SUPRAMOLECULAR ASSEMBLIES OF VARIOUS CYCLOHEXANECARBOXILIC ACIDS

A THESIS
SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
(IN CHEMISTRY)

TO

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BY

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CERTIFICATE

This is to certify that the work presented in this thesis entitled "**Supramolecular Assemblies of Various Cyclohexanecarboxilic Acids**" submitted by **Mr. Manish Dnyaneshwar Raut**, has been carried out by the candidate at National Chemical Laboratory, Pune, India, under my supervision. Such materials as obtained from other sources have been duly acknowledged in the thesis. This work is original and has not been submitted for any other degree or diploma of this or any other university.

September 2013 **Dr. V. R. Pedireddi**

Pune

CANDIDATE'S DECLARATION

I hereby declare that the research work presented in the thesis entitled "**Supramolecular Assemblies of Various Cyclohexanecarboxilic Acids**" was carried out by me at the National Chemical Laboratory, Pune, India, under the supervision of **Dr. V. R. Pedireddi**, Scientist, Division of Organic Chemistry, National Chemical Laboratory, Pune, India and submitted for the degree of Doctor of Philosophy in Chemistry to the University of Pune. This work is original and has not been submitted in part or full by me for any other degree or diploma of this or any other university.

September 2013 **Manish Raut**
Pune


Dedicated to
Aai and Baba

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The blessings and best wishes of my parents keep me active throughout my life. They made me what I am and I owe everything to them. Dedicating this thesis to them is a minor recognition for their invaluable support and encouragement.

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

Manish

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Chapter 4
Supramolecular Assemblies of 1,3-Cyclohexanedicarboxylic Acid with various Aza Donors

Abstract

This thesis entitled "**Supramolecular Assemblies of Various Cyclohexanecarboxilic Acids**" is the compilation of research work carried out to explore the utility of cyclohexanecarboxylic acids in supramolecular synthesis. Various supramolecular architectures, in the form of host-guest complexes, interpenetrated networks, molecular ladders, sheets, etc., obtained by co-crystallization of some cyclohexanecarboxylic acids with different aza donor compounds are summarized into four chapters. Chapter 1 gives an introduction to the bailiwick *"Supramolecular Chemistry"* and its significance in chemical sciences, with some illustrative examples. Chapter 2 deals with the structural analysis of molecular complexes of *cis,cis,cis*-1,2,4,5-cyclohexanetetracarboxylic acid with various *N*-donor compounds. In Chapter 3 supramolecular architectures formed by *cis*- and *trans*-1,2-cyclohexanedicarboxylic acid with different aza- donor compounds are illustrated. Finally, in Chapter 4 supramolecular assemblies of *cis*-1,3-cyclohexanedicarboxylic acid are discussed.

Chapter 1

Supramolecular chemistry refers to the study of *chemistry beyond the molecule* and focus on chemical systems made up of self assembled molecular subunits or components. Preparation of supramolecular assemblies by utilizing the knowledge of intermolecular interactions have gained popular attention in recent times,[1-6] in particular, due to the flexible nature of such bonds for the synthesis of complex and topologically directed materials with tailor made properties. The forces

responsible for the spatial organisation of molecular components may vary from weak or moderate to strong, depending upon the degree of electronic coupling between molecular components. These forces include hydrogen bonds, metal coordination, hydrophobic forces, van der Waals forces, π-π interactions, electrostatic forces, etc.[7]

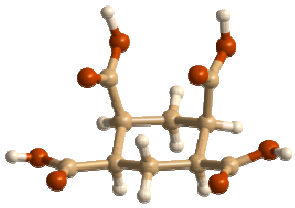
The numerous exotic organic supramolecular assemblies, for example, porous networks, host-guest assemblies, lamellar sheets etc., resulting from the recognition of various organic molecules through a variety of intermolecular interactions in a directed and specific way have been reported by several research groups.[4,8-10] This is not only due to the fascinating structural architectures of the assemblies but also because of the potential applications of such ensembles in many areas including molecular adsorption, ion exchange, and heterogeneous catalysis. A detailed discussion of the contemporary research work in this area is compiled in this chapter.

Chapter 2

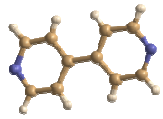
Among numerous organic functional groups known in the literature, the carboxylic acid moiety is well explored within the realm of supramolecular synthesis, particularly, in the form of supramolecular assemblies of aromatic carboxylic acids.[11-13] But, corresponding cyclic aliphatic carboxylic acids are still in scanty[14] as revealed by Cambridge Structural Database analysis[15] except for the few reports of 1,3,5-cyclohexanetricarboxylic acid[16-20] and 1,4- cyclohexanedicarboxylic acid.[21-22]

Taking into account the availability of number of carboxylic acid groups, the conformational flexibility due to cyclohexane ring and better solubility property of such acids in most of the organic solvents, a thorough exploration of various cyclohexanecarboxylic acids have been carried out.

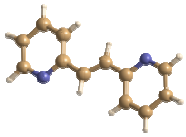
In this Chapter, synthesis and characterisation of molecular adducts of *cis,cis,cis*-1,2,4,5-cyclohexanetetracarboxylic acid, **1**, with various aza donor compounds are discussed.



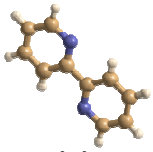
(1) *cis,cis,cis*-1,2,4,5-cyclohexanetetracarboxylic acid



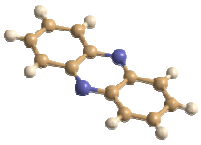
4,4'-bipyridine



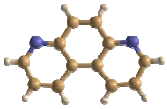
(a) *trans*-1,2-bis(2-pyridyl)ethene



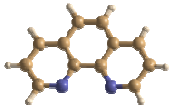
(b) 2,2'-bipyridine



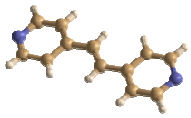
(c) phenazine



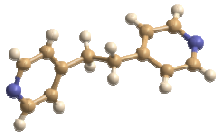
(d) 4,7-phenanthroline



(e) 1,10-phenanthroline



(f) *trans*-1,2-bis(4-pyridyl)ethene

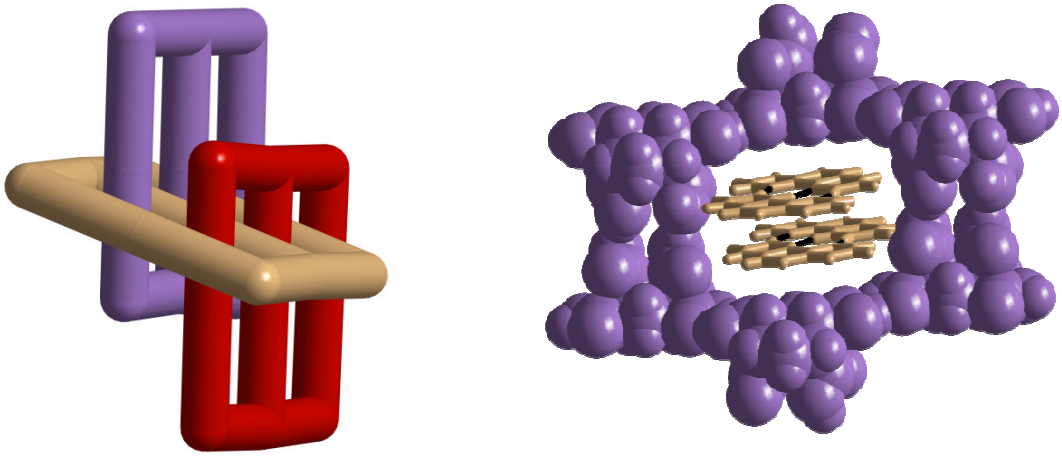


(g) 1,2-bis(4-pyridyl)ethane

Reactants	Solvent of crystallization	Molecular complexes	Composition
1+H_2O	CH_3OH or H_2O	**1.H_2O**	1:2
1+a	CH_3OH	**1a**	1:1
1+b	CH_3OH	**1b**	1:1
1+c	CH_3OH	**1c**	1:1
1+d	C_2H_5OH + CH_3OH (1:1)	**1d**	2:2
1+e	C_2H_5OH + CH_3OH (1:1)	**1e**	1:1
1+f	C_2H_5OH	**1f**	2:3
1+g	C_2H_5OH	**1g**	2:1
1+g	CH_3OH or H_2O	**1g.H_2O**	1:1:1

Co-crystallization of **1** with various aza-donor compounds, **a-g** yielded good quality single crystals of molecular complexes **1a-1g,** respectively, from methanol or ethanol or mixture of solvents (Chart 1). As representative examples, molecular complexes of **1** with 4,4'-bipyridine and 1,10-phenanthroline, **1f** gave 3-fold interpenetrated

ladder and a host-guest assembly, respectively, in the crystal lattices. Packing diagrams of the structures of these molecular complexes are shown in Figure 1. Further exotic features of these structures and also assemblies of other molecular complexes of acid **1,** with aza-donor compounds, as shown in Chart I, would be discussed in detail in this chapter.



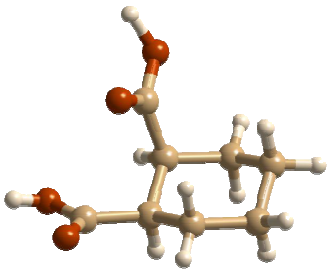
(a) (b)

Figure 1. Supramolecular assemblies formed by 1,2,4,5-cyclohexanetetracarboxylic acid with (a) 4,4'-bipyridine (schematic representation) and (b) 1,10-phenanthroline.

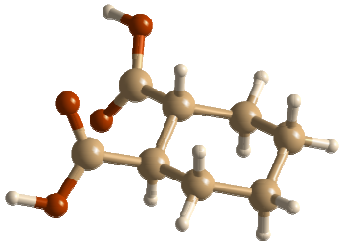
Chapter 3

In continuum, to study the affinity of cyclohexanecarboxylic acids in supramolecular synthesis and formation of a variety of supramolecular assemblies, isomers of 1,2-cyclohexanedicarboxylic acid have been co-crystallized with different N-donor compounds, depending upon the complimentarity of the aza molecules with respect to physical dimensions like volume, length, etc., as well as nature of hydrogen bonding patterns. Various *N*-donors used and molecular

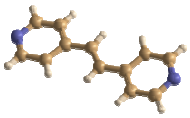
complexes obtained in the co-crystallization experiments are as shown below.



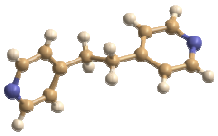
2
cis-1,2-cyclohexanedicarboxylic acid



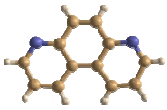
3
trans-1,2-cyclohexanedicarboxylic acid



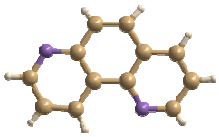
(a)
trans-1,2-*bis*(4-pyridyl)ethane



(b)
1,2-*bis*(4-pyridyl)ethane



(c)
4,7-phenanthroline



(d)
1,7-phenanthroline

Reactants	Solvent of crystallization	Molecular complexes	Composition
2+a	CH_3OH	**2a**	1:1
2+a	$C_6H_5NO_2$	**2a.$C_6H_5NO_2$**	1:1:1
2+b	CH_3OH	**2b**	1:1
2+c	CH_3OH	**2c.H_2O**	1:1:1
3+a	C_2H_5OH + CH_3OH (1:1)	**3a**	2:2
3+d	C_2H_5OH + CH_3OH (1:1)	**3d**	1:1

The structural analysis reveals that both the isomers of 1,2 cyclohexanedicarboxylic acid, **2** and **3**, gave different exotic supramolecular assemblies with various *N*-donor compounds. As representative examples, molecular complex of **2** with *trans*-1,2-*bis*(4-pyridyl)ethane, **2a**, gives discrete tetrameric units, which are further connected through a series of C-H···O hydrogen bonds to yield a sheet structure in two dimensional arrangement (Figure 2a), while molecular complex **3a**, obtained between acid **3** and *trans*-1,2-*bis*(4-pyridyl)ethane, forms zig-zag chains (Figure 2b), via O–H···N hydrogen bonds. The

structural features of these complexes and other molecular assemblies as listed in Chart II, are dealt more in detail in this Chapter.

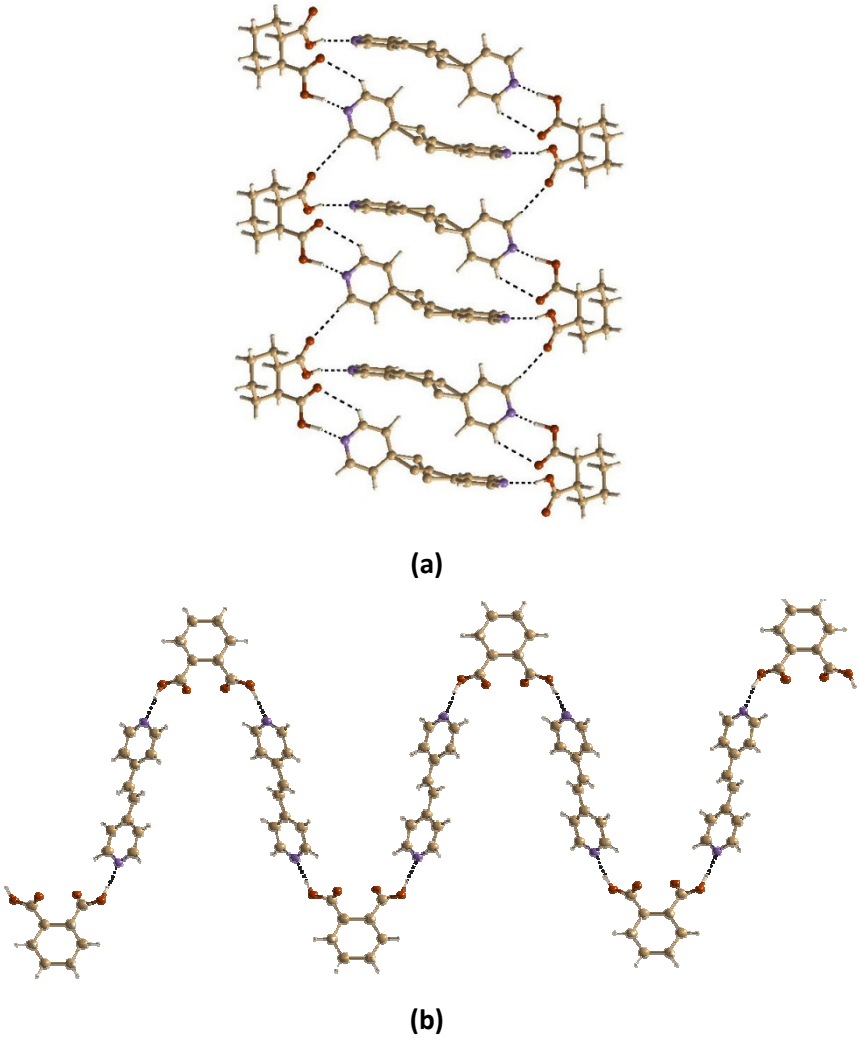
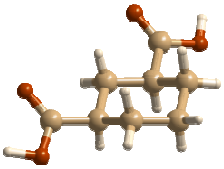


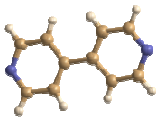
Figure 2. Supramolecular assemblies formed by 1,2-cyclohexanedicarboxylic acid. (a) A ladder like architecture formed acid **2** and *trans*-1,2-*bis*(4-pyridyl)ethane (complex **2a**) where rods of the ladder are being formed by acid molecules and rungs by aza donor. (b) Zig-zag chain formed by acid **3** and *trans*-1,2-*bis*(4-pyridyl)ethane (complex **3a**).

Chapter 4

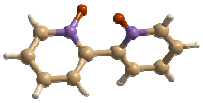
In chapter 4, study of some supramolecular assemblies of 1,3-cyclohexanedicarboxylic acid, **4**, with aza donor compounds as illustrated below are discussed.



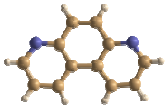
(4)
cis-1,3-cyclohexanedicarboxylic acid



(a)
4,4'-bipyridine



(b)
2,2'-bipyridine-*N,N'*-dioxide



(d)
4,7-phenanthroline

Reactants	Solvent of crystallization	Molecular complexes	Composition
4+a	$C_2H_5OH + CH_3OH$ (1:1)	**4a**	1:1
4+b	CH_3OH	**4b**	1:1
4+c	$C_2H_5OH + CH_3OH$ (1:1)	**4c**	1:1

In a typical example, in molecular complex, **4b**, one of the carboxylic groups of **4** takes part in the formation of carboxylic acid dimer with the adjacent acid molecules, while other carboxylic group is connected to the molecule of **b** via O–H···O/C–H···O pair wise hydrogen bond. Such interactions constitute form infinite molecular chains (Figure 3a) in the solid state structure of **4b**. These chains are further connected to each other through different C–H···O hydrogen bonds to form sheets (Figure 3b), which are stacked in the three dimensional structure, by establishing C-H···O hydrogen bonds between the sheets, as shown in Figure 3c. Additional structural features of molecular complex **4b** and also other complexes, as listed in Chart III, are discussed in detail in this Chapter.

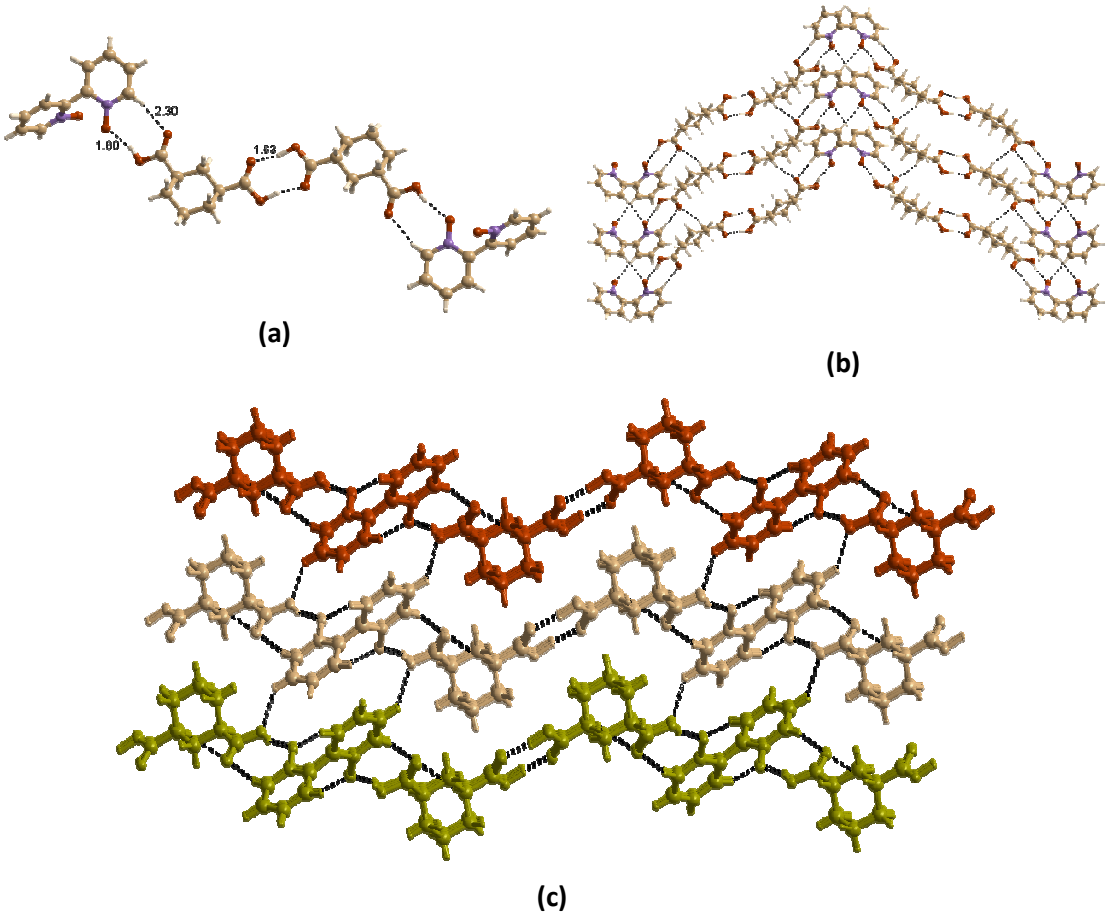


Figure 3. (a) One-dimensional molecular chain formed by acid **4** and 2,2'-bipyridine-*N,N'*-dioxide, in the molecular complex **4b**. Arrangement of chains held together by C-H···O hydrogen bonds in the sheet structure of **4b**. (c) Stacking of sheets in three-dimensional arrangement.

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Chapter 1

Supramolecular Assemblies: A Brief Survey

Supramolecular Assemblies: A Brief Survey

1.1 Introduction

"Where Nature finishes producing its own species, man begins, using natural things and with the help of this nature, to create an infinity of species." The words by Leonardo da Vinci precisely describe the essence of chemical sciences. Main aim of chemists is to prepare molecules with specific physical and chemical properties for applications in several areas, for example, ranging from pharmaceuticals to materials. A molecule is usually considered as a stable collection of atoms connected by forces of attraction, which are generally known as ionic, covalent, coordinate bonds, etc.

Exploration of various methods for the synthesis of desired molecules is generally the central focus in the research areas of chemical sciences. In fact the concepts were successfully demonstrated through development of several types of mechanistic processes, especially in the areas of organic chemistry, which paves the way for the synthesis of even highly complex molecular entities, like vitamin B_{12}, chlorophyll, etc., demonstrating the extraordinary sophistication of synthetic routes. But most of the properties of any compound are not only inherent of the molecules, but also depend on non-covalent interaction between/among the molecules, in particular, within the solid state.

1.2 Supramolecular chemistry

The study of non-covalent interactions and its effect over the properties of compounds is the part of supramolecular chemistry. Nature uses self-assembly strategies, based on non-covalent interactions, such as hydrogen bonds, salt bridges, solvation forces and even metal coordination etc., as observed, for example in the organization of biological systems like DNA, RNA, proteins etc. In supramolecular assemblies, intermolecular interactions act as supramolecular glue between the molecules in the same way as the covalent bonds connect the atoms in the molecule.

According to Nobel Laureate J. M. Lehn, a supermolecule is an organized entity that is being created from the association of two or more chemical species held together by intermolecular forces. In that sense, Lehn defined supramolecular chemistry as "*chemistry beyond the molecules*" [1].

In recent times, much focus is towards the development of various methods for the preparation of complex molecules by viable processes in terms of cost and time effective although a remarkable degree of control is achieved by general methods, over molecular architecture, with the ability to introduce a wide range of substituents in predictable positions on increasingly complex molecular scaffolds and controlling the stereochemistry at particular chiral centres, etc.[2]

To meet such challenges, by proposing a "*bottom-up*" approach, starting from atoms and molecules, Richard Feynman[3] highlighted the concept of small molecules in *supramolecular chemistry*[4]– a discipline which exploits fundamental concepts such as self-assembly, self-organization, and self-replication that are

central to nature's forms and functions–it has experienced an extraordinary development of hybridization of chemistry with biology and physics.

In many of a biological processes, the feature is understood through the projections of Emil Fischer that an enzyme interacts with its substrate as a key does with its lock[5,6] based on two important principles - molecular recognition and supramolecular function. A schematic representation of the function is shown in Figure 1.1.

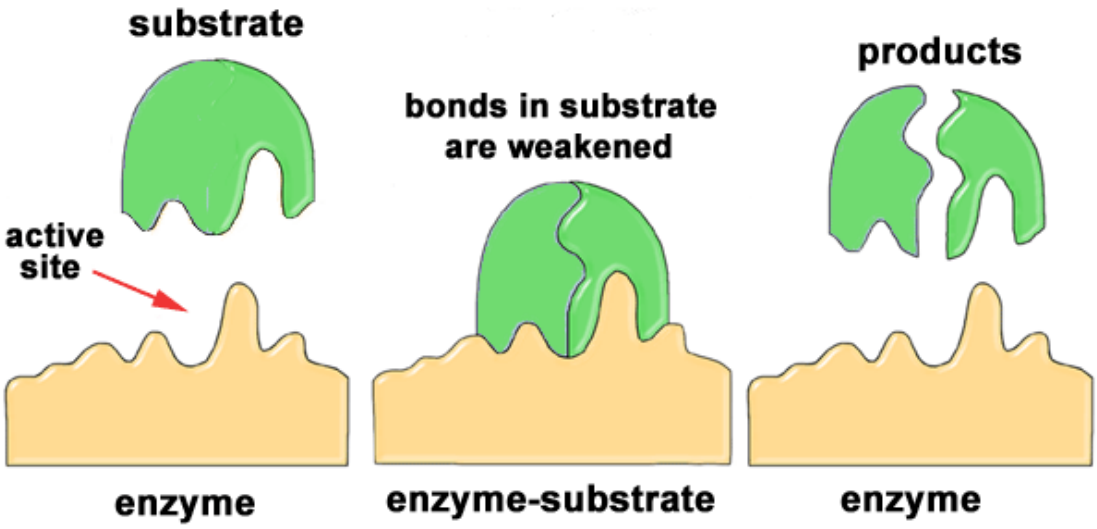


Figure 1.1. Schematic representation of an enzymatic reaction.

In supramolecular chemistry of fine materials also, various molecules recognize each other if their functional group(s) or shape is complementary to each other. The term "*Übermoleküle*",[7] i.e., supermolecules was coined as early as the mid 1930's to describe entities of higher organization, such as dimer of acetic acid. Supramolecular assemblies are the polymolecular entities that result from the spontaneous association of infinite number of supermolecules/ components. Thus, supramolecular chemistry is a highly interdisciplinary field of science with a focus on the study of hybrid of the chemical, physical and biological features of the chemical

species of greater complexity, through the organization utilizing intermolecular non-covalent interactions. Supramolecular chemistry also has a great impact on biotechnology and nanotechnology, which are expected to lead to technological revolutions in near future that will dramatically affect our lifestyles, economy etc., especially towards the development of novel devices. A schematic diagram of supramolecular assemblies formed by hydrogen and co-ordinate bonds are shown in Figure 1.2.[8] In the domain of supramolecular chemistry, the other weak intermolecular interactions like π-π interactions, van der Waals forces etc., are also well studied.

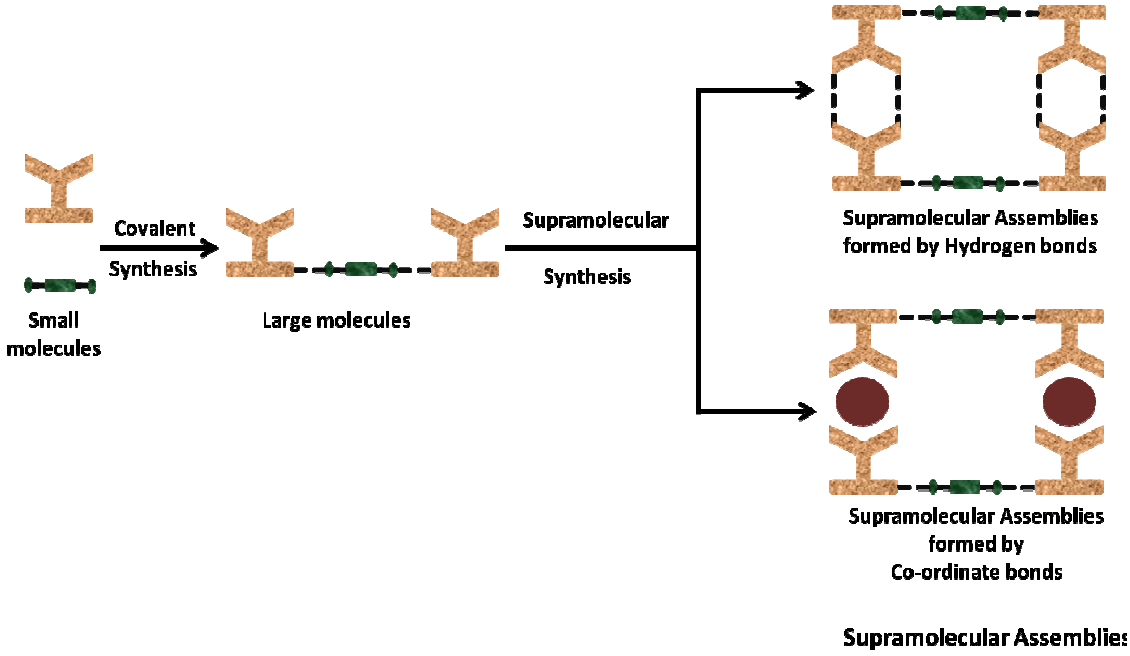


Figure 1.2. Diagram showing the formation of large molecules by covalent synthesis and the formation of supermolecules by hydrogen and co-ordination bonds.

1.2.1 Intermolecular Interactions

The solid and/or liquid phases of a given compound are the direct consequence of attractive forces between the molecules. If the attractive forces

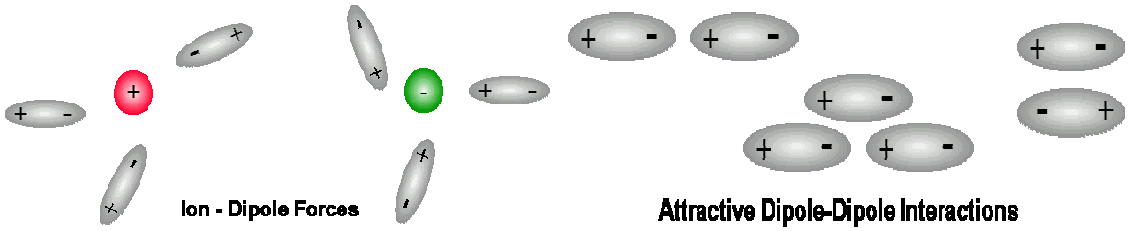
between the molecules are so weak, then a collection of molecules remain in the gas phase. For example, the temperature at which a liquid boils reflects the kinetic energy needed to overcome the attractive intermolecular forces (likewise, the temperature at which a solid melts).

Intermolecular forces are generally much weaker than conventionally well known bonds like covalent bonds in organic compounds. Covalent bonds involve the sharing of electrons while intermolecular forces are simply induced electrostatic in origin (opposite charges attract) without the involvement of electronic configuration. These electrostatic interactions include:

a. ***Dipole-dipole and ion-dipole*** forces
b. ***Hydrogen bonding*** forces

a. Dipole-dipole and ion-dipole Forces

Typically, dipole-dipole and dispersion forces are grouped together and termed as ***van der Waals forces.*** The term van der Waals forces refer to the fact that these forces produce non-ideal behaviour in gases (the effects of which were formalized in the van der Waals equation of non-ideal gases). A dipole-dipole force exists between neutral polar molecules due to the polarization of charge because of the difference in the electronegativity of the atoms that are bonded together. An interaction between a *charged ion* and a *polar molecule* (i.e. a molecule with a *dipole*) is ***ion-dipole interaction***. Dipole-dipole forces are characteristically weaker than ion-dipole forces.

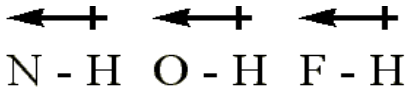


(a) **(b)**

Figure 1.3. Models to explain (a) ion-dipole and (b) dipole-dipole interactions

b. Hydrogen Bonding

Hydrogen bonds are considered to be a **special type of dipole-dipole** interaction. A bond between hydrogen and an electronegative atom such as F, O or N is quite polar:



The hydrogen atom has no inner core of electrons, so the side of the atom facing away from the bond represents a virtually naked proton. This positive charge is attracted to the negative charge of an electronegative atom in a nearby molecule. Because the hydrogen atom in a polar bond is electron-deficient on one side (i.e. the side opposite from the covalent polar bond) this side of the hydrogen atom can get quite close to a neighbouring electronegative atom (with a partial negative charge) and interact strongly with it.

Pauling's early definition of the hydrogen bond

"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 structure that is sufficiently stable to make it convenient for the chemist to consider it as an independent chemical species."

Hydrogen bond (H-bond) is represented as a dashed bond between hydrogen and the acceptors (Y), as shown below.

X-H···Y

Stronger the H-bond, shorter is the H···Y distance. H-bonding interactions lead to increase in the X-H distance. As a consequence, a substantial downward frequency shift is observed for X-H peak in IR spectra of hydrogen bonded systems. IR spectroscopy is also a very good tool to distinguish inter and intramolecular hydrogen bonds. Generally, the bands arising from intramolecular hydrogen bonds are sharp and well defined while the intermolecular hydrogen bonds give rise to broad band. Intermolecular hydrogen bonds are concentration dependent, whereas intramolecular hydrogen bonds are not. The absorption frequency difference between free and associated molecules is smaller in case of intramolecular hydrogen bonding than in intermolecular association. In NMR spectrum, hydrogen bonded protons are shifted downfield since the formation of X-H···Y bond leads to the deshielding of proton involved in hydrogen bond.

The energy of hydrogen bond is estimated to be in the range of 0.2 to 40 kcal mol^{-1}, and depending upon the strength, the hydrogen bonds are classified into three categories- 1) strong 2) moderate and 3) weak. According to system introduced by Jeffrey, the energy of the moderate bonds is in the range of 4 - 15 kcal mol^{-1}, as observed in water molecules and in carbohydrates[9]. Hydrogen bonds with energies above and below this range are called strong and weak, respectively. Some general properties of these categories are listed in Table 1.1. However, it must be

noted that there are no natural borderlines among these categories, to use in stringent way.

Table 1.1. Properties of strong, moderate and weak hydrogen bonds

X-H···Y	**Strong**	**Moderate**	**Weak**
Interaction type	Quasi-covalent	Mostly electrostatic	Electrostatic/Dispersive
Bond length(Å) H···Y	1.2-1.5	1.5-2.2	> 2.2
Lengthening of X-H	0.08-0.25	0.02-0.08	< 0.02
X···Y(Å)	2.2-2.5	2.5-3.2	> 3.2
Directionality	Strong	Moderate	Weak
Bond Energy	15 - 40	~[15]	< 4

Unlike moderate and weak hydrogen bonds, strong hydrogen bonds are quasi-covalent in nature and deserve special discussion. If the hydrogen bond is understood as an incipient proton-transfer reaction, a moderate hydrogen bond represents an early stage of such a reaction, while a strong one represents an advanced stage.

A very strong hydrogen bond is generally a manifestation of the complementary molecules. Depending upon the ΔpK_a (difference in pK_a of the acceptor and donor) either a moderate X-H···Y hydrogen bond or an ionic $X^{-}\cdots H\text{-}Y^{+}$ hydrogen bond is formed, both of which are not very covalent. The quasi-covalent situation occurs in a certain critical range of ΔpK_a, the numerical characteristics of which depend on the particular system.[10]

1.3 Hydrogen Bonding and Supramolecular Assemblies

As early as in 1892, Nernst observed weak interactions between molecules containing hydroxyl groups. But ten years later only Werner included them in his concept of "Nebenvalenz" (minor valence), which was in fact a proper description of the phenomenon of hydrogen bonding. Suggestions that the hydrogen atom was the center of this weak interaction were first made in 1920 by Huggins as well as Latimer and Rodebush. Soon after, it became apparent that association between molecules containing electron rich atom bonded to hydrogen and nonbonding electron pairs on atom, are generally characterized by relatively high interaction energies. Since then, H-bonding interactions have continued to fascinate chemists from theoreticians to biochemists to material scientists.[11]

Water is unusual in its ability to form an extensive hydrogen bonding network. As a liquid, the kinetic energy of the molecules prevents an extensive ordered network of hydrogen bonds. When cooled to a solid the water molecules organize into an arrangement which maximizes the attractive interactions of the hydrogen bonds. The properties of the various polymorphic forms of ice, resulting from hydrogen bond aggregation of water molecules, are different from those of an isolated water molecule in the vapor phase, which, in turn, is different from those of liquid water. The snowflake in Figure 1.4 is an example of an extraordinarily elegant supramolecular aggregate of water molecules through hydrogen bonds.

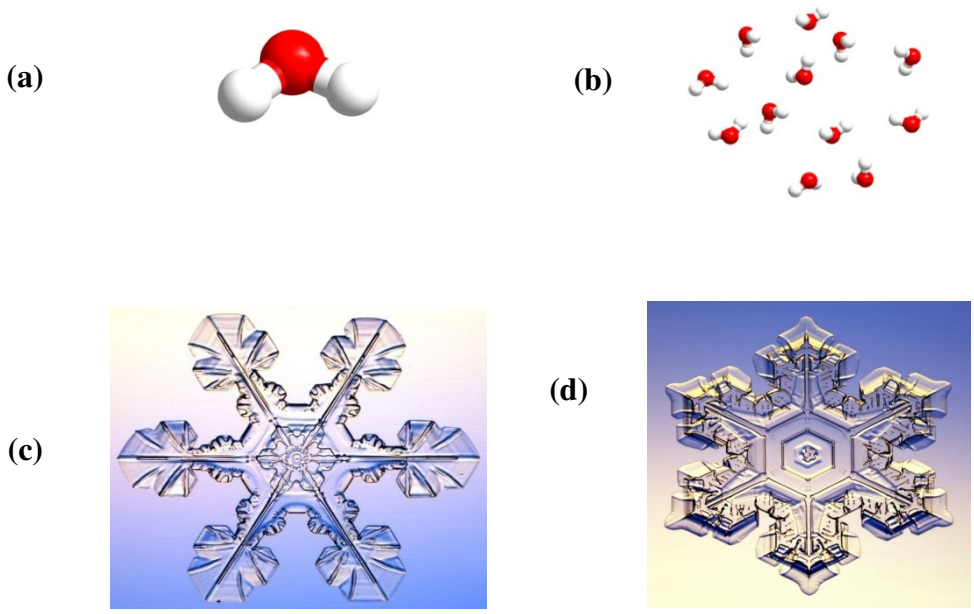
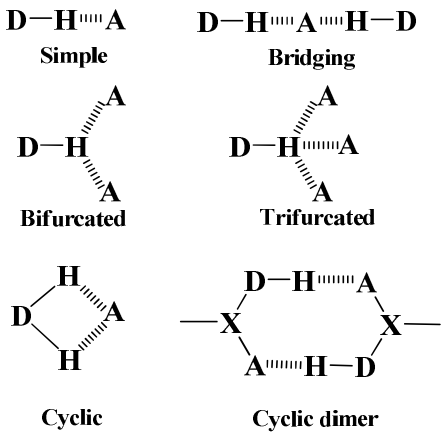


Figure 1.4. **(a)** Ball and stick representation of a gas-phase water molecule and (b) Aggregated water molecules (c) and (d) Elegant supramolecular arrangements of water molecules via O–H···O hydrogen bonds in snowflakes.

Hydrogen bond,[12] the most widely studied non-covalent interaction in biological and chemical sciences plays a vital role in maintaining the structure of various biomolecules like DNA, RNA, proteins, etc., and also for execution of various functions in biology like translation, transcription, cellular recognition, antigen-antibody interaction etc. hydrogen bonds are responsible. Hydrogen bonds are sufficiently strong and directional to control and direct the structure of molecules and also form selective binding with other molecules by molecular recognition. Besides this, the energy of hydrogen bond is such that it can easily form and break at ambient temperatures, which is the requirement for many biological processes like transcription and translation to take place. Though the hydrogen bonds are feeble, easy to break and sometimes even hard to detect, but in conjunction, they become stronger and lean on each other. This phenomenon, which in scientific terms is called

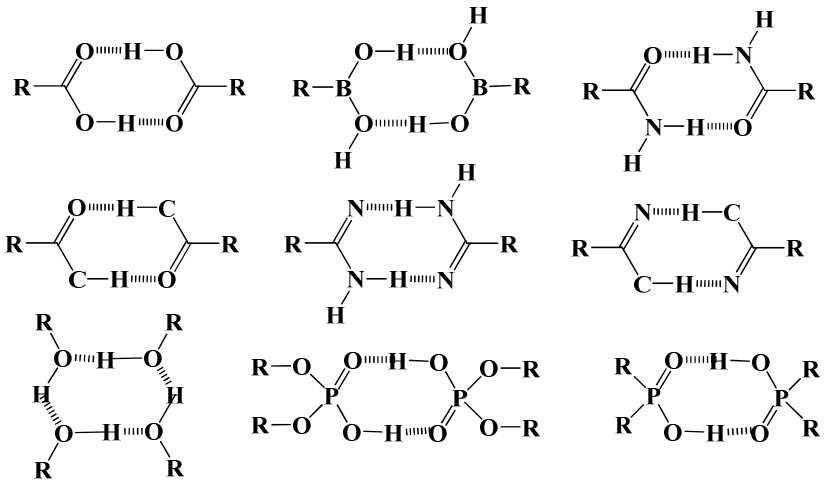
cooperativity,[13] is based on the fact that "a team being greater than the sum of its individuals". Thus, to achieve acceptable stability, molecules in self-assembled aggregates must be joined by many of these weak bonds.

Common arrangements of hydrogen bonds may be described as *simple bifurcated, trifurcated, bridging* or *cyclic* (Scheme 1.1). The most common hydrogen bond donor groups are C–H, N–H, O–H, S–H, P–H, F–H, Cl–H, Br–H and I–H while acceptor groups include N, O, P, S, F, Cl, Br and I as well as alkenes, alkynes, aromatic π-clouds and transition metals.



Scheme 1.1

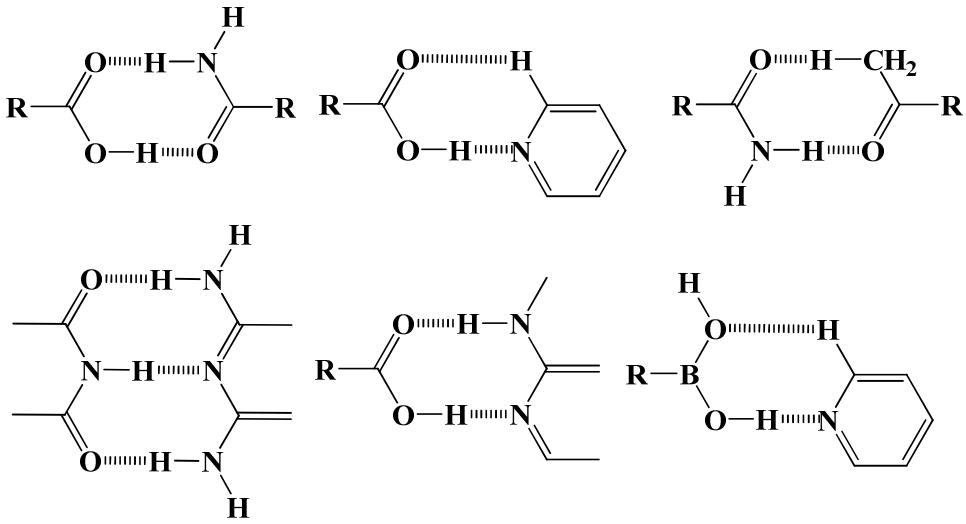
The strength and directionality of the hydrogen bond, as compared with other intermolecular forces, account for its significance and has made it the most important interaction in molecular recognition. Many design strategies for supramolecular synthesis have relied on the complementarity of hydrogen-bond interactions.



Scheme 1.2. Examples of self-complimentary (homomeric) hydrogen bond interactions.

The complimentarity can involve both geometric factors and a suitable balance between the number of hydrogen-bond donors and hydrogen-bond acceptors, as shown in scheme 1.2 for homomeric patterns.

Not only do these complementary supramolecular patterns bring molecules and ions together, they also constrain the relative orientation of those components in much the same way as carbon–carbon double bonds impart specific stereochemistry to individual molecules. More recently, many heteromeric (but still complementary) hydrogen-bond interactions (Scheme 1.3) have been employed in supramolecular synthesis.



Scheme 1.3. Examples of complementary heteromeric hydrogen bonding patterns.

The reliability of and competition between different patterns are most effectively determined through systematic database studies. Etter and coworkers[14] pioneered such explorations through extensive studies of preferential hydrogen-bond patterns in organic crystals and presented following empirical 'rules' as a guide for the design of hydrogen-bonded solids;

(i) All good proton donors and acceptors are involved in hydrogen bonding.

(ii) Six-membered ring intramolecular hydrogen bonds form in preference to intermolecular hydrogen bonds.

(iii) The best proton donor and acceptor remaining after intramolecular hydrogen bond formation will form intermolecular hydrogen bonds.

Graph set analysis of hydrogen bond motifs

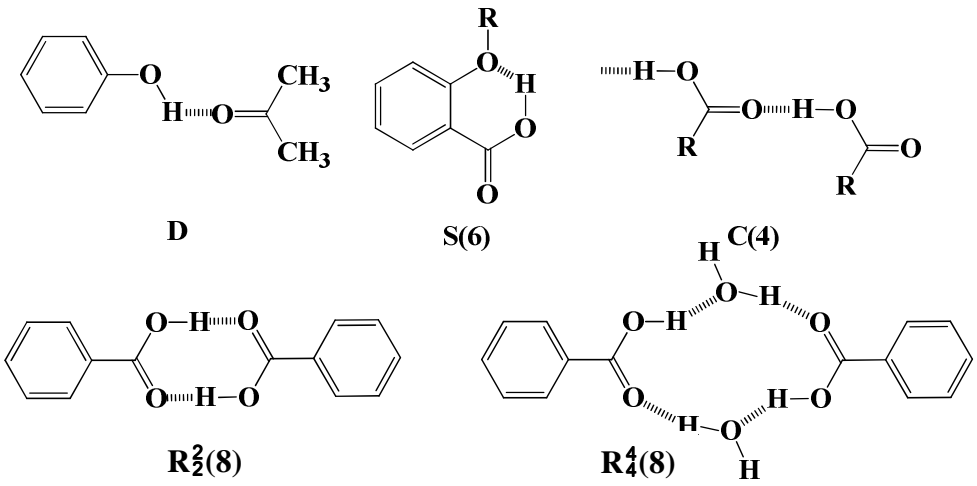
Graph set analysis of hydrogen bond motifs in fact simplifies the complex hydrogen bond networks through specific codes in a systematic process. The method is based on viewing hydrogen bond patterns topologically as if they were intertwined nets with molecules as the nodes and hydrogen bonds as the lines.

An important contribution by Etter, Bernstein and coworkers has been the introduction of a language based upon graph theory for describing and analyzing hydrogen-bonded networks in three-dimensional (3-D) solids.[15] The process of assigning a graph set (Scheme 1.4) begins by identifying the number of different types of hydrogen bonds present in the structure, and then by defining the bonds by the number of its donors and acceptors.

$$G_d^a(n)$$

Scheme 1.4. A generic graph-set descriptor.

A set of molecules connected via hydrogen bonds in a repeat unit, a motif, is characterized by one of four designators, C (chain), R (ring), D (dimer), or S (self, for intramolecular hydrogen bond). The numbers of donors and acceptors used in each motif are assigned as subscripts and superscripts respectively, and the total number of atoms in the repeat unit is denoted in brackets (Scheme 1.5). A benefit of using graph sets is that it brings the focus onto the hydrogen-bonded pattern, and not simply on the geometrical constraints of non-covalent interactions.



Scheme 1.5. Graph-set assignments for some hydrogen-bond motifs.

1.4 Self Assembly

Self-assembly may be defined as the process of spontaneous formation of supramolecular species from its components. For a majority of synthetic systems it appears to be a simple convergent process, giving rise to the assembled target in a straight forward manner.[16] Self-assembly requires molecular components containing two or more interaction sites and thus capable of establishing multiple connections. The self-assembly of a supramolecular architecture is a multistep process implying information and instruct components of one or several types. It is the spontaneous

organization of molecules or objects, under steady-state or equilibrium conditions, into stable aggregates, by noncovalent forces; these aggregates are not necessarily at a minimum in energy. The growth of crystal[17], the formation of liquid crystals[18], the spontaneous generation of synthetic lipid bilayer, the synthesis of metal co-ordination complexes[19], and the alignment of molecules on existing surfaces[20] are but a few of the many manifestations of self- assembly in chemical systems. A system that self-assembles can do so either reversibly or irreversibly. If the latter, the components must be able to adjust their positions within the aggregate if a highly ordered structure is to form. Irreversible aggregation without adjustment leads to glasses. Molecular recognition is the specific interaction between two molecules, which are complimentary in their geometric and electronic features.

1.5 Carboxyl group in self-assembly and supramolecular synthesis

Self-assembly driven by hydrogen bonds through the participation of carboxylic groups is abundant and played a crucial role in development of supramolecular chemistry.[21] For hydrogen bonds, carboxylic groups are very interesting functional units for many reasons. First, they exhibit dual character because the oxygen atom of the carboxyl group can act as an acceptor for hydrogen bonds whereas the hydroxyl group can act as a donor. Thus, with regard to hydrogen bonds, carboxylic groups are self-complimentary (i.e., two adjacent carboxylic groups can form a cyclic dimer interconnected by two equivalent hydrogen bonds). Common binding arrangements for carboxylic acids in molecular assemblies[21] are cyclic dimers, trimers, and catemeric motifs as depicted in Figure 1.5.

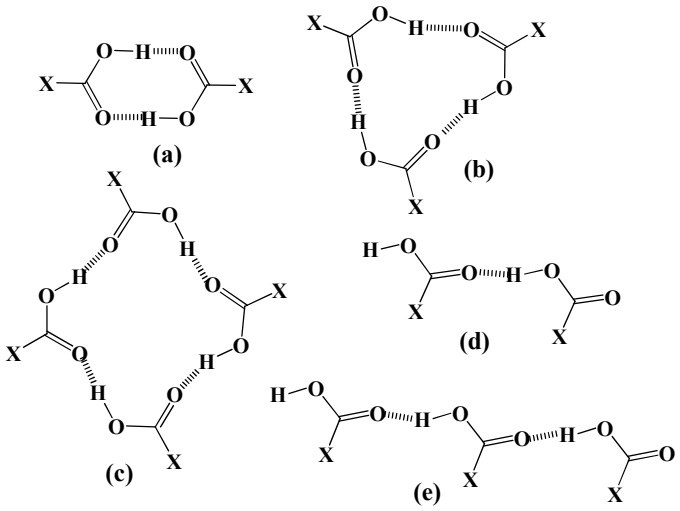


Figure 1.5. Most common modes of carboxylic self-association: (a) cyclic dimer, (b) cyclic trimer, (c) cyclic tetramer, (d) linear dimer, and (e) chain.

The most economical and efficient approach in designing a self-assembling aggregate is through the employment of the self-complementary molecules. This has been the approach used in the preparation of a vast ensemble of supramolecular assemblies; and the examples vary from the simple dimeric assemblies to stable porous three-dimensional networks obtained from various molecular building units. Thus, benzoic acid forms zero-dimensional units, isophthalic acid forms zigzag tapes, terephthalic acid forms one dimensional tapes, trimesic acid with its three fold symmetry forms a two-dimensional chicken wire network and adamantane tetracarboxylic acid group forms a diamondoid network in three-dimension, by utilizing robust dimeric hydrogen bonds as shown in Figure 1.6.[22] In fact the carboxylate groups are also known to be strong acceptors that often bond to multiple donors as noted in the examples thoroughly studied by Gorbitz and Etter. The hydrogen bonding networks and molecular structure organization in crystalline carboxylic acids have been exhaustively investigated by Leiserowitz.[22a]

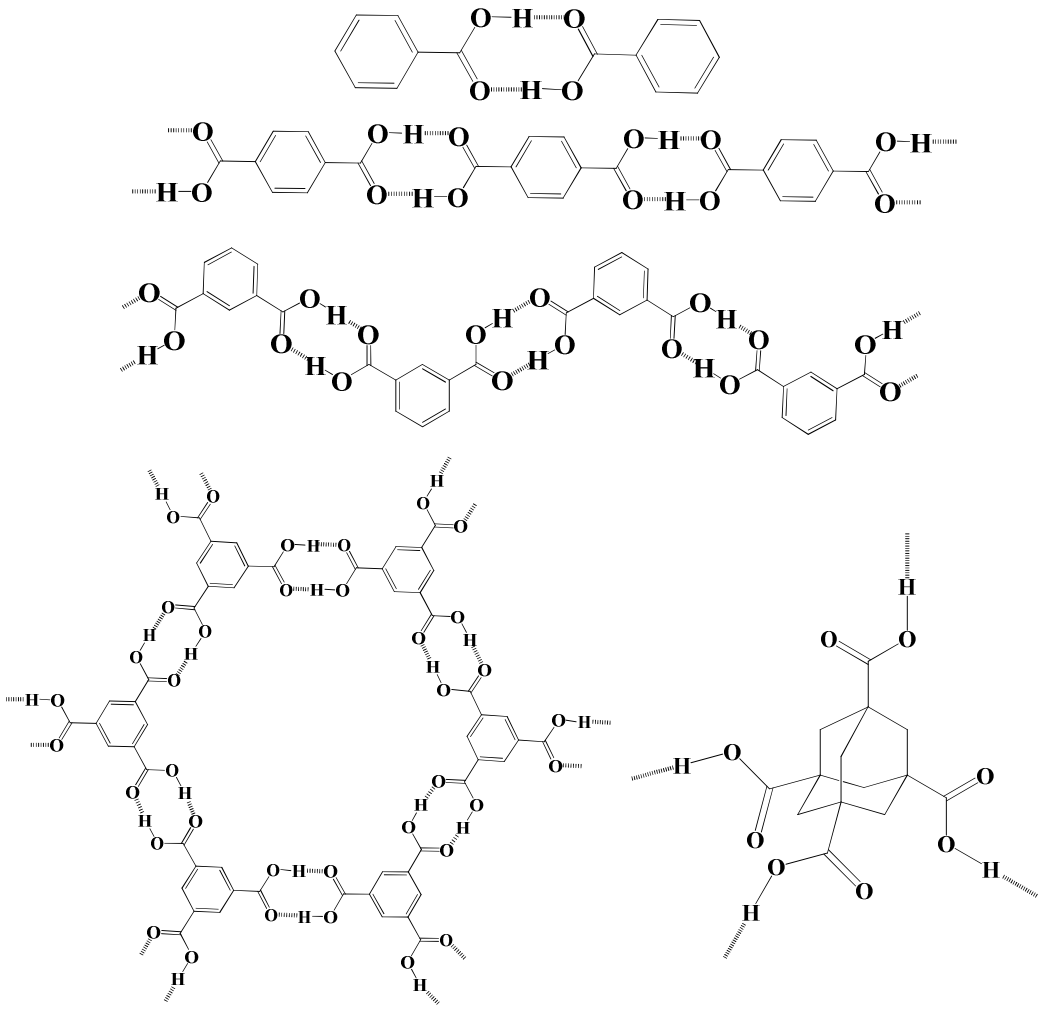


Figure 1.6. Construction of supramolecular assemblies through dimeric hydrogen bonds from different molecular building units.

1.5.1. Carboxyl group in organic assemblies

The strong and directional nature of hydrogen bonds formed by carboxyl groups is exploited in the organized self-assembly of molecules in solution and the solid-state. However, the understanding of factors that direct hydrogen bonding motifs when other functional groups are also present in the molecule is still evolving. For a successful outcome it is necessary to understand the synergy, interplay and competition between different functional groups during self-assembly. For example, interaction of –COOH with several aza compounds forming either O–H···N or O–H···N/ C–H···O pair wise hydrogen bonds[23], which finds applications in many

frontier areas of supramolecular chemistry. Some of the representative examples, observed from literature, are discussed below.

Zimmerman *et al*. reported an exotic hexagonal network of benzene-1,3,5-tricarboxylic acid (trimesic acid, **TMA**).[24] In this case, **TMA** and pyrene were co-crystallized from ethanol and the resulting assembly forms the host guest complex. The hexagonal host network is formed by the **TMA** and ethanol molecules forming cavity which is occupied by pyrene and ethanol molecules respectively as shown in Figure 1.7.

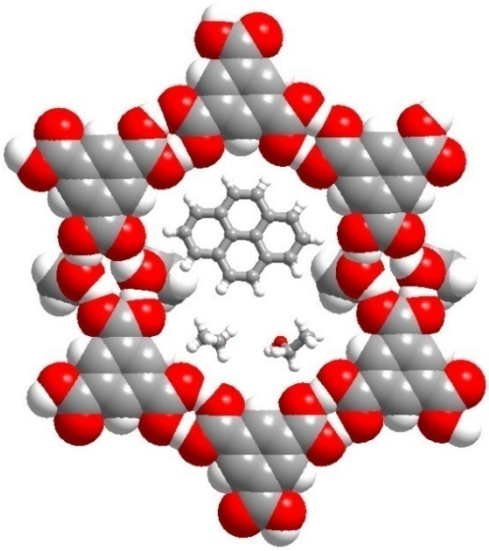


Figure 1.7. Space filling view of hexagonal host network of **TMA** and ethanol molecules to accommodate the guest species.

Zaworotko *et al*.[25] reported the 2:3 cocrystal of **TMA** and 4,4′-bipyridine (***bpy***), which represents a prototypal (6,3) honeycomb network formed by two molecular components. The co-crystal is sustained by pair wise hydrogen bonds and in effect the ***bpy*** molecules act as spacers between acid dimers, thereby expanding the 14 × 14 $Å^2$ **TMA** cavity to ca. 35 × 26 $Å^2$ as shown in Figure 1.8a. This hexagonal cavity is filled by 3-fold parallel interpenetration. Similarly co-crystallization reaction of **TMA** and *trans*-1,2-bis(4-pyridyl)ethane (***bpyea***) exhibit expanded hexagonal (6, 3)

networks of cavity of 41 × 35 $Å^2$ (See Figure 1.8b) dimensions with 3-fold parallel interpenetration occurs once again. Later similar results were reported by Nangia et al. replacing **TMA** with 1,3,5-cyclohexane-tricarboxylic acid. [26]

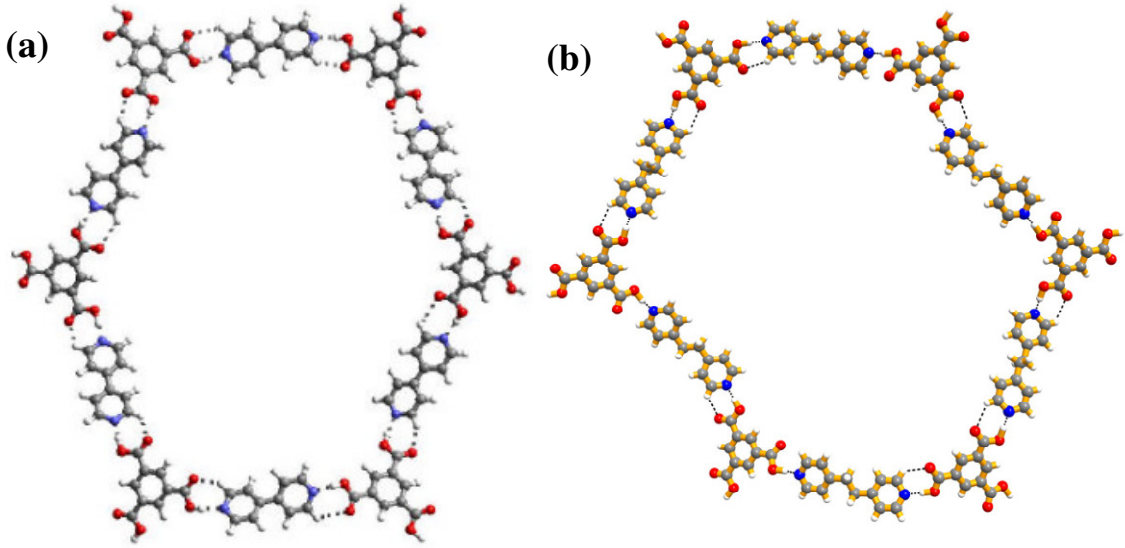


Figure 1.8. Super honeycomb (6,3) network in the molecular complex of **TMA** with ***bpy*** (a) and with ***bpyea*** (b).

Coppens and co-workers[27] developed a host-guest complex by reaction of tridentate ligand 1,3,5-tri(4-pyridyl)-2,4,6-triazine (**TPT**) and **TMA** in the presence of pyrene, which forms a honeycomb framework. The observed three-dimensional structure, with four pyrene molecules in each channel, is shown in Figure 1.9.

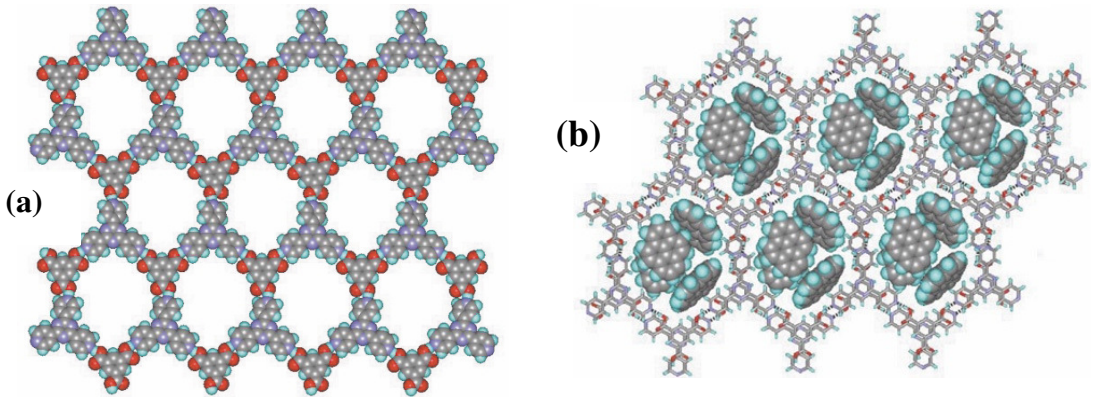


Figure 1.9. (a) Honeycomb framework formed by **TMA** and **TPT** in space filling model (b) Arragment of four pyrene molecules in honeycomb network.

Pedireddi *et al*. reported numerous supramolecular assemblies that primarily possess –COOH and aza-donor moieties to deduce the salient features of recognition patterns in terms of the pK_a of the constituents.[28] The co-crystallization of 2,4-diamino-6-methyl-1,3,5-triazine (**DMT**) with various aliphatic dicarboxylic acids, such as malonic, succinic, or adipic acid. The different types of host–guest arrangement appear to result from differences in the acidity of the dicarboxylic acids, that is, acids with pK_a <3.0 give host networks that consist of **DMT** (Figure 1.10a) and the corresponding acid with water or solvent molecules of crystallization present as guests, whereas acids with pK_a >3.0 host is being constituted by **DMT** and malonate molecules as shown in Figure 1.10b, with the channels are being filled by water molecules.

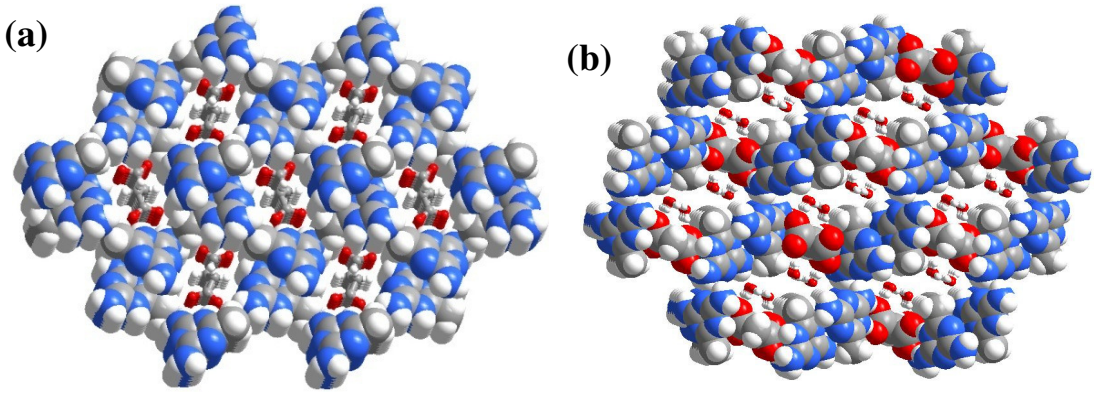
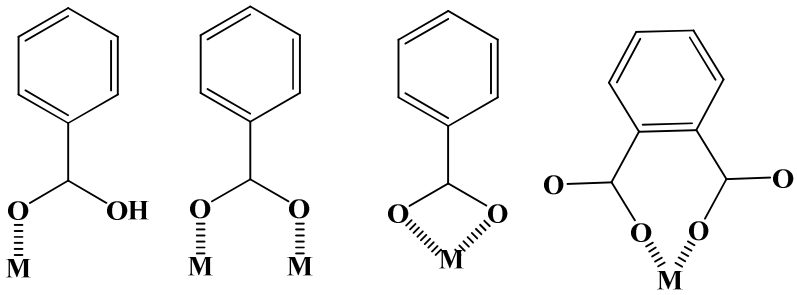


Figure 1.10. (a) Host-guest network observed in complex, **DMT**-Succinic acid, with the host being formed by the molecules of **DMT** and succinate molecules occupying the channels. **(**b) Host-guest network observed in complex **DMT**-malonic acid, with the channels being filled by guest water molecules.

1.5.2 Carboxylate as a ligand for coordination

Metal Organic Frameworks (MOFs) are metal clusters interconnected by organic linker groups, a design that endows the materials with large pores, open channels, and huge internal surface areas for adsorbing molecules. By mixing and

matching metal oxide nodes with a wide variety of organic struts, Yaghi[29], Zaworotko[30], Braga[31], Kitagawa[32], Ferey[33], Rosseinsky[34], have made an enormous variety of MOFs. Construction of MOFs using dative bonds is 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. Amongst a wide range of functional groups used in MOFs carboxylate group is well known for its ability to co-ordinate with metals. Thus carboxylates allow for the formation of more rigid frameworks due to their ability to aggregate with metal ions into M–O–C clusters that refers to as secondary building units (SBUs). There are several bonding modes of the carboxylate group in metal coordination as shown in Scheme 1.6. The SBUs are sufficiently rigid because the metal ions are locked into their positions by the carboxylates; thus, instead of having one metal ion at a network vertex, the SBUs serve as large rigid vertices that can be joined by rigid organic links to produce extended frameworks of high structural stability.



Scheme 1.6

Champness and co-workers[35] synthesized the robust metal-organic framework by hydrothermal reaction of $ZnCl_2$ and 4,4′-bipyridine-2,6,2′,6′-tetracarboxylic acid (H_4L) (See Figure 1.11a), which serves as a representative example with exhaustive studies as illustrated below. Compound **I** crystallizes in a

chiral space group, with the chirality generated by the helical chains of hydrogen-bonded guest water molecules rather than by the coordination framework. Removal of guest water molecules from the crystal affords the porous material, $[Zn_2(L)]$(**II**), which has very high thermal stability and is chemically inert.

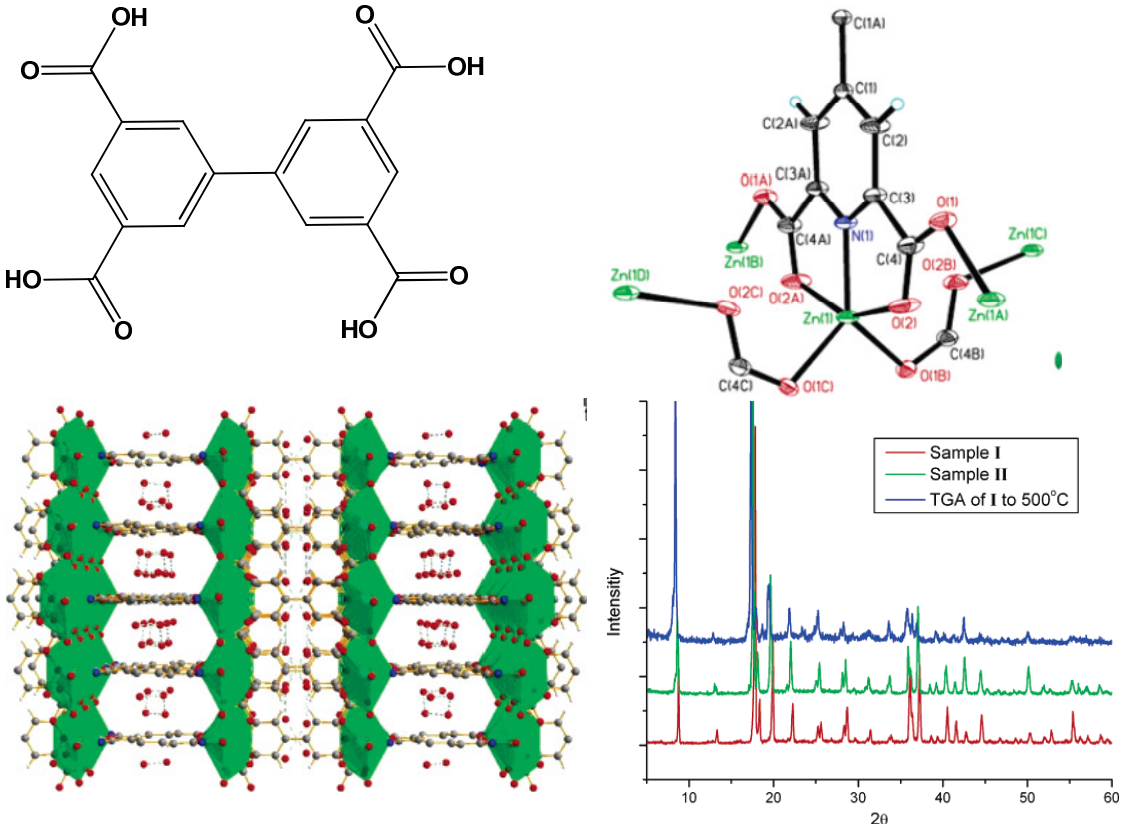


Figure 1.11. (a) Carboxylic acid ligand H_4L, used for synthesis. (b) Coordination geometry of Zn(II) in the crystal structure of {$[Zn_2(L)]\infty 4H_2O$} (**I**). (c) Framework structure of {[Zn2(L)] ∞4H2O} (**I**), in which Zn(II) coordination spheres are represented by green polyhedron and channel occupied by guest water molecules (d) Powder XRD patterns of **I**, **II** and a sample of **I** after TGA to500 °C.

The framework is constructed from Zn(II) ions and anionic ligands, L^{4-}. Zn(II) is coordinated by a tridentate array comprising two O-donors from 2,6-dicarboxylate groups and one pyridyl N-donor, all from the same ligand (Figure 1.11b). The crystal structure of **I** shows a three-dimensional host framework with interconnecting pore cavities containing water molecules as shown in Figure 1.11c. The framework of

compound **I** has a high thermal stability. According to the TGA and DSC data, no phase change was recorded after the removal of the water molecules from the channels up to 250 °C in air or 450 °C under a nitrogen atmosphere, above which the framework starts to decompose. Variable temperature XRPD confirms that considerable crystallinity remains, even after the sample has been heated to 500 °C in a TGA experiment, with only small levels of peak broadening observed (Figure 1.11d).

1.5.2.1 MOFs as gas storage materials

Porous metal organic frameworks can be used as materials for the gas storage, especially, the hydrogen gas adsorbed in metal organic frameworks has potential application as alternative fuel for running motor vehicles.[36] Hydrogen is an ideal fuel for running automobiles, as the chemical energy released on its oxidation (33.9 kcal kg^{-1}) is approximately three times larger than the other chemical fuels (for example, the equivalent value for liquid hydrocarbons is 11.2 kcal kg^{-1}). The other advantage of hydrogen is that, it is a green fuel, as the exhaust gas evolved is only water vapors, when burnt with oxygen. But the only problem for running the vehicles on hydrogen gas is its storage.

One of the first metal–organic frameworks investigated for hydrogen storage was the cubic carboxylate-based framework $Zn_4O(BDC)_3$, also known as MOF-5 or IRMOF-1.[37] Yaghi and co-workers made use of metal-carboxylate cluster chemistry to form this open metal-organic frameworks. They made MOF-5 by the diffusion of triethylamine into a solution of zinc(II) nitrate and terephthalic acid in DMF/chlorobenzene.

In MOF-5, four ZnO_4 tetrahedra with a common vertex form a supertetrahedral cluster, each edge of the Zn tetrahedron is then capped by the $-CO_2$ group, to form octahedral secondary building unit (SBU), having formula $Zn_4O(CO_2)_6$. The octahedral SBU are joined together by benzene links, forming cubic network in which the vertices are the octahedral SBU and the edges are the benzene struts, as shown in Figure 1.12.

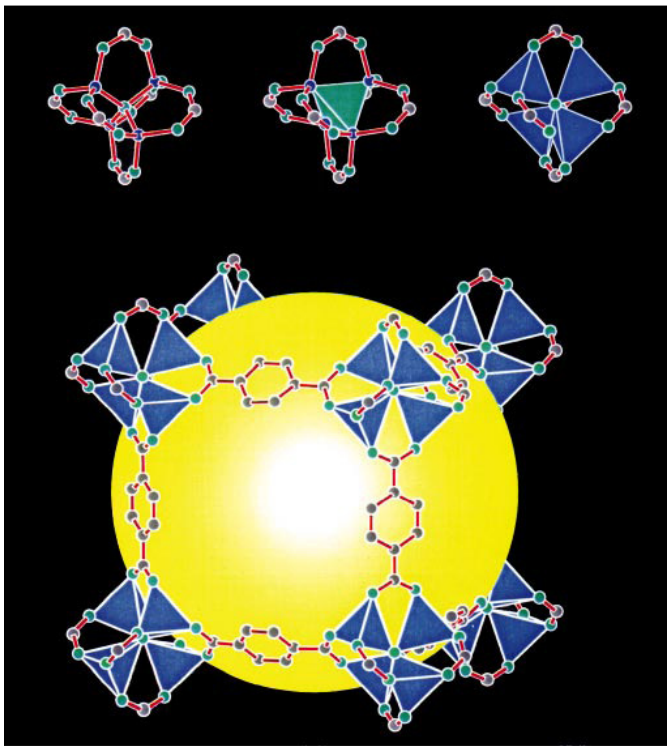


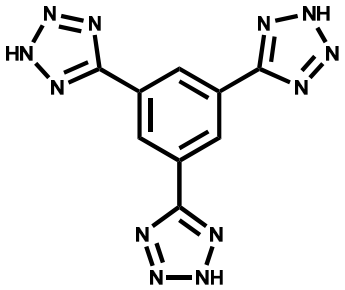
Figure 1.12. Porous network formed by the reaction between terephthalic acid and zinc salt.

In the framework so formed there is a lot of free space and this space is filled by the guest molecules of DMF and C_6H_5Cl. Due to high mobility, the guests can be fully exchanged with chloroform. More significant is that all the chloroform guests can be evacuated from the pores within 3 hours at room temperature and 5×10^{-5} torr, without loss of framework periodicity. They heated the fully desolvated crystals

in the air at 300°C for 24 hours, which has no effect on either their morphology or crystallinity, which gives a further evidence of the stability of the crystals.

MOF-5 shows different H_2 gas storage properties depending upon the procedure of preparation and handling.[38] MOF-5 decomposes in humid air, due to atmospheric water. The best H_2 storage MOF-5 is obtained by minimizing the exposure to water and air. Sample of MOF-5 prepared with exposure of air, adsorbed 5.0 excess wt% H_2, whereas it was 7.1 excess wt% H_2, when MOF-5 was prepared in vacuum.

While $Zn_4O(BDC)_3$ exhibits excellent hydrogen storage characteristics at 77 K, its performance at 298 K is poor due to the weak interactions with H_2. The framework having open metal coordination sites on its surface can increase the strength of H_2 adsorption, resulting in an improved performance at 298 K. This was first demonstrated in $Mn_3[(Mn_4Cl)_3(BTT)_8]_2$, prepared by Long and co-workers,[39a] which contains open Mn^{2+} coordination sites, as shown in Figure 1.13. This framework exhibits a volumetric storage capacity of 60 g L^{-1} at 90 bar and 77 K, despite having a BET surface area of just 2100 m^2 g^{-1}. Most notably, however, at 90 bar and 298 K, a capacity of 12.1 g L^{-1} was observed. This is 77% greater than the density of the compressed H_2 gas, under these conditions.



1,3,5-Tris(2H-tetrazol-5-yl)benzene (H_3BTT)

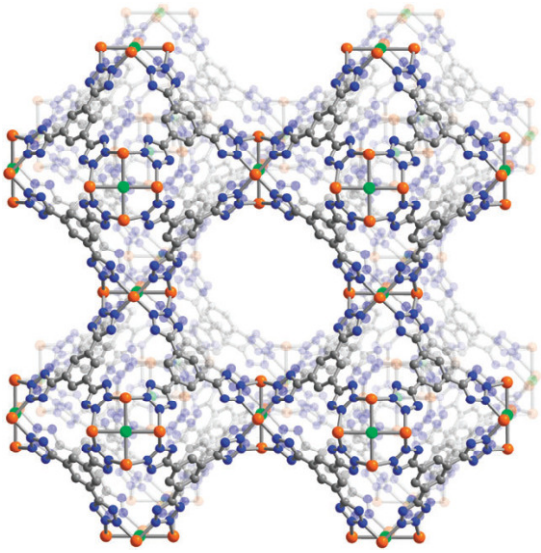


Figure 1.13. Formation of $Mn_3[(Mn_4Cl)_3(BTT)_8]_2$, having open Mn^{2+} coordination sites

One of the challenges in the field of supramolecular chemistry is the design and synthesis of chemical structures with exceptionally high surface area. In this regard, MOF-177 {Zn_4O(1,3,5-benzenetribenzoate)$_2$}, is a representative example for metal-organic framework with a large surface area,[39b] estimated at 4,500m^2 g^{-1}. Block shaped crystals of MOF-177 were produced by heating a mixture of H_3BTB and $Zn(NO_3)_2.6H_2O$ in *N*,*N*-diethylformamide (DEF) to 100° C. The crystals were formulated by elemental analysis as $Zn_4O(BTB)_2.(DEF)_{15}(H_2O)_3$. On heating this sample, solvent guest molecules leave between 50-100° C, yielding a remarkable three dimensional open framework of composition $Zn_4O(BTB)_2$, as shown in Figure 1.14.

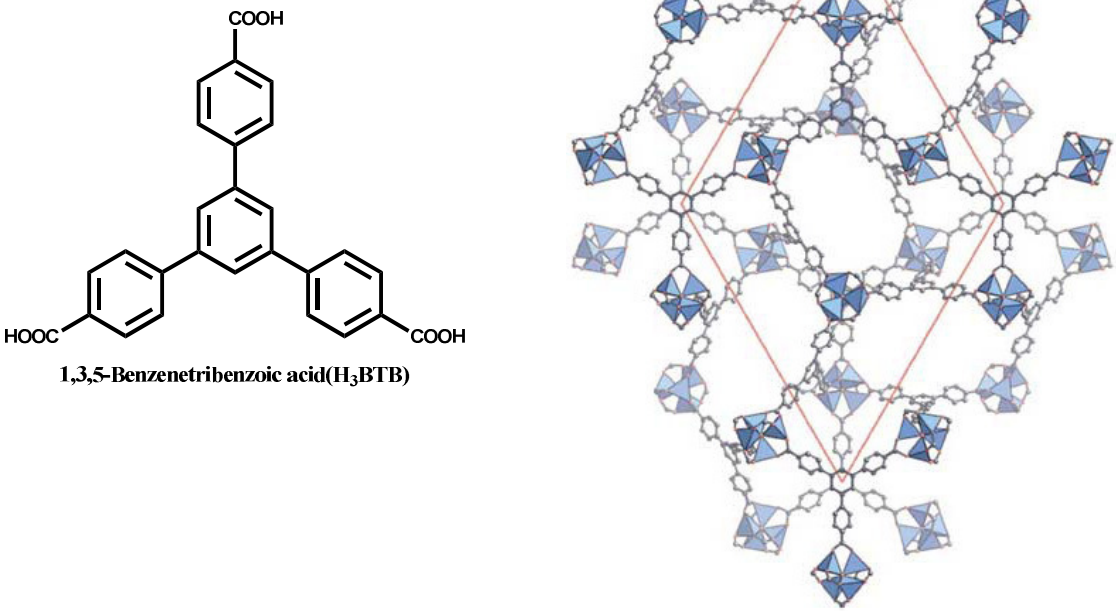


Figure 1.14. Metal organic framework formed between 1,3,5-benzenetribenzoic acid and zinc having high surface area

Hydrogen isotherms up to 90 bar at 77K for MOF-177 show saturation uptake of H_2 between 70 and 80 bar, giving H_2 uptake of 7.5 wt%. Although gravimetric capacity is often a major target for research in H_2 storage materials, there are practical limitations associated with the tank volume required to house the sorbent which makes volumetric capacity just as critical a parameter to consider. So conversion of the gravimetric data to the volumetric data units(g H_2/L), using the crystal density of MOF-177 = 0.477gcm^{-3}, H_2 uptake of 32g/L is obtained, which is well within the realm of the 2010 DOE target of 45g/L.

1.5.2.2 MOFs in separation of molecules

Metal organic frameworks can be utilized for the separation of molecules, as shown by Jing Li et al.[40] They prepared open metal framework of general formula [Cu(4,4'-(hexafluoroisopropylidene)bis(benzoate)(4,4'-(hexafluoroisopropylidene)bis-(benzoic acid)$_{0.5}$], having irregular-shaped micro-channels with alternating large cages and small entrances that connect these cages, as shown in Figure 1.15(a). This network exhibits unique adsorption properties as it adsorbs propane and butane rapidly, but does not adsorb pentane or higher normal or branched hydrocarbons. Thus, the microchannels are unique in being able to seperate normal C_2, C_3 and *n*-C_4 olefins and alkanes from all branched alkanes and all normal hydrocarbons above C4 as shown in Figure 1.15(b).

The unusual property is attributed to a narrowing of channel at intervals of 7.3Å, which is just greater than the length of *n*-C_4 (approximately 6.9 Å), and just less than the length of *n*-C_5 (approximately 8.1 Å). The diameter of the neck is approximately 3.2 Å. This neck is large enough for the passage of normal alkanes but small enough for branched alkanes.

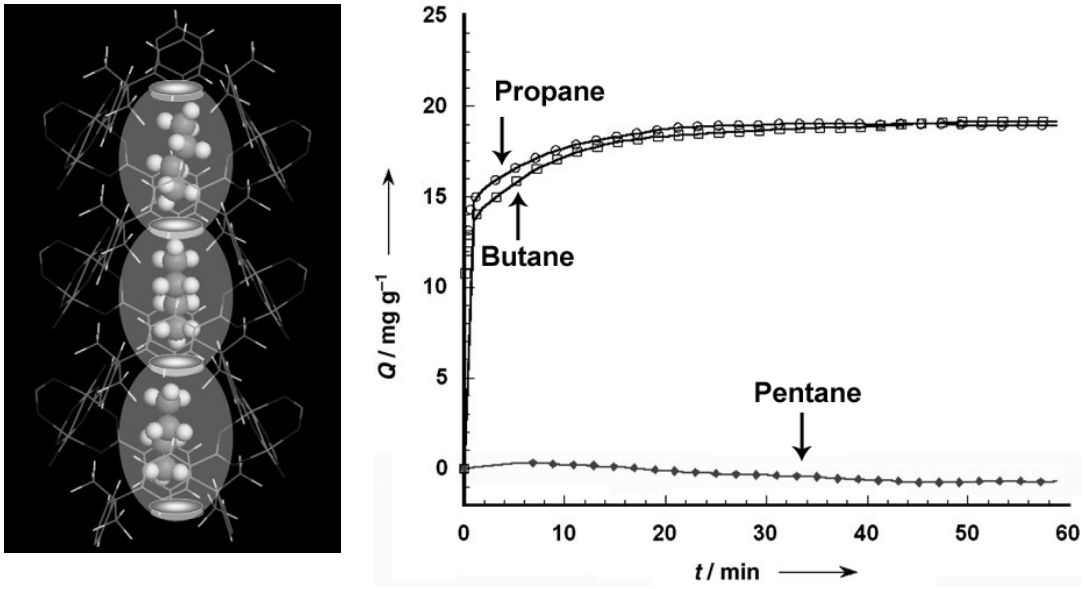


Figure 1.15. (a) Arrangement of butane molecules in the microchannels of the open frame network, with one molecule per cage. (b) Adsorption of propane, butane and pentane at 90°C and 650 torr, as a function of time. Q is the weight of the hydrocarbon molecules adsorbed in the adsorbent

1.5.2.3 MOFs as Catalysts

Metal organic frameworks can catalyze the reactions. In a typical example, Fujita and co-workers showed that a co-ordination network prepared with $Cd(NO_3)_2$ and 4,4'-bipyridine, of composition $\{[Cd(4,4'\text{-bpy})_2(H_2O)_2](NO_3)_2\cdot 4H_2O\}_n$, catalyze cyanosilylation of imines under heterogeneous conditions,[41] as shown in Figures 1.16(a) and (b). Heterogeneous catalytic process is demonstrated by NMR of relatively slow cyanosilylation of CF_3 substituted imine, as shown in Figure 1.17. The solid line in the graph (Figure 1.17 (b) shows progress of the reaction in the presence of catalyst. In a controlled experiment, filtration of this catalyst at any given course of reaction process, retarded the progress of conversion, highlighting the catalytic activity of the metal-organic framework solid described above, which is represented in dashed and dotted lines, in Figure 1.17 (b).

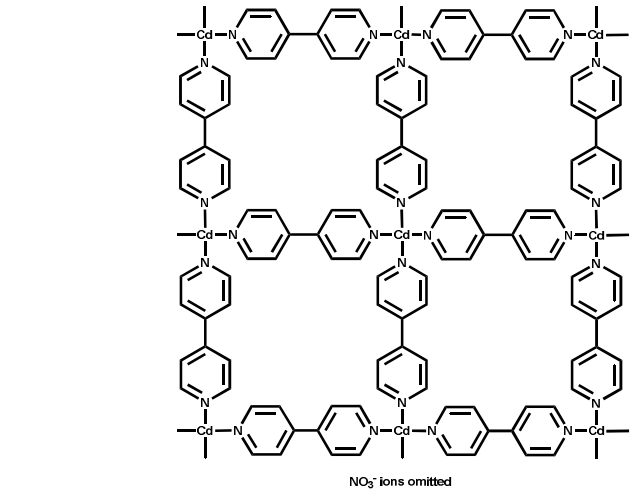


Figure 1.16. (a) Grid network formed by cocrystallizing $Cd(NO_3)_2$ and 4,4'-bpy of composition $\{[Cd(4,4'\text{-bpy})_2(H_2O)_2](NO_3)_2{\cdot}4H_2O\}_n$. (b) catalysed reaction cyanosilylation of imines, under heterogeneous conditions.

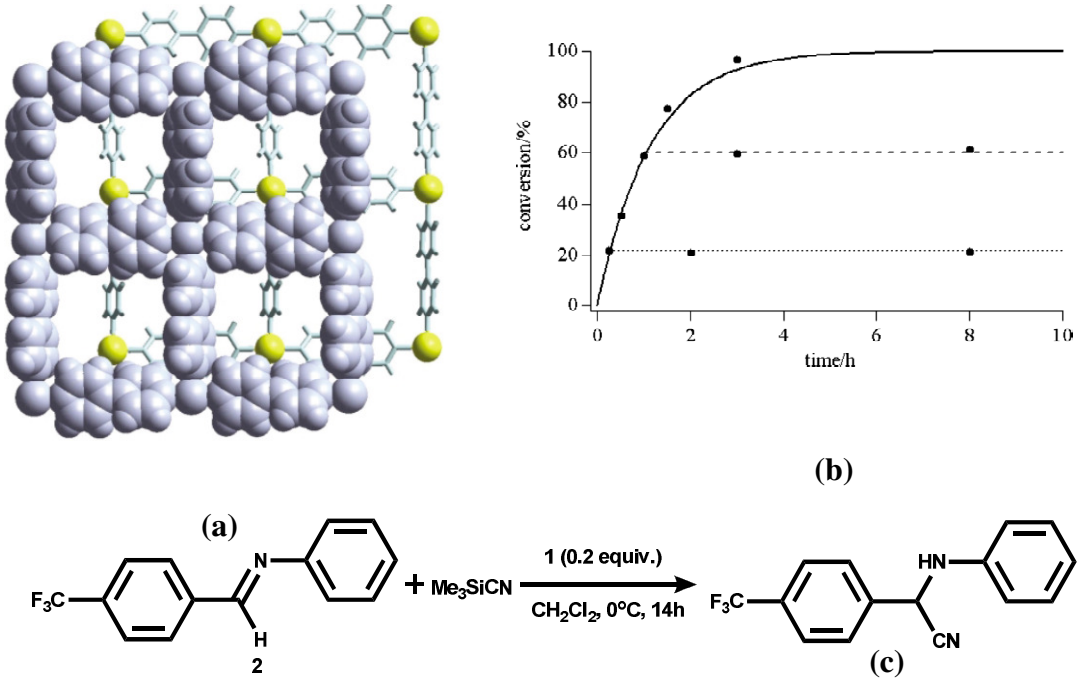


Figure 1.17. (a) Geometrical relationship between the two adjacent layers of **1**. Substrates accommodated in the square cavity of the first layer can interact with Lewis acid Cd(II) center of the second layer. (b) The conversion of the cyanosilylation of CF_3-substituted imine determined by NMR: dot and dashed lines indicate the conversion after filtration of solid at 0.25 and 1 h, respectively and the reaction is shown in the Figure (c)

1.6 Applications of Supramolecular Assemblies

1.6.1 Synthesis of new molecules

Carbon-carbon bond formation lies at the heart of synthetic chemistry. Primary goals in the synthesis of molecules are to obtain possible high yields, limited byproducts, and minimal waste. Novel methods and means of procedures are always on continuous search to develop improved ways to control the formation of covalent bonds. In this process, one of the elegant processes in organic chemistry is C-C bond formation, which is based on topochemical principles for [2+2] photoreactions in the solid state, as described by Schmidt and co-workers through a number of crystallographic investigations. According to this principle, for photodimerization to occur in the solid state, olefinic bonds should be parallel and separated by < 4.2 Å in the solid state structure.[42] Since then chemists have strived to design molecules that will predictably crystallize to allow such reactions to occur. Such an approach to synthesis leads to the formation of covalent bonds 'at will' in solids to facilitate the high yield, solvent-free synthesis of molecules.

MacGillivray and co-workers forwarded novel methodology to achieve controlled [2+2] photodimerization reaction,[43] involving a linear template, based on 1,3-dihydroxybenzene (resorcinol), by enforcing topochemical alignment of olefins in the solid state, creating a template through supramolecular aggregation as demonstrated in the co-crystals of 1,3-dihydroxybenzene (resorcinol) and 1,2-*bis*(4-pyridyl)ethene (Figure 1.18).[44]

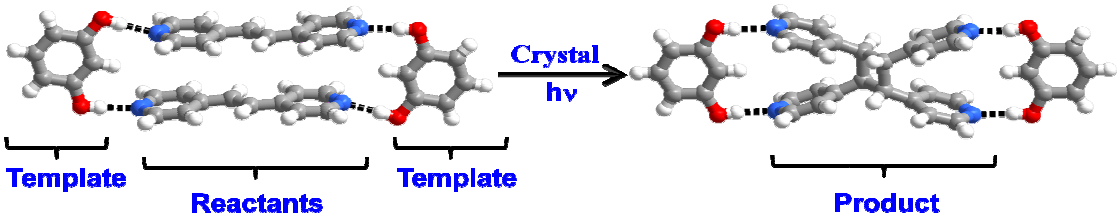


Figure 1.18. New methodology to achieve controlled [2+2] photodimerization reaction

Co-crystallization of recorcinol with 1,2-*bis*(4-pyridyl)ethene yielded a four component assembly, 2(4,4'-bpe).2(resorcinol), in which the olefins of the complex are arranged in parallel fashion, seperated by ~4 Å. Upon photoirradiation, a [2+2] photodimerization reaction took place, yielding *rctt*-tetrakis(4-pyridyl)cyclobutane (tpcb) in 100% yield.

By the similar template directed synthesis [n]-ladderanes[45] were synthesized by most economical and high yields. [n]-ladderane is a molecule that consists of n edge-sharing cyclobutane rings (where n ≥2) that define a molecular equivalent of a macroscopic ladder, as shown in Figure 1.19.

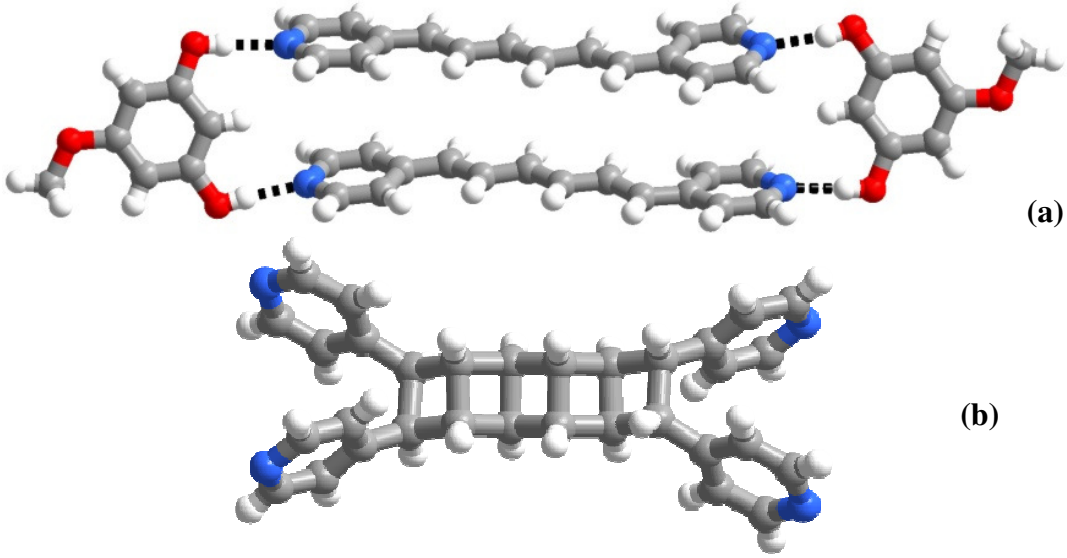


Figure 1.19. a) Co-crystal formed between 5-methoxyresorcinol and 1,6-*bis*(4-pyridyl)hexatriene and b) ladderane formed on irradiating the co-crystal.

Christian Wolf and co-workers utilized pairwise hydrogen bond dimeric interactions between -COOH group of fumaric acid and aza-donor group of 1,8-dipyridylnaphthalene to form a tetrameric assembly stabilized by eight hydrogen bonds.[46] The rigid spatial arrangement of the cofacial pyridyl rings in the template forces two adjacent dicarboxylic acids into close proximity with an intermolecular distance of less than 4.0 Å. Photoirradiation of the crystal resulted in stereoselective conversion of fumaric acid to *cis*, *trans*, *cis*-cyclobutanetetracarboxylic acid in 100% yield as shown in Figure 1.20.

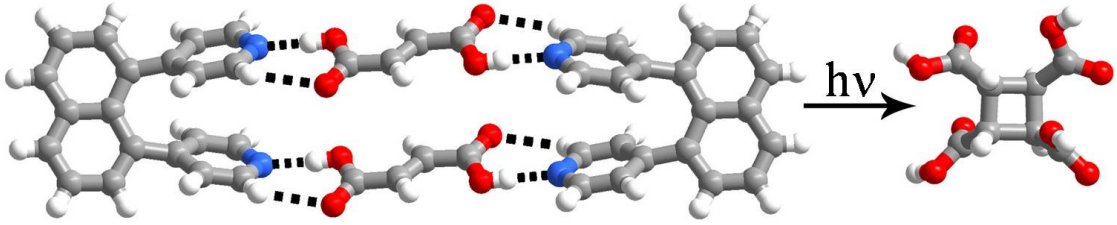


Figure 1.20. Formation of *cis*-cyclobutanetetracarboxylic acid by photodimerization reaction.

Jones and co-workers used polyfunctional templates for the synthesis of [2+2] photodimerized product. On irradiating the co-crystal of 1,2,4,5-benzenetetracarboxylic acid and 1,2-*bis*(4-pyridyl)ethene, in which the adjacent molecules of aza-donor moieties satisfy the criteria of [2+2] photodimerization, the photodimerized product *rctt*-tetrakis(4-pyridyl)cyclobutane (**tpcb**) was obtained in 100% yield.[47] Further, irradiated sample upon co-crystallization from DMSO gave a structure with a porous host network, as shown in Figure 1.21 (a) and (b), with the voids being filled by the guest molecules of DMSO and water.

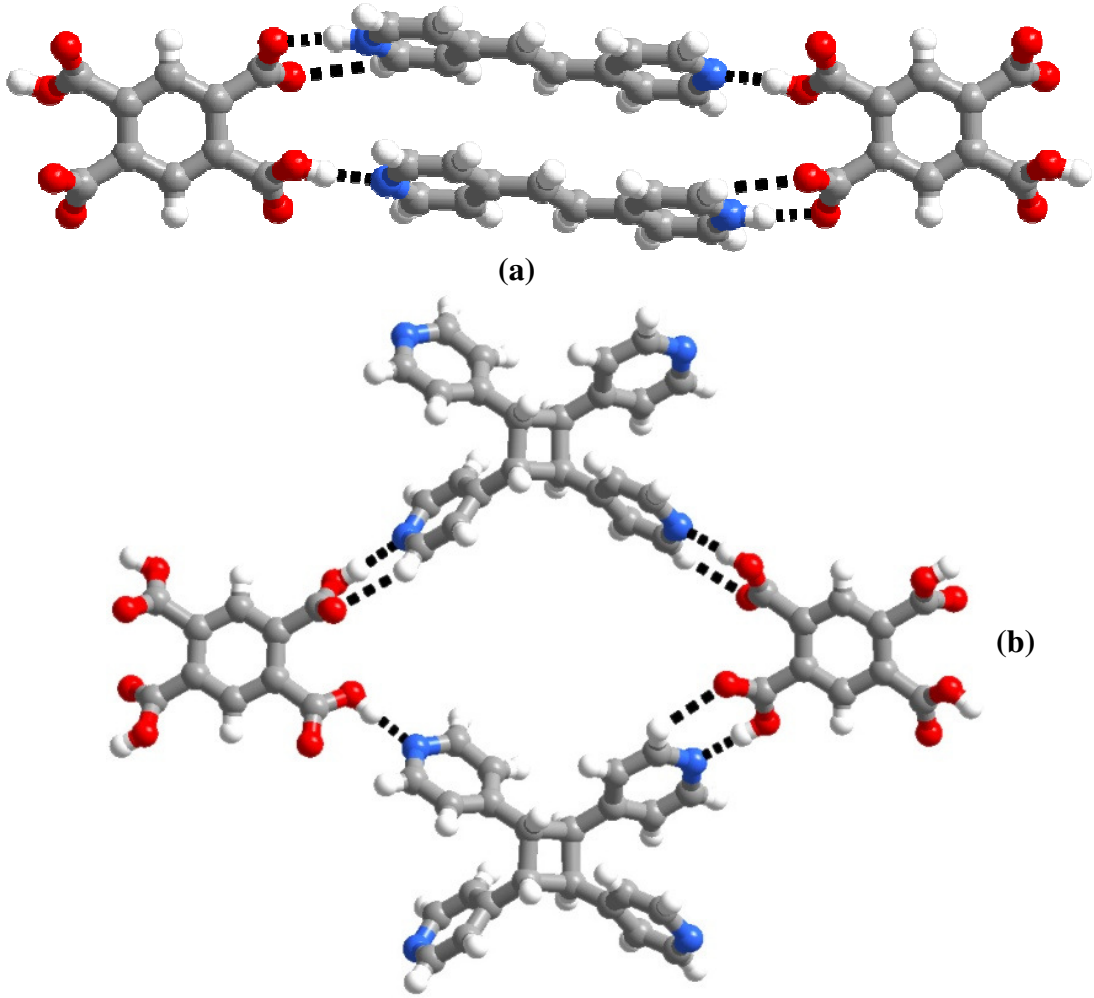


Figure 1.21. (a) Co-crystal formed between 1,2,4,5-benzenetetracarboxylic acid and 4,4'-bipyridine ethene (b) Porous network formed by the irradiation of co-crystal of 1,2,4,5-benzenetetracarboxylic acid and 1,2-*bis*(4-pyridyl)ethene (solvent molecules are removed for clarity)

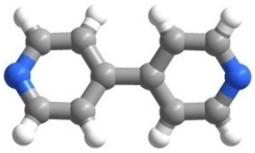
1.6.2 Pharmaceutical Co-crystallisation

Expedition of novel methodologies for the delivery of the active pharmaceutical ingredient (API's) is a continuous challenging task in the process of development.[45] However, recent advancements in the areas of supramolecular chemistry, under the umbrella of polymorphism,[48] reveal that different solid forms of the same compound show different chemical and physical properties. Thus, the solid-state chemistry of API's has become a subject of fundamental, practical and

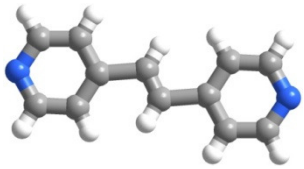
legal interest. As a result, polymorphs, solvates, salts, etc., of API's represent extensions of chemical space, with the enhancement or new chemical and physical properties, leading to extended patent coverage and consequent legal protection of products that may be of great concern to innovator and generic pharmaceutical companies.[49]

Pharmaceutical co-crystals extended the crystal engineering paradigm to control polymorphism in active pharmaceutical ingredients (APIs), patenting of new forms, drug formulations and delivery[50-52]. An effective approach to understanding and designing co-crystals is to apply the crystal engineering strategies, in particular exploitation of supramolecular patterns.

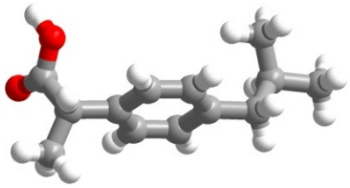
Zaworotko and co-workers co-crystallized 4,4'-bipyridine with ibuprofen, flurbiprofen and aspirin, as well as and 1,2-*bis*(4-pyridyl)ethene with flurbiprofen, involving dimeric interaction between carboxylic acid functional group and aza-donors.[53] In all the co-crystals the drug molecules and the aza-donor compounds co-crystallized in 2:1 ratio, respectively, as shown in Figure 1.22.



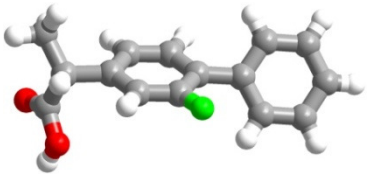
4,4'-Bipyridine
Melting Point = 111-114°C



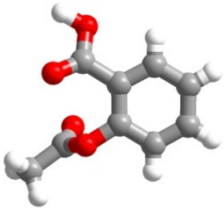
1,2-*bis*(4-pyridyl)ethene
Melting Point = 150-153°C



Ibuprofen
Melting Point = 77-78°C



Flurbiprofen
Melting Point = 113-114°C



Aspirin
Melting Point = 133-135°C

Caffeine is known to exhibit instability with respect to humidity. Jones and co-workers, have prepared co-crystals, A{Caffeine/Oxalic acid (2:1)}, B{Caffeine/malonic acid (2:1)} and D{Caffeine/maleic acid (1:1)}. They also compared the stabilities of caffeine with the co-crystals they formed and also some other already known co-crystals like C{Caffeine/maleic acid (2:1)}, E{Caffeine/glutaric acid (1:1) Form I}, F{Caffeine/glutaric acid (1:1) Form II} and the results obtained are as summarized in Chart 1.[54]

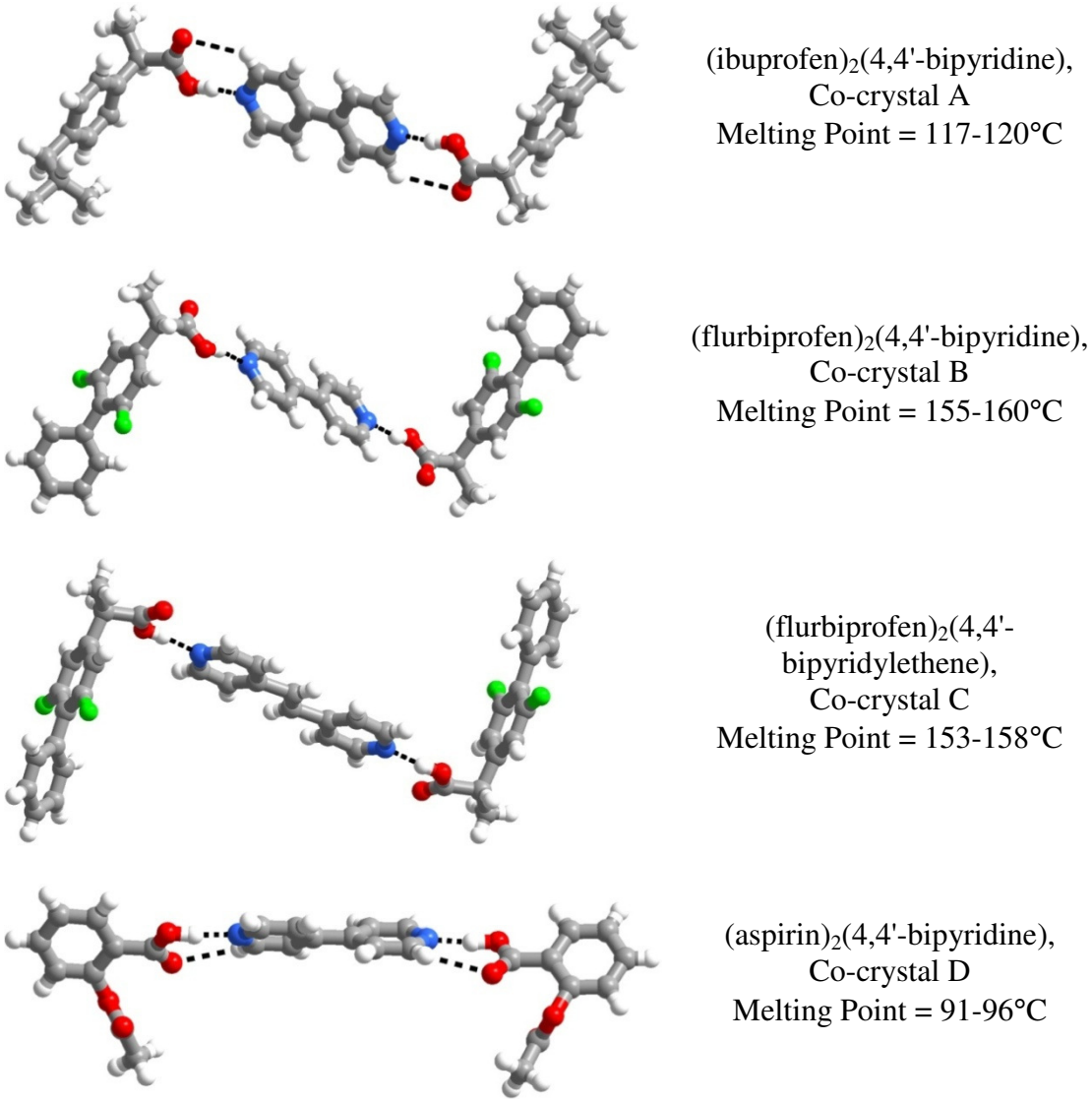


Figure 1.22. Pharmaceutical co-crystals formed between the drug molecules and 4,4'-bipyridine and 1,2-*bis*(4-pyridyl)ethene.

Material	Condition (%RH)	Observed Relative Humidity Stability*			
		1 day	3 days	1 week	7 weeks
Caffeine	0	✓	✓	✓	✓
	43	✓	✓	✓	✓
	75	✓	✓	✓	✓
	98	×	×	×	×
A {Caffeine/Oxalic acid (2:1)}	0	✓	✓	✓	✓
	43	✓	✓	✓	✓
	75	✓	✓	✓	✓
	98	✓	✓	✓	✓
B {Caffeine/malonic acid (2:1)}	0	✓	✓	✓	✓
	43	✓	✓	✓	✓
	75	✓	✓	✓	✓
	98	✓	✓	✓	×
C {Caffeine/maleic acid (2:1)}	0	✓	✓	✓	✓
	43	✓	✓	✓	✓
	75	✓	✓	✓	✓
	98	×	×	×	×
D {Caffeine/maleic acid (1:1)}	0	✓	✓	✓	✓
	43	✓	✓	✓	✓
	75	✓	✓	✓	✓
	98	×	×	×	×
E {Caffeine/glutaric acid (1:1) Form I}	0	✓	✓	✓	✓
	43	✓	×	×	×
	75	×	×	×	×
	98	×	×	×	×
F {Caffeine/glutaric acid (1:1) Form II}	0	✓	✓	✓	✓
	43	✓	✓	✓	✓
	75	✓	✓	✓	✓
	98	✓	✓	×	×

*Note: The symbol ✓ indicates that the crystalline material was stable at that condition and time point. The symbol × indicates that the crystalline material exhibited physical instability at that time point: Caffeine converted to caffeine hydrate, co-crystals B, C, D and F dissociated into molecular components; and the co-crystal E was observed in some instances to convert to polymorph F before dissociating.

Chart 1

From the results so obtained, it is clear that the co-crystals A, B and F are more stable to the moisture as compared to caffeine itself.

Itraconazole is an extremely water-insoluble antifungal drug that is marketed in the amorphous form (Sporanox capsule) to achieve the required oral bioavailability. Remenar and co-workers made co-crystals of itraconazole with fumaric acid, succinic acid, L-malic acid, L-tartaric acid, D-tartaric acid and D, L-tartaric acid and a typical co-crystal formed between itraconazole and succinic acid in 2:1 ratio, is shown in Figure 1.23.[55]

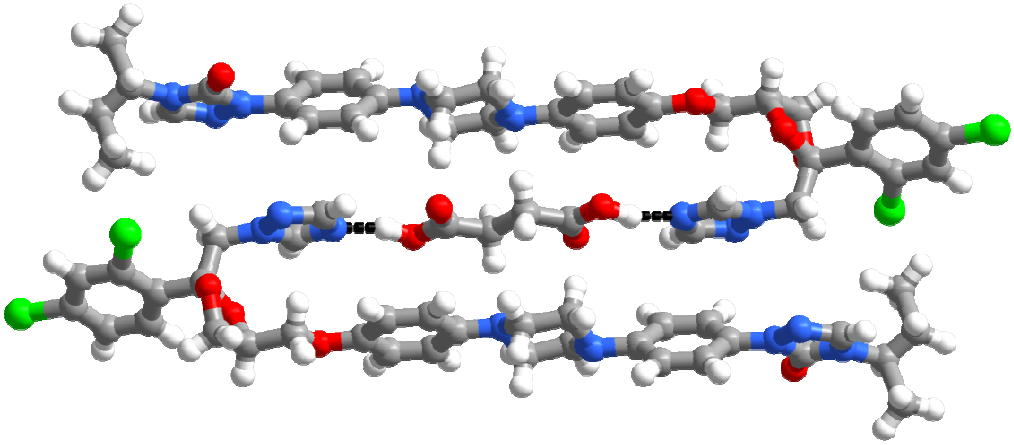


Figure 1.23. Co-crystal formed between itraconazole and succinic acid

The comparison of dissolution studies of amorphous marketed form (Sporanox bead) and crystalline form of itraconazole with co-crystals of itraconazole with succinic acid, L-malic acid, and L-tartaric acid in 0.1N HCl, showed that the co-crystals achieve and sustain from 4- to 20-fold higher concentrations than the crystalline form of itraconazole. The dissolution profile of co-crystals is more similar to amorphous form than that of crystalline form of itraconazole, as shown in Fig 1.24.

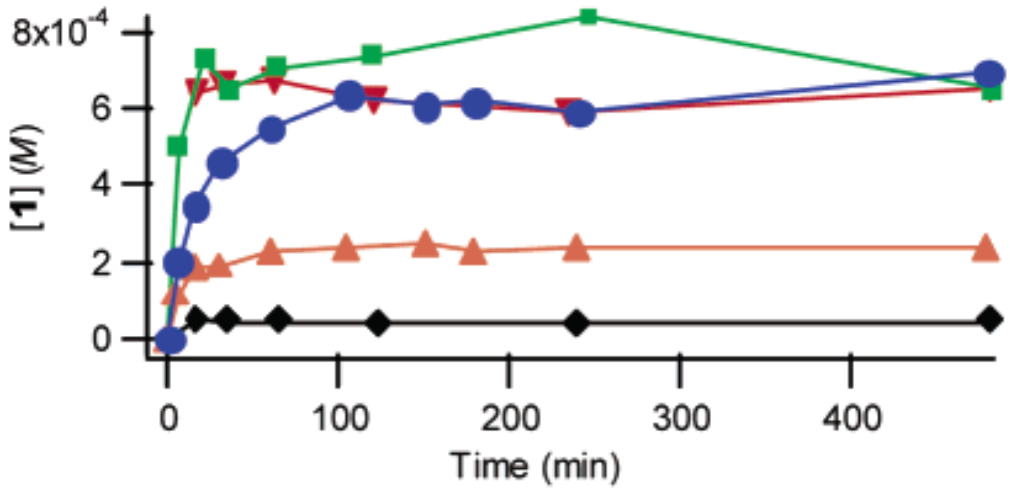


Figure 1.24. Dissolution profile of 0.1 N HCl at 25° C for amorphous form of itraconazole (Sporanox beads (■), itraconazole and L-malic acid co-crystal (▼), itraconazole and L-tartaric acid co-crystal (●), itraconazole and succinic acid co-crystal (▲) and crystalline form of itraconazole 1(◆).

1.7 Conclusion

The architectures formed by supramolecular assemblies utilizing non-covalent interactions are not only fascinating, but also have a lot of applications. Non-covalent interactions, molecular recognition and self-assembly are the keywords that have to be considered for understanding the principles of supramolecular chemistry and were described briefly in the chapter. Design and synthesis of various supramolecular assemblies utilizing various kind of hydrogen bonding recognition patterns are discussed by taking examples from the literature. In the penultimate section, applications of various supramolecular assemblies in synthesis, pharmaceutical co-crystallization, gas storage, separation and catalysis were discussed. Thus supramolecular chemistry not only give us powerful tool to control the physical properties of materials like their solubility, stability and melting point etc., but also make new functional materials for applications like separation,

catalysis and gas storage etc. Considering the effective utilization of supramolecular assemblies based on this discussion presented in the previous sections, supramolecular assemblies of organic molecules alone, with distinct geometry and tailor-made properties are still not as versatile as metal-organic networks.

Taking into account the availability of number of carboxylic groups and the conformational flexibility, various cyclohexanecarboxylic acids in supramolecular synthesis have been employed for the preparation of targeted assemblies. For this purpose, we initiated our co-crystallization experiments of 1,2,4,5-cyclohexanetetracarboxylic acid, 1,2- and 1,3-cyclohexanedicarboxylic acids with different organic substrates, in particular, aza-donor compounds, like 4,4'-bipyridine, 2,2'-bipyridine, 1,2-bis(4-pyridyl)ethane, 1,2-bis(4-pyridyl)ethene, phenazine, etc. The obtained adducts were analyzed by single crystal X-ray diffraction methods and the exotic structural features for the evaluation in possible applications, are described in the following Chapters.

1.9 References

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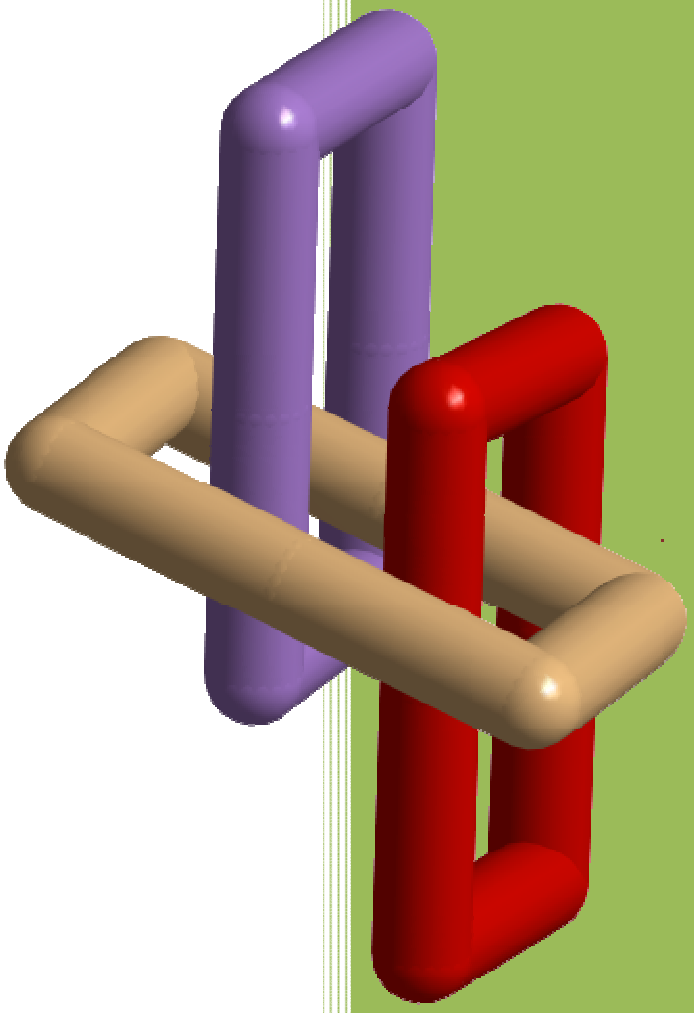
Chapter 2

Supramolecular Assemblies of 1,2,4,5-Cyclohexanetetracarboxylic Acid with various Aza Donors



Supramolecular Assemblies of 1,2,4,5-Cyclohexanetetracarboxylic Acid with various Aza Donors

2.1. Introduction

In Chapter 1 of this compilation, the implication of noncovalent bonds was discussed, thoroughly, in the design of supramolecular assemblies. To achieve, success in such endeavors, a prior knowledge of robust and reliable intermolecular interactions, such as strong hydrogen bonds is important not only to control the assembly and orientation of solid state structures in three-dimensional arrangement, but also to design specific crystal structure with potential specific physical and chemical properties, based on the knowledge of the building blocks.[1,2] Rational analysis of the dominant role played by the hydrogen bonds, because of their selectivity and directionality to control the design of various molecular assemblies, is vital in crystal engineering of organic supramolecular assemblies.[3] Because of the ability of carboxylic (-COOH) group to form robust hydrogen bonds on its own and also with several aza compounds forming either O–H···N or O–H···N/ C–H···O pair wise hydrogen bonds, as well as dative bonds through the carboxylate group, assemblies based on the carboxylic groups are of great important in supramolecular studies.[4-6]

Since benzenepolycarboxylic acids are useful in the creation of extensive arrays through hydrogen bonding and metal-coordination bonds, these acids have been used

extensively by supramolecular chemists.[7] Cambridge Structural Database[8] analysis reveals that co-crystallization studies employing tetrasubstituted acids are not much explored in the supramolecular studies, except a few examples discussed below.

Zaworotko and co-workers[9] exercised a paradigm based on modular design in which co-crystal former can be exploited for their ability to form supramolecular interactions with active pharmaceutical ingredients (APIs). In this regards co-crystallization was carried out with a 1:1 ratio of carbamazepine and adamanatanetetracarboxylic acid (**ATC**) from either methanol or ethanol. The crystal structure contains only heteromeric interactions. The two carboxylic acid groups of the **ATC** generate *heteromeric* interactions with two different carbamazepine molecules, and the exterior hydrogen-bond acceptor/donor sites of the carbamazepine molecules interact with the remaining acid groups by means of catemeric N-H···O and O-H···O hydrogen bonds. In this process, all the hydrogen-bonding donor/acceptor sites of carbamazepine molecule and **ATC** are satisfied as shown in Figure 2.1(a). The acid molecule interact with four different carbamazepine molecules via two dimeric and two catemeric hydrogen bonds, as shown in Figure 2.1(b).

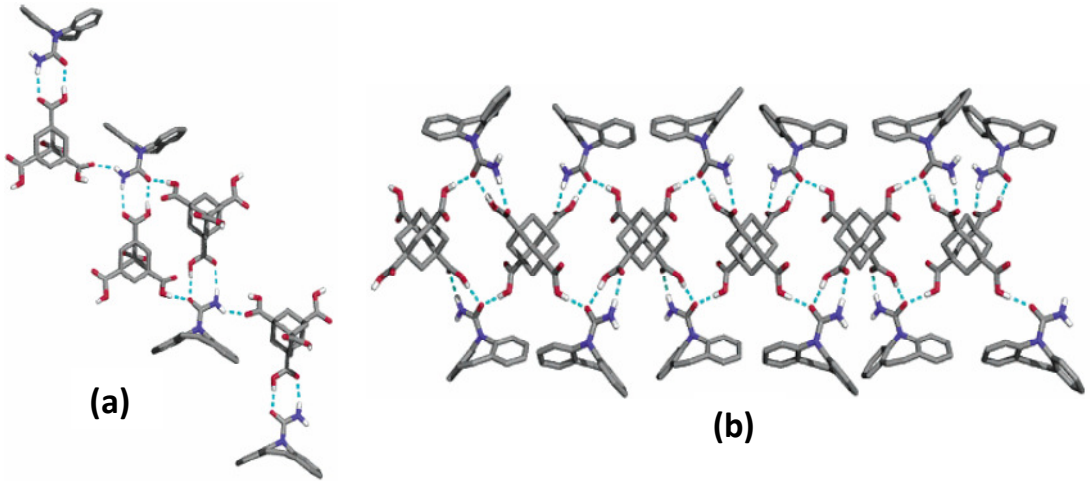


Figure 2.1 (a) Interaction of an amide group of carbamazepine with three different molecules of acid, **ATC**. (b) *Heteromeric* interactions present in the co-crystals of carbamazepine and **ATC**.

Price and co-workers[10] have shown the formation of large cavities in two dimensional network by self assembly process, in the crystal structure of biphenyl-3,3',5,5'-tetracarboxylic acid, which is like an extended tetracarboxylic acid, as shown in Figure 2.2(a). As known for many organic reactions with void space, herein also the cavities are filled by 2-fold interpenetration of three independent networks as shown in Figure 2.2(b).

Further, a systematic study of synthesis of a variety of supramolecular assemblies, employing other polycarboxylic acids, for example 1,2,4,5-benzenetetracarboxylic acid and different types of aza-donors, as reported by Arora *et al.*,[11] demonstrates the significance of the volume of the aza-donors in the formation of specific assembly.

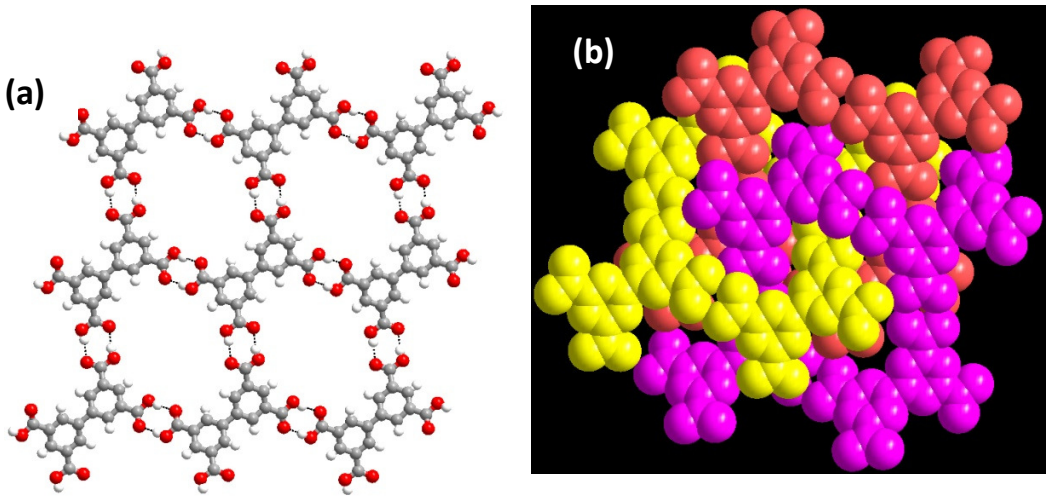


Figure 2.2 (a) Self-assembly of biphenyl-3,3',5,5'-tetracarboxylic acid molecules, through dimeric hydrogen bonds. (b) Hydrogen-bonded interpenetrating networks represented by space-filling model.

When 1,2,4,5-benzenetetracarboxylic acid is cocrystallized with 1,10-phenanthroline, it results into the formation of host-guest assembly, while with 1,2-*bis*-(4-pyridyl)ethane a sheet structure is obtained. Pictorial representation of these assemblies is given in the Figure 2.3. Thus, the carboxylic acid–aza-donor recognition is found to be one of the most reliable supramolecular patterns, even with polycarboxylate acids, also to obtain desirable architectures.

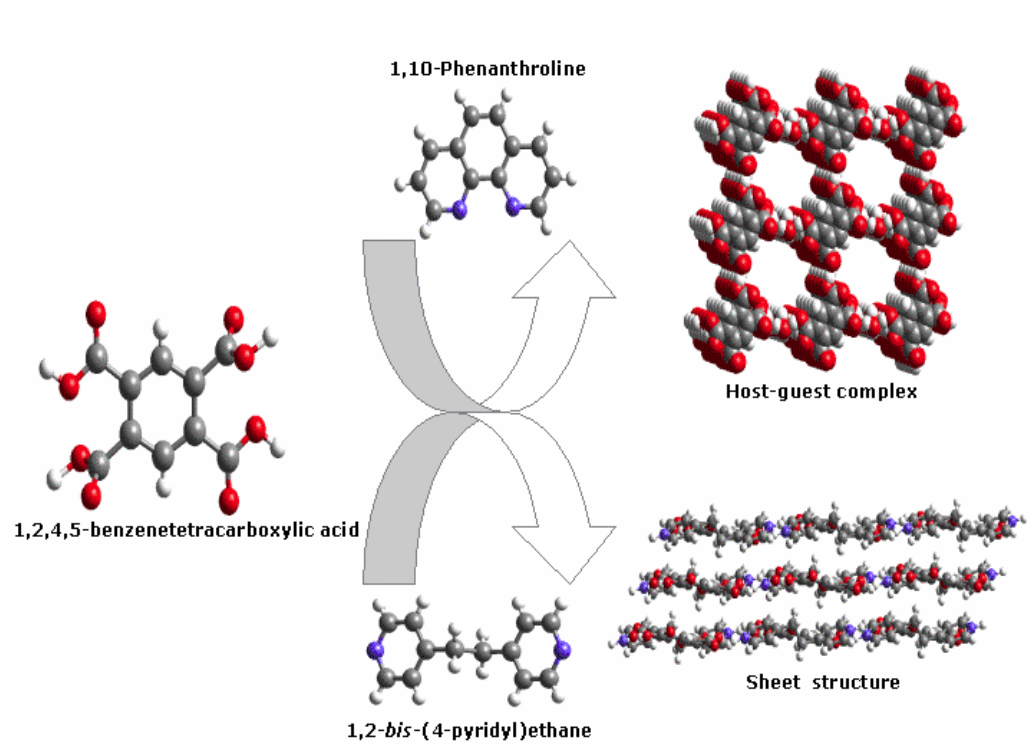


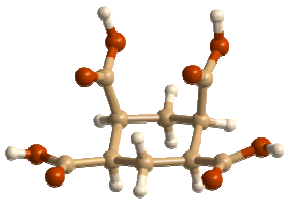
Figure 2.3 Different supramolecular architectures observed in the complexes of 1,2,4,5-benzenetetracarboxylic acid, with different aza-donors.

It is noteworthy to mention that in most of the assemblies, the -COOH group is associated with aromatic moieties. Studies pertain to aliphatic carboxylic acids are very much limited. Thus, to emphasize the significance of such -COOH in the design of supramolecular assemblies, analogues to corresponding aromatic acids are considered.

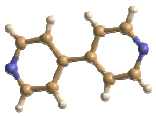
Taken into account some salient features of 1,2,4,5-cyclohexanetetracarboxylic acid (hereafter **1245CTC** or acid **1**), like number of carboxylic groups, its conformational flexibility due to cyclohexane ring and its better solubility in various solvents, a thorough exploration and utilization of **1245CTC** in supramolecular synthesis is formulated. Hence, various co-crystallization experiments of **1245CTC** with several aza donors, as listed in

Chart 1, have been carried out. However, the structure of **1245CTC** with 4,4'-bipyridine (**44bpy**) was found to be known in the literature.[12] Thus, the reported structure has been analyzed for its structural patterns for appropriate correlation with the remaining structures.

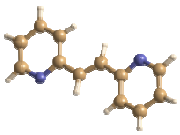
Chart 1



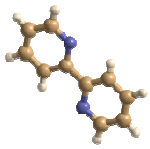
(1)
cis,cis,cis-1,2,4,5-cyclohexanetetracarboxylic acid



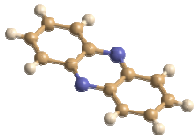
4,4'-bipyridine



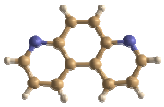
(a)
trans-1,2-bis(2-pyridyl)ethene



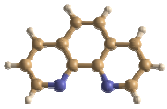
(b)
2,2'-bipyridine



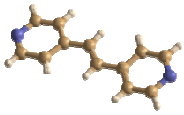
(c)
phenazine



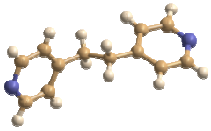
(d)
4,7-phenanthroline



(e)
1,10-phenanthroline



(f)
trans-1,2-bis(4-pyridyl)ethene



(g)
1,2-bis(4-pyridyl)ethane

Reactants	Solvent of crystallization	Molecular complexes	Composition
1+H_2O	CH_3OH or H_2O	**1.H_2O**	1:2
1+a	CH_3OH	**1a**	1:1
1+b	CH_3OH	**1b**	1:1
1+c	CH_3OH	**1c**	1:1
1+d	C_2H_5OH + CH_3OH (1:1)	**1d**	2:2
1+e	C_2H_5OH + CH_3OH (1:1)	**1e**	1:1
1+f	C_2H_5OH	**1f**	2:3
1+g	C_2H_5OH	**1g**	2:1
1+g	CH_3OH or H_2O	**1g.H_2O**	1:1:1

2.2. Results and Discussion

Co-crystallization of acid, **1** with various aza compounds, **a-g** yielded good quality single crystals of molecular complexes, **1a-1g**, respectively, from methanol or ethanol or

mixture of solvents like ethanol and methanol. However, co-crystallization of acid, **1** with hexamethylenetetramine (**HMTA**) resulted in molecular complex **1.H_2O** in which the hydrated form of acid **1** is observed.

Molecular Complex of Acid 1 with 4,4'-bipyridine (44bpy)

Cocrystal of acid **1** with 4,4'-bipyridine **(44bpy)** was reported by Jian-Qiang Liu[14] wherein adjacent acid molecules are held together by well known carboxy acid dimeric pattern of $R_2^2(8)$ interaction via O–H···O hydrogen bond with H···O distance of 1.78 Å, involving equatorial carboxy groups from each acid molecule. Such acid dimeric units are further held together, through two carboxyl groups, by single O–H···O hydrogen bonds (H···O, 1.94 Å), which leads to the formation of one dimensional chain of acid molecule, as shown in Figure 2.4, establishing $R_2^2(14)$ ring pattern.

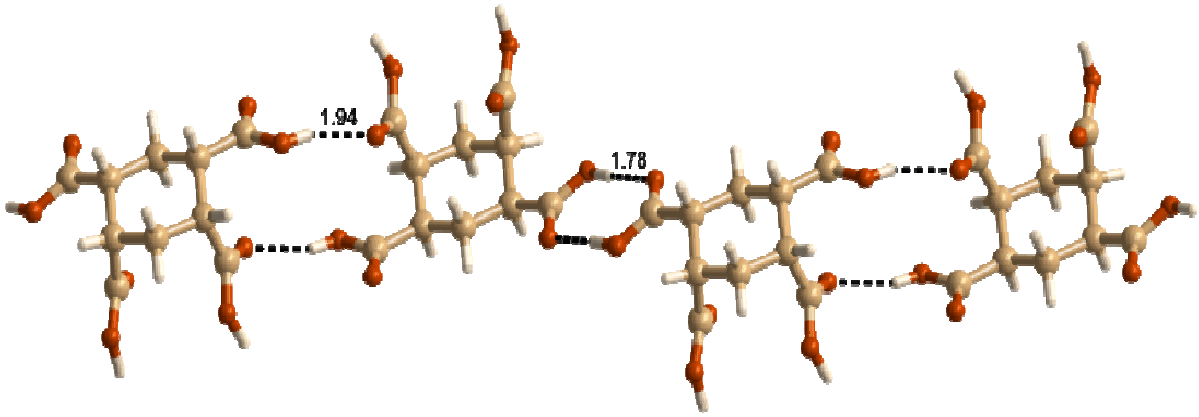


Figure 2.4. One Dimensional acid chain in cocrystals of **1245CTC** and 44bpy.

In two-dimensional arrangement, the adjacent chains related by inversion symmetry are connected to each other by molecules of **44bpy** through two different

hydrogen bonding patterns. While one of them is a single O-H···N hydrogen bond with a distance of 1.87 Å, the other one is a pair-wise O-H···N/C-H···O hydrogen bonds with corresponding H···N and H···O distances being 1.81 and 2.55 Å.

Such an ensemble, as shown in Figure 2.5(a), constitutes a ladder type architecture with acid chains as rods of the ladder and **44bpy** molecules as rungs. Further, it is apparent from Figure 2.6(a) that since the rungs are being separated by a distance 13 Å, a void space of 13 x 16 $Å^2$ is formed. These voids are filled by catenation process in three-dimensional arrangement, as represented schematically in Figure 2.5(b).

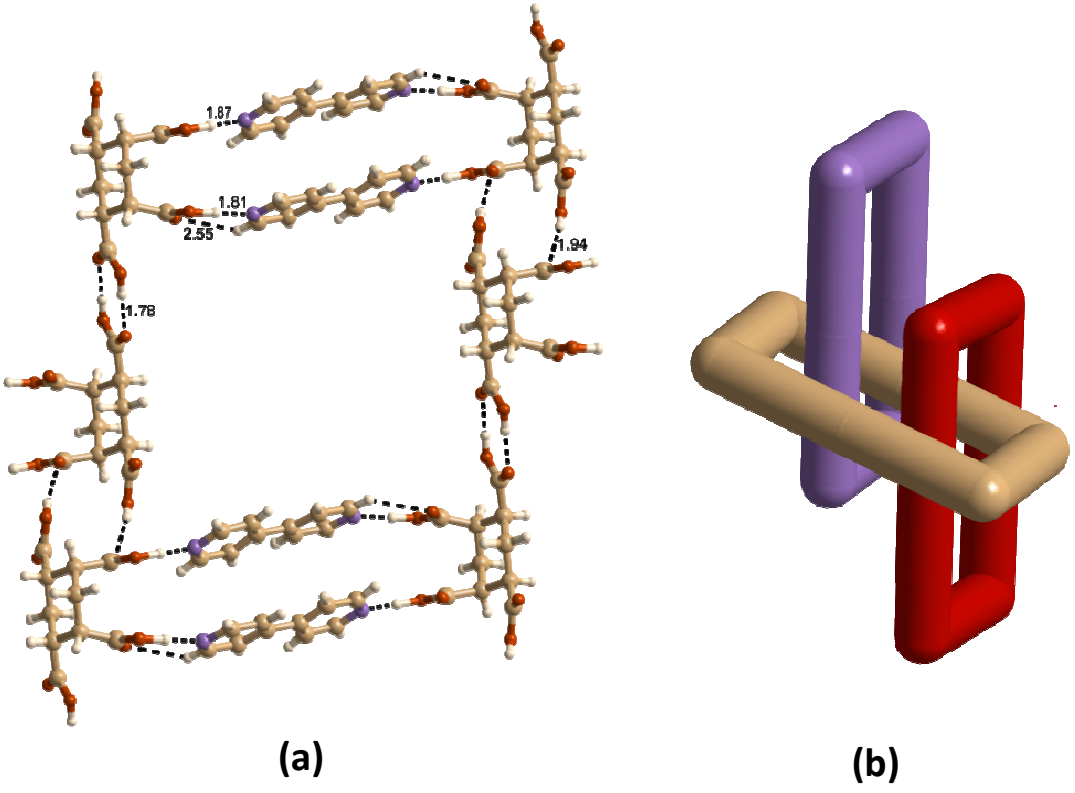


Figure 2.5. (a) Ladder structure observed in the molecular complex of acid **1** and **44bpy**, with void space. (b) Schematic representation of filling of voids by catenation process.

The voids in the assemblies, as observed above, within two-dimensional assemblies, generally, are being filled by self-catenation process due to the non-availability of appropriate molecular component(s) in the co-crystallization process that fit into the voids, by establishing interaction with the host network, either by hydrogen bonds or even by van der Waals forces. Thus, further co-crystallization studies of **1245CTC**, replacing **44bpy** with appropriate aza-donors is apt to obtain perhaps host-guest exotic architectures. Hence, co-crystallization of acid **1** has been carried out with a hydrogen bond acceptor, hexamethylenetetramine.

2.2.1 Structure of Hydrate of Acid 1

Cocrystallization of acid **1** and hexamethylenetetramine gave good quality single crystals. Analysis of the crystals by X-ray diffraction methods reveals that asymmetric unit contains only the acid molecules along with water (solvent of crystallization), as shown in Figure 2.6, in the form of ORTEP, and it is labeled as **1**.H_2O for the purpose of discussion. Characteristic parameters of structure determination are given in Table 2.1. A noteworthy feature is that crystals have adopted an unusual space group, $P4_2/mcb$, which reflected its significance in three-dimensional packing.

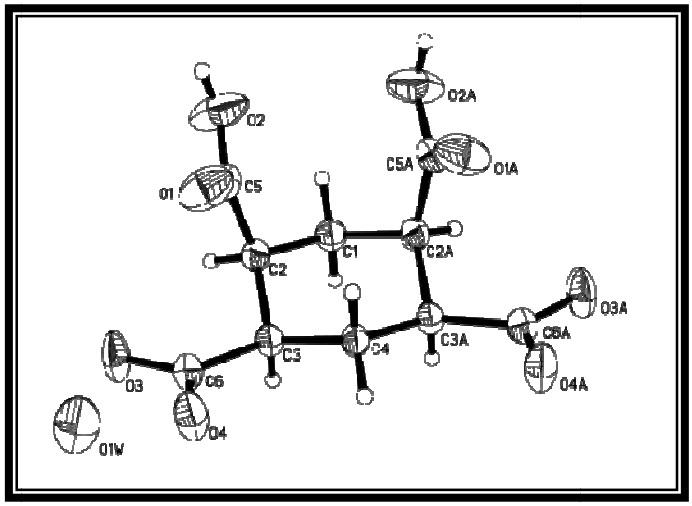


Figure 2.6 ORTEP drawing of acid **1** and water at 50% probability level in the crystals of **1**.H_2O

In the crystal lattice, molecules are found to be arranged in the form of chains by O–H···O hydrogen bonds (H···O, 1.80 Å) that are formed between the equatorial and axial carboxyl groups of adjacent acid molecules in the form of $R_2^2(16)$ pattern, as shown in Figure 2.7(a). Complete details of hydrogen bond parameters are listed in Table 2.2. Such chains are further held together, within two-dimensional arrangement, through C–H···O hydrogen bonds (H···O, 2.73Å, Table 2.2), yielding a corrugated sheet structure. A typical sheet is shown in Figure 2.7(b).

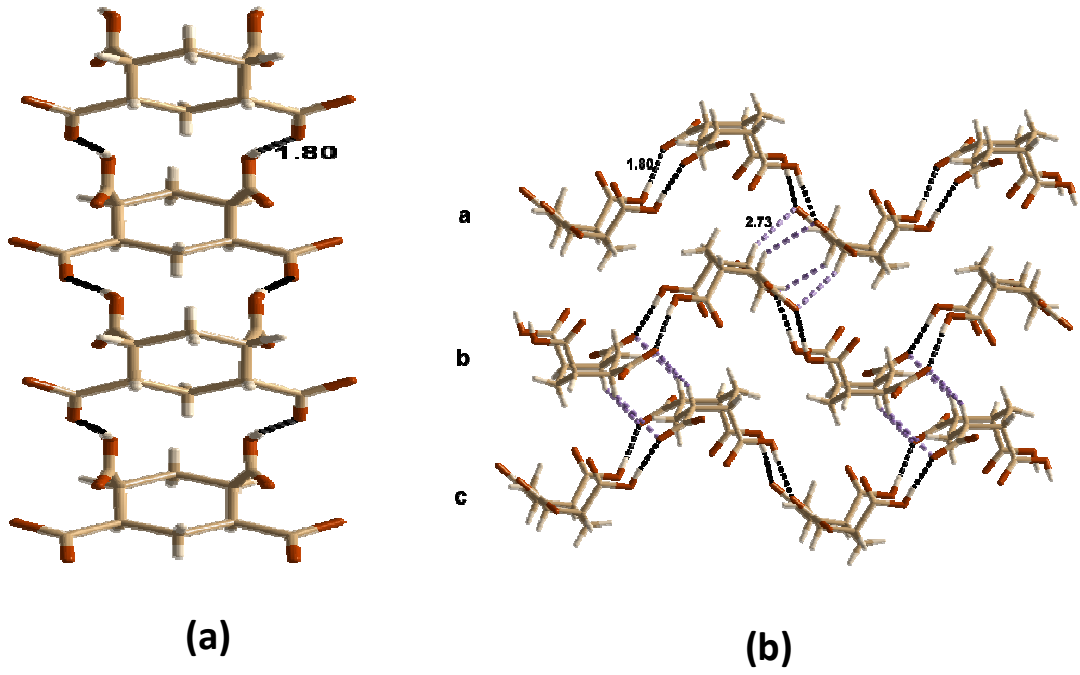
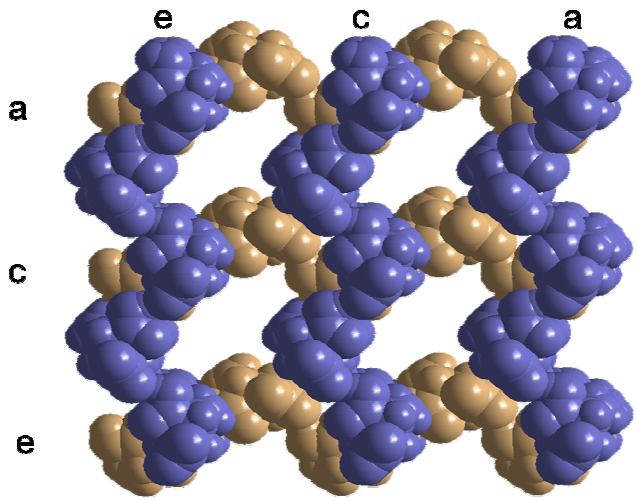
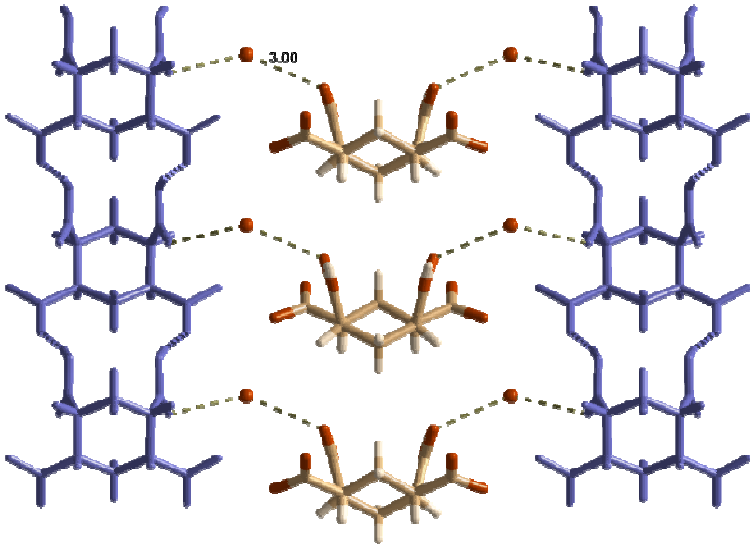


Figure 2.7. (a) One dimensional acid rod and (b) Two dimensional arrangement of molecules in the crystal structure of **1**.H_2O.

Three-dimensional structure is stabilized by stacking of the sheets, but interestingly it has been noted that the adjacent sheets are related by 4-fold symmetry such that the chains of acid molecules in the consecutive layers collectively appear in the form of grids. Such a grid network is shown in Figure 2.8(a) by showing only alternate chains for clear visualization. Water molecules are found to be inserted between sheets along the stacking direction in the form of a water bed. Further, water molecules establish interaction with acid molecules in the consecutive sheets through O-H···O hydrogen bonds, as shown in Figure 2.8(b).



(a)



(b)

Figure 2.8. (a) Three dimensional arrangement in complex **1.H_2O**, with two consecutive acid sheets separated by water molecule (Only alternate layers from a sheet are shown for simplicity). (b) Interaction of water with acid molecules.

Comparison of the water adduct of acid **1**, with the native structure of it, which was reported in literature, indeed reveals that both of them are similar in three-dimensional arrangement except for two aspects - (i) in **1**.H_2O, sheets are separated by water molecules

and (ii) that the chains are linear (in anhydrous structure) within two-dimensional arrangement, as shown in Figure 2.9, as detailed below, and also the adjacent sheets along the stacking direction are related by translational symmetry.

Crystal structure of 1,2,4,5-cyclohexanetetracarboxylic acid (1245CTC).

Crystal structure of native acid **1**, was reported by Uchida et al.[13] Structural analysis unveiled that the equatorial carboxy groups of an acid molecule are connected to axial groups of adjacent acid molecule *via* O–H···O/ C–H···O hydrogen bonds, with H···O distances 1.83 and 2.52 Å, respectively, which leads to the formation of one dimensional chain. These chains are connected to each other through O–H···O hydrogen bond (H···O, 1.89 Å), as shown in Figure 2.9, which results in the formation of a two dimensional sheet. Such planar sheets are stacked to yield a three-dimensional structure stabilized by C–H···O hydrogen bonds between the sheets.

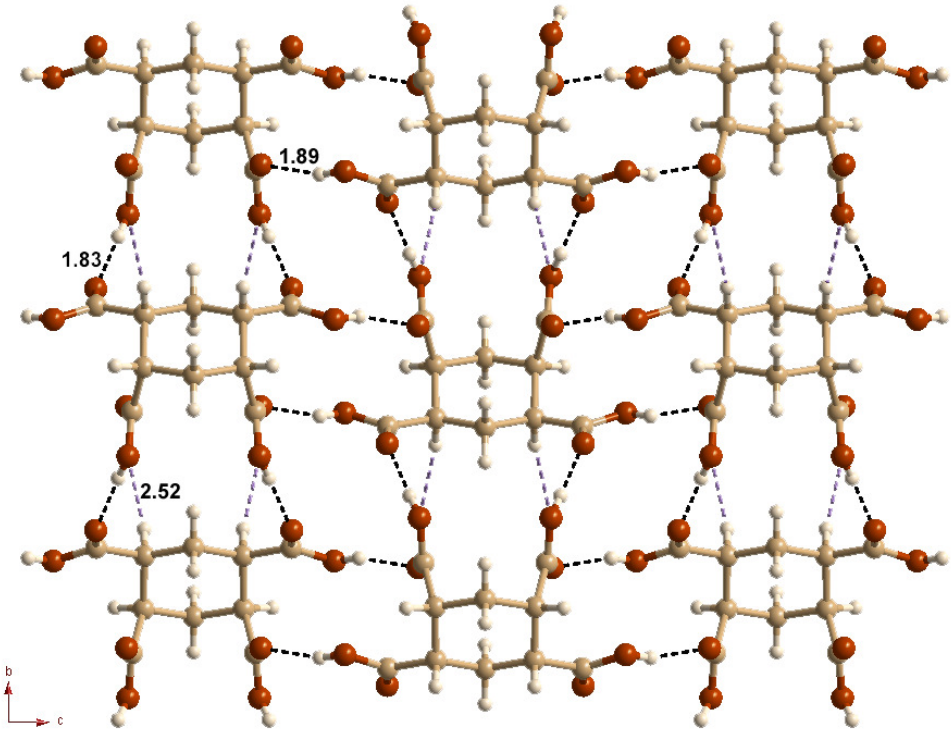


Figure 2.9. Two Dimensional sheet arrangement in native **1245CTC** structure

2.2.2 Molecular Complexes of Acid 1 with *trans*-1,2-*bis*(4-pyridyl)ethene (a), 2,2'-bipyridine (b) and phenazine (c)

Methanolic solution of a mixture of acid, **1** and 1,2-*bis*(4-pyridyl)ethene (**a**) yield good quality single crystals during a period of 72 h. The X-ray structure analysis revealed that a molecular complex, crystallized in an orthorhombic *Pnma* space group is formed, which is labeled as **1a**. Pertinent crystallographic data are given in Table 2.1. Asymmetric unit of complex **1a** consists of 1:1 ratio of acid **1** and molecules of **a**, as shown in Figure 2.10, in the form of ORTEP.

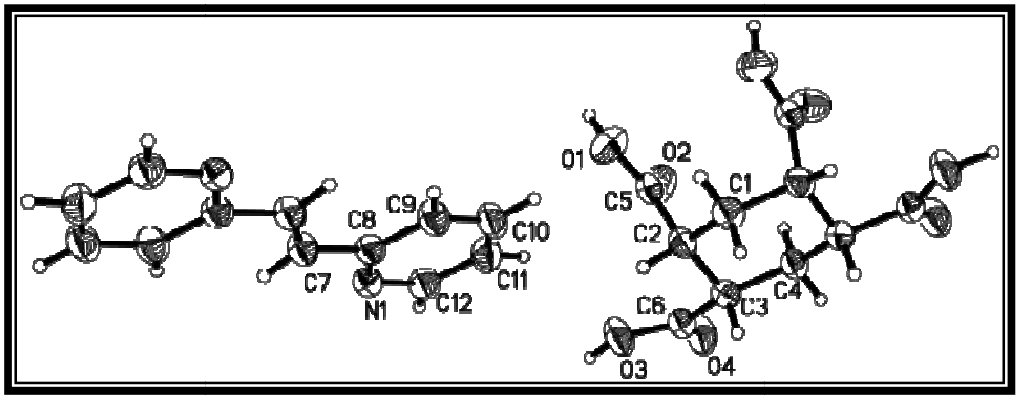


Figure 2.10 ORTEP of acid **1** and molecules of **a** at 50% probability level, in the complex, **1a**.

In complex **1a,** the acid molecules aggregate in the form of chains. A typical arrangement within a chain is shown in Figure 2.11. But unlike in molecular complex of acid **1** and **44bpy**, the arrangement of acid **1,** within the chains, of complex **1a**, is distinctly different through the establishment of intermolecular interactions (hydrogen bonds) between the equatorial and axial carboxyl groups of adjacent acid molecule. The hydrogen bond distance in the noted O–H···O hydrogen bond is H···O, 1.75 Å. It is noteworthy to mention that the arrangement of acid molecules, in chains, in complex **1a** is similar to the arrangement as found in the native structure of acid, **1**.

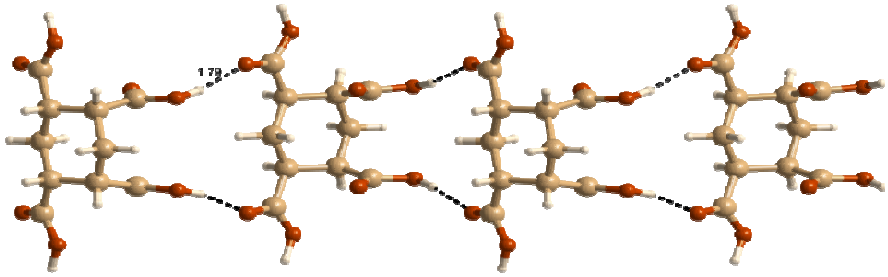
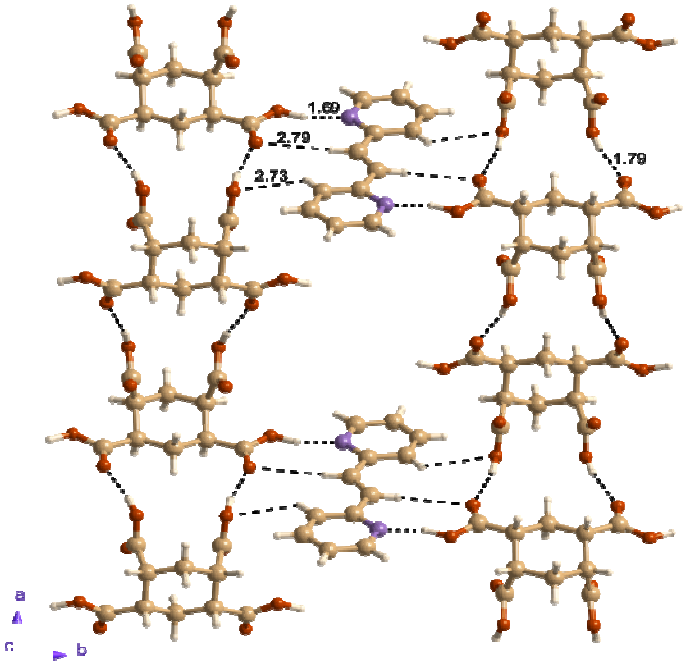
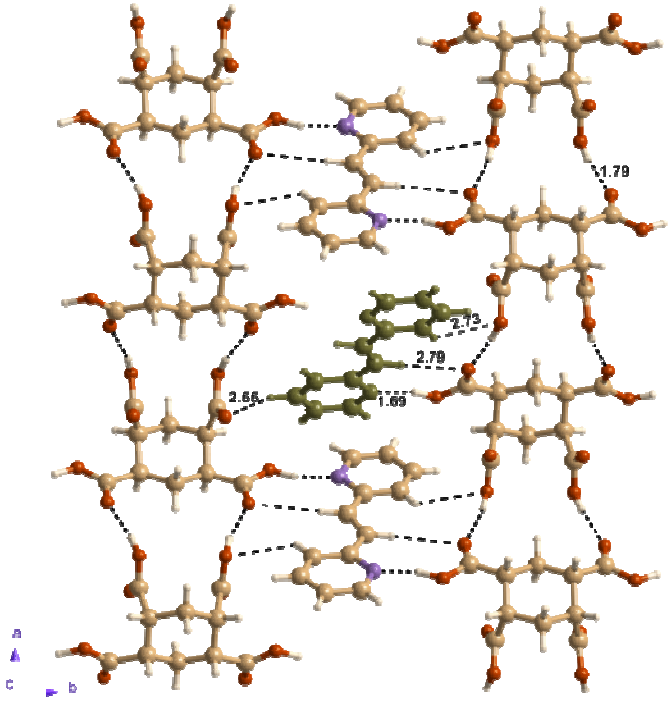


Figure 2.11. Chain of molecules of acid **1**, as observed in molecular complex **1a.**

Within two-dimensional arrangement, between such adjacent chains, that are arranged in *anti* parallel mode, aza-donor ligands are inserted via O–H···N hydrogen bond (H···N, 1.69 Å) formed by the O–H of equatorial carboxyl groups of acid molecules present in both the chains. In addition, the recognition between acid and aza molecules is further strengthened by two auxiliary C–H···O hydrogen bond (H···O, 2.79 and 2.73). The arrangement is shown in Figure 2.12(a). It is clearly evident from such an arrangement, formation of void space of dimension 13 × 13.5 $Å^2$. Thus, complex **1a** has structural features similar to that observed for the complex of acid **1** with **44bpy**. However, in complex **1a**, the void space is not filled in three-dimensional arrangement by catenation process, but *via* stacking of the sheets by sledging such that the void space in a specific sheet is filled by the molecules of aza-donor from the adjacent layers. For a typical sheet, such a filling is shown in Figure 2.12(b). As a result, the stacking energy is further strengthened with acid molecules establishing C–H···O hydrogen bonds (H···O, 2.97 Å, Table 2.2), as shown in Figure 2.12(c), formed between -COOH groups present on the molecules in the adjacent sheets.



(a)



(b)

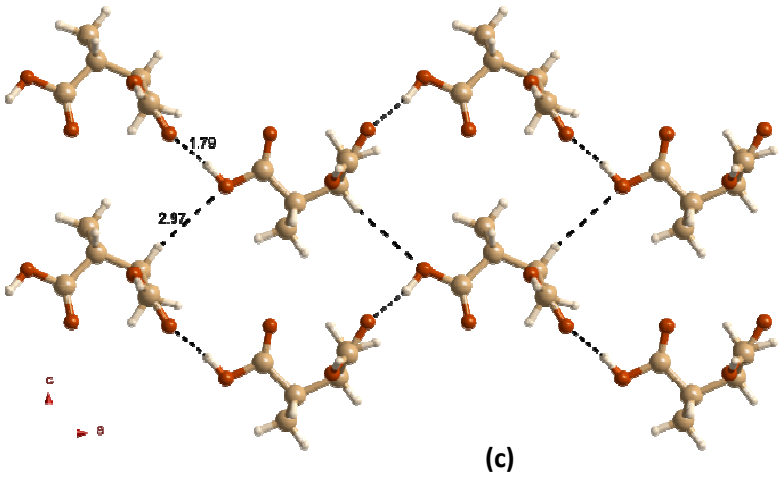


Figure 2.12. (a) Formation of 2D sheet with acid **1** and molecules of **a** in complex **1a** and (b) 3D arrangement of self assembly of acid and aza donor molecules. (c) C–H···O hydrogen bonds mediated acid molecules along stacking direction.

In continuation of co-crystallization of acid **1**, with other aza-donors, experiments performed with 2,2'-bipyridine (**b**) and phenazine (**c**) gave good quality single crystals by slow-evaporation of corresponding methanol solutions. X-ray diffraction analysis further reveals that the co-crystals are 1:1 molecular complexes of **1** with corresponding aza-donor, either **b** or **c**, as the case may be, and the complexes are labeled as **1b** and **1c**, respectively. ORTEP of the contents of asymmetric units are shown in Figure 2.13(a) and (b), respectively for both **1b** and **1c**. Crystallographic parameters are listed in Table 2.1. The lattice parameters for **1b** and **1c** are interestingly found to be closely related to **1a** and also crystallize in the space group, *Pnma*.

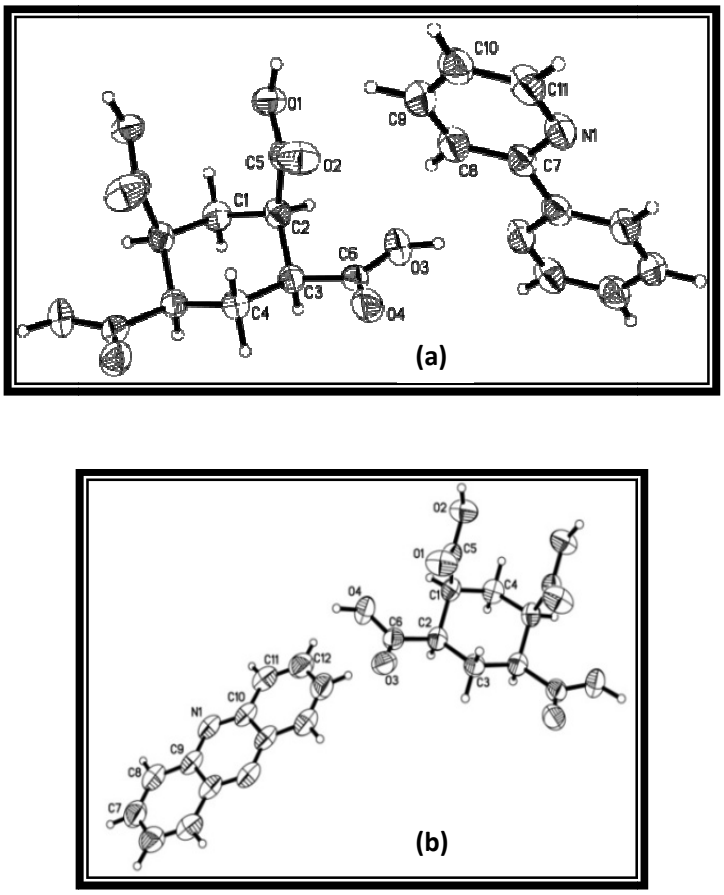
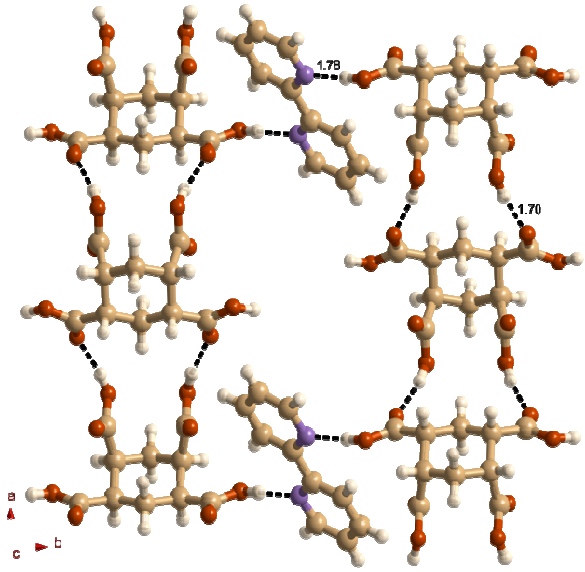
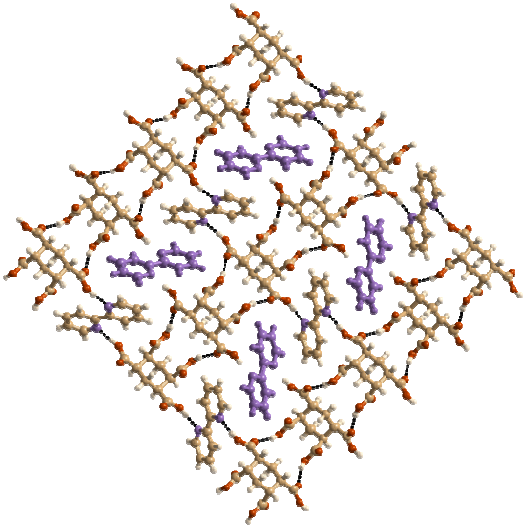


Figure 2.13 ORTEP of acid **1** and (a) 2,2'-bipyridine and (b) phenazine, at 50% probability level, in **1b** and **1c**, respectively.

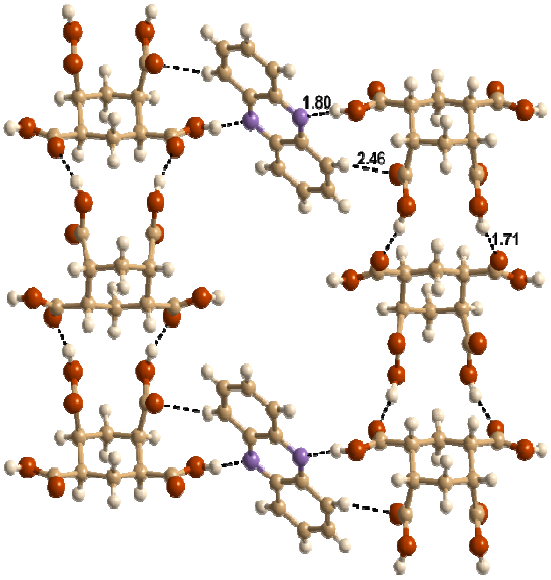
Further, analysis of packing of molecules in crystal lattices indeed reveals that structural features of **1b** and **1c** are also found to be similar to that of molecular complex **1a**. Thus, in **1b** and **1c** also, the acid molecules and aza donors constitute sheets with voids, which are stacked such that void space is effectively being masked by the molecules from the adjacent sheets. Arrangement of molecules in crystal lattices is shown in Figures 2.14 for both **1b** and **1c**.



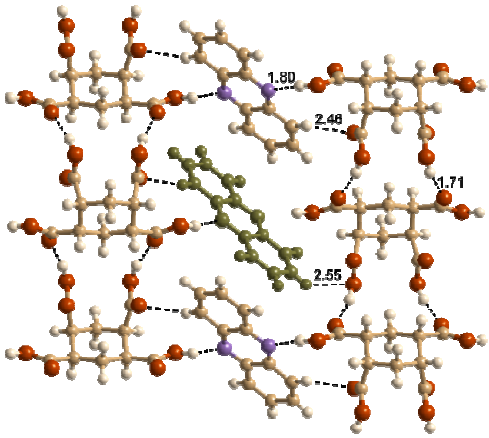
(a)



(b)



(c)



(d)

Figure 2.14 (a) and (b) Structural features of molecular complex **1b** and (c) and (d) for **1c**.

2.2.3. Molecular Complex of Acid 1 with 1,10-phenanthroline (d)

Cocrystallization of acid **1** with 1,10-phenanthroline **(d)** from a 1:1 mixture of ethanol and methanol solvents, gave good quality single crystals. Analysis by X-ray diffraction process determines that the crystals have the co-formers in a 1 : 1 ratio. Also, in the asymmetric unit, two symmetry independent molecules of acid **1**, as well as phenanthroline are present. Contents of the asymmetric unit are shown in Figure 2.15. The complex is labeled as **1d** to brief the structural description. Complete crystallographic information is tabulated in Table 2.1.

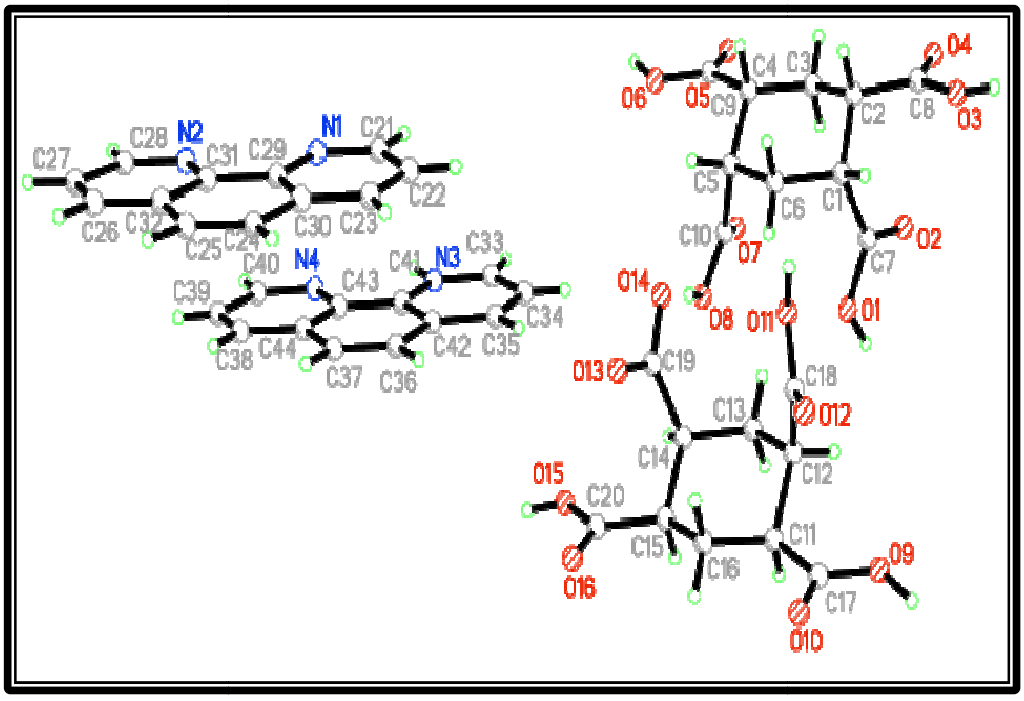


Figure 2.15 Molecules of acid **1** and 1,10-phenanthroline in the crystals of **1d**, at 50% probability level.

Arrangement of molecules (both co-formers) in two and three dimensions is quite intriguing. The observed two symmetry independent acid molecules, (labeled as A and B), are found to be held together by non-centrosymmetric, O-H···O hydrogen bonding pattern in a graphical notation of $R_2^2(8)$ through two axial -COOH group. The arrangement, appear as a chain, is shown in Figure 2.16. The H···O distances in the hydrogen bonds are in the range 1.62 - 1.86 Å.

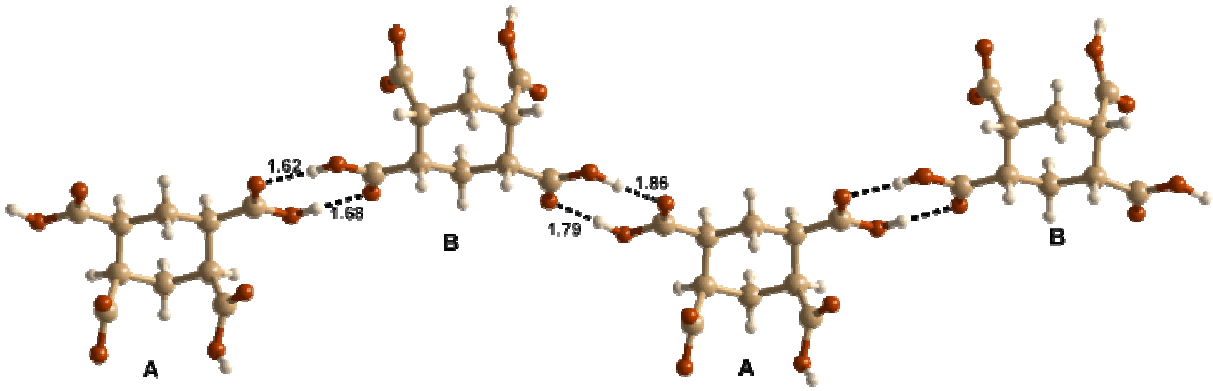


Figure 2.16. Interaction between acid molecules, through O-H···O bonds, in complex **1d**.

Further, such chains, related by inversion symmetry, are held together by O-H···O hydrogen bonds with H···O distance of 1.64 Å, formed between axial equatorial carboxyl groups of acid molecule of same symmetry. Thus, a hexameric aggregation of acid molecules is realized with void space of 17 X 15 $Å^2$. The network is shown in Figure 2.17.

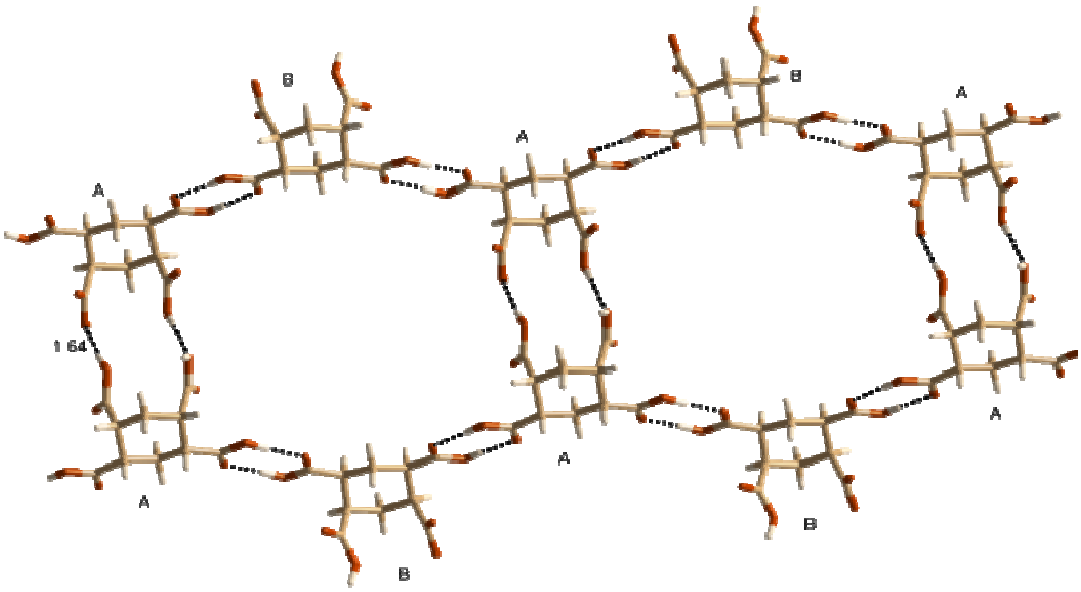
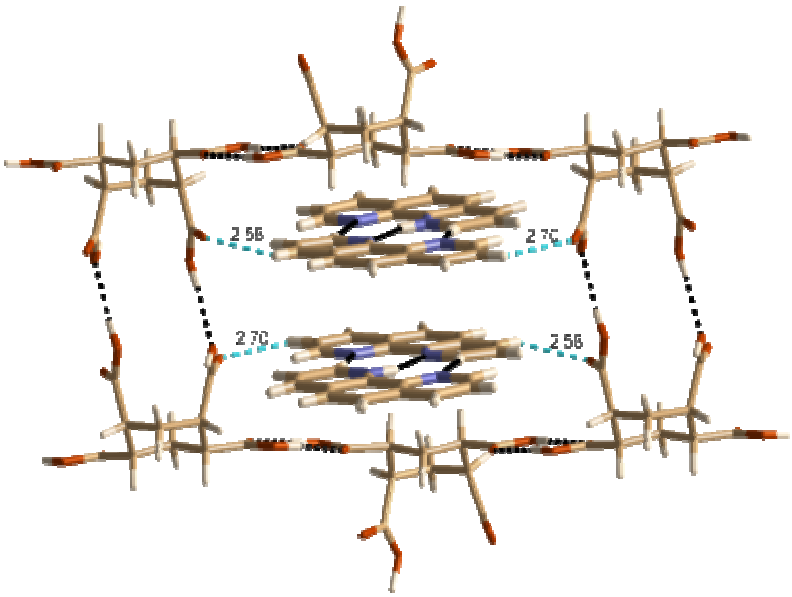
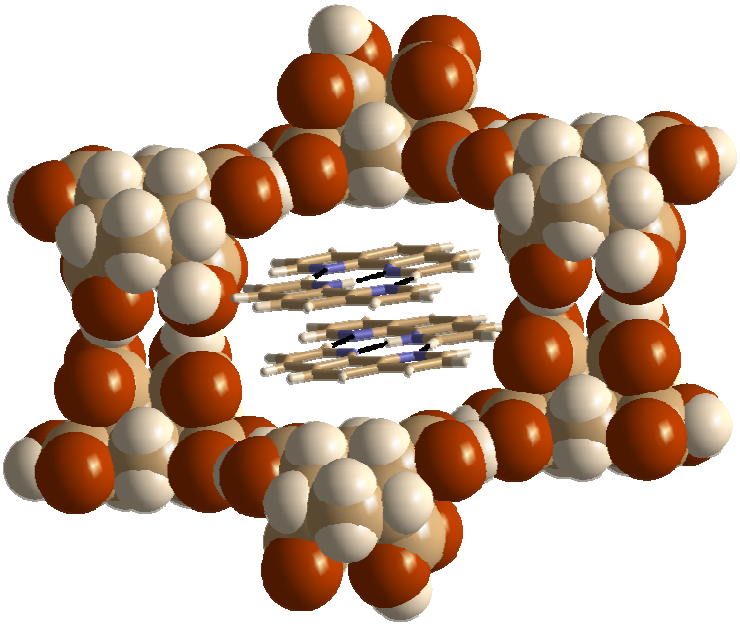


Figure 2.17 Two dimensional molecular host framework formed by acid **1** in complex **1d**.

The sheets with voids created by acid molecules, thus, are stacked along a crystallographic axis through translational symmetry, thereby yielding channels in three-dimensional arrangement.



(a)



(b)

Figure 2.18. (a) host-guest assembly formed by acid and 1, 10 phenanthroline. (b) Space filling fit of host-guest assembly presented in (a).

Within the channels, not just one phenanthroline molecule, but two dimers of it are found to be residing as guest species, by establishing interaction with host network through C-H···O hydrogen bonds with H···O distances of 2.58 and 2.70 Å (Table 2), as shown in Figure 2.18 (a). The close packing model of the same is shown in Figure 2.18(b) for a better appreciation of host-guest fit. In fact, the phenanthroline molecules are also glued to each other through C-H···N hydrogen bonds (H···N, 2.12 -2.48 Å), as represented in Figure 2.19.

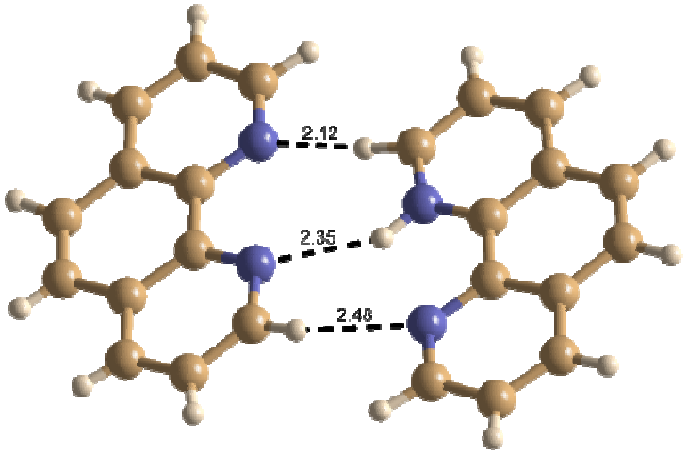


Figure 2.19 Interaction between 1,10 phenanthrolines resided within the channels observed in **1d**.

Considering the effective encapsulation of 1,10-phenanthroline molecules, maintaining the same geometry of aza-donor molecule, co-crystallization of acid **1** has been carried out with 4,7-phenanthroline.

2.2.4 Molecular Complex of Acid 1 with 4,7-phenanthroline (e)

A mixture of acid **1** and 4,7-phenanthroline (e) in a 1:1 mixture of ethanol and methanol solvents, gave crystals of desired quality by slow-evaporation process in 72 h period. Single crystals analysed by X-ray diffraction methods, show the formation of a molecular complex in a 1 : 1 ratio of co-formers, crystallized in an orthorhombic *Pbca* space group. Complete structure determination and refinement parameters are given in Table 2.1. The contents of asymmetric unit are shown in Figure 2.20 as ORTEP.

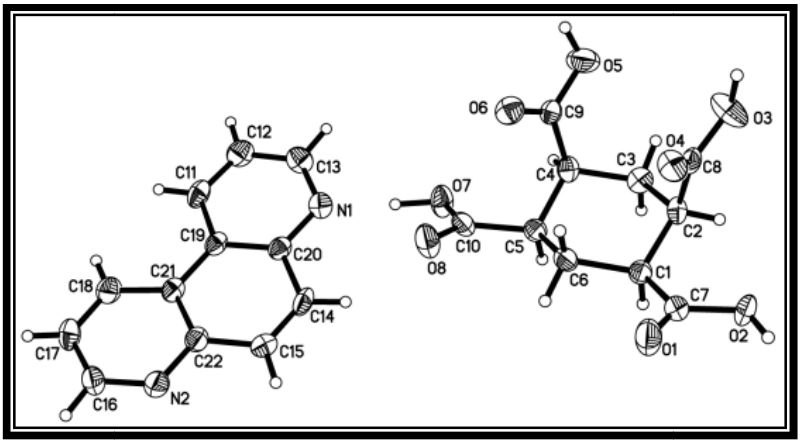


Figure 2.20 ORTEP of acid **1** and 4,7-phenanthroline in the structure of **1e**, at 50% probability level.

In the crystal lattice, structural features reveals that molecules of acid **1**, follow almost similar pattern as observed in the complexes **1a** - **1c**, with the aggregation yielding chains due to the interaction between the adjacent -COOH groups, by O-H···O hydrogen bonds, H···O, 1.71 and 1.82 Å through a $R_2^2(16)$ ring pattern. Complete details of hydrogen bond parameters are given in Table 2.2. Molecules of **e** are joined to carboxyl group at equatorial positions, as pendants, by O–H···N hydrogen bond (H···N, 1.93 and 1.70Å, Table 2.2) by $R_3^3(18)$ ring pattern. A typical ensemble is shown in Figure 2.21.

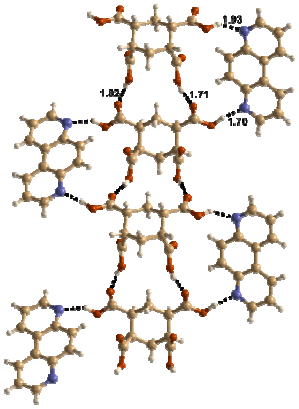


Figure 2.21. Ensemble of molecules of acid, **1** in the form of a chain, to which molecules of **e** are glued.

The ensembles, in fact, are stacked such that the aza-donor molecules in the adjacent moieties establish π–π interaction (~ 3.68 Å), as shown in Figure 2.22.

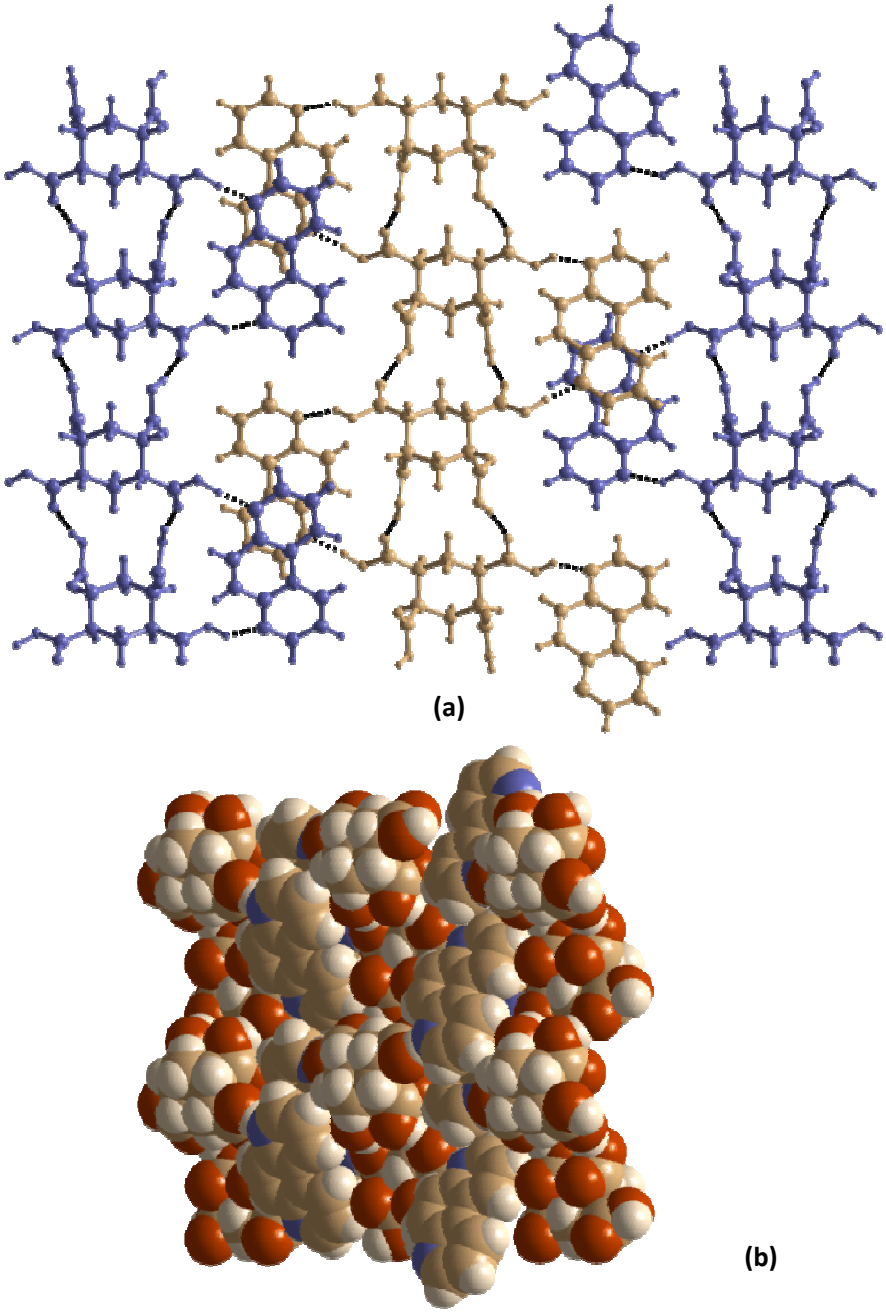


Figure 2.22. (a) Stacking of ensembles of molecules of acid **1** and **e** with π–π interaction between the aza-donor molecules (b) Space filling representation of the arrangement shown in (a).

2.2.5 Molecular Complex of Acid 1 with *trans*-1,2-*bis*(4-pyridyl)ethene (f)

A molecular complex, **1f**, was prepared by co-crystallization of acid **1**, with *trans*-1,2-*bis*(4-pyridyl)ethene (**f**) from their ethanolic solution by slow evaporation process. Single crystal data, obtained from X-ray diffraction process, reveals a composition of acid and aza donors in a 1:2 ratio, respectively, that crystallize into triclinic $P\bar{1}$ space group. Full crystallographic details are listed in Table 2.1. The contents of asymmetric unit are given in Figure 2.23 in the form of ORTEP. It is clearly seen from it, that one of the two molecules of aza-donor in the asymmetric unit is disordered in 1:1.5 population.

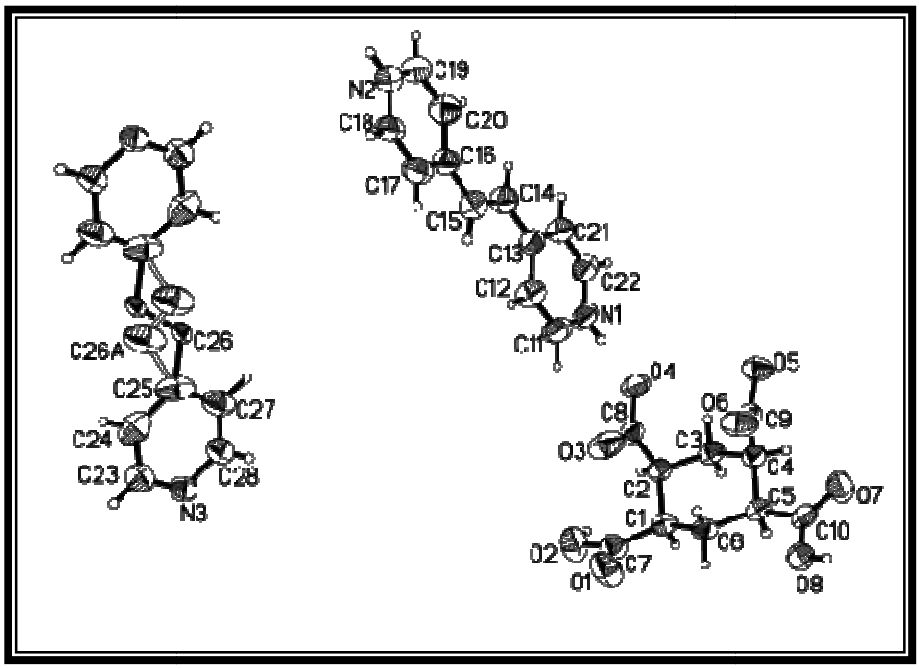


Figure 2.23 ORTEP of acid **1** and *trans*-1,2-bis(4-pyridyl)ethene in the complex **1f**

The structural features, by packing analysis, unveil that, in complex **1f**, the unique ladder type arrangement of acid **1** and aza-donor molecules is observed. A typical ladder is shown in Figure 2.24(a).

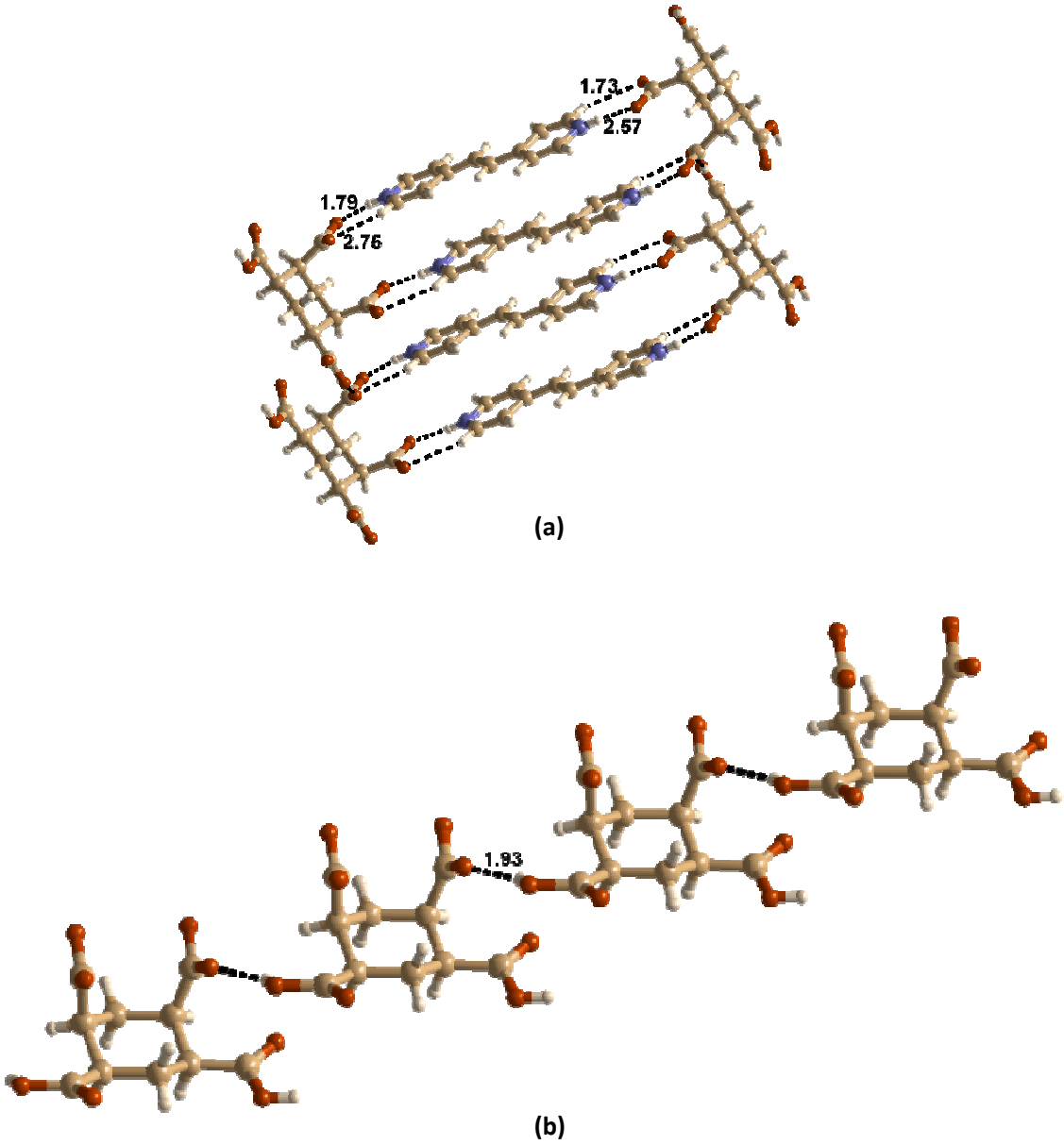


Figure 2.24. (a) Molecular ladder observed in molecular complex, **1f**. (b) Molecules of acid, **1** as rods in the ladder shown in (a).

Within each ladder, the rods are being formed by molecules of acid **1**, held together by single O-H···O hydrogen bond, with a H···O distance of 1.93 Å, as shown in Figure 2.24(b), while the rungs are being formed by one of the molecules of **f**, by establishing N^{+}–H···O^{-} hydrogen bonds (H···O^{-}, 1.73 and 1.79 Å, Table 2.2), which are further supported by C–H···O hydrogen bonds (H···O, 2.57 and 2.75 Å), with axial carboxyl groups of acid **1**. Interestingly, such juxtaposed ladders are further held together by second molecules of **f** (disordered around olefinic moiety) by a pair-wise hydrogen bond O-H···N/C-H···O with the corresponding H…N and H…O distances being 1.90 and 2.59 Å. The arrangement is shown in Figure 2.25.

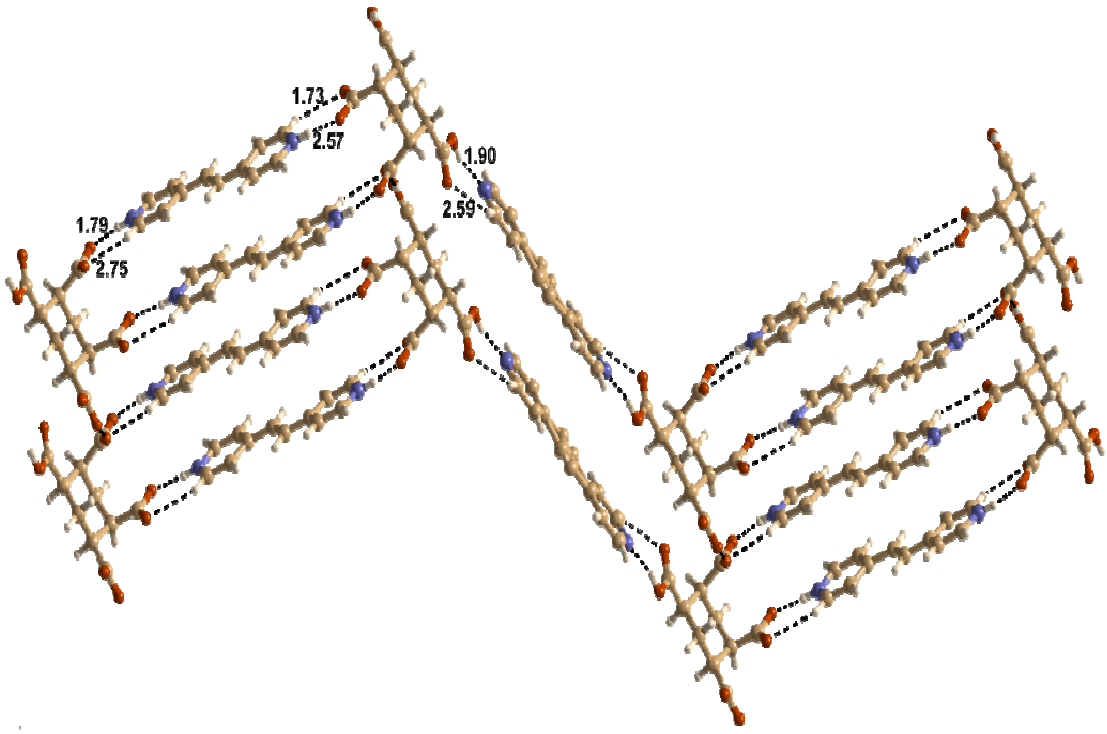


Figure 2.25 Self-assembly of ladders observed in complex **1e** through aza-donor molecules by pair-wise hydrogen bonds.

1,2-*bis*(4-pyridyl)ethane (**g**) is an analogous of molecules of **f** with the replacement of olefinic moiety by methylene moieties. The topological simility, in general, would make the supramolecular assemblies of these two sepcies to be very much similar, as observed in a many complexes. To extend the studies in similar direction with acid **1** also, its co-crystallization has been carried out with molecules of **g**, as detailed below.

2.2.6 Anhydrous and Hydrated Molecular Complexes of Acid 1 with 1,2-*bis*(4-pyridyl)ethane (g)

Cocrystallization of acid **1** and **(g)** in ethanol gave good quality crystals in 72 h period. However, the same composition from methanol gave crystals of different morphology. X-ray diffraction studies on both the types of crystals reveal that they are complexes of **1** and **g** in different composition with the ethanol solvent directed formation of a complex in a 2:1 ratio of co-formers while methanol solvent gave a complex in a 1:1 ratio as a hydrate. The complexes are labeled as **1g** for the anhydrous form and **1g.H_2O** for hydrated complex. In following discussion, the hydrated structure would follow the anhydrous structural analysis.

Crystals of **1g**, crystallize in monoclinic $P2_1/c$ space group. Structure determination and refinement parameters are tabulated in Table 2.1. The contents of asymmetric unit are shown in Figure 2.26.

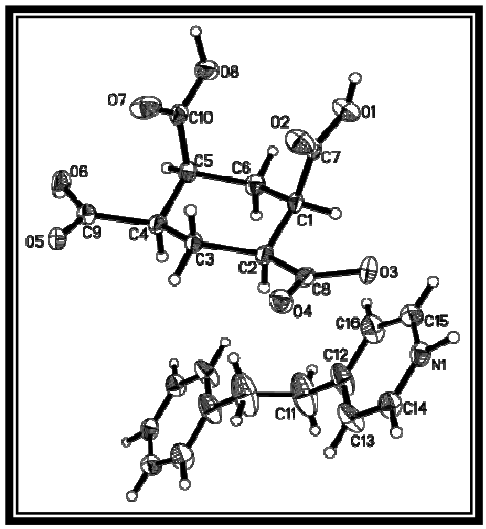
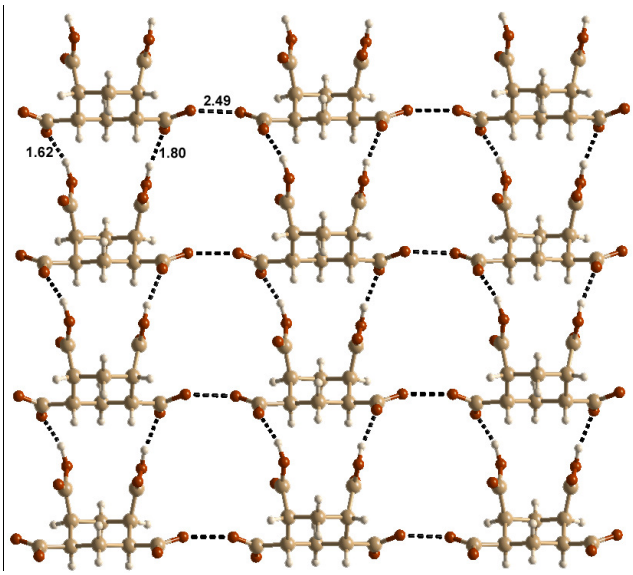
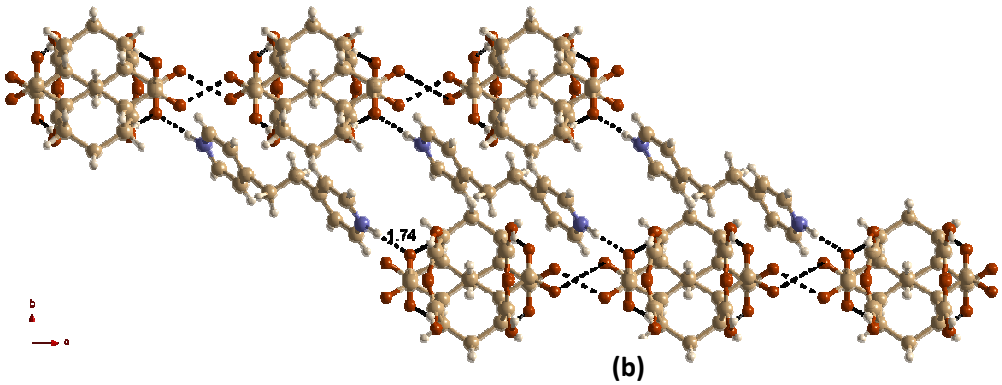


Figure 2.26 ORTEP of molecules in the asymmetric unit of complex, **1g**.

Structural analysis reveals that as observed in the complexes, **1a** - **1c**, acid molecules form chains through O-H…O hydrogen bonds with H…O distance of 1.62 and 1.80 Å. Within two-dimensional arrangement, these chains are juxtaposed to each other through non-conventional short contact (O···O, 2.49 Å) yielding a sheet-like structure. A representative sheet and chains are shown in Figure 2.27 (a). The sheets are stacked in the crystal lattice, in three-dimensional arrangement, being separated by aza-donor molecules. The molecules of **g** are found to be in contact with the acid molecules through N–H···O hydrogen bond (H···O, 1.74 Å). The stacking arrangement is shown in Figure 2.27(b).



(a)



(b)

Figure 2.27. (a) Arrangement of molecules of **1** in a layer in the complex, **1g**. (b) Representation packing of acid molecules in 3D with molecules of **g** being inserted between sheets of **1**.

Crystals of **1g.H_2O** are also found to be adopted monoclinic, *$P2_1/c$* space group as that of the corresponding anhydrous complex. Complete structural parameters are given in Table 2.1, while contents of asymmetric unit are shown in Figure 2.28 in the form of ORTEP.

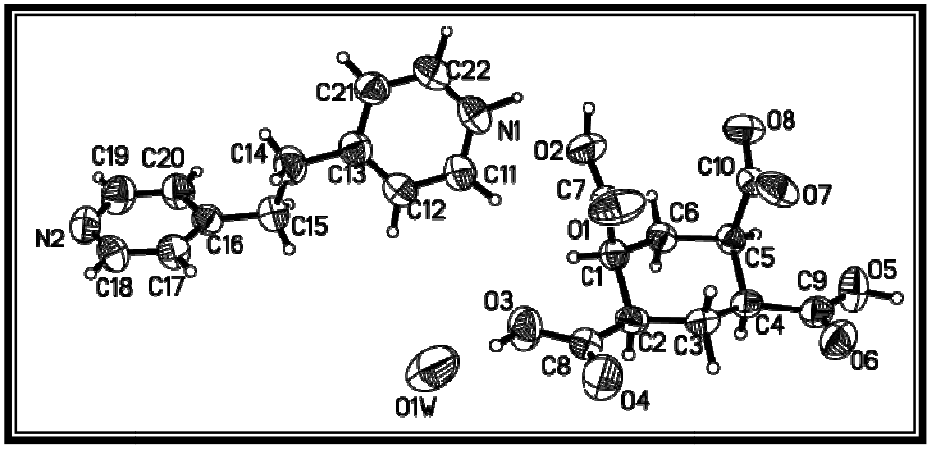


Figure 2.28 ORTEP of molecules in the asymmetric unit of complex, **1g**.H_2O

The packing of molecules is quite intriguing and differ from other structures discussed in the earlier sections. In three-dimensional arrangement, molecules pack in the form of stacked sheets, as shown Figure 2.29(a). Within each sheet, however, the acid molecules did not form chains topology, instead a pair of acids is held together by two molecules of aza-donor. Such an interaction is established through O–H···N hydrogen bonds (H···N, 1.73 and 1.62 Å), formed by equatorial and axial carboxy groups with two molecules of **g**. Thus, a quartet ensemble is realized, which arranges in two-dimensions, through the formation of O–H···O hydrogen bond (H···O, 1.71 Å), between the acid molecules in the adjacent ensembles. The hydrogen bonding pattern is found to be in the form of $R_2^2(16)$ ring pattern.

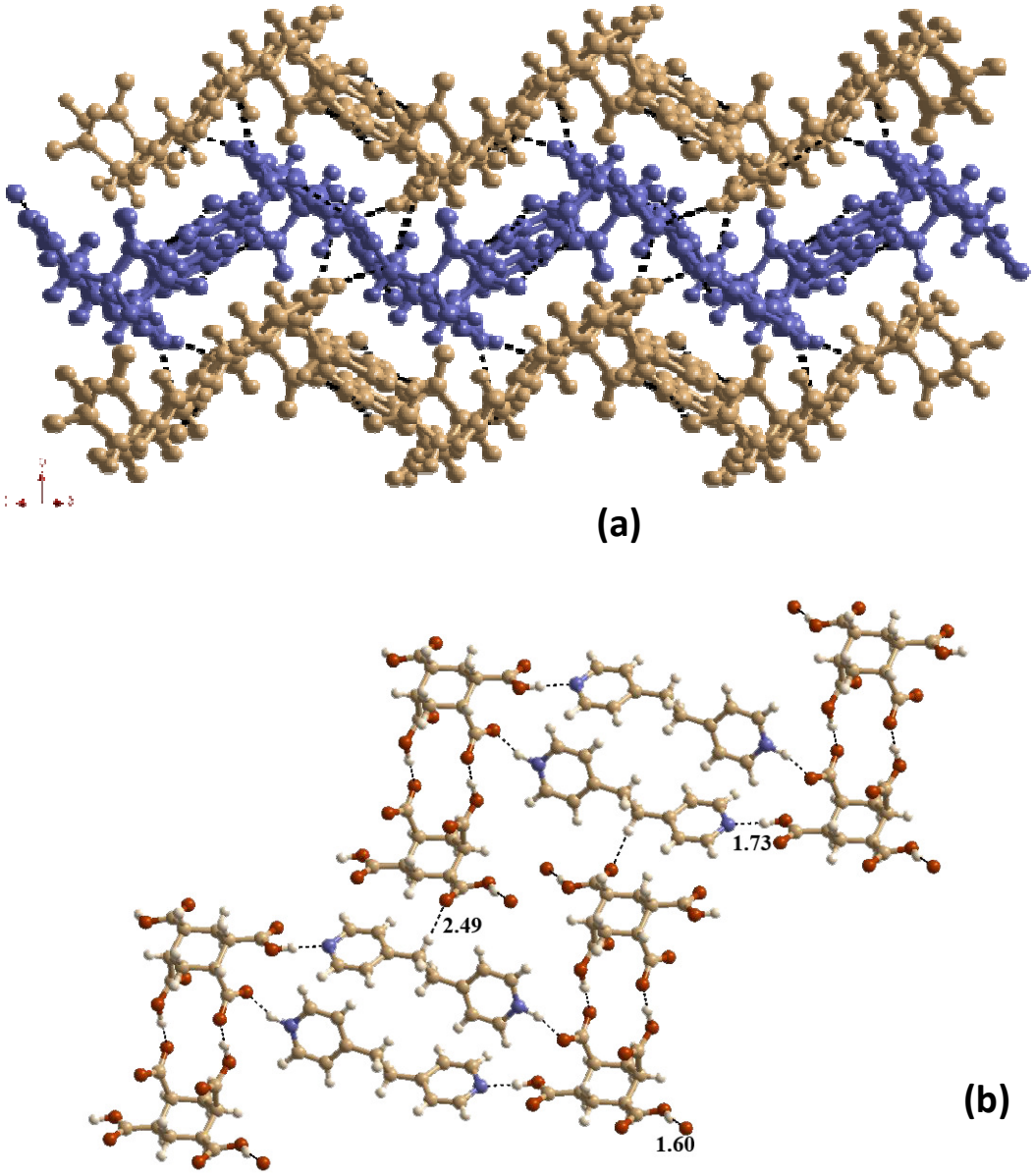


Figure 2.29. (a) Three-dimensional arrangement of molecules in the crystal structure of **1g.H_2O**. (b) Interaction between molecules in a sheet in the complex **1g.H_2O**.

2.3 Conclusion

In this study, co-crystals of 1,2,4,5-cyclohexanetetracarboxylic acid, **1**, have been reported, especially, the ones formed with various aza-donor compounds. In all the

cases, it has been noted the significance of -COOH, even when it is part of aliphatic moiety by yielding exotic supramolecular assemblies. In the examples reported in the above sections, it is apparent that the assemblies have adopted, in general, sheet structure in two-dimensional arrangement. In some instances, for example, the sheets are formed with voids which are self-filled either by interpenetration (acid **1** with **44bpy**) or by the molecules from the adjacent species as observed prominently in **1a**. However, in the structure of acid **1** with 1,10-phenanthroline, **1d**, a host-guest type assembly is realized with the voids aligning along stacking direction, thereby constituting channels. As noted in the structures of **1.H_2O** and **1g**, wherein the sheets are exclusively being constituted by acid molecules, either aza-donor molecules or solvents are sandwiched between such layers, yielding a pillared type structures, well known in many inorganic clay structures. The reported structural features in this study may lead to establish more directed principles and new avenues for the creation of myriad of assemblies through -COOH group either on its own or through hetero functional moieties.

2.4 Experimental Section

2.4.1 Cocrystallization

All chemicals were obtained commercially and used without further purification. The solvents employed for crystallization purpose were of spectroscopic grade of highest available purity. Crystallization experiments were carried out at room temperature by dissolving the acid **1** and aza donor in a 1:1 ratio in either MeOH or EtOH or in the mixture of solvents MeOH and EtOH in 1:1 ratio.

In a typical crystallization, in 25mL Erlenmeyer flask 150mg (0.5mmol) of acid **1** and 78mg (0.5mmol) of 2 were dissolved in MeOH by heating to the boiling temperature of methanol. The reaction mixture was then allowed to cool to room temperature at ambient conditions. Colorless block type single crystals of good quality of complex **2a** were obtained in 72 h, which were used for single crystal structure determination studies by X-ray diffraction method.

2.4.2 X-ray Crystallography

Good quality single crystals of **1.H_2O, 1a-1g**, and **1g.H_2O** were carefully chosen after viewing through a Leica microscope supported by a rotatable polarizing stage and a CCD camera and glued to a glass fiber using an adhesive to mount on a goniometer of Bruker single crystal X-ray diffractometer equipped with APEX CCD detector. The data collection was smooth in all the cases, and no extraordinary methods have been employed, as the crystals were quite stable. The intensity data were processed using Bruker's suite of data processing programs (SAINT),[14] followed by absorption corrections using SADABS. The structure solution of all the complexes have been carried out by direct methods, and refinements were performed by fullmatrix least squares on F^2 using the SHELXTL-PLUS suite of programs. All the structures converged to good *R* factors. All the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms obtained from Fourier maps were refined isotropically. All the refinements were smooth in all the structures. All non-hydrogen atoms were refined anisotropically. All the intermolecular interactions were computed using PLATON.[15]

Table 2.1 Crystallographic data for molecular complexes **1.H_2O, 1a-1g**, and **1g.H_2O**

	1.H_2O	**1a**	**1b**
Formulae	(C_{10} H_{10} O_8), H_2O	(C_{10} H_{12} O_8), (C_{12} H_{10} N_2)	(C_{10} H_{12} O_8), ($C_{10}H_8N_2$)
Mol. wt.	258.18	442.42	416.38
Crystal shape	Block	block	block
Crystal color	Colorless	pale yellow	colorless
Crystal System	Tetragonal	Orthorhombic	Orthorhombic
Space Group	*$P4_2/mbc$*	*Pnma*	*Pnma*
a/ Å	11.849(2)	12.990(3)	12.585(3)
b/ Å	11.849(2)	26.003(6)	25.148(5)
c/ Å	18.381(4)	6.135(1)	5.887(1)
α/^{0}	90	90	90
β/^{0}	90	90	90
γ/^{0}	90	90	90
cell vol./ Å^3	2580.6(8)	2072.4(8)	1863.2(7)
Z	8	4	4
D_{calc} (g cm^3)	1.329	1.418	1.484
***T*/^{0}K**	293(2)	293(2)	293 (2)
Wavelength (Mo, Kα/ Å)	0.71073	0.71073	0.71073
μ/mm^{-1}	0.118	0.109	0.116
2ϑ range /^{0}	50.20	50.50	50.02
F(000)	1072	928	872
Total reflect.	11955	14002	12387
No. unique reflns [*R*(int)]	1185 [0.0498]	1926[0.0520]	1678[0.0400]
Non-zero reflect.	1085	1600	1201
No. parameters	106	196	183
GOF on *F*^{2}	1.137	1.056	0.962
R1 [I>2σ(I)]	0.0640	0.0346	0.0330
wR2	0.1563	0.0926	0.0638

Table 2.1. Continued.....

	1c	1d	1e
Formulae	(C_{10} H_{12} O_8), (C_{12} H_8 N_2)	(C_{10} H_{12} O_8), (C_{12} H_8 N_2)	(C_{10} H_{12} O_8), (C_{10} $H_{11}O_8$), (C_{12} H_9 N_2), (C_{12} H_8 N_2)
Mol. wt.	440.40	440.40	880.80
Crystal shape	needles	needles	block
Crystal color	pale yellow	pale yellow	colorless
Crystal System	Orthorhombic	Orthorhombic	Triclinic
Space Group	*Pnma*	*Pbca*	*Pī*
a/ Å	12.117(2)	11.278(3)	10.743(6)
b/ Å	27.166(5)	12.766(4)	13.928(7)
c/ Å	3.072(1)	27.206(8)	14.159(7)
α/^{0}	90	90	73.33(8)
β/^{0}	90	90	79.47(9)
γ/^{0}	90	90	74.59(8)
cell vol./ Å^3	1998.7(6)	3917(2)	1943.5(2)
Z	4	8	2
D_{calc} (g cm^3)	1.464	1.494	1.505
***T*/^{0}K**	293(2)	293(2)	293(2)
Wavelength (Mo, Kα/ Å)	0.71073	0.71073	0.71073
μ/mm^{-1}	0.113	0.115	0.116
2*ϑ* range /^{0}	50.00	50.02	50.12
F(000)	920	1840	920
Total reflect.	9100	18491	18636
No. unique reflns [*R*(int)]	1799[0.277]	3452[0.0854]	6829[0.0408]
Non-zero reflect.	1420	2814	6068
No. parameters	192	305	737
GOF on F^2	1.110	1.351	1.199
***R*1 [*I*>2σ(*I*)]**	0.0424	0.0969	0.0664
wR2	0.872	0.1678	0.1688

Table 2.1. Continued.....

	1f	**1g**	**1g.H_2O**
Formulae	(C_{10} H_{10} O_8), (C_{12} $H_{12}N_2$), (C_6 H_4 N)	(C_{10} H_{10} O_8), 0.5(C_{12} H_{14} N_2)	(C_{10} H_{11} O_8), (C_{12} H_{13} N_2), H_2O
Mol. wt.	532.52	351.31	460.43
Crystal shape	block	needles	block
Crystal color	colorless	colorless	colorless
Crystal System	Triclinic	Monoclinic	Monoclinic
Space Group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a/ Å	7.216(2)	11.082(2)	16.609(3)
b/ Å	10.604(3)	16.443(2)	9.635(2)
c/ Å	18.914(5)	12.240(1)	13.694(2)
α/^{0}	84.52(4)	90	90
β/^{0}	84.11(4)	122.26(9)	98.12(3)
γ/^{0}	86.58(4)	90	90
cell vol./ Å^3	1431.3(6)	1886.2(4)	2169.4(6)
Z	2	4	4
D_{calc} (g cm^3)	1.236	1.237	1.410
***T*/^{0}K**	293(2)	293(2)	293(2)
Wavelength (Mo, Kα/ Å)	0.71073	0.71073	0.71073
μ/mm^{-1}	0.092	0.101	0.111
2ϑ range /^{0}	50.00	50.04	50.04
F(000)	558	736	968
Total reflect.	13774	13336	15144
No. unique reflns [*R*(int)]	5035[0.0384]	3340[0.0214]	3836[0.0206]
Non-zero reflect.	3174	3025	2743
No. parameters	391	237	386
GOF on F^2	1.015	1.049	1.048
***R*1 [*I*>2σ(*I*)]**	0.0664	0.0537	0.0440
wR2	0.1912	0.1328	0.1235

Table 2.2. Characteristic hydrogen bond distances (Å) and angles (º) of the **1.H_2O, 2a-1g**, and **1g.H_2O**[#]

	1.H_2O			**1a**			**1b**		
O-H···O	1.80	2.60	166	1.71	2.64	168	1.70	2.64	166
O-H···N				1.80	2.79	172	1.78	2.73	168
C-H···O				2.55	3.26	133			
				2.46	3.35	153			

[#] Three columns for each structure represent H···A, D···A distances and D-H···A angle, respectively for a typical hydrogen bond, being represented as D-H···A

Table 2.2. Continued.....

	1c			1d			1e		
O-H···O	1.71	2.64	168	1.71	2.67	166	2.01	2.85	171
				1.82	2.70	164	1.79	2.63	173
							1.68	2.65	168
							1.50	2.54	173
							1.62	2.65	174
							1.64	2.71	173
							1.86	2.66	176
O-H···N	1.80	2.79	172	1.94	2.74	146			
				1.70	2.70	166			
C-H···O	2.55	3.26	133	2.43	3.19	135	2.37	3.20	140
	2.46	3.35	153	2.49	3.25	136	2.56	3.32	140
				2.59	3.24	127	2.34	3.07	130
				2.57	3.25	130	2.33	3.14	136
							2.47	3.42	177
							2.45	3.27	144
							2.40	3.22	141
							2.53	3.51	169
							2.35	3.31	162
C$^-$H···N							2.48	3.41	165
							2.12	3.11	175
N$^-$H···O							1.79	2.64	177
							1.73	2.58	173
N$^-$H···N							2.35	3.15	143

[#] Three columns for each structure represent H···A, D···A distances and D-H···A angle, respectively for a typical hydrogen bond, being represented as D-H···A

Table 2.2. Continued.....

	1f			**1g**			**1g.H_2O**		
O-H···O	1.93	2.70	143	1.80	2.66	165	1.60	2.57	170
				1.62	2.60	159	1.55	2.55	174
O-H···N	1.90	2.71	167				1.73	2.68	169
C-H···O	2.49	3.23	137	2.44	3.35	167	2.55	3.47	158
	2.57	3.20	126	2.55	3.17	124	2.49	3.27	142
	2.59	3.24	128				2.53	3.28	138
N-H···O	1.79	2.64	177	1.74	2.71	153	1.62	2.60	157
	1.73	2.58	173						

[#] Three columns for each structure represent H···A, D···A distances and D-H···A angle, respectively for a typical hydrogen bond, being represented as D-H···A

2.5. References

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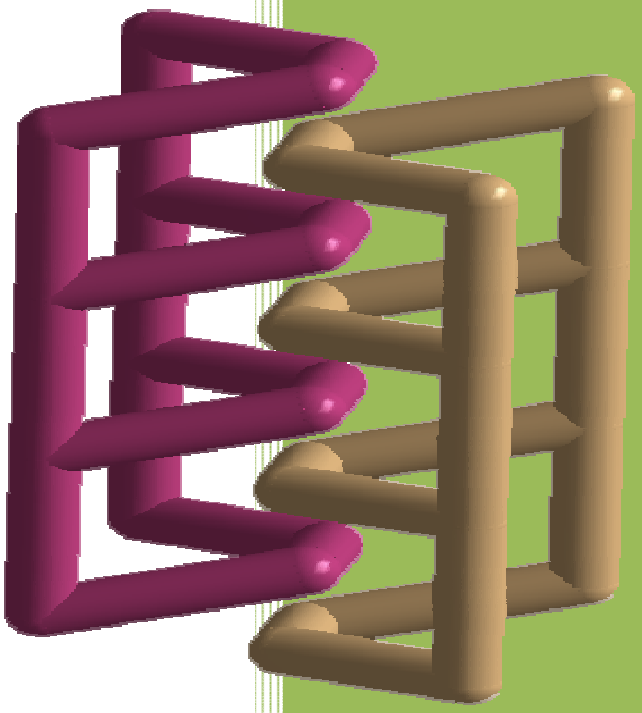
Chapter 3

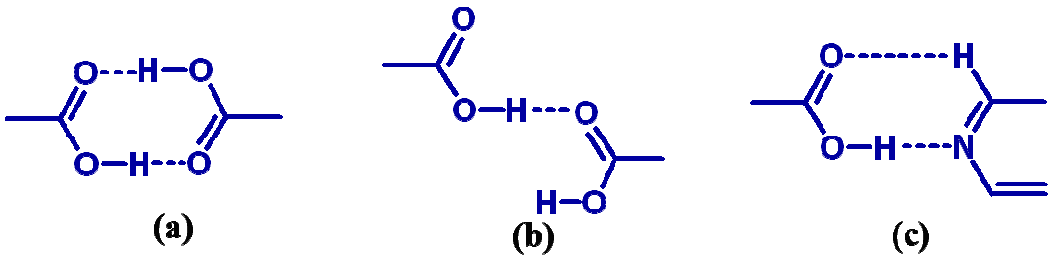
Supramolecular Assemblies of 1,2-Cyclohexanedicarboxylic Acids



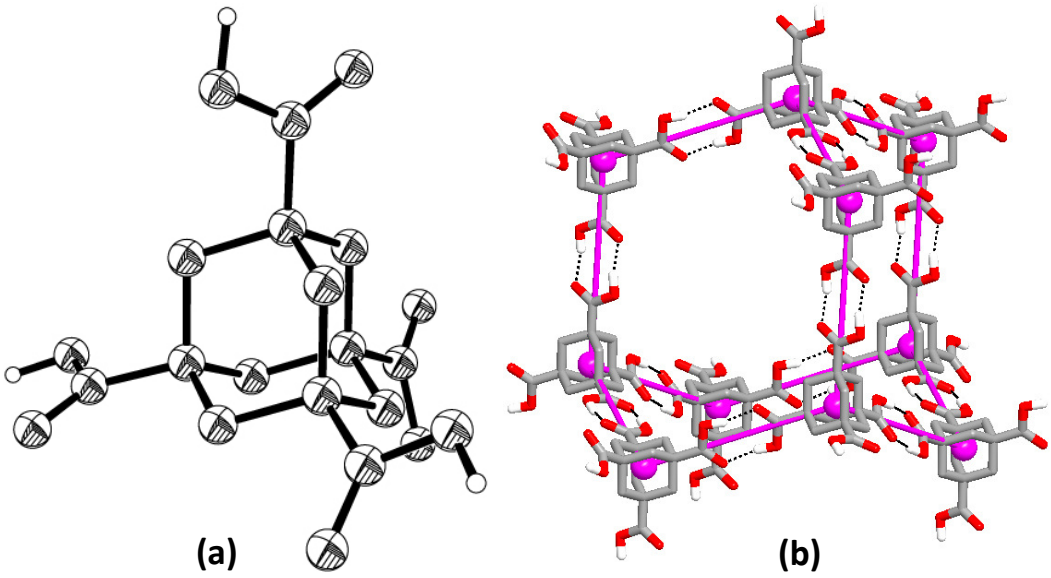
Supramolecular Assemblies of 1,2-Cyclohexanedicarboxylic Acids

3.1 Introduction

Supramolecular assemblies formed by multicomponent ensembles, for example, acid-base complexes, as discussed in the introductory chapter and also the new findings compiled in Chapter 2, in general, yield host-guest architecture at nanoscale, solid state reactions interpenetrated networks, pharmaceutical cocrystals, polymorphism, etc.[1] such an aggregation is generally directed by self-assembly of moieties through non-covalent interactions. However, to obtain a targeted assembly, topology of functional moieties also plays a crucial role apart from the intermolecular interactions that direct self-assembly. In the assemblies derived through aromatic moieties, the topology is considered based on position of the substitution and also orientation of atoms within the functional moiety. The analogy is well extended even for aliphatic cyclic compounds also, like cyclohexane and adamantane mediated assemblies. Assemblies formed by those entities (especially -COOH substituted ones) via homomeric aggregation, and also heteromeric aggregation in the presence of hydrogen bond acceptor moieties like 4,4'-bipyridine, phenazine, phenanthroline, etc. ensues recognition via acid···acid and acid···pyridine recognition patterns, as shown below.[2-18] Some representative examples from literature are discussed in following sections to highlight the topology of functionality.



Ermer demonstrated that infinite diamondoid network of admentane-1,3,5,7-tetracarboxylic acid (**ATC**) in which -COOH groups are tetrahedrally oriented as shown in Figure 3.1(a).[19] **ATC** is a particularly favourable example considering the rigidity of its carbon skeleton and the almost perfect tetrahedral alignment of the carboxylic groups; hence they self-assemble via hydrogen bonded carboxylic acid dimer to afford diamondoid networks with large cavities of roughly 12 Å in diameter, as shown in Figure 3.1(b). However, these cavities are filled by five independent networks that interpenetrate to form five-fold diamondoid networks as shown in Figure 3.1(c).



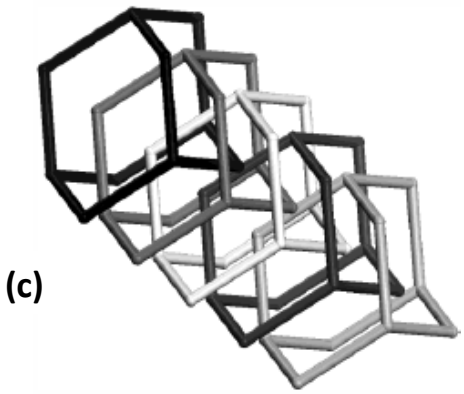


Figure 3.1 (a) Tetrahedrally directed four carboxylic groups of admentane-1,3,5,7-tetracarboxylic acid (**ATC**). (b) Hydrogen-bonded diamondoid framework with a cavity. (c) Five-fold interpenetrating hydrogen-bonded diamondoid networks.

In recent studies, as reported by Bhogala et al.,[20] crystal structure of 1,3,5-cyclohexanetricarboxylic acid **135CTC** with 4,4'-bipyridine, **bpy**, exhibited hexagonal open network formed by acid, **bpy** and water molecule (as shown in Figure 3.2) with void space of dimension 27 × 27 Å.

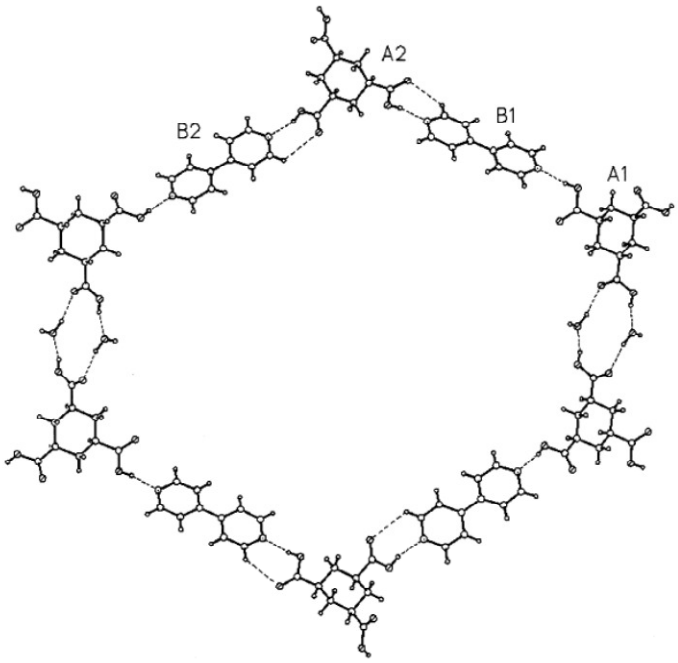


Figure 3.2 A hexagonal open network in hydrated complex of **135CTC** and bpy. The void has dimension of 27 × 27 Å.

Further in a complex of **135CTC** with 1,2-bis(4-pyridyl)ethane, **bpyea**,[21] a super hexagonal network is formed by the acid and **bpyea** molecule where six molecules of each acid and bpyea aggregates to produce a supramolecular hexagon with void space of dimension 34.1 × 36.7 Å as shown in Figure 3.3(a), which resulted in the formation of a honeycomb network of supramolecular hexagon in 2D. Three such networks interwove to give triply interpenetrated network as shown in Figure 3.3(b).

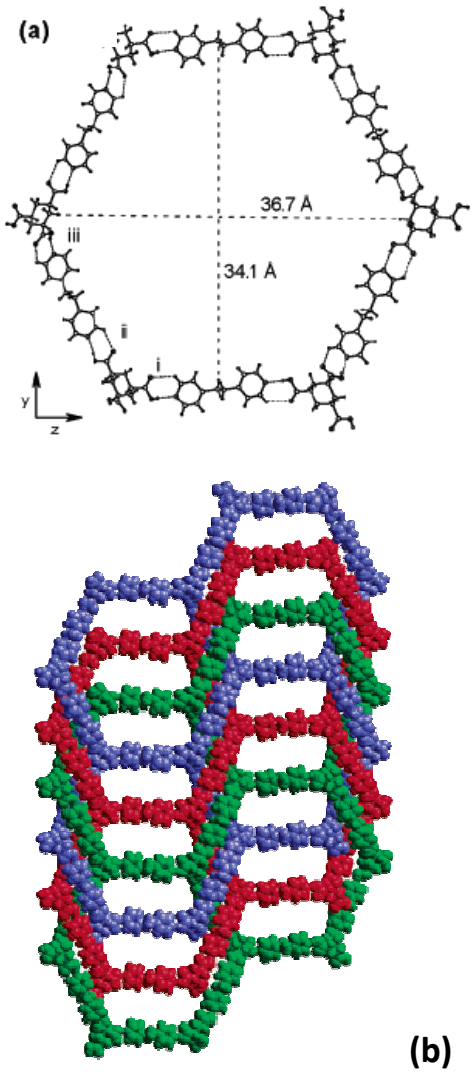
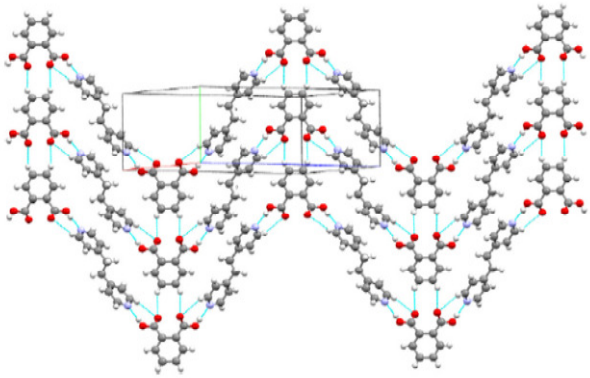
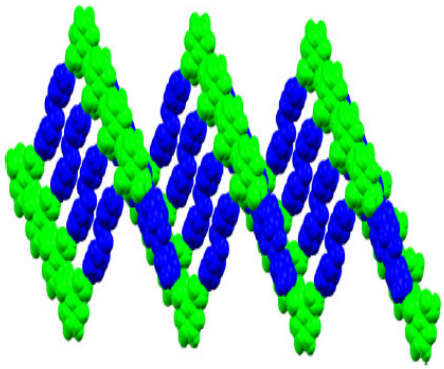


Figure 3.3 (a) A supramolecular super-hexagon network in formed by **135CTC** and **bpyea**. The void has dimension of 34 × 36 Å^2. (b) Three-fold parallel interpenetration of independent networks shown by **135CTC** and **bpyea** complex.

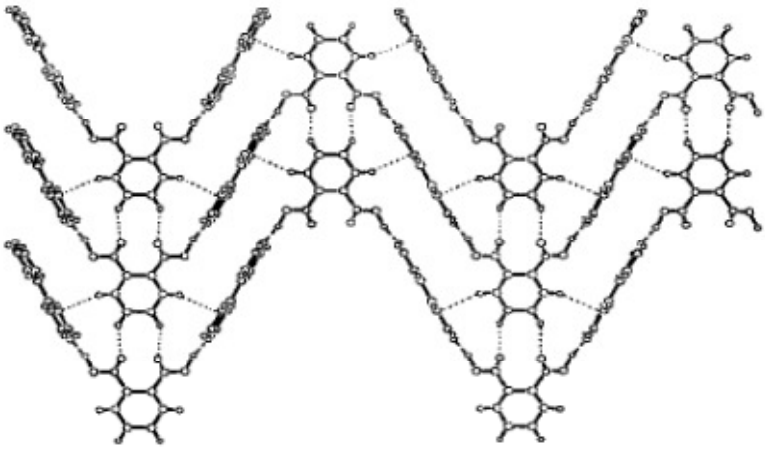
Molecular assemblies formed by phthalic acid, in which the -COOH are positioned in a linear geometry, include formation of one-dimensional chains with many aza-donor compounds.[22] Assemblies of the acid with **bpyee**, **bpy** and 4,4'-dipyridylacetylene are shown in Figure 3.4 in which zigzag network is illustrated.



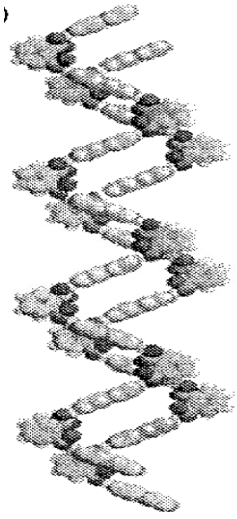
(a)



(b)



(c)



(d)

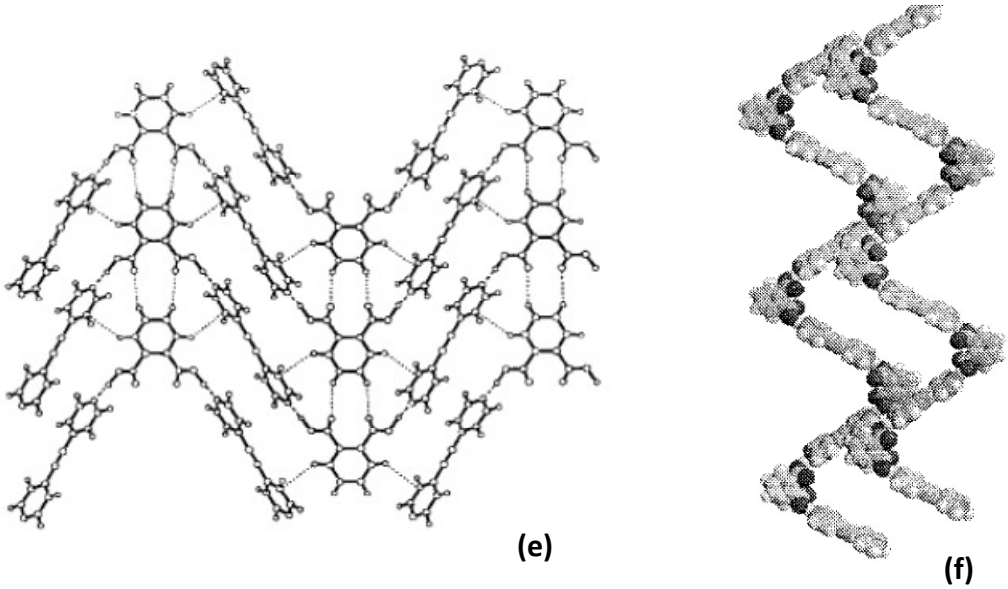
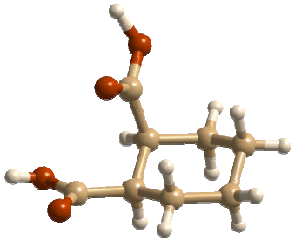


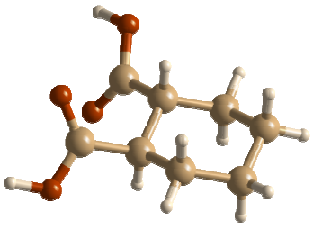
Figure 3.4 One Dimensional zig-zag chains formed by phthalic acid with **bpyee [**(a) and (b)], 4,4'-bipyridine [(c) and (d)] and 4,4'-dipyridylacetylene [(e) and (f)].

However, in reference to aliphatic cyclic compounds, for example 1,3,5-cyclohexanetricarboxylic acid, the topology does not limit to the positional substitution of the -COOH but also conformations in terms of stereochemistry like *cis* and *trans* isomers. To address such features and also in continuum with exploration of supramolecular chemistry of cyclohexanecarboxylic acid moieties, experiments carried out with isomers of 1,2-cyclohexanedicarboxylic acid, viz. *cis*- and *trans*-1,2-cyclohexanedicarboxylic acids, **2** and **3**, respectively, with various aza-donors, as listed in Chart 1. The results of the resultant network structures obtained through self-assembly have been discussed in detail in following sections. The assemblies are found to be crystallized in different architectures, ranging from tapes to molecular ladders to host-guest assemblies.

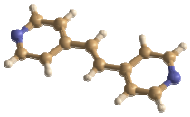
Chart I



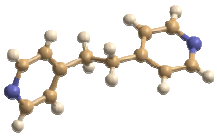
2
cis-1,2-cyclohexanedicarboxylic acid



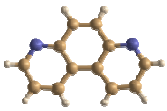
3
trans-1,2-cyclohexanedicarboxylic acid



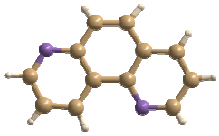
(a)
trans-1,2-bis(4-pyridyl)ethene



(b)
1,2-bis(4-pyridyl)ethane



(c)
4,7-phenanthroline



(d)
1,7-phenanthroline

Reactants	Solvent of crystallization	Molecular complexes	Composition
2+(a)	Methanol	**2a**	1:1
2+(a)	Nitrobenzene	**2a.nb**	1:1:1
2+(b)	Methanol	**2b**	1:1
2+(c)	Methanol	**2c.H_2O**	1:1:1
3+(a)	Ethanol + Methanol (1:1)	**3a**	2:2
3+(d)	Ethanol + Methanol (1:1)	**3d**	1:1

3.2 Results and Discussion

Cocrystallization of acid, **2** with various aza-donors (**a** - **d**) in ethanol, methanol, nitrobenzene or mixture of solvents, as the case be (Chart 1) gave good quality single crystals. Discussion about cocrystals synthesis, structure determination by X-ray diffraction process and analysis of arrangement of molecules in the crystal lattices are compiled in following sections. Parameters pertinent to X-ray data collection strategy, structure solution and refinement are given Table 3.1. Complete characteristics of intermolecular interactions (hydrogen bonds) are listed in Table 3.2.

3.2.1 Molecular Complexes of Acid 2 and *trans*-1,2-bis(4-pyridyl)ethene (a)

Molecular complex of acid, **2** and *trans*-1,2-bis(4-pyridyl)ethene was obtained by co-crystallization of the co-formers in a 1:1 ratio, from a methanol solution. The complex is labelled as **2a** for the purpose of discussion. Crystal structure determination by single crystal X-ray diffraction methods reveals that **2a** crystallizes in triclinic space group, *Pī* (Table 3.1) with both acid **2** and aza-donor (**a**) present in a 2:1 ratio. Contents of asymmetric unit are shown in Figure 3.5.

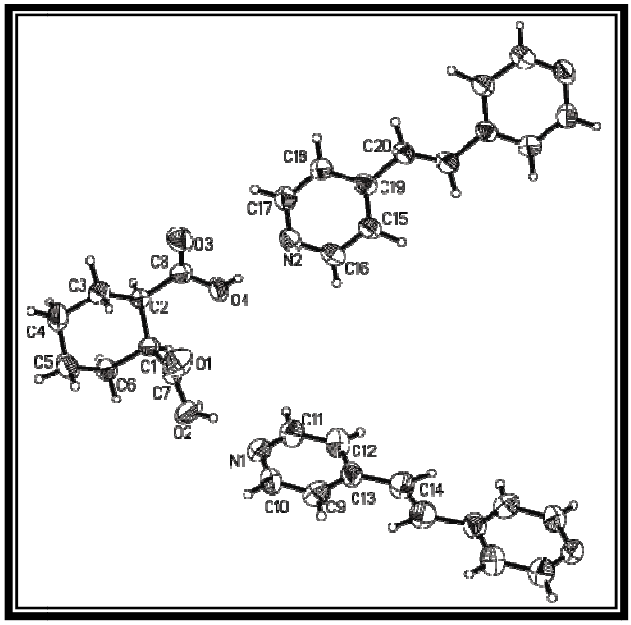


Figure 3.5 ORTEP of acid **2** and aza-donor (**a**) , at 50% probability level, in the crystal structure of **2a**.

Analysis of arrangement of molecule in the crystal lattice of **2a**, gave a projection of stacking of sheets of molecules in three-dimensional arrangement. The arrangement is shown in Figure 3.6.

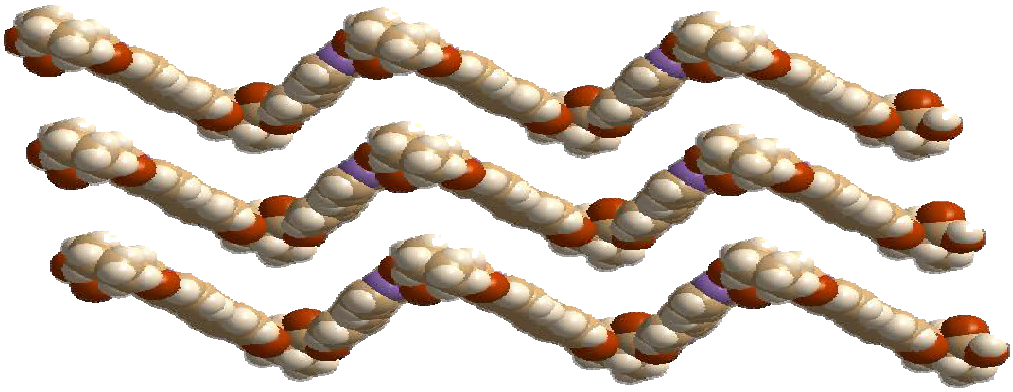


Figure 3.6 Packing of two dimensional sheets in the crystal lattice of complex **2a** .

In a typical sheet, the molecules of **2** and the aza-donors, recognize each other by O-H···N/ C-H···O pairwise hydrogen bonding (H···N, 1.96 and H···O, 2.51 Å), are further held together through a C-H···O hydrogen bond with an H···O distance of 2.56 Å formed by the adjacent acid molecules. As a result, a ladder-type architecture is realized with the rods being formed by acid **2** molecules, while aza-donor molecules act as rungs.

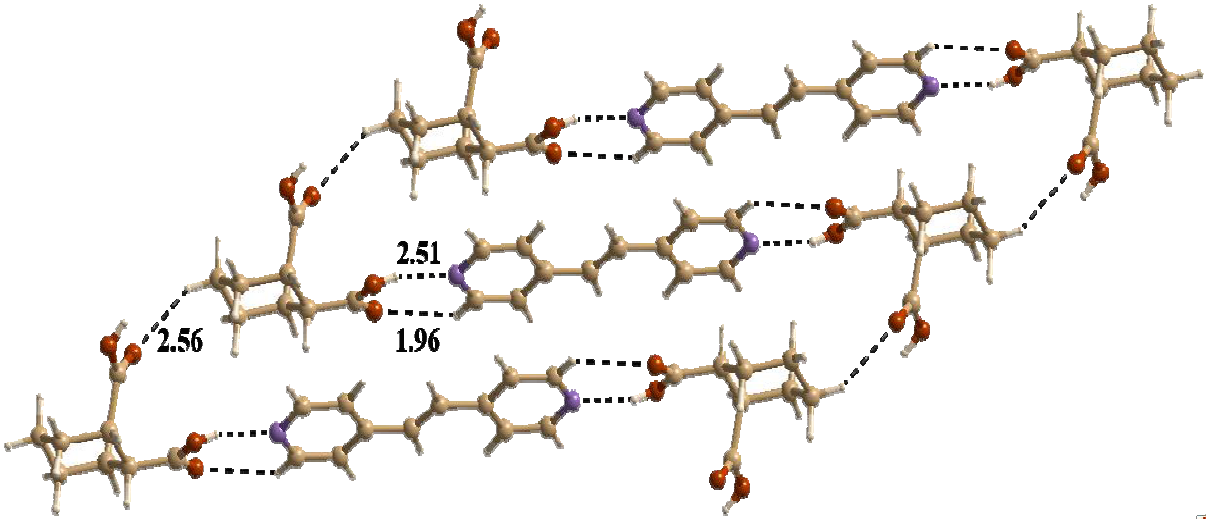


Figure 3.7 Ladder formation in the complex, **2a**, wherein rods are being formed by acid **2** molecules and rungs by the aza-donor.

A representative ladder is shown Figure 3.7 In fact, such adjacent ladders are further connected to each other by the second molecule of **a** through a single O-H···N hydrogen bond with H···N distance of 1.99 Å, as shown in Figure 3.8.

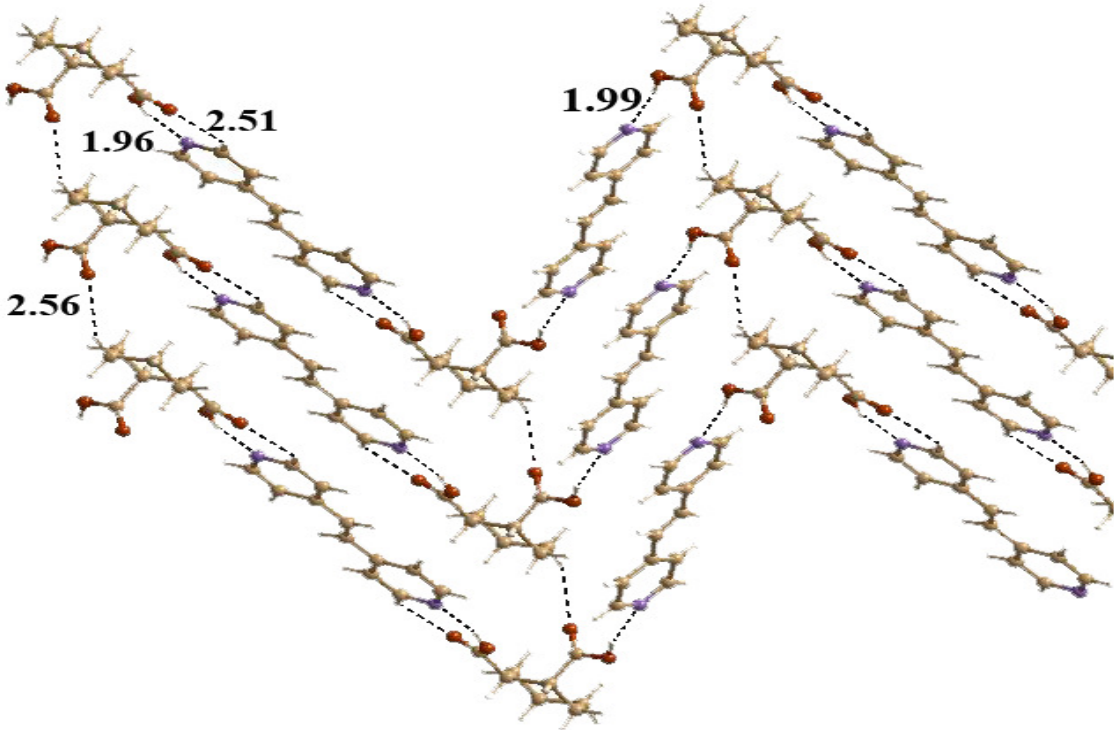


Figure 3.8 Self-assembly of ladders within a sheet structure of complex **2a**.

However, when the co-crystallization experiment between acid **2** and aza-donor in a 1:1 ratio of the co-formers was carried out from other solvents, primarily with an aim to obtain best quality crystals for unambiguous three-dimensional structure determination by single crystal X-ray diffraction methods, the crystals obtained from a nitrobenzene have been found to be crystallized entirely in a different crystal lattice than discussed in the above paragraphs for such crystals obtained from a methanol solution.

Analysis of the X-ray data reveals that, the crystals consist of 2:1 ratio of co-crystal formers and also possess molecules of nitrobenzene, the solvent of crystallization. ORTEP of conformation of molecules is shown in Figure 3.9. This molecular complex is labelled as **2a.nb**, for the purpose of discussion.

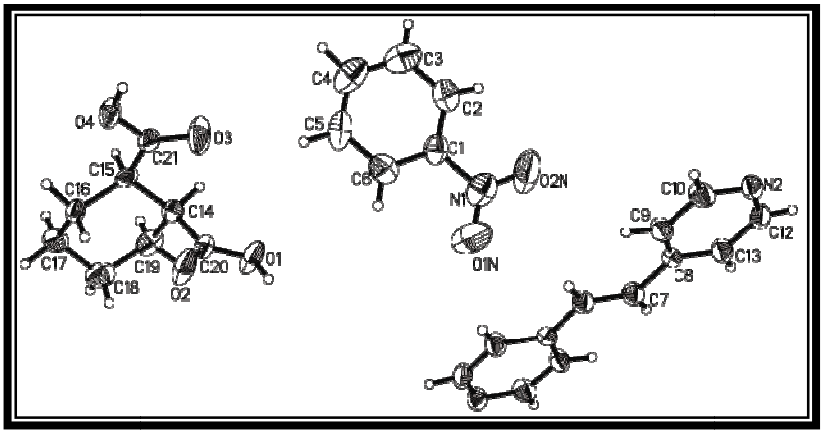


Figure 3.9 ORTEP of molecular complex **2a.nb**, at 50% probability level

Packing analysis of molecules in the crystal lattice highlights that each of acid **2** molecules is bound to a molecule of the aza-donor, **a**, by a pairwise O-H···N/ C-H···O hydrogen bonding pattern (H···N, 1.83, H···O, 2.84 Å). Such pairs of acid **2** and molecules of **a** are further glued together through a centrosymmetric cyclic O-H···O hydrogen bond (H···O, 1.84 Å), formed between the -COOH groups of acid molecules. Thus, an infinite crinkled tape network is established. The arrangement is shown in Figure 3.10.

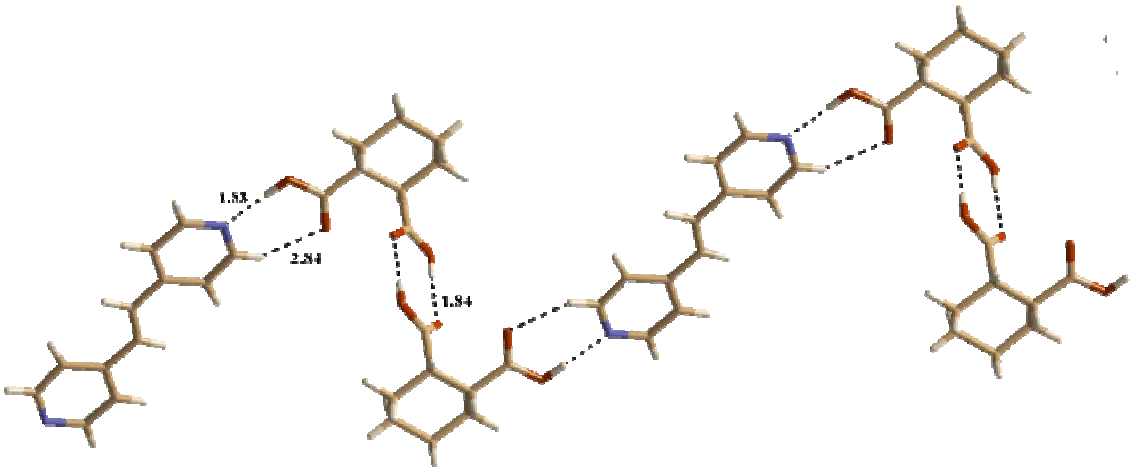


Figure 3.10 Molecular tapes observed in the complex, **2a.nb**.

The tapes are, however, organized in three-dimensional arrangement such that a considerable void space of a dimenison 14.5 × 10.9 $Å^2$ is formed, as shown in

Figure 3.11, in which the solvent molecules (nitrobenzene) reside. The nitrobenzene guest species are found to interact with host molecules through a series of C-H···O hydrogen bonds, with H···O distances in a range 2.51 - 2.68 Å. The observed host-guest feature is depicted in Figure 3.12.

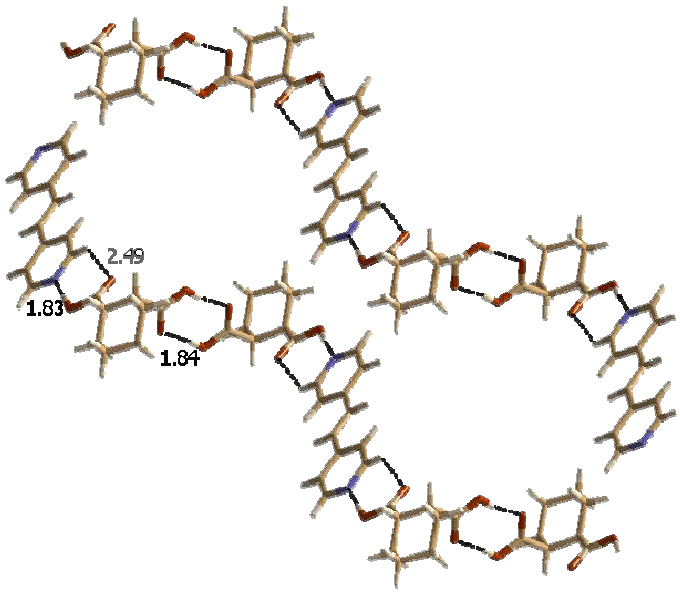
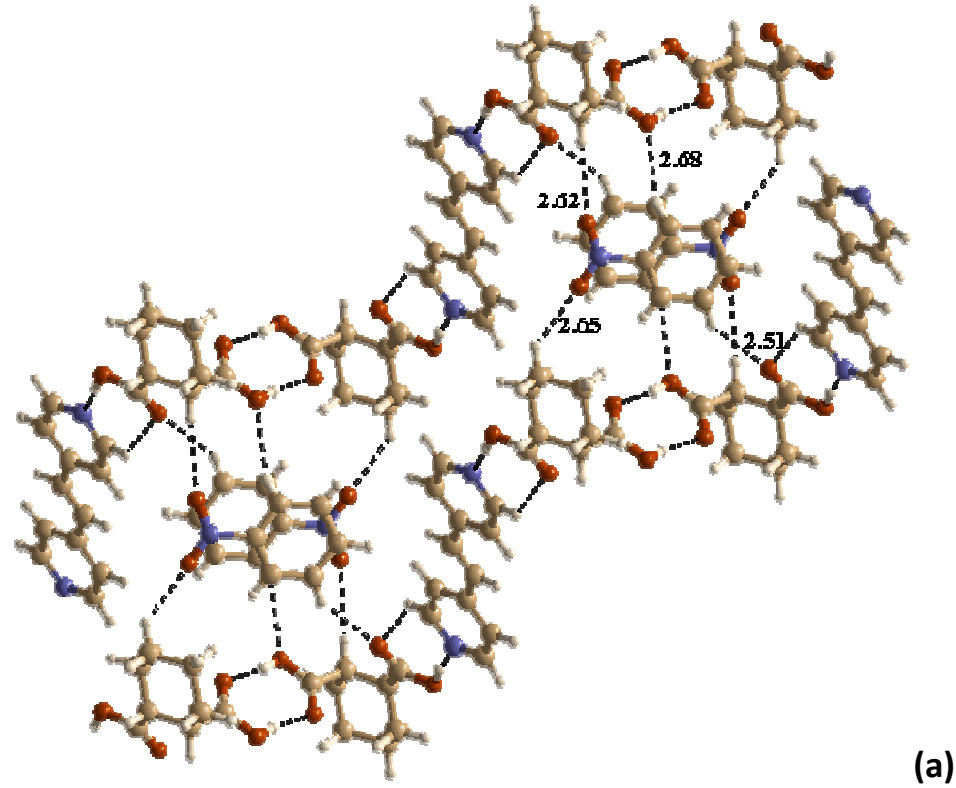
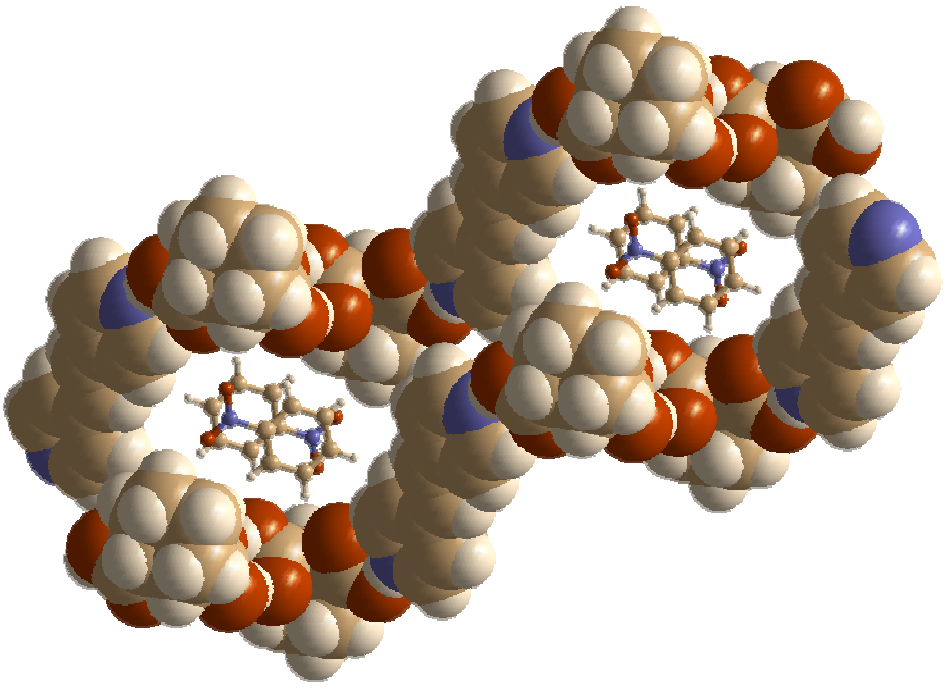


Figure 3.11 Arrangement of molecular tapes, in the form of sheets with void space, observed in complex **2a.nb**.



(a)



(b)

Figure 3.12 (a) Arrangement of nitrobenzene molecules within the host network in **2a.nb**. (b) Space-filling model of the arrangement of host molecules, as shown in (a) and fit of guest molecules.

Taken into account the distinctly different structural assemblies formed by varying the solvent of crystallization, during the co-crystallization process of acid **2** and aza-donor, **a**, attempts to obtain further variant structures from other solvents, however, are futile as crystals obtained thus were always been found to be corresponding to **2a**.

Nevertheless, in continuation of co-crystallization mixture of acid **2** with other aza-donors, molecular complex with 1,2-bis(4-pyridyl)ethane (**b**) has been found to be yielding co-crystals as discussed below.

3.2.2 Molecular Complex of Acid 2 and 1,2-bis(4-pyridyl)ethane (b)

A mixture of acid **2** and 1,2-bis(4-pyridyl)ethane (**b**) dissolved in methanol gave good quality single crystals by slow evaporation of the solution. Characterization of the crystals by X-ray diffraction methods reveals that crystals belong to triclinic *Pī* space group with the asymmetric unit comprising of 1:1 ratio of the components. The molecular complex is labelled as **2b**. Conformations of the molecules in the crystals are shown in Figure 3.13.

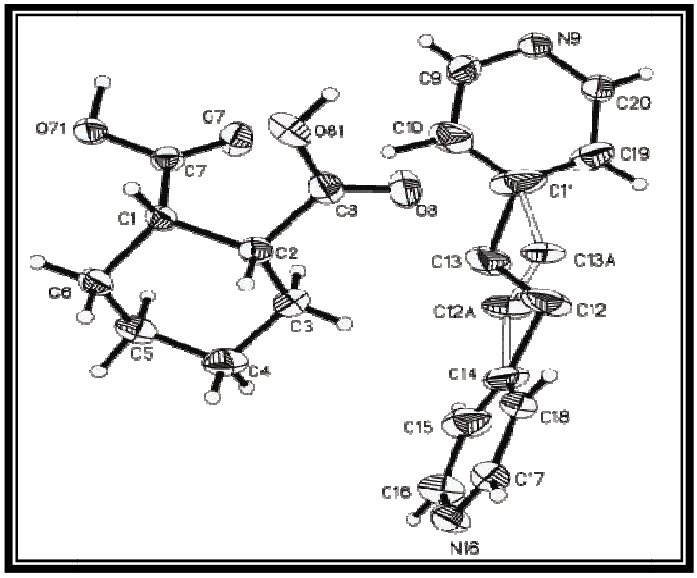


Figure 3.13 ORTEP of molecules in complex **2b** at 50% probability level

A thorough analysis of X-ray data divulges the enthralling features of cocrystal **2b**. Interestingly, two of each of acid **2** and aza-donors are found to be aggregated by yielding a cyclic ensemble, with a graph set notation $R_6^6(36)$, through a pair-wise O–H···N/C-H···O hydrogen bonding (H···N, 1.55 and H···O, 2.74 Å), as well as by a single O–H···N hydrogen bond (H···N, 1.55 Å). A typical ensemble is shown in Figure 3.14.

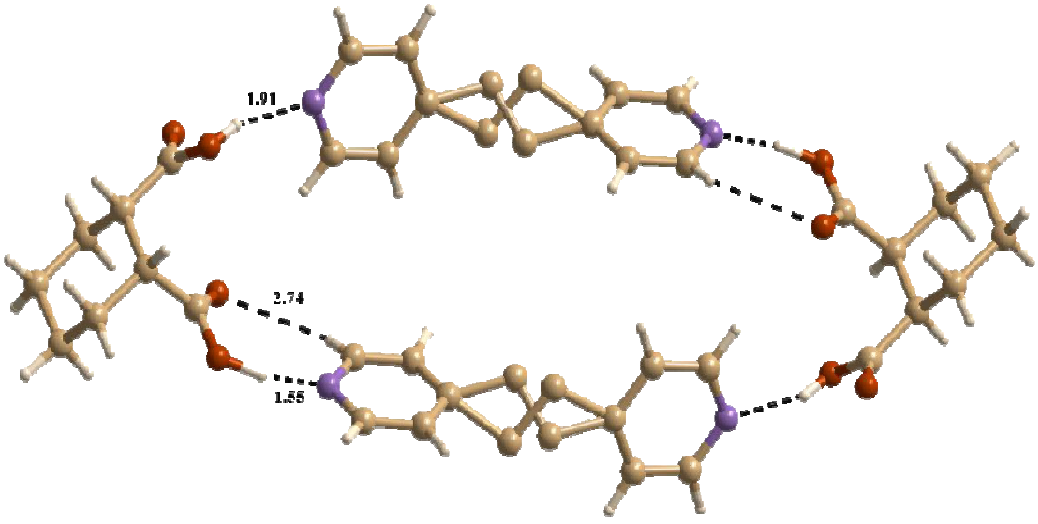


Figure 3.14 A cyclic ensemble of molecules of acid **2** and aza-donor in **2b**.

The adjacent ensembles are further held together through C–H···O hydrogen bonds (H···O, 2.61 Å) which leads to the constitution of sheets, as shown in Figure 3.15. Further, packing analysis projects that the sheets are packed by stacking process, along a crystallographic axis, with the aid of C–H···O and C–H···π interactions, as represented in Figure 3.16.

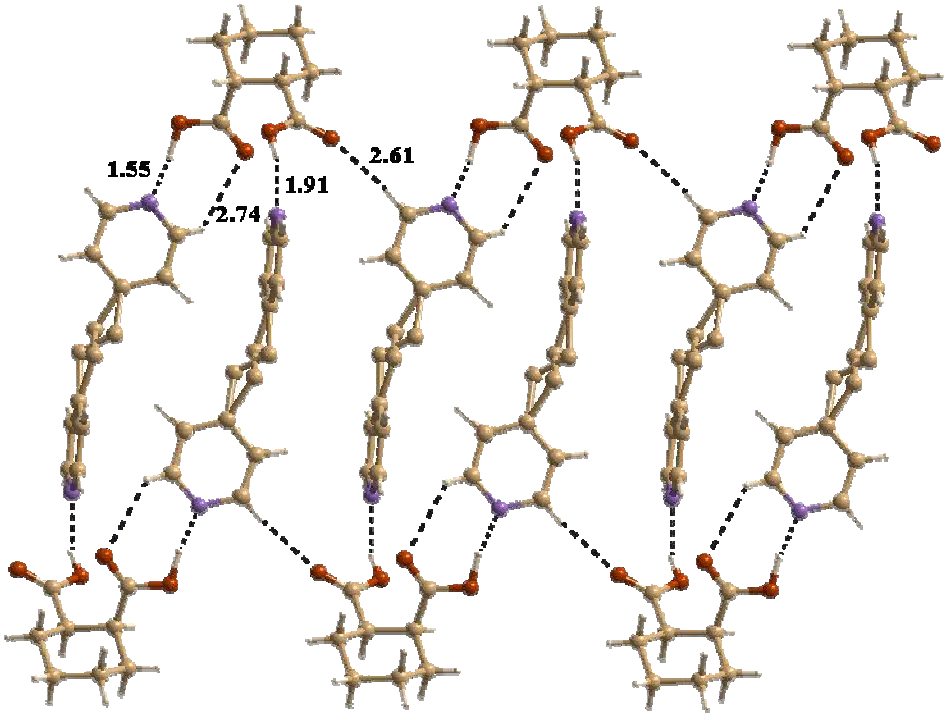


Figure 3.15 A typical sheet observed in **2b**.

The C–H···O hydrogen bonds along the stacking are with a H···O distance of 2.18 Å, while the C–H···π interactions formed between aromatic pyridine ring and equatorial hydrogen atoms of aliphatic cyclohexane are in the range of 3.18 - 3.27 Å.

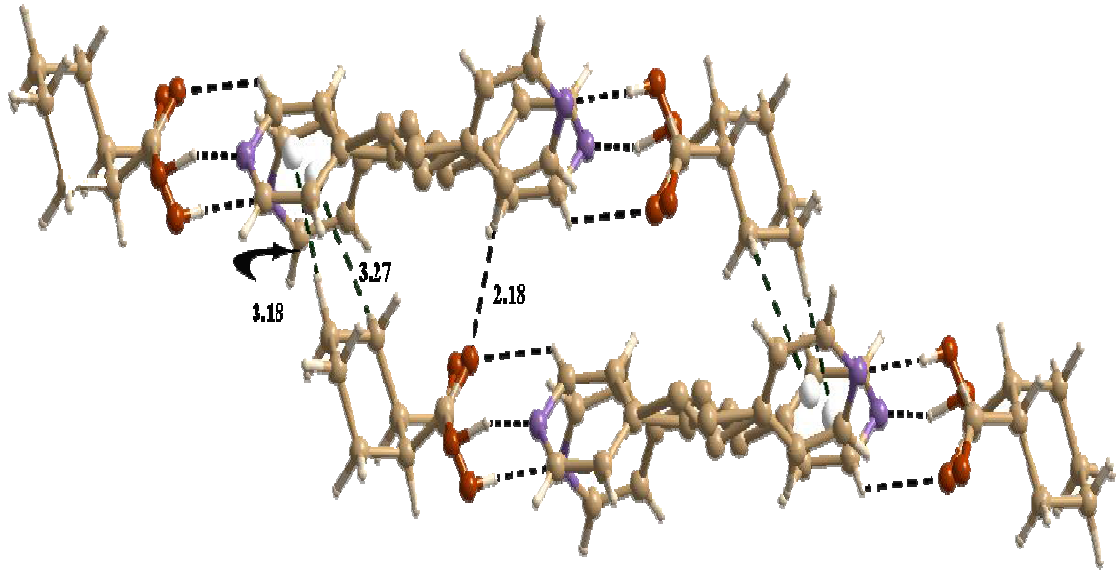


Figure 3.16 Stacking of sheets of molecules in the crystal lattice of **2b**.

3.2.3 Molecular Complex of Acid 2 and 4,7-phenanthroline (c)

Cocrystallization of a 1:1 mixture of Acid **2** and 4,7-phenanthroline (**c**) from a methanol solution gave crystals of high quality, by slow evaporation of the solution. Analysis by X-ray diffraction methods, identifies that crystals belong to a family of triclinic *Pī* space group with asymmetric unit composed of 1:1 ratio of acid **2** and aza-donor, **c**, along with one water molecule. The complex is labelled as **2c**.$\mathbf{H_2O}$. The asymmetric unit of **2c**.$\mathbf{H_2O}$ is shown in Figure 3.17.

(a)

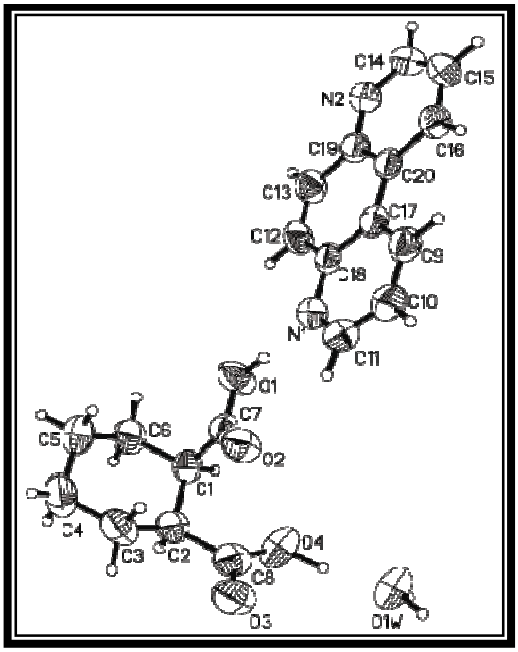


Figure 3.17 ORTEP of molecular adduct **2c.H_2O** at 50% probability level

Packing analysis reveals exotic features of the arrangement of molecules in the crystals **2c**.**H_2O**. A striking feature of molecular arrangement in **2c.H_2O** include the formation of 1-D acid chains and joining of these chains by ligand **c** which contribute to the formation of stand like architecture. The 1-D acid chains are formed through an association between the adjacent molecules, being held together, through water molecules by various O–H···O hydrogen bonds (H···O, 1.58 and 2.06 Å), due to the involvement of axial and equatorial carboxyl groups of adjacent acid molecules, as shown in Figure 3.18.

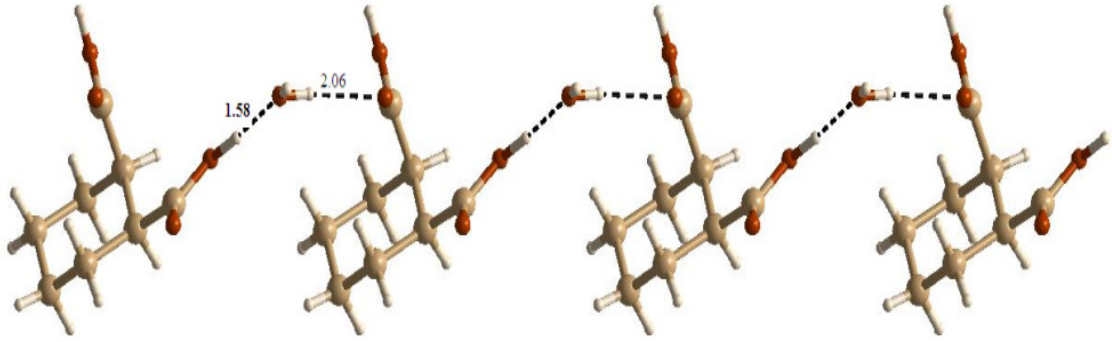


Figure 3.18 Tapes, exclusively formed by, acid **2** and water molecules in **2c.H_2O.**

Such tapes of acid molecules, lie adjacent to each other, are glued together by 4,7-phenanthroline with the help of different O–H···N and O–H···O hydrogen bonds. The binding is shown in Figure 3.19.

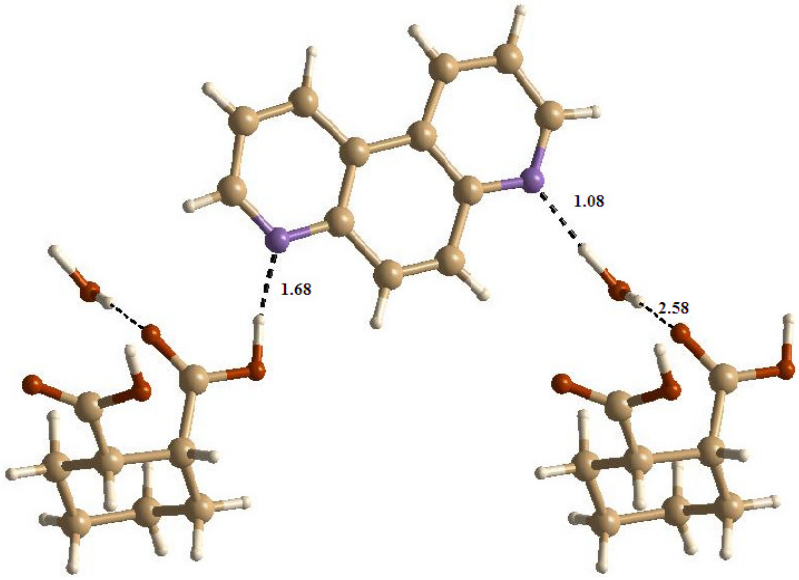
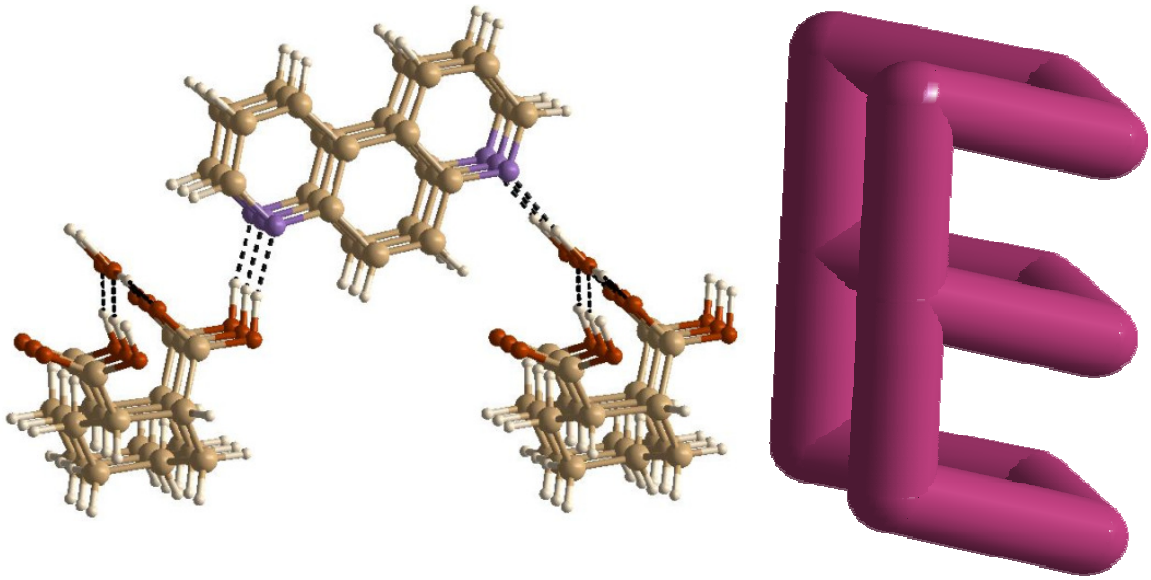


Figure 3.19 Interaction between aza-donor and acid **2** molecules in the tapes found in **2c**.H_2O. Two 1D chains connected by 47phen and water

Such networks ultimately stacked to replicate a stand like architecture with the rods of the stand are made up of 1D acid chains while rungs are of phenanthroline ligand. The molecular arrangement is represented in Figure 3.20(a), while the corresponding schematic presentation is shown in Figure 3.20(b). Further, in three-dimensional arrangement, the ensembles are packed through π-π interaction between phenanthroline rings present in the juxtaposed ensembles, as shown in Figure 3.21.



(a) (b)

Figure 3.20 (a) Top view of stand like architecture wherein the rods of the stand are made up of 1-D acid chains while rungs are of phenanthroline ligand (b) Schematic representation of molecular stand in complex **2c.H_2O**.

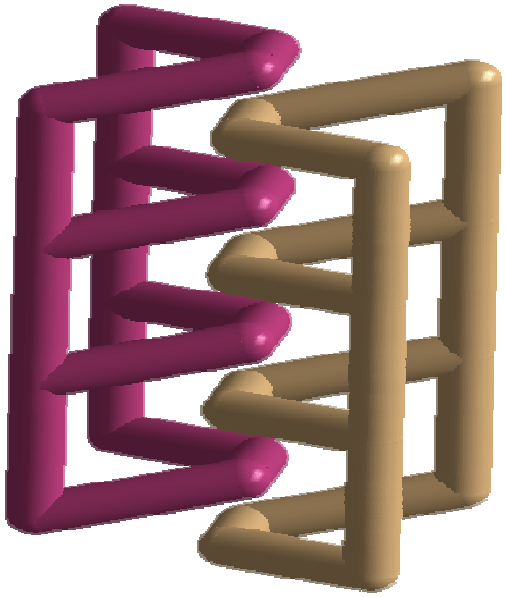


Figure 3.21 Packing of molecules in the crystal lattice, **2c**.H_2O

In continuation of further co-crystallization studies, attempts to obtain single crystals of the acid **2** with the aza-donor, 1,7-phenanthroline (**d**) were not successful. Hence, further experiments were carried out to prepare assemblies of the aza-

donors with acid **3**, an analogue of acid **2** in *trans*-form. However, aza-donors **b** and **c** failed to yield quality single crystals even numerous crystallization experiments were performed but **a** and **d** gave crystals readily, which are suitable for analysis by X-ray diffractions methods.

3.2.4 Molecular Complex of Acid 3 and *trans*-1,2-bis(4-pyridyl)ethene (a)

Solid mixture of *trans*-1,2-cyclohexanedicarboxylic acid, **3** and *trans*-1,2-bis(4-pyridyl)ethene, **a**, in 1:1 mixture of ethanol and methanol solution, gave good quality single crystals. X-ray diffraction analysis reveals an asymmetric unit in orthorhombic space group *C2/c* (Table 3.1). The co-crystals are labelled as **3a** for the ease of discussion. Contents of asymmetric unit are represented in Figure 3.22.

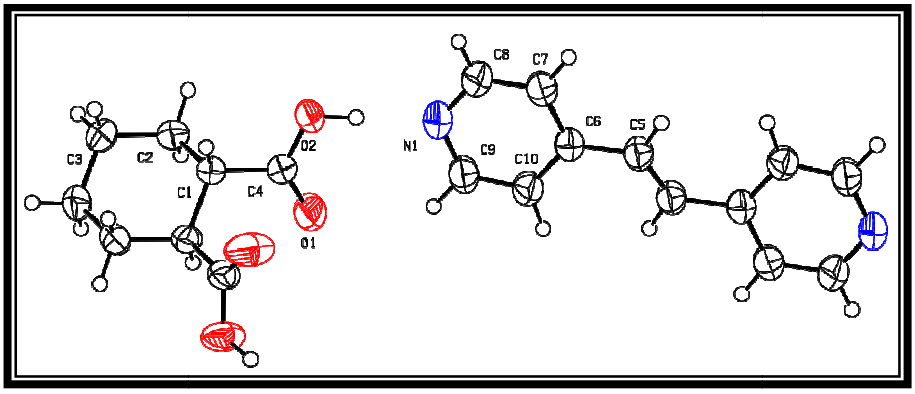
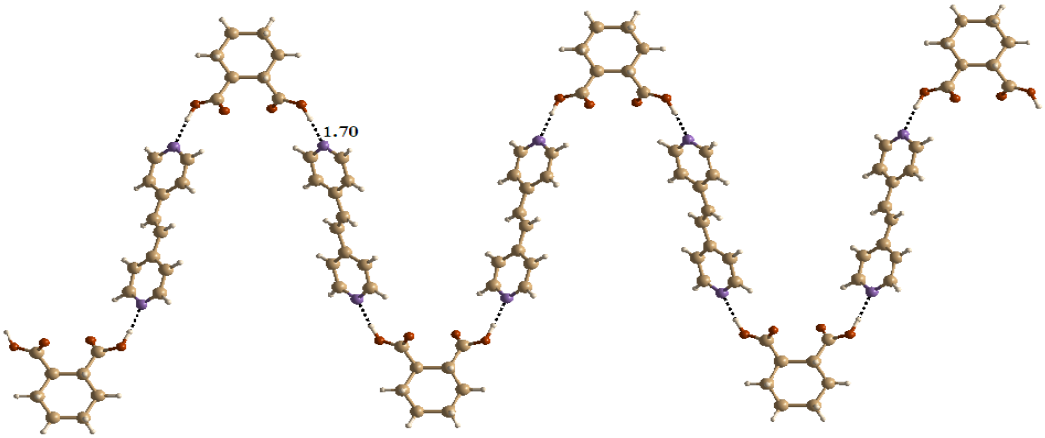
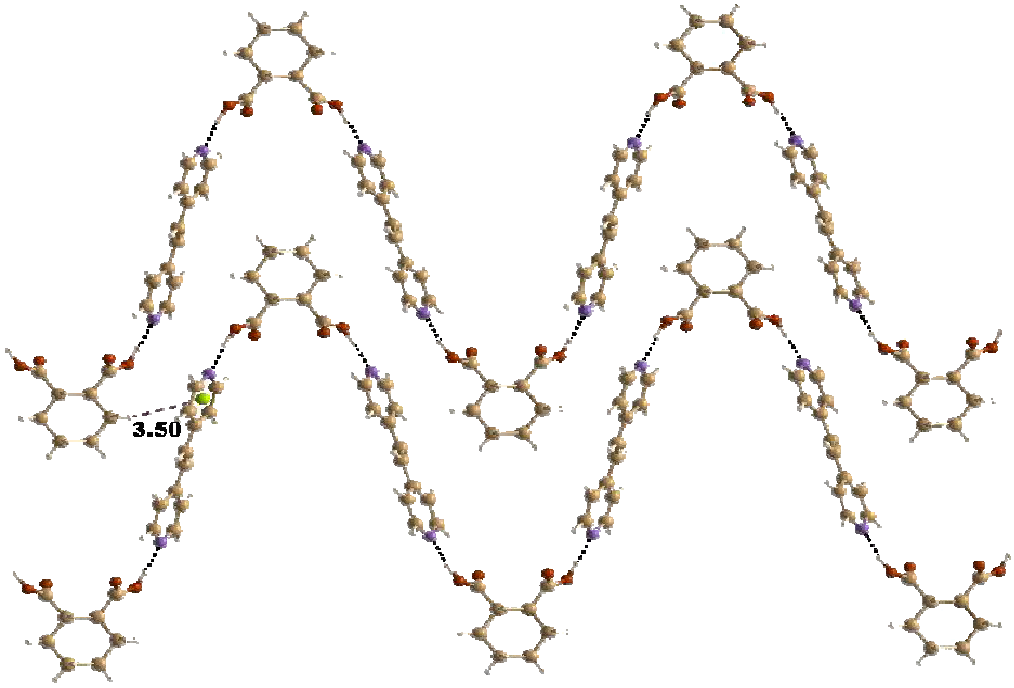


Figure 3.22 ORTEP of molecules in the complex **3a**.

Structural analysis of molecular complex **3a** reveals that acid **3** molecules are connected to aza-donor, **a**, via single O–H···N hydrogen bonding with an H···N distance of 1.70 Å. The recognition pattern extends infinitely, yielding a crinkled tape with the involvement of both equatorial -COOH groups engaged in O–H···N hydrogen bonding with the molecules of **a**. The arrangement is shown in Figure 3.23(a).



(a)



(b)

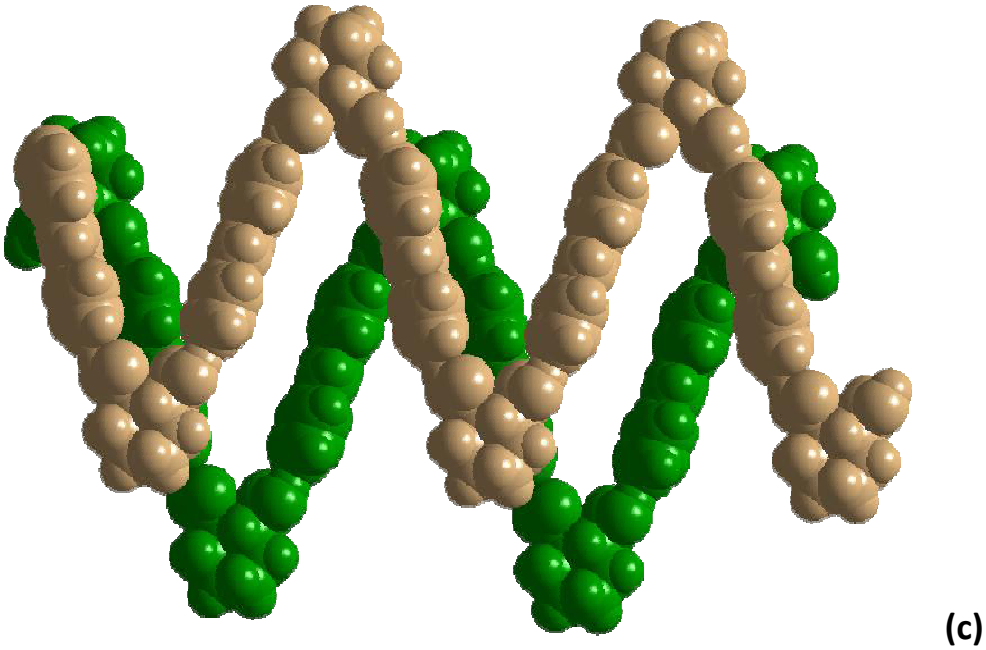


Figure 3.23 (a) Crinkled tape formed by the molecules of acid **3** and **a** in complex **3a**. (b) Arrangement of molecular tapes in the form of sheets through C–H···π interaction. (c) Stacking of corrugated sheets in crystal lattice.

The tapes are arranged within a two-dimensional network, in the form of sheets, through C–H···π interactions (3.50 Å) formed between the adjacent tapes, as represented in Figure 3.23(b). Ultimately the corrugated sheets are stacked in the crystal lattice in the three-dimensional arrangement, as depicted in Figure 3.23(c).

3.2.5 Molecular Complex of Acid 3 and 1,7-phenanthroline (d)

Cocrystallization of acid **3** and 1,7-phenanthroline (**d**) gave good quality single crystals that are suitable for X-ray diffraction studies. Analysis of, X-ray data, thus obtained, indicates formation of a molecular complex, in a 1:1 ratio of acid, **3** and the molecules of **d**, that crystallizes in a triclinic space group *Pī* (Table 3.1). The complex is labelled as **3d** for the purpose of further discussion. The asymmetric unit of the crystal lattice of **3d** is shown in Figure 3.24.

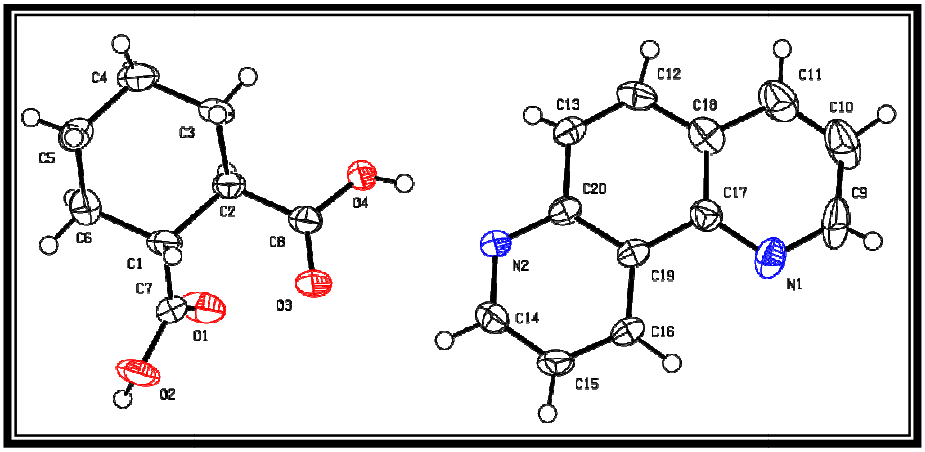
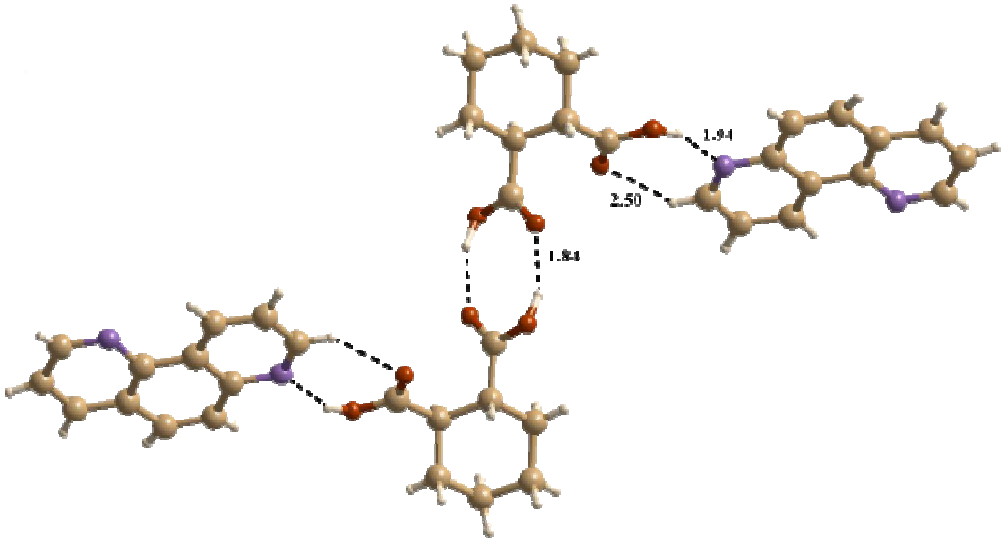
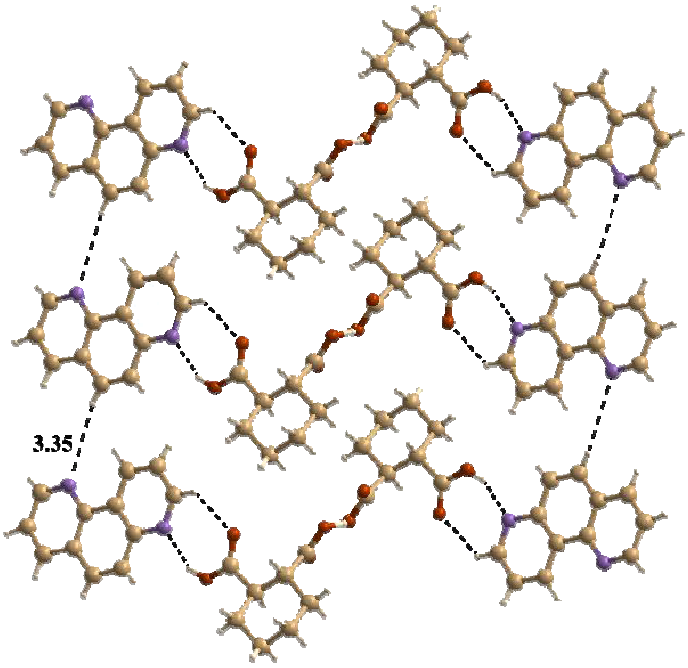


Figure 3.24 ORTEP of the contents of asymmetric unit in molecular complex **3d**.

Structure analysis of molecular complex **3d** shows some interesting features. In this complex, out of the two -COOH groups on each acid molecules, one of it is involved in the formation of a pair-wise hydrogen bonding pattern with the molecules of **d**, through O–H···N and C-H···O hydrogen bonds. The corresponding hydrogen bond distances are H···N, 1.94 Å and H···O, 2.50 Å. Such supermolecules are further held together by the second -COOH, at equatorial position, by a typical *homomeric* $R_2^2(8)$ pattern of -COOH through O-H...O hydrogen bonds with a H···O distance of 1.84 Å. Such an arrangement leads to the formation of molecular tapes, as shown in Figure 3.25(a). The tapes are further self-assembled in two-dimensional arrangement, in the form sheets, as presented in Figure 3.25(b), with the aid of C–H···N hydrogen bonds (H···N, 3.35 Å) formed between phenanthroline molecules.



(a)



(b)

Figure 3.25 (a) Basic recognition pattern between acid **3** and 17phen in complex **3d**. (b) C–H···N interactions between the tapes that aided the formation sheets in complex **3d**.

3.3 Conclusion

Co-crystals of *cis* and *trans* 1,2-cyclohexanedicarboxylic acids, **2** and **3**, respectively, with aza-donors *trans*-1,2-bis(4-pyridyl)ethene (**a**), 1,2-bis(4-pyridyl)ethane (**b**), 4,7-phenanthroline (**c**) and 1,7 phenanthroline (**d**) have been prepared and analyzed by single crystal X-ray diffraction methods. The obtained complexes, **2a**, **2a.nb**, **2b, 2c.H_2O**, **3a** and **3d** were illustrated for their structural

elegancy. It is pertinent to note that influence of solvent of crystallization is well reflected between **2a** and **2a.nb** with the formation of entirely different architectures. The emphasis of this chapter to understand the conformational influence did not give any appreciable variations as we noted similar geometry between **2a** and **3a**. Since analogous structures of **2b**, **2c** and **3d** with their counterparts could not be prepared, study of additional examples necessitates to deduce any conclusive remarks. Thus, the study is extended to analysis of co-crystals of 1,3-cyclohexanedicarboxylic acid as described in Chapter 4.

3.4. Experimental Section

3.4.1. Cocrystallization

All chemicals were obtained commercially and used without any further purification. The solvents employed for the crystallization experiments were of spectroscopic grade of highest available purity. Crystallization experiment were carried out, at room temperature, by dissolving the acid **2** or **3** as the case may be and the corresponding aza donor, in a 1:1 ratio, in MeOH or EtOH or nitrobenzene or the mixture of solvents (MeOH and EtOH in 1:1 ratio). In a typical crystallization process, in a 25mL Erlenmeyer flask 86 mg (0.5 mmol) of acid **2** and 91 mg (0.5 mmol) of the aza-donor **a** were dissolved in MeOH by heating to the boiling temperature of methanol. The reaction mixture was then allowed to cool to room temperature at ambient conditions. Colorless block type single crystals of good

quality of complex **2a** were obtained in 48 h, which were used for single crystal structure determination studies by X-ray diffraction method.

3.4.2. X-ray Crystallography

Good quality single crystals of all complexes were carefully selected after viewing through a Leica microscope supported by a rotatable polarizing stage and a CCD camera and glued to a glass fibre using an adhesive to mount on a goniometer of Bruker single crystal X-ray diffractometer equipped with APEX CCD detector. The data collection was smooth in all the cases, and no extraordinary methods have been employed, as the crystals were quite stable. The intensity data were processed using Bruker's suite of data processing programs (SAINT),[23] followed by absorption corrections using SADABS. The structure solution of all the complexes have been carried out by direct methods, and refinements were performed by fullmatrix least squares on F^2 using the SHELXTL-PLUS suite of programs. All the structures converged to good *R* factors. All the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms obtained from Fourier maps were refined isotropically. All the refinements were smooth in all the structures. All non-hydrogen atoms were refined anisotropically. All the intermolecular interactions were computed using PLATON.[24]

Table 3.1 Crystallographic data for molecular complexes **2a, 2a.nb, 2b, 2c.H_2O, 3a** and **3d**

	2a	**2a.nb**	**2b**
Formulae	(C_8 H_{12} O_4), 0.5($C_{12}H_{10}N_2$), 0.5($C_{12}H_{10}N_2$)	(C_8 H_{12} O_4), 0.5(C_{12} H_{10} N_2), (C_6 H_5 N O_2)	(C_8 H_{12} O_4), (C_{12} H_8 N_2)
Mol. wt.	354.40	386.40	352.38
Crystal shape	'block'	'block'	'needles'
Crystal color	colorless	colorless	colorless
Crystal System	'Triclinic'	'Triclinic'	'Triclinic'
Space Group	*P*$\bar{1}$	*P*$\bar{1}$	*P*$\bar{1}$
a/ Å	6.967(2)	7.202(3)	9.539(5)
b/ Å	7.027(2)	10.954(4)	9.732(5)
c/ Å	19.885(7)	13.103(5)	12.006(9)
α/^{0}	93.73(6)	80.51(7)	107.58(1)
β/^{0}	96.00(5)	77.50(6)	102.90(1)
γ/^{0}	112.12(5)	77.50(6)	110.05(8)
cell vol./ Å^3	891.1(5)	994.4(6)	929.3(1)
Z	2	2	2
D_{calc} (g cm^3)	1.321	1.291	1.259
***T*/^{0}K**	293(2)	293(2)	293(2)
Wavelength (Mo, Kα/ Å)	0.71073	0.71073	0.71073
μ/mm^{-1}	0.093	0.096	0.089
2θ range /^{0}	50.60	50.64	50.58
F(000)	376	408	372
Total reflect.	8786	9784	6881
No. unique reflns [*R*(int)]	3233 [0.1325]	3610 [0.0712]	3354[0.0226]
Non-zero reflect.	2623	2748	3048
No. parameters	332	337	331
GOF on *F*^{2}	1.071	1.284	1.881
***R*1 [*I*>2σ(*I*)]**	0.1090	0.1082	0.0779
wR2	0.2036	0.2221	0.2419

Table 3.1. Continued.....

	2c.H_2O	**3a**	**3d**
Formulae	(C_8 H_{12} O_4), (C_{12} H_8 N_2), H_2 O	**2(C_4 H_6 O_2), 2(C_6 H_5 N)**	**(C_8 H_{12} O_4), (C_{12} H_8 N_2)**
Mol. wt.	370.40	354.40	354.40
Crystal shape	'needles'	'block'	'block'
Crystal color	colorless	colorless	colorless
Crystal System	'Triclinic'	'Monoclinic'	Triclinic
Space Group	*Pī*	$C_{2/c}$	*Pī*
a/ Å	7.265(2)	12.418(2)	7.467(2)
b/ Å	10.464(3)	11.938(2)	7.884(2)
c/ Å	13.727(4)	12.614(2)	15.252(4)
α/^{0}	110.15(5)	90	83.62(5)
β/^{0}	101.14(5)	91.877(3)	88.84(5)
γ/^{0}	91.02(5)	90	73.63(5)
cell vol./ Å^3	957.2(5)	1869.0(6)	856.1(4)
Z	2	4	2
D_{calc} (g cm^3)	1.285	1.259	1.419
***T*/^{0}K**	293(2)	293(2)	293(2)
Wavelength (Mo, Kα/ Å)	0.71073	0.71073	0.71073
μ/mm^{-1}	0.093	0.088	0.128
2*ϑ* range /^{0}	50.76	50.56	50.00
F(000)	392	752	374
Total reflect.	9414	6699	8252
No. unique reflns [*R*(int)]	3492 [0.0814]	1705 [0.0209]	3009 [0.3493]
Non-zero reflect.	2364	1398	2286
No. parameters	332	162	307
GOF on F^2	1.114	1.063	1.506
***R*1 [*I*>2σ(*I*)]**	0.0796	0.0404	0.1259
wR2	0.1868	0.1106	0.2858

Table 3.2 Characteristic hydrogen bond distances (Å) and angles (º) of the **2a, 2a.nb, 1b, 2c.H_2O, 3a** and **3d**[#]

	2a			**2a.nb**			**1b**		
O-H···O				1.85	2.65	174			
O-H···N	1.99	2.67	140	1.93	2.72	174	1.56	2.62	161
	1.96	2.66	158				1.92	2.70	160
C-H···O	2.51	3.29	148	2.49	3.36	156	2.54	3.38	144
	2.56	3.38	148	2.49	3.18	131			

[#] Three columns for each structure represent H···A, D···A distances and D-H···A angle, respectively for a typical hydrogen bond, being represented as D-H···A

Table 3.2 continued…….

	2c.H_2O			**3a**			**3d**		
O-H···O	2.06	2.87	175				1.85	2.62	142
O-H···N	1.58	2.63	165	1.70	2.67	174	1.95	2.68	158
C-H···O	1.70	2.66	172	2.49	3.42	164.1	2.50	3.18	130
	1.71	2.78	173	2.56	3.31	130.8			
	2.36	3.14	135						

[#] Three columns for each structure represent H···A, D···A distances and D-H···A angle, respectively for a typical hydrogen bond, being represented as D-H···A

3.5. References:-

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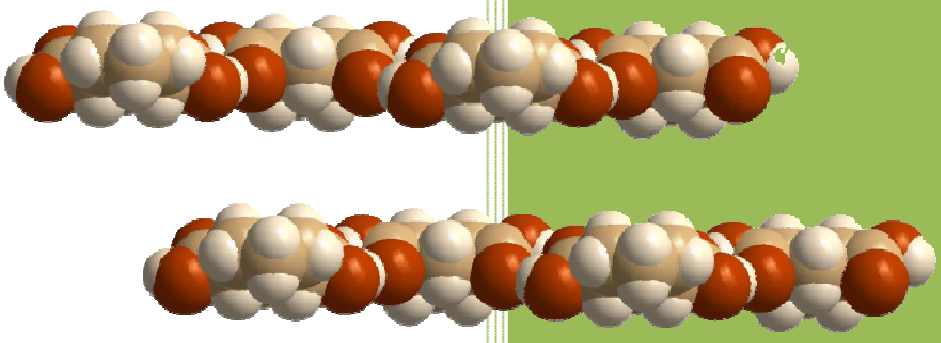
Chapter 4

Supramolecular assemblies of cis-1,3-cyclohexanedicarboxylic acid



Supramolecular assemblies of *cis*-1,3-cyclohexanedicarboxylic acid

4.1. Introduction

In the previous chapters, discussion about necessity of study of supramolecular assemblies formed by cyclohexane based carboxylic acids were emphasized as those assemblies were not well explored as compared to aromatic carboxylic acid in the realm of supramolecular chemistry.[1-15] The study is of special interest taken into account the conformational flexibility associated with the substituted cyclohexanes. In this process, a search performed on Cambridge Structural Database analysis,[16] indeed, reveals that only 19 structures of molecular complexes of 1,3-cyclohexanedicarboxylic acids, corresponding to both *cis* and *trans* forms, are known in the literature. Out of which 17 structures are based on metal-organic assemblies alone. It is interesting to note that except the native structures of the acids, no other only organic mediated assemblies are known in the literature.

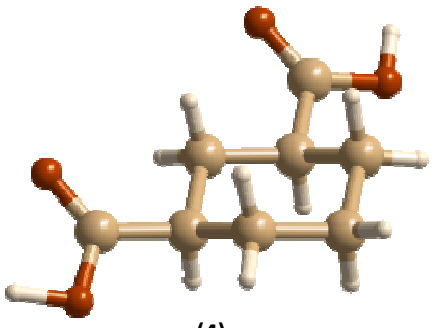
In the metal-organic assemblies of 1,3-cyclohexanedicarboxylic acids, it is noteworthy to mention that the organic ligands employed were 4,4'-bipyridine, 4,7-phenanthroline, etc. Since such ligands are also capable of yielding assemblies with -COOH moiety, preferentially, preparation of those co-crystals is apt for further enrichment of significance of substitution, conformation of functional moieties on the resultant supramolecular assemblies.

In this context, with the accomplished results compiled in Chapters 2 and 3 through *cis,cis,cis*-1,2,4,5-cyclohexanetetracarboxylic acid and the *cis* and *trans*

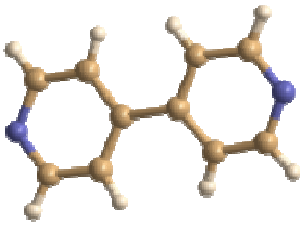
isomers of 1,2-cyclohexanedicarboxylic acids with various aza-donors, it was aimed to explore feasibility of construction of supramolecular architectures of 1,3-cyclohexanedicarboxylic acid.

For this purpose, cocrystallization experiments utilising *cis* and *trans*-1,3-cyclohexanedicarboxylic acids have been proposed with aza donors listed in Chart 1. However, *trans*-1,3-cyclohexanedicarboxylic acid failed to yield good quality single crystals unlike its counterpart *cis* form. Hence, the resultant obtained with cis-1,3-cyclohexanedicarboxylic acid co-crystals have been analyzed for their structural features as described in following section.

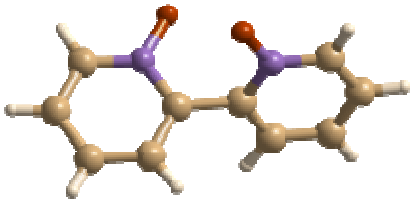
Chart I



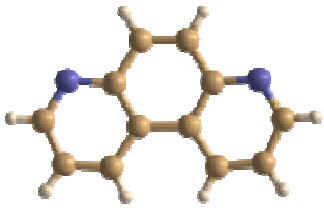
(4)
cis-1,3-cyclohexanedicarboxylic acid



(a)
4,4'-bipyridine



(b)
2,2'-bipyridine-*N,N'*-dioxide

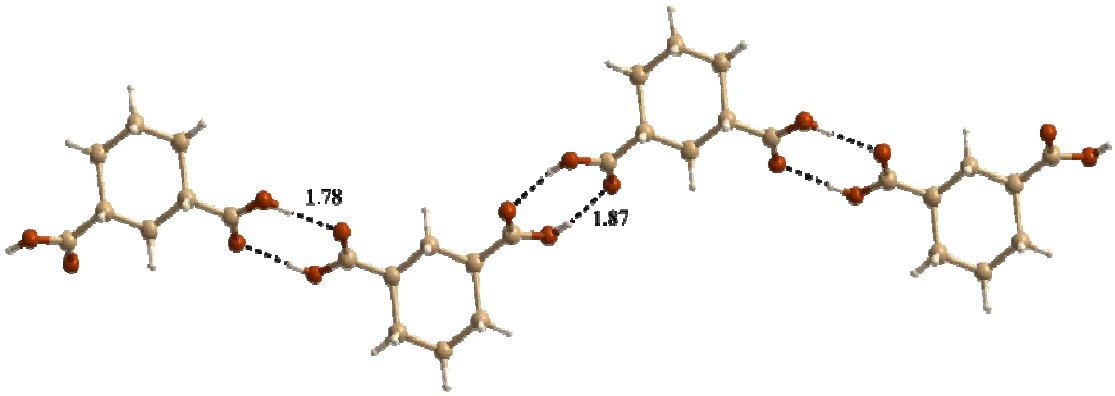


(c)
4,7-phenanthroline

Reactants	Solvent of crystallization	Molecular complexes	Composition
4+a	Ethanol + Methanol (1:1)	**4a**	1:1
4+b	Methanol	**4b**	1:1
4+c	Ethanol + Methanol (1:1)	**4c**	1:1

To begin with, understanding of native structures of the acids would be of a great value addition. However, structure of pure acids (both *cis* and *trans*), were already reported by Koningsveld.[17] Thus, to annotate the self-assembly and arrangement of molecules in the crystal lattices, the data has been retrieved from CSD.

It has been noted that in both *cis* and *trans* forms, the intermolecular interactions and the binding of adjacent molecules are very much the same with the formation of sheets, which are stabilized by staking along a crystallographic axis. A typical analysis done on *cis*-acid, **4**, in which different acid molecules are joined to each other by carboxylic acid dimeric interaction through O-H···O hydrogen bonds (H···O, 178 and 1.87 Å), leading to the formation of molecular tapes, as depicted in Figure 4.1(a). These tapes are held together by C-H···O interactions yielding sheets (Figure 4.1(b)) which stack in three-dimensional arrangement as shown in Figure 4.1(c).



(a)

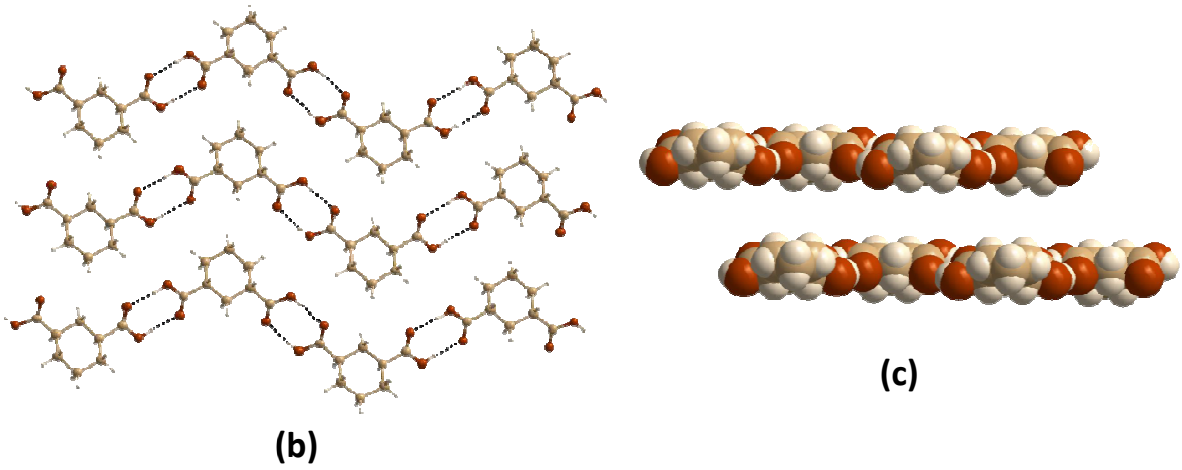


Figure 4.1 (a) 1D tapes formed through carboxylic acids in the form of dimers in the crystal structure of acid, **4**. (b) Formation of sheets by weak C-H···O interaction and (c) stacking of sheets in 3D.

4.2 Results and Discussion

Cocrystallization of acid, **4** with aza-donors, 4,4'-bipyridine (**a**), 2,2'-bipyridine-*N,N'*-dioxide (**b**) and 4,7-phenanthroline (**c**) in ethanol or methanol, or mixture of solvents (methanol and ethanol) gave good quality single crystals. Detailed experimental process of preparation of cocrystals, characterization of the crystals by X-ray diffraction methods are described in experimental section. Pertinent crystallographic data related to structure determination and refinement is listed in Table 4.1, while hydrogen bonds metrics are summarised in Table 4.2.

4.2.1 Molecular Adduct of Acid 4 and 4,4'-Bipyridine (a)

Good quality single crystals of molecular complex suitable for X-ray diffraction studies were obtained by cocrystallization of acid, **4** and 4,4'-bipyridine (a), in 1:1 ratio, from a solution of 1:1 mixture of ethanol and methanol. X-ray

diffraction data reveals that the crystals belong to orthorhombic space group *Pbcn*. Crystal structure determination identifies an asymmetric unit with the co-crystal formers in a 1:1 ratio. The contents of the asymmetric unit are shown in Figure 4.2. The complex is labelled as 4a.

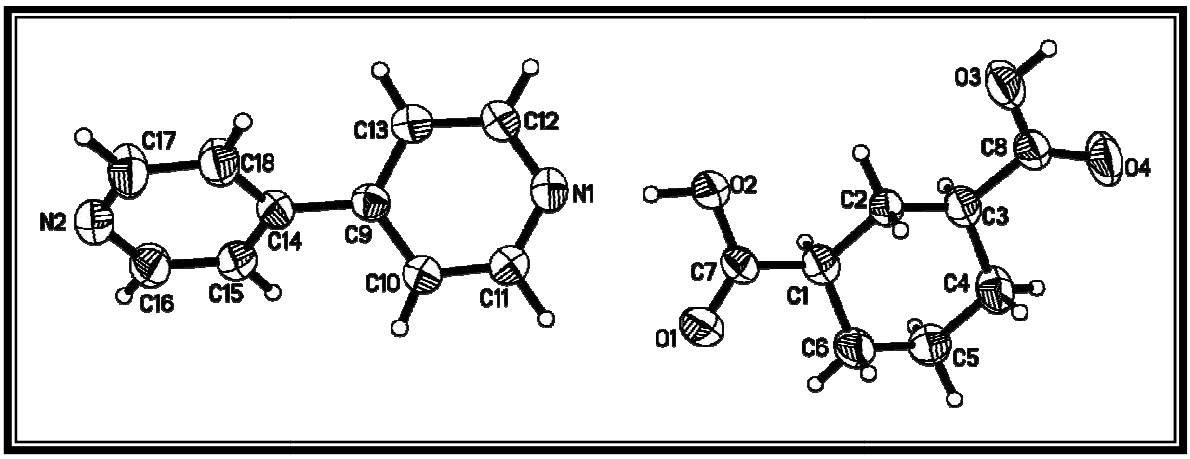


Figure 4.2. ORTEP of acid **4** and 4,4'-bipyridine in co-crystals, **4a**, at 50% probability level

In the crystal lattice of **4a**, both the equatorial carboxy groups of acid **4** are involved in O-H···N/C-H···O pairwise hydrogen bonding (H···N, 1.66 and H···O, 2.55 Å) with the molecules of the aza-donor, **a**. Such a recognition pattern between acid and molecules of **a** leads to the formation of 1D molecular chains, as represented in Figure 4.3.

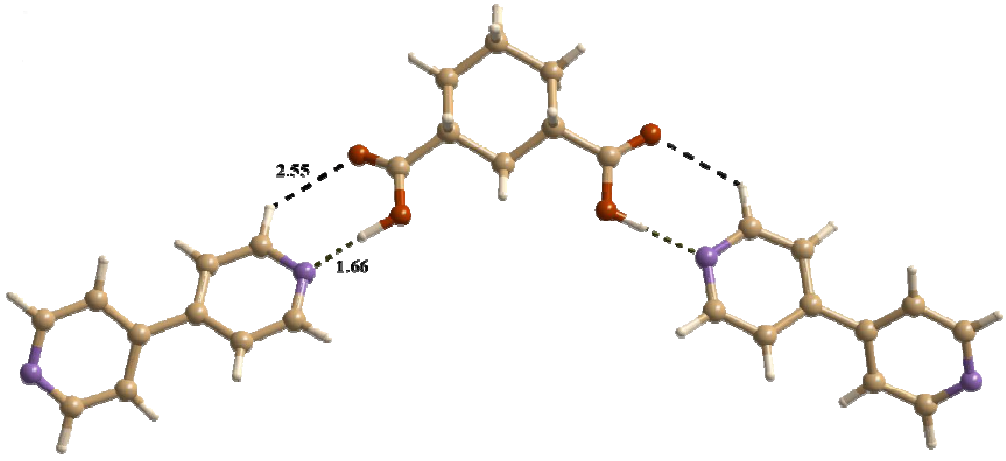
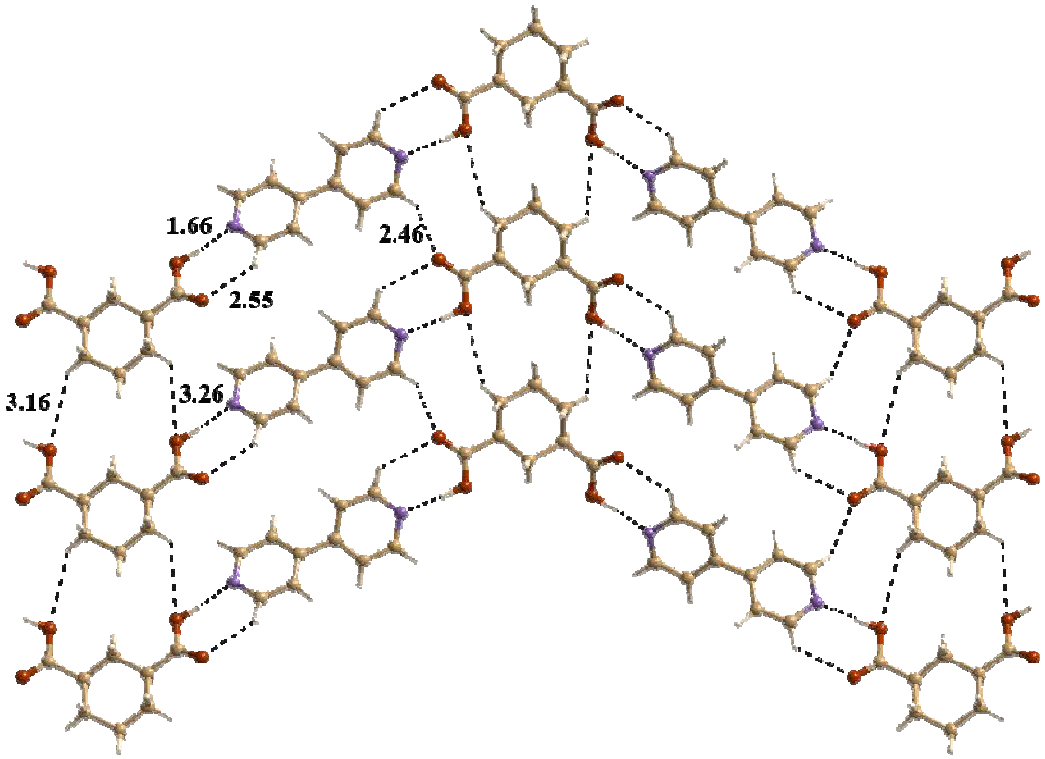


Figure 4.3. Basic recognition pattern between acid **4** and aza-donor molecules in complex **4a**

In further self-assembly, molecular chains are arranged within two-dimensional arrangement, with the adjacent chains being connected to each other via different C-H···O hydrogen bonds. A typical sheet structure is shown in Figure 4.4(a). Such sheets are stacked in the crystal lattice along a crystallographic axis by establishing C-H···O hydrogen bonds with H···O distances in the range 2.43 - 2.68 Å.



(a)

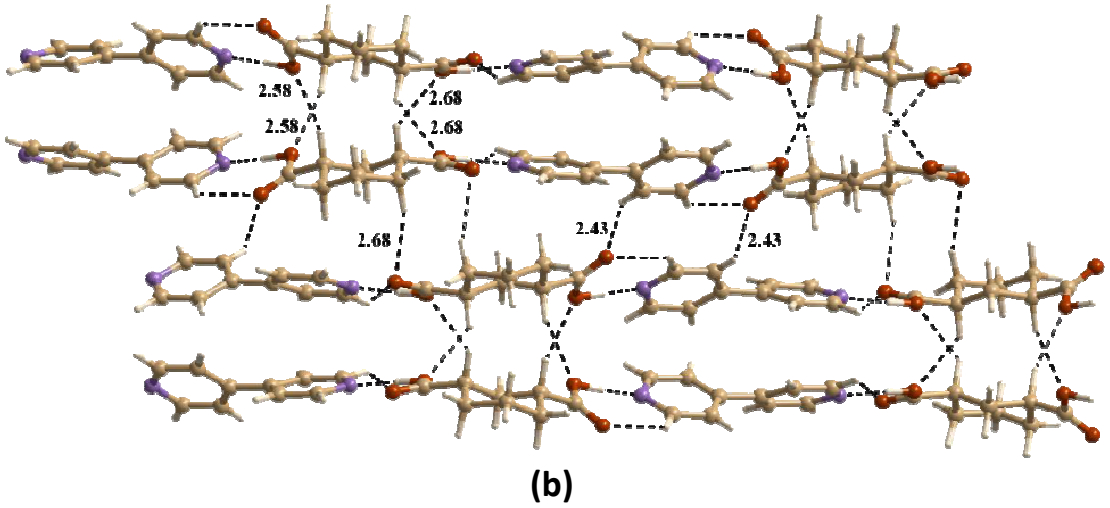


Figure 4.4 (a) Arrangement of molecules within a typical sheet in the crystal lattice of **4a**. (b) stacking of sheets in 3D stabilized by C-H···O hydrogen bonds.

Comparison of structural features of molecular complex **4a** with the native structure of acid **4**, projects that the O-H···O hydrogen bonding pattern between the acid molecules observed in the acid **4** are being replaced by O-H···N/C-H···O pairwise hydrogen bonding and retains all other topological features intact in two and three-dimensional packing.

4.2.2 Molecular Complex of Acid, 4 and 2,2'-Bipyridine-*N,N'*-dioxide (b)

Cocrystallization of acid **4** with 2,2'-bipyridine-N,N'-dioxide (**b**) from a solution of 1:1 mixture of ethanol and methanol gave good quality single crystals. X-ray data analysis confirms the formation of complex with acid **4** and molecules of **b** in a 2:1 ratio, that crystallizes in monoclinic *C2/c* space group. The contents of the asymmetric unit are shown in Figure 4.5.

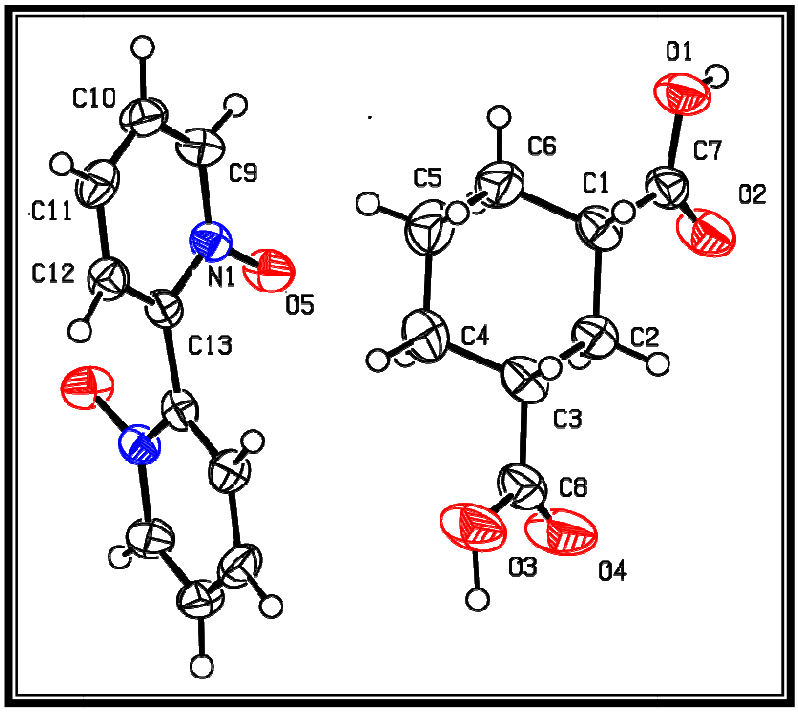


Figure 4.5 ORTEP drawing of acid **4** and aza-donor **b**, at 50% probability level

Packing analysis in terms of intermolecular interactions reveals that, in contrast to the observations made in cocrystals of **4a**, only one of two -COOH groups on acid **4** did establish interaction with the molecules of **b** through a cyclic hydrogen bonding pattern of O-H···O and C-H···O. The corresponding H···O distances in the pattern are 1.80 and 2.30 Å. The second carboxyl acid group at equatorial position on acid **4** is engaged in the formation of carboxylic acid dimeric interaction $R_2^2(8)$ with adjacent acid molecule through O-H···O hydrogen bonds (H···O, 1.63 Å).

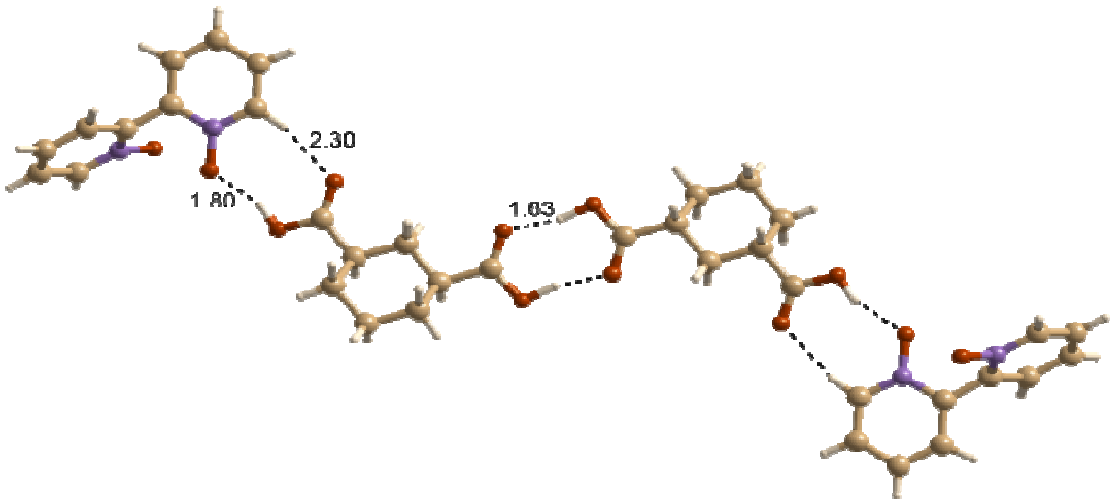
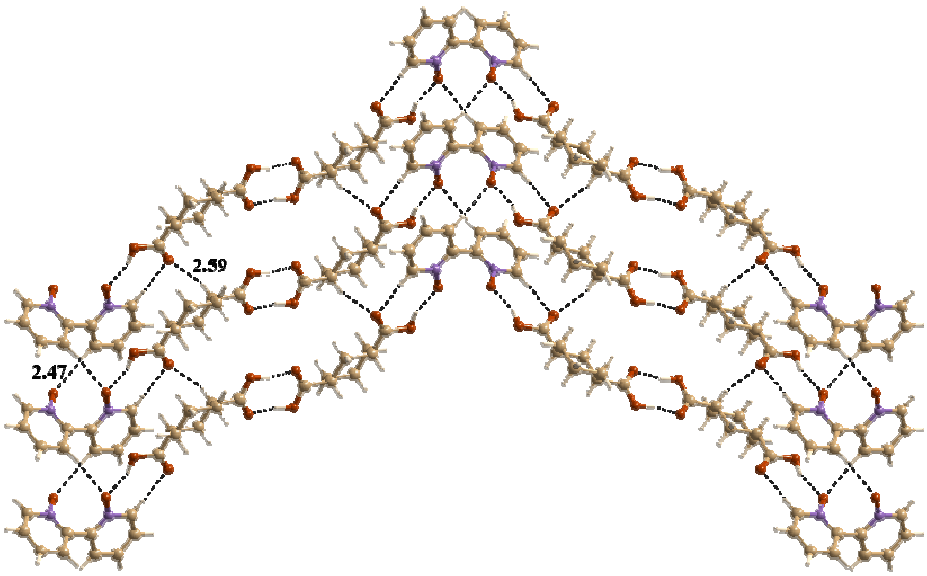
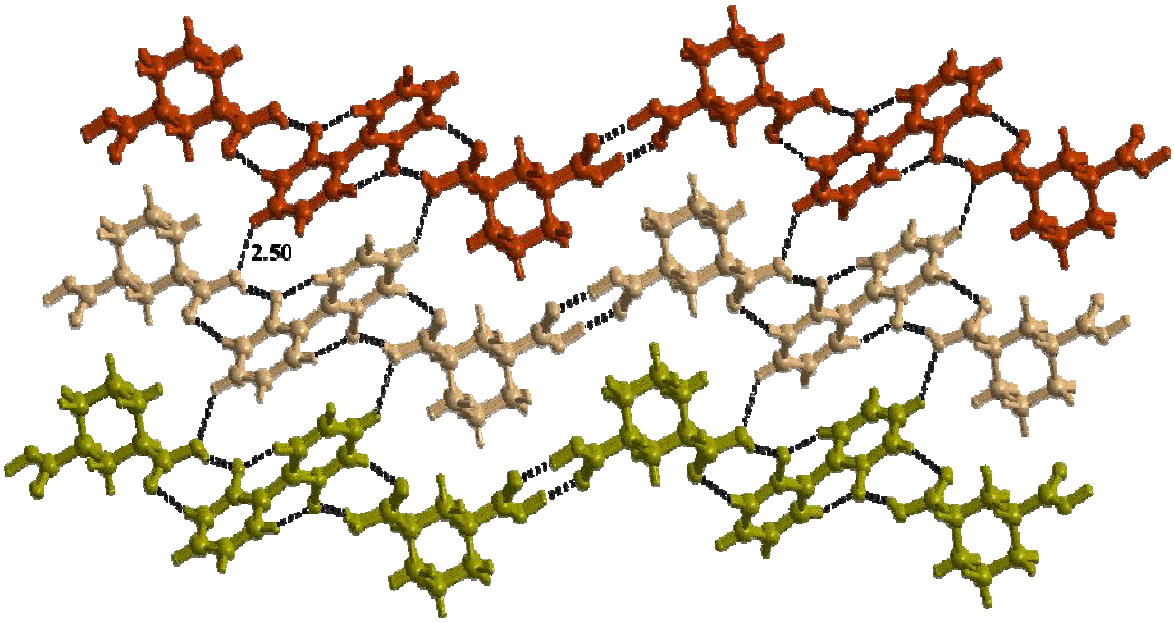


Figure 4.6 Molecular tape formed by acid **4** and molecules of **b** in complex **4b**

Thus, such ensembles constitute molecular tapes as shown in Figure 4.6. In two-dimensional pattern, the tapes are arranged in the form of sheets with the formation of C-H···O hydrogen bonds (H···O, 2.47 and 2.59 Å), as shown in Figure 4.7(a). Such sheets are ultimately stack in three-dimensional arrangement of molecules in the crystal lattice, by C-H···O hydrogen bonds with corresponding H···O distance of 2.50 Å (see Figure 4.7(b)).



(a)



(b)

Figure 4.7 (a) Sheets formed through C-H···O interactions between adjacent molecular tapes in the crystal structure of **4b**. (b) 3D architecture formed by stacking of sheets

4.2.3 Molecular Complex of Acid, 4 and 4,7-phenanthroline (c)

Colourless plate-like crystals were obtained by slow-evaporation of the solution (1:1 mixture of ethanol and methanol) of acid **4** and 4,7-phenanthroline (**c**). Analysis of the crystals by X-ray diffraction method reveals an asymmetric unit with the co-crystal formers in a 1:1 ratio but with four symmetry independent molecules of each acid **4** and the aza-donor. The complex is labelled as **4c** for the purpose of discussion. The contents of the asymmetric unit are shown in Figure 4.8 in the form of ORTEP.

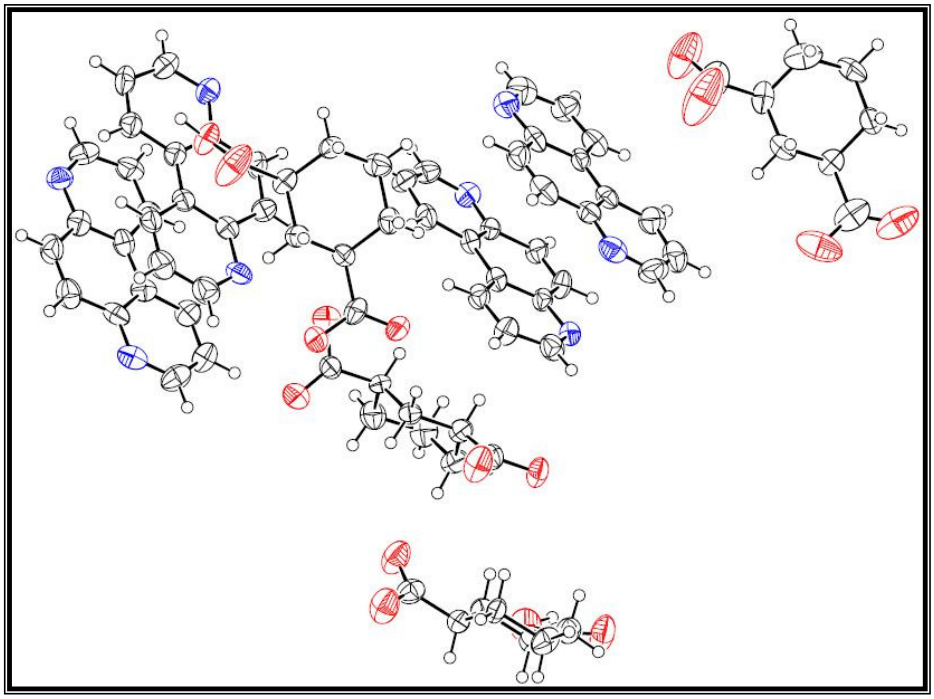


Figure 4.8 ORTEP of co-crystal formers in the asymmetric unit observed in the crystals of **4c**.

Packing analysis reveals that in the crystal lattice of **4c**, the co-crystal formers established interaction as observed in **4a**, but through a single hydrogen bond rather than pair-wise hydrogen bonding pattern, by both the -COOH groups with the aza-donor molecules. The observed O-H···N hydrogen bond is found to be with a distance of H···N, 1.72 Å, as shown in Figure 4.9(a). Because of the flexible conformation of methylene groups in the molecules of c, the ensembles gave an helical arrangement. A typical helix is represented in Figure 4.9(b) and aggregation of adjacent helices is represented in Figure 4.9(c).

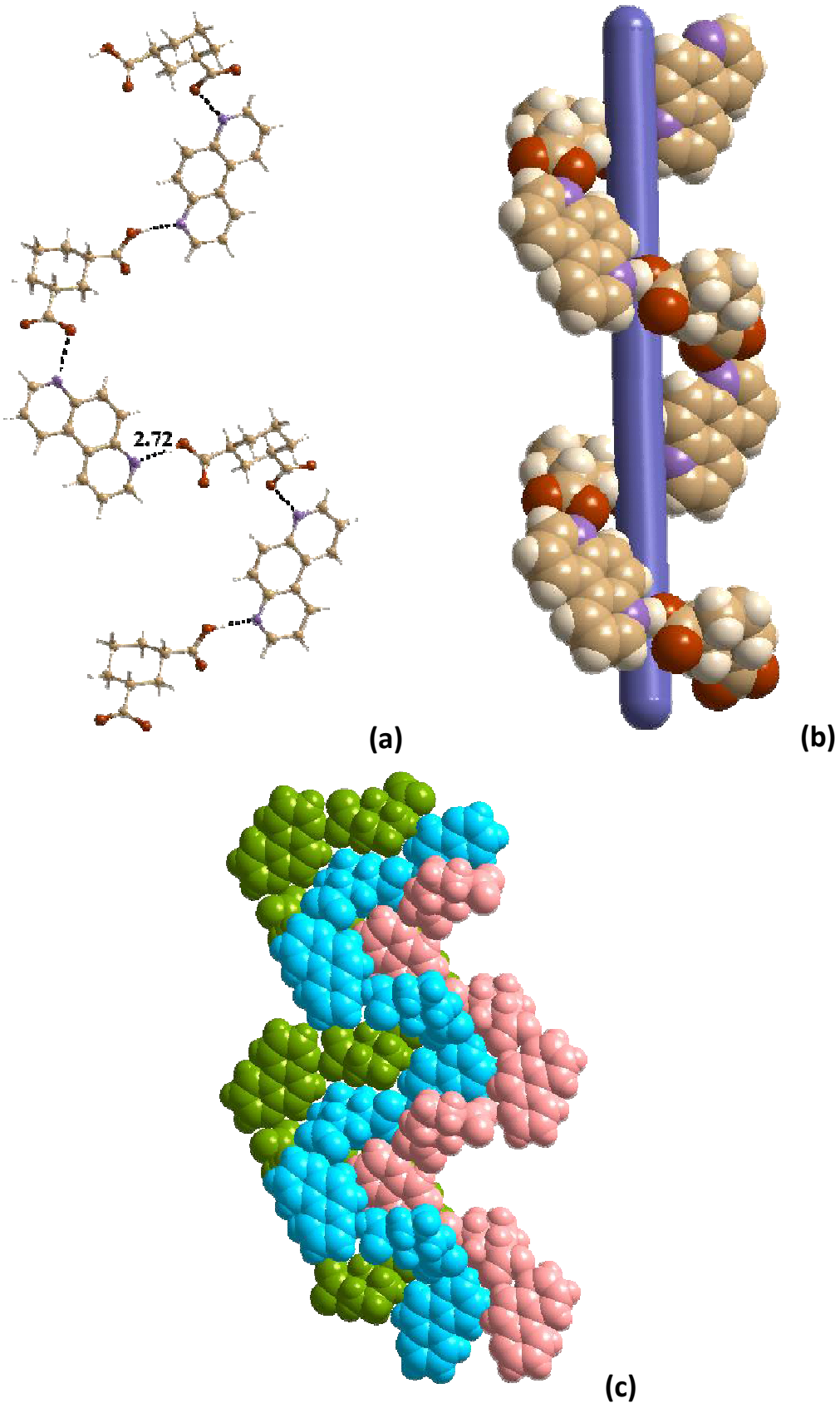


Figure 4.9 Structural features of molecular complex **4c**. (a) 1D helix formed by acid **4** and 47phen. (b) Space filling model of the helix (c) Arrangement of helices in three-dimension.

4.3 Conclusion

In conclusion, molecular complexes of *cis*-1,3-cyclohexanedicarboxylic acid, **4** with different cocrystal formers 4,4'-bipyridine (**a**), 2,2'-bipyridine-*N,N'*-dioxide (**b**) and 4,7-phenanthroline (**c**) have been reported. In all the complexes **4a - 4c**, the aza-donor molecules are inserted between the adjacent acid molecules through different types of hydrogen bonds. However, within the structure of **4b**, one of the acid molecules did not establish interaction with the corresponding aza-donor but interacts with -COOH group on the adjacent acid molecule. The topology in two and three-dimensional arrangement is found to be varied, mostly due to the conformation of the aza-donor molecules as we noted prominently in **4c** with the formation of helical structure.

4.4 Experimental Sections

4.4.1 Synthesis

All chemicals, reagents and solvents were obtained from commercial suppliers and used without further purification. Spectroscopic-grade solvents were used in all co-crystallization studies. All co-crystals, **4a**, **4b** and **4c** were prepared by dissolving the corresponding reactants, in a ratio of 1:1, in methanol or 1:1 mixture of methanol and ethanol and allowing the solvent to evaporate under ambient conditions. In all the cases, single crystals, suitable for X-ray diffraction analysis, were obtained over the period of 72 h.

4.4.2 General procedure for the synthesis of complexes, 4a, 4b and 4c

All co-crystals were prepared by slow-evaporation of respective solutions at ambient laboratory conditions. In a typical preparation, in a 25 mL conical flask, 86 mg (0.5 mmol) of acid **2** and 90 mg (0.5 mmol) of 2,2'-bipyridine-*N,N'*-dioxide were dissolved in MeOH by gentle warming on a water bath. The resultant solution was evaporated under ambient conditions without much external mechanical disturbances. Good quality colourless crystals of **4b** were obtained within 48 h, that were suitable for single-crystal X-ray diffraction studies.

4.4.3 Crystal structures determination

Good quality single crystals of **4a**, **4b** and **4c** were carefully selected with the aid of a polarized Leica microscope equipped with CCD camera, and glued to a glass fiber using an adhesive (cyanoacrylate). In all the cases, the crystals were smeared in the adhesive solution to prevent decay of crystals upon exposure to X-rays. The intensity data were collected on a Bruker single crystal X-ray diffractometer, equipped with an APEX detector, at temperature varying from 100-298 K. Subsequently, the data were processed using Bruker suite of programmes (SAINT)[18] and the convergence was found to be satisfactory with good R_{int} parameters. The details of the data collection and crystallographic information are given in Table 4.1. The structure determination by direct methods and refinements by least-squares methods on F^2 were performed using SHELXTL-PLUS package. The processes were smooth without any complications. All non-hydrogen atoms were refined anisotropically. All the intermolecular interactions were computed using PLATON.[19]

Table 4.1 Crystallographic data for molecular complexes **4a**, **4b** and **4c**.

	4a	**4b**	**4c**
Formulae	(C_8 H_{12} O_4), ($C_{10}H_8N_2$)	2(C_8 H_{12} O_4), (C_{10} H_8 N_2O_2)	2(C8 H11 O4), 2(C8 H10 O4), 4(C12 H8 N2)
Mol. wt.	328.36	532.54	701.74
Crystal shape	'block'	'block'	' block '
Crystal color	colorless	colorless	colorless
Crystal System	'Orthorhombic'	'Monoclinic'	' Orthorhombic '
Space Group	*Pbcn*	*C2/c*	$P2_12_12_1$
a/ Å	14.835(3)	12.565(2)	14.145(5)
b/ Å	6.940(1)	5.3616(1)	19.972(7)
c/ Å	32.399(7)	38.402(7)	24.453(9)
α/^{0}	90	90	90
β/^{0}	90	94.21(3)	90
γ/^{0}	90	90	90
cell vol./ Å^3	3335.6(1)	2580.2(8)	6908(4)
Z	8	4	8
D_{calc} (g cm^3)	1.308	1.371	1.349
***T*/^{0}K**	293(2)	293(2)	293(2)
Wavelength (Mo, Kα/ Å)	0.71073	0.71073	0.71073
μ/mm^{-1}	0.093	0.106	0.095
2θ range /^{0}	50.04	49.96	50.14
F(000)	1392	1128	2952
Total reflect.	15626	8719	28719
No. unique reflns [*R*(int)]	2958 [0.0658]	2274 [0.0450]	12204 [0.1072]
Non-zero reflect.	1867	2748	5496
No. parameters	297	1730	945
GOF on F^2	1.122	1.240	0.996
***R*1 [*I*>2σ(*I*)]**	0.0679	0.0708	0.0887
wR2	0.1319	0.1546	0.1215

Table 4.2 Characteristic hydrogen bond distances (Å) and angles (^{0}) of the supramolecular assemblies **4a, 4b** and **4c**[#].

	4a			**4b**			**4c**		
O-H···O				1.80	2.63	158			
				1.63	2.65	168			
O-H···N	1.66	2.70	175				1.50	2.69	164
	1.75	2.69	177				1.73	2.70	161
C-H···O	2.55	3.65	161	2.59	3.43	153	2.53	3.43	155
	2.63	3.29	131	2.30	3.24	165	2.55	3.24	131
	2.43	3.21	144	2.50	3.28	135	2.39	3.27	156
	2.58	3.29	125	2.47	3.40	160	2.55	3.21	129
	2.46	3.24	134				2.54	3.20	128
							2.47	3.15	130

[#] Three columns for each structure represent H···A, D···A distances and D-H···A angle, respectively for a typical hydrogen bond, being represented as D-H···A.

4.5 References

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List of Publications

1. Manish D. Raut and Venkateswara Rao Pedireddi

   Supramolecular Assemblies of 1,2,4,5-Cyclohexanetetracarboxylic Acid: From Tapes to Ladders to Host-guest Complexes.

   (Manuscript under preparation)

2. Manish D. Raut and Venkateswara Rao Pedireddi

   Molecular Complexes of 1,2-Cyclohexanedicarboxylic Acids with Various Aza-donors.

   (Manuscript under preparation)

3. Manish D. Raut and Venkateswara Rao Pedireddi

   Solid-State Structures of Hydrate of *cis,cis,cis*-1,2,4,5-Cyclohexanetetracarboxylic Acid.

   (Manuscript under preparation)

4. Manish D. Raut and Venkateswara Rao Pedireddi

   Supramolecular Assemblies of 1,3-Cyclohexanedicarboxylic Acids.

   (Manuscript under preparation)

Workshops/Seminars/Symposia

National

- Coursework attended as a part of Ph. D. Program. National Chemical Laboratory, Pune, INDIA.
- *38th National Seminar on Crystallography, 11-13 February 2009,* University of Mysore, Mysore, INDIA.
- *National Workshop on Theory and practice of X-Ray Diffraction Techniques,* TPXRDT-2009, *13-17 July 2009,* School of Physics, Alagappa University, Karaikudi, INDIA.
- *4th J-NOST Conference, 6-9 December 2009,* Madurai Kamaraj University, Madurai, INDIA.
- *National Workshop on "X-ray techniques for material Research" 4-6 December 2009,* IIT, Bombay organized by Panalytical, India and IIT, Bombay.

International

- **AsCA10** *"Tenth Conference of the Asian Crystallographic Association"* 31 Oct-3 Nov 2010, BEXCO, Busan, South Korea.

Awards and Fellowships

- *Junior Research Fellowship*, **CSIR-NET-JRF**, *December 2006,* Council of Scientific and Industrial Research, New Delhi. INDIA.
- *Senior Research Fellowship,* **SRF**, *August 2009,* Council of Scientific and Industrial Research, New Delhi. INDIA.
- **Travel Support Prize** for attending *"Tenth Conference of the Asian Crystallographic Association"* (**AsCA2010**) held at BEXCO, Busan, South Korea.
- **Best Poster Award** at *"Tenth Conference of the Asian Crystallographic Association"* (**AsCA2010**) held at BEXCO, Busan, South Korea.