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Carboxylic Acid and Phenolic Hydroxyl Interactions in the Crystal Structures of Co-Crystals/Clathrates of Trimesic Acid and Pyromellitic Acid with Phenolic Derivatives

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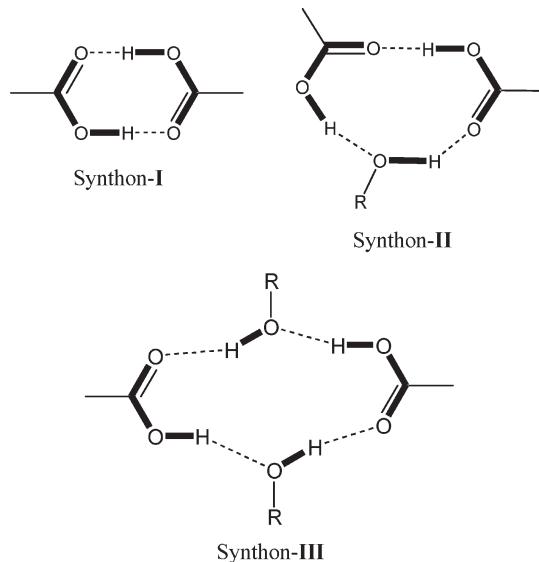
ABSTRACT: Crystallization of trimesic acid (H_3TMA) in the presence of phenol resulted in the single crystals of $[(H_3TMA) \cdot (\text{phenol})]$, **1**. The crystal structure consists of two-dimensional hydrogen bonding layers with herringbone geometry via an acid-phenol synthon in which the O–H group of phenol inserts into a conventional acid dimer in an unsymmetrical fashion. The consistency and robustness of this observed phenomenon were confirmed by reproducing a similar structure by treating H_3TMA with *m*-cresol $[(H_3TMA) \cdot (m\text{-cresol})]$, **2**. On the other hand, similar reactions with H_4PMA resulted in unprecedented clathrates of H_4PMA containing a square grid network via a conventional acid synthon. The square grids have dimensions of $8.3 \times 8.3 \text{ \AA}$ and clathrate phenolic guests. Our studies indicate that H_4PMA can act as a host only for the phenolic derivatives such as phenol $[(H_4PMA) \cdot (\text{phenol})]$, **3**, *o*-cresol $[(H_4PMA)_2 \cdot (o\text{-cresol})]$, **4**, *p*-cresol $[(H_4PMA)_2 \cdot (p\text{-cresol})]$, **5**, and *p*-chlorophenol $[(H_4PMA)_2 \cdot (p\text{-chlorophenol})]$, **6**.

Introduction

Crystal engineering offers an excellent opportunity to synthesize self-assembled structures through a supramolecular synthon approach via noncovalent synthesis.¹ For such an exercise, the precise knowledge of supramolecular synthons, the frequency of synthon occurrence, and the exploration of synthon robustness in the presence of other hydrogen bonding groups is essential. Hydrogen bonded supramolecular synthons are commonly used to build the co-crystals or organic-based self-assembly because of their strength and directionality.^{1,2} Molecules containing multiple carboxylic groups such as trimesic acid (H_3TMA) and pyromellitic acid (H_4PMA) are of particular interest as building blocks for the synthesis of salts, co-crystals, and clathrates.³ The combination of 3-fold symmetry and robustness of the carboxylic acid dimeric synthon makes H_3TMA an ideal building block in crystal engineering. H_3TMA is known to form open and interpenetrated honeycomb networks containing cavities of dimensions $14 \times 14 \text{ \AA}$.⁴ These hexagonal cavities were shown by us to be expanded up to $42 \times 42 \text{ \AA}$ in the co-crystals of H_3TMA with the molecules containing bis-pyridine units (spacers).⁵ Further, recently the honeycomb networks of H_3TMA were shown to be truncated in the crystal structures of acetic acid and MeOH solvates of H_3TMA .⁶ Although the synthon-**I** is a robust synthon, it was shown in several cases that it can be expanded or disrupted by the inclusion of water or alcohols to form synthons-**II** and -**III**. For example, the crystal structure of the mono hydrate of H_3TMA exhibits synthon-**II**.⁷ Further, H_3TMA was also shown to form co-crystal with 1,3,5-trihydroxybenzene in which none of these synthons (**I**–**III**) were observed.⁸ However, the crystal structures of H_3TMA with *p*-hydroquinone or resorcinol exhibit a general honeycomb network in which the O–H group does not show any interference.⁹ These observations motivated us to investigate the effect of phenolic derivatives in the crystallization of H_3TMA and H_4PMA .

On the other hand, pyromellitic acid (H_4PMA) has drawn attention for its 4-fold symmetry and the presence of carboxylic acid groups on the benzene ring, especially for the construction of coordination polymers and preparation of salts with pyridine

containing derivatives.¹⁰ Compared to H_3TMA , H_4PMA has been less explored in organic crystal engineering. H_4PMA crystallizes as a dihydrate in which each water is hydrogen bonded to two carbonyl groups of two different H_4PMA molecules.¹¹ However, in this structure the molecular symmetry is not transferred into the symmetry of network due to the inclusion of water molecule. Therefore, the most expected square grid network via conventional carboxylic acid dimer or clathrates with H_4PMA have not been realized yet. Therefore, herein we report our results on crystallization reactions of H_3TMA and H_4PMA in the presence various phenolic derivatives. We note here that to date no crystal structure of any carboxylic acid containing phenol as solvate was reported. Interestingly, in the case of H_3TMA , the hexagonal cavities were found to transform into rectangular cavities due to the formation of synthon-**II**, while in the case of H_4PMA the phenol derivatives template the square grid networks and form clathrates.



Results and Discussion

The crystallization of H_3TMA and H_4PMA with phenolic derivatives such as phenol, *m*-cresol, *p*-cresol, and *p*-chlorophenol

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Table 1. Crystallographic Parameters for Compounds 1–6

compound	1	2	3	4	5	6
formula	C ₁₅ H ₁₂ O ₇	C ₁₆ H ₁₄ O ₇	C ₁₆ H ₁₂ O ₉	C ₂₇ H ₂₀ O ₁₇	C ₂₇ H ₂₀ O ₁₇	C ₂₆ H ₁₇ ClO ₁₇
mol. wt.	304.25	318.27	348.26	616.44	616.44	636.86
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
system	monoclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	P ₂ 1/c	P ₂ 1/n	C2/m	P ₁	P ₁	C2/c
a (Å)	9.9470(5)	9.179(2)	10.247(1)	8.342(5)	8.537(8)	16.075(9)
b (Å)	15.7431(7)	15.460(3)	15.757(1)	9.621(6)	9.584(8)	10.529(6)
c (Å)	9.9494(5)	10.645(2)	5.093(1)	9.665(6)	9.584(8)	8.551(5)
α (°)	90	90	90	66.405(2)	66.297	90
β (°)	114.942(1)	91.261(7)	115.816(1)	71.27(2)	70.363(2)	114.207(2)
γ (°)	90	90	90	73.37(2)	70.363(2)	90
vol (Å ³)	1412.7(1)	1510.2(5)	740.2(2)	662.0(7)	657.7(1)	1320.0(1)
Z	4	4	2	2	2	4
D (Mg/m ³)	1.430	1.400	1.643	1.817	1.829	1.926
R ₁ (<i>I</i> > 2σ(<i>I</i>))	0.0422	0.0535	0.0654	0.0756	0.0852	0.0769
wR ₂ (on <i>F</i> ² , all data)	0.1394	0.1374	0.1855	0.2213	0.2265	0.1920

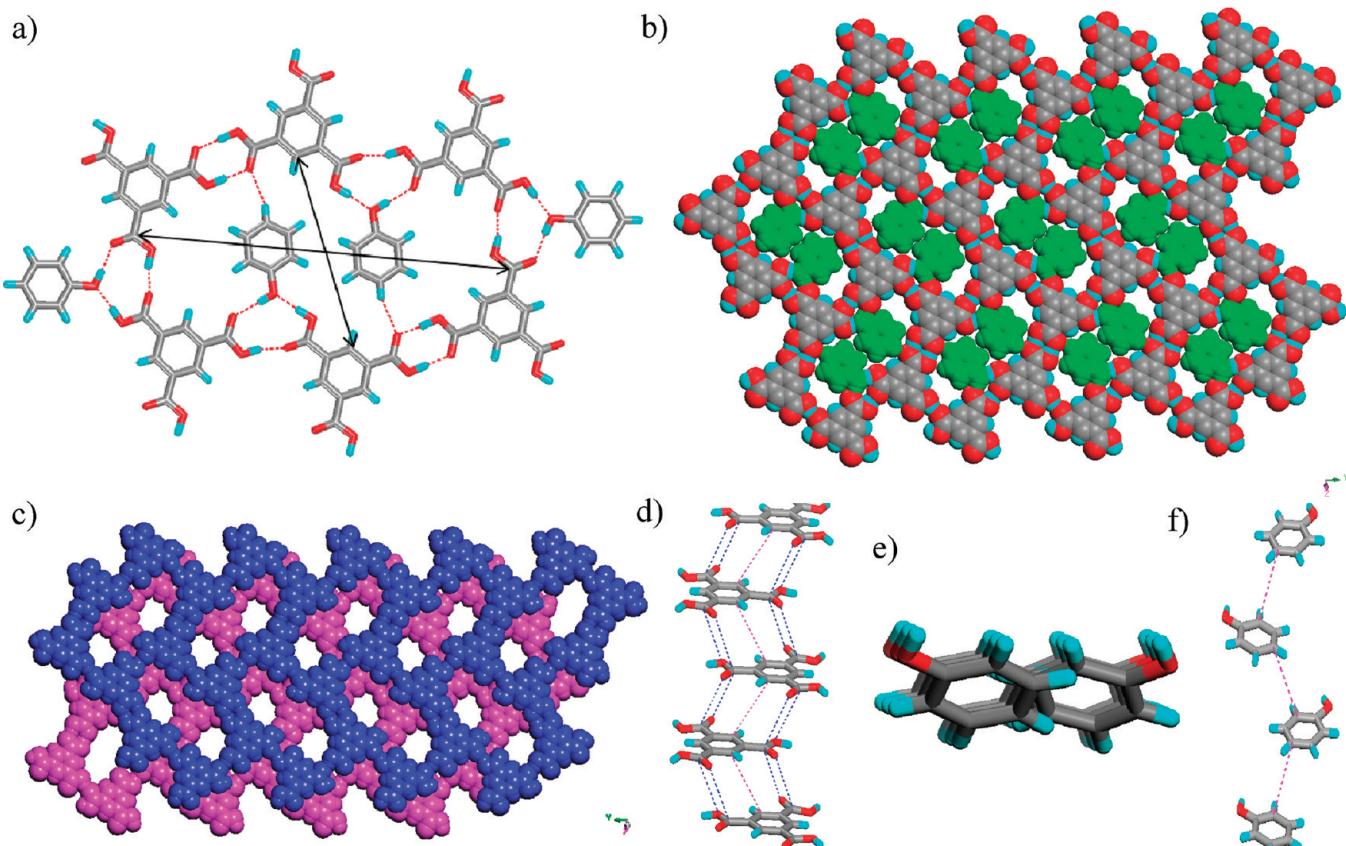


Figure 1. Illustrations for the complex **1**: (a) Part of 2D-layer constructed by synthon-**I** and -**II**; (b) space-fill representation of herringbone layer of H₃TMA units (phenol is shown in green color); (c) packing of adjacent layers; (d) interaction between H₃TMA molecules of adjacent layers; edge-to-edge aromatic interactions between phenols in the column; (e) top view; and (f) side view.

has been carried out by dissolving required amounts of acid and phenol in the minimum amount of MeOH. In the case of H₃TMA, the crystals suitable for single crystal X-ray diffraction analysis were obtained with phenol and *m*-cresol to yield complexes [(H₃TMA)·(phenol)], **1**, and [(H₃TMA)·(*m*-cresol)], **2**, respectively, whereas in the case of H₄PMA, the single crystals were obtained with four phenolic derivatives, namely, [(H₄PMA)·(phenol)], **3**, [(H₄PMA)₂·(*o*-cresol)], **4**, [(H₄PMA)₂·(*p*-cresol)], **5**, and [(H₄PMA)₂·(*p*-chlorophenol)], **6**. The crystallographic parameters and hydrogen bonding parameters for all the crystal structures are given in Tables 1 and 2, respectively.

The complex **1** crystallizes in P₂1/c space group and the asymmetric unit contains one molecule of H₃TMA and one

molecule of phenol. The crystal structure analysis of **1** reveals that the popular hexagonal arrangement of H₃TMA has been disrupted and phenol was inserted into two of the -COOH dimers to form synthon-**II**. One -COOH group exhibits conventional synthon-**I**, while two -COOH groups exhibit acid-phenol synthon-**II** (Figure 1a). Para hydrogen of phenol is also involved in a C–H···O (2.466 Å, 151.55°, 3.313 Å) hydrogen bond with the carbonyl of H₃TMA. Because of the formation of unsymmetrical synthon-**II**, the honeycomb network of H₃TMA has been modulated into a herringbone arrangement as shown in Figure 1b. The interpenetration observed in the crystal structures of H₃TMA (cavity dimension 14 × 14 Å) was eschewed here by the inclusion of aromatic rings of two phenol

units inside the cavity. The herringbone network contains a rectangular cavity of dimension $21.9 \times 11.5 \text{ \AA}$.

In **1**, the adjacent layers pack on to each other in AB fashion such that rectangular cavities of layers are nearly perpendicular to each other. Such arrangement generates the channels with a dimension of half of rectangular cavities across the layers (Figure 1c). The packing of the layers governed by edge-to-edge aromatic interactions between H_3TMA molecules

(closest C \cdots C distance 4.016 \AA) and dipole–dipole interactions between the carbonyl groups of H_3TMA ($\text{C}=\text{O}\cdots\text{C}$, 3.420 \AA) as shown in Figure 1d. Phenyl groups of phenols from adjacent layers also interact with each other via edge-to-edge aromatic interaction (closest C \cdots C distance 3.630 \AA) (Figure 1e,f).

The crystal structure of **2** also exhibits similar herringbone layers as those of **1** with some minor differences (Figure 2a,b). The cavities ($21.5 \times 12.0 \text{ \AA}$) of herringbone layer nicely adjust to accommodate additional methyl group of *m*-cresol. The packing of the layers differs significantly from that of **1**. In **2**, the layers pack in ABC type packing as each layer repeats itself after three layers (Figure 2c). Across the layer, rectangular channels exist which are occupied by a column of *m*-cresol molecules (Figure 2d–f). The phenol and *m*-cresol in **1** and **2** occupy 41% and 45% of crystal volumes, respectively.

The crystal structure of **3** exhibits $C2/m$ space group and the asymmetric unit contains half a molecule of H_4PMA and half a molecule of phenol. Unlike in **1** and **2**, the hydroxyl group of phenol here does not insert into the conventional synthon-**I**; rather it glues to the synthon-**I** via weak O–H \cdots O (2.854 \AA , 117.4° , 3.265 \AA) hydrogen bond with O-atom of -COOH. The H_4PMA units form an elusive 2D layer containing square grid geometry via synthon-**I** (Figure 3a). Each H_4PMA molecule interacts with four of its neighbors (Figure 3b). These layers pack on each other with a perfect overlap such that continuous channels exist across the layers. In these channels, the phenolic columns were included which accounts for 40% of

	type	H \cdots A (Å)	D \cdots A (Å)	D–H \cdots A (deg)
1	O–H \cdots O	hd-aa	1.84	2.703(2)
		ad-aa	1.67	2.640(2)
		ad-ha	1.71	2.657(2)
		Syn- I	1.59	2.647(2)
2	C–H \cdots O		2.47	3.314(3)
	O–H \cdots O	hd-aa	1.86	2.677(3)
		ad-aa	1.78	2.695(3)
		ad-ha	1.78	2.667(2)
3	O–H \cdots O	Syn- I	1.60	2.648(2)
	O–H \cdots O	Syn- I	1.94	2.658(3)
4	O–H \cdots O	Syn- I	2.694(4)	168
			2.685(4)	
			2.696(4)	
5	O–H \cdots O	Syn- I	2.662(5)	
			2.682(5)	
			2.678(6)	
6	O–H \cdots O	Syn- I	2.671(6)	
			2.647(6)	
			2.673(5)	
			2.666(5)	

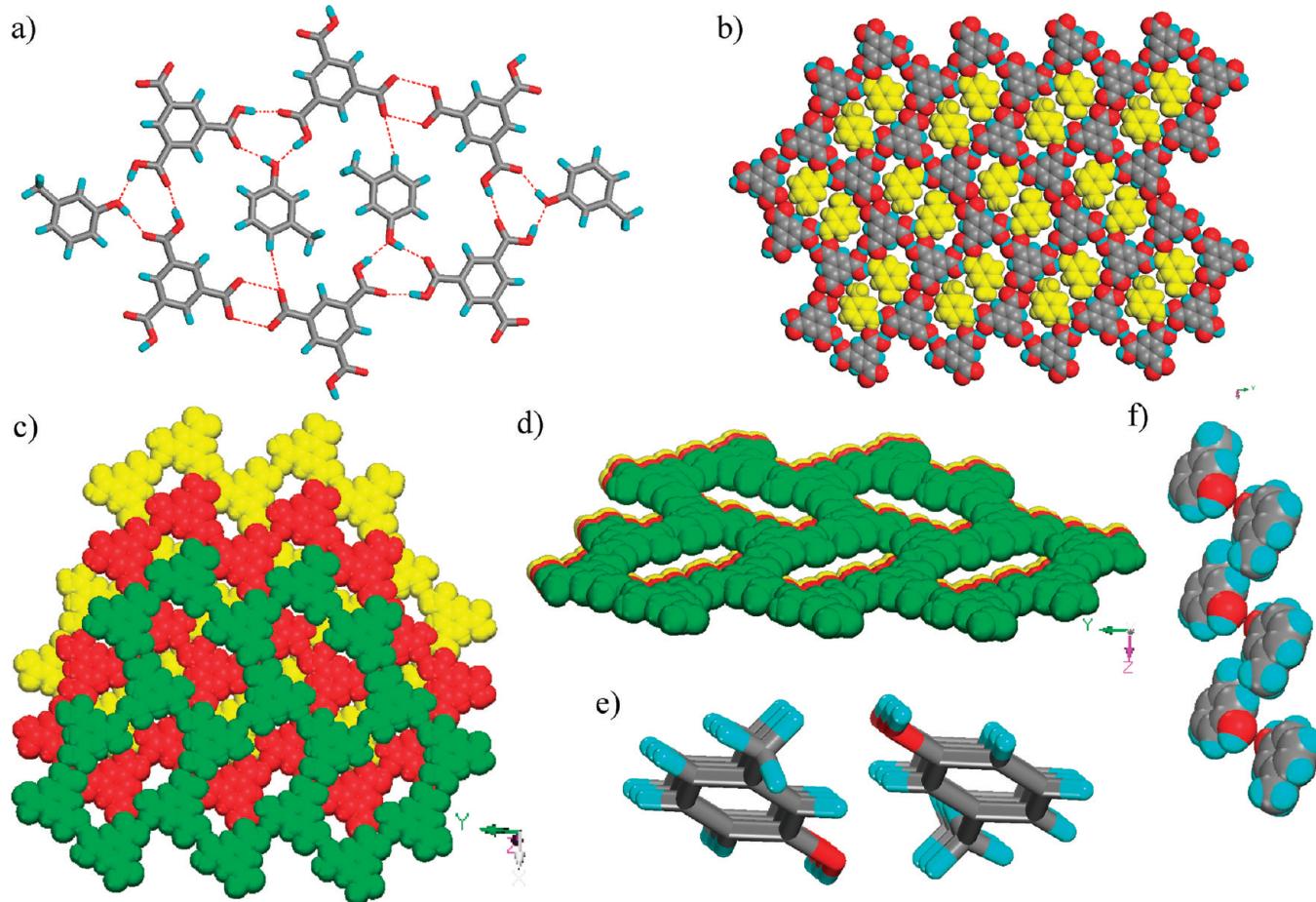


Figure 2. Illustrations for the complex **2**: (a) Part of H_3TMA 2D-layer and *m*-cresol constructed by synthon-**I** and -**II**; (b) space-fill representation of herringbone layer of H_3TMA molecules (phenol is shown in yellow color); (c) slipped packing of adjacent layers; (d) rectangular channels generated across the layers; and column of *m*-cresol: (e) top view and (f) side view (space-fill mode).

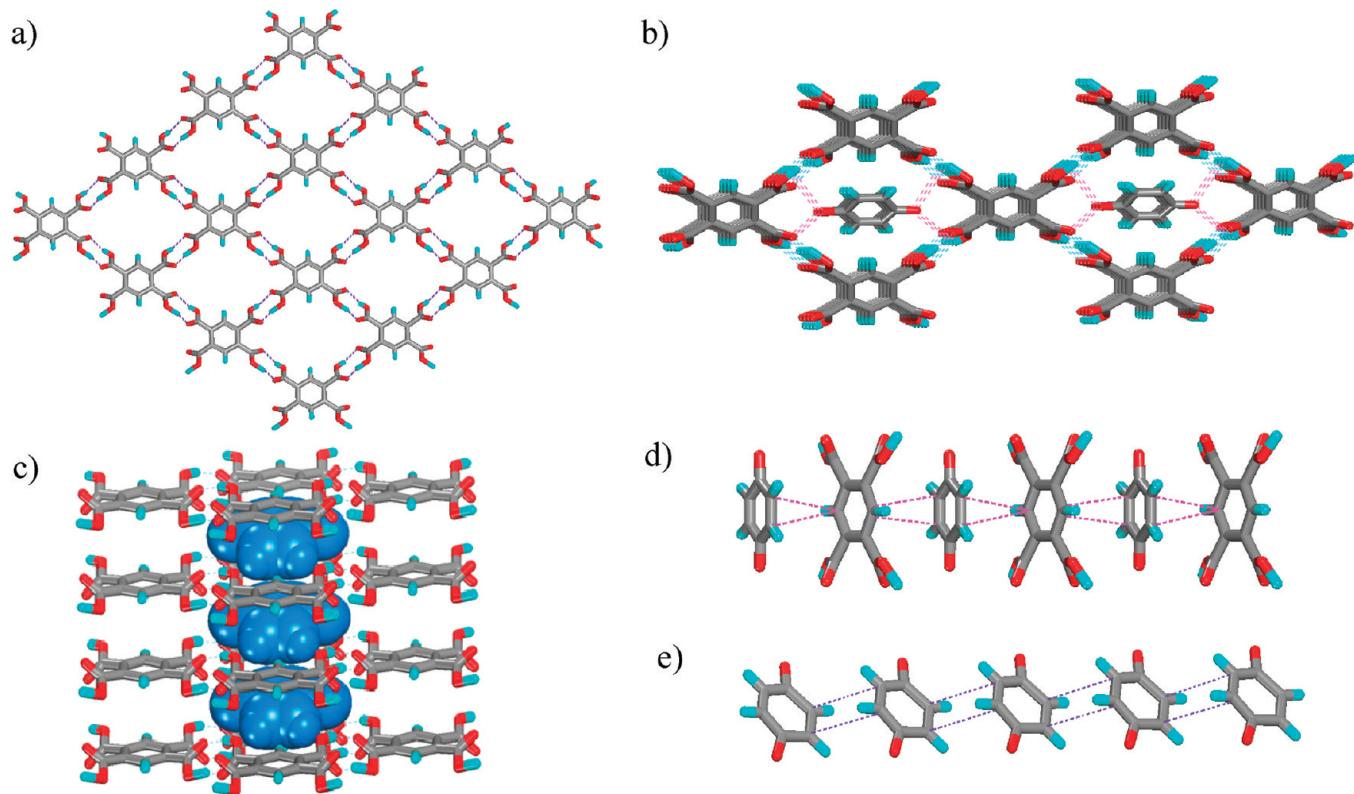


Figure 3. Illustrations for the complex **3**: (a) square grid networks of H₄PMA; (b) one H₄PMA is hydrogen bonded to four H₄PMA via synthon-**I** and weak O-H···O hydrogen bonds between phenol and H₄PMA; (c) enclathration of phenol (disordered) in between the adjacent layers; (d) edge-to-edge aromatic interactions between phenol and H₄PMA; (e) edge-to-edge aromatic interactions between phenols in the column.

the crystal volume. In the column, the phenols interact with each other via edge-to-edge aromatic interactions (closest C···C distance 3.431 Å) (Figure 3c).

Interestingly, somewhat bigger guest molecules such as *o*-cresol, *p*-cresol, and *p*-chlorophenol were also found to include in H₄PMA square nets by reducing the amount of guest to half in **4**, **5**, and **6**, respectively.

Complexes **4** and **5** containing *o*-cresol and *p*-cresol, respectively, crystallize in *P*̄*1* space group. In both cases, the asymmetric unit contains two half units of H₄PMA and a half molecule of cresols. The H₄PMA moieties form similar 2D-layers as observed in **3**. The cresol molecules exhibited disorder which could not be modeled. Although the 2D-layers in **4** and **5** have similar features as those of **3**, the packing of the layers and the geometry of guest inclusion with respect to the layer differ significantly. In **3**, the overlapped synthon-**I** of adjacent layers are parallel to each other, while they are perpendicular to each other in **4** and **5** (Figure 4). This change in orientation could be partly attributed to the change in H₄PMA geometry: in **3**, all the -COOH groups of H₄PMA maintain nearly equal angles (~38°) with a central C₆-ring, while in **4** or **5** the two -COOH groups make different angles (~22° and ~66°) with central C₆-ring. Further, in both cases, the adjacent layers are symmetry independent layers. Because of this type of arrangement of the layers the guest molecules have different orientations of inclusion with respect to the layer. In **3**, the guest molecule phenol is almost parallel to the 2D layer, whereas in **4** or **5** the disordered cresol molecules are inserted within the square unit of H₄PMA such that they are perpendicular to the 2D layers (Figures 3c and 4c). The edge-to-edge aromatic interactions between H₄PMA molecules (closest C···C distance: 3.770 Å)

and dipole–dipole interactions between -COOH groups of H₄PMA (O=C···O=C distance 3.2–3.5 Å) govern the interlayer packing (Figure 3d–f). *o*-Cresol and *m*-cresol occupies 31% and 32% volume of the crystal lattice, respectively.

The crystal structure of **6** exhibits *C*2/*c* space group, and the asymmetric unit is constituted by the half of H₄PMA unit and one-fourth of the guest which is highly disordered and could not be located. The crystal structure has similar features as those of **4** and **5** with the exception that the adjacent layers are symmetry related. The guest *p*-chlorophenol occupies the same volume (32%) as those in **4** and **5**.

We have carried out the CSD analysis for synthons-**II** and -**III** to investigate their frequency of occurrence and geometrical features.¹² Further, it is interesting to note here that the synthon-**II** is constituted by three types of O-H···O hydrogen bonds: acid donor to acid acceptor (ad-aa), hydroxyl donor to acid acceptor (hd-aa), and acid donor to hydroxyl acceptor (ad-ha). Generally, given acid and base strengths one would anticipate the following order in their hydrogen bond strengths: ad-ha > ad-aa > hd-aa. We have carried out the searches for alcohol and water molecules separately. The results are tabulated in Table 3. The synthon-**II** with water and alcohol was observed in 23 and 11 crystal structures, respectively. The mean values of O···O distances confirm the anticipated trend (ad-ha (2.559 Å)>ad-aa (2.619 Å) > hd-aa (2.773 Å)). Similar observations also are found in the case of synthon-**III** where 51 crystal structures were observed with water. Further, the asymmetric (**II**) and symmetric (**III**) nature of synthons was clearly reflected in their O···O distances. Another interesting observation was that both these synthons were found to exhibit by the molecules containing multiple –COOH groups. In the case of synthon-**II**

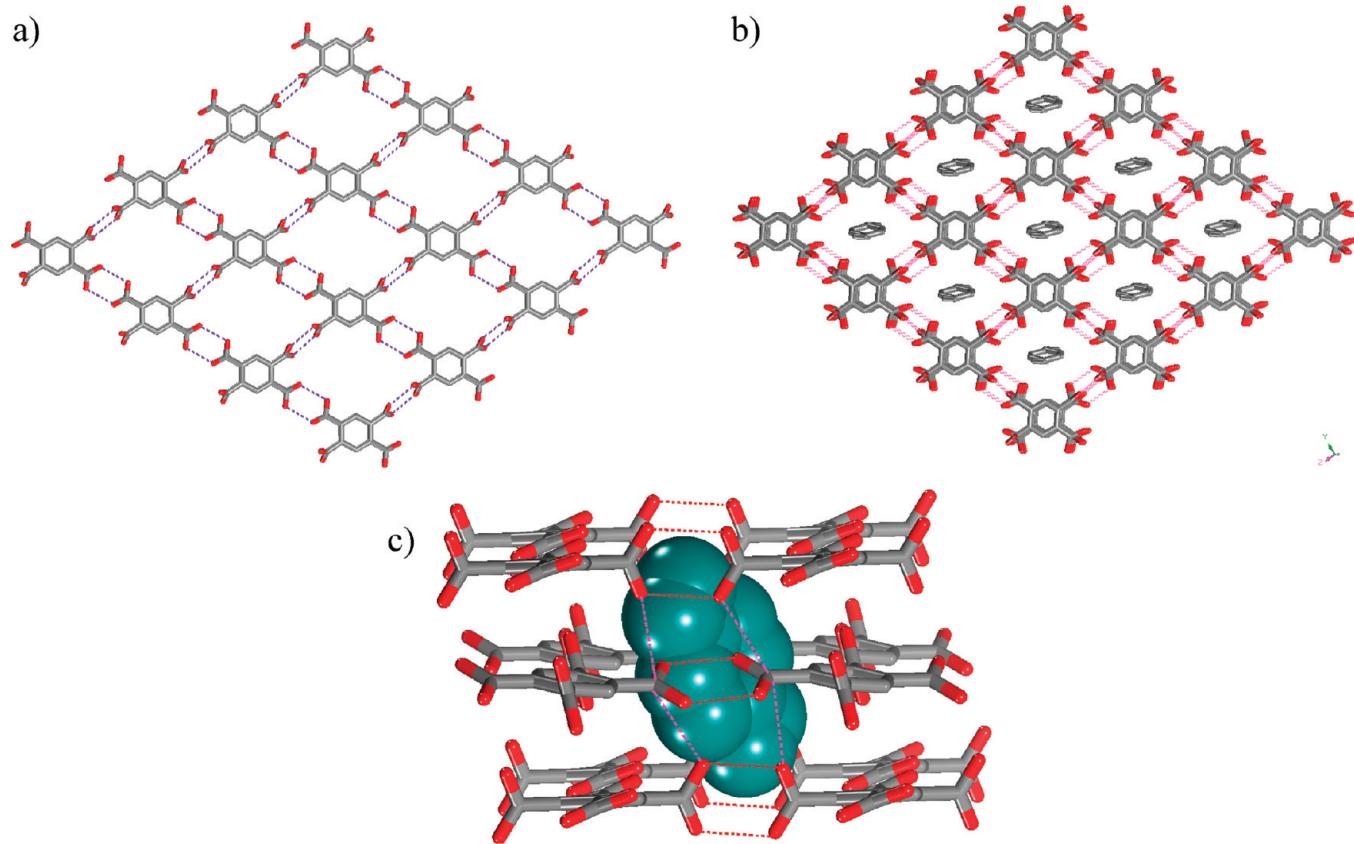


Figure 4. Illustrations for the complex **5**: (a) square grid network of H_4PMA ; (b) packing of the H_4PMA layers; notice the inclusion of disordered *p*-cresol in the channels; (c) enclathration of *p*-cresol in between the adjacent layers (notice the orientation of *p*-cresol with respect to H_4PMA layer and compare with Figure 3c).

Table 3. CSD Analysis for Synthon-II and -III

	O···O	min	max	mean	no. of obs
R=C for II	ad-aa	2.594	2.647	2.619	11
	hd-aa	2.650	2.814	2.773	
	ad-ha	2.476	2.604	2.559	
R=H for II	ad-aa	2.548	2.755	2.634	23
	hd-aa	2.577	2.931	2.829	
	ad-ha	2.489	2.793	2.613	
R=C for III	hd-aa	2.626	2.796	2.738	85
	ad-ha	2.533	2.771	2.625	
	hd-aa	2.626	2.796	2.739	
R=H for III	ad-ha	2.505	2.771	2.626	
	hd-aa	2.646	2.80	2.761	51
	ad-ha	2.493	2.80	2.591	
	hd-aa	2.646	2.80	2.764	
	ad-ha	2.509	2.80	2.592	

in the crystal structures of **1** and **2**, the differences in ad-ha, ad-aa, and hd-aa are reduced as the acidity of phenol hydroxyl is higher than that of alcohol or water.

Conclusion

Crystallization of H_3TMA has shown the tendency for the formation of co-crystals in phenol or *m*-cresol solvents. Hydroxyl group insertion is observed in carboxylic acid dimer for the formation of synthon-II. Because of the change in synthons, the usual honeycomb network of H_3TMA has been distorted to herringbone arrangement. The cavities generated are filled by aromatic moieties of phenols.

However, such phenolic insertion into -COOH synthons is not observed in the case of H_4PMA . For the first time, H_4PMA was shown to form clathrate complexes given the phenolic guests such as phenol, *o*-cresol, *p*-cresol, and *p*-chlorophenol.

The consistent formation of a square grid network through synthon-I is observed in all four complexes. Further, two packing modes were observed for these square nets depending on the host/guest ratios and the size of guest molecules. We note here that the phenol disrupts synthon-I in the case of H_3TMA , while it induces square grid formation via synthon-I in the case of H_4PMA . The phenolic complexes with H_3TMA could be considered as co-crystals, as their hydroxyl groups are part of a network, while those of H_4PMA could be considered as clathrates. The CSD studies of synthon-II and -III clearly illustrates the relation of acid–base strength versus hydrogen bond strength even within a synthon.

Experimental Section

In a typical crystallization process, H_3TMA (0.5 g) was taken in excess phenol (2 mL) and while heating this solution a minimum amount of methanol (\sim 1 mL) was added to dissolve the acid. The solution was kept at room temperature for crystallization by slow evaporation. Colorless prismatic crystals were formed after two days. All the other crystallizations were carried out in a similar fashion.

[$(\text{H}_3\text{TMA}) \cdot (\text{phenol})$] (**1**): Elemental analysis: (Anal. calcd. For $\text{C}_{15}\text{H}_{12}\text{O}_7$: C, 59.21%; H, 3.98%. Observed: C, 59.39%; H, 3.58%).

[$(\text{H}_3\text{TMA}) \cdot (m\text{-cresol})$] (**2**): Elemental analysis: (Anal. calcd. For $\text{C}_{16}\text{H}_{14}\text{O}_7$: C, 60.38%; H, 4.43%. Observed C, 60.92%; H, 4.23%).

[$(\text{H}_4\text{PMA}) \cdot (\text{phenol})$] (**3**): Elemental analysis: (Anal. Calcd. For $\text{C}_{16}\text{H}_{12}\text{O}_9$: C, 55.18%; H, 3.47%. Observed: C, 54.46%; H, 3.02%).

[$(\text{H}_4\text{PMA})_2 \cdot (o\text{-cresol})$] (**4**): Elemental analysis: (Anal. calcd. For $\text{C}_{27}\text{H}_{20}\text{O}_{17}$: C, 52.61%; H, 3.27%. Observed: C, 52.58%; H, 2.94%).

[$(\text{H}_4\text{PMA})_2 \cdot (p\text{-cresol})$] (**5**): Elemental analysis: (Anal. calcd. For $\text{C}_{27}\text{H}_{20}\text{O}_{17}$: C, 52.61%; H, 3.27%. Observed: C, 52.22%; H, 3.12%).

[$(\text{H}_4\text{PMA})_2 \cdot (p\text{-chlorophenol})$] (**6**): Elemental analysis: (Anal. Calcd. For $\text{C}_{26}\text{H}_{17}\text{ClO}_{17}$ Calculated: C, 49.03%; H, 2.69%. Observed: C, 49.72%; H, 2.78%).

Crystal Structure Determination. Single crystal data were collected on a Bruker-APEX-II CCD X-ray diffractometer that uses graphite monochromated Mo K α radiation ($\lambda=0.71073\text{ \AA}$) at room temperature (293 K) by a hemisphere method. The structures were solved by direct methods and refined by least-squares methods on F^2 using SHELX-97.¹³ Non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at calculated positions and refined using a riding model. The H-atoms attached to O-atom are located wherever possible and refined using the riding model. Further the guest molecules were found to be highly disordered in the crystal structures of **4–6**. Therefore, final refinement was done using PLATON squeeze option without guest molecules.¹⁴ PLATON was also used for the calculation of guest available volumes.

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Supporting Information Available: Crystallographic tables of bond lengths, angles, and ORTEP drawings for **1–6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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