Non Covalent Synthesis of Supramolecular Assemblies

Thesis submitted to the

University of Pune

For the degree of

Doctor of Philosophy

in

Chemistry

by

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September 2006

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CERTIFICATE

This is to certify that the work presented in the thesis entitled **"Non Covalent Synthesis of Supramolecular Assemblies"** submitted by J. Prakasha Reddy, was carried out by the candidate at National Chemical Laboratory, Pune, under my supervision. Such materials as obtained from other sources have been duly acknowledged in the thesis.

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DECLARATION

I here by declare that the thesis entitled **"Non Covalent Synthesis of Supramolecular Assemblies"** submitted for the degree of Doctor of Philosophy in Chemistry to the University of Pune has not been submitted by me to any other university or institution. This work was carried out at the National Chemical Laboratory, Pune, India.

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September 2006

ACKNOWLEDGEMENTS

To my prodigious delight, I would like to express my regards and sincere appreciation to my supervisor, Dr. V. R. Pedireddi, for his advice and guidance throughout the course to this work. Thank you for all that I learned from you in our many discussions.

It is my privilege to thank Dr. K. N. Ganesh, former head of the division of Organic Chemistry, NCL, and currently director, IISER Pune, for his constant support and ardent interest shown all along the progress of this work. I take this opportunity to thank Dr. M. K. Gurjar, for his continued support as present head of the division.

I thank Dr. S. Sivaram, director, for giving infrastructure facilities. I also thank Dr. Paul Ratnasamy, former director, and Dr. B. D. Kulkarni, deputy director, for their support and encouragement.

Indelible delectations are due to Dr. C. V. V. Sathyanarayana for his assistance in powder X-ray diffraction analysis. In fact, his interest and enthusiasm for the work, whenever I approach him irrespective of the time, made me to submit more and more samples. It makes the work much more enjoyable when there is an excitement about what is being done. I also thank Dr. P. A. Joy, Dr. C. Ramesh and Dr. C. G. Suresh for scientific discussions and support in many aspects.

I am grateful to Dr. Mohan Bhadbhade, Dr. Mrs. Vedavathi Puranik and Mr. Rajesh Gonnade for their assistance in the single crystal X-ray diffraction. I am thankful to Mrs. Deepa Dhoble, Mrs. Neelakshi and Ms. Smitha for their help in DSC analysis at an early stage of my research here.

I take this opportunity to thank my teachers Drs. Vishnu Kamath, Sureshbabu, Mahendra, Mrs. Shashikala, Mrs. Gayathri, Bangalore University, for their encouragement and motivation. I feel proud to thank my primary school teachers Shri. Rahmath Kahn and Chikkananjudappa for their encouragement at an early level of childhood school days. My stay was so wonderful and pleasant in Jawahar Navodaya Vidayalaya, Kolar, and I thank all the teachers and friends for their guidance and cooperation.

My thanks are due to our group members Kapil, Sunil, Seetha, Marivel, Sathyanarayana, Manish and Amit for their help in various capacities and providing me with an excellent working ambience.

I deeply forever indebted to my friends Suresh, Raman, Umashankar, Srinu, Raghupathi, Shiva, Bhargava, Baasu, Nooks, Swaroop, Sridhar, Rajender, Srinivas, Srikanth, Gnaneshwar, Boje, Govind, Prasanna, Pranjal, Amol and Swarnendu for their help at various stages.

My heart felt thanks to ChandreGowda, NarayanaSwamy, VenkataramanaReddy, Jagadish and Raju for their cheerful company during my MSc days.

It is my sincere thanks to CSIR, New Delhi, for the financial support. In fact the fellowship was the seeding to take up research career at that time and not the real curiosity or interest I had in doing science.

Proud salutations to my childhood friends - Shankara, Seeni, Aaadi, Chandra, Lokesh, cinaBabu and their family and friends whose twinkling memories always come ahead of me.

Special thanks to vaave for care, love, affection and support. I also thank JayaramaReddy babai, Padma chinnamma for their encouragement; Srikanth and chinna (Vaishali) for their cheerful company.

I have no words to express my gratitude to my beloved parents and my sister Geetha, without knowing where and what I am doing, just wishing me all the time with no expectations whose blessings and dreams are definitely everlasting motivation for me and kept me awake all along.

It gives me an immense pleasure and an occasion to remember late Padma Bhushan Prof. Dr. H. Narasimhaiah (fondly called as HN), National Education Society, Karnataka, for his indomitable commitment to the cause of education and whose moral and ethical values and simplicity touched my heart.

I thank all of you again for your kind support and cooperation.

J. Prakasha Reddy

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Abstract

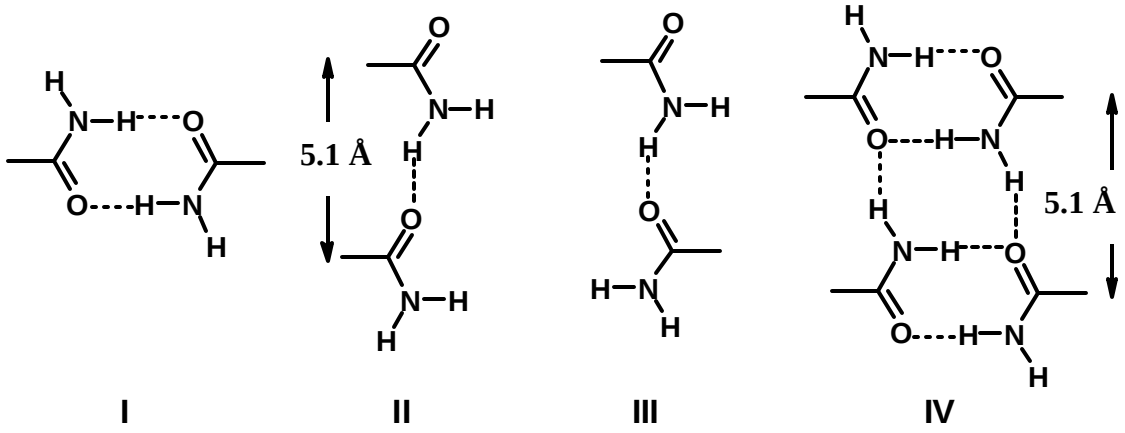
This abstract of thesis entitled "**Non Covalent Synthesis of Supramolecular Assemblies**" consists of four chapters. Chapter 1 comprises of introduction to the frontier area, 'supramolecular chemistry' in the realm of supramolecular synthesis and general terminology along with notations. Chapter 2 describes a study of supramolecular assemblies of carboxamide (3,5-dinitrobenzamide) for the construction of novel network structures followed by structural rationalization of cyclic imides (trithiocyanuric acid). Chapter 3 deals with the polymorphism studies. Finally, in the chapter 4, design and synthesis of pyridyl sulfanyl containing flexible ligands and their utilization in the construction of metal-organic frameworks is discussed.

Chapter 1

Chemical reactions, in general, organic transformations, follow stepwise breaking and making of covalent bonds, yielding desired products following well-established reaction paths. Thus, for more than a century, systematic analyses of chemical reactions lead to the development of pool of synthetic methods. Nowadays, virtually, any chemical transformation, irrespective of the nature of the compounds like high molecular weight and multi-step reaction sequences, for example, synthesis of taxol, can be achieved.[1] However, synthesis of highly complex and topological directed materials, employing pure organic moieties sometimes (often) fail to yield the desired products or otherwise obtainable only in very low yields. Since the focus of research in the chemical sciences is the exploration of novel research methodologies for the synthesis of any desired targets, looking at the natural process of self-assembling of molecules, for example DNA through hydrogen bonds, thrust for the utilization of such bonds in the synthesis of target materials with the aid of the knowledge of hydrogen bonds obtained from a large number of three-dimensional structures of organic compounds lead to the development of frontier area supramolecular chemistry.[2,3] A detailed discussion of these events is compiled in chapter 1.

Chapter 2

In chapter 2, results obtained on the studies of synthesis and structural analysis of supramolecular assemblies formed by 3,5-dinitrobenzamide and trithiocyanuric acid are compiled into two sections with a common theme of exploration of hydrogen bonds formed by N-H moiety in the form of amides and imides. Amide functionality is one of the attractive organic moiety that forms robust hydrogen bonds in different modes depending upon the nature of the -NH moiety. Analysis of solid-state structures of numerous amides reported in the literature by Leisorowitz and co-workers[4] revealed that while primary monoamides commonly form ribbon-like motifs, diamides yield infinite layers. However, in secondary amides, such as N-methyl amides, the resulting motif is commonly an infinite chain. Different motifs/patterns that are commonly found in primary amides are shown in the Scheme 1.



Scheme 1

However, in the supramolecular synthesis, utility of amide functional group (-$CONH_2$), is not that well explored in comparison with other functional moieties like -COOH.[5] Thus, a study of synthesis of supramolecular assemblies of 3,5-dinitrobenzamide (**DNBA**) has been considered. For this purpose, the endeavour was initiated with the determination of solid-state structure of **DNBA** itself, as it is not known in the literature, which was confirmed by performing a search on the Cambridge Structural Database (CSD).[6]

Part A: Assemblies of 3,5-dinitrobenzamide

Crystal structure of 3,5-dinitrobenzamide revealed several intriguing and unique features. Firstly, an unusual arrangement of **DNBA** molecules in its crystal structure, by not forming 5.1 Å structure, which is usually observed in primary amides (see Scheme 1) without any steric constraints.[7] The arrangement of **DNBA** molecules in the crystalline lattice is shown in Figure 1. This kind of unusual arrangement may suggests that **DNBA** is an ideal substrate for the formation of polymorphs, solvates, molecular complexes, etc. Hence, we attempted crystallization of **DNBA** from various solvents, with varying polarity, such as ethanol, propanol, butanol, iso-propanol, chloroform, dichloromethane, carbon tetrachloride, nitromethane, ethylacetate, benzene etc., under various conditions. But, only dimethyl sulfoxide (DMSO) and pyridine (hydrogen bond receptor solvents) formed solvated structures with **DNBA**. In DMSO adduct, recognition between **DNBA** and the solvent molecules is established through the formation of N-H···O hydrogen bond while in the pyridine complex the recognition is through the formation N-H···N hydrogen bond. In both the solvated structures, amide molecules exist as dimers with the formation of eight membered centro symmetric cyclic motifs.

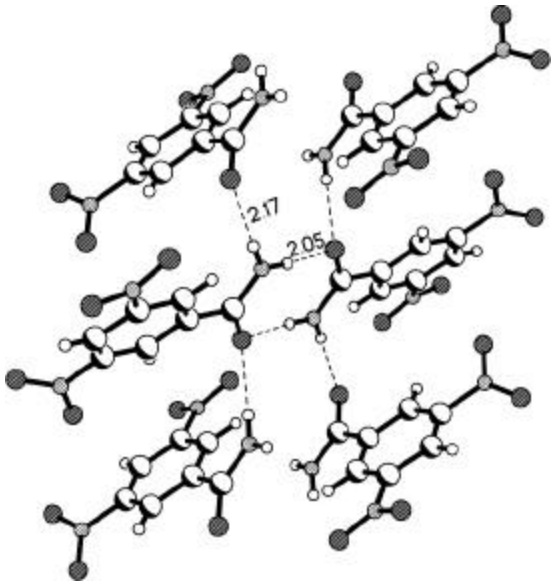


Figure 1. Arrangement of molecules of 3,5-dinitrobenzamide in its crystal lattice.

Further, to evaluate **DNBA** as a potential substrate to form novel supramolecular assemblies/architectures, co-crystallization with several substrates possessing hydrogen bond donor/acceptor functionalities, for example, aza-donor compounds was carried out. Co-crystallization of **DNBA** with bpy from methanol or water gave molecular complexes of **DNBA** and bpy in a 2:1 ratio, along with the corresponding solvent of crystallization. Both the complexes form channel structures with channels being occupied by bpy molecules. However, the two complexes differ from each other about the arrangement of molecules around the channels. In water adduct, the stacking of the planar sheets with cavities form channels. While in methanol adduct, such channels are formed by the stacking of helical chains, running in an anti-parallel manner, constituting a double helix (Fig. 2).

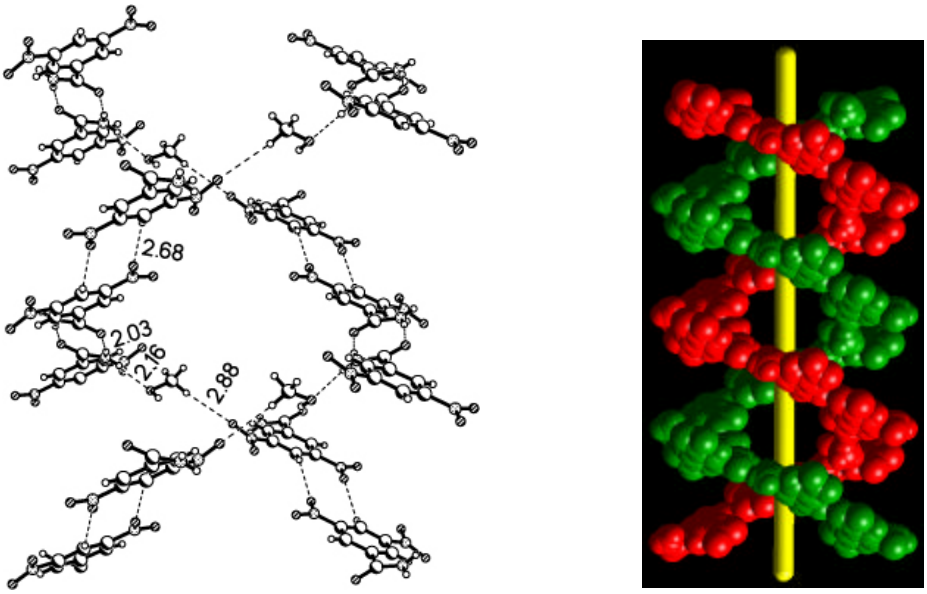


Figure 2. Two-dimensional arrangement of constituent molecules in methanol adduct.

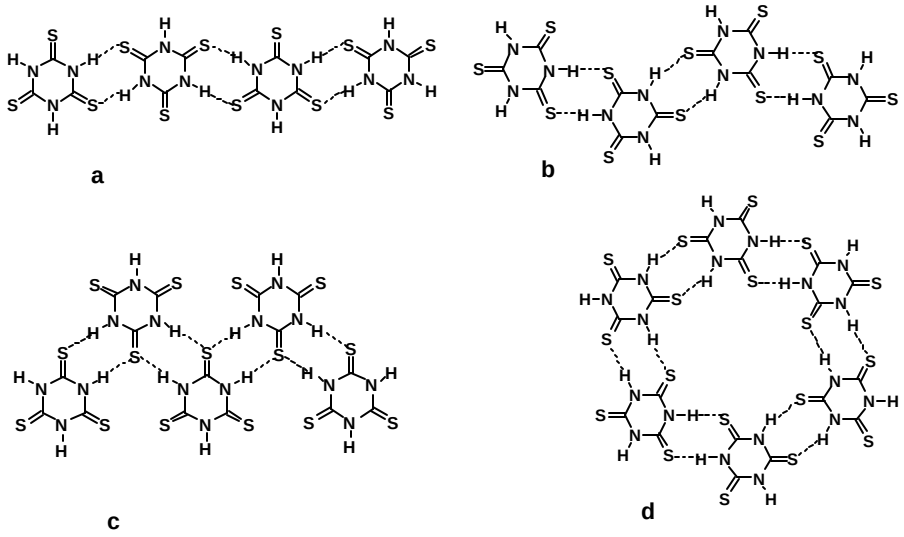
Similarly, co-crystallization of **DNBA** with 1,2-bis(4-pyridyl)ethene (bpyee) and 1,2-bis(4-pyridyl)ethane (bpyea) also gave solvent dependent host-guest complexes. In these complexes, **DNBA** molecules in the form of dimers, through the formation of N-H···O hydrogen bonds, constitute a host framework along with the solvent of

crytallization yielding channels with the aza-donor molecules, while bpyee and bpyea occupying the void space. Further, an interesting observation is that in the water adducts bpyee and bpyea, form triplet supramolecular pattern with **DNBA**. The experiments were continued with other substrates and full details of the features of these assemblies would be discussed in detail in this chapter.

Part B: Structural rationalization of some solvated structures of trithiocyanuric acid

The observation of the effective role of -NH moiety in $CONH_2$ group to form different type of assemblies, cyclic imides which possess -NH moiety appeared to be of potential targets for the creation of exotic assemblies.[8] In fact cyanuric acid (CA),[9] was well explored by many research groups for this purpose, but studies pertain to its thio analogue trithiocyanuric acid (**TCA**) are limited in the literature except for its structure with acetone.[10] Thus, looking at the hexagonal network structure formed by **TCA** along with acetone, it might be possible to have structures of **TCA** with other solvent molecules. Hence, crystallization of **TCA** from different solvents having hydrogen bonding receptor nature like DMSO, DMF, acetonitrile, methanol and butanone was carried out.

Crystal structure analyses reveal the formation of solvated **TCA** structures. The structures, thus obtained, can be classified into two different groups depending upon the topological arrangement of the **TCA** molecules in the lattices. Thus, three infinite single tape arrangements (Scheme 2(a-c)) of **TCA** molecules and one infinite double tape type arrangement (Scheme 2(d)) of **TCA** molecules are identified. In all the solvated structures, recognition is established between the molecules through the involvement of N-H bonds of **TCA** and the other molecule. Detailed rationalization of the structural properties of all the structures will be presented in the thesis.



Scheme 2

Chapter 3

Polymorphism,[11] a phenomenon dealing with the study of ability of a compound to exist in more than one crystalline form has gained paramount importance in academic and commercial sectors. In particular, a precise knowledge of the stability between/among the polymorphs at ambient and non-ambient conditions is essential, especially in the crystallization processes of bioactive compounds like drugs, to create different types of formulations.

Current approaches for the preparation and isolation of polymorphs of a compound include crystallization with tailor-made soluble additives, epitaxial growth, laser induced nucleation, crystallization in capillaries, pressure induced crystallization and more common and traditional method such as crystallization from various solvents/mixture of solvents at different conditions of temperature.[12] Recently, Matzger et al., introduced polymers as heteronuclei for the preparation and isolation of polymorphs of acetaminophen, carbamazepine, 5-methyl-2-[(2-nitrophenyl)amino]-3-thiophenecarbonitrile (commonly known as ROY) and sulfamethaxazole.[13]

Polymorphism, however, appears to be still in its infant stage and clear mechanistic explanation for the formation of polymorphs is not well established except the recent efforts of systematic analysis, which suggest that (i) the interplay of intermolecular

interactions (ii) interaction between structure of growing surface and the solvent i.e., action of the solvent at various crystal faces (iii) solvent-solute and solute-solute interactions etc. may direct the formation of polymorphs. So, a large number of polymorphism studies are still quite essential for targeted preparation of the forms. In this direction, thus, we have chosen carboxamide (-$CONH_2$), which may exhibit polymorphism due to the nature of forming different types of intermolecular interactions and these features are discussed in this chapter.

Synthesis and Analysis of Four Polymorphs of 4-amino-3,5-dinitrobenzamide

Crystallization of 4-amino-3,5-dinitrobenzamide (**ADNBA**) from various solvents with different polarities and under variant conditions, yielded different crystal habits such as blocks, plates, needles etc. The samples were examined using different analytical techniques such as differential scanning calorimeter (DSC), variable/high temperature powder X-ray diffraction (PXRD), hot stage microscopy (HSM) and single crystal X-ray diffraction.

Crystals obtained from tetrahydrofuran (THF), methanol, water (hydrothermal process) and benzene gave different unit cell parameters while the parameters from all the remaining other solvents as well as from mixture of solvents gave same cell parameters as obtained from methanol. For convenience, we labeled the forms obtained from THF, methanol, hydrothermal process and benzene as Forms I, II, III and IV respectively.

In all the four forms, -NH_2 group which is sandwiched between two -NO_2 groups forms intramolecular N-H···O hydrogen bonding. Further, although, difference in the unit cell parameters do exists between the Forms I and II, both of them are iso-structural by forming N-H···O hydrogen bonded catemer networks in a helical manner. In Form III and IV, unlike in Forms I and II, the adjacent amide moieties are held together by N-H···O hydrogen bonds in dimeric form. The detailed structural characterization and features of the four forms and further insights into the stability, inter-conversion of the forms in the solid-state as characterized by HSM, PXRD, DSC, etc., will be presented in the thesis.

Chapter 4

Principles of crystal engineering, originally formulated through the studies of solid-state structures of organic compounds, were later on extended for the preparation of new materials using coordination complexes also.[14] Crystal engineering of metal-organic frameworks (MOFs) using dative bonds are not only well known for their fascinating, esthetic architectures but also find potential applications such as in catalysis, ion-exchange, molecular sensing, gas storage, chiral separation, etc.[15] A remarkable development in this area may be the possibility of selecting suitable ligand/building block and assemble them into structures with specific topologies using metal nodes. A wide variety of supramolecular coordination polymers and discrete networks exhibiting different types of topologies, such as capsules, honeycomb networks, chicken wire frameworks, cages, helices, channels, rosettes, tubes etc. have been well demonstrated and showed that the different type of architectures formed primarily depend on the structure of the ligands as well as the coordination geometry of the metal center.[16]

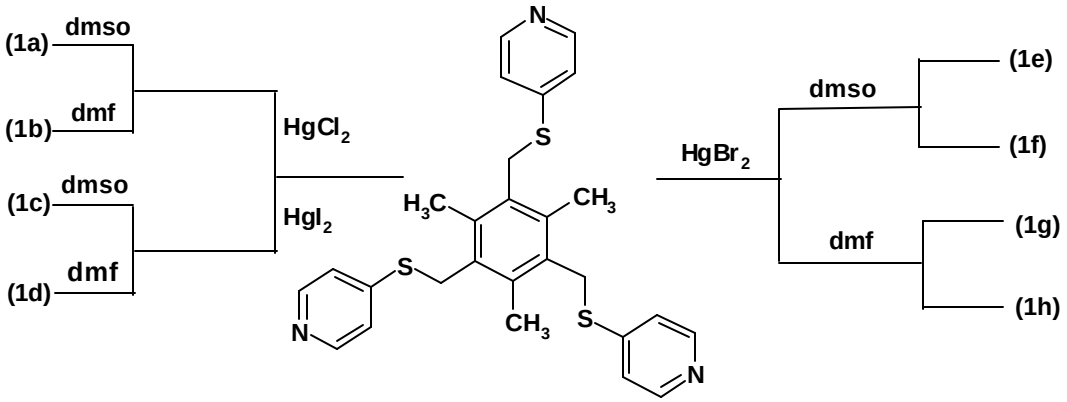
Studies towards the design and synthesis of MOFs, employing flexible ligands, such as tripodal ligands, are limited and are considered to be one of the most useful building blocks.[17] Thus, a considerable efforts in this area has recently been devoted to develop novel multi dentate/multi armed molecules with arene moieties as core unit that can form unique supramolecular network topologies. These molecules also have been shown to act as hosts for a wide range of solvent molecules and also for the development of dendrimers. In this direction, three pyridyl sulfanyl ligands, 1,3,5-tris(4-pyridylsulfanylmethyl)mesitylene, $\mathbf{L_1}$, 9-(4-pyridylsulfanyl)phenanthrene, $\mathbf{L_2}$, and 2,2'-bis(4-pyridylsulfanylmethyl)biphenyl, $\mathbf{L_3}$, have been synthesized and structurally characterized by single crystal X-ray diffraction. Further, metal-organic supramolecular assemblies of ligand L_1 with different Hg(II) halides, have been synthesized and structural characterization by X-ray diffraction methods and analysis of molecular packing in the crystalline lattice were carried out.

Synthesis and self-assembly of pyridyl sulfanyl ligands.

All the ligands have been synthesized in one-step reaction from the corresponding bromo derivatives. The ligand, **L_1**, was prepared by refluxing 1,3,5-tris (bromomethyl)mesitylene and 4-mercaptopyridine for 48 hours in methanol. Crystal structure analysis showed that the three-pyridyl thio groups adopt a *cis, cis, cis,* confirmation i.e. the three pyridyl groups lie on the same side of the plane of the central benzene ring. Packing analysis revealed that the molecules recognize each other through the formation of a weak C-H···N hydrogen bond. The ligands, **L_2** and **L_3** were prepared by the reaction of 2,2'-bis(bromomethyl)biphenyl and 4-mercaptopyridine in methanol, by refluxing at 80 ^{o}C and 35 ^{o}C respectively, for 24 hours. The crystal structure analysis revealed that in both **L_2** and **L_3**, the adjacent molecules are held together by C-H···N hydrogen bonds.

Coordination assemblies of L_1 with Mercury (II) halides

A Schematic representation of the formation of coordination complexes of Ligand **L_1** with different mercury halides is shown in Scheme 3. A detailed discussion of their assemblies is presented in the thesis.



Scheme 3

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Chapter ONE

AN OVERVIEW OF SUPRAMOLECULAR CHEMISTRY

"The chemist finds illustration, inspiration, and stimulation in natural processes, as well as confidence and reassurance since they are proof that such highly complex systems can indeed be achieved on the basis of molecular components".

Jean-Marie Lehn, 1995

1.1 INTRODUCTION

Organic compounds synthesized by conventional synthetic methods using covalent bonds, can be regarded as an ensemble of atoms that result from overlap of atomic orbitals. Chemical reactions, in general, involve stepwise breaking and making of covalent bonds, have been studied in a systematic way that has ultimately lead to the development of pool of synthetic methods.[1] Virtually nowadays any chemical transformation can be achieved irrespective of dimensionality, complexity, etc., as exemplified with the synthesis of taxol, one of the high molecular weight compounds, known till today. However, it still remains a challenge to synthesize designer compounds with complex structural features such as supramolecular architectures and networks, nanoscale or polymeric systems through the stepwise reorganization of bonds that often involve tedious processes and also generally end up in a low overall yield of desired product. Thus, thrust for novel methodologies and tools became essential to meet the demands of 21st century technology revolution.

1.2 Noncovalent synthesis

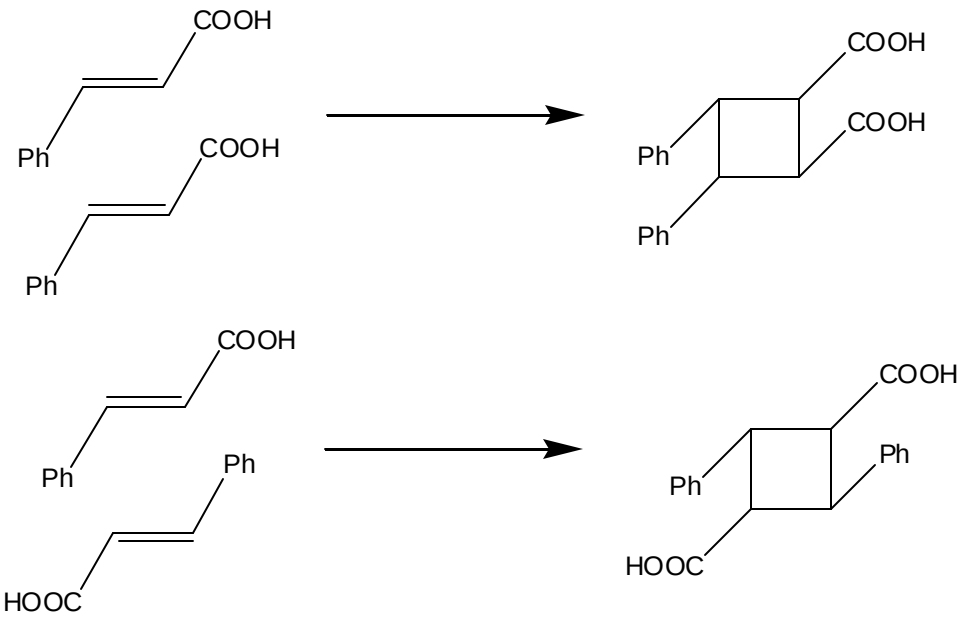
Crown ethers, a novel class of macro cyclic compounds with their ability to capture small charged and neutral molecules, as explored by the research groups of Lehn and Cram, for which they were awarded the Nobel Prize in 1987, laid foundation for the introduction of novel synthetic methodologies for the creation of assemblies with tailor-made properties. In a systematic evaluation of the new processes, drifting from mere molecular dimensions matchability approach in terms of lock and key mechanism,

the concepts were extended focusing on the analysis of binding affinity between the constituents studies in terms of interaction between host and guest compounds through noncovalent bonds such as hydrogen bonds. Further, Lehn defined it as supramolecular chemistry - '*chemistry beyond molecule'* - and in his own words that "*supermolecules are to molecules and the intermolecular bond what molecules are to atoms and covalent bonds*".[2] Thus, beyond the molecular chemistry, lies the field of supramolecular chemistry, the aim of which is to gain control over the intermolecular bond. Therefore, the understanding of intermolecular interactions is as important to supramolecular chemistry as the understanding of covalent bond to molecular chemistry. This novel synthetic approach, also referred in the literature as noncovalent synthesis/supramolecular synthesis is well explored with applications in various disciplines (such as in biology, physics, materials preparation) making supramolecular synthesis as a interdisciplinary area of research.[3] The progress in the last several decades demonstrates that noncovalent interactions have an enormous potential for the construction of chemical structures exhibiting a high degree of structural complexity.[4]

1.3 Crystal engineering

The phrase crystal engineering came into existence when G. M. J. Schmidt carried out his work on the topochemical reactions (Scheme 1.1) of crystalline *trans*-cinnamic acids, about three decades ago.[5] However, as it was mentioned in the recent report by Zaworotko,[6] crystal engineering was first coined by R. Pepinsky at the American Physical Society Meeting in 1955,[7] with an abstract entitled *Crystal Engineering*: *A New Concept in Crystallography* and wrote:

crystallization of organic ions with metal containing complex ions of suitable sizes, charges and solubilities, results in structures with cell and symmetries determined chiefly by the packing of complex ions. These cells and symmetries are to a good extent controllable: hence crystals with advantageous properties can be 'engineered'…

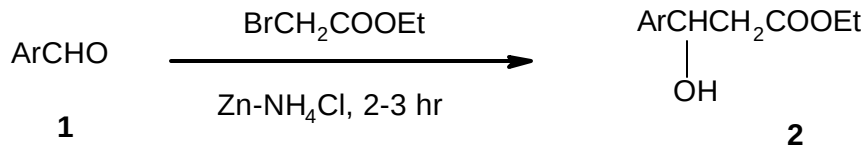


Scheme 1.1: Photo activation of *trans*-cinnamic acid giving different cyclobutane products depending on the arrangement of reactant molecules in the crystal structure.

However, prolific utilization of the concepts and principles of crystal engineering became so popular with the increasing knowledge of noncovalent interactions that play a significant role in the supramolecular synthesis.8 Thus, pioneering work carried out by different research groups in the direction of rationalization of crystal structures and packing patterns within a series of related compounds lead to the development of strategical approaches for crystal engineering of supramolecular assemblies.[9]

The design element or sub structural unit within a molecule that can be identified by crystal engineering principles is the key factor for producing new systems with tailor-made properties and novel applications. In the realm of solid-state chemistry,

the goals of crystal engineering are the design and preparation of materials with specific properties (conductivity, thermochromism, photoactivity, second-harmonic generation, etc.).[10,11] The properties of a crystalline material are due to the arrangement of molecules in the crystal lattice that are controlled by intermolecular interactions. Crystals, in the form of collection of molecules which are held together by numerous intermolecular interactions directs the structural properties. Hence, a precise knowledge and understanding of the various intermolecular interactions is essential which may also further be useful in the prediction of crystal packing for a given compound. Progressive research efforts in those directions, indeed, lead to the evolution of different frontier areas of research such as polymorphism, self assembled thin films, liquid crystals, drug design, solid state (solvent less chemical reactions), etc.[12-14] In fact, engineering of crystal structures is not just limited for the synthesis of different supramolecular architectures, but also to perform numerous chemical reactions. For example, it has been shown that several common and named organic reactions can be carried out in solid state based on the structural arrangement by grinding and/or heating the reactants. Often, solid-state reactions are found to be most efficient and also selective than reactions in the solution media and furthermore proceed with increased environmental friendliness, especially for industrial scale processes. Toda et al. reported numerous organic reactions in the solid state that proceeded very efficiently and selectively.[15] For example, treatment of the aromatic aldehydes **1a-d** with ethylbromoacetate and Zn-NH_4Cl at room temperature for 2-3 hr, as shown in the Scheme 1.2, gave the corresponding Reformatsky reaction products **2a** (91%), **2b** (94%), **2c** (83%) and **2d** (80%).[16]



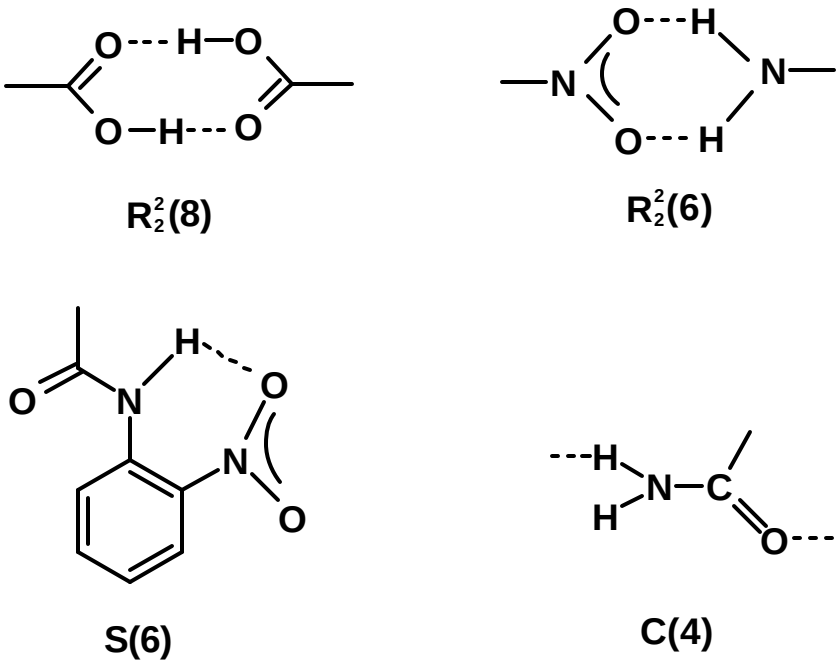
1 **2**

a) Ar = Ph, b) Ar = *p*-BrC_6H_4
c) Ar = *p*-PhC_6H_4, d) Ar = 2-naphthyl

Scheme 1.2

In the supramolecular synthesis, hydrogen bonding is a powerful/ resourceful interaction in the targeted synthesis. So several studies of systematic analysis of hydrogen bonding patterns have been carried out.[17] Thus, it could be emphasized that hydrogen bonding is not random but show directional strength to tune the spatial arrangement of molecules and/or ions in the solid state and hence the design of functional solids.[18] Thus, a *graph set analysis*[19] (see Scheme 1.3) with empirical rules in order to define the formation of hydrogen bonded arrays was developed by Etter and further refined by Bernstein.[20] The process of assigning a graph set begins with identification of a number of different types of hydrogen bonds, as defined by the nature of the donors and acceptors in a hydrogen bond, that are present in the structure. Different types of hydrogen bonds are characterized by one of the four designators. These designators are **C** (chain), **R** (ring), and **D** (finite set), while **S** denotes self or an intramolecular hydrogen bond. The number of donors (**D**) and acceptors (**A**) used are assigned as subscripts and superscripts, respectively, and the motif (the number of atoms in the repeat unit) is indicated in parentheses. A major outcome of this analysis is evolution of some principles, which have more impact than the actual numerical codings developed. Some of the postulates or rules given by Etter are mentioned below.[19a]

1. All good proton donors and acceptors are used in hydrogen bonding.
2. Six-membered-ring intramolecular hydrogen bonds form in preference to intermolecular hydrogen bonds.
3. The best proton donors and acceptors remaining after intramolecular hydrogen-bond formation form intermolecular hydrogen bonds to one another.



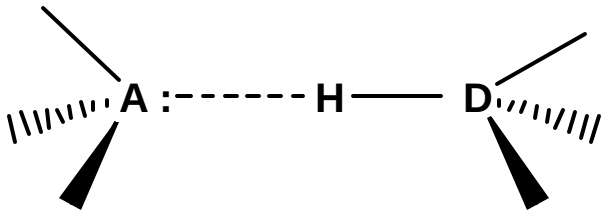
Scheme 1.3: Graph set notation for some hydrogen bonding networks.

1.4 Various intermolecular interactions operating in the solids

In an ensemble of molecules, recognition between the molecules occurs through weak interactions, such as hydrogen bonding, van der Waals or dispersive forces, C-H···p, p-p, ionic, dative bonds, etc. Hydrogen bonding, due to its strength and the directionality, is the most reliable of all the noncovalent/intermolecular interactions known. They play a crucial role in aligning molecular components and exist in simple molecules like water to complex biological systems like in DNA and protein structure.[21]

Pauling's early definition of the hydrogen bond:[22]

A hydrogen bond is an interaction that directs the association of a covalently bound hydrogen atom with one or more other atoms, groups of atoms, or molecules into an aggregate structures that is sufficiently stable to make it convenient for the chemist to consider it as an independent chemical species.

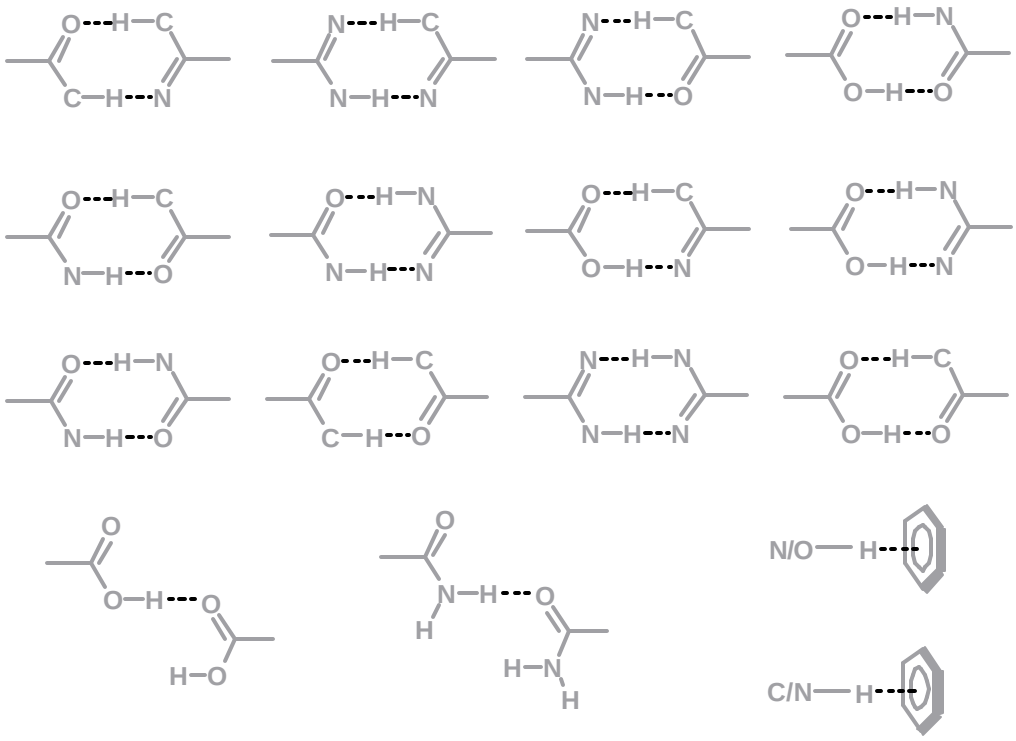


A = F, Cl, O, S, N, ?-system D = F, Cl, O, S, N, C

Figure 1.1: A Hydrogen bond formed between an acidic hydrogen atom and an appropriate acceptor.

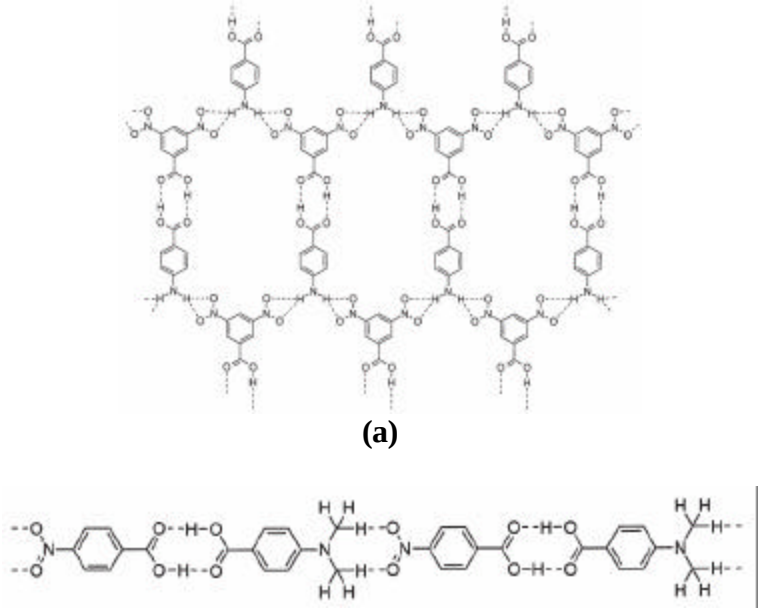
The hydrogen bond, usually denoted as D-H···A (Fig. 1.1), is an interaction between a hydrogen atom covalently bonded to a proton donor D and interacting with proton acceptor A.[23] The hydrogen bond is mainly electrostatic in nature. Geometrical properties also contribute to a greater extent to estimate the nature of the hydrogen bond. The geometry of the hydrogen bonds has been studied extensively by statistical and neutron diffraction methods.[24] Dunitz pointed out that the energy required to extend a covalent bond by 0.2 Å is of the order of 50 kcal mol^{-1} while that to extend a hydrogen bond the same amount is only 1.2 kcal mol^{-1}.[25] This illustrates the difference in strength on the two types of bonds. Some of the intermolecular interactions which are involved in the construction and stabilization of large noncovalently linked supramolecular architectures, are listed in Chart 1.1.

Chart 1.1



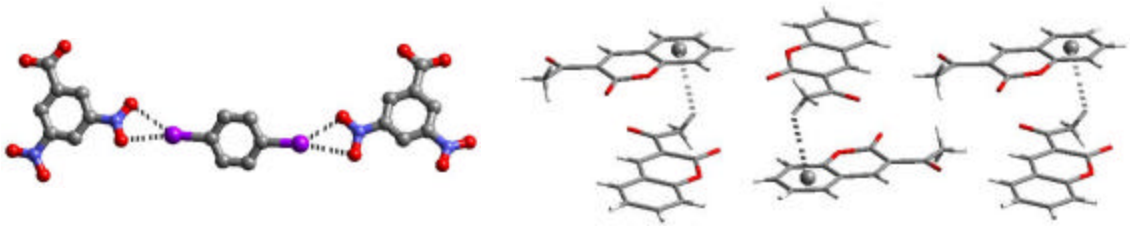
Hydrogen bonds, further, may be divided into strong (for example, O/N-H···O, O/N-H···N) and weak (for example C-H···O/N) hydrogen bonds. One of the examples of strong hydrogen bonds is shown in Figure 1.2(a) in which the recognition between molecules 3,5-dinitrobezoic acid and 4-aminobenzoic acid is established through O-H···O and N-H···O hydrogen bonds forming sheet structure in two-dimension.[26] But, in the complex formed between 4-nitrobenzoic acid and 4-(N,N'-dimethylamino)benzoic acid both strong and weak hydrogen bonds constitute the observed tapes in the crystal structure (Fig. 1.2(b)).[27] Weak interactions such as O/N-H···p, C/N-H···p, p-p, X···X (X = Cl, Br, I), iodo···nitro etc., also play crucial role in stabilizing supramolecular architectures and hence the properties. For example, in the molecular complex between 3,5-dinitrobenzoic acid and 1,4-diiodobenzene, the molecules recognize through iodo-

nitro interactions in addition to O-H···O hydrogen bond (see Figure 1.3(a)).[28] In the crystal structure of the forms of 3-acetylcoumarin, molecules recognize each other through C-H···p interactions (see Figure 1.3(b)) in addition to C-H···O hydrogen bond, generating a sheet structure.[29]



(a) **(b)**

Figure 1.2: (a) Strong hydrogen bonds that stabilize the sheet structure found in the complex between 3,5-dinitrobenzoic acid and 4-aminobenzoic acid. (b) Presence of C-H···O hydrogen bonding is evident in the tapes formed by 4-nitrobenzoic acid and 4-(N,N'-dimethylamino)benzoic acid in addition to strong hydrogen bonds.



(a) **(b)**

Figure 1.3: (a) Recognition between the molecules in the complex of 3,5-dinitrobenzoic acid and 1,4-diiodobenzene. (b) Arrangement of molecules in 3-acetylcoumarin. Notice C-H···p interactions.

1.5 Various supramolecular architectures and interactions

Using noncovalent protocols a wide variety of exotic supramolecular architectures, both organic and organometallic, formed due to intermolecular interactions and dative bonds, described as self assembled capsules, cages, helices, channels, tubes, rosette aggregates, tapes, ordered hydrogen bonded arrays, etc., are reported in the literature.[30-33] All these hydrogen bonded assemblies are based on self complimentarity between the interacting species and evolution of an assembly depends on the functional group associated with various compounds under consideration. In this respect, assemblies based on carboxylic acid group (-COOH) are well studied because of the robust hydrogen bonds that it can form on its own as well as with appropriate receptors.[34,35] For instance, benzoic acid forms zero dimensional units, terephthalic acid forms one dimensional tapes, trimesic acid with its threefold symmetry forms a two dimensional chicken wire network and adamantane-1,3,5,7-tetracarboxylic acid with its tetrahedrally disposed carboxylic acid group forms a diamondoid network in three-dimension (see Figure 1.4(a)-(d)).[36] Further, with various other substrates -COOH forms a variety of hydrogen bonding patterns by reorganizing the motifs known in the native structure which illustrates the efficacy of the -COOH group to yield novel hydrogen bonding patterns, for example, interaction with aza aromatic molecule, shown in Figure 1.5, a seven membered pair-wise hydrogen bonded dimer is formed preferably in a majority of the complexes.[37]

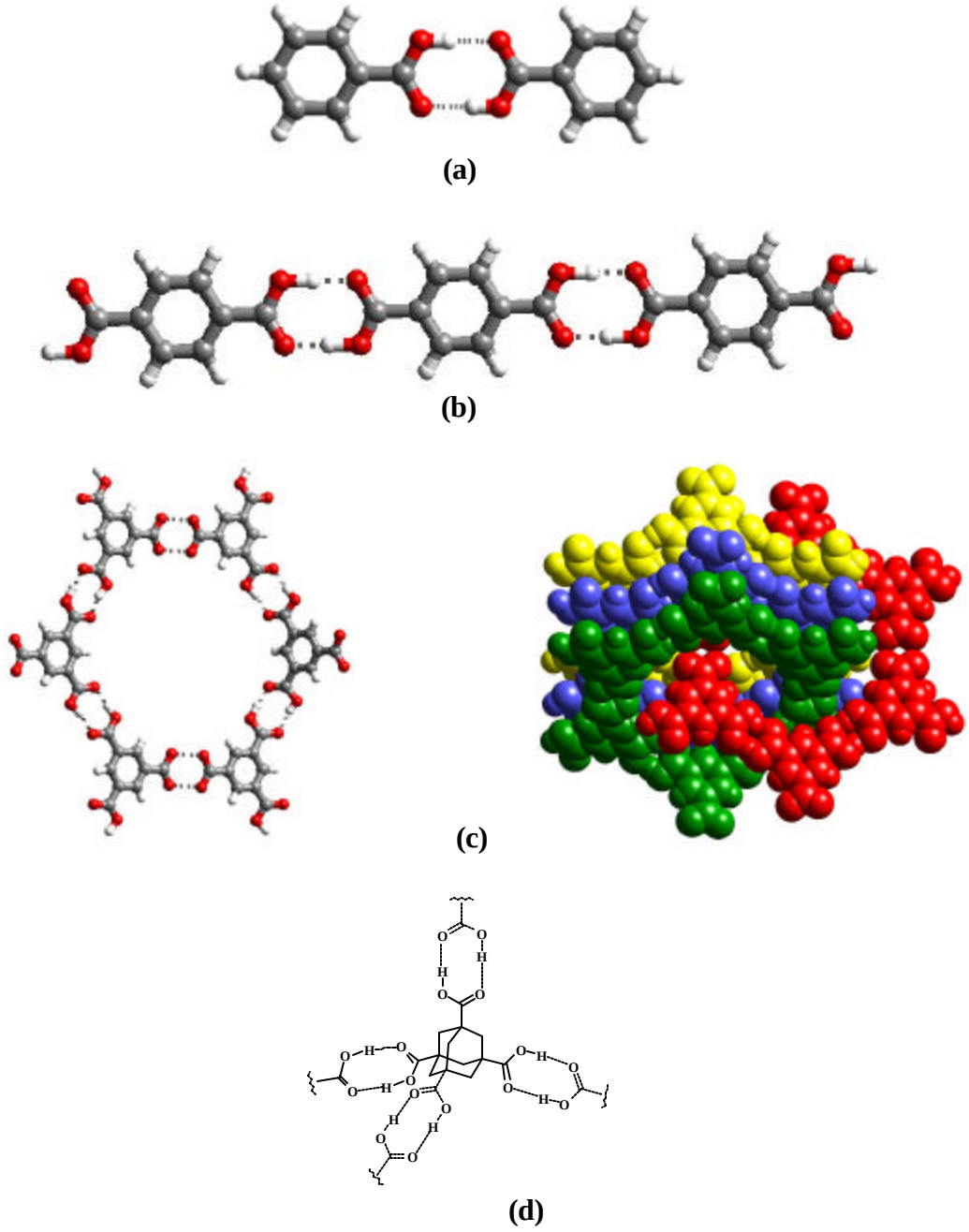


Figure 1.4: Various hydrogen bonded networks formed by -COOH associated with various compounds. (a) Benzoic acid forms zero-dimensional units. (b) Hydrogen bonded tape formed by terephthalic acid in one-dimension. (c) Trimesic acid forms chicken wire network in two-dimension, channels or cavities are not present as a result of extensive interpenetration (mutual triple catenation). (d) Forms diamondoid network in Adamantanetetracarboxylic acid.

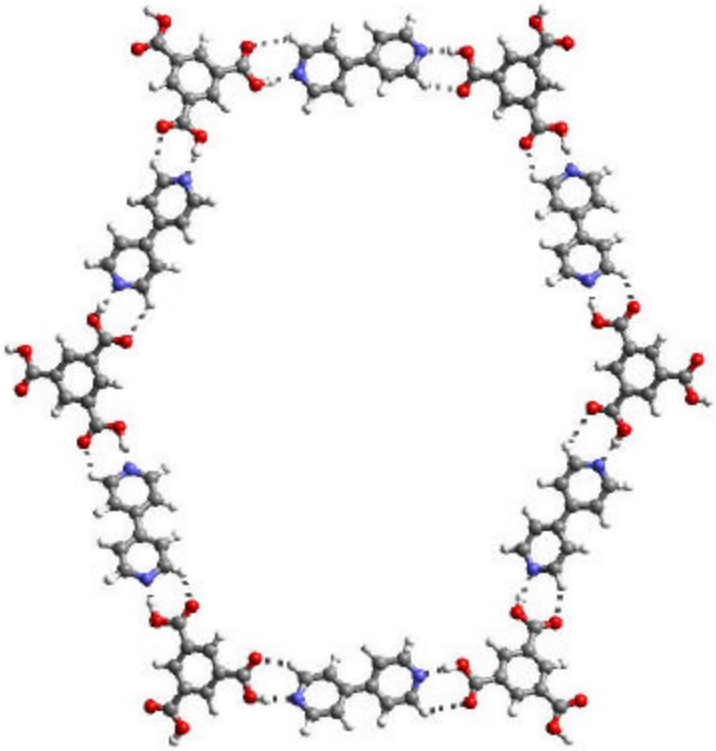


Figure 1.5: Interaction between carboxylic acid (trimesic acid) and 4,4'-bipyridyl.

Hamilton and co-workers reported the formation of hexameric cyclic networks by appropriately modifying isophthalic acid. Substitution with a bulky group at C-5 position on isophthalic acid disrupted the tape packing motif in the solid-state. The structure of 5-decyloxyisophthalic acid was successfully characterized by X-ray diffraction yielding the anticipated hydrogen-bonding pattern (Fig. 1.6).[38] Zimmerman et al. reported an exotic hexagonal network when trimesic acid and pyrene were co-crystallized from ethanol in which pyrene and ethanol molecules acting as guest molecules and trimesic acid and ethanol molecules forming host network as shown in Figure 1.7.[39]

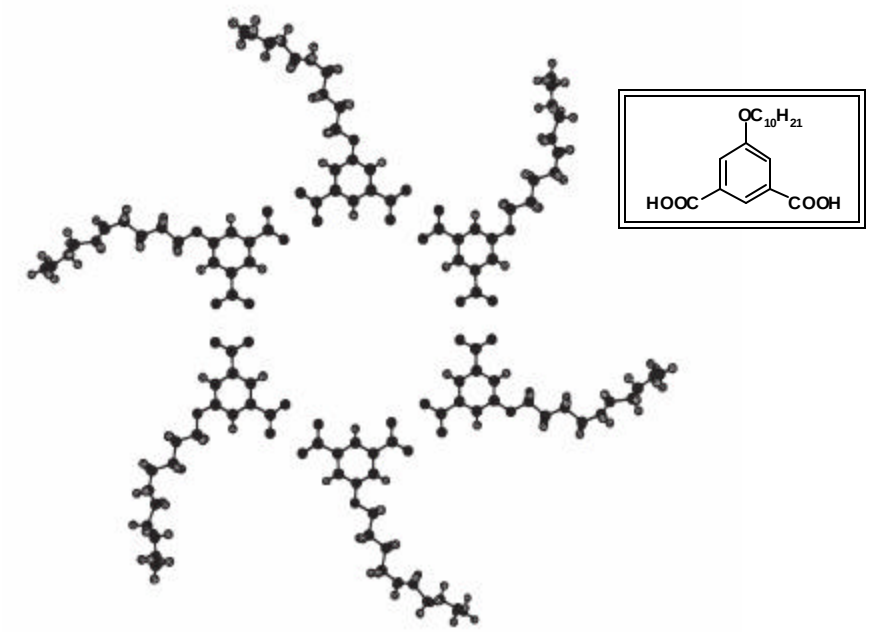


Figure 1.6: Cyclic hexameric aggregate formed by 5-alkoxyterephthalic acid in the solid-state.

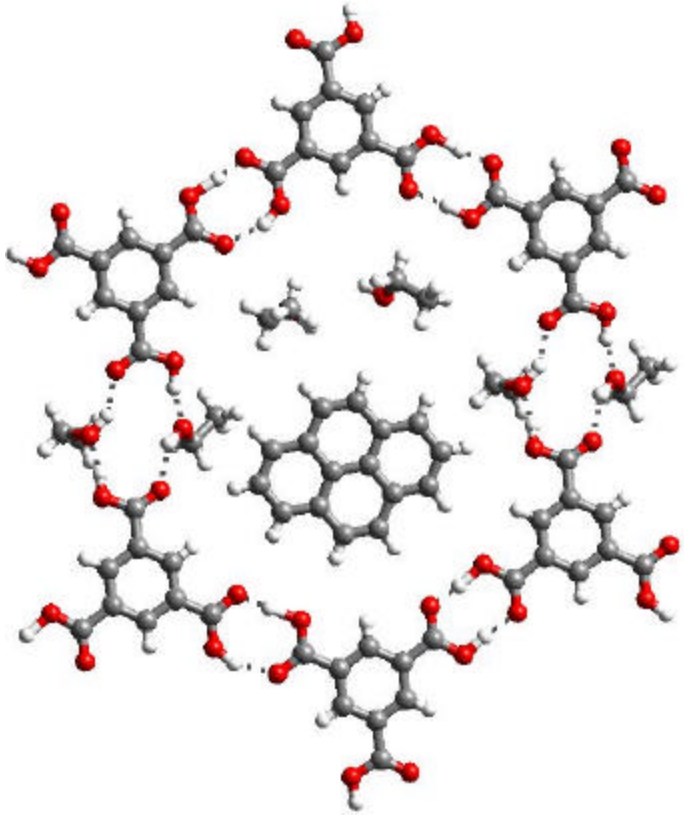
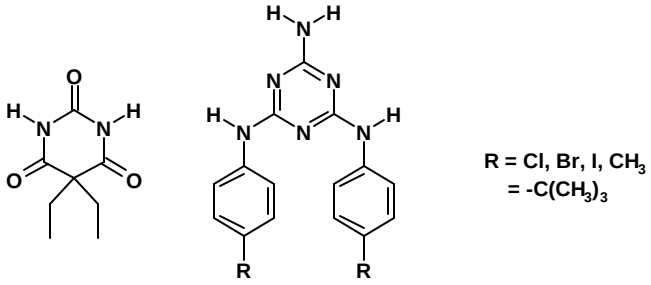


Figure 1.7: Trimesic acid forming of hexagonal network in two-dimensional arrangement.

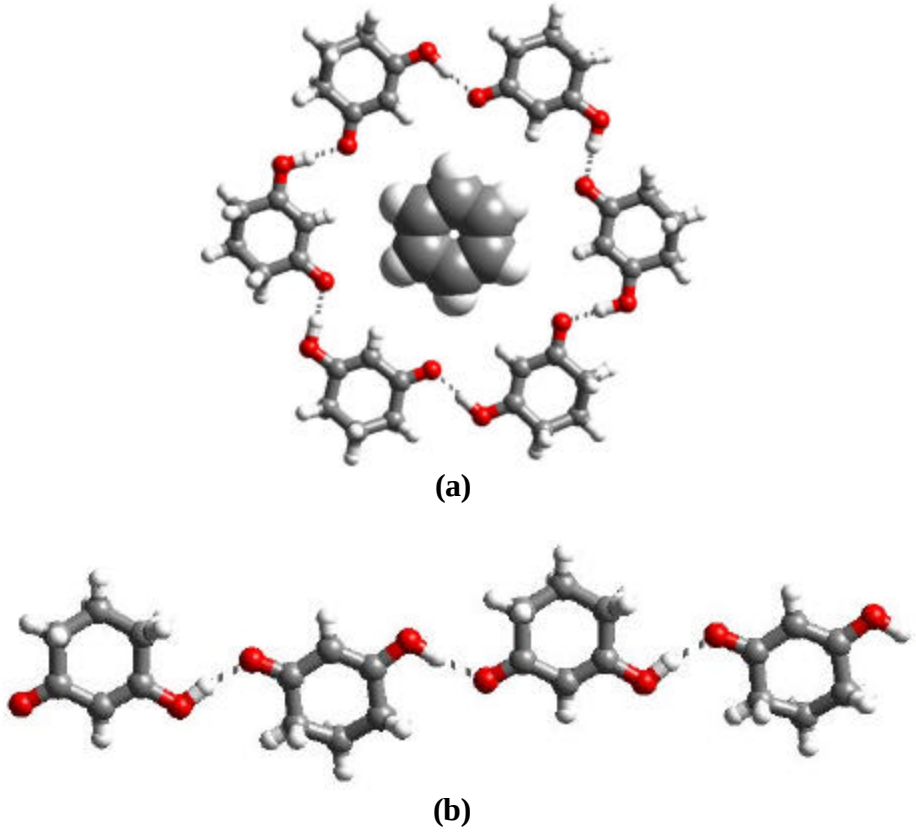
Apart from -COOH, studies with compounds possessing other complimentary functional groups such as substituted melamines and cyanuric acids (barbituric acid) were also known in the literature through the pioneering contribution of Whitesides and workers.[40] It was found that the solid-state structures/architectures formed by compounds **3** and **4**, are dependent on steric interactions and variations in the substituents form various supramolecular architectures. For example, Cl, Br, I and CH_3 substituted melamines gave tape structures and in the case of methyl or ethyl ester substituted melamines, the components self assemble to form ribbons. However, when the substituents are *t*-butyl group, a cyclic hexamer is formed.[41] Also, Lehn and coworkers designed elegant strategies in the creation of variety of supramolecular aggregates based on hydrogen bonding functionalities as exemplified through the seminal work on triaminopyrimidine substituents and barbituric acids.[42]



3 **4**

Etter et al. showed the formation of a cyclic hexamer when 1,3-hexanedione was co-crystallized with benzene or deuterated benzene. The elegancy of this work is that the hexamer aggregate is only formed when the guest solvent molecules are present. However, 1,3-hexanedione forms a tape in the absence of guest (Fig. 1.8).[43] Fenniri et al. utilized heterroaromatic bases possessing both the Watson and Crick DDA pattern of guanine (where A is acceptor and D is donor) and AAD pattern of cytosine to design

homomeric rosette aggregates.[44] Calix[4]arene linked melamine and cyanurate units were used by Reinhoudt et al. to build a family of 3D double-rosette assemblies and their growth on gold surface was further studied.[45] In a remarkable study by the same group, the quantitative formation of a 15-component 3D tetra-rosette nanoscale assembly held together by hydrogen bonds was demonstrated. Design of discrete nanoscale motifs was further explored to generate 3D heteromeric hexa- and octa-rosette assemblies. The spontaneous formation of this 27-component octa-rosette structure (~20 kDa) demonstrates the huge potential of this approach in engineering nanoscale 3D aggregates.[46]

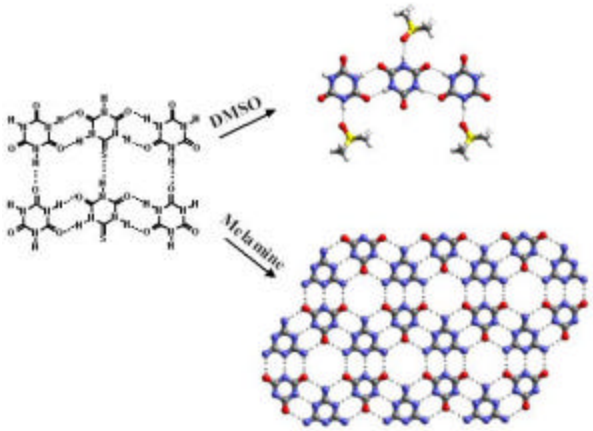


(a)

(b)

Figure 1.8: Formation of (a) cyclic hexamers in the presence of guest; (b) tapes in the absence of guest.

Some organic functional groups, however, form more than one type of motif in practice and, as a result, structural modifications depend upon the nature of the substrates employed to synthesize supramolecular networks. For example, cyanuric acid, a cyclic imide, with two types of patterns (cyclic and acyclic) in its solid-state structure, forms different assemblies with DMSO and melamine as shown in Scheme 1.4.[47] Thus, preparation of supramolecular assemblies of amide (3,5-dinitrobenzamide) and a cyclic imide (trithiocyanuric acid) which form similar hydrogen bonds are discussed in chapter two.



Scheme 1.4: Formation of different networks depending upon the substrate employed. Cyanuric acid with (i) DMSO (ii) melamine.

1.6 Introduction to polymorphism

Polymorphism, a phenomenon of existence of a compound in different crystalline forms, is one of the contemporary areas of solid-state studies as an interdisciplinary subject embracing all major sections of science (biology, chemistry, physics, etc.).[48] The phenomenon of polymorphism is not limited to molecular compounds, but indeed, it was recognized long ago in elements as 'allotropy'. For example, carbon with different structural forms differentiated by the bonding between

the atoms, exist in different forms known as graphite, diamond and fullerenes is a famous representative example. Its importance is now well appreciated both in the context of fundamental aspects of structural features as well as in terms of its impact on the preparation and formulation of specialty chemicals, pharmaceuticals, explosives, dyes, pigments, flavors, agrochemicals, etc.[49,50] The phenomenon has gained paramount importance especially in pharmaceutical industry, because of the relevance of a particular form in formulations and bioavailabilty. Polymorphs, exhibiting diverse packing arrangements, due to different arrangement and/or conformation, might differ significantly in their physico-chemical properties such as solubility, stability, change in free energy, melting point, density, etc. Hence, preparation of particular polymorph of an active substrate has become utmost important consideration in the synthesis of pharma compounds to ensure that the same form/modification is always being produced consistently and reproducibly.

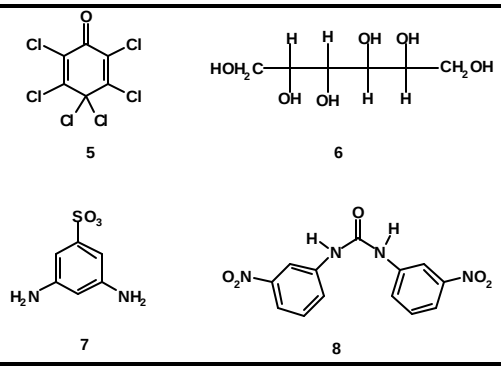
Crystallization of compounds into different polymorphs is governed by a combination of thermodynamic and kinetic factors. The occurrence of polymorphic modifications often follows Ostwald's rule of stages which states that the meta-stable form is often obtained first and the stable form crystallizes subsequently. For example, a stable form of sulfathiazole (form IV) crystallizes from hot aqueous solution through the transformation of meta stable forms I, II and III.[51] The practical implication is that it should be possible to isolate the different polymorphs of a given compound at different levels of solution supersaturation and hence exercise some control over the crystallization process. Preparation of new form of a compound/drug, on one hand, is of utmost importance because of novel properties/activity that it can exhibit, whereas, on

the other hand, is a problem to pharmaceutical researchers as a point of legal exposure for companies whose intellectual property can be threatened leading to a general attribution of *'Chemistry in the Court'*.[52] A well-documented example is ranitidine hydrochloride case (see box 1).

1.7 Some examples of polymorphic compounds from the literature

The first recognized example of a polymorphic organic substance is dimorphism of benzamide as described by Wohler and Liebig in 1832.[53] They synthesized the compound for the first time and found having a melting point of 115 ^{o}C (later called as unstable form). But, re-examination of the melting point of the compound lead to the discovery of new polymorph (stable form), which melts at 128 ^{o}C. The unstable or the lower melting form crystallizes as needles while the stable or higher melting form as blocks. Recently, Davey et al. reported the crystal structure of unstable form by synchrotron diffraction.[54] Groth was apparently the first person to compile a number of cases of compounds exhibiting polymorphism.[55,56] Some compounds of his interest include hexachloro-keto-dihydrobenzene C_6Cl_6O (**5**), mannitol $C_6H_{14}O_6$ (**6**), *m*-diaminobenzenesulfonic acid ($C_6H_3(NH_2)_2SO_3H$) (**7**), di-*m*-nitro-*s*-diphenyl carbamide $CO(NHC_6H_4NO_2)_2$ (**8**), etc (Chart 1.2).

Chart 1.2



5 6

7 8

Box 1

Ranitidine was developed in the 1970s by Allen & Mansburys Ltd., of the Glaxo group (now Glaxo SmithKline) for the treatment of peptic ulcers. In 1977, David Collin, a Glaxo chemist, first prepared ranitidine hydrochloride (**RHCl**) and obtained a U.S. patent which gives the procedure for the preparation of the hydrochloride from ranitidine base. In 1980, for unknown reasons, **RHCl** prepared produced crystals that gave different IR spectra & X-ray powder diffraction pattern than the previously observed. Glaxo concluded that a new polymorph, designated Form 2, had been produced, and the earlier form was designated as Form 1. Glaxo subsequently developed a process to manufacture all the **RHCl** it has sold commercially as the active ingredient in Zantac. In 1981, Glaxo obtained a new patent on Form 2. The abstract of the Form 2 states simply, 'A new form of ranitidine.....hydrochloride, designated Form 2, and having favorable filtrate and drying characteristics, is characterized by its infrared spectrum and /or by X-ray powder diffraction pattern'.

By 1991, Zantac sales had reached nearly $3.5 billions, nearly twice the sales of the next best selling drug. A number of generic drug firms under took efforts to prepare to go on the market with Form 1 in 1995, upon anticipated expiration of the Form 1 patent. One of these generic companies was Novopharm Ltd., the defendant in the first **RHCl** litigation that went to trial. Novopharm scientists were not successful in preparing Form 1 by following the procedure of the Form 1 patent and therefore sought approval to market Form 2, claiming that the product is and always has been, Form 2 **RHCl**. Novopharm notified Glaxo of its contention that the Form 2 patent was invalid. Glaxo sued Novopharm for infringement of Form 2 patent. Novopharm admitted infringement of the Form 2 patent, but contended that it was invalid, claiming that Form

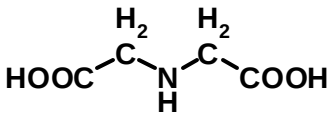
Box 1 contd…..

2 was inherent in the Form 1 patent. Glaxo proved that they can get Form 1 using reported procedure in the filed patent. In addition, they presented the evidence of notebooks that were used at Oxford university that lead to the Form 1 product and that the Form 2 patent was valid. Novopharm then examined the possibility of marketing Form 1 and sought approval to market Form 1 **RHCl** upon the expiration of the Form 1 patent. Shortly thereafter, Glaxo sued Novopharm again, alleging that Novopharm had sought permission to manufacture and market a product which would contain not pure Form 1, but rather a mixture of Forms 1 and 2, thereby infringing upon Glaxo's Form 2 patent. Novopharm, however, submitted X-ray evidence at trial that demonstrated that its actual samples of RHCl did not contain detectable Form 2. The court found that Novopharm had established that its product would not contain Form 2, and that if the product did contain Form 2, then it would be present as an independent component or impurity, not as the basis for some improvement or equivalent. The court thus allowed Novopharm to market mixtures of Forms 1 and 2. The two Glaxo v. Novopharm cases (and many other generic companies, like Glaxo v. torpharm) involved many aspects of the study and analysis of polymorphic materials.

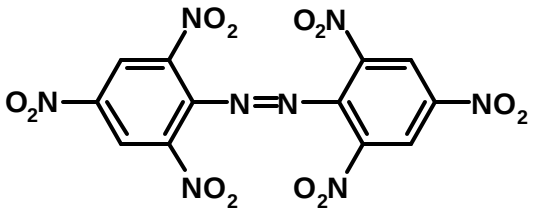
1.8 Classification of polymorphs

Polymorphs may be classified into different groups depending upon the arrangement of molecules and/or conformation adopted by different functional groups present on the molecule. Thus, conformational polymorphs, concomitant polymorphs, conformational isomers, structural polymorphs, configurational polymorphs, etc. are the representative classes in the area of polymorphism. Conformational polymorphs are

generally due to the different conformers of the same molecule crystallize into different polymorphic modifications. For example, iminodiacetic acid, shown below, exists in three forms.[57] Of the four independent molecules in the three polymorphic structures, two are identical. However, there are torsional differences of up to 30^{o} about C-N bonds. Another example is 2,2',4,4',6,6'-hexanitroazobenzene as shown below.[58]

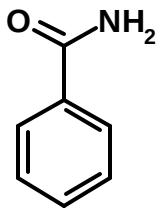


iminodiacetic acid

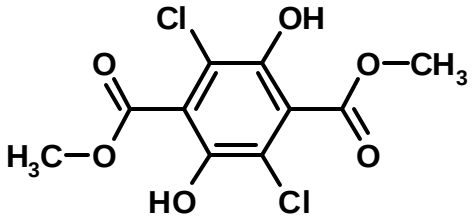


2,2',4,4',6,6'-hexanitroazobenzene

Crystallization of two or more polymorphic modifications under identical conditions lead to the formation of concomitant polymorphs.[59] For example if a hot saturated aqueous solution of benzamide is allowed to cool rapidly, one is able to observe by microscopy that two modifications of it crystallize concomitantly.[53,54] Another example is the trimorphic concomitant crystallization of methyl-2,5-hydroxy-3,6-dichloroterephthalate.[60]



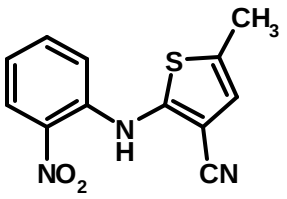
benzamide



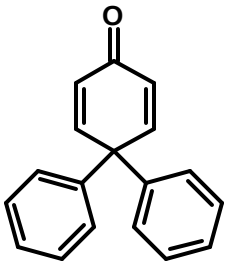
methyl-2,5-hydroxy-3,6-dichloroterephthalate

Conformational isomers are due to the existence of different conformers of the molecule in the same crystal structure. For example, 5-methyl-2-[(2-nitro phenyl) amino]-3-thiophene carbonitrile (commonly known as ROY) give conformational

isomers.[61] Recently, Howard and co-workers also reported conformational isomers of 4,4-diphenyl-2,5-cyclohexadienone in four polymorphic modifications.[62]

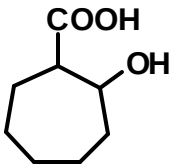


ROY



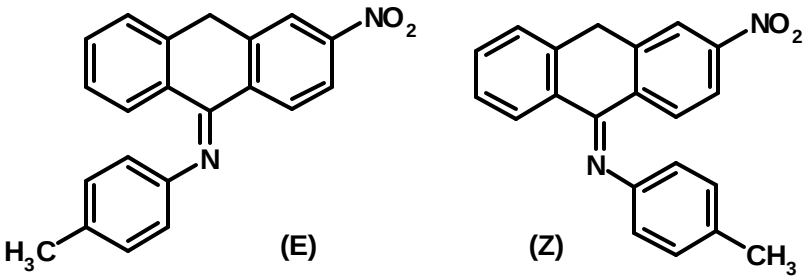
4,4-diphenyl-2,5-cyclohexadienone

Structural polymorphs are obtained when different polymorphic modifications have nearly the same or identical structural arrangement (also referred to as isostructurality). For example, *trans*-2-hydroxycycloheptanecarboxylic acid exists in two different forms and both forms are isostructural.[63]



***trans*-2-hydroxycycloheptanecarboxylic acid**

Configurational polymorphs correspond to molecule/compound that exists in same or different configuration (E or Z) in same/different polymorphic forms. Matthews et al. described the crystal structures of three crystalline forms of 4-methyl-N-(4-nitro-a-phenylbenzylidene)-aniline.[64] In solution, the material exists as a mixture of stereoisomers with Z and E configurations. In the solid state it is trimorphic, namely forms A, B and C. The A form exhibits Z configuration, while, B and C forms exhibits E configuration.

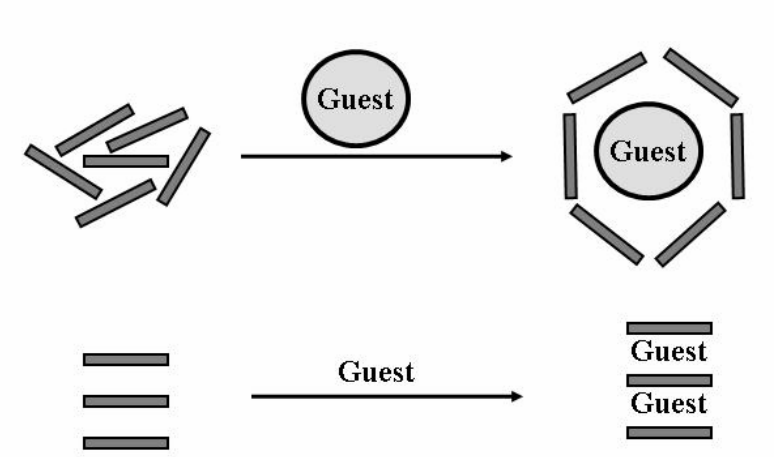


4-methyl-N-(4-nitro-a-phenylbenzylidene)-aniline

1.9 Introduction to coordination complexes

Structural chemistry studies in terms of supramolecular synthesis were originally formulated through the studies of solid-state structures of organic compounds. However, knowing the potentiality of coordination bonds (dative bonds) in terms of directionality, facile synthetic routes, preparation of novel materials, coordination complexes as well have become attractive reagents in supramolecular chemistry.[65] Construction of metal-organic frameworks (MOFs) using dative bonds are not only well known for their fascinating, esthetic architectures but also find potential applications in catalysis, ion-exchange, molecular sensing, gas storage, chiral separation, etc.[66-70] In addition to a wide range of functional materials designed using crystal engineering concepts, rational design of layered structures and porous solids, obtained by the combination of organic building blocks and metal ions (also referred to as *supramolecular coordination chemistry*), to mimic the functional properties of natural clays and zeolites, have attracted greater attention in recent times.[71] This may be because, the design strategies to synthesize these materials are relatively simple, for example, a three-dimensional open frame work structure filled with guest/s molecules

may be considered as a porous solid or sometimes it can also form intercalated structure as shown schematically below.



A wide variety of supramolecular coordination polymers and discrete networks exhibiting different types of topologies, such as capsules, honeycomb networks, chicken wire frameworks, cages, helices, channels, rosettes, tubes etc., have been well demonstrated.[32,33] Since Robson's seminal work on MOFs,[72] a great deal of effort has been directed towards the design of various MOFs exhibiting novel properties. Several efficient new methods have been developed for the preparation of novel materials. Amongst all the techniques explored, metal coordination and hydrogen bonding motifs are the most celebrated means of producing structurally rich supramolecular architectures.[73] The selection of appropriate metal ion and ligand is crucial for the construction of different type of architectures, as is witnessed in a number of publications, reviews and books.[74] Yaghi et al. reported numerous supramolecular entities of 1-D, 2-D, 3-D polymeric networks utilizing carboxylate group ($-COO^-$) as

building block with appropriate metal ion.[75] For instance, a reaction between trimesic acid and cobalt nitrate forms a cavity structure in two-dimension. (see Figure 1.9).[76]

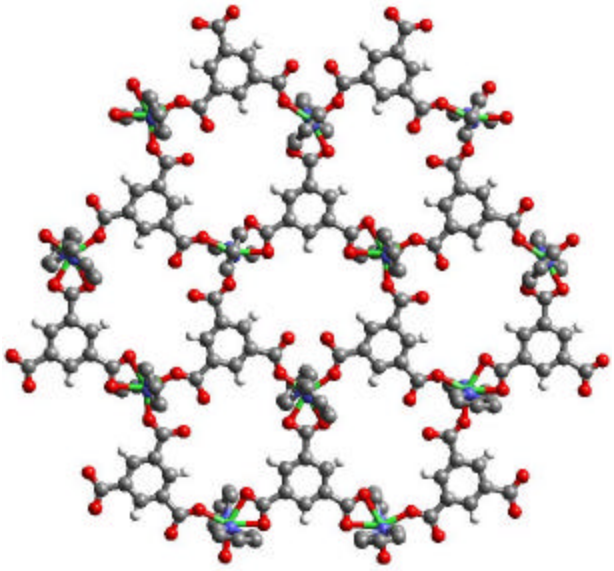
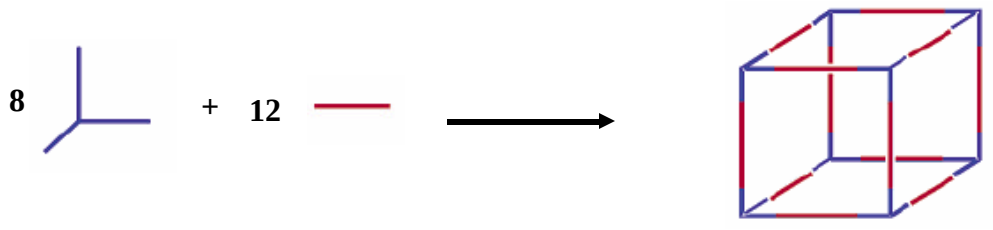


Figure 1.9: Formation of hexagonal network by the interaction between trimesic acid (organic moiety) and cobalt ion (coordination center).

The *molecular library approach* or *directional bonding approach*, as coined by Stang and Mirkin, involves mainly rigid, complementary precursors with predefined angles.[77] For instance, preparation of a supramolecular cube involves eight tritopic, 90^{o} corner units which react with twelve ditopic, linear linkers to form a supramolecular cube as shown in Scheme 1.5.[74(c)] However, a number of other factors, such as the order of precursor addition, choice of solvent system, concentration, temperature, including the rate of mixing of the two building blocks, have profound effect on the target product of any given self-assembly reaction. In addition, weaker supramolecular forces such as hydrogen bonding, p-p interactions, the coordination ability of the counter ions etc., may also strongly influence the ultimate geometry of the framework.[65-77]



Scheme 1.5: Self assembled supramolecular cube.

Stang et al. prepared a family of nanoscale 3D arrays using rigid tritopic bridging ligands and rectangular corner units.[74(c)] The highly symmetrical cage compounds are described as face-directed, self-assembled truncated tetrahedra with T_d symmetry. A nanoscale adamantanoid framework was constructed using an angle-directed, coordination driven approach by combining six angular ditopic units with four angular tritopic units.[77(a)] Zaworotko, Braga, Kitagawa and several others have also carried out extensive research work utilizing some of the pyridyl containing rigid ligands with appropriate metal ion.[78] Lin et al. demonstrated the construction of one-pot self assembly of molecular polygons ranging from triangle to octagon assemblies (with 1.4-4.3 nm cavity), as shown in Figure 1.10.[79] Recently, helical architectures have received special attention because of their structural similarity with double-stranded DNA.[80] Lehn and others have reported several circular helicates by utilising bipyridine and other bidentate ligands as chelating groups.[81] All these networks/supramolecular architectures involve the utilization of pyridine containing rigid ligands (some of them are listed in Scheme 1.6).

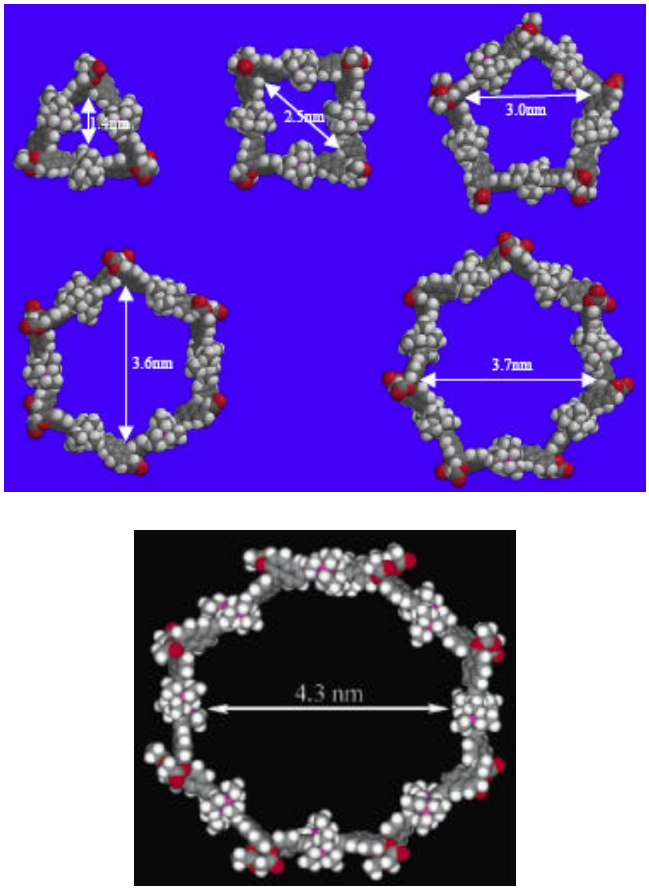
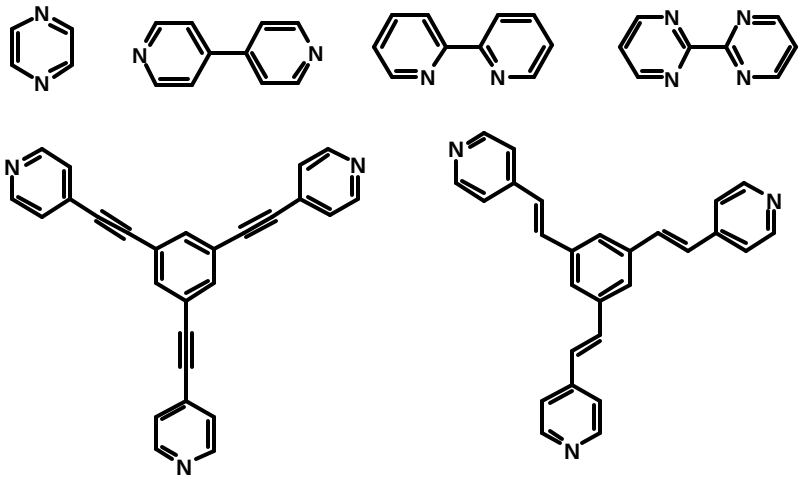


Figure 1.10: Self-assembly of molecular triangle to octagon in space filling model.



Scheme 1.6: Some of the rigid ligands used in the construction of metal-organic frameworks.

However, studies towards the design and synthesis of MOFs, employing flexible ligands, such as tripodal ligands with an arene core, are limited and are considered to be one of the most useful building blocks.[82] Thus, a great effort in this area has recently been devoted to develop novel multi dentate/multi armed molecules with an arene as core unit that can form a unique supramolecular network topology. Such molecules are of great interest to a wide community of researchers because these molecules find applications in many ways such as in discotic liquid crystals and they have recently been shown to form micelles in aqueous solutions.[83] These molecules also have been shown to act as hosts for a range of solvent molecules and used as core units for dendrimers[84] and above all, they can be utilized in the formation of unprecedented supramolecular architectures with the appropriate metal salts. Thus, preparation and utilization of some of the sulphur containing flexible ligands are discussed in chapter 4.

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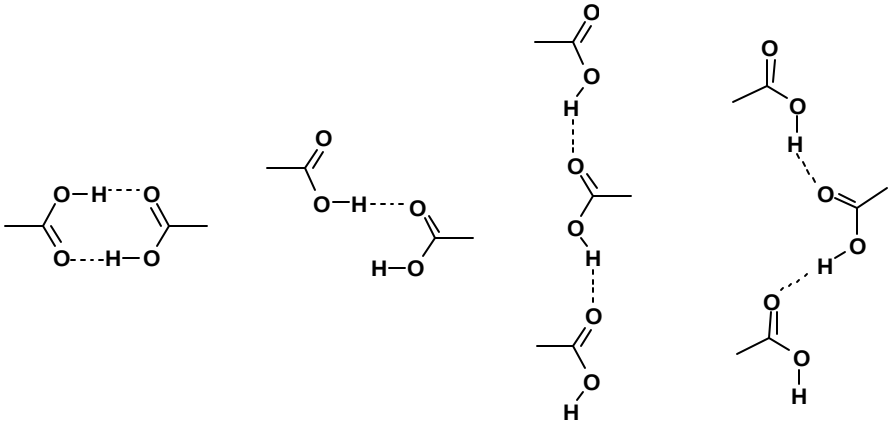
Chapter TWO

SYNTHESIS AND RATIONAL ANALYSIS OF SOME SUPRAMOLECULAR ASSEMBLIES OF 3,5-DINITROBENZAMIDE AND TRITHIOCYANURIC ACID

PART - A

2.1 INTRODUCTION

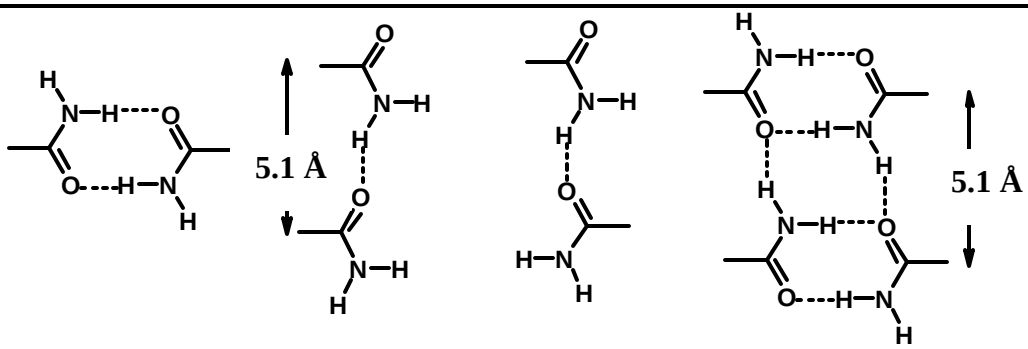
Synthesis of supramolecular assemblies, using a knowledge of intermolecular interactions, utilizing different functional groups associated with various compounds and self-complimentary groups has become a focal point for the synthesis of functional solids with tailor-made properties.[1-5] In this respect, carboxylic acid (-COOH) group, as illustrated in detail in chapter one, is one of the well studied functional group in supramolecular chemistry and noncovalent synthesis.[6,7] Carboxylic acids form different types of hydrogen bonding patterns based on the symmetry of their O-H···O hydrogen bond as shown in Scheme 2.1. They can form dimer motifs that contain a center of inversion and catemers that aggregate into acentric one-dimensional chains.



Scheme 2.1: Hydrogen bonding patterns in carboxylic acids.

Another functional group which mimics in the formation of hydrogen bonds is the amide group. It is also one of the versatile functional groups that has potential importance in the general organic synthesis and also to a greater extent in biology in the form of peptide bonds. In fact, the geometry around the peptide bond is the cause for the

variety of architectures that are adopted by the proteins. It is evident from the literature that amide group is not well explored when compared to carboxylic acid in the noncovalent synthesis of supramolecular assemblies.[8] The commonly found motifs/patterns in primary amides are shown in the Scheme 2.2.

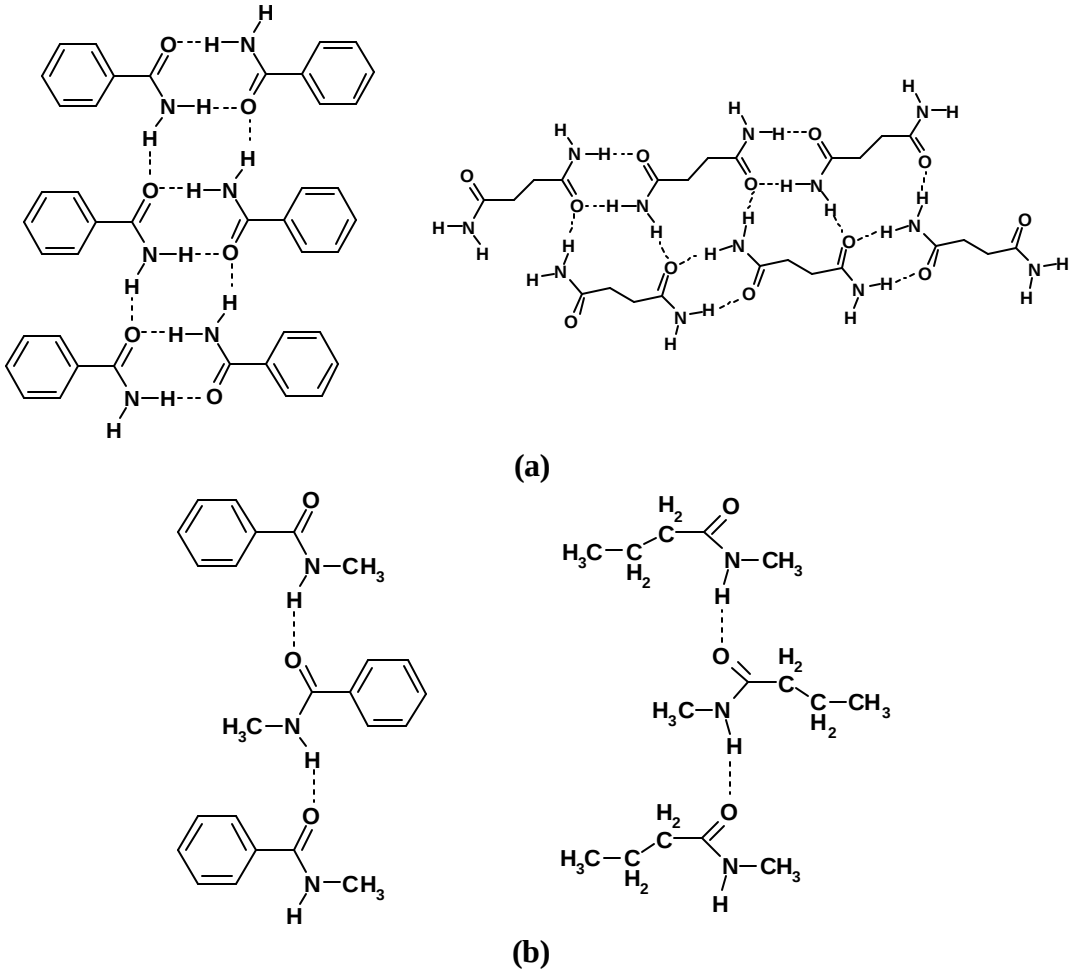


Scheme 2.2: Four different types of patterns/motifs found in primary amides.

Leiserowitz and co-workers were among the first to appreciate the importance of structural analysis and packing patterns within a series of amide related compounds which, in turn, made it possible to identify hydrogen bond preferences.[9] For example, primary amides form ribbon-like motif (see Scheme 2.3(a)), while, in secondary amides like N-methyl amide, the resulting motif is commonly an infinite chain as shown in Scheme 2.3(b).[10]

Initial efforts in this direction were initiated in our research group for the creation of supramolecular asseblies of different aliphatic amides (malonamide, succinamide, glutaramide, adipamide and pimelamide) with 4,4'-bipyridyl (bpy), to mimic molecular complexes of carboxylic acids and bpy.[11] However, it was found that the amides did not show interaction towards bpy.[12] Also attempts to synthesize a molecular complex between benzamide and bpy were unsuccessful. Nevertheless, knowing the influence of other functional groups on the hydrogen bonding patterns of

amides,[12] substituted aromatic amides have been chosen. In this respect, 3,5-dinitrobenzamide (**DNBA**) was chosen as information of its solid-state structure itself is not known in the literature as confirmed by analysis performed on Cambridge Structural Database (CSD) version 5.24.[13]



Scheme 2.3: Formation of (a) ribbon motif (b) infinite chains.

2.2 Crystal structure analysis of 3,5-dinitrobenzamide (DNBA), 1

Crystallization of **DNBA** from a methanol solution gave block-like colorless crystals suitable for X-ray diffraction studies. **DNBA** crystallizes in orthorhombic, *P*bca space group and complete crystallographic details are given in Table 2.1. An ORTEP

diagram along with atom labels is shown in Figure 2.1. Structure analysis revealed that **DNBA** molecules recognize each other through the formation of well-known eight-membered centrosymmetric cyclic N-H···O hydrogen bonds (H···O, 2.05 Å), by $R_2^2(8)$ arrangement formed between the adjacent molecules related by inversion symmetry, utilizing *syn*- hydrogen atoms (see Fig. 2.2). However, the adjacent dimers interact with each other by a single N-H···O hydrogen bond (H···O, 2.17 Å), through *anti*- hydrogen atom as shown in Fig. 2.2. Thus, each dimer is connected to four different amide dimers and, as a result, the structure is stabilized by the cyclic as well as acyclic hydrogen bonds. The hydrogen bonding arrangement observed is uncommon in amides but it has a resemblance to cyclic imides like cyanuric acid and trithiocyanuric acid molecules which also possess cyclic and acylic hydrogen bonded networks.[14]

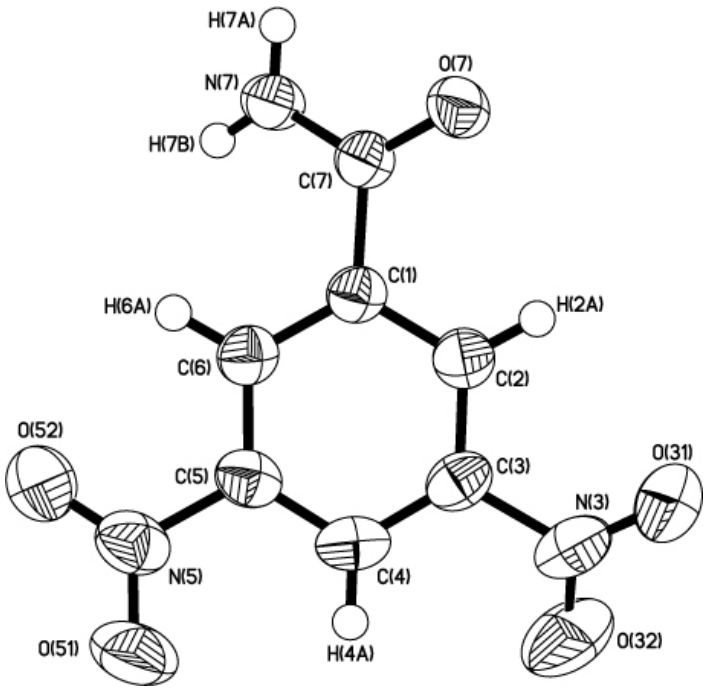


Figure 2.1: ORTEP drawing of 3,5-dinitrobenzamide.

Another unique feature is that **DNBA** molecules did not form 5.1 Å structure, in three-dimensional arrangement unlike as observed in many amides,[9,10] reminiscates with 4-chloro-1-cubanecaboxamide and corresponding bromo and iodo derivatives, perhaps due to the bulky nature of the substituents. Observing the unusual features in the native crystal structure of **DNBA** its crystallization was carried out under various conditions of temperature and from various solvents, with varying polarity, such as ethanol, propanol, butanol, *iso*-propanol, chloroform, dichloromethane, carbon tetrachloride, nitromethane, ethylacetate, benzene etc., to study the influence of the solvents in the crystal packing. In all these cases (the crystals obtained from different solvents) the unit cell parameters are identical to that of the crystals obtained from methanol. However, crystals obtained from dimethyl sulfoxide (DMSO), a high polar solvent and a good hydrogen bond acceptor, resulted in a solvated structure.

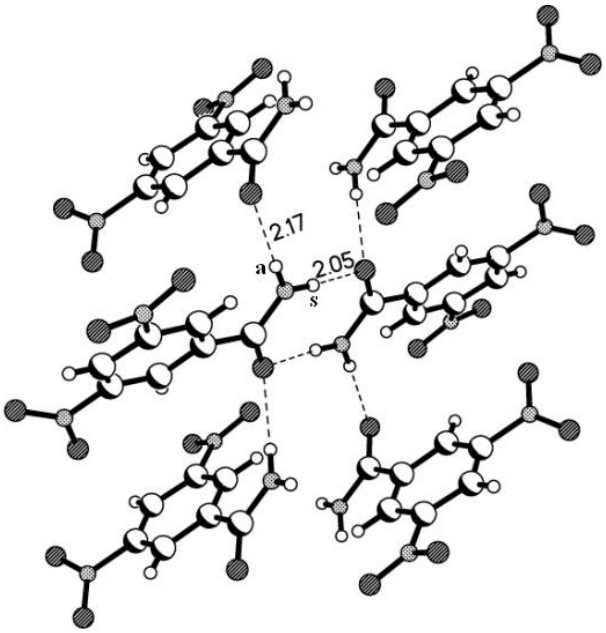


Figure 2.2: Typical arrangement of molecules of 3,5-dinitrobenzamide in its crystal structure. ‘s’ and ‘a’ refers to *syn* and *anti* hydrogen atoms respectively.

2.3 Solvated structures of 3,5-dinitrobenzamide

2.3.1 Two forms of 3,5-dinitrobenzamide with DMSO, 1a and 1b.

Crystallization of **DNBA** from DMSO gave two different types of crystals differentiated by morphology depending upon the crystallization conditions. While, crystals of plate-like geometry, **1a**, were obtained from DMSO at room temperature, needles type crystals were obtained by warming DMSO on a water bath. Crystals of **1a** and **1b** show different unit cells (Table 2.1) and the structure analysis further reveals the characteristic differences between them. ORTEP drawings of **1a** and **1b** are shown in Figure 2.3.

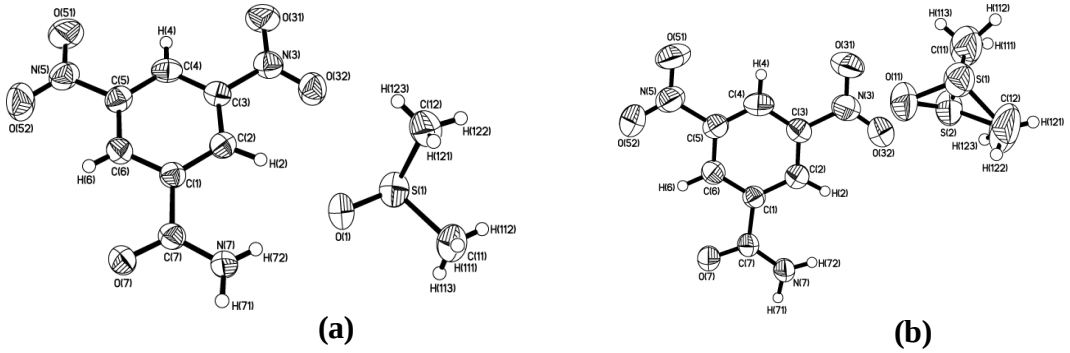
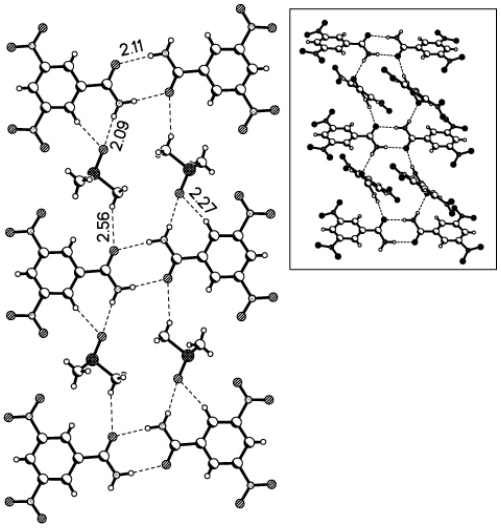


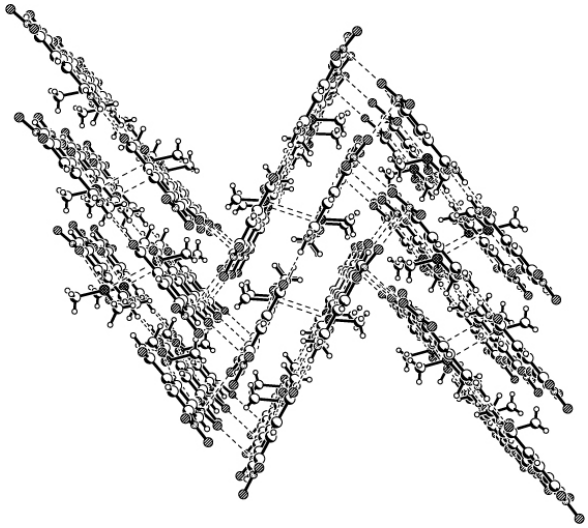
Figure 2.3: ORTEP diagrams in the crystal structures of **1a** and **1b** showing DMSO molecule (a) ordered and (b) disordered.

Packing analysis of **1a** revealed that the recognition between **DNBA** and DMSO molecules is established through *anti*-hydrogen atom of amide group and S=O group of DMSO by forming N-H···O hydrogen bond (H···O, 2.09Å; N-H···O, 164.5^{o}). The adjacent molecules of **DNBA** interact with each other forming a 8-membered cyclic network through N-H···O hydrogen bond with a H···O distance of 2.11Å. In fact, the arrangement of **DNBA** and DMSO molecules shows close resemblance with the arrangement of molecules found in the parent crystal structure of **DNBA**, which is

shown as an inset in Figure 2.4(a), with the replacement of molecules of **DNBA** related by pseudo-glide symmetry by DMSO molecules. In addition, the molecules of DMSO form C-H···O hydrogen bonds with the molecules of **DNBA**. The assembly yields a herringbone structure in three dimensions as shown in Figure 2.4(b).



(a)



(b)

Figure 2.4: (a) Recognition between **DNBA** and DMSO molecules in **1a** and compare with the **DNBA** structure shown in the inset. (b) Three-dimensional arrangement in the crystal structure of **1a**.

Packing analysis revealed that **1b** is *iso*-structural with **1a** in all the aspects of two- and three-dimensional arrangements except for the hydrogen bond distances. Molecular arrangement in the structure of **1b** is shown in Figure 2.5. It is apparent from Figures 2.4 and 2.5 that molecules in **1b** are more densely packed than in **1a** as identical hydrogen bonds are formed with shorter distances in **1b** than in **1a**. For example, the N-H···O hydrogen bond that holds **DNBA** and DMSO molecules is 1.99 Å in **1b**, whereas it is 2.09 Å in **1a**. Similarly, the N-H···O hydrogen bond in the centrosymmetric coupling is 2.00 and 2.11 Å in **1b** and **1a** respectively (Table 2.2).

Thus, the analysis of **1a** and **1b** reveals the affinity of amides to interact with hydrogen bond acceptor moieties through the utilization of *anti*- hydrogen atom. To further explore the features, crystallization of **DNBA** from pyridine has been carried out, in anticipation of N-H···N hydrogen bonds between **DNBA** and pyridine.

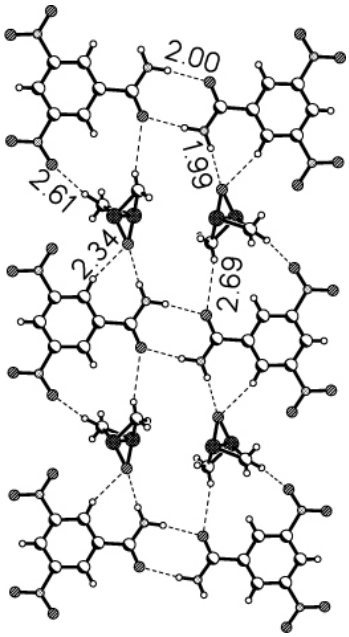
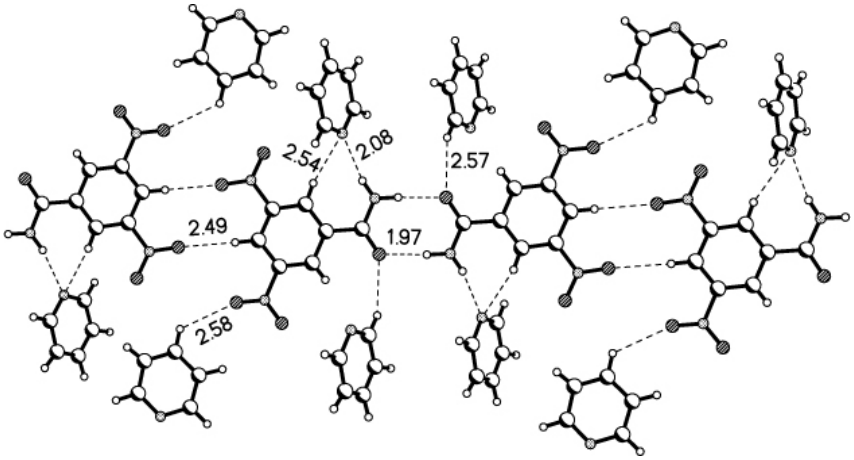


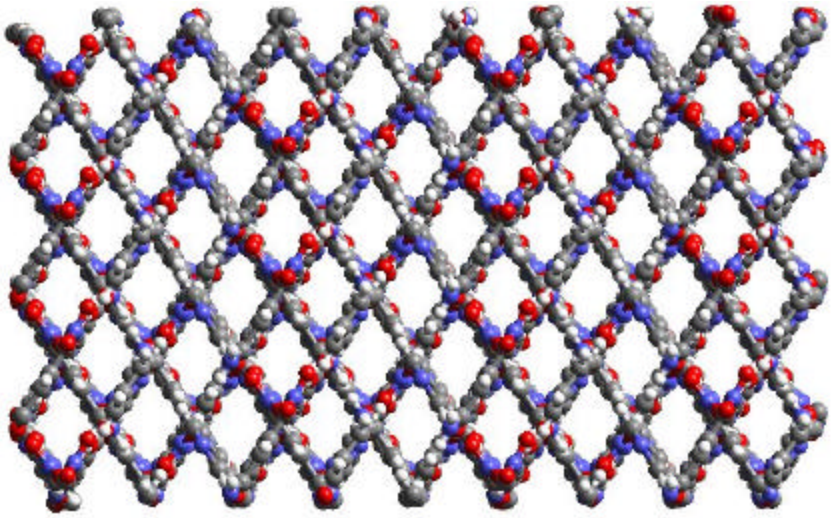
Figure 2.5: Arrangement of molecules of **DNBA** and DMSO in the structure **1b**. Compare with that of the Figure 2.4(a).

2.3.2. 3,5-dinitrobenzamide and pyridine structure, 1c.

Crystallization of **DNBA** from pyridine yielded block-like crystals, **1c**, and structure analysis revealed that it is a pyridine adduct of **1**. Both the components recognize each other through the formation of N-H···N hydrogen bond between the *anti*-hydrogen atom of amide group and the pyridyl nitrogen (see Fig. 2.6(a)) with H···N distance of 2.08 Å.



(a)



(b)

Figure 2.6: (a) Pyridine molecules lying as pendants to the tapes formed by **DNBA** are shown. (b) View of the arrangement of molecules in three-dimension.

In addition, pyridine molecules interact through C-H···O hydrogen bond formed between aromatic H atom of the amide and N atom of pyridine molecules. Amide molecules exist as an infinite molecular tape in such a manner that pyridine molecules lying as pendants to a chain of amide molecules that are connected together by cyclic centrosymmetric N-H···O as well as C-H···O hydrogen bonds with H···O distances of 1.97 and 2.49 Å respectively. This arrangement is shown in the Figure 2.6(a). Further, the adjacent tapes which are perpendicular to each other arrange in a crossed manner in three-dimension as shown in Figure 2.6(b).

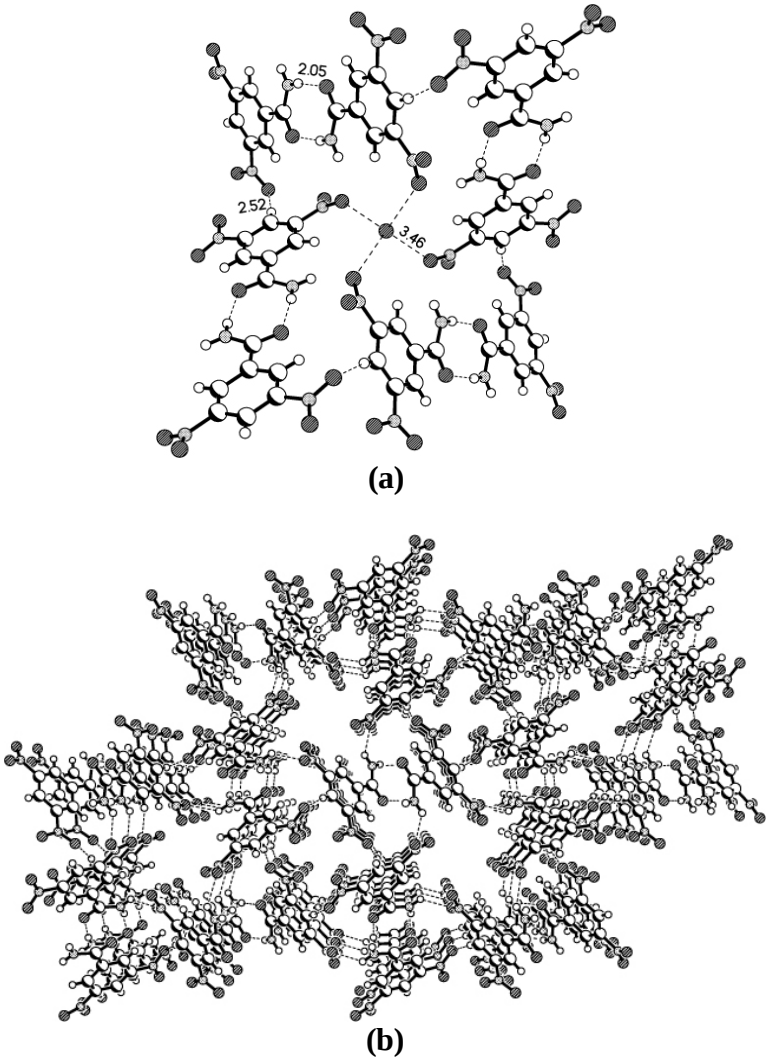
However, attempts to prepare solvates of **DNBA** with dimethyl formamide (DMF), dimethylamine (DMA) etc., which also possess hydrogen bond donor/acceptor groups, were not successful as pure crystals of **DNBA** only obtained all the time. But, when co-crystallization of **DNBA** with 4-chloro or 4-amino benzamide was carried out from a methanol solution, a hydrate structure of **DNBA** was obtained instead of corresponding molecular complexes. In fact, water was not present in the reaction medium but was absorbed from the atmosphere, which is a well-known process in many crystallization studies[16] and further more the hydrate could not be synthesized by crystallization of **DNBA** directly from water. In addition, the structure analysis reveals exotic supramolecular architecture in the form of host-guest assembly,[17] as described in the following section.

2.4 Host-Guest Complexes

2.4.1 3,5-dinitrobenzamide with water, 1d.

The molecules of **DNBA** and water crystallized in 4:1 ratio in a tetragonal space group, $P4_2/n$ and the other crystallographic parameters are given in Table 2.1. The

structure forms channels in three dimensions, in which water molecules are accommodated. Packing analysis reveals that channels are the resultant of self-assembly of each of eight molecules of **1**, rather than the usually observed six molecules in many organic supramolecular assemblies.[18] In each cavity, as shown in Figure 2.7(a), the amide molecules form centrosymmetric dimers held together by N-H···O hydrogen bonds with an H···O distance of 2.05 Å.



(a)

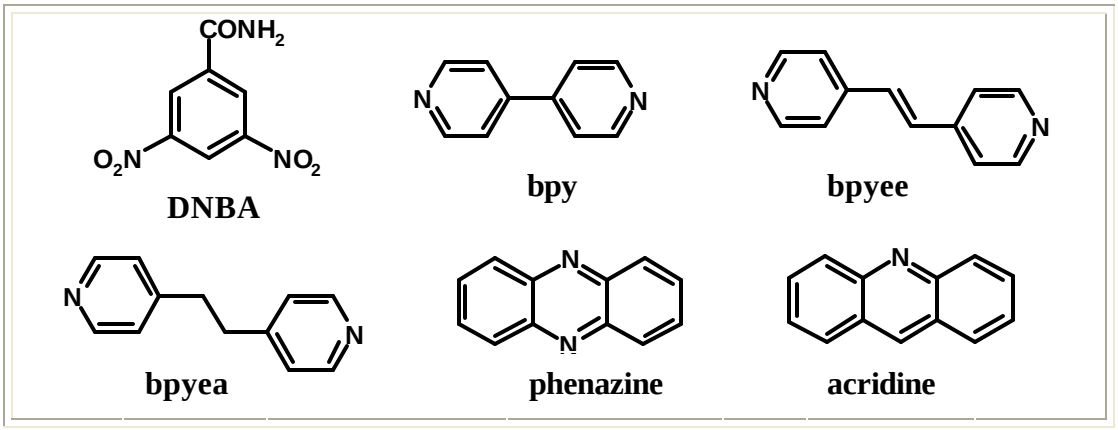
(b)

Figure 2.7: (a) Formation of a cavity involving eight molecules of **DNBA**. (b) Formation of channels in three-dimension in which host network formed by **DNBA** is shown.

Four such dimers are held together by C-H···O hydrogen bonds[19] (H···O, 2.52 Å) constituting cavities which are filled by water molecules. The adjacent octagons are held together by C-H···O hydrogen bonds (H···O, 2.52 Å) to yield two-dimensional sheet structure. These sheets, in turn, are stacked through p-p interaction forming channel structure in three-dimension (see Fig. 2.7(b)). Interestingly, the water molecules do not have any interaction with the host material **DNBA**, as the interaction between the oxygen atoms of water and $-NO_2$ groups (protruded into the channels) is 3.46 Å.

This suggests that **DNBA** may also be a potential host to accommodate large guest species provided the channel dimension is increased. Also, **1a**, **1b** and **1c** demonstrate not only the ability of **DNBA** to yield different solvated structures, but also its affinity to interact with hydrogen bonding receptor substrates. Hence, formation of novel supramolecular assemblies/networks could be envisaged between amide and molecules possessing different functionalities to form hydrogen bonds. For this purpose, synthesis of molecular complexes between **DNBA** and aza donor molecules such as 4,4'-bipyridyl (bpy), 1,2-bis(4-pyridyl)ethene (bpyee), 1,2-bis(4-pyridyl)ethane (bpyea), phenazine and acridine as listed in Chart 2.1 has been carried out.

Chart 2.1



2.4.2 3,5-dinitrobenzamide and 4,4'-bipyridine complex from methanol

Co-crystallization of **DNBA** and bpy was carried out from a methanol solution anticipating N-H···N hydrogen bond through *anti*- hydrogen atom of amide and N atom of bpy molecules, as noted in the case of **DNBA**/pyridine structure, **1c**. X-ray diffraction studies revealed that **DNBA** forms a 2:1 complex, **2a**, with bpy along with two molecules of methanol (Table 2.1). Packing analysis revealed that the three-dimensional arrangement of the molecules form channel structure, as shown in Figure 2.8, which are being occupied by bpy molecules as guest molecules; the guest molecules are not shown for the purpose of clear vision of channels (see Fig. 2.8). An analysis of channels revealed that they are formed due to the stacking of helical chains. A fascinating feature is that the chains running in an *anti*-parallel manner constitute a double helix. A typical double helix, viewed perpendicular to the direction of the channels, is shown in Figure 2.9. Thus, **DNBA** and methanol molecules together form a host lattice, through the formation of centrosymmetric cyclic N-H···O (H···O, 2.03 Å) and C-H···O (H···O, 2.68 Å) hydrogen bonds between amide molecules, while, methanol molecules interacting with **DNBA** forming N-H···O (H···O, 2.16 Å) and C-H···O (H···O, 2.88 Å) hydrogen bonds. In addition, methanol molecules are also connected to bpy molecules through O-H···N (H···N, 1.85 Å) hydrogen bonds (see Table 2.2). In further exploration, to prepare such channel structures, co-crystallization of **DNBA** and bpy was carried out from different solvents such as ethanol, propanol, *iso*-propanol, butanol, chloroform, DCM, water, etc. While the quality of single crystals was so poor from many other solvents, the crystals from water gave a different unit cell than **2a**.

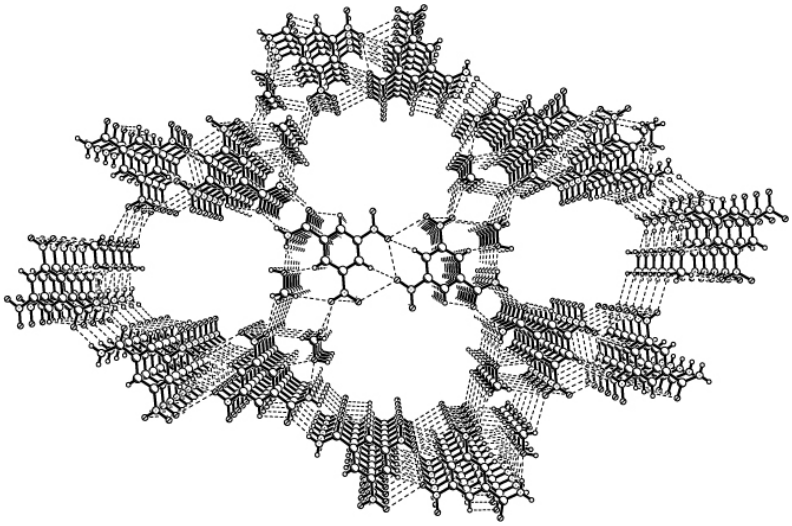
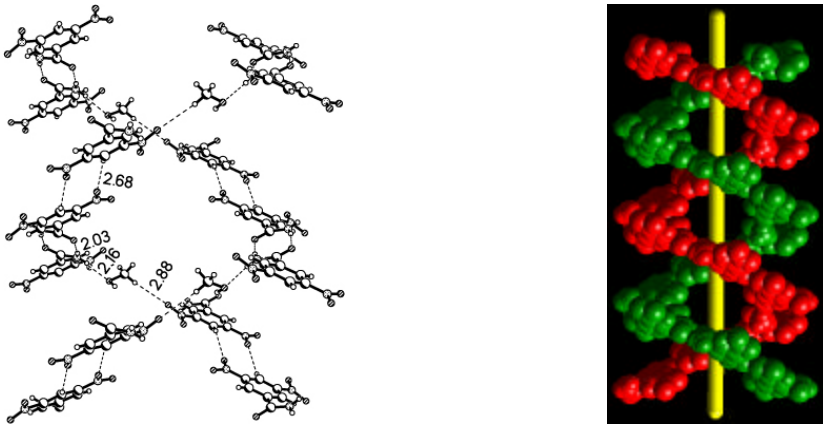


Figure 2.8: Formation of channel structure in three-dimension, in the crystal structure of **2a**.



(a) **(b)**

Figure 2.9: (a) Arrangement of **DNBA** and methanol molecules forming a double helix structure in the complex **2a**. (b) A typical double helix in space-filling model.

2.4.3 3,5-dinitrobenzamide and 4,4'-bipyridine complex from water, 2b.

X-ray diffraction studies on the single crystals, **2b**, obtained from water revealed that **DNBA** forms a 2:1 complex with bpy along with two molecules of water. The complex **2b** forms channel structure in three dimensions (Fig. 2.10) through the

stacking of planar sheets, as shown in Figure 2.11(b), in contrast to the helical chains formed in **2a**. The arrangement of molecules in a typical sheet is shown in Figure 2.11(a).

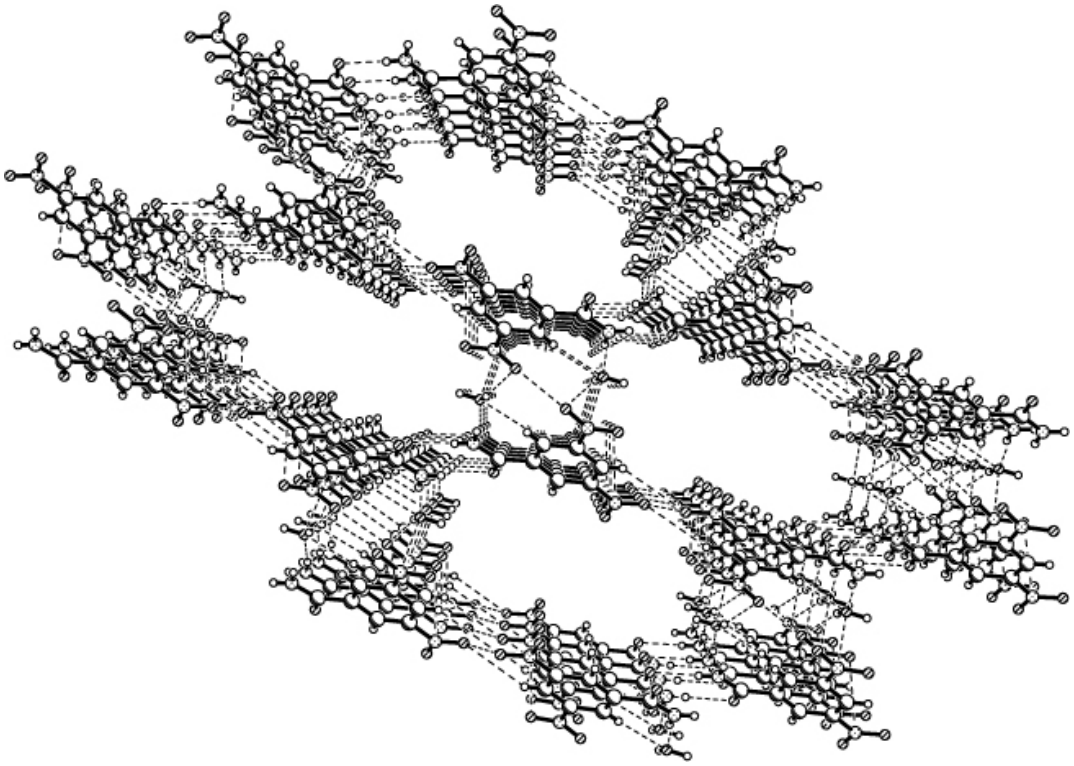


Figure 2.10: DNBA along with water molecules forming host network is shown.

In each layer, **DNBA** and water molecules together constituted a host network and interact through the formation of centrosymmetric cyclic N-H···O (H···O, 2.10 Å) and C-H···O (H···O, 2.94 Å) hydrogen bonds formed between the amide and $-NO_2$ groups respectively. The H_2O molecules are attached to **DNBA** molecules through N-H···O (H···O, 2.02 Å) hydrogen bonds involving the *anti*-hydrogen atom of amide functional group. In addition, there is also a $NO_2\cdots O_2N$ close contact with O···O distance of 3.19 Å. Such an arrangement forms an elliptical cavity of 7×11 $Å^2$ in

dimension, which is occupied by bpy molecules. The guest molecules (bpy) interact with **DNBA** through H_2O molecules forming O-H···N (H···N, 1.99 Å) hydrogen bonds. Interaction between host and the guest molecules is further strengthened by the formation of C-H···O hydrogen bonds, with the H···O distances in the range 2.34–2.66 Å (Table 2.2), involving all the hydrogen atoms of the bpy molecule. Thus, **DNBA** has formed two different solvated supramolecular assemblies with bpy. To extend the observation for generalization, co-crystallization of **DNBA** with some other aza-donor compounds like 1,2-bis(4-pyridyl)ethene (bpyee) and 1,2-bis(4-pyridyl)ethane (bpyea) were performed.

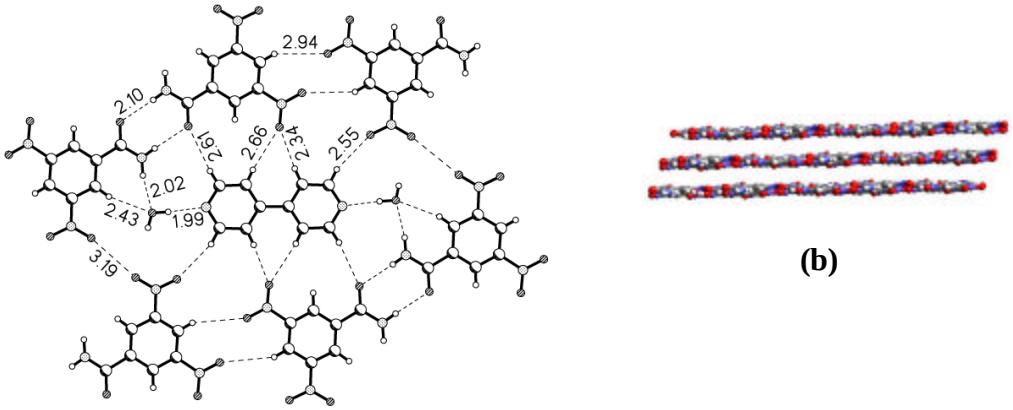


Figure 2.11: (a) Recognition pattern between constituent molecules in the complex **2b**. Notice that the bpy molecule is planar.

2.4.4 3,5-dinitrobenzamide with 1,2-bis(4-pyridyl)ethene (bpyee), 3a, and 1,2-bis(4-pyridyl)ethane (bpyea), 3b, from methanol.

Co-crystallization of **DNBA** and bpyee from a methanol solution also gave single crystals in a 2:1 composition along with solvent molecules in the asymmetric

unit. The packing analysis revealed that the channel structure is formed in three-dimension (Fig. 2.12), as observed in **2a** and **2b**, which is formed due to the stacking of two-dimensional planar sheets (Fig. 2.13(b)). The arrangement of the molecules in a typical sheet is shown in Figure 2.13(a).

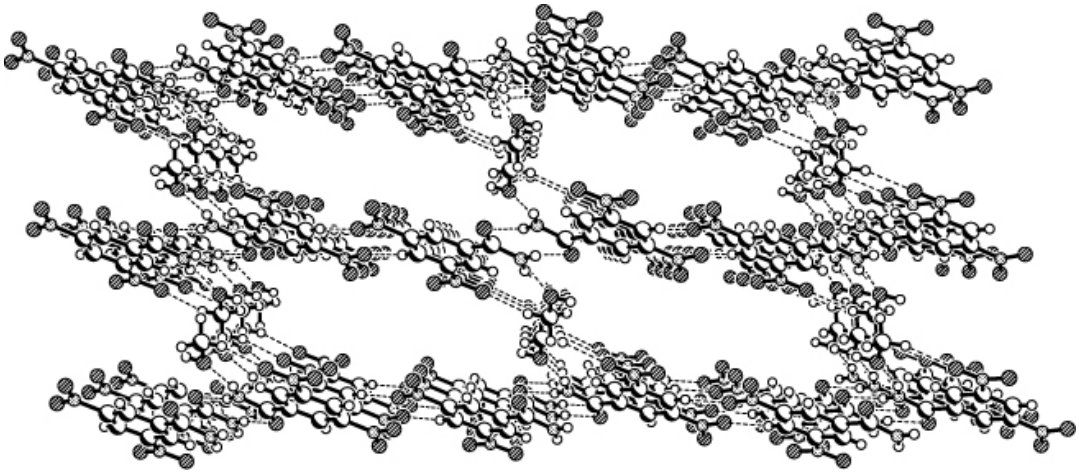


Figure 2.12: Formation of channels in three dimensions due to the stacking of two-dimensional sheets. Guest molecules have been omitted for clarity.

The molecules of **DNBA** form centrosymmetric cyclic N-H···O hydrogen bonded dimer (H···O, 2.11 Å), which further interacts with the adjacent dimers by forming centrosymmetric cyclic C-H···O hydrogen bonds (H···O, 2.56 Å). This assembly further interacts with methanol molecules through the *anti*- hydrogen atom of amide group and oxygen atom of the methanol to form host network and is further stabilized by C-H···O hydrogen bonds between methanol and $–NO_2$ groups, thus, leading to the formation of a cavity, which is filled by the molecules of bpyee acting as guest molecules. The bpyee interact with the host network through the formation of O-H···N and C-H···O hydrogen bonds (see Table 2.2) with methanol molecules and $–NO_2$ groups of amide respectively (Figure 2.13(a)).

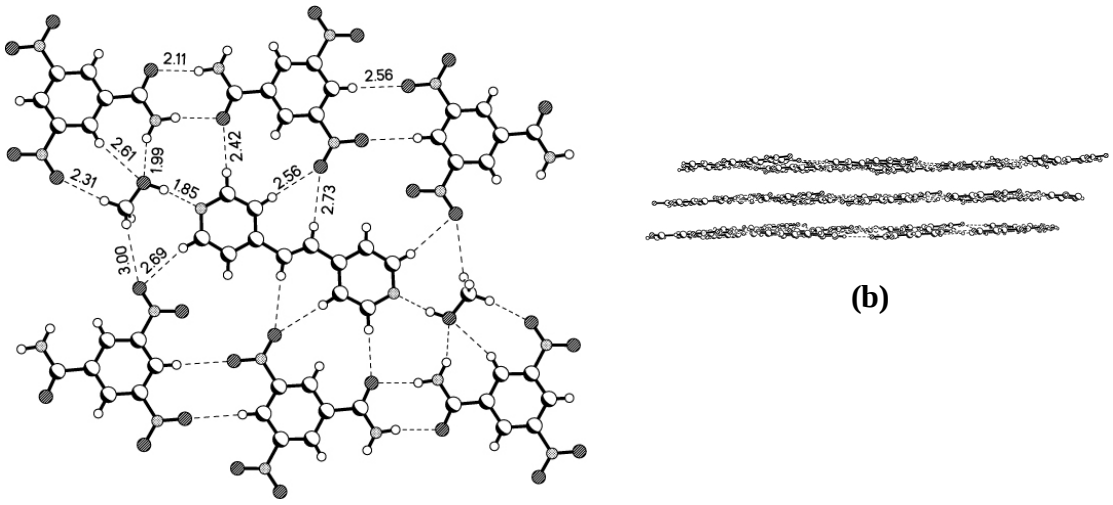


Figure 2.13: (a) Recognition between host and the guest molecules, and (b) Formation of layers in two-dimension.

Similarly, co-crystallization of **DNBA** and bpyea from a methanol solution gave a molecular complex, **3b**, in a 1:1 ratio along with solvent molecules. Packing analysis revealed that **DNBA** and methanol molecules form host network and bpyea acting as guest molecules. A close observation reveals that the complexes **3a** and **3b** are *iso*-structural in all the aspects except for the variations in the distances of the hydrogen bonds. The recognition between host and the guest molecules along with hydrogen bond distances is shown in Figure 2.14 (see also Table 2.2). Change of solvent of crystallization from methanol to water gave assemblies with sheet structures rather than host-guest type complexes with bpyee and bpyea.

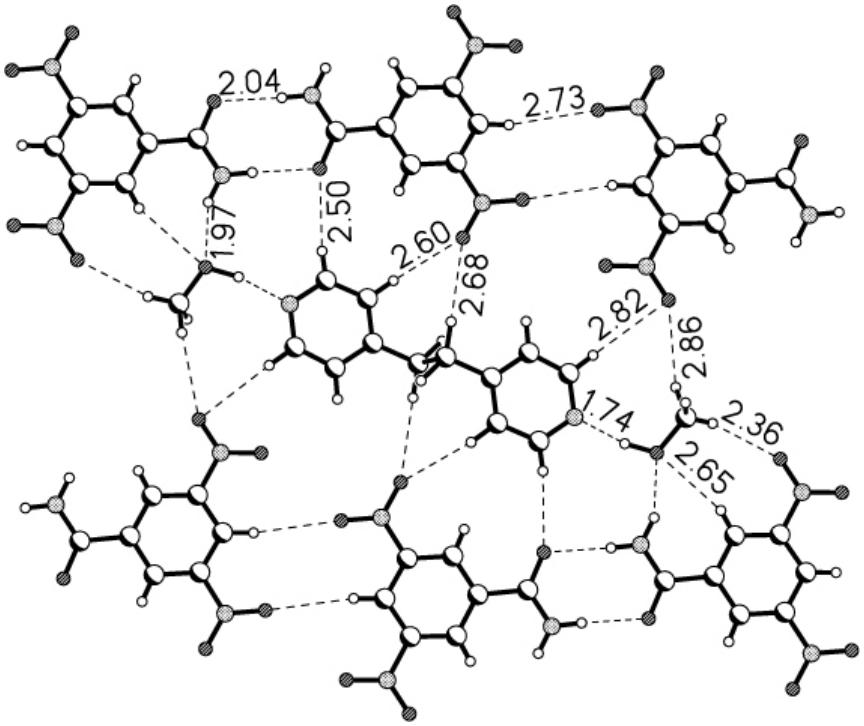


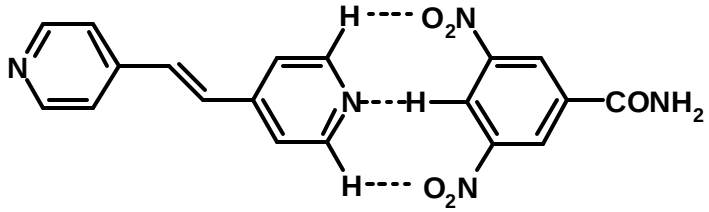
Figure 2.14: Recognition among molecules of **DNBA**, bpyea and solvent molecules in the complex **3b**.

2.5 Sheet Structures

2.5.1 3,5-dinitrobenzamide with 1,2-bis(4-pyridyl)ethene (bpyee), 4a, and 1,2-bis(4-pyridyl)ethane (bpyea), 4b, from water.

X-ray structure analysis revealed that the single crystals, **4a** and **4b**, obtained from water upon co-crystallization of **DNBA** with bpyee and bpyea respectively formed a 1:1 complex, along with water molecules. In the complex **4a**, two symmetry independent molecules each of **DNBA** and bpyea are present. The molecules of **DNBA** are labeled as A and B whereas molecules of bpyee as C and D. The interaction between the molecules and recognition pattern between the constituents are shown in Figure 2.15(a). It is apparent from the packing analysis that both the molecules of

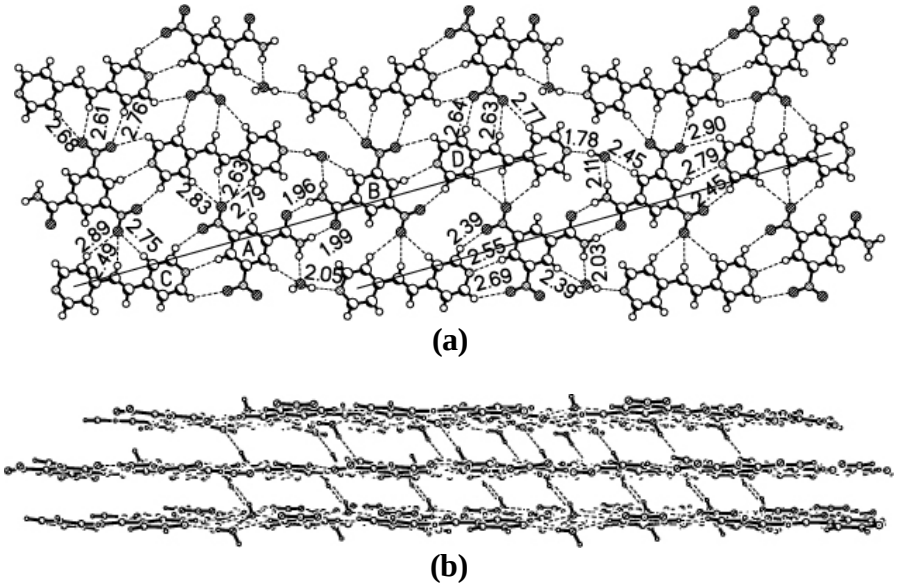
DNBA (A and B) interact with each other through the non-centrosymmetric cyclic N-H···O hydrogen bond. The hydrogen bond distances are 1.96 and 1.99 Å. The recognition between **DNBA** and bpyee occurs through pyridyl nitrogen, $-NO_2$ groups and phenyl hydrogens, forming a unique recognition pattern with three hydrogen bonds, as shown in Scheme 2.4, consisting of two C-H···O and one C-H···N hydrogen bonds. The other related motifs, known in the literature, consist either of strong hydrogen bonds (for example, cyanuric acid and melamine complex)[20] or a combination of weak and strong hydrogen bonds (for example, a molecular complex of N-methylcyanuric acid and 9-ethyladenine).[21] However, in the complex, **4a**, all the hydrogen bonds in the recognition pattern are weak hydrogen bonds (Table 2.2). Another interesting feature is that only one of the pyridyl nitrogens of bpyee is involved in this unique pattern, while the other nitrogen is attached to a water molecule through O-H···N hydrogen bond with a H···N distance of 1.78 Å as shown in Figure 2.15(a).



Scheme 2.4: Formation of a triplet supramolecular recognition motif.

Thus, in the two-dimensional arrangement, a supermolecule, comprising of four molecules (two from each **DNBA** and bpyee), is established, which are shown by straight lines in Figure 2.15(a). Such adjacent supermolecules interact with each other through water molecules by forming N-H···O hydrogen bonds (H···O, 2.03 and 2.11 Å). In addition, the interaction between the supermolecules is further strengthened by C-

H···O hydrogen bonds (H···O range 2.49–2.89 Å), formed between the $–NO_2$ groups and hydrogen atoms of ethene and aromatic ring. These two-dimensional sheets stack to yield three-dimensional structure stabilized by O-H···N hydrogen bonds (H···N, 2.10 Å) formed by water molecules as well as p-p interaction as shown in Figure 2.15(b).



(a)

(b)

Figure 2.15: (a) Recognition between constituent molecules and the formation of supermolecule (shown in straight line). (b) Stacking of the two-dimensional sheets.

In the crystals of **4b**, however, there is only one molecule each in the asymmetric unit. Structure analysis reveals that the recognition pattern between the molecules in **4b** is identical to that of **4a** in all most all the aspects of hydrogen bonding features. The arrangement of molecules and straight lines joining the individual molecules representing each supermolecule is shown in Figure 2.16(a). Complexes **4a** and **4b,** however, differ with respect to the interaction between the supermolecules. In the complex **4b** the adjacent supermolecules are connected together by centrosymmetric cyclic C-H···N hydrogen bonds, with an H···N distance of 2.94 Å. As a consequence of

this, the supermolecules constitute infinite molecular tapes, which are held together by C-H···O hydrogen bonds formed between $-NO_2$ groups and aromatic hydrogen atoms. These two-dimensional sheets further stack in three-dimensions stabilized by O-H···N hydrogen bonds (H···N, 2.08 Å, Table 2.2) and p-p interactions, as in **4a**, and the arrangement of molecules is shown in Figure 2.16(b).

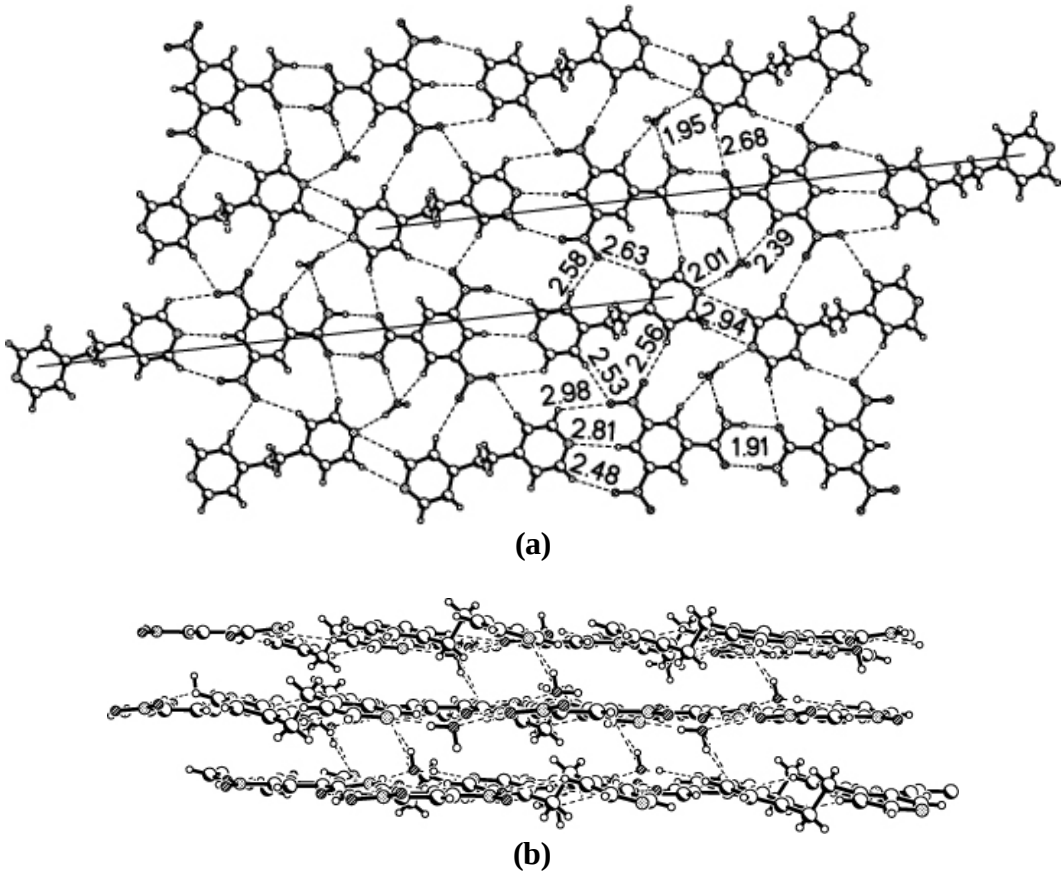


Figure 2.16: (a) Arrangement of molecules in the complex **4b**. (b) Stacking of two-dimensional sheets.

2.6 Comparison of complexes 2a, 2b, 3a, 3b, 4a and 4b.

Complexes **2a**, **2b**, **3a** and **3b** form channel structures in three dimension, whilst, the complexes **4a** and **4b** form sheet structures. However, the way in which the channels

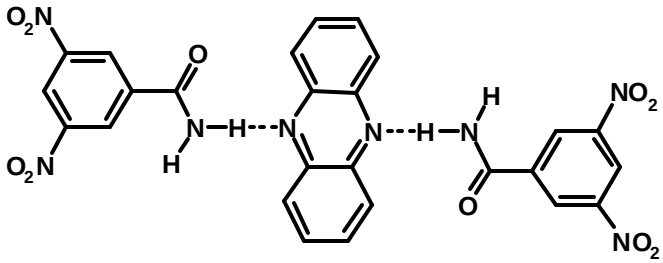
are formed is different in **2a** from that of **2b**, **3a** and **3b**. In the case of complex **2a**, channels are formed due to the stacking of helical chains where as in other complexes (**2b**, **3a** and **3b**) the channels are formed due to the stacking of planar sheet structures. An interesting feature about the bpy molecules, particularly, in the complexes **2a** and **2b**, is that the two aromatic rings are twisted with a dihedral angle of about 35^{o} unlike those found in water complex in which the two aromatic rings are almost planar. The conformational variations in bpy molecules is well known in the literature,[22] but, the differences in the conformations of bpy molecules observed in the complexes **2a** and **2b**, commensurate with the host arrangement, perhaps a coincidence, nevertheless, is unique. Further, it is apparent from the description of the structural features of **3a**, **3b**, **4a** and **4b** that the structures possessing the same solvent of crystallization, namely **3a** and **3b**; **4a** and **4b**, are *iso*-structural rather than structures with the same aza molecules i.e., **3a** and **4a**; **3b** and **4b**. This feature, in fact, supports the involvement of solvent molecules within the host framework for the creation of a fixed void space to accommodate appropriate guest molecules. Hence, methanol, which is bigger in dimension than water, creates the required space to accommodate bpyee and bpyea in **3a** and **3b**, respectively. Another, noteworthy feature is the formation of different types of interactions by the pyridyl nitrogens of bpyee and bpyea, despite being the same, chemically. For example, in **3a** and **3b**, both the pyridyl nitrogen atoms of bpyee and bpyea form same type of O-H···N hydrogen bonds (Figs. 2.13 and 2.14) with CH_3OH molecules, where as in **4a** and **4b**, each pyridyl nitrogen atom have different interactions (Figs. 2.15(a) and 2.16(a)), with one of them forming O-H···N hydrogen bond with water molecule and the other one forming a triplet recognition pattern

(Scheme 2.4) with the molecules of **DNBA**. Furthermore, in none of these structures, direct interaction between the amide group and aza group is observed, and moreover the centrosymmetric N-H···O hydrogen bonded motif of amide moiety is always retained. So, in order to test the robustness of the amide dimer, reaction of **DNBA** with some other aza compounds such as phenazine and acridine has been carried out. Analysis of the resultant structures revealed that the solvent molecules are not incorporated in the crystal structure in contrast to the complexes discussed above.

2.7 Molecular complexes of DNBA without solvent molecules.

2.7.1 3,5-dinitrobenzamide and phenazine complex, 5a.

Taking into account the presence of both donors and acceptors in **DNBA** and phenazine one would anticipate a 2:1 molecular complex, as shown in Scheme 2.5. In contrast, upon co-crystallization from a methanol solution, a 1:1 molecular complex, **5a**, was obtained which crystallized into a monoclinic, non-centrosymmetric space group, $P2_1$ (see Table 2.1). Unlike **1a** – **4b** discussed above, no solvent of crystallization was observed in the crystal structure. However, our efforts to get a 2:1 complex, by varying concentration of reactants and crystallizing from various solvents and/or mixture of solvents at different conditions of temperature and pressure, were not successful.



Scheme 2.5: Anticipated molecular complex (recognition) between **DNBA** and phenazine.

The arrangement of molecules in the complex is shown in Figure 2.17. The molecules recognize each other through the formation of N-H···N hydrogen bond with H···N distance of 2.33 Å (see Table 2.2). However, adjacent ensembles of **DNBA** and phenazine are joined together through the formation of catemeric N-H···O hydrogen bonds between the molecules of **DNBA**. This arrangement lead to the formation of an unusual unsymmetrical cyclic recognition pattern of C-H···O hydrogen bonds (H···O, 2.63, 2.72 Å) between the aromatic hydrogen atoms of phenazine and $-NO_2$ group of **DNBA** as shown in Figure 2.17. As a consequence of the recognition between amide group and phenazine through N-H···N hydrogen bond, **5a** is the first example so far discussed in this study wherein the regular cyclic N-H···O hydrogen bonded amide dimer is broken to have interaction with the co-crystallizing substrate. A noteworthy feature of complex **5a** is that only one of the two nitrogen atoms of phenazine is involved in the formation of hydrogen bonds. Thus, packing arrangement in **5a** suggests that acridine, which possess only one nitrogen atom also may form *iso*-structural supramolecular assembly with **DNBA**. Hence, co-crystallization of acridine with **DNBA** has been carried out from a methanol solution.

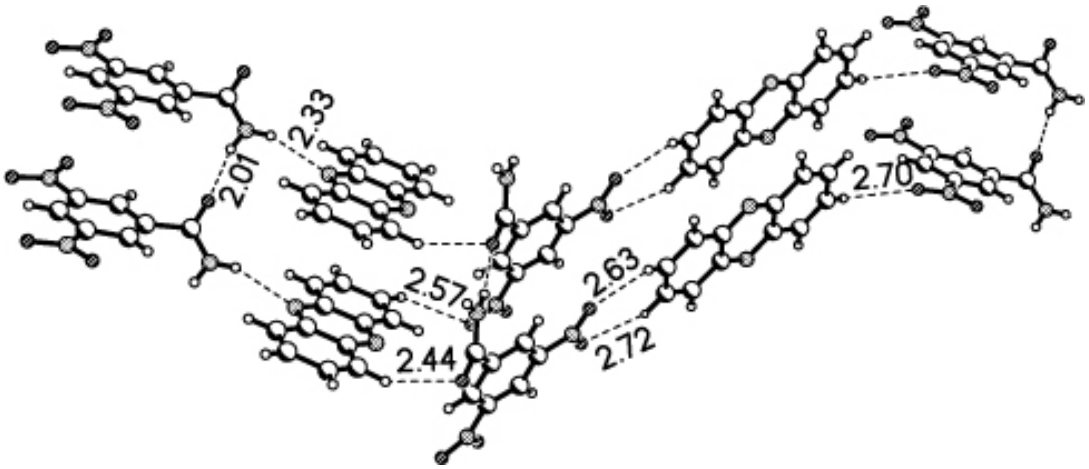


Figure 2.17: Arrangement of molecules in the complex **5a**.

2.7.2 3,5-dinitrobenzamide and acridine complex, 6a.

X-ray crystal structure determination of the complex revealed that **DNBA** and acridine co-crystallized in a 1:1 molar ratio (see Table 2.1), with three molecules each in the asymmetric unit. The interaction between the symmetry independent molecules **DNBA** and acridine is established through the formation of N-H···N hydrogen bonds with H···N distances ranging from 2.07-2.25 Å (Table 2.2). The packing arrangement of these molecules is shown in Figure 2.18. As observed in the complex **5a**, symmetry independent **DNBA** molecules are held together by forming infinite catemeric N-H···O hydrogen bonds (H···O, 2.06, 2.07 and 2.08 Å, Table 2.2), constituting a zigzag chain, with the acridine molecules connected to this chain as pendant groups, through N-H···N hydrogen bonds.

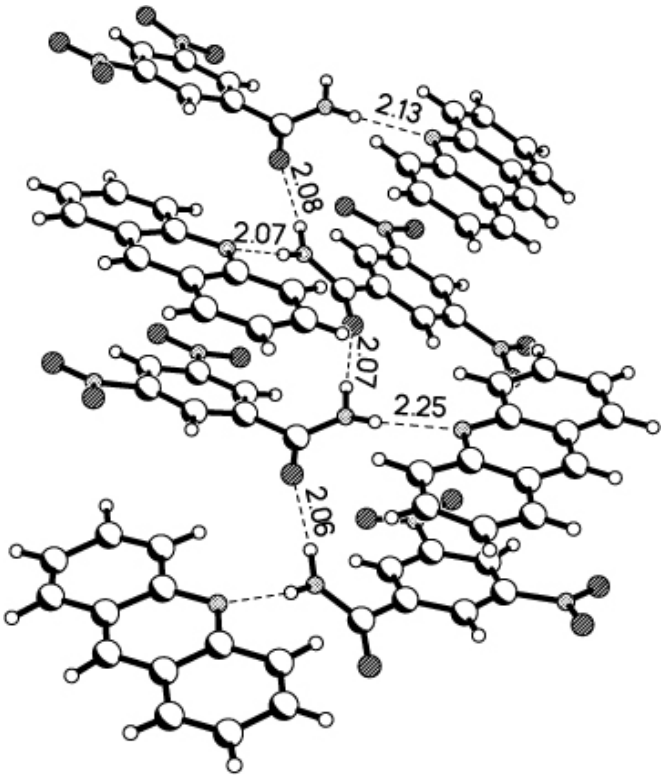


Figure 2.18: Arrangement of three symmetry independent molecules of **DNBA** and acridine molecules. Notice the acridine molecules lying as pendants.

Such adjacent chains are held together by C-H···O hydrogen bonds through hydrogen atoms of acridine and $-NO_2$ groups of **DNBA**. Further, to expand the horizon of supramolecular assemblies of **DNBA** by utilizing the ability of anti- hydrogen atom, co-crystallization of **DNBA** with 3,5-dinitrobenzonitrile, 3,5-dinitrobenzoic acid, 4-chloro-3,5-dinitrobenzoic acid and 9-anthracenecarboxylic acid were carried out. Each structure showed distinct features that are of intriguing in the supramolecular synthesis of molecular complexes.

2.7.3 3,5-dinitrobenzamide and 3,5-dinitrobenzonitrile complex, 7a.

Co-crystallization of **DNBA** and 3,5-dinitrobenzonitrile from a methanol solution resulted in a 2:1 complex (Table 2.3). The three-dimensional arrangement of the molecules in the complex is unique and fascinating. The packing analysis reveals that **DNBA** and DNBN molecules are arranged in alternate columns in such a fashion that clusters of **DNBA** molecules are placed next to the chains of 3,5-dinitrobenzonitrile molecules and *vice versa*, as shown in Figure 2.19. The molecules of 3,5-dinitrobenzonitrile, in each chain, are held together by C-H···N hydrogen bonds with a H···N distance of 2.79 Å, whilst, the **DNBA** molecules exist as dimers through the formation of N-H···O hydrogen bond with a H···O distance of 2.08 Å. These dimers, in turn, are held together by single hydrogen bonds through *anti*- hydrogen atom (H···O, 2.07 and 2.16 Å, Table 1.2). This kind of molecular packing has a close resemblance with the arrangement found in the native crystal structures of **DNBA** and 3,5-dinitrobenzonitrile which is shown as an inset in the Figure 2.19.

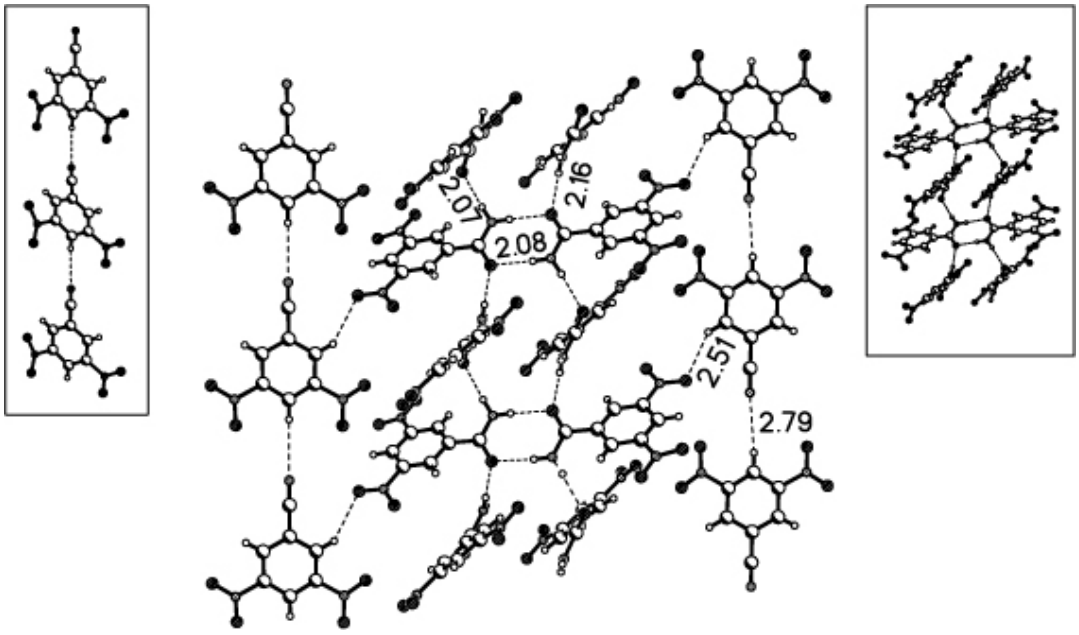


Figure 2.19: Arrangement of constituent molecules in the crystal structure of the additive assembly of the complex **7a**. The insets correspond to the arrangement of 3,5-dinitrobenzonitrile (left) and **DNBA** (right) molecules in their parent crystal structures.

2.7.4 3,5-dinitrobenzamide and 4-chloro-3,5-dinitrobenzoic acid complex, 8a

Co-crystallization of **DNBA** with 4-chloro-3,5-dinitrobenzoic acid gave a 1:1 molecular complex, **8a**, and crystallizes in a triclinic, *P*?, space group and the corresponding crystallographic details are given in Table 2.1. Complex forms a zigzag sheet structure which is, in turn, stacked in three-dimensions as shown in Figure 2.20(a). A typical sheet structure in two-dimensions is shown in Figure 2.20(b). Molecules of **DNBA** and 4-chloro-3,5-dinitrobenzoic acid did recognize each other through the formation of a catemeric O-H···O hydrogen bond, in contrast to the anticipated cyclic $R_2^2(8)$ pattern noted in many other amide-acid molecular complexes.[23]

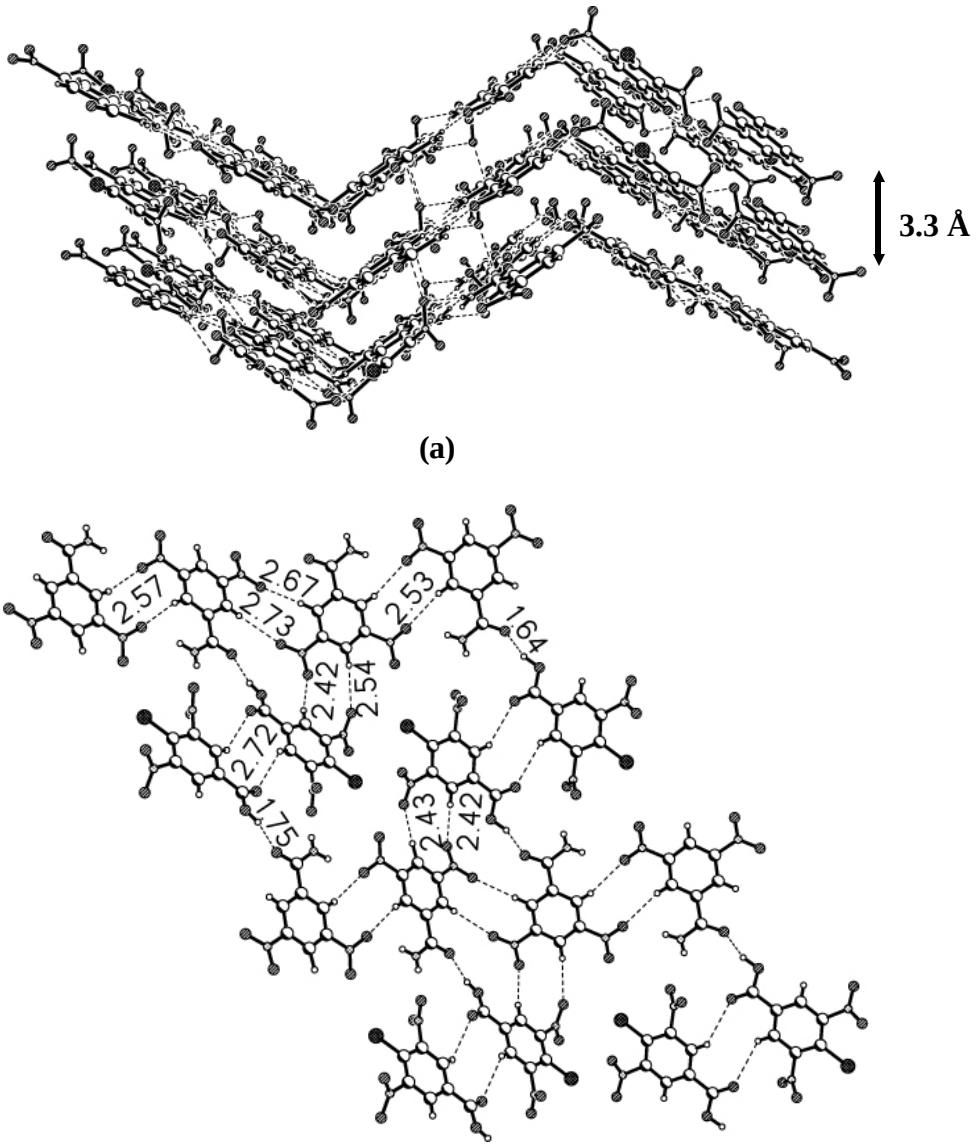


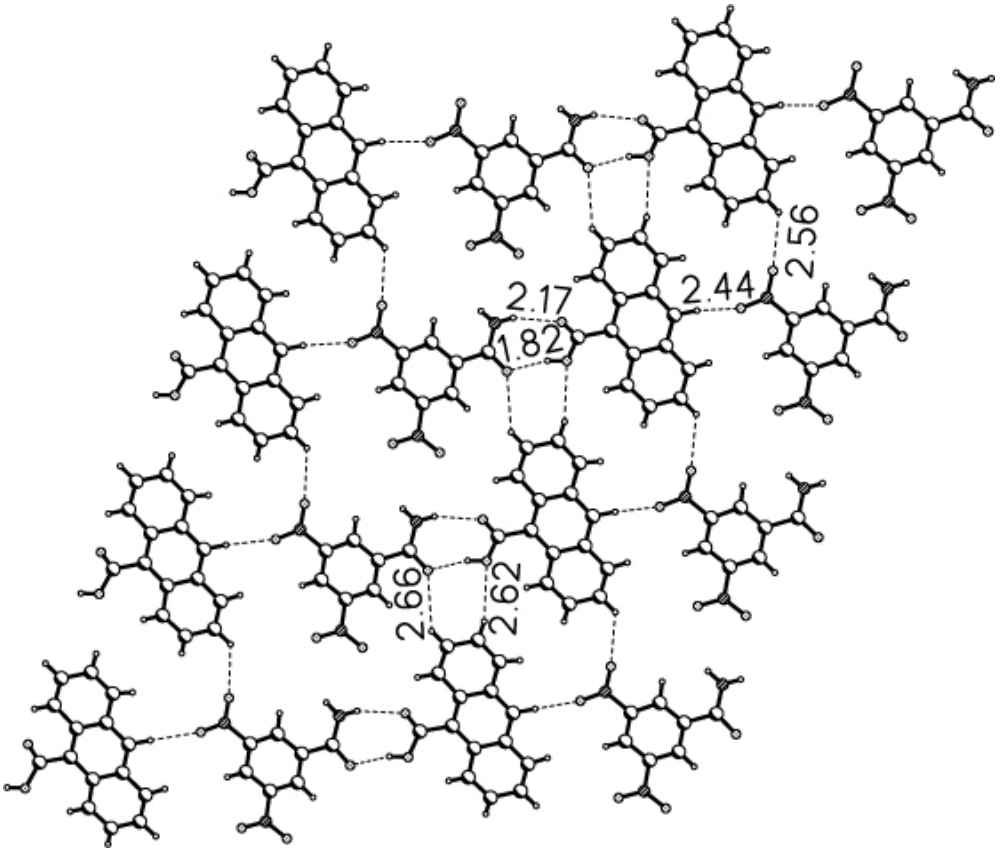
Figure 2.20: (a) Three-dimensional packing of molecules in the molecular complex, **8a**. Notice the stacking of the zigzag sheets. (b) Arrangement of amide and acid molecules in a two-dimensional sheet, in the complex **8a**.

The molecules within a sheet arrange in such a manner that **DNBA** and 4-chloro-3,5-dinitrobenzoic acid are arranged alternately such that the dimers of 4-chloro-3,5-dinitrobenzoic acid are inserted between the tapes of **DNBA**. The molecules of **DNBA** in each layer are held together by both centrosymmetric and non-centrosymmetric

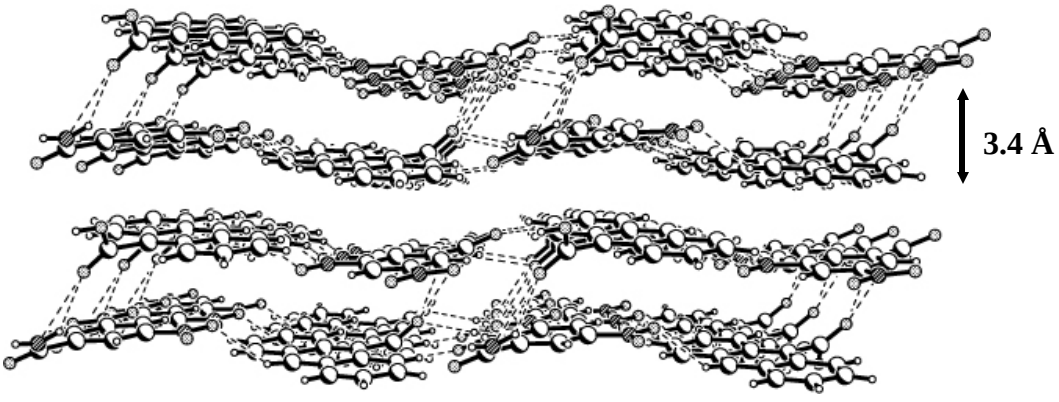
cyclic C-H···O hydrogen bonds. The centrosymmetric bonds are formed between symmetry dependent molecules, whereas the non-centrosymmetric bonds are formed between symmetry independent molecules with H···O distances ranging from 2.53 - 2.73 Å. In addition, each dimer of 4-chloro-3,5-dinitrobenzoic acid interacts with the tapes of **DNBA** through the formation of asymmetric cyclic C-H···O hydrogen bonds with H···O distances in the range 2.42 - 2.54 Å (see Table 2.2).

2.7.5 3,5-dinitrobenzamide and 9-anthracenecarboxylic acid complex, 9a

A 1:1 molecular complex is obtained between **DNBA** and 9-anthracenecarboxylic acid as determined from single crystal X-ray diffraction methods and full crystallographic information is given in Table 2.1. Recognition pattern and arrangement of molecules in a two-dimensional sheet is shown in Fig. 2.21(a). The two reactants interact with each other through hydrogen-bonded dimer formed between acid and amide moieties. Thus, a cyclic, eight membered hydrogen-bonding motif, consisting of strong O-H···O and N-H···O hydrogen bonds, with H···O distances of 1.82 and 2.17 Å, respectively, is formed between **DNBA** and 9-anthracenecarboxylic acid. Further, such adjacent dimers are connected together by a C-H···O hydrogen bond (H···O, 2.44 Å) and yield an infinite molecular tape, in one-dimensional arrangement. It is evident from Figure 2.21(a) that these molecular tapes constitute two-dimensional sheets through C-H···O hydrogen bonds (see Table 2.2). These two-dimensional sheets stack in three-dimensional arrangement with the aid of N-H···O hydrogen bonds (H···O, 2.17 Å) as well as p-p interaction with a distance of 3.4 Å as shown in Figure 2.21(b).



(a)



(b)

Figure 2.21: (a) Interaction between the molecules of amide (**DNBA**) and acid (9-anthracenecarboxylic acid) in two-dimensional sheet structure of complex **9a**. (b) Stacking of sheets in three-dimensional packing.

Table 2.1 Crystallographic information of 3,5-dinitrobenzamide (**DNBA**), its solvated structures (**1a-1d**) and molecular complexes (**2a-9a**).

	1	**1a**	**1b**	**1c**	**1d**
Formula	$C_7H_5N_3O_5$	$(C_7H_5N_3O_5)$: $(C_2H_6O_1S_1)$	$(C_7H_5N_3O_5)$: $(C_2H_6O_1S_1)$	$(C_7H_5N_3O_5)$: $(C_5H_5N_1)$	$4(C_7H_5N_3O_5)$: (H_2O)
Fw	211.14	289.27	289.27	290.24	860.56
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	tetragonal
Space group	*P*bca	$P2_1/c$	$P2_1/c$	$C2/c$	$P4_2/n$
***a*(?)**	8.226(2)	10.720(2)	10.874(1)	19.950(2)	17.217(5)
***b*(?)**	8.897(2)	19.642(4)	6.243(1)	5.789(1)	17.217(5)
***c*(?)**	23.610(5)	5.952(1)	18.915(3)	24.245(2)	5.999(3)
***a*(deg)**	90	90	90	90	90
***ß*(deg)**	90	94.37(1)	94.72(1)	104.29(1)	90
***?*(deg)**	90	90	90	90	90
***V*(? ^{3})**	1727.9(7)	1249.6(4)	1279.7(3)	2713.4(2)	1778.3(12)
Z	8	4	4	8	2
D_{calc}(g cm^{-3})	1.623	1.538	1.501	1.421	1.607
No. reflections measured	6751	5344	5242	5632	3442
No. unique reflns [R(int)]	1242[0.0226]	1794[0.0256]	1819[0.0414]	1985[0.0856]	1274[0.0452]
No. reflns used	1095	1584	1157	1295	1023
GOF on F^2	1.054	1.058	0.845	0.904	1.242
R1[I>2s(I)]	0.0365	0.0511	0.0466	0.0393	0.0608
wR2	0.0989	0.1369	0.1166	0.0798	0.1630
Final diff. four map (e^- . Å^{-3}) max, min	0.20, -0.26	0.95, -0.24	0.19, -0.13	0.12, -0.14	0.69, -0.23

Table 2.1 contd…..

2a	**2b**	**3a**	**3b**	**4a**	**4b**
$2(C_7H_5N_3O_5)$: $(C_{10}H_8N_2)$: $2(CH_4O)$	$2(C_7H_5N_3O_5)$: $(C_{10}H_8N_2)$: $2(H_2O)$	$2(C_7H_5N_3O_5)$: $(C_{12}H_{10}N_2)$: $2(C_1H_4O_1)$	$2(C_7H_5N_3O_5)$: $(C_{12}H_{12}N_2)$: $2(C_1H_4O_1)$	$2(C_7H_5N_3O_5)$: $2(C_{12}H_{10}N_2)$: $2(H_2O)$	$(C_7H_5N_3O_5)$: $(C_{12}H_{12}N_2)$: (H_2O)
642.55	307.25	334.29	335.30	822.75	390.39
monoclinic	triclinic	triclinic	triclinic	triclinic	triclinic
*P*2/n	*P*?	*P*?	*P*?	*P*?	*P*?
15.722(3)	5.788(3)	7.319(3)	6.946(1)	7.240(2)	7.592(1)
3.789(1)	8.899(5)	7.625(4)	7.832(2)	13.294(1)	9.965(1)
24.405(5)	13.41(7)	14.420(7)	14.764(1)	20.483(2)	13.927(2)
90	98.84(1)	76.32(1)	83.97(1)	75.65(1)	76.45(1)
91.85(1)	96.93(1)	75.85(1)	76.50(1)	85.19(1)	75.55(1)
90	90.19(1)	75.03(1)	79.28(1)	84.16(1)	72.42(1)
1453.1(6)	677.4(6)	740.8(6)	765.8(5)	1896.5(2)	958.1(5)
2	2	2	2	2	2
1.469	1.506	1.499	1.454	1.441	1.433
5684	2846	6082	6198	8259	7764
2095[0.0273]	1937[0.0260]	2133[0.0212]	2211[0.0270]	5393[0.0305]	2746[0.0205]
1638	1492	1958	1963	3194	2686
1.031	1.061	1.063	1.707	1.000	1.178
0.0397	0.0565	0.0362	0.0582	0.0540	0.0393
0.0983	0.1397	0.0999	0.1879	0.1141	0.1000
0.18, -0.13	0.25, -0.27	0.33, -0.45	0.60, -0. 72	0.43, -0.47	0.31, -0.31

Table 2.1 contd……

5a	**6a**	**7a**	**8a**	**9a**
$(C_7H_5N_3O_5)$: $(C_{12}H_8N_2)$	$3(C_7H_5N_3O_5)$: $3(C_{13}H_9N_1)$	$2(C_7H_5N_3O_5)$: $(C_7H_3N_3O_4)$	$2(C_7H_5N_3O_5)$: $2(C_7H_3N_2O_6Cl)$	$C_7H_5N_3O_5$: $C_{15}H_{10}O_2$
391.34	1171.06	615.40	915.41	433.37
monoclinic	monoclinic	monoclinic	triclinic	triclinic
$P2_1$	$P2_1/n$	$P2_1/c$	*P*?	*P*?
4.993(1)	6.934(3)	7.978(2)	6.016(4)	7.305(2)
13.461(3)	27.885(12)	8.961(2)	13.250(7)	9.392(2)
12.987(3)	27.308(11)	35.620(6)	22.894(13)	15.325(3)
90	90	90	81.37(11)	83.53(1)
95.64(1)	95.41(1)	93.30(1)	82.77(11)	77.89(1)
90	90	90	82.08(11)	73.07(1)
868.6(3)	5257(4)	2542.3(10)	1776.8(17)	982.0(4)
2	4	4	2	2
1.496	1.480	1.608	1.711	1.466
3684	23047	10704	11298	4243
1902[0.0242]	7626[0.1120]	3662[0.0449]	5145[0.0536]	2788[0.0391]
1814	4267	2530	4178	2261
1.065	0.873	1.043	1.132	1.156
0.0282	0.0577	0.0455	0.0595	0.0584
0.0703	0.1199	0.1016	0.1442	0.1611
0.11, -0.13	0.26, -0.27	0.19, -0.15	0.87, -0.33	0.27, -0.26

Table 2.2 Characteristics of hydrogen bonds (distances/Å and angles/deg)[#]

Hydrogen bonds	**1**	**1a**	**1b**	**1c**	**1d**
O-H···O					
O-H···N					
N-H···O	2.05 2.91 168.9 2.17 3.02 171.9	2.09 2.87 164.5 2.11 2.96 174.1	1.99 2.84 170.8 2.00 2.92 171.8	1.97 2.90 173.1 2.08 2.94 166.9	2.05 2.90 169.8
N-H···N					
C-H···O		2.27 3.18 164.7 2.56 3.35 154.5 2.89 3.73 163.0	2.34 3.24 161.7 2.61 3.76 169.4 2.69 3.43 152.3	2.49 3.43 168.1 2.57 3.47 155.4	2.52 3.44 171.7
C-H···N				2.54 3.37 151.9	

[#] The three numbers in each column indicate H···N(O), O(N/C)···O(N) and angles, respectively.

Table 2.2 *contd*…..

2a	2b	3a	3b	4a	4b
1.85 2.80 166.9	1.99 2.82 171.2	1.85 2.77 170.9	1.74 2.76 168.2	1.78 2.81 170.0 2.05 2.88 167.1 2.10 3.03 166.8	2.01 2.89 164.3 2.08 2.93 158.3
2.03 2.92 168.8 2.16 2.99 173.1	2.02 2.93 169.8 2.10 2.94 177.7	1.99 2.82 157.3 2.11 2.99 170.4	1.97 2.82 156.0 2.04 2.95 176.8	1.96 2.89 171.4 1.99 2.93 177.4 2.03 2.95 172.4 2.11 3.01 170.7	1.91 2.84 178.1 1.95 2.86 171.9
2.56 3.47 176.4 2.66 3.57 173.9 2.68 3.52 150.8 2.78 3.66 153.4 2.86 3.52 150.8 2.88 3.79 167.0 3.01 3.93 176.8	2.34 3.24 165.2 2.43 3.31 164.7 2.54 3.45 162.8 2.61 3.51 162.0	2.31 3.28 164.8 2.42 3.38 169.2 2.56 3.47 170.5 2.56 3.48 173.9 2.61 3.46 158.9 2.69 3.59 161.8 2.73 3.57 154.5 3.00 3.64 123.6	2.36 3.27 154.0 2.50 3.38 169.1 2.60 3.47 144.4 2.65 3.48 159.4 2.68 3.67 149.3 2.73 3.64 164.7 2.82 3.70 150.9 2.86 3.58 117.3	2.39 3.22 143.2 2.39 3.28 160.4 2.45 3.26 159.0 2.45 3.30 149.5 2.49 3.39 167.7 2.61 3.65 176.6 2.63 3.64 165.1 2.64 3.51 161.3 2.68 3.59 163.7 2.75 3.60 154.2 2.76 3.60 152.2 2.77 3.69 164.1 2.79 3.66 147.8 2.82 3.62 144.3 2.83 3.67 158.6 2.89 3.72 145.3	2.39 3.28 155.2 2.48 3.34 148.4 2.53 3.48 176.1 2.56 3.44 156.5 2.58 3.39 146.0 2.63 3.47 151.0 2.68 3.56 156.2 2.98 3.47 114.2
				2.55 3.49 174.2 2.79 3.64 161.1	2.81 3.70 168.3 2.94 3.77 147.2

Table 2.2 *contd*…..

5a	6a	7a	8a	9a
			1.64 2.58 159.8 1.75 2.58 156.8	1.82 2.65 165.3
2.01 2.88 165.8	2.06 2.99 174.5 2.07 2.98 176.3 2.08 2.99 166.3	2.07 3.00 175.0 2.08 2.92 170.9 2.16 3.01 175.1		2.17 2.89 136.7 2.17 2.95 156.0
2.33 3.09 149.2	2.07 3.01 170.4 2.13 3.00 168.6 2.25 3.08 170.8			
2.44 3.35 153.0 2.57 3.31 134.0 2.63 3.50 150.6 2.68 3.49 142.6 2.70 3.47 137.8 2.72 3.57 142.7	2.51 3.34 135.3 2.52 3.45 149.4 2.57 3.41 148.3	2.51 3.30 144.7	2.42 3.31 169.6 2.42 3.34 173.8 2.43 3.50 165.2 2.53 3.39 166.8 2.54 3.46 172.8 2.57 3.37 166.3 2.67 3.58 157.6 2.72 3.36 136.6 2.73 3.59 174.2	2.44 3.29 142.7 2.56 3.30 131.8 2.62 3.48 155.3 2.66 3.42 136.8
		2.79 3.68 162.4		

PART - B

With the structural features observed in **DNBA**, a primary amide, possessing both cyclic and acyclic hydrogen bonds, characteristic pattern of cyclic imides like cyanuric acid (CA), a study of hydrogen bonding features in cyclic imides has been chosen to compare with the amides. In this connection, taking into consideration the pioneering work of Whitesides, Lehn and many other researchers on cyanuric acid, triaminopyrimidine, barbituric acids etc., and their complexes with many substrates, yielding exotic supramolecular assemblies,[24] trithiocyanuric acid (**TCA**), a thio analogue of CA has been chosen as a substrate for the study of its hydrogen bonding features, as only a very limited number of structures of **TCA** are known in the literature.[20, 25] It is known from the literature that in the acetone solvated structure of **TCA**, a hexagonal arrangement formed by six **TCA** molecules is resulted through cyclic N-H···S hydrogen bond, due to the interaction between free N-H present on **TCA** with oxygen atom of the acetone molecule (see Fig. 2.22).[26]

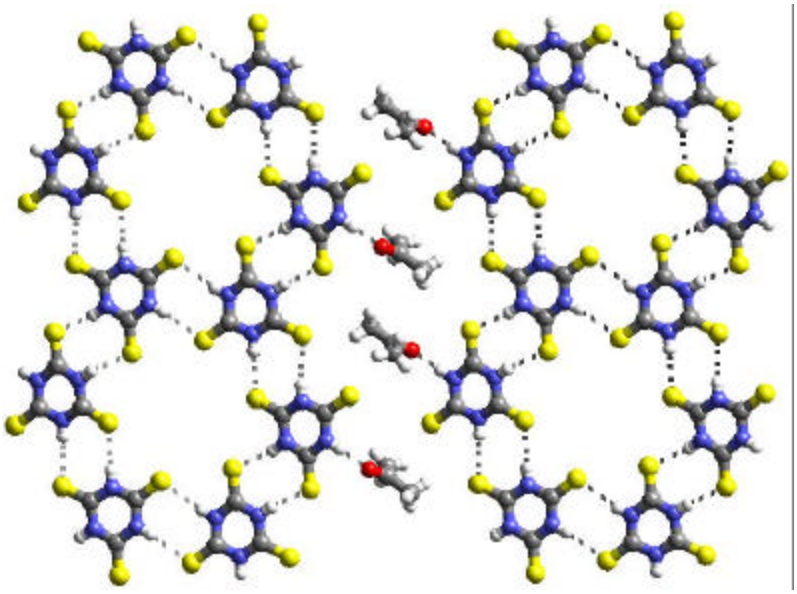


Figure 2.22: Two-dimensional arrangement of molecules in the **TCA**/acetone structure.

This suggests that it might be possible to prepare solvated structures with other solvent molecules that are capable of forming hydrogen bonds with **TCA**. Thus, crystallization of **TCA** from various solvents like 2-butanone, DMSO, DMF, acetonitrile and methanol, has been carried out.

2.8 Solvated structures of trithiocyanuric acid with some solvent molecules containing hydrogen-bonding functionality.

2.8.1 Structure of trithiocyanuric acid with 2-butanone (TCA/2-butanone)

Trithiocyanuric acid crystallizes from 2-butanone in a 2:1 molecular ratio as determined by single crystal X-ray diffraction methods (see Table 2.3). The structure analysis reveals that it has a close resemblance with that of **TCA**/acetone adopting essentially the same packing arrangement. A typical layer formed by **TCA** molecules in two-dimension, as shown in Figure 2.23, consists of hexagonal units in which the symmetry dependent pairs of **TCA** molecules are held together by cyclic N-H···S hydrogen bond with H···S distance of 2.57 Å. Further, these pairs are connected to each other through symmetry independent molecules again through N-H···S hydrogen bond with H···S distances ranging from 2.45-2.59 Å. The free N-H present forms N-H···S hydrogen bond with the oxygen atom of the 2-butanone lying as pendants to the tapes formed by **TCA** (Fig. 2.23). On either side of a given tape, there are two other tapes in the same plane, with the directions of these tapes running parallel to each other and the pendant 2-butanone molecules of adjacent tapes alternate with one another in the region between adjacent tapes. Although, Figure 2.23 gives an impression that open channels are present along an axis (see also Fig. 2.24(b) for the arrangement of molecules in

three-dimension), such channels do not actually exist, as cavities are capped by the -C-CH_3 group of 2-butanone from the adjacent layer (Fig. 2.24(a)). The perpendicular distance between adjacent layers is about 3.6 Å and the relative positions of the **TCA** molecules in adjacent layers is such that S atoms of one sheet lie almost directly above N atoms of the adjacent sheet, and *vice versa*.

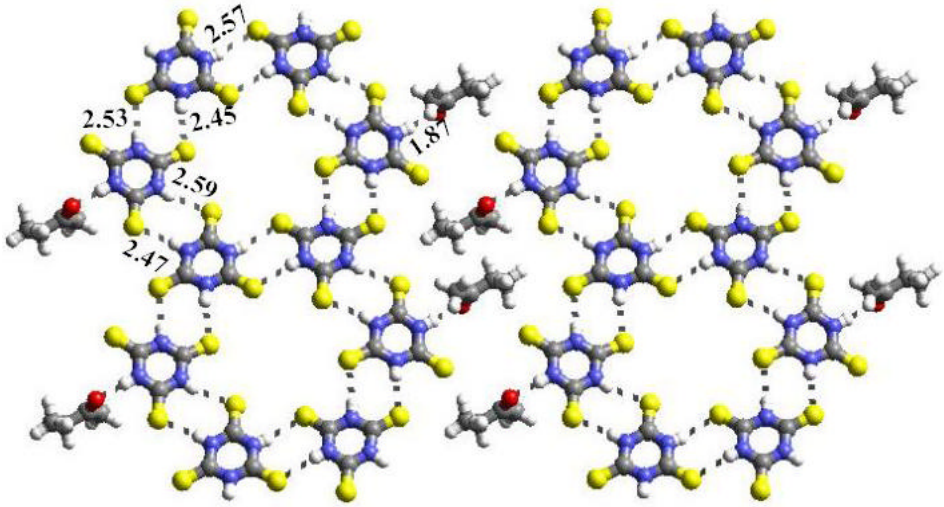


Figure 2.23: A single sheet structure showing hexagonal arrangement of **TCA** molecules in two-dimension.

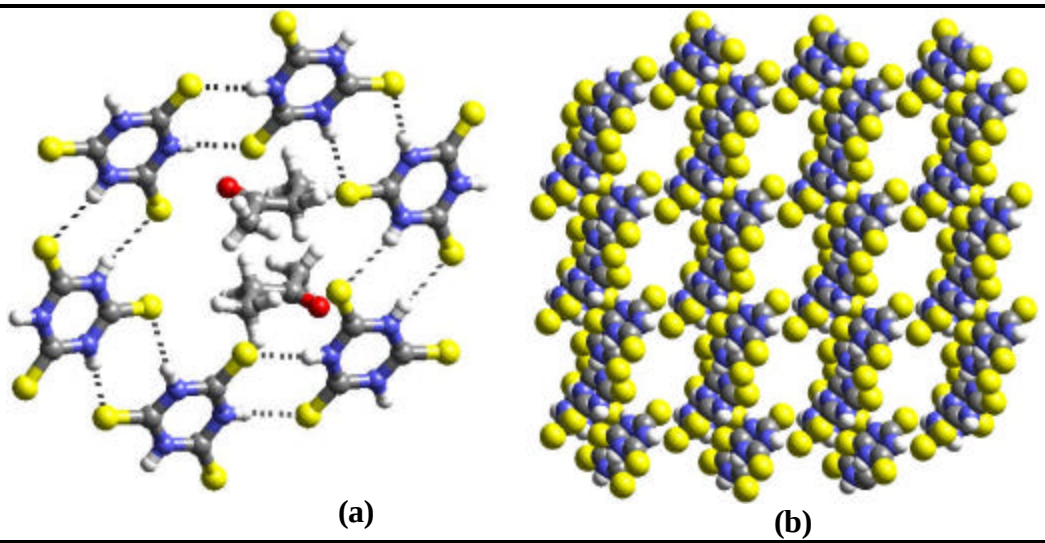


Figure 2.24: (a) Diagram showing 2-butanone molecules from adjacent layers pointing towards cavity. (b) Three-dimensional view of the structure, along the z-axis (solvent molecules have been removed).

2.8.2 Structure of trithiocyanuric acid with dimethylsulfoxide (TCA/DMSO)

Crystal structure determination by single crystal X-ray diffraction method reveals that the **TCA** crystallized along with solvent molecule in a 1:1 molar ratio and crystallographic information is given in Table 2.3. A two-dimensional arrangement of these molecules, in which **TCA** molecules connected to each other through the cyclic N-H···S hydrogen bond, with H···S distance of 2.57 Å, forming tapes is shown in Figure 2.25(a).

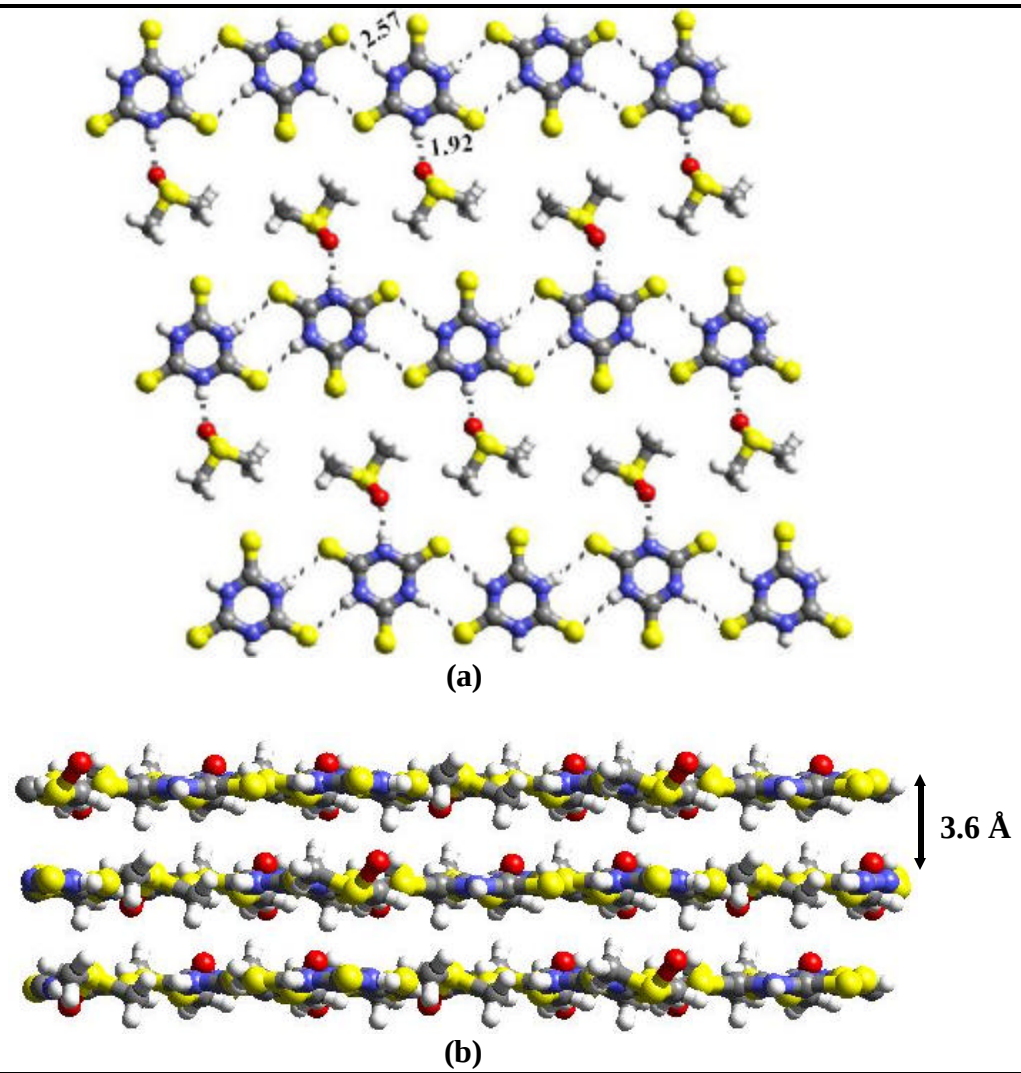


Figure 2.25: (a) Recognition pattern between **TCA** and DMSO molecules. (b) Stacking of layers in three-dimensional arrangement in **TCA**/DMSO structure.

The free N-H group of each **TCA** molecule in the tape involves in the formation of an N-H···O (H···O, 1.92 Å) hydrogen bond to the oxygen atom of a dimethyl sulfoxide (DMSO) molecule lying as pendant molecules as observed in **TCA**/acetone and **TCA**/2-butanone. On each side of a given tape, there is another tape in the same plane, giving rise to a two-dimensional layer. Within this layer, all tapes run parallel to each other and in the region between adjacent tapes, the pendant DMSO molecules of adjacent tapes alternate with one another and interact through van der Waals interactions. The two-dimensional layers discussed above are stacked parallel to each other and the perpendicular distance between adjacent layers is about 3.6 Å (Fig. 2.25(b)).

2.8.3 Structure of trithiocyanuric acid with dimethylformamide (TCA/DMF)

The solvated structure of **TCA** with dimethylformamide (DMF) crystallizes in a monoclinic, space group $P2_1/c$ (see Table 2.3). The packing arrangement of **TCA** and DMF molecules is topologically similar without any major deviation from the features already noted in the **TCA**/DMSO structure. **TCA** molecules connected to each other through the cyclic N-H···S hydrogen bond, with H···S distance of 2.55 Å, forming tapes and the free N-H bond of each **TCA** molecule in the tape forms an N-H···O hydrogen bond to the oxygen atom of a DMF molecule and these solvent molecules lie as pendants between the tapes of **TCA** (Fig. 2.26(a)). The two-dimensional layers discussed above are stacked parallel to each other; the perpendicular distance between adjacent layers is about 3.4 Å as shown in Fig. 2.26(b).

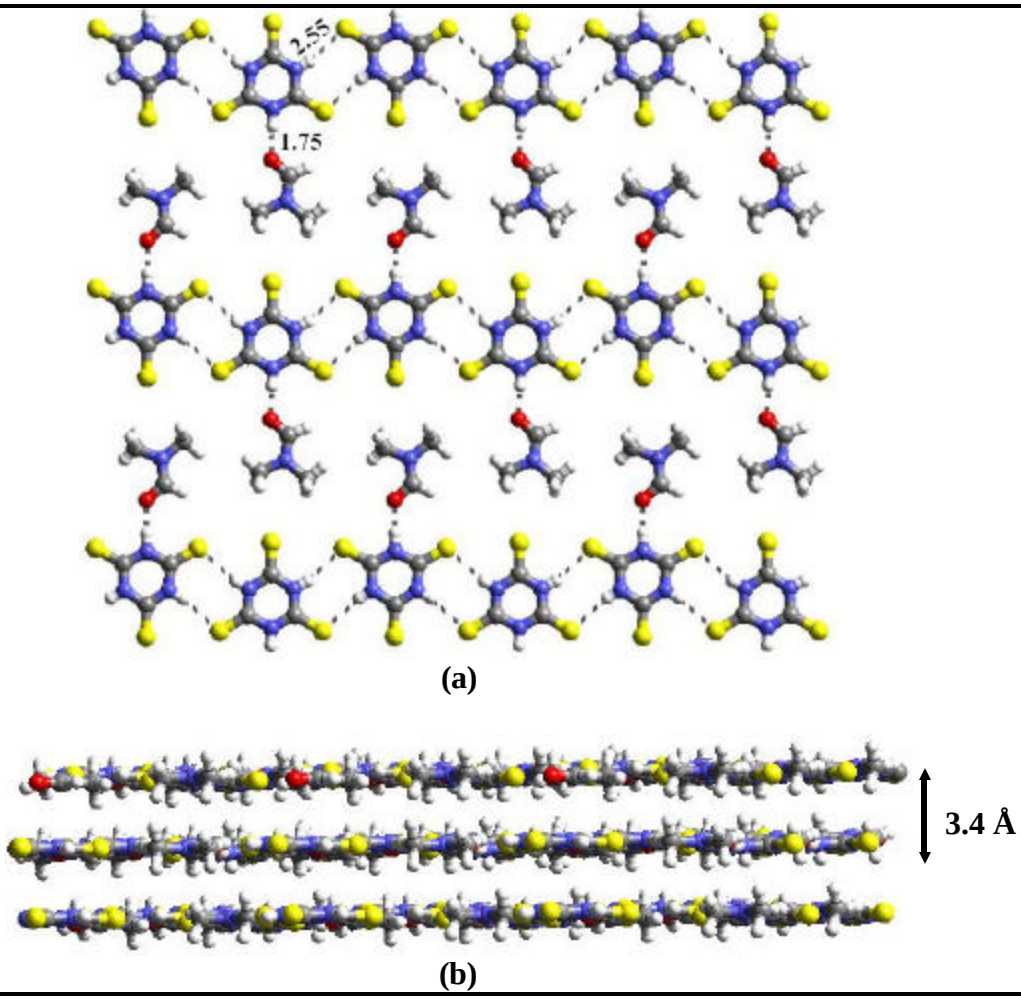


Figure 2.26: (a) Arrangement of molecules of **TCA** in its solvated structure with DMF. (b) Stacking of molecules to form layered structure in three-dimension.

2.8.4 Structure of trithiocyanuric acid with acetonitrile (TCA/acetonitrile)

TCA with acetonitrile has a 1:1 ratio of the two components and structure consists of tapes of **TCA** molecules held together by cyclic N-H···S hydrogen bond, with H···S distance of 2.39 Å. The free N-H bond of each **TCA** molecule in the tapes form an N-H···N hydrogen bond to the nitrogen atom of acetonitrile molecule and these solvent molecules lie as pendants between the tapes formed by **TCA** molecules (Fig. 2.27(a)). On each side of a given tape there is another tape in the same plane, giving rise

to a two-dimensional layer. The pendant acetonitrile molecules of adjacent tapes alternate with one another in the region between the tapes. The layers stack in three-dimension and the perpendicular distance between adjacent layers is about 3.4 Å as shown in Fig. 2.27(b). The relative positions of the **TCA** molecules in adjacent layers is such that S atoms of one layer lie almost directly above N atoms of the adjacent layer, and *vice versa*.

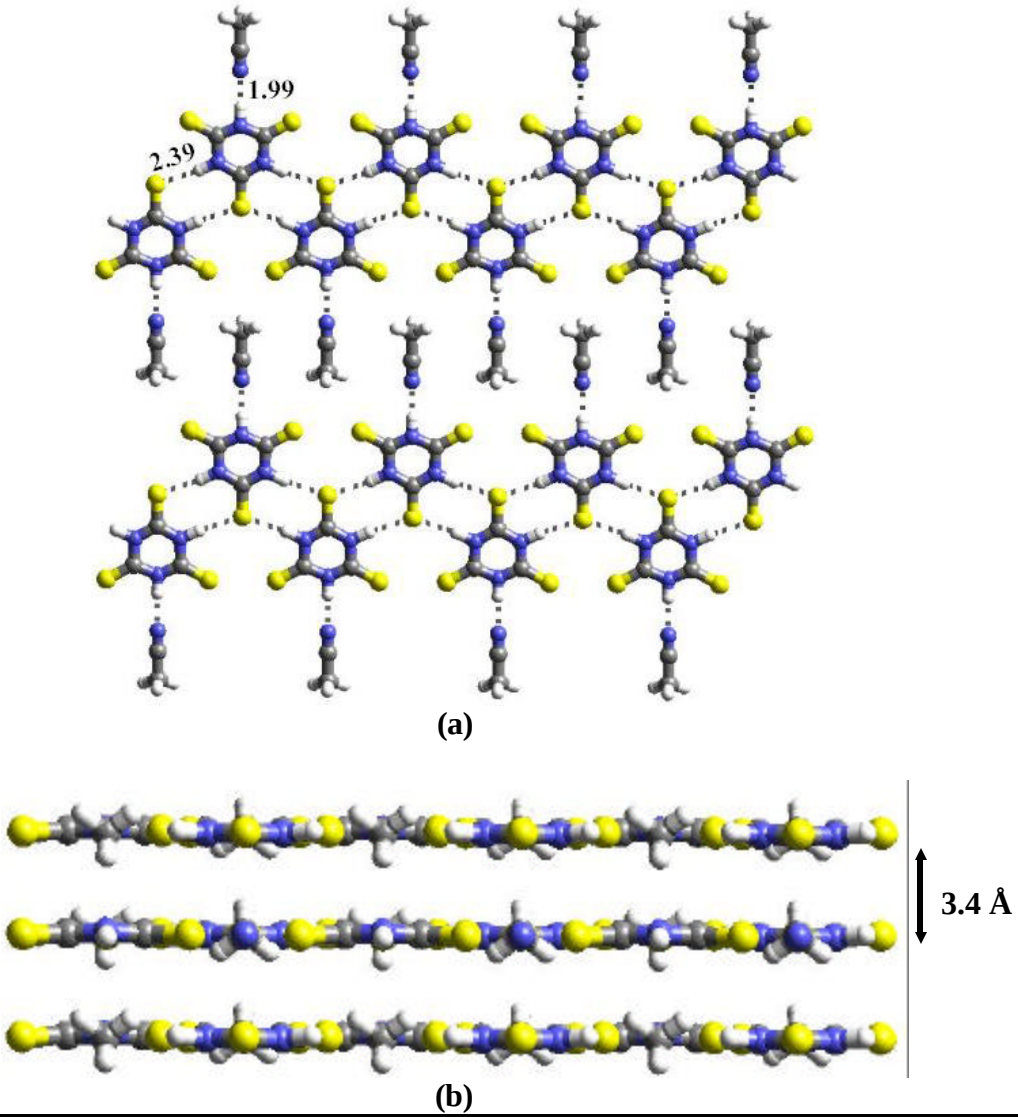
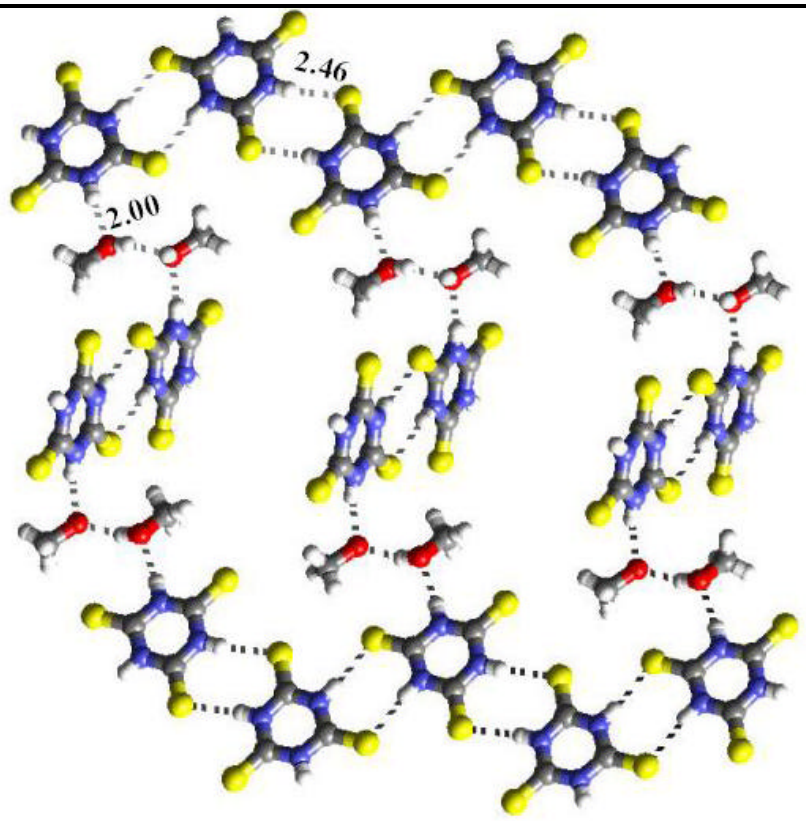


Figure 2.27: (a) Formation of **TCA** tapes and interaction with acetonitrile molecules lying as pendants. (b) Stacking of layers in three-dimension.

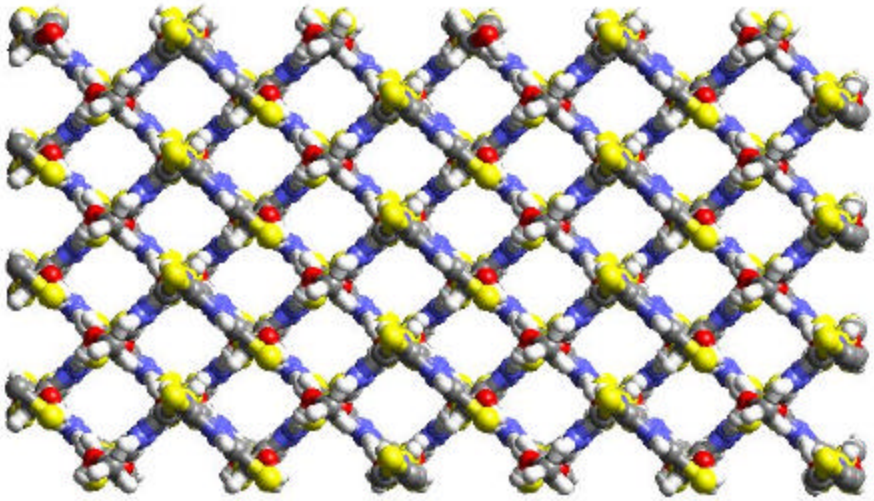
2.8.5 Structure of trithiocyanuric acid with methanol (TCA/methanol)

The solvent molecules, incorporated along with **TCA** discussed above, contain good hydrogen bond acceptor but does not contain good hydrogen bond donor. It is not surprising that, in all of these structures, each of these molecules engages as a hydrogen bond acceptor in a hydrogen bond with a free N-H bond of a **TCA** molecule. The solvated structure formed between **TCA** and methanol possesses additional features, as methanol can behave both as a hydrogen bond donor and as a hydrogen bond acceptor.

The structure of **TCA** and methanol has a 1:1 ratio of the two components and crystallographic information is given in Table 2.3. In this structure, **TCA** molecules are arranged as tapes, and the free N-H bond of each **TCA** molecule forms an N-H···O hydrogen bond to the oxygen atom of a methanol molecule as shown in Figure 2.28(a). The methyl group of the methanol molecule lies approximately in the plane of the tape. While the existence of a **TCA** tape with pendant solvent molecules hydrogen bonded through the free N-H bonds on the tape is a common feature of all the solvated structures of **TCA** reported here. However, the arrangement of tapes relative to each other differs significantly between the **TCA**/methanol structure and the other structures. The **TCA** methanol solvated structure does not contain two-dimensional layer. Instead, the tapes are stacked on top of each other such that the adjacent tapes run alternately *in* and *out* of the page. In three-dimension, adjacent tapes cross each other which gives the appearance of an approximately square grid arrangement of the **TCA** tapes as shown in Figure 2.28(b).



(a)



(b)

Figure 2.28: (a) Formation of tapes of **TCA** molecules and the interaction with the methanol. Notice that the tapes are not in the same plane but run alternately *in* and *out* of page. (b) View of the packing of molecules in three-dimension resembling an approximately square grid-like arrangement.

The methanol molecules that are pendant to a given tape, as discussed above, at the interface between the adjacent tapes, form a zigzag ···O-H···O-H···O-H··· hydrogen bonded chain (Fig. 2.29) as found in the structures of polymorphs of pure methanol.[27] Thus, each methanol oxygen atoms acts as a hydrogen bond acceptor to both the N-H bond of a **TCA** molecule and the O-H bond of another methanol molecule, thus, acting as both hydrogen bond donor and as well as acceptor.

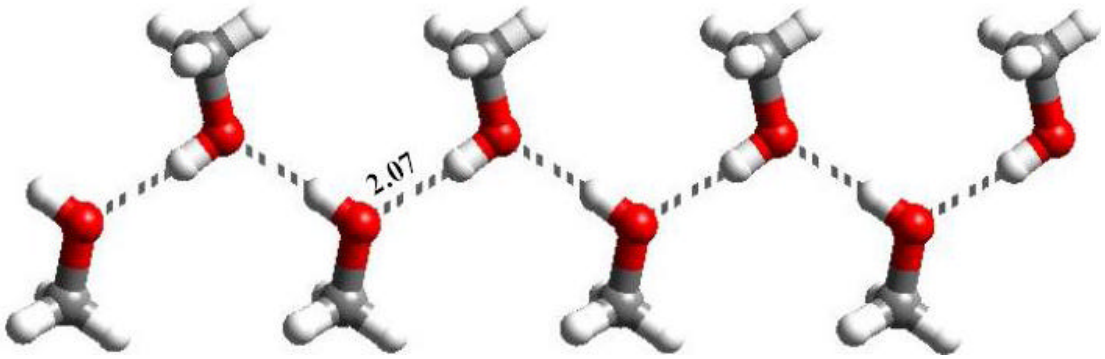


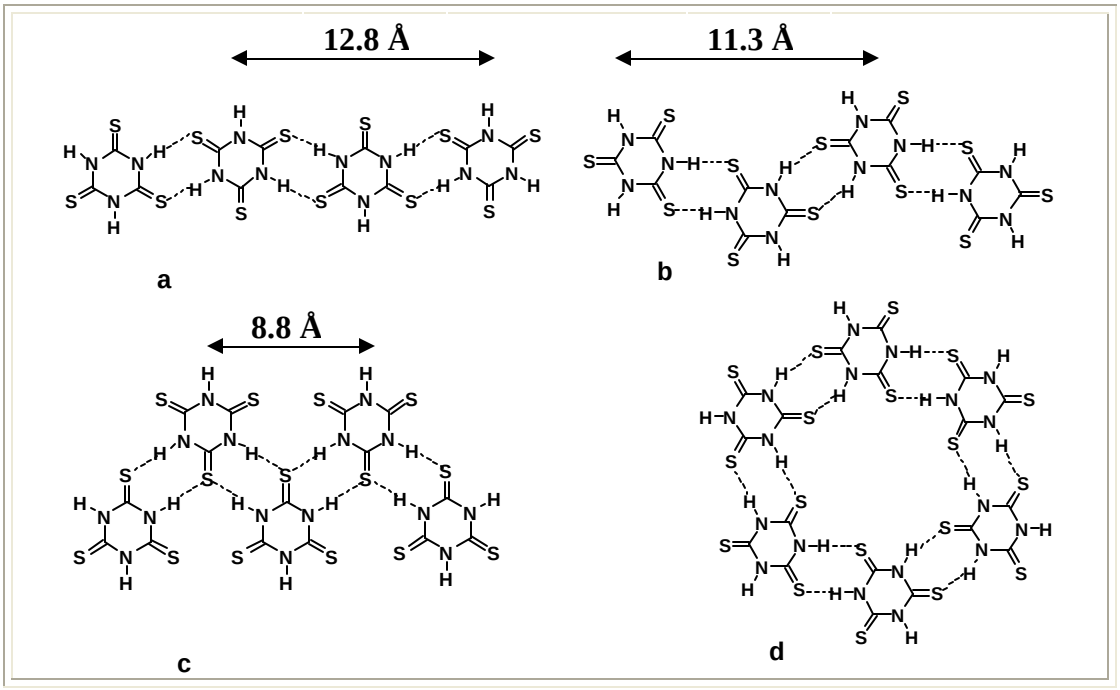
Figure 2.29: Formation of a zigzag hydrogen bonded chain between methanol molecules in the solvated structure of **TCA**/methanol. Hydrogen bonding is shown in dashed lines.

2.9 Identification of characteristic packing modes for TCA molecules

Structural rationalization of solvated structures of **TCA** reveals two structural classes - (i) formation of infinite single-tape arrangement (Scheme 2.6(a-c)) and (ii) formation of infinite double tape arrangement (Scheme 2.6(d)). Single tape arrangement consists of three different types of tapes – type I - III as shown in Scheme 2.6(a-c) respectively. In all three types of single-tape, each **TCA** molecule interacts with two neighbours. Each of these interactions involves a pair of N-H···S hydrogen bonds in a

cyclic $R_2^2(8)$ arrangement. Further, in tapes of types I and II, these interactions involve two N-H bonds and two C=S bonds of the **TCA** molecule, and thus one N-H bond and one C=S bond in each molecule are not involved in these interactions. In type I, the free N-H bond and C=S bond are at opposite corners of the molecule, whereas in type II, the free N-H bond and C=S bond are at adjacent corners of the molecule. In type III, the $R_2^2(8)$ hydrogen-bonding arrangement between adjacent molecules involves two N-H bonds but only one C=S bond of each **TCA** molecule, and thus one N-H bond and two C=S bonds of each molecule are not involved in these interactions. Thus, in all types of single-tape arrangement, there is one free N-H bond per molecule that is involved in hydrogen bonding with solvent molecule. Also the direction of the free N-H bond alternates between opposite sides of the tape on moving from one molecule to its neighbour along the tape. In tapes of types I and III, the free N-H bond points perpendicular to the direction of the tape, whereas in tapes of type II, the free N-H bond forms an angle of about 60^o with the direction of the tape. Furthermore, the periodic repeat unit of the tape comprises two **TCA** molecules, but because the packing of **TCA** molecules is different in each case, the distance along the direction of the tape is different for each type of tape. Thus, the distance decreases from type I to III and is about 12.8 Å for tapes of type I, about 11.3 Å for tapes of type II and about 8.8 Å for tapes of type III. Corresponding to the trend of decreasing periodicity from type I to type III, the width of the tapes becomes greater on moving from type I to type III. The **TCA**/DMSO and **TCA**/DMF structures form type I arrangement while **TCA**/methanol structure adopts type II where as **TCA**/acetonitrile forms type III arrangement.

The **TCA**/2-butanone structure, on the other hand, forms double tape arrangement, which consists of two single-tapes of type II in which every second molecule is linked to a molecule of the other single-tape by N-H···S hydrogen bonds in cyclic $R_2^2(8)$ arrangements forming hexagonal units. The molecules which are involved in cross-linking between the two individual single-tapes, all N-H bonds and all C=S bonds are engaged in N-H···S hydrogen bonds to other **TCA** molecules. The other molecules, having one free N-H bond and one free C=S bond are not involved in hydrogen bonding to other **TCA** molecules. These free N-H and C=S bonds are at adjacent corners of the **TCA** molecule and point outwards from the double-tape and interact with solvent molecule.



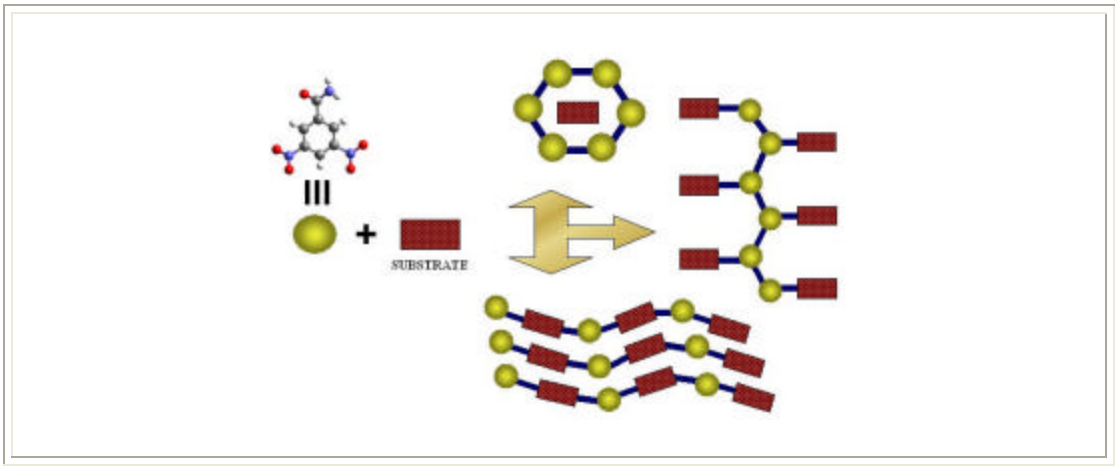
Scheme 2.6: Identification of different types of TCA tapes.

Table 2.3 Crystallographic data for the **TCA** solvated structures.

	TCA/ 2-butanone	**TCA/ dmso**	**TCA/ dmf**	**TCA/ acetonitrile**	**TCA/ methanol**
Formula	$2(C_3H_3N_3S_3)$: (C_4H_8O)	$(C_3H_3N_3S_3)$: (C_2H_6OS)	$(C_3H_3N_3S_3)$: (C_3H_7ON)	$(C_3H_3N_3S_3)$: (C_2H_3N)	$(C_3H_3N_3S_3)$: (CH_4O)
Fw	426.64	255.39	250.36	218.32	209.31
Crystal system	triclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	*P*?	*P*?	$P2_1/c$	$P2_1/m$	$C2/c$
***a*(?)**	10.130(2)	4.666(1)	9.789(1)	5.266(2)	17.472(3)
***b*(?)**	10.358(2)	10.423(1)	12.763(1)	8.814(1)	4.611(1)
***c*(?)**	9.606(1)	11.777(2)	9.285(1)	10.525(3)	22.593(4)
***a*(deg)**	99.33(1)	85.39(1)	90	90	90
***ß*(deg)**	110.53(1)	87.73(1)	91.19(1)	102.70(1)	94.96(1)
***?*(deg)**	90.57(2)	78.58(1)	90	90	90
***V*(? ^{3})**	929.0(2)	559.4(2)	1159.8(2)	476.5(2)	1813.4(6)
Z	2	2	4	2	8
D_{calc}(g cm^{-3})	1.525	1.516	1.434	1.521	1.533
No. reflns measured	5701	2190	4389	2330	3247
No. unique reflns	3010	1555	1663	1617	1294
No. reflns used	2884	1351	1069	1313	835
GOF on F^2	1.11	1.04	1.19	1.18	1.22
R1[I>2s(I)]	0.038	0.033	0.053	0.075	0.054
wR2	0.093	0.084	0.119	0.198	0.089

2.10 Conclusions

Solvated structures and molecular complexes of **DNBA** have shown the ability of amide functionality to form various supramolecular networks such as planar sheets, helices, herring bone structures, host-guest complexes. A schematic representation of different supramolecular architectures formed in different adducts is shown in Scheme 2.7. In this study, amide moiety of **DNBA** has always shown preference to form dimer and its *anti*- hydrogen atom is associated with a solvent molecule (DMSO in **1a** and **1b**; pyridine in **1c**; CH_3OH in **2a**, **3a** and **3b**; H_2O in **2b**, **4a** and **4b**) is mainly observed. It is noteworthy to mention an intriguing feature that in none of the complexes (**2a-4b**) aza donor compounds did participate as spacer ligand as observed in a majority of molecular complexes. It is further interesting to note that the channel dimensions are tuned with the aid of the solvent of crystallization to accommodate the guest molecules unlike other known host–guest complexes, wherein this feature is totally dominated by the nature of host compound alone. Also, amide group of **DNBA** adopts different conformations in different complexes and hence, different supramolecular architectures.



Scheme 2.7: Schematic representation of various supramolecular networks

Further, structural features of solvated structures of **TCA**, obtained by crystallisation of **TCA** from different solvents containing hydrogen-bonding functionality are reported. The solvated structures are conveniently classified according to the structural arrangement of the **TCA** molecules, which comprises either double- or single-tapes of **TCA** molecules. In all structures, the solvent molecule engages in hydrogen bonding involving free N-H bonds on the **TCA** tapes as the hydrogen bond donor. Also, the solvent molecules behave exclusively only as a hydrogen bond acceptor (except **TCA**/methanol), and the crystal structures in these cases can be rationalized on the basis of the packing of the **TCA** tapes with pendant hydrogen bonded solvent molecules. Thus, the formation of single-tapes of type III in **TCA**/acetonitrile in comparison to the formation of single-tapes of type I in **TCA**/DMF and **TCA**/DMSO can be rationalized on the basis of the periodicity of these tapes with the size of the pendant solvent molecule. The formation of double-tapes in the **TCA**/2-butanone structure can be rationalized on the basis of efficient packing of adjacent two-dimensional layers on top of each other. The solvated structure formed between **TCA** and methanol introduces additional structural features, arising from the fact that each methanol molecule can participate in hydrogen bonding both as a donor and as an acceptor. Clearly the rationalization of the structural features of solvated structures of **TCA** established from the present study will serve as a systematic basis for predicting and rationalizing interactions formed between **TCA** and solvent molecules containing hydrogen-bonding functionality.

2.11 Experimental Section

All the chemicals used in this study were obtained commercially and used as such without any further purification. HPLC grade solvents were used for carrying out experiments. The synthesis of molecular complexes was carried out, by dissolving the reactants in the appropriate solvents either at room temperature or by warming on a water bath and subsequently cooling by a slow-evaporation method. In a typical experiment, 105 mg (0.5 mmol) of 3,5-dinitrobenzamide and 78 mg (0.5 mmol) of 4,4'-bipyridyl were dissolved in a methanol solution on a water bath and then subsequently cooled to room temperature. Colorless rectangular block shaped single crystals of good quality were obtained over a period of three days and were used for X-ray diffraction studies.

In the solvated structures of **TCA,** good quality single crystals were prepared by dissolving **TCA** (Aldrich) in 2-butanone, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), methanol and acetonitrile. Slow evaporation of solvent from these solutions gave good quality single crystals suitable for X-ray diffraction. The **TCA**/methanol systems yielded single crystals within 24 hr, whereas the other systems gave single crystals over a longer time (typically one week). In all cases, crystals were found to be unstable under ambient conditions, leading to the loss of crystal quality over time.

2.12 Structure determination by single crystal X-ray diffraction method

Good quality single crystals (3,5-dinitrobenzamide, its solvated and molecular complexes) have been carefully selected looking under a polarized Leica microscope

equipped with CCD camera and glued to a glass fiber using an adhesive (cyano acrylate). In all the cases, the crystals were smeared in the adhesive solution to prevent decay of crystals due to solvent evaporation or direct exposure to ambient conditions. The intensity data were collected on a Bruker single crystal X-ray diffractometer, equipped with an APEX detector, at room temperature (298 K), except for **1c**, **3a** and **3b**, which were collected at the temperature 133 K due to the instability of the crystals. In the case of solvated structures of **TCA**, the crystals were smeared in araldite to protect them from direct exposure to atmosphere because of the susceptibility of the crystals to degradation. Subsequently, the data were processed using Bruker suite of programmes[28] and the convergence was found to be satisfactory with good R_{ini} parameters. The details of the data collection and crystallographic information for all the structures are given in Table 2.1 and 2.3. The structure determination by direct methods and refinements by least-squares methods on F^2 were performed using SHELXTL-PLUS package.[29] All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were taken from a difference Fourier maps and were refined isotropically. All the intermolecular interactions were computed using PLATON.[30]

2.13 References

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Chapter THREE

SYNTHESIS AND RATIONAL ANALYSIS OF FOUR POLYMORPHS OF 4-AMINO-3,5-DINITROBENZAMIDE

"The number of forms known for a given compound is proportional to the time and money spent in research on that compound."

Mc Crone, 1995

3.1 INTRODUCTION

Polymorphism, besides its academic interest, has also gained technological importance especially in pharmaceutical industry (see box 1). The concept of polymorphism became so powerful in recent years with an explosive growth in the form of publications, patents, books, meetings, symposia, etc.[1-6] The more common and traditional method of crystallization from solution, to prepare polymorphs, has great technological importance, as it is one of the most successful and reliable methods for the preparation and purification of industrially important chemicals. The other methods/approaches developed in recent times for the preparation and isolation of polymorphs of a compound include crystallization with tailor-made additives,[7] epitaxial growth,[8] laser induced nucleation,[9] crystallization in capillaries,[10] pressure induced crystallization,[11] etc. Further, Matzger *et al*. introduced the method of using polymers as heteronuclei for the preparation and isolation of polymorphs.[12] This method is proven to be successful in achieving selective production of polymorphs of acetaminophen, carbamazepine, 5-methyl-2-[(2-nitro phenyl) amino]-3-thiophene carbonitrile (commonly known as ROY) and sulfamethaxazole by varying exclusively the identity of the polymer employed.[13] Jones and co-workers used the method of solid-state grinding to obtain a particular form of a polymorphic system. For instance, solid- state grinding together with a small quantity of a certain solvent has been demonstrated to allow for selective conversion toward particular polymorphs of anthranilic acid and succinic acid.[14] The transformations that occur with minimal solvent addition also indicate a green chemistry application.[15] Further, this approach may represent a novel method of revealing undiscovered metastable crystalline modifications in other systems.

Box 1

THE IMPORTANCE OF POLYMORPHISM IN THE PHARMA INDUSTRY †

Many of the inconsistencies/problems encountered in product performance in the chemical, pharmaceutical, food and related industries can be attributed to polymorphism. An important example is inconsistent behaviour of drug substances upon dissolution which may have a direct influence on bioavailability. Production of '*wrong*' polymorph at the crystallization stage following synthesis or at any of the intermediate processing stages can therefore result in pharmaceutical dosage forms which are either ineffective or toxic. Liquid preparations of metastable drugs sometimes lose their effectiveness due to precipitation of less soluble, thermodynamically more stable polymorphs or solvated forms. A case in point is the antiprotozoal agent metronidazole benzoate which, when stored as an aqueous suspension below 38 °C is metastable, leading to precipitation and growth of the insoluble monohydrate. Dunitz and Bernstein have recently documented several cases of "vanishing" polymorphs. These are usually metastable forms which, despite their thermodynamic instability, might have crystallized due to more rapid nucleation. Attempts to regenerate the original polymorph are frequently met with failure. Specific compounds with such a history include e.g. 1,2,3,5-tetra-*O*-acetyl-*ß*-D-ribofuranose, benzocaine picrate and xylitol. This disturbing phenomenon extends to solvates. A previously known monohydrate of the antibiotic ampicillin has not been obtained since the appearance of the trihydrate.

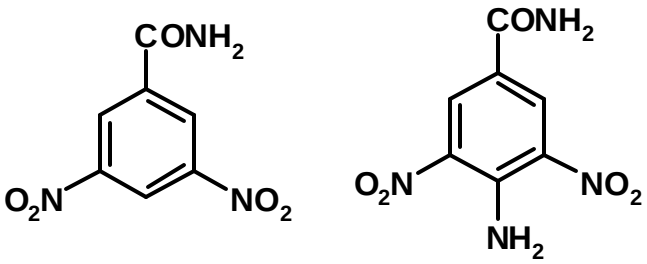
During manufacturing processes (crystallization scale-up, drying, heating, compression, milling, etc.) careful quality control is necessary at all stages to monitor the appearance of undesirable forms/solvated structures. Identification of the different polymorphic forms of a drug substance, determination of their chemical and physical properties, thermodynamic stabilities, and temperatures and rates of interconversion are essential for ensuring drug preparations. Hence, a deeper understanding of the processes of nucleation, crystal growth and polymorphic transformation is essential to overcome the problems or complex phenomenon associated with polymorphism.

† Caira, M. R. *Top. Curr. Chem*. **1998**, *198*, 163-208.

Despite the successful correlation observed with some factors that have influence on the process, such as (i) the interplay of intermolecular interactions (ii) interaction between structure of growing surface and the solvent i.e., action of the solvent at various crystal faces (iii) solvent-solute and solute-solute interactions etc., still in general, the phenomenon remains as a complex process.[16] A systematic study of crystal polymorphism from both theoretical and practical point of view may also help or provide better information about which of the many likely structures a compound/molecule will adopt.[17] It is also apparent from the recent studies that compounds possessing functional groups that have the ability to form different types of intermolecular interactions may also exhibit polymorphism.[18] In this direction, -$CONH_2$ functional group has been chosen to explore its ability to direct the formation of different polymorphs. The results obtained in the process are compiled in the following sections for 4-amino-3,5-dinitrobenzamide.

3.2 Synthesis and structural analysis of polymorphs of 4-amino-3,5-dinitrobenzamide

Initially experiments were begun with 3,5-dinitrobenzamide but no polymorphs were obtained. But, upon extending the study to its derivatives, we were successful with 4-amino-3,5-dinitrobenzamide which gave four polymorphs, labeled as Forms I, II, III and IV, by varying the crystallization conditions and solvents as discussed below. Manual crystallization screening using a range of solvents (32 solvents) or a mixture of solvents under various crystallization techniques has been employed in this study. These



DNBA **ADNBA**

include slow/fast solvent evaporation, vapour diffusion with ethyl acetate/petroleum ether/hexane acting as anti-solvents, solvent evaporation at 5 ^{o}C (in a domestic refrigerator), etc. Different forms of crystals and the preparative conditions are given in Table 3.1. Crystals obtained from tetrahydrofuran (THF), methanol and benzene gave different unit cell parameters. While, the crystals obtained from all other solvents gave cell parameters corresponding to methanol form. It is noteworthy to mention that the four forms are easily distinguishable by morphology as shown in Figure 3.1.

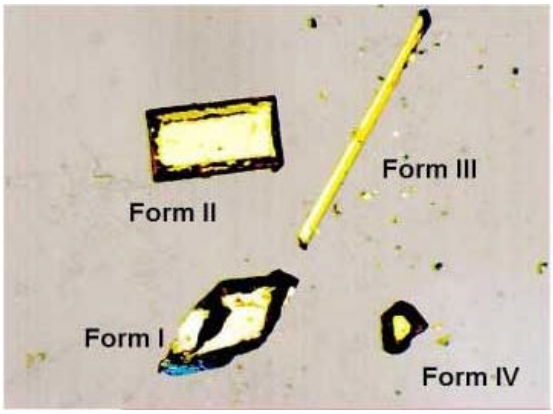


Figure 3.1: Crystal morphology of four forms of 4-amino-3,5-dinitrobenzamide.

The crystallographic details are given in Table 3.2. Further, taking into account the growing interest of employing hydrothermal techniques, which is quite versatile for the synthesis of organic-inorganic hybrids,[19] its applicability to polymorphism studies was

Table 3.1 Crystallization experiments performed on 4-amino-3,5-dinitrobenzamide.

Solvent	Solubility	Crystallization method	Crystal Form
methanol	Soluble	SE at RT and at (5 ^{o}C)	Form II
acetonitrile	Soluble	SE	Form II
acetone	Soluble	SE at RT and at (5 ^{o}C)	Form II
ethanol	Soluble	SE	Form II
propanol	Soluble	SE	Form II
1-butanol	Soluble	SE	Form II
2-butanol	Soluble	SE	Form II
2-propanol	Soluble	SE	Form II
THF	Soluble	SE at RT and at 5 ^{o}C	Forms I and II
pyridine	Soluble	SE	Form II
DMF	Soluble	SE	Form II
DMSO	Soluble	SE at RT and at 5 ^{o}C	Form II
Acetyl acetone	Soluble	SE	Form II
nitrobenzene	Soluble	SE	Form II
chlorobenzene	Soluble	SE	Form II
nitromethane	Soluble	SE	Form II
chloroform	Sparing	SE	Form II
DCM	Sparing	SE	Form II
carbontetrachloride	Sparing	SE	Form II
dichloroethane	Sparing	SE	Form II
ethyl acetate	Sparing	SE	Form II
benzene	Sparing	SE	Form IV
1,4-dioxane	Sparing	SE	Form II
water	Sparing	SE at RT and at 5 ^{o}C	Form II
acetic acid	Sparing	SE	Form II
trifluroacetic acid	Sparing	SE	Form II
diethyl ether	Insoluble	-	-
toluene	Insoluble	-	-
cyclohexane	Insoluble	-	-
hexane	Insoluble	-	-
Methanol	Soluble	VD/ether	Form II
acetone	Soluble	VD/benzene	Form II
acetonitrile	Soluble	VD/Toluene	Form II
benzene	Sparing	VD/ether	Form II
water	Sparing	Hydrothermal method	Form III
Methanol/benzene	Soluble	Solvothermal method	Form II
Methanol/benzene	Soluble	Solvothermal method	Form III

SE – Solvent Evaporation, **VD** – Vapour Diffusion

explored, as such attempts are not found in the literature. Thus, an aqueous solution of **ADNBA** kept in an autoclave, gave single crystals having different unit cell dimensions than the other forms without any solvent molecule/s, as characterized by X-ray diffraction methods (Table 3.2). It is, indeed, rather surprising that the crystallization of **ADNBA** from water at ambient conditions did yield the form corresponding to the crystals obtained from methanol. We labeled the forms obtained from THF, methanol, hydrothermal technique and benzene as Forms I, II, III and IV respectively. ORTEP drawings for all the four forms are shown in Figure 3.2. At the outset, it is noteworthy to mention that in all the four forms, intramolecular N-H···O hydrogen bond exists between -NH_2 and -NO_2 groups.

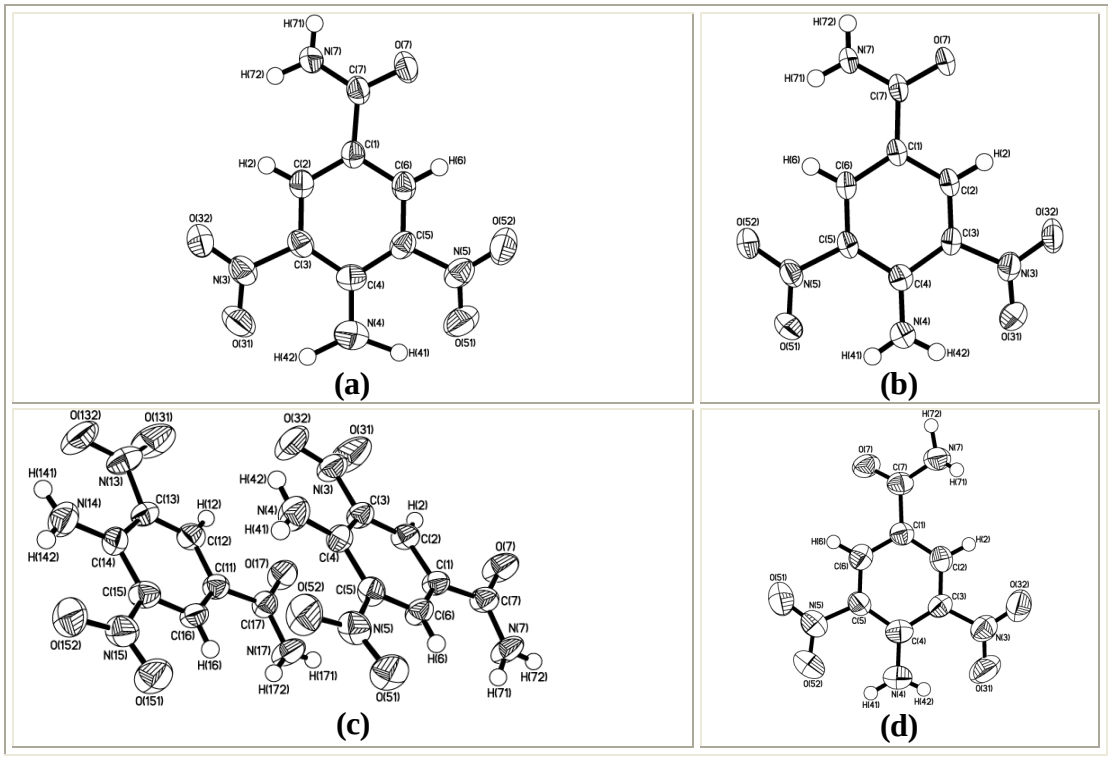


Figure 3.2: ORPEP drawings of (a) Form I, (b) Form II, (c) Form III and (d) Form IV.

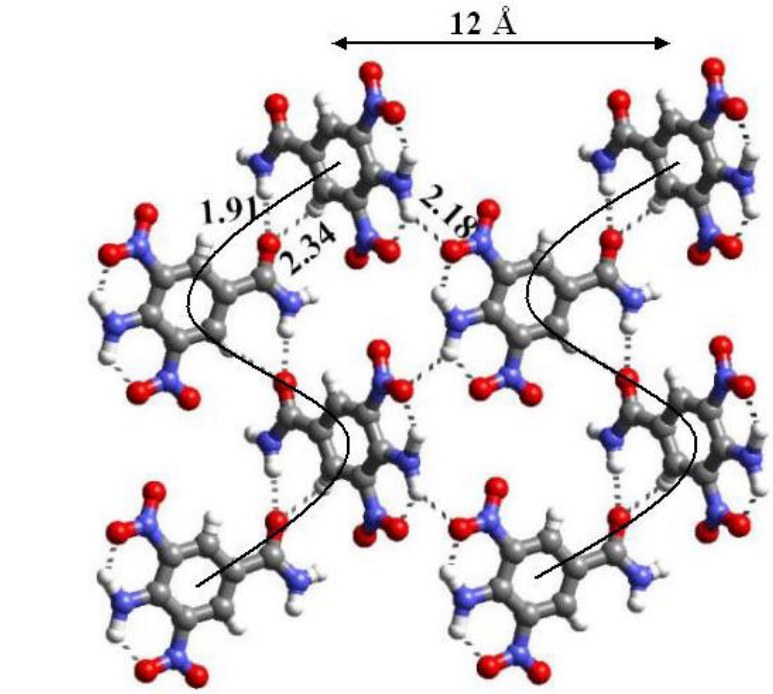
Table 3.2 Crystal data of Forms I, II, III and IV of 4-amino-3,5-dinitrobenzamide.

	Form I	**Form II**	**Form III**	**Form IV**
Formula	$C_7H_6N_4O_5$	$C_7H_6N_4O_5$	$C_7H_6N_4O_5$	$C_7H_6N_4O_5$
Fw	226.16	226.16	226.16	226.16
Crystal habit	hexagonal blocks	rectangular blocks	plates	small blocks
Crystal color	yellow	yellow	yellow	yellow
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	$P2_1/n$	$Pbca$	$P2_1/c$	$P2_1/c$
a(Å)	7.910(2)	9.983(2)	8.564(2)	13.968(4)
b(Å)	12.419(3)	10.919(2)	8.845(2)	7.608(2)
c(Å)	9.539(2)	16.054(3)	23.778(5)	8.663(2)
a(deg)	90	90	90	90
ß(deg)	111.78(1)	90	98.58(1)	94.19(1)
?(deg)	90	90	90	90
V(Å^3)	870.2(4)	1750.0(6)	1781.0(7)	918.1(4)
Z	4	8	8	4
D_{calc}(g cm^{-3})	1.726	1.717	1.687	1.636
µ (mm^{-1})	0.149	0.149	0.146	0.142
2? range (deg)	46.58	46.52	46.56	46.60
Limiting indices	-8 = h = 8 -13 = k = 13 -10 = l = 10	-11 = h =11 -12 = k = 12 -17 = l = 13	-8 = h = 9 -9 = k = 9 -26 = l = 23	-15 = h = 15 -8 = k = 8 -9 = l = 9
F(000)	464	928	928	464
Total reflns	5295	6987	7490	7284
No. unique reflns [R(int)]	1255[0.0239]	1256[0.0299]	2564[0.0420]	1324[0.0725]
No. reflns used	1087	1076	1697	586
No. parameters	169	169	338	169
GOF on F^2	1.070	1.045	1.036	0.765
R1[I>2s(I)]	0.0379	0.0320	0.0575	0.0439
wR2	0.1064	0.0844	0. 1216	0.0783

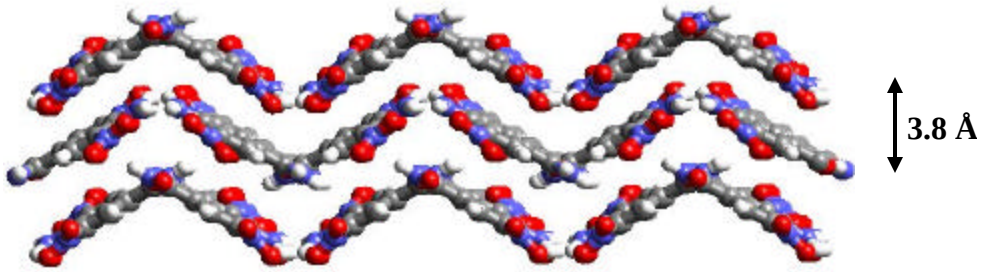
Final diff. Fouriermap (e^-. $Å^{-3}$) max, min	0.167, -0.175	0.200, -0.227	0.212, -0.252	0.180, -0.187

3.2.1 Preparation and structural analysis of Form I

Crystallization of **ADNBA** from a THF solution, by slow evaporation method, gave block-like, yellow colored crystals suitable for single crystal X-ray diffraction. Structural analysis revealed that the adjacent molecules of **ADNBA** interact through catemeric or single N-H···O hydrogen bond (H···O, 1.91 Å). The arrangement is shown in Figure 3.3(a).



(a)



(b)

Figure 3.3: (a) Two-dimensional arrangement of molecules in Form I. (b) Three-dimensional arrangement in the crystal structure of Form I.

Further, each oxygen atom of amide group forms C-H···O hydrogen bond (H···O, 2.34 Å) with an aromatic hydrogen atom. Such an arrangement constituted a helical chain network and the adjacent chains are connected to each other through a N-H···O hydrogen bond (H···O, 2.18 Å) formed between $-NH_2$ and $-NO_2$ groups, leading to the formation of corrugated sheet structure in three-dimension (see Fig. 3.3(b)). The corrugated sheets were hold together by p-p interactions with a distance of 3.8 Å in three-dimensional arrangement.

3.2.2 Preparation and structural analysis of Form II

Crystallization of **ADNBA** from methanol and many other organic solvents (Table 3.1) gave yellow colored rectangular crystals. The ensemble of molecules forms a crinkled sheet structure, stabilized by p-p interactions with a distance of 3.6 Å, arrange in three-dimension as shown in Figure 3.4(a). The arrangement of molecules in a typical sheet structure is shown in Figure 3.4(b). The adjacent molecules recognize each other through the formation of catemeric N-H···O hydrogen bond like in Form I (compare with Figure 3.3(a)) constituting helical chains. All the N-H···O hydrogen bonds in Form II are longer than that in Form I. Further, the chains are held together by N-H···O hydrogen bonds. A close observation of the arrangement of molecules, in Form I and II, reveals that within the sheets, the chains are packed more densely along the direction of the formation of layers in Form II (see Figure 3.5). As a result, the distance between the molecules of adjacent chains is less in Form II (~10 Å) when compared to

Form I (~12 Å). Thus, Forms I and II are iso-structural (structural polymorphs) with identical nature of intermolecular interactions except for the length of the hydrogen bonds, although crystallographic differences do exist between the two forms (see Table 3.2).

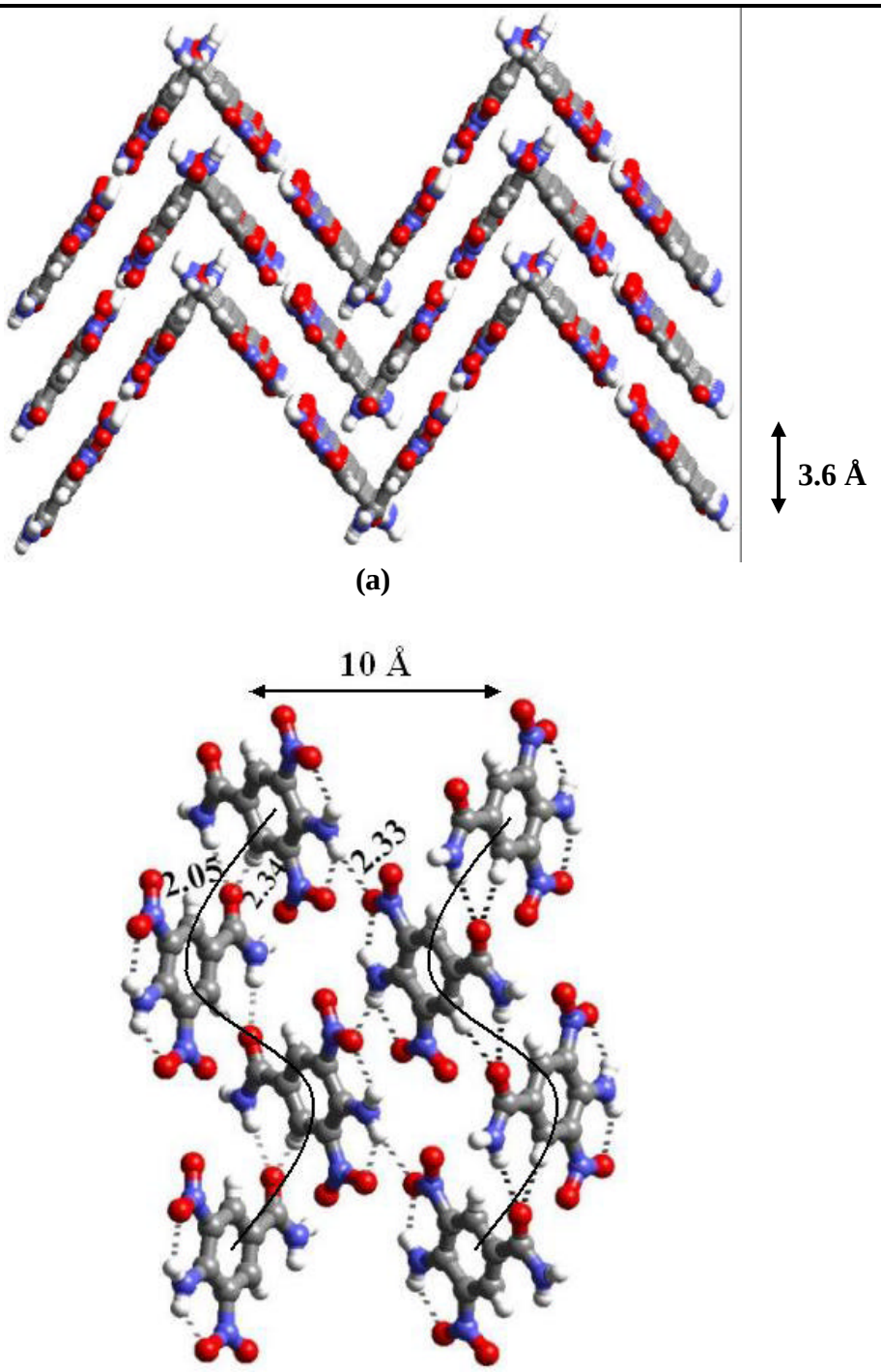


Figure 3.4: (a) Three-dimensional arrangement in Form II. (b) Arrangement of molecules in a typical sheet structure in Form II.

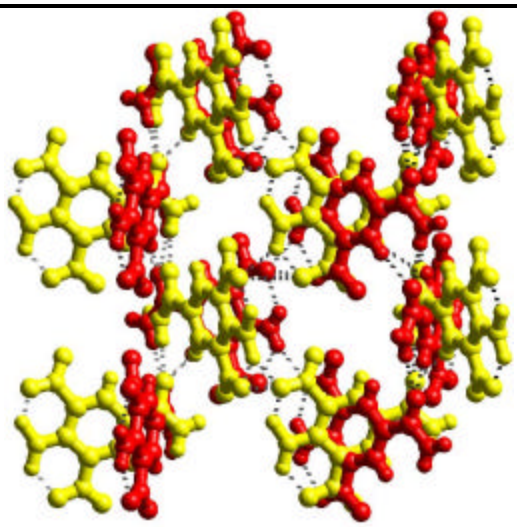
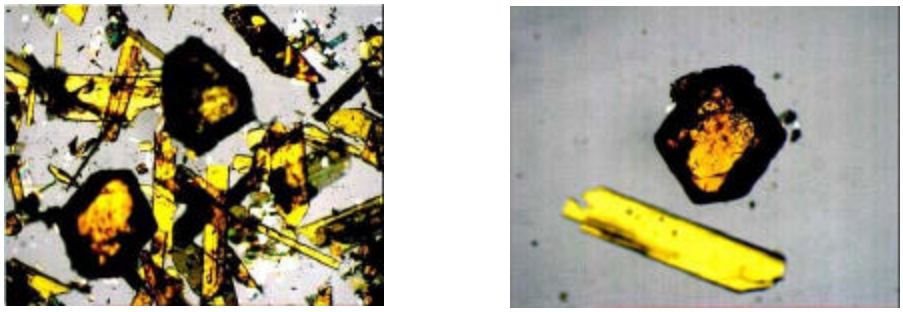


Figure 3.5: Overlay diagram showing the arrangement of molecules in two-dimensions in Form I (yellow) and Form II (red).

Furthermore, we observed that Forms I and II also obtained as concomitant forms (see Fig. 3.6) in co-crystallization experiments of **ADNBA** with different amide and acid compounds. It may be perhaps due to the structural similarity between the two forms, as it is known in the literature that such closely related structures could be prepared concomitantly by introducing subtle variations.[7b, 20] In the present case, the other amide and acid components might have influenced the crystallization process as additives leading to the formation of Forms I and II concomitantly.



(a) **(b)**

Figure 3.6: Two different morphologies of the crystals obtained concomitantly corresponding to polymorphs of Forms I (hexagonal blocks) and II (thin plates) of **ADNBA**; (b) isolated single crystals of Forms I and II of **ADNBA**.

3.2.3 Preparation and structural analysis of Form III

Crystal structure determination of the single crystals, obtained by hydrothermal technique reveals that asymmetric unit consists of two molecules of **ADNBA** unlike Forms I and II which contains only one molecule in the asymmetric units (see Figure 3.2). In Form III, in contrast to the Forms I and II, the adjacent molecules are held together by dimeric motif formed by N-H···O hydrogen bonds, a well known recognition pattern between the amide groups. The arrangement is shown in Figure 3.7(a).

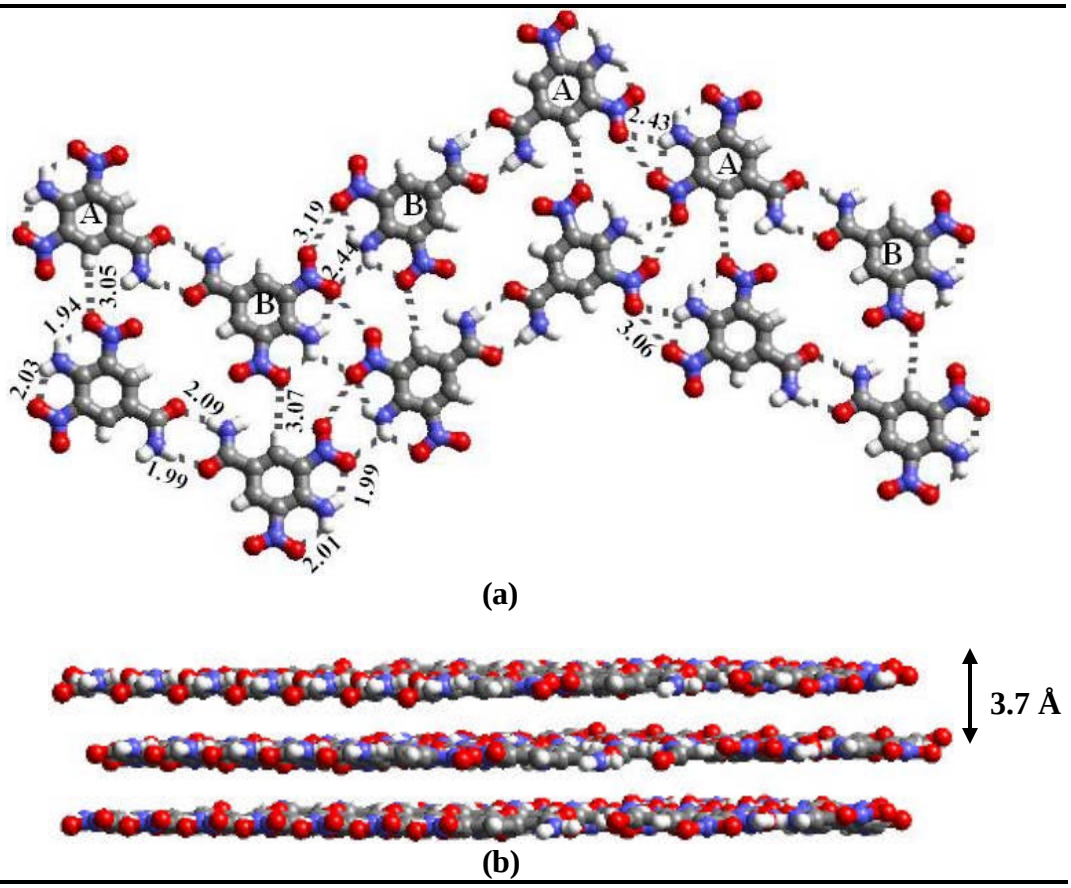
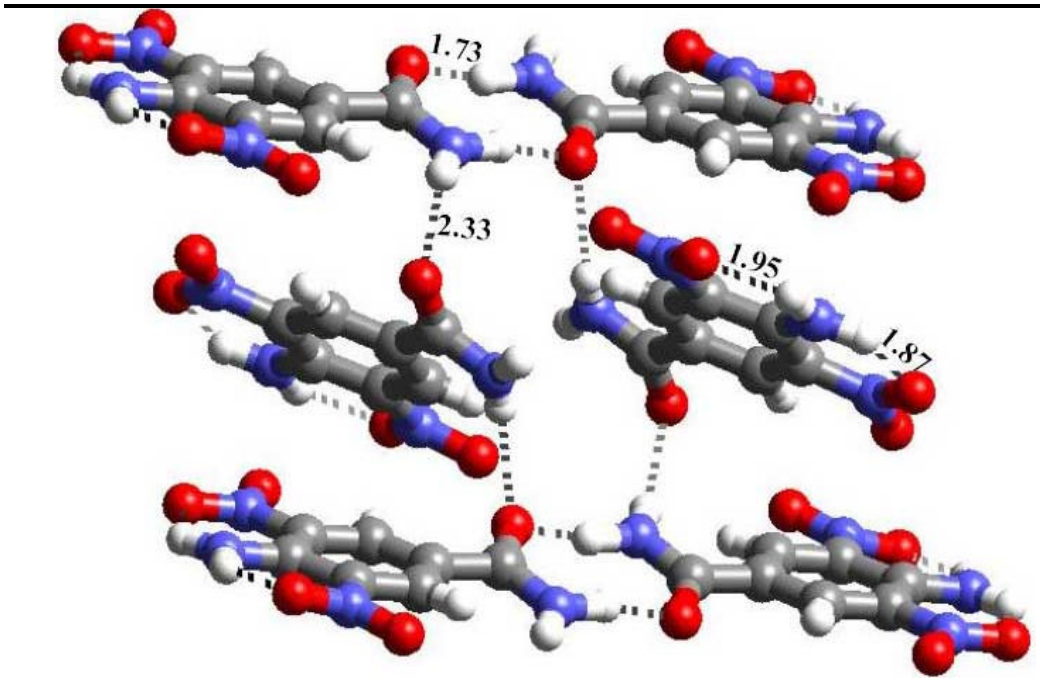


Figure 3.7: (a) Interaction between the molecules in two-dimension in Form III. Notice the formation of a dimer in contrast to a catemer observed in Forms I and II. (b) Stacking of layers in three-dimensional arrangement.

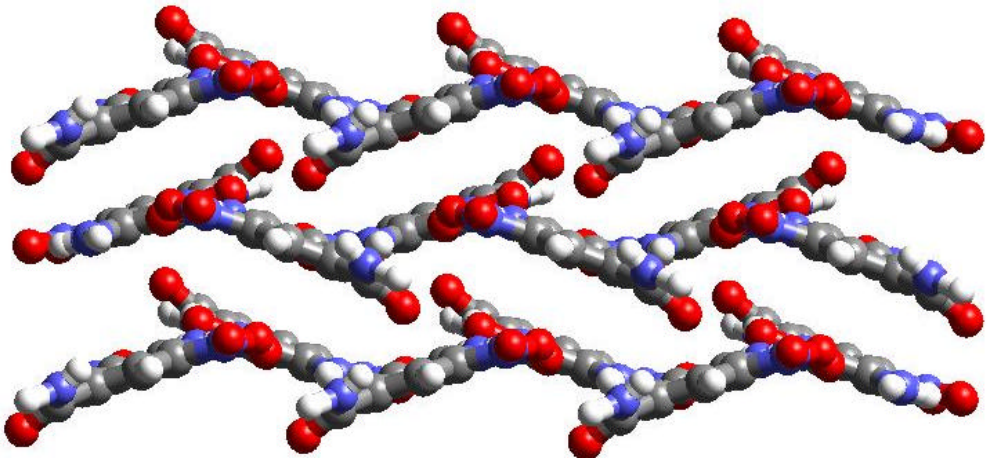
The dimers are formed between symmetry independent molecules, denoted as A and B, through a non-centrosymmetric N-H···O hydrogen bonded coupling with H···O distances of 1.99 and 2.09 Å. Further, the adjacent dimers interact through N-H···O hydrogen bonds formed as a result of the interactions between $-NH_2$ and $-NO_2$ groups. Thus, a one-dimensional zigzag tape with ABBAAB… arrangement prevails in the structure of Form III. Such adjacent tapes interact with each other through C-H···O hydrogen bonds (H···O, 3.05 and 3.07 Å). The molecular ensemble, thus, forms a planar sheet structure and stacks in three-dimensions, stabilized by **p-p** interactions (see Fig. 3.7(b)) with distance between the adjacent sheets is being 3.7 Å.

3.2.4 Preparation and structural analysis of Form IV

Form IV is obtained by the crystallization of **ADNBA** from a benzene solution by slow evaporation method. Packing analysis reveals that Form IV has a quite distinct feature with the incorporation of both the types of hydrogen bonding patterns of the amide compounds – catemer and dimer. Arrangement of molecules is shown in Figure 3.8 (a). The adjacent molecules related by inversion symmetry form dimers through $R_2^2(8)$ pattern consisting of N-H···O hydrogen bonds, formed by *syn* H atoms of amide group, with a H···O distance of 1.73 Å. These dimers further interact with each other through catemeric hydrogen bonding involving the *anti* H atom of the amide group forming N-H···O hydrogen bond with a H···O distance of 2.33 Å. As a result, both cyclic as well as acyclic hydrogen bonds, as observed in 3,5-dinitrobenzamide, stabilize the structure. In three-dimensions, the ensemble yields a herringbone pattern as shown in Figure 3.8(b).



(a)



(b)

Figure 3.8: Arrangement of molecules of **ADNBA** in Form IV in (a) two and (b) three-dimensions.

Encouraged by the result obtained with the preparation of four polymorphs, further studies were carried out to evaluate the physical properties, stability, relative energy of the forms, etc. The observations revealed several salient properties of the

forms as described in the following sections. In the process of determining the melting point of the four polymorphs, surprisingly, we found that all the forms melt at the same temperature (254 - 256 ^{o}C), despite the distinct differences in the crystal packing and nature of intermolecular interactions. This exciting observation lead to study thermal behavior of the forms in detail by hot-stage microscopy (HSM), differential scanning calorimetry (DSC), powder X-ray diffraction (PXRD) methods.

3.3 Hot-Stage Microscopy (HSM) analysis

The variations observed in the crystals during heating were recorded and represented in Figure 3.9. Crystals of Form I did not show any visual changes such as in its morphology, color etc., (see Figure 3.9) during heating of the crystals and melting occurred at 254 ^{o}C and upon cooling the melt recrystallized at 216 ^{o}C. In the case of crystals of Form II, however, around 175-176 ^{o}C, quite remarkable changes were observed in its color (Figure 3.9) and eventually melted at 254 ^{o}C (m. p. of Form I) and subsequently recrystallized at 214 ^{o}C just like observed in Form I. Similarly, Forms III and IV crystals showed changes in crystal characteristics before melting, but at different temperatures than in Form II. In Form III, the change in crystal characteristics were observed around 225 ^{o}C, while, Form IV showed changes around 185 ^{o}C. However, both the Forms III and IV melted and recrystallized around the same temperature as observed in Form I and II. Thus, hot stage microscopy analysis suggests a phase transition in the Forms II, III, and IV, possibly to Form I. To explore further the nature of phase transition, differential scanning calorimetry (DSC) measurements were carried out.

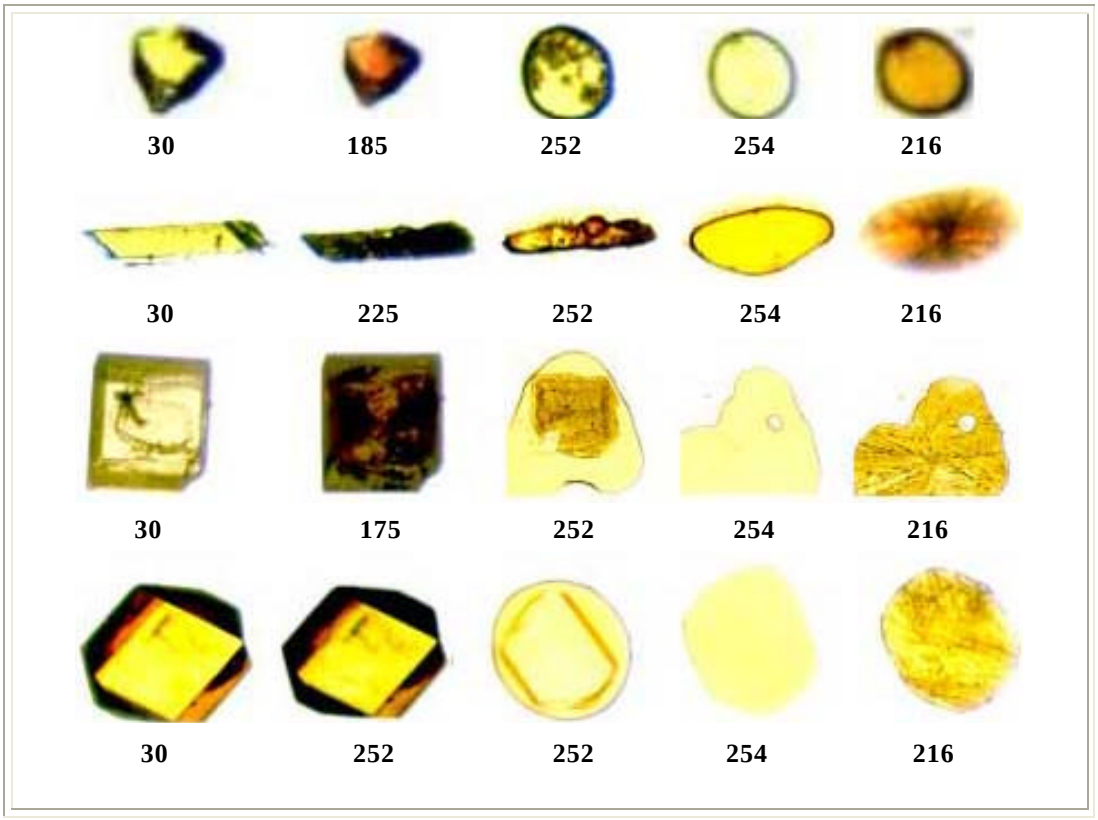
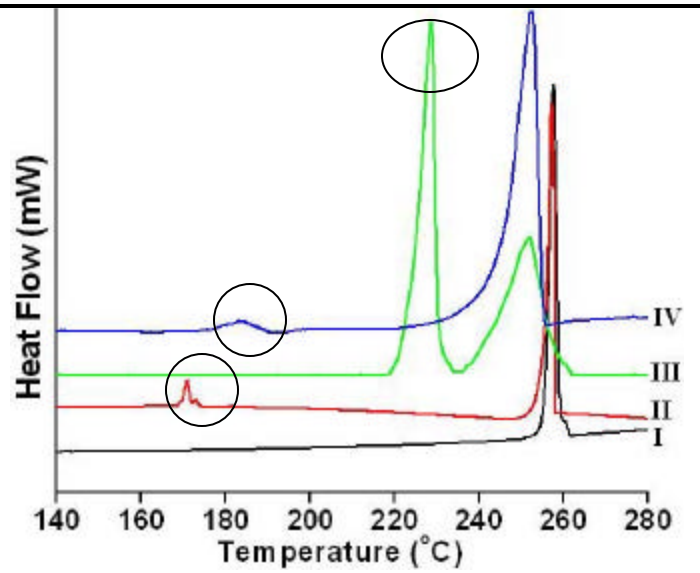


Figure 3.9: Hot stage microscopy pictures at different temperatures (^{o}C) during the heating of Forms I-IV (bottom to top). Heat progress is from left to right and last picture in each row is recrystallization temperature of melt during cooling.

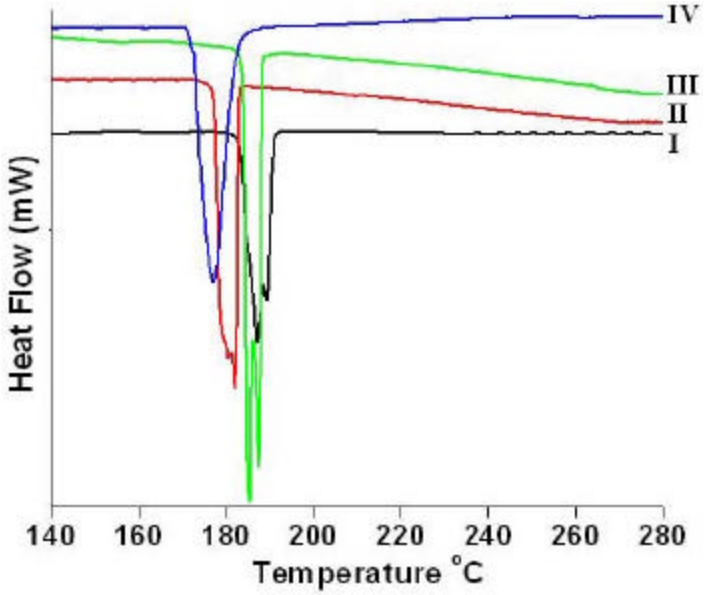
3.4 Differential Scanning Calorimetry (DSC) analysis

It is evident from Figure 3.10(a) that no changes were observed in the energy profile for Form I, except a sharp endothermic peak at 257 ^{o}C, which is due to the melting of Form I. However, for Form II (Fig. 3.10(a)) two endothermic peaks (172 and 257 ^{o}C) were observed. Since the latter peak corresponds to the melting point of Form I, it suggests that a phase transition of Form II ? I might have occurred at 172 ^{o}C and subsequently melted at 257 ^{o}C. Similarly, for Forms III and IV, two endothermic peaks corresponding to phase transition were observed at 184 and 227 ^{o}C respectively and eventually melting was observed at 257 ^{o}C as shown in Fig. 3.10(a). Further, it was

noted that all the forms recrystallized around the same temperature upon cooling as shown in Fig. 3.10(b). It demonstrated that Forms IV, III and II transformed into I within the solid state, upon heating. This phase transition was further confirmed by performing *insitu* powder X-ray diffraction (PXRD).



(a)



(b)

Figure 3.10: DSC traces of Forms I-IV, (a) heating just above melting point and (b) *insitu* cooling.

3.5 Powder X-Ray Diffraction (PXRD) Analysis

The diffraction patterns for all the four forms recorded at ambient conditions are shown in Figure 3.11. From the initial experiments it is clearly evident that the Forms II, III and IV trasformed into Form I quantitatively much below the melting point as observed from differential scanning calorimetry and hot stage microscopy experiments. So, we preceded further with *insitu* variable temperature powder X-ray diffraction experiments to identify the transition temperatures and also to assess the solid-state behavior after the transformation.

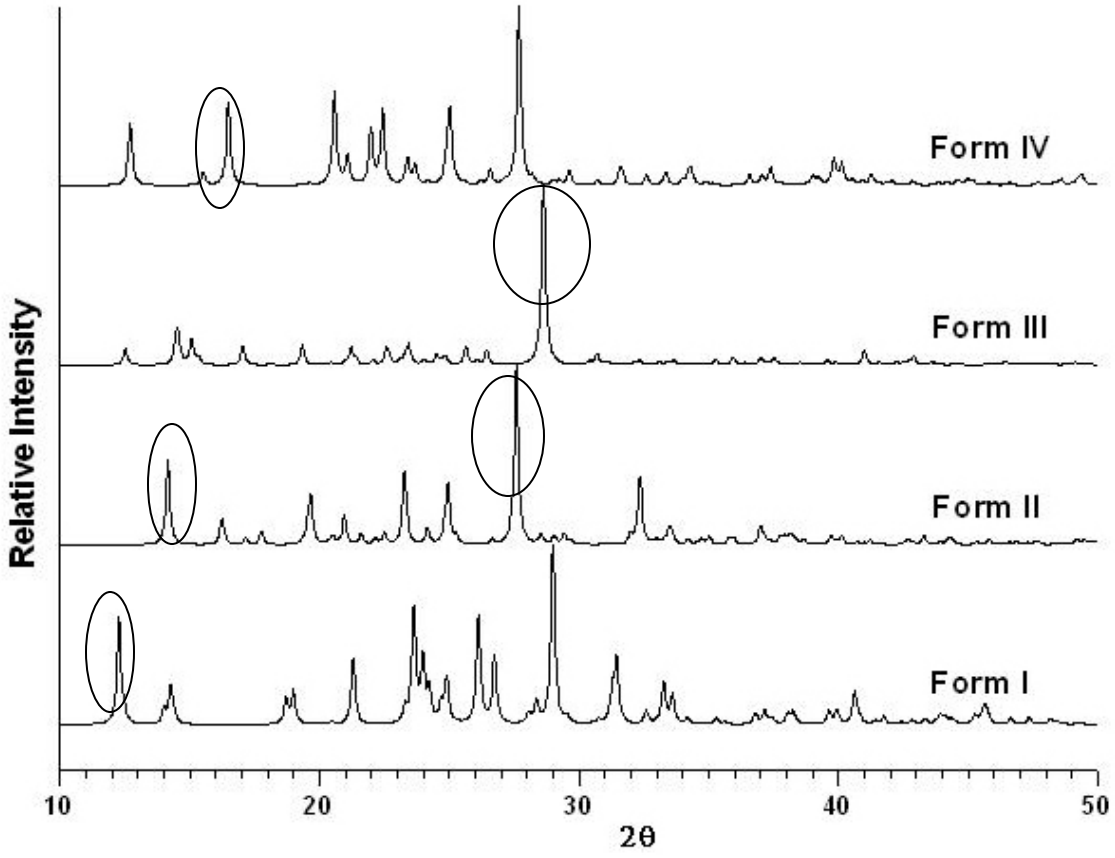


Figure 3.11: Powder X-ray diffractions patterns for (a) Form I (b) Form II (c) Form III and (d) Form IV as obtained from the native crystallization experiments.

3.6 *Insitu* variable temperature Powder X-Ray Diffraction (PXRD) analysis

Insitu diffraction patterns of powder samples of Forms I – IV are shown in Figure 3.12. It is clearly evident from the Figure 3.12 that Form I did not show any phase transition as the position and intensity of the peaks did remain intact throughout the process, irrespective of the temperature variations. However, phase transition of Forms II, III and IV to Form I is evident from the appearance of new peaks during the heating. The transformations are shown in blue in Figure 3.12. The patterns in blue are exactly identical with that of the patterns shown in Figure 3.12 for Form I. This unequivocally confirms the transition of Forms II, III and IV into I before the melting of the forms. In Form II, the transition is observed in between 170-180 ^{o}C (with the appearance of the new peaks at the 2? of 12, 18, 27^{o} and disappearance of peaks at 16, 18, 32^{o}), while similar transformation is observed for Form III in between 220-230 ^{o}C with a clear observation of the characteristic peaks of Form I in the above mentioned 2? positions. However, in Form IV, such a transformation was found in between 180-190 ^{o}C. Thus, polymorphic transformations were well characterized with a high degree of correlation of transition temperature from different experiments as tabulated in Table 3.3. It is further observed that Form I is stable as no reversible transition was observed during cooling as well. Taking into account the polymorphic transformations within the solid state and also the close similarities between the forms in their structural arrangements, especially Forms I and II, further focus on the investigations on single crystals reveals that Form II converted topotactically to Form I around 170 ^{o}C, while, Forms III and IV showed degradation. Detailed methodology and observations are as discussed below.

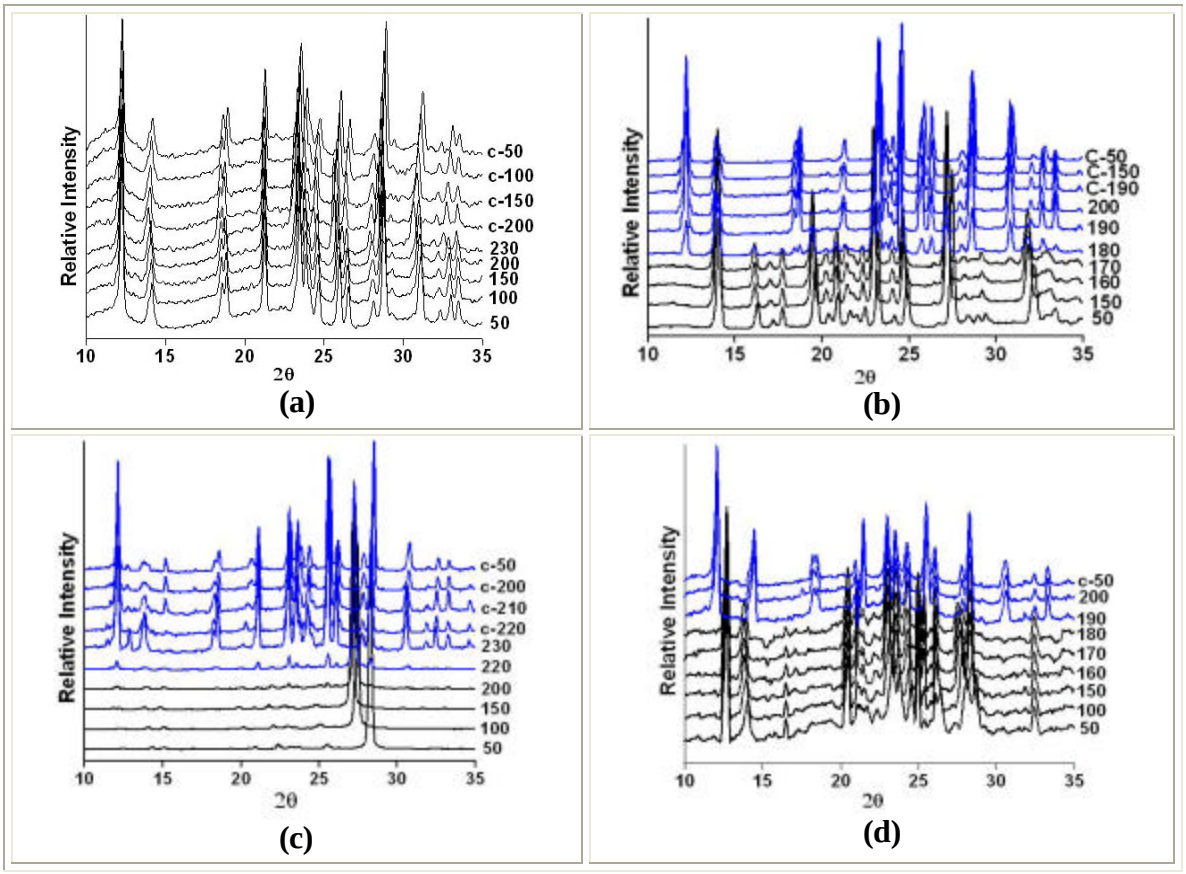
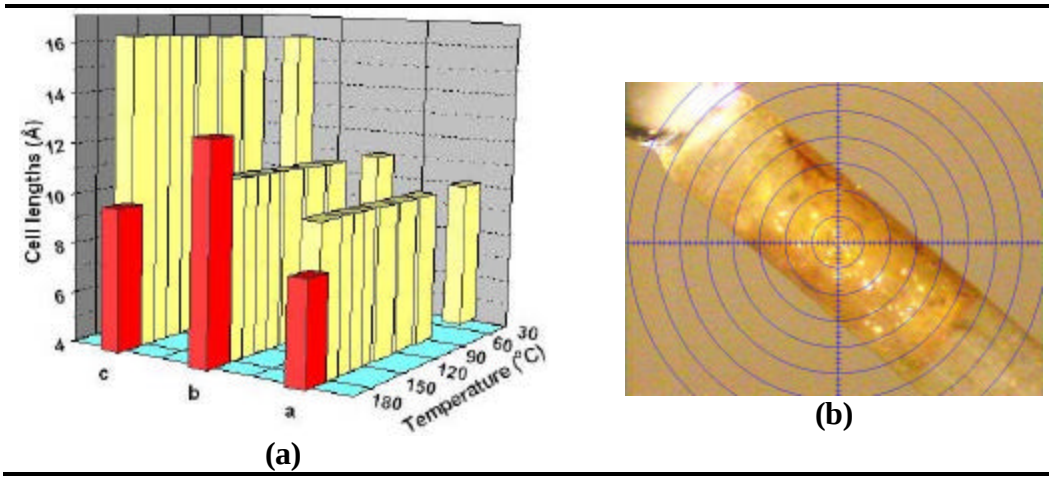


Figure 3.12: Variable temperature powder X-ray diffraction patterns for the polymorphs of a) Form I, b) conversion of Form II-I, c) conversion of Form III-I and d) conversion of Form IV-I. Patterns during cooling are prefixed with 'c'.

3.7 Single-crystal-to-single-crystal polymorph transformations

Single crystals of Form I did not show any changes in the unit cell dimensions upon heating even up to 200 ^{o}C. Thus, further demonstrates the stability of Form I. However, single crystals of Form II showed sudden change in the unit cell parameters in the temperature range 167-177 ^{o}C which correspond to Form I (monoclinic), as shown in Figure 3.13 in red. Further, the intensity data collected at 177 ^{o}C refined to a R-factor of 4.9 %, without any complications with the molecular packing as shown in Figure 3.3. Thus, transformation II? I was found be to topotactic unambiguously. In

contrast, Forms III and IV, however, did remain intact without any changes up to 175 ^{o}C but after that the diffraction pattern failed to converge to yield unit cell. This may be attributed to the facts that since, Forms III and IV show a large structural deviation from that of Form I, for example, transformation of dimeric hydrogen bonding between amides into a catemeric hydrogen bonding, which requires higher degree of freedom for reorientation of molecules than one would find in the constructional solid state environment. In fact, higher phase transition temperature for Form III is also indicative of lattice relaxation before transformation occurs.



(a) **(b)**

Figure 3.13: (a) Variations in the unit cell dimensions during *insitu* heating performed on a single crystal. (b) Color of Form II crystal at 177 ^{o}C mounted by capillary method.

Table 3.3 Transition temperatures (^{o}C) observed for the polymorphic transformations by different analytical methods.

Forms	Hot-stage microscopy	DSC	Variable temp PXRD	SC-SC
I	-	-	-	-
II - I	176	172	170-180	167-177
III - I	225	227	220-230	-
IV - I	185	184	180-190	-

3.8 Conclusions

Four polymorphs of **ADNBA** have been prepared by following conventional as well as non-ambient conditions like hydrothermal crystallization methods and their features have been evaluated by different techniques such as X-ray diffraction, differential scanning calorimetry, hot-stage microscopy etc. All the observed four forms are well differentiated in terms of hydrogen bonding networks (catemer in Forms I and II; dimer in Forms III and IV) formed by -$CONH_2$ moiety. Further, polymorph transformations of **ADNBA** have been reported and *insitu* single-crystal-to-single-crystal transformation (topotactic) has been demonstrated. Further, it could be summarized that all the polymorphs of **ADNBA**, except the Form IV, could be obtained through eco-friendly methods - Form I by heating, Form II by original synthesis and Form III by hydrothermal methods which is important from the view point of green chemistry. The cross over experiments carried out, especially at high temperatures in solid-state, would provide ample opportunities to explore/prepare polymorphs of new compounds or new forms for the existing polymorphic compounds. Careful consideration of the thermal behavior/analysis of polymorphs may provide several insights or information about the relationship among the phases and suggest conditions for growing different polymorphic forms. This strategy may be useful for the exploratory search for polymorphs, the development of robust procedures for obtaining polymorphs by choice. In this study, at least two hundred crystallization experiments were performed and mounted about hundred single crystals for the identification of the four forms and also to study the transformations. Thus, this study also has demonstrated

the reality of the statement that *'polymorphism study is a test of time and patience of the researcher'*.[21]

3.10 Experimental Section

All the chemicals used in this study were obtained from commercial suppliers and used as such without any further purification. Forms I, II and IV were prepared by slow evaporation method in which approximately 20 mg of the compound (**ADNBA**) was dissolved in respective solvents. Form III was obtained by hydrothermal method. A Teflon flask containing an aqueous solution of 20 mL of **ADNBA** (50 mg), placed in a stainless steel autoclave. It was kept in a hot-air oven and heated to 180 ^{o}C for 24 hrs. Single crystals of long needles look-like were obtained upon cooling the apparatus to the laboratory temperature over a period of 6 hr. The experiment is repeated at every 10 ^{o}C decrease in oven temperature i.e., at 170, 160, 150, 140, 130, 120, 110, 100, 90 ^{o}C. Similarly, experiment was repeated by employing various solvents such as methanol, acetone and benzene (solvothermal technique).

In the case of hot stage microscopy experiments, a single crystal of a particular form was placed on a glass slide with a cover slip and the sample was heated at the rate of 10 ^{o}C/min. Observations were made during heating using a Leica microscope equipped with a hot stage attachment. Temperatures at which phase transition occurred, melting started, completely melted and recrystallization occurred were determined by visual observation. For DSC analysis, samples of approximately 4 mg were weighed and encapsulated in flat-bottomed aluminium pans with pressed-on lids. The sample was heated from 30 ^{o}C to 280 ^{o}C at a rate of 10 ^{o}C/min and cooled at the same rate. For

insitu variable temperature PXRD, finely powdered samples 30-35 mg were used. In these experiments, the samples were heated from 50 ^{o}C to either 200 or 230 ^{o}C (below the melting of Form I), at the rate of 10 ^{o}C/min and PXRD patterns were recorded with a scan rate of 2 ^{o}/sec., followed by cooling under similar conditions. Oxford cryo system, attached to Bruker APEX, was made use in characterizing single-crystal-to-single-crystal (sc-sc) phase transition and crystal was mounted by capillary method. A single crystal of Form II that was used for the structure determination at 25 ^{o}C subjected to *insitu* heating and unit cell measurements were carried out at 77, 97, 117, 137, 147, 157, 167, 177 ^{o}C.

3.11 References

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Chapter FOUR

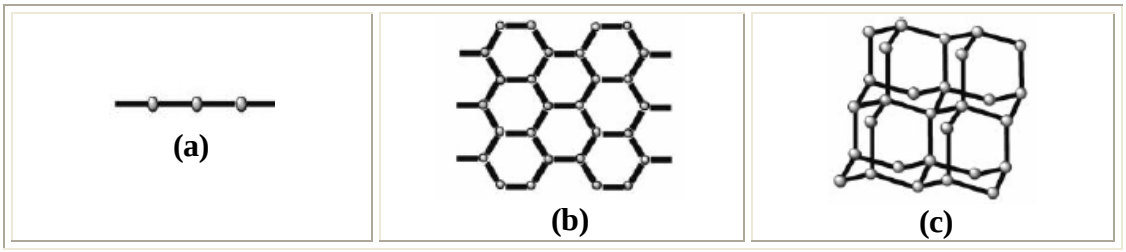
DESIGN AND SYNTHESIS OF SOME PYRIDYLSULFANYL LIGANDS AND THEIR UTILITY FOR THE CREATION OF METAL-ORGANIC FRAMEWORKS

4.1 INTRODUCTION

The synthesis and investigation of novel coordination polymers or metal-organic frameworks (MOFs), may also referred as organic-inorganic hybrid materials, is of current interests in the contemporary supramolecular chemistry.[1-4] Due to rapid advances during the past several years, the field of supramolecular chemistry has progressed to such an extent where a desired network structures can often be synthesized via self-assembly of judiciously selected building blocks under controlled reaction conditions.[5,6] The synthesis of supramolecular coordination networks has been extensively studied in recent years owing to their potential applications as functional materials.[7-9] More significantly, absorption and storage of different gases like H_2, CO_2, N_2, O_2, SO_2, acetylene, etc., are well studied recently in the area of MOFs.[10] Success of such synthesis is critically dependent on identifying chemical units with specific geometry that would assemble into a target structure. Hence, a great interest has been focused on this rapidly expanding field of crystal engineering of one- (1D), two- (2D) and three-dimensional (3D) coordination polymers and much effort has been made towards the connection of suitable building blocks (metal ions with organic linkers) into networks in order to obtain the desired materials.[11-13]

A wide range of infinite coordination polymers such as diamondoid, octahedral, honeycomb, molecular ladders/bilayers and many other frameworks have been reported, especially with bipyridine type rigid, linear, *N,N*-donor spacers.[14] For example, silver and 4,4'-bipyridine (bpy) system exhibits several interesting structural topologies, as shown in Scheme 4.1, depending upon the choice of counter anions.[15] Compared to the rigid and robust organic ligands, there has been a growing interest, in recent times, in

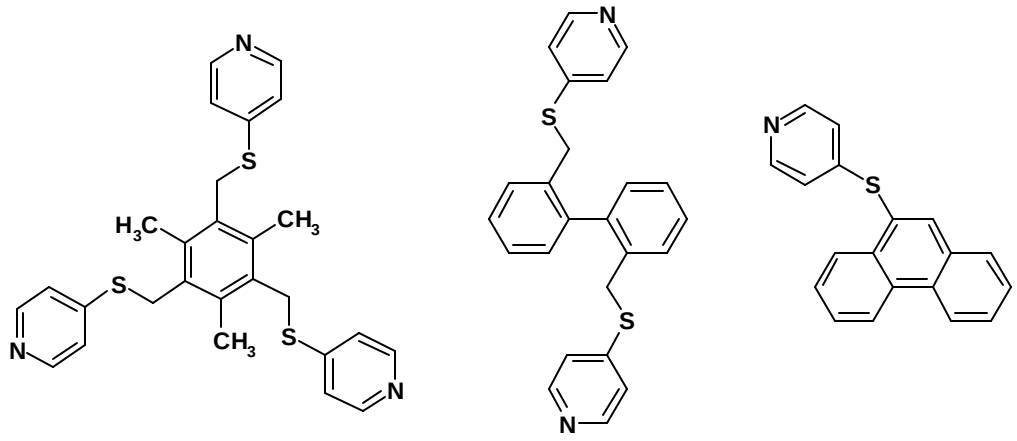
the design and synthesis of flexible ligands and their utilization in the preparation of metal-organic frameworks.[16,17] This chapter focuses on strategies for the design and synthesis of some flexible ligands and their utilization in the construction of metal-organic frameworks.



Scheme 4.1: Schematic representation of various structural topologies (a) 1D chain, (b) 2D honeycomb network and (c) 3D diamondoid nework.

In continuation of creation of supramolecular assemblies employing different types of ligands,[18] synthesis of some pyridylsulfanyl flexible ligands (Chart 4.1) and to study the influence of such flexible armed molecules for the creation of novel supramolecular assemblies with tailor-made properties have been carried out. The solid-state structures of the new multi-armed molecules are of interest, because of the possibility of more than one conformation which may yield different products. Thus, some of the pyridylsulfanyl compounds (see Chart 4.1) 1,3,5-tris(4-pyridylsulfanylmethyl)-2,4,6-trimethylbenzene, **L_1**, 2,2'-bis(4-pyridylsulfanylmethyl)-1,1'-biphenyl, **L_2**, 9-(4-pyridylsulfanyl)phenanthrene, **L_3,** were synthesized as well as their solid-state structures have been determined by X-ray crystallographic methods.

Chart 4.1



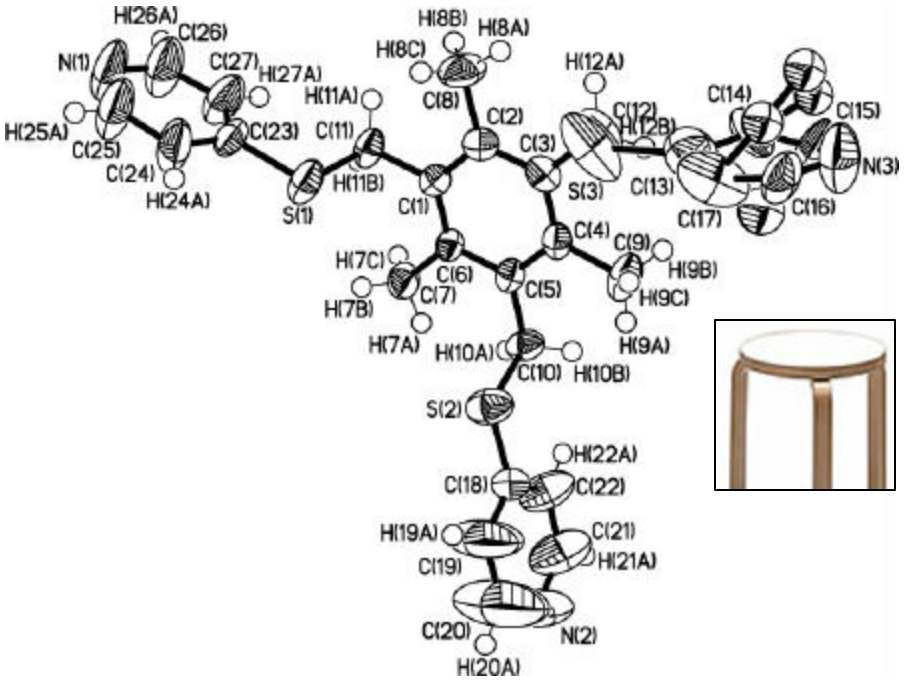
(L_1) (L_2) (L_3)

4.2 Synthesis and Self-assembly of Pyridylsulfanyl Ligands

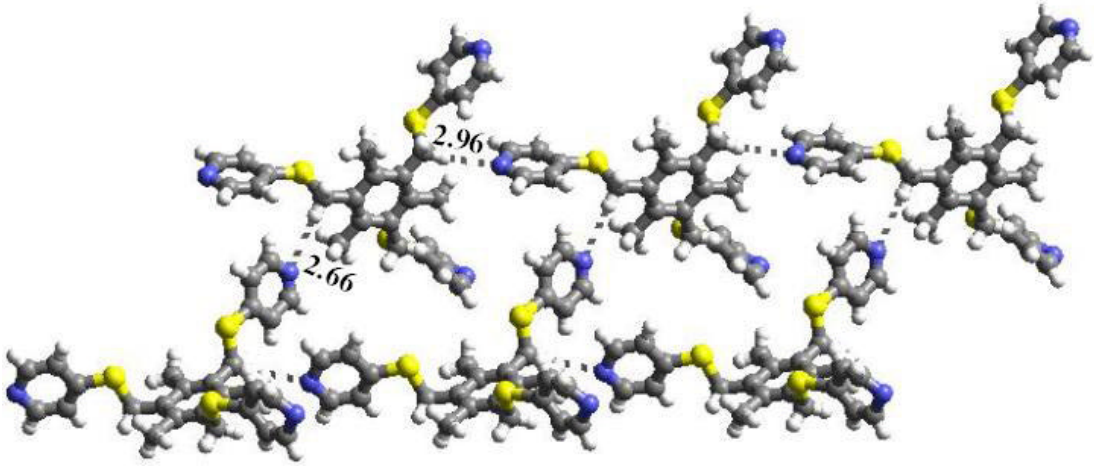
4.2.1 Solid-state structure of 1,3,5-tris(4-pyridylsulfanylmethyl)-2,4,6-trimethyl benzene, L_1

The ligand **L_1** crystallizes in a monoclinic system with one molecule in the asymmetric unit, as shown in Figure 4.1(a), with one of the three pyridyl moieties is disordered, and the ligand **L_1** adopts *cis, cis, cis* – conformation i.e., the three thio pyridyl groups lie on the same side of the plane of the central benzene ring and looks like a three legged stool as shown in the inset (Figure 4.1(a)). Full crystallographic details are given in Table 4.1. The arrangement of molecules in two-dimensions is shown in Figure 4.1(b) and we omitted disordered orientation of the pyridyl moiety for the purpose of clarity. The adjacent molecules interact through C-H···N hydrogen bonds, formed between the pyridyl -N atoms and methylene hydrogen atoms, with H···N distance of 2.66 and 2.96 Å. Such an association led to the formation of a layered

structure due to the self-assembly of the molecules into quartets with void space, which is being filled by the bulky pyridyl moieties (Figure 4.1(b)).



(a)



(b)

Figure 4.1: (a) ORTEP drawing of 1,3,5-tris(4-pyridylsulfanylmethyl)-2,4,6-trimethylbenzene. (b) Self-assembly of molecules in the crystal structure of $\mathbf{L_1}$ into sheet network. Dashed lines represent C-H···N hydrogen bonds.

4.2.2 Solid state structure of 2,2'-bis(4-pyridylsulfanylmethyl)-1,1'-biphenyl, L_2

The ligand, $\mathbf{L_2}$, crystallizes into a triclinic space group *P*? and the full crystallographic details are given in Table 4.1. The molecules are fully ordered in the ligand $\mathbf{L_2}$ unlike in $\mathbf{L_1}$. The asymmetric unit is shown in Figure 4.2. The two-phenyl moieties of biphenyl core are approximately arranged in perpendicular direction to each other.

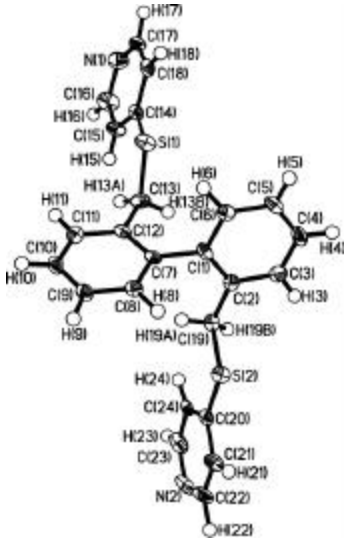


Figure 4.2: ORTEP drawing of asymmetric unit in the crystal structure of $\mathbf{L_2}$.

The adjacent molecules interact with the surrounding ones through C-H···N hydrogen bonds (H···N, 2.47 Å) as it was observed in $\mathbf{L_1}$. However, in the structure of $\mathbf{L_2}$, the hydrogen bonds are formed between pyridyl -N atoms and -CH group of pyridyl moieties rather than by methylene groups. Thus, cyclic networks of dimers are present in the crystal structure of $\mathbf{L_2}$, as shown in Figure 4.3(a). Such dimers are further held together through C-H···N hydrogen bonds (H···N, 2.69 Å) using methylene hydrogen atoms and pyridyl -N atoms constituting a bracelet network, as shown in Figure 4.3(b). The molecules arrange in three-dimensions as shown in Figure 4.4.

Table 4.1 Crystallographic data of Ligands **L_1**, **L_2** and **L_3**

	L_1	**L_2**	**L_3**
Formula	$C_{27}H_{27}N_3S_3$	$C_{24}H_{20}N_2S_2$	$C_{19}H_{13}NS$
Fw	485.66	400.54	287.36
Crystal habit	blocks	blocks	blocks
Crystal color	colorless	colorless	colorless
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	*P*?	$P2_1$
a (Å)	13.385(1)	9.337(5)	9.223(4)
b (Å)	9.443(7)	9.923(5)	5.517(2)
c (Å)	20.324(15)	12.939(6)	14.147(6)
a (deg)	90	110.52(1)	90
ß (deg)	104.41(1)	94.01(1)	105.20(1)
? (deg)	90	113.29(1)	90
V(Å^3)	2488(3)	1000.5(9)	694.7(5)
Z	4	2	2
D_{calc}(g cm^{-3})	1.297	1.330	1.374
T(K)	298	298	298
Mo ka	0.71073	0.71073	0.71073
µ (mm^{-1})	0.318	0.278	0.224
2? range (deg)	47.18	46.70	46.74
Limiting indices	-14 = h = 14 -10 = k = 10 -22 = l = 22	-10 = h = 10 -10 = k = 11 -11 = l = 14	-10 = h = 10 -6 = k = 6 -15 = l = 15
F(000)	1016	420	300
No. reflns measured	20100	4232	5846
No. unique reflns [R(int)]	3636 [0.0475]	2844 [0.0349]	2001[0.0466]
No. reflns used	2845	2332	1916
No. parameters	318	333	185
GOF on F^2	1.734	1.144	1.214
R1[I>2s(I)]	0.0993	0.0717	0.0506
wR2	0.2603	0.1595	0.1110
Final diff. Fouriermap (e$^-$. Å^{-3}) max, min	0.881, -0.734	0. 359, -0. 408	0.197, -0.173

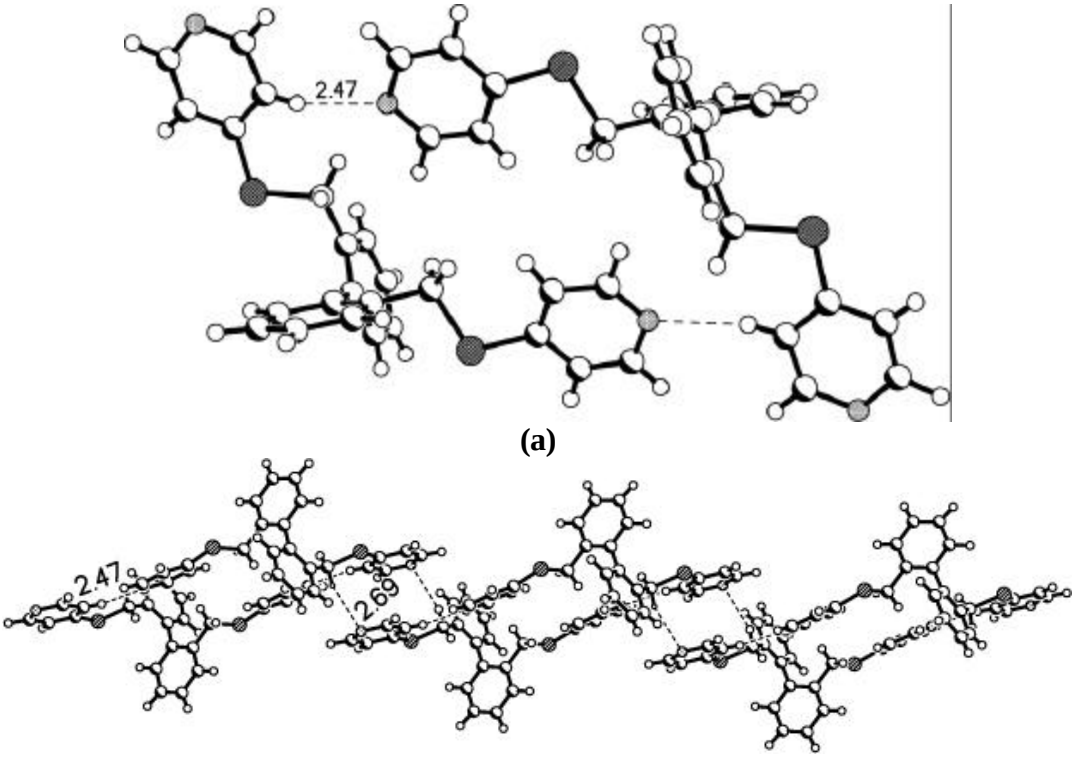


Figure 4.3: (a) Dimers of molecules of $\mathbf{L_2}$ formed through C-H···N hydrogen bonds. (b) packing of molecules into infinite tapes in one-dimension.

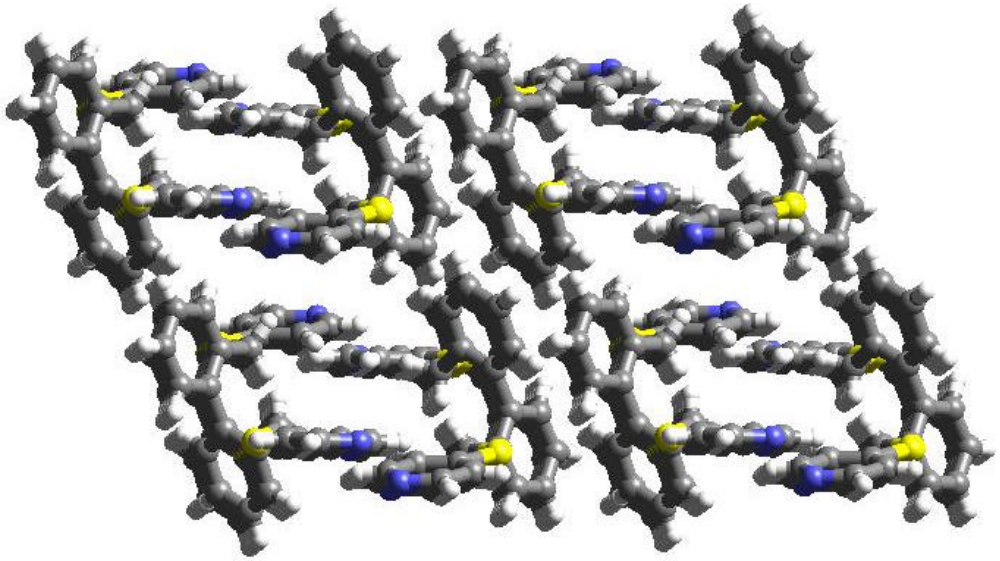


Figure 4.4: Arrangement of ligand molecules, $\mathbf{L_2}$ in three-dimensions.

4.2.3 Solid state Structure of 9-(4-pyridylsulfanyl)phenanthrene, $\mathbf{L_3}$

Compound $\mathbf{L_3}$ crystallizes in a non-centrosymmetric and chiral space group ($P2_1$), unlike $\mathbf{L_1}$ and $\mathbf{L_2}$, which are centrosymmetric ($P2_1/n$ and $P?$, respectively). The asymmetric unit is shown in Figure 4.5. The salient features of the crystal structure parameters are given in Table 4.1. The molecules recognize each other through C-H···N hydrogen bond with a H···N distance of 2.64 Å with nitrogen atom of pyridine ring and hydrogen atom of phenanthrene group. Thus, in accordance with the chiral space group, the arrangement of molecules leads to the formation of helical assembly (single stranded right handed) as shown in Figure 4.6(a). In addition, the structure is stabilized by C-H···p interactions, with a H···p distance of 3.4 - 3.7 Å, which exists between the adjacent helical chains. The arrangement of molecules in three-dimension is shown in Figure 4.6(b).

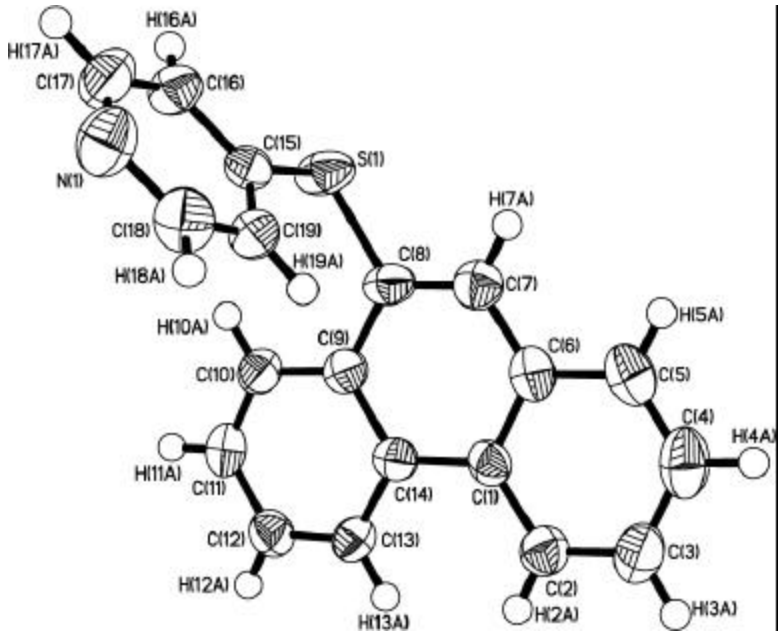
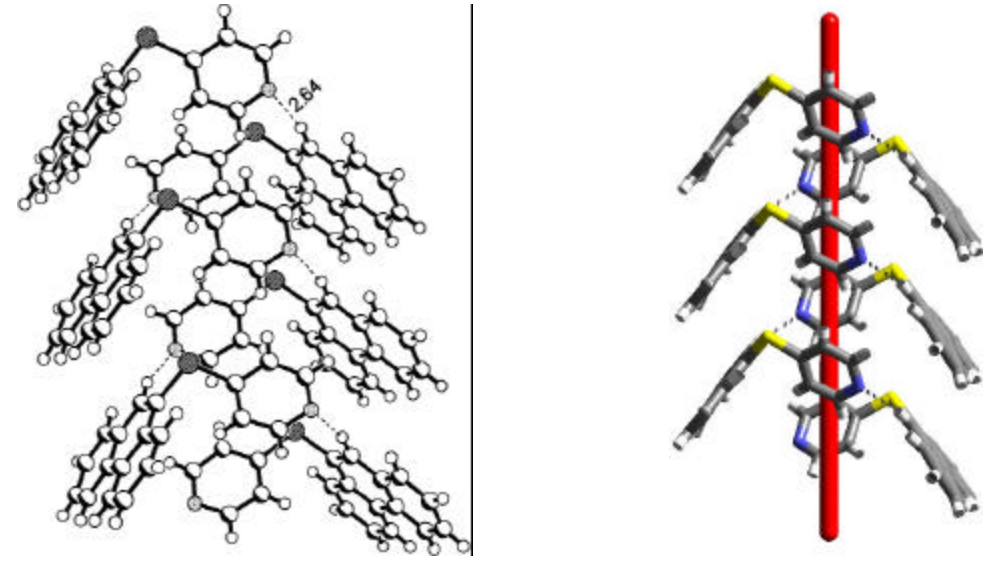
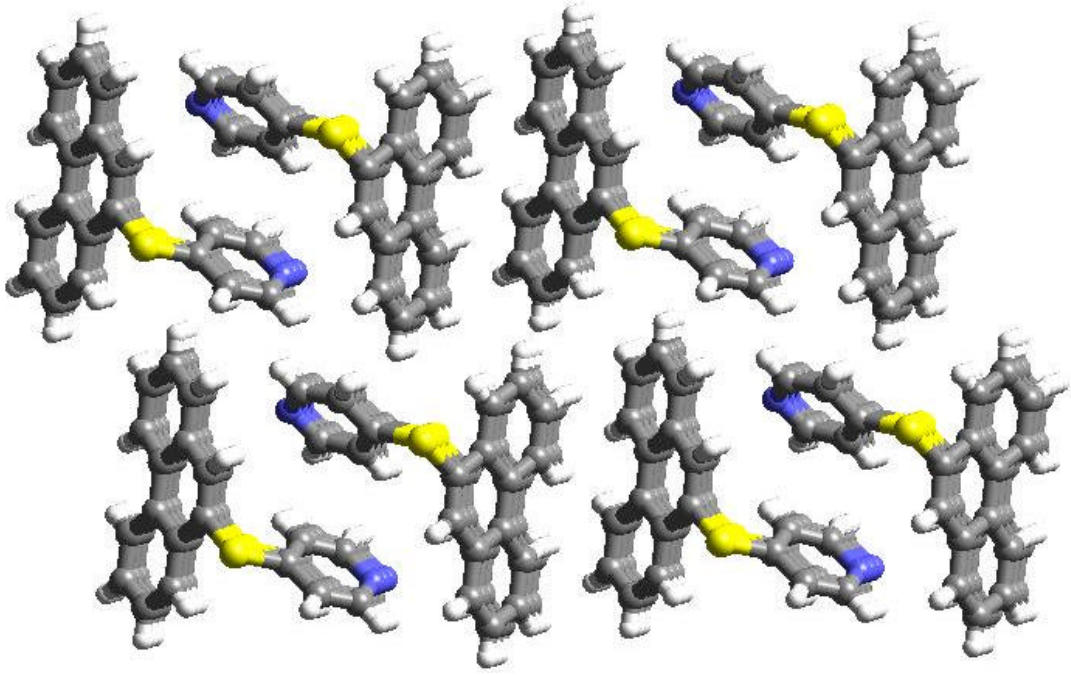


Figure 4.5: ORETP drawing of the asymmetric unit in the crystal structure of $\mathbf{L_3}$.



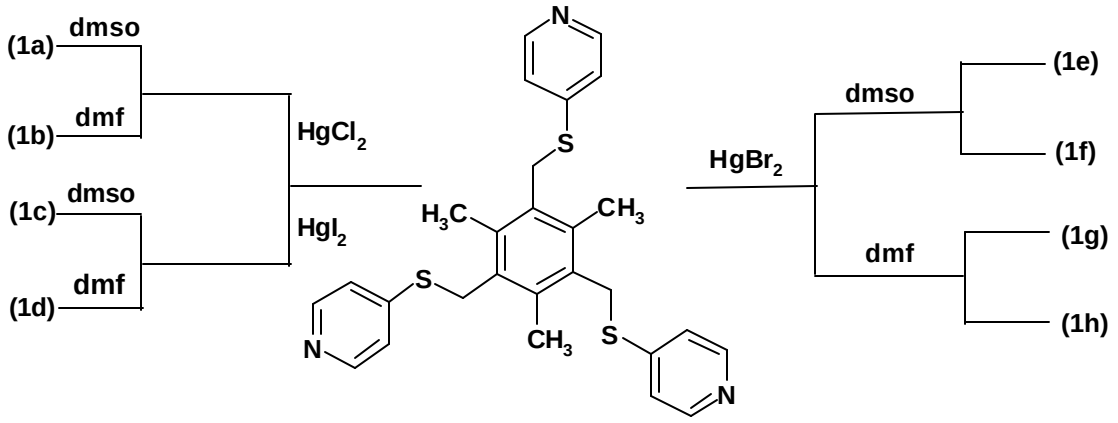
(a)



(b)

Figure 4.6: (a) (left) Recognition between the adjacent molecules in a helix formed in the crystals of $\mathbf{L_3}$. (right) Cylindrical model of a typical helical arrangement. (b) Arrangement of ligand molecules, $\mathbf{L_3}$ in three-dimensions.

Comparing the structures of **L_1 - L_3**, reveals self-assembly of the molecules into open-frame network structures, through hydrogen bonds, which could be evaluated for the synthesis of supramolecular assemblies by co-crystallization with a variety of complimentary receptors. However, attempts to obtain co-crystals with pure organic receptors were not successful but, knowing affinity of pyridyl N and S atoms towards metal ions, in particular mercury ions, reactions were carried out with different mercuric halides and the assemblies obtained are shown in Scheme 4.2. A detailed discussion of their assemblies is presented in the following sections.



Scheme 4.2

4.3 Coordination assemblies of L_1 with Mercury (II) halides

4.3.1 Solid state Structure of Complex $[Hg(L_1)Cl_2].(DMSO)_2$, 1a

Crystallization of precipitate of **L_1** and $HgCl_2$ from DMSO gave single crystals that were suitable for analysis by X-ray diffraction methods. The crystal structure determination (see Table 4.2) reveals that the pyridyl -N atoms of the **L_1** have formed coordination bonds with Hg(II) (Figure 4.7). The observed Hg-N bonds distances (2.457 - 2.479 Å) are in agreement with the similar distances known in the literature.[19]

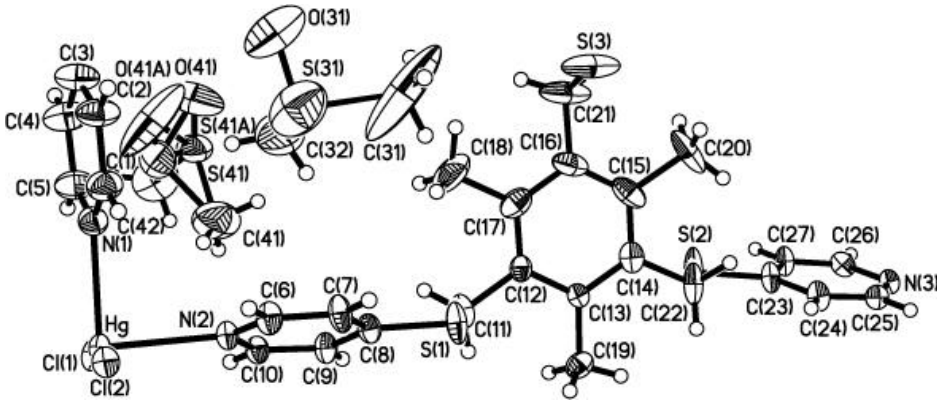
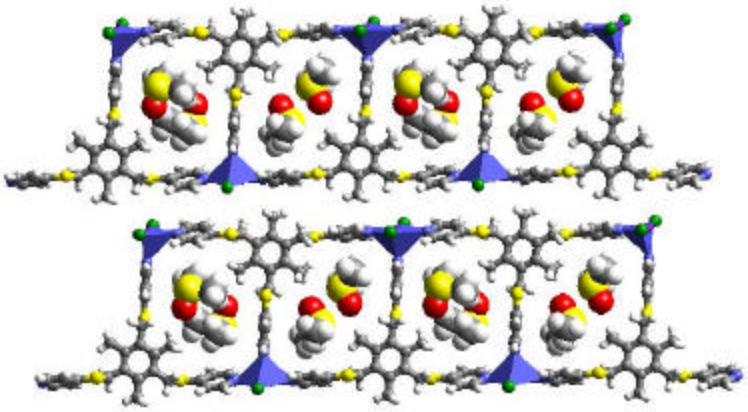
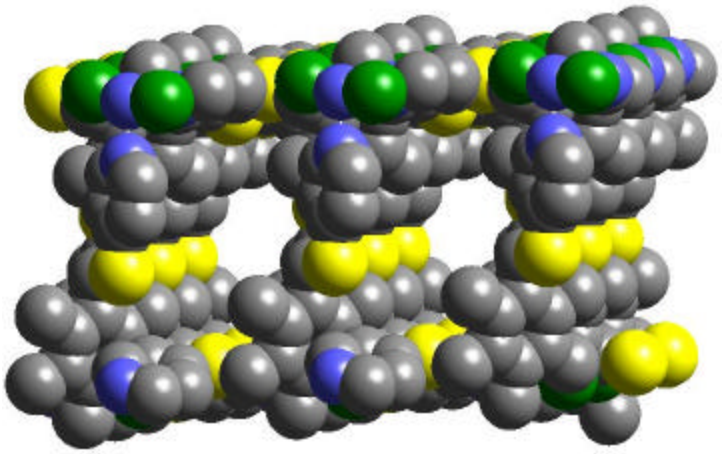


Figure 4.7: ORTEP drawing of the asymmetric unit in the coordination complex, **1a**, along with DMSO.

Further, each Hg(II) is connected to two halide ions forming Hg-Cl bonds with distances of 2.458 and 2.491 Å. Complete coordination bond lengths and angles are given in Table 4.3. Thus, each Hg(II) with *penta* coordination show square-pyrimidal geometry. Such interaction indeed resulted in the formation of a cavity of dimension 9 x 12 $Å^2$ such that each cavity is being created by two molecules of $\mathbf{L_1}$ and Hg(II) as shown in Figure 4.8(a). The cavities are further aligned in three-dimensional arrangement yielding channels (see Fig. 4.8(b)) that are being occupied by DMSO molecules (solvent of crystallization), which exist in order and disorder forms. Further, both the types of DMSO molecules exist as dimers independently; while the ordered form interact through bifurcated C-H···O hydrogen bonds (H···O, 2.58 and 2.61 Å), as shown in the Figure 4.9, the disordered form exist as cyclic 8-membered units through C-H···O hydrogen bonds (see Figure 4.9).



(a)



(b)

Figure 4.8: (a) Presentation of cavities occupied by DMSO molecules in the crystal structure of complex **1a**. (b) Formation of channels in three-dimensions.

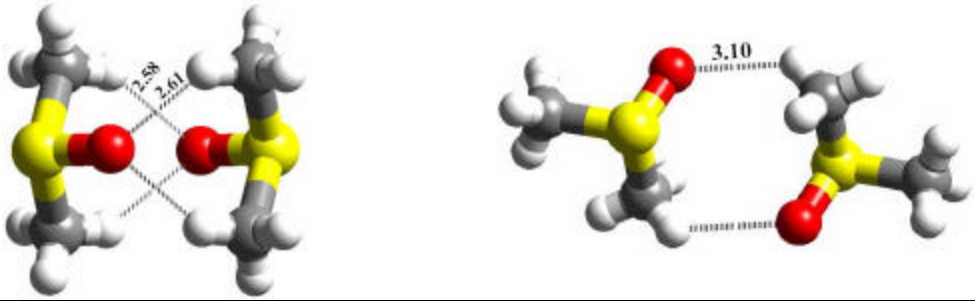


Figure 4.9: Interactions observed between (left) ordered and (right) disordered DMSO molecules found in the complex, **1a**. Disorder has been removed for the clarity.

Table 4.2 Crystallographic data of metal complexes of **L_1**, **1a - 1h**.

	1a	**1b**	**1c**	**1d**
Formula	$(C_{27}H_{27}N_3S_3)$: $2(C_2H_6SO)$:$(HgCl_2)$	$(C_{27}H_{27}N_3S_3)$: $2(C_3H_7NO)$:$(HgCl_2)$	$2(C_{27}H_{27}N_3S_3)$:$3(HgI_2)$	$2(C_{27}H_{27}N_3S_3)$:$3(HgI_2)$
Fw	917.44	905.36	2342.56	2342.56
Crystal habit	blocks	blocks	blocks	blocks
Crystal color	colorless	colorless	colorless	colorless
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	*P*?	*P*?	*C*2/c	*C*2/c
a (Å)	9.049(2)	8.979(3)	27.661(7)	27.050(13)
b (Å)	13.646(4)	13.611(5)	18.821(4)	18.653(9)
c (Å)	16.298(4)	16.355(5)	15.786(4)	15.361(8)
a (deg)	111.99(1)	111.57(1)	90	90
ß (deg)	90.43(1)	92.37(1)	113.13(1)	108.69(1)
? (deg)	101.57(1)	101.07(1)	90	90
V ($Å^3$)	1820.6(8)	1810.5(11)	7558(3)	7342(6)
Z	2	2	4	4
Dcalc(g cm^{-3})	1.674	1.661	2.059	2.119
T(K)	133	133	133	133
Mo ka	0.71073	0.71073	0.71073	0.71073
µ (mm^{-1})	4.693	4.609	8.730	8.986
2? range (deg)	46.54	52.12	46.66	52.26
F(000)	912	900	4296	4296
Total reflns	15091	18822	15672	37776
No. unique reflns [R(int)]	5225 [0.0469]	7103 [0.0468]	5451 [0.1232]	7284 [0.0502]
No. reflns used	4931	6481	2929	5703
No. parameters	403	425	339	339
GOF on F^2	1.512	0.747	0.927	1.265
R1[I>2s(I)]	0.0532	0.0354	0.0570	0.0375
wR2	0.1486	0.0928	0.1374	0.1358

Table 4.2 Contd……

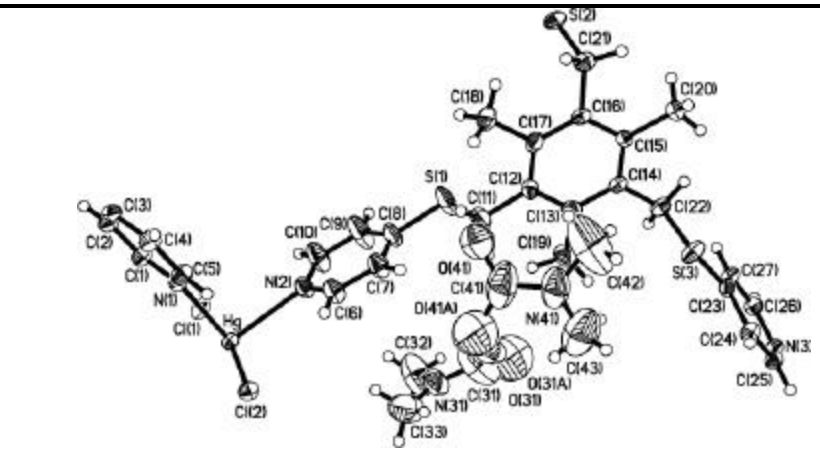
1e	**1f**	**1g**	**1h**
$(C_{27}H_{27}N_3S_3)$: (C_2H_6SO):$(HgBr_2)$	$2(C_{27}H_{27}N_3S_3)$:3$(HgBr_2)$	$(C_{27}H_{27}N_3S_3)$: (C_3H_7NO):$(HgBr_2)$	$2(C_{27}H_{27}N_3S_3)$:3$(HgBr_2)$
928.23	2060.62	922.19	2060.62
thin plates	blocks	thin plates	blocks
colorless	colorless	colorless	colorless
monoclinic	monoclinic	monoclinic	monoclinic
$P2_1/c$	$C2/c$	$P2_1/n$	$C2/c$
17.950(5)	26.753(15)	17.697(10)	26.898(11)
9.031(2)	18.415(10)	9.224(5)	18.426(8)
22.200(6)	14.940(7)	21.933(12)	14.930(6)
90	90	90	90
113.62(1)	109.50(1)	112.50(1)	108.77(1)
90	90	90	90
3297.3(15)	6938(6)	3308(3)	7006(5)
4	4	4	4
1.870	1.973	1.852	1.954
133	133	133	133
0.71073	0.71073	0.71073	0.71073
7.373	10.295	7.289	10.195
46.62	46.82	46.62	46.72
1800	3864	1788	3864
13942	4747	13554	14191
4755 [0.0543]	4002 [0.0255]	4758 [0.1469]	5001 [0.1170]
4411	2542	3305	3018
356	339	320	339
1.380	1.265	1.142	1.005
0.0729	0.0517	0.1079	0.0617
0.1558	0.1493	0.3029	0.1453

Table 4.3 Selected bond lengths (Å) and bond angles (^{o}) around the coordination sphere in complexes **1a - 1h**.

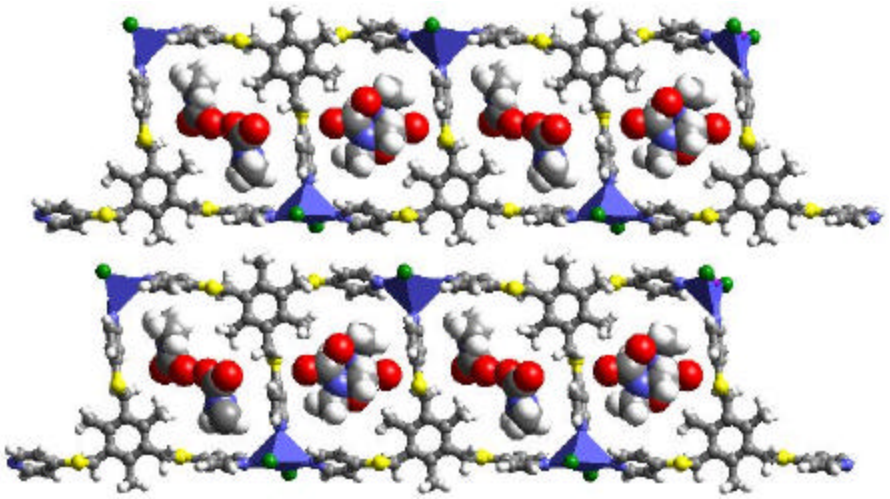
1a		**1b**	
Hg-N(1) 2.457(7)	N(1)-Hg-N(2) 88.1(2)	Hg-N(1) 2.464(4)	N(1)-Hg-N(2) 90.2(1)
Hg-N(2) 2.462(6)	N(1)-Hg-N(3) 86.5(2)	Hg-N(2) 2.493(4)	N(1)-Hg-N(3) 178.3(1)
Hg-N(3) 2.479(6)	N(2)-Hg-N(3) 174.5(2)	Hg-N(3) 2.515(4)	N(2)-Hg-N(3) 88.7(1)
Hg-Cl(1) 2.491(2)	N(1)-Hg-Cl(1) 92.0(2)	Hg-Cl(1) 2.430(1)	Cl(1)-Hg-N(2) 99.4(1)
Hg-Cl(2) 2.458(2)	N(1)-Hg-Cl(2) 97.2(2)	Hg-Cl(2) 2.451(1)	Cl(1)-Hg-N(1) 91.3(9)
	N(2)-Hg-Cl(1) 89.8(2)		Cl(1)-Hg-N(3) 87.5(9)
	N(3)-Hg-Cl(1) 90.9(2)		Cl(1)-Hg-Cl(2) 167.9(4)
	Cl(2)-Hg-Cl(1)170.7(7)		Cl(2)-Hg-N(3) 91.3(9)
	Cl(2)-Hg-N(2) 91.3(2)		Cl(2)-Hg-N(1) 90.1(9)
	Cl(2)-Hg-N(3) 88.8(2)		Cl(2)-Hg-N(2) 92.7(1)
1c		**1d**	
Hg(1)-N(1) 2.353(1)	N(1)-Hg(1)-N(1) 83.0(7)	Hg(1)-N(1)2.386(8)	N(1)-Hg(1)-N(1) 82.7(4)
Hg(2)-N(2) 2.440(2)	N(3)-Hg(2)-N(2) 85.6(6)	Hg(2)-N(2) 2.402(8)	N(1)-Hg(1)-I(1) 105.6(2)
Hg(2)-N(3) 2.406(2)	N(1)-Hg(1)-I(1) 105.0(4)	Hg(2)-N(3) 2.417(8)	N(1)-Hg(1)-I(1) 102.1(2)
Hg(1)-I(1) 2.634(2)	N(1)-Hg(1)-I(1) 104.7(4)	Hg(1)-I(1) 2.638(1)	N(2)-Hg(2)-N(3) 88.1(3)
Hg(2)-I(2) 2.623(2)	N(3)-Hg(2)-I(3) 101.1(4)	Hg(2)-I(2) 2.661(2)	N(2)-Hg(2)-I(2) 101.6(2)
Hg(2)-I(3) 2.653(2)	N(2)-Hg(2)-I(2) 102.2(4)	Hg(2)-I(3) 2.635(1)	N(2)-Hg(2)-I(3) 106.3(2)
	N(3)-Hg(2)-I(2) 107.8(4)		N(3)-Hg(2)-I(2) 100.6(2)
	N(2)-Hg(2)-I(3) 101.3(4)		N(3)-Hg(2)-I(3) 101.5(2)
	I(2)-Hg(2)-I(3) 143.8(7)		I(1)-Hg(1)-I(1) 142.9(5)
	I(1)-Hg(1)-I(1) 140.0(9)		I(3)-Hg(2)-I(2) 144.7(4)
1e		**1f**	
Hg-N(2) 2.342(1)	N(2)-Hg-N(3) 119.6(4)	Hg(1)-N(1) 2.421(2)	N(1)-Hg(1)-N(1) 81.9(9)
Hg-N(3) 2.348(1)	N(2)-Hg-Br(1) 103.0(3)	Hg(2)-N(2) 2.346(2)	N(1)-Hg(1)-Br(1) 102.0(4)
Hg-Br(1) 2.520(2)	N(2)-Hg-Br(2) 101.2(3)	Hg(2)-N(3) 2.370(2)	N(2)-Hg(2)-N(3) 88.1(7)
Hg-Br(2) 2.515(2)	N(3)-Hg-Br(1) 98.8(3)	Hg(2)-Br(2) 2.485(3)	N(2)-Hg(2)-Br(2) 99.9(4)
	N(3)-Hg-Br(2) 101.0(3)	Hg(2)-Br(3) 2.448(3)	N(2)-Hg(2)-Br(3) 105.4(4)
	Br(2)-Hg-Br(1) 135.3(7)	Hg(1)-Br(1) 2.455(3)	N(3)-Hg(2)-Br(2) 100.5(4)
			N(3)-Hg(2)-Br(3) 99.6(3)
			Br(1)-Hg(1)-Br(1) 148.1(1)
			Br(3)-Hg(2)-Br(2) 148.0(1)
1g		**1h**	
Hg-N(1) 2.310(2)	N(1)-Hg-N(2) 116.7(9)	Hg(1)-N(1) 2.402(1)	N(1)-Hg(1)-N(1) 80.4(6)
Hg-N(2) 2.380(2)	N(1)-Hg-Br(1) 100.8(6)	Hg(2)-N(2) 2.372(1)	N(1)-Hg(1)-Br(1) 102.3(4)
Hg-Br(1) 2.486(4)	N(1)-Hg-Br(2) 103.5(6)	Hg(2)-N(3) 2.432(1)	N(1)-Hg(1)-Br(1) 101.8(4)
Hg-Br(2) 2.509(3)	N(2)-Hg-Br(2) 98.6(7)	Hg(1)-Br(1) 2.465(2)	Br(1)-Hg(1)-Br(1) 148.3(11)
	N(2)-Hg-Br(1) 98.6(8)	Hg(2)-Br(3) 2.458(2)	N(2)-Hg(2)-N(3) 87.4(4)
	Br(1)-Hg-Br(2) 139.7(1)	Hg(2)-Br(2) 2.488(2)	N(2)-Hg(2)-Br(2) 100.2(4)
			N(2)-Hg(2)-Br(3) 104.2(4)
			N(3)-Hg(2)-Br(2) 100.0(4)
			N(3)-Hg(2)-Br(3) 100.9(4)
			Br(3)-Hg(2)-Br(2) 148.4(8)

4.3.2 Solid state Structure of Complex $[Hg(L_1)Cl_2].(DMF)_2$, 1b

Precipitate of ligand $\mathbf{L_1}$ with $HgCl_2$ gave solvent incorporated crystals from dimethylformamide (DMF) as confirmed by X-ray diffraction methods and each Hg(II) is connected to ligand $\mathbf{L_1}$ exactly in the same mode as observed in **1a**, and it is shown in Figure 4.10. The Hg-N distances are in the range 2.464 - 2.515 Å, the Hg-Cl distances are 2.430 and 2.450 Å.



(a)



(b)

Figure 4.10: (a) ORTEP drawing of the asymmetric unit in the crystal structure of **1b** along with solvent of crystallization DMF molecules. (b) Arrangement of DMF molecules in the cavities formed in two-dimensions.

Thus, in the crystals of **1b**, two DMF molecules present in cavities like DMSO molecules in **1a**, but both the DMF molecules are disordered in **1b**. Further, the symmetry independent DMF molecules interact with each other through C-H···O hydrogen bonds with C···O distances of 3.07 and 3.13 Å. A typical hydrogen-bonding network between the DMF molecules is shown in Figure 4.11. However, no interaction exists between symmetry dependent molecules as observed in **1a**.

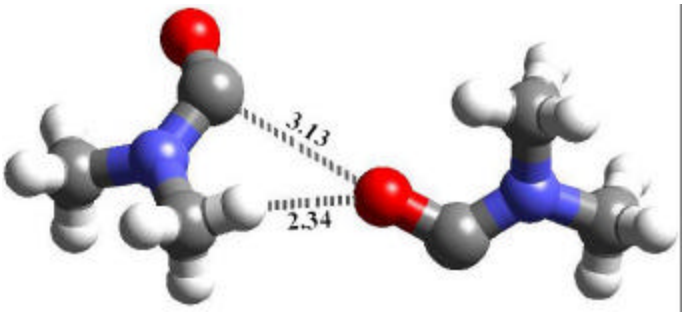


Figure 4.11: Interaction between the DMF molecules in the complex **1b**.

4.3.3 Solid state Structure of Complex [Hg(L_1)I_2], 1c, from DMSO.

Replacement of $HgCl_2$ with HgI_2 resulted in a drastic change in the ultimate co-ordination polymer structure. Single crystals suitable for X-ray diffraction were obtained by dissolving the precipitate of $\mathbf{L_1}$ and HgI_2 in DMSO solution. Crystal structure analysis of the complex showed that the metal to ligand ratio is 3:2 unlike the complexes **1a** and **1b** and the asymmetric unit is shown in Figure 4.12. Complete crystallographic details are given in Table 4.2. In the complex **1c**, ligand $\mathbf{L_1}$ forms coordination bonds with Hg(II) with Hg-N distances of 2.353 - 2.440 Å and Hg-I coordination bonds with the distances in the range 2.623 - 2.653 Å.

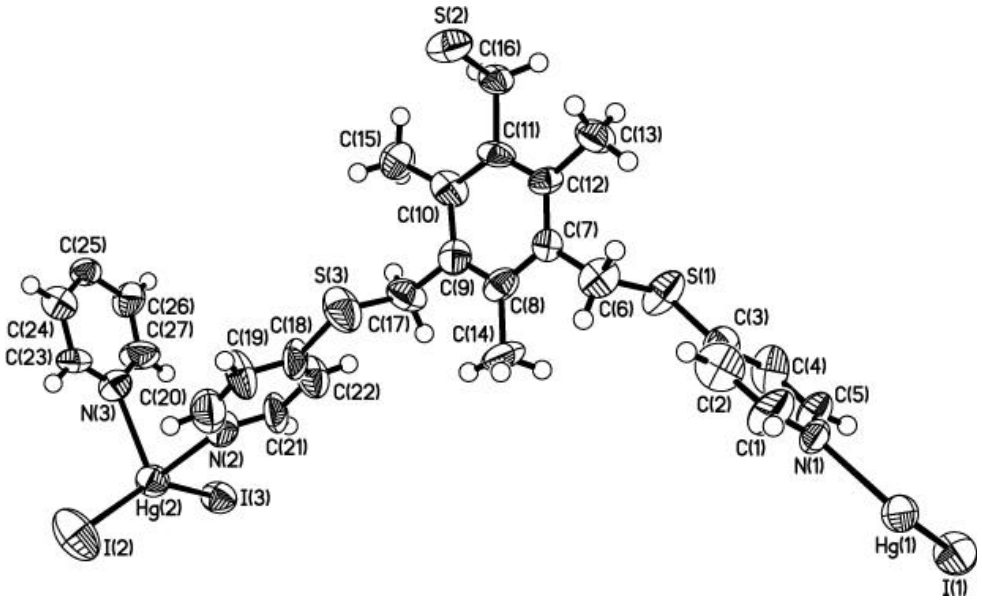
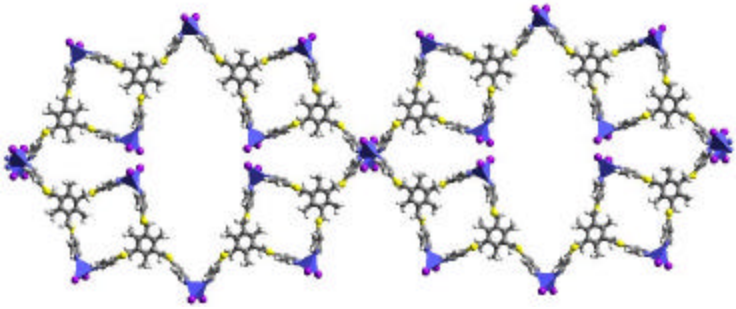


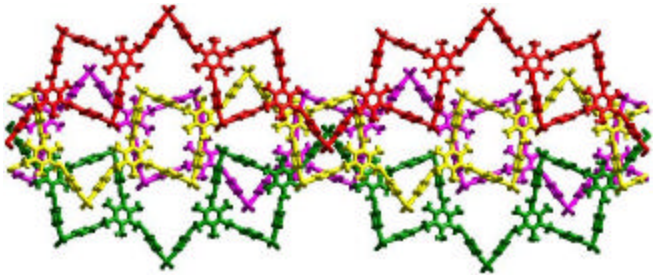
Figure 4.12: ORTEP drawing of coordination geometry in the crystal structure of **1c**.

In comparison with complexes formed by $HgCl_2$ (**1a** and **1b**), there are two different Hg(II) centers present in the complex. At one position, one molecule of ligand $\mathbf{L_1}$ and a molecule of mercuric chloride form a discrete square network while these discrete networks are further joined together at the second position of the coordination center. In total, the coordination geometry around Hg(II) is distorted tetrahedron unlike square pyramidal geometry observed in **1a** and **1b**. Thus, the coordination moieties yield a polymer network comprising of interconnected square grids with cavities (Figure 4.13(a) and (b)) in two-dimensions. However, the cavities did not constitute channels in three-dimensional arrangement as the void space is filled by the moieties from the adjacent chains as shown in Figure 4.13(c).

(a)



(b)



(c)

Figure 4.13: (a) Square-grid network mediated coordination polymers in the crystal structure of **1c**. (b) Arrangement of two-adjacent polymer networks. (c) The three-dimensional arrangement of the coordination polymers. Each polymer network is shown in different colors.

4.3.4 Solid state Structure of Complex [Hg(L_1)I_2], 1d from DMF.

Complex **1d** is obtained in a 3:2 metal to ligand ratio when the precipitate of $\mathbf{L_1}$ and HgI_2 was dissolved in DMF. The asymmetric unit is shown in Figure 4.14. Structure analysis further confirms that both the complexes **1c** and **1d** are isostructural as well as isomorphous although significant differences in the unit cell parameters are

noticed (see Table 4.2). Each mercury center in **1d** has a distorted tetrahedral geometry with two nitrogen atoms from ligand and the two remaining sites coordinated by iodine atoms. Like the complex **1c**, two different Hg(II) centers are present.

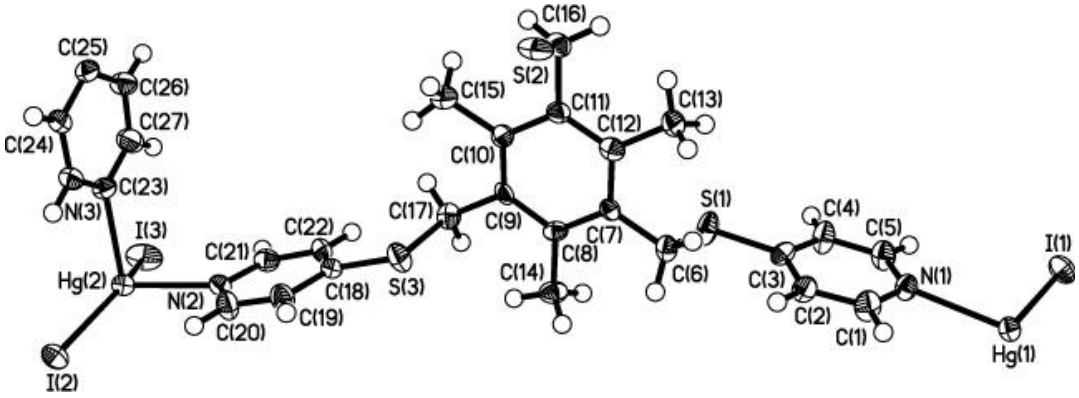
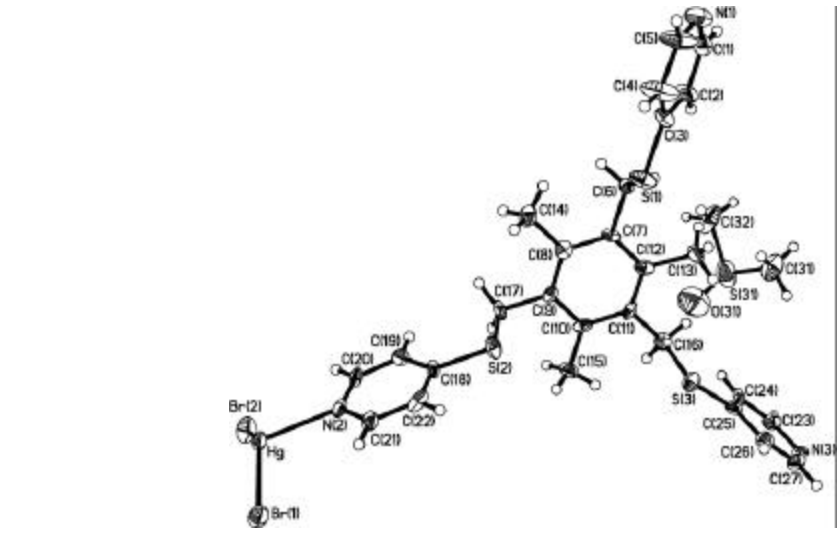


Figure 4.14: The asymmetric unit in the complex **1d**. Notice two different metal centers.

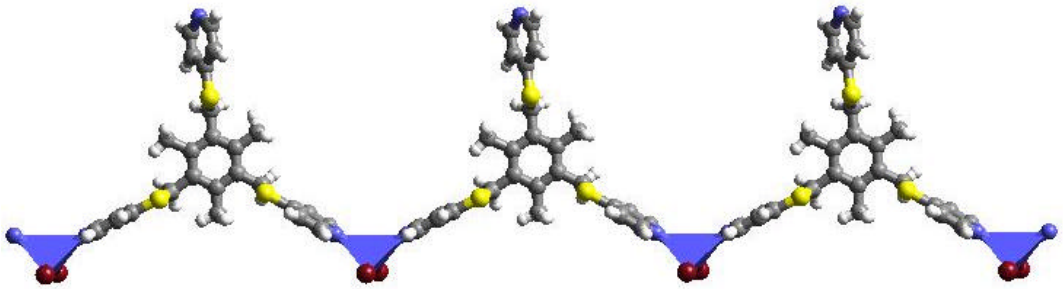
However, crystallization of a solid mixture of $\mathbf{L_1}$ and $HgBr_2$ from DMSO and DMF gave crystals of two different morphologies, concomitantly, from each solvent. Structure analysis reveals that, while one of the morphologies from each solvent (**1e** and **1g**) corresponds to solvated structure like in $HgCl_2$ (**1a** and **1b**), the other morphologies (**1f** and **1h**) gave structures without the solvent of crystallization, like **1c** and **1d** formed by HgI_2.

4.3.5 Solid state Structure of Complex $[Hg(L_1)Br_2].(DMSO)$, 1e

The complex **1e** crystallizes in space group, $P2_1/c$ and the asymmetric unit is shown in Figure 4.15(a). In a typical interaction, as shown in Figure 4.15(b), the ligand $\mathbf{L_1}$ interacts with Hg(II) by forming Hg-N bonds with a distance of 2.342 Å (Table 4.3), with only two pyridyl moieties, yielding infinite coordination polymer chain.



(a)

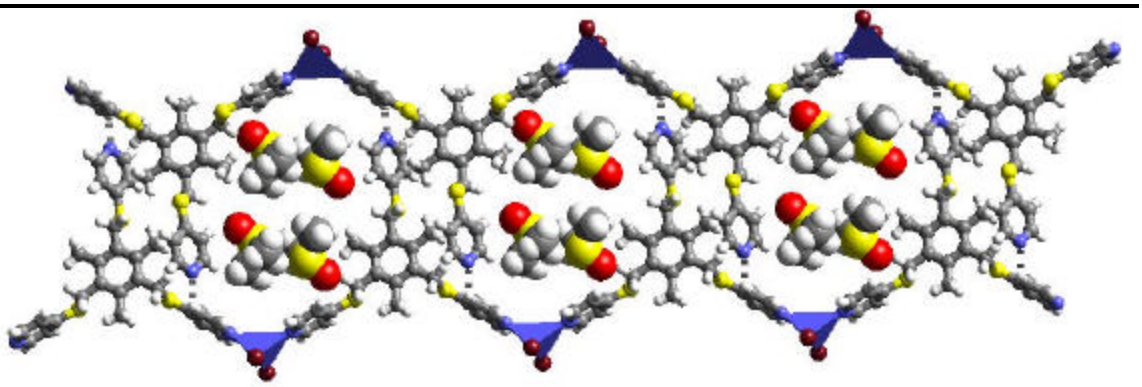


(b)

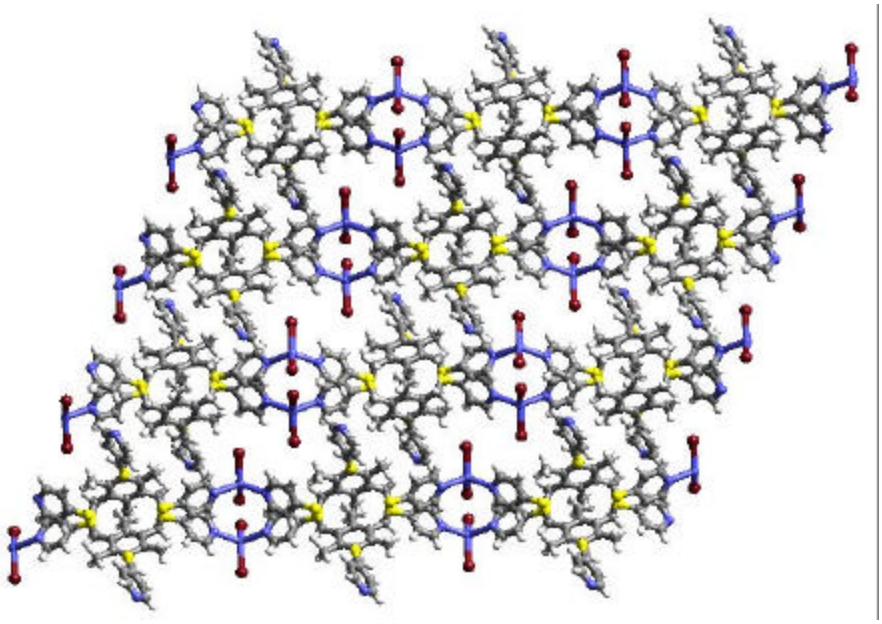
Figure 4.15: (a) ORTEP drawing of the asymmetric unit showing the complex **1e** along with solvent of crystallization, DMSO. (b) Coordination polymer formed between $\mathbf{L_1}$ and $HgBr_2$ yielding a polymer chain.

Also, each Hg(II) is bonded to two Br atoms (Table 4.3) to yield a coordination geometry around each Hg(II) in a distorted tetrahedron form. Such adjacent chains are held together by C-H···N hydrogen bonds with an H···N distance of 2.66-2.89 Å, forming cavities of dimension 11 x 16 $Å^2$ (Figure 4.16(a)), which are aligned in three-dimensional arrangement to yield channels as shown in Figure 4.16(b). The channels were occupied by solvent molecules (DMSO). Thus, **1e** shows some similarities with **1a** and **1b** in the formation of open-frame network. However, the metal coordination and

geometry around each Hg(II) has a close resemblance to **1c** and **1d**. Further, the solvent molecules present in channels of structures **1e** are completely ordered and did not have any interaction among them as observed in the complexes **1a** and **1b** but they are bound to the host lattice through numerous intermolecular interactions.



(a)



(b)

Figure 4.16: (a) Representation of cavities formed with the interaction of the adjacent polymeric chains through C-H···N hydrogen bonds in the crystal structure **1e** along with the DMSO molecules. (b) Formation of channels in three-dimension. Solvent molecules have been removed for clarity.

4.3.6 Solid state Structure of Complex [Hg(L_1)Br_2].(DMF), 1g

Complex **1g** was prepared by dissolving the solid precipitate of ligand $\mathbf{L_1}$ and $HgBr_2$ in DMF. The asymmetric unit is shown in Figure 4.17. Although **1e** and **1g** have similar unit cell parameters, they are not isomorphous, as crystallize in different space groups, $P2_1/c$ and $P2_1/n$ respectively. The full crystallographic details are given in Table 4.2. However, structure analysis reveals that both **1e** and **1g** are iso-structural with the formation of identical three-dimensional arrangement. In a typical interaction, the ligand $\mathbf{L_1}$ interacts with Hg(II) through Hg-N bonds (Table 4.3), forming distorted tetrahedron geometry around Hg(II) center which lead to the formation of one-dimensional infinite coordination polymer chain. Such adjacent chains are held together by C-H···N hydrogen bonds with an H···N distance of 2.66 - 2.89 Å, forming cavities of dimension 11 x 16 $Å^2$ (Figure 4.18), which are aligned in three-dimensional arrangement to yield channels. The channels were occupied by DMF molecules and did not have any interaction among them rather interact with host lattice through numerous intermolecular interactions as observed in the complex **1e**.

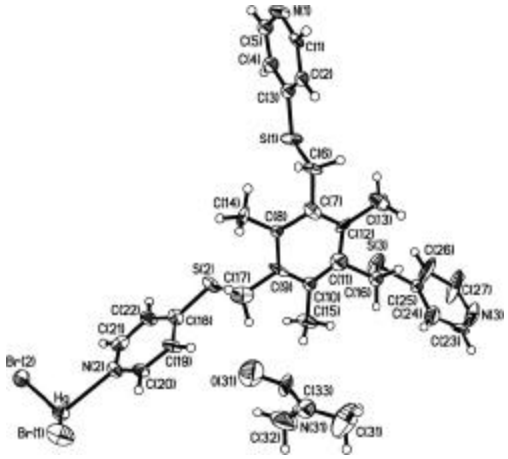


Figure 4.17: ORTEP drawing of the asymmetric unit showing the complex **1g** along with the solvent of crystallization, DMF.

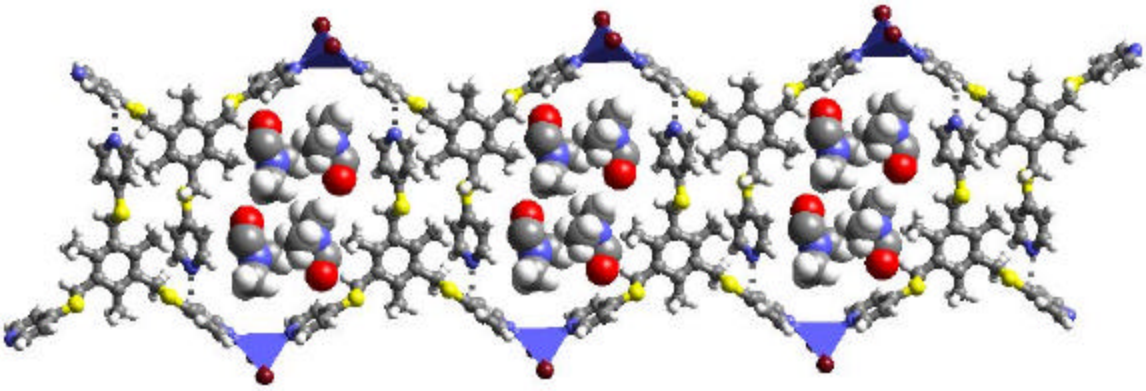


Figure 4.18: Representation of cavities formed with the interaction of the adjacent polymeric chains through C-H···N hydrogen bonds in the crystal structure **1g**.

4.3.7 Solid state Structures of Complexes 1f and 1h

The complexes **1f** and **1h**, obtained as concomitant crystals along with **1e** and **1g**, respectively, gave similar unit cell parameters and crystallizes in monoclinic space group, *C*2/c. Further, packing analysis reveals that both **1f** and **1h** are also isostructural and are identical to the structures formed by HgI_2 (**1c** and **1d**) in all respects except for the difference of the halogen atoms. A typical structural arrangement in the complexes **1f** and **1h** is shown in Figure 4.19 to appreciate the comparison with the similar structures formed by **1c** and **1d**.

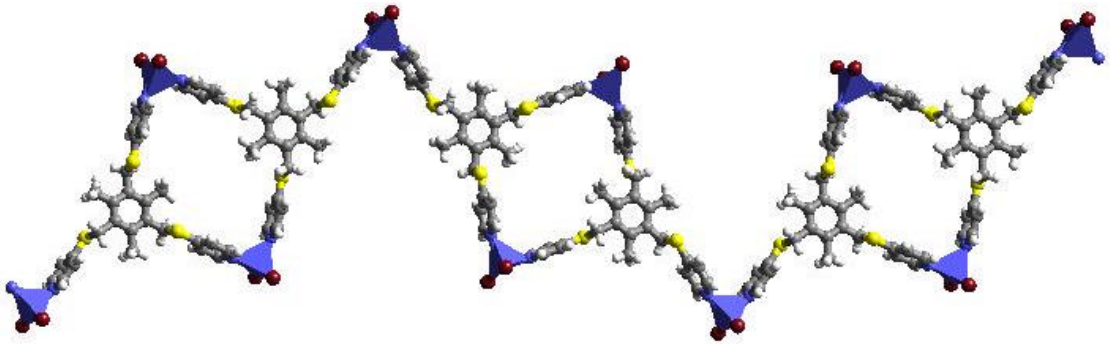


Figure 4.19: Square-grid network found in the solid-state structures of complexes, **1f** and **1h**.

4.4 Conclusions

Comparing the structures of the metal complexes described above (**1a - 1h**), it is clearly evident that the structures obtained are in agreement with the proposition of utilization of pyridylsulfanyl ligands in the supramolecular synthesis as in all the metal complexes, the coordination polymers gave a host network comprising of purely dative bonds or a combination of dative bonds and hydrogen bonds (**1f** and **1g**). Another intriguing feature of these metal complexes is the pivotal role of counter ion (halogen) in the formation of different metal-organic frameworks. While $HgCl_2$ form solvated structures, HgI_2 form structures exclusively without solvents of crystallization. However, $HgBr_2$ being in between $HgCl_2$ and HgI_2 gave both types of complexes, concomitantly, reinforcing the schizophrenic nature of Br that was observed in different crystal structures.[20] Just for the appreciation, the nature of Br is compared to the amber sign that is observed at traffic signal as it could turn out to be in any direction but green and red have definite message either go or stop, respectively.

One more interesting feature that evolves in the comparison is the conformational changes in the ligand $\mathbf{L_1}$ as shown in Figure 4.20. It is apparent that all the metal complexes except **1e** and **1g**, adopted the same conformation (*cis, trans, trans*), which is different from that of the conformation observed in the pure structure of $\mathbf{L_1}$ (*cis, cis, cis*). It is well known in the literature that tripodal ligands like $\mathbf{L_1}$ show both the types of the conformations observed in this study but often it was attributed to the nature of the anion present in the structures.[17] However, it is apparent from this study that coordination environment of metal species as well as denticity of the ligands also play a significant role. In particular, the complexes formed by $HgBr_2$ are quite

significant in this respect. Since, the same halogen (Br) gave structures of both the conformations, which are differentiated by number of metal coordination centres, it may be understood that, interaction with three metal ions like Hg(II) lead to strained crowding in *cis, cis, cis* geometry, which might have forced the transformation of the conformation to *cis, trans, trans* in **1f** and **1h**, whereas in **1e** and **1g**, with only two Hg(II) involved in the complex formation, the conformation is retained as such, like in $\mathbf{L_1}$. In particular, the variations observed in the conformations of the ligand $\mathbf{L_1}$ are intriguing and may provide further insights in modeling experiments especially for the evaluation of metal-hybrids as catalysts, which has increased demands in the current research themes.

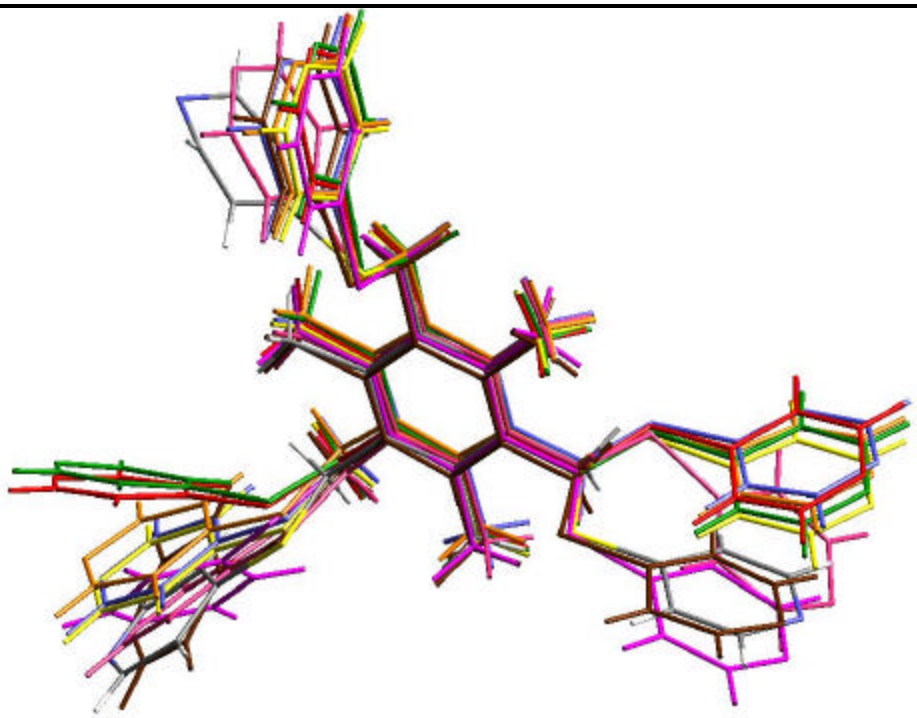


Figure 4.20: An over-lay diagram of molecular conformation of ligand $\mathbf{L_1}$ in its crystal structure (gray) and also in the complexes **1a - 1h**. Brown and pink correspond to **1e** and **1g**.

4.5 Experimental Section

4.5.1 Synthesis of Ligands

Synthesis of 1,3,5-Tris(4-pyridylsulfanylmethyl)-2,4,6-trimethylbenzene, L_1

1,3,5-tris-(bromo-methyl)mesitylene (399 mg, 1 mmol) was added to a ice-cooled solution of 4-mercaptopyridine (333 mg, 3 mmol) and KOH (560 mg, 10 mmol, slightly excess) in methanol under stirring. The mixture was refluxed for 48 hours at 80 ^{o}C (see Chart 4.2). The solution was poured into ice-cold water, filtered the crude product and separated by column chromatography. The product is obtained as colorless microcrystalline solid, **L_1**. Yield: 72%, melting point: 228-230 ^{o}C. ^{1}H NMR ($CDCl_3$, 200 MHz, ppm) d 1.6-1.9 (9H, -CH_3), 3.5-3.7 (6H, -CH_2), 6.5-6.7 (6H, -2CH), 7.6-7.8 (6H, -1CH). Analysis. $C_{27}H_{27}N_3S_3$ calculated: C, 66.26; H, 5.52; N, 8.59; S, 19.63. Found: C, 65.96; H, 5.34; N, 8.36; S, 17.69. Single crystals of **L_1** suitable for X-ray diffraction were obtained from methanol solution after 2 - 3 days.

Synthesis of 2,2'-Bis(4-pyridylsulfanylmethyl)-1,1'-biphenyl, L_2

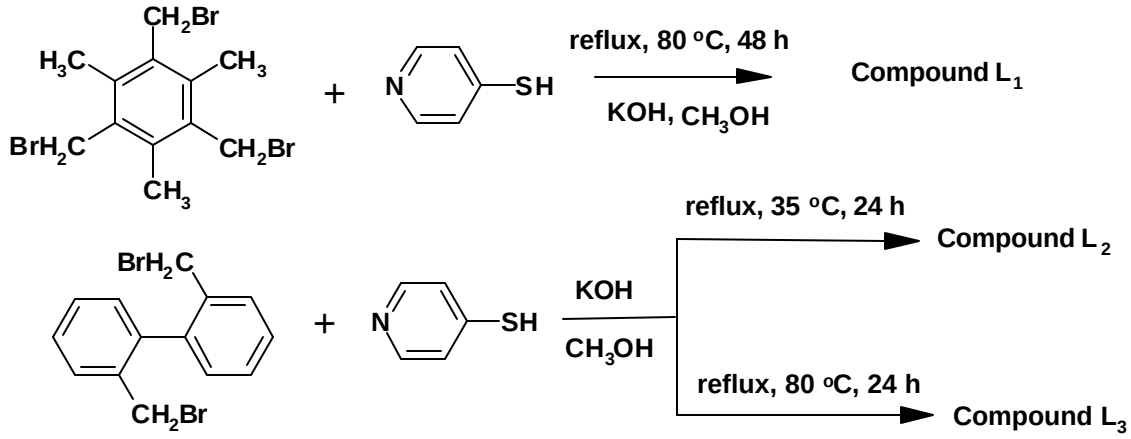
4-mercaptopyridine (222 mg, 2 mmol) and KOH (560 mg, 10 mmol, slightly excess) were stirred in methanol at 0 ^{o}C. To the above mixture 2,2'-bis(bromomethyl)-1,1'-biphenyl (340 mg, 1 mmol) was added slowly and stirred for about 24 hours at room temperature. The mixture was poured into ice-cold water, filtered the crude product and pure product was separated by column chromatography to give colorless microcrystalline solid. Yield: 75%, melting point: 137-139 ^{o}C. ^{1}H NMR ($CDCl_3$, 200

MHz, ppm) d 4.2-4.4 (4H, -CH_2), 7.1-7.7 (8H, -CH), 7.7-7.9 (4H, -2CH) 8.5-8.9 (4H, -1CH). Analysis. $C_{24}H_{20}N_2S_2$ calculated: C, 71.91; H, 4.99; N, 6.99; S, 15.98. Found: C, 71.10; H, 4.82; N, 6.76; S, 12.69. Crystals of **L_2**, suitable for single crystal X-ray diffraction, were obtained by diffusion of petroleum ether into a solution of ethyl acetate.

Synthesis of 9-(4-pyridylsulfanyl)phenanthrene , L_3

The same procedure, as that of the preparation of ligand **L_2**, was followed for the preparation of **L_3** as well except that the mixture was refluxed at 80 ^oC (see Scheme 4.3). The formation of compound **L_3** is serendipitous and may be attributed due to the *insitu* generation of 9-bromophenanthrene from 2,2'-bis(bromomethyl)-1,1'-biphenyl through cyclization prior to the reaction with mercaptopyridine. The solution was poured into ice-cold water, filtered the crude product and separated by column chromatography to give pure colorless microcrystalline solid. Yield: 70%, melting point: 185-187 ^oC. ^1H NMR ($CDCl_3$, 200 MHz, ppm) d 7.5-8.0 (8H, -CH), 8.2-8.4 (2H, -CH), 8.7-8.8 (2H, -CH). Analysis. $C_{19}H_{13}NS$ calculated: C, 79.44; H, 4.53; N, 4.88; S, 11.14. Found: C, 79.28; H, 4.32; N, 4.56; S, 9.19. Single crystals of **L_3** suitable for X-ray diffraction were obtained from chloroform solution after 2 days.

Scheme 4.3



4.5.2 Synthesis of metal complexes

Preparation of complexes $[Hg(L_1)Cl_2].(DMSO)_2$, 1a and $[Hg(L_1)Cl_2].(DMF)_2$, 1b

A solution of $HgCl_2$ (81 mg, 0.3 mmol) in methanol was added to a solution of **L_1** (49 mg, 0.1 mmol) in methanol and white precipitate was obtianed. The precipitate was filtered and dissolving it in DMSO/DMF gave colourless crystals, **1a** and **1b** respectively, suitable for single crystal X-ray diffraction studies.

Preparation of complexes $[Hg(L_1)I_2]$, 1c and $[Hg(L_1)I_2]$, 1d

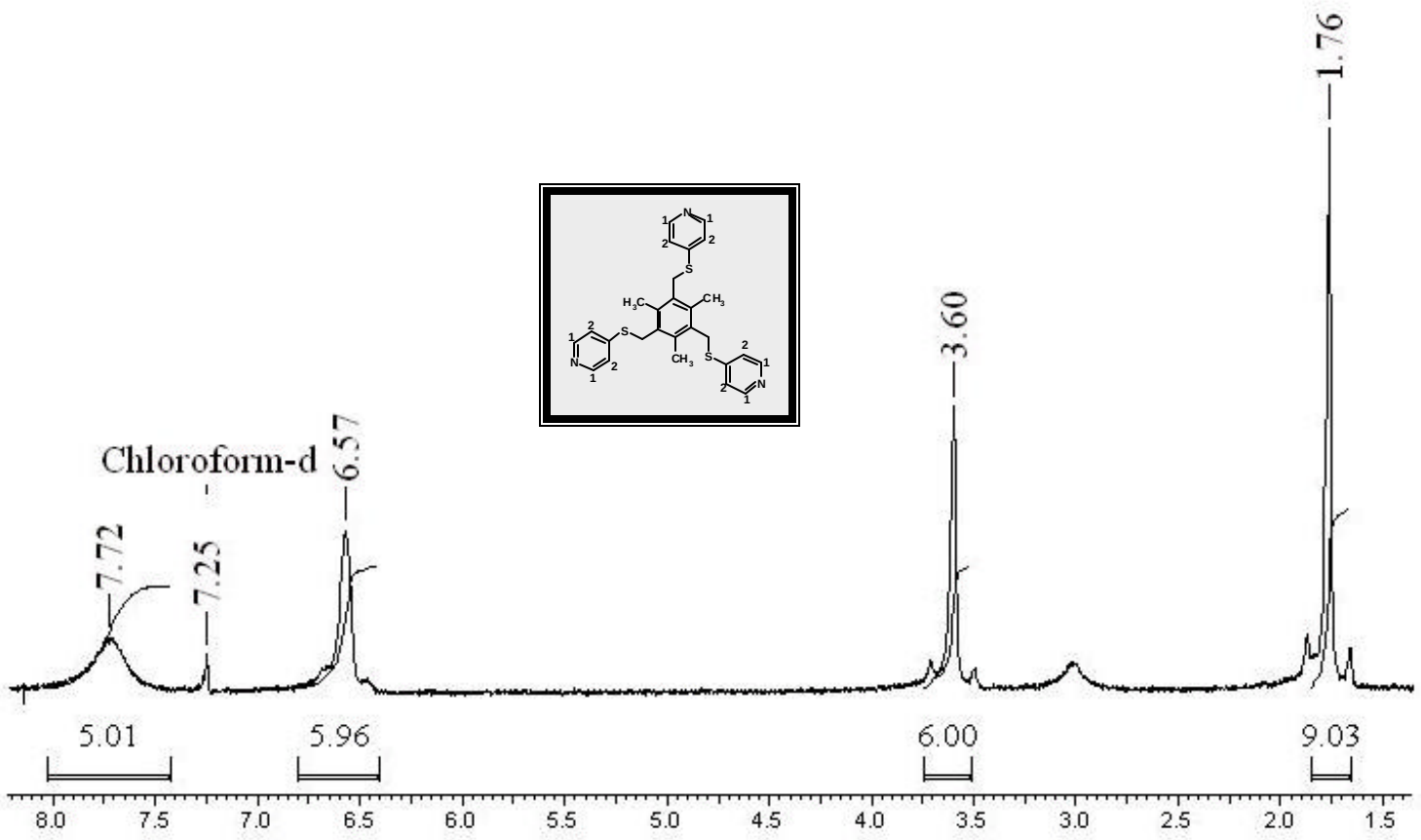
A solution of HgI_2 (135 mg, 0.3 mmol) in methanol was added to a solution of **L_1** (49mg, 0.1mmol) in methanol and white precipitate was obtained. The precipitate was filtered and dissolved in DMSO/DMF. Colorless crystals, **1c** and **1d**, respectively, were obtained within 10 minutes.

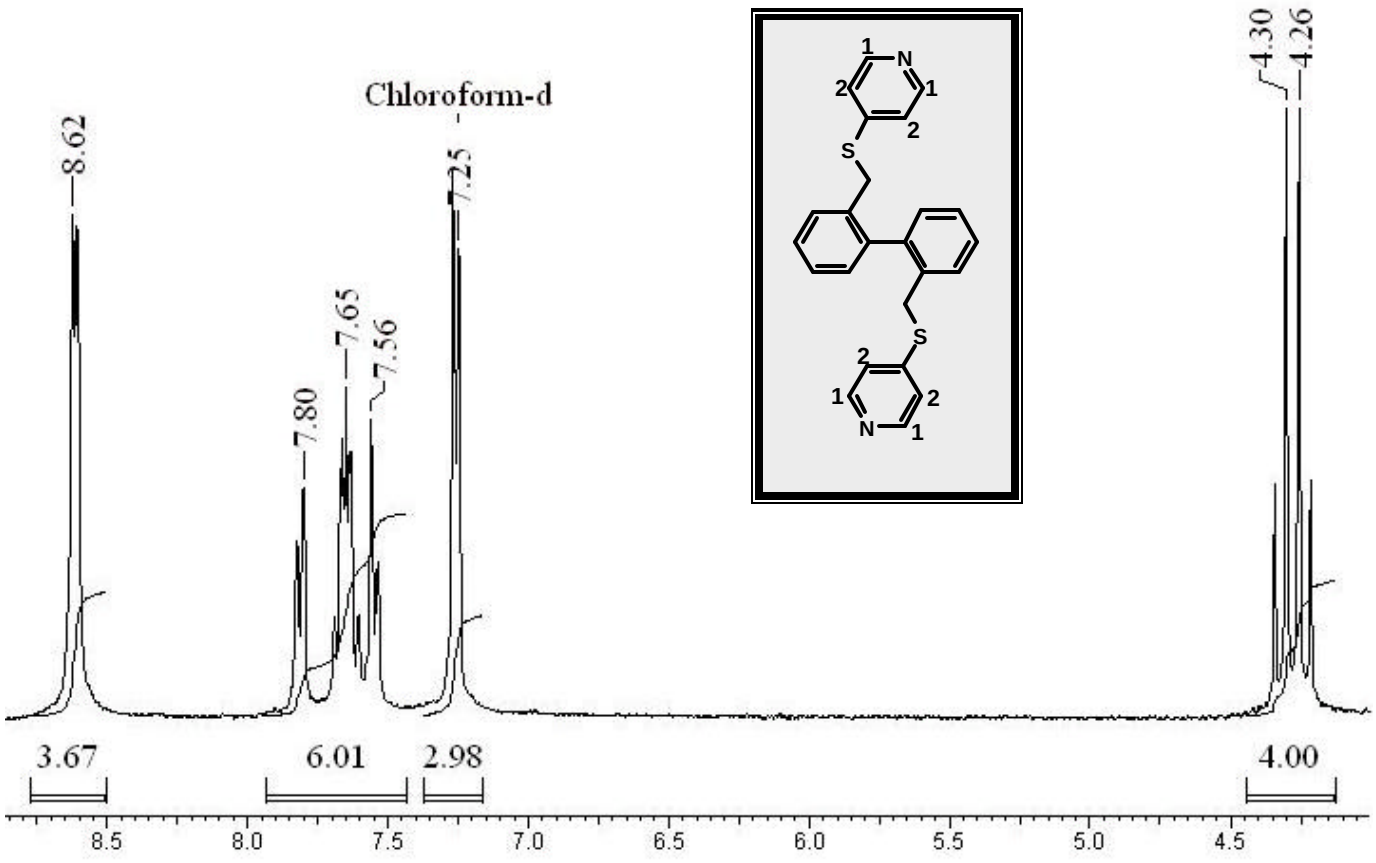
Preparation of complexes of L_1 with $HgBr_2$, 1e - 1h

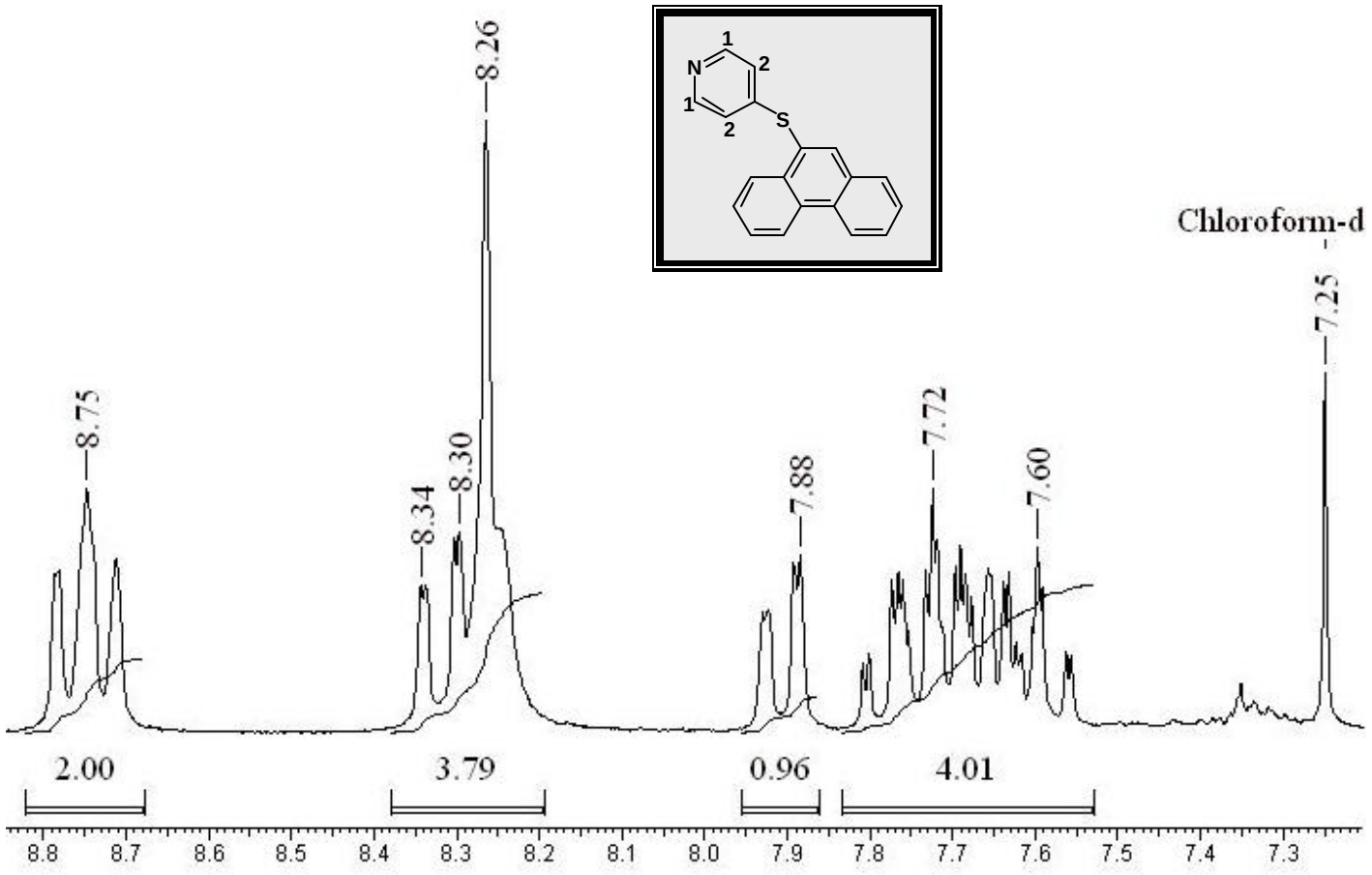
A solution of $HgBr_2$ (108 mg, 0.3 mmol) in methanol was added to a solution of **L_1** (49 mg, 0.1 mmol) in methanol. A white precipitate was formed immediately. The precipitate was filtered and dissolved in DMSO/DMF. Colorless crystals of two morphologies (plates and small blocks), were obtained within twelve hours from each solvent. Thus, **1e** and **1f** were isolated from DMSO, while **1g** and **1h** from DMF.

4.6 Crystal Structure Determinations

Good quality single crystals of **L_1 - L_3** and **1a - 1h**, grown as described above were carefully chosen with the aid of polarized optical microscope and glued to glass fiber to mount on a goniometer equipped with CCD area detector. The data collection proceeded without any complication and processed using the Bruker suite of software. The structures were determined and refined using SHELXTL suite of programmes,[21] and absorption corrections were made on all the crystals using SADABS. All the non-hydrogen atoms were refined by anisotropically except an atom in **1e** and few atoms in **1g** (nine atoms). All hydrogen atoms were placed in the calculated positions. The structural parameters were given in Tables 4.1 and 4.2. All the intra and intermolecular distances were computed using PLATON software.[22] The packing drawings were generated either by XP package of SHELXTL or Cerius^2 of Accelyrs, Inc.[23]


Chloroform-d
7.72
7.25
6.57
3.60
1.76
5.01
5.96
6.00
9.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5


8.62
Chloroform-d
7.80
7.65
7.56
7.25
4.30
4.26
3.67
6.01
2.98
4.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5


8.26
8.75
8.34
8.30
7.88
7.72
7.60
Chloroform-d
7.25
2.00
3.79
0.96
4.01
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3

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Symposia/invited talk etc.

- Fourth National Symposium in chemistry (Chemical Research Society of India), Feb 1-3, 2002, National Chemical Laboratory, Pune – 411008 INDIA.
- BCA Intensive X-ray structure analysis course held at the university of Durham, April 7-14, 2003, U. K.
- XXXIII National Seminar on Crystallography, 8-10 January 2004, National Chemical Laboratory, Pune – 411008- INDIA.
- RSC-student symposium, West India section, 24-25th Sept 2004, Bombay, INDIA.
- ACS-CSIR joint international conference, 7th – 9th January 2006, National Chemical Laboratory, Pune – 411008 INDIA.