

A Rational Study of Crystal Engineering of Supramolecular Assemblies of 1,2,4,5-Benzenetetracarboxylic Acid

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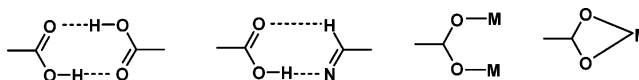
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Supramolecular assemblies of 1,2,4,5-benzenetetracarboxylic acid, **1**, with *aza* donor molecules such as 1,10-phenanthroline, **2**, 1,7-phenanthroline, **3**, phenazine, **4**, 4-(*N,N*-dimethylamino)pyridine, **5**, 1,2-bis(4-pyridyl)ethene, **6**, and 1,2-bis(4-pyridyl)ethane, **7**, have been synthesized and characterized by single-crystal X-ray diffraction methods. All the complexes crystallize in the triclinic, $P\bar{1}$ space group. In the complexes of **2** and **4**, water is also present in the resultant assembly, but the complexes of **5**, **6**, and **7** crystallize without any water molecules or solvent of crystallization. However, **3** forms two types of complexes, a hydrate and a nonhydrate complex, depending upon whether water is used as a solvent or not. These assemblies divide into two classes, host-guest systems (with *aza* molecules being in the channels created by the acid molecules) and assemblies with infinite molecular tapes. While the assemblies of the compounds **2**, **4**, and **5** belong to the former class, the assemblies of compounds **6** and **7** form molecular tapes, which are arranged in two dimensions to form sheet structures. The two structures of **3**, in fact, bridge the two classes with each one falling into different categories.

Introduction

Crystal engineering of organic supramolecular assemblies employing two or more components is a two step process, formation of a supermolecule between the constituents followed by self-assembly or packing of the supermolecules in the three-dimensional space.^{1,2} In this direction, solid-state structures with well-defined molecular networks of different types such as molecular tapes, molecular sheets, three-dimensional architectures possessing cavities and channels, and so forth have been synthesized by employing both hydrogen bonds as well as dative bonds.^{3–8} However, in all these cases, invariably, evolution of an assembly depends on the properties of the functional group under consideration. In this respect, assemblies based on the carboxylic group (–COOH) are very well-known because of its ability to form robust hydrogen bonds on its own and also with several *aza* compounds forming either O–H···N or O–H···N/C–H···O pairwise hydrogen bonds, as well as dative bonds through

SCHEME 1

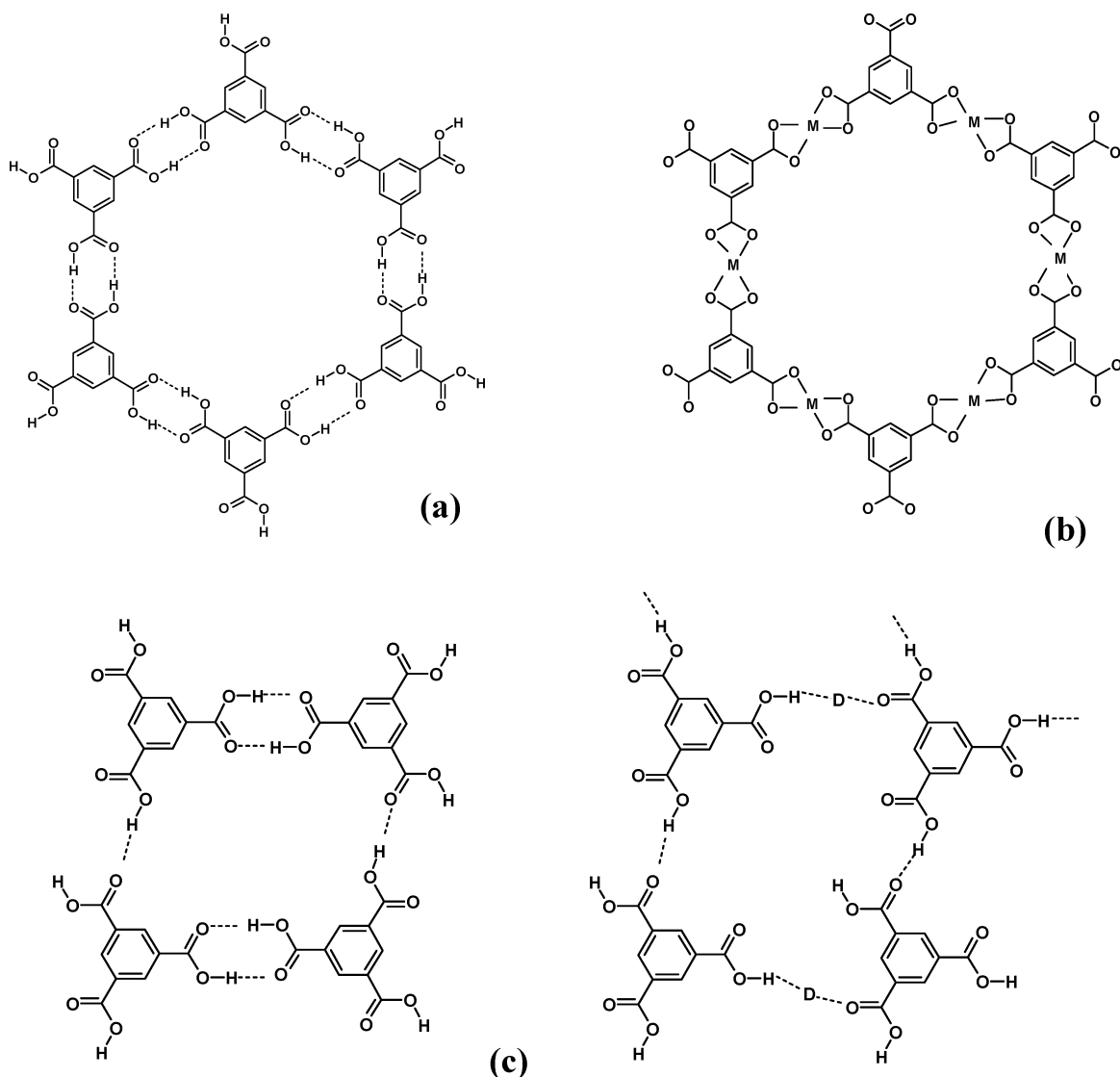


the carboxylate group.^{3c,3d,9} A schematic representation of some of these networks is shown in Scheme 1.

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SCHEME 2



For instance, trimesic acid forms a well-known chicken-wire frame network on its own (Scheme 2a)^{9a} and also forms hexagonal networks with pyrene, *N,N*-dimethylamine, and so forth.¹⁰ In addition, several researchers demonstrated the robustness of carboxylate and metal bond for the creation of a myriad of channel structures employing trimesic acid (Scheme 2b).^{9k-o} Also, we recently reported the formation of four-membered networks by trimesic acid, involving simple molecules such as

methanol to a long-chain molecule like tetramethylethylenediamine (Scheme 2c).¹¹ Similarly, terephthalic acid was employed very much in the synthesis of metal-based functional solids.¹²

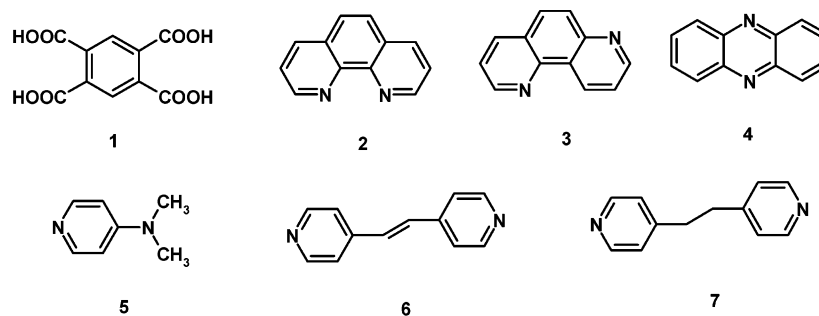
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Reactants	Solvent of crystallization	Molecular complexes	Composition (Including solvent molecules)
1 + 2	Methanol or water	2a. H ₂ O	1:1:1
1 + 3	Methanol	3a	1:2
1 + 3	Water	3b.H ₂ O	1:1:2
1 + 4	Methanol or water	4a. H ₂ O	1:2:4
1 + 5	Methanol or water	5a	2:2
1 + 6	Dimethylsulfoxide or water	6a	1:1
1 + 7	Dimethylsulfoxide or water	7a	1:1

FIGURE 1. Molecular structures and designations of compounds and complexes.

To our knowledge, however, cocrystallization studies employing tetrasubstituted acids are fewer in number. Among the known structures, cyclic network mediated supramolecular assemblies of 1,2,4,5-benzenetetracarboxylic acid, **1**, with pyridine and some of its derivatives is quite significant.¹³ Nevertheless, structures of pure organic assemblies are very much limited as compared to the structures formed by the acid **1** with metal salts.¹⁴ In this connection, looking at the geometries obtained as square networks formed by trimesic acid, we find it is evident that the -COOH groups situated at *meta* position to each other are potential precursors for the synthesis of cyclic networks. When this feature is taken into account and also the geometries noted in the supramolecular assemblies of the acid **1** (though limited in number), it is apparent that the acid **1** can form host-guest type lattices very easily. Hence, we were interested to study the synthesis of molecular complexes of 1,2,4,5-benzenetetracarboxylic acid with various aza derivatives hoping that the *tetra*-substitution would help to extend the hydrogen bonds in all three directions to yield novel supramolecular assemblies. For this purpose, we have synthesized assemblies of the acid **1** with 1,10-phenan-

throline, **2**, 1,7-phenanthroline, **3**, phenazine, **4**, 4-(*N,N*-dimethylamino)pyridine, **5**, 1,2-bis(4-pyridyl)ethene, **6**, and 1,2-bis(4-pyridyl)ethane, **7**. The resulting complexes are labeled as given in Figure 1.

Results and Discussion

Cocrystallization of 1,2,4,5-benzenetetracarboxylic acid, **1**, with aza compounds **2–7** yielded good quality single crystals of molecular complexes **2a–7a** respectively, from either methanol or dimethyl sulfoxide (DMSO) as the case may be. However, compound **3** forms one more complex **3b** upon crystallization from water. Structure determination of these complexes reveals several common features as well as distinctly unique features. Also, the complexes divide into two categories with respect to the arrangement of the molecules in three dimensions. We discuss these aspects in two steps, first by describing the structural features of the complexes **2a–7a** and **3b** independently followed by comparison of the structures.

Acid 1 and 1,10-Phenanthroline (Complex 2a). Acid **1** with 1,10-phenanthroline, **2**, forms a molecular complex, **2a**, from a CH₃OH solution. The structure determination reveals that the complex exists as a hydrate with the constituents in the asymmetric unit being in a 1:1:1 ratio. Arrangement of the molecules in the complex **2a** is shown in Figure 2. The structure analysis reveals that one of the four acid moieties is converted to a carboxylate by a deprotonation process. These molecules are then arranged in such a manner that adjacent acid molecules constitute chains through O–H···O[−] hydrogen bonds (H···O, 1.68 Å) as shown in Figure 2(i). The other characteristics of the hydrogen bonds are given in Table 1.

In the two-dimensional arrangement, water molecules hold these chains together by forming O–H···O hydrogen bonds (H···O, 1.55 and 1.87 Å; Table 1) leading to the formation of a closed network with a cavity of 9 × 12 Å²

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TABLE 1. Hydrogen Bond Distances, Donor–Acceptor Distances, and Angles of Different Types of Hydrogen Bonds Observed in the Molecular Complexes 2a–7a and 3b^a

hydrogen bonds	2a			3a			3b			4a			5a			6a			7a					
O–H···O	1.87	2.73	165.2	1.66	2.61	172.1	1.74	2.67	175.3	1.48	2.68	178.3	1.72	2.56	158.3									
	1.55	2.55	170.2				1.84	2.79	172.1	1.93	2.85	176.1												
							1.50	2.51	177.6	1.82	2.86	136.7												
										1.38	2.53	173.3												
O–H···O ⁻	1.68	2.66	164.0				2.09	2.95	172.8				1.79	2.65	170.0	1.46	2.41	161.3	1.38	2.40	170.6			
							1.59	2.61	174.5															
							1.37	2.40	170.6															
O–H···N	2.26	3.00	163.2	1.30	2.56	176.9	1.94	2.81	170.0	1.99	2.89	173.6												
										1.68	2.65	164.6												
N ⁺ –H···O	2.02	2.74	129.3				1.91	2.78	172.3							2.41	3.12	142.1						
																2.32	2.89	124.9						
N ⁺ –H···O ⁻																								
C–H···N				2.89	3.79	152.9										1.64	2.67	173.1	1.69	2.72	176.2			
				2.84	3.56	135.0																		
C–H···O	2.45	3.10	127.5	2.74	3.36	121.1	2.62	3.21	120.0	2.59	3.33	132.5	2.63	3.25	123.1	2.99	3.73	138.9	2.67	3.46	143.6			
	2.37	3.25	175.6	2.69	3.34	126.1	2.47	3.10	123.5	2.41	3.35	153.6	2.68	3.31	126.7	2.78	3.50	130.7	2.69	3.42	133.5			
	2.79	3.61	145.5	2.50	3.29	140.7	2.92	3.80	155.6	2.61	3.47	152.3	2.34	2.98	122.1	2.53	3.43	153.3	2.88	3.61	134.3			
	2.63	3.41	136.8	2.86	3.50	126.8	2.67	3.35	131.1	2.86	3.51	128.2	2.36	3.17	140.4	2.28	3.15	157.9	2.73	3.37	125.0			
	2.80	3.42	127.6	2.66	3.28	123.4	2.68	3.51	148.8	2.84	3.53	127.3	2.78	3.55	142.5				2.46	3.28	142.5			
	2.86	3.66	139.1	2.65	3.47	138.9	2.27	3.20	161.9	2.54	3.48	151.5	2.65	3.48	142.2				2.90	3.83	155.7			
	2.97	3.79	143.8	2.69	3.45	133.0	2.83	3.64	144.0				2.79	3.51	139.0				2.71	3.65	158.6			
	2.56	3.35	141.9	2.85	3.74	153.9							2.78	3.47	123.6									
	2.47	3.32	145.8																					
C–H···O ⁻	2.64	3.37	137.3				2.59	3.49	166.5				2.98	3.78	143.4	2.51	3.32	143.6	2.42	3.32	156.8			
	2.31	3.26	162.5										2.66	3.53	153.0	2.46	3.11	130.1	2.36	3.06	130.8			
	2.65	3.49	156.4										2.70	3.33	126.2									

^a In each column, the three numbers correspond to distances of H···acceptor and acceptor···donor and angles of donor–H···acceptor, respectively.

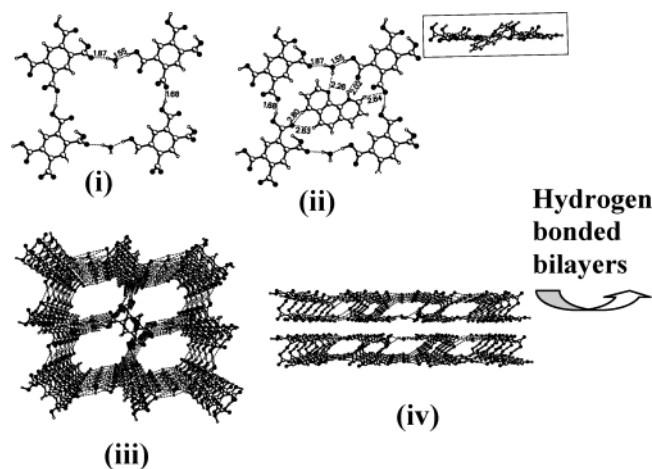


FIGURE 2. Arrangement of molecules of acid **1** and 1,10-phenanthroline, **2**, in the molecular complex **2a**. (i) Cavity ($9 \times 12 \text{ \AA}^2$) formed by the acid molecules in two-dimensional arrangement; (ii) 1,10-phenanthroline molecule in the cavity (actual orientation is shown in inset); (iii) channels in three-dimensional arrangement. (iv) Representation of bilayers and their stacking.

in dimension. The molecules of **2** are filling these cavities. In fact, the phenanthroline molecules are not in the plane of the acid layers but protrude through the cavity as shown in the inset of Figure 2(ii). In the three-dimensional arrangement, the layers are stacked such that the cavities align to yield channels as shown in Figure 2(iii). Phenanthroline molecules, which lie in the channels, are removed for the purpose of clarity. Further, the stacking of the sheets is quite interesting as each of the two adjacent layers, with an interlayer distance of 3.88 \AA , connected by catemeric O–H···O hydrogen bonds (H···O, 1.22 \AA ; Table 1), constitute bilayers. These

bilayers stack with a separation distance of 4.13 \AA as shown in Figure 2(iv).

Acid 1 and 1,7-Phenanthroline (Complexes 3a and 3b). Cocrystallization of 1,7-phenanthroline, **3**, and acid **1** from a methanol solution gave a complex, **3a**, in a 1:1 ratio. The two reactants primarily recognize each other through the formation of O–H···N and C–H···O pairwise hydrogen bonds and bifurcated C–H···O hydrogen bonds (Table 1) as shown in the inset on the left side of Figure 3a, forming a cyclic assembly. The H···O and H···N distances, respectively, in this assembly are 2.66 and 1.30 \AA in the pairwise hydrogen bond pattern and 2.69 and 2.74 \AA in the bifurcated pattern.¹⁵ This kind of assembly, indeed, is known to exist in some other complexes of carboxylic acids with 4,4'-bipyridyl.^{3e} Among them, particularly, a molecular complex of acid **1** and 4,4'-bipyridyl shows a close relation to the pattern observed in the complex **3a**.¹⁶

Complex **3a**, however, is unique in the three-dimensional arrangement, forming a novel staircase type structure as shown in Figure 3a. Within this ensemble, the acid molecules are connected with the adjacent molecules by O–H···O hydrogen bonds (H···O, 1.66 \AA ; Table 1) formed between the –COOH groups positioned *ortho* to each other as shown in the inset on the right side of Figure 3a. Such linear acid chains are further linked together by phenanthroline molecules in a step-wise manner such that adjacent molecules of **3** are separated by two types of distances 3.77 and 2.56 \AA , alternately.

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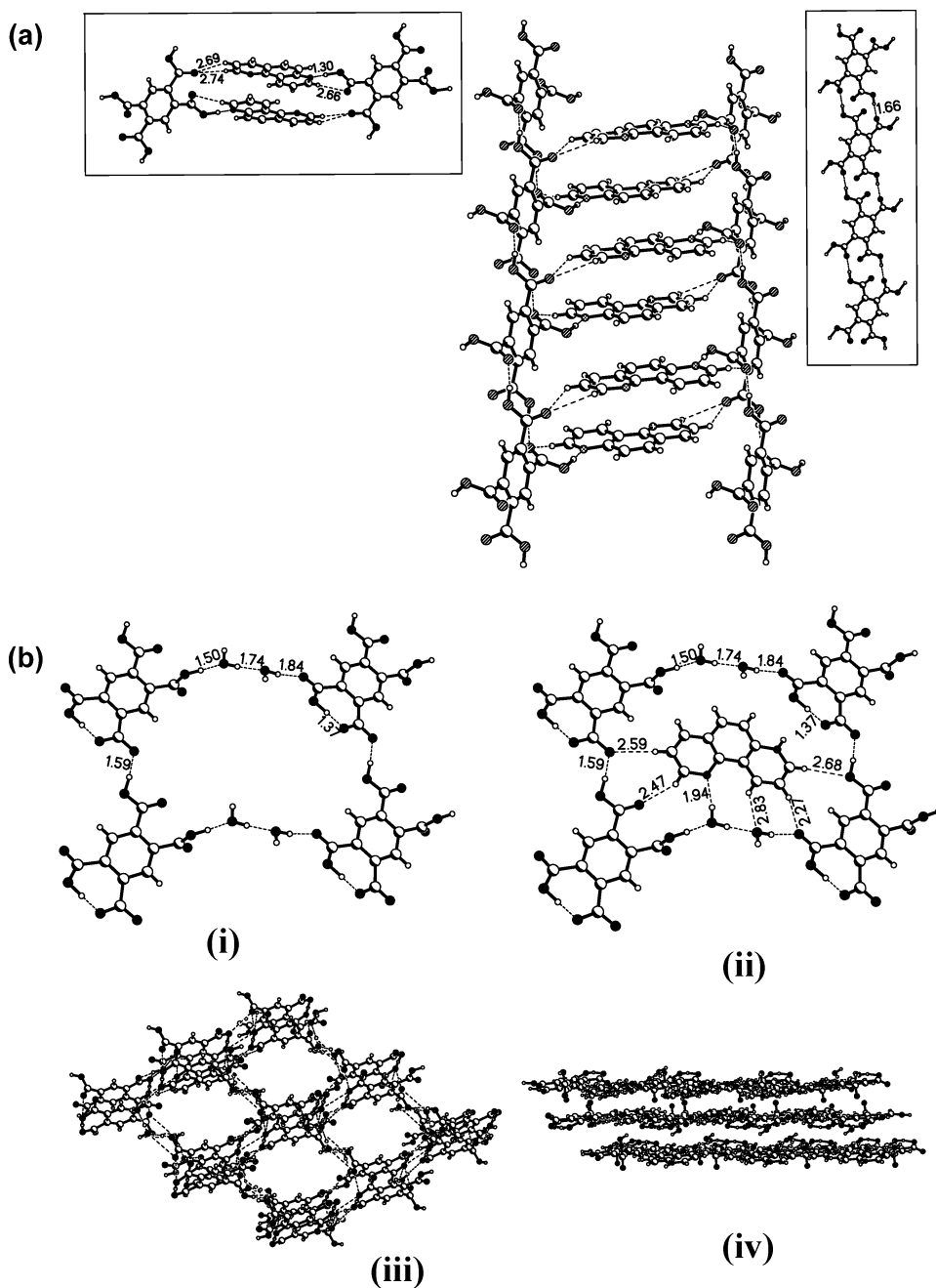


FIGURE 3. (a) Staircase structure observed in the molecular complex, **3a**. The basic recognition pattern between the acid and 1,7-phenanthroline molecules is shown in the left inset and interaction among the adjacent acid molecules is shown in the inset on the right side. (b) Recognition and packing of molecules in the crystal structure of molecular complex, **3b**. (i) Cavity ($7 \times 13 \text{ \AA}^2$) created by the acid molecules along with water molecules; (ii) occupation of the cavity by 1,7-phenanthroline molecule in the two-dimensional arrangement; (iii) channels noted in the three-dimensional arrangement; (iv) planar geometry of the sheets with both the acid and 1,7-phenanthroline molecules remain coplanar with each other.

It is interesting, however, to note that, though complexes **2a** and **3a** were crystallized from CH_3OH , the later one did not absorb water from atmosphere. Indeed, the water molecules played a crucial role in the formation of channel structure in the complex **2a**. In the case of **3a**, though a novel staircase structure was obtained, we were interested to see whether a channel structure could be synthesized between the acid **1** and phenanthroline **3**. For this purpose, we deliberately cocrystallized acid **1** and phenanthroline **3** from water to obtain a complex, **3b**.

The single crystals of **3b** obtained from water gave an entirely different unit cell, suggesting, at least, a different

packing arrangement between acid **1** and phenanthroline. However, the structure determination revealed that, in fact, two molecules of water (solvent of crystallization) are present in the asymmetric unit, with other constituents in a 1:1 ratio. Molecular arrangement in the complex **3b** is shown in Figure 3b. It is evident from Figure 3b that one of the $-\text{COOH}$ group is deprotonated unlike in the complex **3a** and akin to complex **2a**. However, complex **3b** distinctly differs from the complexes **2a** and **3a** with respect to the conformation of acid molecules. The acid molecules in **3b** form an intramolecular hydrogen bonding (Table 1) between one pair of $-\text{COOH}$

groups situated at *ortho* position to each other. The structural analysis reveals that the complex **3b** also adopts a similar arrangement that was noted in complex **2a** by forming a chain of molecules of acid **1** connected together by O–H \cdots O $^-$ hydrogen bonds with an H \cdots O distance of 1.59 Å (see Figure 3b(i)), which are further held together by water molecules, forming a network with larger cavities (7 × 13 Å²), and these cavities are occupied by phenanthroline molecules as shown in Figure 3b(ii). These two-dimensional sheets align to form channels in the three-dimensional arrangement as shown in Figure 3b(iii). Thus, it appears that water plays a crucial role in the formation of channel structures in the supramolecular assemblies of acid **1**. In the complex **2a**, while one water molecule is holding the chains, in the complex **3b**, two water molecules, which are interconnected to each other by O–H \cdots O hydrogen bonds (H \cdots O, 1.74 Å; Table 1), join the adjacent chains of acid **1**. It is also interesting to note that phenanthroline molecules interact with the host lattice through O–H \cdots N hydrogen bonds formed by water molecules rather than by –COOH groups, being another distinct difference between the complexes **2a** and **3b**. Also, in contrast to **2a**, the phenanthroline molecules were found to be coplanar with the layers of acid molecules as shown in Figure 3b(iv).

Acid 1 and Phenazine (Complex 4a). Phenazine, **4**, and acid **1** form a 1:2 complex, **4a**, along with four molecules of water in the asymmetric unit irrespective of solvent employed for crystallization. In this complex, in contrast to the molecular complexes **2a** and **3b**, none of the carboxylic acid moieties of **1** are deprotonated and it is somewhat similar to the complex **3a**. The molecular interactions and their characteristics among the constituents are shown in Figure 4(i) and Table 1, respectively. It is interesting to note that each acid molecule interacts with two phenazine molecules through the formation of O–H \cdots N and C–H \cdots O pairwise hydrogen bonds (H \cdots N, 1.68 Å and H \cdots O, 2.54 Å, respectively). Such adjacent supermolecules further join together through two water molecules forming O–H \cdots N and C–H \cdots O hydrogen bonds (H \cdots N, 1.99 and H \cdots O, 2.61 Å, respectively) leading to the formation of infinite tapes. The two water molecules in the assembly are in turn coupled through O–H \cdots O hydrogen bond with an H \cdots O distance of 1.48 Å. And ultimately, these infinite tapes are arranged in two dimensions in such a manner that two types of void space are generated. One of these voids is occupied by two symmetry related water molecules, forming O–H \cdots O hydrogen bonds (H \cdots O, 1.82 and 1.93 Å; Table 1) with the free acid groups that are not participated in the interaction with phenazine molecules. However, the second cavity remains unoccupied in a two-dimensional arrangement, but it is being masked by the molecules from the adjacent layers in a three-dimensional packing as shown in Figure 4(ii). As a result, complex **4a** could not yield a channel structure like **2a** and **3b**.

Acid 1 and 4-(*N,N*-Dimethylamino)pyridine (Complex 5a). Crystal structure determination of complex **5a**, obtained between acid **1** and 4-(*N,N*-dimethylamino)pyridine, **5**, reveals that it forms a 2:2 complex upon cocrystallization from a CH₃OH solution. Structural analysis reveals that the symmetry independent acid molecules adopt different conformations. In one of the acids (B), all the four carboxylic acids are intact without

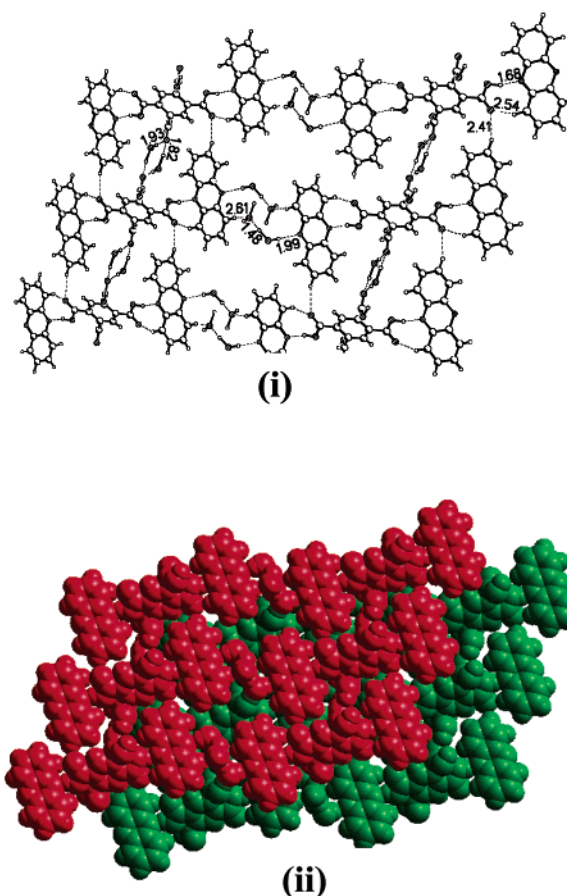


FIGURE 4. (i) Two-dimensional arrangement of molecules of acid **1** and phenazine, **4**, with two types of cavities, of which one is being filled by water molecules; (ii) stacking of two-dimensional sheets with the masking of vacant cavities by the molecules from the adjacent sheets.

deprotonation, but in the second acid molecule (A), two of the –COOH moieties were deprotonated and also form intramolecular hydrogen bonding (Table 1) between the *ortho* substituents. Such different conformations of acid **1** are indeed known in the crystal structure of molecular complexes of **1** with 2,2'-bipyridyl.¹⁷ It is noteworthy to mention that in the complexes **2a–4a** and **3b** the conformation of the acid molecules is unique by forming either intramolecular hydrogen bonding or intermolecular hydrogen bonding. Hence, complex **5a** with dual patterns could be considered as a bridge between the complexes possessing either of the types of hydrogen bonds. The recognition pattern between the acid **1** and pyridine **5** is established through C–H \cdots O hydrogen bonds (H \cdots O, 2.70 and 2.79 Å; Table 1) formed between –N(CH₃)₂ and a keto group of acid moieties as shown in Chart 1b. Such a molecular recognition phenomenon is known from the literature in the molecular complex of 3,5-dinitrobenzoic acid and 4-(*N,N*-dimethylamino)benzoic acid.^{3h} Further arrangement of the molecules in the crystal is shown in Figure 5. It is evident from Figure 5(i) that the two symmetry independent acid molecules do form a cyclic network with the aid of O–H \cdots O and O–H \cdots O $^-$ hydrogen bonds (1.72 and 1.79 Å, respectively)

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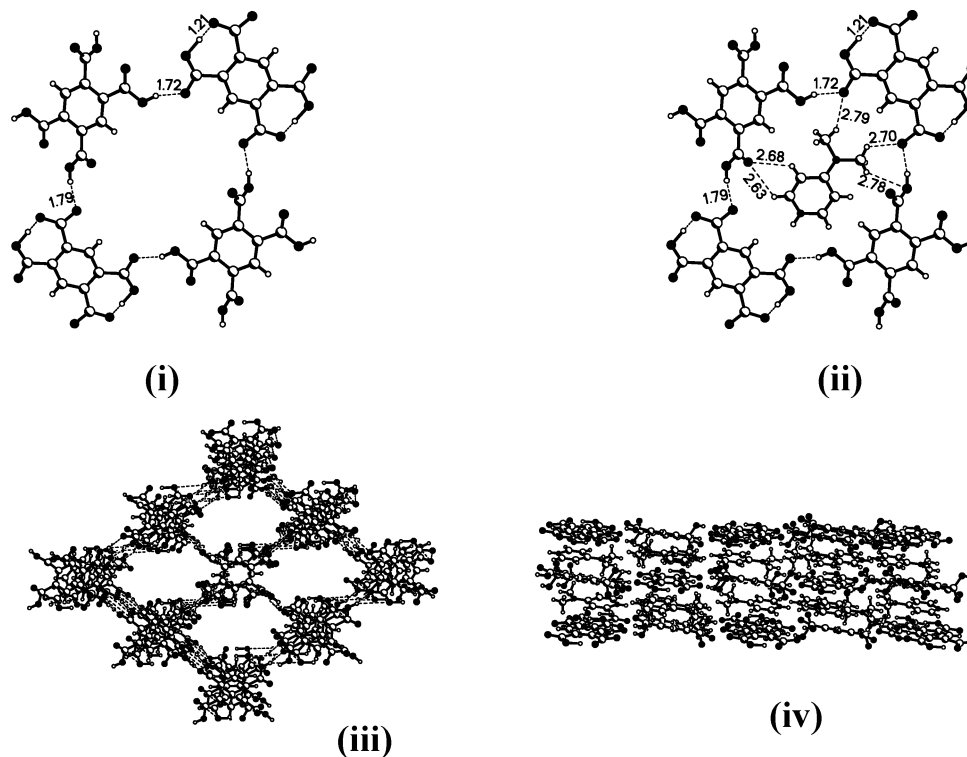
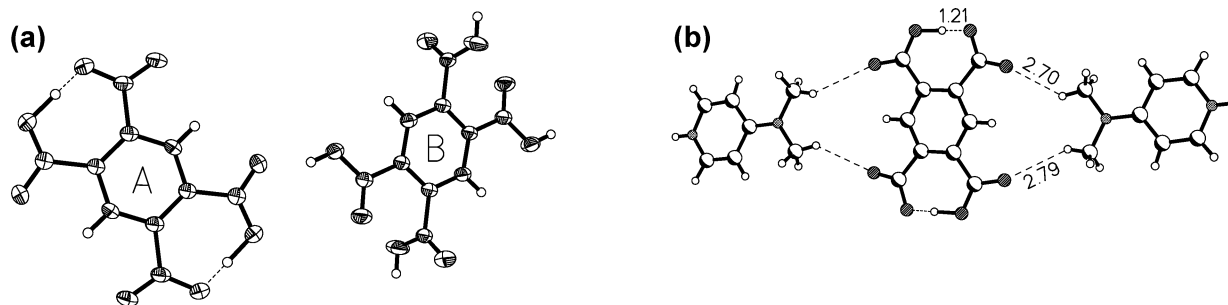


FIGURE 5. Assembly of molecules in the molecular complex **5a**. (i) Formation of cavities ($7 \times 11 \text{ \AA}^2$) by each of the four acid molecules connected together by $\text{O-H}\cdots\text{O}$ and $\text{O-H}\cdots\text{O}^-$ hydrogen bonds; (ii) arrangement of guest molecules, pyridine **5** in the voids (please note that the pyridine molecules are not in the same plane of ensemble of acid molecules); (iii) channels created in the three-dimensional arrangement by the stacking of layers of acid molecules (pyridine molecules in the channels are not shown); (iv) arrangement of sheets of acids separated by the molecules of pyridine **5**.

CHART 1. Acid 1 and 4-(*N,N*-dimethylamino)pyridine (Complex **5a): (a) Different Conformations of Two Acid Molecules in the Crystal Structure of Complex **5a** (Molecules Labeled **A** exhibit Intramolecular Hydrogen Bonding); (b) Recognition Pattern between the Acid Molecules and Pyridine **5** in Complex **5a**.**



forming cavities of a $7 \times 11 \text{ \AA}^2$ dimension which are being filled by the molecules of pyridine, **5** as shown in Figure 5(ii). The pyridine molecules interact with the host through a series of $\text{C-H}\cdots\text{O}$ hydrogen bonds (Table 1), and the $\text{H}\cdots\text{O}$ distances are in the range 2.61–2.78 Å. In the three-dimensional arrangement, the sheets are aligned to form channels as shown in Figure 5(iii).

When all the channel structures **2a**, **3b**, and **5a** are compared, it is apparent that the positions of the guest molecules within the channels vary in a systematic manner, in the three structures, with respect to the plane of the acid sheets. While in the complex **3b**, the guest molecules and acid sheets are coplanar (Figure 3a(iv)); in the complexes **2a** and **5a**, they are non-coplanar. An interesting aspect about **2a** and **5a** is that, in **2a**, the guest molecules protrude through the cavities (inset in

Figure 2a(ii)) but, in **5a**, the guest molecules lie between the sheets (Figure 5a(iv)).

Complex 6a and 7a (Acid 1 with 1,2-Bis(4-pyridyl)ethene and 1,2-Bis(4-pyridyl)ethane, Respectively). Complexes **6a** and **7a** were prepared by cocrystallization of acid **1** with 1,2-bis(4-pyridyl)ethene, **6**, and 1,2-bis(4-pyridyl)ethane, **7**, respectively, from dimethyl sulfoxide (DMSO) solution. Both the complexes **6a** and **7a** are isomorphous, crystallizing in a 1:1 ratio, and are also in the same space group, *P1*, with similar unit cell dimensions. Further, structural analysis reveals that complexes **6a** and **7a** are also *iso*-structural adopting identical packing arrangement both in two dimensions as well as in three dimensions. The arrangement of molecules is shown in Figures 6 and 7 for the complexes **6a** and **7a**, respectively.

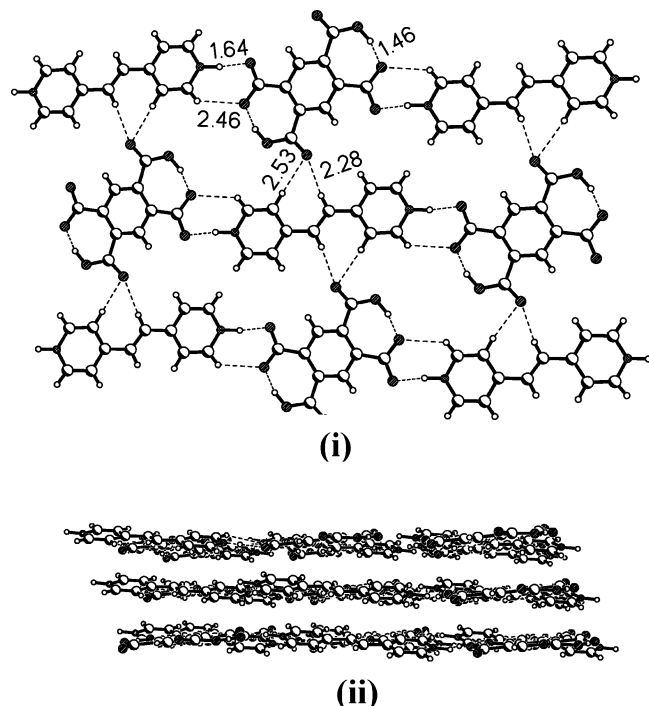


FIGURE 6. (i) Interaction between the molecules of acid **1** and pyridine **6** in the molecular complex **6a**. Notice the formation of molecular tapes through pairwise hydrogen bonds; (ii) stacking of the planar sheets in three-dimensional arrangement.

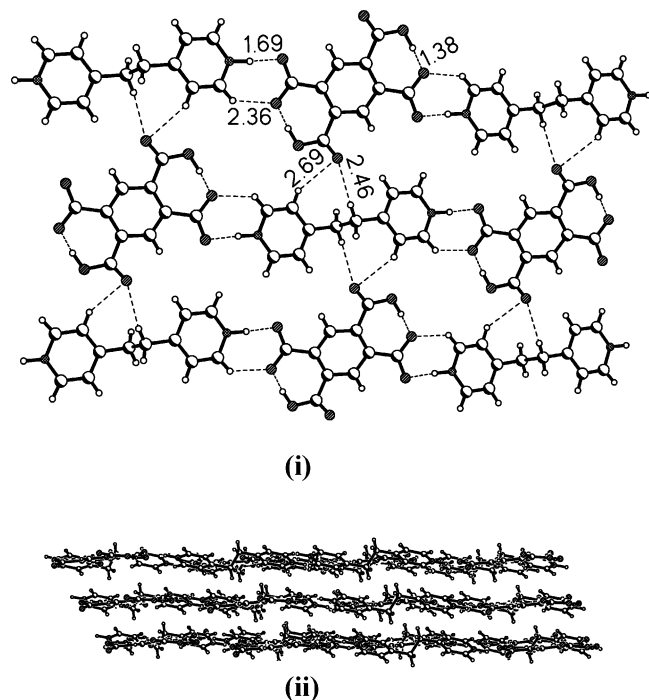


FIGURE 7. (i) Arrangement of acid **1** and pyridine **7** in the molecular complex **7a** in two dimensions. Notice the formation of molecular tapes through pairwise hydrogen bonds as in **6a**; (ii) stacking of the planar sheets in three-dimensional arrangement.

Further, this arrangement is distinctly different from the molecular complex formed by acid **1** with 4,4'-bipyridyl, an analogue of **6** and **7**.¹⁶ Acid molecules in both the

SCHEME 3



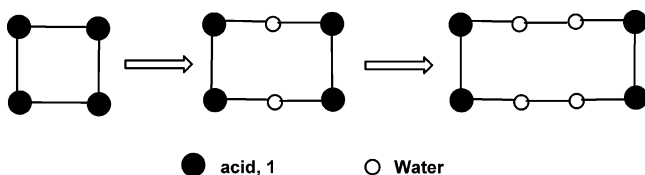
complexes exist in a deprotonated form with intramolecular hydrogen bonding (Table 1) between the adjacent ortho substituents. Further, the constituent reactants interact with each other forming $N^+-H\cdots O^-$ and $C-H\cdots O^-$ pairwise hydrogen bonds and constitute infinite tapes. These tapes are held together by $C-H\cdots O$ hydrogen bonds with $H\cdots O$ distances of 2.28 and 2.53 Å in the complex **6a** (Figure 6(i)) and by 2.46 and 2.69 Å in the complex **7a** (Figure 7(i)), in the two-dimensional arrangement. The planar sheets are stacked to yield a three-dimensional structure with $C-H\cdots O$ hydrogen bonds between the sheets as shown in Figures 6(ii) and 7(ii). The corresponding $H\cdots O$ distances are 2.51 Å (complex **6a**) and 2.42 and 2.71 Å (complex **7a**). Other characteristics of these hydrogen bonds are given in Table 1.

Cavities and Channels versus Plain Sheets: Intra- and Intermolecular Hydrogen Bonding in Acid 1. The supramolecular assemblies of the molecular complexes **2a–7a** and **3b** that have been described in the earlier sections reveal that, in none of the structures, the acid molecules form centrosymmetric cyclic hydrogen bonding patterns that are well-known for $-COOH$ groups.^{2b,18} In all the structures, the acid molecules do interact with the adjacent molecules by single $O-H\cdots O$ or $O-H\cdots O^-$ hydrogen bonds. Further, all the structures **2a–7a** and **3b** basically form sheet structures in a two-dimensional arrangement as shown in Scheme 3. Within these sheets, in the complexes **2a**, **3b**, and **5a**, void space exists, which is translated into channels in a three-dimensional arrangement: the void space observed in the complex **4a** is stabilized by the electron density from the adjacent layers, and hence, no channels are observed in this structure. In the remaining complexes, while **6a** and **7a** form perfect planar sheet structures, complex **3a** adopts a staircase structure. Other noteworthy features of these structures are intra- and intermolecular hydrogen bonding patterns shown by acid **1** molecules and the presence of water in the complexes **2a**, **3b**, and **4a**.

We were interested to deduce a correlation between the observed supramolecular assembly and the nature of the intermolecular interactions and the constituents. In this direction, we focused our attention mainly toward the role of water, which is embedded into some of the crystal lattices, irrespective of whether it is used for crystallization or not. All the hydrated structures invariably possessed cavities in the two-dimensional sheets (complexes **2a**, **3b**, and **4a**) with complex **5a** as an exception, wherein the structure possesses cavities with-

(18) Deviation from the regular dimeric pattern of $-COOH$ in these complexes could be attributed to the preference of intramolecular hydrogen bonding (Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120) and also for the formation of acid–base aggregation through $O-H\cdots N$ hydrogen bonds.

SCHEME 4



out the aid of water. If the constituents in the complexes are taken into consideration, in the complexes **2a**, **3b**, and **4a**, apart from acid **1**, the other reactant is a bulky molecule like phenanthroline **2** or **3** and phenazine, **4**, but in the complex **5a**, the reactant is quite simple, being pyridine **5**. It suggests that water plays a definite role for the creation of cavities and channels of the required dimensions in the supramolecular assemblies of acid **1**. For this purpose, dependent upon the dimension of the guest molecules, different amounts of water would be incorporated into the crystal lattices of the assemblies. In this study, the number of water molecules entered into the crystal lattices are 0 → 4 for the complexes **2a**, **3b**, **4a**, and **5a**. This is clearly evident from Scheme 4 in which the increase in the cavity dimension could be noticed easily.

However, if the molecular dimension is beyond a threshold limit, naturally a large number of water molecules may be required to create the required cavity to insert the guest molecule. Hence, such components may adopt other structural patterns, for instance, simple sheet structures as observed in the molecular complexes of **6a** and **7a**, as the reactants pyridine **6** and **7** are certainly quite large in dimension compared to **2**, **3**, and **4**.

Conclusions

We have reported synthesis and rational analysis of supramolecular assemblies **2a–7a** and **3b** formed by 1,2,4,5-benzenetetracarboxylic acid with aromatic aza compounds 1,10-phenanthroline, 1,7-phenanthroline, phenazine, 4-(*N,N*-dimethylamino)pyridine, 1,2-bis(4-pyridyl)ethene, and 1,2-bis(4-pyridyl)ethane. All these assemblies form invariably two-dimensional sheet structures but differ in the mode of stacking. While the complexes **2a**, **3b**, and **5a** form channel structures in three-dimensional lattices, complexes **4a**, **6a**, and **7a** yielded simple planar sheet structures. However, complex **3a** gave a unique staircase structure. These differences in the three-dimensional lattice arrangement are accounted for the ability of the water molecules to be part of the lattices of the assemblies.

Experimental Section

Cocrystallization. All the chemicals were obtained commercially, and the crystallization experiments were carried out

at room temperature by dissolving the constituent reactants in the spectroscopic grade solvents as the case may be. For a typical crystallization, in a 25 mL conical flask, 127 mg (0.5 mmol) of acid **1** and 90 mg (0.5 mmol) of **2** were dissolved in methanol by heating CH₃OH to the boiling temperature and then subsequently cooling to room temperature at ambient conditions. Colorless rectangular block type single crystals of good quality were obtained within 2 days, which were used for single-crystal structure determination studies by X-ray diffraction methods. However, in the case of **6a** and **7a**, reactants **6** and **7** formed an insoluble precipitate from CH₃OH upon mixing with **1**. The resultant precipitate was dissolved in dimethyl sulfoxide (DMSO) to obtain single crystals over a period of 7 days.

X-ray Crystallography. Good quality single crystals of **2a**, **3a**, **3b**, and **4a–7a** were carefully chosen after viewing through a Leica microscope supported by a rotatable polarizing stage and a CCD camera. The crystals were glued to a thin glass fiber using an adhesive (cyano acrylate) and mounted on a diffractometer equipped with an APEX CCD area detector. The X-ray intensity data were collected into 2424 frames with varying exposure time (5 s – **3b**, **5a**; 15 s – **2a**, 20 s – **3a**; 25 s – **7a**; 30 s – **4a**, **6a**) depending upon the quality of the crystal(s). The data collection was smooth in all the cases, and no extraordinary methods have been employed, as the crystals were quite stable. The intensity data were processed using Bruker's suite of data processing programs (SAINT),¹⁹ and absorption corrections were applied using SADABS.²⁰ The structure solution of all the complexes have been carried out by direct methods, and refinements were performed by full-matrix least squares on F^2 using the SHELXTL-PLUS²¹ suite of programs. All the structures converged to good R factors. All the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms obtained from Fourier maps were refined isotropically. All the refinements were smooth in all the structures.

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Supporting Information Available: X-ray data with details of refinement procedures (cif files), ORTEP drawings, lists of bond parameters (bond lengths and angles), and structure factors of molecular complexes **2a**, **3a**, **3b**, and **4a–7a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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