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A Study of Supramolecular Hydrogen Bonded Complexes formed by Aliphatic Dicarboxylic Acids with Azaaromatic Donors

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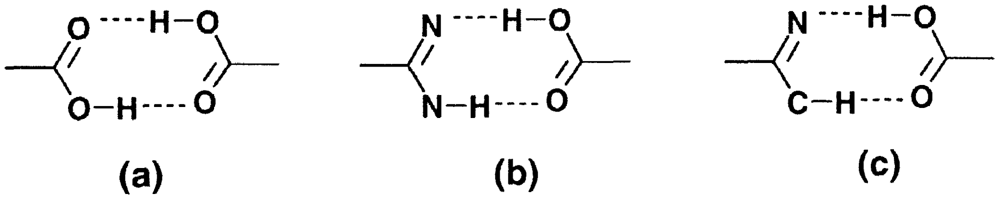
Abstract: Crystal structures of the hydrogen bonded, 1:1 molecular complexes of malonic, glutaric, adipic, thiodiglycolic and thiodipropionic acids with 4,4'-bipyridyl have been investigated in detail. All the dicarboxylic acids form molecular tape-like structures, but thiodiglycolic acid gives a cyclic structure, favoured by intermolecular π - π interaction between the heteroatom-rings. The cyclic structure is indeed unique, in the sense that it represents a noncovalent synthesis of a rectangle. Crystal structures of hydrogen bonded molecular complexes of malonic, succinic, glutaric, adipic and thiodipropionic acids with 2,4,6-triaminopyrimidine have been studied. By and large, only tape-like structures are formed, the crossed ribbon network being favoured in the complexes of malonic and glutaric acids with an odd number carbon atoms. In all the complexes of 2,4,6-triaminopyrimidine, proton transfer occurs from the carboxyl group to the heteroatom nitrogen, giving rise to a strong hydrogen bonded cyclic system.

Introduction

Noncovalent synthesis of supramolecular structures mediated by hydrogen bonds has gained considerable importance in the last few years.[1-6] A variety of hydrogen bonds such as O-H...O, N-H...O, O-H...N, N-H...N, N-H...S and C-H...O have been employed in the synthesis of such assemblies.[7-15] We wanted to explore supramolecular hydrogen bonded assemblies formed by aliphatic dicarboxylic acids, with donor molecules providing more than one bonding site, such as 4,4'-bipyridyl. The motivation for the study was that the carboxylic group can form stable cyclic hydrogen bonded systems with different donor molecules as shown below in Scheme 1, wherein couplings such as 1b and c are indeed very robust.[8-10] A recent study of the assemblage of acylaminopyrimidine and aliphatic carboxylic acids has shown the influence of the spacer present between recognisable moieties.[8]



Scheme 1

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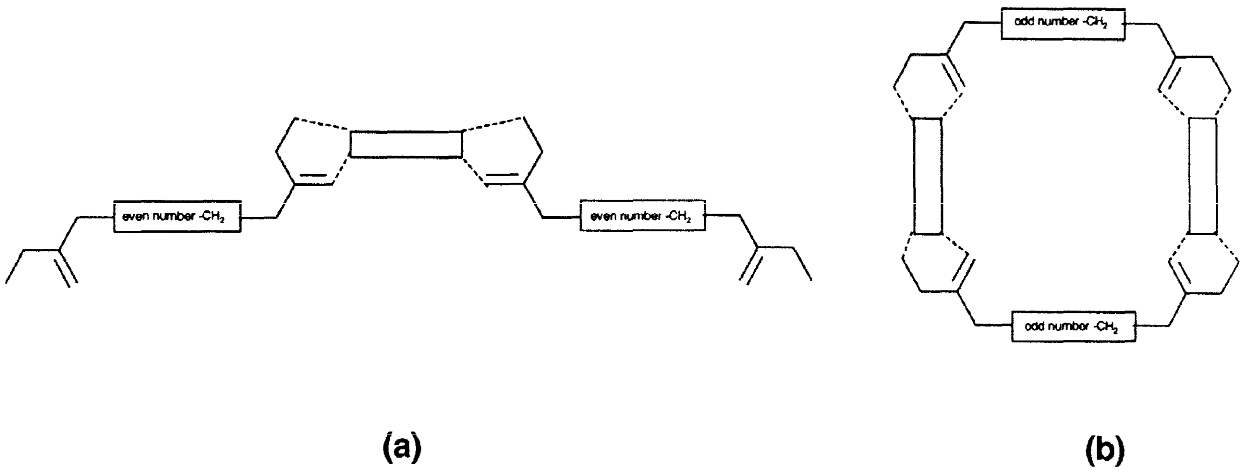
In the present study, we have investigated the hydrogen bonded complexes formed by 4,4'-bipyridyl with several aliphatic dicarboxylic acids, which include malonic acid, **1**, glutaric acid, **2**, adipic acid, **3**, thiodiglycolic acid, **4** and thiodipropionic acid, **5**. One of the features that we expected in these hydrogen bonded complexes was the possible dependence of the structure on the number of carbon atoms in the acid. That is even and odd number dicarboxylic acids could show differences with respect to the hydrogen bonded structure in the complex. We show two possible structures of the complexes in Scheme 2, one involving the formation of tape-like structures (a) and the other of cyclic structures (b).

We have investigated the supramolecular hydrogen bonded structures of complexes formed by the dicarboxylic acids, with a more complex donor molecule, 2,4,6-triaminopyrimidine which can form the type (b) coupling in Scheme 1 and other possible structures. The dicarboxylic acids examined with the pyrimidine are acids, **1**, **2**, **3**, **5** and succinic acid.



Scheme 2

Experimental

Hydrogen bonded molecular complexes were prepared by the co-crystallization of the two components, a dicarboxylic acid along with the donor (4,4'-bipyridyl or 2,4,6-triaminopyrimidine) in a methanol solution. The two components were taken in a 1:1 molar ratio. The dicarboxylic acids (Figure 1) and their complexes examined in the present study are listed below along with the stoichiometry and symbols used to represent them.

Acid (Figure 1)	**4,4'-bipyridyl**		**2,4,6-triaminopyrimidine**	
	symbol	**stoichiometry**	**symbol**	**stoichiometry**
Malonic, **1**	**1a**	1:1	**6a**	1:1
Glutaric, **2**	**2a**	1:1	**7a**	1:1
Adipic, **3**	**3a**	1:1	**8a**	3:2
Thiodiglycolic, **4**	**4a**	1:1	-	-
Thiodipropionic, **5**	**5a**	1:1	**10a**	1:1
Succinic	-	-	**9a**	1:1

The crystal structures were determined and refined using the Siemens SHELXTL-PLUS package.[16] The analyses were uncomplicated and all the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically except in the structures **7a** and **8a** wherein the atoms are being placed in calculated positions. We have listed all the crystal structure data of all the hydrogen bonded complexes studied by us in Tables 1 and 3. All the noncovalent bonds were calculated using the program PLATON.[17] The unique and representative bonds are given in Table 2 and 4.

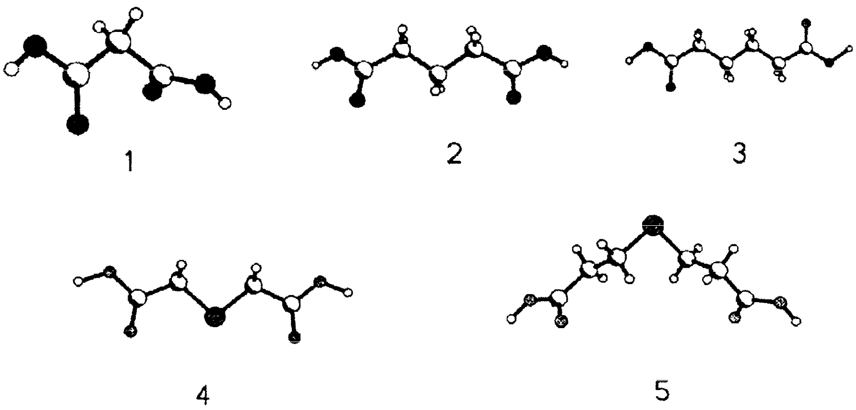


Figure 1: Molecular structures of malonic acid, **1**, glutaric acid, **2**, adipic acid, **3**, thiodiglycolic acid, **4** and thiodipropionic acid, **5**. Notice the difference in the orientation of -COOH with respect to the number of $-CH_2$ groups.

Results and Discussion

4,4'-bipyridyl forms good crystalline 1:1 molecular complexes with malonic acid, **1**, glutaric acid, **2** and adipic acid, **3**. We were not able to get good crystals of 4,4'-bipyridyl with succinic acid.

We have examined the crystal structures of 1:1 complexes **1a**, **2a** and **3a**, formed by 4,4'-bipyridyl with **1**, **2** and **3** respectively in detail.

Molecular complexes of 4,4'-bipyridyl with aliphatic dicarboxylic acids, 1, 2 and 3: The crystal structures of the complexes **1a**, **2a** and **3a** (see Table 1) reveal that the recognition between acid and pyridyl moiety occurs primarily through the formation of O-H...N / C-H...O couplings as shown in scheme (1c). The hydrogen bond distances and angles in these complexes are listed in Table 2. Contrary to our expectations (scheme 2) all the three complexes **1a** - **3a** form molecular tapes independent of whether the acid has an even or an odd number of carbon atoms. The molecular tapes in the structures of **1a** and **2a** differ distinctly from the tapes in **3a** in the three-dimensional arrangement as can be seen from Figure 2. The linear tapes in **3a** are arranged in two-dimensions to form planar sheets, stacked in a three-dimensional arrangement. The tapes **1a** and **2a** are arranged in a crossed fashion, as commonly found crinkled tapes as shown in Figure 3 in the case of **1a**. This difference in the three-dimensional packing between the complexes of aliphatic dicarboxylic acids with even or odd -CH_2 groups is noteworthy.

The features of hydrogen bonds listed in Table 2 suggest that the affinity of interaction between the acids and the bipyridyl in the complexes, **1a** – **3a**, is nearly the same with similar H...N distances. The H...N distances in the O-H...N bonds are in the range of 1.59 – 1.80Å while the H...O distances in the C-H...O bonds fall in the range of 2.62 – 2.77Å.[18]

Molecular complexes of 4,4'-bipyridyl with thiodicarboxylic acids, 4 and 5: We have investigated the hydrogen bonded complexes of thiodiglycolic acid, 4 and thiodipropionic acid, 5, with 4,4;-bipyridyl to see in what way the presence of a heteroatom instead of a –CH_2 group affects the structure. These two thioacids are analogous to glutaric and pimelic acids respectively. 4,4'-bipyridyl forms good crystalline 1:1 complexes, **4a** and **5a**, with the acids **4** and **5** respectively. The complexes **4a** and **5a** show unique structural features (Table 1). In the complex, **4a**, the molecules of bipyridyl and thiodiglycolic acid molecules interact in a manner that a cyclic supermolecule is formed as shown in Figure 4. Each supermolecule consists of two molecules of each of bipyridyl and the acid, **4** (four molecules in total) connected through four O-H...N / C-H...O couplings. Each coupling is formed between the nitrogen atoms of bipyridyl and the carboxyl group of the acid. The couplings formed by acid molecules are all similar and the hydrogen bond distances are also approximately the same, with H...N distances of ~1.57Å and H...O distances in the C-H...O bonds

Table 1: Crystal structures of 1:1 molecular complexes, **1a** – **5a**, formed between dicarboxylic acids **1** – **5** and 4,4'-bipyridyl.

	1a	**2a**	**3a**	**4a**	**5a**
Formulae	$C_{10}H_8N_2:C_3H_4O_4$	$C_{10}H_8N_2:C_5H_8O_4$	$C_{10}H_8N_2:C_6H_{10}O_4$	$C_{10}H_8N_2: C_4H_6O_4S_1$	$C_{10}H_8N_2: C_6H_{10}O_4S_1$
Mol. wt.	260.25	288.30	302.32	306.33	367.43
Crystal system	Monoclinic	monoclinic	triclinic	triclinic	Monoclinic
Space group	C2/c	$P2_1/c$	P-1	P-1	$P2_1/n$
a	19.579(8)	5.572(1)	5.481(1)	7.991(1)	11.444(6)
b	4.085(2)	9.966(1)	10.442(1)	8.140(1)	4.925(3)
c	15.967(6)	50.685(1)	13.863(1)	12.205(2)	15.793(7)
α	90	90	106.44(1)	70.03(1)	90
β	104.83(2)	91.48(1)	94.72(1)	81.50(1)	109.55(4)
γ	90	90	96.98(1)	68.73(1)	90
Cell vol. $Å^3$	1234.5(9)	2813.6(6)	749.6(2)	723.6(2)	838.8(8)
Z	4	8	2	2	2
F(000)	544	1216	320	320	352
D_{calcd}, g. cm^{-3}	1.400	1.361	1.339	1.406	1.495
λ, Å	0.7107	0.7107	0.7107	0.7107	0.7107
μ, mm^{-1}	0.106	0.100	0.097	0.241	0.240
Crystal size, mm	0.5 x 0.45 x 0.5	0.25 x 0.25 x 0.25	0.35 x 0.25 x 0.25	0.25 x 0.15 x 0.10	0.3 x 0.25 x 0.3
Diffractometer	Smart, CCD area detector	Smart, CCD area detector	Smart, CCD area detector	Smart, CCD area detector	Smart, CCD area detector
T, K	273	273	273	273	273
X-radiation	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α
θ range, deg	2 – 24	1 - 24	1 - 24	2 - 24	1 – 24
h	-18 to 20	-5 to 6	-6 to 5	-8 to 4	-10 to 10
k	-4 to 4	-10 to 11	-11 to 9	-9 to 6	-5 to 5
l	-17 to 0	-56 to 52	-9 to 15	-6 to 8	-7 to 17
Total reflectn.	960	10853	2953	1309	1462
Non-zero reflectn.	731	4074	2096	1305	1062
σ-level	3	3	3	3	3
R	0.043	0.053	0.073	0.044	0.043
R_w	0.090	0.096	0.143	0.148	0.100
Max. e $Å^{-3}$	0.146	0.171	0.183	0.178	0.126

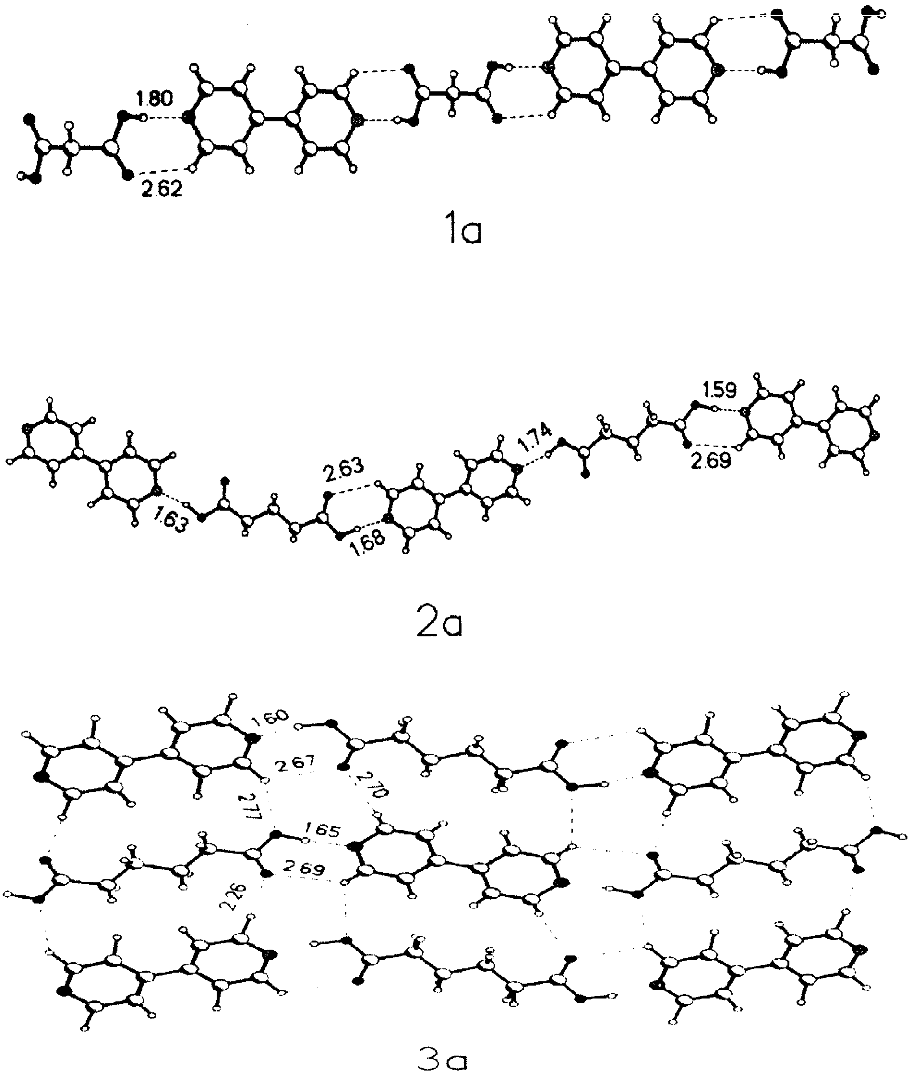


Figure 2: Molecular tapes in the complexes **1a**, **2a** and the two-dimensional arrangement of tapes in complex **3a**. Dashed lines represent hydrogen bonds.

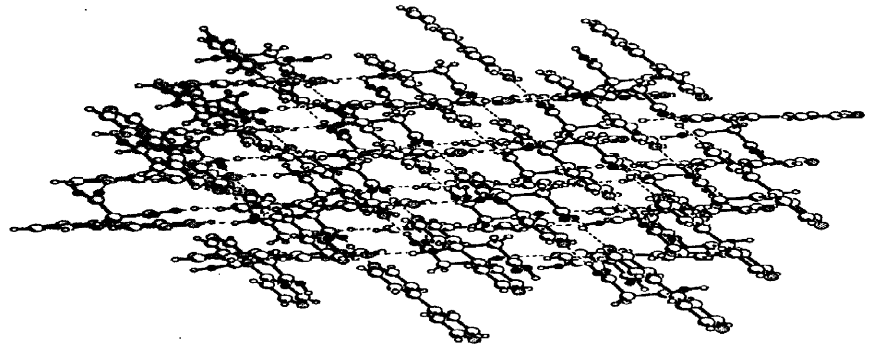
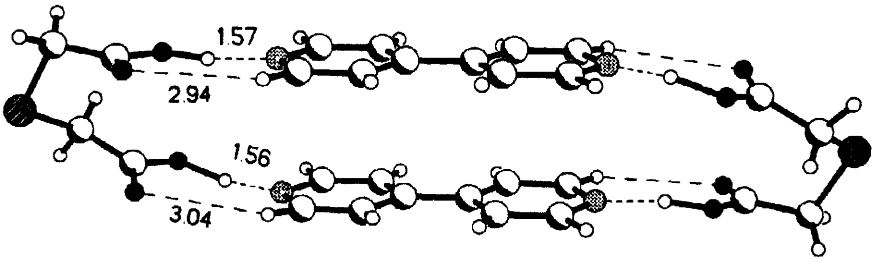


Figure 3: Three-dimensional arrangement in the crystal structure of the complex, **1a**.

Table 2: Relevant hydrogen bond distances and angles in the hydrogen bonded complexes **1a** – **5a**.

complex	Interaction	H...donor (D) distance (Å)	acceptor (A)...donor (D) distance (Å)	D-H...A angle (°)
1a	O(212)-H(212)...N(14)	1.80	2.61	172
	C(15)-(H15)...O(211)	2.62	3.31	128
2a	O(312)-H(312)...N(11)	1.63	2.62	164
	O(352)-H(23)...N(21)	1.68	2.64	173
	O(452)-H(452)...N(22)	1.74	2.65	165
	O(412)-H(412)...N(12)	1.59	2.64	176
	C(18)-H(18)...O(411)	2.69	3.39	128
	C(23)-H(23)...O(351)	2.63	3.31	128
3a	O(212)-H(212)...N(14)	1.60	2.66	166
	O(412)-H(412)...N(34)	1.65	2.67	166
	C(13)-H(13)...O(211)	2.67	3.32	115
	C(13)-H(13)...O(412)	2.77	3.77	146
	C(15)-H(15)...O(411)	2.26	3.46	164
	C(33)-H(33)...O(411)	2.69	3.33	128
	C(35)-H(35)...O(211)	2.70	3.45	166
4a	O(212)-H(212)...N(10)	1.57	2.61	162
	O(252)-H(252)...N(4)	1.56	2.63	167
	C(5)-H(5)...O(251)	2.94	3.68	141
	C(6)-H(6)...O(251)	3.04	3.43	114
5a	O(231)-H(231)...N(14)	1.67	2.64	169
	C(13)-H(13)...O(232)	3.05	3.66	125

are ~ 3Å. Three-dimensional arrangement of the supermolecules formed in this structure is shown in Figure 5.



4a

Figure 4: A cyclic unit formed between thiodiglycolic acid and 4,4'-bipyridyl in the complex, **4a**. Hydrogen bonds are shown in as dashed lines.

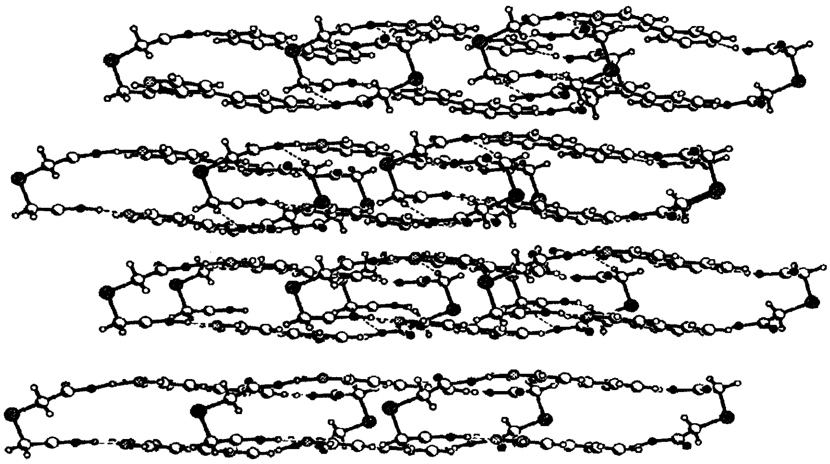


Figure 5: Three-dimensional arrangement in the cyclic units of the complex, **4a**.

The complex **5a** formed by thiodipropionic acid, **5** with 4,4'-bipyridyl has features which are completely different from those of **4a** formed by thiodiglycolic acid, **4**. In the crystal structure of **5a** (Table 1) molecules of bipyridyl and the dicarboxylic acid interact through O-H...N / C-H...O hydrogen bonds yielding molecular tapes, just as the hydrogen bond complexes **1a** - **3a** between bipyridyl and simple aliphatic dicarboxylic acids. The molecular tapes in **5a** are shown in Figure 6. Furthermore, the three dimensional arrangement of the tapes in complex **5a** exhibits features similar to those in the complexes **1a** and **2a** formed by other aliphatic dicarboxylic acids. In addition, we see from Table 2 that the hydrogen bond distances in **4a** and **5a** are close to those in **1a** – **3a**. The H...N and the H...O (in C-H...O) distances are in the range of 1.56 – 1.67Å and 2.94 – 3.04Å respectively.

Molecular Tapes vs Cyclic Supermolecules: From Figure 4, it appears that the cyclic structure of the complex **4a** is stabilized by π-π interaction between the bipyridyl molecules. This could be crucial in the design of such assemblies. We note from Scheme (2b) that the distance between the bipyridyl units is dependent of the length of the acid chain, which will allow π-π interaction only at a critical chain length of the acid molecule. It is possible that in complexes **1a** - **3a** and **5a**, the chain length of the acids is inappropriate to facilitate the π-π interaction between the bipyridyl units, there by favouring the tape structure. The formation of the cyclic structure only in **4a** consisting of acid, **4** but not in the complex **2a** which consists of glutaric acid, analogous to acid, **4** is rather surprising. Based on an analysis of the structures of the parent acids **2** and **4** (Figure 1), we see that the angle around the sulfur atom is 96° in **4** whereas the angle around corresponding carbon atom in the acid, **2** is 115°. The small angle around the central atom noticed in **4** could facilitate the adjacent chains to form the cyclic structure through π - π interactions. While sulfur certainly seems to play a crucial role to be used as a basis for the design of a tailor-made assemblies, as we see in the complex, **5a** length of acid chain seems to decide the formation of the tape structure, in spite of the presence of the central sulfur atom.

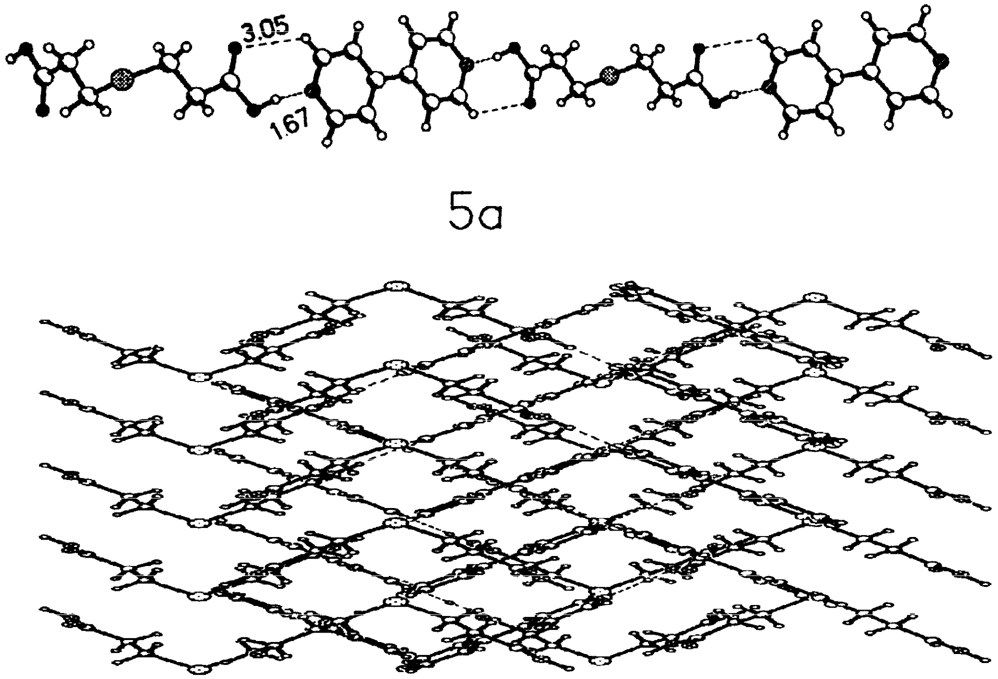
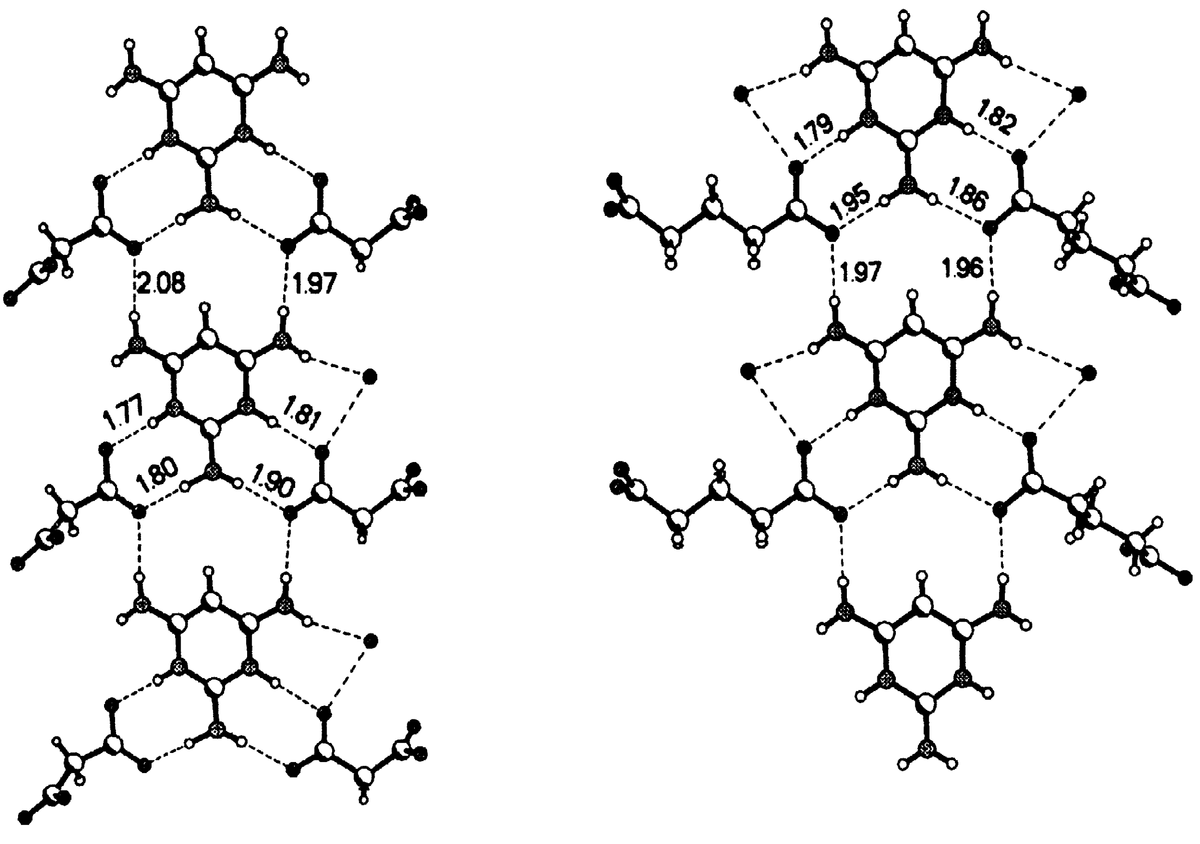


Figure 6: Two dimensional planar sheet arrangement in the molecular complex, **5a** of thiodipropionic acid and 4,4'-bipyridyl is shown along with the three-dimensional arrangement. Notice the similarity between **5a** and **1a**.

Molecular Complexes of 2,4,6-triaminopyrimidine with acids 1, 2 and 3: In order to examine the hydrogen bonded structures formed in a system where the nitrogens of the hetero cyclic ring as well as of the amino side chain can interact simultaneously with the carboxyl group to form molecular complexes with aliphatic dicarboxylic acids, we have investigated the complexes of 2,4,6-triaminopyrimidine. Co-crystallization of 2,4,6-triaminopyrimidine with acids, **1**, **2** and **3** resulted in the formation of molecular complexes which we designate as **6a**, **7a** and **8a** respectively. Crystal structures of these complexes (Table 3) reveal a new structural feature related to the hydrogen bonds involving the carboxylic group and heterocyclic nitrogen. The basic recognition between the pyrimidine and the acid occurs between the carboxylic group and the pyridyl nitrogen. The complexes **6a** – **8a** differ from one with other in some aspects, the common feature being that the pyrimidine and the acid molecules are held together by the couplings consisting of O^-...H^+-N / N-H...O bonds as shown in Figures 7 and 8.



6a

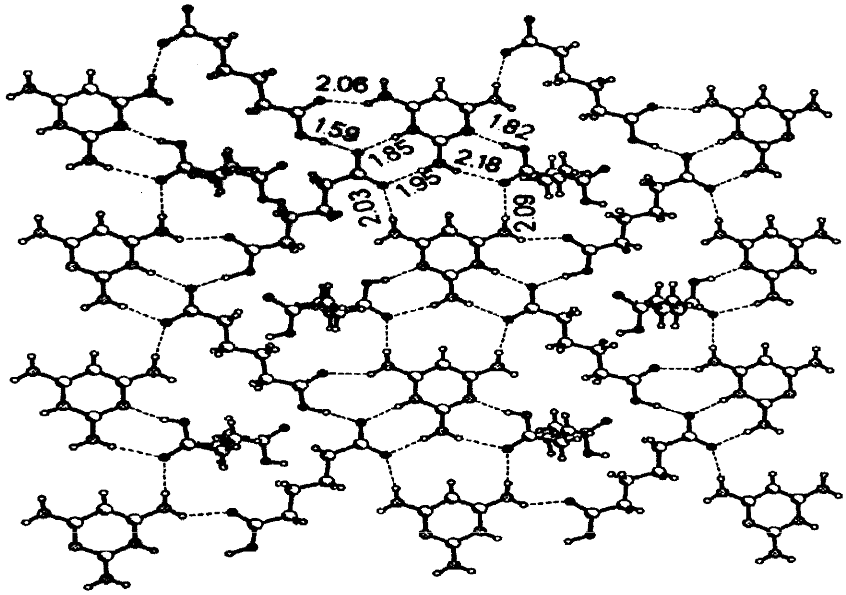
7a

Figure 7: Molecular tapes formed by 2,4,6-triaminopyrimidine in the complexes, **6a** and **7a**. Notice the similar recognition pattern between the pyrimidine and acid molecules. Lone atoms represent water molecules.

Table 3: Crystal structures of molecular complexes of dicarboxylic acids with 2,4,6-triaminopyrimidine.[a]

	6a	7a	8a	9a	10a
Formulae	$C_4H_7N_5$:$C_3H_4O_4$:0.5(H_2O)	$C_4H_7N_5$:$C_5H_8O_4$:1.5(H_2O)	2($C_4H_7N_5$): 3($C_6H_{10}O_4$)	$C_4H_7N_5$: $C_6H_{10}O_4S_1$: 2(CH_3OH)	$C_4H_7N_5$:$C_4H_6O_4$:H_2O
Mol. wt.	237.21	281.26	688.71	367.43	261.25
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	C2/c	C2/c	$P2_1/c$	C2/m	P-1
a	12.060(2)	11.929(3)	9.808(1)	14.095(1)	5.190(1)
b	10.748(2)	10.883(3)	16.104(1)	14.691(1)	8.568(1)
c	16.501(2)	20.559(5)	10.182(1)	8.136(1)	13.338(1)
α	90	90	90	90	103.66(1)
β	107.22(9)	98.77(3)	93.07(2)	104.24(1)	94.55(1)
γ	90	90	90	90	92.86(1)
Cell vol. $Å^3$	2043.0(6)	2638.1(2)	1605.9(1)	1633.0(3)	573.1(1)
Z	8	8	2	4	2
F(000)	992	1184	732	784	276
D_{calcd}, g. cm^{-3}	1.542	1.416	1.424	1.495	1.514
λ, Å	0.7107	0.7107	0.7107	0.7107	0.7107
μ, mm^{-1}	0.130	0.118	0.114	0.240	0.126
Crystal size, mm	0.30 x 0.25 x 0.25	0.20 x 0.25 x 0.15	0.40 x 0.35 x 0.25	0.30 x 0.30 x 0.30	0.40 x 0.20 x 0.20
Diffractometer	Smart, CCD area detector	Smart, CCD area detector	Smart, CCD area detector	Smart, CCD area detector	Smart, CCD area detector
T, K	273	273	273	273	273
X-radiation	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α
θ range, deg	2 - 24	2 - 24	2 - 24	2 - 24	1 - 24
h	-13 to 13	-13 to 9	-7 to 10	-15 to 15	-5 to 5
k	-11 to 7	-6 to 12	-16 to 17	-12 to 16	-9 to 9
l	-14 to 18	-20 to 21	-8 to 11	-8 to 9	-12 to 14
Total reflectn.	3788	2359	2246	3222	2255
Non-zero reflectn.	1477	1609	2323	1243	1611
σ-level	3	3	3	3	3
R	0.074	0.056	0.044	0.063	0.045
R_w	0.120	0.105	0.083	0.102	0.088
Max. e $Å^{-3}$	0.572	0.422	0.373	0.299	0.242

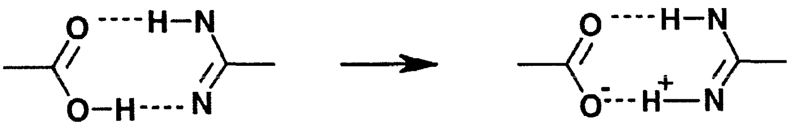
[a] The complexes **6a** – **8a** are formed by dicarboxylic acids **1** – **3** with 2,4,6-triaminopyrimidine. The stoichiometry is 1:1 in **6a** and **7a** but 3:2 in **8a**. The complexes **9a** and **10a** are formed by 2,4,6-triaminopyrimidine with succinic acid and thiodipropionic acid, **5** respectively.



8a

Figure 8: Arrangement of molecules of adipic acid, **3** and 2,4,6-triaminopyrimidine, in a two-dimensional planar sheet of complex, **8a**.

A comparison with the structures of **1a** - **5a** as well as the literature data on aminopyrimidines,[19] we would expect the hydrogen bond coupling in **6a** - **8a** to be O-H...N and N-H...O. However, the couplings actually observed by us in **6a** - **8a** involve proton transfer from the carboxylic group to the heterocyclic nitrogen as shown below in Scheme 3. Such proton transfer occurs because of strong hydrogen bond initially formed between the carboxyl and the pyridyl nitrogen atoms. The H...O distances in the cyclic hydrogen bond structures also supports the occurrence of proton transfer (see Table 4). The H^+...O^- and H...O distances in the O^-...H^+-N and O...H-N bonds are comparable (~1.80Å), showing thereby the high stability and strength of the cyclic hydrogen bond structure.



Scheme 3

Further, unlike in **1a** – **5a**, the complexes **6a** and **7a** are stabilized by the incorporation of guest molecules. In the case of **6a** and **7a**, water molecules are the guest molecules. The interaction of the water molecules with the acids and the pyrimidine is shown in Figure 7. However, in **8a**, additional acid molecule has been incorporated as guest molecule. It appears that the large chain length of the acid, **3** facilitated the formation of larger voids as shown in Figure 9 (right) which are

Table 4: Relevant hydrogen bond distances and angles in the hydrogen bonded complexes **6a** – **10a**.

complex	Interaction	H...donor (D) distance (Å)	Acceptor (A)...donor (D) distance (Å)	D-H...A angle (°)
6a	N(21)-H(21A)...O(111)	1.97	2.81	170
	N(22)-H(22)...O(112)	1.81	2.75	179
	N(23)-H(23A)...O(111)	1.90	2.74	164
	N(23)-H(23B)...O(132)	1.80	2.84	174
	N(24)-H(24)...O(131)	1.77	2.62	173
	N(25)-H(25B)...O(132)	2.08	2.93	170
7a	N(22)-H(22B)...O(111)	1.97	2.83	175
	N(23)-H(23A)...O(112)	1.79	2.64	174
	N(24)-H(24A)...O(111)	1.95	2.81	177
	N(24)-H(24B)...O(152)	1.86	2.72	175
	N(25)-H(25A)...O(151)	1.82	2.67	173
	N(26)-H(26B)...O(152)	1.96	2.81	173
8a	O(132)-H(132)...N(36)	1.82	2.61	162
	O(212)-H(212)...N(262)	1.59	2.60	172
	N(31)-H(31A)...O(131)	2.18	3.02	167
	N(31)-H(31B)...O(261)	1.95	2.81	178
	N(32)-H(32A)...O(262)	1.85	2.70	179
	N(33)-H(33A)...O(131)	2.09	2.95	174
	N(33)-H(33B)...O(211)	2.06	2.80	143
	N(35)-H(35B)...O(261)	2.03	2.89	171
9a	O(100)-H(1)...O(222)	2.11	2.95	169
	O(100)-H(2)...O(122)	1.96	2.85	176
	O(222)-H(222)...O(121)	1.52	2.56	167
	N(31)-H(31A)...O(122)	1.91	2.84	177
	N(33)-H(33A)...O(221)	2.14	3.07	169
	N(33)-H(33B)...O(100)	2.03	2.88	168
	N(35)-H(35A)...O(221)	2.16	2.89	136
	N(35)-H(35B)...N(34)	2.08	2.98	172
	N(36)-H(36)...O(121)	1.83	2.79	177
10a	O(1)-H(1)...O(231)	1.90	2.67	157
	N(11)-H(11a)...O(232)	1.77	2.73	175
	N(12)-H(12)...O(231)	1.63	2.68	175
	N(13)-H(13)...O(232)	2.10	2.84	174
	N(13)-H(13B)...O(1)	1.90	2.85	165
	C(1)-H(1B)...S(21)	2.76	3.72	173

filled by the additional acid molecules (Figure 9 – left). In fact, the three-dimensional arrangement resembles a typical inorganic pillared type structure.

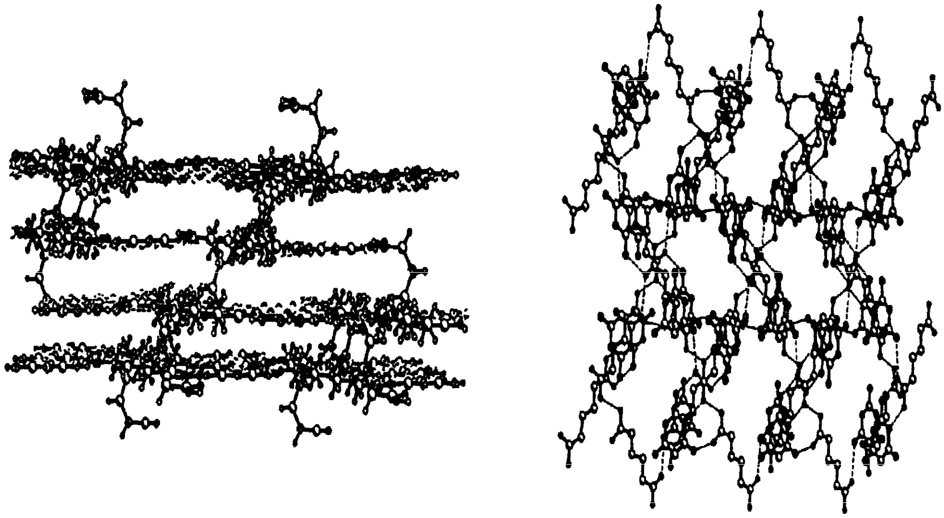


Figure 9: Left: Three dimensional arrangement of planar sheets found in the co-crystals of 2,4,6-triaminopyrimidine and adipic acid, **3**. Notice the acid molecules pillaring the sheets. Right: Channels viewed along a crystallographic axis in which adipic acid molecules fit. The acid molecules are not shown for a clear vision of the channels.

A comparison of crystal packing of the complexes **6a** – **8a**, reveals that the number of -CH_2 groups in the constituent acid dictate the pattern of crystallization. This becomes evident from the two-dimensional network observed in **8a** (Figure 8), consisting of adipic acid, an acid with even number -CH_2 groups. The complexes, **6a** and **7a** with acids possessing an odd number -CH_2 groups, constitute three- dimensional crossed networks (Figure 10). The guest molecules are situated within the two-dimensional cavities in **8a** but are located at the intercepts of the crossed networks in **6a** and **7a**. Incorporation of the guest molecules in complexes **6a** - **8a** appears to be possible due to the incompatible dimensions between the acids and the pyrimidine molecules. Such a situation is not encountered in the complexes **1a** - **5a**, as 4,4'-bipyridyl and the acids are proportionate to each other in dimension. Although the basic recognition pattern in **6a** – **8a**, is similar the nature of association of the supermolecules is somewhat different. For instance, **6a** and **7a** are formed in a 1:1 ratio, with each pyrimidine attached to two acid molecules (Figure 7), through O^-...H^+-N / N-H...O hydrogen bonds. In **8a**, however, the complex is formed in 3:2 ratio of adipic acid and 2,4,6-triaminopyrimidine (Figure 8), and each pyrimidine is attached to two acid molecules as in **6a** and **7a** but one of the acid molecules is not deprotonated and forms O-H...N / N-H...O bonds. In addition, the acid which is not deprotonated bridges the adjacent sheets as shown in Figure 9.

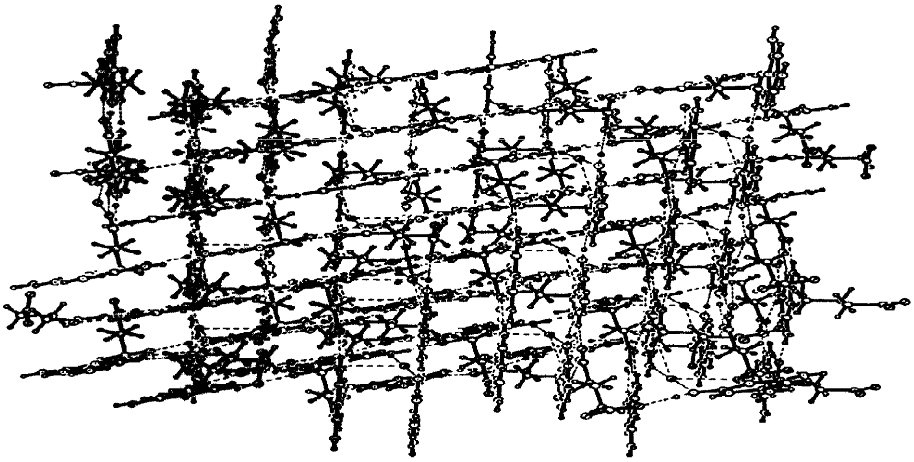
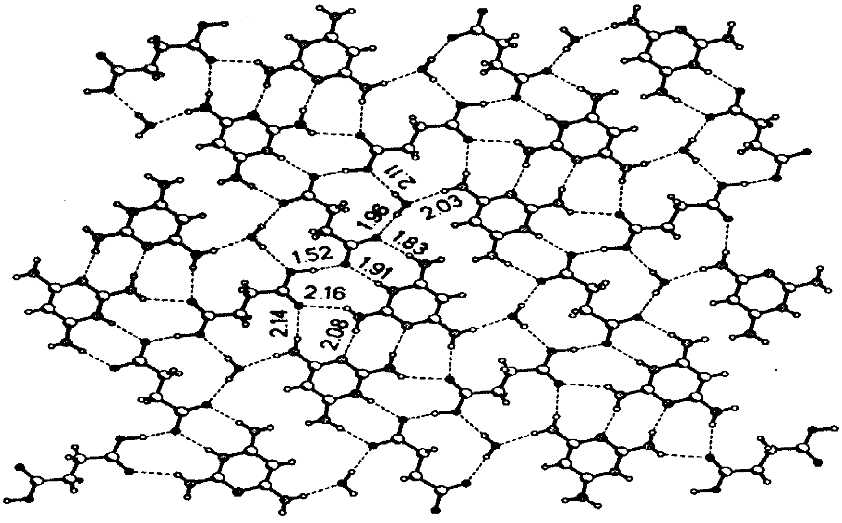


Figure 10: Three-dimensional arrangement of molecular tapes observed in the crystal structure of complex **6a** of 2,4,6-triaminopyrimidine and malonic acid.

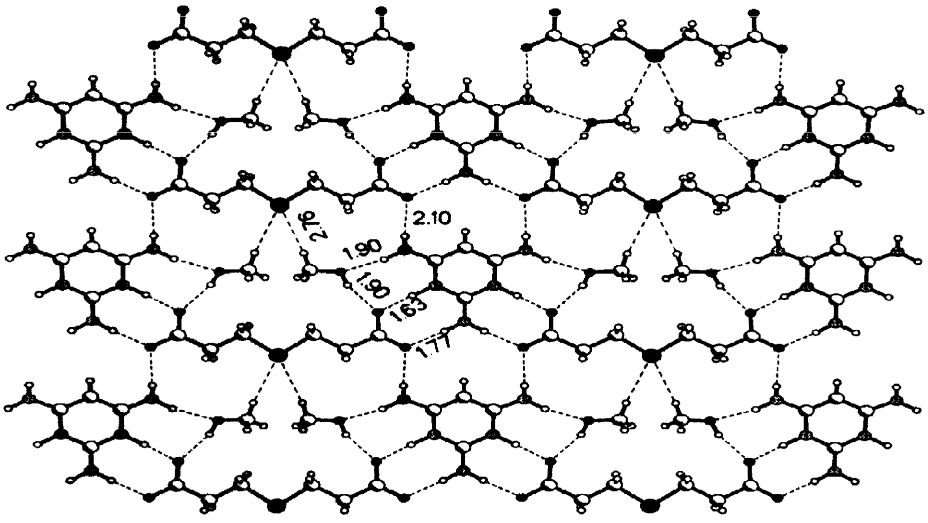
Other hydrogen bonded complexes of 2,4,6-triaminopyrimidine with diacids:

Unlike 4,4'-bipyridyl, where we could not obtain satisfactory crystals with succinic acid, we could isolate good crystals of the complex between 2,4,6-triaminopyrimidine and succinic acid, **9a**. The structure of **9a** (Table 3) is similar to complexes **6a** - **8a**. The molecules of pyrimidine and succinic acid interact again through $O^{-}...H^{+}$-N / N-H...O hydrogen bonds, but each of the pyrimidine is attached to only one acid molecule. The recognition pattern shown in Figure 11, has the adjacent pyrimidine molecules interacting with each other through the formation of centrosymmetric N-H...O hydrogen bonds.



9a

Figure 11: Recognition pattern of 2,4,6-triaminopyrimidine with succinic acid and arrangement of the molecular tapes into planar sheets.



10a

Figure 12: Arrangement of molecules of 2,4,6-triaminopyridine and thiodipropionic acid in the molecular complex, **10a**. A two-dimensional arrangement of molecular tapes is shown.

We have also examined the structure of the complex **10a**, formed between thiodipropionic acid, **5**, and 2,4,6-triaminopyrimidine. The two-dimensional arrangement of the molecules in **10a** (Table 3) is shown in Figure 12. This complex has the same recognition pattern and forms a regular hydrogen bonded coupling of $O^-...H^+-N$ / N-H...O with H...O distances of 1.63 and 1.77, as in **6a** - **8a**. However, the adoption of a planar sheet arrangement as in Figure 12 is reminiscent of the structures of the complexes **3a**, **8a** and **9a**, rather than of **1a**, **2a**, **5a**, **6a**, and **7a**. An interesting feature of **10a** is that the solvent of crystallization, methanol, is located in the available void space in the crystal structure. It would appear that the sulfur atom in the acid plays a subtle role in determining the structure of the complex. As a result, larger molecules like $-CH_3OH$ rather than H_2O molecules, as noted in the complexes **6a** and **7a**, could be incorporated.

Conclusions

The present systematic study of hydrogen bonded molecular complexes of aliphatic dicarboxylic acids with 4,4'-bipyridyl have shown that molecular tape structures are generally formed in all the systems, independent of whether the acid has an even or an odd number of carbon atoms. The only exception was in the case of thiodiglycolic acid where π - π interactions between the heterocylic molecules seems to favour the cyclic structure. Alhough such a cyclic structure is rare, the one found by us provides a nice rectangle by noncovalent synthesis. Synthesis of such rectangles has been reported in recent years in the literature.[20-23] The hydrogen bonded molecular complexes of dicarboxylic acids with 2,4,6-triaminopyrimidine also yielded tape structures, involving cyclic hydrogen bonded motifs where there is proton transfer from carboxylic group to the heterocyclic ring nitrogen, through the initial formation of a strong hydrogen bond. In this system, the acids with an odd number of carbon atoms seem to form cross ribbon networks. The composition of the complex with adipic acid consist of even number of carbon atoms differs slightly from those with an odd number of carbon atoms. While we have obtained some interesting and useful hydrogen bond structures formed by supramolecular organization, the present study indicates how we are still far away from being able to do a complete rational supramolecular design of hydrogen bonded molecular assemblies.

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