Thio-18-Crown-6 (-S)		
Donor	Acceptor	E^2	Donor	Acceptor	E^2
LP (1) O1	BD*(1) Xe 43 - O44	0.61 (0.75)	LP (2) S5	BD*(1)Xe1 - O3	0.76 (0.83)
LP (1) O3	BD*(1) Xe 43 - O45	0.61 (0.75)	LP (2) S5	BD*(1)Xe1 - O4	0.81 (0.88)
LP (1) O24	BD*(1) Xe 43 - O46	0.61 (0.75)	LP (2) S6	BD*(1)Xe1 - O3	2.65 (2.93)
LP (2) O2	BD*(1) Xe 43 - O44	0.14 (0.16)	LP(2) S19	BD*(1)Xe1 - O2	0.81 (0.88)
LP (2) O2	BD*(1) Xe 43 - O45	0.14 (0.16)	LP(2) S19	BD*(1)Xe1 - O4	0.76 (0.83)
LP (2) O23	BD*(1) Xe 43 - O45	0.14 (0.16)	LP(2) S20	BD*(1)Xe1 - O2	0.76 (0.83)
LP (2) O23	BD*(1) Xe 43 - O46	0.14 (0.16)	LP(2) S20	BD*(1)Xe1 - O3	0.81 (0.88)
LP (2) O25	BD*(1) Xe 43 - O46	0.14 (0.16)	LP(2) S21	BD*(1)Xe1 - O4	2.66 (2.94)
LP (2) O25	BD*(1) Xe 43 - O44	0.14 (0.16)	LP(2) S22	BD*(1)Xe1 - O2	2.67 (2.95)

^aThe E^2 values are in kcal/mol. The bracketed E^2 values are from the NBO 6 output.

Table 4. Energy Decomposition Analysis (EDA) of All of the Complexes of XeO_3 at the BP86-D3BJ/TZ2P Level of Theory^a

	ΔE	E_{Pauli}	E_{elstat}	%	E_{oi}	%	E_{disp}	%
XeO_3 :9O3	-21.31	37.81	-32.46	55	-17.08	29	-9.58	16
XeO_3 :12O4	-25.96	41.48	-36.94	55	-18.68	28	-11.82	18
XeO_3 :15O5	-32.24	49.16	-43.92	54	-22.35	27	-15.13	19
XeO_3 :18O6	-33.99	40.62	-40.13	54	-17.81	24	-16.67	22
XeO_3 :21O7	-34.58	53.09	-45.36	52	-22.97	26	-19.34	22
XeO_3 :9S3	-23.57	44.94	-34.24	50	-23.05	34	-11.22	16
XeO_3 :12S4	-26.69	48.01	-36.62	49	-24.13	32	-13.95	19
XeO_3 :15S5	-33.89	53.67	-42.36	48	-26.84	31	-18.36	21
XeO_3 :18S6	-40.86	69.79	-54.22	49	-33.72	30	-22.71	21
XeO_3 :21S7	-48.09	96.05	-68.43	47	-51.51	36	-24.2	17

^aThe energy values are in kcal/mol. Contributions to the sum of all attractive energy terms are shown as percentages. E_{Pauli} represents Pauli repulsion, E_{elstat} represents electrostatic interactions, E_{oi} represents orbital interaction, and E_{disp} represents the dispersion interaction.

corresponding to the bond critical points, along with their respective electron density (ρ , in a.u.) and the Laplacian of the electron density ($\nabla^2\rho$, in a.u.), are deposited in the SI (Tables S8–S10). The C–H $\cdots$ O interactions were found to be highest (up to 9) in the complexes of 21S7. The more attractive aerogen bonding interactions, as indicated from the NCI plots along with the highest number C–H $\cdots$ O hydrogen bonding interactions, agree well with the interaction energy trend, which suggests that 21S7 binds to NgO_3 the strongest, as compared to the other crown ethers in the present study. It also revealed the existence of six BCPs between 18S6 and XeO_3 , indicating that all six sulfur atoms are interacting with the Xe, as compared to the three BCPs in its oxygen analogues. This further validates the coordination number of 9 (3 oxygen atoms of parent XeO_3 and 6 sulfur atoms of 18S6) for Xe in the complex of 18S6 and XeO_3 . The same is also true for KrO_3 , whereas for the case of ArO_3 only three BCPs were observed, owing to its lowest polarizability and thus lowest σ -hole strength. As evident from the BCPs, the exodentate nature of thio-crown ethers restricts proper C–H $\cdots$ O interactions compared to their oxygen analogues, with the exception of thio-21-crown-7 (21S7). The smaller thio-crown ethers are more significantly affected, while thio-18-crown-6 (18S6) compensates for the loss of additional support from C–H $\cdots$ O interactions by binding to NgO_3 via all six sulfur atoms. Notably, 21S7 exhibits strong binding with NgO_3 , and its binding mode allows for the maximum C–H $\cdots$ O interactions among the crown ethers studied. This explains why the smaller thio-crown ethers with NgO_3 show less favorable binding as compared to their oxygen counterparts, whereas the larger thio-analogues show more favorable binding with NgO_3 .

3.5. Natural Bond Orbital Analysis (NBO). To elucidate the orbital effects within the context of aerogen crown-ether/thio-crown-ether complexes, NBO calculations were conducted. These calculations aimed to shed light on the donor–acceptor interactions between the crown-ether/thio-crown-ether molecules and aerogen species, quantified as second-order perturbation energy (E^2). For the lighter aerogens, such as ArO_3 and KrO_3 , we observed relatively lower orbital interactions between the donor orbitals (lone pairs, LPs) originating from the oxygen atoms of the crown ether/the sulfur atoms of the thio-crown ether and the antibonding orbitals (BD*) associated with Ng–O bonds. Specifically, these interactions fell within the ranges of 0.06–0.38 kcal/mol for ArO_3 and 0.06–0.88 kcal/mol for KrO_3 . A similar trend emerged in the case of thio-crown-ether complexes with lighter aerogens, with interactions in the range of 0.10–2.07 kcal/mol for ArO_3 and 0.23–5.92 kcal/mol for KrO_3 . These findings align reasonably well with the lower total interaction energies observed in these complex types compared to those in XeO_3 complexes. The significance of orbital contributions becomes more pronounced in xenon complexes (XeO_3), where second-order perturbation interaction energies ranged from 0.05 to 1.65 kcal/mol for crown ether complexes and from 0.34 to 8.96 kcal/mol for thio-crown-ether complexes. In all XeO_3 complexes (both crown ether and thio-crown ether), the total interaction energies were markedly higher compared to their counterparts involving argon or krypton (ArO_3 and KrO_3). These results are concisely summarized in Table S11. It is also worth noting that across all cases involving NgO_3 , the aerogens paired with thio-crown-ether consistently exhibited more pronounced orbital inter-

actions compared to their oxygen analogues in crown-ether complexes as shown in Tables S12–S14. This contributes to the enhanced coordination number of 9 for Xe in the $\text{XeO}_3\cdot 18\text{S6}$ complex. In this complex, the lone pairs of all six sulfur atoms exhibit increased orbital interactions with the antibonding (σ^*) $\text{Xe}-\text{O}$ orbital, in contrast to the $\text{XeO}_3\cdot 18\text{O6}$ complex (as shown in Table 3). It is worth mentioning that the highest coordination number for Xe previously reported in the literature was 8 for the adduct of XeO_3 with 15-crown-5.³¹ Table S15 summarizes the NBO data for the alternative binding modes of 21-crown-7 with the noble gas trioxides ($\text{NgO}_3\cdot 21\text{O7}'$). A comparison between the data obtained from NBO 3.1 and 6 was conducted. It was noted that the absolute values corresponding to E^2 values slightly improved with the use of NBO 6. However, the overall trends described above remained the same.

3.6. Energy Decomposition Analysis (EDA). All of the above findings were further supported by Ziegler–Rauk energy decomposition analysis. Although the absolute interaction energies differ from the higher-level computations due to the varying functional/basis set (cf. Tables 4, S16–S18), the relative trends are conserved and allow additional interpretations. Overall, the attractive interaction is around 50–60% electrostatic and 50–40% orbital/London dispersive in nature. As expected, the thio-crown ethers show larger orbital and London dispersive contributions compared to the oxygen analogs. Along the line $\text{Ar} > \text{Kr} > \text{Xe}$, all three attractive contributions (electrostatic, orbital, and dispersion) increase irrespective of the type and size of the crown ether. Thus, a more efficient σ -hole (electrostatic) and orbital overlap-based interaction is responsible for the strongest binding of XeO_3 , emphasizing that this type of “special interaction” behaves similarly to the conventional Lewis acid–base type of interaction. The percentage contribution changes along the elements: while the relative amount of orbital interaction increases from $\text{Ar} < \text{Kr} < \text{Xe}$, the relative importance of electrostatic and dispersive attraction decreases, $\text{Ar} > \text{Kr} > \text{Xe}$. Considering the effect of ring size, it was interesting to observe that the percentage of electrostatic contribution gradually decreases with the increase in the size of the crown ether (from 55 to 52% for XeO_3 , from 55 to 51% for KrO_3 , and from 58 to 51% for ArO_3). A similar observation was also made for the complexes of thio analogues of XeO_3 and KrO_3 , with the exception of 18S6, which could be due to its unusually high coordination number of 9 in the $\text{NgO}_3\cdot 18\text{S6}$ complexes. No particular trend was observed in the thio complexes of ArO_3 , except for an initial decrease in the percentage contribution (of electrostatic interaction) from 9S3 to 15S5. Additionally, we also found that the percentage of orbital contribution decreases with the increase in the size of the crown ethers (from 9-crown-3 to 18-crown-6) and their thio analogues, with the exception of 21O7 and 21S7. Finally, we also observed that the percentage contribution from dispersion interactions increases progressively with the increase in the size of the crown ether complexes for all three noble gas trioxides (from 16 to 22% for XeO_3 , from 18 to 28% for KrO_3 , and from 21 to 32% for ArO_3). With the exception of 21S7, the percentage contribution for the complexes of thio analogues was also found to increase with an increase in the size of the crown from 9-crown-3S (9S3) to 18-crown-6S (18S6). All of the relevant EDA data discussed above are presented in Table 4 (for XeO_3), Table S16 (for KrO_3), and Table S17 (For ArO_3). It is worth noting that the alternative binding modes of 21O7

with NgO_3 (Table S18) show increased contributions from orbital interactions and decreased contributions from electrostatic as well as dispersion interactions.

4. CONCLUSIONS

Our investigation into the formation of adducts between various crown ethers and noble gas trioxides has revealed key insights into the factors governing their stability. Interestingly, the complexation of different crowns with noble gas trioxides was observed to be more favorable with the increase in the ring size of the crowns and less favorable while going from XeO_3 to ArO_3 . The pivotal role of $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonding interactions in stabilizing the complexes of larger crown ethers has also been revealed. Furthermore, our analysis demonstrated that thio-crown ethers exhibit larger orbital/London dispersive contributions than their oxygen analogs. A noteworthy highlight of our work is the revelation of a coordination number of 9 for xenon in the complex formed between XeO_3 and the thio analogue of 18-crown-6. This surpasses the previously recorded highest coordination number of Xe, 8, as observed in the synthetically reported complex of XeO_3 with 15-crown-5.³¹ Finally, our investigation revealed that, with a few exceptions, the percentage contribution from electrostatic interactions tended to decrease as the size of the crown ethers increased. In contrast, the percentage contribution from dispersion interactions increased with a larger crown size. This distinction in interaction types provides valuable insights into the nature of bonding within these complexes. We are aware of the high thermodynamic and kinetic difficulties regarding any potential synthesis or handling of compounds ArO_3 and KrO_3 and that this challenge most likely will prevent any synthetic realization. However, we believe that the strong thermodynamic and kinetic stabilization under the described conditions might guide the way for future strategies to at least temporarily get a glimpse of such elusive species. In summary, our study provides insights into the intricate factors that influence the stability of crown ether-noble gas trioxide host–guest complexes, particularly as the crown size varies. These findings contribute to the broader understanding of σ -hole-mediated noble gas complexes as well as supramolecular chemistry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.3c03782>.

Figures of optimized geometries with the bond parameters, NCI plots and tables containing data for charge analysis, WBI bond order, BCP analysis, NBO analysis, and EDA (DOCX)

Optimized Cartesian coordinates (PDF)

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Author Contributions

The manuscript was written through the contributions of all authors. S.R.D. has made the bulk of the calculations discussed in the manuscript. H.S. has done the NBO analysis. M.K.T. has provided insights into the localization effects of the charge density. L.G. has performed the EDA analysis discussed in the manuscript and provided his insights on the analysis of other data. K.V. has helped write the manuscript and provided input on the localization effects of the charge density and also supervised the project overall. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Exploring Unconventional σ -Hole Interactions: Computational Insights into the Interaction of XeO_3 with Non-Aromatic Coordinating Solvents

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In order to control the explosiveness and shock sensitivity of XeO_3 , we have investigated its plausible interaction with various non-aromatic coordinating solvents, serving as potential Lewis base donors, through density functional theory (DFT) calculations. Out of twenty six such solvents, the top ten were thus identified and then thoroughly examined by employing various computational tools such as the mapping of the electrostatic potential surface (MESP), Wiberg bond indices (WBIs), non-covalent interaction (NCI) plots, Bader's theory of atoms-in-molecules (AIM), natural bond orbital (NBO) analysis, and the energy decomposition analysis (EDA). The amphoteric nature of XeO_3 was also explored by investigating the extent of back

donation from the lone pair of Xe to the antibonding orbital of the donating atom/group of the solvent molecules. The C–H...O interactions were also found to be a contributing factor in the stabilization of these adducts. Although these aerogen-bonding interactions were found to be predominantly electrostatic, significant contributions from the orbital contributions, as well as dispersion interactions, were observed. The top three non-aromatic solvents (among the twenty six studied) which form the strongest adducts with XeO_3 are proposed to be hexamethylphosphoramide (HMPA), N,N'-dimethylpropyleneurea (DMPU) and tetramethylethylenediamine (TMEDA).

Introduction

Noncovalent interactions (NCIs) such as hydrogen bonding, π – π stacking, and van der Waals forces, which are primarily driven by electrostatic forces, Pauli repulsion, dispersion, polarization, and charge transfer, serve as the backbone of supramolecular chemistry.^[1–6] While NCIs may be weaker than covalent interactions, the growing interest in NCIs extends beyond theoretical considerations, given their pivotal role in developing functional materials, crystal engineering, ion recognition, protein folding, and drug (guest)-receptor (host) interactions.^[7–11] Besides the extensively studied hydrogen bond,^[12] 21st-century supramolecular chemistry is renewing interest in different kinds of unconventional NCIs and challenging the established perspectives by introducing novel interaction types named after the involved groups of elements.^[13,14] The localized region of positive electrostatic potential, which is positioned on a σ^* orbital on the extension of a covalent bond between the recipient atom bound to an electron-withdrawing atom/group, also known as a sigma hole, gives rise to the NCIs (Figure 1, left).^[15] These include halogen, chalcogen, pnictogen, tetrel,

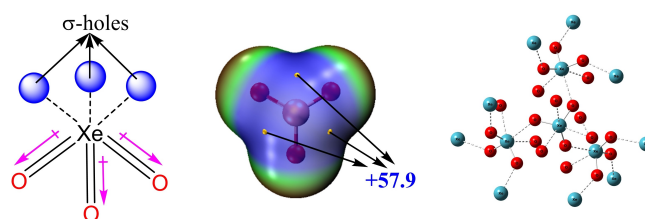


Figure 1. Left: Pictorial representation of σ -holes present at the extension of the covalent Xe–O double bond, in the pyramidal XeO_3 , created due to withdrawal of electron density from xenon by more electronegative oxygen atoms (dipole moment vector is shown by pink arrow). Middle: the molecular electrostatic surface potential (MESP) plot of XeO_3 with the maxima ($V_{s,\text{max}}$ in kcal/mol) around the σ -holes, obtained at the APFD/def2-TZVPD level of theory. Right: Network-like crystal structure of XeO_3 in the solid state.^[26,27] Dotted lines represent the σ -hole mediated NCIs.

icosagen (or triel), and, more recently, spondium, regium, and aerogen bonds.^[16–25]

In the case of aerogen bonding or noble gas bonding, the existence of unconventional σ -holes was revealed by Bauza and Frontera,^[18] and provided key insights into the unique crystal structure of XeO_3 .^[26,27] In the crystal structure, the three σ -holes present at the extension of each Xe=O bond provide three binding sites that direct the interaction with the nucleophilic oxygens of neighboring XeO_3 molecules, leading to a network-like structure (Figure 1), which is highly shock-sensitive and explosive in nature.^[28] However, interestingly, the σ -holes that are responsible for the explosive nature of XeO_3 also enable/direct other nucleophiles such as anions and Lewis bases to interact with XeO_3 , thus disrupting the Xe...O secondary interactions present in the parent XeO_3 crystal, making the newly obtained adduct of XeO_3 stable and shock-insensitive. Considering the hospitalization of Bartlett and Rao due to the

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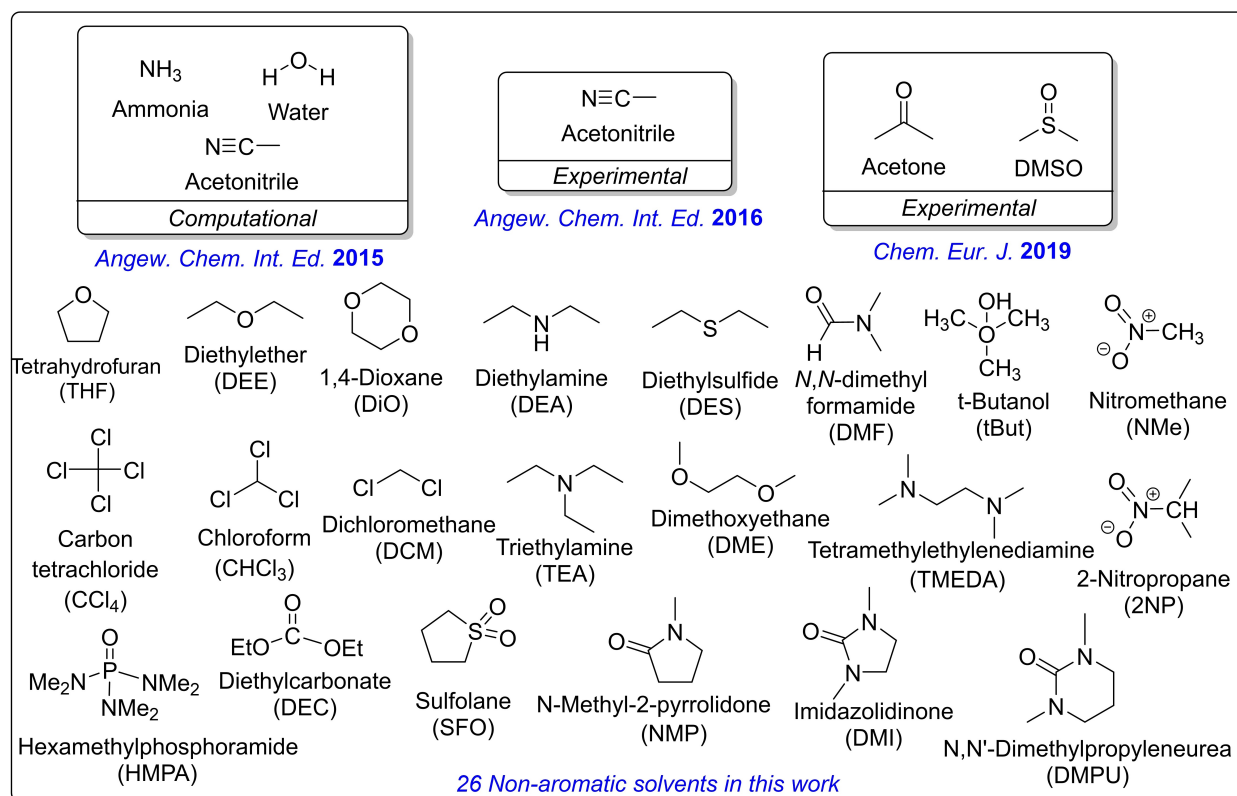
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detonation of XeO_3 , who were the first to experimentally verify its explosive nature,^[29] brave efforts by the group of Schrobilgen in utilizing this principle led to the successful experimentally obtained stable adducts of XeO_3 with different nucleophilic molecules.^[30–33] On the computational front, while there have been many studies on aerogen bonding with different types of anions, nucleophiles, crown ethers, and aromatic molecules such as benzene and its derivatives (aerogen- π interactions),^[34–41] we observed a paucity in the number of detailed studies on non-aromatic coordinating solvents.

Although the pioneering work by Bauza and Frontera shows the interaction between ammonia, water and acetonitrile with XeO_3 , only a 1:1 binding mode between them has been discussed.^[18] Experimentally, only three non-aromatic solvents have been explored for stabilizing XeO_3 , the first among them being acetonitrile,^[30] inspired by the computational prediction (Scheme 1).^[18] The other two were acetone and DMSO,^[33] among which acetone was lost from the XeO_3 crystal, due to adduct dissociation at room temperature, which could be attributed to the evaporation of acetone, which is a low boiling point solvent. Lastly, the 1:3 adduct of DMSO was successfully characterized, and the crystalline product was found to be less shock-sensitive than the parent solid XeO_3 . However, over the course of multiple days, DMSO decomposed to yield the redox product Me_2SO_2 due to the oxidant nature of XeO_3 .^[42–44] The risk associated with the explosiveness of XeO_3 , although it has a promising future to lead the noble gas chemistry, hinders a vast experimental exploration, which in turn makes pre-computa-

tional analysis of possible hosts or suitable candidates for stabilizing XeO_3 very important.^[45–49] There are undoubtedly other factors, such as the possibility of unwanted side reactions leading to the decomposition of the adduct, which would influence the choice of optimal solvent(s) for XeO_3 . Nevertheless, among the numerous factors influencing the stability of XeO_3 in the solid state, a computationally screenable aspect is the binding capability of potential hosts.

In this study, we aim to gain a deeper understanding of such unconventional aerogen bonding interactions, and hope to obtain/predict some alternatives that can overcome the drawbacks mentioned above and lead to a highly stable XeO_3 adduct. Inspired and motivated by the previous reports, we have selected twenty six different non-aromatic coordinating solvents (Scheme 1) as Lewis base donors to investigate their interactions with XeO_3 . Considering the presence of three σ -holes associated with XeO_3 , three plausible binding modes 1:1, 1:2, and 1:3 have been investigated. Beginning with the molecular electrostatic potential surface analysis (MESP), we have carried out a comparative analysis of the interaction energies for all the adduct formations. To further our understanding and to unveil the underlying physical properties governing the interactions between XeO_3 and different non-aromatic coordinating solvents, a comprehensive analysis of geometrical characteristics, natural population charge (NPA), Wiberg bond indices (WBIs), NCI plot, bond critical points (BCP), natural bond orbital (NBO) and energy decomposition analysis (EDA) have been conducted.



Scheme 1. Previous computational and experimental reports on XeO_3 :solvent adducts and different non-aromatic coordinating solvents used in this study.

Results and Discussion

Molecular Electrostatic Potential Surface (MESP) Study

MESP, being a real physically observable property, has found extensive utility in σ -hole mediated non-covalent interactions, which are majorly driven by electrostatic interactions.^[50] Nevertheless, it is essential to highlight that MESP involves not just the influences of electrons but also those of the nuclei.^[51] Figure 1 (Middle) depicts the MESP plot for XeO_3 , which shows the presence of three σ -holes (orange dots) in the positively charged zone (blue color), opposite to each Xe–O double bond, and associated with a $V_{s,\text{max}}$ (MESP maxima) value corresponding to +57.9 kcal/mol, which also correlates well with the previously reported value at the MP2/aug-cc-pVTZ level of theory.^[18,47] The MESP values have also been evaluated for isolated non-aromatic solvent molecules to examine their negative potential sites (red-colored regions) for possible binding with XeO_3 , as shown in Figure 2.

The $V_{s,\text{min}}$ (MESP minima) for each isolated solvent are shown as blue dots, and the corresponding values are listed below. Compared to the well-explored DMSO,^[33] a higher negative potential was observed for the case of HMPA, DMPU, DMI, and NMP, suggesting a possibility of stronger electrostatic interaction with XeO_3 . Among the twenty six non-aromatic solvents, in this study, TMEDA and DME provide a bidentate binding site,

each of which has a MESP minima of –28.95 and –27.04 respectively. SFO which is widely proposed as a possible alternative to DMSO,^[52] has a lower $V_{s,\text{min}}$ value as compared to DMSO, due to the presence of an additional electronegative oxygen atom bound to sulfur, although two $V_{s,\text{min}}$ corresponding to both the oxygen atoms were observed to be at –37.25 kcal/mol, which increases its overall nucleophilicity. It is also observed that, in accordance with the electronegativity trends, nitrogen donor solvents have higher negative potential, when there is a one-to-one comparison with oxygen donor solvents, such as DEA vs DEE, TMEDA vs DME, NH_3 vs H_2O . Halogen donor solvents such as DCM, CHCl_3 , and CCl_4 were found to be having the lowest $V_{s,\text{min}}$ values, and are probably the worst possible candidates for the current cause, as they have their own σ -holes along the extension of C–Cl bond (corresponding to the halogen bonds), with a $V_{s,\text{max}}$ of +9.05, +14.95, +19.10 kcal/mol respectively.

Interaction Energies

The solvents are ordered as per their decreasing MESP ($V_{s,\text{min}}$) values, and their interaction energies (BSSE corrected) with XeO_3 were evaluated considering three binding modes, such as $\text{XeO}_3\text{:Solvent}$ (1:1), $\text{XeO}_3\text{:}(\text{Solvent})_2$ (1:2), and $\text{XeO}_3\text{:}(\text{Solvent})_3$ (1:3), as shown in Table 1. It is to be noted that the correlation

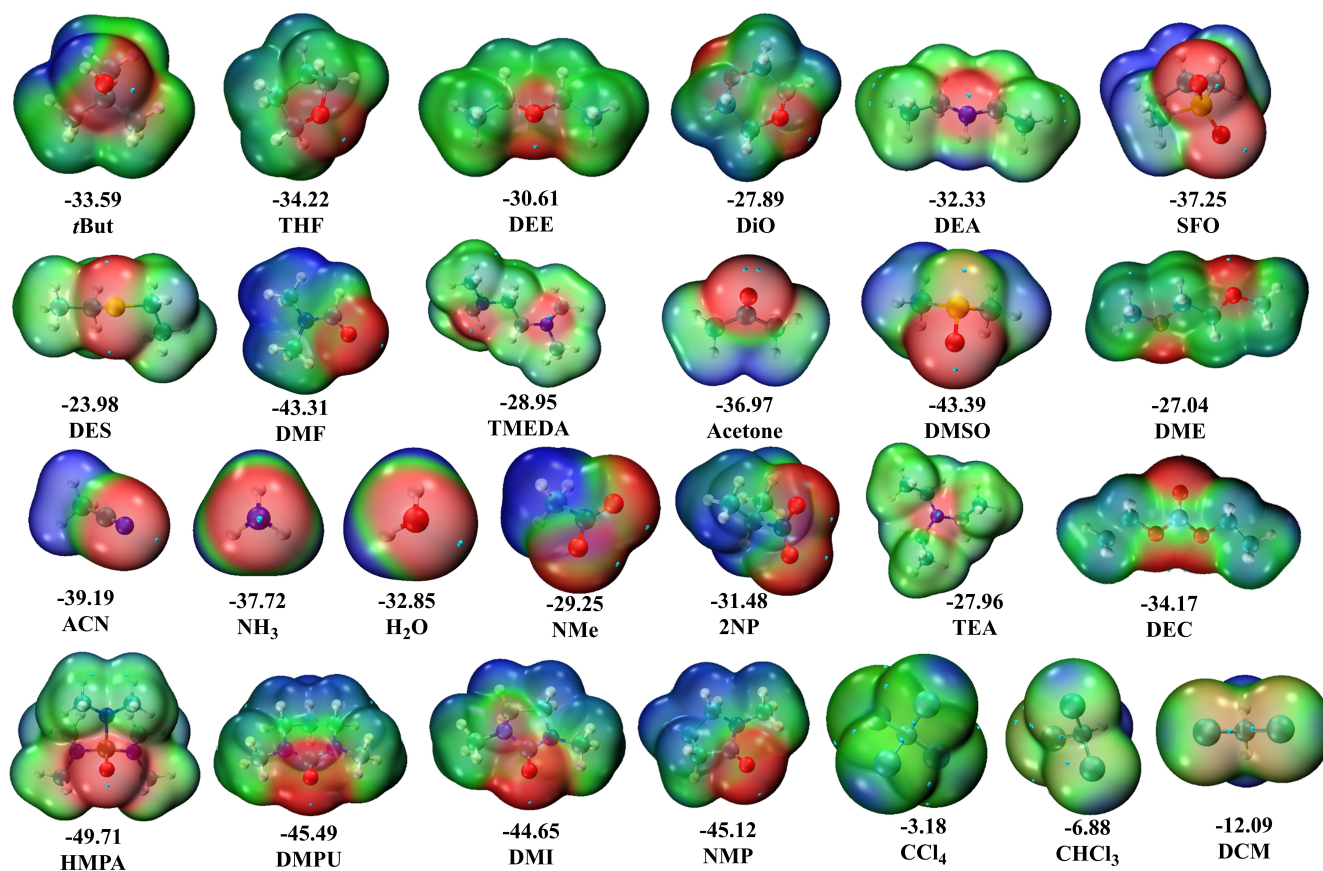


Figure 2. MESP values for different solvents with their corresponding minima ($V_{s,\text{min}}$ in kcal/mol) generated using the RGB color scale (isovalue 0.001 a.u.), where red represents negative regions, blue denotes positive regions, and green signifies the intermediate zone between them.

Table 1. Comparative interaction energies (with counterpoise correction) of XeO₃ with various solvents across three binding modes (1:1, 1:2, and 1:3) evaluated at the APFD/def2-TZVPD level of theory.

Solvent	V _{s,min} (in kcal/mol)	ΔE_{BSSE} (in kcal/mol)		
		1:3	1:2	1:1
HMPA	−49.71	−70.65	−47.99	−25.87
DMPU	−45.49	−62.11	−41.63	−22.08
NMP	−45.12	−55.83	−37.55	−19.71
DMI	−44.65	−57.84	−38.25	−19.90
DMSO	−43.39	−58.43	−41.17	−21.91
DMF	−43.31	−44.56	−32.29	−17.83
ACN	−39.19	−32.44	−20.88	−11.09
NH ₃	−37.72	−36.53	−25.62	−13.58
SFO	−37.25	−56.33	−37.25	−19.23
Acetone	−36.97	−42.01	−29.67	−15.78
THF	−34.22	−48.44	−32.70	−16.54
DEC	−34.17	−52.88	−33.18	−17.41
tBut	−33.59	−44.10	−29.75	−15.19
H ₂ O	−32.85	−32.66	−22.12	−11.31
DEA	−32.33	−54.33	−36.98	−19.27
2NP	−31.48	−35.86	−23.97	−11.97
DEE	−30.61	−47.14	−30.58	−15.18
NMe	−29.25	−36.81	−24.90	−12.67
TMEDA	−28.95	−58.08	−52.05	−33.52
TEA	−27.96	−51.98	−39.11	−20.91
DiO	−27.89	−41.90	−27.73	−13.74
DME	−27.04	−46.74	−35.99	−20.14
DES	−23.98	−52.59	−33.94	−16.46
DCM	−12.09	−24.18	−16.02	−8.23
CHCl ₃	−6.88	−23.16	−15.57	−7.61
CCl ₄	−3.18	−18.47	−11.22	−5.29

of MESP values with the interaction energies is not always straightforward, as there are many factors other than electrostatic interactions, such as orbital contribution, dispersion interactions, and intramolecular interactions, which influence the binding strength. Apart from DMSO, the top three solvents in terms of interaction energy values were revealed as HMPA, DMPU, and TMEDA across the different modes of binding. As expected from MESP values, the halogen donor solvents (DCM, CHCl₃, and CCl₄) were found to be associated with the lowest interaction energies. Furthermore, consistent with the MESP trend, nitrogen donor solvents demonstrate stronger interaction energies in one-to-one comparisons with oxygen donor solvents. For example, DEA > DEE, TMEDA > DME, and NH₃ > H₂O across the three binding modes.

Among other solvents, considering 1:3 binding mode, HMPA > DMPU > DMSO > TMEDA > DMI > SFO > NMP > DEA > DEC > TEA, makes the list of top ten candidates for stabilizing XeO₃. It is to be noted that, although DES has slightly better interaction energy as compared to TEA, there is a high chance that its adduct with XeO₃ will be short-lived, leading to a redox

decomposition of DES, as observed experimentally for the case of DMSO.^[29] Considering the same, among the sulfur-containing solvents, SFO might be a good candidate for stabilizing XeO₃, as it has a higher chance to resist oxidation, and trails only by 2.1 kcal/mol ($\Delta\Delta E_{\text{BSSE}}$) with respect to DMSO for the case of the 1:3 binding mode. It should be noted that SFO also has the highest boiling point (287.3 °C) among all the 26 solvents in this study. The interaction energy order for 1:2 binding mode was observed to be slightly changed, where TMEDA > HMPA > DMPU > DMSO > TEA > DMI > NMP > SFO > DEA > DME, makes the list of top ten candidates. TMEDA being a bidentate ligand tops the chart among the top three. Similarly, DME which is also another bidentate ligand makes the top ten list. Significant improvement in ranking for TEA was observed in the 1:2 binding case due to its bulky nature, which has more accommodative space in 1:2, thus lesser steric repulsion as compared to its 1:3 adduct. The top ten non-aromatic solvents (in this study) for 1:1 binding mode constitutes the same group of solvents, with slight change in their order; TMEDA > HMPA > DMPU > DMSO > TEA > DME > DMI > NMP > DEA > SFO. Again, the improvement in the ranking of DME can be attributed to its bidentate nature, which allows it to interact with two out of the three σ -holes present in XeO₃, leading to a higher stabilization. As, evident from Table 1, MEPs alone cannot serve as the exclusive indicator for the strength of these non-covalent interactions, thus prompting us to employ different computational tools to obtain further insights into the factors influencing the stability of these aerogen bond adducts.

Geometrical Characteristics, Wiberg Bond Indices (WBI), and Charge Analysis

The optimized cartesian coordinates for all the adducts are provided in the electronic supporting information (ESI) file. The optimized geometries corresponding to XeO₃ and the adducts of the top ten solvents (1:3, 1:2, and 1:1) along with their bonding parameters, such as primary Xe–O bond length, secondary Xe...X (X = donating atom of the solvent) bond distances, bond angles associated with the aerogen bonds, natural population charge analysis (obtained from NBO), and Wiberg bond indexes are shown in Figures S1–S11. A comparative summary of the above-mentioned parameters for the top three solvents is listed in Table 2. In general, elongation of Xe–O bond upon adduct formation was observed for all cases, and follows the order 1:1 > 1:2 > 1:3, with a couple of exceptions. The increase in Xe–O bond lengths is found to be highest in TMEDA for 1:1 and 1:2 adducts, where TMEDA is bound to XeO₃ in a bidentate fashion. For the 1:3 adduct of TMEDA, a monodentate binding mode had to be considered, which showed lesser elongation of the Xe–O bond as compared to its 1:2 and 1:1 adducts. Similar observations were also made for DME, which is another bidentate solvent in this study. However, no bidentate mode of binding could be observed for its cyclic analogue DiO, due to the rigid backbone of the latter.

The secondary bond distances corresponding to the σ -hole interactions and their associated bond angles were also found

Table 2. Geometrical parameters. X denotes the donating atom of different solvents. WBI values are listed along with the atomic charges (in a.u.) obtained from the natural population analysis at the APFD/def2-TZVPD level of theory.

Solvent	Ratio	Xe–O (in Å)	Xe...X (in Å)	<O–Xe...X (in °)	WBI (XeO ₃)	WBI (Xe...X)	NPA (XeO ₃)
HMPA	1:3	1.7701	2.6420	166.74	Xe1 = 3.3125	0.0458	Xe1 = +3.016
		1.7720	2.6414	166.28	O2 = 1.4259	0.0481	O2 = –1.021
		1.7734	2.6391	167.37	O3 = 1.4153	0.0500	O3 = –1.031
					O4 = 1.4094		O4 = –1.038
	1:2	1.7666	2.6169	165.36	Xe1 = 3.3212	0.0509	Xe1 = +2.957
		1.7675	2.6011	163.37	O2 = 1.4367	0.0585	O2 = –0.997
		1.7675			O3 = 1.4541		O3 = –0.999
					O4 = 1.4405		O4 = –1.016
	1:1	1.7644	2.5688	161.79	Xe1 = 3.3436	0.0699	Xe1 = +2.868
		1.7645			O2 = 1.4723		O2 = –0.969
		1.7641			O3 = 1.5006		O3 = –0.965
					O4 = 1.4711		O4 = –0.972
DMPU	1:3	1.7712	2.7353	170.86	Xe1 = 3.3278	0.0420	Xe1 = +2.945
		1.7711	2.7366	170.71	O2 = 1.4345	0.0419	O2 = –1.009
		1.7711	2.7318	170.85	O3 = 1.4346	0.0425	O3 = –1.009
					O4 = 1.4343		O4 = –1.010
	1:2	1.7677	2.6445	165.43	Xe1 = 3.3343	0.0576	Xe1 = +2.905
		1.7731	2.7076	167.42	O2 = 1.4432	0.0466	O2 = –0.992
		1.7638			O3 = 1.4438		O3 = –1.009
					O4 = 1.4816		O4 = –0.970
	1:1	1.7616	2.6115	162.07	Xe1 = 3.3508	0.0659	Xe1 = +2.844
		1.7668			O2 = 1.4918		O2 = –0.955
		1.7647			O3 = 1.4655		O3 = –0.975
					O4 = 1.5041		O4 = –0.960
TMEDA	1:3	1.7702	2.9278	177.96	Xe19 = 3.3458	0.0596	Xe19 = +2.897
		1.7707	2.9220	177.33	O20 = 1.4366	0.0604	O20 = –1.005
		1.7708	2.9275	177.30	O21 = 1.4361	0.0594	O21 = –1.006
					O22 = 1.4359		O22 = –1.006
	1:2	1.7759	2.8110	158.90	Xe12 = 3.3521	0.0644	Xe12 = +2.888
		1.7754	2.7986	162.22	O13 = 1.4400	0.0707	O13 = –1.009
		1.7720	2.8875	176.64	O14 = 1.4412	0.0597	O14 = –1.009
					O15 = 1.4246		O15 = –1.009
	1:1	1.7684	2.7591	160.51	Xe1 = 3.3601	0.0776	Xe1 = +2.850
		1.7729	2.7156	159.39	O2 = 1.4314	0.0862	O2 = –0.990
		1.7728			O3 = 1.4708		O3 = –0.990
					O4 = 1.4698		O4 = –0.990

to be increasing from the 1:1 to the 1:3 adducts, which could be attributed to an increase in steric crowding. It is also interesting to note that adducts of HMPA have the shortest secondary bond distance among the top three, enabling it to have a stronger interaction with the σ -hole of XeO₃. It must be noted that the intermolecular secondary bond distances (Xe...X) were observed to be shorter than the sum of their respective van der Waals radii ($\Sigma(\text{Xe–O})_{\text{vdW}} = 3.68 \text{ Å}$, $\Sigma(\text{Xe–N})_{\text{vdW}} = 3.71 \text{ Å}$, according to Bondi^[53] and larger than the sum of their corresponding covalent radii ($\Sigma(\text{Xe–O})_{\text{cov}} = 2.03 \text{ Å}$, $\Sigma(\text{Xe–N})_{\text{cov}} = 2.11 \text{ Å}$). Consistent with the observed bond elongation, there was a gradual decrease in the Wiberg bond indices of both Xe and O upon the formation of adducts, following the order of 1:1 > 1:2 > 1:3. A similar trend was also noted for the aerogen bonds (Xe...X), with an overall reduction in WBI values following the order of 1:1 > 1:2 > 1:3. Furthermore, natural population analysis revealed that, upon the formation of the adducts, the charges on Xe and O within XeO₃ were enhanced. In particular, Xe demonstrated an increase in positive charge, whereas oxygen exhibited an increase in negative charge, while both

follow the trend 1:3 > 1:2 > 1:1 (more $\pm$ to less $\pm$). These results indicate an increased polar-covalent character in the primary Xe–O bonds of XeO₃ upon adduct formation. It is interesting to note that the adducts of HMPA show the maximum enhancement in the charges of Xe and O, suggesting a stronger charge transfer from HMPA to XeO₃ among the top three.

Non-Covalent Interaction (NCI) Plots and Bond Critical Points (BCP) Analysis

To obtain more insights into the binding between XeO₃ and the various non-aromatic coordinating solvents, NCI plot analyses were carried out, which unveiled that beyond the aerogen bonds involving the donor atom of the solvents and Xe, there exist attractive regions indicative of hydrogen bonding interactions, specifically C–H...O interactions. NCI plots for the adducts of XeO₃ with the top three solvents are illustrated in Figure 3 and Figure S12. The σ -hole mediated aerogen bonds

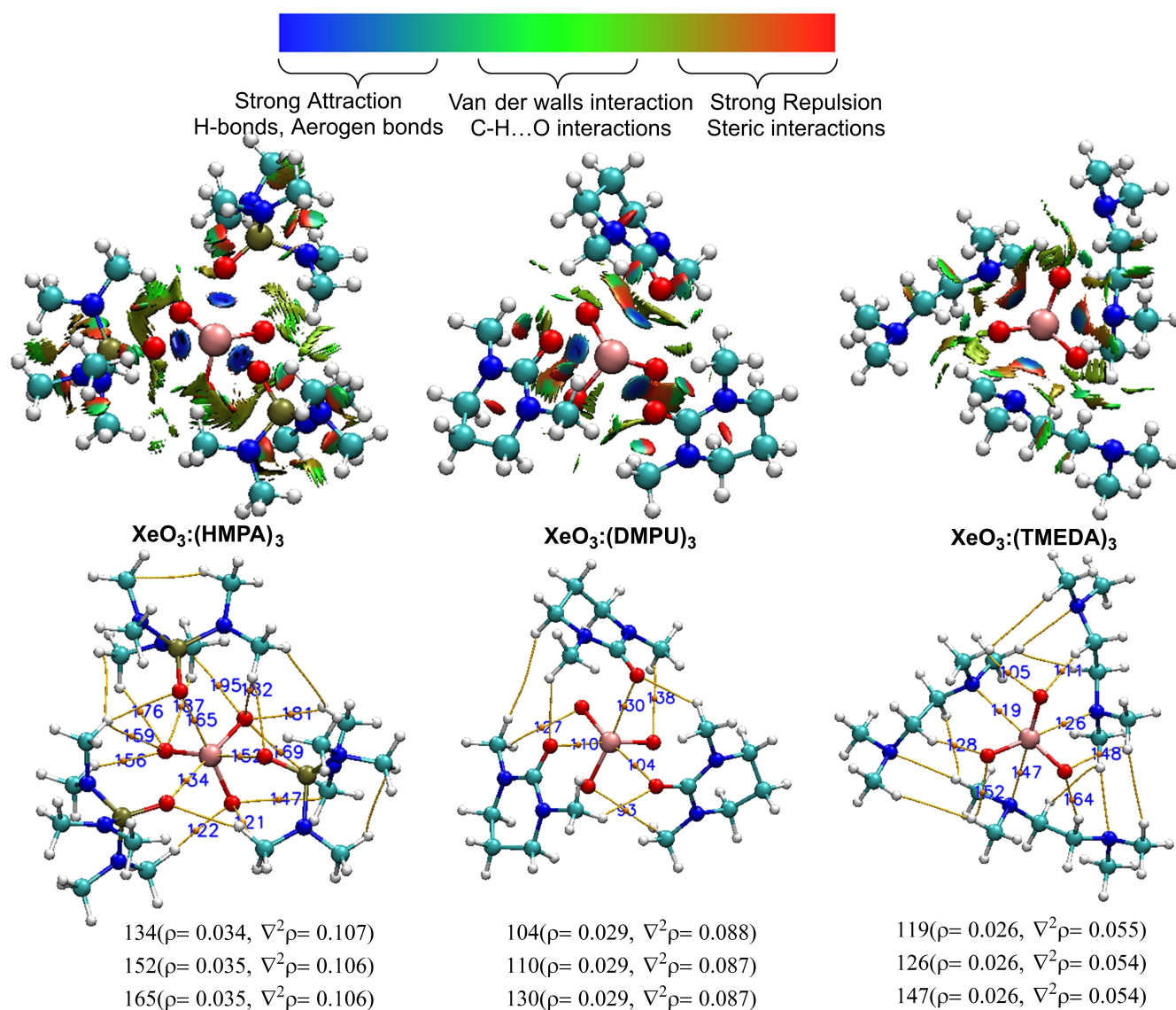


Figure 3. NCI plots (isovalue 0.5 a.u.) and bond critical points (of aerogen bonds) obtained from the AIM analysis of the adducts of XeO_3 with the top three solvents, for the 1:3 binding mode and their respective electron density (ρ , in a.u.) and Laplacian of the electron density ($\nabla^2\rho$, in a.u.).

are depicted by an intense blue-colored region, suggesting very strong stabilizing interactions, whereas, the C-H...O interactions are revealed as weakly stabilizing interactions, which are indicated by the greenish surface associated with them. Some intermolecular stabilizing weak interactions between the solvent molecules were also observed, as indicated by the greenish surface between them. Owing to the greater number of neighboring atoms, the number of C-H...O interactions increases in the order 1:1 < 1:2 < 1:3. These observations are further corroborated by bond critical point (BCP) analyses.

As revealed by NCI plots, bond critical points were observed corresponding to aerogen bonds as well as C-H...O hydrogen bonding interactions. A consistent trend in electron density (ρ) and the Laplacian ($\nabla^2\rho$) of the electron density associated with the BCPs of aerogen bonds was observed to follow the order 1:3 < 1:2 < 1:1, consistent with the shorter secondary (Xe...X) bond distances in the same order. From BCP analysis, it is

evident that the number of C-H...O interactions are highest for HMPA adducts, the best among the top three. Some intermolecular C-H...N and C-H...O hydrogen bonding interactions were also observed from the AIM/BCP analysis. The Laplacian values were found to be positive for all the cases, which suggests a close-shell system as per Bader's AIM theory. These BCPs are shown in Figure 3 and Figure S13 along with their respective electron density (ρ , in a.u.) and Laplacian of electron density ($\nabla^2\rho$, in a.u.). The largest value of ρ at the BCPs corresponding to the aerogen bonds was observed for the adducts of HMPA, which provides a clear indication that the interactions between HMPA and XeO_3 are the strongest. In general, by comparing the absolute value of ρ , it can also be implied that the 1:1 adducts show stronger aerogen bonding interactions as compared to 1:2 and 1:3 adducts. The NCI plots and BCPs related to the remaining top ten solvents are shown in Figures S14–S20.

Table 3. Second-order perturbation energy values (E^2 , in kcal/mol) obtained from natural bond orbital (NBO) analysis of selected adducts of XeO_3 at the APFD/def2-TZVPD level of theory.

Solvent	Ratio	Donor	Acceptor	E^2
HMPA	1:3	LP (1)Xe1	BD*(1)O5–P9	0.92
		LP (1)Xe1	BD*(1)O6–P10	0.81
		LP (1)Xe1	BD*(1)O7–P8	0.79
		LP (1)O5	BD*(1)Xe1–O3	2.33
		LP (3)O5	BD*(1)Xe1–O3	4.30
		LP (1)O6	BD*(1)Xe1–O2	1.94
		LP (3)O6	BD*(1)Xe1–O2	5.26
		LP (1)O7	BD*(1)Xe1–O4	1.92
		LP (3)O7	BD*(1)Xe1–O4	5.53
		LP (1)Xe1	BD*(1)O5–P8	1.14
		LP (1)Xe1	BD*(1)O6–P7	1.01
		LP (1)O5	BD*(1)Xe1–O3	2.54
	1:2	LP (3)O5	BD*(1)Xe1–O3	4.23
		LP (1)O6	BD*(1)Xe1–O4	2.00
		LP (3)O6	BD*(1)Xe1–O4	6.49
	1:1	LP (1)Xe1	BD*(1)O5–P6	1.23
		LP (1)O5	BD*(1)Xe1–O3	2.04
		LP (3)O5	BD*(1)Xe1–O3	6.90
DMPU	1:3	LP (1)Xe1	BD*(1)O5–C27	0.25
		LP (1)Xe1	BD*(2)O5–C27	0.30
		LP (1)Xe1	BD*(1)O6–C8	0.25
		LP (1)Xe1	BD*(2)O6–C8	0.30
		LP (1)Xe1	BD*(1)O7–C18	0.25
		LP (1)Xe1	BD*(2)O7–C18	0.31
		BD (2) O5–C27	BD*(1)Xe1–O3	2.84
		LP (1) O5	BD*(1)Xe1–O3	0.92
		BD (2) O6–C8	BD*(1)Xe1–O2	2.84
		LP (1) O6	BD*(1)Xe1–O2	0.92
		BD (2) O7–C18	BD*(1)Xe1–O4	2.87
		LP (1)O7	BD*(1)Xe1–O4	0.95
	1:2	LP (1)Xe1	BD*(2) O5–C16	0.57
		LP (1)Xe1	BD*(2) O6–C7	0.39
		LP (1)Xe1	BD*(1) O6–C7	0.29
		BD (2) O5–C16	BD*(1)Xe1–O3	3.55
		LP (1)O5	BD*(1)Xe1–O3	1.37
		BD (2) O6–C7	BD*(1)Xe1–O4	3.08
		LP (1) O6	BD*(1)Xe1–O4	0.92
	1:1	LP (1)Xe1	BD*(1) O5–C6	0.49
		LP (1)Xe1	BD*(2) O5–C6	0.70
		BD (2) O5–C6	BD*(1)Xe1–O4	4.00
		LP (1)O5	BD*(1)Xe1–O4	1.41
TMEDA	1:3	LP (1)Xe19	BD*(1) C1–N25	0.36
		LP (1)Xe19	BD*(1) N25–C41	0.28
		LP (1)Xe19	BD*(1) C3–N23	0.36
		LP (1)Xe19	BD*(1) N23–C73	0.28
		LP (1)Xe19	BD*(1) C14–N27	0.36
		LP (1)Xe19	BD*(1) N27–C57	0.27
		LP (1)N25	BD*(1)Xe19–O20	4.92
		LP (1)N23	BD*(1)Xe19–O21	4.86
		LP (1)N27	BD*(1)Xe19–O22	4.83
	1:2	LP (1)Xe12	BD*(1) C1–N33	0.41
		LP (1)Xe12	BD*(1) C2–N33	0.25
		LP (1)Xe12	BD*(1) C3–N34	0.29
		LP (1)Xe12	BD*(1) C24–N34	0.34
		LP (1)Xe12	BD*(1) N33–C49	0.38
		LP (1)Xe12	BD*(1) N34–C45	0.45
		LP (1)Xe12	BD*(1) C7–N35	0.35
		LP (1)Xe12	BD*(1) C16–N35	0.29
		LP (1)Xe12	BD*(1) N35–C37	0.20
		LP (1) N 35	BD*(1)Xe12–O15	5.41
		LP (1) N 33	BD*(1)Xe12–O13	6.08
		LP (1) N 34	BD*(1)Xe12–O14	6.68
	1:1	LP (1)Xe 1	BD*(1) C5–N12	0.36
		LP (1)Xe 1	BD*(1) C6–N11	0.33
		LP (1)Xe 1	BD*(1) N11–C21	0.58

Table 3. continued

Solvent	Ratio	Donor	Acceptor	E^2
		LP (1)Xe 1	BD*(1) N11–C25	0.32
		LP (1)Xe 1	BD*(1) N12–C13	0.61
		LP (1)Xe 1	BD*(1) N12–C17	0.35
		LP (1) N 11	BD*(1)Xe1–O4	7.20
		LP (1) N 12	BD*(1)Xe1–O3	8.15

Natural Bond Orbital (NBO) Analysis

NBO calculations were carried out to enhance our understanding of the donor-acceptor nature of these adducts by investigating the orbital interactions between the solvent molecules and XeO_3 quantified through second-order perturbation energy (E^2).^[54] Some interesting results from NBO analysis were observed, and are summarized in Table 3 (for the top three solvents), and Tables S1–S3 (for the remaining solvents among the top ten candidates). It was observed that the E^2 values corresponding to the interaction between the lone pair on the donating atom and the acceptor $\sigma^*(\text{Xe}–\text{O})$ orbital (corresponding to the σ -hole) increase while moving from 1:3 to 1:1 adducts, in accordance with the decrease in their secondary bond distances ($\text{Xe}\cdots\text{X}$). Considering the amphoteric Lewis acid/base nature of XeO_3 , the strength of back donation from the lone pair on Xe to the antibonding orbital of the donating atom/group was also examined for individual solvent molecules, which although smaller, but not negligible, follows the order 1:1 > 1:2 > 1:3. This provides another explanation for the trend in secondary bond distances, which follows the same order. It should be noted that the cumulative strength of back-donation was found to be highest for the adducts of HMPA for the 1:3 binding mode, and TMEDA for the 1:2 and the 1:1 binding mode (due to its bidentate nature), among the top three solvents, which correlates with the interaction energy trends.

A very interesting observation from NBO analysis was the revelation of a stronger donation from the bonding $\text{O}=\text{C}$ orbital of DMPU to the σ -hole of XeO_3 ($\pi \rightarrow \sigma^*$), as compared to the donation from the lone pair of oxygen to the same ($n \rightarrow \sigma^*$), for each binding mode, in the order of 1:1 > 1:2 > 1:3. The absence of such interaction, in case of HMPA, can be attributed to the enhanced polar character of the $\text{O}=\text{P}$ orbital, due to larger electronegativity difference between O and P. It should be noted that two bonding NBOs corresponding to $\text{O}=\text{C}$ in DMPU (one σ and one π) were observed, whereas only one bonding NBO related to $\text{O}=\text{P}$ in HMPA (only σ) was observed. However, this leads to the accumulation of charge on the donor oxygen atom of HMPA leading to a stronger $n \rightarrow \sigma^*$ (lone pair of oxygen to the σ -hole) interactions in its aerogen bond complexes, as compared to that of DMPU, which overcompensates the absence of earlier mentioned $\pi \rightarrow \sigma^*$ interactions in HMPA adducts. The NBO analysis also confirms the presence of $\text{C}\cdots\text{H}\cdots\text{O}$ hydrogen bonds. However, they are significantly weaker than the aerogen bonds, with the associated E^2 values ranging only 0.07–1.43 kcal/mol for HMPA, 0.05–0.18 kcal/mol

for DMPU, and 0.05–1.86 kcal/mol for TMEDA (Table S4), in the order of 1:3 > 1:2 > 1:1.

Energy Decomposition Analysis (EDA)

The aforementioned observations were additionally corroborated through the Ziegler-Rauk energy decomposition analysis.^[61] The energy decomposition analysis was carried out for all the adducts across the three binding modes (1:1, 1:2, and 1:3). While the absolute interaction energies may vary with different functional/basis set combinations (Tables S5–S7), the same group of solvents were found to constitute the top ten (except DES), with variation in their order, enabling further interpretations. In summary, ignoring the halogen-containing solvents, the attractive interaction consists of approximately 47–64% electrostatic, 26–34% orbital, and 8–24% dispersion components. For halogenated solvents (DCM, CHCl₃, and CCl₄), the electrostatic nature of NCIs reduces to 35–55%, whereas an increased contribution from dispersion factors (18–43%) was observed. Overall, apart from a few exceptions (highlighted in Table—S8), going from 1:1 to 1:3 mode of binding, the percentage contributions from electrostatic and orbital interactions were found to be decreasing, with increased contribution from the dispersion interaction. In general, electrostatic interactions remain the dominant contributor for all the cases except for CCl₄, where the contribution from dispersion interactions overcomes that of the electrostatic (Table S8). A comparative summary of the energy decomposition analysis for the top three solvents is listed in Table 4.

It is to be noted that, the order of interaction energy obtained from EDA varies from the BSSE corrected interaction energy. This difference in the interaction energy from EDA as compared to earlier trends also could be attributed to the BSSE correction, and the variation in the level of theory. Consistent with the interaction energy, BCP and the NBO analysis trend, HMPA shows the highest orbital interaction, as well as electrostatic and dispersion interaction among the top three, for 1:3 adducts, whereas TMEDA was observed to be the highest for 1:2 and 1:1 adducts. Although TEA breaks into the top three adducts for 1:2, and 1:1 binding mode, considering the

interaction energy obtained from EDA, it could be attributed to its higher contribution from dispersion as well as orbital interaction. It is also observed that in agreement with the MESP and interaction energy trends, nitrogen donor solvents have a higher percentage contribution from orbital interactions, as compared to oxygen donor solvents when there is a one-on-one comparison, such as DEA vs DEE, TMEDA vs DME, NH₃ vs H₂O (for all three binding modes).

Conclusions

Our probe into the adduct formation between diverse non-aromatic coordinating solvents and XeO₃ has provided crucial insights into the factors dictating their strength. Nitrogen donor solvents were found to have a stronger affinity towards the σ -holes of XeO₃, as compared to their analogous oxygen donor solvents. The top three solvents which form the strongest adducts with XeO₃, among the twenty six non-aromatic solvents in the current study, were found to be hexamethylphosphoramide (HMPA with a O=P donating site), N,N'-dimethylpropyleneurea (DMPU with an O=C donating site) and tetramethylethylenediamine (TMEDA, a bidentate solvent with two nitrogen donating sites). Other solvents that constitute the top ten list, apart from the experimentally well-explored DMSO,^[33] are imidazolidinone (DMI), sulfolane (SFO), N-Methyl-2-pyrrolidone (NMP), diethylamine (DEA), diethylcarbonate (DEC), triethylamine (TEA) and dimethoxyethane (DME). In a happy coincidence, seven out of the top ten solvents identified possess high boiling points (> 100 °C), with SFO (285 °C) being the highest among them. This feature is expected to inhibit solvent evaporation and prevent adduct dissociation – a phenomenon observed experimentally with the low-boiling-point solvent acetone (56 °C).^[33] The important role of the C–H...O hydrogen bonding interaction, as well as that of back bonding from the lone pair of Xe to the antibonding orbital corresponding to the donating atom/group of solvent, in stabilizing these adducts has also been revealed. Lastly, it was also confirmed from the energy decomposition analysis that these σ hole-mediated interactions are predominantly electrostatic in nature. However significant contributions from orbital interactions (up to 34%)

Table 4. The energy decomposition analysis (EDA) of selected adducts of XeO₃ with different solvents at the BP86-D3BJ/TZ2P level of theory. Percentage contribution to the total attractive energy is shown below, where electrostatic interactions are denoted as E_{elstat} , orbital interactions as E_{oi} , and dispersion interactions as E_{disp} .

Solvent	Ratio	ΔE	E_{Pauli}	E_{elstat}	%	E_{oi}	%	E_{disp}	%
HMPA	1:3	−64.09	118.32	−91.83	50	−52.44	29	−38.15	21
	1:2	−43.24	80.95	−66.65	54	−36.94	30	−20.59	17
	1:1	−23.16	44.4	−37.71	56	−20.67	31	−9.18	14
DMPU	1:3	−53.74	98.99	−78.26	51	−43.75	29	−30.72	20
	1:2	−35.96	69.04	−55.48	53	−31.32	30	−18.2	17
	1:1	−19.34	37.85	−31.56	55	−18.15	32	−7.48	13
TMEDA	1:3	−55.43	109.02	−80.32	49	−48.07	29	−36.06	22
	1:2	−48.6	102.57	−79.09	52	−46.32	31	−25.76	17
	1:1	−31.59	75.72	−58.82	55	−35.77	33	−12.72	12

and dispersion interactions (up to 24%) were also noted. In conclusion, our investigation sheds light on the key factors influencing the strength of the aerogen-bonded adducts, highlighting variations in their stability when bound in 1:1, 1:2, and 1:3 configurations. Our findings not only contribute to the broader understanding of sigma hole-mediated non-covalent interactions but also offer insights into the nucleophilicity (coordinating ability) of non-aromatic solvents as Lewis base donors. We note here that there are other factors, such as the possibility of unwanted side reactions,^[33] that can influence the choice of the optimal solvent for XeO₃. Nevertheless, the current work can serve as a guide for experimentalists and aid them in screening for the best solvent(s) for preparing XeO₃ adducts.

Computational Methods

The Gaussian 09 suite of programs was utilized for conducting all the density functional theory (DFT) calculations.^[55] Optimization of each model in the gas phase was carried out by employing the APFD^[56] functionals along with the def2-TZVPD basis set.^[57] This specific theoretical approach was chosen based on its established reputation for reliability, as demonstrated in benchmarks against experimentally obtained adducts of XeO₃, by Schrobilgen's research group.^[32,33] Additionally, all the stationary points were confirmed to be minima by performing harmonic frequency calculations. Furthermore, Grimme's semi-empirical Conformer–Rotamer Ensemble Sampling Tool (CREST)^[58] was employed for conformational search analysis at the xTB-GFN2 levels of theory.^[59–61] The models or conformers obtained from CREST underwent additional optimization through DFT. With a few exceptions, a consensus between the CREST and DFT models was observed concerning the orientation and binding mode of the solvents. Only the most stable geometry for all the adducts was considered. It is to be noted that CREST was employed solely to ensure that no lower energy conformer (or a more stable binding mode) was omitted from our study.^[58] In order to enhance the accuracy of interaction energy (ΔE) values via rectifying the basis set superimposition error (BSSE), the counterpoise correction method was utilized.^[62] The MultiWFN program^[63] was used to generate and evaluate ESP, NCI plot, and AIM analysis, and the Visual Molecular Dynamics (VMD) software^[64] was used for visualization. NBO analysis was performed using the incorporated module in the Gaussian 09 software. For EDA^[65], the BP86/TZ2P^[66,67] level of theory was applied along with Grimme's DFT-D3 correction with Becke–Johnson damping (BJ) as implemented in ADF 2023. The frozen core approximation with scalar relativistic effect was used and the numerical quality was set to good. A strictly closed-shell fragmentation scheme was chosen. The APFD functional, as well as the def2TZVPD basis set are not implemented in ADF 2023 and the EDA has not been checked for consistency and robustness with this method, whereas it is well established for BP86/TZ2P level of theory. Additionally, a recent publication has shown that the selection of the functional is not a determining factor in deriving meaningful conclusions from the EDA analysis.^[68]

Supporting Information

Optimized cartesian coordinates and other related information as discussed in the manuscript are deposited to the electronic supporting information.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Taming XeO₃ with Aza-Crowns: Computational Studies into σ -Hole Mediated Host-Guest Interactions

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Various aza-crowns with different sizes and substituents have been explored computationally as potential hosts for stabilizing the explosive guest xenon trioxide (XeO₃) through σ -hole-mediated aerogen bonding interactions. Interestingly, aza-crowns demonstrate superior binding towards XeO₃ compared to their oxygen and thio counterparts. However, unlike the

latter cases, where the binding was found to be increasingly favorable with the increase in the size of the crowns, aza-crowns exhibit a variable size preference for XeO₃, peaking with aza-15-crown-5, and reducing thereafter with increase in crown size.

Great science often demands sacrifices and encourages people to take risks, as was the case for the discovery of the explosive nature of XeO₃, leading to the hospitalization of Bartlett and Rao.^[1] However, ironically, the curse of σ -holes (a positively charged localized region present at the extension of the Xe=O bond),^[2–4] which is responsible for the explosiveness of XeO₃, could also act as a boon to stabilize it, if XeO₃ were to be provided with an appropriate host.^[5,6] The host could be a Lewis base or an anion willing to share its electrons to quench the electron deficiency of the σ -hole regions, as the aerogen bonding is predominantly electrostatic, similar to the halogen bonds as well as the pnictogen bonds as defined by IUPAC recently.^[7–13] Among the few experimental attempts to stabilize XeO₃ by utilizing this principle, its adduct with 15-crown-5 stands out, achieving high stability and shock insensitivity in comparison to the others.^[14–16] In a continuous effort to further improve the stability of the XeO₃ adducts, different crown ethers, along with their thio analogues, have been investigated computationally.^[17,18] While experimental and computational studies have explored the aerogen bonding interactions of nitrogen based donors with XeO₃,^[2,13,19–21] there have been no reports thus far on macrocyclic nitrogen based donors in this context. Hence, herein, we have investigated the aza-crowns, which are nitrogen analogues of the crown ethers, as a potential macrocyclic host to stabilize XeO₃ by means of different computational techniques. Our goal is to find the “chosen one”, that is, the best among the pool of potential aza-crown hosts, explore the leading causes for stabilization, and determine guidelines to minimize the risk associated with an experimental exploration. In addition to their role as poly-

dentate macrocyclic ligands, aza-crowns offer the advantage of having substituents bound to the nitrogen atoms,^[22] whose effect on the strength of host-guest complexes is also investigated in this study, along with the ongoing exploration on the impact of increasing crown sizes. Different alkyl groups (Figure 1) were considered as the substituents, as they exhibit +I effects that can enhance the nucleophilicity of the nitrogen atoms towards the σ -holes of XeO₃. These groups can also potentially facilitate C–H...O interactions when properly aligned, which could further strengthen the binding of XeO₃.

While the negative potential obtained from the molecular electrostatic potential surface (MESP) analysis does not increase with the size of the substituent from Me to ^tBu (Figures S1–S5, Table S1), natural population analysis (Table S2) reveals the expected rise in charge on the nitrogen atoms (Me < Et < ⁱPr < ^tBu). Among the different sizes of aza-crowns (Figure 2, Table S1), the shared negative potential was found to be highest for aza-18-crown-6 (18N6) with Me, Et, and ⁱPr

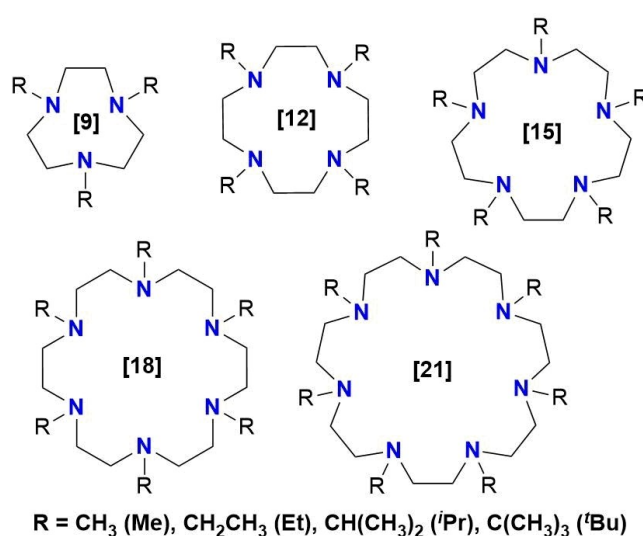


Figure 1. Different aza-crowns (with increasing crown size) having different substituents (with increasing steric bulk) used as potential hosts for XeO₃ in this study.

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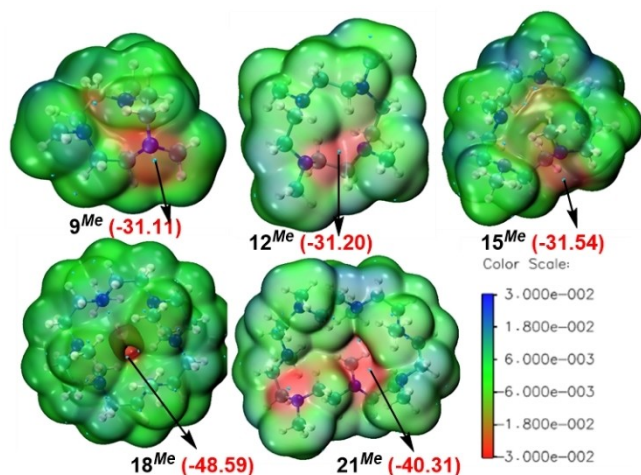


Figure 2. The MESP (color scale: RGB, isovalue = 0.001 a.u.) of different aza-crowns with their corresponding highest $V_{s,min}$ in kcal/mol. See Table S1 for details.

substituents. Except for ^tBu substituents, a decrease in shared negative potential was observed in the order Me > Et > ⁱPr.

The interaction energies, accounting for the basis set superposition error (Table 1), indicate higher values for the host-guest complexation between aza-crowns and XeO₃ as compared to their oxygen and thio analogues.^[17] However, interestingly, unlike crown ethers and thio-crown ethers, the interaction energies do not tend to increase with the increase in the size of the aza-crowns. Instead, they show an increase from aza-9-crown-3 (9N3) to aza-15-crown-5 (15N5), followed by a decrease up to aza-21-crown-7 (21N7), for Me, Et, and ⁱPr substitutions. Among the ^tBu substituted complexes, aza-12-crown-4 (12N4) shows the highest interaction energy.

The deformation energies associated with the complexation of aza-crowns with XeO₃ (listed in Table S3) were observed to be higher (except for 9N3^{Me}) in comparison to their oxygen and thio analogues, which could be attributed to the loss of intramolecular C–H...N interactions present in the parent aza-crowns. Additionally, deformation energies were found to rise with increasing steric bulk of the substituents. With a few

exceptions, they were found to increase as the size of the aza-crowns expanded up to 18N6, followed by a decrease for 21N7.

The optimized geometries of the host-guest complexes formed by aza-crowns and XeO₃ are depicted in Figures 3, S6–S10. An alternative mode of binding was observed for the Me ($\Delta E_{BSSE} = -50.5$ kcal/mol) and Et ($\Delta E_{BSSE} = -51.2$ kcal/mol) substituted 21N7 (21N7') cases, where Xe binds to three of nitrogen donor atoms instead of four (Figure S11). In all cases, the Xe=O bond lengths were observed to elongate upon complexation. This elongation can be attributed to the transfer of electron density from the lone pair of nitrogen atoms to the σ -holes located at the antibonding (σ^*) Xe–O orbital. Consequently, an increase in the polar covalent character of the primary Xe–O bonds was observed, which is also reflected by the enhanced charges (natural population analysis), and reduced Wiberg bond indices (WBI) corresponding to Xe and O atoms (Tables 2, S4–S7). The secondary bond distances associated with the interacting nitrogen atoms and Xe were found to fall within the range of the sum of their corresponding covalent radii ($\Sigma(Xe-N)_{cov} = 2.11$ Å) and van der Waals radii ($\Sigma(Xe-N)_{vdW} = 3.71$ Å, as per Bondi).^[23] It was observed that the Xe...N secondary bond distances increased with the increase in the crown size from 9N3 to 18N6, followed by a decrease for 21N7 and 21N7'. The longer Xe...N distance in the 18N6 complexes can also be attributed to the steric factors, which prevent XeO₃ from approaching the nitrogen donor sites more closely. With a few exceptions, the Xe...N distances generally increased with the increase in the substituent size. The bond orders associated with the secondary Xe...N interactions, as determined from the WBI analysis, align with the trends observed in bond distances (Tables 2, S4–S7).

The non-covalent interactions (NCI) plot analysis reveals a gradual decrease in aerogen bonding strength, indicated by a colour shift on the surface between nitrogen atoms and Xe, transitioning from bluish to greenish from 9N3 to 18N6, followed by an increase for 21N7 and 21N7', albeit with less coordination with the donor atoms. Similar to observations in crown ethers, C–H...O interactions were found to increase with

Table 1. BSSE corrected interaction energies (in kcal/mol) for the complexation of XeO₃ with various aza-crowns, computed at the APFD/def2-TZVPD level of theory.

ΔE_{BSSE}	Me	Et	ⁱ Pr	^t Bu
9N3	–42.3 (–41.8)	–43.4 (–43.0)	–46.3 (–45.9)	–46.6 (–46.3)
12N4	–52.7 (–52.5)	–53.8 (–53.6)	–52.0 (–52.0)	–53.6 (–53.5)
15N5	–58.2 (–58.2)	–59.4 (–59.4)	–54.9 (–55.0)	–42.5 (–42.5)
18N6	–55.6 (–55.8)	–54.9 (–55.1)	–52.9 (–53.0)	–40.5 (–40.5)
21N7	–50.6 (–50.7)	–51.5 (–51.6)	–53.0 (–53.1)	–42.3 (–42.3)

[a] bracketed values at the APFD/aug-cc-pVTZ (–PP for Xe) level of theory.

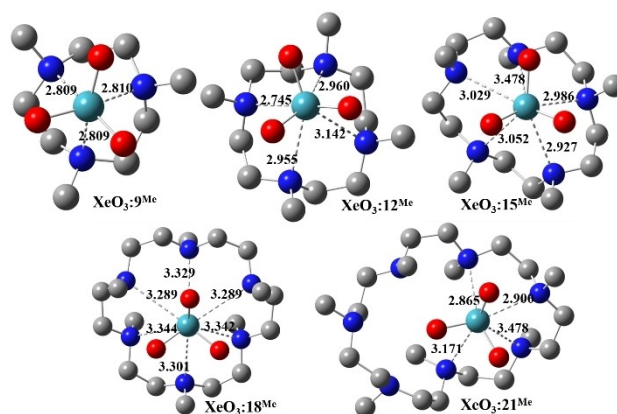


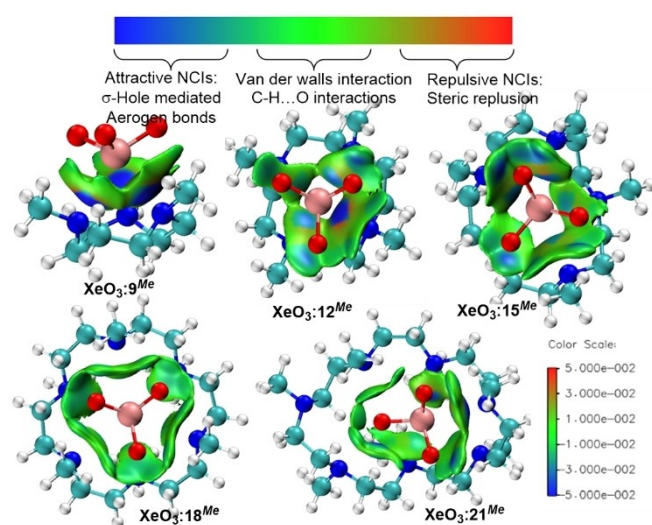
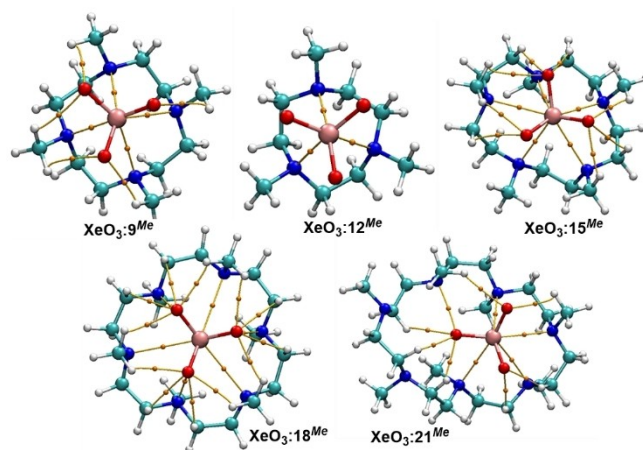
Figure 3. Optimized models of host-guest complexes of aza-crowns (Me) and XeO₃ with increasing crown size. Bond distances corresponding to Xe...N interactions are shown in Å. Hydrogen atoms have been omitted for clarity.

Table 2. Bond parameters host-guest complexes of aza-crowns (Me) and XeO₃. The electron density (ρ) and the Laplacian of electron density ($\nabla^2\rho$) values of the BCPs corresponding to the aerogen bonds are listed.

Me	Xe–O (in Å)	Xe...N (in Å)	WBI (Xe...N)	ρ (in a.u.)	$\nabla^2\rho$ (in a.u.)
9N3	1.776	2.809	0.0555	0.038	0.073
	1.776	2.809	0.0554	0.033	0.073
	1.776	2.810	0.0552	0.033	0.073
12N4	1.774	2.745	0.0767	0.036	0.074
	1.773	2.960	0.0393	0.024	0.056
	1.772	2.955	0.0374	0.024	0.057
		3.142	0.0185	0.017	0.044
15N5	1.775	3.029	0.0431	0.020	0.050
	1.772	3.052	0.0250	0.020	0.047
	1.772	2.927	0.0483	0.025	0.058
		2.986	0.0435	0.025	0.052
		3.478	0.0071	0.008	0.024
18N6	1.766	3.289	0.0221	0.012	0.031
	1.766	3.342	0.0122	–	–
	1.766	3.301	0.0213	0.011	0.035
		3.344	0.0121	–	–
		3.289	0.0221	0.012	0.031
		3.329	0.0127	0.011	0.030
21N7	1.760	2.900	0.0578	0.027	0.058
	1.769	2.865	0.0569	0.029	0.063
	1.775	3.773	0.0026	–	–
		3.478	0.0072	0.008	0.024
		3.171	0.0288	0.016	0.038
		4.439	0.0011	–	–
		5.235	0.0004	–	–

the increase in the crown size.^[17] A gradual decrease in aerogen bond strength and an increase in C–H...O interactions were also noted with the increase in the substituent size, except for ^tBu substituted aza-crowns, as illustrated in the NCI plot analysis (Figures 4, S6–S11).

The bond critical points (BCPs) obtained from the AIM analysis (Figures 5, S6–S11) align with the NCI plot analysis. In the case of 9N3 (for all substituents), three BCPs corresponding

**Figure 4.** NCI plots (IGM method: intramolecular interactions are excluded for clarity) of the host-guest complexes of aza-crowns (Me) and XeO₃ with increasing crown size (isovalue = 0.01 a.u.).**Figure 5.** Bond critical points (intramolecular interactions are excluded for clarity) corresponding to the interactions between the XeO₃ with various aza-crowns (Me) in their host-guest complexes. Please see the ESI (Figures S6–S11) for enlarged images with their associated values.

to aerogen bonds between the three nitrogen donor atoms and xenon were observed. Similar observations were made for 12N4 (four BCPs). However, for the ^tBu substituted aza-crowns, as the crown size increases to 15N5, 18N6, and 21N7, only two BCPs were obtained for aerogen bonding, indicating the binding of xenon with only two of the nitrogen donor atoms *via* two σ -holes of XeO₃, leaving the third σ -hole unquenched. This explains why, among ^tBu substituted aza-crowns, 12N4, and not 15N5, exhibits the strongest binding with XeO₃, even though the supporting strength from C–H...O interactions were found to be increased for larger crowns. Among different substituents in 18N6, six BCPs were observed only for ⁱPr (Figure S9). In general, ρ and $\nabla^2\rho$ values associated with BCPs for aerogen bonds were found to decrease with increase in the size of aza-crowns from 9N3 to 18N6, followed by an increase for 21N7 and 21N7'. With the exception of ^tBu substituted aza-crowns, these values were also seen to decrease with the increasing size of the substituents. It is to be noted that these changes were observed to be marginal for 21N7'.

The natural bond orbital (NBO) analysis further reveals that among the various orbital interactions between the aza-crowns and XeO₃, the aerogen bonding interaction, which involves the donation of electron density from the lone pair of the nitrogen atom to the antibonding Xe–O orbital, is the dominant interaction (Tables 3 and S8–S10). Additionally, a weak interaction corresponding to the back-donation from the lone pair of Xe to the antibonding C–N orbital was also observed. Both of these interactions were found to be weakest in the case of 18N6 due to the longer Xe...N distance. It is noteworthy that the orbital interactions for the complexes of aza-crowns were also found to be stronger, as indicated by higher E^2 energy values compared to their oxygen analogues.^[17] When compared to thio analogues, smaller aza-crowns (9N3, 12N4, 15N5) exhibit better orbital interactions, whereas 18N6, 21N7, and 21N7' show weaker orbital interactions due to the steric hindrance of additional substituents, leading to their distorted binding nature. Additionally, it was observed that an increase in the size

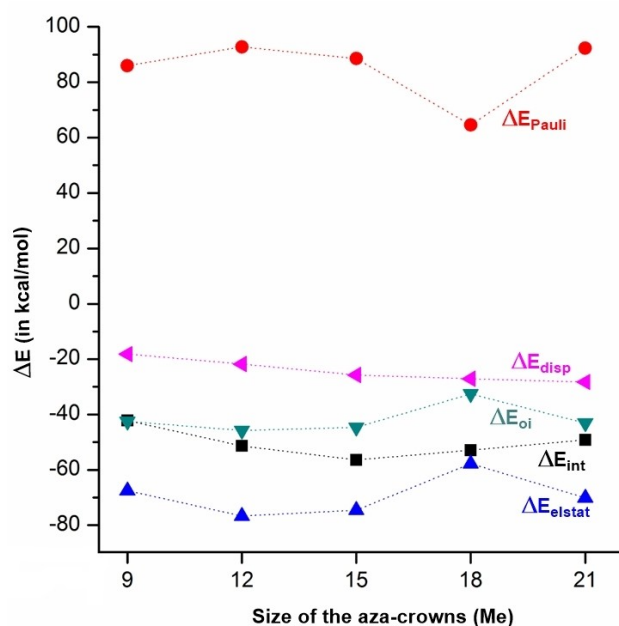
Table 3. Natural bond orbital (from NBO 7.0) analysis of complexes of different aza-crowns with XeO₃ at the APFD/def2-TZVPD level of theory. E² represents sums of second-order perturbation energy values (Threshold = 0.10 kcal/mol).

Me	Donor	Acceptor	E ²
9N3	LP N	BD* Xe–O	18.32
	LP Xe	BD* C–N	2.22
	LP O	BD* C–H	1.58
12N4	LP N	BD* Xe–O	20.21
	LP Xe	BD* C–N	3.05
	LP O	BD* C–H	4.48
15N5	LP N	BD* Xe–O	17.29
	LP Xe	BD* C–N	3.34
	LP O	BD* C–H	7.22
18N6	LP N	BD* Xe–O	9.17
	LP Xe	BD* C–N	–
	LP O	BD* C–H	6.77
21N7	LP N	BD* Xe–O	16.37
	LP Xe	BD* C–N	1.9
	LP O	BD* C–H	8.65
21N7'	LP N	BD* Xe–O	18.27
	LP Xe	BD* C–N	2.07
	LP O	BD* C–H	14.76

of the substituents led to lower orbital interaction, with a few exceptions. With the exception of the ^tBu substituted complex and 21N7^{Et}, the second order perturbation energy of C–H...O interactions was observed to increase from 9N3 to 15N5, followed by a decrease for 18N6, and then an increase again for 21N7 and 21N7'.

The EDA analysis reveals that aza-crowns exhibit enhanced electrostatic, orbital, and dispersive interactions compared to crown ethers (Tables S11–S14) in all cases.^[17] As illustrated in Figure 6 (Me substituted aza-crowns), despite a decrease in the Pauli repulsion, a reduction in interaction energy was observed for the 18N6 complex due to lower contributions from stabilizing orbitals and electrostatic interactions. This could be the consequence of the inimical steric interactions, which is reflected in the EDA, resulting in one favourable effect – the reduction of the Pauli repulsion, and two unfavourable effects: the decrease in the orbital and electrostatic interactions. This eventually leads to the overall reduction in the interaction energy for 18N6 complexes. Although both factors slightly improved for 21N7, an increase in Pauli repulsion led to an overall decrease in interaction energy for the related complex compared to 15N5. Similar trends were observed for Et and ⁱPr substituted complexes. This also explains why 15N5 (Me, Et, and ⁱPr) exhibits the highest binding affinity towards XeO₃. It is noteworthy that while the interactions between aza-crowns and XeO₃ are primarily electrostatic (47–54%), there is also a substantial contribution from orbital (27–33%) and dispersion (14–24%) interactions.

In summary, aza-crowns exhibit a remarkably high binding affinity towards the σ -holes of XeO₃, positioning them as promising hosts for stabilizing the highly explosive and shock-sensitive XeO₃. Smaller aza-crowns (9N3, 12N4, and 15N5) outperform their oxygen and thio analogues not only in terms of interaction energy but also in their individual components

**Figure 6.** The energy decomposition analysis (EDA) evaluated at the BP86-D3BJ/TZ2P level of theory for the host-guest complexes of aza-crowns (Me) and XeO₃. ΔE_{int} = Interaction energy, ΔE_{pauli} = Pauli repulsion, ΔE_{elstat} = electrostatic interactions, ΔE_{oi} = orbital interactions, and ΔE_{disp} = dispersion interactions.

(electrostatic, orbital, and dispersion) during complexation with XeO₃. Similar to crown ethers, aza-crowns demonstrate an increase in the secondary bond distances and C–H...O interactions with the increase in the crown sizes. However, unlike crown ethers, the increased number of C–H...O interactions fails to compensate for the diminished strength of the primary binding force – the σ -hole mediated aerogen bonds associated with larger aza-crowns (18N6 and 21N7). This leads to size selectivity of aza-crowns towards XeO₃, as evidenced by the case of aza-15-crown-5 (Me, Et, and ⁱPr substituted 15N5). Overall, our findings provide new insights, not only into the σ -hole mediated host-guest complexes of aza-crowns, but also into the broader aspects of molecular recognition and supramolecular chemistry.

Supporting Information

Computational methods, optimized Cartesian coordinates and other relevant data as discussed in the manuscript are added to the supporting information.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Host-guest systems • Noncovalent interactions • aza-crowns • sigma (σ) hole • Xenon

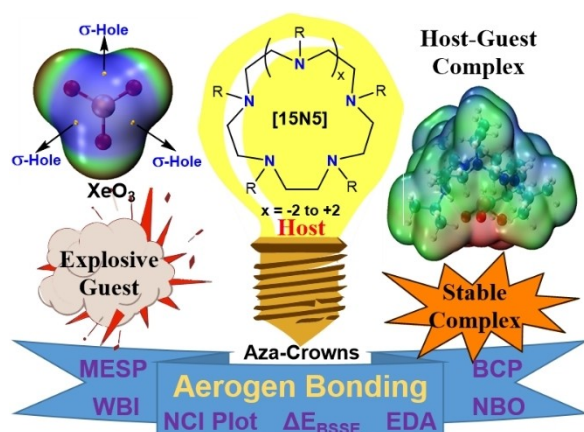
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1 – 6

Taming XeO₃ with Aza-Crowns: Computational Studies into σ -Hole Mediated Host-Guest Interactions



Aza-crowns showcase a notably strong affinity for binding to the σ -holes of XeO₃, making them compelling candidates for stabilizing the highly explosive XeO₃. The effect of

both increasing the crown size and altering the substituent groups on the binding strength has been explored using a variety of computational tools.

Unveiling the Inverse Sandwich Complexes of XeO₃: A Computational Exploration

Soumya Ranjan Dash and Kumar Vanka*

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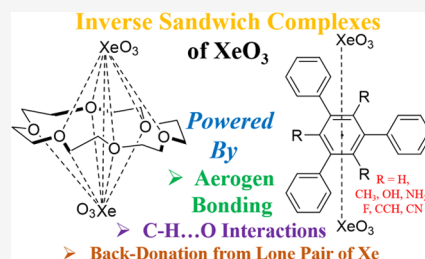


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Supporting Information

ABSTRACT: Our study introduces the design of inverse sandwich (iSw) complexes incorporating a noble gas compound: xenon trioxide (XeO₃). Through comprehensive computational analyses, we have investigated the critical factors influencing their stability by employing a variety of state-of-the-art computational tools. We demonstrated that the coordination number of xenon in the iSw complex of XeO₃ with 18-crown-6 is influenced by the presence of a rare, weakly stabilizing Xe...Xe interaction between the XeO₃ molecules. Furthermore, we observed that the stability of iSw complexes of 1,3,5-triphenylbenzene (TPB) and its derivatives is not solely attributed to aerogen bonding, but also involves contributions from C–H...O interactions and back-donation from the lone pair of Xe to the antibonding C–C orbitals of TPB. Additionally, the significant contributions from orbital interactions and dispersion interactions in the TPB derivatives highlight the multifaceted amphoteric properties of XeO₃ and reveal that the iSw complexes of TPB and derivatives are not predominantly governed by electrostatic interactions, contrary to conventional belief.



1. INTRODUCTION

The allure of novel sandwich and inverse sandwich complexes continues to captivate researchers, expanding the horizons of organometallic chemistry.¹ Sandwich complexes made their debut with the serendipitous discovery of ferrocene in 1951,² while the term “inverse sandwich” was coined by Professor Hoffmann much later in 1976,^{3,4} to describe complexes featuring a planar ring coordinated by Lewis conjugates, both above and below the plane of the ring. The initial experimental evidence of such inverse sandwich (iSw) complexes was provided by Schmidbaur.^{5–7} Intriguingly, the stability of the first experimentally obtained inverse sandwich complex, [C₆(CH₃)₆][BiCl₃]₂, and the subsequent discovery of iSw complexes of group 15 halides, can be attributed to pnictogen bonding via σ -hole interactions, a concept yet to be recognized at that time.⁸ A σ -hole denotes a confined area of positive electrostatic potential situated on a σ^* orbital along the extension of a covalently bound parent atom with an atom/group of electron-withdrawing nature. Initially introduced for halogen bonds,⁹ this idea was later extended to chalcogen, pnictogen, tetrel, triel, spondium, regium, and aerogen bonds.^{10–18}

The term “aerogen bonding” was introduced by the group of Bauza and Frontera to delineate the σ -hole interactions of noble gas compounds.¹² Among the recipients of aerogen bonding stabilization is the xenon trioxide (XeO₃) molecule, notorious for its instability in the solid state due to its high shock sensitivity and explosiveness,^{19,20} attributable to the presence of sigma holes (depicted as orange spheres in Figure 1a).^{21,22} The hazardous nature of XeO₃ makes computational studies an ideal means of exploring new chemistry with this

important compound, prior to experimental investigations. While investigating different crown ethers for stabilizing the explosive XeO₃,^{23–25} we realized that 18-crown-6 (18O6) provides a distinctive binding site, where three alternating oxygen donor atoms are bound to XeO₃ via three σ -holes (in a 1:1 complex), and the remaining three free oxygen atoms face the opposite side (Figure 1b), making them available for further binding. The availability of these free oxygen donor atoms, in principle, should allow another XeO₃ to approach them to quench its electron-deficient σ -holes, which could lead to an inverse sandwich complex of XeO₃. Remarkably, in the rapidly evolving field of inverse sandwich complexes,^{26–31} no reports of such complexes involving noble gas compounds have surfaced, to the best of our knowledge.

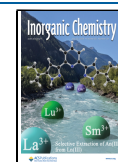
This further motivated us to search for potential hosts capable of providing a uniform nucleophilic donating center, preferably binding with three σ -holes at the top and three σ -holes at the bottom to allow complexation with XeO₃. One of the usual suspects for such a role is arenes; however, the question arises: which arene to choose? Simple benzene (Figure 1c) could potentially host two pyramidal AB₃-type molecules with electron-deficient σ -hole centers. The 1:1 complexes of XeO₃ with benzene and its derivatives have been

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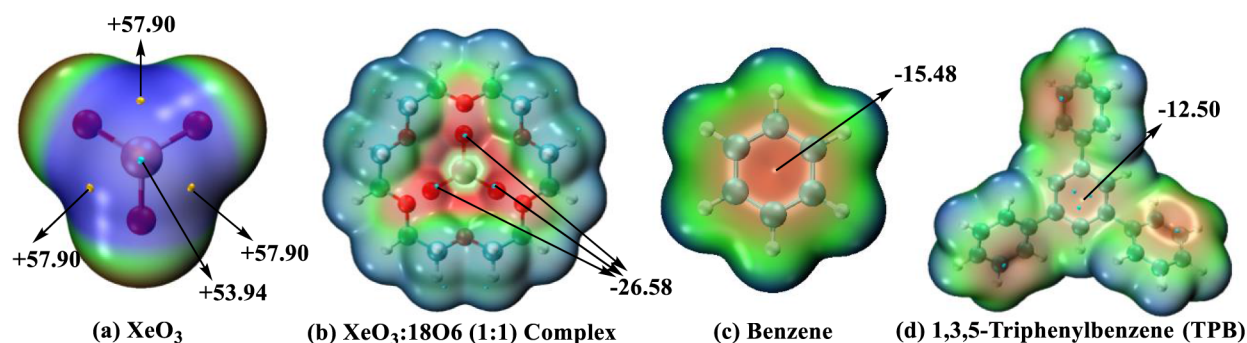
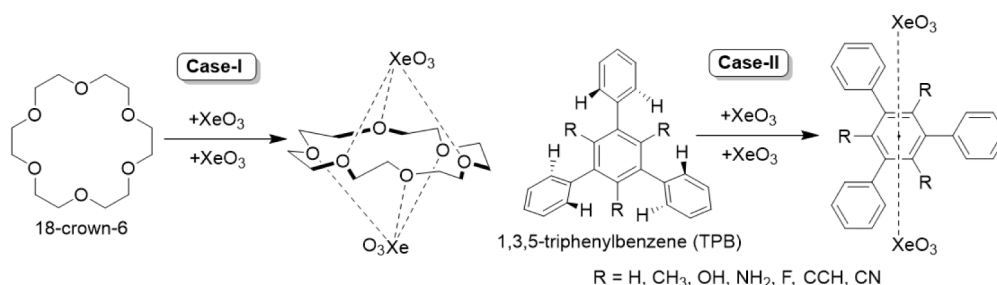


Figure 1. Molecular electrostatic potential (MEP) plots of (a) XeO_3 , (b) 1:1 complex of XeO_3 and 18-crown-6, (c) benzene, (d) 1,3,5-triphenylbenzene, produced at the APFD/def2-TZVPD level of theory. The plots were generated utilizing the RGB color scale (isovalue 0.001 au), where blue and red depict the positive and negative regions, respectively, while green signifies the intermediate zone between them.

Scheme 1. Proposed Inverse Sandwich Complexes of XeO_3 and the Ligands/Hosts Used in This Study



previously explored;^{32,33} however, they lacked secondary support via C–H $\cdots$ O interactions, which has proven to be crucial in enhancing the stability of such aerogen bonding complexes.^{25,34,35} In our quest for such a host, we came across a highly intriguing benzene derivative, 1,3,5-triphenylbenzene (TPB-H), which was utilized to synthesize an inverse sandwich complex of $\text{Ca}(\text{THF})_3$.³⁶ It is noteworthy that the binding nature of calcium to the π -center was entirely different from the context of this study, leading to a debate over the true oxidation states of calcium and the existence of Ca–Ca interactions through the π -center.^{37–39}

However, the TPB-H ligand in its unperturbed state (Figure 1d) satisfies both criteria for hosting two XeO_3 molecules to form an inverse sandwich complex: (1) the central π -ring provides the binding site for the sigma holes of XeO_3 , and (2) the substituent phenyl groups can provide secondary C–H $\cdots$ O interactions. Keeping these parameters in mind, we investigated the σ -hole mediated complexation between 1,3,5-triphenylbenzene (TPB) and XeO_3 , leading to the formation of an inverse sandwich complex between them. Furthermore, different electron withdrawing and donating groups were carefully chosen, satisfying the criterion that they are planar to the central ring, as any large deviation from planarity might lead to distortion in the formation of the desired inverse sandwich complex (Scheme 1). The factors governing the stability of these inverse sandwich complexes of XeO_3 have been investigated using various computational tools, such as the mapping of the molecular electrostatic potential (MEP), Wiberg bond indices (WBIs), natural population charge analysis (NPA), Bader's theory of atoms-in-molecules (AIM), noncovalent interaction (NCI) plots, natural bond orbital (NBO), and energy decomposition analyses (EDA).

2. METHODOLOGY

Gaussian 09 suite of programs was employed to carry out all the density functional theory (DFT) calculations.⁴⁰ All the models were optimized by utilizing the APFD⁴¹ functionals in combination with the def2-TZVPD basis set in gas phase.⁴² This choice of theory was made based on its benchmarking as the most reliable combination, particularly in comparison to the experimentally derived adduct of 15-Crown-5 with XeO_3 by Schrobilgen's research group.²³ Additionally, all the stationary points were confirmed to be minima by conducting harmonic frequency calculations. Grimme's semiempirical Conformer–Rotamer Ensemble Sampling Tool (CREST)⁴³ at the xTB-GFN2 levels of theory was also employed to carry out Conformational search analyses.^{44–46} In order to obtain more accurate interaction energy (ΔE) values, the counterpoise correction method was applied to correct for basis set superimposition error (BSSE).⁴⁷ Interaction energy was computed as the difference between the energy of the complex and the energy of the isolated monomers in the complex configuration. For each complexation the deformation energies required by the hosts were also computed. The typical accuracy level of the reported energy values is ± 0.5 kcal/mol. *Ab initio* molecular dynamics (AIMD) simulations were conducted using the GPU-based TeraChem software package for a duration of 50 ps at 298.15 K with a time step of 0.5 fs to assess the stability of the proposed iSw complexes.⁴⁸ The simulations employed the ω B97X functional along with the 6–31+G* basis set for all atoms except Xe, for which the crenbl_ecp basis set was utilized. This specific combination of functional and basis set was chosen based on recommendations from TeraChem support, given the limited availability of suitable level of theory. MultiWFN program⁴⁹ was utilized to generate and evaluate ESP, NCI plot and AIM analysis along with the Visual Molecular Dynamics (VMD) software for

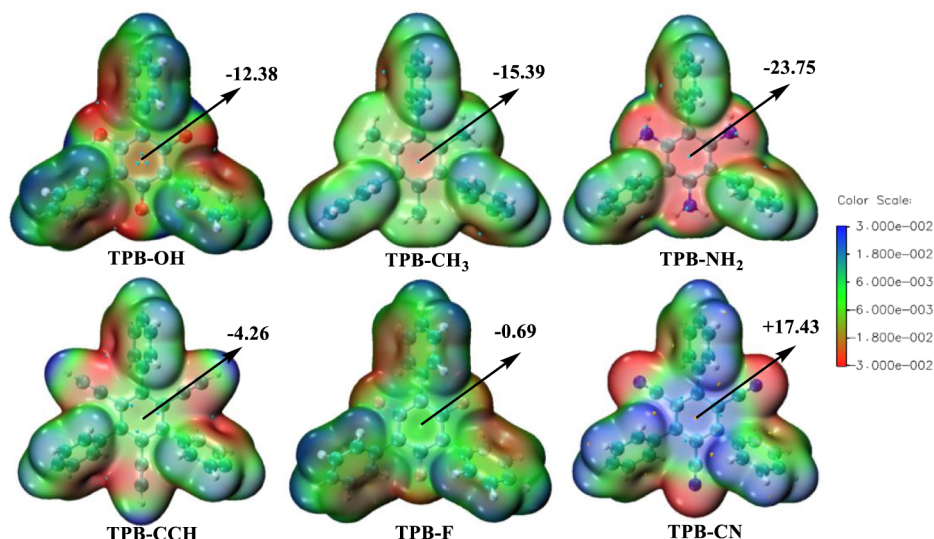


Figure 2. Chosen MEPs of the central arene ring along with their corresponding energy values at minima ($V_{s,\min}$ in kcal/mol). The plots were generated utilizing the RGB color scale (isovalue 0.001 au), where blue and red depict the positive and negative regions, respectively, while green signifies the intermediate zone between them.

visualization.⁵⁰ NBO analysis were performed using the Gaussian 09 module. The BP86⁵¹ functional along with Grimme's D3 dispersion correction and Becke-Johnson damping (BJ) was employed with the TZ2P⁵² basis set to carry out energy decomposition analysis (EDA) as implemented in ADF 2023.101.⁵³ A strictly closed-shell fragmentation scheme (three fragments: the host and 2 XeO₃ units for iSw complexes) was chosen along with the ZORA relativistic effect, frozen core approximation, and good numerical quality for the EDA calculations.

3. RESULTS AND DISCUSSION

3.1. Molecular Electrostatic Potentials of Isolated Molecules. The analysis of noncovalent interactions (NCIs) can be effectively conducted through the examination of the molecular electrostatic potential (MEP), given that NCIs are predominantly coulombic in nature.⁵⁴ It is important to highlight that MEP reflects not only the influence of electrons but also that of nuclei.⁵⁵ Figure 1a shows the computed MEP plot of XeO₃ confirming the presence of three σ -holes at the extension of Xe–O bond. These σ -holes are represented by the orange dots residing in the electron deficient region, as indicated by the blue color. The $V_{s,\max}$ value associated with the σ -holes of XeO₃ computed at the APFD/def2-TZVPD level of theory closely matched earlier reported values at the MP2/aug-cc-pVTZ level of theory.¹² Furthermore, it should be noted that an area of accumulated positive charge was observed at the position of the lone pair of Xe, previously assumed to be the site of the σ -hole, as indicated by the blue dot in Figure 1a.^{12,22}

Figure 1b confirms the presence of three unbound oxygen atoms serving as electron-rich donors (blue dots) in the 1:1 complex (mono) of XeO₃ with 18-crown-6 (18O6). As anticipated, the electron density was observed to be withdrawn from the central π -ring of the TPB-H as compared to the benzene ring (Figure 1c,d), due to the presence of three electron-withdrawing phenyl groups. The $V_{s,\min}$ corresponding to the central π -ring of the substituted TPB ligands follow the trend: CN < F < CCH < OH $\approx$ H < CH₃ < NH₂, as depicted by Figure 2.

3.2. Interaction Energies. The evaluation of BSSE corrected interaction energies for all adduct formations was conducted as shown in Table 1. The 1:1 complexes are

Table 1. Interaction Energies (ΔE in kcal/mol), Incorporating the Counterpoise (BSSE) Corrections Calculated at the APFD/def2-TZVPD Level of Theory, along with the Deformation Energies (ΔE_{deform}) associated with the Hosts Upon Complexation

hosts	1:1 (Mono)		1:2 (iSw)	
	ΔE_{BSSE}	ΔE_{deform}	ΔE_{BSSE}	ΔE_{deform}
18O6	−40.2 ^a	1.5 ^a	−72.0	4.5
TPB-NH ₂	−29.6	0.7	−49.7	1.9
TPB-CH ₃	−23.6	0.7	−40.8	1.2
TPB-OH	−22.1	0.5	−37.8	0.9
TPB-H	−18.3	0.3	−32.1	0.7
TPB-CCH	−16.5	0.1	−29.8	0.3
TPB-F	−14.7	0.3	−25.6	0.7
TPB-CN	−10.3	0.1	−18.5	0.2

^aValues obtained from previous study.²⁵

denoted as Mono, while the 1:2 inverse sandwich complexes are labeled as iSw. The interaction energies exhibited a similar trend in both the Mono and iSw complexes: CN < F < CCH < H < OH < CH₃ < NH₂. It is noteworthy that TPB–OH, which had a negligible difference in MEP compared to TPB–H, demonstrated favorability by 3.8 kcal/mol ($\Delta\Delta E_{\text{BSSE}}$) for Mono and 5.7 kcal/mol ($\Delta\Delta E_{\text{BSSE}}$) for the iSw complexes of XeO₃. Interestingly, the interaction energy of XeO₃ was observed to be more favorable for 1:1 complexes of TPB (−H, −F, −CCH) compared to benzene (ΔE_{BSSE} = −13.0 kcal/mol), despite the withdrawal of electron density from the central ring.

It was observed that very less deformation energy was consumed by the TPB ligands for complexation with XeO₃, which is <1.0 kcal/mol for Mono and <2.0 kcal/mol for iSw complexes. For 18-crown-6, a notably strong interaction with XeO₃ was observed for both the Mono and the iSw cases. This high interaction energy enables 18O6 to offset the necessary

Table 2. Geometrical Parameters of Different Inverse Sandwich Complexes of XeO₃^a

hosts	Xe–O (avg.)	Xe...Xe	Xe... π	<O–Xe–Xe–O	NPA (avg.)		WBI (avg.)
					Xe	O	Xe...C ^{π}
Only XeO ₃	1.760	-	-	-	2.765	−0.922	
TPB-NH ₂	1.767	5.750	2.857	32.12	2.835	−0.955	0.016
TPB-CH ₃	1.765	5.840	2.928	29.41	2.844	−0.946	0.012
TPB-OH	1.764	5.879	2.942	33.84	2.826	−0.946	0.012
TPB-H	1.763	5.967	2.984	40.54	2.828	−0.941	0.010
TPB-CCH	1.762	6.052	3.026	43.53	2.831	−0.936	0.008
TPB-F	1.763	6.059	3.030	37.15	2.811	−0.935	0.009
TPB-CN	1.762	6.202	3.101	49.00	2.811	−0.926	0.007

^aXe... π represents the distance (in Å) of Xe from the centre of the central π -ring. C ^{π} represents the carbon atoms of central π ring and avg. represents the average values.

deformation energy for complexation. These patterns discussed above imply that MEPs alone cannot serve as the exclusive indicator of such noncovalent interactions. Consequently, additional computational tools were utilized to gain insights into the factors influencing the interaction energy for the iSw complexes of XeO₃.

3.3. Structural Characteristics, WBI, and Charge Analysis. For all the complexes, the optimized geometries, along with their respective primary Xe–O bond lengths, secondary Xe...X (X = O/C) bond distances, Wiberg bond indexes, and charge analysis values obtained from natural population analysis, are illustrated in Figures S1–S7 (for Mono) and Figures S8–S15 (for iSw). A comparative analysis of the aforementioned parameters is also presented in Table 2 for the TPB derivatives. AIMD simulations confirmed the stability of the iSw complex of 18-crown-6 and XeO₃, which remained intact throughout the 50 ps simulation at 298.15 K (i.e., XeO₃ did not dissociate). In the case of the iSw complex of TPB-H, XeO₃ was observed to hover around the central arene ring for up to 21 ps before relocating (one of the XeO₃) to a neighboring phenyl group for the remainder of the simulations. The optimized shifted complex (Figure S16) was found to be 1.7 kcal/mol more favorable ($\Delta\Delta E_{\text{BSSE}}$) than the proposed inverse sandwich structure. Nevertheless, the stability of the inverse sandwich complex of TPB-H for up to 21 ps was encouraging, prompting further investigation into iSw complexes. Although, upon lowering the temperature to 273.15 K (0 °C), both XeO₃ remained with the central arene ring throughout the entire 50 ps simulation. Figure 3 depicts the optimized geometry for the iSw complexes of 18-crown-6 (18O6) and TPB-H.

Upon complex formation, Xe–O bonds were observed to be elongated for both the cases (Mono and iSw). The intermolecular distances of secondary Xe...X (X = O/C) interactions, illustrated in Figures S1–S16, were found to be less than the sum of their respective van der Waals radii ($\Sigma(\text{Xe}–\text{O})_{\text{vdW}} = 3.68$ Å, $\Sigma(\text{Xe}–\text{C})_{\text{vdW}} = 3.86$ Å, as per Bondi⁵⁶ across all scenarios. Intriguingly, in the iSw complex of 18O6 (Figure S15), the Xe...Xe distance measured 3.82 Å, falling below the sum of their corresponding van der Waals radii ($\Sigma(\text{Xe}–\text{Xe})_{\text{vdW}} = 4.32$ Å).⁵⁶ This suggests the potential existence of a rare Xe...Xe interaction, which could be one of the reasons for the slight tilt of XeO₃ away from the central axis of 18O6, unlike its 1:1 counterpart.^{24,25}

The Xe...Xe distance for the iSw complexes of TPB derivatives was observed to be much longer, following the reverse pattern compared to the interaction energies: CN > F > CCH > H > OH > CH₃ > NH₂. This further supports the

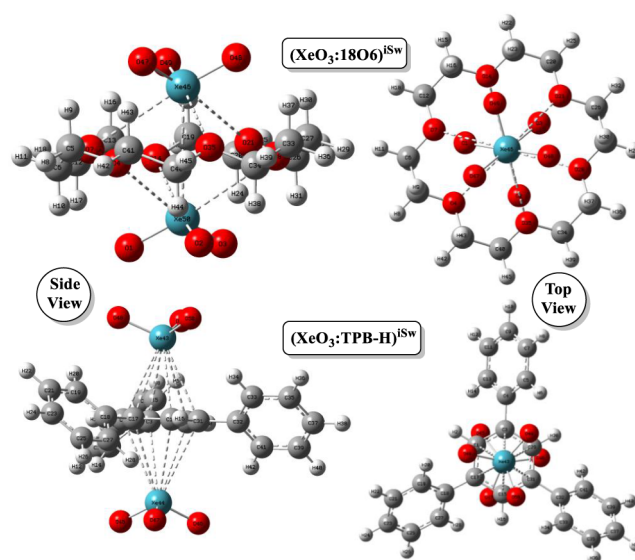


Figure 3. Optimized geometries of the inverse sandwich complexes involving XeO₃ with 18-crown-6 (top) and with TPB-H (bottom).

notion that the primary force driving the formation of the iSw complexes is the σ -hole-mediated aerogen bonding, where stronger interactions lead to shorter Xe...Xe distances. The distance of Xe from the center of the central arene ring also follows a similar trend as mentioned above. Interestingly, the <O–Xe–Xe–O dihedral angle around the C1 atom was also observed to follow a similar trend, except for TPB-NH₂ and TPB-F.

Consistent with the observed bond elongation, a decrease in the Wiberg bond indices (WBI)⁵⁷ of Xe and O was observed during complexation. For comparative purposes, Table 2 presents the WBI values as averages for the Xe...C ^{π} interaction, as XeO₃ binds to the central arene (π) ring in an η^6 fashion. However, individual WBI values are detailed in the ESI (Figures S1–S15). The average bond orders of Xe...C secondary interactions were found to mirror the same order as the interaction energies, except for the case of TPB-F. It was also observed that the bond orders corresponding to the carbon atoms with phenyl substituents are slightly higher than those relate to the carbon atoms with the varying functional groups. Interestingly, the WBI value corresponding to the Xe...Xe interaction in (XeO₃:18O6)^{iSw} complex was found to be 0.77, which further indicates the presence of a rare Xe...Xe interaction. Moreover, natural population analysis indicated that, upon complex formation, the charges on Xe and O within

XeO₃ increased, suggesting enhanced polar-covalent character in the primary Xe–O bonds of XeO₃.

3.4. NCI and AIM Analysis. To obtain further insights into the nature of interaction between XeO₃ with 18O6 and TPB derivatives, analyses of noncovalent interaction (NCI) plots were conducted (refer to Figures 4, S17, and S18).⁵⁸ These

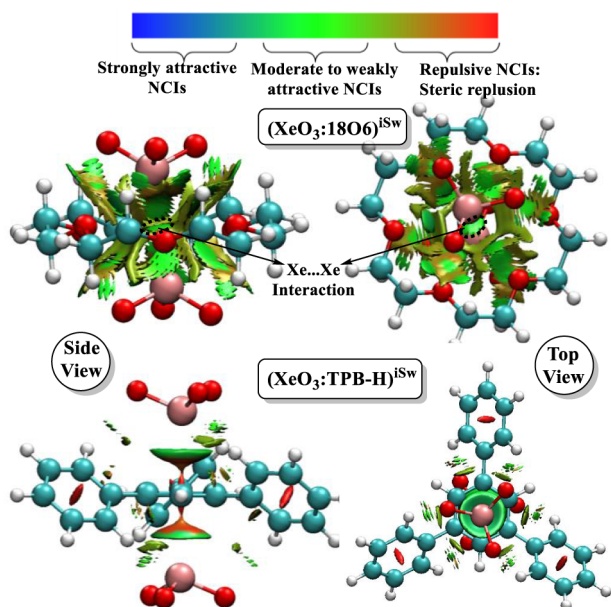


Figure 4. Noncovalent interaction (NCI) plots (isovalue 0.5 au) for the inverse sandwich complexes involving XeO₃ with 18-crown-6 (top) and with TPB-H (bottom).

analyses revealed that, in addition to conventional aerogen bonds (such as the interaction between the host's donor atom–oxygen for 18O6, carbon atoms of the central arene ring for TPBs—and Xe), there are attractive regions indicating C–H...O interactions. Furthermore, a green region suggesting a weak noncovalent interaction between Xe...Xe in the (XeO₃:18O6)^{isw} complex was also observed, confirming previous observations. For TPB derivatives, the intensity of the red region indicating repulsive interactions at the center of the arene ring linking both XeO₃ molecules followed similar trends with the interaction energies (refer to Figures S17 and S18), intensifying with the increase in interaction energy and shorter Xe...Xe distance, and diminishing with the decrease in interaction energy and longer Xe...Xe distance. It is also to be noted that additional regions of greenish surface indicative of weak attractive interactions were uniformly observed between XeO₃ and the substituted phenyl ring, both at the top and at the bottom.

The examination of bond critical points (BCPs, indicated by orange sphere) derived from the AIM analysis of the (XeO₃:18O6)^{isw} complex reveals the intriguing binding nature of the inverse sandwich complex. The slight distortion of XeO₃, as discussed in Section 3.3, enables Xe to bind with five of the oxygen atoms (resulting in 5 BCPs between each Xe and the 18O6) both at the top and bottom (Figure 5), elevating its coordination number to 8 at each xenon center, unlike the 6 coordination number observed in the 1:1 complex. Additionally, one BCP corresponding to Xe...Xe interaction was also observed. In the case of TPB-H (Figure 5) three BCPs were noted between each Xe and the three carbon atoms (which are

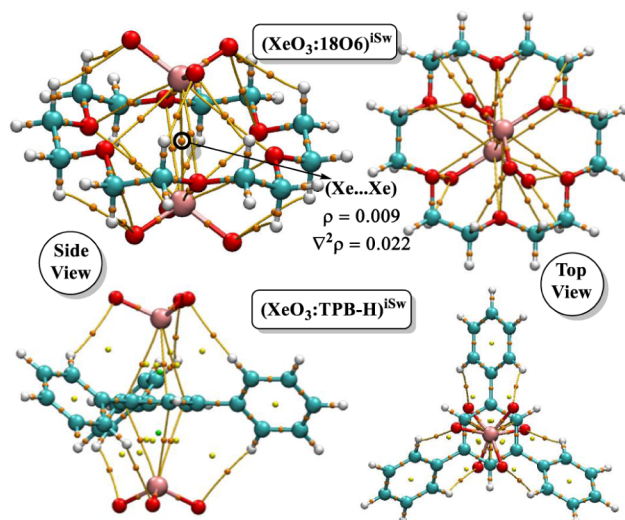


Figure 5. AIM analysis for the inverse sandwich complexes involving XeO₃ with 18-crown-6 (top) and with TPB-H (bottom). The associated values (ρ , $\nabla^2\rho$, H) are shown in Table S1.

subjected to substitution by different groups) of the central arene ring. Each oxygen atom was found to be associated with one BCP corresponding to C–H...O interaction with the C–H of the substituent phenyl group. Additionally, three ring critical points (RCP, indicated by yellow spheres) were obtained between each Xe and the C–C bond of the central arene ring.

For TPB derivatives, except for the case of TPB-CN, three RCPs, as mentioned above, were observed between Xe and the central carbon atoms with varying substitutions, whereas three BCPs were observed between Xe and the central carbon atoms with phenyl substituent (Figures S19 and S20). The combination of these three RCPs and three BCPs corresponds to the aerogen bonding interactions, with their electron density (ρ) and the Laplacian of electron density ($\nabla^2\rho$) values mirroring the interaction energy trend, except for the case of TPB-F (Table S1). Three additional RCPs were observed between each XeO₃ and the C–C linker bond connecting the central arene ring and the phenyl substituents, for all cases. Alongside these, a cage critical point (green sphere) was also observed between each Xe and the central π -ring, whose ρ and $\nabla^2\rho$ values also followed the above-mentioned trend. The energy density values (H) were determined to be positive across all cases, which is typical for closed shell calculations.

3.5. Natural Bond Orbital Analysis (NBO). To explore the orbital interactions, NBO calculations were conducted for the Mono (Table S2) and iSw (Tables 3 and S3) complexes of XeO₃. Consistent with previous observations, second-order perturbation energies ($E^{(2)}$) corresponding to orbital interactions ($n \rightarrow \sigma^*$) between lone pairs of five oxygen donor atoms and the σ^* antibonding Xe–O orbital were obtained for the (XeO₃:18O6)^{isw} complex (see Table 3). Additionally, $n \rightarrow \sigma^*$ orbital interactions were observed between the lone pair of Xe and the σ^* antibonding Xe–O orbital ($E^{(2)} = 0.18$ kcal/mol, for each Xe), providing further evidence of the presence of a weakly attractive noncovalent Xe...Xe interaction between the two XeO₃ molecules. Significant orbital interactions from C–H...O interactions were also noted. For TPB derivatives, $\pi \rightarrow \sigma^*$ orbital interactions between the C–C bonding orbital of the central arene ring and the antibonding Xe–O orbital

Table 3. Second Order Perturbation Energies (Summed Up ΔE^2 Values in kcal/mol) Derived from NBO Analysis at the APFD/def2-TZVPD Level of Theory for the iSw Complexes of XeO_3 ^a

iSw	donor	acceptor	ΔE^2
18O6	LP O	σ^* (Xe–O)	–5.74
	LP Xe	σ^* (Xe–O)	–0.36
	LP O	σ^* (C–H)	–7.28
NH_2	π (C–C) ^{arene}	σ^* (Xe–O)	–8.54
	LP Xe	σ^* (C–C ^{Ph})	–1.83
	LP Xe	σ^* (C–NH ₂)	–1.50
	LP O	σ^* (C–H)	–6.67
	LP O	π^* (C–C) ^{arene}	–0.24
CH_3	π (C–C) ^{arene}	σ^* (Xe–O)	–6.79
	LP Xe	σ^* (C–C ^{Ph})	–2.10
	LP Xe	σ^* (C–CH ₃)	–2.13
	LP O	σ^* (C–H)	–6.01
OH	π (C–C) ^{arene}	σ^* (Xe–O)	–6.39
	LP Xe	σ^* (C–C ^{Ph})	–1.62
	LP Xe	σ^* (C–OH)	–0.66
	LP O	σ^* (C–H)	–5.18
H	π (C–C) ^{arene}	σ^* (Xe–O)	–5.40
	LP Xe	σ^* (C–C ^{Ph})	–1.68
	LP O	σ^* (C–H)	–1.44
CCH	π (C–C) ^{arene}	σ^* (Xe–O)	–4.10
	LP Xe	σ^* (C–C ^{Ph})	–1.58
	LP Xe	σ^* (C–CCH)	–1.38
	LP O	σ^* (C–H)	–6.03
F	π (C–C) ^{arene}	σ^* (Xe–O)	–4.52
	LP Xe	σ^* (C–C ^{Ph})	–1.29
	LP O	σ^* (C–H)	–2.78
CN	π (C–C) ^{arene}	σ^* (Xe–O)	–2.85
	LP Xe	σ^* (C–C ^{Ph})	–1.38
	LP Xe	σ^* (C–CN)	–0.72
	LP O	σ^* (C–H)	–3.76

^a(C–C)^{arene} indicates the carbon atoms of the central arene ring, CPh indicates the carbon attached to the phenyl substituents.

corresponding to the aerogen bonds were observed. The summed E^2 values corresponding to the above interactions followed the interaction energy trend, except for the case of TPB-F: CN (–2.9) < CCH (–4.1) < F (–4.5) < H (–5.4) < OH (–6.4) < CH_3 (–6.8) < NH_2 (–8.5). In concurrence with the NCI plot analysis and the RCPs, $n \rightarrow \sigma^*$ orbital interactions were noted originating from the lone pair of Xe to the antibonding C(arene)–C(phenyl) orbital. In complexes where carbon-containing substituents (CH_3 , CCH, CN) had

replaced H of the C(arene), $n \rightarrow \sigma^*$ orbital interactions were also observed between the lone pair of Xe and the antibonding C(arene)–C(substituent) orbital. These observations provide testament to the amphoteric nature of XeO_3 . Additionally, non-negligible orbital interactions corresponding to the C–H...O interactions were also observed.

3.6. Energy Decomposition Analysis (EDA). The conclusions drawn above were additionally substantiated by the Ziegler-Rauk energy decomposition analysis. It was found that while the absolute interaction energies varied from those obtained through higher-level computations, due to differences in functional and basis set (Table 4, refer Table S4 for Mono), the relative trends remained consistent, enabling further insights. In all cases, the percentage contribution from electrostatic interactions decreased upon the formation of 1:2 iSw complexes, as compared to the 1:1 Mono complexes. This reduction occurs due to the sharing of electron-rich sources between the two XeO_3 molecules. At the same time, the percentage contribution from dispersion interactions increased for the same. No clear trend was observed in the percentage contribution from orbital interactions. Regarding the TPB derivatives, electrostatic interactions were found to increase with higher interaction energies and decrease with lower interaction energies, aligning with the electron donating and withdrawing abilities of the substituents. Conversely, a reverse trend was noted for dispersion interactions. Interestingly, for the most electron-deficient TPB-CN case, interactions were predominantly due to dispersive interactions (50% for iSw, 46% for Mono), with electrostatic interactions contributing only about 14% for iSw and 19% for Mono. With the exception of the TPB- NH_2 case, significant contributions from orbital and dispersion interactions were observed for all TPB derivatives, even those with electron-donating groups attached.

Furthermore, the natural orbitals for chemical valence (NOCV), combined with EDA, also known as ETS-NOCV analysis,⁵⁹ confirmed the existence of a weakly attractive Xe...Xe interaction in the $(\text{XeO}_3:18\text{O6})^{\text{iSw}}$ complex. For TPB derivatives, the orbital interaction energies corresponding to the aerogen bonds were identified using ETS-NOCV analysis, and were observed to follow the trend: CN (–9.1) < F (–12.9) $\approx$ CCH (–12.9) < H (–14.6) < OH (–18.5) $\approx$ CH_3 (–18.4) < NH_2 (–24.2). Figure 6 depicts NOCVs associated with the Xe...Xe interaction in the $(\text{XeO}_3:18\text{O6})^{\text{iSw}}$ complex along with the corresponding NBOs, and the aerogen bonding NOCVs for the iSw complex of TPB-H.

Table 4. Energy Decomposition Analysis of iSw (Three Fragments Were Considered: The Host and 2 XeO_3 Units) Complexes of XeO_3 at the BP86-D3BJ/ZORA/TZ2P Level of Theory^a

iSw	ΔE_{int}	ΔE_{Pauli}	ΔE_{elstat}	%	ΔE_{oi}	%	ΔE_{disp}	%
18O6	–63.0	70.3	–64.1	48	–34.9	26	–34.3	26
TPB- NH_2	–49.0	70.1	–46.2	39	–42.0	35	–30.8	26
TPB- CH_3	–39.8	63.2	–36.7	36	–34.4	33	–32.0	31
TPB-OH	–36.8	57.5	–32.4	34	–33.0	35	–28.8	31
TPB-H	–31.3	45.2	–25.2	33	–25.3	33	–25.9	34
TPB-CCH	–30.2	46.8	–20.7	27	–26.2	34	–30.1	39
TPB-F	–25.3	42.5	–17.7	26	–24.0	35	–26.1	39
TPB-CN	–19.8	37.3	–8.1	14	–20.4	36	–28.5	50

^aThe energy values are in kcal/mol. Contribution to the sum of all attractive energy terms are shown as percentages. E_{Pauli} indicates Pauli repulsion, E_{elstat} denotes electrostatic interactions, E_{oi} signifies orbital interaction and the E_{disp} indicates the dispersion interaction.

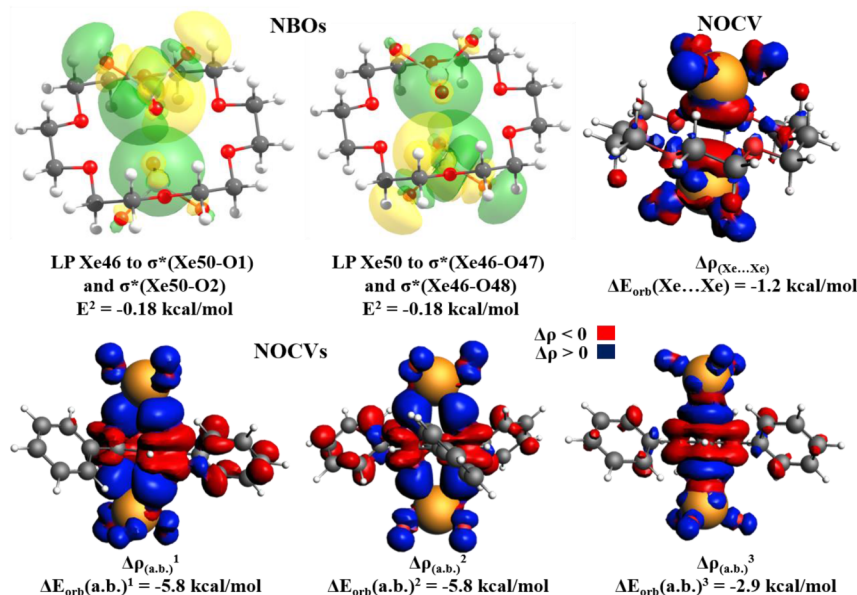


Figure 6. Top: NBOs and NOCV associated with the Xe...Xe interaction in the $(\text{XeO}_3:18\text{O}_6)^{\text{iSw}}$ complex; Bottom: aerogen bonding (a.b.) NOCVs for the iSw complex of TPB-H. Red region represents outflow of electron density (charge depletion) and blue region represents inflow of electron density (charge accumulation). $\Delta\rho$ were plotted with isovalues ± 0.0001 au for clarity.

4. CONCLUSIONS

In this study, we have offered insights into the rational design of inverse sandwich complexes involving XeO_3 , along with a thorough computational investigation into the key factors governing their stability. The NCI plot, BCP, NBO, and ETS-NOCV analysis all confirmed the presence of a rare, weak, attractive Xe...Xe interaction in the inverse sandwich complex of XeO_3 with 18-crown-6. This interaction caused XeO_3 to tilt away from the central axis of the crown, enabling its interaction with five oxygen atoms and increasing its coordination number to 8. This stands in contrast to the monomeric 1:1 complex, where Xe was bound to only three oxygen atoms, resulting in a coordination number of 6.^{24,25} For the inverse sandwich complexes of 1,3,5-triphenylbenzene (TPB) and its derivatives, besides C-H...O interactions and aerogen bonding, interactions between the lone pair of Xe and the antibonding C-C orbitals were found to contribute to the overall orbital interactions, showcasing the non-negligible amphoteric prowess of the XeO_3 molecule. It is noteworthy that the inverse sandwich complexes of TPB and derivatives exhibit significant contributions from orbital interactions (33–36%) and dispersion interactions (26–50%) as compared to conventional electrostatic interactions (14–39%). This study presents the first report of inverse sandwich complexes of XeO_3 , stabilized by aerogen bonding, alongside C-H...O interactions, and back-donation from the lone pair of xenon. Overall, we believe this study has the potential to initiate the development of novel inverse sandwich complexes of noble gas compounds, thereby impacting our broader understanding of supramolecular chemistry and σ -hole mediated non covalent interactions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.4c01744>.

Optimized Cartesian coordinates (PDF)

Figures S1–S7. Optimized geometries of XeO_3 and its 1:1 (Mono) adducts with TPB and derivatives. Figures S8–S15. Optimized geometries of XeO_3 and its 1:2 (iSw) adducts with TPB derivatives and 18-crown-6. Figure S16. Optimized geometry, NCI plot, and AIM analysis of XeO_3 and its 1:2 (shifted) adduct with TPB-H. Figures S17–S18. NCI plots of the Mono and iSw complexes of XeO_3 with TPB derivatives. Figures S19–S20. AIM analysis of the Mono and iSw complexes of XeO_3 with TPB derivatives. Table S1. AIM analysis. Tables S2–S3. NBO analyses of the Mono and iSw complexes. Table S4. Energy decomposition analysis of the Mono complexes of XeO_3 (PDF)

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Notes

The authors declare no competing financial interest.

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