DESIGN OF ORGANIC SOLIDS BASED ON SUPRAMOLECULAR HYDROGEN-BONDED ASSEMBLIES

A PROJECT REPORT SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENT OF THE DEGREE OF MASTER OF SCIENCE AS PART OF INTEGRATED Ph. D. PROGRAMME

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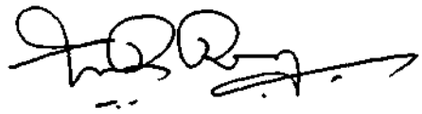
STATEMENT

Certified that the work here has been done under my supervision at Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore.



Professor C.N.R.Rao

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Summary

A variety of supramolecular assemblies involving O-H...O, N-H...O, O-H...N, N-H...N and other hydrogen bonds are known. In the present study, we have carried out co-crystallization experiments between different donor and acceptor molecules to obtain supramolecular assemblies consisting of two-dimensional layered networks, cavities, three-dimensional channels, and related structures.

We have studied the layered hydrogen-bonded structures formed by aliphatic dicarboxylic acids and dinitrobenzoic acids with azaaromatics. The hydrogen-bonded molecular complexes of malonic, glutaric and adipic acids with 2,4,6-triaminopyrimidine show crossed ribbon networks in the case of malonic and glutaric acids and a two-dimensional network in the case of adipic acid. 3,5-dinitrobenzoic acid and 3,5-dinitro-4-methylbenzoic acid form layered structures with 4,4'-bipyridyl.

Co-crystallization of cyanuric acid and 4,4'-bipyridyl gave two

* Papers based on some of the work described here have appeared in Tetrahedron (1998), J.Am.Chem.Soc. (1997, 1999).

different types of molecular complexes on varying the solvent of crystallization. A 2:1 adduct was formed from methanol and a 1:1 adduct from water. Such a difference is attributed to the difference in the hydrogen-bonded networks formed within the crystal structures of cyanuric acid upon crystallization from methanol and water. N-methylcyanuric acid, when crystallized from methanol or water forms two different chain structures but consist of only one type of hydrogen-bonded network with single hydrogen bonds. The presence of the methyl group does not favour cyclic hydrogen-bonded dimers. However, co-crystallization of N-methylcyanuric acid with 4,4'-bipyridyl forms the same structure irrespective of the solvent of crystallization.

We have examined the supramolecular assemblies obtained from crystallization of trithiocyanuric acid and a donor molecule like 4,4'-bipyridyl along with a variety of aromatic guest molecules. All the complexes form channel structures. Thermogravimetric analyses have been performed on all the complexes of trithiocyanuric acid and 4,4'-bipyridyl with the aromatic guest molecules to study the nature of the channels in the absence of the guest molecules.

We have prepared 1:1 co-crystals of cyanuric acid and melamine (also trithiocyanuric acid and melamine) by hydrothermal synthesis. A rosette structure giving rise to channels was obtained in both the cases. In order to extend the study of novel channel structures, we have

investigated the channel structures formed by self-assembled four-membered networks of trimesic acid.

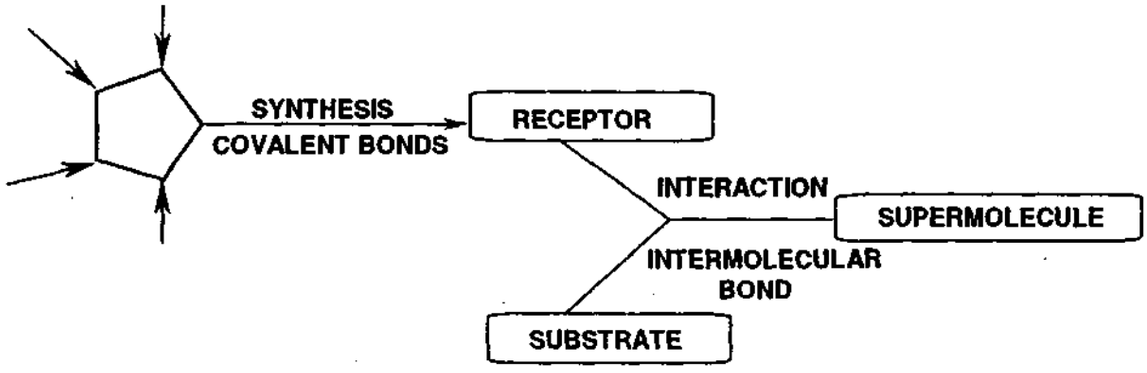
Crystallization of trimesic acid from DMF/benzene yields a crystal structure comprising of two-dimensional molecular tapes formed between trimesic acid and DMF through hydrogen bonds. Crystallization of trimesic acid from methanol/benzene gives four-membered networks (rather than the hexagonal network) with a polymeric chain of methanol molecules with O-H...O hydrogen bonds, present inside the channels. Crystallization of trimesic acid from acetone yields a structure identical to the one obtained from methanol/benzene, with the acetone molecules residing in the channels.

DESIGN OF ORGANIC SOLIDS BASED ON SUPRAMOLECULAR HYDROGEN-BONDED ASSEMBLIES

1. Introduction

In organic chemistry, the term *synthesis* implies the construction of molecular systems using covalent bonds. However, chemists have explored recently another type of bond, the hydrogen bond, referred to as the noncovalent bond to synthesize a variety of novel molecular assemblies which are often either difficult to synthesize through covalent synthesis or economically not viable. Hydrogen bonds are one of the many noncovalent bonds quite popular in the synthesis of supramolecular assemblies.[1] These bonds bring molecules together to form aggregates. The properties of these noncovalent bonds are comparable to the covalent bonds both in energy and directional aspects. Construction of molecular assemblies employing noncovalent bonds has been referred to as non-covalent synthesis by Lehn[2,3] and Whitesides.[4] This new methodology, noncovalent synthesis, has indeed started to bridge the gap between molecular and macromolecular structures. In recent years, various multimolecular assemblies have been synthesized employing the noncovalent bonds, which has led to the birth of a highly interdisciplinary field of chemical research, i.e., ***supramolecular chemistry***.[1-3] Supramolecular chemistry was defined in the words of Lehn[3] "Just as there is a field of *molecular chemistry* based on the covalent bond, there is a field of *supramolecular chemistry*, the chemistry of molecular

assemblies and of the intermolecular bond." The Scheme 1.1 depicts this. Supramolecular science deals with the chemical, physical and the biological features of the species of greater complexity than molecules themselves, that are held together and organized by means of intermolecular binding interactions.



Scheme 1.1: From molecular to supramolecular chemistry: molecules and supermolecules

There are two facets of modern-day chemical synthesis which are influenced by supramolecular chemistry. They are (1) The creation of multicomponent supramolecular architectures using noncovalent bonding interactions, that is, *supramolecular noncovalent synthesis*[5] and (2) the synthesis of discrete molecular entities - held together using wholly covalent and mechanical bonds - aided and abetted by noncovalent, intermolecular interactions, i.e., *supramolecular assistance to molecular synthesis. Self-assembly*, the spontaneous generation of well-defined supramolecular architectures from engineered building blocks is the impetus for the development of both the aspects of synthetic supramolecular chemistry (1) and (2) mentioned above.

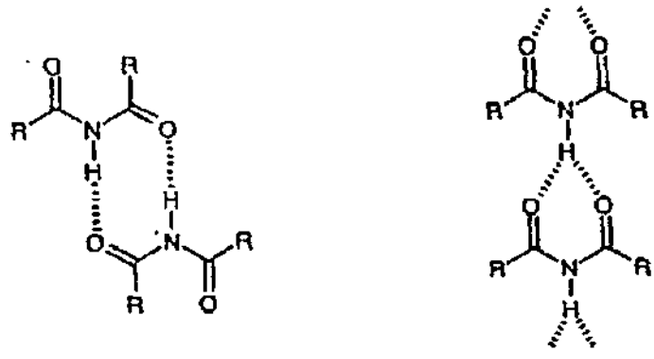
The resemblance of noncovalent synthesis to classical organic chemistry is so well marked as various methodological strategies are being used, taking into account the geometric and energetic properties of various types of intermolecular interactions, to construct supramolecular assemblies just as molecular chemists employ a variety of synthetic methods to combine atoms into molecules. Thus, predicting solid-state structure and controlling the intermolecular forces that determine molecular packing patterns in crystals attracted various researchers to synthesize novel supramolecular assemblies. In this regard, the design of hexagonal rosette structures by Whitesides is a stunning example.[6]

Among the numerous noncovalent bonds, hydrogen bonds have been widely used as the nature of these bonds is well understood both theoretically and experimentally than other bonds. Hydrogen bonds are formed when a donor with an available acidic hydrogen atom is brought into intimate contact (i.e., a separation less than the sum of the appropriate van der Waals radii) with an acceptor carrying available nonbonding lone pairs of electrons. Hydrogen bonds are moderately strong (1-5 kcal mol^{-1}) with directional nature. They are feeble compared with the familiar covalent bonds that bind atoms to each other in molecules, or the ionic bonds that exist in salts and minerals.

A few examples are available in the literature using non-hydrogen bonds also in the design and synthesis of supramolecular assemblies. The non-hydrogen bonds are mainly Cl...O, Br...O, I...O, I...I, O...I, N...Cl and so on. A 1:1 supramolecular assembly between 3,5-dinitrobenzoic acid and

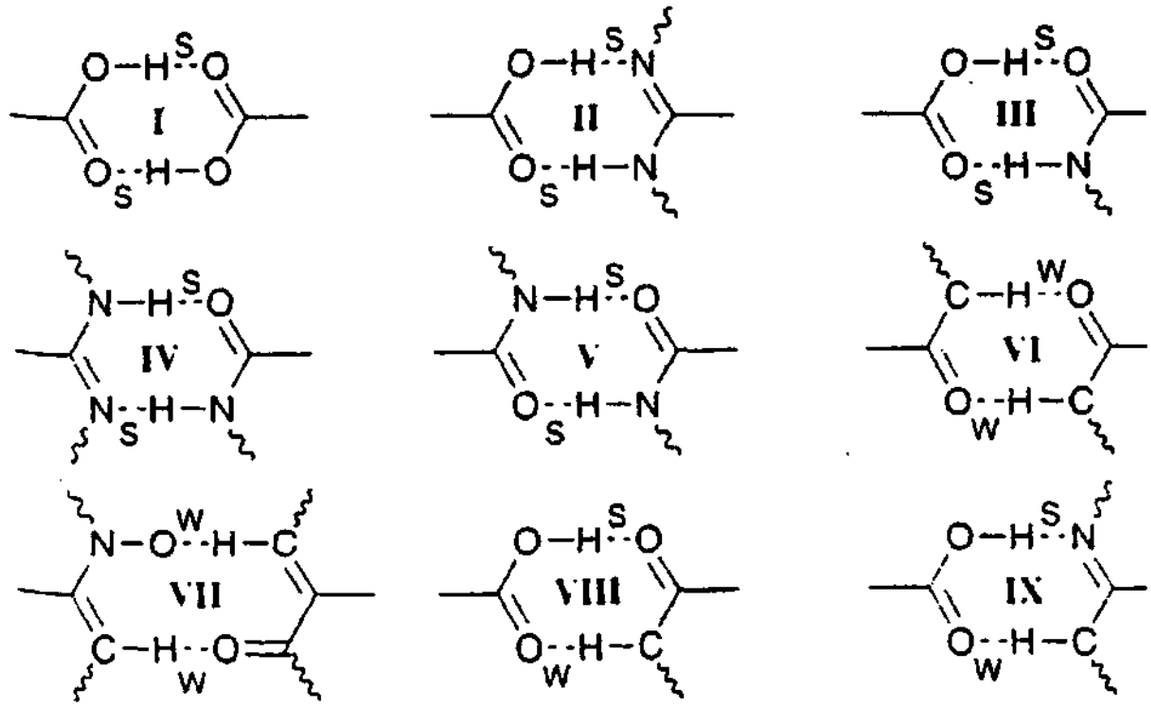
1,4-diiodobenzene formed through I...O interactions is a representative example.[7]

In the early attempts of systematic study of application of hydrogen bonds to noncovalent synthesis, Etter[8] proposed a set of rules that describe the selectivity of different functional groups in forming hydrogen bonds. A representative case for amide group is shown in Scheme 1.2.



Scheme 1.2

Various forms of hydrogen-bonded networks were represented as *motifs* and formulated graph set theory to represent the motifs in a much simpler fashion. For instance, motifs formed by –COOH group and of motifs similar in nature as shown in Scheme 1.3 were assigned a notation, $R^2(8)$ wherein, superscript and subscript numbers represent number of acceptor and donor atoms and the number within the parenthesis denoting the number of bonds in the motif. However, such a representation fails to distinguish the chemical differences among the motifs with identical notation.



Scheme 1.3: Some of the cyclic motifs involving hydrogen bonds

Several researchers later on attempted to postulate a new definition for the motifs to elaborate their chemical and other features. Although, no definite mechanism has evolved out, different nomenclature came into existence such as couplings, synthons based on the topology and dimensionality of the hydrogen bonds.[5,9] In such a work, it has also been notified that weak hydrogen bonds with nonconventional donors and acceptors also play a crucial role in the construction of many supramolecular assemblies. The use of C-H...O[10] hydrogen bonds are one of such weak hydrogen bonds quite often employed in crystal structure design but have still not been explored to the full extent.

Synthetic strategies

The highly selective and directional nature of the hydrogen bond makes it ideal for use in the construction and stabilization of large noncovalently linked molecular and supramolecular architectures. Recent developments in the understanding of the nature of the hydrogen bond resulted in the development of a variety of new synthetic strategies for the preparation of supramolecular assemblies. This strategy is based on molecular self-assembly, a phenomenon in which the individual subunits are quickly driven together and held in place by multiple, accurately positioned hydrogen bonds.

The great versatility and power of these bonds is illustrated by the recent elegant investigation of nanoporous molecular sandwiches by Ward *et al.*[11] the synthesis of self-organized nanostructures by Stupp and coworkers,[12] the rosette aggregate,[6] two- and three-dimensional self-assembly of mesoscale objects by Whitesides and coworkers,[13] and three-dimensional tennis-ball-like capsules of Rebek,[14] the ordered hydrogen-bonded arrays of Hamilton,[15] the dipyridine-based aggregates of Wuest,[16] and many others. A few representative examples are discussed in the following paragraphs.

The crystal structure of aminopyrimidine shows that all donors and acceptors are used in forming continuous chains of hydrogen bonds[17] (Figure 1.1). However the addition of either carboxylic acids or dicarboxylic acids can produce four distinct structural motifs, depending on the nature of the added dicarboxylic acid as shown in Figure 1.1.

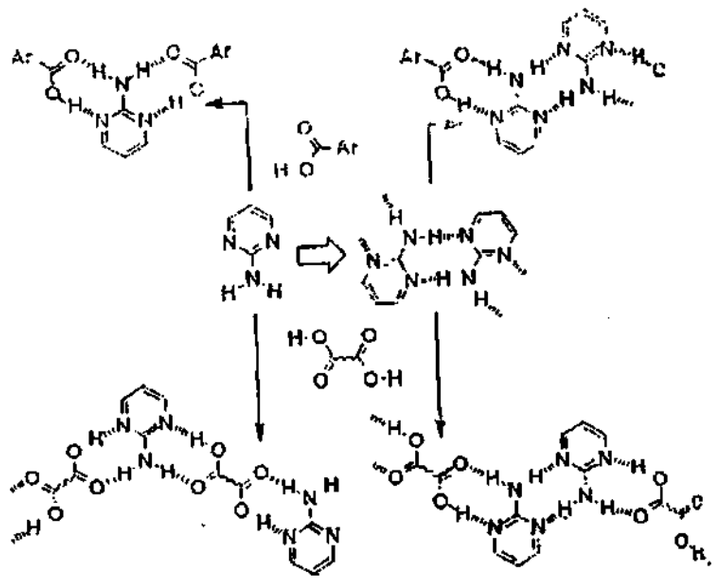


Figure 1.1: Interplay of hydrogen bonding networks of aminopyrimidine with various substrates.

2,6-Diamidopyridine has a parallel alignment of hydrogen bond donors and acceptors in its free base form (Figure 1.2). Protonation at the pyridine nitrogen atom produces a conformational change: the amide carbonyl oxygen atoms form intramolecular hydrogen bonds and the amide protons are directed outwards. In this conformation, the pyridinium ion can form continuous hydrogen bonds with its diaryl phosphate counterions in the solid state.

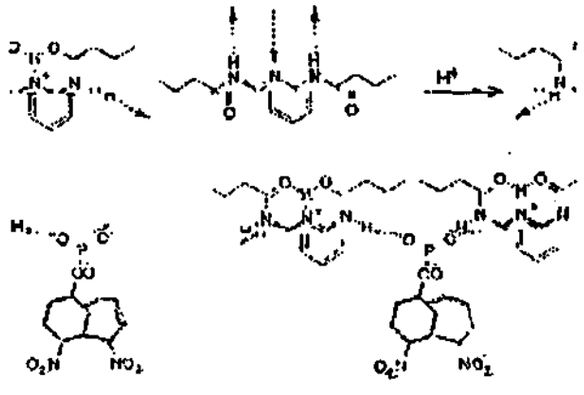


Figure 1.2: *Hydrogen bonding pattern in the complexes of* 2,6-diamidopyridine

Crystallization of triamide (Figure 1.3) from CH_2Cl_2 and MeOH results in the growth of large rod-shaped crystals. X-ray diffraction analysis demonstrates that the triamide molecules form stacks which are stabilized by hydrogen bonds between the three amide N-H groups of one molecule and the amide CO groups of the next molecule in the stack.

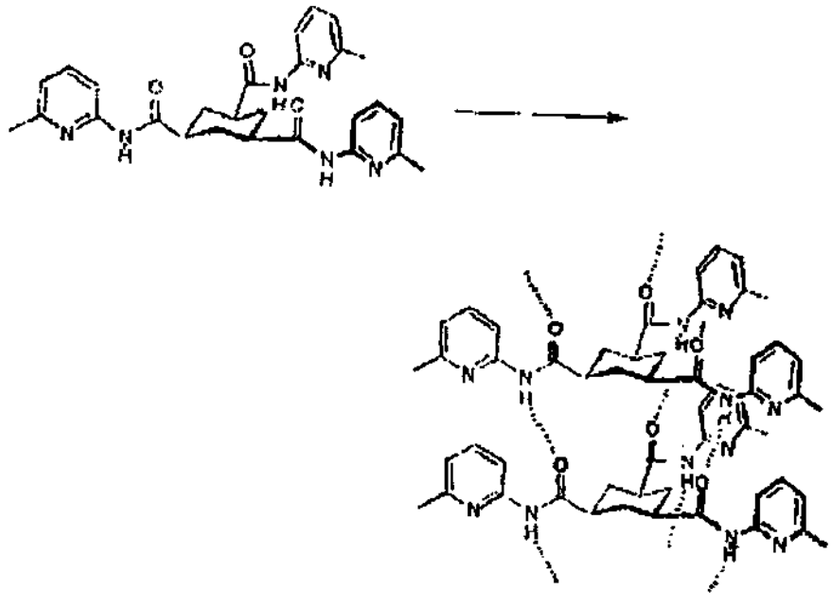


Figure 1.3: The hydrogen bond directed self-assembly of molecular rods through hydrogen bonding between amide groups

Kelly *et al*[18] have reported the design and synthesis of a "bisubstrate reaction template" as shown in Figure 1.4 which is capable of a six-fold acceleration in the reaction between the benzylic bromide and the amine (see path (a) in Figure 1.4).

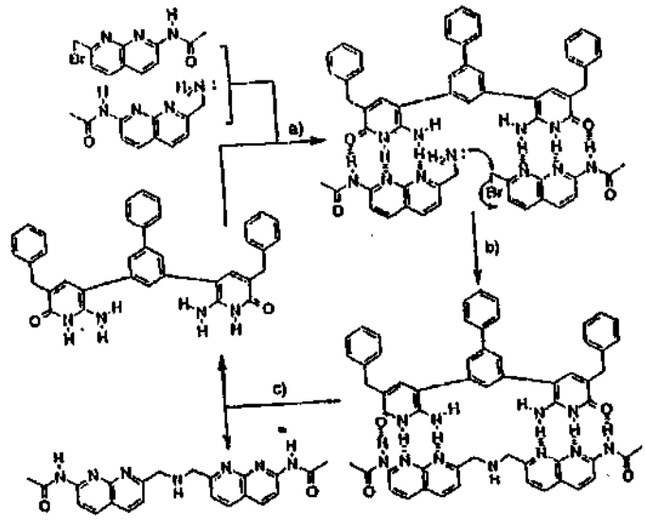
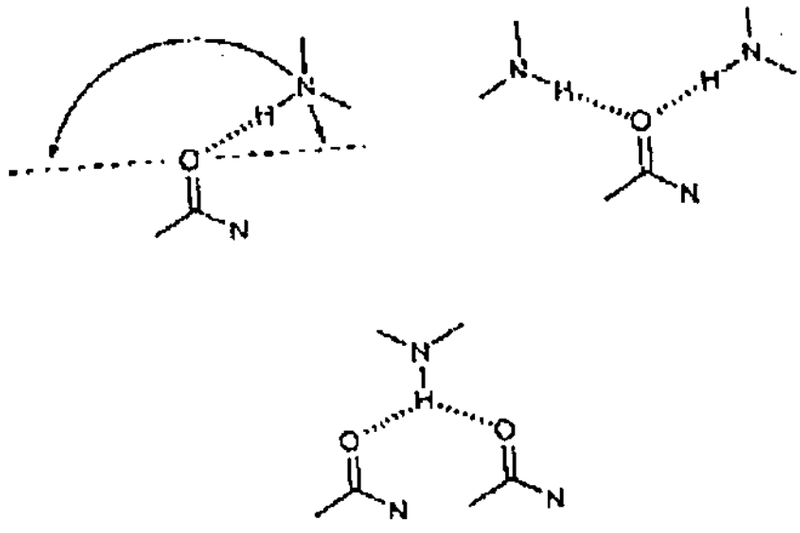


Figure 1.4: Rate acceleration through hydrogen bond directed binding of reactants in a bisubstrate reaction template. a. Association, b. Reaction, c. Dissociation.

The amide group is one of the attractive functional groups to use in designing hydrogen-bonded tape structures in the solid state: it forms hydrogen bonds with well understood geometrical constraints and is itself planar (Scheme 1.4).



Scheme 1.4

Whitesides and coworkers have exploited the strong and multiply hydrogen-bonded lattice formed between cyanuric acid and melamine to construct rosette type structures.[6] In addition, they forwarded a variety of strategies to design molecules that will form intermolecular motifs with well-defined structures - spheres, sheets,[19,20] tapes,[21,22] helices[23] etc., (Figure 1.6).

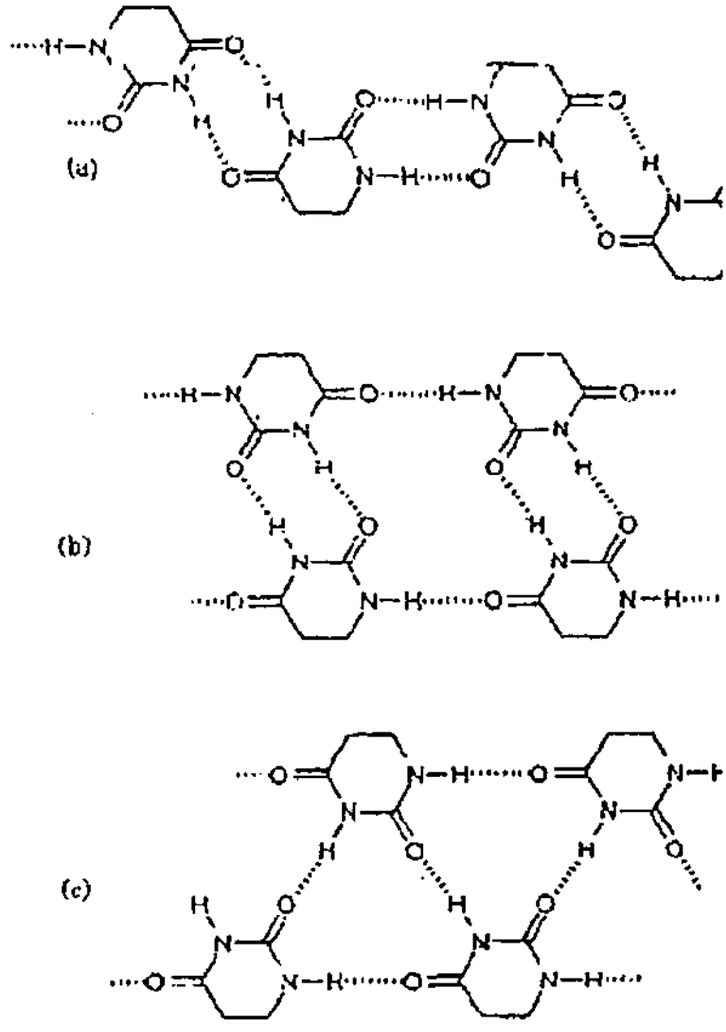


Figure 1.6: Examples of tapes and ribbons

Tapes and ribbons are distinguished as: A tape motif is generated when each molecule is hydrogen-bonded to two neighbouring molecules, and when the hydrogen bonds between two molecules form a cyclic ring (Figure

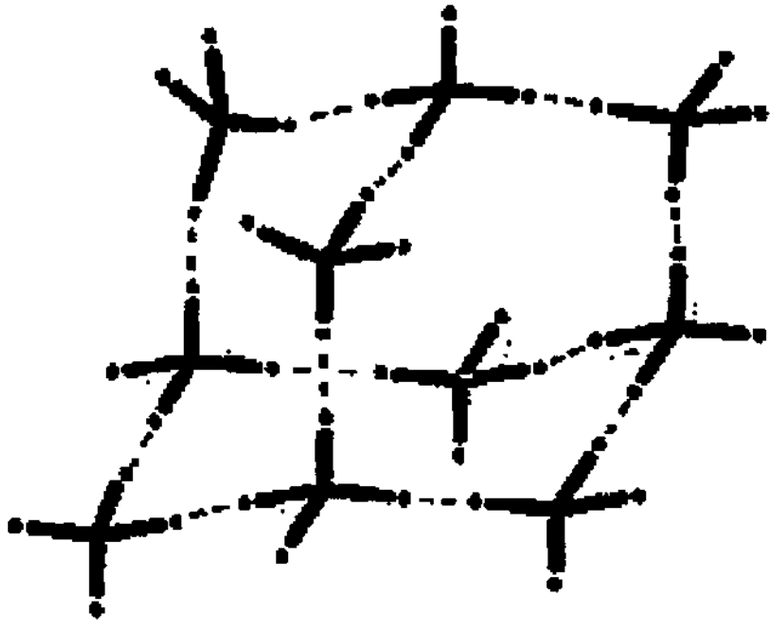
1.6a); a ribbon motif is generated when each molecule is hydrogen- bonded to the adjacent molecules by single hydrogen bonds only (Figure 1.6b and c).

Inorganic microporous minerals like zeolites have networks of molecular-scale pores, channels and cavities.[24,25] Analogous microporous solids based on organic building blocks have the potential for a precise rational design, through control of the shape and size of the pores.[26-28] Yaghi *et al*[26,29,30] have designed many metal-organic frameworks that bind aromatic guest molecules selectively. Yaghi's group often employed hydrothermal method as one of the synthetic routes.

Moore and co-workers[31] have made porous materials from ring-shaped units that stack themselves by hydrogen bonding. Each ring is made up of six rigid rod-like units and six corner pieces to form a regular hexagon. Acetylenic groups, however, gave rods. The corner pieces were benzene rings with hydroxy groups which provide connections needed to make hexagons. The benzenes in neighbouring sheets interact in a way that encourages the rings to stack on top of one another, creating parallel channels about 9Å in diameter.

A slightly different approach has been developed by Wuest's group.[32] They used building blocks that create channels as they assemble themselves into a network. Wuest, in fact introduced the concept of *tectons* into supramolecular chemistry. Tectons are the molecules with sticky ends that can participate in intermolecular interactions that are strong, specific and directional. The geometry of the tectons determines that of the network into which they assemble. For instance, a diamondoid network as shown in Scheme 1.5. can be synthesized from tectons with four sticky hydrogen

bonding sites in a tetrahedral orientation. Such self-assembly often results in the formation of channel structures which are being filled by solvent molecules.



Scheme 1.5

In this thesis, results of an extensive investigation of organic solids obtained by supramolecular hydrogen-bonded aggregation are discussed. The scope of these investigations is discussed in the next section.

2. Scope of the Present Investigations

In what follows, the scope of the investigations reported in this thesis is presented.

Hydrogen bonds like O-H...O, N-H...O, N-H...N, O-H...N are being extensively used in the design and synthesis of novel supramolecular assemblies with tailor-made properties such as non-linear optics, catalytic properties etc. In order to explore the possible formation of two-dimensional layered and cavity structures as well as three-dimensional channel structures using hydrogen bond assemblies, we have carried out several co-crystallization experiments between different molecules (Figure 2.1), possessing acceptor and donor moieties. In what follows, the strategies employed in the synthesis of the assemblies are described.

2.1 Layered hydrogen-bonded structures formed by carboxylic acids with azaaromatics

The carboxylic group can form stable cyclic hydrogen-bonded systems with a donor molecule as shown in Scheme 2.1[33-35] in which coupling (b) is very robust.[33] A recent study of the assemblage of acylaminopyrimidine and aliphatic carboxylic acids has shown the design of novel assemblies using coupling (b).[33]

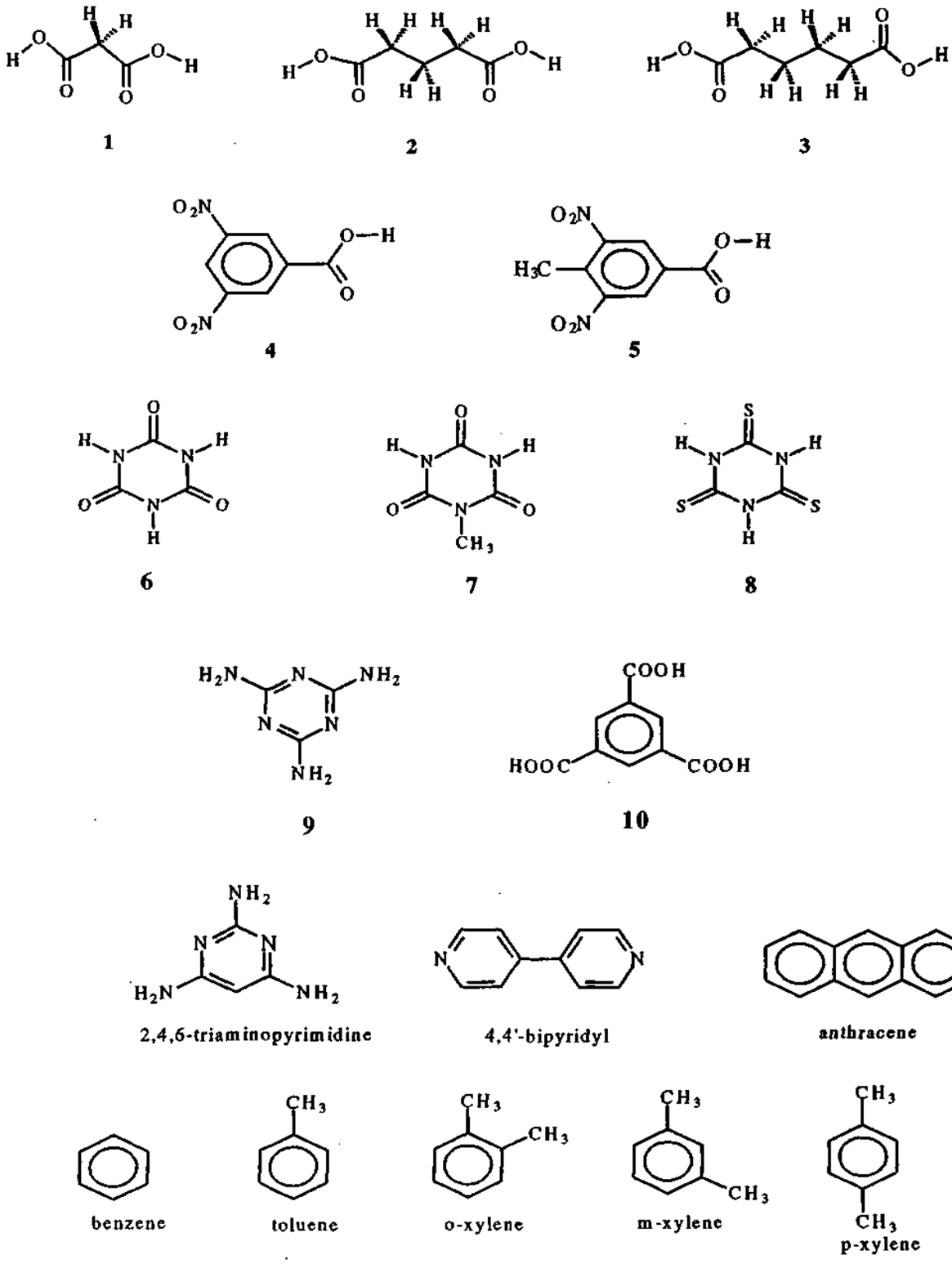
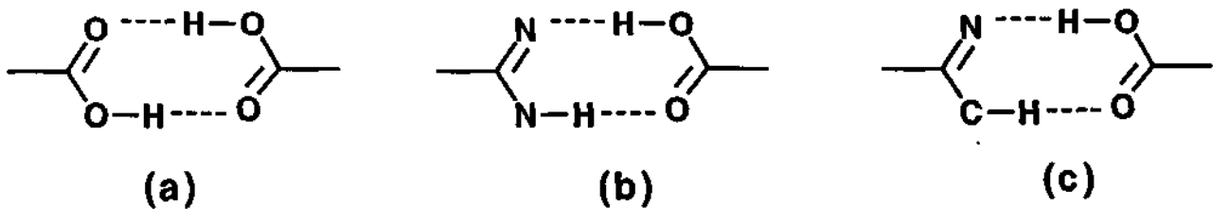

1
2
3
4
5
6
7
8
9
10
2,4,6-triaminopyrimidine
4,4'-bipyridyl
anthracene
benzene
toluene
o-xylene
m-xylene
p-xylene

Figure 2.1



Scheme 2.1

We wanted to explore supramolecular hydrogen-bonded assemblies formed by aliphatic dicarboxylic acids with a donor molecule such as 2,4,6-triaminopyrimidine involving the coupling (b). In this regard, crystal structures of hydrogen-bonded molecular complexes of malonic, **1**, glutaric, **2** and adipic, **3** acids with 2,4,6-triaminopyrimidine have been studied in order to examine the hydrogen-bonded structures formed in a system where the nitrogens of the heterocyclic ring as well as of the amino side chain of an azaaromatic compound can interact simultaneously with the carboxyl group. The results are discussed in section 4.1.1. Interestingly, we have found that the complexes differ among themselves depending upon the number of $-CH_2$ groups present in a given carboxylic acid.

Formation of coupling (c) was reported to occur when carboxylic groups interact with hetero nitrogen atoms as was described for the first time in the complexes of phenazine with 3,5-dinitrobenzoic acid, **4** and 3,5-dinitro-4-methylbenzoic acid, **5**.[9] The assemblies obtained formed linear tapes which are arranged in three dimension to yield either herringbone or crossed-ribbon networks. However, recently, a complex between trimesic acid and 4,4'-bipyridyl has been found to form a layered structure in which 4,4'-bipyridyl

expanded the two-dimensional cavities of trimesic acid by inserting in between the carboxyl group. Hence, we have chosen to co-crystallize acids, **4** and **5** in the presence of 4,4'-bipyridyl to examine the perturbation of hydrogen bonding network present in the parent crystal structures to obtain layered structures. It has been noticed that 4,4'-bipyridyl simply breaks the cyclic O-H...O hydrogen bonding coupling between the adjacent acid groups and insert in between the acid moieties forming O-H...N and C-H...O coupling. The results are elaborated in section 4.1.2.

2.2 Hydrogen-bonded structures formed by cyanuric acid and N-methylcyanuric acid

Apart from the carboxyl group, the other potential functional groups to form hydrogen-bonded networks are the amide groups. In particular, cyclic amide groups, present in molecules like cyanuric acid are of special interest with the availability of symmetrically substituted amide groups to form cyclic hydrogen bond networks.[37] Such networks may yield cavities or channel type structures like in trimesic acid.[44] For this purpose, we wished to co-crystallize cyanuric acid, **6**, with 2,4,6-triaminopyrimidine and 4,4'-bipyridyl. We were not successful to get co-crystals with 2,4,6-triaminopyrimidine, but interesting crystal structures were obtained with 4,4'-bipyridyl. Cyanuric acid, **6** and 4,4'-bipyridyl form two different crystals depending upon the solvent of crystallization and such solvent dependence on the formation of co-crystals is hitherto unknown. The feature is related to the formation of different

hydrogen-bonded networks by the cyanuric acid upon crystallization from different solvents. This is further confirmed by the formation of only one assembly by 4,4'-bipyridyl with N-methylcyanuric acid, **7**, which forms only one type of hydrogen bonding network in its pure crystal structures, irrespective of the solvent of crystallization. The results are discussed in detail in section 4.2.

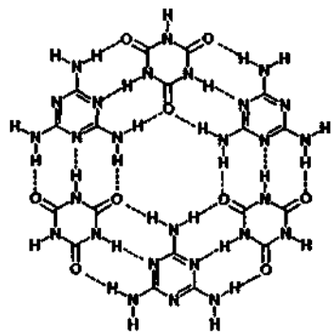
2.3 Organic porous solids formed by the hydrogen-bonded self-assembly of trithiocyanuric acid and 4,4'-bipyridyl

As mentioned in Section 2.2, cyanuric acid forms interesting co-crystals with other substrates. This is partly because of the formation of strong N-H...O hydrogen bonds between cyanuric acid molecules. It was of interest to prepare channel structures of zeolite type using organic molecules alone.[38] Such structures are very few in the literature, the noted examples being the self-assembly of three-dimensional networks with large chambers by using a pyridone as the tecton[39] and complexes of urea and thiourea with channels as well as the quinol clathrates with cages. We were interested to synthesize materials of that kind by noncovalent synthesis, as they can be easily used in the industry for the purification of various chemicals or in catalysis, etc. In this connection, we have chosen trithiocyanuric acid, **8**, as a model compound as it can form N-H...S hydrogen bonds[40] which are weaker in nature, leading to greater flexibility.

We have investigated the hydrogen-bonded adduct formed between **8** and 4,4'-bipyridyl that has nice three-dimensional channels accommodating benzene. We have carried out detailed study to explore whether other aromatic compounds can be introduced in these channels and if so, there is any shape selectivity as in zeolites. We find that supramolecular hydrogen-bonded porous structures formed by **8** and 4,4'-bipyridyl is not only thermally stable but also accommodates several aromatic molecules like toluene, *o*-, *m*-, *p*-xylenes and anthracene, with some shape selectivity. The results are explained in Section 4.3.

2.4 Hydrothermal synthesis of organic channel structures formed by the hydrogen bonding interaction of melamine with cyanuric and trithiocyanuric acids

Cyanuric acid-melamine adduct is expected to form a hexagonal network through the formation of hydrogen bonds as shown in Scheme 2.2. Such a network was referred to as a rosette by Whitesides.[6]



Scheme 2.2

Whitesides and coworkers synthesized a family of self-assembled hydrogen-bonded aggregates, stable in solution, based on this template.[41,42] However, the structure of the parent lattice, formed between pure cyanuric acid, **6** and melamine, **9**, has not been established by single crystal X-ray crystallography[42] as single crystals of suitable quality could not be prepared by the generally known crystallization methods such as slow evaporation, sublimation etc. The difficulty in growing crystals of the adduct is partly because both the reactants **6** and **9** are hydrogen-bonded solids melting at very high temperatures, with limited solubility in most organic solvents. We have therefore, made use of hydrothermal conditions,[43] commonly employed in the synthesis of quartz, zeolites and inorganic open-framework structures, to obtain the crystals of the 1:1 adduct. Crystals of the 1:1 adduct of trithiocyanuric acid, **8** and **9** could also not be obtained by any other crystallization methods, but have been prepared by employing this procedure. The structure determination reveals that the rosette arrangement form channels of ~ 4Å in dimension. The results are discussed in Section 4.5. These examples highlight the application of hydrothermal technique for the synthesis of organic supramolecular assemblies which is well known for the synthesis of inorganic or organometallic assemblies.

2.5 Channel structures formed by self-assembled four-membered networks of trimesic acid

In our continued interest to synthesize channel structures, we have extended our studies to trimesic acid, **10**, as well. Trimesic acid, **10** with huge cavities (~10Å) in its two-dimensional arrangement attracted various researchers for the design of organic porous solids. For instance, Herbstein and Marsh[44] determined the structures of molecular complexes formed by hydrates of **10** and found that hydrogen-bonded layers of the composition trimesic acid-H_2O gave rise to channels wherein picric acid molecules could reside. Further, Kolotuchin *et. al.*[45] have described hexagonal channel structures of **10** containing ethanol, pyrene and tetrahydrofuran. In our investigation, surprisingly, simple crystallization of **10** from methanol/benzene mixture or acetone resulted in the formation of a channel structure with the incorporation of the solvent molecules within the channels. These results have been discussed in section 4.5 along with the co-crystals of **10** with dimethylformamide (DMF).

3. Experimental

All the chemicals used in the present studies, except N-methylcyanuric acid, were obtained from commercial sources. N-methylcyanuric acid was prepared in the laboratory. (Courtesy of Dr.K.N.Ganesh, NCL, Pune.) Preparation of N-methylcyanuric acid: Melamine (5gm) and dimethyl sulphate (5gm) were refluxed in dioxane (20mL) for 4 hours in an atmosphere of argon. The reaction was stripped of the solvent and subjected to exhaustive hydrolysis

by refluxing in a mixture of glacial acetic acid, concentrated hydrochloric acid and water for 24 hours. The solid residue obtained by evaporating the solvents under reduced pressure, was triturated with 20mL chilled water and filtered and the solid obtained was characterized by ^{1}H NMR and chemical analysis.

3.1 Preparation of molecular complexes

3.1.1 Hydrogen-bonded complexes formed by aliphatic dicarboxylic acids and dinitrobenzoic acids with azaaromatic donors

(a) Co-crystals of the azaaromatic donor, 2,4,6-triaminopyrimidine (12.5mg) with aliphatic dicarboxylic acids, malonic (10.4 mg), glutaric (13.2 mg) and adipic (14.6 mg) acids were prepared in a 1:1 molar ratio from a methanol solution by slow evaporation method. Good quality single crystals were obtained in all the cases.

(b) Co-crystals, of 3,5-dinitrobenzoic acid (21.2 mg) and 3,5-dinitro-4-methylbenzoic acid (22.6 mg) respectively with 4,4'-bipyridyl (15.6 mg), were also prepared from a methanol solution. In both the cases, complexes were obtained in a 2:1 stoichiometry. Further, co-crystallization of the adducts with anthracene was carried out. 3,5-dinitrobenzoic acid did not yield any co-crystals with anthracene, but 3,5-dinitro-4-methylbenoic acid gave crystals of good quality with anthracene (17.8 mg) in a 1:1 molar ratio that were suitable for single crystal X-ray diffraction studies.

3.1.2 Molecular complexes of cyanuric acid and N-methylcyanuric acid with 4,4'-bipyridyl

Co-crystals formed between 4,4'-bipyridyl (15.6 mg) and cyanuric acid (12.9 mg) as well as N-methylcyanuric (15.0 mg) were prepared from a methanol solution and from water. Crystals of N-methylcyanuric acid with 4,4'-bipyridyl, were obtained from a methanol solution.

3.1.3 Synthesis of trithiocyanuric acid and 4,4'-bipyridyl adduct and its various host-guest type complexes

The adduct of trithiocyanuric acid with 4,4'-bipyridyl was prepared by the co-crystallization of the two components from a methanol solution, but the crystals were not very stable. In the presence of benzene, toluene, *o*-, *m*- or *p*-xylene or anthracene, however, stable crystals, were obtained accommodating respective aromatic guest molecules. In a typical preparation, 354 mg of trithiocyanuric acid and 156 mg of 4,4'-bipyridyl were taken in 15mL of methanol in the presence of an aromatic compound (5mL). After slow evaporation, crystals of the adduct of trithiocyanuric acid-4,4'-bipyridyl, containing the aromatic compound were obtained. In all these cases, good quality single crystals were obtained and these were employed for the determination of molecular and crystal structures, by single crystal X-ray diffraction. The ratio of trithiocyanuric acid, 4,4'-bipyridyl and the aromatic molecule in the adducts containing benzene, toluene, *o*- and *m*-xylene was 2:1:1. The ratio was 2:1:0.5 in the adducts containing p-xylene and anthracene.

3.1.4 Hydrothermal synthesis of molecular complexes of melamine with cyanuric acid and trithiocyanuric acid

Single crystals of melamine with cyanuric acid as well as trithiocyanuric acid could not be obtained by the usual crystallization methods from organic solvents. There was however evidence for the formation of the adduct from the powder X-ray diffraction patterns of the polycrystalline precipitates obtained on mixing the two in methanol. Since, all the compounds (cyanuric acid, trithiocyanuric acid and melamine) are solids with high melting points (>300°C), we made use of hydrothermal conditions, commonly employed in the synthesis of quartz, zeolites and inorganic framework structures, to obtain the crystals.

Aqueous solutions of cyanuric acid (129 mg) and melamine (126 mg) were mixed in a teflon flask and the mixture (15mL) was kept in a stainless steel bomb. The bomb was sealed and maintained in a furnace at 180°C. Rectangular plate-like crystals of good quality separated from the solution, upon cooling the bomb to room temperature over a period of 4 hours. These crystals were used for collecting intensity data on the single crystal X-ray diffractometer. Crystals of the trithiocyanuric acid and melamine adduct were also obtained by a similar procedure except that the temperature of the furnace was maintained at 100°C. This was because trithiocyanuric acid decomposed when the temperature was maintained at 180°C as in the case of cyanuric acid.

3.1.5 Crystallization of Trimesic acid adducts with various organic solvents

The adduct of trimesic acid and methanol was prepared by the crystallization of the acid (21.0 mg) from a mixture of 1:1 solution of methanol and benzene. However, the adduct of the acid and acetone, was obtained from the crystallization of trimesic acid (21.0 mg) from a solution of acetone. Crystals of trimesic acid and dimethylformamide (DMF), were obtained by crystallization of trimesic acid (21.0 mg) from a 1:1 solution of DMF and benzene. Single crystals obtained in all the cases were of good quality, suitable for crystal structure analysis to characterize by single crystal diffraction method.

3.2 Methods of characterization

3.2.1 Single crystal X-ray diffraction

Molecular and crystal structures of all the co-crystals mentioned in the earlier sections have been determined using single crystal X-ray diffraction method. Good quality single crystals carefully chosen from the available samples prepared as discussed in the above section were attached to the tip of a glass fiber using an adhesive. Intensity data were collected on a diffractometer equipped with CCD area detector of Siemens. The structures were solved and refined by full-matrix least-square on F^2 using the SHELXTL-PLUS package.[46] The analyses were uncomplicated and all the non-hydrogen atoms were refined anisotropically. The essential crystallographic information is given in Table 3.1. Fractional coordinates (along with the ORTEP diagrams

showing the labelling schemes) are given in tables as an Appendix to the thesis. Non-covalent bonds were calculated using the program PLATON.[47]

3.2.2 *Thermogravimetric analysis*

Thermogravimetric analysis (TGA) has been carried out to study the porous nature of the host-guest complexes formed by the adduct trithiocyanuric acid and 4,4'-bipyridyl (section 3.1.3) using a Mettler-Toledo TG850 instrument. Initially, the complexes as-prepared were heated in the furnace attached to the instrument over the temperature range 25-200°C. This led to the removal of the aromatic guest molecules as confirmed by the weight loss noted in process. The host material obtained after removing the aromatic molecule was immersed in the aromatic liquid for several hours. The crystals were then taken out, and TGA repeated. This procedure was repeated more than once to find out whether the inclusion of the guest molecule was reversible and also whether there was any change in the temperature of decomposition or in the proportion of the aromatic compound in the adduct, with such cycling.

Table 3.1. Crystallographic data for molecular complexes **1a - 10b**[(a)]

compound	a, Å	b, Å	c, Å	α, °	β, °	γ, °	Crystal System, Space Group	Z	Volume Å^3	R_1, wR_2
1a	12.060(2)	10.748(2)	16.501(2)	90	107.22(9)	90	monoclinic, C2/c	8	2043.0(6)	0.074, 0.120
2a	11.929(3)	10.883(3)	20.559(5)	90	98.77(3)	90	monoclinic, C2/c	8	2638.1(2)	0.056, 0.105
3a	9.808(1)	16.104(1)	10.182(1)	90	93.07(2)	90	monoclinic, $P2_1/c$	2	1605.9(1)	0.044, 0.083
4a	6.226(1)	22.150(2)	9.417(1)	90	99.17(1)	90	monoclinic, $P2_1/n$	2	1282.1(3)	0.065, 0.087
5a	9.852(1)	11.297(2)	14.827(1)	67.72(1)	89.77(2)	64.85(1)	triclinic, $P\bar{1}$	2	1357.7(2)	0.049, 0.098
5b	9.121(1)	9.260(1)	11.199(2)	73.83(1)	89.58(1)	81.78(1)	triclinic, $P\bar{1}$	1	898.6(2)	0.055, 0.085
6a	4.320(1)	9.202(1)	11.702(2)	78.75(1)	82.64(2)	86.36(1)	triclinic, $P\bar{1}$	1	452.1(1)	0.033, 0.087
6b	6.845(1)	28.779(3)	7.139(1)	90	115.47(1)	90	monoclinic, $P2_1/n$	4	1269.6(3)	0.058, 0.125
7a	3.878(1)	16.943(1)	20.830(1)	90	90.75(1)	90	monoclinic, P2/n	4	1368.5(4)	0.063, 0.111
8a	7.018(1)	10.344(1)	10.757(1)	63.75(1)	75.78(1)	73.82(1)	triclinic, $P\bar{1}$	1	665.8(1)	0.032, 0.077
8b	7.112(1)	10.489(1)	10.681(1)	65.40(1)	76.58(1)	73.05(1)	triclinic, $P\bar{1}$	1	687.4(1)	0.070, 0.154
8c	7.282(1)	10.621(1)	10.648(1)	66.30(1)	76.53(1)	70.42(1)	triclinic, $P\bar{1}$	1	705.9(1)	0.056, 0.149
8d	10.324(1)	11.615(1)	12.319(1)	102.16(1)	93.46(1)	90.68(1)	triclinic, $P\bar{1}$	2	1441.0(2)	0.083, 0.153
8e	10.359(1)	11.467(1)	18.412(1)	83.65(1)	75.06(1)	67.94(1)	triclinic, $P\bar{1}$	2	1957.7(3)	0.058, 0.132
8f	10.472(1)	11.419(1)	12.932(1)	100.46(1)	107.69(2)	111.28(2)	triclinic, $P\bar{1}$	2	1296.5(2)	0.049, 0.098
9a	14.853(2)	9.641(2)	3.581(2)	90	92.26(1)	90	monoclinic, C2/m	2	512.4(2)	0.056, 0.141
9b	14.862(3)	9.650(2)	3.588(1)	90	92.32(1)	90	monoclinic, C2/m	2	514.2(2)	0.062, 0.134
10a	3.679(1)	8.971(2)	18.038(1)	72.76(1)	86.86(1)	88.04(1)	triclinic, $P\bar{1}$	2	580.8(2)	0.133, 0.308
10b	16.912(6)	14.475(1)	7.390(1)	90	90.55(1)	90	monoclinic, P2/c	4	1809.0(1)	0.059, 0.116

(a) For description of the complexes, see the Results and Discussion (Section 4).

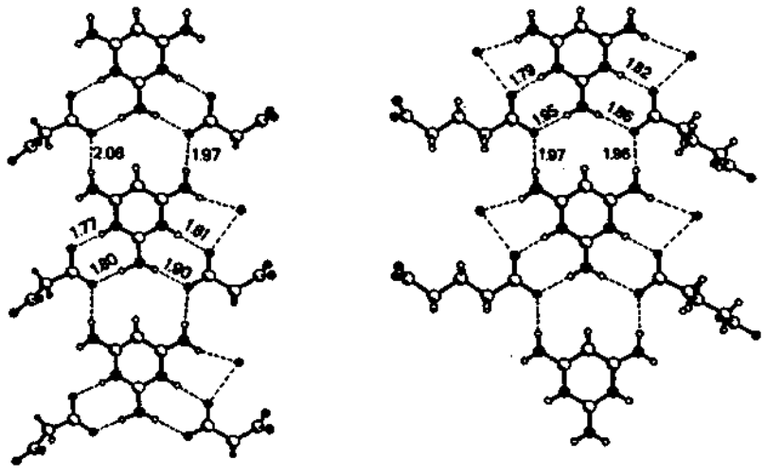
FRACTIONAL COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS OF THESE COMPLEXES ARE LISTED AT THE END OF THE THESIS.

4. Results and discussion

4.1 Layered hydrogen-bonded structures formed by carboxylic acids with azaaromatics

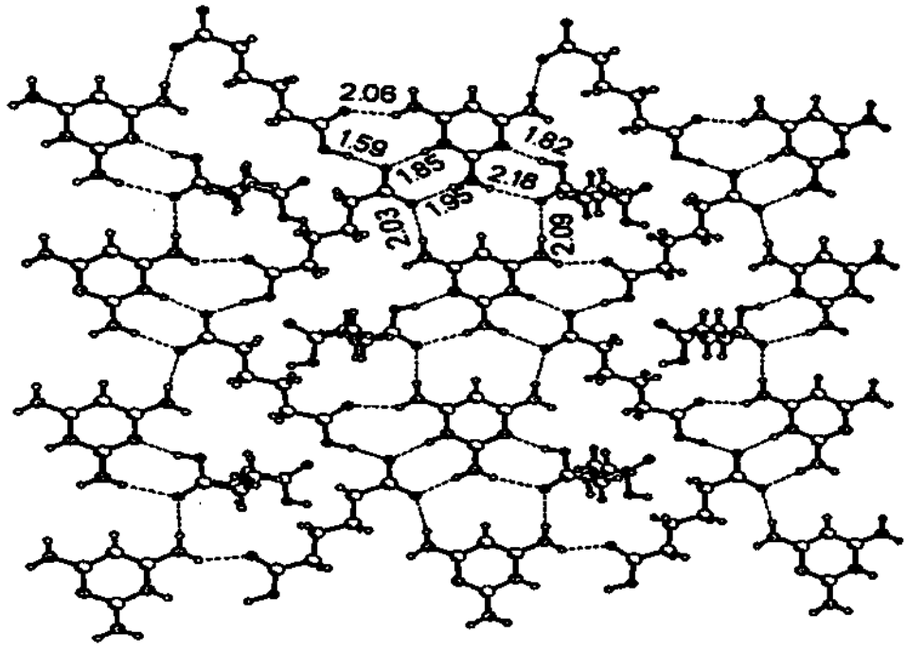
4.1.1 Crystal structures of the hydrogen-bonded complexes of 2,4,6-triaminopyrimidine with aliphatic dicarboxylic acids

Co-crystallization of 2,4,6-triaminopyrimidine with malonic, glutaric, and adipic, acids resulted in the formation of molecular complexes which are designated as **1a**, **2a** and **3a** respectively. The crystal structures of these complexes reveal a new structural feature related to the hydrogen bonds involving the carboxylic group and the heterocyclic nitrogen. The basic recognition between the pyrimidine and the acids occurs between the carboxylic group and the pyridyl nitrogen. The complexes **1a-3a** differ from one another in some aspects, the common feature being that the pyrimidine and the acid molecules are held together by the couplings consisting of $O^{-}...H^{+}$-N / N-H...O bonds as shown in Figures 4.1 and 4.2. While **1a** and **2a** are formed in a 1:1 ratio, with each pyrimidine attached to an acid molecule through $O^{-}...H^{+}$-N / N-H...O hydrogen bonds (Figures 4.1) the complex **3a** between adipic acid and the pyrimidine is formed in the 3:2 ratio.



1a **2a**

Figure 4.1: Molecular tapes formed by 2,4,6-triaminopyrimidine in the adducts **1a** (left) and **2a** (right).



3a

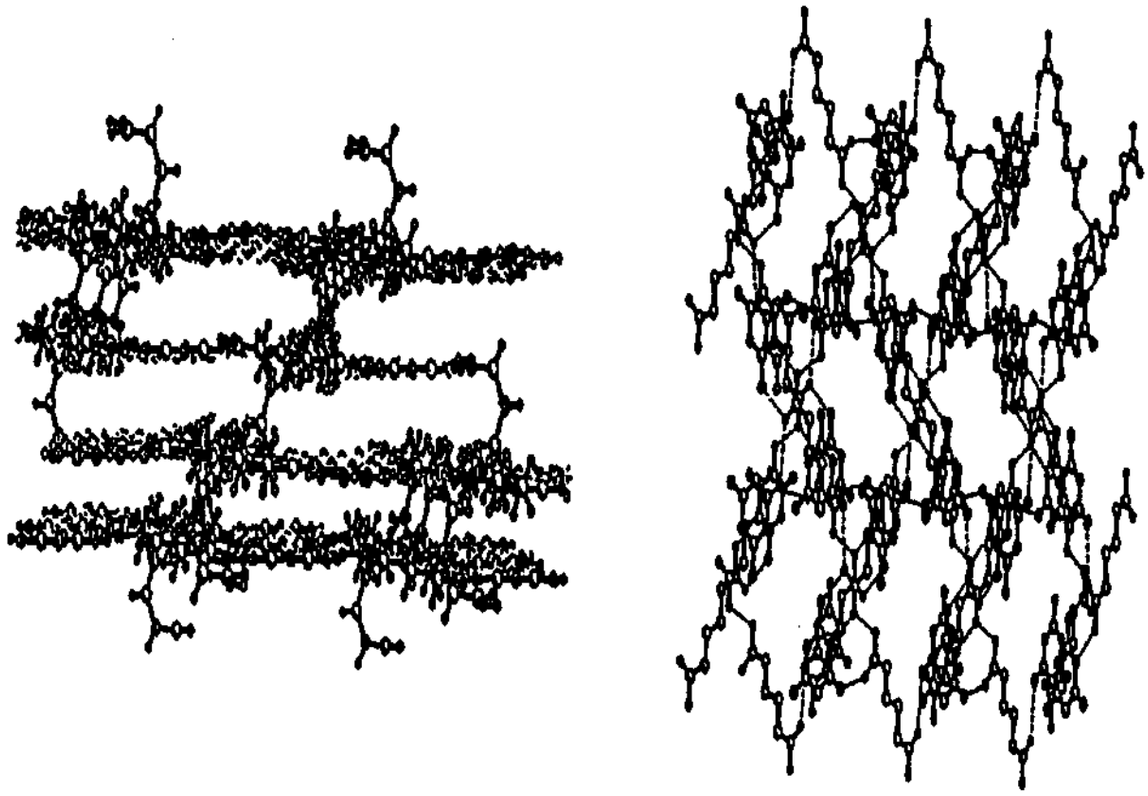
Figure 4.2: Arrangement of molecules of adipic acid and 2,4,6-triaminopyrimidine in a two-dimensional planar sheet of the complex, **3a**

On comparison with the literature data on aminopyrimidines,[48] we would expect the hydrogen bond coupling in **1a-3a** to be O-H...N and N-H...O. However the couplings actually observed by us in **1a-3a**

involve proton transfer from the carboxylic group to the heterocyclic nitrogen as shown below in Scheme 4.1.

Scheme 4.1

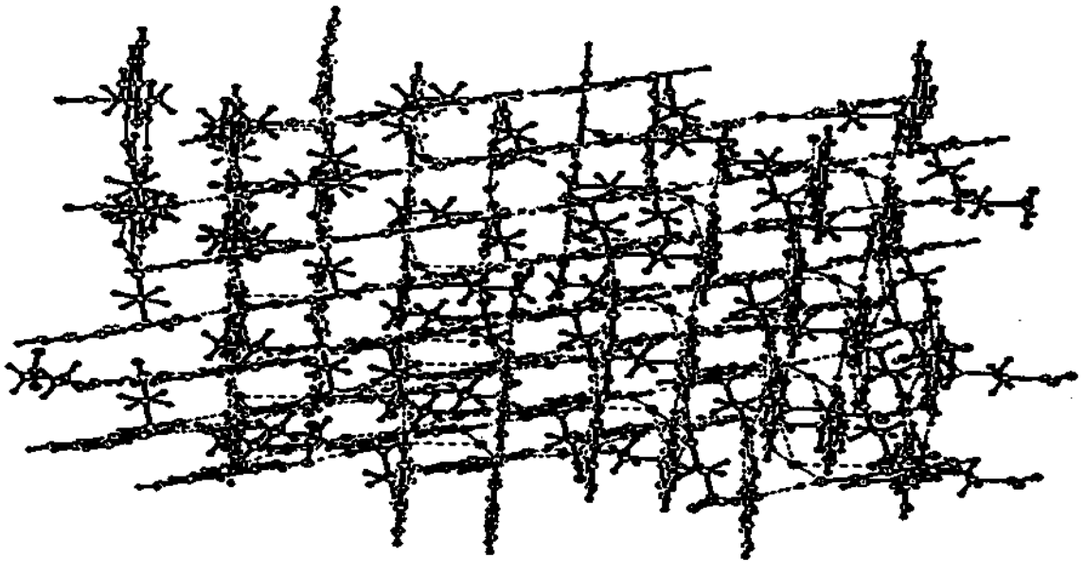
Such proton transfer occurs because of strong hydrogen bonds initially formed between the carboxyl and the pyridyl nitrogen atoms. The H...O distances in the cyclic hydrogen bond structures also supports the occurrence of proton transfer as the $H^+...O^-$ and H...O distances in the $O...H^+$-N and O...H-N bonds are comparable (~1.80Å). The complexes **1a-3a** are stabilized by the incorporation of guest molecules. In the case of **1a** and **2a**, water molecules are the guest molecules. The interaction of the water molecules with the acids and the pyrimidine is shown in Figure 4.1. However in **3a**, additional acid molecule has been incorporated as guest molecule. It appears that the large chain length of adipic acid, **3** facilitated the formation of larger voids as shown in Figure 4.3 (right) which are filled by the additional acid molecules. Furthermore, the three-dimensional arrangement resembles a typical inorganic pillared type structure as depicted in the Figure 4.3 (left).



3a

Figure 4.3: Three-dimensional arrangement of the planar sheets formed in the co-crystals, **3a** formed by 2,4,6-triaminopyrimidine and adipic acid

In addition, a comparison of the crystal packing of the complexes **1a-3a** reveals another noteworthy feature that the number of $-CH_2$ groups in the constituent acid play an important role in the pattern of crystallization. This becomes evident as **3a** consisting of an acid with even number $-CH_2$ groups yields two-dimensional network (Figure 4.2) whereas complexes **1a** and **2a** with acids possessing an odd number CH_2 groups, constitute three-dimensional crossed networks. Such a network corresponding to **1a** is shown in Figure 4.4

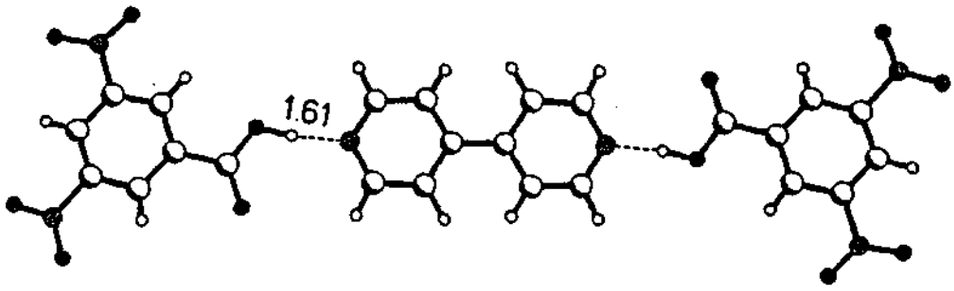


1a

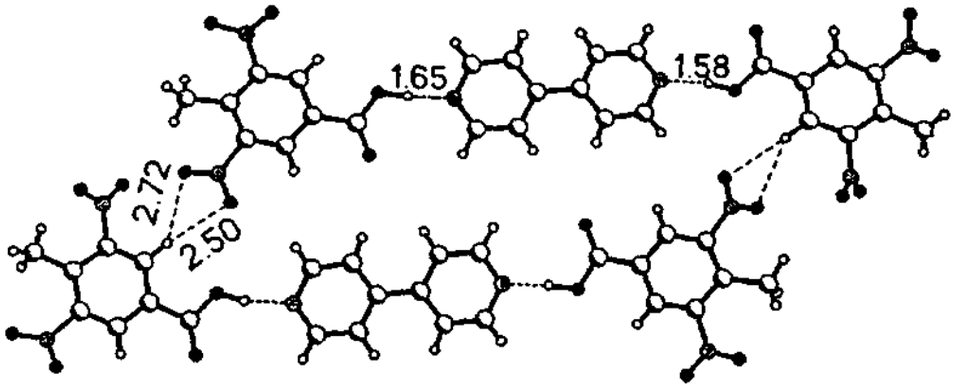
Figure 4.4: Three-dimensional arrangement of molecular tapes observed in the crystal structure of the complex between 2,4,6-triaminopyrimidine and malonic acid, **1a**

4.1.2 Layered structures formed by 3,5-dinitrobenzoic acid, 4 and 3,5-dinitro-4-methylbenzoic acid, 5, with 4,4'-bipyridyl

3,5-dinitrobenzoic acid, **4** is known to form a structure with cavities when crystallized from benzene solution, the cavities accommodating anthracene.[49] In the absence of benzene, however, it does not form a layered structure. Crystallization of 3,5-dinitro-4-methylbenzoic acid, **5** from most solvents, yields structures with cavities in a two-dimensional arrangement, which can accommodate anthracene.[49a] We have investigated whether the cavities formed by **4** and **5** could be modified by incorporating an azaaromatic donor molecule such as 4,4'-bipyridyl. Crystallization of **4** and **5** in the presence of bipyridyl gave complexes **4a** and **5a** respectively in a 2:1 stoichiometry. In both **4a** and **5a**, bipyridyl molecules break up the hydrogen bonds between the carboxyl groups as shown in Figure 4.5.



4a



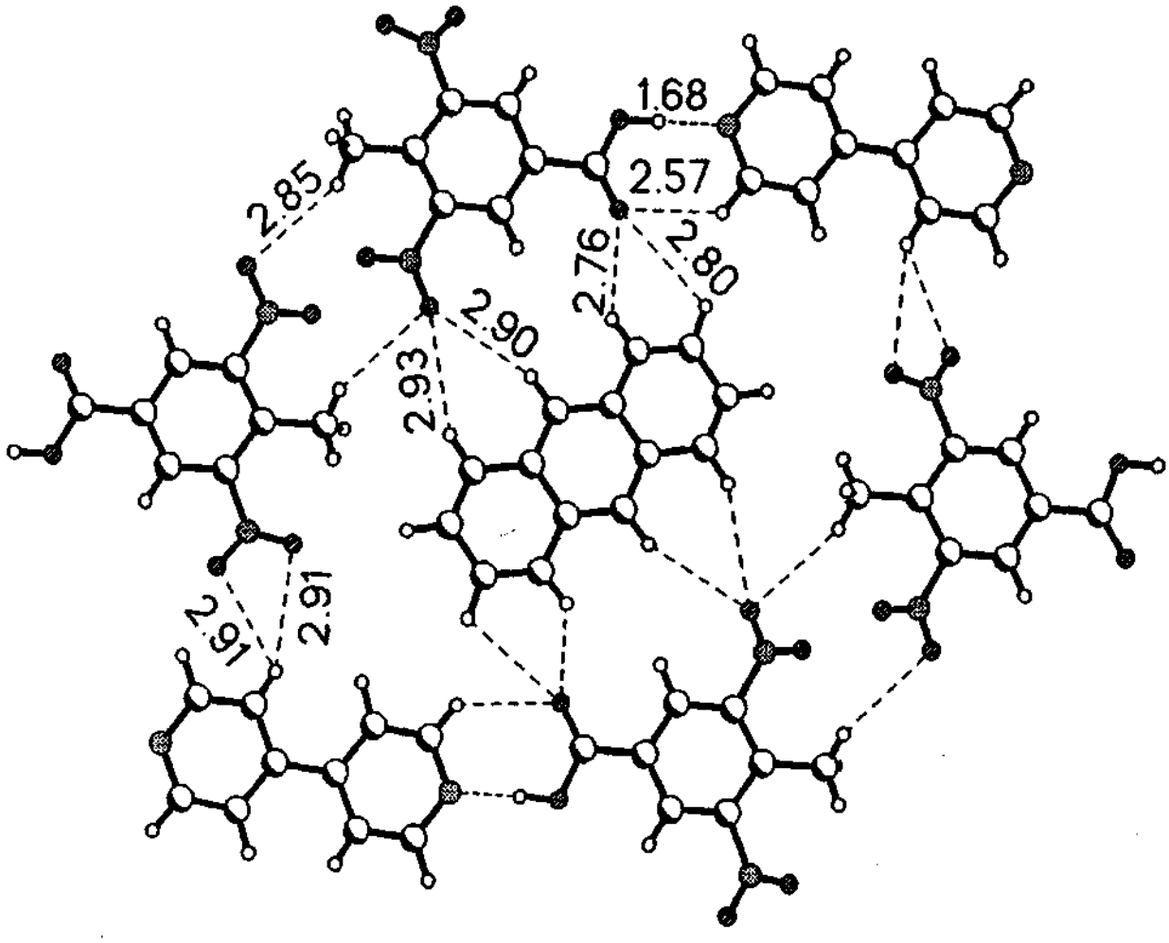
5a.

Figure 4.5: (top) Recognition pattern between 3,5-dinitrobenzoic acid, 4 and 4,4'-bipyridyl in the molecular complex, **4a**. (bottom) Two-dimensional arrangement of supermolecules of 3,5-dinitro-4-methylbenzoic acid, 5 and 4,4'-bipyridyl in **5a**. The dashed lines represent hydrogen bonds.

Interestingly, interaction between the carboxylic acid and the bipyridyl molecule in these complexes occur through the formation of a single O-H...N hydrogen bond (Figure 4.5), unlike the pair-wise hydrogen bond coupling observed in other related systems. The H...N distances in **4a** and **5a** are 1.61 and 1.65Å respectively. Furthermore, molecules of **5a** are arranged in two dimensions to yield planar sheets (Figure 4.5, bottom) which in turn are stacked in the three-dimensional packing while molecules of **4a** adopt a herringbone packing pattern.

Although both **4a** and **5a** do not possess cavities, the two-dimensional arrangement in **5a**, (Figure 4.5, bottom), which is similar

to that of the structures of pure acid, **5** encouraged us to investigate the co-crystallization of **4a** and **5a** in the presence of anthracene. **4a** did not yield any co-crystals with anthracene but **5a** gave crystals of good quality suitable for single crystal X-ray diffraction studies. The complex of **5a** with anthracene (designated as **5b**) is stabilized by the formation of O-H...N and C-H...O hydrogen bonds coupling (Figure 4.6), not found either in **4a** or **5a**.



5b

Figure 4.6: Two-dimensional arrangement of hexagonal cavity, formed by acid, **5** and 4,4'-bipyridyl which is filled by molecules of anthracene in the complex, **5b**.

The H...N and H...O distances between **5** and 4,4'-bipyridyl in the anthracene adduct, **5b** are 1.68 and 2.57Å respectively. Figure 4.7 shows that the supermolecules are arranged in two dimensions in a hexagonal mode through the formation of C-H...O hydrogen bonds between anthracene and the neighbouring molecules of carboxylic acid, **5** such that a cavity of dimension 10×12Å results. The anthracene molecules are accommodated in these cavities through the formation of C-H...O hydrogen bonds. The H...O distances are in the range of 2.76-2.93Å. A comparison of the structure of **5b** (Figure 4.6) with the anthracene adduct formed by the parent carboxylic acid, **5** alone indicates that the recognition pattern between anthracene and the acid **5** is not perturbed with the presence of bipyridyl molecules in **5b**.

4.2 Self-assembled hydrogen-bonded structures formed by cyanuric acid and N-methylcyanuric acid

Cyanuric acid crystallized from methanol has a planar sheet structure wherein adjacent molecules are held together by symmetrical cyclic N-H...O hydrogen bonds (H...O, 1.90Å), as shown in Figure 4.7a.[50a] This bonding gives rise to molecular tapes connected to each other by single N-H...O hydrogen bonds (H...O, 1.80 Å). Cyanuric acid crystallized from water, however, incorporates the solvent of crystallization into the structure giving the composition cyanuric acid.H_2O. This has a chain structure where adjacent molecules are connected together by single N-H...O bonds (H...O, 2.01Å) rather than by the cyclic hydrogen-bonded dimers[50b] (Figure 4.7b). The chains are

held together by O-H...O and N-H...O hydrogen bonds with the water molecules (H...O, 2.00-2.15Å). The N-H...O bonds forming the chains in cyanuric acid.H_2O (Figure 4.7b) are considerably longer than those in cyanuric acid crystallized from methanol.

Co-crystallization of cyanuric acid, **6** and 4,4'-bipyridyl forms two different types of molecular complexes depending upon the solvent of crystallization. From methanol, a complex, **6a**, in a ratio of 2:1 results while co-crystallization from water gives a 1:1 adduct, **6b**.

In **6a**, adjacent molecules of **6** are held together by two different cyclic N-H...O hydrogen-bonded dimers (H...O, 1.94 and 1.96Å) as shown in Figure 4.8. The bipyridyl molecules interact with **6** through a N-H...N hydrogen bond (H...N, 1.77Å). There is also some C-H...O interaction between bipyridyl and **6** (H...O, 2.40Å). The structure of the 1:1 hydrogen-bonded adduct, **6b**, crystallized from water is altogether different from that of the 2:1 hydrogen-bonded adduct **6a**, crystallized from methanol. We show the structure of **6b** in Figure 4.9. In this structure, molecules of **6** form a chain held together by single N-H...O hydrogen bonds (H...O, 2.02Å). The bipyridyl molecules hold the chains together through N-H...N bonds (H...N, 1.92, 1.94Å). The N-H...O bonds forming the chains in **6b** are very much longer than those in **6a**. The N-H...N bond between bipyridyl and **6** is also considerably longer in **6b**.

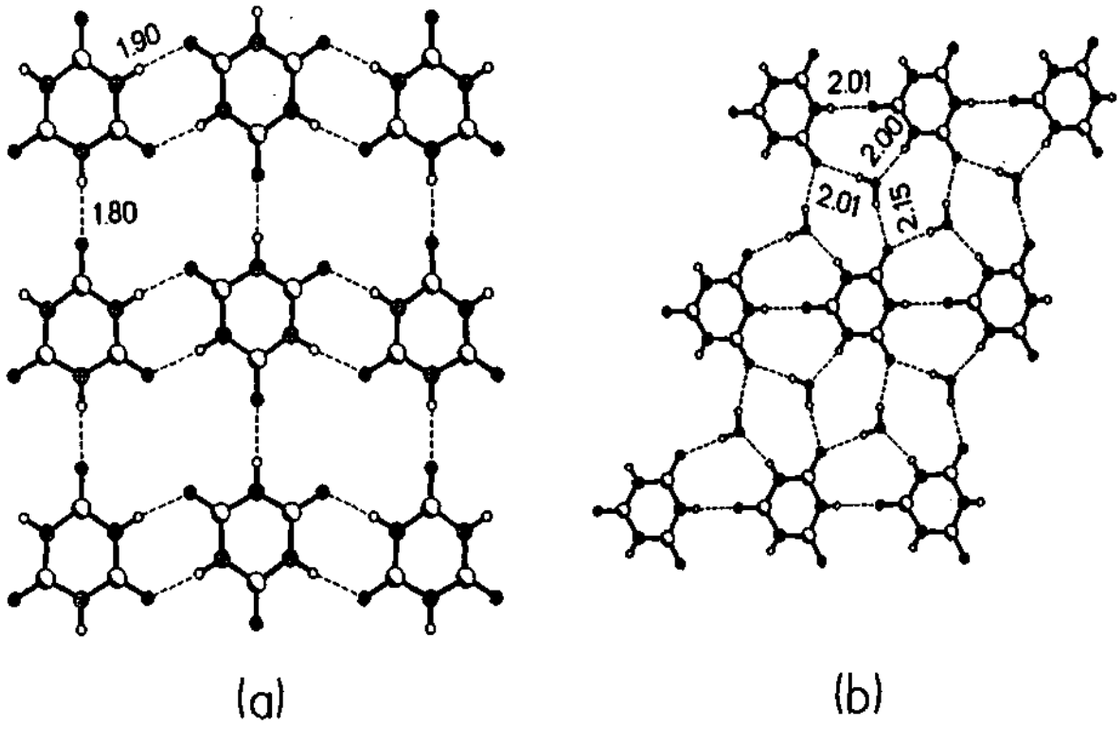
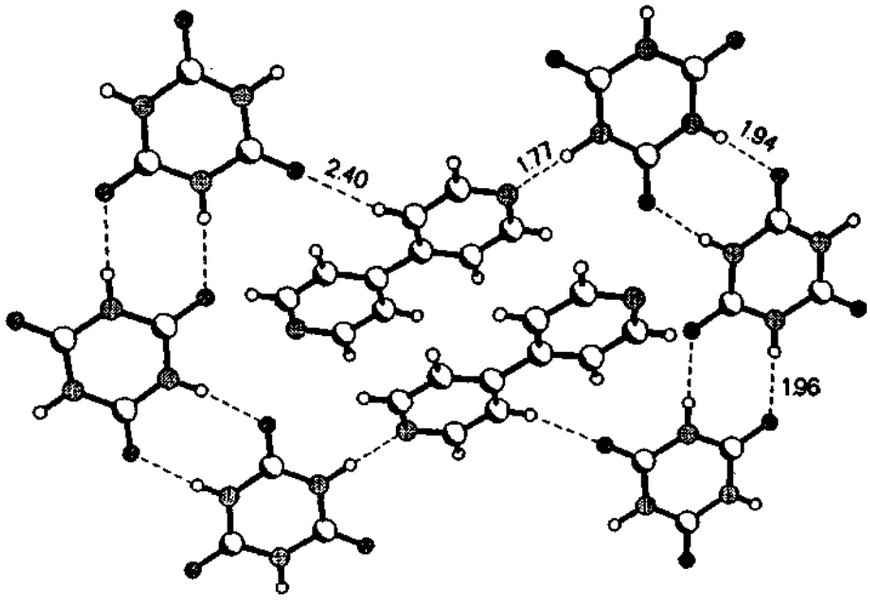


Figure 4.7: (a) Arrangement of cyanuric acid molecules forming tapes and chains in its crystal structure (b) Interaction of water molecules with cyanuric acid forming a planar sheet structure in a two-dimensional arrangement



6a

Figure 4.8: Arrangement of molecules of cyanuric acid, and 4,4'-bipyridyl in the crystal structure of the complex, **6a**. Dashed lines represent hydrogen bonds. Unique hydrogen bond distances are quoted.

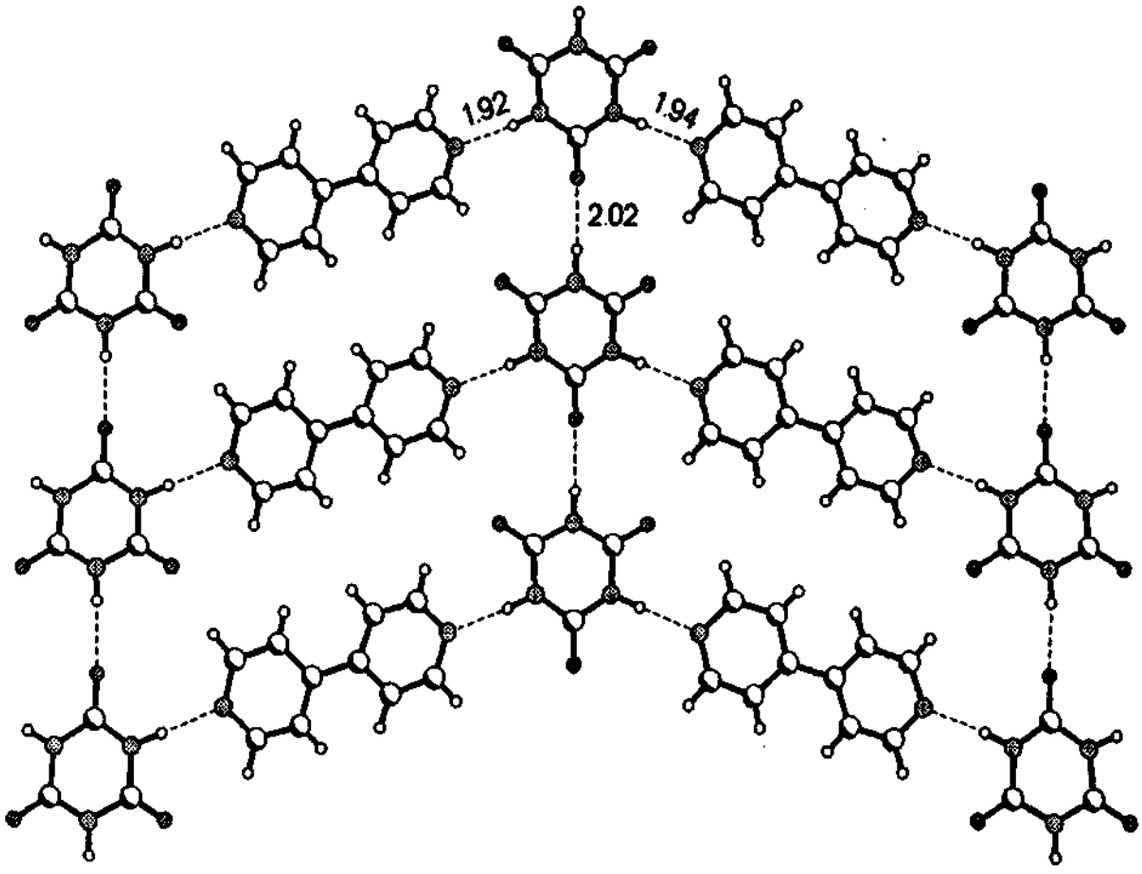


Figure 4.9: Two-dimensional arrangement of molecules of cyanuric acid and 4,4'-bipyridyl in a planar sheet of complex, **6b**

The chain structure of the 1:1 adduct between bipyridyl and **6** (Figure 4.9) is comparable to that of the crystal structure of **6** obtained from crystallization from water (Figure 4.7b), the water being replaced by bipyridyl forming N-H...N bonds (instead of the O-H...O or N-H...O bonds). Interestingly, the N-H...O bonds forming the chains are of comparable length. Similarly, the structure of the 2:1 adduct between **6** and bipyridyl (Figure 4.8) crystallized from methanol bears resemblance to the structure of **6** crystallized from the same solvent (Figure 4.7a) both having cyclic hydrogen bond couplings between

adjacent molecules of **6**. The N-H...O hydrogen bonds in the dimers have comparable dimensions. Thus, the formation of two different hydrogen-bonded adducts between **6** and bipyridyl from methanol and water solvents can be attributed to the presence of different hydrogen bonding networks in the parent structures of **6** crystallized from these solvents.

When one of the N-H groups in **6** is methylated to form N-methylcyanuric acid, **7**, we would expect differences in the nature of the hydrogen-bonded structures formed by them. For example, the formation of the cyclic (dimeric) hydrogen bonds between the amide groups would not be as favoured in **7** compared to **6**. A search on the Cambridge Crystallographic Database (CSD) showed that there was no structural information on **7** in the literature. We have, therefore, carried out a structural study of **7** crystallized from methanol and water. The structural data of **7** crystallized from methanol and water are given in Table 4.1.

N-methylcyanuric acid, **7** yields different hydrogen-bonded assemblies when crystallized from methanol and water, incorporating the solvent of crystallization in the latter case. The structure of **7** crystallized from methanol solution has linear chains formed by N-H...O hydrogen bonds (H...O, 1.87Å). These chains are held together through N-H...O (H...O, 1.78Å) bonds on one side and by weak C-H...O interaction (H...O, 2.87Å) on the other. This results in a hexagonal network involving molecules of **7** as shown in Figure 4.10a.

Table 4.1: Structural data for N-methylcyanuric acid crystallized from methanol and water

	a, Å	b, Å	c, Å	α, °	β, °	γ, °	Crystal System, Space group	Z	Volume Å^3	R_1, wR_2
N-methylcyanuric acid	6.743(2)	6.306(2)	13.612(4)	90	90	90	orthorhombic, Pnma	4	578.8(1)	0.050, 0.107
N-methylcyanuric acid.H_2O	6.695(2)	6.275(2)	8.375(2)	90	105.06(4)	90	monoclinic, $P2_1/m$	2	339.8(2)	0.057, 0.088

Table 4.2: Hydrogen bond distances [in Å] in cyanuric acid, N-methylcyanuric acid and their adducts, with 4,4'-bipyridyl

Hydrogen bond	cyanuric acid	6a	cyanuric acid.H_2O	6b	N-methylcyanuric acid	N-methylcyanuric acid.H_2O	N-methylcyanuric acid.bipyridyl
H...O (N-H...O)[a]	1.80	-	2.01	2.02	1.87[f]	1.82	-
H...O (N-H...O)[b]	1.90	1.94, 1.96	-	-	-	-	-
H...N (N-H...N)[c]	-	1.77	-	1.92, 1.94	-	-	1.83
H...O (C-H...O)[d]	-	2.40	-	-	2.87	-	2.49, 2.73
H...O (O-H...O)[e]	-	-	2.01, 2.15	-	-	1.88, 2.05	-

a) single N-H...O bond forming chains between cyanuric acid molecules; b) cyclic dimer formed between two cyanuric acid molecules; c) N-H...N bond between 4,4'-bipyridyl and cyanuric acid (N-methylcyanuric acid) d) C-H...O interaction; e) O-H...O bonds formed by water molecules; water molecules also form N-H...O bonds using the oxygen lone pair with H...O distances of 2.00 and 1.92Å respectively in cyanuric acid.H_2O and N-methylcyanuric acid. f) There is an additional N-H...O bond (H...O, 1.78Å) between the N-methylcyanuric acid molecules.

N-methylcyanuric acid obtained by crystallization from water, has a structure similar to that of cyanuric acid obtained from water (see Figure 4.7).

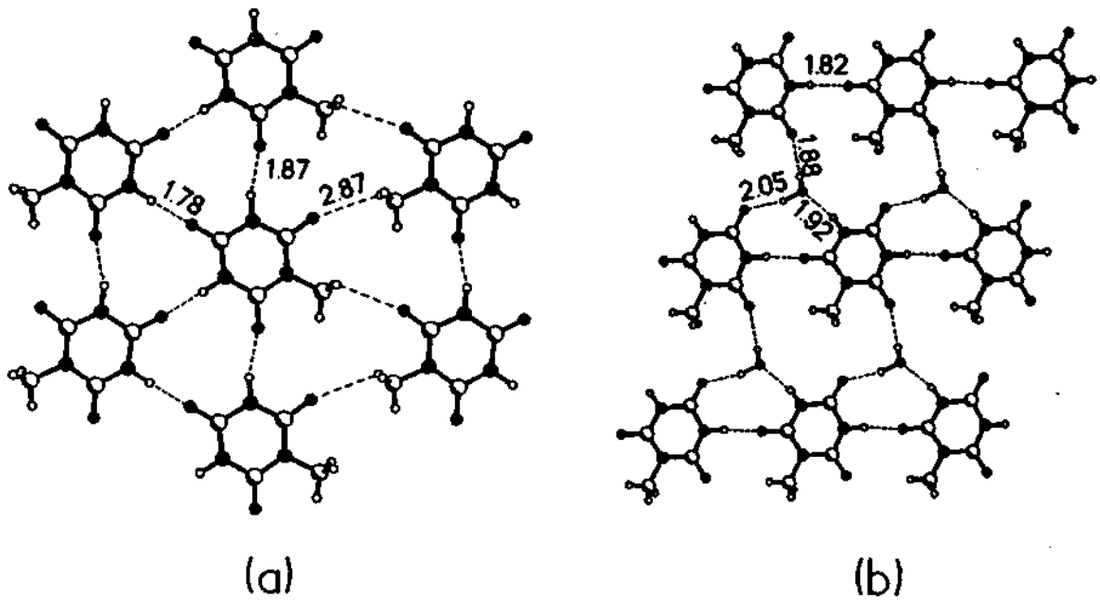
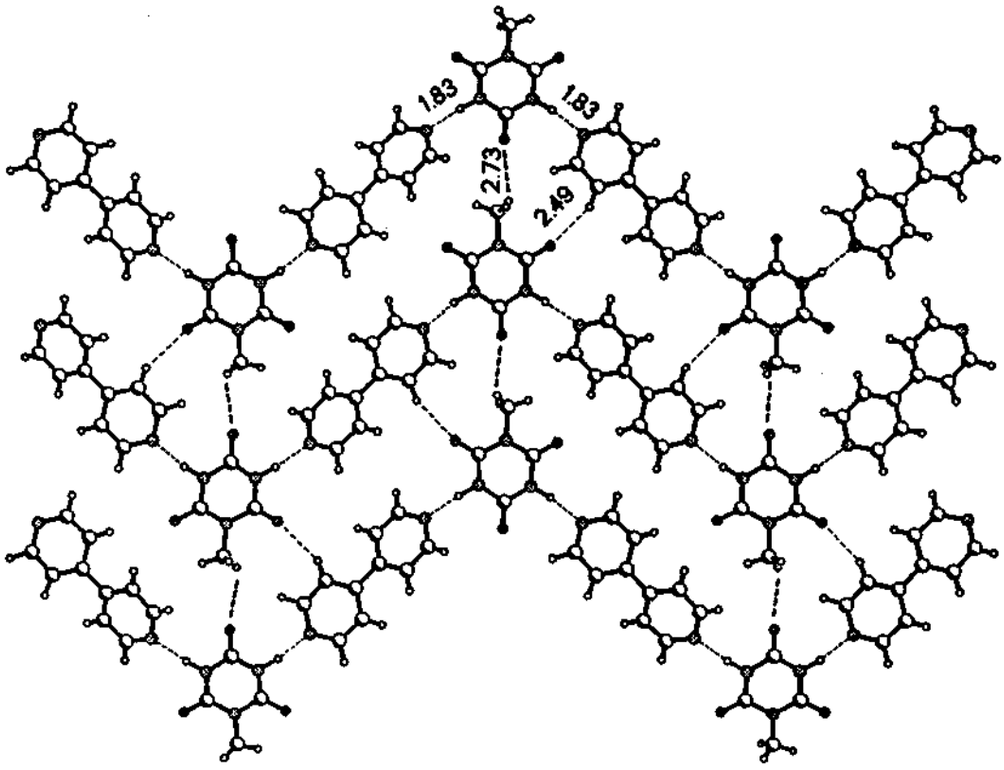


Figure 4.10: (a) Hexagonal arrangement of molecules of N-methylcyanuric acid, crystallized from methanol. (b) Interaction of water molecules with N-methylcyanuric acid in a two-dimensional planar sheet

The structure involves chains of molecules of **7** formed by N-H...O hydrogen bonds (H...O, 1.82Å), are connected together by water molecules forming O-H...O and N-H...O hydrogen bonds (H...O 1.88 - 2.05Å) as shown in Figure 4.10b. It is evident from Figure 4.10 that unlike cyanuric acid, N-methylcyanuric acid crystallizes in chain structures involving single hydrogen bonds from both the solvents, the cyclic hydrogen-bonded dimers being disfavoured by the presence of the methyl group.

The 1:1 adduct, **7a** formed between N-methylcyanuric acid and 4,4'-bipyridyl crystallized from either methanol and water has the same

structure. The two-dimensional arrangement of molecules in **7a** is shown in Figure 4.11. Amazingly, the linear chains of molecules of **7** only involve weak C-H...O interaction (H...O, 2.73Å).



7a

Figure 4.11: Arrangement of molecules of N-methylcyanuric acid and 4,4'-bipyridyl in the crystal structure of the complex, **7a**

The chains are actually the consequence of the positioning of the molecules of **7** along the chain, through strong N-H...N bonds (H...N, 1.83Å) with bipyridyl, besides the strong C-H...O interaction (H...O, 2.49Å) between the two molecules. This C-H...O interaction is considerably stronger than that between the molecules of **7** in the linear chain or in the parent **7** crystals (Figure 4.10a).

In Table 4.2, we have listed the hydrogen-bonded distances in cyanuric acid and N-methylcyanuric acid structures.

4.3 Organic porous solids formed by the hydrogen-bonded self-assembly of trithiocyanuric acid and 4,4'-bipyridyl

We have carried out a systematic study of the supramolecular hydrogen-bonded assemblages obtained from the crystallization of trithiocyanuric acid with 4,4'-bipyridyl in a variety of solvents.

4.3.1 Adduct of trithiocyanuric acid, 8 and 4,4'-bipyridyl from methanol solution

Co-crystallization of trithiocyanuric acid, **8** with 4,4'-bipyridyl from methanol solution gives a 2:1 hydrogen-bonded adduct containing the solvent of crystallization. The crystal structure of the adduct reveals the presence of intermolecular N-H...N hydrogen bonds between **8** and the bipyridyl as shown in Figure 4.12. This hydrogen-bonded structure has a cavity of 10Å in dimension, occupied by methanol molecules. These crystals are unstable under ambient conditions because of the evaporation of methanol.

4.3.2 Adduct of trithiocyanuric acid, 8, 4,4'-bipyridyl and benzene

The 2:1 adduct of **8** with 4,4'-bipyridyl incorporating benzene was highly stable. The molar ratio of benzene and bipyridyl was 1:1. These crystals also gave the same two-dimensional hydrogen-bonded structure as in Figure 4.12. Besides the N-H...N bonds (H...N, 2.77Å) responsible for the formation of the cavity, there are weak C-H...S bonds (H...S, 2.91, 2.93Å) between **8** and 4,4'-bipyridyl. There are N-H...S hydrogen bonds between the trithiocyanuric acid molecules (H...S, 2.5Å).

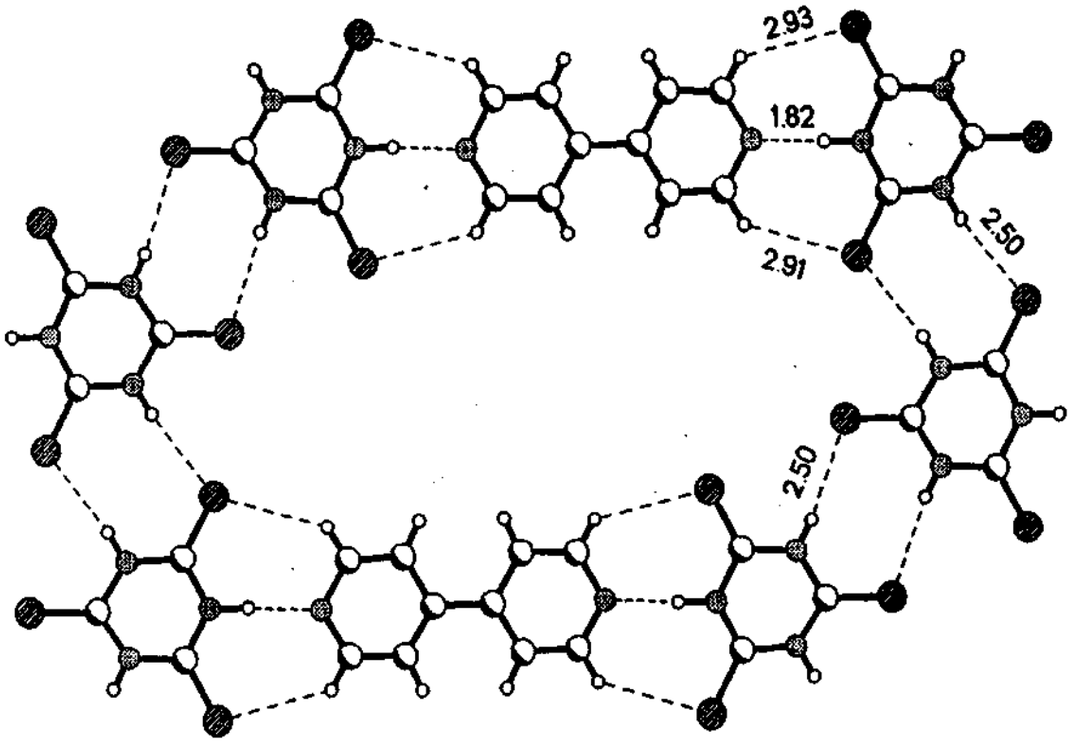
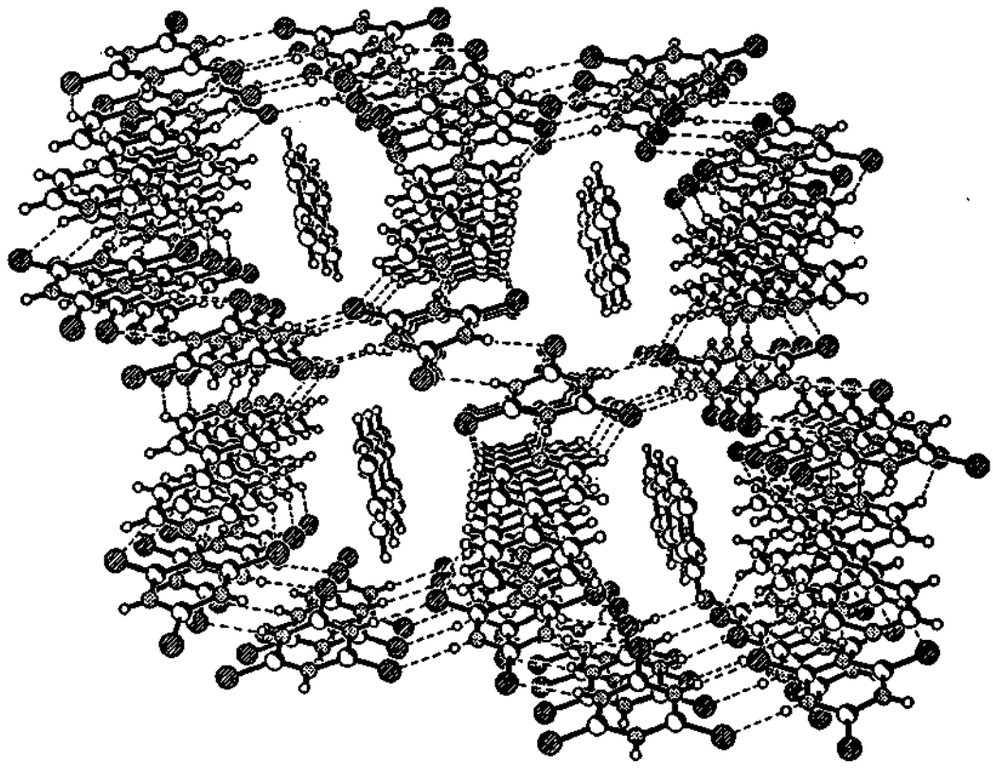


Figure 4.12: Self-assembly of trithiocyanuric acid, **8** and 4,4'-bipyridyl forming a layered network with a cavity

Besides the N-H...N bonds (H...N, 2.77Å) responsible for the formation of the cavity, there are weak C-H...S bonds (H...S, 2.91, 2.93Å) between **8** and 4,4'-bipyridyl. There are N-H...S hydrogen bonds between trithiocyanuric acid molecules (H...S, 2.5Å).

The three-dimensional structure of the 2:1 adduct of trithiocyanuric acid, **8** and 4,4'-bipyridyl with benzene is shown in Figure 4.13. The structure clearly reveals the presence of channels formed by the stacking of the layers with cavities. The channels accommodate benzene molecules as can be seen in Figure 4.8.



8a

Figure 4.13: Three-dimensional structure of the 2:1 trithiocyanuric acid-4,4'-bipyridyl adduct, **8a** containing benzene in the channels

Furthermore, an interesting feature is that the crystals were stable and heating them to 180°C or slightly higher did not destroy the crystals. Hence, we were interested to see whether the channel structure will remain intact even after the removal of benzene molecules to have zeolite type structure. In this connection, thermogravimetric analysis was carried out for the crystals of **8a**.

In Figure 4.14(a), the TGA curve of the benzene adduct is shown, recorded at a heating rate of 2°C min^{-1}. We see that all the benzene (mass loss, 13%) is removed around 190°C which is well above the boiling point of benzene (shown in curve 1). After the removal of benzene, the host crystals soaked in benzene for several hours were

again subjected for TGA. These crystals showed a loss of benzene at a lower temperature (158°C).

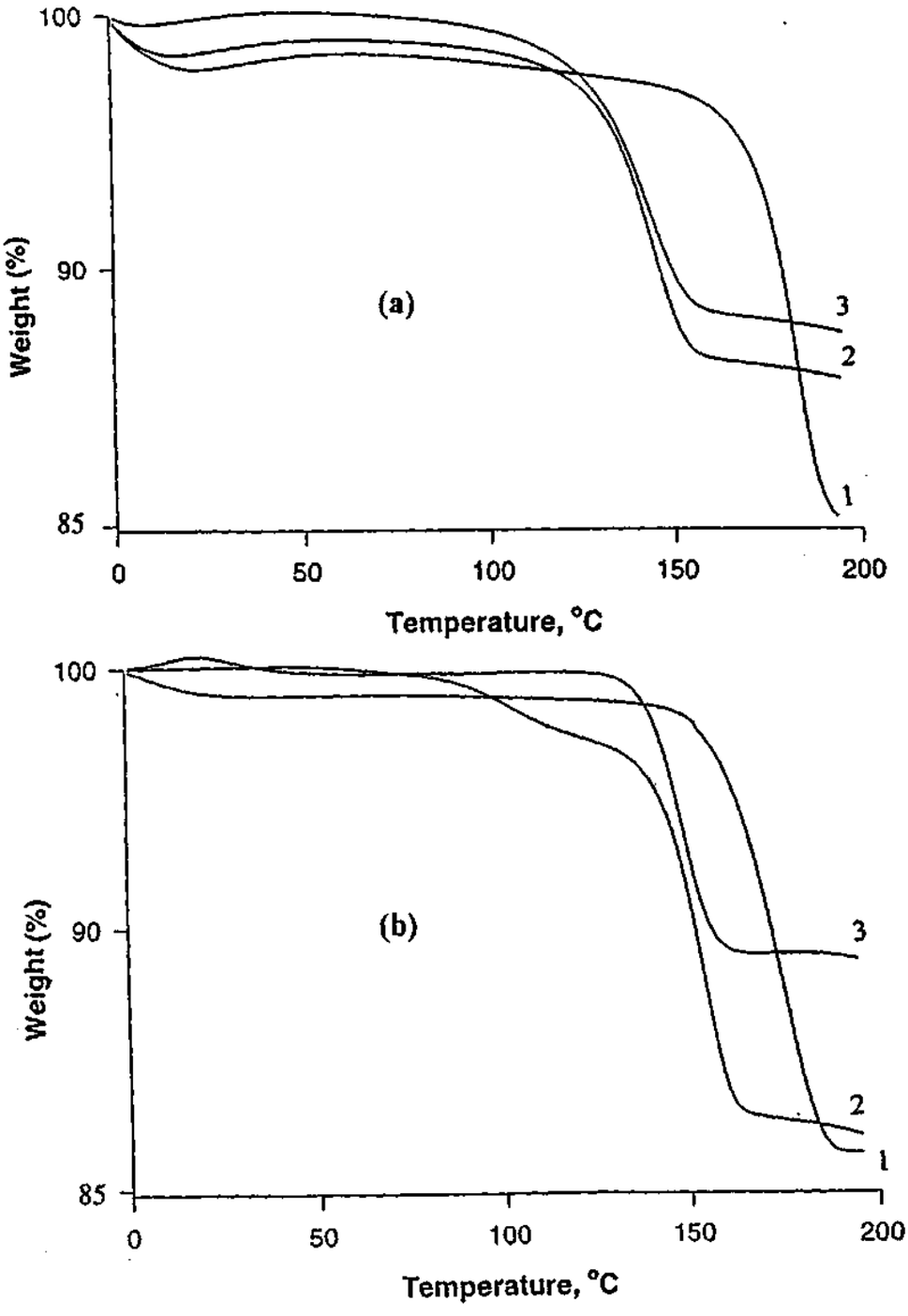


Figure 4.14: Thermogravimetric analysis of the adducts, (a) **8a** and (b) **8b**

Furthermore, the amount of benzene in the channels is less by about 4% as can be seen from curve 2 in Figure 4.14a (see Table 4.3 for results for TGA). A repetition of this procedure showed that the removal of benzene continued to occur around the same temperature (158°C) with the same mass loss (curve 3 in Figure 4.14a). It thus appears that after the benzene in the channels of the initial adduct is removed, the empty channel can accommodate benzene which is removed around 158°C.

The crystal structure of the adduct, **8a** heated to 200°C (to remove all the benzene) gave a single crystal X-ray diffraction pattern, although the data were not sufficiently good to obtain the detailed structure. The dimensions of the unit cell remained essentially the same as those of the parent adduct. The unit cell parameters of the adduct with empty channels were: a=7.181, b=10.455, c=10.956Å, α=63.80°, β=77.70° and γ=75.82°. Encouraged by the findings, we were interested to see whether the solvent molecules, benzene, in the channels can be exchangeable with other molecules and also prevalence of shape selectivity. So, **8** and 4,4'-bipyridyl were co-crystallized in various solvents like toluene, different isomers of xylenes and anthracene.

4.3.3 Adduct of trithiocyanuric acid, 4,4'-bipyridyl and toluene

Trithiocyanuric acid, **8** and 4,4'-bipyridyl indeed formed a structure, **8b**, with toluene, identical to that of **8a**, with a three-dimensional channel structure (refer Figure 4.13) except that benzene molecules are replaced by the toluene molecules. Further, TG analysis reveals that the channel structure remains intact even in the absence of the toluene molecules. TGA of the toluene adduct (Figure 4.14b) shows

a mass loss of 14.8% at 183°C (curve 1). The host crystal with the empty channels soaked in toluene and then subjected to TGA, gives a mass loss of 9.2% at 166°C (curve 2). A repetition of the procedure shows that the same mass loss occurs at 162°C (curve 3). The behaviour is similar to that of the benzene adduct (Table 4.3).

4.3.4 Adduct of trithiocyanuric acid, 4,4'-bipyridyl and p-xylene

Co-crystallization of **8** with 4,4'-bipyridyl from *p*-xylene yields a complex, **8c**, in 2:1:1 ratio similar to that of **8a** and **8b**. TGA of the p-xylene adduct shows a mass loss (12.2%) due to the removal of *p*-xylene around 167°C (curve 1 in Figure 4.15a). After re-incorporation of *p*-xylene in the channels, the mass loss occurs around 139°C, but the magnitude of mass loss is smaller (7%) as can be seen from curve 2 in Figure 4.15a. The temperature of decomposition and the mass loss remain the same in further cycling (curve 3 of Figure 4.15a). The TGA data of **8a-8e** are summarized in Table 4.3.

4.3.5 Adduct of trithiocyanuric acid and 4,4'-bipyridyl with o- and m-xylenes

Unlike **8a-8c**, co-crystallization of trithiocyanuric acid and 4,4'-bipyrdiyl with *o*- and *m*-xylenes formed slightly different lattices, **8d** and **8e** respectively as evident from the unit cell dimensions as shown in Table 3.1. Although, the basic recognition pattern and cavity structure is similar to **8a-8c**, the two-dimensional network shows expanded cavity as shown in Figure 4.16 for the adduct of **8e** obtained from *m*-xylene. The corresponding three-dimensional channel structure is given in Figure 4.17.

In addition, an interesting feature is that the crystals of **8d** and **8e** appear to be unstable with the removal of the corresponding solvent molecules as they could not be re-incorporated after their removal from the *as-prepared* crystals.

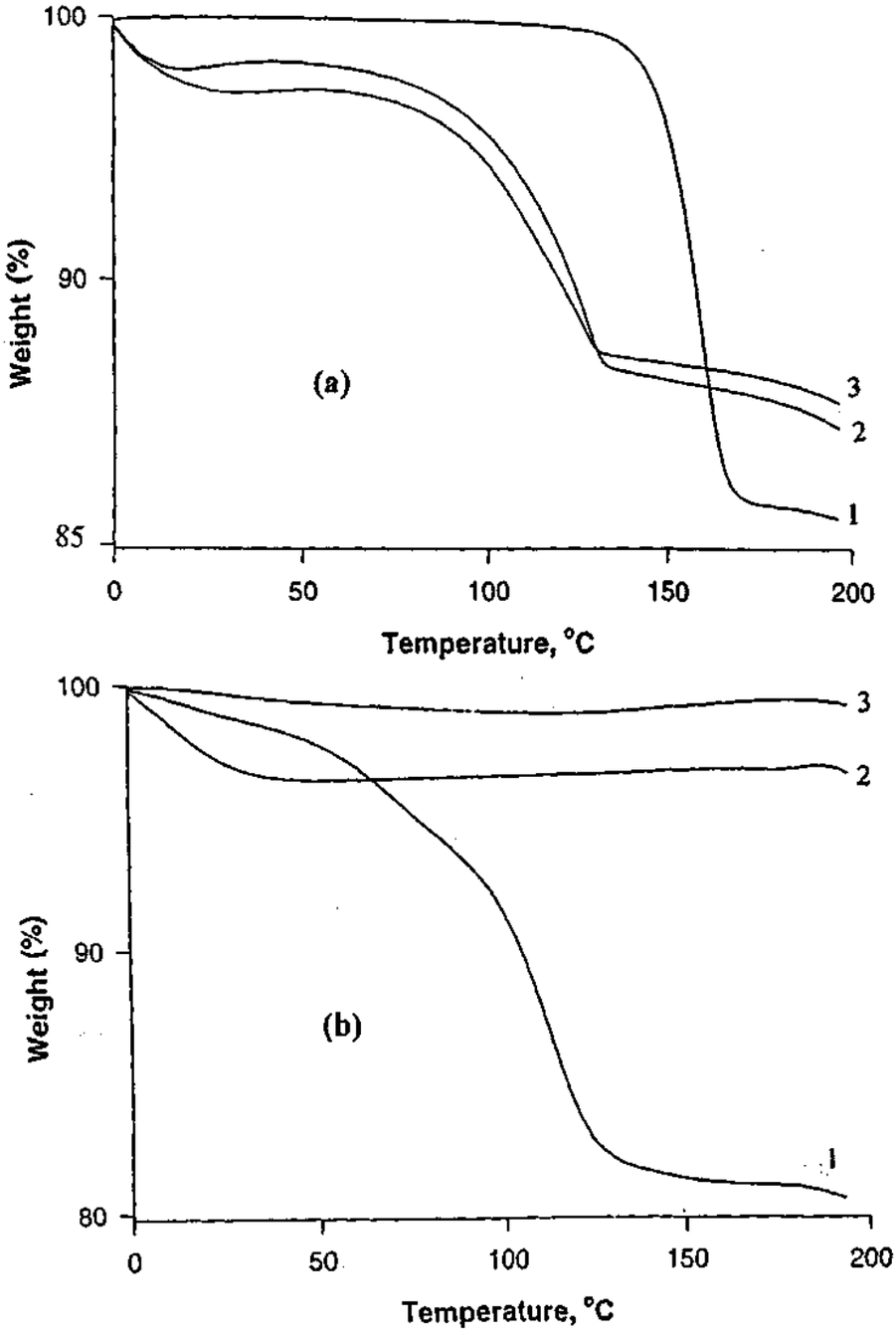
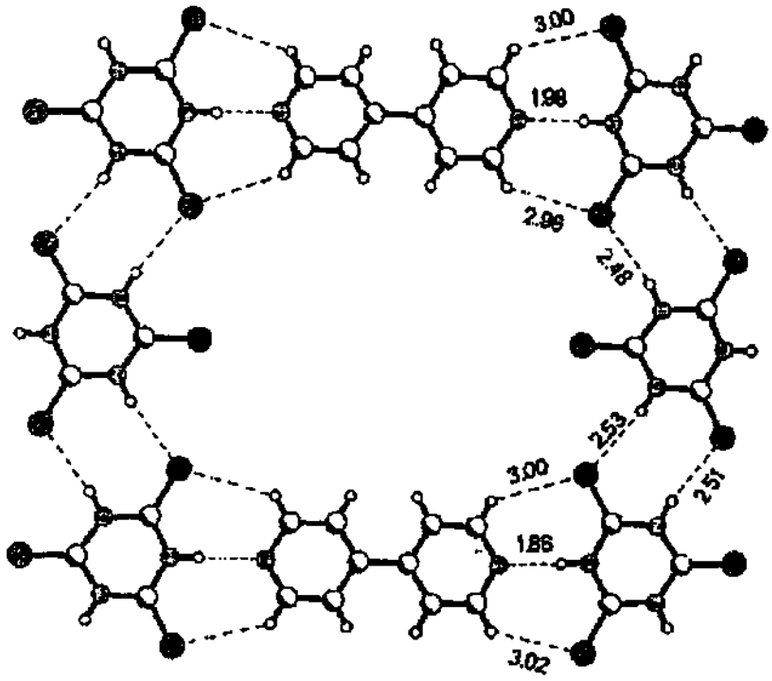


Figure 4.15: Thermogravimetric analysis curves of the adducts (a) **8d** and (b) **8e**

Table 4.3: Summary of the results of thermogravimetric analysis (TGA)

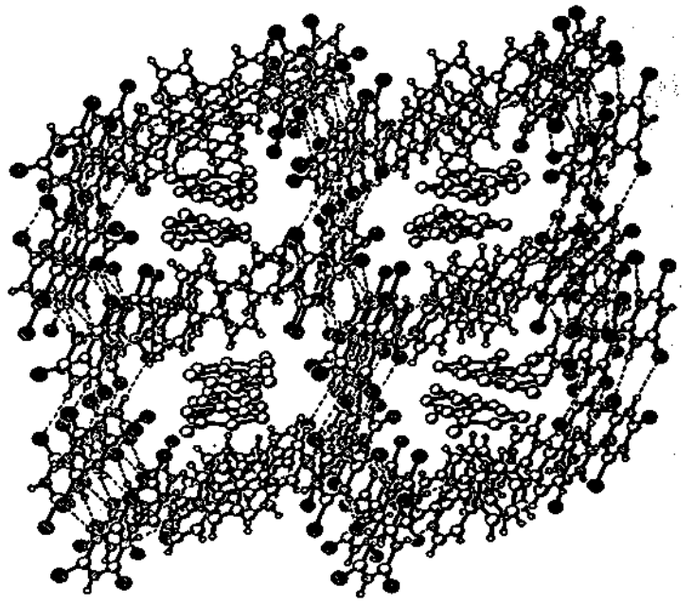
Complex	First heating		Second heating		Third heating	
	Weight loss[a] (%)	Temp. °C	Weight loss (%)	Temp °C	Weight loss (%)	Temp. °C
Benzene	13.86(13.26)	192	9.70	158	9.24	157
Toluene	14.81(15.26)	183	9.23	166	9.26	162
o-Xylene	16.16(17.18)	172	-	-	-	-
m-Xylene	17.67(17.18)	131	-	-	-	-
p-Xylene	12.24(12.15)	167	6.84	139	7.96	143

[a] numbers in the parenthesis correspond to the calculated weight loss based on the contents of the unit cell.



8e

Figure 4.16: Two-dimensional arrangement of the molecules of **8** and 4,4'-bipyridyl in the complex, **8e**, with m-xylene



8e

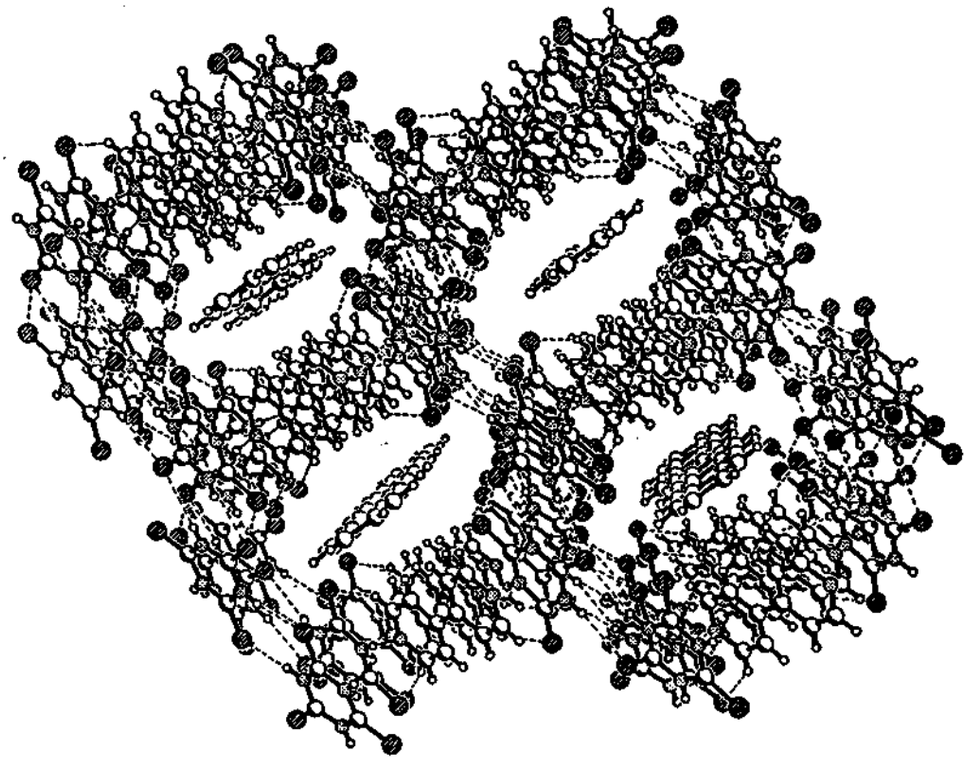
Figure 4.17: Three-dimensional arrangement of molecules in the crystal structure of **8e** shown channels occupied by *m*-xylene molecules

Typical TGA data is shown for the *m*-xylene adduct in Figure 4.15b. The as-prepared adduct of *m*-xylene undergoes a mass loss (17%) at 131°C (curve 1). However *m*-xylene could not be put back in the channels even after soaking the host crystals with empty channels in *m*-xylene for long periods. This is confirmed by the TGA curves 2 and 3 in Figure 4.11b which shows no mass loss corresponding to m-xylene (Table 4.3). The behaviour of the *o*-xylene adduct was similar to that of the *m*-xylene adduct, in that *o*-xylene could not be reintroduced into the channels once it was removed at 172°C from the as-prepared adduct. Clearly, there is some selectivity in the channels of the trithiocyanuric acid-4,4'-bipyridyl adduct. This can be understood from the obvious differences in the shapes of *p*-, *o*- and *m*-xylenes. In *p*-xylene, the two methyl groups are symmetrically positioned and favour the ready re-incorporation into the channels of the host crystal. This is not the case in the other two isomers. Accordingly, the empty channels of the trithiocyanuric acid-4,4'-bipyridyl adduct only take in *p*-xylene from a mixture of the three xylene isomers. Furthermore, no crystals were obtained when mesitylene is the solvent of crystallization to form an adduct between **8** and 4,4'-bipyridyl and supports the shape selectivity of the channels towards guest molecules.

4.3.6 Adduct of trithiocyanuric acid and 4,4'-bipyridyl with anthracene

In the further continuation of the work, we intended to accommodate larger molecules like naphthalene and anthracene in the channels of the adduct of **8** and 4,4'-bipyridyl. We present here, the results obtained with anthracene. **8** and 4,4'-bipyridyl upon co-crystallization with anthracene from methanol solution yields a

structure, **8f**, as shown in Figure 4.18. The molecules of **8** and bipyridyl form a hexagonal network with channels in three-dimensional arrangement which are being occupied by anthracene molecules. The three-dimensional structure of the adduct of trithiocyanuric acid and 4,4'-bipyridyl with anthracene is shown in Figure 4.18. It is seen that trithiocyanuric acid and bipyridyl form channels that accommodate anthracene.



8f

Figure 4.18: Three-dimensional structure of adduct, **8f** with anthracene in the channels

The three-dimensional channels of the organic porous solid formed by the supramolecular hydrogen-bonded assembly of trithiocyanuric acid and 4,4'-bipyridyl can accommodate aromatic molecules like benzene, toluene, p-xylene and anthracene. This porous

solid is thermally stable upto 200°C and exhibits shape selectivity with respect to the xylene isomers. The channels do not accommodate mesitylene.

4.4 Hydrothermal synthesis of organic channel structures formed by melamine with cyanuric and trithiocyanuric acids

The 1:1 adduct, **9a**, between cyanuric acid, **6** and melamine, **9** prepared by hydrothermal methods has asymmetric unit consisting of the molecules of **6** and **9** with 50% occupancy of each. An ORTEP drawing of the superimposed asymmetric unit is shown in Figure 4.19. Packing analysis shows that **6** and **9** are held together by N-H...O and N-H...N hydrogen bonds yielding the hexamer (rosette) shown in Figure 4.20.

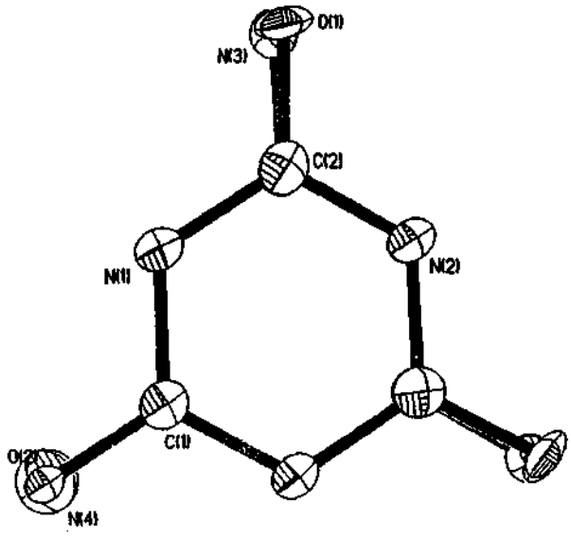
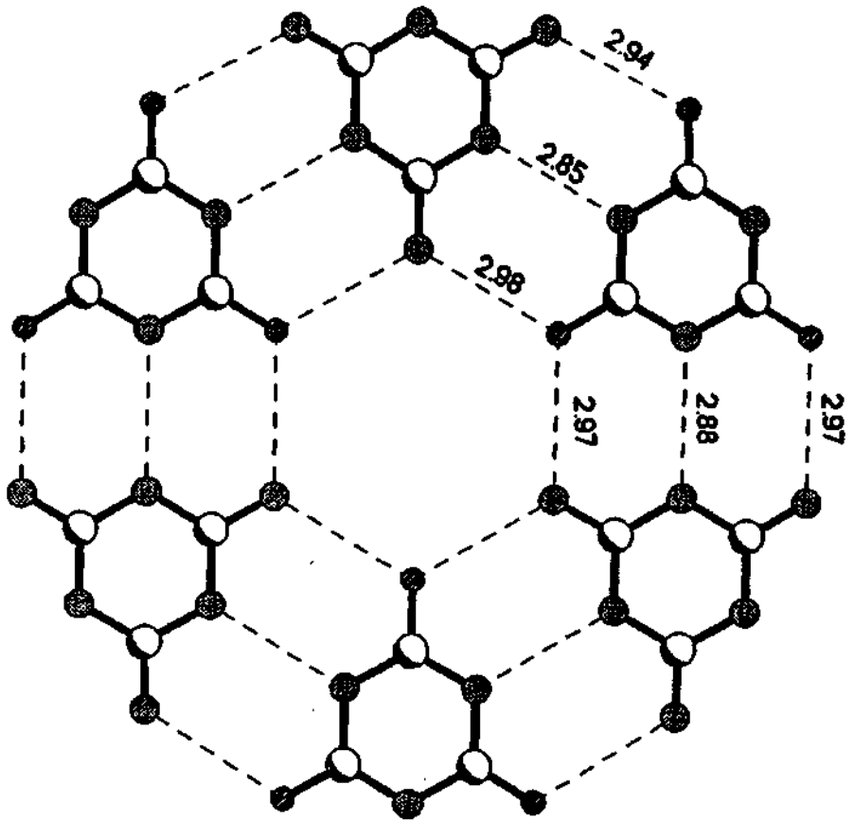


Figure 4.19: An ORTEP drawing showing the superimposed asymmetric unit in the crystal lattice of **9a**



9a

Figure 4.20: Hexagonal arrangement of the molecules of **6** and **9** forming a rosette structure in the adduct, **9a**.

The interatomic N...O and N...N distances corresponding to N-H...O and N-H...N bonds are in the range of 2.94-2.98Å and 2.85-2.88Å respectively. The hexamers are arranged in two dimensions to form planar sheets, the structure being exactly as predicted by Whitesides (refer Scheme 2.2). A significant feature is that the planar sheets are stacked in three dimensions to give channels with a diameter of 4Å (Figure 4.21). These channels are comparable to the cavities in cryptands.

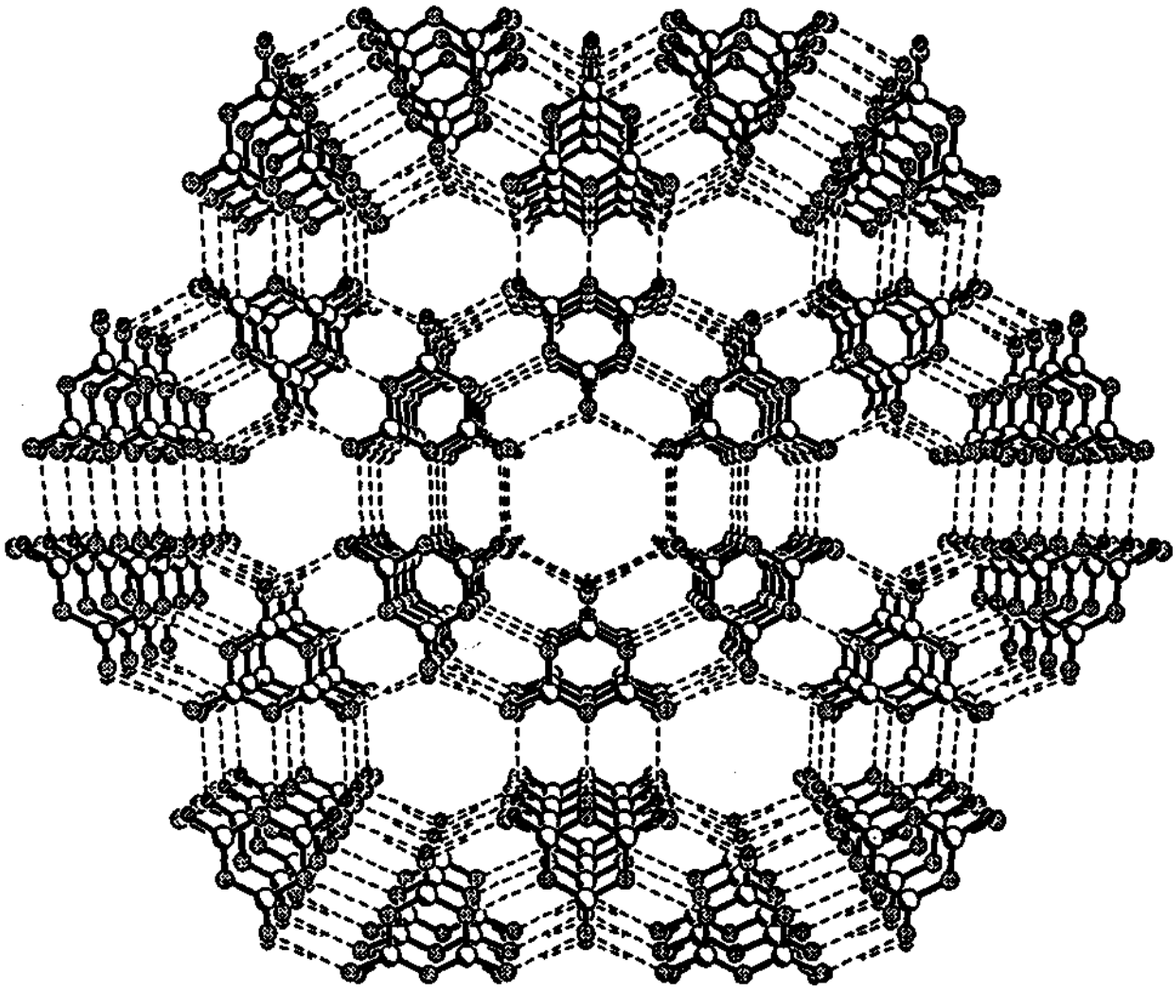


Figure 4.21: Three-dimensional arrangement of the sheets in the adduct **9a** forming channels.

Crystal structure of the adduct, **9b**, corresponding to trithiocyanuric acid, **8** and melamine, **9** reveals that it also has features similar to those of **9a** with a superimposed asymmetric unit (Figure 4.22), except that the N-H...O hydrogen bonds are replaced by the N-H...S hydrogen bonds as shown in Figure 4.23.

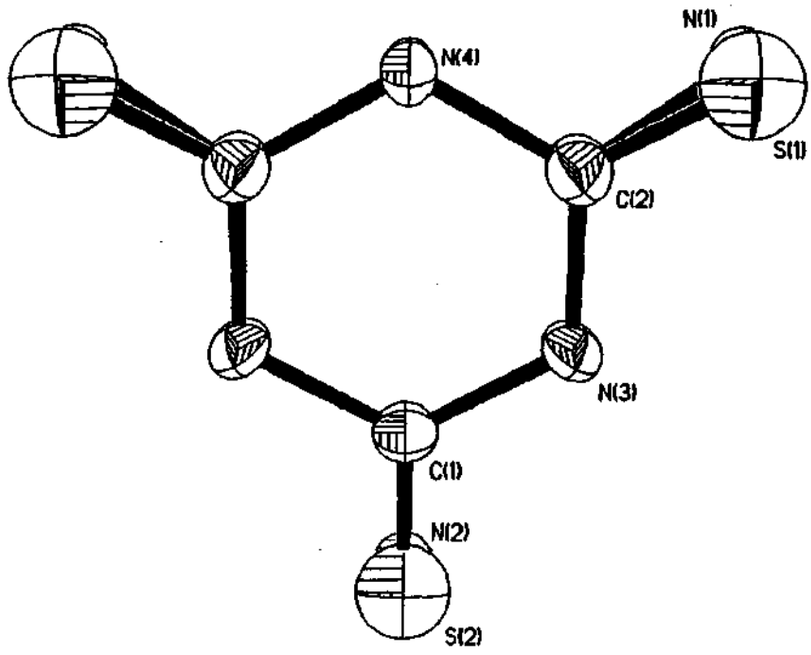
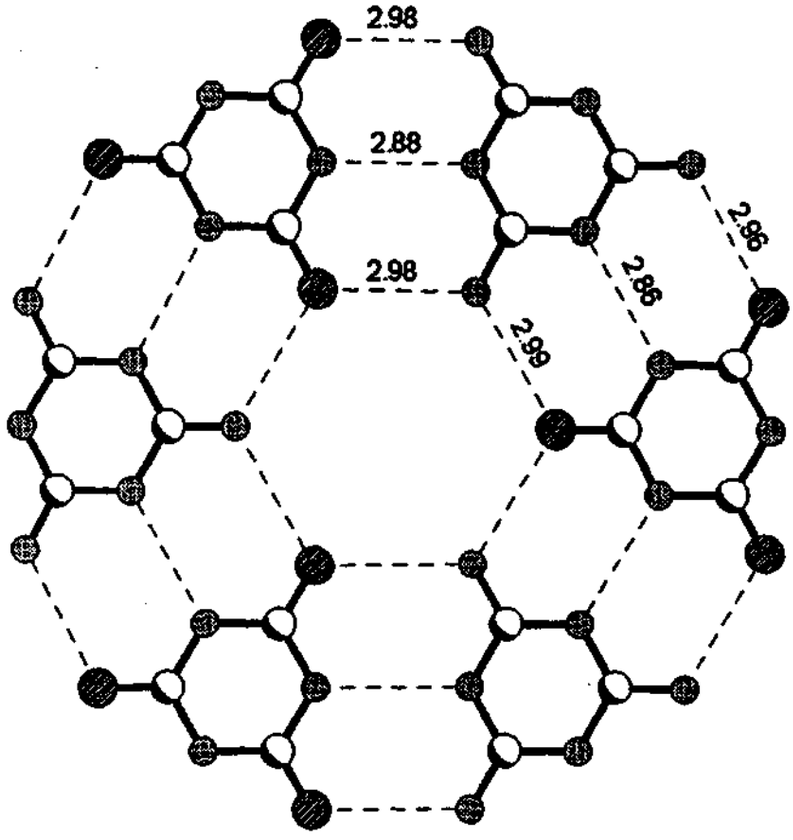


Figure 4.22: Asymmetric unit of the crystal lattice, **9b**.



9b

Figure 4.23: Rosette structure noticed in the adduct, **9b**.

The N...S and N...N distances corresponding to N-H...S and N-H...N bonds are in the range of 2.96-2.98Å and 2.86-2.88Å respectively. The sheets are stacked in a three-dimensional channel arrangement as depicted in Figure 4.24. The diameter of the channel as shown in Figure 4.24 is approximately 4Å here as well.

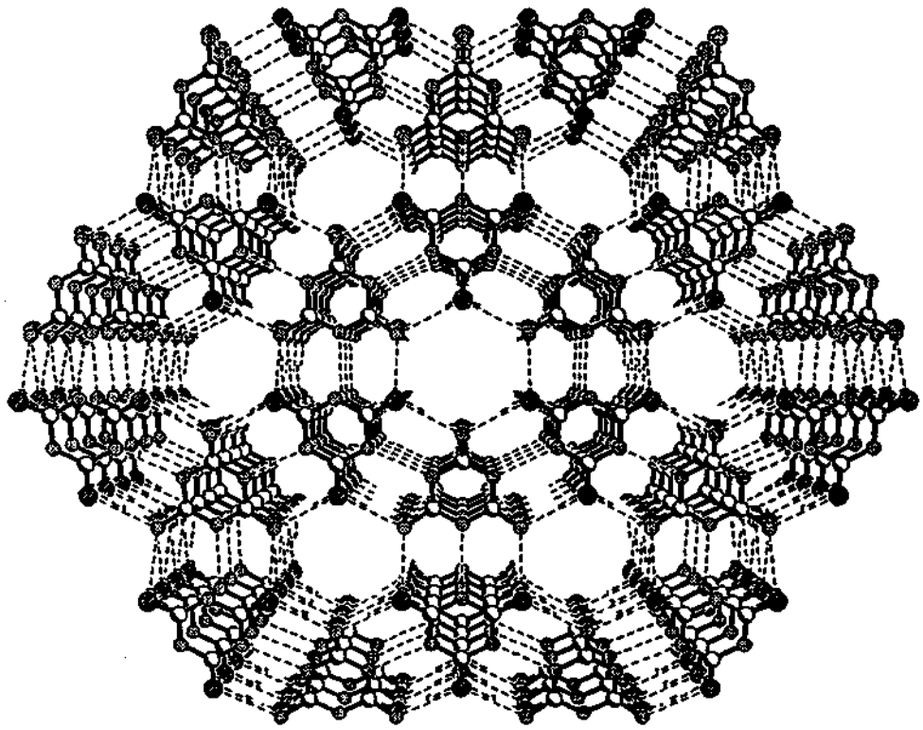


Figure 4.24: Three-dimensional arrangement of the sheets in the crystal structure of **9b**

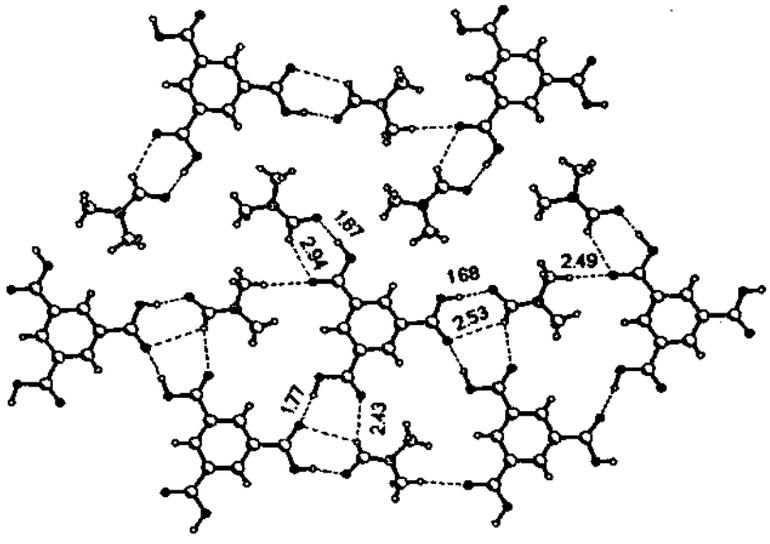
4.5 Channel structures formed by self-assembled four - membered networks of trimesic acid

Trimesic acid generally forms hexagonal networks which are formed through the formation of O-H...O hydrogen bond couplings between the adjacent carboxylic groups. However, in our exploration, we have found that a rectangular network as was reported by Herbstein in the complex of trimesic acid with picric acid is also equally

promising in the formation of novel assemblies and indeed gives nice channel structures. Our investigation in fact was originated with the attempts to crystallize trimesic acid, **10**, with dimethylformamide (DMF). It is known in the literature that the acid **10** forms a crystal structure with dimethylamine rather than DMF upon crystallization of the acid from DMF.[51] This prompted us to explore the possible methods to incorporate DMF itself into the crystal structure of the acid, **10**. In this connection, we attempted to crystallize acid, **10** from a mixture of DMF and benzene solvent with a view that **10** while crystallizing from benzene, can trap DMF molecules into the lattice.

4.5.1 Hydrogen-bonded adduct of trimesic acid with dimethylformamide

Crystallization of **10** with DMF in the presence of benzene yields **10a** which comprises of two-dimensional molecular tapes formed between the molecules of **TMA** and DMF through hydrogen bonds.



10a

Figure 4.25: Two-dimensional sheet structure formed between trimesic acid, **10** and DMF in the crystal structure of **10a**.

The two-dimensional arrangement of the molecules in a sheet are shown in Figure 4.25. Out of the three carboxyl groups, two of them interact with DMF molecules forming a cyclic coupling consisting of O-H...N and C-H...O hydrogen bonds. The corresponding H...O distances are 1.67, 1.68 and 2.53, 2.94Å respectively. The third carboxyl group forms O-H...O (H...O, 1.77Å) and C-H...O (H...O, 2.43Å) hydrogen bonds. In the further continuation to explore the influence of mixed solvents on the pattern of crystallization of acid **10**, we attempted to crystallize it from methanol/benzene.

4.5.2 Trimesic acid with methanol

Interestingly, acid, **10** forms crystals, **10b** upon crystallization from methanol/benzene in which four adjacent trimesic acid molecules are connected to each other through regular symmetrical O-H...O hydrogen bonds as well as by single O-H...O hydrogen bonds leading to the formation of a four-membered network rather than usual hexagonal network. Here, two sides of the network are made up of dimeric hydrogen bonds between the trimesic acid molecules (O...O, 2.61 and 2.64Å) and these sides are connected to each other through H_2O molecules by O-H...O bonds (O...O, 2.61 and 2.87Å), to yield planar sheets. This structure is similar to the one described by Herbstein and Marsh. These sheets are stacked in a three-dimensional arrangement yielding channels occupied by methanol molecules as shown in Figure 4.26.

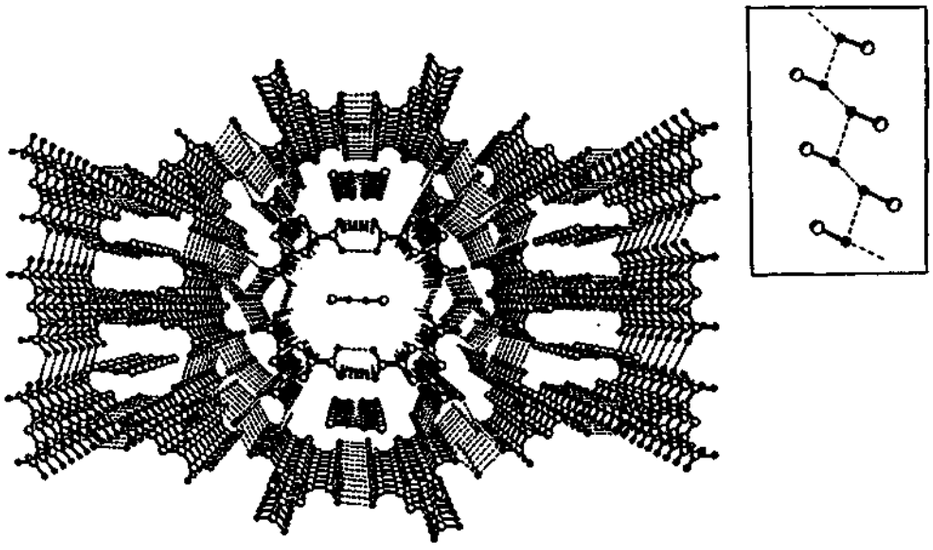


Figure 4.26: Three-dimensional arrangement in the crystal structure of trimesic acid, obtained from the crystallizaton from methanol/benzene. In the inset, a polymeric chain of methanol molecules present in the channels are shown.

The methanol molecules are hydrogen-bonded to one another (as shown in the inset of Figure 4.26). Such a polymeric chain of methanol molecules with O-H...O hydrogen bonds (O...O, 2.43Å) has not been isolated or characterized hitherto and this has been possible in the present study since the methanol molecules are present in the channel.

4.5.3 Trimesic acid with acetone

Structures exactly identical to the one shown in Figure 4.26 are also obtained for trimesic acid upon its crystallization from acetone. The only difference between the structures with methanol and acetone is that the methanol molecules in Figure 4.26 are replaced by molecules of acetone in Figure 4.27. However, the positions of the

atoms corresponding to the acetone molecules could not be refined to a satisfactory level.

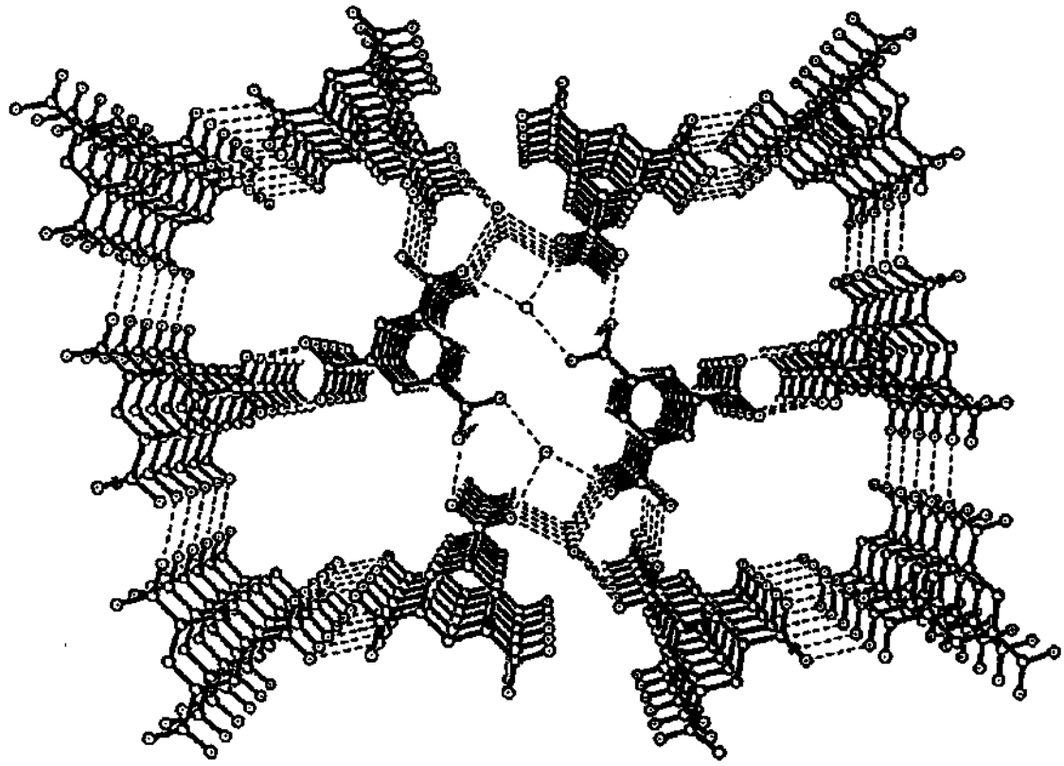


Figure 4.27: Three-dimensional arrangement in the crystal structure of trimesic acid, obtained by crystallization from acetone. Acetone molecules are not shown in the channels

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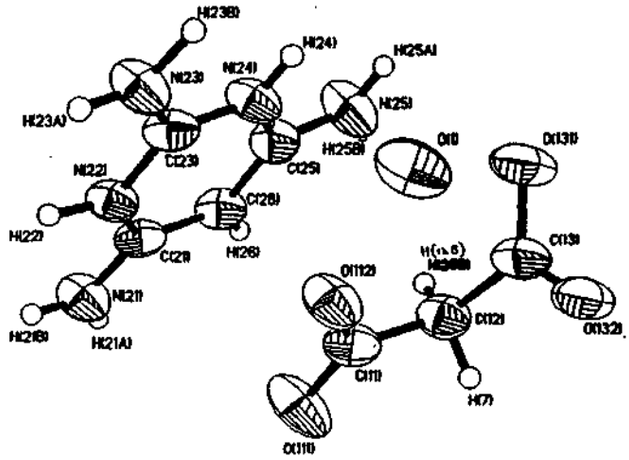
Table A1. Fractional Coordinates and Equivalent Isotropic Displacement Parameters [$Å^2$] of 2,4,6-triaminopyrimidine + malonic acid, **1a**.

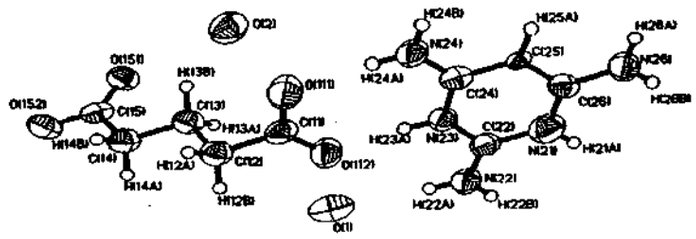
Atom	x/a	y/b	z/c	U_{eq}
N(22)	0.7435(2)	0.0997(3)	0.5425(3)	0.040(1)
N(23)	0.5600(3)	0.1798(4)	0.4870(3)	0.051(1)
N(25)	0.6562(3)	-0.1750(4)	0.3694(3)	0.064(1)
C(26)	0.8000(3)	-0.0809(4)	0.4835(3)	0.044(1)
N(24)	0.6099(2)	0.0036(3)	0.4271(3)	0.045(1)
N(21)	0.9287(3)	0.0262(3)	0.6011(3)	0.053(1)
C(25)	0.6904(3)	-0.0854(4)	0.4270(3)	0.043(1)
C(23)	0.6376(3)	0.0934(4)	0.4845(3)	0.040(1)
C(21)	0.8275(3)	0.0127(4)	0.5429(3)	0.040(1)
O(112)	0.7209(2)	0.2235(3)	0.3316(2)	0.055(1)
O(132)	0.6606(2)	0.1476(3)	0.1347(2)	0.058(1)
O(111)	0.9034(2)	0.1632(3)	0.3767(3)	0.069(1)
C(12)	0.7832(3)	0.0566(5)	0.2598(4)	0.047(1)
O(131)	0.5886(2)	-0.0051(3)	0.1936(3)	0.063(1)
C(13)	0.6710(3)	0.0701(4)	0.1903(4)	0.047(1)
C(11)	0.8040(3)	0.1560(4)	0.3277(3)	0.044(1)
O(1)	0.5000	0.3079(4)	0.2500	0.059(1)
H(25A)	0.5869(3)	-0.1744(4)	0.3351(3)	0.076
H(25B)	0.7034(3)	-0.2336(4)	0.3665(3)	0.076
H(24)	0.5422(2)	0.0014(3)	0.3905(3)	0.054
H(21A)	0.9837(3)	-0.0260(3)	0.6040(3)	0.064
H(21B)	0.9396(3)	0.0873(3)	0.6363(3)	0.064
H(26)	0.8535(31)	-0.1433(39)	0.4797(30)	0.043(11)
H(23B)	0.4815(40)	0.1713(44)	0.4396(37)	0.069(15)
H(23A)	0.5818(33)	0.2350(40)	0.5260(34)	0.039(13)
H(7)	0.8467(41)	0.0691(47)	0.2371(36)	0.076(15)
H(22)	0.7561(36)	0.1597(50)	0.5856(38)	0.062(15)
H(25B)	0.7855(41)	-0.0201(54)	0.2854(41)	0.078(18)



1a

Table A2. Fractional Coordinates and Equivalent Isotropic Displacement Parameters [Å^2] of 2,4,6-triaminopyrimidine + glutaric acid, **2a**.

Atom	x/a	y/b	z/c	U_{eq}
O(1)	1.0000	-0.1891(5)	0.7500	0.080(2)
O(2)	0.9729(5)	0.3159(4)	0.6765(2)	0.087(2)
C(11)	0.8649(5)	0.0423(5)	0.8431(3)	0.049(2)
C(12)	0.7608(5)	0.0272(5)	0.7904(3)	0.050(2)
C(13)	0.7710(5)	0.1111(5)	0.7322(3)	0.046(2)
C(14)	0.6640(5)	0.1022(5)	0.6802(3)	0.049(2)
C(15)	0.6660(5)	0.1849(4)	0.6213(3)	0.045(2)
C(21)	1.3108(5)	-0.1015(4)	0.9769(2)	0.045(2)
N(22)	1.1945(4)	-0.1899(4)	0.8830(2)	0.057(1)
C(22)	1.2121(5)	-0.1060(4)	0.9305(3)	0.044(1)
N(23)	1.1312(4)	-0.0185(3)	0.9320(2)	0.044(1)
N(24)	1.0591(4)	0.1492(4)	0.9786(2)	0.052(1)
C(24)	1.1380(5)	0.0707(4)	0.9775(2)	0.040(1)
N(25)	1.2358(4)	0.0762(3)	1.0229(2)	0.045(1)
N(26)	1.4108(4)	0.0032(4)	1.0697(2)	0.055(1)
C(26)	1.3193(5)	-0.0081(4)	1.0234(3)	0.041(1)
O(111)	0.8666(4)	0.1310(4)	0.8817(2)	0.074(2)
O(112)	0.9433(4)	-0.0335(4)	0.8452(2)	0.063(1)
O(151)	0.7482(3)	0.2531(3)	0.6171(2)	0.053(1)
O(152)	0.5763(4)	0.1824(3)	0.5775(2)	0.061(1)
H(13A)	0.8369(5)	0.0877(5)	0.7126(3)	0.055
H(13B)	0.7813(5)	0.1953(5)	0.7474(3)	0.055
H(14A)	0.6551(5)	0.0179(5)	0.6650(3)	0.058
H(14B)	0.5985(5)	0.1230(5)	0.7007(3)	0.058
H(21A)	1.3685(5)	-0.1589(4)	0.9767(2)	0.054
H(22A)	1.1335(4)	-0.1876(4)	0.8547(2)	0.069
H(22B)	1.2440(4)	-0.2465(4)	0.8806(2)	0.069
H(23A)	1.0723(4)	-0.0205(3)	0.9021(2)	0.053
H(24A)	0.9991(4)	0.1461(4)	0.9496(2)	0.062
H(24B)	1.0659(4)	0.2053(4)	1.0084(2)	0.062
H(25A)	1.2439(4)	0.1346(3)	1.0514(2)	0.054
H(26A)	1.4149(4)	0.0624(4)	1.0976(2)	0.066
H(26B)	1.4654(4)	-0.0489(4)	1.0714(2)	0.066

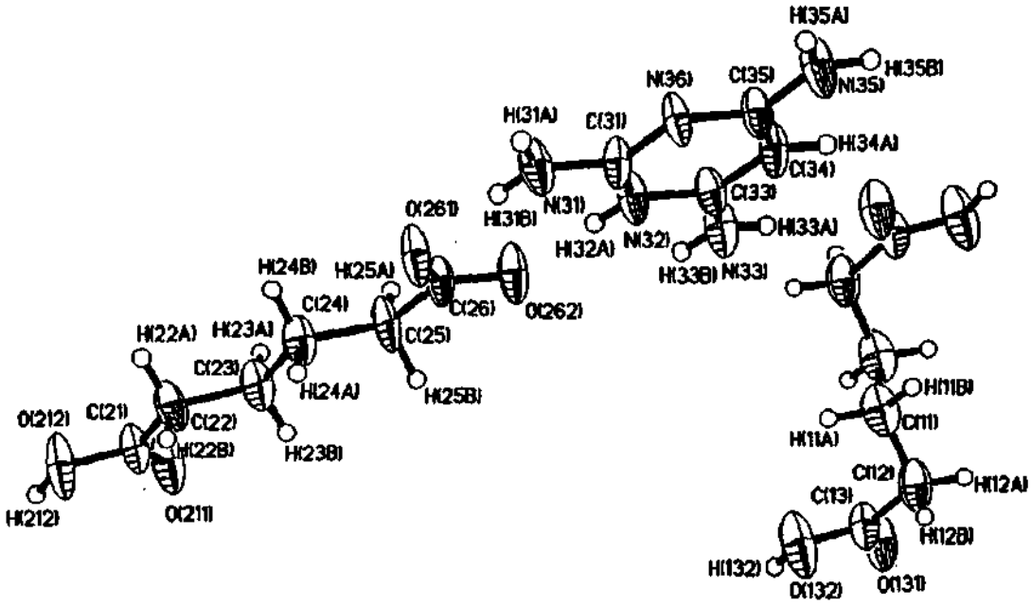


2a

Table A3. Fractional Coordinates and Equivalent Isotropic Displacement Parameters [$Å^2$] of 2,4,6-triaminopyrimidine + adipic acid, **3a**.

Atom	x/a	y/b	z/c	U_{eq}
C(11)	0.4677(7)	0.4825(4)	-0.0629(5)	0.056(2)
C(12)	0.3269(8)	0.5185(4)	-0.0995(5)	0.057(2)
C(13)	0.2266(7)	0.4919(4)	-0.0060(5)	0.049(2)
O(131)	0.1646(5)	0.5381(2)	0.0644(4)	0.059(1)
O(132)	0.2061(5)	0.4114(3)	-0.0047(4)	0.074(2)
C(21)	0.4215(7)	-0.2880(3)	0.3089(5)	0.043(2)
C(22)	0.5214(7)	-0.2615(3)	0.2112(5)	0.048(2)
C(23)	0.5460(8)	-0.1691(3)	0.2096(5)	0.049(2)
C(24)	0.6450(7)	-0.1412(3)	0.1099(5)	0.043(2)
C(25)	0.6601(9)	-0.0468(3)	0.1127(6)	0.047(2)
C(26)	0.7515(6)	-0.0091(3)	0.0142(5)	0.040(2)
O(261)	0.8157(5)	-0.0515(2)	-0.0612(3)	0.052(1)
O(262)	0.7547(5)	0.0705(2)	0.0144(3)	0.056(1)
C(31)	0.9794(6)	0.1154(3)	-0.2405(5)	0.039(2)
N(32)	0.9043(5)	0.1564(2)	-0.1557(4)	0.043(1)
C(33)	0.9054(7)	0.2414(3)	-0.1553(5)	0.039(2)
C(34)	0.9835(6)	0.2826(3)	-0.2404(5)	0.043(2)
C(35)	1.0584(6)	0.2370(3)	-0.3245(5)	0.040(2)
N(36)	1.0561(5)	0.1527(2)	-0.3260(4)	0.038(1)
N(31)	0.9803(5)	0.0330(3)	- 0.2352(4)	0.048(2)
N(33)	0.8265(6)	0.2789(3)	-0.0713(4)	0.054(2)
N(35)	1.1393(6)	0.2722(3)	-0.4093(4)	0.055(2)
O(211)	0.3666(5)	-0.2422(2)	0.3816(4)	0.067(2)
O(212)	0.4017(6)	-0.3683(2)	0.3105(4)	0.066(2)
H(11A)	0.4596(7)	0.4227(4)	-0.0538(5)	0.068
H(11B)	0.5273(7)	0.4932(4)	-0.1339(5)	0.068
H(12A)	0.3323(8)	0.5787(4)	-0.1000(5)	0.069
H(12B)	0.2974(8)	0.5004(4)	-0.1873(5)	0.069
H(132)	0.1490(5)	0.4003(3)	0.0486(4)	0.112
H(22A)	0.6076(7)	-0.2895(3)	0.2310(5)	0.058
H(22B)	0.4879(7)	-0.2789(3)	0.1242(5)	0.058
H(23A)	0.5806(8)	-0.1519(3)	0.2964(5)	0.059
H(23B)	0.4594(8)	-0.1412(3)	0.1914(5)	0.059
H(24A)	0.6122(7)	-0.1588(3)	0.0227(5)	0.052
H(24B)	0.7332(7)	-0.1668(3)	0.1293(5)	0.052
H(32A)	0.8558(5)	0.1296(2)	-0.1020(4)	0.051
H(34A)	0.9860(6)	0.3403(3)	-0.2415(5)	0.052
H(31A)	1.0299(5)	0.0051(3)	-0.2866(4)	0.058
H(31B)	0.9312(5)	0.0076(3)	-0.1804(4)	0.058
H(33A)	0.8228(6)	0.3322(3)	-0.0687(4)	0.065
H(33B)	0.7791(6)	0.2498(3)	-0.0196(4)	0.065
H(35A)	1.1855(6)	0.2418(3)	-0.4602(4)	0.066

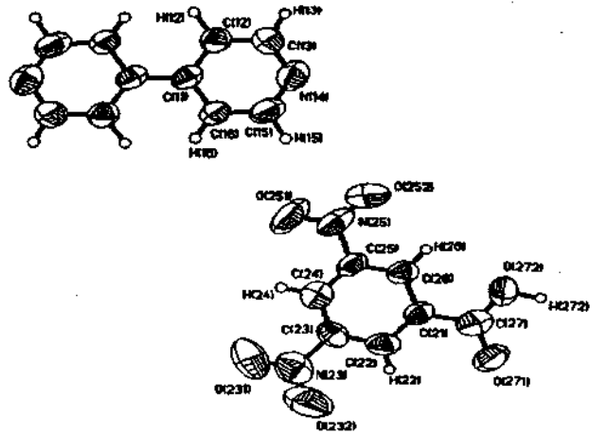
H(212)	0.3335(88)	-0.3887(53)	0.3765(70)	0.120(30)
H(25B)	0.5591(73)	-0.0142(43)	0.1082(55)	0.071(21)
H(25A)	0.7009(55)	-0.0266(33)	0.1930(49)	0.040(16)
H(25A)	0.7009(55)	-0.0266(33)	0.1930(49)	0.040(16)



3a

Table A4. Fractional Coordinates and Equivalent Isotropic Displacement Parameters [$Å^2$] of 3,5-dinitrobenzoic acid + 4,4'-bipyridyl, **4a**.

Atom	x/a	y/b	z/c	U_{eq}
C(11)	1.9105(8)	-0.0134(2)	-0.4693(5)	0.065(2)
C(12)	1.8224(10)	-0.0697(3)	-0.5161(6)	0.074(2)
C(13)	1.6518(10)	-0.0935(3)	-0.4564(7)	0.081(2)
N(14)	1.5696(8)	-0.0660(3)	-0.3531(6)	0.083(2)
C(15)	1.6518(11)	-0.0140(3)	-0.3064(6)	0.087(2)
C(16)	1.8187(11)	0.0139(3)	-0.3609(6)	0.082(2)
C(21)	1.0146(9)	0.1679(3)	0.1799(5)	0.061(1)
C(22)	1.1290(12)	0.2222(3)	0.2083(6)	0.075(2)
C(23)	1.3043(11)	0.2321(3)	0.1407(6)	0.072(2)
N(23)	1.4348(11)	0.2890(3)	0.1767(6)	0.106(2)
C(24)	1.3710(11)	0.1922(3)	0.0478(6)	0.074(2)
C(25)	1.2547(10)	0.1406(3)	0.0193(5)	0.068(2)
N(25)	1.3286(10)	0.0956(3)	-0.0794(5)	0.101(2)
C(26)	1.0783(10)	0.1272(3)	0.0827(5)	0.066(2)
C(27)	0.8314(10)	0.1533(3)	0.2590(6)	0.079(2)
O(231)	1.6072(9)	0.2923(2)	0.1313(6)	0.134(2)
O(232)	1.3597(10)	0.3270(2)	0.2442(6)	0.158(2)
O(251)	1.4769(8)	0.1110(2)	-0.1408(5)	0.146(2)
O(252)	1.2364(9)	0.0477(2)	-0.0923(5)	0.142(2)
O(271)	0.7749(6)	0.1873(2)	0.3494(4)	0.096(1)
O(272)	0.7404(7)	0.1020(2)	0.2222(4)	0.094(1)
H(12)	1.9042(80)	-0.0928(19)	-0.5913(47)	0.112(19)
H(16)	1.8864(75)	0.0514(21)	-0.3253(43)	0.092(20)
H(24)	1.5111(74)	0.1950(17)	0.0121(42)	0.071(17)
H(22)	1.0743(77)	0.2549(22)	0.2473(49)	0.107(23)
H(26)	1.0166(65)	0.0871(16)	0.0693(37)	0.064(16)
H(272)	0.6270(65)	0.0912(15)	0.2783(39)	0.045(13)
H(15)	1.5868(66)	0.0098(19)	-0.2312(39)	0.089(17)
H(13)	1.5983(79)	-0.1335(22)	-0.4948(45)	0.110(21)

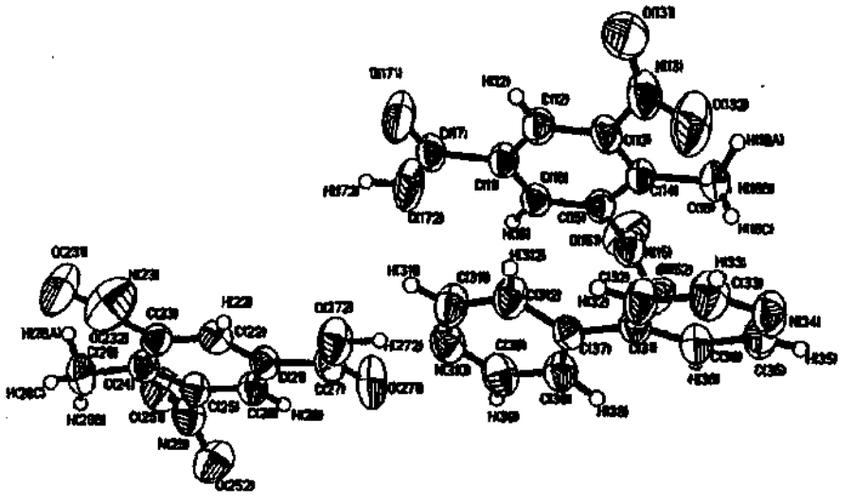


4a

Table A5. Fractional Coordinates and Equivalent Isotropic Displacement Parameters [$Å^2$] of 3,5-dinitro-4-methylbenzoic acid + 4,4'-bipyridyl, **5a**.

Atom	x/a	y/b	z/c	U_{eq}
C(11)	-0.0658(3)	0.5369(3)	0.3177(2)	0.046(1)
C(12)	-0.1651(3)	0.5615(3)	0.3817(2)	0.052(1)
C(13)	-0.3118(3)	0.6711(3)	0.3460(2)	0.050(1)
C(14)	-0.3697(3)	0.7631(3)	0.2453(2)	0.046(1)
C(15)	-0.2639(3)	0.7312(3)	0.1848(2)	0.046(1)
C(16)	-0.1162(3)	0.6239(3)	0.2169(2)	0.045(1)
C(17)	0.0960(3)	0.4188(3)	0.3571(2)	0.052(1)
C(18)	-0.5331(4)	0.8781(4)	0.2037(3)	0.063(1)
N(13)	-0.4103(3)	0.6925(4)	0.4198(2)	0.072(1)
N(15)	-0.3104(3)	0.8231(3)	0.0763(2)	0.056(1)
O(131)	-0.3984(3)	0.5852(3)	0.4898(2)	0.110(1)
O(132)	-0.4940(3)	0.8153(3)	0.4081(2)	0.104(1)
O(151)	-0.3135(3)	0.7680(3)	0.0212(2)	0.088(1)
O(152)	-0.3370(3)	0.9482(3)	0.0486(2)	0.081(1)
O(171)	0.1449(2)	0.3426(3)	0.4442(2)	0.086(1)
O(172)	0.1729(3)	0.4098(3)	0.2878(2)	0.086(1)
C(21)	0.6314(3)	0.4659(3)	0.1687(2)	0.046(1)
C(22)	0.7189(3)	0.3743(3)	0.2626(2)	0.048(1)
C(23)	0.8698(3)	0.2793(3)	0.2726(2)	0.049(1)
C(24)	0.9441(3)	0.2683(3)	0.1937(2)	0.050(1)
C(25)	0.8483(3)	0.3624(3)	0.1013(2)	0.049(1)
C(26)	0.6973(3)	0.4585(3)	0.0875(2)	0.050(1)
C(27)	0.4677(3)	0.5738(4)	0.1532(3)	0.057(1)
C(28)	1.1133(4)	0.1748(5)	0.2035(4)	0.069(1)
N(23)	0.9528(3)	0.1841(3)	0.3774(2)	0.068(1)
N(25)	0.9089(3)	0.3627(4)	0.0101(2)	0.065(1)
O(231)	1.0609(3)	0.0681(3)	0.3944(2)	0.106(1)
O(232)	0.9054(4)	0.2266(3)	0.4401(2)	0.104(1)
O(251)	0.9838(3)	0.2474(3)	0.0053(2)	0.083(1)
O(252)	0.8786(3)	0.4795(3)	-0.0573(2)	0.092(1)
O(271)	0.3883(3)	0.6512(3)	0.0714(2)	0.088(1)
O(272)	0.4264(3)	0.5772(3)	0.2358(2)	0.076(1)
C(31)	-0.2728(3)	1.0396(3)	0.2752(2)	0.044(1)
C(32)	-0.2952(4)	1.0341(3)	0.3691(2)	0.057(1)
C(33)	-0.4350(4)	1.1255(4)	0.3806(3)	0.065(1)
N(34)	-0.5522(3)	1.2195(3)	0.3057(2)	0.062(1)
C(35)	-0.5303(4)	1.2244(4)	0.2165(3)	0.059(1)
C(36)	-0.3956(3)	1.1395(3)	0.1970(2)	0.052(1)
C(37)	-0.1241(3)	0.9444(3)	0.2597(2)	0.043(1)

C(38)	-0.0837(3)	0.9740(4)	0.1667(2)	0.054(1)
C(39)	0.0570(4)	0.8818(4)	0.1563(3)	0.062(1)
N(310)	0.1574(3)	0.7647(3)	0.2325(2)	0.060(1)
C(311)	0.1199(4)	0.7371(4)	0.3214(3)	0.064(1)
C(312)	-0.0182(3)	0.8215(3)	0.3382(2)	0.056(1)
H(12)	0.1312(30)	0.5025(28)	0.4503(19)	0.052(8)
H(16)	-0.0477(29)	0.6068(25)	0.1687(17)	0.046(7)
H(18A)	-0.6019(46)	0.8540(39)	0.2393(27)	0.106(14)
H(18B)	-0.5556(51)	0.8843(46)	0.1424(32)	0.134(19)
H(18C)	-0.5462(48)	0.9696(48)	0.2053(27)	0.129(16)
H(172)	0.2737(43)	0.3343(38)	0.3038(23)	0.090(11)
H(22)	0.6739(28)	0.3872(26)	0.3166(18)	0.043(7)
H(26)	0.6409(31)	0.5199(29)	0.0240(19)	0.053(8)
H(28A)	1.1354(54)	0.0658(54)	0.2217(31)	0.149(18)
H(28B)	1.1517(49)	0.2023(44)	0.1424(30)	0.0127(17)
H(28C)	1.1697(40)	0.1675(36)	0.2580(25)	0.090(13)
H(272)	0.3181(46)	0.6480(41)	0.2298(25)	0.106(13)
H(32)	-0.2130(35)	0.9684(33)	0.4255(21)	0.070(10)
H(33)	-0.4521(35)	1.1263(32)	0.4425(21)	0.072(10)
H(35)	-0.6127(36)	1.2897(32)	0.1647(21)	0.068(10)
H(36)	-0.3897(31)	1.1540(29)	0.1312(20)	0.057(9)
H(38)	-0.1504(32)	1.0624(30)	0.1104(19)	0.057(9)
H(39)	0.0843(36)	0.8980(33)	0.0913(23)	0.080(10)
H(311)	0.1960(43)	0.6578(39)	0.3744(25)	0.097(12)
H(312)	-0.0346(34)	0.7935(31)	0.4037(21)	0.070(10)

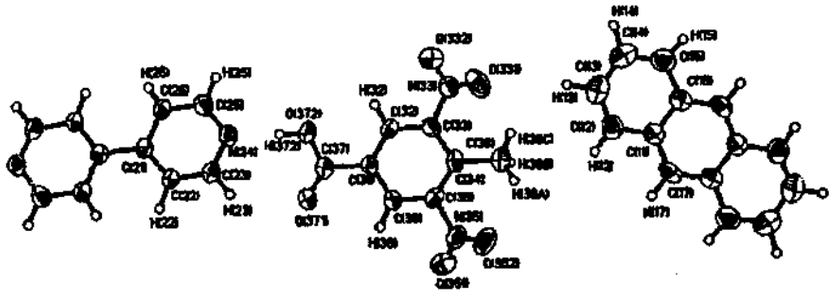


5a

Table A6. Fractional Coordinates and Equivalent Isotropic Displacement Parameters [$Å^2$] of 3,5-dinitro-4-methyl-benzoic acid + 4,4'-bipyridyl + anthracene, **5b**.

Atom	x/a	y/b	z/c	U_{eq}
O(372)	0.3112(3)	0.1179(3)	-0.0010(2)	0.051(1)
C(34)	0.2446(3)	0.3397(3)	0.3584(3)	0.039(1)
C(21)	0.4754(3)	0.0123(3)	-0.4397(2)	0.036(1)
C(33)	0.1705(3)	0.2494(3)	0.3066(3)	0.038(1)
N(24)	0.3803(3)	0.0581(3)	-0.2125(2)	0.045(1)
C(22)	0.5496(4)	0.0920(4)	-0.3780(3)	0.043(1)
N(33)	0.0377(3)	0.1883(4)	0.3650(2)	0.056(1)
C(31)	0.3293(3)	0.2658(3)	0.1347(3)	0.035(1)
C(26)	0.3503(4)	-0.0427(4)	-0.3838(3)	0.049(1)
O(371)	0.4641(3)	0.2924(3)	-0.0505(2)	0.062(1)
C(32)	0.2103(4)	0.2114(4)	0.1991(3)	0.039(1)
N(35)	0.4593(4)	0.4826(4)	0.3352(2)	0.059(1)
C(36)	0.4076(4)	0.3568(4)	0.1805(3)	0.042(1)
C(37)	0.3762(4)	0.2277(4)	0.0167(3)	0.043(1)
C(25)	0.03071(4)	-0.0179(4)	-0.2720(3)	0.052(1)
C(35)	0.3654(4)	0.3897(3)	0.2899(3)	0.042(1)
C(23)	0.4990(4)	0.1120(4)	-0.2663(3)	0.047(1)
O(352)	0.3975(3)	0.5833(3)	0.3762(2)	0.081(1)
O(351)	0.5935(3)	0.4533(3)	0.3266(2)	0.084(1)
O(332)	0.0218(3)	0.0612(3)	0.3599(2)	0.083(1)
C(38)	0.2076(5)	0.3718(6)	0.4810(4)	0.056(1)
O(331)	-0.0483(3)	0.2667(3)	0.4132(2)	0.083(1)
C(11)	0.0322(3)	0.4354(4)	0.9001(3)	0.045(1)
C(17)	0.1121(4)	0.5447(4)	0.9199(3)	0.049(1)
C(16)	-0.0834(4)	0.3896(4)	0.9836(3)	0.045(1)
C(12)	0.0605(5)	0.3689(5)	0.8001(3)	0.059(1)
C(13)	-0.0178(5)	0.2635(5)	0.7836(4)	0.071(1)
C(15)	-0.1636(4)	0.2782(4)	0.9610(4)	0.062(1)
C(14)	-0.1316(5)	0.2174(5)	0.8654(4)	0.072(1)
H(17)	0.1935(29)	0.5719(27)	0.8632(23)	0.036(8)
H(36)	0.4907(29)	0.3981(29)	0.1370(23)	0.041(9)
H(32)	0.1548(28)	0.1511(28)	0.1681(23)	0.038(8)
H(26)	0.2915(32)	-0.0926(32)	-0.4195(26)	0.056(10)
H(23)	0.5515(27)	0.1652(28)	-0.2202(23)	0.036(8)
H(25)	0.2144(34)	-0.0548(33)	-0.2355(27)	0.066(10)
H(22)	0.6444(33)	0.1329(33)	-0.4098(26)	0.068(11)
H(14)	-0.1986(36)	0.1373(37)	0.8555(29)	0.081(11)
H(38C)	0.1594(35)	0.2885(36)	0.5341(28)	0.068(11)

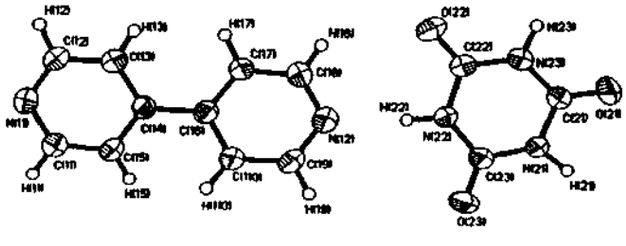
H(15)	-0.2398(31)	0.2536(31)	1.0185(25)	0.049(10)
H(38B)	0.1412(45)	0.4694(47)	0.4653(34)	0.108(16)
H(38A)	0.2916(38)	0.3813(36)	0.5252(29)	0.072(13)
H(12)	0.1437(39)	0.3979(39)	0.7480(31)	0.091(13)
H(372)	0.3325(42)	0.1032(42)	-0.0799(36)	0.110(15)
H(13)	-0.0048(38)	0.2240(39)	0.7082(33)	0.091(13)



5b

Table A7. Fractional Coordinates and Equivalent Isotropic Displacement Parameters [$Å^2$] of Cyanuric acid + 4,4'-bipyridyl + water, **6a**.

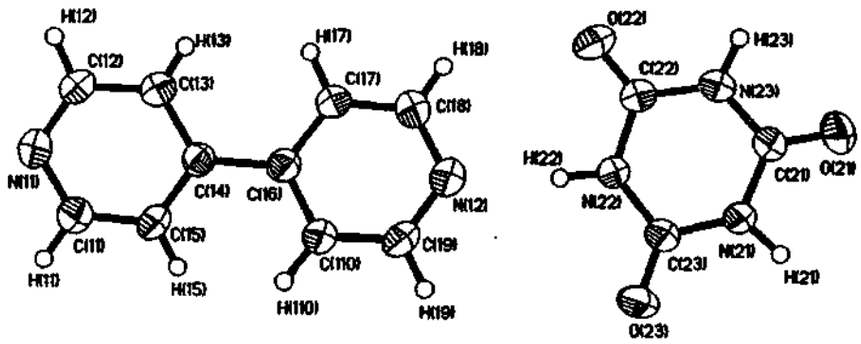
Atom	x/a	y/b	z/c	U_{eq}
N(23)	0.6364(5)	0.0626(1)	0.2098(5)	0.042(1)
N(22)	0.9433(5)	0.0227(1)	0.2422(5)	0.041(1)
N(21)	0.9387(5)	0.1029(1)	0.2372(5)	0.040(1)
O(23)	1.2358(4)	0.0639(1)	0.2636(4)	0.053(1)
N(12)	1.1113(5)	-0.0686(1)	0.2699(5)	0.046(1)
O(22)	0.6529(4)	-0.0161(1)	0.2359(4)	0.060(1)
O(21)	0.6331(4)	0.1414(1)	0.1933(5)	0.063(1)
C(23)	1.0525(5)	0.0634(1)	0.2499(5)	0.036(1)
C(16)	1.2183(5)	-0.1623(1)	0.2474(5)	0.036(1)
N(11)	1.3805(5)	-0.3048(1)	0.2103(5)	0.046(1)
C(22)	0.7387(6)	0.0204(1)	0.2304(6)	0.041(1)
C(14)	1.2720(5)	-0.2114(1)	0.2317(5)	0.034(1)
C(21)	0.7286(6)	0.1048(1)	0.2124(6)	0.041(1)
C(110)	1.3722(6)	-0.1271(1)	0.3021(6)	0.042(1)
C(15)	1.4494(6)	-0.2241(1)	0.1966(6)	0.044(1)
C(19)	1.3119(7)	-0.0816(1)	0.3110(6)	0.045(1)
C(13)	1.1501(6)	-0.2476(1)	0.2521(6)	0.041(1)
C(17)	1.0091(6)	-0.1485(1)	0.2072(6)	0.043(1)
C(12)	1.2069(6)	-0.2931(1)	0.2390(6)	0.045(1)
C(18)	0.9635(7)	-0.1025(1)	0.2212(6)	0.048(1)
C(11)	1.4986(7)	-0.2700(1)	0.1894(6)	0.045(1)
H(11)	1.6256(58)	-0.2789(1)	0.1685(53)	0.053(11)
H(12)	1.1141(55)	-0.3152(15)	0.2562(52)	0.059(12)
H(13)	1.0373(52)	-0.2406(11)	0.2862(48)	0.033(9)
H(15)	1.5286(53)	-0.2020(11)	0.1712(49)	0.039(10)
H(17)	0.8935(54)	-0.1728(13)	0.1706(50)	0.055(11)
H(21)	0.9938(57)	0.1333(13)	0.2458(54)	0.052(11)
H(110)	1.5193(67)	-0.1370(13)	0.3359(58)	0.068(13)
H(22)	1.0075(68)	-0.0061(15)	0.2534(64)	0.074(14)
H(19)	1.4182(57)	-0.0583(11)	0.3397(52)	0.044(10)
H(18)	0.8222(57)	-0.0945(13)	0.1956(53)	0.057(12)
H(23)	0.5057(77)	0.0641(13)	0.2152(65)	0.071(13)



6a

Table A8. Fractional Coordinates and Equivalent Isotropic Displacement Parameters [$Å^2$] of Cyanuric acid + 4,4'-bipyridyl (methanol), **6b**.

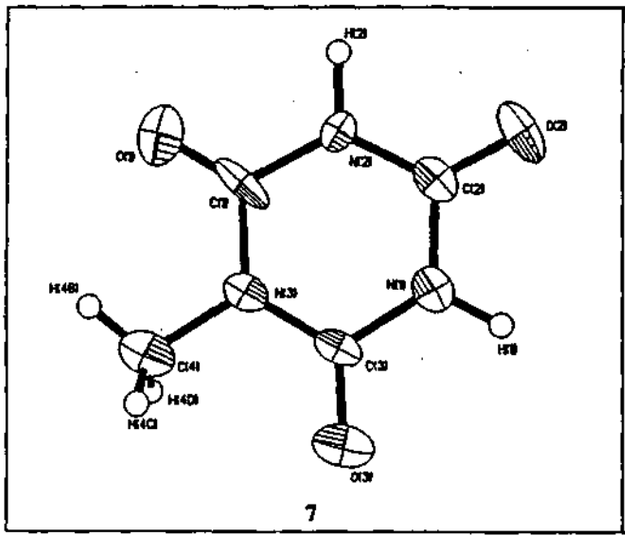
Atom	x/a	y/b	z/c	U_{eq}
N(26)	0.1952(3)	0.1613(1)	0.0346(1)	0.043(1)
O(25)	0.2527(3)	0.3985(1)	-0.0612(1)	0.056(1)
O(23)	0.7272(3)	0.2324(1)	0.2669(1)	0.061(1)
N(24)	0.4824(3)	0.3193(2)	0.1056(1)	0.047(1)
O(21)	0.1762(3)	-0.0805(1)	0.1235(1)	0.054(1)
N(22)	0.4440(3)	0.0738(1)	0.2001(1)	0.044(1)
C(11)	0.0758(4)	0.4303(2)	-0.4702(1)	0.042(1)
N(14)	0.3594(3)	0.1670(2)	-0.3584(1)	0.053(1)
C(25)	0.3075(4)	0.3004(2)	0.0208(1)	0.042(1)
C(12)	0.0867(5)	0.3002(2)	-0.5135(2)	0.060(1)
C(16)	0.2150(5)	0.4231(2)	-0.3691(2)	0.055(1)
C(15)	0.3517(5)	0.2919(2)	-0.3174(2)	0.059(1)
C(23)	0.5610(4)	0.2101(2)	0.1966(1)	0.044(1)
C(21)	0.2663(4)	0.0441(2)	0.1203(1)	0.041(1)
C(13)	0.2262(5)	0.1735(2)	-0.4553(2)	0.062(1)
H(26)	0.0853(45)	0.1410(19)	-0.0200(17)	0.054(5)
H(15)	0.4541(48)	0.2872(22)	-0.2509(19)	0.071(6)
H(24)	0.5606(48)	0.4072(25)	0.0967(17)	0.067(6)
H(16)	0.2206(49)	0.5078(24)	-0.3343(19)	0.076(6)
H(13)	0.2273(52)	0.0832(24)	-0.4838(19)	0.082(7)
H(12)	-0.0083(53)	0.2953(24)	-0.5829(20)	0.081(6)
H(22)	0.5036(47)	0.0100(24)	0.2629(18)	0.068(6)



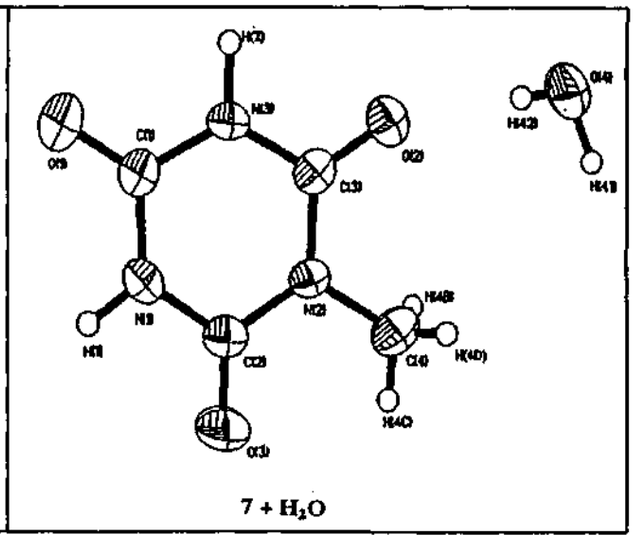
6b

Table A9. Fractional Coordinates and Equivalent Isotropic Displacement Parameters [$Å^2$] of N-methylcyanuric acid, 7 and its adduct with water (7 + H_2O).

	7				7 + H_2O			
Atom	x/a	y/b	z/c	U_{eq}	x/a	y/b	z/c	U_{eq}
N(3)	0.7346(21)	0.2500	0.5534(5)	0.034(3)	0.0183(5)	0.2500	0.8052(4)	0.040(1)
N(2)	0.7145(19)	0.2500	0.3824(5)	0.030(3)	0.2636(5)	0.2500	0.6537(4)	0.038(1)
N(1)	1.0237(20)	0.2500	0.4578(6)	0.036(3)	0.3626(5)	0.2500	0.9419(4)	0.044(1)
O(3)	1.0438(15)	0.2500	0.6233(4)	0.049(3)	0.6014(4)	0.2500	0.7961(3)	0.073(1)
O(1)	0.4389(17)	0.2500	0.4741(6)	0.054(3)	0.1176(4)	0.2500	1.0849(4)	0.063(1)
C(2)	0.9147(24)	0.2500	0.3708(7)	0.033(4)	0.4224(7)	0.2500	0.7973(5)	0.040(1)
C(3)	0.9359(25)	0.2500	0.5500(6)	0.029(3)	0.0583(6)	0.2500	0.6530(5)	0.038(1)
O(2)	0.9990(14)	0.2500	0.2917(4)	0.058(3)	-0.0816(4)	0.2500	0.5268(3)	0.053(1)
C(1)	0.6163(26)	0.2500	0.4700(7)	0.041(4)	0.1645(7)	0.2500	0.9540(5)	0.042(1)
C(4)	0.6427(23)	0.2500	0.6502(5)	0.051(4)	0.3150(9)	0.2500	0.4918(6)	0.057(2)
H(4B)	0.5011(23)	0.2500	0.6432(5)	0.076	0.2716(73)	0.1160(77)	0.4284(59)	0.181(22)
H(4C)	0.6832(23)	0.3743	0.6856(5)	0.076	0.4544(84)	0.2500	0.4987(57)	0.084(19)
H(4D)	0.6832(23)	0.1257	0.6856(5)	0.076	0.2716	0.3839	0.4284	0.062(10)
H(2)	0.6330(350)	0.2500	0.3208(109)	0.198(79)	-0.1237(61)	0.2500	0.8087(42)	0.038(11)
H(1)	1.1653(179)	0.2500	0.4514(57)	0.015(28)	0.4722(70)	0.2500	1.0332(51)	0.060(14)
O(4)					-0.2612(5)	0.2500	0.1884(5)	0.061(1)
H(41)					-0.1419(108)	0.2500	0.1329(73)	0.148(26)
H(42)					0.2154(86)	0.2500	0.2773(67)	0.093(24)



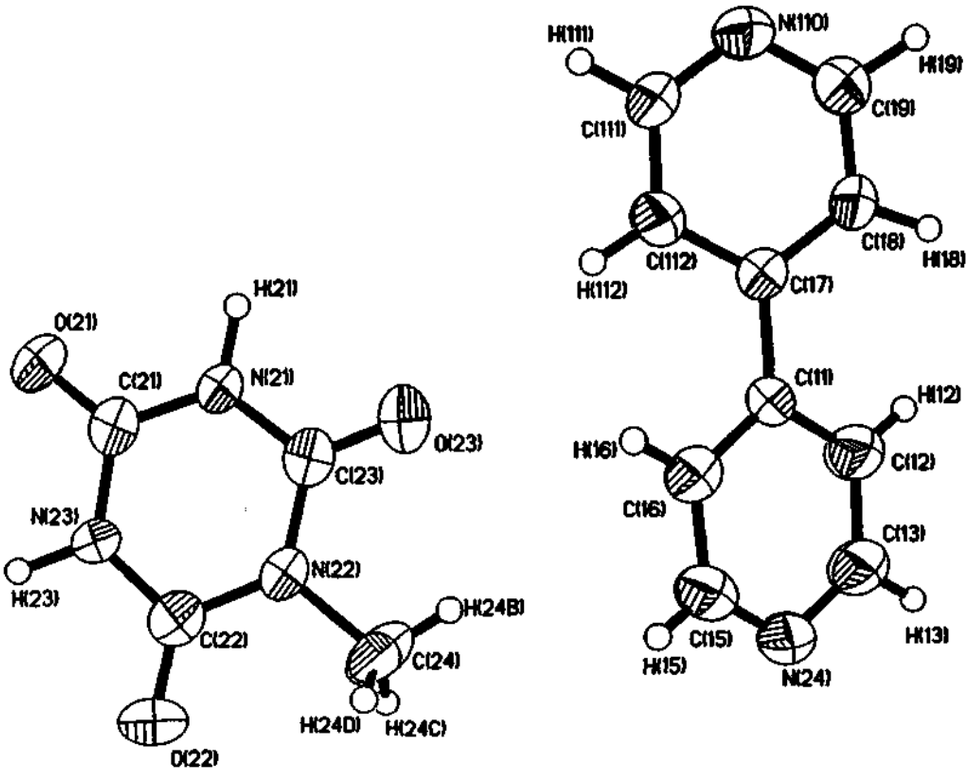
7



7 + H_2O

Table A10. Fractional Coordinates and Equivalent Isotropic Displacement Parameters [$Å^2$] of N-methylcyanuric acid + 4,4'-bipyridyl, **7a**.

Atom	x/a	y/b	z/c	U_{eq}
O(21)	0.1233(9)	0.6208(2)	0.7333(1)	0.065(1)
O(23)	0.6138(10)	0.3992(2)	0.6540(2)	0.075(1)
O(22)	0.1084(9)	0.3958(2)	0.8507(1)	0.072(1)
N(24)	0.7560(10)	0.0963(2)	0.6157(2)	0.057(1)
N(23)	0.1024(11)	0.5077(2)	0.7914(2)	0.049(1)
N(22)	0.3559(10)	0.3935(2)	0.7518(2)	0.049(1)
C(11)	1.0090(12)	0.2134(2)	0.5332(2)	0.043(1)
N(21)	0.3673(11)	0.5104(2)	0.6924(2)	0.052(1)
C(17)	1.1370(12)	0.2756(2)	0.4893(2)	0.045(1)
C(16)	0.9767(14)	0.2266(3)	0.5980(2)	0.055(2)
C(21)	0.1946(13)	0.5506(3)	0.7383(2)	0.053(1)
C(18)	1.2777(13)	0.2586(3)	0.4307(2)	0.053(2)
N(110)	1.3779(11)	0.3938(2)	0.4070(2)	0.057(1)
C(22)	0.1870(13)	0.4298(3)	0.8011(2)	0.053(1)
C(23)	0.4599(14)	0.4322(3)	0.6967(2)	0.055(2)
C(112)	1.1215(14)	0.3556(3)	0.5056(2)	0.057(2)
C(13)	0.7911(15)	0.0836(3)	0.5534(2)	0.062(2)
C(111)	1.2410(14)	0.4110(3)	0.4630(2)	0.061(2)
C(15)	0.8543(15)	0.1666(3)	0.6364(3)	0.062(2)
C(19)	1.3942(15)	0.3179(3)	0.3917(2)	0.064(2)
C(24)	0.4461(14)	0.3092(2)	0.7579(2)	0.072(2)
C(12)	0.9099(15)	0.1393(3)	0.5104(3)	0.062(2)
H(24B)	0.5625(14)	0.2921(2)	0.7199(2)	0.108
H(24C)	0.2397(14)	0.2787(2)	0.7631(2)	0.108
H(24D)	0.5949(14)	0.3018(2)	0.7946(2)	0.108
H(18)	1.3171(93)	0.2071(20)	0.4155(16)	0.036(12)
H(19)	1.5064(106)	0.3008(22)	0.3493(19)	0.063(13)
H(112)	1.0171(93)	0.3707(20)	0.5424(16)	0.030(11)
H(16)	1.0644(98)	0.2761(21)	0.6162(16)	0.046(12)
H(12)	0.9234(106)	0.1274(23)	0.4670(18)	0.056(14)
H(23)	0.0182(108)	0.5359(24)	0.8266(18)	0.069(15)
H(21)	0.4755(124)	0.5391(27)	0.6560(22)	0.090(17)
H(13)	0.7158(105)	0.0316(25)	0.5373(16)	0.057(14)
H(111)	1.2217(108)	0.4666(24)	0.4737(17)	0.057(13)
H(15)	0.8620(106)	0.1770(23)	0.6772(18)	0.050(14)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H(19)
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C(17)
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N(24)
H(21)
O(21)
C(21)
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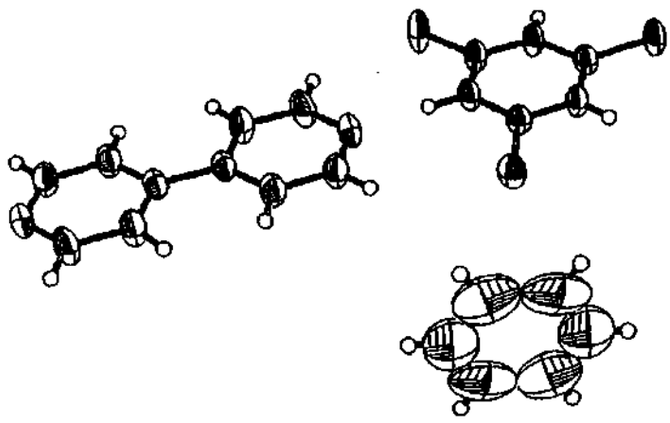
O(23)
C(23)
N(23)
N(22)
H(23)
H(24B)
C(22)
C(24)
H(24D)
H(24C)
O(22)

7a

Table A11. Fractional Coordinates and Equivalent Isotropic Displacement Parameters [$Å^2$] of Trithiocyanuric acid + 4,4'-bipyridyl + benzene, **8a**.

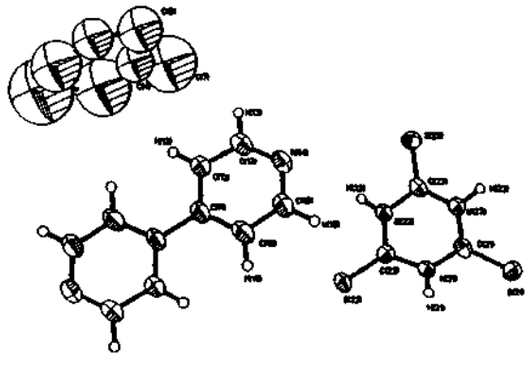
Atom	x/a	y/b	z/c	U_{eq}
S(15)	0.4757(1)	0.7270(1)	0.3620(1)	0.043(1)
S(13)	0.9800(1)	0.4111(1)	0.7293(1)	0.048(1)
S(11)	0.2342(1)	0.6153(1)	0.9005(1)	0.061(1)
N(16)	0.3739(3)	0.6593(2)	0.6355(2)	0.036(1)
C(21)	-0.3963(3)	0.9607(2)	0.5142(2)	0.036(1)
C(23)	-0.0531(4)	0.8696(3)	0.4405(3)	0.046(1)
N(14)	0.7055(3)	0.5770(2)	0.5607(2)	0.037(1)
C(15)	0.5177(3)	0.6511(2)	0.5256(2)	0.034(1)
N(12)	0.5991(3)	0.5221(2)	0.7932(2)	0.040(1)
C(26)	-0.3457(4)	0.8970(3)	0.6486(3)	0.048(1)
C(13)	0.7538(3)	0.5065(2)	0.6919(2)	0.036(1)
N(24)	-0.0067(3)	0.8083(2)	0.5699(2)	0.042(1)
C(25)	-0.1530(4)	0.8227(3)	0.6718(3)	0.050(1)
C(22)	-0.2433(3)	0.9453(3)	0.4087(3)	0.044(1)
C(11)	0.4090(3)	0.5985(3)	0.7697(2)	0.038(1)
C(32)	0.3681(15)	0.9161(10)	0.0145(5)	0.123(2)
C(31)	0.3024(11)	1.0570(11)	0.0053(5)	0.124(2)
C(33)	0.5667(18)	0.860(7)	0.0086(5)	0.122(2)
H(23)	0.0475(41)	0.8619(27)	0.3709(28)	0.049(7)
H(26)	-0.4415(44)	0.9004(29)	0.7257(31)	0.060(8)
H(14)	0.7929(41)	0.5731(27)	0.4937(29)	0.046(7)
H(22)	-0.2631(41)	0.9883(29)	0.3162(31)	0.056(8)
H(12)	0.6280(40)	0.4826(28)	0.8750(29)	0.049(8)
H(25)	-0.1214(4)	0.7764(30)	0.7641(31)	0.059(8)
H(16)	0.2427(53)	0.7100(35)	0.6155(33)	0.080(10)
H(31)	0.1776(81)	1.0854(61)	0.0109(54)	0.144(25)
H(32)	0.2666(93)	0.8621(66)	0.0190(60)	0.178(26)
H(33)	0.6066(90)	0.7661(65)	0.0139(56)	0.166(25)



8a

Table A12. Fractional Coordinates and Equivalent Isotropic Displacement Parameters [$Å^2$] of Trithiocyanuric acid + 4,4'-bipyridyl + toluene, **8b**.

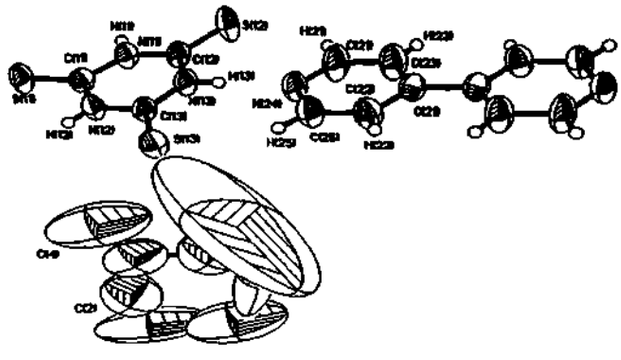
Atom	x/a	y/b	z/c	U_{eq}
S(23)	-0.0276(2)	0.7242(2)	-0.1392(2)	0.050(1)
S(22)	0.4802(2)	0.4203(2)	0.2265(2)	0.055(1)
S(21)	-0.2620(3)	0.6208(3)	0.3969(2)	0.078(1)
N(23)	-0.1254(8)	0.6632(6)	0.1327(5)	0.042(1)
C(11)	0.8962(8)	0.0391(7)	-0.0133(6)	0.040(2)
C(15)	0.5564(10)	0.1329(8)	0.0619(7)	0.051(2)
N(22)	0.2043(7)	0.5796(6)	0.0585(5)	0.040(2)
C(12)	0.8423(10)	0.0982(8)	-0.1467(7)	0.053(2)
C(23)	0.0167(8)	0.6525(7)	0.0242(6)	0.039(2)
C(16)	0.7474(9)	0.0571(8)	0.0918(8)	0.051(2)
N(21)	0.1018(7)	0.5305(7)	0.2890(6)	0.047(2)
C(22)	0.2548(9)	0.5123(7)	0.1899(6)	0.041(2)
N(14)	0.5063(7)	0.1881(6)	-0.0667(6)	0.048(1)
C(21)	-0.0887(9)	0.6041(8)	0.2668(7)	0.048(2)
C(13)	0.6479(10)	0.1720(9)	-0.1680(8)	0.060(2)
C(4)	0.9720(27)	0.1184(19)	-0.5106(15)	0.134(5)
C(3)	0.6239(56)	0.0387(50)	-0.4805(40)	0.387(21)
C(5)	0.7661(42)	0.1080(32)	-0.4984(24)	0.219(9)
C(2)	0.8348(53)	-0.1315(38)	-0.4787(31)	0.307(15)
C(6)	0.8490(32)	-0.0158(27)	-0.4903(19)	0.171(7)
C(7)	0.8592(49)	0.2378(36)	-0.5181(30)	0.301(14)
H(16)	0.7713(105)	0.0241(79)	0.1887(78)	0.069(23)
H(15)	0.4484(101)	0.1363(72)	0.1438(71)	0.061(20)
H(12)	0.9390(95)	0.0952(69)	-0.2257(67)	0.051(19)
H(13)	0.6230(99)	0.2074(75)	-0.2653(76)	0.065(21)
H(21)	0.1252(95)	0.4881(72)	0.3658(69)	0.046(21)
H(22)	0.2859(139)	0.5801(84)	-0.0161(81)	0.076(26)
H(23)	-0.2518(139)	0.7025(102)	0.1114(94)	0.112(34)



8b

Table A13. Fractional Coordinates and Equivalent Isotropic Displacement Parameters [$Å^2$] of Trithiocyanuric acid + 4,4'-bipyridyl + o-xylene, **8c**.

Atom	x/a	y/b	z/c	U_{eq}
S(13)	0.0302(2)	0.2795(1)	0.1381(1)	0.055(1)
S(11)	-0.4810(2)	0.5733(1)	-0.2250(1)	0.058(1)
S(12)	0.2609(2)	0.3787(2)	-0.3947(1)	0.068(1)
N(13)	0.1239(5)	0.3367(4)	-0.1315(4)	0.044(1)
C(21)	0.8963(6)	0.0385(4)	-0.0134(4)	0.044(1)
N(12)	-0.2024(5)	0.4197(4)	-0.0591(4)	0.045(1)
C(25)	0.5595(7)	0.1345(6)	0.0617(5)	0.060(1)
C(13)	-0.0159(6)	0.3478(4)	0.0234(4)	0.041(1)
N(11)	-0.1035(5)	0.4655(4)	-0.2874(4)	0.045(1)
C(12)	0.0878(6)	0.3940(5)	-0.2654(4)	0.044(1)
N(24)	0.5059(5)	0.1878(4)	-0.0646(4)	0.051(1)
C(23)	0.8374(8)	0.0949(6)	-0.1429(5)	0.068(2)
C(11)	-0.2554(6)	0.4837(4)	-0.1879(4)	0.043(1)
C(22)	0.7495(7)	0.0608(6)	0.0915(5)	0.060(1)
C(21)	0.6453(7)	0.1672(7)	-0.1639(6)	0.072(2)
C(4)	-0.0971(70)	0.2325(26)	0.4832(21)	0.298(22)
C(3)	-0.2649(46)	0.1190(39)	0.5024(17)	0.377(25)
C(5)	0.1772(74)	0.1242(29)	0.4741(16)	0.305(26)
C(1)	0.0651(29)	-0.0916(14)	0.5038(8)	0.148(4)
C(2)	-0.1651(23)	-0.0080(23)	0.5137(11)	0.162(4)
C(7)	-0.3157(125)	-0.0530(141)	0.5063(106)	1.499(154)
H(12)	-0.2814(62)	0.4275(40)	0.0027(44)	0.033(11)
H(22)	0.7720(77)	0.0356(54)	0.1768(60)	0.069(15)
H(25)	0.4582(81)	0.1526(52)	0.1302(56)	0.068(15)
H(11)	-0.1281(60)	0.5003(42)	-0.3596(46)	0.031(12)
H(23)	0.9185(81)	0.0866(53)	-0.2134(58)	0.064(16)
H(21)	0.6177(107)	0.2047(76)	-0.2473(79)	0.119(25)
H(13)	0.2398(96)	0.2926(63)	-0.1141(62)	0.086(19)

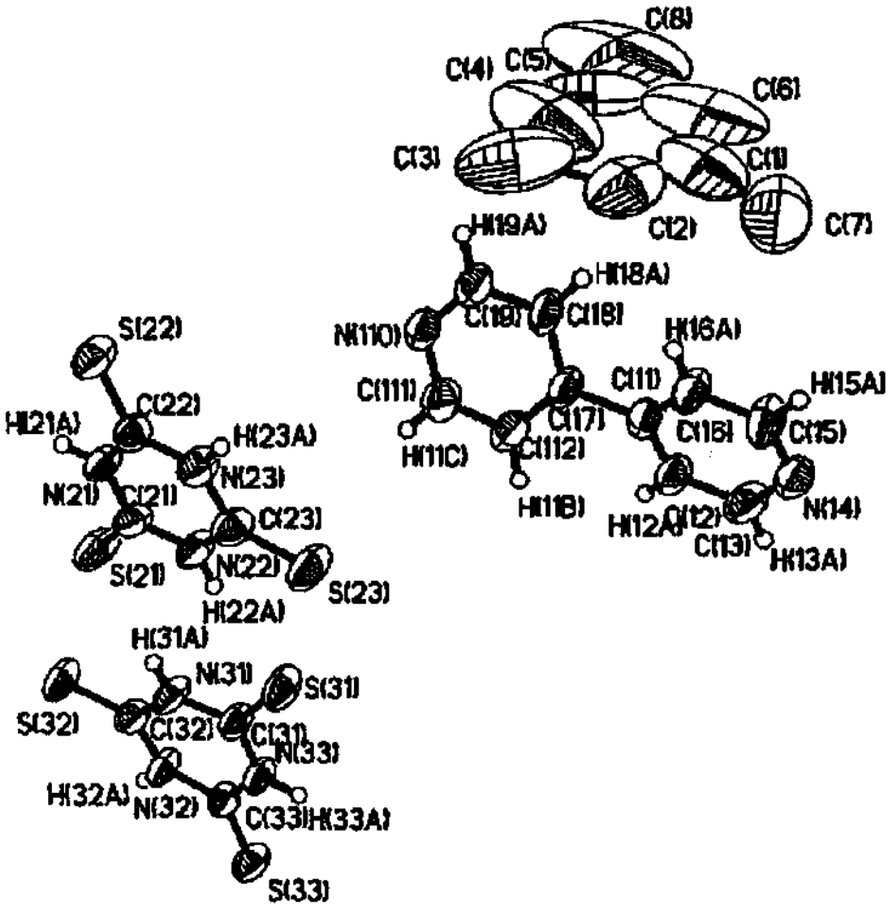


8c

Table 14. Fractional Coordinates and Equivalent Isotropic Displacement Parameters [$Å^2$] of Trithiocyanuric acid + 4,4'-bipyridyl + m-xylene, **8d**.

Atom	x/a	y/b	z/c	U_{eq}
S(33)	0.3383(3)	0.7219(2)	0.2772(3)	0.060(1)
S(22)	1.4957(3)	0.6680(2)	0.6127(2)	0.060(1)
S(31)	0.8137(3)	0.5610(2)	0.3076(3)	0.066(1)
S(32)	0.6975(3)	0.9696(2)	0.5530(3)	0.065(1)
S(21)	1.0324(3)	0.8363(3)	0.5421(3)	0.072(1)
S(23)	1.1430(3)	0.4044(3)	0.3413(3)	0.073(1)
N(33)	0.5786(8)	0.6509(7)	0.3012(3)	0.049(2)
N(23)	1.3073(8)	0.5515(7)	0.4783(7)	0.053(3)
N(32)	0.5312(7)	0.8346(7)	0.4074(7)	0.048(2)
N(22)	1.1055(8)	0.6227(7)	0.4495(7)	0.053(3)
C(33)	0.4894(9)	0.7350(9)	0.3312(8)	0.044(3)
N(110)	1.5019(9)	0.4567(7)	0.1401(7)	0.054(2)
C(23)	1.1859(10)	0.5290(9)	0.4243(9)	0.052(3)
N(21)	1.2577(7)	0.7371(7)	0.5703(7)	0.049(2)
C(32)	0.6512(9)	0.8520(9)	0.4620(9)	0.048(3)
C(15)	1.4452(11)	-0.0401(9)	-0.2144(10)	0.064(3)
C(16)	1.4806(10)	0.0568(9)	-0.1341(9)	0.061(3)
N(14)	1.3305(9)	-0.0522(8)	-0.2729(8)	0.061(3)
C(112)	1.3408(11)	0.3267(10)	0.0359(10)	0.068(4)
C(22)	1.3472(9)	0.6522(8)	0.5519(8)	0.044(3)
C(11)	1.3978(10)	0.1495(9)	-0.1090(9)	0.050(3)
N(31)	0.7334(8)	0.7596(7)	0.4274(7)	0.056(3)
C(12)	1.2800(10)	0.1386(9)	-0.1699(9)	0.056(3)
C(18)	1.5611(11)	0.2931(9)	0.0054(9)	0.061(3)
C(17)	1.4322(10)	0.2582(9)	-0.0218(9)	0.050(3)
C(31)	0.7034(10)	0.6605(8)	0.3461(9)	0.049(3)
C(111)	1.3787(12)	0.4231(9)	0.1136(10)	0.067(4)
C(21)	1.1350(9)	0.7278(9)	0.5194(9)	0.049(3)
C(19)	1.5901(11)	0.3924(10)	0.0851(10)	0.067(4)
C(13)	1.2501(11)	0.0371(10)	-0.2498(10)	0.063(3)
C(7)	1.8245(20)	-0.0783(22)	-0.1626(18)	0.152(8)
C(4)	1.9104(35)	0.2574(57)	0.0537(35)	0.251(28)
C(2)	1.8521(17)	0.0846(18)	0.0069(27)	0.140(8)
C(1)	1.8663(18)	0.0544(28)	-0.1108(29)	0.150(10)
C(3)	1.8786(29)	0.2157(30)	0.1251(37)	0.208(18)
C(5)	1.9341(24)	0.2726(31)	-0.0352(49)	0.177(20)
C(6)	1.9121(22)	0.1457(54)	-0.1616(32)	0.243(21)
C(8)	1.9649(30)	0.3288(71)	-0.1027(52)	0.459(46)
H(33A)	0.5554(8)	0.5889(7)	0.2518(7)	0.059
H(23A)	1.3631(8)	0.4969(7)	0.4642(7)	0.064
H(32A)	0.4772(7)	0.8908(7)	0.4219(7)	0.058
H(22A)	1.0285(8)	0.6139(7)	0.4177(7)	0.064

H(21A)	1.2791(7)	0.8013(7)	0.6172(7)	0.059
H(15A)	1.5037(11)	-0.1009(9)	-0.2293(10)	0.077
H(16A)	1.5615(10)	0.0604(9)	-0.0959(9)	0.074
H(11B)	1.2531(11)	0.3065(10)	0.0214(10)	0.081
H(31A)	0.8101(8)	0.7647(7)	0.4597(7)	0.067
H(12A)	1.2209(10)	0.1991(9)	-0.1537(9)	0.068
H(18A)	1.6270(11)	0.2494(9)	-0.0303(9)	0.074
H(11C)	1.3150(12)	0.4687(9)	0.1507(10)	0.081
H(19A)	1.6769(11)	0.4157(10)	0.1013(10)	0.081
H(13A)	1.1698(11)	0.0311(10)	-0.2894(10)	0.076

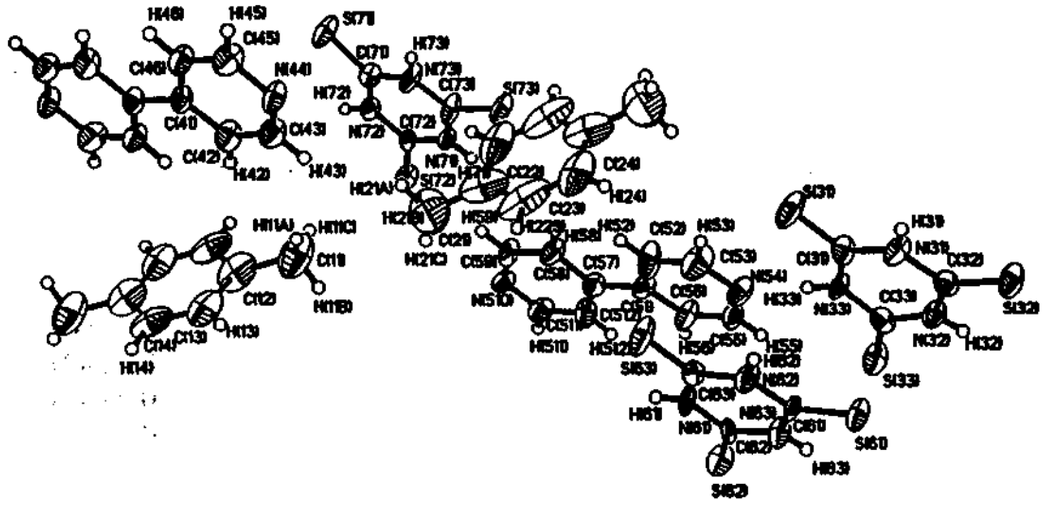


8d

Table A15. Fractional Coordinates and Equivalent Isotropic Displacement Parameters [$Å^2$] of Trithiocyanuric acid + 4,4'-bipyridyl + p-xylene, **8e**.

Atom	x/a	y/b	z/c	U_{eq}
C(11)	0.1540(13)	0.4761(12)	0.3386(7)	0.095(5)
C(12)	0.0723(14)	0.4867(16)	0.4217(9)	0.074(5)
C(13)	0.0633(13)	0.3877(15)	0.4666(10)	0.067(5)
C(14)	-0.0071(15)	0.3950(13)	0.5422(10)	0.075(5)
C(21)	0.3399(15)	0.4697(16)	0.1514(8)	0.134(8)
C(22)	0.4219(18)	0.4815(22)	0.0741(11)	0.089(6)
C(23)	0.4954(23)	0.3858(15)	0.0240(15)	0.099(7)
C(24)	0.5688(16)	0.4048(22)	-0.0487(12)	0.089(7)
N(31)	0.7886(8)	0.1010(7)	-0.4436(4)	0.039(3)
S(31)	0.7537(3)	0.2045(3)	-0.3161(2)	0.064(1)
C(31)	0.6968(10)	0.1744(9)	-0.3842(5)	0.035(3)
S(32)	0.8706(3)	-0.0138(3)	-0.5752(2)	0.051(1)
N(32)	0.6100(8)	0.1249(7)	-0.5020(4)	0.038(2)
C(32)	0.7529(10)	0.0713(9)	-0.5060(6)	0.036(3)
S(33)	0.3355(3)	0.2454(3)	-0.4452(2)	0.048(1)
N(33)	0.5547(8)	0.2174(7)	-0.3863(4)	0.034(2)
C(33)	0.5028(10)	0.1925(9)	-0.4445(6)	0.034(3)
C(41)	0.5493(10)	0.4616(9)	0.4666(5)	0.033(3)
C(42)	0.4973(10)	0.4350(10)	0.4100(5)	0.046(3)
C(43)	0.5926(11)	0.3632(10)	0.3504(6)	0.045(3)
N(44)	0.7330(9)	0.3131(8)	0.3422(4)	0.042(3)
C(45)	0.7836(11)	0.3395(10)	0.3961(6)	0.049(3)
C(46)	0.6961(10)	0.4106(9)	0.4583(5)	0.042(3)
C(51)	0.1641(10)	0.5173(9)	-0.1476(6)	0.036(3)
C(52)	0.3041(11)	0.4571(11)	-0.1506(6)	0.060(4)
C(53)	0.3933(12)	0.3843(11)	-0.2112(7)	0.066(4)
N(54)	0.3485(9)	0.3652(8)	-0.2695(5)	0.044(3)
C(55)	0.2119(11)	0.4242(10)	-0.2663(6)	0.044(3)
C(56)	0.1167(11)	0.4990(10)	-0.2080(6)	0.050(3)
C(57)	0.0648(10)	0.5985(9)	-0.0822(6)	0.035(3)
C(58)	0.1193(11)	0.6214(9)	-0.0248(6)	0.044(1)
C(59)	0.0246(11)	0.6935(9)	0.0354(5)	0.043(3)
S(61)	-0.5574(3)	1.1074(3)	0.3712(2)	0.044(1)
C(61)	-0.4533(11)	1.0193(9)	0.2968(5)	0.031(3)
N(61)	-0.2838(8)	0.8811(7)	0.1717(4)	0.036(2)
S(62)	-0.0479(3)	0.8147(3)	0.2247(2)	0.047(1)
N(62)	-0.5035(8)	1.0057(8)	0.2382(4)	0.040(2)
C(62)	-0.2172(10)	0.8864(9)	0.2277(5)	0.027(3)
S(63)	-0.4993(3)	0.9332(3)	0.1066(2)	0.060(1)
N(63)	-0.3086(7)	0.9537(7)	0.2893(4)	0.038(3)

C(63)	-0.4262(10)	0.9414(9)	0.1740(5)	0.033(3)
S(71)	0.1348(3)	1.1583(3)	0.2762(2)	0.056(1)
N(71)	-0.448(8)	1.0773(7)	0.1057(4)	0.031(2)
C(71)	0.0651(10)	1.1217(9)	0.2142(5)	0.031(3)
S(72)	-0.3138(3)	1.2120(3)	0.1694(2)	0.042(1)
C(72)	-0.1407(10)	1.1519(9)	0.1641(5)	0.031(3)
N(72)	-0.0794(8)	1.1699(7)	0.2180(4)	0.036(2)
S(73)	0.2063(3)	0.9330(3)	0.0265(2)	0.046(1)
N(73)	0.1462(8)	1.0464(7)	0.1550(4)	0.040(3)
C(73)	0.0983(10)	1.0218(9)	0.0985(5)	0.040(3)
N(510)	-0.1142(9)	0.7425(7)	0.0431(5)	0.038(2)
C(511)	-0.0803(10)	0.6513(10)	-0.0724(6)	0.047(3)
H(11C)	0.1457(13)	0.5585(12)	0.3180(7)	0.142
H(11B)	0.1140(13)	0.4374(12)	0.3111(7)	0.142
H(11A)	0.2532(13)	0.4256(12)	0.3348(7)	0.142
H(13)	0.1077(13)	0.3082(15)	0.4453(10)	0.081
H(14)	-0.0115(15)	0.3225(13)	0.5691(10)	0.091
H(21C)	0.3437(15)	0.3845(16)	0.1607(8)	0.201
H(21B)	0.2420(15)	0.5254(16)	0.1571(8)	0.201
H(21A)	0.3808(15)	0.4914(16)	0.1867(8)	0.201
H(223)	0.4965(23)	0.3053(15)	0.0389(15)	0.119
H(24)	0.6132(16)	0.3371(22)	-0.0812(12)	0.107
H(31)	0.8777(8)	0.0697(7)	-0.4426(4)	0.047
H(32)	0.5831(8)	0.1151(7)	-0.5407(4)	0.046
H(33)	0.4930(8)	0.2627(7)	-0.3496(4)	0.041
H(42)	0.3994(10)	0.4655(10)	0.4127(5)	0.055
H(43)	0.5554(11)	0.3486(10)	0.3129(6)	0.053
H(45)	0.8822(11)	0.3084(10)	0.3914(6)	0.059
H(46)	0.7362(10)	0.4242(9)	0.4948(5)	0.050
H(52)	0.3412(11)	0.4647(11)	-0.1112(6)	0.072
H(53)	0.4902(12)	0.3461(11)	-0.2118(7)	0.079
H(55)	0.1770(11)	0.4148(10)	-0.3062(6)	0.052
H(56)	0.0205(11)	0.5375(10)	-0.2088(6)	0.059
H(58)	0.2173(11)	0 .5887(9)	-0.0275(6)	0.053
H(59)	0.0619(11)	0.7080(9)	0.0729(5)	0.051
H(61)	-0.2311(8)	0.8365(7)	0.1329(4)	0.043
H(62)	-0.5944(8)	1.0417(8)	0.2423(4)	0.048
H(63)	-0.2729(7)	0.9553(7)	0.3263(4)	0.046
H(71)	-0.0788(8)	1.0647(7)	0.0706(4)	0.037
H(72)	-0.1352(8)	1.2140(7)	0.2565(4)	0.043
H(73)	0.2364(8)	1.0109(7)	0.1529(4)	0.048
H(511)	-0.2652(11)	0.7593(10)	-0.0063(6)	0.057
H(512)	-0.1222(10)	0.6385(10)	-0.1083(6)	0.057

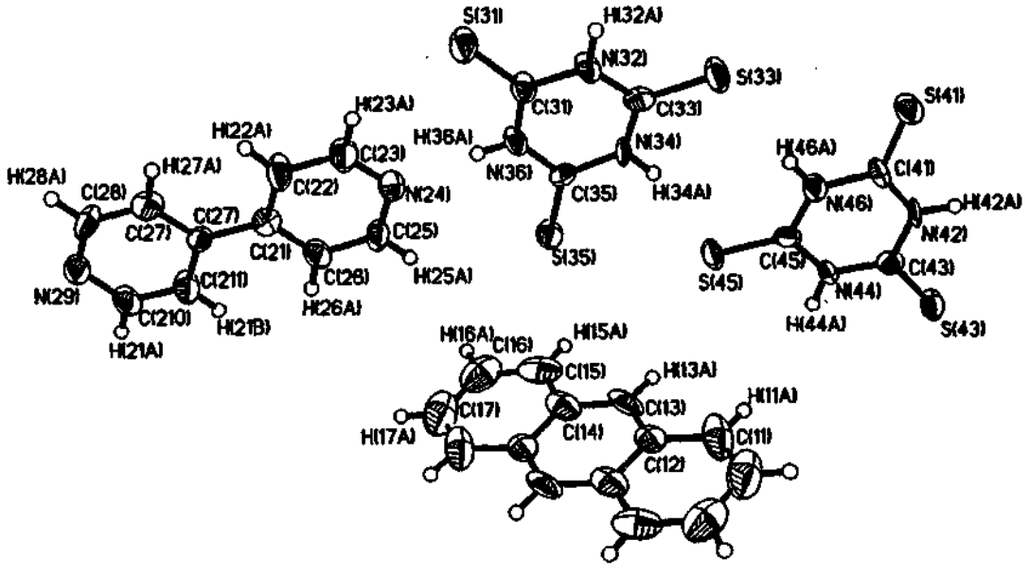


8e

Table A16. Fractional Coordinates and Equivalent Isotropic Displacement Parameters [$Å^2$] of Trithiocyanuric acid + 4,4'-bipyridyl + anthracene, **8f**.

Atom	x/a	y/b	z/c	U_{eq}
S(43)	0.4758(3)	0.3144(3)	0.3843(3)	0.046(1)
S(41)	0.9776(3)	0.4704(3)	0.3140(3)	0.045(1)
S(35)	1.1107(3)	1.1648(3)	0.7228(3)	0.045(1)
S(45)	0.8934(3)	0.8109(2)	0.5871(2)	0.042(1)
S(31)	1.6450(3)	1.3765(3)	0.7092(3)	0.053(1)
S(33)	1.2719(3)	0.8696(3)	0.4767(3)	0.045(1)
N(44)	0.6998(9)	0.5581(7)	0.4789(7)	0.035(2)
N(42)	0.7342(9)	0.4046(7)	0.3609(7)	0.033(2)
N(36)	1.3731(9)	1.2565(8)	0.7067(7)	0.032(2)
N(46)	0.9109(9)	0.6248(8)	0.4437(7)	0.039(2)
N(34)	1.2157(9)	1.0337(7)	0.6070(7)	0.034(2)
N(32)	1.4412(8)	1.1294(8)	0.5964(7)	0.034(2)
C(21)	1.5090(10)	1.7524(9)	1.0035(9)	0.029(2)
C(35)	1.2367(11)	1.1508(9)	0.6777(9)	0.033(3)
C(27)	1.5558(11)	1.8881(9)	1.0810(9)	0.032(2)
C(33)	1.3107(10)	1.0167(10)	0.5620(9)	0.031(2)
C(45)	0.8331(11)	0.6594(10)	0.4993(8)	0.032(2)
N(29)	1.6393(10)	2.1448(8)	1.2230(7)	0.039(2)
C(210)	1.5074(13)	2.0442(11)	1.1964(10)	0.046(3)
C(28)	1.7289(12)	2.1181(10)	1.1783(10)	0.047(3)
C(43)	0.6441(11)	0.4300(10)	0.4096(9)	0.033(3)
C(26)	1.3738(13)	1.6454(10)	0.9754(10)	0.049(3)
N(24)	1.4274(9)	1.5001(8)	0.8554(7)	0.035(2)
C(211)	1.4648(12)	1.9176(11)	1.1277(10)	0.047(3)
C(25)	1.3368(12)	1.5226(10)	0.9016(10)	0.045(3)
C(41)	0.8694(11)	0.4990(9)	0.3746(8)	0.031(2)
C(22)	1.6055(12)	1.7275(11)	0.9601(10)	0.052(3)
C(27)	1.6936(12)	1.9936(10)	1.1088(10)	0.044(3)
C(31)	1.4817(11)	1.2514(9)	0.6705(9)	0.034(3)
C(23)	1.5580(13)	1.6003(11)	0.8851(10)	0.053(3)
C(13)	0.9156(13)	0.9345(13)	0.8815(10)	0.056(4)
C(15)	0.8955(13)	1.1405(15)	0.8613(12)	0.061(4)
C(14)	0.9464(12)	0.8671(11)	0.9297(10)	0.052(3)
C(12)	0.9698(12)	0.8671(11)	0.9490(10)	0.047(3)
C(17)	1.0132(18)	1.3353(15)	1.0326(18)	0.089(6)
C(16)	0.9316(16)	1.2721(16)	0.9127(16)	0.074(4)
C(11)	0.9373(14)	0.7304(13)	0.9018(14)	0.070(4)
H(44A)	0.6463(9)	0.5760(7)	0.5123(7)	0.042

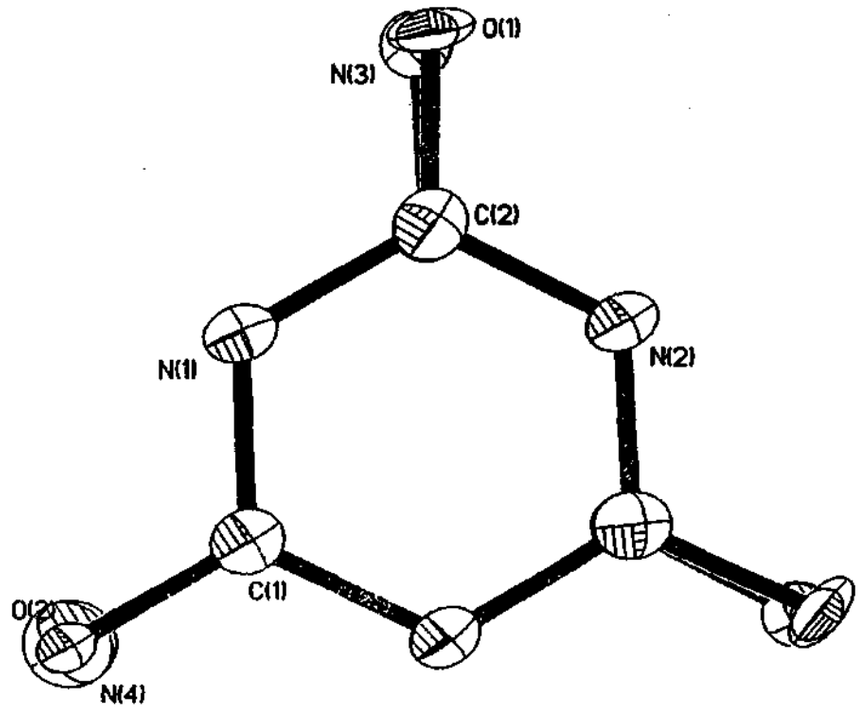
H(42A)	0.7040(9)	0.3243(7)	0.3190(7)	0.039
H(36A)	1.3916(9)	1.3319(8)	0.7511(7)	0.038
H(46A)	0.9941(9)	0.6870(8)	0.4522(7)	0.046
H(34A)	1.1337(9)	0.9644(7)	0.5898(7)	0.041
H(32A)	1.504398)	1.1231(8)	0.5687(7)	0.041
H(21A)	1.4415(13)	2.0596(11)	1.2251(10)	0.055
H(28A)	1.8211(12)	2.1877(10)	1.1949(10)	0.056
H(26A)	1.3073(13)	1.6557(10)	1.0059(10)	0.059
H(21B)	1.3718(12)	1.8501(11)	1.1125(10)	0.056
H(25A)	1.2443(12)	1.4523(10)	0.8834(10)	0.054
H(22A)	1.7010(12)	1.7944(11)	0.9805(10)	0.062
H(27A)	1.7614(12)	1.9808(10)	1.0811(10)	0.052
H(23A)	1.6231(13)	1.5864(11)	0.8546(10)	0.064
H(13A)	0.8580(13)	0.8909(13)	0.8032(10)	0.068
H(15A)	0.8384(13)	1.0994(15)	0.7827(12)	0.073
H(17A)	1.0327(18)	1.4226(15)	1.0660(18)	0.107
H(16A)	0.9017(16)	1.3198(16)	0.8675(16)	0.089
H(11A)	0.8803(14)	0.6863(13)	0.8235(14)	0.084



8f

Table A17. Fractional Coordinates and Equivalent Isotropic Displacement Parameters [Å^2] of Cyanuric acid + Melamine, **9a**.

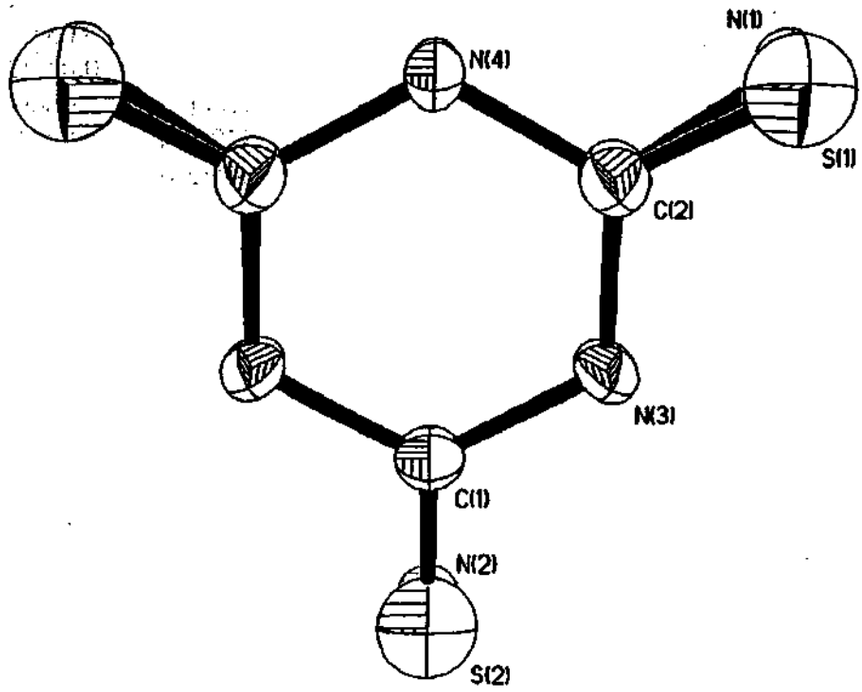
Atom	x/a	y/b	z/c	U_{eq}
N(2)	0.0879(3)	0.0000	0.3511(12)	0.026(1)
N(1)	0.2114(2)	0.1228(3)	0.1158(8)	0.025(1)
C(2)	0.1293(2)	0.1217(4)	0.2674(10)	0.026(1)
C(1)	0.2529(3)	0.0000	0.0420(14)	0.023(1)
O(2)	0.3247(12)	0.0000	0.1382(50)	0.026(3)
O(1)	0.0832(6)	0.2355(9)	0.2944(25)	0.027(2)
N(4)	0.3360(17)	0.0000	0.0517(65)	0.028(6)
N(3)	0.0973(8)	0.2381(15)	0.3887(31)	0.024(3)



9a

Table A18. Fractional Coordinates and Equivalent Isotropic Displacement Parameters [$Å^2$] of Trithiocyanuric acid + Melamine, **9b**.

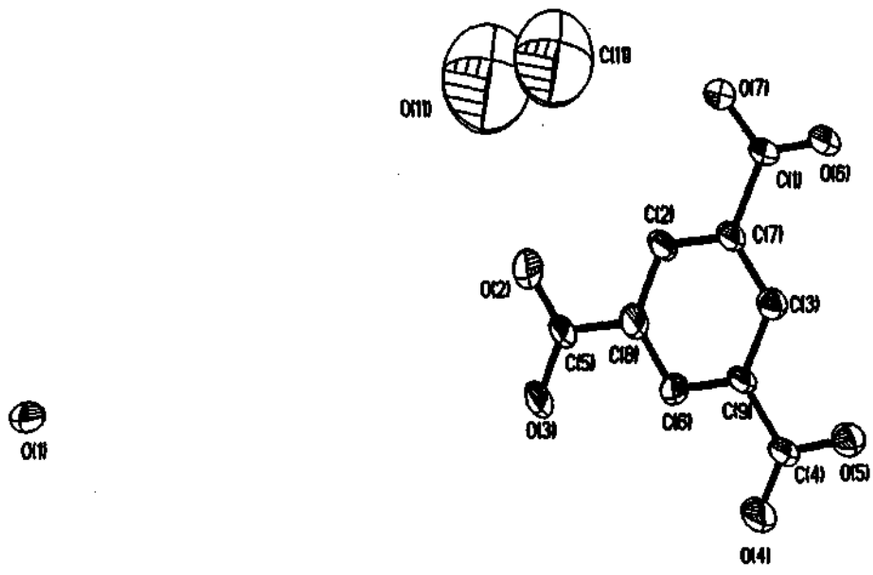
Atom	x/a	y/b	z/c	U_{eq}
N(4)	0.0877(3)	0.0000	0.3053(14)	0.025(1)
N(3)	0.2115(2)	0.1226(3)	0.1161(9)	0.024(1)
C(2)	0.1289(3)	0.1213(4)	0.2681(12)	0.025(1)
C(1)	0.2522(4)	0.0000	0.0449(17)	0.023(2)
S(1)	0.0934(4)	0.2371(5)	0.3634(17)	0.053(2)
N(1)	0.0798(11)	0.2359(17)	0.2633(48)	0.023(6)
N(2)	0.3212(12)	0.0000	-0.1745(57)	0.022(6)
S(2)	0.3331(5)	0.0000	-0.0702(23)	0.052(3)



9b

Table A19. Fractional Coordinates and Equivalent Isotropic Displacement Parameters [$Å^2$] of Trimesic acid (methanol), **10a**.

Atom	x/a	y/b	z/c	U_{eq}
C(9)	0.2357(24)	-0.0030(9)	0.8047(9)	0.034(2)
C(8)	0.2261(26)	-0.0777(10)	0.6844(5)	0.039(2)
O(7)	0.6573(23)	-0.4979(7)	0.7820(4)	0.065(2)
O(5)	0.2405(22)	0.0784(7)	0.9219(4)	0.060(2)
O(6)	0.7049(20)	-0.4383(7)	0.8949(4)	0.054(2)
O(4)	-0.0146(22)	0.2336(8)	0.8259(4)	0.061(2)
O(3)	-0.0196(22)	0.0850(8)	0.5762(4)	0.064(2)
C(7)	0.4567(24)	-0.2522(9)	0.7930(5)	0.032(2)
O(2)	0.2220(23)	-1.0422(9)	0.5639(4)	0.071(2)
C(6)	0.0175(24)	0.0324(10)	0.7285(5)	0.035(2)
C(5)	0.1456(28)	-0.0414(10)	0.6029(5)	0.046(3)
C(4)	0.1452(26)	0.1158(9)	0.8515(5)	0.039(2)
C(3)	0.3848(25)	-0.1433(10)	0.8380(5)	0.037(2)
C(2)	0.3769(24)	-0.2202(9)	0.7167(5)	0.035(2)
C(1)	0.6172(26)	-0.4070(10)	0.8294(5)	0.040(2)
O(1)	0.0306(24)	0.2991(7)	-0.0108(4)	0.066(2)
O(11)	0.2026(86)	-0.5111(48)	0.5328(22)	0.365(19)
C(11)	0.4159(116)	-0.5440(54)	0.6045(26)	0.276(19)

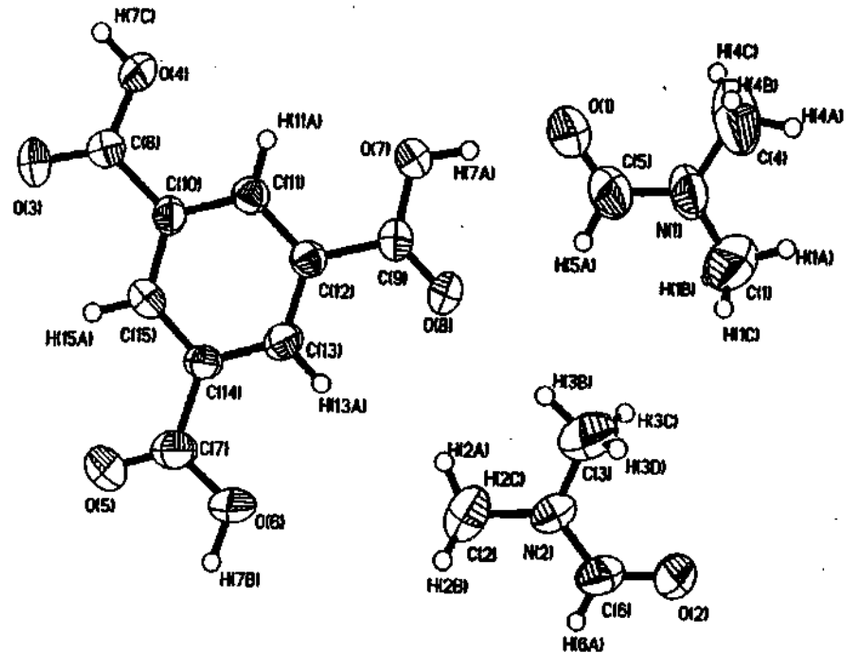


10a

Table A20. Fractional Coordinates and Equivalent Isotropic Displacement Parameters [$Å^2$] of Trimesic acid (dimethylformammide), **10b**.

Atom	x/a	y/b	z/c	U_{eq}
O(6)	0.4809(2)	0.4170(2)	0.2127(5)	0.074(1)
O(8)	0.2154(2)	0.4330(2)	-0.0668(4)	0.066(1)
C(10)	0.3359(2)	0.1421(2)	0.0736(5)	0.037(1)
O(4)	0.2650(2)	0.0076(2)	0.0109(5)	0.068(1)
O(7)	0.1464(2)	0.3035(2)	-0.1036(5)	0.066(1)
O(5)	0.5401(2)	0.2812(2)	0.2570(5)	0.087(1)
C(12)	0.2771(2)	0.2913(3)	0.0106(5)	0.037(1)
C(14)	0.4089(2)	0.2823(3)	0.1364(5)	0.039(1)
C(9)	0.2109(3)	0.3500(3)	-0.0572(6)	0.043(1)
C(13)	0.3458(2)	0.3338(3)	0.0745(5)	0.042(1)
C(15)	0.4039(2)	0.1863(3)	0.1357(5)	0.044(1)
C(11)	0.2726(2)	0.1953(2)	0.0117(5)	0.038(1)
O(3)	0.3825(2)	-0.0095(2)	0.1439(5)	0.071(1)
C(8)	0.3309(3)	0.0394(3)	0.0818(6)	0.046(1)
N(2)	0.2742(2)	0.6898(2)	0.0656(5)	0.063(1)
O(2)	0.2351(2)	0.8381(2)	0.0429(5)	0.087(1)
O(1)	0.0318(2)	0.4127(2)	-0.2076(5)	0.084(1)
C(7)	0.4843(3)	0.3254(3)	0.2067(6)	0.054(1)
N(1)	-0.0010(3)	0.5598(3)	-0.2869(5)	0.070(1)
C(6)	0.2873(3)	0.7783(3)	0.0578(7)	0.066(2)
C(5)	0.0491(3)	0.4945(4)	-0.2406(7)	0.078(2)
C(4)	-0.0840(4)	0.5400(4)	-0.2977(8)	0.108(2)
C(3)	0.1943(3)	0.6556(3)	0.0577(9)	0.117(2)
C(2)	0.3364(3)	0.6215(3)	0.0827(7)	0.085(2)
C(1)	0.0224(3)	0.6534(4)	-0.3203(9)	0.132(3)
H(15A)	0.4465(2)	0.1513(3)	0.1773(5)	0.053
H(11A)	0.2268(2)	0.1663(2)	-0.0295(5)	0.046
H(6A)	0.3395(3)	0.7982(3)	0.0637(7)	0.079
H(5A)	0.1022(3)	0.5107(4)	-0.2318(7)	0.093
H(4A)	-0.1122(4)	0.5947(4)	-0.3330(8)	0.162
H(4B)	-0.1022(4)	0.5197(4)	-0.1816(8)	0.162
H(4C)	-0.0932(4)	0.4923(4)	-0.3856(8)	0.162
H(3B)	0.1948(3)	0.5894(3)	0.0651(9)	0.175
H(3C)	0.1700(3)	0.6742(3)	-0.0543(9)	0.175
H(3D)	0.1649(3)	0.6803(3)	0.1571(9)	0.175
H(2A)	0.3135(3)	0.5608(3)	0.0860(7)	0.127
H(2B)	0.3658(3)	0.6322(3)	0.1924(7)	0.127
H(2C)	0.3711(3)	0.6261(3)	-0.0189(7)	0.127
H(1A)	-0.0234(3)	0.6895(4)	-0.3521(9)	0.198
H(1B)	0.0594(3)	0.6549(4)	-0.4179(9)	0.198
H(1C)	0.0467(3)	0.6786(4)	-0.2132(9)	0.198

H(7C)	0.2601(25)	-0.0512(32)	0.0220(61)	0.077(17)
H(7B)	0.5299(29)	0.4431(34)	0.2620(66)	0.116(20)
H(7A)	0.1084(29)	0.3433(33)	-0.1577(68)	0.111(20)



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