Solid State Supramolecular Synthesis of Organic Networks: Some Studies in Crystal Engineering

A Thesis
Submitted for the Degree of
DOCTOR OF PHILOSOPHY

By
D. Shekhar Reddy

School of Chemistry
University of Hyderabad
Hyderabad - 500 046
India
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To
My Parents

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Statement

I hereby declare that the matter embodied in this Thesis is the result of investigations carried out by me in the School of Chemistry, University of Hyderabad, India under the supervision of Professor Gautam R. Desiraju.

In keeping with the general practice of reporting scientific observations due acknowledgements have been made wherever the work described is based on the findings of other investigators.

Hyderabad
June, 1995

D.Shekhar Reddy

Certificate

Certified that the work **"Solid State Supramolecular Synthesis of Organic Networks: Some Studies in Crystal Engineering"** has been carried out by D.Shekhar Reddy under my supervision and that the same has not been submitted elsewhere for a degree.

Gautam R. Desiraju

Dean
School of Chemistry

Prof. Gautam R. Desiraju
Thesis Supervisor

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Finally, I wish to thank my wife Madhavi for her patience and consistent encouragement.

D.Shekhar Reddy

Preface

Supramolecular chemistry is the chemistry beyond the molecule and is the designed chemistry of the intermolecular bond just as molecular chemistry is that of covalent bond. The mainstream of synthetic chemistry is involved in the synthesis of molecules by joining atoms with covalent bonds. A very high degree of control over covalent bond formation has been achieved during this century. Supramolecular chemistry is now a rapidly growing subject and desirable supermolecules may be synthesised if intermolecular interactions are handled in a predictable fashion. Conventional hydrogen bonds have been exaustively used in the architecture of supermolecules. The work involved in this thesis uses several weak intermolecular interactions in solid-state supramolecular synthesis.

This thesis consists of four chapters. The first chapter gives a brief account of various supramolecular networks found in many inorganic and organic structures that are constructed with strong intermolecular interactions and metal-ligand bonds. The knowledge gained from these networks is then utilised in the construction of similar and new supramolecular networks using weaker intermolecular interactions.

Geometrical characteristics of $C\equiv N\cdots Cl$ interactions have been thoroughly described in the second chapter using the Cambridge Structural Database(CSD). The knowledge obtained from the CSD studies, is exploited in the design of one- and two-dimensional networks using $C\equiv N\cdots Cl$ interactions.

The third chapter discuss the use of C–H···N≡C hydrogen bonding in the crystal engineering of organic networks. For this purpose, β-hydrogen containing organic cyano compounds are selected.

The supramolecular synthesis of organic diamondoid networks is presented in the fourth chapter. In this study, several weak intermolecular interactions such as N···Br, C–H···N, Br···Br, Br···π and I···I are utilised in the design of diamondoid networks. Besides this, the topological relationship between organic and inorganic structures is also discussed.

CHAPTER ONE

INTRODUCTION

Supramolecular chemistry is the study of the structures and functions of molecular assemblies.[1] This branch of science lies at the interface of chemistry, biology and materials science and has emerged as a very important, interdisciplinary subject. Molecular association through intermolecular interactions leads to the formation of supermolecules. Such association which results from molecular recognition is a key step in supramolecular synthesis. Much of the early work in supramolecular chemistry has been done in the solution state. Solid-state supramolecular chemistry has taken advantage of crystallography and it is now well-recognised that a crystal is the ultimate supermolecule - "a supermolecule *par excellence*".[2] The systematic strategies by which useful solid-state structures are produced defines the subject of crystal engineering which is "the understanding of intermolecular interactions in the context of crystal packing and in the utilisation of such understanding in the design of new solids with desired physical and chemical properties".[3] The aim of crystal engineering is to establish rigorous connections between molecular and supramolecular chemistry via intermolecular interactions. If a crystal is the supramolecular equivalent of a molecule, crystal engineering is the supramolecular equivalent of organic synthesis. Therefore crystal engineering can be termed solid state supramolecular synthesis.

The construction of solid state supramolecular assemblies in one-, two- and three-dimensional networks is important because these solids are not only fascinating but also exhibit many desirable physical and chemical properties. Such supramolecular construction therefore represents an important challenge in structural chemistry.[3] The rationalisation and prediction of these molecular organisations is extremely helpful in understanding complex structures such as three-dimensional organic and inorganic networks, double helical characteristics of nucleic acids, liquid crystalline phases, molecular films and mesophases.[1,4]

This chapter gives a brief account of various supramolecular networks found in many inorganic and organic structures that are constructed with strong intermolecular interactions and metal-ligand bonds. The knowledge gained from these networks will then be utilised to construct similar or new supramolecular networks using weaker intermolecular interactions.

1.1. Inorganic networks

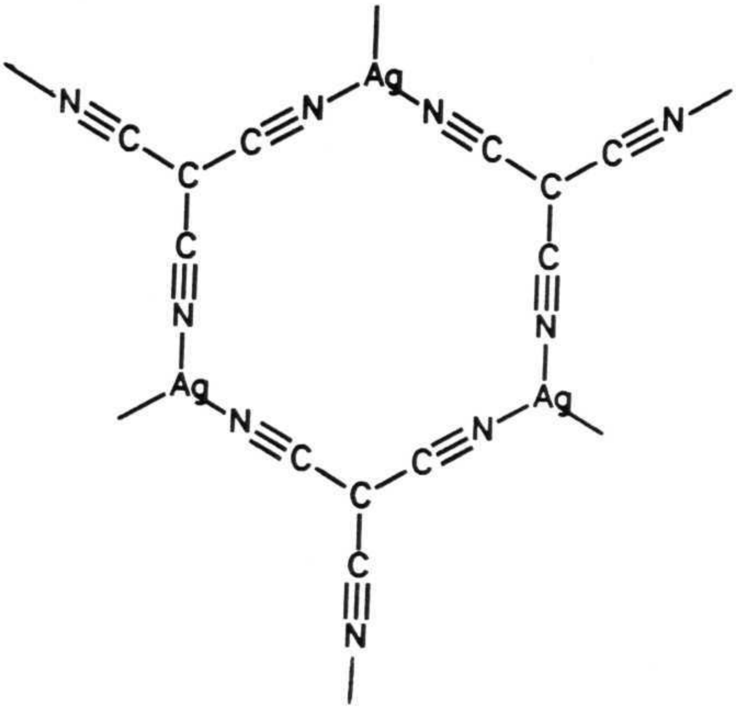
The description of crystal structures in terms of nets is one of the most promising of systematic approaches and is an easy technique to communicate structural information in a precise fashion.[5] This technique is excellently described by Wells in his well-known book *"Structural Inorganic Chemistry"*.[6] This type of analogy between known and unknown structures results in a dramatic reduction in the time and effort required to elucidate a crystal structure because it does not require much with regard to terminology or notation. Originally, this concept was applied only to inorganic networks but it has been realised that it is also highly useful in the understanding of organic crystal structures. In the application of network theory to organic structures, the molecular residues are taken as nodes and the supramolecular bonds are taken as node connections. The importance of this method is that, the knowledge gained from the large body of inorganic networks can be successfully applied to easily understand complicated organic crystal structures.[5] This method has been applied to understand many organic structures and is very useful in elucidating relationships between different structures.

Among several examples found in the inorganic literature, a simple 'Metal–C≡N–Metal' example is considered here. In this system, the metal is a node and '–C≡N–' is a node connection. This system is selected because of the linearity and rigidity of the cyano group, which enables the cyano group to be used as a node connector. The following examples show one-, two- and three-dimensional nets formed by Metal–C≡N–Metal system.

Linear one-dimensional arrays formed by C≡N-metal bonds are found in AgCN and AuCN and a schematic diagram of these arrays is shown in **1**.[6] The crystal structures of $AgC(CN)_3$[7] and $CuC(CN)_2$[6] show two-dimensional networks formed through C≡N-metal connectivities with cyclic hexameric cavities and the hexameric cavity of $AgC(C{\equiv}N)_3$ is shown in **2**. The hexameric cavities are filled by self-catenation in the crystal structure of $AgC(CN)_3$ and water molecules are enclathrated in the crystal structure of $CuC(CN)_2$.

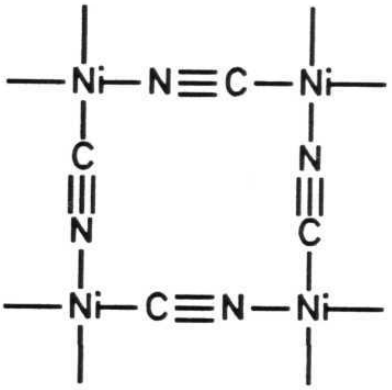
$$\text{—}\,Ag\text{–}C{\equiv}N\text{—}Ag\,\text{—} \qquad\qquad \text{—}\,Au\text{–}C{\equiv}N\text{—}Au\,\text{—}$$

(1)



(2)

The crystal structure of $Ni(CN)_2.NH_3.C_6H_6$[8] is another classical example for the formation two-dimensional networks with C≡N-metal bonds. In this structure, Ni atoms are linked through the cyano groups, leading to the formation of a two-dimensional layer which consists of square grid units as shown in 3. The benzene molecules are enclathrated into the host cavity. Three-dimensional networks are also constructed with -C≡N- node connections. For example the crystal structures of $Zn(CN)_2$[9] and $Cd(CN)_2$[9] show two-fold diamondoid lattices. The interpentration in the $Cd(CN)_2$ structure is removed by quenching with CCl_4 molecules.



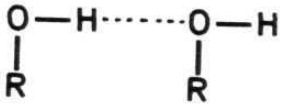
(3)

1.2. Hydrogen bonded networks

It is well known that the properties of solids are critically dependent upon their structure.[3] The structural features of solids are optimised by various intermolecular interactions which are directional and/or non-directional. It is well-recognised that the crystal is a result of a near perfect balance between different intermolecular interactions and that it consists of specific structural units.[10,11] Although different intermolecular interactions are involved in the formation of a crystal, the strength and directionality of the hydrogen bond places it at the centre of many research efforts aimed at controlling solid state structures. Most structural studies show that the hydrogen bond association is not random but leads to the formation of specific patterns. Certain patterns are specific for some functional groups and display a clear preference over other patterns. Such knowledge is quite useful in the design of the organic solids with desired properties. The improved understanding of hydrogen bonds in organic molecular solids leads to the classification of hydrogen bonding. In this context, two major types of classification proposed by Etter[10] and Desiraju[11] have appeared. Etter proposed graph-set rules for understanding hydrogen bonded networks in the solid state. This graph theory explains the hydrogen bonded networks in terms of encoding and decoding hydrogen bonding networks. This theory is restricted to hydrogen bonded and similar networks because it is based on donor and acceptor groups. Desiraju's explanation of structures is based on the fact that the crystal is the ultimate supermolecule and that all organic crystal structures can be considered as networks. In the crystal, molecules are connected to each other with intermolecular interactions in specific reproducible patterns. These geometrically and chemically meaningful patterns are called "*supramolecular synthons*". This is analogous to the inorganic nomenclature described in Section 1.1. Here the molecules are nodes and the node connections are the supramolecular synthons. In other words, this concept takes advantage of synthetic organic chemistry (the synthon concept) and inorganic crystal chemistry (description of structure in terms of networks) thus bridging two major areas of chemistry at the supramolecular level. The beauty of this supramolecular synthon concept is that it not only includes hydrogen bonding patterns but also patterns formed by other weak intermolecular interactions. Several patterns involving strong hydrogen bonding based on different functional groups are now described.

1.2.1. Alcohols

In alcohols, the $\mathrm{O{-}H\cdots O}$ hydrogen bonded motif **4** is the most common while the trimeric motif **5** is also observed frequently in many crystal structures.[12] The $\mathrm{O{-}H\cdots O}$ hydrogen bonded zig-zag chains are also seen in many crystal structures. For instance solid methanol, ethanol and other higher aliphatic alcohols form infinite molecular chains.[13] The schematic diagram is depicted in **6**.



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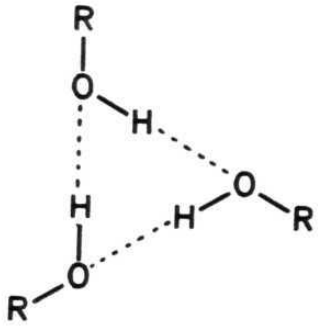

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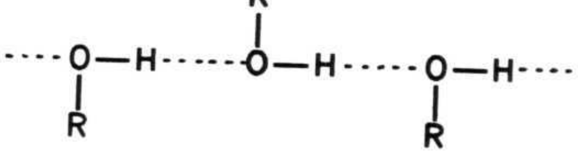
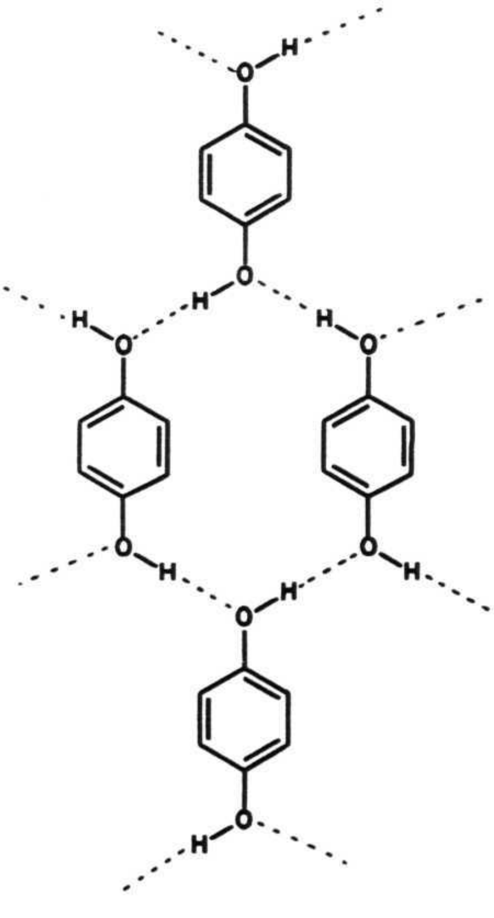


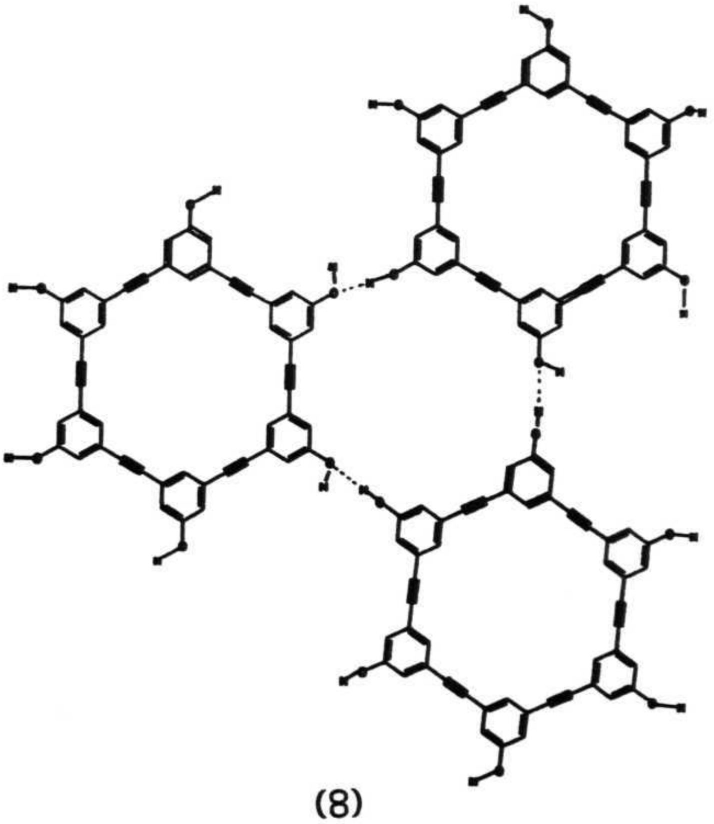
(6)

The formation of the two-dimensional hydrogen bonded networks in alcohols usually appears when the molecules have two hydroxy functionalities at terminal positions. For example γ-hydroquinone[14] has two OH functionalities at terminal positions and these can act independently as donor and acceptor, leading to the formation of two-dimensional hydrogen bonded sheets as shown in **7**. The two-dimensional hydrogen bonded networks formed by alcohols have cavities and are capable of enclosing guest molecules.



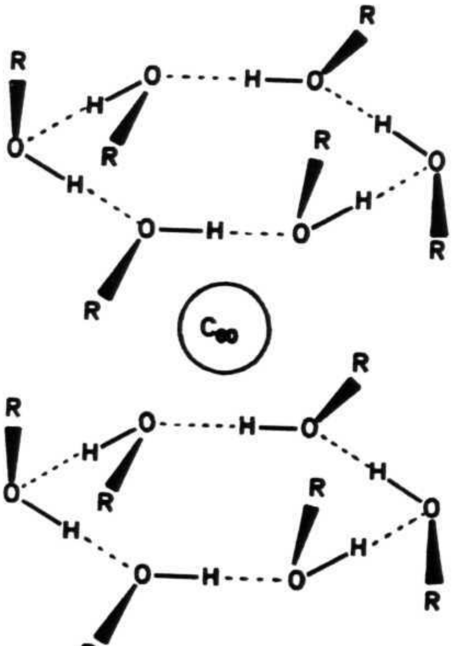
(7)

Moore and co-workers[15] have recently constructed a two-dimensional hydrogen bonded sheet with a macrocycle with phenolic groups on the exterior. The crystal structure of this compound shows wide cyclic hexameric cavities, **8** that are filled by solvent molecules instead of self-catenation. These authors noticed that the size of the host molecule is bigger than the supramolecular cavity formed by host molecules and the possibility of the self-catenation is thus ruled out in its crystal structure. This type of design helps in avoiding self-catenation but in practice, it involves tedious synthetic work and it is also difficult to anticipate the exact size of the supramolecular cavity because foreign solvent molecules may be included into the host network and enlarge the size of supramolecular cavity.



(8)

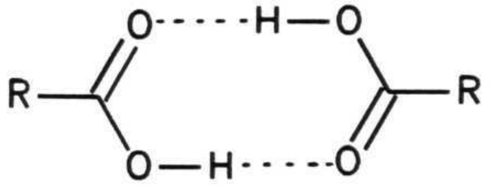
Three-dimensional hydrogen bonded networks formed by alcohols have long been known. The three-dimensional hydrogen bonded networks are commonly produced when the O-H group utilises the lone pair and its hydrogen atom for hydrogen bonding. For instance, ice forms diamondoid networks through O-H···O hydrogen bonds.[16] Similarly, β-hydroquinone[17] forms three-dimensional hydrogen bonded networks (super cube). In this structure, the super cube is filled by the other identical networks and the remaining space is useful for the incorporation of small guest molecules. The super cube of this structure is completely utilised by quenching the interpenetration with C_{60} molecules as shown in 9.[18] This study clearly conforms that the inclusion of foreign guest molecules is always preferred to self-catenation when the host cavity and guest molecules are complementary in size. It is believed that this type of quenching is an efficient method to avoid self-catenation in supramolecular host structures.



(9)

1.2.2. Carboxylic acids

Carboxylic acid functionalities self-assemble in two different ways. The centrosymmetric dimer motif **10** is commonly observed in many crystal structures whereas the catemer motif **11** is rarely observed.[3] Thus the predictability of motif **10** is greater and the following examples show the usage of motif **10** in systematic supramolecular synthesis.



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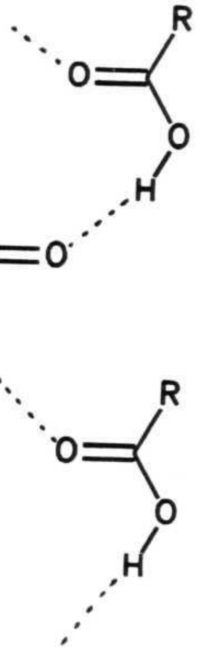
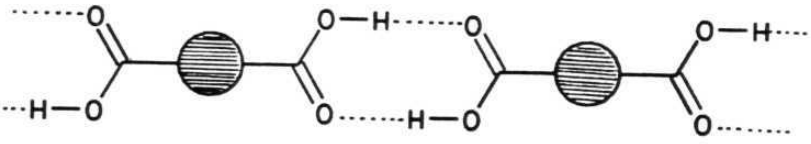
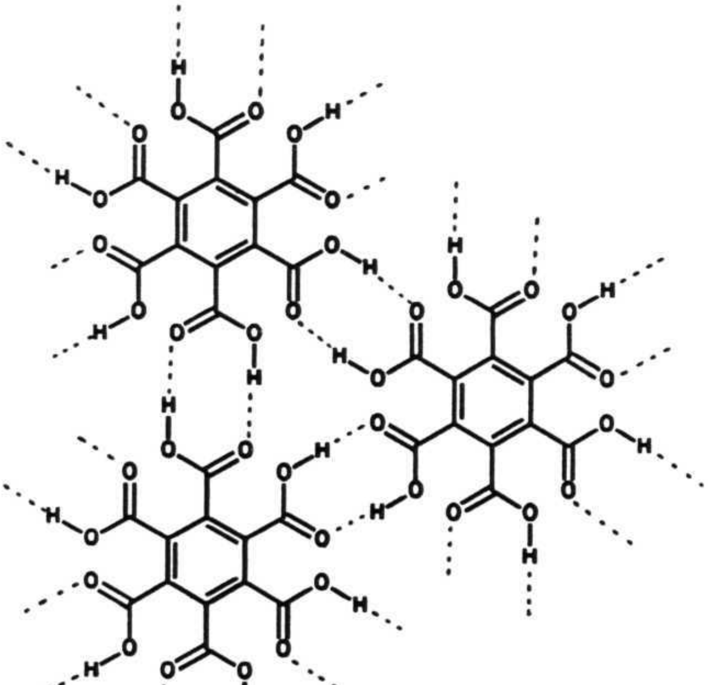


(11)

The carboxylic acid dimer motif **10** is used to generate one-dimensional ribbon structures. This dimer motif is robust and is not perturbed even though drastic changes are made at the molecular level. For instance in the crystal structures of β-oxalic acid, fumaric acid and terephthalic acid, the molecules are interlinked with each other with dimer motif **10** resulting in the formation of linear one-dimensional molecular ribbons as shown in **12**.[19]

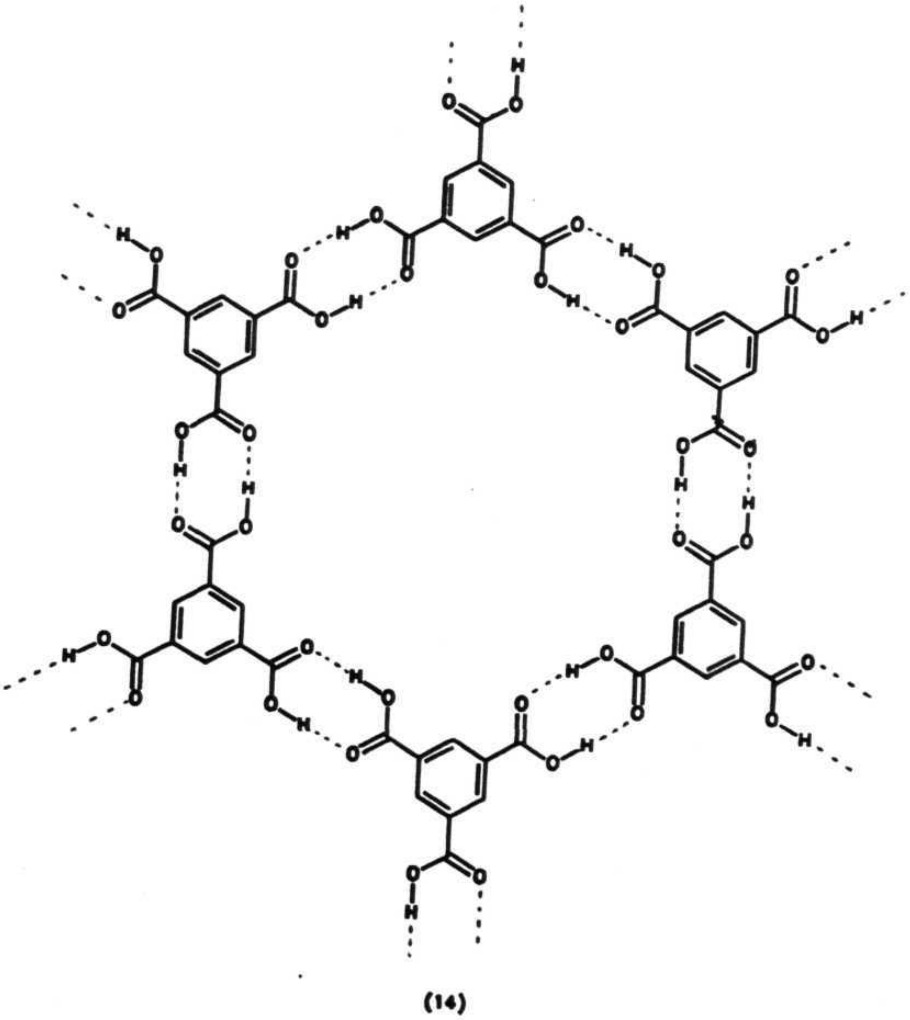


(12)



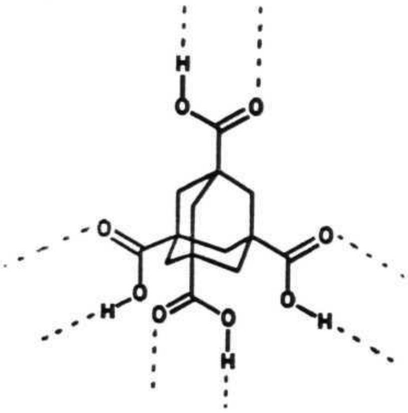
(13)

Two-dimensional hexagonal sheets may be observed in the crystal structures of acids containing molecular three-fold symmetry. In the crystal structure of mellitic acid,[20] each molecule is connected by six such molecules, resulting in the formation of hexagonal hydrogen bonded sheet as shown in **13**. Accordingly, in the crystal structure of trimesic acid (benzene-1,3,5-tricarboxylic acid),[21] each molecule is connected by three other molecules leading to the formation of very large hexagonal cavities **14** which are self-catenated by three other such identical hydrogen bonded networks.



(14)

Diamondoid networks were first observed by Ermer in the crystal structure adamantane-1,3,5,7-tetracarboxylic acid **15.**[22] In this molecule, the carboxylic acid functionalities are tetrahedrally disposed resulting in the formation of super-adamantane structure through carboxylic dimer units in the crystal. The super-adamamtane cavity is completely filled by self-catenation resulting in a five-fold diamondoid structure. Accordingly, the crystal structure of methanetetraacetic acid **16**[23] produces three-fold diamondoid lattices due to its smaller size.



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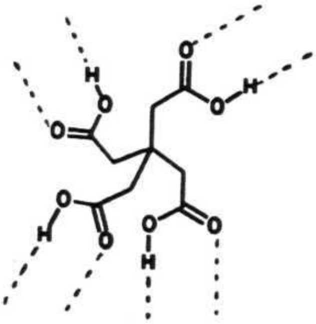
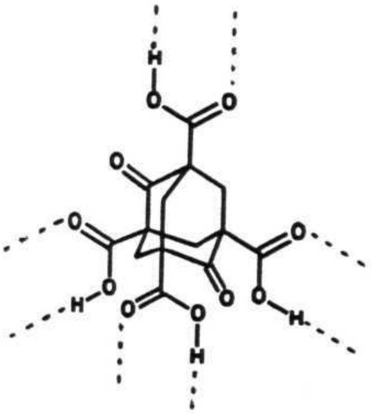


(16)

However, in these two solids, the super-adamantane cavity is completely filled by self-catenation and is not useful for the enclosure of foreign guest molecules. Till now, two types of procedures, have been developed to avoid self-catenation in supramolecular host structures. One way is to select a suitable guest molecules and incorporate it into the host cavity so as to avoid catenation.[18] The second way is to introduce some steric factors disfavouring catenation by insertion of some appropriate functionality in the host molecules.[24] Ermer and co-workers adopted the second method to avoid the self-catenation in the super-adamantoid cavities and introduced the oxo or methylene groups in compound **15**. Consequently the degree of interpenetration was reduced in the crystal structure of adamantane-2,6-dione -1,3,5,7-tetracarboxylic acid **17**[24] and small guest molecules such as acetic acid molecules are incorporated into the host cavity along with the three interpenetrating networks. In the crystal structure of adamantane-2,6-dimethylene-1,3,5,7-tetracarboxylic acid **18**[24] the degree of interpenetration is further reduced and larger molecules such as mesitylene are incorporated into the host cavity along with two interpenetrating diamondoid lattices.



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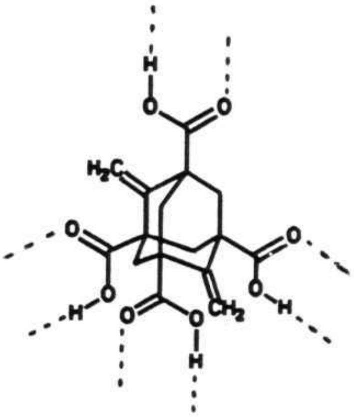
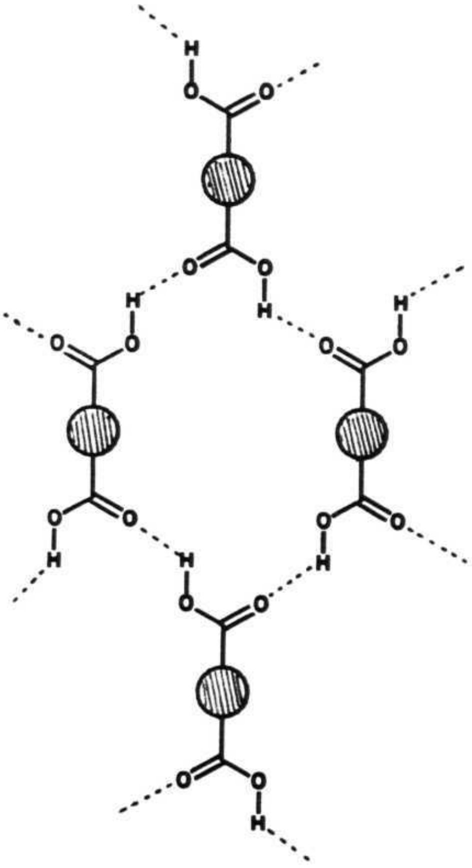


(18)

The catemer type of hydrogen bonding appears infrequently when compared to the cyclic dimer motif. The one-dimensional networks are known with this type hydrogen bonded networks in the crystal structure of formic acid, acetic acid and (p-chlorophenyl)propiolic acid.[25] It is believed that in the last case, the driving force for the formation of hydrogen bonded catemer networks is due to the influence of weak C-H···O and Cl···Cl interactions. A schematic view of the one-dimensional catenated network is depicted in **11**.

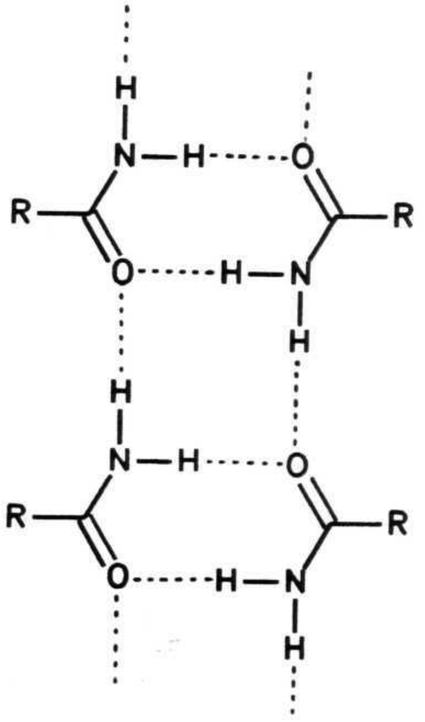
Two-dimensional layered structures are also noticed with the catemer type of hydrogen bonding when the catemer hydrogen bonded networks are properly linked. The best examples are α-oxalic acid[26] and 1,4-dicarboxycubane[27] and the network structure of which are shown in 19.



(19)

1.2.3. Amides

Hydrogen bonded networks are well studied in amides.[28,29] Primary amides usually form centrosymmetric dimers and these dimers are again connected to each other with hydrogen bonds forming one-dimensional ribbon structures 20.[28] Two-dimensional layered structures are also noticed when the one-dimensional ribbons are connected through covalent moieties as shown in 21.[28] The formation of this type of two-dimensional hydrogen bonded network is possible when the molecule has two primary amide functionalities. The crystal structure of adamantane-1,3,5,7-tetracarboxamide 22[22] is a unique example of a diamondoid solid in which four-fold diamondoid lattices are interconnected to each other by hydrogen bonding.



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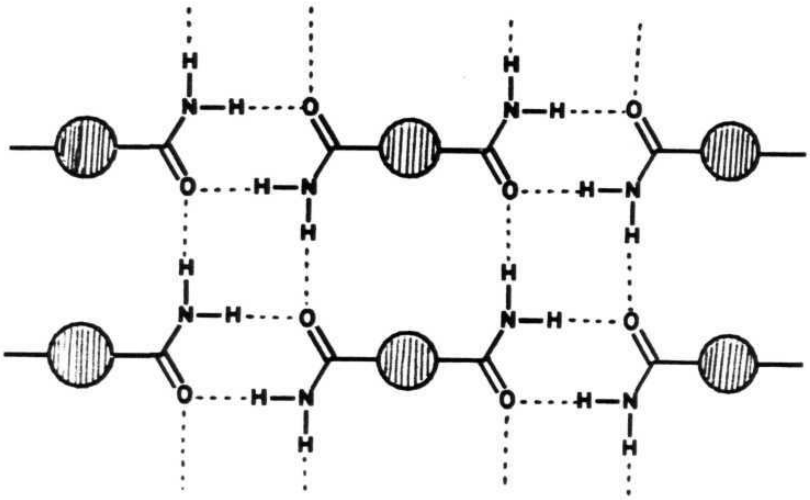

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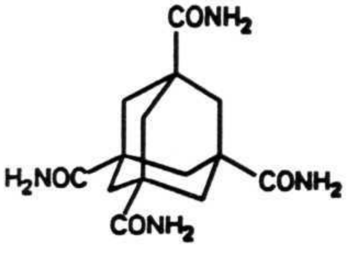
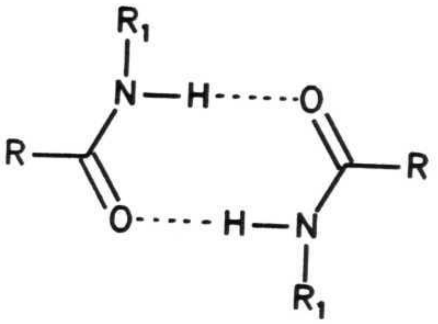


(22)

The secondary amides may be divided into *cis*- and *trans*-amides with respect to the geometry of hydrogen and oxygen atoms in the amide functionality. The *cis*-amides generally form the centrosymmetric dimer motif **23** as in carboxylic acids while the *trans*-amides form catenated hydrogen bonded networks.



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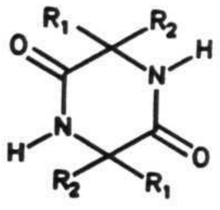
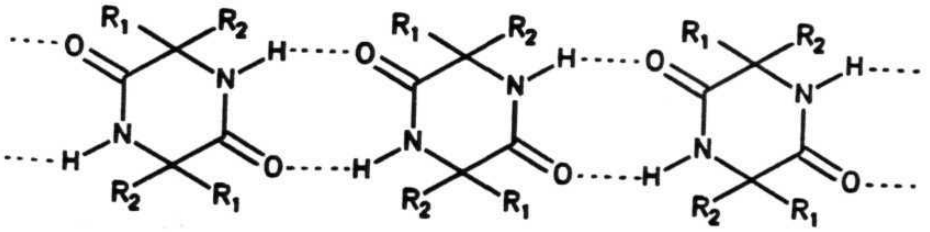


(24)

The *cis*-amide groups are most promising functionalities like carboxylic acids and have fine self-complementary binding sites. One- and two-dimensional hydrogen bonded networks are well-studied in many classes of compounds with the *cis*-amide functionality.[28,29] For instance, the diketopiperazine, **24** and its derivatives may be considered for the study of the organisation of hydrogen bonds in generating one- and two-dimensional networks using *cis*-amide functionalities. The molecular ribbon formation through the dimer motif is dipicted in **25**. The formation of hydrogen bonded square grids, **26** extends to two-dimensional layers.



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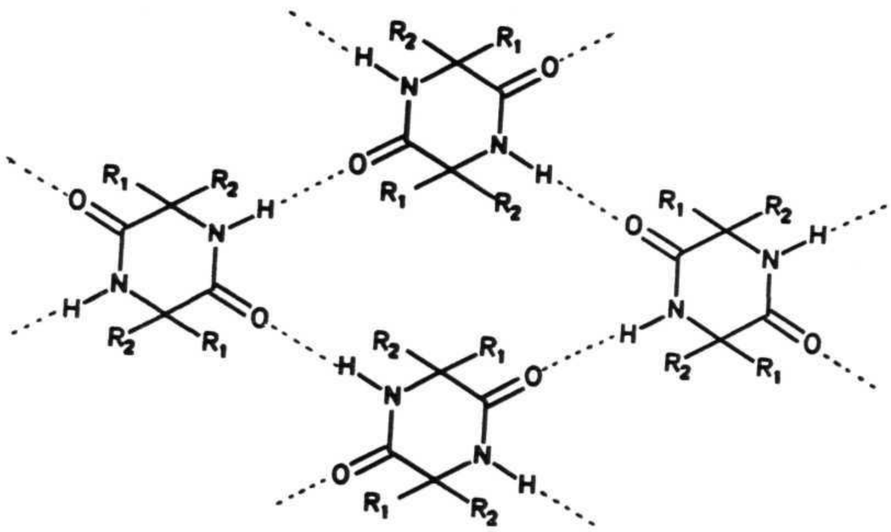
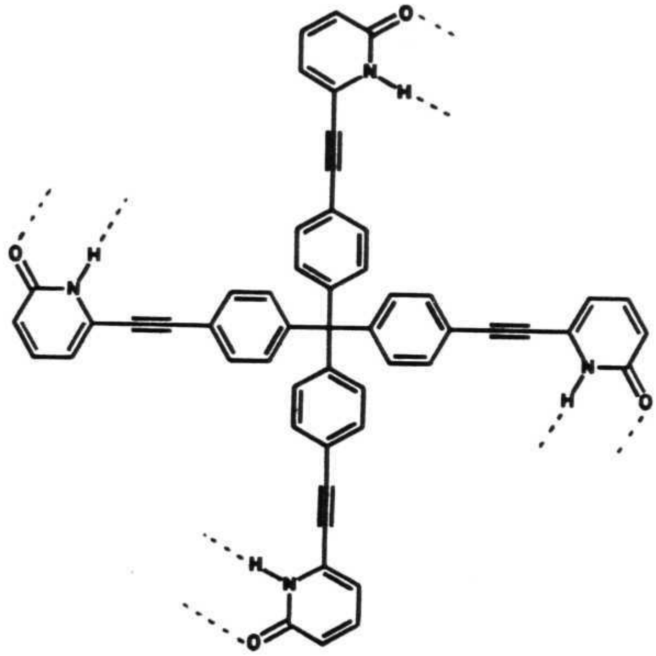


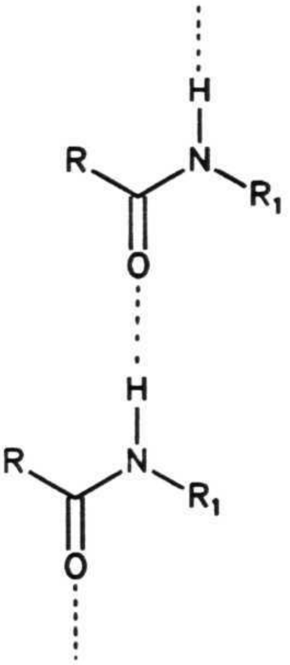
(26)

Wuest and co-workers[30] have synthesised super-adamantoi hydrogen bonded networks using the *cis*-amide functionalities. These authors used tetrakis(4-((6-oxopyrid-2-yl)-ethynyl)phenyl)methane **27** and related metal compounds are taken as precusors to devolop the super-adamantanoid cavities. Because of the long arms, a huge super-adamantoid cavity is generated but unfortunately these group of solids have extensive interpenetration of seven-fold diamondoid lattices.



(27)

The *trans*-amides molecules connect with each other through hydrogen bonds and resulting in the formation of infinitive one-dimensional networks as shown in **28**.[28] If the molecules have more than one *trans*-amide functionality, then the possibility of two-dimensional networks arises as shown in **29**.[28]



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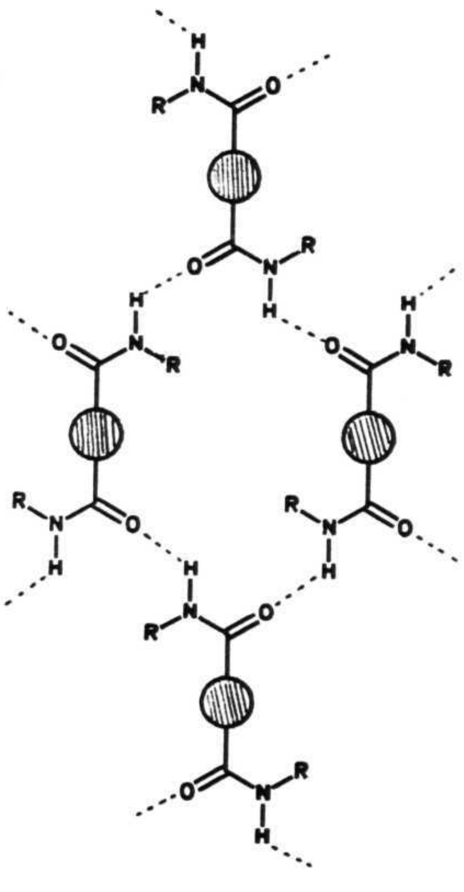
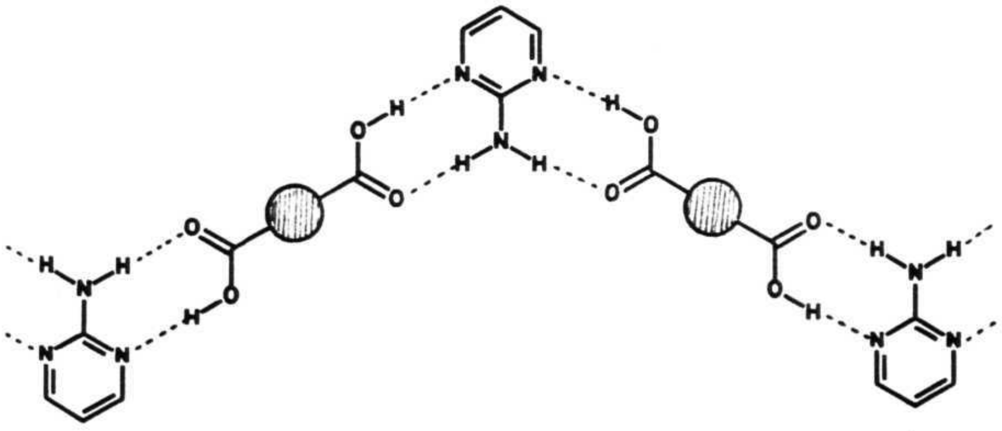


(29)

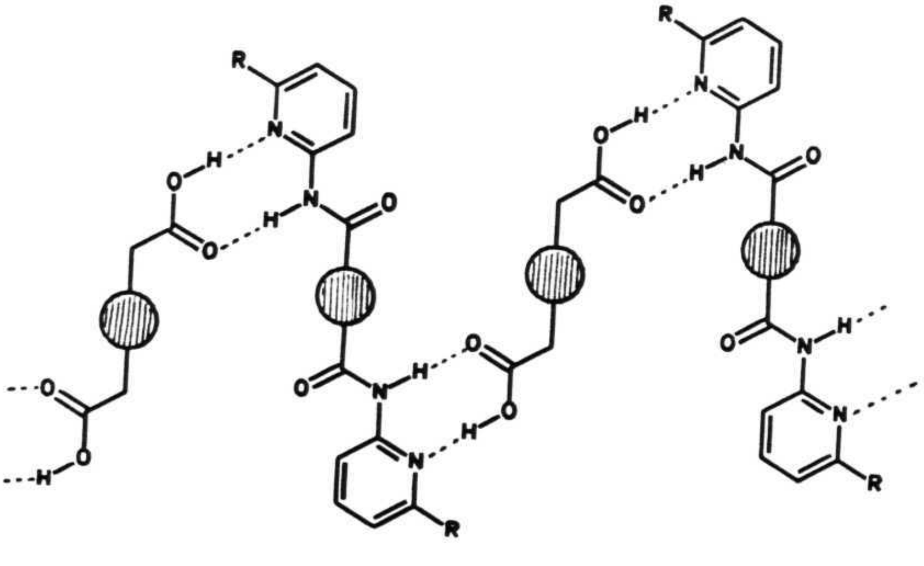
1.2.4. Molecular complexes

Intermolecular interactions between different molecules are the basis for the formation of molecular complexes. The analysis of single component crystal structures is useful for studying the structures of ensembles of molecules after association has taken place, while molecular complexation studies are useful for monitoring competitive interactions that determine the selectivity of recognition processes. In other words, molecular complexes generally contain stronger or more specific interactions than do either of the starting materials. A substantial amount of work has been done in this area and some of these studies are particularly relevant in the design of one-, two- and three-dimensional hydrogen bonded networks.



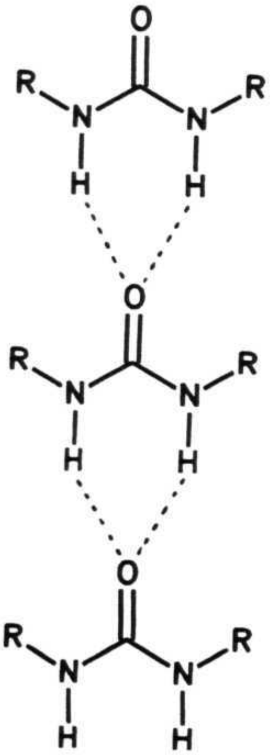
(30)

Etter and co-workers[31] developed one-dimensional supramolecular arrays utilising the hydrogen bond preferences of 2-aminopyrimidines and dicarboxylic acids as shown in **30**. Hamilton and co-workers[32] extended these ideas to one-dimensional hydrogen bonded networks utilising similar hydrogen bond preferences. In a series of structures, bis(amidopyrimidines) and dicarboxylic acids of different size are used as precursors to develop one-dimensional hydrogen bonded chains. This is depicted in **31**.



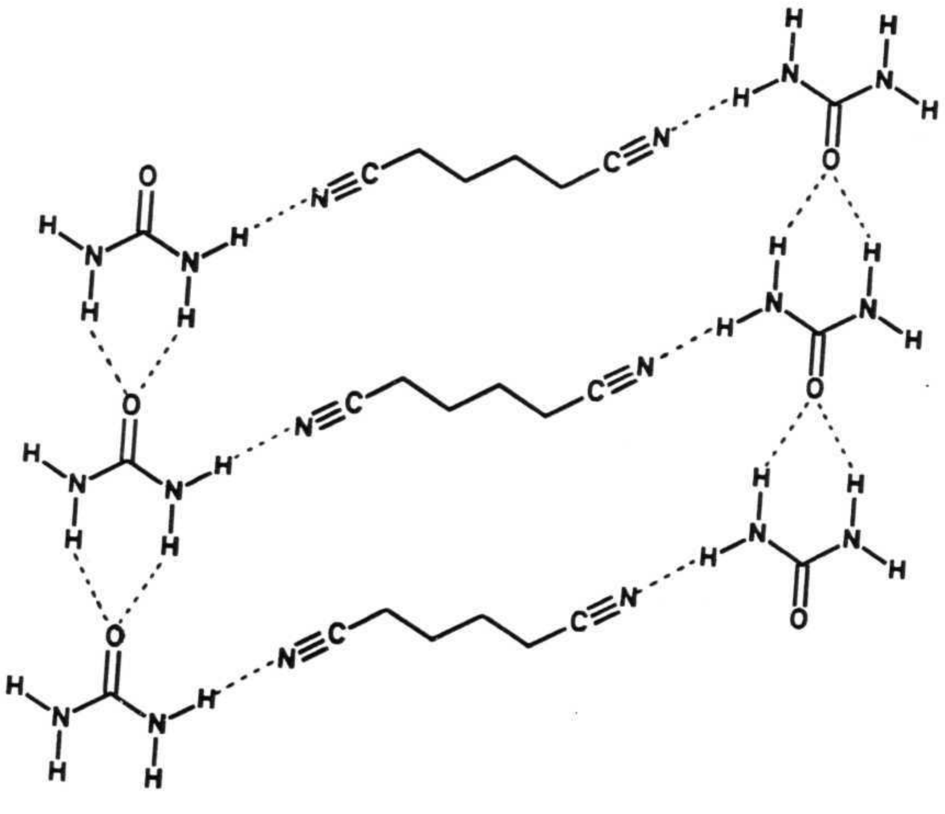
(31)

The N N' disubstituted urea derivatives have two proton donors and one proton acceptor (oxygen atom) that can participate in hydrogen bonding resulting in the formation of a one-dimensional linear molecular ribbon structure as shown in **32**.[33] The reproducibility of this ribbon motif in many structures is utilised in the design of two-dimensional hydrogen bonded networks using the N,N' disubstituted urea derivaties. Along these lines, Hollingsworth and co-workers[34] devoloped two-dimensional layered materials with the co-crystallisation of N,N' disubstituted urea



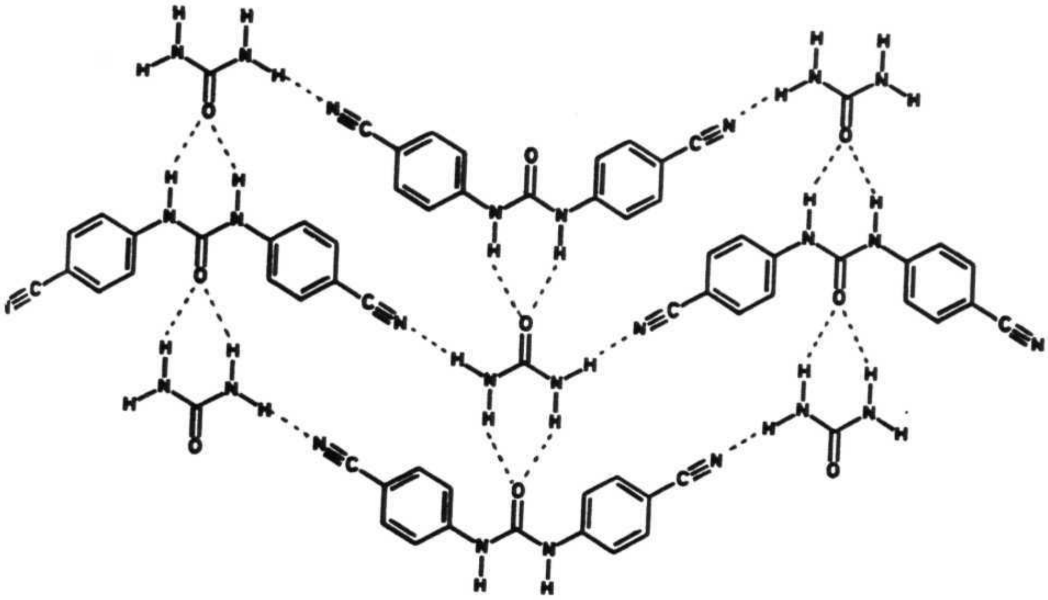
(32)

derivaties and linear aliphatic dinitrile spacer molecules. Interestingly, some of these two-dimensional networks showed inclusion properties. In their study, the cyano groups acts as a hydrogen acceptor and N,N' disubstituted urea derivatives donates



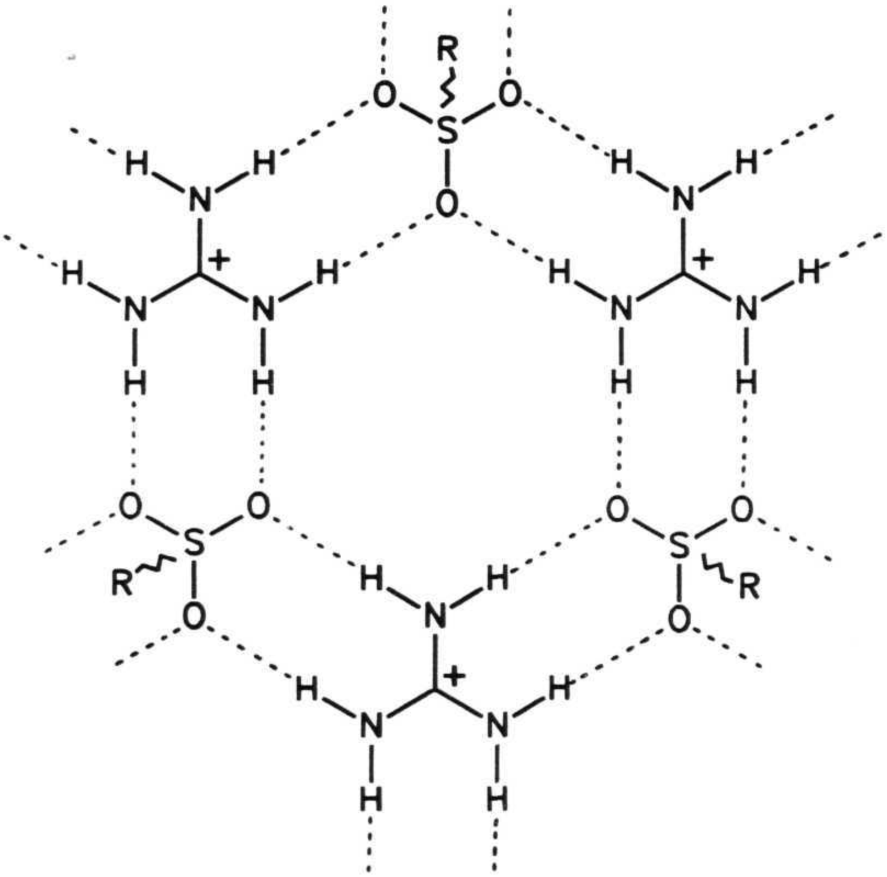
(33)

hydrogen atoms. The resulting layered two-dimensional $C\equiv N\cdots H-N$ hydrogen bonded networks is shown in **33**. Curiously, the 1:1 complex of urea and bis (4-cyanophenyl) urea exhibits a two-dimensional hydrogen bonded layered structure as shown in **34**.



(34)

One- and two-dimensional hydrogen bonded networks have also been designed with the co-crystallisation of 3-fold symmetrical molecules. In this connection, Ward and co-workers[35] studied hydrogen bonded molecular ribbons and sheets in a series of crystal structures of guanidinium and para-substituted benzenesulfonates. In these structures, hydrogen bonded sheets **35** are observed in these cases where the para-substituent is a poor hydrogen bonding functionality which does not interfere with the guanidinium-sulfonate hydrogen-bonded network. In cases where the para-substituent is a good hydrogen-bonding functionality, the guanidinium sulfonate hydrogen-bonded network is disrupted and results in the fomation of molecular ribbons as shown in **36**.



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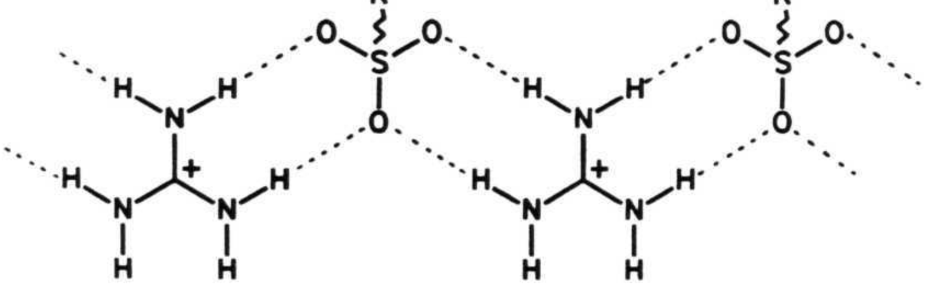
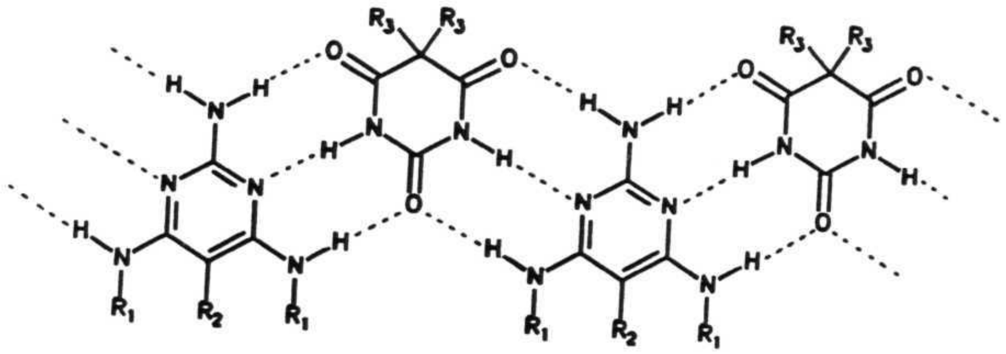


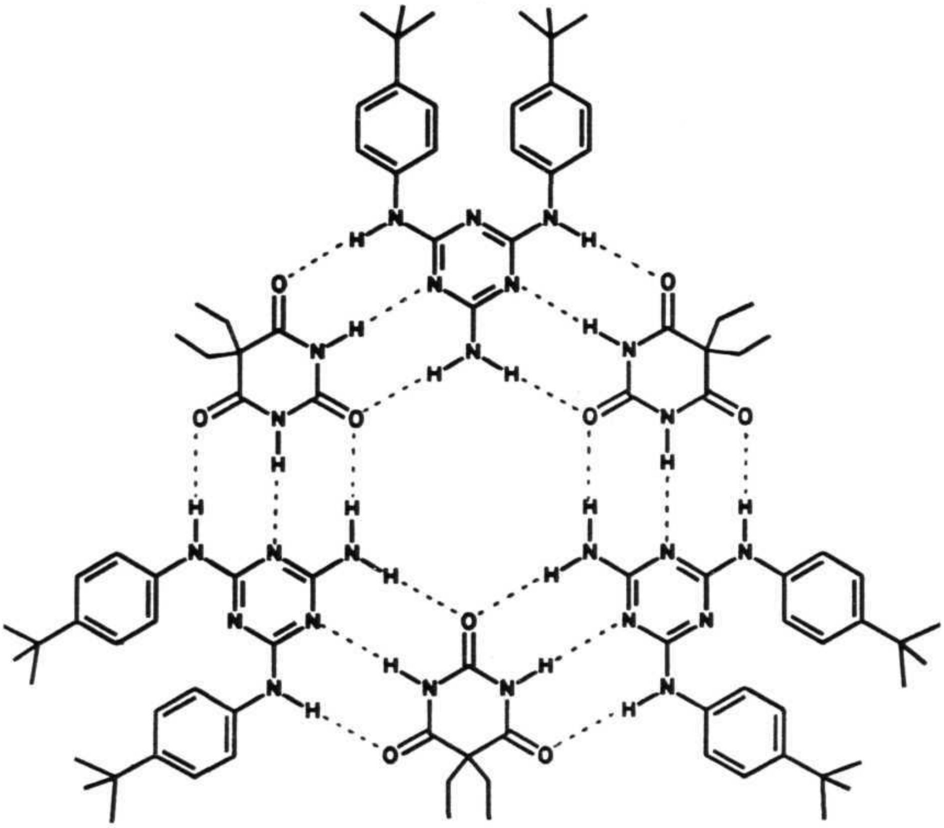
(36)

The groups of Lehn and Whitesides[36] have observed one-dimensional networks with multiple hydrogen bonds in the 1:1 molecular complexes of barbituric acid and melamine derivatives as shown in **37**. Interestingly, the multiple hydrogen bonding is strategically and successfully utilised by Whitesides and co-workers to develop the cyclic hexameric aggregates as shown in **38**.



(37)

Zaworotko and co-workers[37] have developed super diamondoid networks by allowing molecular complexation between $[Mn(CO)_3(\mu_3\text{-}OH)]_4$ **39** and different linear and rigid molecular spacer units which have the hydrogen accepting capacity. In this architecture, different sizes of spacer molecules are utilised and levels of interpenetration are logically employed based upon the length and volume of the spacer molecules.



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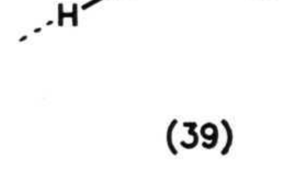
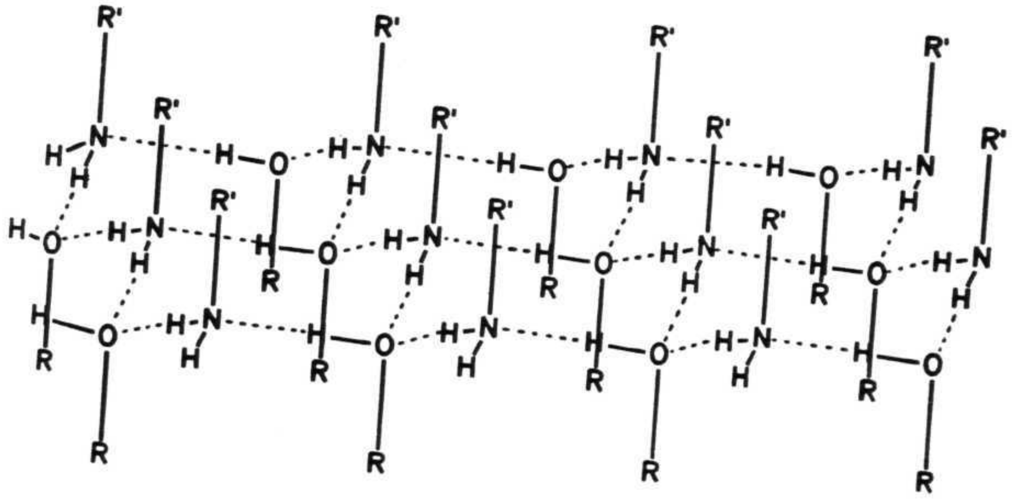


(39)

Ermer and co-workers[38] showed that due to the complementarity of the hydroxy and amino groups, molecular recognition occurs among alcohols and primary amines leading to the formation of tetrahedral clusters with N-H···O and O-H···N hydrogen bonds. This concept is successfully exploited for crystal engineering purposes by drawing upon linear diphenols and aromatic diamines as supramolecular partners. The super-tetrahedral crystal architecture is shown in 40.



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CHAPTER TWO

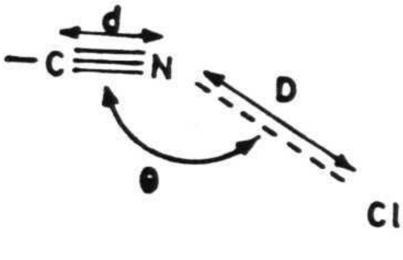
SOLID STATE SUPRAMOLECULAR SYNTHESIS WITH CYANO···CHLORO INTERACTIONS

An organic crystal is one of the best examples of a supermolecule because in it, a mutual recognition of molecules is sharpened by geometrical factors and long-range structural periodicity to generate a near-perfect supramolecular array.[1-3] Simultaneously, it is well-recognised that the construction of molecular assemblies utilising the directional characteristics of intermolecular forces is a cornerstone of supramolecular chemistry.[4] In the solid state, such rational design of supramolecular structure is referred to as crystal engineering and has important implications for the development of new materials with useful physical and chemical properties.[5]

It has been clearly evidenced that, besides conventional hydrogen bonding, weak intermolecular interactions such as C–H···O, C–H···N, C–H···halogen, halogen···halogen, N···Br, C≡N···halogen and hydrophobic interactions can be used as building blocks in the construction of supermolecules.[6] Though these interactions are not as strong as conventional hydrogen bonds they may be equally directional in nature. This realisation leads to the anticipation of similar one- and two-dimensional networks with these weaker interactions. In the preceding chapter, the synthesis of various supramolecular networks using conventional hydrogen bonds has been described. This chapter discusses the identification and robustness of patterns involving C≡N···Cl interactions and their use in the supramolecular synthesis of one- and two-dimensional networks. The motivation for this study of weaker interactions is that the scope of compounds which can be used for supramolecular construction is greatly enhanced but because of their weakness, multipoint rather than single-point recognition is often the key to their successful implementation. In this connection a series of crystalline 1,4-disubstituted 2,3-dicyano-5,6-dichlorobenzenes **1-8** have been studied and the Cambridge Structural Database (CSD) is used to understand the geometrical features of $C\equiv N\cdots Cl$ interactions.

2.1. Cyano...chloro interactions

The structural chemistry of the cyano group has been discussed previously.[7] This group can accept acidic H-atoms forming conventional hydrogen bonds and also participate in donor-acceptor interactions with polarisable, electron-deficient groups like the halogens. Such cyano···halogen interactions were first studied by Hassel[8] and much early work was reviewed by Britton[9] and in a more general context by Bent.[10] More recently, Desiraju and Harlow studied these interactions in greater detail with the CSD and found that the shortest of these contacts (N···Cl 3.00-3.20Å) are the result of halogen atom polarisation $[C\equiv N(\delta^-)\cdots X(\delta^+)]$.[11] The basicity of an sp hybridised N-atom is less than that of sp^2 and sp^3 hybridised N-atoms. Despite this, the sp-hybridised N-atom can form effective cyano···halogen interactions because of the compact cylindrical shape of the cyano group and the fact that the radii of the Cl-atom and the cyano group are similar (3.60Å). The approach of the cyano group towards the Cl-atom is shown below.



Since the study of Desiraju and Harlow,[11] the CSD has almost doubled in size (69691 versus 119939 entries in the April 1994 release of Version 5.07) and it was felt desirable to repeat the CSD study of C≡N···Cl interactions. Retrieval of non-metal atom containing, error-free (0.02Å level) crystal structures of compounds containing both chloro and cyano groups yielded 166 entries (76 entries formerly). Duplicate entries with higher R-factors were removed. Of these 166 entries, 46 crystal structures gave 65 C≡N···Cl contacts less than 3.50Å (formerly 37 contacts). Histograms of the N···Cl distances, D and the C≡N···Cl angles, θ are shown in **Figure** 1. The distance distribution shows that there are two types of contacts, a shorter one (3.00–3.20Å) caused by atom polarisation and a more 'normal' or van der Waals one (3.20–3.50Å) which is longer. The histogram of C≡N···Cl angles is much more featured than that observed previously and there is a clear preference for θ to be around 120°. In the earlier study, it had been observed that the distribution is 'seemingly featureless' between 80 and 180°. It is interesting to note that with a near doubling of the data, this ' seeming' featurelessness has resolved

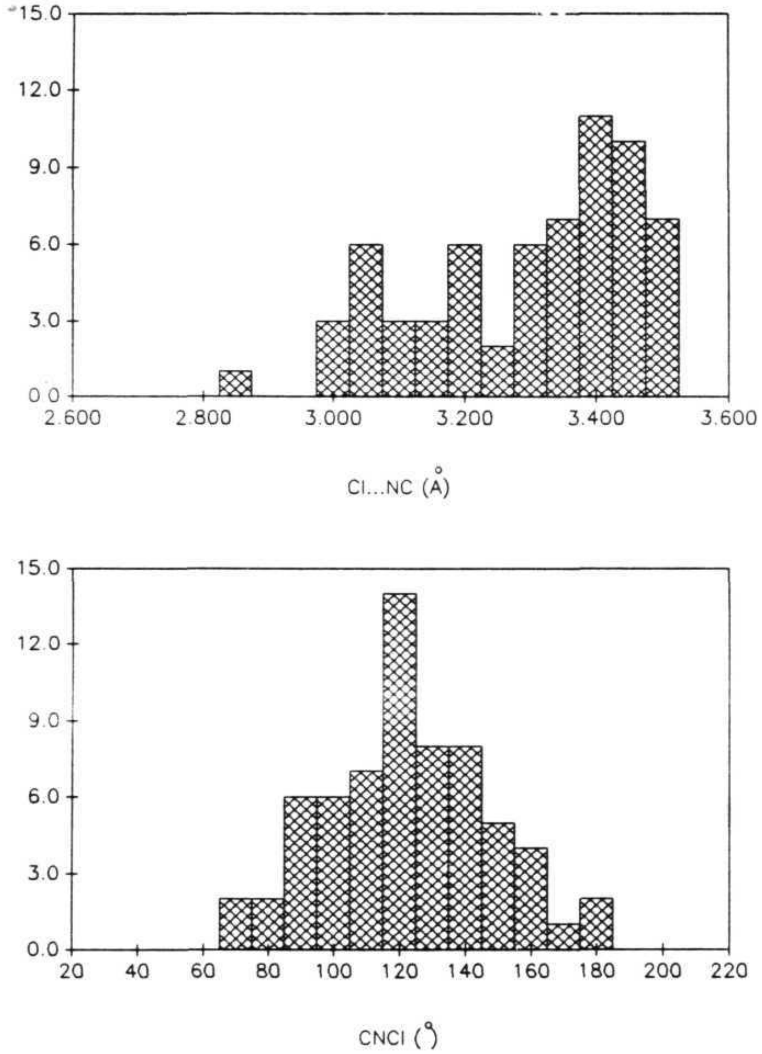


Fig 1

Figure 1. a) Histogram of $C\equiv N\cdots Cl$ bond lengths. b) Histogram of $C\equiv N\cdots Cl$ bond angles. Notice that maximum number of hits appear at 120°

into a distinct maximum at 120^0. Such an observation is also of general relevance to CSD research because it suggests that even with the ever-increasing size of the database, changes in statistical profiles may not be unusual with the passage of time. This 120^0 trajectory towards the C≡N bond has been noted in studies of conventional hydrogen bonding by the cyano group[7] and may have to do with the importance of canonical forms wherein the N-atom is formally sp^2 hybridised. To summarise, the CSD results show that the C≡N···Cl interaction has definite length and angle attributes and therefore has a definite structure-defining ability which one might attempt to use in crystal engineering.

2.2. Simple cyano...chloro motifs

An inspection of the 46 crystal structures retrieved above showed that, in many cases, C≡N···Cl contacts are responsible for supramolecular assembly. Figures 2a-c show some of these crystal structures and Scheme 1 shows some of the supramolecular fragments found therein. The simplest supramolecular fragment observed is just the interaction, **I** and may be found for example, in chlorocyanoacetylene[12] and 4-chlorobenzonitrile[11] wherein it alternates with spacer ethynyl or phenyl groups. When C≡N···Cl contacts are taken in pairs, the symmetrical and unsymmetrical motifs **II** and **III** are obtained. Both these motifs take the form of dimeric loops. Motif **II** may be observed in dichlorofumaronitrile[13] and also in 1,2-dicyano- 3,4,5,6-tetrachlorobenzene[14] where it occurs along with motif **III** and the more intricate **IV** and **V**. Many other compounds, retrieved from the CSD have more complicated crystal structures because they contain other structurally-perturbing functional groups such as hydroxy, amino,

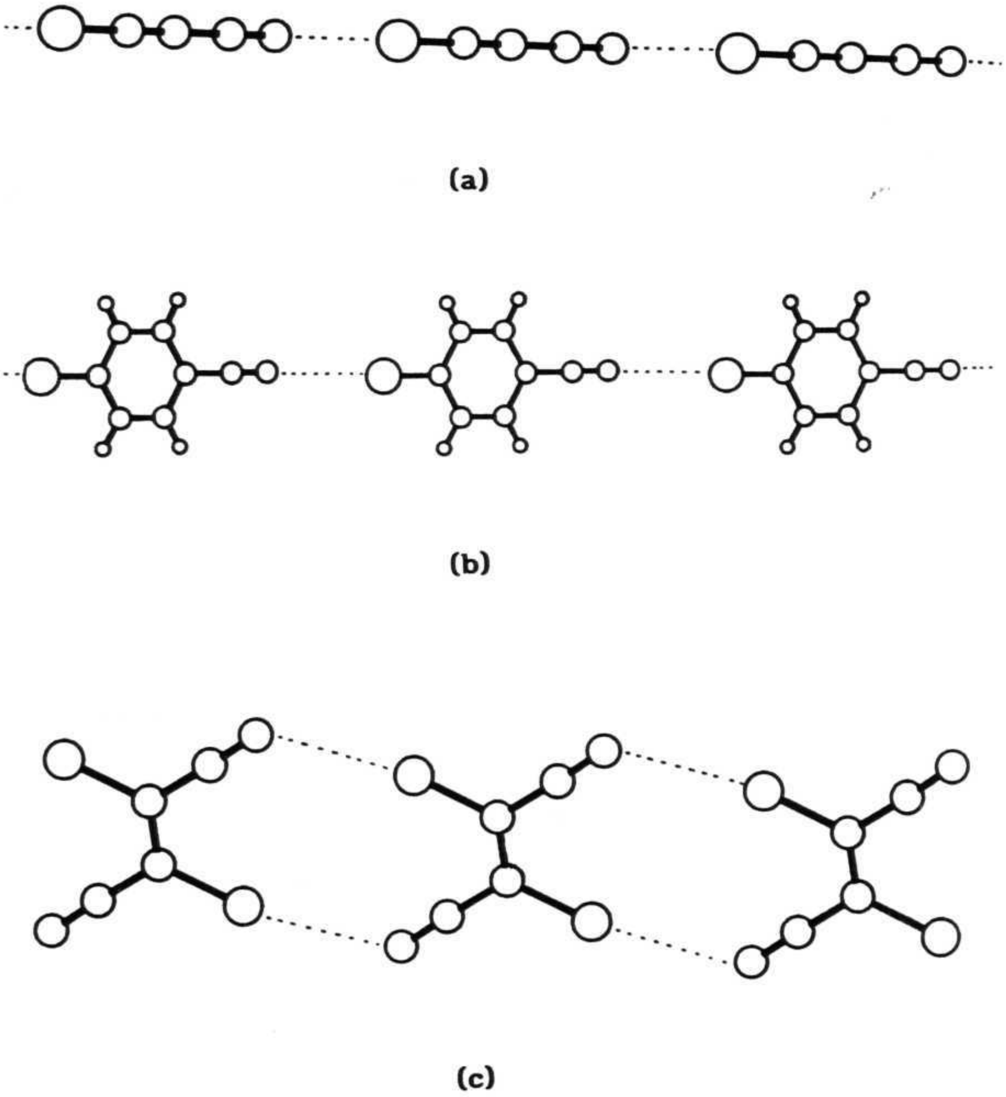
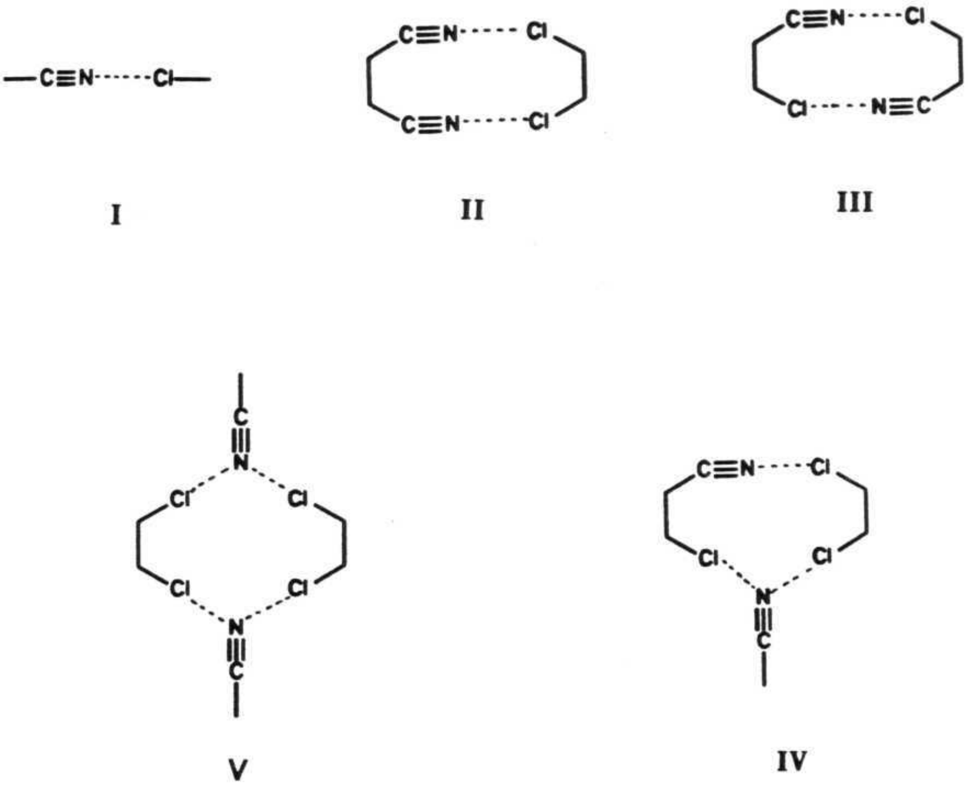


Figure 2. Supramolecular networks based on C≡N···Cl interactions in the crystal structures of some simple compounds. Linear chains are shown in (a) Chlorocyanoacetelene, (b) 4-Chlorobenzonitrile and (c) molecular tapes are shown in Dichlorofumaronitrile through C≡N···Cl interactions.



I

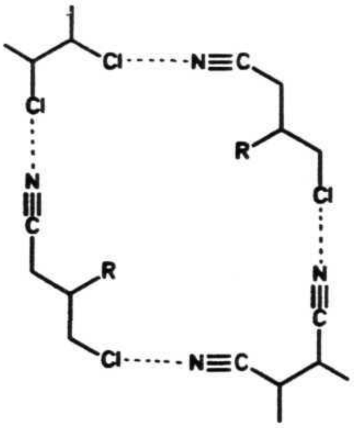
II

III

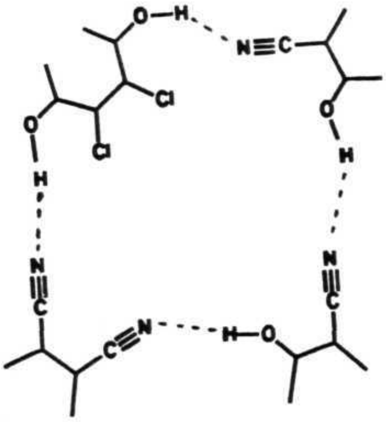
V

IV

Scheme 1



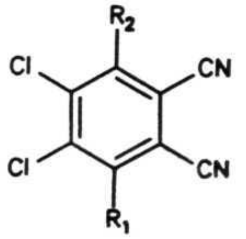
VI



VII

quinone and so on. Systematic crystal engineering appeared to be difficult through an analysis of these largely random structures and it was felt appropriate to examine new crystal structures of specially chosen compounds.

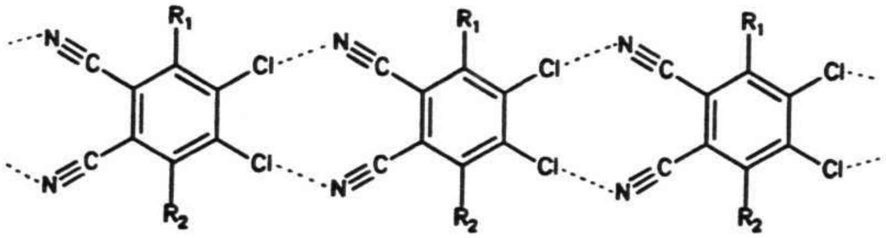
The starting point for the crystal engineering exercise used in this study was the motif **I** mediated linear ribbon structure of 4-chlorobenzonitrile. In this structure, $\mathrm{C{\equiv}N\cdots Cl}$ ribbons are laid side-by-side but the lack of lateral interactions (along the C-H bond directions) leads to mistakes in the alignment of ribbons resulting in subtle disorder.[11] Noting that, in general, any control of supramolecular structure will improve with multipoint recognition, attention was drawn to substituted 2,3-dicyano-5,6-dichlorobenzenes which were felt to be good candidates for the formation of $\mathrm{C{\equiv}N\cdots Cl}$ mediated molecular tapes such as is shown in Scheme 2.[15,16] Accordingly several 1,4-dialkoxy derivatives **1-5**, the 1-hydroxy-4-n-octyloxy derivative **6**, the 1,4- dihydroxy derivative **7** and the 1,4-di-n-octyloxy derivative **8** were prepared.



1 $R_1=R_2=H$
2 $R_1=R_2=OMe$
3 $R_1=R_2=OEt$
4 $R_1=R_2=OPr$
5 $R_1=R_2=OBu$
6 $R_1=OH$, $R_2=n\text{-}Oc$
7 $R_1=R_2=n\text{-}Oc$
8 $R_1=R_2=OH$

2.3. Molecular tapes in the parent hydrocarbon 1 and the dimethoxy derivative 2

The simplest member of the series is 2,3-dicyano-5,6-dichlorobenzene, 1. The structure consists of molecular tapes which are constructed by linking the dimeric loop III with spacer phenyl groups exactly as anticipated in Scheme 2 (Figure 3). The 1,2,4,5-substitution pattern ensures that the tape is linear. The C≡N···Cl contacts are short and linear (D=3.21Å, θ=155.5^{0}). The tape pattern is stabilised by intertape C–H···N hydrogen bonding (C···N 3.47Å; C–H···N, 152.2^{0}) to generate sheets and the three-dimensional structure is completed by stacking of the sheets. This tape structure is retained with a similar dimeric loop III in 1,4-dimethoxy-2,3-dicyano-5,6-dichlorobenzene, 2 (Figure 4). Here, molecules are bisected by a two fold axis and the tape length is along [010]. The C≡N···Cl contacts (D=3.10Å, θ=137.50) are again very short. In this structure, crystallographic symmetry dictates that the tape is perfectly flat and undistorted, there being no offset of molecules within, or perpendicular to the molecular planes. Intertape C–H···N interactions (C···N 3.31Å; C–H···N,



Scheme 2

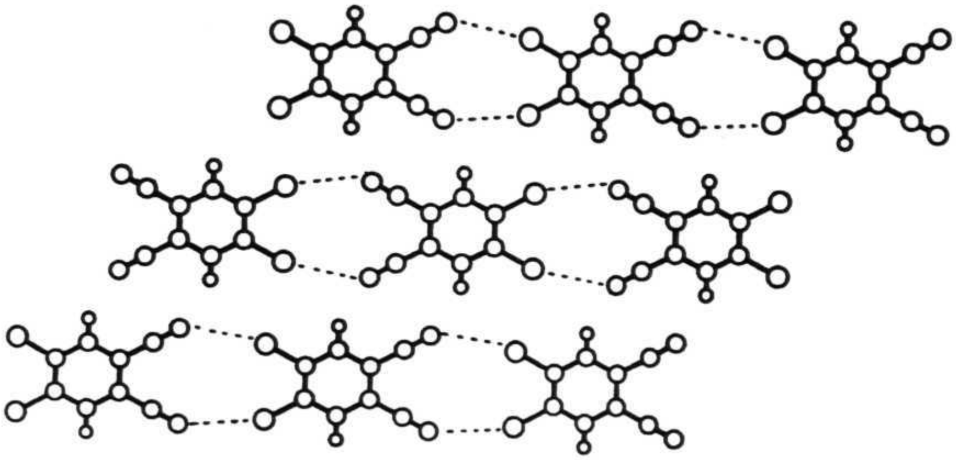


Figure 3. C≡N···Cl mediated molecular tapes in the crystal structure of compound 1.

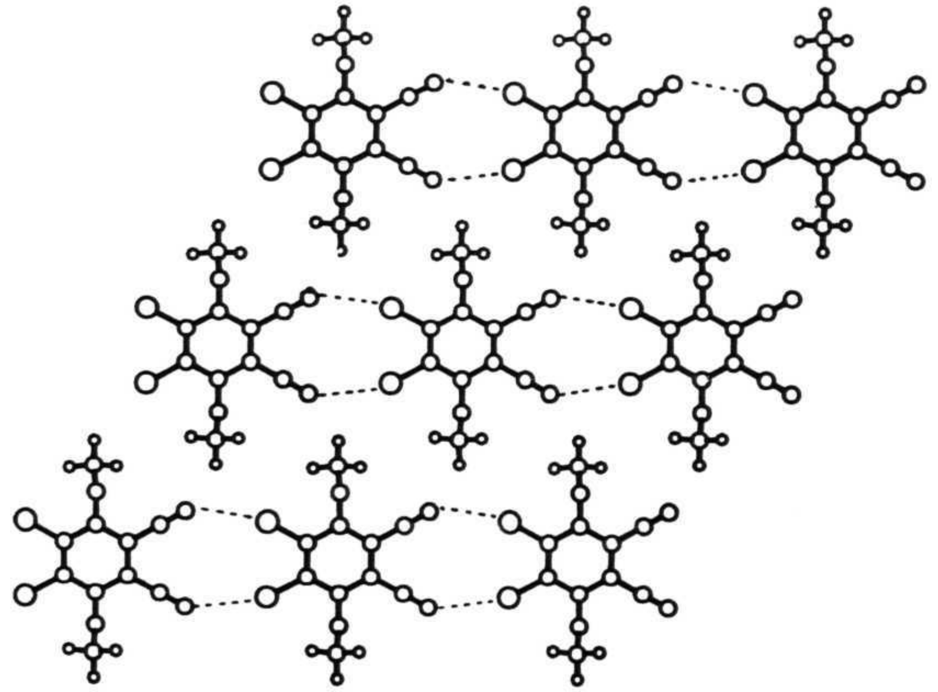


Figure 4. Crystal structure of compound **2** showing C≡N···Cl mediated molecular tapes.

96.8^0) are again important, in this case between methoxyl and cyano groups. The three-dimensional structure is again generated by stacking (plane-to-plane perpendicular distance, 3.67Å). These two structures show that the tape structure with C≡N···Cl dimeric loops is a stable one but that additional intertape stabilisation via C-H···N interactions could also be important.

2.4. Tetramer structure in the diethoxy derivative 3

The structure is layered and each layer consists of molecules connected to four others with short C≡N···Cl interactions (D=3.15Å, θ=153.43^0; D=3.31Å, θ=170.0^0). These contacts lead to the formation of the C≡N···Cl mediated tetrameric loop **VI** with the empty spaces in the square network being filled by the ethoxy groups (Figure 5). The shortest C···C distance between the ethoxy groups is 3.82Å and so these groups are reasonably well-packed. The tetramer-loop **VI** is more robust than the dimer-loop **III** (as observed in structures **1** and **2**) because the two distinct functionalities, namely the cyano and chloro groups on the one hand and the alkoxy groups on the other are structurally well-insulated unlike in **1** and **2** where the pendant groups (H-atom in **1**, methoxy group in **2**) are C-H···N hydrogen bonded dimeric loop **III**. Conceptually, one might even consider the ethoxy groups as being intercalated within a tubular host framework of cyano and chloro groups. It was therefore anticipated that this tetramer-loop **VI** would be carried over into the structure of the dipropoxy derivative.

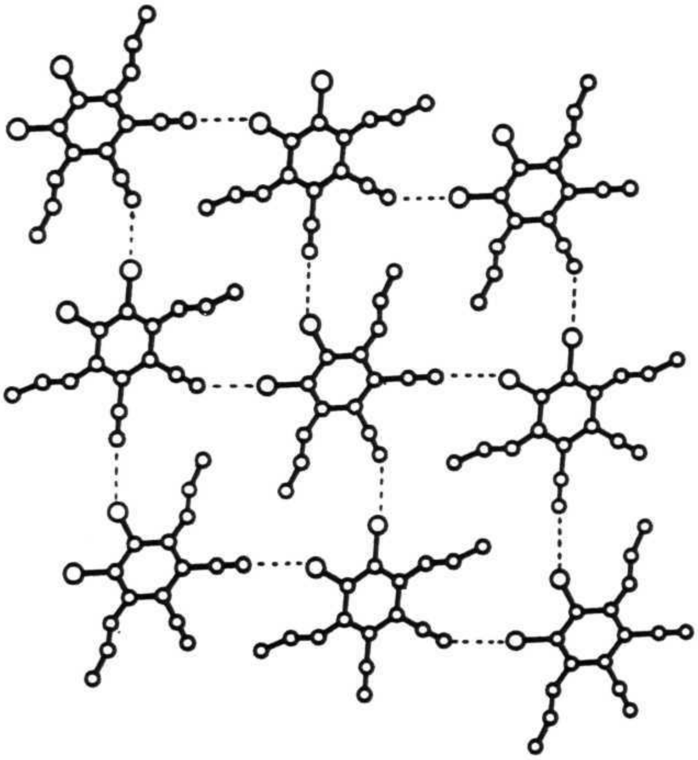


Figure 5. Tetrameric loops through C≡N···Cl interactions in the crystal structure of compound 3.

2.5. Disordered and ordered forms of the di-n-propoxy derivative 4

The tetrameric loop **VI** is retained as expected but close-packing of the larger propoxy groups within a loop framework as compact as that found in compound **3**, is now difficult. Two alternative structural compromises are possible, resulting in dimorphism. In the Pbcn room temperature polymorph, there is a substantial elongation of loop **VI** (D=3.82Å, θ=132^0) in the direction of the (longer) propoxy substituents which are disordered (Figure 6a). The shortest C···C distance between propoxy substituents is 3.90Å. In the terminology of host-guest complexes alluded to above, the host framework is distorted and the guest is disordered. In the Pc low temperature ordered polymorph (Figure 6b), the tetramer-loop **VI** is broken (D=3.34Å, θ=148.19^0; D=3.59Å, θ=136.83^0; D=3.59, θ =112.44^0; D=4.55Å, θ=130.94^0). There are two symmetry-independent molecules which differ only in the conformations of the propoxy groups. The closest C···C distances between propoxy groups are 3.23 and 3.26Å, expectedly shorter than that found in compound **3** and in the disordered polymorph. Essentially, more efficient close-packing of alkoxy groups has been achieved in the ordered polymorph at the expense of one of the four C≡N···Cl interactions in the tetramer-synthon **VI** while in the disordered polymorph, the entropy contribution from the disordered propoxy groups is sufficient to compensate for the very long N···Cl distances.

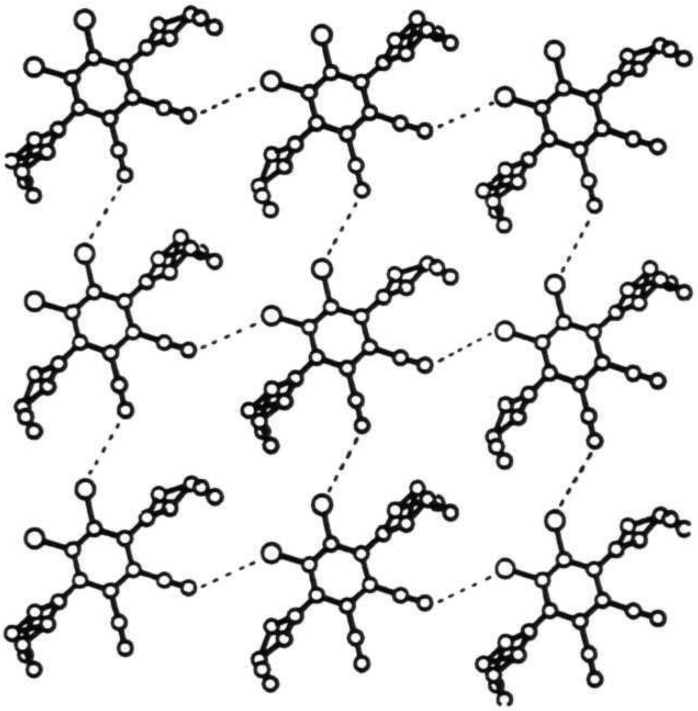


Figure 6. a) Elongated tetrameric loops obsereved in the room temperature form of compound **4**. Notice that the disordered propoxy groups are located in the tetrameric cavity.

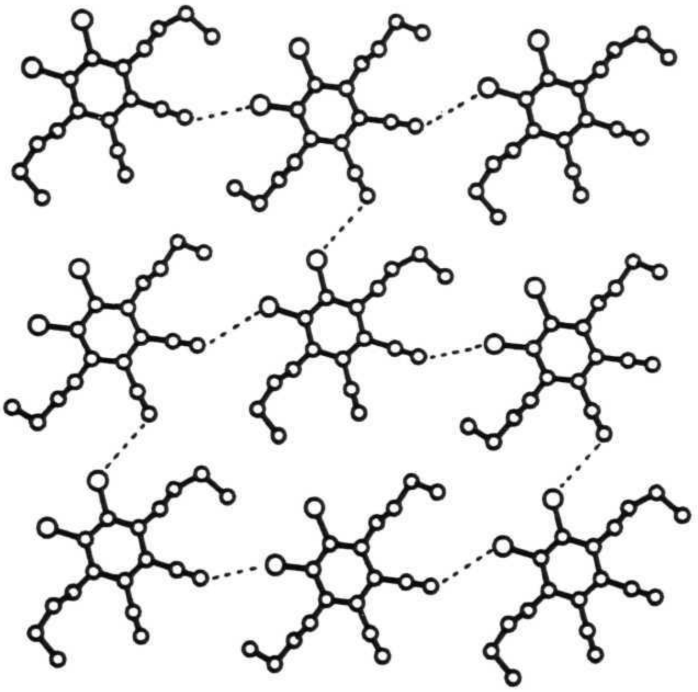


Figure 6. b). Broken tetrameric loops in the low temparature form of compound **4** with the loss of one C≡N···Cl interaction.

2.6. Onset of hydrophobic interactions in the di-n-butoxy derivative 5

In any structural series, the existence of polymorphic modifications, especially ordered and disordered variants as seen in the dipropoxy derivative **4**, signals the onset of a change in structure type. The alkoxy groups in the dibutoxy derivative **5** are definitely too long to be accomodated in the tetramer-loop **VI** which is now broken into two (Figure 7). Of the four 'original' links in the tetramer-loop, two have elongated to 6.081Å while the two

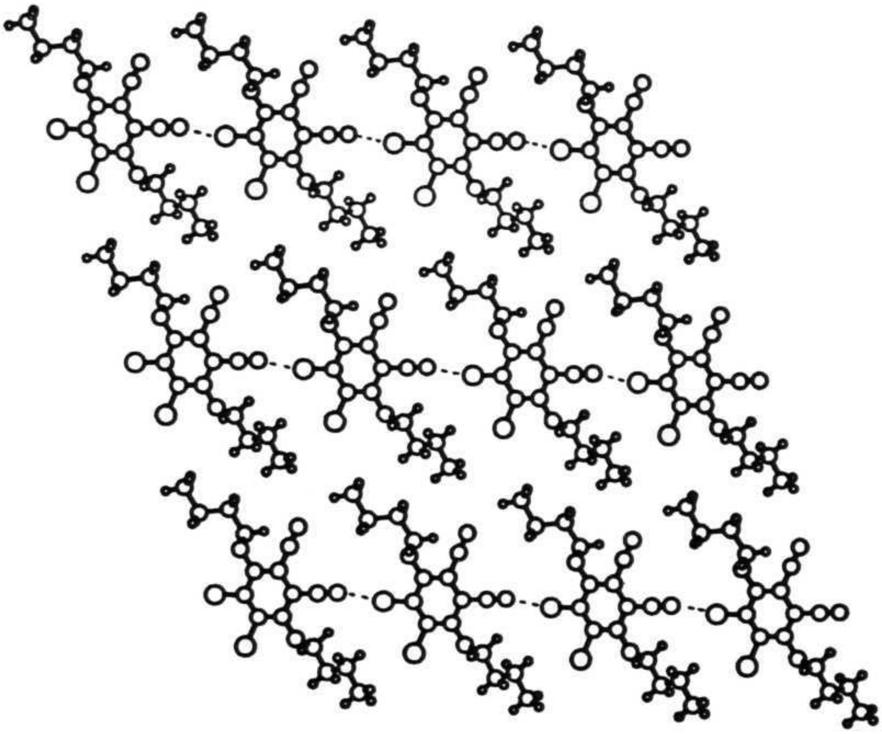


Figure 7. C≡N···Cl mediated linear chains in the crystal structure of compound **5**. Notice that the tetrameric loop is completely broken.

others (connecting glide-related molecules) have contracted to 3.18Å (106.90^0). Alternatively, this structure may be viewed as an example of the simple linear motif **I**. Figure 7 shows clearly that this dissection of the tetramer-loop is caused by the approach of the bulky butoxy groups which are packed better than the alkyl groups in the dimorphs of compound **4**. Even so, these groups are still not very compactly packed and they do not have the parallel saw-tooth geometry characteristic of efficient hydrophobic interactions. For example, the shortest C···C distances between butoxy groups is still 3.90Å (shortest H···H 2.62Å). However, this is probably a satisfactory arrangement for there was no evidence of a phase transition at low temperatures as was observed in compound **4**. To summarise, the (albeit not very efficient) packing of the butoxy groups is still worth the two disrupted C≡N···Cl interactions in the motif **VI** and one might say that this structure represents the onset of alkyl···alkyl hydrophobic interactions in this family of compounds.

2.7. Three types of intermolecular interactions in the hydroxy-n-octyloxy derivative 6

The length of the n-octyl chain ensures that hydrophobic interactions are the major determinants of the structure of compound **6**. Parallel alkyl groups are compactly arranged and the saw-tooth conformation can be observed clearly in Figure 8 which also shows the reappearance of motif **III** and with it of the tape structure ($D=3.40$Å, $\theta= 146.1^0$; $D=3.45$Å, $\theta=132.4^0$). However, this tape is stabilised for reasons which are different from **1** and **2**. It does not interfere with the close-packing of octyloxy groups (C···C 3.49Å; H···H 2.55Å) and further, adjacent tapes are connected with strong, helical O-H···N hydrogen bonds bewteen phenolic and cyano groups. It was anticipated that the di-n-octyloxy derivative, 7 would incorporate the tape structure with the C≡N···Cl mediated dimeric loop. The compound was prepared as a liquid and crystals were obtained with some difficulty in situ with the low-temperature attachment on the diffractometer. However, the diffraction obtained was so poor that even a unit cell could not be obtained.

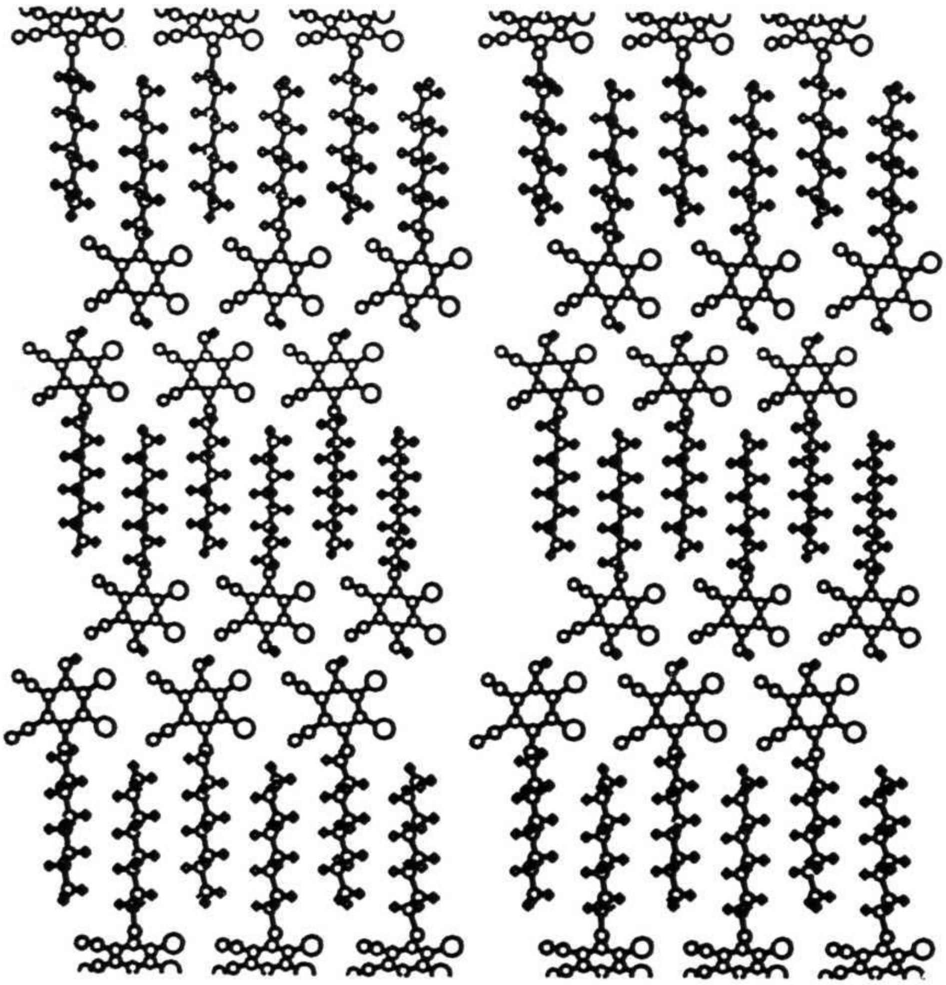


Figure 8. Stereoview of compound 6 showing molecular tapes formed through C≡N···Cl interactions and close-packing of octyloxy groups.

2.8. Topological analogies and the structure of dihydroxy derivative 8

The crystal structure of **8** is shown in Figure 9 and though there are drastic differences at the molecular level in comparison with **1–5**, there are similarities in the crystal structure, especially with respect to the diethoxy derivative **3**. Molecules are again linked in tetramer-loops **VII** but these are formed via conventional N···H–O hydrogen bonds (N···O, 2.75Å; N···H, 2.08Å; θ=160.2^0, N···O, 2.76Å; N···H, 1.98Å; θ=148.5^0). Conceptually, one could visualise OH and Cl groups as δ^+ groups which could make short contacts with the δ^- cyano groups. In **3**, there are no OH groups and the tetramer is formed with N···Cl interactions. In **8**, the Cl^- group is unable to compete with the OH groups and the tetramer is formed with C≡N···H–O hydrogen bonds. However, the effects of the Cl^- groups are still seen in the form of three-centre interactions (D=3.26Å, θ=104^0; D =3.35Å, θ =121^0). The C≡N···Cl contact is, in effect, the chloro equivalent of a C≡N···H–O hydrogen bond. It is important to note that motifs **VI** and VII have similar topological properties and therefore similar effects on the crystal structure even though they are derived from rather dissimilar chemical functionalities. This is a rather general observation in crystal engineering studies and a comparison of such crystal structures is greatly facilitated by their dissection in terms of supramolecular networks.

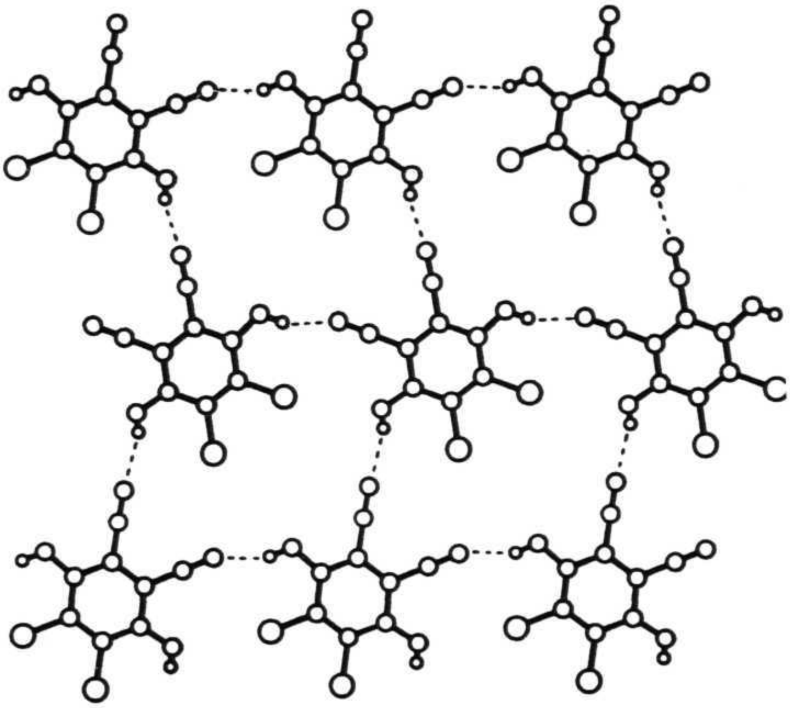


Figure 9. Crystal structure of compound **8** showing tetrameric loops formed through C≡N···H–O and C≡N···Cl interactions.

2.9. Conclusions

This work shows that the conceptualisation and dissection of crystal structures into their constituent substructural motifs facilitates their deeper analysis and enables the definition of other target networks which may be obtained by an appropriate choice of monomer precursor. These substructural motifs cannot be viewed in isolation but interfere with each other, thereby affecting their stability. Such interference is problematic and means that motif robustness, or an ability to withstand interference, is a valued attribute in crystal engineering. There are clear topological parallels between networks formed by strong and weak intermolecular interactions and this means that the weaker interactions may just as effectively be used in crystal engineering.

2.10. Experimental

General Methods and Instrumentation

Infrared spectra were obtained using a JASCO FT/ IR-5300 spectrometer. ^{1}HNMR spectra were measured with a Jeol-Fax-100 spectrometer. Chemical shifts are reported as d values relative to TMS. Starting meterials were purchased from Aldrich. Compound **1** was obatained from the DuPont company. All solvents were purified by distillation before use. The CSD was implemented on a MicroVax 3300 computer

2,3-Dichloro-5,6-dicyano-1,4-dihydroxybenzene (8)

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone(DDQ) 2.27g (1.00 mmol), and 1.1g (1.00mmol) of 1,4-dihydroxybenzene were taken in

100mL of dry 1,4-dioxane and were refluxed for 12h. The reaction mixture was allowed to cool to room temperature and a pale yellow solid settled down. This was filtered, dried and purified by recrystallization from acetone to yield 1.83g of compound **8**.

m.p.	:317 ^{0}C.
I.R ν_{max}(KBr)	:3209, 2253, 1574, 512, 1452, 1358, 1275 cm^{-1}

2,3-Dichloro-5,6-dicyano-1,4-dimethoxybenzene (**2**)

Compound **8** (0.4g, 1.75mmol) and anhydrous K_2CO_3 (0.966g, 3.5mmol) were taken in dry acetone (30mL) and an excess of methyl iodide (1mL) was added to this solution and refluxed for 3h. The reaction mixture was cooled to room temperature and was poured into ice water. Compound **2** which precipitated was filtered, dried and recrystallised from $CHCl_3$.

m.p.	:187 ^{0}C.
I.R ν_{max}(KBr)	:2890, 2220, 1450, 1360,1210 cm^{-1}.
NMR δ_H($CDCl_3$)	:4.1(6H, s, O–CH_3).

2,3-Dichloro-5,6-dicyano-1,4-diethoxybenzene (**3**)

Compound **8** (0.3g, 1.3215 mmol) and anhydrous K_2CO_3 (0.7294g, 2.643 mmol) were taken in dry DMF (20mL), and an excess of ethyl iodide (2mL) was added to this solution followed by stirring for 8h at room temperature. The reaction mixture was poured into ice water and 5% HCl solution was added dropwise to yield a colourless precipitate which was filtered and then purified by recrystallization from petroleum ether. Crystals of compound **3** were obtained from absolute ethanol.

m.p:	:110–113 ^{0}C.
I.R ν_{max}(KBr)	:3000, 2250, 1580, 1380, 1350, 1240, 1010, 920, 810, 800 cm^{-1}.

NMR $\delta_H(CDCl_3)$:4.3(4H, q, OCH_2), 1.5(6H, t,$-CH_3$).

NMR $\delta_C(CDCl_3)$:15.5($-CH_3$), 72.51($-OCH_2$), 109.02(-O-C=C), 112.16(-Cl-C=C), 135.44(NC-C), 155.23(-C≡N)

2,3-Dichloro-5,6-dicyano-1,4-dipropoxybenzene (**4**)

Compound **8** (0.3g, 1.321mmol) and anhydrous K_2CO_2 (0.7294g, 2.643mmol) were taken in dry DMF(20mL) and an excess of n-propyl iodide (2mL) was added to this solution and stirred at room temperature for 8h. A colourless solid, compound **4** (0.207g) was recrystallised from petroleum ether. Crystals of compound **4** were obtained from absolute ethanol.

m.p. :70 ^{0}C.

I.R ν_{max}(KBr) :2950, 2250, 1440, 1380, 1240, 1050, 1000, 940, 880, 800 cm^{-1}.

NMR $\delta_H(CDCl_3)$:4.2(4H, t, OCH_2), 1.8(4H, m, $-CH_2$), 1.2(6H, t $-CH_3$).

NMR $\delta_C(CDCl_3)$:10.37($-CH_3$), 23.1($-CH_2$), 75.3($-O-CH_2$), 108.6(-O-C=C), 112.1(-Cl-C=C), 145.17(N≡C-C), 155.04(-C≡N).

2,3-Dichloro-5,6-dicyano-1,4-dibutoxybenzene (**5**)

Compound **8** (0.3g, 1.321mmol) and anhydrous K_2CO_3 (0.7294g, 2.643mmol) were taken in dry DMF(20mL) and an excess of n-butyl iodide (2mL) was added to this solution followed by stirring at room temperature for 8h. A colourless solid, compound **5** (0.227g) was obtained and recrystallised from $CHCl_3$.

m.p. :60 ^{0}C.

I.R ν_{max}(KBr) :2900, 2250, 1520, 1420, 1340, 1280, 1050 cm^{-1}.

NMR $\delta_H(CDCl_3)$:4.2(4H, t, $O-CH_2$), 1.8(4H, m, $-CH_2$) 1.6(4H, t,$-CH_2$), 1.0(6H, t,$-CH_3$).

NMR $\delta_C(CDCl_3)$:13.7($-CH_3$), 18.83($-CH_2$), 31.97($-CH_2$), 76.39 ($-OCH_2$), 108.82($-O-C=C$), 112.17($Cl-C=C$), 135.36($N\equiv C-C$), 155.37($-C\equiv N$).

2,3-Dichloro-5,6-dicyano-4-n-octyloxyphenol (6)

Compound **8** (0.3g, 1.321mmol) and anhydrous K_2CO_3(0.729g, 2.643mmol) were taken in dry acetone (100mL) and an excess of n-octyl iodide (3mL) was added to this solution followed by refluxing for 3 days. The reaction mixture was allowed to cool to room temperature and poured into ice water. The resulting colourless solid was recrystallized from $AcOH-CCl_4$.

m.p. :115 ^{0}C.

I.R ν_{max}(KBr) :3400, 2900, 2250, 1580, 1460, 1200 cm^{-1}.

^{1}HNMR (acetone-d6) :3.95(2H, t, $O-CH_2$), 1.8(2H, m), 1.35(10H, m) 0.9(3H, t, $O-CH_3$).

2,3-Dichloro-5,6-dicyano-1,4-di-n-octyloxybenzene (**7**)

Compound **8** and anhydrous K_2CO_3 were taken in dry DMF (15mL) and excess n-octyl iodide (3mL) was added to this solution and stirred at room temperature for 24h. The reaction mixture was poured in ice water and 5% HCl solution added slowly. After removal of DMF with several washings with water, a brown liquid was obtained. The traces of DMF and unreacted n-octyl iodide were distilled in vacuum (0.1 mm Hg). Compound **7** was obtained in the fraction which distilled at 120^0 as a yellow liquid.

I.R ν_{max}(KBr) :2928, 2856, 2235, 1547, 1466, 1429,1367, 1242, 1091, 1014, 947, 785, 723 cm^{-1}.

NMR $\delta_H(CDCl_3)$:0.9(6H, t, $(CH_3)_2$), 1.2(24H, m, $(CH_2)_{12}$), 4.16 (t, 4H, $(OCH_2)_2$).

X-Ray Crystallography

The single crystal X-ray data for the compounds discussed here were collected by Dr.T.Pilati (University of Milano) and Professor Y.T.Struchkov (INEOS, Moscow). The structure solution of the compounds were carried out with SHELXS86 and the refinements were carried out with SHELX76.[17] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were located from difference Fourier maps. All the relevant crystallographic information is given in Appendix A-1. The atomic coordinates and thermal parameters are given in Appendix A-2

Database Studies

Data were retrieved form the 1994 update of version 5.07 of the CSD (119939 entries) for all the ordered crystal structures with an exact match between chemical and crystallographic connectivity (screen 153, -28). No R-factor restriction was employed because the structures were found to be of good accuracy with R factors very rarely in excess of 0.10. Geometrical calculations were performed on the retrieved data for intermolecular C≡N···Cl interactions using QUEST3D-GSTAT, an automatic graphics non-bonded search program of the CSD. Duplicate hits (identified by the same REFCODE) were removed manually by eliminating all but the structure with the lowest R value in each case.

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16. A tape is defined as a linear array of molecules which are linked at multiple sites. In a ribbon, any two molecules are linked at a single site.

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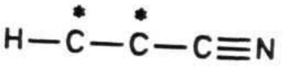
CHAPTER THREE

C-H···N≡C HYDROGEN BONDED NETWORKS IN ORGANIC CYANO COMPOUNDS

The synthesis of three-dimensional solid state structures is a difficult problem since it involves the control and prediction of various intermolecular interactions.[1] Among the various intermolecular interactions conventional hydrogen bonds (O–H···O and N–H···O) have been used extensively in the supramolecular synthesis because of their strength and directionality.[2] From the vast amount of literature available on these strong hydrogen bonds it may be observed that they usually assemble into specific patterns with implicit chemical and geometrical information and that the patterns show pronounced reproducibility from structure to structure.[3] The systematic usage of these patterns in crystal engineering leads to the production of solids with desired physical and chemical properties. Along these lines, weak hydrogen bonds such as C–H···O, C–H···N, O···I, O–H···π and N–H···π have also been investigated (but to a relatively lesser extent) in supramolecular synthesis.[4] The reasons for incorporating weak hydrogen bonds in supramolecular synthesis are as follows: (1) These weak forces are quite useful in the design of supermolecules, as most organic compounds contain functional groups incapable of forming strong hydrogen bonds; (2) The understanding of crystal structures is incomplete if only strong hydrogen bonds are considered because the crystal packing is governed by a balance between strong and weak forces; (3) The incorporation of these weak forces into supramolecular synthesis would greatly enhance the scope of the subject.

The frequent occurrence of oxygen and nitrogen atoms in organic compounds suggests the use of C–H···O and C–H···N hydrogen bonds in the synthesis of supramolecular networks. Consequently C–H···O hydrogen bonds have been explored in this direction and have been proved to have significant effects on the modes of crystal packing.[4] Curiously, C–H···N hydrogen bonds have not been much used in the same direction in spite of the frequent occurrence of nitrogen atom in several organic compounds. A survey on the presence of C–H···N hydrogen bonds in the literature reveals that they are identified in heterocyclic chemistry.[5] Organic cyano compounds are also expected to show these interactions but this aspect has not been studied adequately.[6]

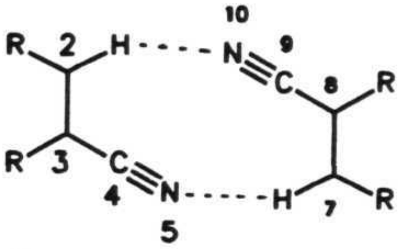
The preceding chapter in this thesis describes the use of cyano group in the construction of supramolecular networks through its ability to form donor–acceptor intermolecular interactions with the chloro group. The present chapter discuss the use of β–hydrogen–atom containing organic cyano compounds (see fragment I and in which the H atom is attached to the β–carbon atom to the C≡N group) in the construction of C–H···N mediated supramolecular networks and their role in crystal engineering. The motivation of this study is prompted by the identification of the C–H···N≡C hydrogen bonded cyclic dimer, **II** which is obtained from the dimerisation of fragment **I** in the crystal structures of 3–cyanocinnamic acid and 4–cyanocinnamic acid.[6] Interestingly, in both these structures the molecules are held together by carboxylic dimer units and the resultant dimeric molecular aggregates again connected by C–H···N≡C hydrogen bonded dimer **II** units. Consequently it was felt that dimer **II** can be usful in supramolecular synthesis.



$H-\overset{*}{C}-\overset{*}{C}-C\equiv N$

* = sp^3 or sp^2

I



II

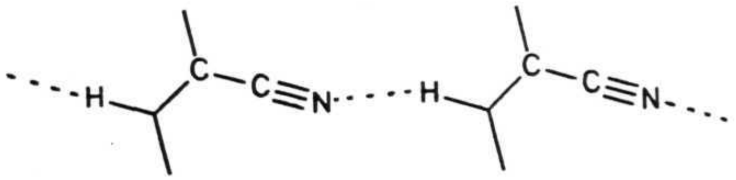
$P_1 = 2,3,4,5$

$P_2 = 7,8,9,10$

In the light of these ideas, the Cambridge Structural Database (CSD)[7] was used to retreive all crystal structures containing fragment **I**. It was found that in most of these structures, C-H···N≡C mediated dimers **II** are present.

3.1. Database studies on C-H···N≡C hydrogen bonded networks

It is observed that fragment **I** exists in *cis* and *trans* configurations depending on the geometry of hydrogen and cyano groups. It is also observed that while *trans* compounds form catemers **III**, *cis* compounds form cyclic dimers **II** through C-H···N≡C hydrogen bonds. From the 278 crystal structures observed in the *trans* configuration, only 173 hits show the presence of catemer **III**.



III

Among the 455 crystal structures containing *cis* configuration, 380 hits show the dimer **II**. From a close observation of the geometrical characteristics of dimer **II**, it may be seen that it is stabilised by both dipole···dipole interactions of cyano groups and C–H···N≡C hydrogen bonds. It is expected that the dipole···dipole interactions are significant at a centroid to centroid distance of 3.0–3.6Å between interacting cyano groups. Therefore it is understood that the collective influence of dipole···dipole and C–H···N≡C interactions leads to the formation of dimer **II**.

Since dimer **II** consists of two fragments of **I**, it can be geometrically described in terms of three parameters: (1) The interplanar angle between the planes of the two fragments with hydrogen atoms ignored. Figure 1a represents a histogram of the interplanar angles from which it can be seen that most of the points are located below 7.5° Therefore the two fragments are coplanar; (2) The vertical offset or the translation perpendicular to the planes of the two fragments. To represent this offset the average interplanar distances of the two planes have been calculated. These distances are shown in Figure 1b. This Figure shows that most of the points are located in between –0.2 and 0.1Å, within a coplanar arrangement; (3) The lateral offset of the planes of two fragments, that is, the translation in the mean of two fragment planes. This parameter may be described in terms of the difference between the distances of diagonally disposed C and N atoms of dimer **II**. This is shown in Figure 1c. Small and large differences in these diagonal distances indicate that dimer **II** may exist in two ways as shown Figure 2. Now the formation of dimer II may be easily rationalised with C–H···N≡C hydrogen bonds and dipole···dipole interactions of cyano groups.

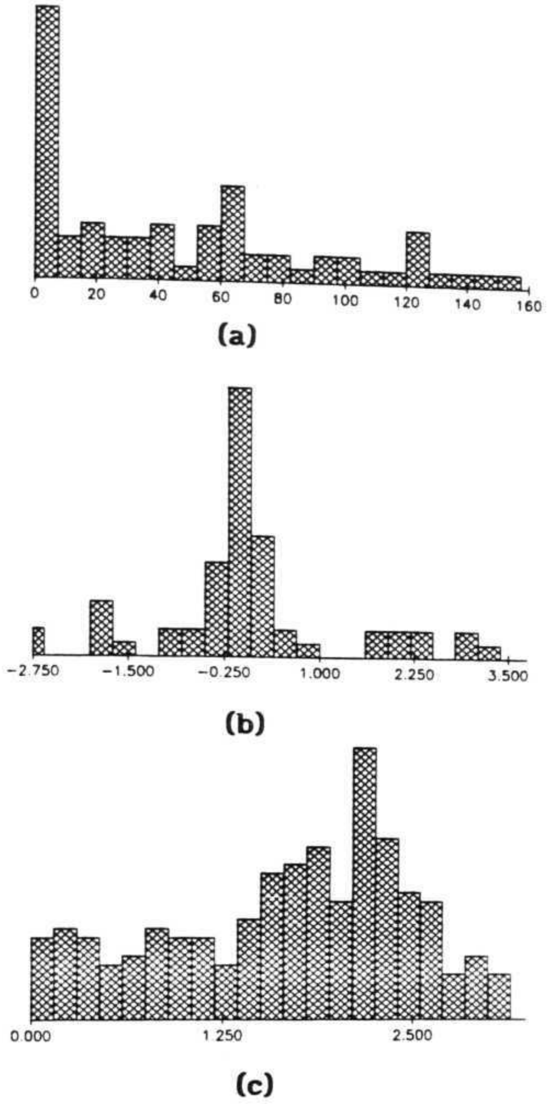
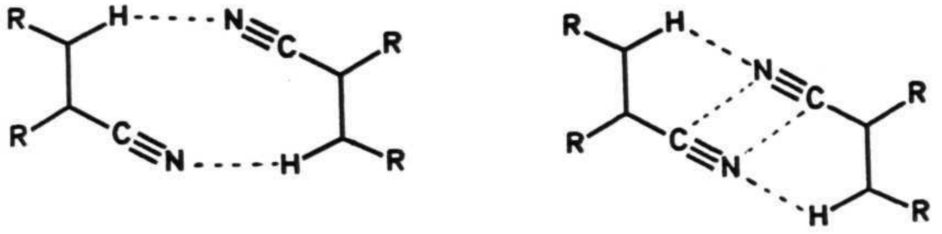


Figure 1. Histograms of three parameters which represent dimer **II** formation. (a) Interplanar angle($^{\circ}$) between the planes of fragment I. (b) Vertical offset translation (Å) perpendicular to the planes of fragment **I**. (C) Lateral offset translation (Å) between the fragment **I**.



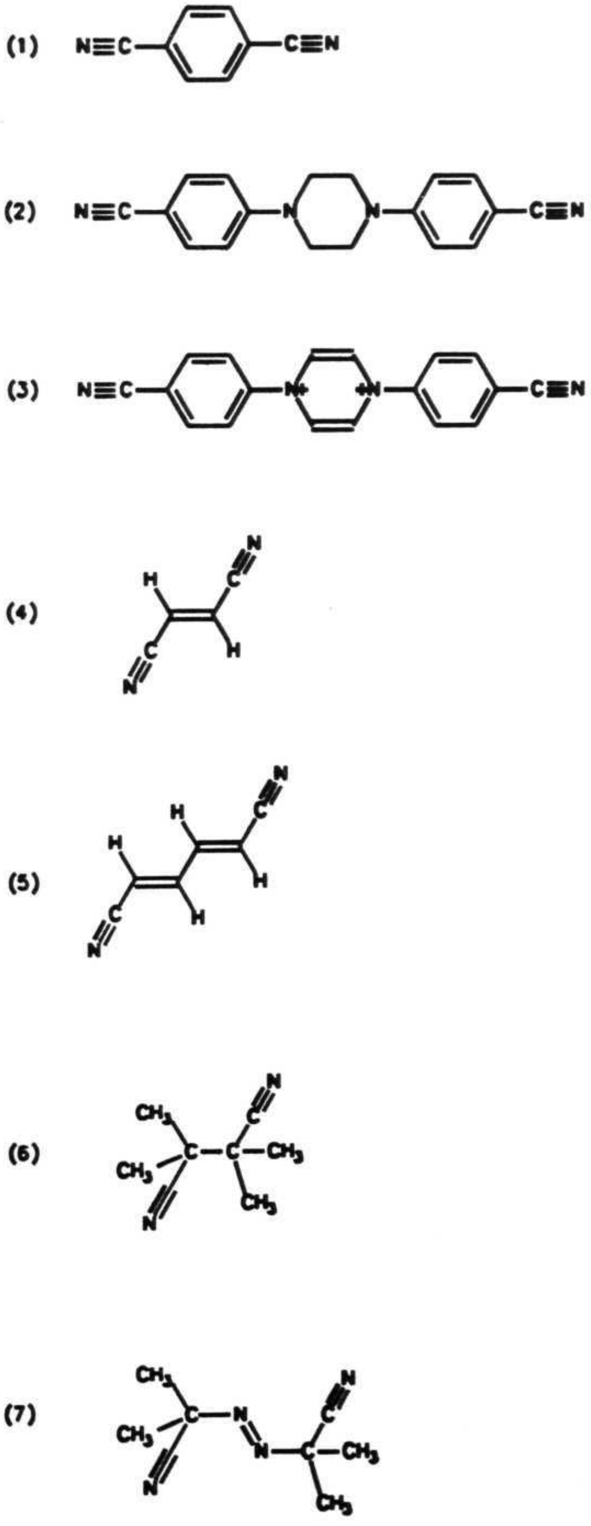
(a) (b)

Figure 2. Fragment **I** dimerises in two ways to give dimer **II**. (a) Dimer **II** formed exclusively with C–H···N≡C hydrogen bonds; (b) Dimer **II** formed with both C–H···N≡C hydrogen bonds and dipole···dipole interactions.

3.2. One-dimensional networks with C–H···N≡C hydrogen bonds

From the observations of the crystal structures of various compounds, which contain two or more units of fragment **I** it may be shown that dimer **II** can be used as a dependable building block in crystal engineering. The discussion that follows clearly illustrates the importance of C–H···N≡C hydrogen bonds in stabilising the crystal structures of different classes of organic compounds. The structural formulae of selected crystal structures form CSD is shown in Scheme 1.

Scheme 1



A simple example in the series is 1,4-dicyanobenzene, **1**.[8] In this structure dimer **II** is flanked by two phenyl rings and this is extended to the one-dimensional network, **1**. Figure 3 shows the crystal structure of **1** wherein phenyl rings and dimer **II** units alternate to form the one-dimensional network. In this network, the phenyl ring is the molecular core and dimer **II** is the supramolecular glue. The synthesis of similar one-dimensional networks by changing the molecular core and keeping the

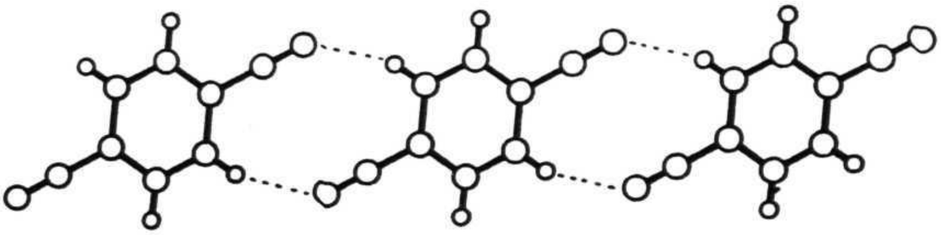


Figure 3. The C–H···N≡C hydrogen bonded molecular tape in the crystal structure of 1,4-dicyanobenzene, **1**.

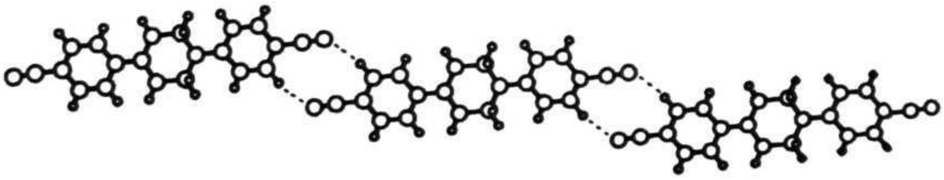


Figure 4. The crystal structure of N,N'-bis(4-cyanophenyl) piperazine, **2**. Notice that the dimer **II** units are separated by piperazine units.

supramolecular glue unchanged will be a test for the robustness of the dimer **II** units. For instance, in the structure of N,N'-bis(4-cyanophenyl)piperazine, **2**[9] the molecular spacer is extended by piperazine units as is shown in Figure 4. The molecular spacer may be further extended by a lengthier unit in the structure of the 1,1'-bis(4-cyanophenyl) -4,4'-bipyridinium cation **3** (Figure 5).[10]

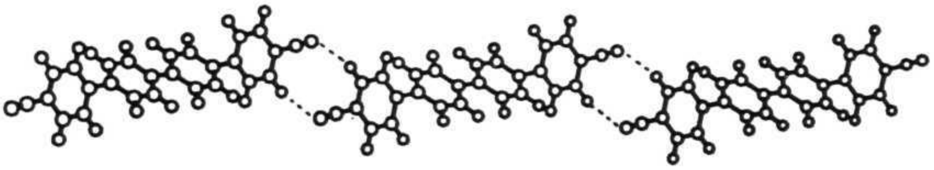
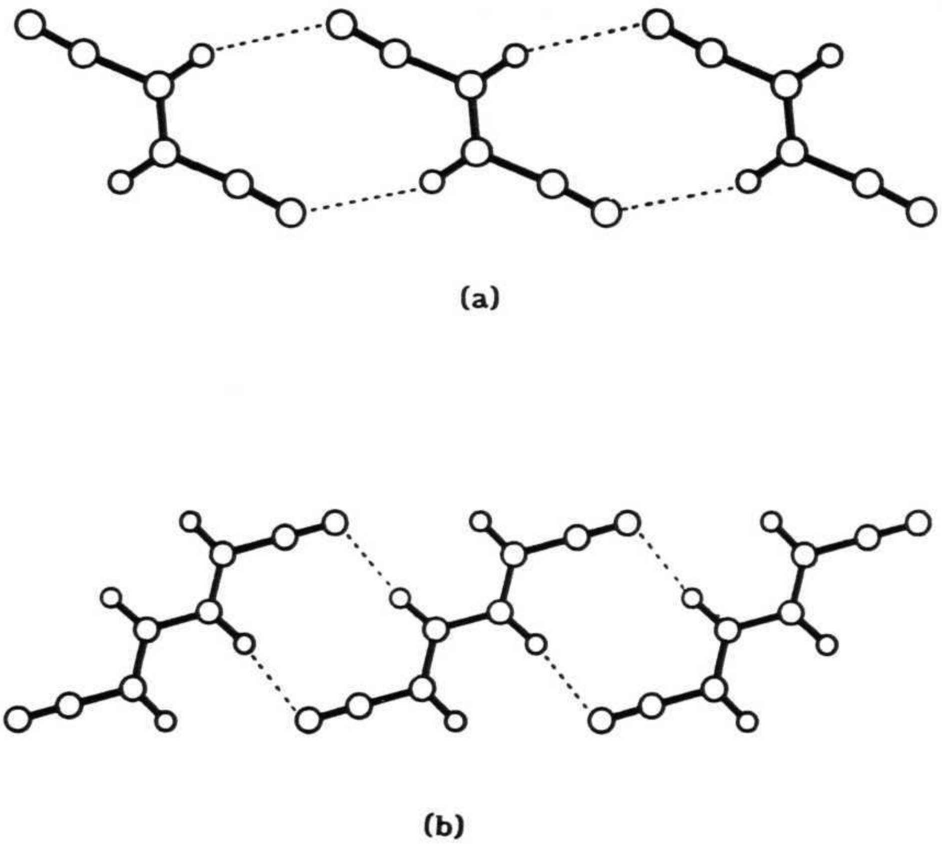


fig 5

Figure 5. The crystal structure of compound **3**. Notice that the dimer **II** units are separated by bipyridinium units.

In all the preceding examples, the molecular spacer is aromatic in nature and in the following examples non-aromatic compounds are taken as molecular spacers. In the structures of fumaronitrile, **4**,[11] mucononitrile, **5**,[12] tetramethyl succinonitrile, **6**[13] and azo-bis(isobutyronitrile), **7**,[14] aliphatic spacers are used to produce supramolecularly similar one-dimensional networks. The structures of **4** and **5** are shown in Figures 6 and while the structures of **6** and **7** are shown in Figure 7.



(a)

(b)

Figure 6. One-dimensional hydrogen bonded networks in some non-aromatic compounds. (a) Crystal structure of fumaronitrile, 4. (b) Crystal structure of mucononitrile, 5.

From the above examples it is evident that dimer **II** is robust enough to form supramolecular one-dimensional networks and that it resists the structural variability at the level of the molecular core. To summarise, the use of motifs such as dimer **II** in producing similar supramolecular networks in various crystal structures would lead to the identification and production of new motifs based on C-H···N≡C interactions.

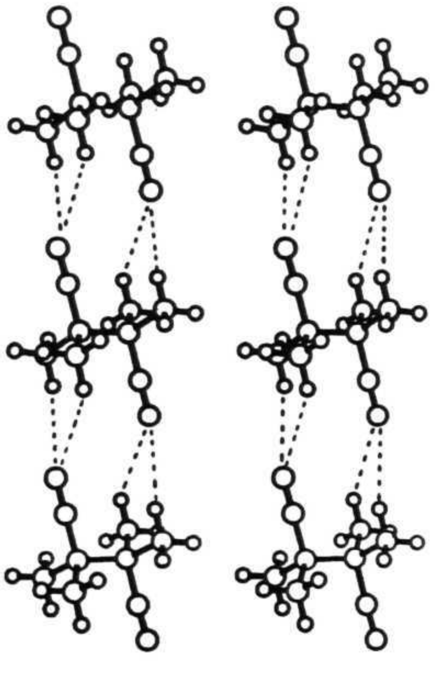


Figure 7. (a) Stereoview of the crystal structure of succinonitrile, **6**.

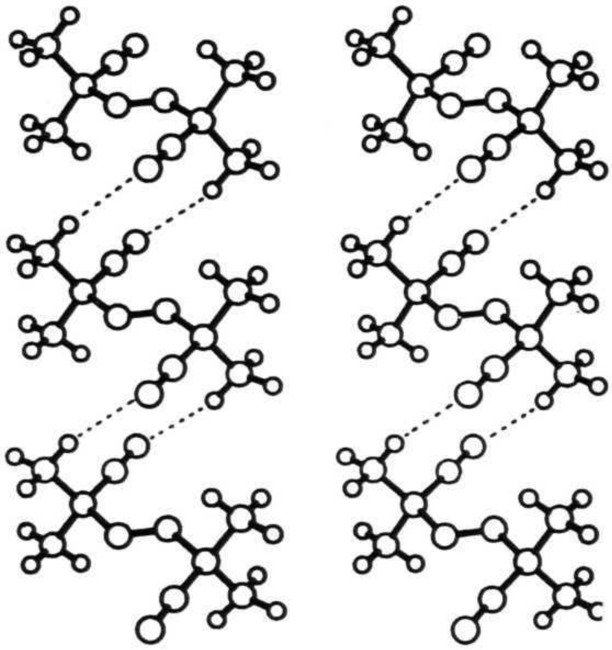


Figure 7. (b) Stereoview of the crystal structure of azo-bis(isobutyro)nitrile, **7**.

3.3. Hexagonal networks with C-H···N≡C hydrogen bonds

The observations above show that C-H···N≡C hydrogen bonding can be used as an efficient tool in supramolecular synthesis. Along these lines, 1,3,5-tricyanobenzene(TCB) was selected to exploit the C-H···N≡C hydrogen bonding in constructing supramolecular networks. It was expected that the hydrogen bonding sites in fragment **I** and the three-fold symmetry of the molecule would be an advantage in the synthesis of two and three-dimensional networks because there are no other supramolecular functionalities present in the molecular skeleton and the cyano and C-H groups are present in equal numbers. In this connection, the crystal structures of 1:1 complex of TCB and hexamethylbenzene(HMB)[17] and of pure TCB were studied.[18]

The crystal structure of the TCB-HMB complex consists of alternating layers of molecules of TCB and HMB (Figure 8). These layers are shown separately in Figures 9 and 10. In the crystal, they are stacked along [001] at a centroid-to-centroid separation

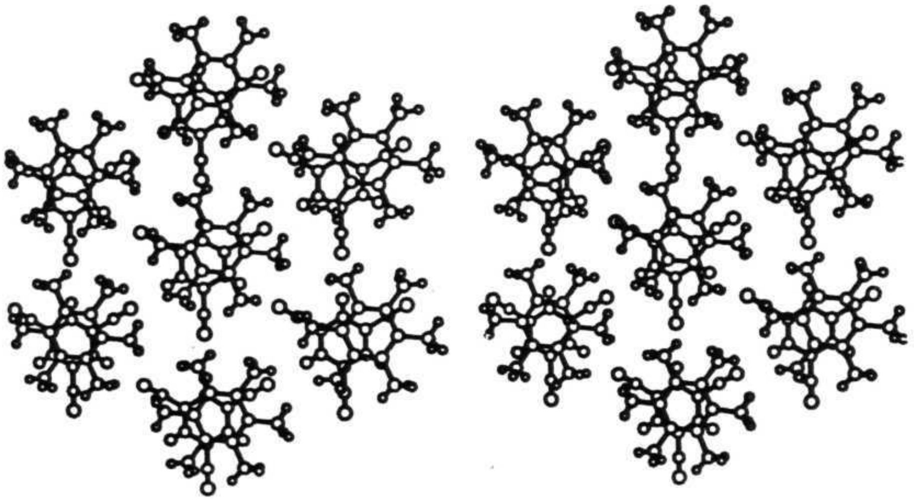


Figure 8. Stacking of successive layers of 1,3,5-tricyanobenzene and hexamethylbenzene in the crystal structure of TCB-HMB complex to optimise $\pi\cdots\pi$ interactions.

of 3.85Å to optimise $\pi\cdots\pi$ interactions. Figure 9 reveals that the molecules of TCB crystallise according to a hexagonal network which is built through C–H···N≡C hydrogen bonded trimeric units. Both TCB and HMB molecules lie on special positions but curiously, these are different. While the molecules of TCB are bisected by twofold axes, those of HMB are located on inversion centres. Such a site symmetry of TCB necessitates that therefore four of the six moderately strong C–H··N≡C hydrogen bonds encircling the molecule [C···N 3.47Å; C–H...N, 172^0] must be equal must while the other twc must be perfectly linear (C···N, 3.51Å; C–H···N, 180^0).

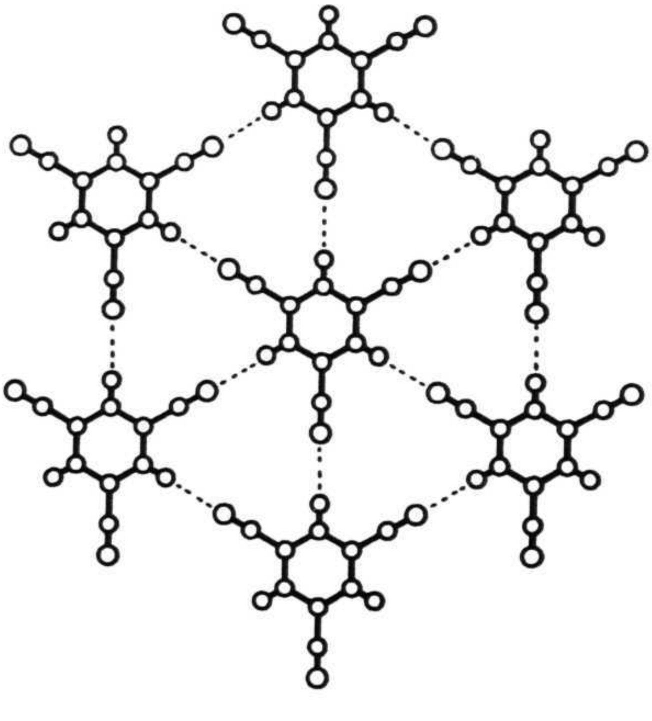


Figure 9. Layer structure parallel to (110) of 1,3,5-tricyanobenzene molecules in TCB-HMB complex.

Additionally, the molecular plane of TCB is nearly parallel to (110), but this is not required by the crystallographic symmetry. The overall effect is a flat hexagonal array of molecules of TCB linked efficiently by C–H···N hydrogen bonds. It is noteworthy that the entire layer is assembled with interactions which are far weaker than the conventional hydrogen bonds, the traditional glue for supramolecular construction. Interestingly, a topologically similar network is observed in the crystal structure of cyanuric chloride in which N···Cl interactions are employed.[19]

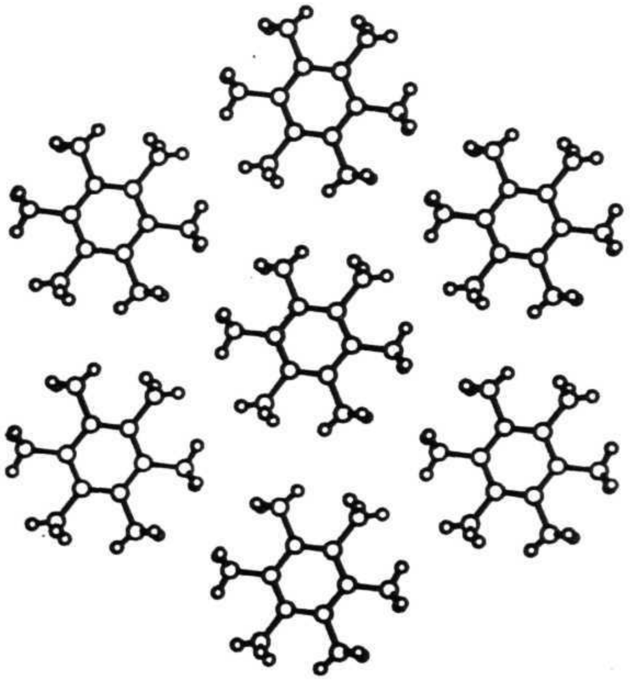


Figure 10. Layer structure parallel to (110) of hexamethylbenzene molecules in TCB-HMB complex.

The layers of molecules of HMB in the crystal structure of complex TCB–HMB closely resemble the molecular layers in the crystal structure of pure HMB itself but in general, layering of a planar aromatic hydrocarbon is difficult and the crystal structure of pure HMB is exceptional. Retrieval of all HMB containing structures from the CSD yielded 15 hits (no metal atom) but in many of these, the molecules of HMB are arranged in a herringbone or quasi-herringbone fashion

The crystal structure of pure TCB is slightly different. Each molecule is connected with six similar molecules through C–H···N≡C hydrogen bonds (C···N 3.25–3.39Å, C–H···N, 105.6–162^{0}). In other words, each H atom is bifurcated (three-centred) by two N atoms and each N atom is bifurcated by two H atoms. These bifurcated hydrogen bonds result in infinite C–H...N≡C mediated helices which when combined give quasi-hexagonal networks (Figure 11). The hexagonal network in the 1:1 complex is two-dimensional while in the pure compound it is three-dimensional.

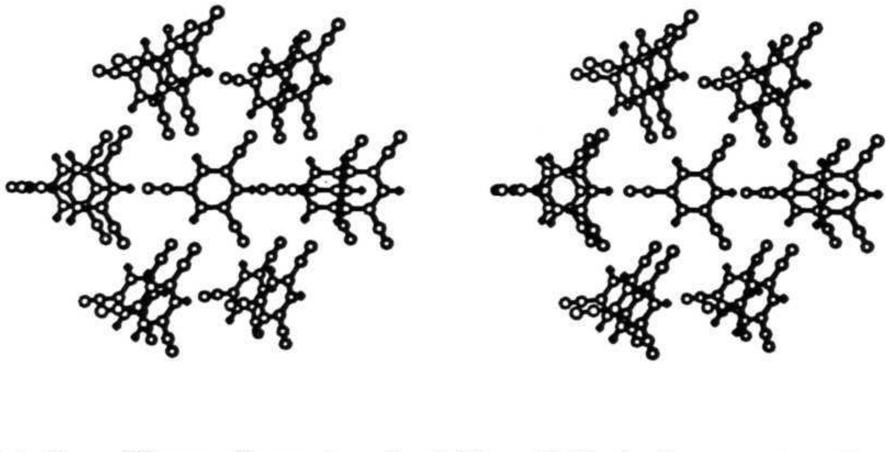


Figure 11. Three-dimensional C–H···N≡C hydrogen bonding in the crystal structure of 1,3,5-tricyanobenzene.

The formation of two-dimensional C–H···N≡C hydrogen bonded hexagonal networks in the TCB–HMB complex and three-dimensional helices in the pure TCB structure may be due to the interplay between directional C–H...N≡C hydrogen bonds and non directional forces such as C···C and $\pi\cdots\pi$ interactions. In the TCB–HMB complex structure, the C–H···N≡C hydrogen bonds, the C···C and the $\pi\cdots\pi$ interactions are all perfectly disposed resulting in a hexagonal network whereas in the case of the pure TCB structure, the C–H···N≡C hydrogen bonds are the only principal forces stabilising the crystal packing. Hence, three-dimensional C–H····N≡C hydrogen bonded helices are formed.

3.4. Conclusion

The study on β-hydrogen containing organic cyano compounds indicates that the C–H···N≡C hydrogen bonds are robust in nature and that these hydrogen bonds are expected to be most promising agents in supramolecular synthesis. The C–H···N≡C hydrogen bonded supramolecular motifs and networks presented in this chapter may be useful in designing new solid state structures with desired structural properties. The results presented in this chapter are also useful in the understanding of the interplay between directional hydrogen bonds and non-directional forces.

3.5. Experimental

1,3,5-Tricyanobenzene (TCB)[20]

TCB was prepared according to the literature procedure from trimesamide. Trimesamide (4.6g) was dissolved in dry DMF (35mL) and thionyl chloride (6mL) was added and stirred for 1h at 60 °C. The solution was poured into ice cold water and the resulting suspension was extracted with $CHCl_3$. The $CHCl_3$ layer was washed twice with 5% aqueous HCl, dried, concentrated and the colourless solid was obtained.

m.p. :260 ^{0}C
I.R ν_{max}(KBr) :3100, 2250, 1550, 1400, 1300, 1200, 820 cm^{-1}.
NMR $\delta_H(CDCl_3)$:8.2 (s)

TCB-HMB complex

Crystals of the TCB-HMB complex were obtained as colourless needles from an equimolar mixure of TCB and HMB in $CHCl_3$.

m.p. :255 ^{0}C
I.R ν_{max}(KBr) :3200, 2255, 1440, 920, 680 cm^{-1}.

X-Ray Crystallography

The data for the TCB-HMB complex and pure TCB were collected by Dr. H.L Carrell, Fox Chase Cancer Center, Philadelphia, U.S.A. The structure solution of both the TCB-HMB complex and pure TCB was carried out with SHELXS86 and the refinements were carried out with SHELX76.[21] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were located from difference Fourier maps. All the relevant crystallographic information is given in Appendix B-1. The atomic coordinates and thermal parameters are given in Appendix B-2

Database studies

All the cyano compounds were retrieved from the CSD (version 5.07) using the 3D graphics option. Screens -28, 153 were set to eliminate compounds with metal atoms and without coordinates. Entries with R-factors greater than 0.10 were also excluded to create a subsidiary IDX file of 950 compounds. All further 3D graphical searches for *cis* and *trans* compounds were made from this subsidary file. A distance of 2.7Å to 3.9Å was specified for C···N atoms between two fragments of I. The dimers are characterised by two C···N distances d1 and d2 and two C-H···N angles θ1 and θ2.

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CHAPTER FOUR

CONSTRUCTION OF DIAMONDOID NETWORKS BASED ON S_4 MOLECULAR RECOGNITION

The synthesis of inorganic three-dimensional networks having large cavities, windows and channels is a well-studied subject.[1] Such networks are characteristic of porous solids which have potential applications in materials science. This realization leads to the investigation of organic porous solids to achieve similar benefits.[2] Along these lines, different classes of organic porous solids have been designed and have proved to have many useful applications. Among these solids, the supramolecular synthesis of organic diamondoid materials has received much current interest for the following reasons: (1) They represent a new family of organic host materials which make use of molecular symmetry and self-assembly to generate three-dimensional networks; (2) In the context of crystal engineering, they test the robustness of intermolecular interactions, particularly of weak intermolecular interactions since complex three-dimensional networks are produced; (3) The structures are fascinating and aesthetically appealing. In effect, these diamondoid solids are believed to act as organic zeolites which mimic inorganic zeolites and consequently can be utilized as molecular sieves and catalysts.

Organic diamondoid networks were first discussed by Ermer with reference to the crystal structures of adamantane-1,3,5,7-tetracarboxylic acid **1**[3] and methanetetraacetic acid[4] and based on self-assembly sustained by hydrogen bonding between carboxylic acid groups. These networks are largely hollow and can be filled either by self-catenation or guest clathration in accordance with the close-packing principle. In the structures of 1 and methanetetraacetic acid, the super-adamantoid cavities are filled by extensive self-catenation and lead to the formation of five-fold and three-fold diamondoid lattices. Ermer later demonstrated that the degree of interpenetration can be reduced in these solids by changing the molecular skeleton properly and without changing the carboxylic functionalities. For example, self-catenation in super-adamantane cavities is partially removed in the structures of adamantane-2,6-dione-1,3,5,7-tetracarboxylic acid[5a] and adamantane-2,6-dimethylene-1,3,5,7-tetracarboxylic acid[5b] with the enclathration of foreign guest molecules of different sizes.

Wuest and co-workers[6] extended this concept and used the *cis*-amide functionality in the place of the carboxylic acid functionality, so that the anticipated super-diamondoid networks are achieved through centrosymmetric N-H···O hydrogen bonding of *cis*-amide units. However, because of the huge super-adamantane cavities in these solids, a high degree of interpenetration is encountered. Later Zaworotko and co-workers[7] constructed diamondoid networks by the co-crystallisation of S_4 symmetry organometallic moieties (which have four tetrahedrally orginated hydroxy supramolecular functionalities) and different rigid and linear spacer units. The resultant solids showed self-catenation in some cases whilst in others, inclusion of guest molecules along with the self-catenation was observed.

From all these examples it is clear that the synthesis of diamondoid networks is achieved by the association of molecules containing S_4 symmetry. In all cases, the intermolecular interactions used are strong and directional hydrogen bonds. However, all these reported structures show self-catenation. In particular, the degree of interpenetration is pronounced and therefore these networks cannot be completely utilised for the inclusion of foreign guests.

This chapter describes the supramolecular synthesis of diamondoid networks using intermolecular interactions weaker than conventional hydrogen bonding. It is shown that in some of these supramolecular networks, self-clathration is effectively avoided and that guest molecule inclusion is therefore possible. To construct diamondoid solids with weak intermolecular interactions, S_4 molecules with appropriate functionalities are used as tetrahedral centres. These centres are connected by weak interactions such as N···Br,[8] C–H···N,[9] Br···Br, Br···phenyl and I···I.[10] Besides this, similarities between organic and inorganic networks are also discussed. In this connection the O–H···O hydrogen bonded network in the crystal structure of 1,3,5,7-tetrahydroxyadamantane, **8**[11] is similar to the network found in the CsCl family of inorganic solids.

4.1. N···Br Mediated diamondoid networks

As mentioned above, organic diamondoid networks are necessarily built with molecules with S_4 (or pseudo-S_4) symmetry or tetrahedral bonding. Our search for new diamondoid networks concentrated therefore on molecules with S_4 symmetry and a propensity to form weak yet directional interactions. The short N···Br interactions have been described by Hassel in the structure of $CHBr_3$-hexamethylenetetramine (HMT).[12] Later these interactions were studied in the structures of the DABCO (1,4-diazabicyclo[2.2.2]octane)[13a] and quinuclidine complexes of CBr_4.[13b] Despite the presence of short N···Br contacts, none of these structures have diamondoid networks because one of the two components in the mixed crystal falls short of S_4 symmetry and in this sense acts as a 'network stopper' in the solid. Building on this earlier work, an equimolar mixture of the two S_4-symmetry molecules, CBr_4 and HMT and was co-crystallised to yield molecular complex **2**.

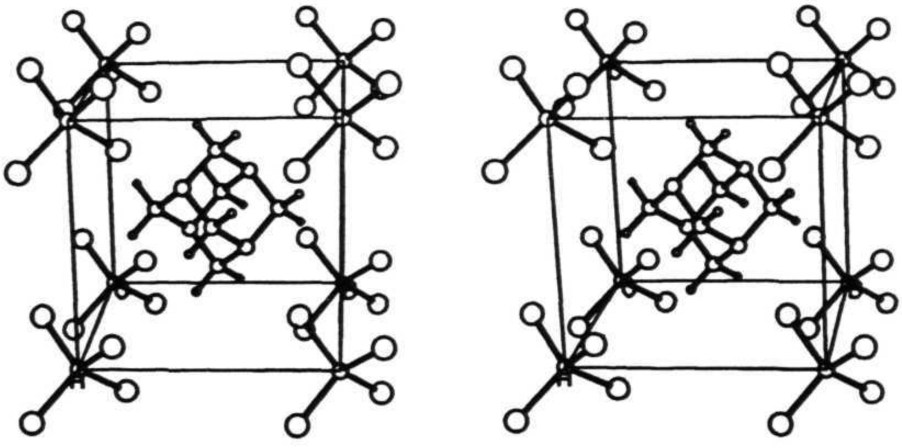


Figure 1. Stereoview of the crystal structure of CBr_4-HMT complex, **2**. The CBr_4 molecules have been placed at the cell corners and the HMT molecules at the cell centre to show the N···Br interactions. This is an idealised view of the structure, which in reality adopts a disordered body centred cubic packing.

The body-centred cubic structure of the complex **2** contains CBr_4 and **HMT** molecules disordered at each of the lattice positions. The crystallographic evidence for the body-centred cell was unequivocal and a detailed search for larger unit cells (of possibly lower symmetry) yielded no alternative possibility. Therefore the CBr_4 and HMT species are disordered. Figure 1 is obtained by placing the CBr_4 molecules at the unit cell corners and the **HMT** molecule at the cell centre. This creates two non-connected but catenated diamondoid (actually sphalerite or cubic ZnS) networks as shown in Figure 2. It is important to note that each

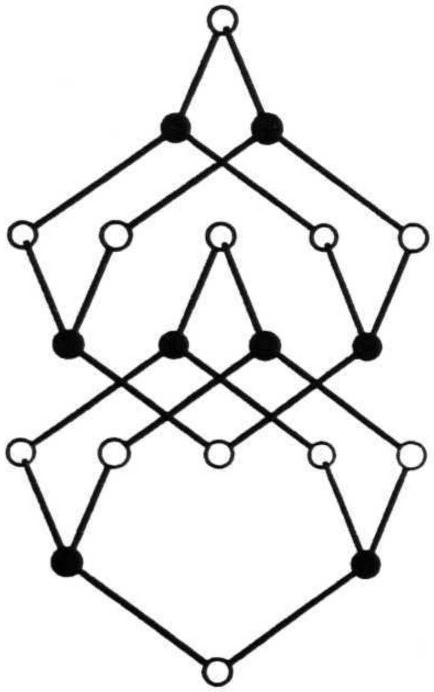


Figure 2. Idealised ordered structure of CBr_4-HMT complex, **2** to show the two identical supramolecularly catenated diamondoid networks. Shaded and unshaded circles represent complete CBr_4-HMT.

sphere in Figure 2 (shaded or unshaded) represents a complete molecule of CBr_4 or HMT and that the shaded and unshaded lines represent the N···Br interactions. The catenation is therefore completely supramolecular and each network is formed with N···Br interactions of 2.61Å. These interactions are tetrahedrally disposed about the CBr_4 and HMT molecules and are constrained by crystallographic symmetry to lie exactly on the body diagonal of the unit cell.

A random positioning of CBr_4 and HMT molecules at all the lattice sites in other words, a solid solution structure for complex **2** would yield the observed body centering. However, there is good evidence that the interaction of a length similar to that observed here in CBr_4-DABCO (2.88, 2.76Å),[13a] CBr_4-quinuclidine (2.53Å)[13a] CBr_4-2,3-diazabicyclo[2.2.2]octene (2.91Å),[13b] $CHBr_3$-HMT (3.00Å)[12] and others. Secondly, the mixed crystals obtained from 3:1, 1:1 and 1:3 mixtures of CBr_4 and HMT in solution have identical melting points and IR spectra and were found (by elemental analysis) to have CBr_4:HMT ratios of 1:0.99, 1:1.06 and 1:1.23 showing the absence of solid solution behaviour.

Significantly, crystals of the complex obtained from solutions rich in HMT were found to contain a slight excess of HMT in the crystal but when the mother liquor was rich in CBr_4, this component was not correspondingly incorporated into the mixed crystal in excess. This observation, coupled with the fact that pure HMT[14] crystallises in a unit cell of nearly the same dimensions as complex **2** and with the same space group $I\bar{4}3m$ (pure HMT is cubic, a=7.02Å) provides a mechanism for the observed body centering in **2** while retaining a largely ordered network, which is chemically more reasonable than the solid solution model. In the crystal of pure HMT, molecules translated along the vector [1/2,1/2,1/2) are linked with sets of three identical C–H···N hydrogen bonds (C···N 3.88Å). It is proposed that the CBr_4–HMT networks in **2** are nearly ordered but that occasionally there is a misregistry of molecules, with two HMT molecules next to each other (as in the pure HMT crystal). This necessitates a switch of molecules within the network, which when averaged over the entire crystal produces the body-centering.

The switching could be due to the coincidental equality of molecular sizes of CBr_4 and HMT and also because all the intermolecular interactions are very weak. The fact that some excess HMT can be incorporated in the crystal seems to suggest that the C–H···N interactions in an HMT···HMT linkage do not compete favourably with the N···Br interaction in an HMT···CBr_4 linkage. Additionally, the fact that an excess of CBr_4 is not incorporated in these crystals shows that both N···Br and C–H···N interactions are perhaps stronger than Br···Br interactions. In effect, the N···Br interactions are sufficiently specific to create a largely ordered network but not so strong as to result in a fully ordered structure. Complex **2** is therefore an example of a supramolecular structure poised between complete order and complete disorder.

The N···Br contact in complex **2** is of a very unusual length (2.61Å) being short for an intermolecular interaction(3.2–3.4Å) and long for a covalent bond(1.9–2.3Å) and suggests extensive atomic polarisation or charge transfer. These N···Br interactions are in general the shortest to be found among the several CBr_4 complexes already reported.

4.2. C–H···N hydrogen bonded diamondoid networks

Our observations on the 1:1 complex HMT–CBr_4 above arise from the similarity in molecular dimensions of HMT and CBr_4 molecules. Therefore different tetrahedral molecules with unequal molecular sizes were examined as possible constitaents of ordered diamondoid networks. However, it was noted that the molecular synthesis of tetrahedral species with appropriate functionalities is somewhat difficult. In these circumstances, the easily available HMT was considered as a good building block for the formation of diamondoid networks because it can form both N···Br interactions with bromo compounds and C–H···N hydrogen bonds with both hydrogen donor and acceptor compounds. To synthesise the supramolecular diamondoid networks with weak interactions wherein the molecular components are not disordered, 1,3,5,7-tetrabromoadamantane ($AdBr_4$) was selected instead of CBr_4 for complexation with HMT, as $AdBr_4$ and HMT are of dissimilar sizes. Co-crystallisation of $AdBr_4$ and HMT resulted in a 1:2 complex, **3**.

The crystal structure of complex **3** is face-centred cubic with $AdBr_4$ molecules at the cell corners and HMT molecules tetrahedrally situated in the alternating octants (as in cubic ZnS). We will refer to these HMT molecules as HMT(1/4,1/4,1/4). Interestingly these molecules are held together by four sets each of three equivalent C–H···N hydrogen bonds (C···N 3.77Å, θ 151°) rather than by N···Br interactions as in the HMT–CBr_4 complex. In these 12 identical C–H···N hydrogen bonds, the hydrogen atoms are provided by $AdBr_4$ and the nitrogen atoms by HMT. These alternating $AdBr_4$ and HMT(1/4,1/4,1/4) molecules form a super-adamantoid cage. Figure 3 is a schematic view of the structure and Figure 4 is a stereoview

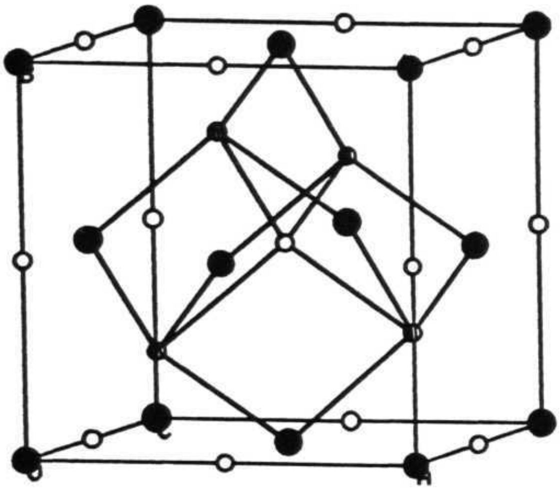


Figure 3. Schematic representation of the crystal structure of complex **3**. Molecules are shown as circles: filled ($AdBr_4$); shaded with lines (hmt 1/4,1/4,1/4); unshaded (hmt 1/2,1/2,1/2). The super-adamantoid cage is marked as the co-ordination between the two types of hmt molecule.

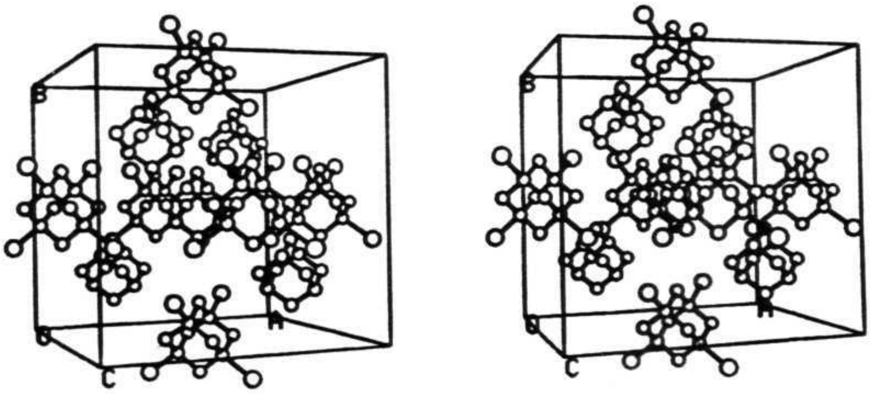


Figure 4. Stereoview of the structure of complex **3** showing inclusion of the hmt(1/2,1/2,1/2) molecule in the super-adamantoid cage. The hmt(1/2/,1/2,1/2) molecule is shown in one of its two possible orientations.

of the actual structure. Because of the relatively distant spacing of molecules in this cage, there is sufficient room within for a second type of HMT molecule at the cell-centre. This is referred to as HMT(1/2,1/2,1/2). Significantly, the HMT(1/2,1/2,1/2) molecules are disordered about a molecular inversion centre, the space group being non-centrosymmetric.

Two questions are of structural interest: (1) Why are only alternate octants occupied by HMT(1/4, 1/4, 1/4) molecules? (2) Why are the HMT(1/2, 1/2, 1/2) molecules disordered? To answer the first question, it is relevant to note that four $AdBr_4$ molecules converge tetrahedrally to give six identical Br···Br contacts of 4.08Å. This Br_4-cluster occupies alternate octants leaving alternate octants for the HMT(1/4,1/4,1/4) molecules. The Br_4-cluster is shown in Figure 5. The disorder of the

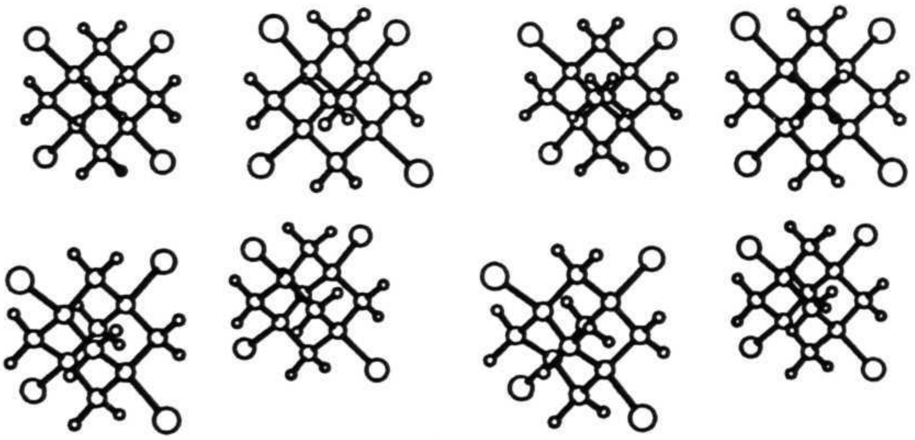


Figure 5. Br···Br Interactions formed by four molecules of $AdBr_4$ in the crystal structures of complexs **3** and **4**. The four central Br atoms form a bromine-cluster.

HMT(1/2,1/2,1/2) molecules is in turn rationalised because each HMT(1/2,1/2,1/2) molecule can have only 12 C–H···N contacts to the neighbouring HMT(1/4,1/4,1/4) molecules (C···N 3.74Å, θ=148^0) rather than the 24 such contacts possible for HMT(1/4,1/4,1/4) molecules. Each HMT(1/4,1/4,1/4) molecule forms 24 C–H···N contacts. Of these, 12 are to $AdBr_4$ wherein HMT(1/4,1/4,1/4) acts as a hydrogen bond acceptor. The other 12 are to HMT(1/2,1/2,1/2) wherein HMT(1/4,1/4,1/4) acts as a hydrogen bond donor. All these latter 12 contacts are found in only one of the two disordered orientations of HMT(1/2,1/2,1/2) and the enthalpic contribution from these interactions is probably insufficient to ensure ordering.

The disordered HMT(1/2,1/2,1/2) molecule is encapsulated within the super-adamantoid cages formed by $AdBr_4$ and HMT(1/4,1/4,1/4) but this clathrating behaviour is demonstrated more strikingly by substituting the HMT(1/2,1/2,1/2) by CBr_4 which is already known to be a good structural mimic for HMT. As predicted, co-crystallisation of an equimolar mixture of $AdBr_4$, HMT and CBr_4 from chloroform yielded exclusively crystals of the 1:1:1 complex **4**.

The crystal structure of complex **4** is isostructural to that of complex **3** and is shown in Figures 6 and 7. The CBr_4 molecule in complex **4** is, however, ordered unlike the HMT(1/2,1/2,1/2) molecule in complex **3**. The reason for this is that CBr_4 can form 12 Br···Br contacts of 3.90Å with $AdBr_4$ molecules in only one orientation (which is the one found in here). Clearly these 12 Br···Br interactions are of greater enthalpic significance than the 12 C–H···N interactions formed by HMT(1/2,1/2,1/2) in complex **3**. In

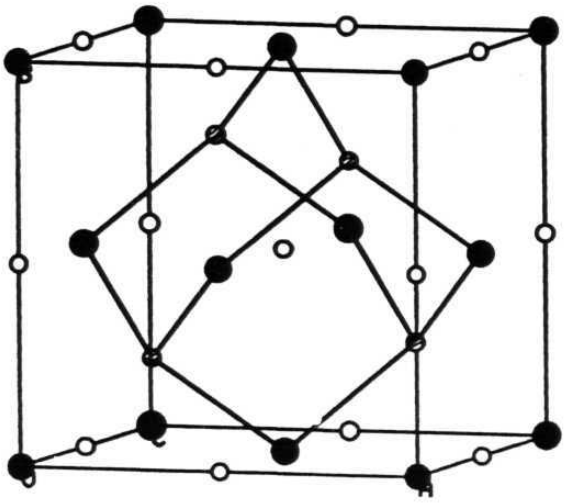


Figure 6. Schematic representation of the crystal structure of complex **4**. Compare this with Figure 3. CBr_4 molecules are shown as unshaded circles.

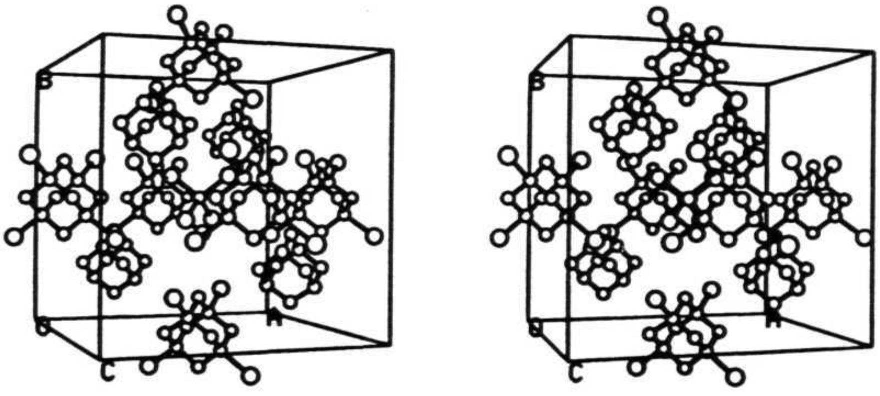


Figure 7. Stereoview of the structure of complex **4** showing inclusion of the CBr_4 molecule. Notice that the CBr_4 molecule makes contacts with the bromine-clusters formed by the $AdBr_4$ molecules.

both 1:2 and 1:1:1 complexes the Br_4-cluster(1/4,1/4,1/4) resulting from the $AdBr_4$ molecules has a shape and size identical with those of HMT or CBr_4 molecules. In summary therefore, there are four types of molecules or supertetrahedral species present in the 1:2 or 1:1:1 complexes: $AdBr_4$(0,0,0), HMT(1/4,1/4,1/4), HMT(1/2,1/2,1/2) or CBr_4 and the Br_4-cluster(3/4,3/4,3/4). Both structures consist of ordered and simple diamondoid networks with C-H···N hydrogen bonds and these super-adamantane cavities are filled by either HMT(1/2,1/2,1/2), CBr_4 or the Br_4-cluster. The relationship between such structures and inorganic alloys is apparent and the term 'organic alloys' has been suggested for such compounds.

4.3. Diamondoid Networks with Br...Br and Br...Phenyl Interactions

From the analysis of these organic-alloys above it may be learned that there are two types of supramolecular fragments. These are the super-adamantane units formed through multiple C-H···N hydrogen bonds and super-tetrahedral species, such as the Br_4-cluster formed by the aggregation of $AdBr_4$ molecules. The repetitive occurrence of this super-tetrahedral Br_4-cluster in the crystal structures of **3** and **4** suggests that this can be used as a design element in the crystal engineering of diamondoid networks. As the size of this super-tetrahedral cluster is identical to the CBr_4 or HMT molecule it is expected that CBr_4 or HMT may be incorporated wherever this super-tetrahedral cluster is encountered. The following examples show how this principle may be used to generate new diamondoid networks with a reasonable level of predictability.

Keeping these aspects in mind, the crystal structure of tetrakis(4-bromophenyl)methane **5** was studied. From the molecular structure it was anticipated that the crystal packing would be controlled by Br···Br interactions. Continuing this line of thought it was further expected that, there are two possible ways in which molecules **5** can of pack. One way is to form diamondoid networks with weak linear Br···Br intermolecular interactions similar to the crystal structure of AdI_4.[10] The second possibility is via formation of a Br_4-cluster by the aggregation of four molecules of **5**.

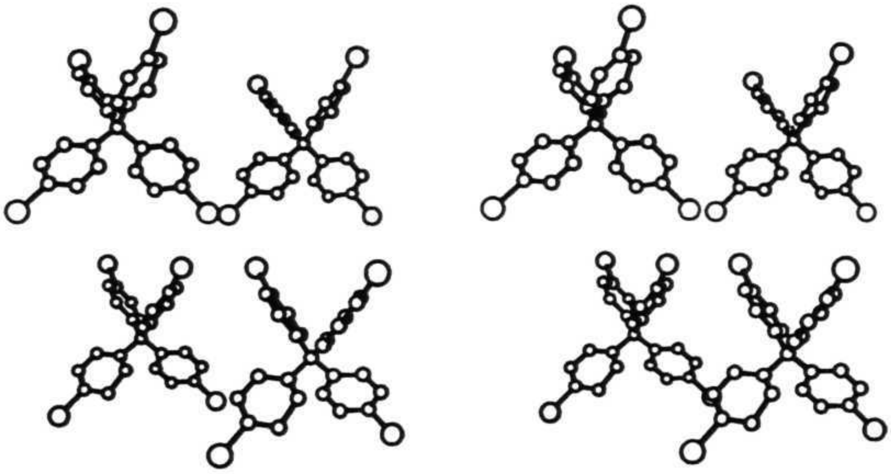


Figure 8. Br···Br Interactions formed by four molecules of **5**. The four central Br atoms form a bromine-cluster.

In reality and interestingly, compound **5** crystallises in the tetragonal system and the crystal structure shows the presence of the Br_4-cluster rather than diamondoid networks with linear Br···Br intermolecular interactions. The Br_4-cluster found in **5** is shown in Figure 8. In this cluster, four Br atoms are arranged in a tetrahedral fashion and the distance between any two Br atoms is 3.91Å. If the centroid of the Br_4-cluster considered as a C atom, the cluster then appears as a super-CBr_4 molecule. The C–Br bond distance of the super-CBr_4 is 2.146Å and Br–C–Br angles are 108.35^0 (four) and 110.04^0 (two). These parameters match with parameters of the actual CBr_4 molecule of complex **6** and in which the C–Br distance is 1.926Å and the Br–C–Br angles are 108.92^0 (two) and 110.58^0 (four). The structure of **5** may now be easily understood in terms of the combination of two tetrahedral moieties, the tetraphenylmethane moiety and the super-CBr_4 moiety. If the centres of these two tetrahedral moieties are considered as spheres, distorted diamondoid networks are produced when the spheres are joined. Figure 9 is a schematic view of the structure and Figure 10 is a stereoview of the actual structure.

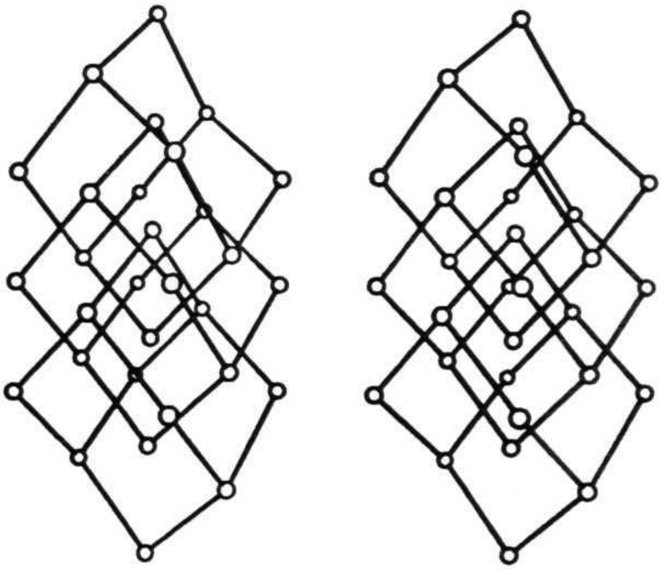


Figure 9. Three interpenetrating diamondoid networks of **5**. Both super-CBr_4 and tetraphenyl moity are shown as circles.

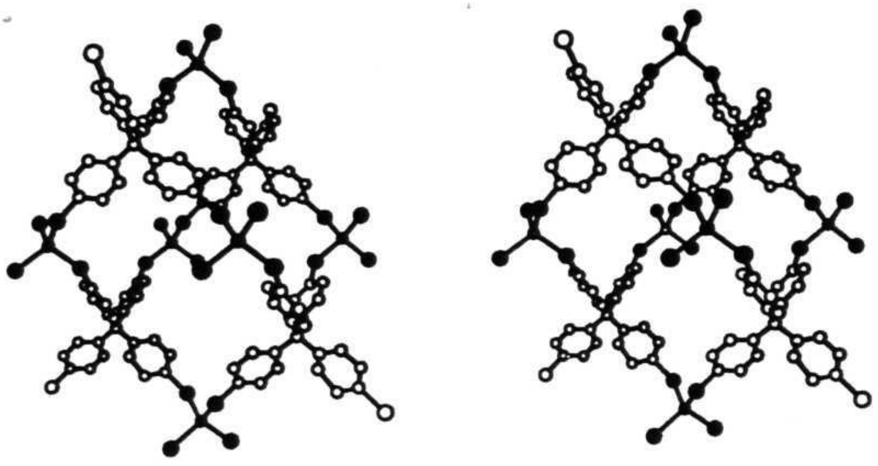


Figure 10. Stereoview of the structure of compound **5**. Notice that the super-CBr_4 molecules are shaded. For clarity the other two interpenetrating networks are not shown.

As described above, two types of tetrahedral species are present in the crystal structure of **5**. The super-CBr_4 molecules are connected with tetraphenyl moiety through Ph–Br covalent bonds. By observing these structural features it is expected that the Ph-Br bonds can be replaced with Br···phenyl interactions if the super-CBr_4 is replaced by a CBr_4 molecule. This leads to the preparation of the 1:1 complex **6** of tetraphenylmethane(TPM) and CBr_4. As expected, this structure is isostructural with **5**. In this structure, TPM molecules are connected by four CBr_4 molecules through Br···phenyl interactions (Br···phenyl 3.67Å) and accordingly the CBr_4 molecules are connected to four TPM molecules through Br··phenyl interactions. Figure 11 shows the CBr_4 molecule is tetrahedrally surrounded by four TPM molecules. As in the structure of **5**, the centroids of the CBr_4 and TPM may be considered as spheres and joined to form distorted diamondoid networks. The schematic view of this structure is shown in Figure 12 and a stereoview of the actual structure is presented in Figure 13.

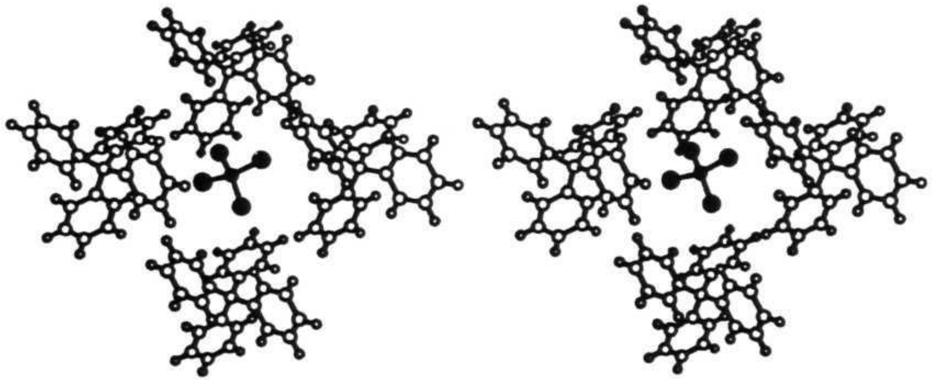


Figure 11. Shows Br···π ineteractions in the crystal structure of complex **6**. Notice that the CBr_4 molecule is surrounded by four TPM molecules.

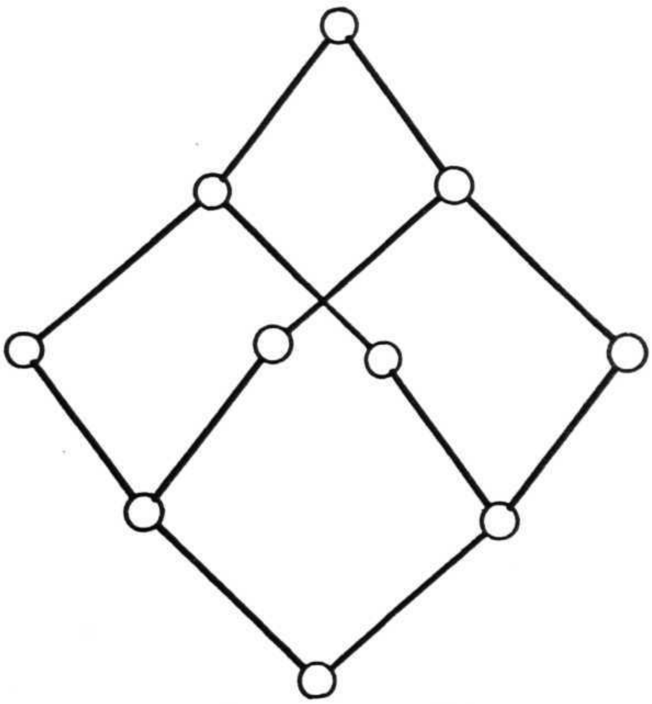


Figure 12. Schematic representation of the crystal structure of complex **6**. Both TPM amd CBr_4 molecules are shown as circles.

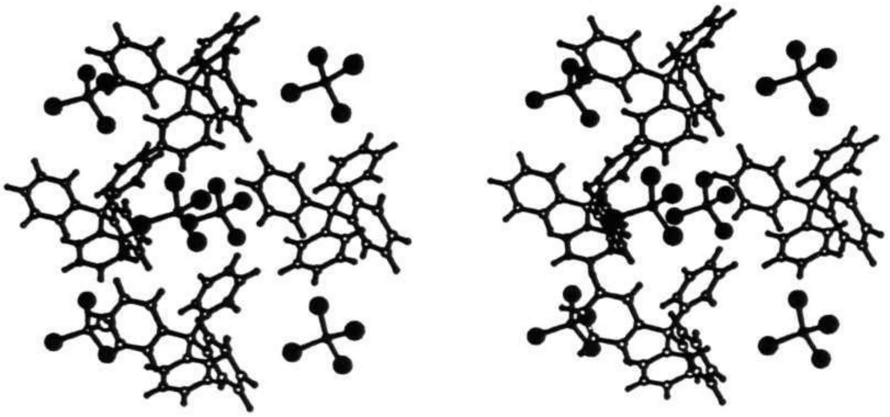


Figure 13. Stereoview of the structure of compound **6**. Notice that the CBr_4 molecules are shaded.

Thus **5** and **6** have close similarities at the molecular and supramolecular levels in that they produce identical distorted diamondoid networks respectively with Br···Br and Br···phenyl intermolecular interactions. It is clear that the super-CBr_4 molecule in the crystal structure of **5** is equivalent to CBr_4 molecule in complex **6**. Hence, a covalent bond (Ph–Br) in the structure of **5** is replaced by an intermolecular interaction (Br···phenyl) in complex **6** and conversely an intermolecular interaction (Br···Br) in the structure of **5** is replaced by a covalent connection (Br–C–Br) in complex **6** without changing the supramolecular structure.

In these two structures, besides the presence of Br···Br or Br···phenyl interactions which form the supramolecular diamondoid networks, another common structural element is present in the form of phenyl···phenyl interactions. Though these interactions are disposed in a three-dimensional fashion, the molecular arrangement is quite clear as all the molecules are stacked along the common tetragonal axis. Interestingly, the molecular stacking in these two crystal structures is similar to the molecular stacking in the parent compound i.e, in the crystal structure of pure TPM. The general arrangement of the molecules in all the three structures is shown in Figure 14. This arrangement seems to be quite important in the TPM family of structures and leads to compression along the tetragonal(common) axis. In turn, this leads to crystallisation in the tetragonal system instead of the cubic system. The molecular stacking in all the three compounds is shown individually in Figure 15.

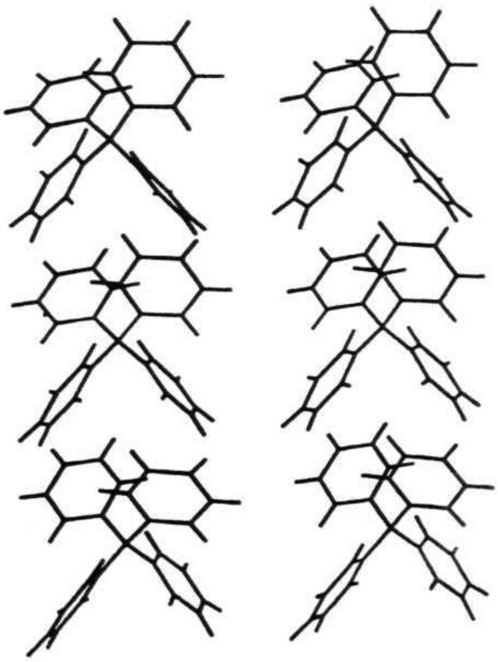
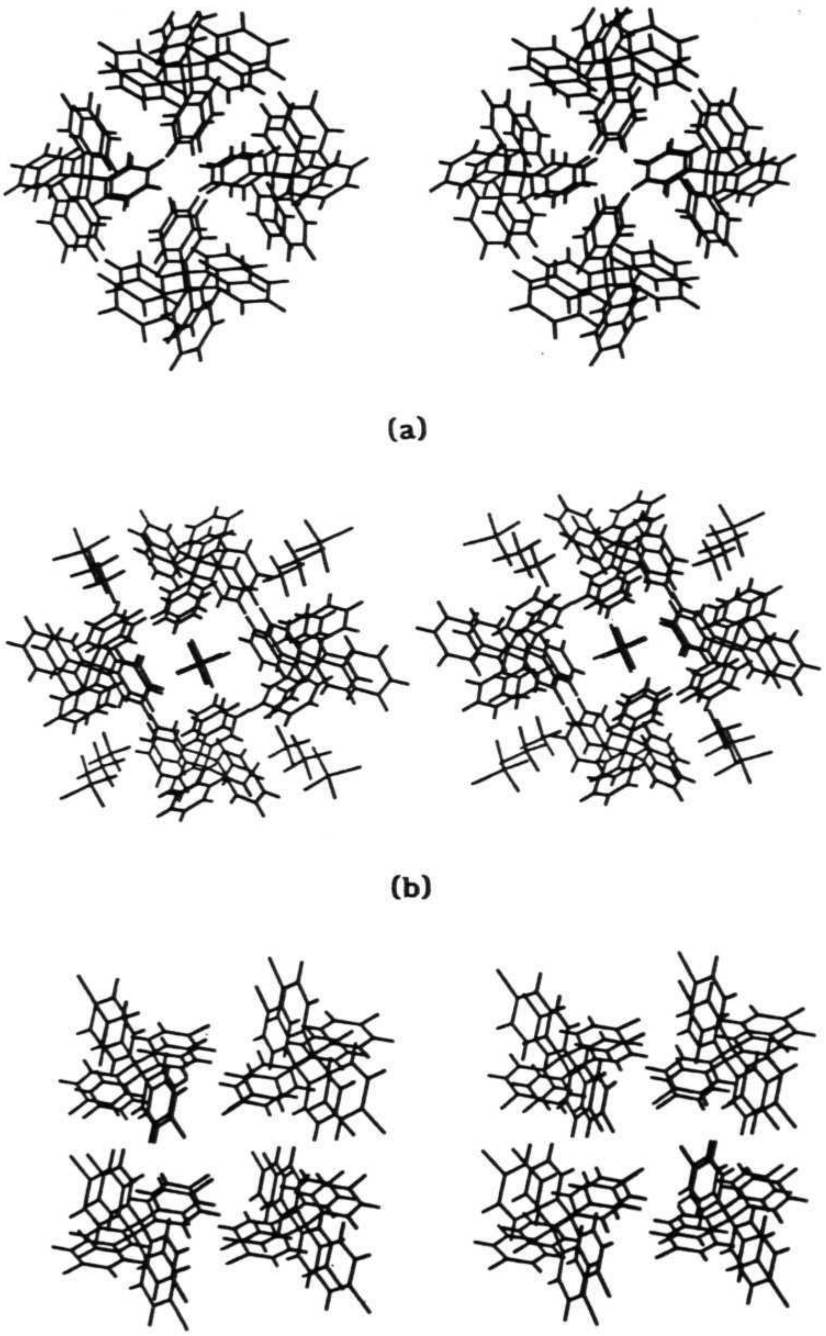


Figure 14. Shows genreral arrangement of molecules along common axis in the TPM family of crystals.



(a)

(b)

(c)

Figure 15. Shows molecular arrangement along the common axis in the crystal structures of (a) pure TPM, (6) compound 5 and (b) complex 6.

4.4. Diamondoid Networks with I···I Interactions

Halogen···halogen interactions have been known for several decades. It is noticed that these forces are strong enough to govern crystal packing.[15] The following examples clearly show the role of these interaction. While 1,3,5,7-tetrachloroadamantane and 1,3,5,7-tetrabromoadamantane form plastic crystals as do other symmetrical adamantanes, Schleyer and co-workers reported[16] that the 1,3,5,7-tetraiodo derivative, **7**, crystallises in a tetragonal space group and is disordered. Continuing the trend, 1,3-difluoro-5,7- diiodoadamantane and 1,3,5-trifluoro-7-iodoadamantane have ordered structures.[16] Such differences in crystallisation behaviour were attributed to the importance of I···I interactions (in compound **7**) and to the importance of the unsymmetrical I···F interactions (in the fluoro iodo derivatives) in other words, to the importance of halogen atom polarisability in X···X interactions. Some of these results of Schleyer and co-workers are, however, ambiguous because the crystal structure of 7, was determined to an unacceptably high R-value of 0.203. Therefore it seemed appropriate to re-examine this crystal structure.

The structure in $I4_1/a$, Z=4, has individual molecules of implicit $\bar{4}2m$ symmetry on sites of $\bar{4}$ symmetry in the crystal (Figure 16). The origin was chosen to lie on an inversion centre. Figure 17 shows that the structure can be described in terms of 4_1 screw related layers of molecules, each layer consisting entirely of molecules related by simple translations na+mb where n and m are integers. The symmetry of such a layer is very nearly $P\bar{4}2m$. An intramolecular I···I vector for I atoms at the same height along c

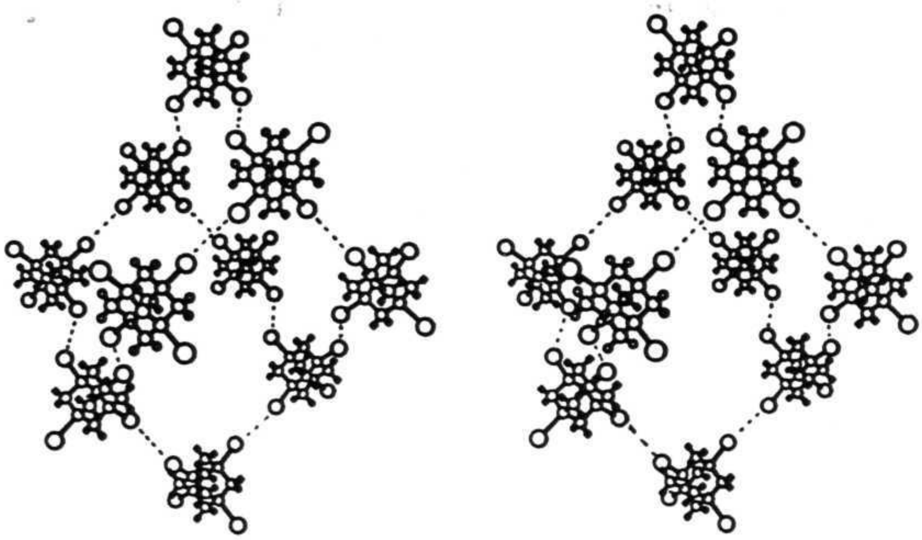


Figure 16. I···I mediated diamondoid network in the crystal structure of 1,3,5,7-Tetraiodoadamantane, **7**. I···I contacts are shown as dashed lines.

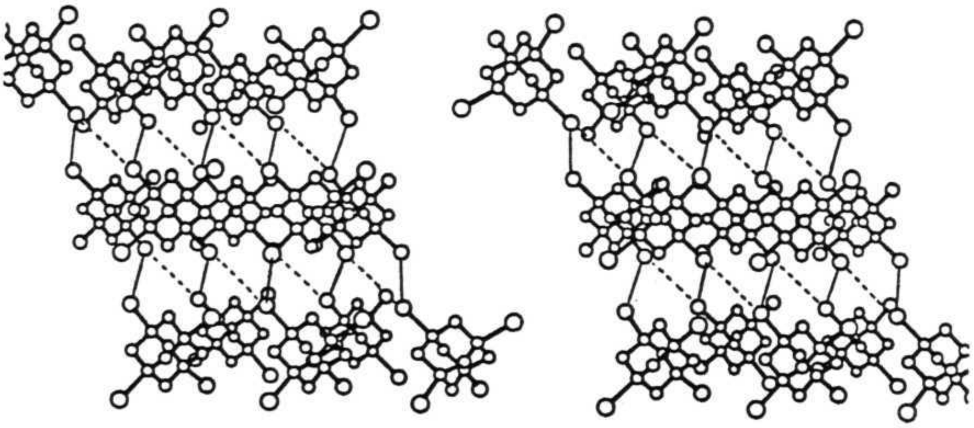


Figure 17. Crystal structure of **7** to show a layer of molecules perpendicular to (001). Molecules within a particular super-adamantoid network as shown in figure 19 are connected with undashed lines(—). Molecules in different networks are connected with dashed lines(---). Molecules in all five independent networks are shown in the figure.

structural option in the sense that the frequency of appearance of misaligned layers is greater in the disordered portions of the crystal. However, it should be emphasised that the refinement is able to treat these two phenomena separately and indeed the identification of both twinning and disorder parameters is essential for meaningful refinement. Such a treatment has been recently reported in the successful refinement of the crystal structure of the Aurivillius phase $Bi_2SrTa_2O_9$.

Since crystal systems of compound **7** and **1** are similar it is worthwhile to compare both structures. In **7**, the shortest I···I contact distance of 4.063Å is between centrosymmetrically related molecules of $\bar{4}$ site symmetry at 0,1/4,1/8 and 1,3/4,-1/8, a vector of **a**+1/2**b**-1/4**c**. The $\bar{4}$ symmetry operation creates a tetrahedrally related vector -1/2**a**+**b**+1/4**c**. The sum of these vectors is 1/2**a'**=1/2**a**+3/2**b** and the $\bar{4}$ operation acting on this vector creates the vector 1/2**b'**=-3/2**a**+1/2**b**. The cell **a'=a+3b**, **b'=-3a+b**, **c'=c** can then be used to describe a network of molecules connected by the 4.063Å contact distance and is shown in Figure 18. The distribution of molecules in this network is exactly the same as in the diamond structure, using 8 molecules per F centred cell with a volume 10 times that of the Z=4 structure corresponding to **a,b,c**. There are thus five interpenetrating networks of contacting molecules in the structure. This is topologically analogous to the structure of acid 1 described by Ermer.[3] The structure of acid **1** has molecules connected by hydrogen bonds about centres of inversion with no other connections with so strong a bonding. However, Figure 19 hints that the structure of **7** has an almost equal I···I contact distance of 4.167Å connecting molecules related by 2 fold rotation

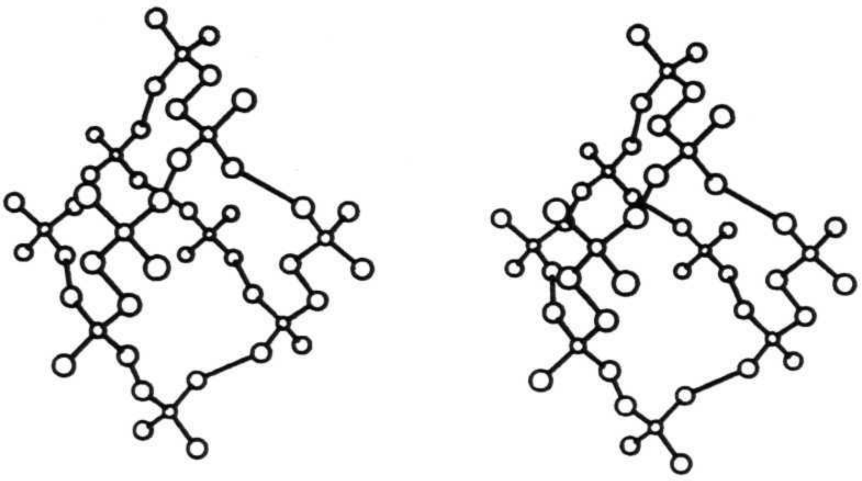


Figure 18. Schematic drawing of diamondoid network of molecules of **7**. Compare this with figure 16. Only the I atoms and the centroids of the molecules are shown for simplicity. The I···I interactions are indicated as dashed lines.

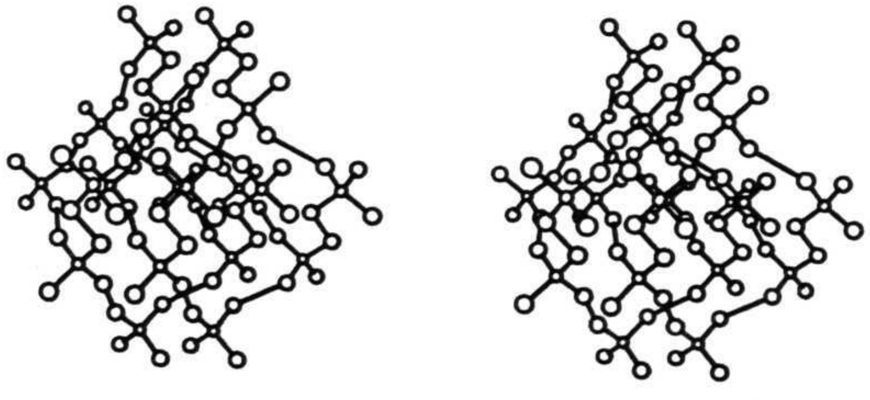


Figure 19. Two interpenetrating diamondoid networks of **7**. Compare this with figure 17. Only two networks are shown for simplicity.

for the reference molecule at 0,1/4,1/8 is 0.609,0.573,0 compared with 0.586,0.586,0 if the molecule were aligned with the [110] direction for the idealised symmetry. The adjacent layers have molecules b-glide related at 0,3/4,-1/8 and a-glide related at 1/2,1/4,3/8. If the pseudo mirror plane of the pseudo P$\bar{4}$2m layer is imposed on these molecules, adjacent layers perpendicular to [001] could have molecules at 1/2,1/4,-1/8 or 0,3/4,3/8. Alternative I···I contact distances associated with twinning or disorder are then possible and these distances depend on how the alternative layers are created. A stacking fault of (a+b)/2 translation creates an I···I contact distance of 4.285(1)Å whereas a two fold rotation 3/4-y,1/4-x,-z between adjacent layers creates a contact distance of 4.172(1)Å. These distances may be compared with distances of 4.063(1)Å for the normal interlayer contact and 4.167(1)Å for the closest intermolecular contact between I atoms of molecules at the same z value.

The possible stacking fault mechanism replaces a P2/b bilayer with a P2/a bilayer using a translation of (a+b)/2 for one layer relative to the other. This stacking fault option would reduce the scale of l=2n+1 data relative to that l=2n. Because of the I-centering, a translation of (a+b)/2 is equivalent to a translation of c/2. However, a twinning that superimposes the diffraction patterns of two orientations of the crystal is observed and this is not possible using the stacking fault mechanism. Failure to identify this twinning was the major cause of failure of the previous refinement[16] attempt and not the fact that "unfortunately the iodine atoms are severely disordered". It should be appreciated additionally that the subtle disorder actually present mimics the twinning mechanism and is not a distinct axes. There are 4 such contacts per molecule and these contacts link molecules at the same z value (not shown in Figure 19). The central molecule and the four surrounding molecules each belong to a different one of the five diamond-like substructures. Thus each substructure is connected to each of the other substructures by the symmetry equivalents of this 4.167Å contact. The contact is facilitated by the rotation of the molecule to align a mirror plane of the inherent $\bar{4}2m$ symmetry of the molecule with the [110] direction rather than the [210] direction as is the case for acid 1.

Orthonormal crystal coordinates of the I atom from the $\bar{4}$ centre are 2.192, 2.062,-2.132Å giving a distance of the I atom from the $\bar{4}$ centre of 3.688Å. If compound 7 had taken up an idealised structure of five interpenetrating diamond lattices with linear C–I···I–C contacts and had the same unit cell volume as the actual structure (presumably the packing co-efficient is inherently constant), the axial lengths would then be a=b=7.7658Å, c=$\sqrt{10}$a=24.558Å. For the idealised structure, the vector a+1/2b-1/4c has a magnitude of 10.634Å, giving a contact distance for I···I of 3.258Å, compared to the actual distance of 4.063Å. The actual c/a ratio in 7 is 3.971 which contrasts with the 2.915 value in acid 1 and $\sqrt{10}$=3.162 for the idealised structure. The structure has rotated the molecule in the idealised structure and shrunk the a and b axes to facilitate the extra contact while at the same time expanding the c-value in order to lengthen the existing contact. The C–I···I angle is 138.4(2)° for the 4.063Å contact. This compares to 180° for the idealised structure. A similar angle of 144.5(2)° is obtained for C–I···I involving the 4.167Å contact. For the twin plane the C–I···I angle involving the 4.172Å close contact is 134.7(1)°.

4.5. Topological equivalences between organic and inorganic crystal structures

The study of organic and inorganic crystal chemistry has proceeded, for the most part, along independent lines.[17] Of course, propositions such as the need to fill space most economically and the conflict between close-packing and directionality are of universal applicability. However, when these are considered along with the many differences between the molecular and ionic building blocks, characteristic respectively of organic and inorganic crystals, any possible similarity between these two vast groupings of substances seems to rapidly disappear.

However there are certain instances when it is most profitable to seek similarities between organic and inorganic crystal structures. Naturally, such similarities must be purely topological in nature, equivalences being found between intermolecular interactions in organic solids (≈40 KJ mol-1) and ionic and covalent bonds in inorganic solids (≈400 KJ mol-1). For example 1,3,5,7-tetracarboxyadamantane **1** and 1,3,5,7-tetraiodoadamantane **7** have crystal structures which are topologically related to diamond; the hydrogen bonded dimer rings in **1** and I···I interactions in **7** replaces the C–C bonds in diamond with the adamantyl skeleton becoming a super-carbon atom. Again, the 1:1 complex between HMT and CBr_4 is analogously related to cubic $ZnCN_2$,[18] $CdCN_2$[18] group of solids with N···Br interactions instead of Zn–N≡C, Cd–N≡C covalent bonds while the 1:2 and 1:1:1 complex of $AdBr_4$, HMT and CBr_4 may be likened to ZnS and LiAlSi[19] group of solids. Similarly, structure of complex **6** and the structure of compound **5** may compared with crystal structure of grey tin.[1]

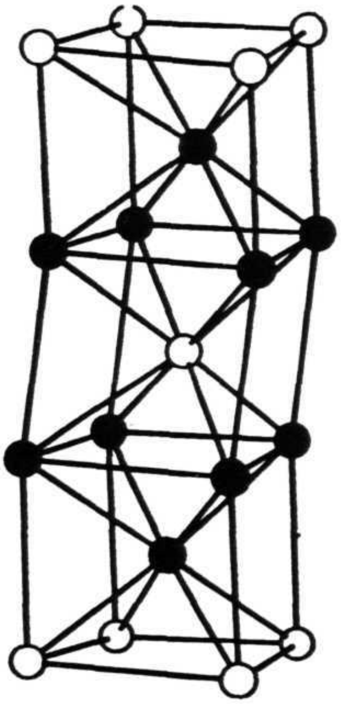


Figure 20. The crystal structure of 1,3,5,7-Tetrahydroxyadamantane **8** showing its topological relationship to the CsCl family. The molecules are represented as circles.

The crystal structure of 1,3,5,7-tetrahydroxyadamantane **8**[11] shows complex hydrogen bonded networks because of its high molecular symmetry and strong hydrogen-bonding compulsions. Therefore for an alternative strategy, one can develop a structural analogy between **8** and a simple inorganic structure. The crystal structure of compound **8** is intricate with an unusual space group, *Pbcn*, and molecules both in general and special positions. Both these molecules are connected to eight neighbouring molecules with strong hydrogen bonds (O···O, O–H···O, 2.719, 170.3; 2.763, 170.4; 2.739, 177.2; 2.722, 175.3; 2.785 177.6^0). The general position molecule is connected with four general position molecules and four special position molecules through hydrogen bonds. Accordingly, the special position molecule is connected with eight general position molecules with hydrogen bonding. To make a clear analysis of this unusual hydrogen bonding between two independent molecules in the crystal structure, the molecules are reduced to spheres and the resultant eight connected hydrogen bonded nets is seen to be clearly similar to the CsCl family of structures. The topological relation between the crystal structure of compound **8** and CsCl structures is shown in Figure 20. The four hydroxy functionalities are conceptually connected to the centroid of the adamantane moiety and hydrogen bonds are explicitly shown Figure 21. All the hydrogen atoms are ordered and the hydrogen bonds have geometrical features within the typical distance and angle ranges. The hydrogen bonding with complete molecules is shown in Figure 22.

This kind of analysis has several utilitarian features: (1) complex hydrogen bond and other networks in molecular crystals can be described with a very simple, classical terminology and without recourse to new and still untested schemes for structural decoding.

(2) The method is general.

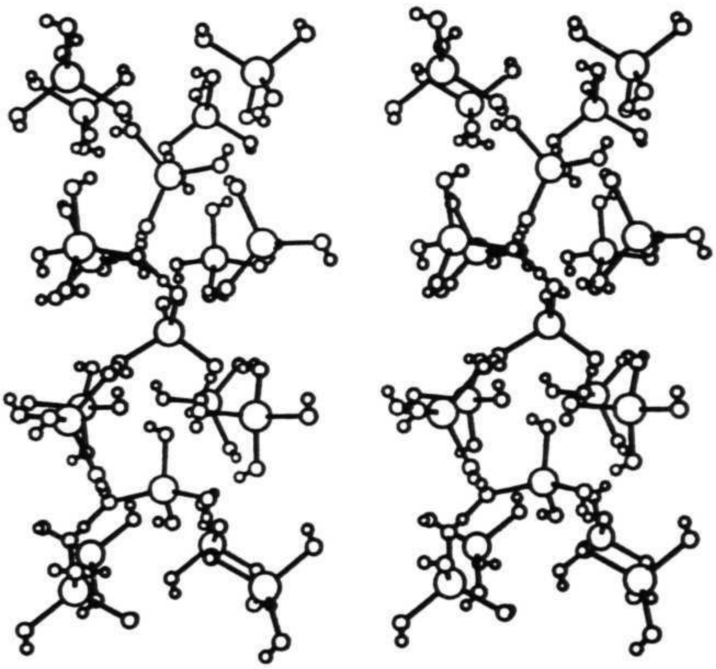


Figure 21. Crystal structure of **8** with the hydrogen bonds explicitly shown. Notice the eight-coordination of the molecules.

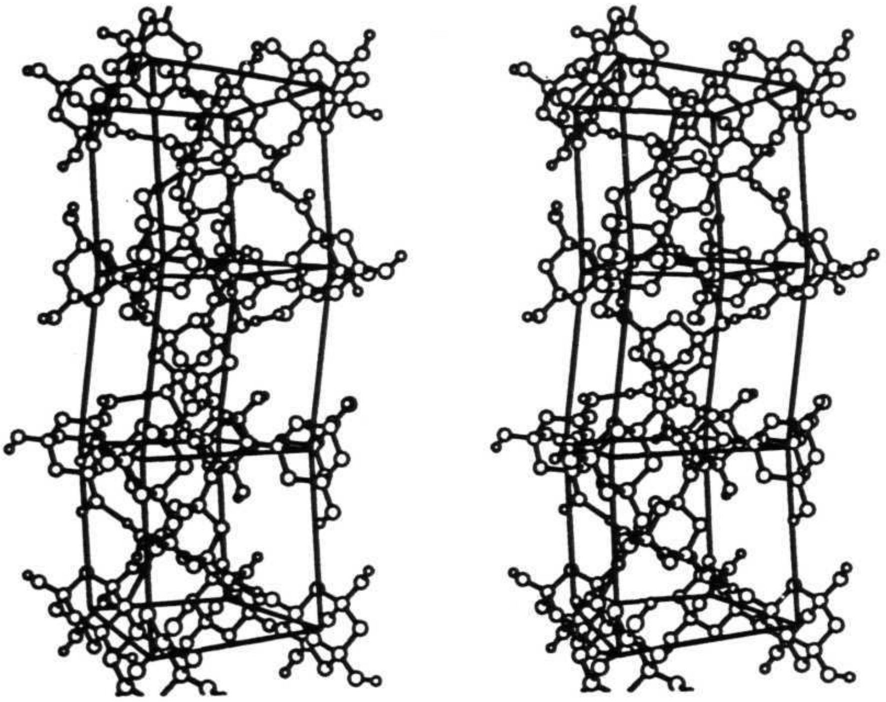


Figure 22. Crystal structure of 8 showing the molecules in full. Notice the pseudo-cubic unit cells.

4.6. Conclusions

The architecture of diamondoid networks is very important becuase these fascinating solids have many applications in materials science this is particularly useful in the area of host-guest chemistry which covers selective enclatheration, microporosity and catalysis. The synthesis of these complex supramolecular networks with intermolecular interactions has the principal advantage that these structures with specific architectural or functional features are formed reversibly by spontaneous self-assembly, and not by tedious bond-by-bond synthesis. Besides these general advantages, this chapter presents results which shows that super-diamondoid networks can be synthesised with interactions weaker than conventional hydrogen bonding and that in some cases the super-adamantane cavity is efficiently utilised for the inclusion of foreign guest molecules. These experimental results also highlight the analogy between organic and inorganic crystal chemistry at the supramolecular level and it may be stated that the present and yet almost always hidden similarity between organic and inorganic crystal structures is more easily revealed for these symmetrical molecules and may provide a new handle in the study of complex crystal packing arrangements.

4.7. Experimental

General methods and Instrumentation

Infrared spectra were obtained using JASCO FT/IR-5300 spectrometer. ^{1}H NMR spectra were measured with a Jeol-Fax-100 spectrometer. Chemical shifts are reported as δ values relative to TMS. Starting materials and some of the compounds (Adamantane, HMT,

CBr_4) are purchased from Aldrich. The remaining compounds were prepared according to literature procedures.

1,3,5,7-Tetrabromoadamantane (AdBr$_4$)[20a]

To a 100 mL, three-necked dry round bottomed flask equipped with a water condenser, magnetic stirrer, and a rubber septum connected to a nitrogen inlet, were added bromine (21mL, 65.14g). This mixture was cooled to 5-10^0 with an ice bath. Adamantane (5.0 g,) was added over a period of 30 min with constant stirring. The mixture was then refluxed at 70 ^{0}C for 24h, which led to vigorous HBr evolution. Excess bromine was distilled off. The residue was treated with aqueous sodium sulfite and then stirred with 50 mL of a 6 M HCl solution. The solid precipitate was filtered off, and washed several times with water. The compound was recrystallised from glacial acetic acid give to 8.0g of $AdBr_4$.

m.p. :260^{0}C.
I.R ν_{max}(KBr) :2942, 1440, 1310, 1250, 1200, 1020, 980, 840, 740, 720 cm^{-1}
NMR δ_H($CDCl_3$) :2.7(s).

Tetraphenylmethane (TPM)[20b]

A mixture of triphenylmethanol(52g), aniline (28mL), concentrated hydrochloric acid (90mL), and glacial acetic acid (600mL) was heated under reflux for 48h. The intermediate product was isolated, dissolved in 1.5 L of ethanol and 100mL of concentrated sulphuric acid and diazotised at -10°C with 60 mL of isopentyl nitrite, and after 45 min deaminated with 150mL of 60% hypophosphorous acid under reflux. The yield after recrystallisation from 1,2-dichloroethane was 38.3g

mp :282-283°C.

I.R ν_{max}(KBr) :3030, 2359, 1591, 1491, 1182, 1035, 1001, 937, 889, 750, 700 cm^{-1}

NMR δ_H($CDCl_3$) :7.2(m)

Preparation of tetrakis tetrabromo(tetraphenyl-)methane 5[20b]

Tetraphenylmethane (TPM) (9.0g) was added to 30 mL of pure bromine at room temperature; the mixture was stirred for 45 min and then diluted with ethanol in an ice cooled vessel until no further crude product precipitated. The crude product was filtered off and washed with sodium bisulphite solution. The yield after recrystallisation from chloroform/ethanol 11.0g of **5**; mp 312°C.

I.R ν_{max}(KBr) :3000, 1479, 1396, 1184, 1076, 1006, 810, 748, 532, 509 cm^{-1}.

NMR δ_H($CDCl_3$) :7.4(m).

1,3,5,7-Tetraiodoadamantane 7[20a]

Methylene iodide (24 mL, 79.8g) and aluminium powder (2g) were added to a round bottomed flask equipped with a magnetic stirrer and a water condenser. Bromine (0.13 mL) was added to this mixture and the combined mixture stirred for 35 min in an oil bath at 80-82°C. $AdBr_4$ (2.0g) was added in one portion and allowed to react for 15 min at the same temperature. The reaction mixture was poured into 40 mL of cold water with constant stirring. Sodium sulphite was added to remove any colour of Bromine. The methylene iodide layer was separated and washed well. The solvent was removed by vacuum distillation. The solid residue was washed well. The solvent was removed by vacuum distillation. The solid residue was washed successively with 10mL each of $CHCl_3$ and acetone. The colourless solid obtained was recrystallised from chloroform to give 1.8g of the product as shiny white isodimensional crystals.

mp :360°C.
I.R ν_{max}(KBr) :3302, 2945, 2866, 1334, 1122, 1049, 970 cm^{-1}.
NMR δ_H(CDCl$_3$) :3.2(s).

1,3,5,7-Tetrahydroxyadamantane 8[20c]

AdBr$_4$(5.0) and 7.6g of dry silver sulphate and 10mL of concentrated H_2SO_4 were taken in a dry round bottomed flask and stirred for 30 min at 80 ^{0}C. The reaction mixture was added to the water and filtered. The filtrate was neutralised with KOH solution and evaporated until the solid was obtained. The crude product was dried and recrystallised from dry ethanol/benzene. yield; 2.0g.

m.p. :317-320^{0}C.
I.R ν_{max}(KBr) :3302, 2945, 2866, 1334, 1122, 1049, 970 cm^{-1}.
NMR δ_H(CDCl$_3$) :4.6(s)

Complex **2**

Colourless crystals of complex **2** (235 ^{0}C) were obtained readily from an equimolar solution of HMT and CBr$_4$ in chloroform.

I.R ν_{max}(KBr) :2800, 1450, 1380, 1220, 1000, 800, 680 cm^{-1}.

Complex **3**

Colourless crystals of complex **3** (260 C^{0}) were obtained from an the solution of one equivalent of AdBr$_4$, and two equivalent of HMT in chloroform.

I.R ν_{max}(KBr) :3000, 1450, 1390, 1360, 1220, 1000, 810, 840, 710, 680 cm^{-1}.

Complex **4**

Colourless crystals of complex **4** (260 C^{0}) were obtained from a equimolar solution of AdBr$_4$, HMT and CBr$_4$ in chloroform.

I.R ν_{max}(KBr) :3000, 1450, 1380, 1220, 1000, 820, 800, cm^{-1}

Complex 6

Colourless crystals of complex **6** (280 °C) were obtained readily from an equimolar solution of TPM and CBr_4 in chloroform.

I.R ν_{max}(KBr) :3030, 2359, 1591, 1491, 1182, 1035, 1001, 937, 889, 750, 700 cm^{-1}

X-ray Crystallographic Studies

Crystal data for all these compounds were collected by Mr. D.C. Craig, University of New South Wales, Australia on an Enraf-Nonius CAD-4 diffractometer. The structures were determined using MULTAN80 and refined with BLOCKLS.[21] All non-hydrogen atoms were refined anisotropically and the final R-factors and other crystallographic information are presented in Appendix C-1. Tables of coordinates and thermal vibrational parameters are given in Appendix C-2.

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APPENDICES

Appendix A-1

Table 2.1

Crystallographic Details for compounds 1-7

	1	2	3	4
Formulae	$C_8H_2N_2Cl_2$	$C_{10}H_6N_2O_2Cl_2$	$C_{12}H_{10}N_2O_2Cl_2$	$C_{14}H_{14}N_2O_2Cl_2$
Mol.Wt	193.0	257.0	287.0	286.76
Crystal sys.	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	C2/c	Pc	Pc
a Å	6.251(1)	16.46(1)	4.204(2)	13.549(12)
b Å	8.252(2)	9.11(2)	10.909(3)	14.588(14)
c Å	9.283(3)	7.33(1)	14.198(4)	7.444(9)
$\alpha(^0)$	64.48(2)	90	90	90
$\beta(^0)$	72.78(2)	93.24(8)	91.58(20)	91.08(9)
$\gamma(^0)$	78.63(2)	90	90	90
Cell Volume Å	411.4(2)	1097(3)	650.9(7)	1471(3)
Z	2	4	2	4
F(000)	196	520	292	640
$D_{cald.gcm^{-1}}$	1.593	1.556	1.455	1.414
λ, Å	0.7107	0.7107	0.7107	0.7107
Diffractometer	SiemensR3m	CAD-4	SiemensP3/Pc	SiemensP3/Pc
T,K	293	293	140	140
X-radiation	MoKα	MoKα	MoKα	MoKα
Total reflctn	1808	921	2403	3168
Non-zero refl	1401	760	1636	2082
R	0.045	0.073	0.079	0.128

Table 2.1 (contd)

	5	6	8
Formulae	$C_{16}H_{18}N_2O_2Cl_2$	$C_{16}H_{18}N_2O_2Cl_2$	$C_8H_2N_2O_2Cl_2$
Mol.Wt	343.10	343.10	227.0
Crystal sys.	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1/c$	Pbca	$Pna2_1$
a Å	12.854(3)	47.023(3)	16.503(2)
b Å	8.778(2)	9.424(1)	8.542(1)
c Å	16.983(3)	7.607(2)	6.421(2)
$\alpha(^0)$	90	90	90
$\beta(^0)$	108.23(2)	90	90
$\gamma(^0)$	90	90	90
Cell Volume Å	1820(1)	3371(2)	905(1)
Z	4	8	4
F(000)	712	1424	456
$D_{cald.gcm^{-1}}$	1.245	1.345	1.66
λ, Å	0.7107	0.7107	0.7107
Diffractometer	Siemens P3/Pc	CAD-4	CAD-4
T,K	293	293	293
X-radiation	MoKα	MoKα	MoKα
Total reflctn	2230	969	1210
Non-zero refl	1038	654	876
R	0.063	0.034	0.023

Appendix A-2

Table 2.2

Fractional co-ordinates and equivalent thermal parameters for 2,3-Dicyano-5,6-dichlorobenzene (1) (e.s.d's are in parentheses).

Atom	x/a	y/b	z/c	U_{eq}
Cl(1)	0.2482(1)	0.1573(1)	0.0085(1)	0.005(1)
Cl(2)	-0.2354(1)	0.3527(1)	0.0325(1)	0.061(1)
N(1)	-0.3218(3)	0.3830(3)	-0.6168(2)	0.060(1)
N(2)	0.2919(3)	0.0959(3)	-0.6342(3)	0.062(1)
C(1)	0.1090(3)	0.2061(2)	-0.1415(2)	0.037(1)
C(2)	-0.1043(3)	0.2974(2)	-0.1330(2)	0.039(1)
C(3)	-0.2142(3)	0.3417(2)	-0.2565(2)	0.041(1)
C(4)	-0.1121(3)	0.2919(2)	-0.3875(2)	0.038(1)
C(5)	0.1010(3)	0.1966(2)	-0.3948(2)	0.038(1)
C(6)	0.2110(3)	0.1546(3)	-0.2716(2)	0.040(1)
C(7)	-0.2259(3)	0.3409(3)	-0.5169(2)	0.046(1)
C(8)	0.2066(3)	0.1426(3)	-0.5296(3)	0.047(1)
H(3)	-0.0362(4)	0.0401(3)	-0.0246(3)	0.005(1)
H(6)	0.0354(4)	0.0094(3)	-0.0280(3)	0.006(1)

Table 2.3

Final anisotropic thermal vibrational parameters for non-H atoms for 2,3-Dicyano-5,6-dichlorobenzene (1) (e.s.d's are in parentheses).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl(1)	0.042(1)	0.061(1)	0.055(1)	-0.025(1)	-0.020(1)	0.005(1)
Cl(2)	0.048(1)	0.081(1)	0.060(1)	-0.046(1)	-0.009(1)	0.015(1)
N(1)	0.057(1)	0.069(1)	0.056(1)	-0.027(1)	-0.023(1)	0.010(1)
N(2)	0.052(1)	0.081(1)	0.059(1)	-0.042(1)	-0.009(1)	0.009(1)
C(1)	0.030(1)	0.038(1)	0.042(1)	-0.016(1)	-0.008(1)	0.000(1)
C(2)	0.031(1)	0.040(1)	0.043(1)	-0.019(1)	-0.004(1)	0.001(1)
C(3)	0.029(1)	0.042(1)	0.047(1)	-0.018(1)	-0.007(1)	0.005(1)
C(4)	0.032(1)	0.037(1)	0.040(1)	-0.013(1)	-0.007(1)	0.001(1)
C(5)	0.031(1)	0.038(1)	0.041(1)	-0.017(1)	-0.002(1)	0.001(1)
C(6)	0.028(1)	0.042(1)	0.047(1)	-0.020(1)	-0.006(1)	0.004(1)
C(7)	0.040(1)	0.046(1)	0.048(1)	-0.018(1)	-0.012(1)	0.003(1)
C(8)	0.038(1)	0.054(1)	0.049(1)	-0.025(1)	-0.008(1)	0.003(1)

Table 2.4

Fractional co-ordinates and equivalent thermal parameters for 2,3-Dicyano-5,6-dichloro-1,4,-dimethoxybenzene (**2**) (e.s.d's are in parentheses).

Atom	x/a	y/b	z/c	U_{eq}
Cl1	0.4118(1)	0.6424(1)	0.1652(1)	0.039(1)
C2	0.4604(3)	0.4795(5)	0.2142(7)	0.037(3)
C3	0.4207(3)	0.3475(5)	0.1725(7)	0.038(3)
C4	0.4605(3)	0.2169(6)	0.2115(7)	0.037(3)
C5	0.4204(3)	0.0820(7)	0.1580(8)	0.045(3)
N6	0.3881(3)	-0.0222(5)	0.1123(7)	0.058(3)
O7	0.3443(2)	0.3468(4)	0.0932(10)	0.048(2)
C8	0.2811(3)	0.3568(8)	0.2172(10)	0.073(5)
H81	0.222(3)	0.355(8)	0.143(9)	0.009(3)
H82	0.287(3)	0.457(8)	0.295(9)	0.018(4)
H83	0.285(3)	0.264(8)	0.309(9)	0.012(3)

Table 2.5

Final anisotropic thermal vibrational parameters for non-H atoms for 2,3-Dicyano-5,6-dichloro-1,4-dimethoxybenzene (**2**) (e.s.d's are in parentheses).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl(1)	0.049(1)	0.040(1)	0.065(1)	0.004(1)	0.007(1)	0.015(1)
C(2)	0.031(2)	0.032(3)	0.048(3)	0.003(2)	0.006(2)	0.006(6)
C(3)	0.024(3)	0.042(3)	0.049(3)	-0.002(2)	0.005(2)	0.003(2)
C(4)	0.026(2)	0.036(3)	0.049(3)	-0.000(2)	0.005(2)	-0.001(2)
C(5)	0.026(3)	0.045(3)	0.063(4)	0.001(3)	-0.001(2)	-0.001(2)
N(6)	0.043(3)	0.044(3)	0.087(4)	-0.006(3)	0.000(3)	-0.009(2)
O(7)	0.021(2)	0.060(3)	0.062(2)	-0.004(2)	-0.006(2)	0.004(2)
C(8)	0.019(3)	0.108(6)	0.090(5)	-0.017(4)	0.006(3)	0.001(3)

Table 2.6

Fractional co-ordinates and equivalent thermal parameters for 2,3-Dicyano-5,6-dichloro-1,4,-diethoxybenzene (**3**) (e.s.d's are in parentheses).

Atom	x/a	y/b	z/c	U_{eq}
Cl(1)	0.0716(1)	0.4669(2)	0.2125(1)	0.026(1)
Cl(2)	0.9198(7)	0.1920(2)	0.1753(2)	0.024(1)
O(1)	0.3325(14)	0.4967(5)	0.3841(4)	0.020(1)
O(2)	0.7286(14)	0.0206(4)	0.3207(4)	0.021(1)
N(1)	0.0241(22)	0.3448(7)	0.5739(5)	0.034(2)
N(2)	0.2783(21)	-0.0056(7)	0.5277(5)	0.033(2)
C(11)	0.6130(17)	0.3526(6)	0.2900(5)	0.017(2)
C(12)	0.4382(19)	0.3812(6)	0.3680(5)	0.019(2)
C(13)	0.3554(18)	0.2879(6)	0.4297(5)	0.017(2)
C(14)	0.1779(21)	0.3187(6)	0.5107(5)	0.022(2)
C(15)	0.5579(19)	0.5739(7)	0.4358(6)	0.022(2)
C(16)	0.3849(31)	0.6883(8)	0.4626(8)	0.043(3)
C(21)	0.7062(18)	0.2316(6)	0.2733(5)	0.017(2)
C(22)	0.6264(17)	0.1362(6)	0.3357(4)	0.015(2)
C(23)	0.4488(17)	0.1653(6)	0.4137(4)	0.016(2)
C(24)	0.3624(20)	0.0696(7)	0.4772(5)	0.022(2)
C(25)	0.5009(22)	-0.0550(6)	0.2663(6)	0.026(2)
C(26)	0.6759(25)	-0.1679(8)	0.2349(8)	0.037(3)

Table 2.7

Final anisotropic thermal vibrational parameters for non-H atoms for 2,3-Dicyano-5,6-dichloro-1,4-diethoxybenzene (**3**) (e.s.d's are in parentheses).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl(1)	0.029(1)	0.025(1)	0.024(1)	0.005(1)	0.015(1)	-0.002(1)
Cl(2)	0.019(1)	0.033(1)	0.022(1)	-0.002(1)	0.017(1)	0.003(1)
O(1)	0.016(3)	0.018(2)	0.026(2)	-0.000(2)	0.011(2)	-0.000(2)
O(2)	0.021(3)	0.019(2)	0.024(2)	-0.003(2)	0.008(2)	0.005(2)
N(1)	0.042(5)	0.027(3)	0.035(3)	-0.001(3)	0.027(3)	0.003(3)
N(2)	0.041(5)	0.026(3)	0.034(3)	0.003(2)	0.025(3)	-0.004(3)
C(11)	0.007(3)	0.022(3)	0.023(3)	0.004(2)	0.012(2)	0.002(2)
C(12)	0.017(4)	0.019(3)	0.021(3)	-0.001(2)	0.012(3)	-0.000(3)
C(13)	0.016(3)	0.018(3)	0.016(3)	-0.001(2)	0.009(2)	-0.001(2)
C(14)	0.024(4)	0.018(3)	0.025(3)	0.001(2)	0.016(3)	0.001(3)
C(15)	0.013(3)	0.023(3)	0.031(3)	-0.005(3)	0.003(3)	0.001(3)
C(16)	0.047(6)	0.024(4)	0.057(6)	-0.016(4)	0.003(5)	0.003(4)
C(21)	0.011(3)	0.025(3)	0.015(2)	-0.001(2)	0.001(2)	0.002(2)
C(22)	0.009(3)	0.020(3)	0.017(3)	-0.002(2)	0.009(2)	0.003(2)
C(23)	0.009(3)	0.020(3)	0.018(3)	-0.000(2)	0.001(1)	-0.002(2)
C(24)	0.025(4)	0.022(3)	0.018(3)	0.000(2)	0.009(3)	0.003(3)
C(25)	0.025(4)	0.021(3)	0.033(4)	-0.004(3)	0.009(3)	0.004(3)
C(26)	0.022(4)	0.032(4)	0.058(5)	-0.019(4)	0.003(4)	-0.003(3)

Table 2.8

Fractional co-ordinates and equivalent thermal parameters for 2,3-Dicyano-5,6-dichloro-1,4-dipropoxybenzene (low-temperature) (**4**) (e.s.d's are in parentheses).

Atom	x/a	y/b	z/c	U_{eq}
Cl(1A)	0.9576(1)	1.0936(2)	0.2251(1)	0.034(1)
Cl(2A)	1.1766(2)	1.0588(2)	0.3497(7)	0.034(1)
O(1A)	0.8468(3)	0.9289(8)	0.1478(8)	0.036(1)
O(2A)	1.2240(3)	0.8634(8)	0.4034(8)	0.031(1)
N(1A)	0.8641(11)	0.6847(7)	0.1371(17)	0.060(1)
N(2A)	1.1304(11)	0.6399(4)	0.3420(18)	0.053(1)
C(11A)	1.0023(3)	0.9837(2)	0.2453(17)	0.032(1)
C(12A)	0.9382(3)	0.9093(2)	0.2065(12)	0.026(1)
C(13A)	0.9746(4)	0.8196(2)	0.2274(16)	0.038(1)
C(14A)	0.9107(5)	0.7448(3)	0.1782(16)	0.042(1)
C(15A)	0.7753(5)	0.9235(10)	0.2954(9)	0.037(1)
C(16A)	0.6748(3)	0.9435(7)	0.2094(14)	0.036(1)
C(17A)	0.6389(10)	0.8663(10)	0.0872(16)	0.049(1)
C(21A)	1.0985(3)	0.9682(2)	0.3065(13)	0.017(1)
C(22A)	1.1341(3)	0.8778(2)	0.3315(12)	0.023(1)
C(23A)	1.0708(4)	0.8041(2)	0.2900(15)	0.028(1)
C(24A)	1.1072(5)	0.7127(2)	0.3190(15)	0.023(1)
C(25A)	1.2999(4)	0.8611(10)	0.2632(9)	0.034(1)
C(26A)	1.3985(3)	0.8538(7)	0.3636(14)	0.039(1)
C(27A)	1.4217(11)	0.9385(8)	0.4761(17)	0.047(1)
Cl(1B)	0.6118(3)	0.6147(2)	0.1839(7)	0.033(1)
Cl(2B)	0.3933(3)	0.6099(2)	0.3133(7)	0.031(1)
O(1B)	0.6973(3)	0.4295(8)	0.1242(8)	0.029(1)
O(2B)	0.3170(3)	0.4197(8)	0.3711(8)	0.024(1)
N(1B)	0.6429(9)	0.1959(5)	0.1317(17)	0.050(1)
N(2B)	0.3783(12)	0.1915(6)	0.3571(17)	0.052(1)

Table 2.8 (contd)

Atom	x/a	y/b	z/c	U_{eq}
C(11B)	0.5527(4)	0.5117(2)	0.2152(15)	0.031(1)
C(12B)	0.6057(4)	0.4294(2)	0.1878(12)	0.026(1)
C(13B)	0.5570(4)	0.3455(2)	0.2151(14)	0.029(1)
C(14B)	0.6072(6)	0.2627(2)	0.1668(16)	0.037(1)
C(15B)	0.7714(5)	0.4419(9)	0.2708(10)	0.040(1)
C(16B)	0.8708(4)	0.4211(8)	0.1880(15)	0.055(1)
C(17B)	0.880(1)	0.3213(9)	0.1310(19)	0.076(1)
C(21B)	0.4562(4)	0.5096(2)	0.2753(15)	0.024(1)
C(22B)	0.4080(3)	0.4250(2)	0.3053(12)	0.018(1)
C(23B)	0.4615(4)	0.3435(2)	0.2815(14)	0.024(1)
C(24B)	0.4135(5)	0.2582(2)	0.3207(15)	0.039(1)
C(25B)	0.2412(5)	0.4317(8)	0.2274(10)	0.041(1)
C(26B)	0.1435(3)	0.4059(7)	0.3117(14)	0.031(1)
C(27B)	0.1353(10)	0.3036(8)	0.3484(17)	0.043(1)

Table 2.9

Final anisotropic thermal vibrational parameters for non-H atoms for 2,3-Dicyano-5,6-dichloro-1,4-dipropoxybenzene(low-temperature) (**4**) (e.s.d's are in parentheses).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl(1A)	0.026(2)	0.017(1)	0.059(2)	-0.001(1)	-0.001(1)	-0.004(1)
Cl(2A)	0.019(1)	0.020(1)	0.062(2)	0.003(1)	-0.001(1)	0.006(1)
O(1A)	0.013(2)	0.032(2)	0.062(2)	0.001(2)	-0.009(2)	-0.026(2)
O(2A)	0.018(2)	0.032(2)	0.043(2)	0.004(2)	-0.009(2)	-0.005(2)
N(1A)	0.046(2)	0.019(2)	0.112(2)	-0.014(2)	-0.027(2)	0.021(2)
N(2A)	0.027(2)	0.025(2)	0.110(2)	-0.003(2)	0.015(2)	-0.020(2)
C(11A)	0.028(2)	0.014(2)	0.056(2)	0.007(2)	-0.010(2)	-0.022(2)
C(21A)	0.001(2)	0.043(2)	0.082(2)	-0.002(2)	0.006(2)	0.011(2)
C(12A)	0.027(2)	0.021(2)	0.031(2)	-0.004(2)	-0.009(2)	0.012(2)
C(22A)	0.000(2)	0.046(2)	0.024(2)	-0.001(2)	0.010(2)	0.009(2)
C(13A)	0.038(2)	0.031(2)	0.043(2)	-0.011(2)	-0.005(2)	-0.006(2)
C(23A)	0.005(2)	0.048(2)	0.032(2)	0.001(2)	0.004(2)	0.016(2)
C(14A)	0.074(2)	0.011(2)	0.041(2)	0.012(2)	-0.029(2)	0.002(2)
C(24A)	0.000(2)	0.020(2)	0.048(2)	-0.001(2)	0.012(2)	0.008(2)
C(15A)	0.011(2)	0.050(2)	0.050(2)	0.004(2)	-0.004(2)	-0.000(2)
C(25A)	0.000(2)	0.068(2)	0.033(2)	0.004(2)	0.010(2)	-0.003(2)
C(16A)	0.017(2)	0.014(2)	0.078(2)	0.013(2)	0.007(2)	0.002(2)
C(26A)	0.002(2)	0.016(2)	0.100(2)	-0.005(2)	-0.007(2)	0.001(2)
C(17A)	0.039(2)	0.041(2)	0.065(2)	0.019(2)	-0.005(2)	0.019(2)
C(27A)	0.051(2)	0.018(2)	0.072(2)	0.002(2)	-0.023(2)	-0.010(2)
Cl(1B)	0.027(2)	0.020(1)	0.053(2)	-0.001(1)	-0.008(1)	0.006(1)
Cl(2B)	0.016(1)	0.011(1)	0.065(2)	0.005(1)	-0.001(1)	-0.005(1)
O(1B)	0.012(2)	0.038(2)	0.037(2)	0.006(2)	0.005(2)	0.009(2)
O(2B)	0.000(2)	0.032(2)	0.040(2)	0.002(2)	0.008(2)	0.003(2)
N(1B)	0.007(2)	0.000(2)	0.144(2)	0.008(2)	0.010(2)	-0.010(2)
N(2B)	0.057(2)	0.037(2)	0.063(2)	-0.004(2)	-0.003(2)	0.015(2)

Table 2.9 (contd)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(11B)	0.036(2)	0.000(2)	0.056(2)	0.010(2)	-0.016(2)	-0.016(2)
C(21B)	0.005(2)	0.040(2)	0.027(2)	-0.002(2)	0.001(2)	-0.032(2)
C(12B)	0.031(2)	0.002(2)	0.047(2)	-0.006(2)	-0.001(2)	-0.01(2)
C(22B)	0.00(2)	0.024(2)	0.029(2)	-0.002(2)	0.001(2)	-0.01(2)
C(13B)	0.044(2)	0.010(2)	0.034(2)	0.001(2)	-0.017(2)	0.018(2)
C(23B)	0.026(2)	0.009(2)	0.036(2)	-0.006(2)	-0.017(2)	0.013(2)
C(14B)	0.058(2)	0.000(2)	0.051(2)	-0.009(2)	-0.010(2)	0.017(2)
C(24B)	0.028(2)	0.063(2)	0.025(2)	-0.009(2)	-0.018(2)	0.013(2)
C(15B)	0.004(2)	0.046(2)	0.072(2)	0.009(2)	0.005(2)	-0.030(2)
C(25B)	0.069(2)	0.016(2)	0.036(2)	0.000(2)	-0.031(2)	-0.008(2)
C(16B)	0.017(2)	0.072(2)	0.079(2)	0.002(2)	0.010(2)	0.000(2)
C(26B)	0.00(2)	0.040(2)	0.053(2)	-0.002(2)	0.003(2)	0.000(2)
C(17B)	0.00(2)	0.049(2)	0.179(2)	0.034(2)	0.017(2)	-0.018(2)
C(27B)	0.030(2)	0.050(2)	0.048(2)	-0.017(2)	-0.014(2)	-0.003(2)

Table 2.10

Fractional co-ordinates and equivalent thermal parameters for 2,3-Dicyano-5,6-dichloro-1,4-dibutoxybenzene (**5**) (e.s.d's are in parentheses).

Atom	x/a	y/b	z/c	U_{eq}
Cl(1)	0.5552(5)	0.1738(7)	0.5970(4)	0.306(2)
Cl(2)	0.7783(5)	0.2418(7)	0.5585(4)	0.337(2)
O(1)	0.3513(1)	0.3145(2)	0.4737(1)	0.262(6)
O(2)	0.7366(1)	0.4090(2)	0.3992(1)	0.277(6)
N(1)	0.2444(2)	0.4955(3)	0.2766(2)	0.460(10)
N(2)	0.5249(2)	0.5771(3)	0.2257(2)	0.429(9)
C(11)	0.5499(2)	0.2708(3)	0.5071(1)	0.237(8)
C(12)	0.4454(2)	0.3258(3)	0.4531(1)	0.227(8)
C(13)	0.4386(2)	0.4021(3)	0.3791(1)	0.247(8)
C(14)	0.3306(2)	0.4544(3)	0.3225(2)	0.313(9)
C(15)	0.2844(2)	0.1731(3)	0.4446(2)	0.350(10)
C(16)	0.1798(2)	0.1888(4)	0.4667(2)	0.350(10)
C(17)	0.2012(2)	0.1836(4)	0.5602(2)	0.350(10)
C(18)	0.0915(3)	0.1893(5)	0.5782(2)	0.540(10)
C(21)	0.6477(2)	0.2983(3)	0.4894(2)	0.253(8)
C(22)	0.6416(2)	0.3763(2)	0.4162(2)	0.234(8)
C(23)	0.5375(2)	0.4284(3)	0.3612(1)	0.237(8)
C(24)	0.5311(2)	0.5113(3)	0.2857(2)	0.300(9)
C(25)	0.7696(2)	0.2834(3)	0.3538(2)	0.340(10)
C(26)	0.8730(2)	0.3378(3)	0.3380(2)	0.350(10)
C(27)	0.8500(2)	0.4713(4)	0.2758(2)	0.360(10)
C(28)	0.9564(3)	0.5255(5)	0.2622(2)	0.530(10)

Table 2.10 (contd)

Atom	x/a	y/b	z/c	U_{eq}
H(151)	0.0269(2)	0.0164(3)	0.3841(2)	0.440(80)
H(152)	0.0333(3)	0.0083(4)	0.470(2)	0.470(80)
H(161)	0.0132(3)	0.0107(4)	0.440(2)	0.480(80)
H(162)	0.0142(2)	0.0288(3)	0.443(2)	0.320(70)
H(171)	0.0248(2)	0.0267(4)	0.590(2)	0.380(70)
H(172)	0.0240(3)	0.094(4)	0.582(2)	0.480(80)
H(181)	0.0111(3)	0.0179(4)	0.638(2)	0.600(100)
H(182)	0.0054(3)	0.0292(5)	0.554(2)	0.700(100)
H(183)	0.0040(3)	0.0117(5)	0.548(2)	0.800(100)
H(251)	0.0785(2)	0.0199(4)	0.391(2)	0.410(80)
H(252)	0.0704(3)	0.0262(3)	0.295(2)	0.410(80)
H(261)	0.0902(3)	0.0249(4)	0.320(2)	0.450(80)
H(262)	0.0928(3)	0.0371(3)	0.392(2)	0.430(80)
H(271)	0.0812(2)	0.0559(4)	0.292(2)	0.410(80)
H(272)	0.0795(2)	0.0437(3)	0.222(2)	0.390(70)
H(281)	0.0942(3)	0.0615(4)	0.227(2)	0.560(90)
H(282)	0.109(3)	0.0557(4)	0.316(2)	0.600(100)
H(283)	0.0991(3)	0.0445(5)	0.236(2)	0.700(100)

Table 2.11

Final anisotropic thermal vibrational parameters for non-H atoms for 2,3-Dicyano-5,6-dichloro-1,4-dibutoxybenzene (5) (e.s.d's are in parentheses).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl(1)	0.033(1)	0.031(1)	0.031(1)	0.006(1)	0.015(1)	0.001(1)
O(1)	0.025(1)	0.023(1)	0.036(1)	-0.006(1)	0.018(1)	-0.004(1)
N(1)	0.034(1)	0.052(1)	0.049(1)	0.010(1)	0.012(1)	0.006(1)
C(11)	0.028(1)	0.018(1)	0.027(1)	-0.003(1)	0.012(1)	-0.002(1)
C(12)	0.024(1)	0.018(1)	0.031(1)	-0.007(1)	0.015(1)	-0.003(1)
C(13)	0.027(1)	0.018(1)	0.029(1)	-0.005(1)	0.010(1)	0.000(1)
C(14)	0.030(1)	0.031(1)	0.036(1)	0.002(1)	0.015(1)	0.003(1)
C(15)	0.031(1)	0.034(1)	0.047(2)	-0.015(1)	0.022(1)	-0.012(1)
C(16)	0.026(1)	0.038(2)	0.043(2)	-0.010(1)	0.017(1)	-0.008(1)
C(17)	0.035(1)	0.029(1)	0.042(2)	-0.001(1)	0.015(1)	-0.005(1)
C(18)	0.052(2)	0.069(2)	0.052(2)	-0.017(2)	0.032(2)	-0.023(2)
Cl(2)	0.023(1)	0.038(1)	0.038(1)	0.004(1)	0.08(1)	0.001(1)
O(2)	0.029(1)	0.022(1)	0.041(1)	-0.003(1)	0.023(1)	-0.003(1)
N(2)	0.058(2)	0.038(1)	0.040(1)	0.007(1)	0.027(1)	0.009(1)
C(21)	0.025(1)	0.018(1)	0.033(1)	-0.004(1)	0.010(1)	-0.001(1)
C(22)	0.026(1)	0.016(1)	0.033(1)	-0.005(1)	0.017(1)	-0.004(1)
C(23)	0.029(1)	0.016(1)	0.028(1)	-0.003(1)	0.013(1)	0.001(1)
C(24)	0.034(1)	0.025(1)	0.035(1)	-0.000(1)	0.019(1)	0.004(1)
C(25)	0.037(1)	0.024(1)	0.051(2)	-0.002(1)	0.028(1)	0.002(1)
C(26)	0.029(1)	0.038(2)	0.044(2)	-0.002(1)	0.020(1)	0.003(1)
C(27)	0.029(1)	0.047(2)	0.033(1)	-0.002(1)	0.013(1)	-0.010(1)
C(28)	0.046(2)	0.071(2)	0.050(2)	-0.005(2)	0.028(2)	-0.021(2)

Table 2.12

Fractional co-ordinates and equivalent thermal parameters for 2,3-Dicyano-5,6-dichloro-4-octyloxyphenol (6) (e.s.d's are in parentheses).

Atom	x/a	y/b	z/c	U_{eq}
Cl(1)	0.0919(1)	0.1003(1)	0.0334(1)	0.054(1)
Cl(2)	0.0308(1)	0.1254(1)	-0.1330(1)	0.052(1)
O(1)	0.0122(1)	0.4260(2)	-0.1834(1)	0.050(1)
O(2)	0.1184(1)	0.3740(2)	0.1177(2)	0.047(1)
N(1)	0.0288(1)	0.7643(3)	-0.1413(4)	0.064(1)
N(2)	0.1032(1)	0.7466(3)	0.1330(4)	0.072(2)
C(1)	0.0770(1)	0.2640(3)	-0.0038(3)	0.039(2)
C(2)	0.0500(1)	0.2737(3)	-0.0780(3)	0.038(1)
C(3)	0.0379(1)	0.4061(3)	-0.1099(3)	0.037(1)
C(4)	0.0527(1)	0.5281(3)	-0.0615(3)	0.037(1)
C(5)	0.0795(1)	0.5176(3)	0.0184(3)	0.037(1)
C(6)	0.0920(1)	0.3859(3)	0.0430(3)	0.038(1)
C(7)	0.0400(1)	0.6619(3)	-0.1023(4)	0.044(1)
C(8)	0.0933(1)	0.6445(3)	0.0805(4)	0.047(2)
C(9)	0.1415(1)	0.3982(5)	-0.0024(5)	0.063(2)
C(10)	0.1685(1)	0.3545(4)	0.0802(5)	0.058(2)
C(11)	0.1948(1)	0.3968(4)	-0.0179(5)	0.058(2)
C(12)	0.2225(1)	0.3497(4)	0.0619(6)	0.063(3)
C(13)	0.2489(1)	0.3992(4)	-0.0276(6)	0.064(2)
C(14)	0.2768(1)	0.3530(4)	0.0510(6)	0.066(3)
C(15)	0.3029(1)	0.4058(5)	-0.0377(7)	0.081(3)
C(16)	0.3309(1)	0.3622(7)	0.039(1)	0.100(4)

Table 2.12 (contd)

Atom	x/a	y/b	z/c	U_{eq}
H(O1)	0.005(1)	0.353(3)	-0.214(6)	0.08(1)
H(91)	0.142(1)	0.496(5)	-0.024(6)	0.13(2)
H(92)	0.137(1)	0.354(5)	-0.112(6)	0.14(2)
H(101)	0.169(1)	0.254(4)	0.094(6)	0.12(1)
H(102)	0.168(1)	0.388(3)	0.200(5)	0.07(1)
H(111)	0.196(1)	0.507(4)	-0.011(5)	0.10(1)
H(112)	0.192(1)	0.369(3)	-0.145(5)	0.09(1)
H(121)	0.222(1)	0.238(5)	0.050(5)	0.13(2)
H(122)	0.223(1)	0.365(3)	0.189(5)	0.08(1)
H(131)	0.248(1)	0.514(5)	-0.012(5)	0.12(1)
H(132)	0.249(1)	0.383(3)	-0.152(6)	0.10(1)
H(141)	0.277(1)	0.239(5)	0.025(5)	0.12(1)
H(142)	0.277(1)	0.369(4)	0.175(5)	0.09(1)
H(151)	0.302(1)	0.511(6)	-0.012(6)	0.17(2)
H(152)	0.302(1)	0.385(4)	-0.163(6)	0.13(2)
H(161)	0.347(1)	0.398(4)	-0.021(5)	0.11(1)
H(162)	0.334(1)	0.373(6)	0.160(8)	0.17(3)
H(163)	0.333(1)	0.262(7)	0.032(9)	0.19(3)

Table 2.13

Final anisotropic thermal vibrational parameters for non-H atoms for 2,3-Dicyano-5,6-dichloro-4-octyloxyphenol (6) e.s.d's are in parentheses).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl(1)	0.055(1)	0.045(1)	0.062(1)	0.005(1)	0.004(1)	0.015(1)
Cl(2)	0.051(1)	0.041(1)	0.064(1)	-0.007(1)	0.002(1)	-0.009(1)
O(1)	0.035(1)	0.048(1)	0.067(1)	-0.003(1)	-0.017(1)	-0.001(1)
O(2)	0.028(1)	0.064(1)	0.048(1)	0.004(1)	-0.003(1)	0.006(1)
N(1)	0.055(1)	0.050(2)	0.087(2)	0.006(1)	-0.014(1)	0.006(1)
N(2)	0.056(1)	0.065(2)	0.094(2)	-0.012(2)	0.005(2)	-0.015(1)
C(1)	0.036(1)	0.041(1)	0.039(2)	0.002(1)	0.006(1)	0.007(1)
C(2)	0.035(1)	0.039(1)	0.041(2)	-0.002(1)	0.002(1)	-0.003(1)
C(3)	0.028(1)	0.044(1)	0.040(1)	-0.001(1)	0.001(1)	-0.000(1)
C(4)	0.031(1)	0.036(1)	0.043(2)	0.001(1)	0.000(1)	0.000(1)
C(5)	0.027(1)	0.043(1)	0.041(2)	-0.000(1)	0.001(1)	-0.002(1)
C(6)	0.028(1)	0.049(2)	0.038(1)	0.001(1)	0.001(1)	0.002(1)
C(7)	0.030(1)	0.043(2)	0.057(2)	-0.002(1)	-0.005(1)	-0.003(1)
C(8)	0.031(1)	0.050(2)	0.059(2)	-0.001(1)	-0.002(1)	-0.002(2)
C(9)	0.029(2)	0.092(3)	0.070(2)	0.012(2)	0.006(2)	0.004(2)
C(10)	0.032(2)	0.078(2)	0.064(2)	0.004(2)	-0.004(1)	0.004(1)
C(11)	0.030(2)	0.074(2)	0.069(2)	-0.002(2)	-0.001(1)	-0.000(1)
C(12)	0.030(2)	0.083(3)	0.077(3)	0.002(2)	-0.002(2)	0.004(1)
C(13)	0.031(2)	0.081(2)	0.079(3)	0.001(2)	-0.001(2)	0.001(1)
C(14)	0.032(2)	0.084(3)	0.081(3)	0.000(2)	-0.000(2)	0.005(2)
C(15)	0.032(2)	0.106(3)	0.106(4)	0.003(3)	0.002(2)	-0.000(2)
C(16)	0.035(2)	0.123(4)	0.141(5)	0.005(4)	-0.004(2)	0.007(2)

Table 2.14

Fractional co-ordinates and equivalent thermal parameters for 2,3-Dicyano-5,6-dichloro-1,4-dihydroxybenzene (8) (e.s.d's are in parentheses).

Atom	x/a	y/b	z/c	U_{eq}
C(1)	0.1702(2)	0.4054(3)	0.3663(17)	0.018(1)
C(2)	0.2222(2)	0.5349(4)	0.3625(16)	0.018(1)
C(3)	0.1921(2)	0.6890(4)	0.3700(17)	0.020(1)
C(4)	0.1076(2)	0.7082(3)	0.3634(19)	0.019(1)
C(5)	0.0553(2)	0.5784(4)	0.3667(16)	0.018(1)
C(6)	0.0851(2)	0.4264(4)	0.3727(17)	0.018(1)
C(7)	0.0751(2)	0.8649(4)	0.3668(17)	0.022(1)
C(8)	-0.0313(2)	0.6032(3)	0.3688(17)	0.018(1)
N(1)	0.0488(2)	0.9892(3)	0.3570(20)	0.032(1)
N(2)	-0.992(2)	0.6268(3)	0.3580(19)	0.026(1)
O(1)	0.2368(1)	0.8192(3)	0.3626(16)	0.025(1)
O(2)	0.0305(1)	0.3097(3)	0.3695(14)	0.024(1)
Cl(1)	0.2076(1)	0.2176(1)	0.3642(5)	0.023(1)
Cl(2)	0.3256(1)	0.5079(1)	0.3652(6)	0.024(1)
H(1)	0.2768(2)	0.8142(5)	0.3471(2)	0.054(20
H(2)	0.494(27)	0.2182(50)	0.4063(1)	0.029(17

Table 2.15

Final anisotropic thermal vibrational parameters for non-H atoms for 2,3-Dicyano-5,6-dichloro-1,4-dihydroxybenzene (**8**) (e.s.d's are in parentheses).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	0.019(2)	0.014(1)	0.020(2)	0.09(5)	0.006(5)	0.003(1)
C(2)	0.009(1)	0.024(2)	0.022(2)	-0.017(4)	-0.002(4)	0.002(1)
C(3)	0.014(2)	0.021(2)	0.025(2)	-0.013(4)	0.014(4)	-0.001(1)
C(4)	0.015(2)	0.016(2)	0.025(2)	-0.004(4)	0.011(4)	0.003(1)
C(5)	0.014(1)	0.020(2)	0.021(2)	-0.017(4)	0.010(4)	-0.001(1)
C(6)	0.017(2)	0.017(2)	0.021(2)	0.007(4)	0.00(4)	-0.001(1)
C(7)	0.014(1)	0.019(2)	0.033(2)	0.017(5)	-0.03(5)	-0.003(1)
C(8)	0.019(2)	0.013(1)	0.023(2)	0.004(4)	-0.014(4)	-0.001(1)
N(1)	0.025(2)	0.016(2)	0.053(3)	-0.008(4)	-0.006(4)	0.000(1)
N(2)	0.018(1)	0.025(2)	0.034(2)	0.010(4)	-0.011(4)	0.002(1)
O(1)	0.014(1)	0.018(1)	0.042(2)	-0.013(4)	0.000(4)	-0.002(1)
O(2)	0.017(1)	0.013(1)	0.041(2)	0.007(4)	-0.001(4)	0.001(1)
Cl(1)	0.021(1)	0.015(1)	0.033(1)	0.001(1)	-0.001(1)	0.002(1)
Cl(2)	0.012(2)	0.023(1)	0.036(1)	-0.002(2)	0.001(1)	0.003(2)

Appendix B-1

Table 3.1

Crystallographic Details for TCB and TCB-HMB complex

	TCB-HMB	TCB
Formulae	$C_9H_3N_3.C_{12}H_{18}$	$C_9H_3N_3$
Mol.Wt	315.41	153.14
Crystal sys.	monoclinic	monoclinic
Space group	C2/c	$P2_1$
a Å	15.207(3)	13.719(2)
b Å	8.839(2)	7.726(1)
c Å	14.460(2)	3.875(1)
$\alpha(^0)$	90	90
$\beta(^0)$	110.48(7)	95.5(2)
$\gamma(^0)$	90	90
Cell Volume Å	1826(1)	408.8(2)
Z	4	2
F(000)	672	156
$D_{cald.gcm^{-1}}$	1.51	1.244
λ, Å	0.7107	0.7107
Diffractometer	CAD-4	CAD-4
T,K	293	293
X-radiation	MoKα	MoKα
Total reflctn	1680	1416
Non-zero refl	1380	1128
R	0.049	0.052

Appendix B-2

Table 3.2

Fractional co-ordinates and equivalent thermal parameters for 1:1 copmlex of 1,3,5-Tricyanobenzene and hexamethylbenzene (TCB-HMB) (e.s.d's are in parentheses).

Atom	x/a	y/b	z/c	U_{eq}
C(1)	0.5000	0.2449(4)	0.7500	0.0510(2)
C(2)	0.4201(2)	0.1674(3)	0.7474(2)	0.0530(2)
C(3)	0.4207(2)	0.0120(3)	0.7463(2)	0.0480(2)
C(4)	0.5000	-0.0667(4)	0.7500	0.0500(2)
C(5)	0.5000	0.4080(5)	0.7500	0.0770(2)
C(6)	0.3370(2)	-0.0699(4)	0.7407(2)	0.0700(2)
N(1)	0.5000	0.5355(5)	0.7500	0.1240(4)
N(2)	0.2703(2)	-0.1339(4)	0.7350(2)	0.1070(2)
H(2)	0.3660(2)	0.2200(3)	0.7450(2)	0.0600(1)
H(4)	0.5000	-0.1770(5)	0.7500	0.0700(1)
C(7)	0.5369(2)	0.1443(3)	0.5006(2)	0.0460(1)
C(8)	0.4425(2)	0.1265(3)	0.4882(3)	0.0460(1)
C(9)	0.4053(2)	-0.0179(3)	0.4873(2)	0.0450(1)
C(10)	0.5753(3)	0.3026(4)	0.5014(3)	0.0790(2)
C(11)	0.3799(3)	0.2630(4)	0.4762(4)	0.0780(2)
C(12)	0.3025(2)	-0.0387(5)	0.4726(3)	0.0790(2)
H(41)	0.6390(3)	0.3161(5)	0.5500(4)	0.1600(2)
H(42)	0.5280(6)	0.3701(8)	0.4810(6)	0.2800(4)
H(43)	0.6140(3)	0.3030(5)	0.4610(4)	0.1500(2)
H(51)	0.3710(4)	0.3040(6)	0.4210(4)	0.1600(2)
H(52)	0.4100(4)	0.3350(6)	0.5270(4)	0.1700(2)
H(53)	0.3250(5)	0.2760(1)	0.4860(6)	0.2900(4)
H(61)	0.2760(4)	0.0570(7)	0.4880(4)	0.1800(2)
H(62)	0.2680(3)	-0.1090(5)	0.4170(3)	0.1300(1)
H(63)	0.2820(3)	-0.0970(5)	0.5280(4)	0.1700(2)

Table 3.3

Final anisotropic thermal vibrational parameters for non-H atoms for 1:1 copmlex of 1,3,5-Tricyanobenzene and hexamethylbenzene (TCB-HMB) (e.s.d's are in parentheses).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	0.064(2)	0.041(2)	0.047(2)	0.000	0.021(2)	0.000
C(2)	0.051(2)	0.060(2)	0.049(2)	-0.001(1)	0.021(1)	0.012(2)
C(3)	0.047(2)	0.054(2)	0.043(1)	-0.003(1)	0.019(1)	-0.006(1)
C(4)	0.063(3)	0.039(2)	0.048(2)	0.000	0.020(2)	0.000
C(5)	0.116(4)	0.052(3)	0.064(3)	0.000	0.030(3)	0.000
C(6)	0.061(2)	0.095(2)	0.055(2)	-0.003(2)	0.022(1)	-0.026(2)
N(1)	0.211(6)	0.045(3)	0.116(4)	0.000	0.055(4)	0.000
N(2)	0.083(2)	0.156(3)	0.082(2)	-0.007(2)	0.029(2)	-0.059(2)
C(7)	0.051(2)	0.039(1)	0.047(1)	0.000(1)	0.017(1)	-0.008(1)
C(8)	0.049(2)	0.046(2)	0.044(1)	-0.003(1)	0.017(1)	0.007(1)
C(9)	0.038(1)	0.051(2)	0.045(1)	-0.002(1)	0.019(1)	-0.003(1)
C(10)	0.080(2)	0.055(2)	0.101(3)	0.005(2)	0.025(2)	-0.021(2)
C(11)	0.085(2)	0.058(2)	0.091(3)	-0.006(2)	0.024(2)	0.028(2)
C(12)	0.049(2)	0.096(3)	0.091(3)	-0.003(2)	0.034(2)	-0.008(2)

Table 3.4

Fractional co-ordinates and equivalent thermal parameters for 1,3,5-Tricyanobenzene(TCB) (e.s.d's are in parentheses).

Atom	x/a	y/b	z/c	U_{eq}
C(1)	0.3209(2)	−0.1833(4)	0.0931(5)	0.0434(4)
C(2)	0.3323(3)	−0.0144(4)	0.2138(5)	0.0433(4)
C(3)	0.2470(3)	0.0826(3)	0.1607(4)	0.0406(4)
C(4)	0.1623(2)	0.0130(3)	−0.0110(4)	0.0398(4)
C(5)	0.1644(2)	−0.1561(3)	−0.1302(4)	0.0382(4)
C(6)	0.2488(4)	−0.2560(3)	−0.0801(4)	0.0418(4)
C(7)	0.4200(2)	−0.2871(5)	0.1493(7)	0.0704(8)
C(8)	0.2467(2)	0.2570(4)	0.2919(6)	0.0619(6)
C(9)	0.0773(2)	−0.2309(4)	−0.3094(5)	0.0560(6)
N(1)	0.4893(2)	−0.3663(7)	0.1975(8)	0.1145(14)
N(2)	0.2465(2)	0.3933(4)	0.4012(7)	0.0959(10)
N(3)	0.0093(2)	−0.2902(5)	−0.4519(7)	0.0875(9)
H(2)	0.3907(18)	0.0295(39)	0.3413(70)	0.0531(7)
H(4)	0.1050(20)	0.0746(49)	−0.0621(76)	0.0651(8)
H(6)	0.2448(16)	−0.3673(41)	−0.1592(65)	0.0633(7)

Table 3.5

Final anisotropic thermal vibrational parameters for non-H atoms for TCB-HMB complex(e.s.d's are in parentheses).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	0.0396(8)	0.0506(1)	0.0391(7)	0.0022(8)	-0.0003(6)	0.008(8)
C(2)	0.0407(8)	0.0504(1)	0.0377(7)	-0.0023(8)	-0.0016(6)	-0.010(8)
C(3)	0.0536(9)	0.0308(7)	0.0372(7)	-0.0010(6)	0.0038(6)	-0.005(7)
C(4)	0.0394(8)	0.0401(9)	0.0393(7)	0.0011(7)	0.0006(6)	0.004(7)
C(5)	0.0374(7)	0.0413(9)	0.0351(7)	-0.0023(7)	-0.0002(5)	-0.009(7)
C(6)	0.0537(1)	0.0325(8)	0.0387(7)	-0.0026(6)	0.0022(6)	0.000(7)
C(7)	0.0583(1)	0.092(2)	0.0592(1)	-0.0001(1)	-0.0026(1)	0.030(2)
C(8)	0.099(2)	0.0376(1)	0.0493(1)	-0.0049(8)	0.0086(1)	-0.010(2)
C(9)	0.0494(1)	0.0703(2)	0.0468(9)	-0.0048(1)	-0.0030(8)	-0.019(3)
N(1)	0.086(2)	0.161(4)	0.094(2)	-0.001(2)	-0.0054(1)	0.068(2)
N(2)	0.165(3)	0.0453(2)	0.078(2)	-0.0178(1)	0.015(2)	-0.011(2)
N(3)	0.0694(1)	0.116(3)	0.0741(2)	-0.014(2)	-0.0112(1)	-0.039(2)

Appendix C-1

Table 4.1

Crystallographic Details for crystal structures of **2-8**

	2	**3**	**4**	**5**
Formulae	$C_7H_{12}Br_4N_4$	$C_{22}H_{36}N_8Br_4$	$C_{23}H_{36}N_8Br_8$	$C_{25}H_{16}Br_4$
Mol.Wt	471.8	732.2	923.6	636.0
Crystal sys.	cubic	cubic	cubic	tetragonal
Space group	$I\bar{4}3m$	$F\bar{4}3m$	$F\bar{4}3m$	$I\bar{4}$
a Å	6.955(7)	13.801(1)	13.571(1)	12.713(2)
c Å				7.113(2)
$\alpha(^0)$	90	90	90	90
$\beta(^0)$	90	90	90	90
$\gamma(^0)$	90	90	90	90
Cell Volume Å	336.54(4)	2628.3(3)	2499.1(1)	1149.7(3)
Z	1	4	4	2
F(000)	408	1456	1640	612
$D_{cald.gcm^{-1}}$	2.33	1.85	2.45	1.837
λ, Å	0.7107	0.7107	0.7107	0.7107
Diffractometer	CAD-4	CAD-4	CAD-4	CAD-4
T,K	293	293	293	293
X-radiation	MoKα	MoKα	MoKα	MoKα
Total reflctn	72	155	146	596
Non-zero refl	63	135	135	443
R	0.034	0.032	0.028	0.59

Table 4.1 (contd)

	6	7	8
Formulae	$C_{26}H_{20}Br_4$	$C_{10}H_{12}I_4$	$C_{10}H_{16}O_4$
Mol.Wt	652.1	640.10	200.2
Crystal sys.	tetragonal	tetragonal	orthorhombic
Space group	$I\bar{4}$	$I4_1/a$	Pbcn
a Å	12.638(2)	7.1984(7)	24.481(6)
b Å			10.991(2)
c Å	7.297(1)	28.582(4)	11.242(2)
$\alpha(^0)$	90	90	90
$\beta(^0)$	90	90	90
$\gamma(^0)$	90	90	90
Cell Volume Å	1165.6(2)	1481.3(1)	3025.2(1)
Z	2	4	12
F(000)	632	1136	1296
$D_{cald.gcm}{}^{-1}$	1.858	2.869	1.32
λ, Å	0.7107	0.7107	0.7107
Diffractometer	CAD-4	CAD-4	CAD-4
T,K	293	293	293
X-radiation	MoKα	MoKα	MoKα
Total reflctn	603	655	2871
Non-zero refl	507	600	2561
R	0.027	0.035	0.036

Appendix C-2

Table 4.2

Fractional co-ordinates and equivalent thermal parameters for 1:1 complex of HMT and CBr_4, **2** (e.s.d's are in parentheses).

Atom	x/a	y/b	z/c	U_{eq}
C(1)	0.0000	0.0000	0.0000	0.0271(1)
Br(1)	0.1599(6)	0.1599	0.1599	0.0323(1)
N(1)	0.3762(46)	0.3762	0.3762	0.0283(7)
C(2)	0.5000	0.5000	0.2536(36)	0.0421(1)

Table 4.3

Final anisotropic thermal vibrational parameters for non-H atoms for 1:1 complex of HMT and CBr_4, **2** (e.s.d's are in parenthesis).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	0.027(1)	0.027	0.027	0.0000	0.0000	0.0000
Br(1)	0.0323(1)	0.0333	0.0323	-0.0051(1)	-0.0051(1)	-0.0051
N(1)	0.0283(7)	0.0283	0.0283	-0.0020(5)	-0.0020	-0.0020
C(2)	0.054(1)	0.0543	0.0192(4)	-0.0284(8)	0.0000	0.0000

Table 4.4

Fractional co-ordinates and equivalent thermal parameters for 1:2 complex for HMT and $AdBr_4$, 3 (e.s.d's are in parentheses).

Atom	x/a	y/b	z/c	U_{eq}
Br(1)	0.14514(6)	−0.14514(6)	−0.14514(6)	0.080(1)
C(1)	−0.0628(5)	−0.0628(5)	−0.0628(5)	0.041(1)
C(2)	0.0000	0.0000	−0.1301(6)	0.045(1)
N(1)	0.4376(3)	0.4376(3)	0.4376(3)	0.117(5)
C(3)	0.5000	0.5000	0.3799(7)	0.133(6)
N(2)	0.1876(3)	0.1876(3)	0.1876(3)	0.051(2)
C(4)	0.2500	0.2500	0.1299(7)	0.055(2)
N(1')	0.5624(3)	0.5624(3)	0.5624(3)	0.117(5)
H(C2)	−0.0461(19)	0.0461(19)	−0.1763(19)	0.059(1)
H(C3)	0.4539(19)	0.5461(19)	0.3338(19)	0.239(13)
H(C4)	0.2039(19)	0.2961(19)	0.0838(19)	0.079(6)
H(C3')	0.5461(19)	0.5461(19)	0.3338(19)	0.239(15)

Table 4.5

Final anisotropic thermal vibrational parameters for non-H atoms for 1:2 complex of HMT and $AdBr_4$, 3 (e.s.d's are in parentheses).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br(1)	0.080(1)	0.080(1)	0.080(1)	-0.024(1)	-0.024(1)	-0.024(1)
C(1)	0.041(1)	0.041(1)	0.041(1)	-0.004(1)	-0.004(1)	-0.004(1)
C(2)	0.052(1)	0.052(1)	0.032(1)	0.000(1)	0.000	0.000
N(1)	0.117(5)	0.117(5)	0.117(5)	-0.035(3)	-0.035(3)	-0.035(3)
C(3)	0.177(8)	0.177(8)	0.046(7)	0.000(1)	0.000	0.000
N(2)	0.051(2)	0.051(2)	0.051(2)	-0.008(2)	-0.008(2)	-0.008(2)
C(4)	0.065(3)	0.065(3)	0.035(4)	0.000(1)	0.000	0.000
N(1')	0.117(5)	0.117(5)	0.117(5)	-0.035(3)	-0.035(3)	-0.035(3)
H(C2)	0.070(1)	0.070(1)	0.037(1)	0.002(1)	-0.009(1)	0.009(1)
H(C3)	0.316(18)	0.316(18)	0.084(5)	0.019(2)	-0.070(6)	0.070(6)
H(C4)	0.096(9)	0.096(9)	0.044(2)	0.004(1)	-0.016(3)	0.016(3)
H(C3)'	0.316(18)	0.316(18)	0.084(5)	-0.019(2)	0.070(6)	0.070(6)

Table 4.6

Fractional co-ordinates and equivalent thermal parameters for 1:1:1 complex of HMT, CBr_4 and $AdBr_4$, **4** (e.s.d's are in parentheses).

Atom	x/a	y/b	z/c	U_{eq}
Br(1)	-0.1480(2)	-0.1480	-0.1480	3.42(4)
C(1)	-0.0635(16)	-0.0635	-0.0635	1.76(24)
C(2)	0.0000	0.0000	-0.1304(9)	2.62(31)
Br(2)	0.5812(3)	0.5812	0.5812	6.69(7)
C(3)	0.5000	0.5000	0.5000	3.88(81)
N(1)	0.1867(20)	0.1867	0.1867	3.84(32)
C(4)	0.2500	0.2500	0.1245(10)	3.47(32)
HC(2)	-0.0425	0.0425	-0.1722	-
HC(4)	0.2925	0.2075	0.0819	-

Table 4.7

Final anisotropic thermal vibrational parameters for non-H atoms for 1:1:1 complex of HMT, CBr_4 and $AdBr_4$, 4 (e.s.d's are in parentheses).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br(1)	0.080(1)	0.080(1)	0.080(1)	-0.024(1)	-0.024(1)	-0.024(1)
C(1)	0.041(1)	0.041(1)	0.041(1)	-0.004(1)	-0.004(1)	-0.004(1)
C(2)	0.052(1)	0.052(1)	0.032(1)	0.000(1)	0.000	0.000
N(1)	0.117(5)	0.117(5)	0.117(5)	-0.035(3)	-0.35(3)	-0.035(3)
C(3)	0.117(8)	0.117(8)	0.046(7)	0.000(1)	0.000	0.000
N(2)	0.051(2)	0.051(2)	0.051(2)	-0.008(2)	-0.008(2)	-0.008(2)
C(4)	0.065(3)	0.065(3)	0.035(4)	0.000(1)	0.000	0.000
N(1')	0.117(5)	0.117(5)	0.117(5)	-0.035(3)	0.35(3)	-0.035(3)
H(C2)	0.070(1)	0.070(1)	0.037(1)	0.002(1)	-0.009(1)	0.009(1)
H(C3)	0.316(1)	0.316(1)	0.084(5)	0.019(2)	-0.070(6)	0.070(6)
H(C4)	0.096(9)	0.096(9)	0.044(2)	0.004(1)	-0.016(3)	0.016(3)
H(C3)'	0.316(1)	0.316(1)	0.084(5)	-0.019(2)	0.070(6)	0.070(6)

Table 4.8

Fractional co-ordinates and equivalent thermal parameters for Tetrabromophenylmethane, **5** (e.s.d's are in parentheses).

Atom	x/a	y/b	z/cB_{eq}	
Br(1)	0.3692(1)	-0.0831(1)	0.5563(2)	7.12(5)
C(1)	0.0000	0.0000	0.0000	3.58(5)
C(2)	0.0952(8)	-0.0236(8)	0.1305(15)	3.12(26)
C(3)	0.1200(9)	0.0478(9)	0.2700(17)	3.89(30)
C(4)	0.2003(8)	0.0328(8)	0.3957(14)	3.36(28)
C(5)	0.2600(9)	-0.0575(9)	0.3757(17)	4.30(33)
C(6)	0.2413(6)	-0.1298(9)	0.2450(18)	4.25(33)
C(7)	0.1568(9)	-0.1125(9)	0.1166(16)	4.09(31)
HC(3)	0.0761	0.1130	0.2804	-
HC(4)	0.2151	0.0856	0.4965	-
HC(6)	0.2844	-0.1964	0.2381	-
HC(7)	0.1415	-0.1652	0.0147	-

Table 4.9

Final anisotropic thermal vibrational parameters for non-H atoms for Tetrabromophenylmethane, **5** (e.s.d's are in parentheses).

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br1	0.0092(1)	0.0102(1)	0.0436(5)	0.0004(1)	-0.0110(2)	0.0005(2)
C(1)	0.0046(2)	0.0046(1)	0.0235(6)	0.0000)	0.0000	0.0000(1)
C(2)	0.0051(7)	0.0049(7)	0.0144(2)	0.0001(6)	0.0018(2)	-0.0006(1)
C(3)	0.0064(8)	0.0054(7)	0.0197(2)	0.0003(6)	0.0005(1)	0.0000
C(4)	0.0064(8)	0.0057(8)	0.0112(2)	-0.0013(6)	-0.0009(3)	0.0009(1)
C(5)	0.0057(8)	0.0067(8)	0.0243(3)	-0.0006(7)	-0.0027(1)	0.0016(3)
C(6)	0.0066(8)	0.0068(9)	0.0201(2)	0.0014(7)	-0.0014(1)	0.0007(3)
C(7)	0.0061(8)	0.0067(8)	0.0195(2)	0.0008(7)	-0.0013(2)	-0.0009(4)

Table 4.10

Fractional co-ordinates and equivalent thermal parameters for 1:1 complex of TPM and CBr_4, 6 (e.s.d's are in parentheses).

Atom	x/a	y/b	z/c	B_{eq}
Br(1)	0.1169(1)	0.0451(1)	0.1503(1)	5.21(2)
C(1)	0.0000(1)	0.0000	0.0000	3.83(3)
C(2)	0.5000	0.0000	0.2500	1.83(21)
C(3)	0.5378(4)	0.0902(4)	0.1235(8)	2.09(12)
C(4)	0.6347(4)	0.1424(4)	0.1439(9)	2.56(12)
C(5)	0.6636(5)	0.2243(4)	0.0276(1)	3.57(16)
C(6)	0.5977(5)	0.2552(4)	-0.1130(1)	3.75(18)
C(7)	0.5016(5)	0.2033(4)	-0.1386(9)	3.32(14)
C(8)	0.4729(4)	0.1216(4)	-0.0211(8)	2.77(14)
HC(3)	0.6839	0.1202	0.2440	-
HC(4)	0.7328	0.2612	0.0459	-
HC(5)	0.6187	0.3143	-0.1960	-
HC(6)	0.4534	0.2241	-0.2408	-
HC(7)	0.4040	0.0844	-0.0409	-

Table 4.11

Final anisotropic thermal vibrational parameters for non-H atoms for 1:1 complex of TPM and CBr_4, 6 (e.s.d's are in parentheses).

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br1	0.0076(1)	0.0060(1)	0.0325(2)	0.0002(1)	-0.0057(1)	-0.0015(1)
C1	0.0047(9)	0.0047	0.0255(36)	0.0000	0.0000	0.0000
C2	0.0025(7)	0.0025	0.0108(20)	0.0000	0.0000	0.0000
C3	0.0034(3)	0.0034(3)	0.0089(10)	0.0002(2)	0.0010(5)	0.0003(5)
C4	0.0034(3)	0.0041(3)	0.0134(10)	-0.0001(3)	0.0005(6)	-0.0005(7)
C5	0.0052(4)	0.0040(4)	0.0226(17)	-0.0017(3)	0.0020(7)	0.0017(7)
C6	0.0071(4)	0.0034(4)	0.0213(19)	0.0004(3)	0.0023(8)	0.0033(7)
C7	0.0067(4)	0.0042(3)	0.0141(11)	0.0012(3)	0.0006(8)	0.0021(7)
C8	0.0044(4)	0.0046(4)	0.0118(11)	0.0001(3)	-0.0004(5)	-0.0001(6)

Table 4.12

Fractional co-ordinates and equivalent thermal parameters for 1,3,5,7-Tetraiodoadamantane, **7** (e.s.d's are in parentheses).

Atom	x/a	y/b	z/c	U_{eq}
I(1)	0.3044(1)	0.5366(1)	0.0504(0)	0.061(0)
C(1)	0.1252(8)	0.3664(8)	0.0946(2)	0.033(1)
C(2)	0.0000	0.2500	0.0631(3)	0.035(2)
C(3)	0.0079(10)	0.4976(9)	0.1248(2)	0.035(1)
H(1)	0.0779	0.1665	0.0432	0.035
H(2)	0.0907	0.5754	0.1449	0.035
H(3)	−0.0704	0.5785	0.1043	0.035

Table 4.13

Final anisotropic thermal vibrational parameters for non-H atoms for 1,3,5,7-Tetraiodoadamantane, **7** (e.s.d's are in parentheses).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I(1)	0.050(0)	0.069(0)	0.064(0)	−0.019(0)	0.012(0)	0.025(0)
C(1)	0.029(3)	0.035(4)	0.035(3)	−0.007(3)	0.001(3)	0.006(3)
C(2)	0.036(5)	0.035(5)	0.034(4)	0.002(4)	0.000(−)	0.000(−)
C(3)	0.030(3)	0.026(3)	0.048(3)	0.001(5)	−0.003(3)	0.006(4)

Table 4.14

Fractional co-ordinates and equivalent thermal parameters for 1,3,5,7-Tetrahydroxyadamantane, **8** (e.s.d's are in parentheses).

Atom	x/a	y/b	z/c	B_{eq}
O(1)	0.15259(4)	0.1779(1)	-0.0215(1)	2.47(3)
O(2)	0.2772(4)	0.2394(1)	0.3084(1)	3.04(3)
O(3)	0.16258(4)	0.5689(1)	0.1831(1)	2.88(3)
O(4)	0.08144(5)	0.2212(1)	0.3760(1)	2.79(3)
C(1)	0.1608(1)	0.2395(1)	0.0892(1)	1.73(3)
C(2)	0.2170(1)	0.2074(1)	0.1392(1)	1.99(3)
C(3)	0.2249(1)	0.2679(1)	0.2608(1)	1.99(3)
C(4)	0.2206(1)	0.4061(1)	0.2452(1)	2.25(3)
C(5)	0.1644(1)	0.4389(1)	0.1953(1)	2.02(3)
C(6)	0.1200(1)	0.3950(1)	0.2809(1)	2.24(3)
C(7)	0.1241(1)	0.2571(1)	0.2957(1)	1.93(3)
C(8)	0.1165(1)	0.1957(1)	0.1745(1)	1.97(3)
C(9)	0.1564(1)	0.3775(1)	0.0741(1)	2.10(3)
C(10)	0.1805(1)	0.2239(1)	0.3458(1)	2.28(3)
O(5)	0.57485(4)	0.4726(1)	0.1139(1)	2.36(3)
O(6)	0.56304(4)	0.1525(1)	0.4129(1)	2.47(3)
C(11)	0.5394(1)	0.3936(1)	0.1795(1)	1.79(3)
C(12)	0.5000	0.4740(2)	0.2500	1.97(4)
C(13)	0.5326(1)	0.2320(1)	0.3356(1)	1.80(3)
C(14)	0.5000	0.1515(2)	0.2500	1.98(4)
C(15)	0.5069(1)	0.3125(1)	0.0938(1)	1.92(3)
C(16)	0.5719(1)	0.3134(1)	0.2654(1)	1.98(3)

Table 4.14 (contd)

Atom	x/a	y/b	z/c
H(O1)	0.1790	0.1997	-0.0758
H(O2)	0.2946	0.1768	0.2697
H(O3)	0.1296	0.5866	0.1466
H(O4)	0.0784	0.1308	0.3821
H(1C2)	0.2458	0.2374	0.0830
H(2C2)	0.2199	0.1173	0.1473
H(1C4)	0.2494	0.4346	0.1883
H(2C4)	0.2257	0.4474	0.3235
H(1C6)	0.0833	0.4170	0.2483
H(2C6)	0.1252	0.4354	0.3598
H(1C8)	0.0797	0.2172	0.1417
H(2C8)	0.1192	0.1056	0.1845
H(1C9)	0.1197	0.3983	0.0407
H(2C9)	0.1854	0.4060	0.0172
H(1C10)	0.1860	0.2641	0.4255
H(2C10)	0.1836	0.1337	0.3562
H(O11)	0.6016	0.4216	0.0774
H(O12)	0.5701	0.1962	0.4834
H(1C13)	0.4788	0.5271	0.1938
H(1C14)	0.4743	0.0988	0.2963
H(1C15)	0.4857	0.3654	0.0376
H(2C16)	0.5327	0.2605	0.0474
H(2C17)	0.5976	0.2615	0.2194

Table 4.15

Final anisotropic thermal vibrational parameters for non-H atoms 1,3,5,7-Tetrahydroxyadamantane, **8** (e.s.d's are in parentheses).

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	0.0011(1)	0.0069(1)	0.0031(1)	-0.0008(1)	0.0000(1)	-0.0010(1)
O(2)	0.0010(1)	0.0070(1)	0.0065(1)	0.0008(1)	-0.0013(1)	-0.0019(1)
O(3)	0.0011(1)	0.0031(1)	0.0091(1)	-0.0001(1)	-0.0004(1)	0.0005(1)
O(4)	0.0014(1)	0.0054(1)	0.0047(1)	-0.0006(1)	0.0012(1)	-0.0005(1)
C(1)	0.0008(1)	0.0039(1)	0.0028(1)	-0.0003(1)	-0.0001(1)	-0.0003(1)
C(2)	0.0008(1)	0.0044(1)	0.0039(1)	0.0001(1)	-0.0001(1)	-0.0005(1)
C(3)	0.0008(1)	0.0043(1)	0.0041(1)	0.0003(1)	-0.0006(1)	-0.0005(1)
C(4)	0.0008(1)	0.0040(1)	0.0055(1)	-0.0002(1)	0.0003(1)	-0.0006(1)
C(5)	0.0008(1)	0.0027(1)	0.0054(1)	-0.0001(1)	-0.0001(1)	0.0000(1)
C(6)	0.0009(1)	0.0040(1)	0.0050(1)	0.0001(1)	0.0003(1)	-0.0006(1)
C(7)	0.0009(1)	0.0040(1)	0.0034(1)	-0.0002(1)	0.0004(1)	-0.0002(1)
C(8)	0.0009(1)	0.0043(1)	0.0035(1)	-0.0004(1)	0.0001(1)	-0.0001(1)
C(9)	0.0008(1)	0.0045(1)	0.0041(1)	-0.0001(1)	-0.0001(1)	0.0010(1)
C(10)	0.0013(1)	0.0044(1)	0.0034(1)	0.0001(1)	-0.0003(1)	0.0001(1)
O(5)	0.0009(1)	0.0040(1)	0.0061(1)	-0.0002(1)	0.0008(1)	0.0004(1)
O(6)	0.0012(1)	0.0048(1)	0.0042(1)	0.0008(1)	-0.0005(1)	0.0003(1)
C(11)	0.0007(1)	0.0036(1)	0.0040(1)	-0.0001(1)	0.0002(1)	0.0003(1)
C(12)	0.0007(1)	0.0034(2)	0.0049(1)	0.0000	0.0002(1)	0.0000(1)
C(13)	0.0008(1)	0.0037(1)	0.0034(1)	0.0003(1)	-0.0002(1)	0.0002(1)
C(14)	0.0010(1)	0.0036(2)	0.0036(1)	0.0000	-0.0000(1)	0.0000(1)
C(15)	0.0009(1)	0.0042(1)	0.0033(1)	-0.0001(1)	0.0000(1)	0.0002(1)
C(16)	0.0007(1)	0.0044(1)	0.0044(1)	0.0002(1)	0.0000(1)	-0.0001(1)

VII

List of Publications

1. Molecular Tapes based on $\mathrm{C{\equiv}N\cdots Cl}$ Interactions.
   D.Shekhar Reddy, K.Panneerselvam, T.Pilati and G.R.Desiraju,
   J.Chem.Soc., *Chem.Commun.*, 1993, 661.

2. $\mathrm{C{-}H\cdots N}$ Mediated Hexagonal Network in the Crystal Structure of the 1:1 Molecular Complex 1,3,5-Tricyanobenzene-Hexamethylbenzene.
   D.Shekhar Reddy, B.S.Goud, K.Panneerselvam and G.R.Desiraju,
   J.Chem.Soc., *Chem.Commun.*, 1993, 663.

3. $\mathrm{N\cdots Br}$ Mediated Diamondoid Network in the Crystalline Complex Carbon Tetrabromide:Hexamethylenetetramine.
   D.Shekhar Reddy, D.C.Craig, A.D.Rae and G.R.Desiraju
   J.Chem.Soc., *Chem.Commun.*, 1993, 1737.

4. Organic Alloys: Diamondoid Networks in Crystalline Complexes of 1,3,5,7-Tetrabromoadamantane, Hexamethylenetetramine and Carbon Tetrabromide.
   D.Shekhar Reddy, D.C.Craig and G.R.Desiraju
   J.Chem.Soc., *Chem.Commun.*, 1994, 1457.

5. The Nature of Halogen$\cdots$Halogen Interactions and the Crystal Structure of 1,3,5,7-Tetraiodoadamantane.
   V.R.Pedireddi, **D.Shekhar Reddy**, B.S.Goud, D.C.Craig, A.D.Rae and G.R.Desiraju
   J.Chem.Soc., *Perkin Trans. 2*, 1994, 2353-2360

6. **Molecular and Crystal Structure of 1-(8-Carboxyoctyl)-1,3,5,7- tetra- azaadamantan-1-ium bromide and 1-(6-Bromohexyl)- 1,3,5,7- tetraaza- adamantan- 1-ium bromide.**
   D.Shekhar Reddy, K.Panneerselvam, L.Shimoni, H.L.Carrell and G.R.Desiraju
   J.Mol. Str., 1994, 113-120

7. Topological Equivalences between Organic and Inorganic Crystal Structures: 1,3,5,7- Tetrahydroxyadamantane and Caesium Chloride.
   D.Shekhar Reddy, D.C.Craig and G.R.Desiraju
   J.Chem.Soc., *Chem.Commun.*, 1995, 339.

8. 1,3,5-Tricyanobenzene.
   D.Shekhar Reddy, K.Panneerselvam, C.J.Carrell, H.L.Carrell and G.R.Desiraju
   Acta.Crystallogr., 1995, in the press.