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A Competitive Molecular Recognition Study: Syntheses and Analysis of Supramolecular Assemblies of 3,5-Dihydroxybenzoic Acid and Its Bromo Derivative with Some N-Donor Compounds

Sunil Varughese and Venkateswara Rao Pedireddi*[a]

Abstract: A molecular recognition study of 3,5-dihydroxybenzoic acid (**1**) and its bromo derivative 4-bromo-3,5-dihydroxybenzoic acid (**2**) with the N-donor compounds 1,2-bis(4-pyridyl)ethene (bpyee), 1,2-bis(4-pyridyl)ethane (bpyea), and 4,4′-bipyridine (bpy) is reported. Thus, the syntheses and structural analysis of molecular adducts **1a**–**1c** (**1** with bpyee, bpyea, and bpy, respectively) and **2a**–**2c** (**2** with bpyee, bpyea, and bpy, respectively) are discussed. In all these adducts, recognition between the constituents is established through either O−H⋯N and/or O−H⋯N/C−H⋯O pairwise hydrogen bonds. In all the adducts both OH and COOH functional groups available on **1** and **2** interact with the N-donor compounds, except in **2a**, in which only COOH (COO$^-$) is involved in the recognition process. The COOH moieties in **1a**, **1b**, and **2b** form only single O−H⋯N hydrogen bonds, whereas in **1c** and **2c**, they form pairwise O−H⋯N/C−H⋯O hydrogen bonds. In addition, subtle differences in the recognition patterns resulted in the formation of cyclic networks of different dimensions. In fact, only **1c** forms a four-molecule cyclic moiety, as was already documented in the literature for this kind of assemblies. All complexes have been characterized by single-crystal X-ray diffraction. The supramolecular architectures are quite elegant and simple, with stacking of sheets in all adducts, but a rather complex network with a threefold interpenetration pattern was found in **2c**.

Keywords: crystal engineering · hydrogen bonds · molecular recognition · self-assembly · supramolecular chemistry

Introduction

Molecular recognition,[1] the process of bringing different chemical entities together through noncovalent forces, is a powerful tool for the development of novel targeted assemblies with tailor-made properties.[2–4] Initial studies towards host–guest-type assemblies, in which the guest molecules are captured in the cavities/channels formed by host molecules, such as crown ethers,[5] cryptands,[6] and so on, indeed brought about dramatic changes in organic synthesis and led to the development of novel synthetic strategies for the preparation of complex molecules to be employed in molecular recognition studies. As a result, the synthesis of host structures[7,8] by using noncovalent bonds (e.g., hydrogen bonds), which are weaker than conventional covalent bonds (σ and π bonds) and also have the advantage of flexibility for fine-tuning to obtain the desired network or architecture, evolved as a general synthetic strategy for the creation of exotic assemblies that can be utilized in molecular recognition studies.[9] Numerous examples of host–guest systems generated through noncovalent synthetic procedures have appeared in the recent literature. For example, adducts of trimesic acid,[10] 3,5-dinitrobenzoic acid,[11] 3,5-dinitrobenzonitrile,[12] cyanuric acid,[13] trithiocyanuric acid,[14] 1,2,4,5-benzenetetracarboxylic acid,[15] and so on, representing a variety of host–guest systems of different architectures (Scheme 1), demonstrate the elegance and reliability of molecular recognition process.

In further developments aimed at increased knowledge of hydrogen bonds,[16] attention was also directed towards utilization of hydrogen bonds for synthesis of targeted assemblies to perform unusual chemical transformations that otherwise appear to be either infeasible or complex in nature.[17,18] In this regard, the elegant studies by MacGillivray et al. on the synthesis of ladderanes by cocrystallization and subsequent photochemical reaction by irradiation of the adducts of resorcinol and unsaturated N-donor molecules such as 1,2-bis(4-pyridyl)ethene, prepared by inducing recognition between the constituents through O−H⋯N hydro-

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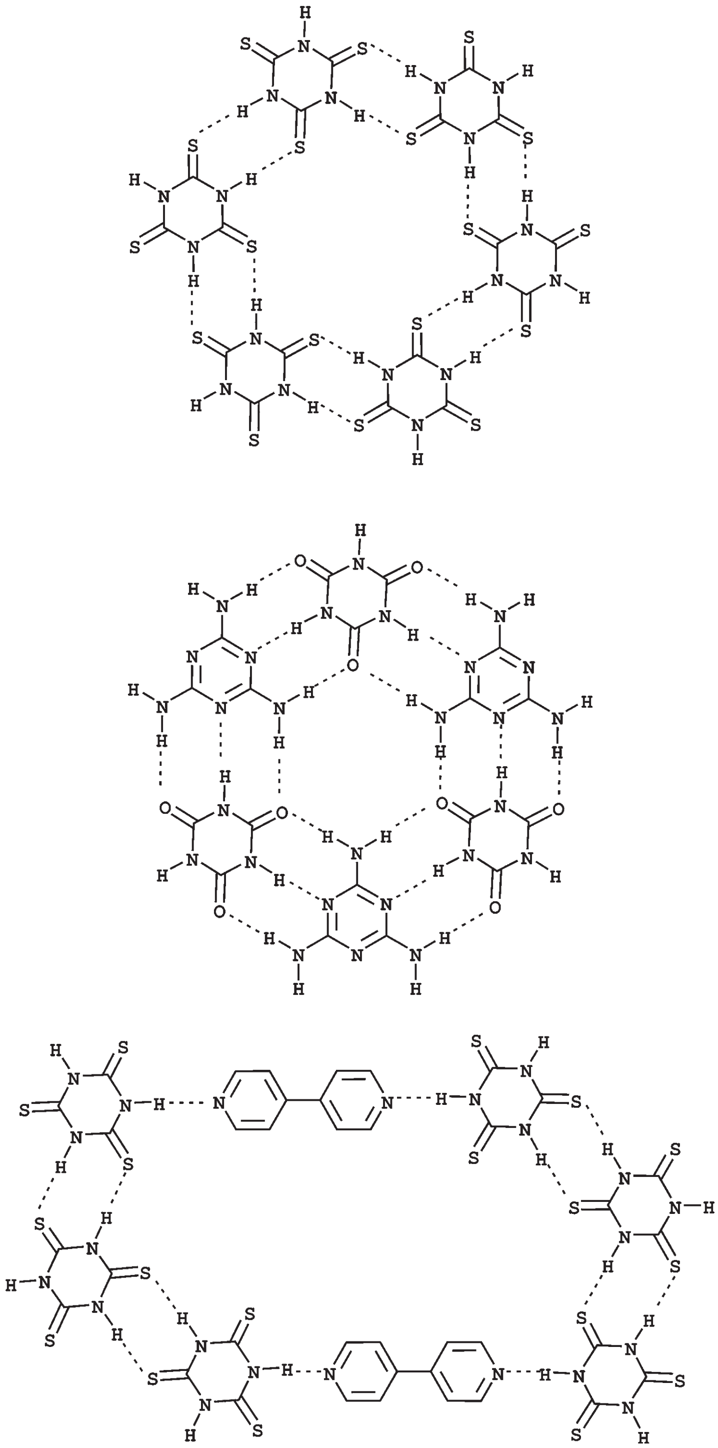
[a] S. Varughese, Dr. V. R. Pedireddi
Solid State & Supramolecular Structural Chemistry Lab
Division of Organic Chemistry, National Chemical Laboratory
Dr. Homi Bhabha Road, Pune 411 008 (India)
Fax: (+91) 20-258-93153
E-mail: vr.pedireddi@ncl.res.in



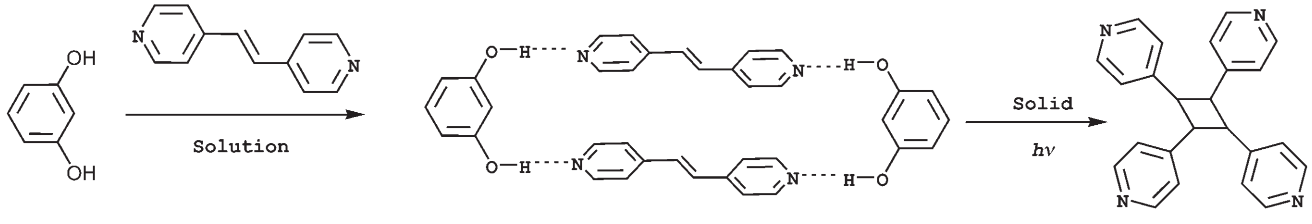
Scheme 1.

gen bonds, are superb examples that highlight the use of molecular recognition phenomenon for the generation of complex chemical systems (Scheme 2).[19] From those studies, it was further noted that the recognition pattern between the OH groups in the *meta*-positions and aromatic N-donor compounds was not affected by the presence of different functional groups, as was shown recently in a case study on a homologous series of phluroglucinols.[20] However, studies on the influence of functional group such as COOH, which is also capable of forming O−H⋯N hydrogen bonds, on the topological arrangement shown in Scheme 2, is not well explored. Thus, studies towards understanding the competition of COOH and OH for N-donor compounds would provide valuable information for the development of hitherto unknown assemblies.

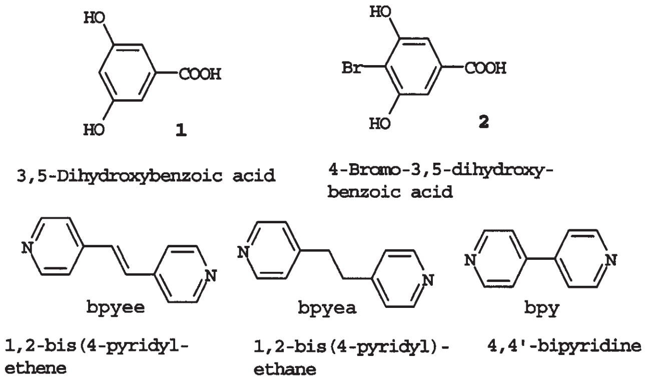
In our continued exploration of utilization of O−H⋯N and O−H⋯N/C−H⋯O pairwise hydrogen bonds[21] in supramolecular synthesis and molecular recognition, we carried out such competitive recognition studies employing molecular entities having both OH and COOH groups by cocrystallization with different heteroaromatic compounds, which can exploit the robustness of the four-membered recognition pattern (Scheme 2) or may lead to new assemblies generated through different recognition schemes. Thus, we chose 3,5-dihydroxybenzoic acid (**1**) for cocrystallization with 1,2-bis(4-pyridyl)ethene (bpyee), 1,2-bis(4-pyridyl)ethane, (bpyea), and 4,4′-bipyridine (bpy). Furthermore, the study was extended to halo derivatives of **1**, as such substitution did not have any effect on the basic molecular recognition features in the resultant assemblies, as known from the earlier studies of MacGillivray et al.[22] Hence, cocrystallizations of 4-bromo-3,5-dihydroxybenzoic acid with bpyee, bpyea, and bpy were also carried out. The synthetic strategies and the nature of the products are illustrated in Scheme 3.

Results and Discussion

Cocrystallization of 3,5-dihydroxybenzoic acid (**1**) with the N-donor compounds 1,2-bis(4-pyridyl)ethene (bpyee), 1,2-bis(4-pyridyl)ethane (bpyea) and 4,4′-bipyridyl (bpy) from CH_3OH gave single crystals of **1a**–**1c**, respectively. Similarly, 4-bromo-3,5-dihydroxybenzoic acid gave cocrystals **2a**–**2c** with bpyee, bpyea, and bpy, respectively. Single-crystal X-ray diffraction revealed that the reactants recognize each other by interaction of OH and/or COOH groups of **1** and **2** with the N atoms of N-donor compounds. Each adduct is unique in aspects of structural arrangements with respect to



Scheme 2.



Reactants	Ratio	Molecular Complexes
1 + bpyee	2:3	1a
1 + bpyea	1:1	1b
1 + bpy	2:3	1c
2 + bpyee	2:1	2a
2 + bpyea	2:2	2b
2 + bpy	1:1	2c

Scheme 3.

the conformation and the nature of the hydrogen bonds formed by OH and COOH groups. However, collectively, they exhibit many common features, especially in the formation of ladderlike structures. Thus, descriptions of the unique features of each adduct are followed by a comparison to deduce common features which may be useful for evaluating literature examples and formulating new systems.

Molecular complex of 3,5-dihydroxybenzoic acid and 1,2-bis(4-pyridyl)ethene (1a): Cocrystallization of 3,5-dihydroxybenzoic acid (**1**) and bpyee in a 1:1 ratio from methanol gave single crystals suitable for X-ray diffraction. Structure determination (Table 1)[23] revealed that **1** and bpyee are present in a 2:3 ratio in the molecular complex **1a**, and the asymmetric unit is shown in Figure 1. The two OH groups on **1** are arranged in a *syn–syn* orientation with respect to the H atom in the *para* position, and one of the bpyee molecules is disordered around the olefinic bridge in a 53:47 distribution. The ordered bpyee molecules are denoted as B, and the disordered molecules as C. These mole-

Table 1. Crystallographic data for **1a**, **1b** and **2a**–**2c**

	1a	**1b**	**2a**	**2b**	**2c**
formula	$2(C_7H_6O_4):3(C_{12}H_{10}N_2)$	$(C_7H_6O_4):(C_{12}H_{12}N_2)$	$2(C_7H_4O_4Br):(C_{12}H_{12}N_2)$	$2(C_7H_5O_4Br):2(C_{12}H_{12}N_2)$	$(C_7H_5O_4Br):(C_{10}H_8N_2)$
M_r	852.88	338.35	648.26	830.48	389.20
crystal habit	blocks	blocks	blocks	blocks	blocks
crystal system	triclinic	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a [Å]	9.035(8)	7.234(2)	6.693(2)	7.321(2)	10.247(4)
b [Å]	10.648(9)	13.914(3)	16.425(4)	8.047(2)	9.270(3)
c [Å]	12.813(9)	17.141(4)	11.197(3)	16.817(5)	17.130(6)
α [°]	107.46(9)	78.54(4)	90	98.34(5)	90
β [°]	102.50 (9)	82.50(4)	91.55(5)	90.74(5)	99.39(5)
γ [°]	109.12(9)	84.00(4)	90	114.91(4)	90
V [Å^3)	1041.0(2)	1671.0(7)	1230.5(6)	886.0(4)	1605.4(10)
Z	1	4	2	1	4
ρ_{calcd} [g cm^{-3}]	1.360	1.345	1.750	1.556	1.610
T [K]	298(2)	298(2)	298(2)	298(2)	298(2)
$\lambda(Mo_{K\alpha})$	0.71073	0.71073	0.71073	0.71073	0.71073
μ [mm^{-1}]	0.094	0.095	3.350	2.347	2.585
2θ range [°]	46.74	46.66	46.58	46.62	46.56
index ranges	$-10 \leq h \leq 10$	$-8 \leq h \leq 8$	$-7 \leq h \leq 7$	$-8 \leq h \leq 8$	$-11 \leq h \leq 10$
	$-11 \leq k \leq 11$	$-15 \leq k \leq 15$	$-18 \leq k \leq 18$	$-8 \leq k \leq 8$	$-10 \leq k \leq 10$
	$-14 \leq l \leq 13$	$-18 \leq l \leq 19$	$-11 \leq l \leq 12$	$-18 \leq l \leq 18$	$-19 \leq l \leq 18$
$F(000)$	446	712	648	420	784
total reflns	6482	14115	5235	7360	9552
unique reflns	3000	4816	1785	2554	2306
reflns used	1924	2213	1399	2072	1939
parameters	374	455	212	305	266
GOF on F^2	1.038	0.819	0.930	0.910	1.013
$R1$ [$I > 2\sigma(I)$]	0.0527	0.0493	0.0267	0.0363	0.0275
$wR2$	0.1069	0.0973	0.0623	0.0914	0.0740
max./min. residual electron density [e Å^{-3}]	0.366/−0.144	0.194/−0.180	0.331/−0.404	0.492/−0.243	0.305/−0.399

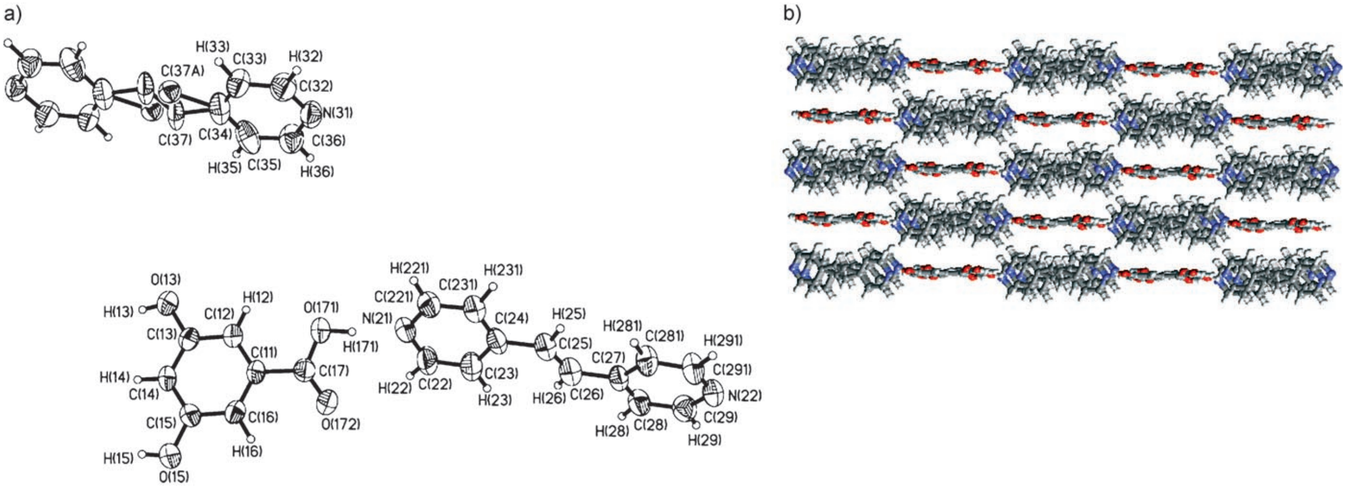


Figure 1. a) ORTEP plot of molecular entities in the asymmetric unit of **1a**. b) Packing of molecules in stacked layers in the crystal lattice (view down *c* axis).

cules are arranged in the crystal lattice to yield a sheet structure, stacked along the *a* axis (Figure 1b).

In each sheet, recognition between **1** and bpyee is established through O−H···N hydrogen bonds. The basic recognition pattern is shown in Figure 2a. Each molecule of **1** is connected one ordered and one disordered bpyee molecule by O−H···N hydrogen bonds (H···N 1.77, 1.97 Å) involving the OH groups. The characteristics of the hydrogen bonds are listed in Table 2. Furthermore, these two bpyee molecules in turn interact with a pair of molecules of **1**, which themselves are held together by cyclic C−H···O hydrogen bonds (H···O 2.68 Å), by formation of O−H···N hydrogen bonds (H···N 1.97 and 1.62 Å, Table 2) involving OH and COOH groups (see Figure 2a). Thus, a five-membered supramolecular entity is established in such a manner that the disordered bpyee forms O−H···N hydrogen bonds exclusively with OH groups, while the ordered bpyee molecules interact with both OH and COOH groups. As a result, it appears that the presence of COOH group disturbed the recognition pattern, which was otherwise expected be a four-membered unit, as shown in Scheme 2. However, adjacent supramolecular ensembles interact with each other to form a ladder structure in which bpyee molecules are inserted as rungs between the rods of acid **1** (Figure 2b).

The distance between the rungs is 4.2 Å (Figure 2b), which is a reactive distance for photodimerization. Thus, even though COOH is able to influence the fundamental recognition pattern, the gross structure still did not deviate from the required topological arrangement, and thus the properties of the structures remain intact for utilization in further reactions, such as [2+2] cycloaddition. Retention of such three-dimensional packing irrespective of the nature of substitutuents on the acid molecules is further reflected in a more elegant manner in adduct **1b**, in which not only the basic recognition interaction is totally different than that observed in **1a**, but also from that of the pattern shown in Scheme 2.

Molecular complex of 3,5-dihydroxybenzoic acid and 1,2-bis(4-pyridyl)ethane (1b): Complex **1b** was prepared under

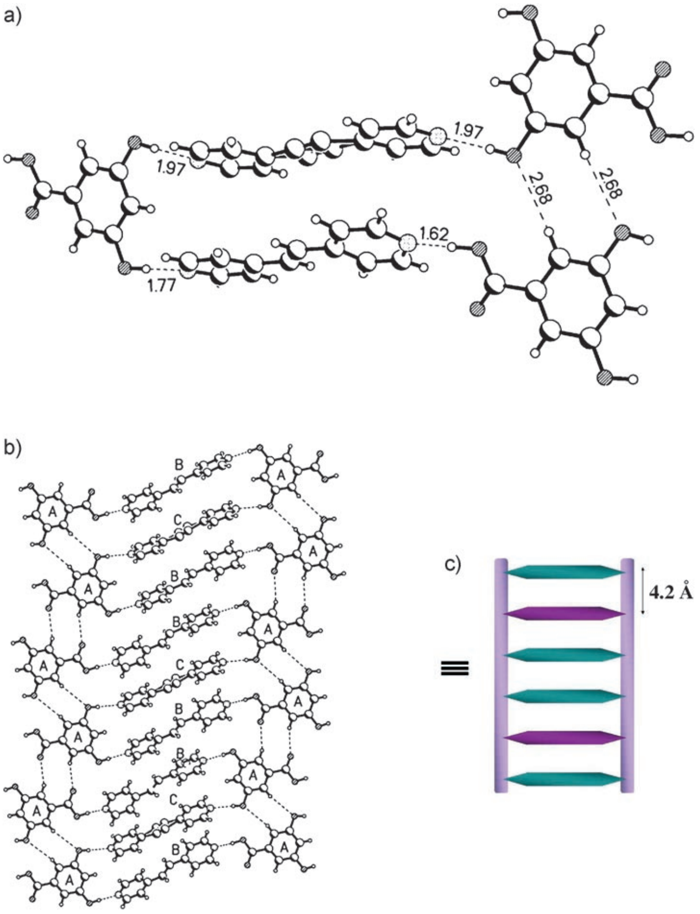


Figure 2. a) Recognition pattern between **1** and bpyee to give a five-membered cyclic moiety. b) and c) Ladderlike structure observed in **1a** along with a schematic representation. The different colors of the rungs represent ordered and disordered bpyee.

Table 2. Characteristics of hydrogen bonds [bond lengths in Å, angles in °] in **1a**–**1c** and **2a**–**2c**.

	1a			**1b**			**1c**			**2a**			**2b**			**2c**		
O–H···O				1.812	2.631	177				1.778	2.595	169	2.034	2.708	150	1.888	2.668	169
				1.846	2.666	178				1.830	2.655	173						
	1.624	2.599	178	1.717	2.535	175	1.853	2.685	171				1.703	2.539	173	1.744	2.557	171
	1.773	2.692	179	1.729	2.547	175	1.882	2.721	177				1.919	2.633	174	1.917	2.741	172
O–H···N	1.965	2.814	174	1.767	2.681	163	1.886	2.720	172									
				1.898	2.673	157	1.918	2.750	170									
							1.917	2.756	178									
							1.976	2.814	176									
N^+–H···O^-										1.667	2.608	179						
										2.529	3.121	121						
	2.359	3.321	174	2.666	3.578	167	2.450	3.342	156	2.400	3.077	129	2.680	3.523	167	2.443	3.429	175
	2.567	3.431	144	2.674	3.329	128	2.496	3.393	157	2.482	3.281	149	2.791	3.755	172	2.709	3.305	124
	2.626	3.332	128	2.693	3.547	153	2.515	3.373	151	2.835	3.440	124	2.916	3.741	147	2.827	3.389	121
	2.669	3.473	143	2.708	3.339	126	2.569	3.236	128	2.874	3.636	141	3.018	3.871	164			
	2.680	3.565	153	2.730	3.416	131	2.582	3.264	129									
	2.711	3.594	147	2.730	3.463	136	2.618	3.486	152									
C–H···O	2.936	3.857	166	2.781	3.688	165	2.655	3.572	162									
				2.785	3.636	153	2.662	3.452	141									
				2.831	3.740	156	2.676	3.429	137									
				2.839	3.625	143	2.687	3.364	129									
				2.841	3.454	125	2.748	3.414	128									
				2.876	3.796	170	2.756	3.367	123									
				2.910	3.634	136	2.764	3.479	133									
							2.792	3.403	123									
							2.936	3.641	132									
							2.972	3.628	127									
							2.973	3.612	126									
							2.980	3.568	122									
	2.701	3.342	128	2.913	3.676	136	2.522	3.254	134				2.882	3.473	123	2.910	3.455	128
	2.782	3.472	133	2.892	3.643	135	2.611	3.304	130									
C–H···N							2.690	3.375	130									
							2.737	3.679	171									
							2.815	3.477	128									
							2.911	3.837	165									
							2.979	3.692	133									

the same conditions as **1a** and is a 1:1 complex of **1** and bpyea (Table 1), but with two symmetry-independent molecules in the asymmetric unit (Figure 3a), without any abnormal features, such as the disorder that was observed in **1a**.

The two symmetry-independent molecules of **1** are denoted as A and B, and those of bpyea as C and D. While the molecular geometries of A and B are more or less the same, the differences in C and D are mainly due to the variable conformational arrangement of methylene bridge; the two phenyl moieties in bpyea are twisted by 5.2° in C and 7.3° in D. The molecules form a stacked planar sheet structure along the c axis. However, the interactions between the molecules in each layer are quite intriguing.

Unlike in **1a**, the recognition between **1** and bpyea is established such that each symmetry-related molecule of bpyea is held by both symmetry-independent molecules (A and B) of **1** with formation of O–H···N hydrogen bonds (H···N 1.73 and 1.90 Å; 1.72 and 1.77 Å; Table 2) involving both OH and COOH groups. This arrangement is shown in Figure 3b and c, respectively, for molecules C and D. Thus, an infinite one-dimensional crinkled tape is formed. In two dimensions, adjacent tapes are arranged in antiparallel manner such that the two symmetry-independent molecules of **1** interact with each other through an O–H···O hydrogen bond (H···O, 1.81 and 1.85 Å, Table 2) between OH and COOH groups, which is supplemented by C–H···O hydrogen bonds (H···O, 2.67–2.79 Å, Table 2), as shown in Figure 3d. Thus, a ladderlike network is established in which the rods are the two symmetry-independent molecules of **1**, and the molecules of bpyea of particular symmetry (C or D) are rungs. Hence, two different types of ladders are formed, which are arranged in a crinkled manner, as shown schematically in Figure 3d. Thus, although the basic recognition pattern in **1b** is entirely different to either known pattern (Scheme 2) or that observed in **1a**, retention of the global packing motif and formation of a ladderlike structure suggests its stabilization in the solid state. However, cocrystallization of **1** and 4,4′-bipyridine gave an assembly (**1c**) that is clearly different from **1a** and **1b**.

Molecular complex of 3,5-dihydroxybenzoic acid and 4,4′-bipyridine (1c): Cocrystallization of **1** and bpy in a 1:1 ratio from methanol gave single crystals of **1c**. However, a CSD search[24] revealed that the crystal structure of **1c** with a 2:3 ratio is known. Furthermore, the unit-cell dimensions of **1c** synthesized by us ($a=9.666$, $b=14.359$ $c=14.769$ Å, $\alpha=63.21$, $\beta=83.22$, $\gamma=80.14°$) were similar to those of the reported structure ($a=9.683(1)$, $b=14.378(3)$, $c=14.797$

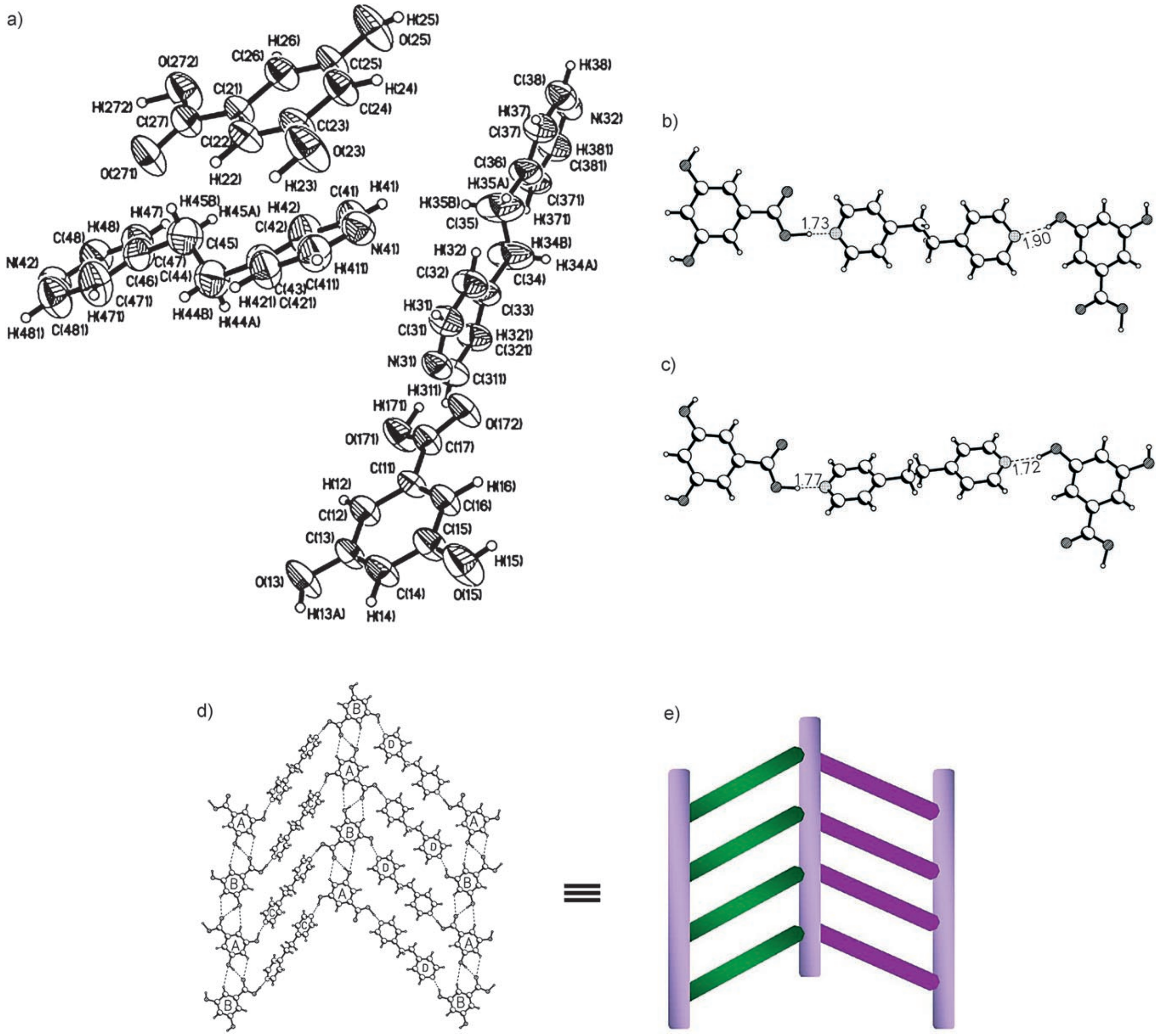


Figure 3. a) ORTEP plot of asymmetric unit of **1b**. b) and c) Different recognition patterns formed by the two symmetry-independent molecules of bpyea. d) and e) Two-dimensional ladderlike arrangement in the crystal lattice and its schematic representation. The different colors of rungs in the ladder represent different symmetry-independent molecules.

(3) Å, $\alpha = 63.17(6)$, $\beta = 83.25(11)$, $\gamma = 80.17(10)$°), so we did not proceed with the determination of the crystal structure of **1c**.

However, the focus of the study was to compare the ability of the COOH group to yield O−H···N hydrogen bonds with N-donor compounds in a series of carboxylic acids. Thus, emphasis on the three-dimensional networks was altogether different, and the competitive nature of different functional groups was not addressed. Hence, we continued our analysis using the data retrieved from the CSD, as it is an accurate structure with good *R* factor.

In **1c**, the basic recognition pattern (Figure 4) is quite intriguing, as the recognition feature shown in Scheme 2 is formed, with a network of cyclic tetramers comprising two molecules each of **1** and bpy, formed through O−H···N hydrogen bonds (H···N, 1.89–1.98 Å, Table 2) involving the OH groups. Such adjacent units are held together by an additional molecule of bpy by forming O−H···N/C−H···O pairwise hydrogen bonds (H···N 1.85 Å, H···O 2.97 Å) between the COOH group and the N atom (see Figure 4a). As a result an infinite open braceletlike structure is formed, which is represented in a close-packing mode in Figure 4b.

Thus, the two functional groups OH and COOH interact with bpy as if they were on two different molecules. Furthermore, adjacent bracelets are held together differently in different directions of packing. The two orientations are shown in Figure 4c and d. Along the *a* axis, adjacent bracelets are held together by a combination of C−H···O hydrogen bonds and π–π interactions, as shown in Figure 4c. Along the *b* axis, however, a combination of O−H···N (H···O 1.89 Å) and

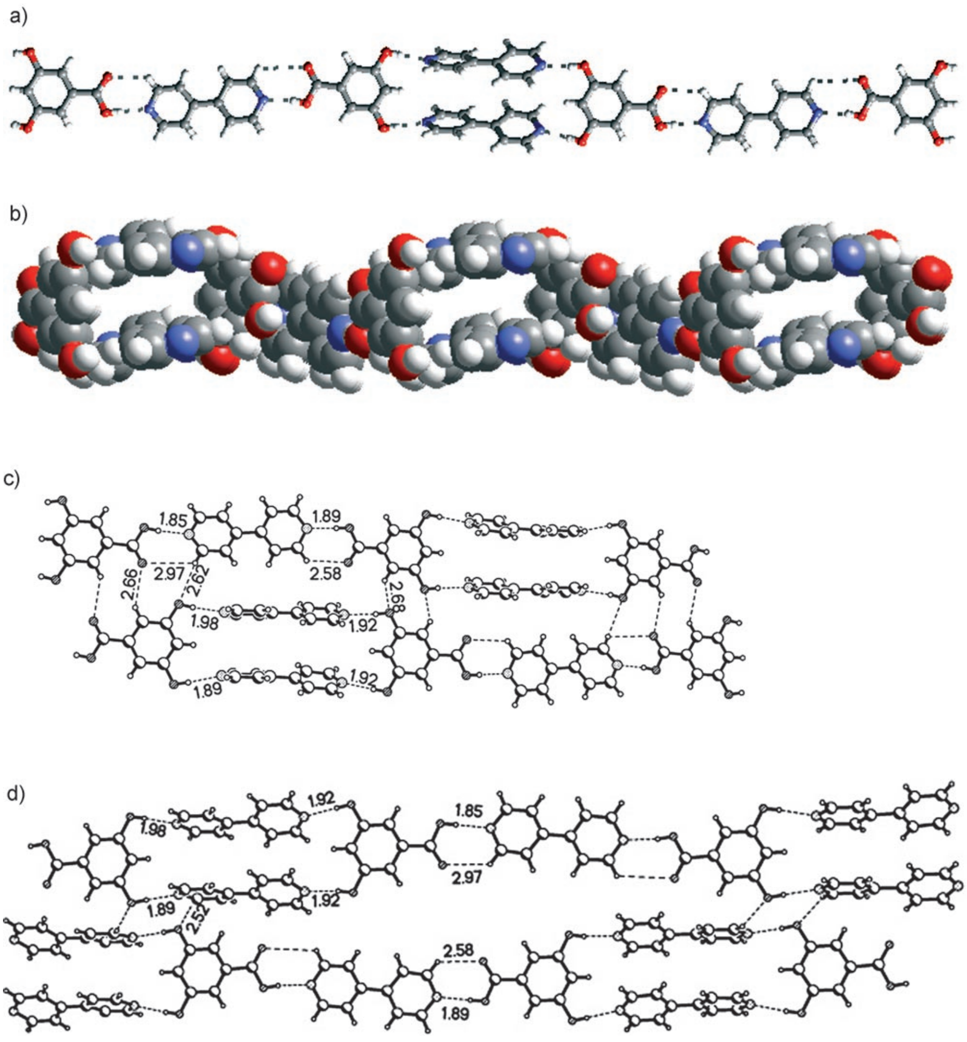


Figure 4. a) Basic recognition pattern and formation of molecular tape in **1c**. b) Arrangement of adjacent tapes in a braceletlike network. c) Close-packed model of the bracelet (along *a* axis) shown in b). d) Arrangement of the tapes in the perpendicular direction forming an unusual tetrameric hydrogen-bonding network.

C–H···O (H···O, 2.52 Å) hydrogen bonds binds adjacent rings in a quartet manner. In fact, this quartet network is a novel pattern in supramolecular structures and may be utilized in strategic design to prepare novel assemblies in future.

However, it is quite surprising that in the three-dimensional arrangement, despite its having the expected cyclic molecular component, a ladderlike structure did not form. Since subtle variations have been observed among **1a**–**1c**, the study was extended to further molecular complexes while keeping the OH and COOH groups intact. To this end, we considered bulky halo substituents, with their anomalous electronic effects on aromatic moieties and their ability to form the pattern shown in Scheme 2, as exemplified by the studies of MacGillivray et al.,[22] and attempted cocrystallization of halo derivatives of **1** with the N-donor compounds. However, we were successful only in obtaining single crystals of complexes of 4-bromo-3,5-dihydroxybenzoic acid with bpyee, bpyea, and bpy.

Molecular complex of 4-bromo-3,5-dihydroxybenzoic acid and 1,2-bis(4-pyridyl)ethene (2a): Cocrystallization of 4-bromo-3,5-dihydroxybenzoic acid (**2**) and bpyee from methanol gave single crystals of (**2a**) with a 2:1 ratio of **2** and bpyee in the asymmetric unit (Table 1). The structure is fully ordered (Figure 5a).

Among the complexes studied so far, deprotonation of COOH occurred only in **2a**. Furthermore, recognition between **2** and bpyee is established through the carboxylate group and the protonated N atom of bpyee by formation of $N^+–H···O^-$ ($H···O^-$ 1.67 Å) and C–H···O (H···O 2.40 Å) pairwise hydrogen bonds. The recognition pattern is shown in Figure 5b. The resultant three molecular ensembles are further held together in a perpendicular direction by an interaction between carboxylate and OH groups (Figure 5c) by formation of O–H···O hydrogen bonds (H···O 1.78 and 1.83 Å). Thus, in the two-dimensional arrangement, in each chain Br atoms on molecules of **2** lie on the same side of the chain (Figure 5d).

It is also evident from Figure 5d that complex **2a** also has a ladder structure, but not exactly as was observed in **1a** and **1b**. All the acid molecules that constituted rods of the ladders in **1a** and **1b** lie in the same plane, while they are twisted by almost 90° in **2a**. Also, the ladders are formed as discrete units, whereas in **1a** and **1b** adjacent ladders share edges. It could be rationalized that the Br substituent could perturb the basic recognition patterns, perhaps due to electronic effects on the molecular structures of the reactants, without any significant dramatic changes in the three-dimensional arrangement in the crystal lattice. This is indeed well reflected in the structure of **2b**, which was synthesized to evaluate the influence of the heavy atom Br in the light of the unusual observations made in **2a**, such as deprotonation and subtle variations in the formation of ladders.

Molecular complex of 4-bromo-3,5-dihydroxybenzoic acid and 1,2-bis(4-pyridyl)ethane (2b): Cocrystallization of **2** and bpyea resulted in formation of 2:2 complex **2b**, with two molecules of each reactant in the unit cell (Table 1). An

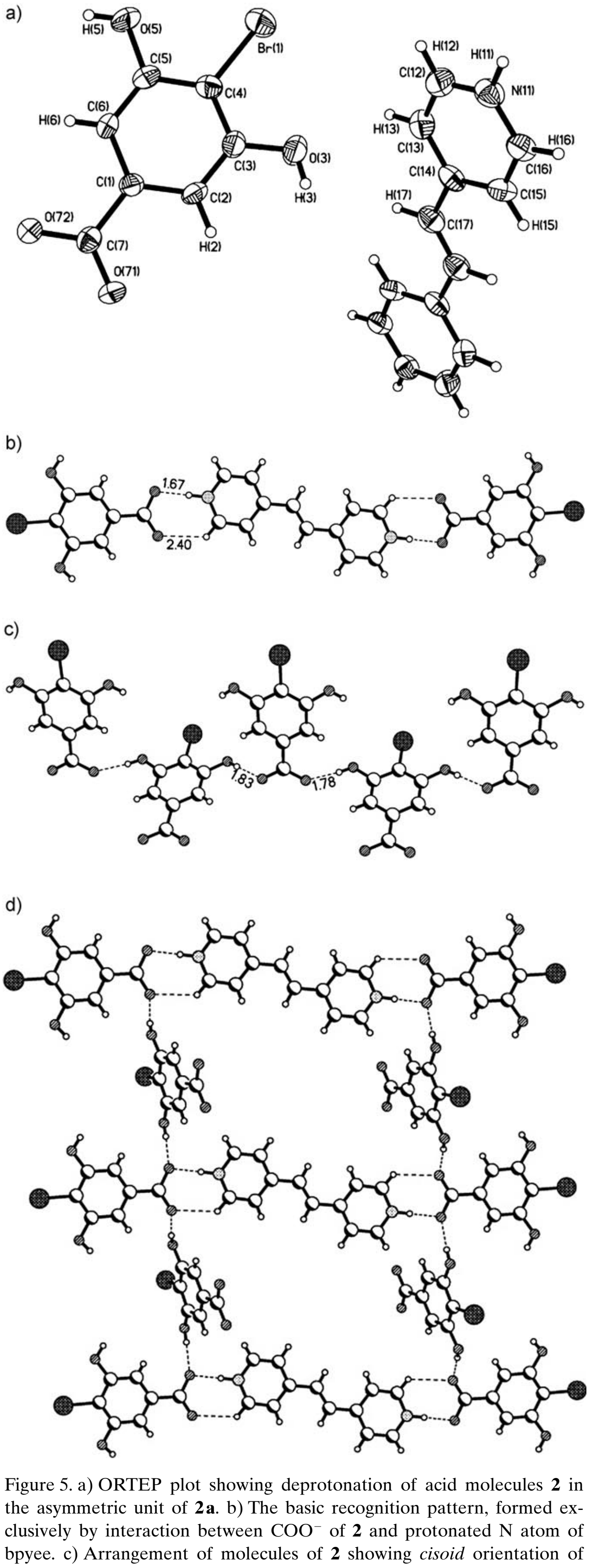


Figure 5. a) ORTEP plot showing deprotonation of acid molecules **2** in the asymmetric unit of **2a**. b) The basic recognition pattern, formed exclusively by interaction between COO^- of **2** and protonated N atom of bpyee. c) Arrangement of molecules of **2** showing *cisoid* orientation of Br atoms. d) Two-dimensional arrangement of the molecular ensembles in **2a** (viewed along *a* axis).

ORTEP plot of **2b** is shown in Figure 6a. The two molecules of bpyea in **2b** differ in the ethylene bridges, one of which is fully ordered, while the other is disordered in the ratio of 68:32.

In the three-dimensional arrangement, these molecules pack to form sheets stacked along the *b* axis (Figure 6b). The interactions among the molecules in the sheets are quite intriguing and show many common features with the packing observed in **1b**.

As observed in **1b**, the two molecules of bpyea interact with **2** in different modes. In one case, a disordered molecule of bpyea forms O−H···N hydrogen bonds (H···N 1.70 Å) exclusively by interacting only with a COOH group. The second molecule of bpyea, with a perfectly ordered ethylene bridge, interacts with **2** exclusively by forming O−H···N hydrogen bonds (H···N 1.92 Å) involving only OH groups. Thus, an infinite chain of alternately ordered and disordered bpyea molecules are separated by molecules of **2**, results. These chains, in two-dimensions, yield a sheet structure by formation of O−H···O hydrogen bonds (H···O 2.03 Å) between OH and COOH groups (Figure 6d). As a result, a ladderlike structure is formed, exactly as observed in **1b**, in which alternating ladders have bpyea molecules of different orientation. Such similar global packing between **1b** and **2b** further supports that the role of Br is limited to variations in the molecular geometry and basic recognition patterns, without any influence on the ultimate three-dimensional packing features. However, the influence of the Br atom in a unilateral manner is observed in complex **2c**, formed between **2** and bpy.

Molecular complex of 4-bromo-3,5-dihydroxybenzoic acid and 4,4-bipyridine (2c): Cocrystallization of acid **2** with bpy from methanol occurred in a 1:1 ratio to give **2c** (Table 1). There are no anomalous features about the molecular geometry of the product, as the structure is well refined without any ambiguity. However, the packing arrangement in the crystal lattice is fascinating in many aspects. The basic recognition between **2** and bpy involves both COOH and OH groups, which form O−H···N hydrogen bonds as in **1c**.

In **2c**, each bpy interacts with two molecules of **2** forming O−H···N hydrogen bonds (H···N 1.92 Å) with OH groups and pairwise O−H···N (H···N 1.74 Å) and C−H···O (H···O, 2.71 Å) hydrogen bonds formed by COOH groups. Thus, a one-dimensional crinkled tape (Figure 7a) is formed, which is quite usual feature of this type of recognition process that was observed in earlier examples, too. However, the interaction between adjacent tapes and the resulting three-dimensional arrangement is quite fascinating.

The one-dimensional units are held together by forming a four-membered O−H···N and C−H···O hydrogen-bond coupling (inset of Figure 7b). The H···N and H···O distances are 1.92 and 2.44 Å, respectively. Interestingly, a similar network was observed in the crystal structure of complex **1c**, which is formed by bpy with **1** instead of **2**. Thus a huge void space, (12×29 Å^2) results, as observed in many other organic assemblies (see Figure 7c). Since such void structures are quite

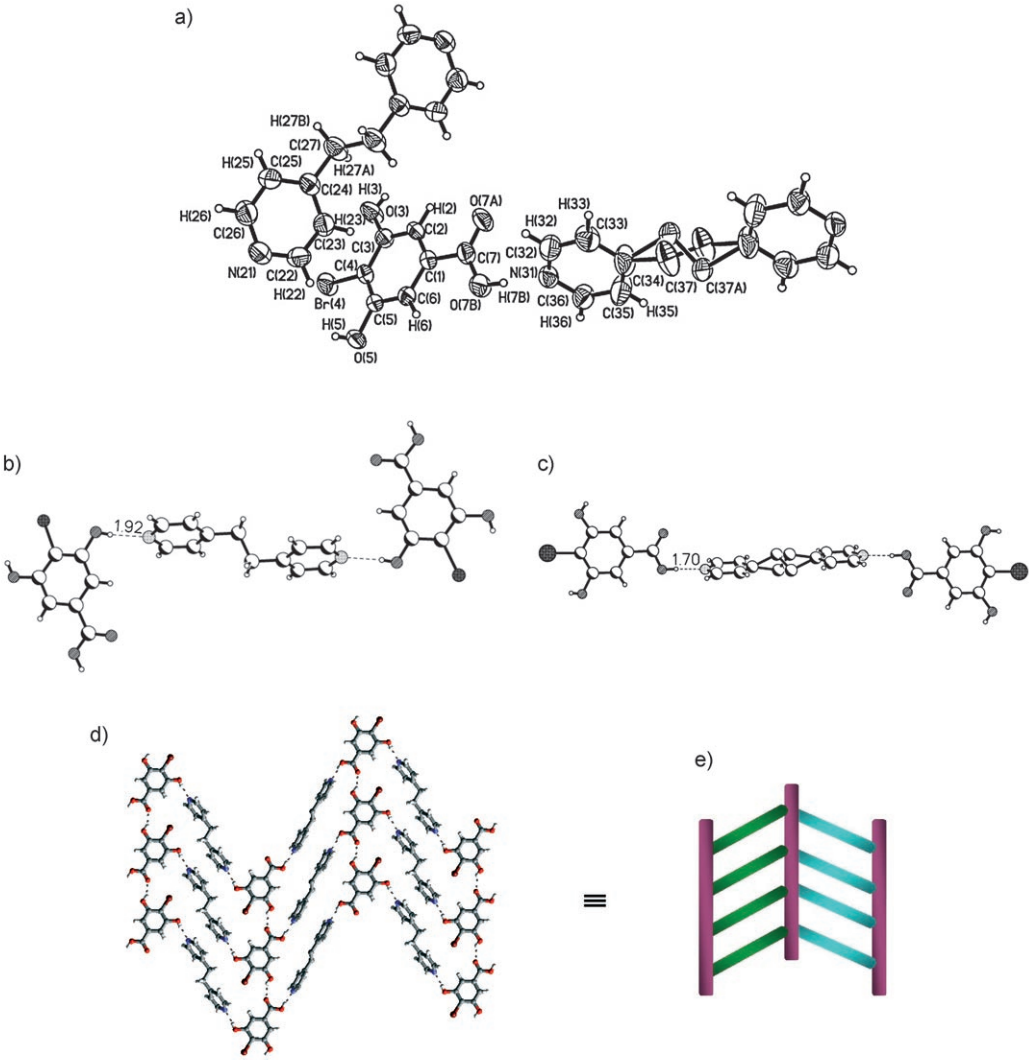


Figure 6. a) ORTEP plot of **2b** showing disorder around the methylene bridge in one of the molecules of bpyea. b) and c) Different recognition patterns shown by the two molecules of bpyea with acid **2**. d) Two-dimensional arrangement of the ensembles formed by the two different molecules of bpyea with **2**, yielding a ladderlike structure. e) Schematic representation of the ladder (viewed along *c* axis).

unstable, they are generally occupied by guest species if an appropriate molecule is available; otherwise, catenation or interpenetration result through self-assembly. In complex **2c**, as no guest species is present, the void space is filled by a self-assembly process leading to exotic threefold interpenetration (Figure 7d). The three units are shown in different colors for a better understanding of the interpenetration. Although the Br atom is not involved directly in any appreciable nonbonding interactions or hydrogen bonds, its effect is fully reflected in the formation of an interpenetrated network structure, despite the similar nature of interactions to those observed in **1c**, perhaps due to its bulky nature.

From ladders to interpenetration and host–guest networks: It is apparent from the study of molecular complexes **1a**–**1c** and **2a**–**2c** that ladderlike structure are predominately formed in **1a**, **1b**, **2a**, and **2b**, whereas **1c** and **2c** completely deviate from this behavior. In particular, it is noteworthy that bpy as spacer molecule did not yield ladderlike structures with either **1** or **2**. However, bpyea, irrespective of the nature of the acid, gave the same type of supramolecular structure, whereas bpyee showed variations, and it is not possible to draw firm conclusion on its behavior, as the deprotonation of the acid molecule in complex **2a** can significantly change the overall packing pattern. However, the observed transition from ladders to interpenetration could be related to the dimensions of the molecular components and their ability to form closed ensembles. In this process, if the dimension of the void space is within the van der Waals limits, a regular ladderlike structure results, otherwise an interpenetrated or host–guest network would be formed. A schematic representation of the relations among the global architectures is shown in Scheme 4.

Conformational differences of the OH groups in complexes 1a–1c and 2a–2c: A collective analysis of all the complexes

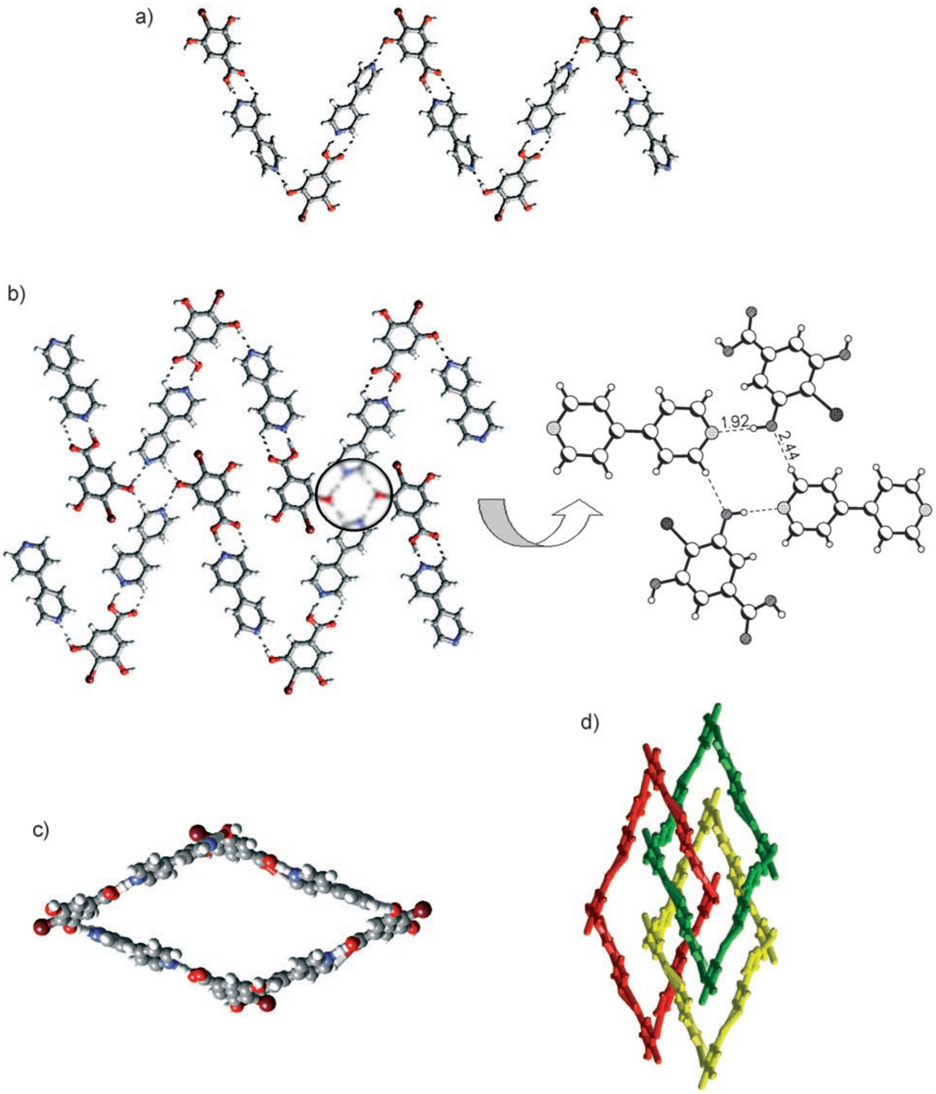
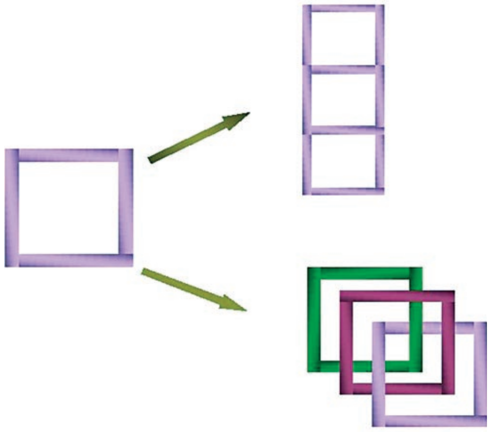


Figure 7. a) Recognition pattern between **2** and bpy through the formation of O−H⋯N and O−H⋯N/C−H⋯O pairwise hydrogen bonds between OH and COOH, respectively, with N atoms to form a crinkled tape. b) Arrangement of the adjacent tapes, held together by a fourfold hydrogen-bonding pattern involving O−H⋯N and C−H⋯O hydrogen bonds. c) Void space in tetrameric unit shown in b). d) Filling of the void space by interaction between the adjacent tapes and threefold interpenetration (viewed along *a* axis).



Scheme 4.

reveal that the conformations of acids **1** and **2** in **1a**–**1c** and **2a**–**2c** are different due to the differences in the arrangement of OH groups, and it appears that this is the prime factor in the formation of specific structural arrangements. The different conformations observed are shown in Figure 8. In **1a** and **1c** the OH group adopts a *syn–syn* arrangement, while in **2a** and **2c** the hydroxyl groups are in *anti–anti* arrangements. In **1b** and **2b**, the arrangement is *syn–anti*.

The above classification is with respect to the orientation of the H atom on the OH group towards the H/Br atom at the *para* position on molecules **1** and **2**. It is apparent that bpy and bpyee directed the *syn–syn* conformation in **1**, while they induced the *anti–anti* conformation in **2**. In contrast, bpyea always strongly favored the *syn–anti* conformation. This could be the reason for the formation of same lad-

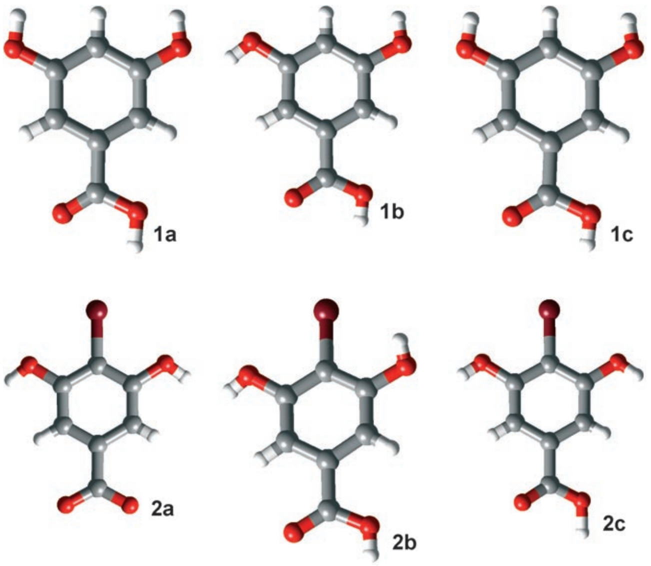


Figure 8. Representation of different conformations of **1** in complexes **1a**–**1c** and **2** in complexes **2a**–**2c**.

derlike structure in **1b** and **2b**, whereas the nature of the global structure varied in the other complexes due to the variations in the conformations of the OH groups. Furthermore, the *syn–anti* arrangement is intact in both **1b** and **2b**, irrespective of the presence of a Br atom. Similarly, the *anti–anti* arrangements in **2a** and **2c** could also be attributed to the bulky nature of the Br atom. Although global packing and molecular interactions could not give conclusive information about the role of the Br atom, the conformational analysis more or less demonstrates its size effect, based on the observed variations in the lattice arrangements between **1a**–**1c** and **2a**–**2c**.

Conclusion

We have synthesized and structurally evaluated molecular complexes **1a**–**1c** and **2a**–**2c** to account for the basic recognition pattern between the constituents. It is evident that the affinities of COOH and OH groups towards N-donor compounds are fairly competitive, and this is in a way reflected in the formation of different recognition patterns. However, the global packing arrangement is not much perturbed, perhaps due to the operation of same principles in all the complexes, that is, effective space filling in accordance with crystallographic symmetry rules. Thus, ladderlike structures and interpenetrated networks appeared, depending on the size of the available molecular components and dimensions of resultant void space. Furthermore, the role of a Br substituent is enigmatic, as it appears to be dominated by its electronic nature in the basic recognition aspect, but in a molecular analysis, the role of its bulky nature is more predominant. Nevertheless, the packing arrangements in **2a**–**2c** are not that different from those of unsubstituted structures **1a**–**1c**, except for **2c**. We believe that a large number of further examples are required to draw authentic conclusions on the effects of various functional groups on the robustness of formation of four-membered cyclic units as depicted in Scheme 2. To this end, we are synthesizing and analyzing other halogen derivatives and also those with other functional groups such as nitrile, nitro, and amide moieties.

Experimental Section

Preparation of molecular complexes 1a–1c and 2a–2c: All chemicals, reagents, and solvents were obtained from commercial suppliers and used without further purification. We used spectroscopic-grade solvents in all cocrystallization studies. All cocrystals **1a**–**1c** and **2a**–**2c** were prepared by dissolving the respective reactants in a ratio of 1:1 in CH_3OH and allowing the solvent to evaporate under ambient conditions. In all cases, single crystals suitable for X-ray diffraction analysis were obtained within 3 d.

In a typical cocrystallization experiment 4-bromo-3,5-dihydroxybenzoic acid (**2**, 0.094 g, 0.400 mmol) and 1,2-bis(4-pyridyl)ethene (bpyea, 0.072 g, 0.400 mmol) were dissolved in MeOH (8 mL) in a 25 mL conical flask by warming on a water bath. The resultant solution was allowed to evaporate under ambient conditions, and colorless single crystals were obtained in 2 d. The crystals were separated from the mother liquor by filtration, washed with ice-cold CH_3OH, and dried under vacuum.

Crystal structure determination: Single crystals were analyzed under a Leica microscope equipped with a CCD camera, and good-quality crystals were chosen for structure determination by x-ray diffraction with a Polaroid detector. The crystals were mounted on a goniometer by gluing to a glass fiber with cyanoacrylate adhesive, and crystal data were collected on a CCD diffractometer with APEX detector. The intensity data were processed using SAINT[23] software of the Bruker suite of programs. The structures were solved and refined using the SHELXTL package,[23] and no anomalies were observed at any stage of structure solutions. The final crystallographic details and data collection strategies are given in Table 1. All calculations of intermolecular interactions listed in Table 2 were done with PLATON.[25]

CCDC-278691–278695 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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