Three-Dimensional Hexagonal Structures from a Novel Self-Complementary Molecular Building Block

C. V. Krishnamohan Sharma and Abraham Clearfield*

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas, 77843-3255

Received October 4, 1999

Abstract: Nitrilotri(methylphosphonic acid), **1H$_6$**, exists as a zwitter ion in its pure form and reveals a complex three-dimensional structure with no predictable structural patterns. However, when acid **1H$_6$** is reacted with 1,7-phenanthroline, **2**, 1,10-phenanthroline, **3**, acridine, **6**, and tripropylamine, **8**, in a 1:1 molar ratio, monodeprotonation of **1H$_6$** triggers a prototypal self-complementary 3D hexagonal architecture in complexes **9** (**1H$_5$·H·**2H$_2$O), **10** (**1H$_5$·3H**), **11** (**1·5H**)·(**5**)$_{0.5}$, and **12** (**1·8H**). The networks are stabilized by very strong ionic hydrogen bonds and offer a viable new strategy for the design of stable and predictable 3D open organic networks. However, monodeprotonation of acid **1H$_6$** with quinoline, **6**, does not lead to the expected open hexagonal structure in **13** (**1·6H**) as quinolinium cations cannot effectively fill the void space if open hexagonal open structures were formed. The unique three-dimensional connectivity of these open networks does not permit interweaving, and template effects play a critical role in the formation of open structures. The double deprotonation of acid **1H$_6$** with amines **2**, 4,7-phenanthroline, **3**, and diisopropylamine, **7,** leads to the formation of complexes **14** (**1H$_4$·(2H)**$_2$·2H$_2$O), **15** (**1H$_4$·(4H)**$_2$·5H$_2$O), and **16** (**1H$_4$·**7H) with one-dimensional chain structures only. Crystal structures of **9**−**16** together indicate the importance of the ionic hydrogen bond donor: acceptor ratio in determining 3D hexagonal network formation. Further, the proton transfer from acid **1H$_6$** to phenanthrolines influences the absorption properties of **9**, but has no effect on **10**. 1,7-Phenanthroline (mp 80 °C) changes its color from pale yellow to deep orange-red upon protonation and exhibits stability up to 325 °C. These results bring out a new concept, that we may be able to control absorption properties and heat stability of pigments/colorants by encapsulating different structural forms into a rigid three-dimensional host matrix by optimizing hydrogen bond properties.

Introduction

In recent years, crystal engineering strategies directed toward the design of open hexagonal networks successfully produced several exotic designer networks.[1−3] Nevertheless, the two-dimensional nature of such architectures led to the formation of interpenetrated and/or offset stacked structural motifs that avoid the formation of continuous open channel structures.[1i,3,4] Therefore, development of new strategies for the construction of rigid *three-dimensionally networked hexagonal architectures* have become absolutely essential to design functional solids. Indeed, construction of such three-dimensional networks is of fundamental importance, because the only predictable three-dimensional organic *open networks* to date are based on molecular building blocks with T_d symmetry.[5,6] In this article we report a new strategy to generate self-complementary three-dimensional hexagonal open networks by combining trigonal

(1) For a very good overview of recent developments in crystal engineering see the following multiauthored volumes and review articles: (a) *Crystal Engineering: From Molecules and Crystals To Materials*; Braga, D., Orpen, A. G., Eds.; NATO ASI series; Kluwer: Dordecht, The Netherlands, 1999. (b) Weber, E., Ed. *Design of Organic Solids*; Topics in Current Chemistry; Springer-Verlag, Heidelberg, 1998; Vol. 198. (c) *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vogtle, F., Lehn, J.-M., Eds.; Pergamon: Oxford, 1996; Vol. 6. (d) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311−2327. (e) Aakeroy, C. B. *Acta Crystallogr.* **1997**, *B53*, 569−583. (f) Braga, D.; Grepioni, F.; Desiraju, G. R. *Chem. Rev.* **1998**, *98*, 1375−1405. (g) Bernstein, J.; Davis, R. E.; Shimoni, L.; Chang, N. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1555−1573. (h) MacDonald, J. C.; Whitesides, G. M. *Chem. Rev.* **1994**, *94*, 2383−2420. (i) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1460−1494. (j) Zaworotko, M. J. Coordination Polymers. In *Crystal Engineering: The Design and Applications of Functional Solids*; Seddon, K. R., Zaworotko, M. J., Eds.; NATO ASI series; Kluwer: Dordecht, The Netherlands, 1998. (k) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2639−2684. (l) Alivisatos, A. P.; Barbara, P. F.; Castelman, A. W.; Chang, J.; Dixon, D. A.; Klein, M. L.; McLendon, G. L.; Miller, J. S.; Ratner, M. A.; Rossky, P. J.; Stupp, S. I.; Thompson, M. E. *Adv. Mater.* **1998**, *10*, 1297−1336.

(2) (a) Russell, V. A.; Evans, C. C.; Li, W.; Ward, M. D. *Science* **1997**, *276*, 575−579. (b) Kolotuchin, S. V.; Fenlon, E. E.; Wilson, S. R.; Loweth, C. J.; Zimmerman, S. C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2654−2657. (c) Ranganathan, A.; Pedireddi, V. R.; Rao, C. N. R. *J. Am. Chem. Soc.* **1999**, *121*, 1752−1753. (d) Zerkowski, J. A.; Seto, C. T.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 5473−5475. (e) Yang, J.; Marendaz, J-L.; Geib, S. J.; Hamilton, A. D. *Tetrahedron Lett.* **1994**, *35*, 3665−3668. (f) Thalladi, V. R.; Brasselet, S.; Blaser, D.; Boese, R.; Zyss, J.; Nangia, A.; Desiarju, G. R. *Chem. Commun.* **1997**, 1841−1842. (g) Tadokoro, M.; Isobe, K.; Uekusa, H.; Ohashi, Y.; Toyoda, J.; Tashiro, K.; Nakasuji, K. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 95−98. (h) Sharma, C. V. K.; Zaworotko, M. J. *Chem. Commun.* **1996**, 2655−2656. (i) Melendez, R. E.; Sharma, C. V. K.; Zaworotko, M. J.; Bauer, C.; Rogers, R. D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2213−2215. (j) Coe S.; Kane J. J, Nguyen, T. L.; Toledo L. M.; Wininger, E.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 86−93.

(3) (a) Yaghi, O. M.; Li, G.; Li, H. *Nature* **1995**, *378*, 703−706. (b) Gardner, G. B.; Venkataraman, D.; Moore, J. S.; Lee, S. *Nature* **1995**, *374*, 792−795. (c) Choi, H. J.; Lee, T. S.; Suh, M. P. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1405−1408. (d) Asefa, T.; MacLachlan, M. J.; Coombs, N.; Ozin, G. A. *Nature*, **1999**, *402*, 867−871. (e) Stang, P. J.; Persky, N. E.; Mana, J. *J. Am. Chem. Soc.* **1997**, *119*, 4777−4778. (f) Fujita, M.; Kwon, Y. J.; Sasaki, O.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 7287−7288.

(4) Sharma, C. V. K. In *Crystal Engineering: From Molecules and Crystals to Materials*; Braga, D., Orpen, G., Eds.; NATO, ASI series; Kluwer: Dordecht, The Netherlands, 1999; pp 481−500.

10.1021/ja9935512 CCC: $19.00
Published on Web 04/22/2000

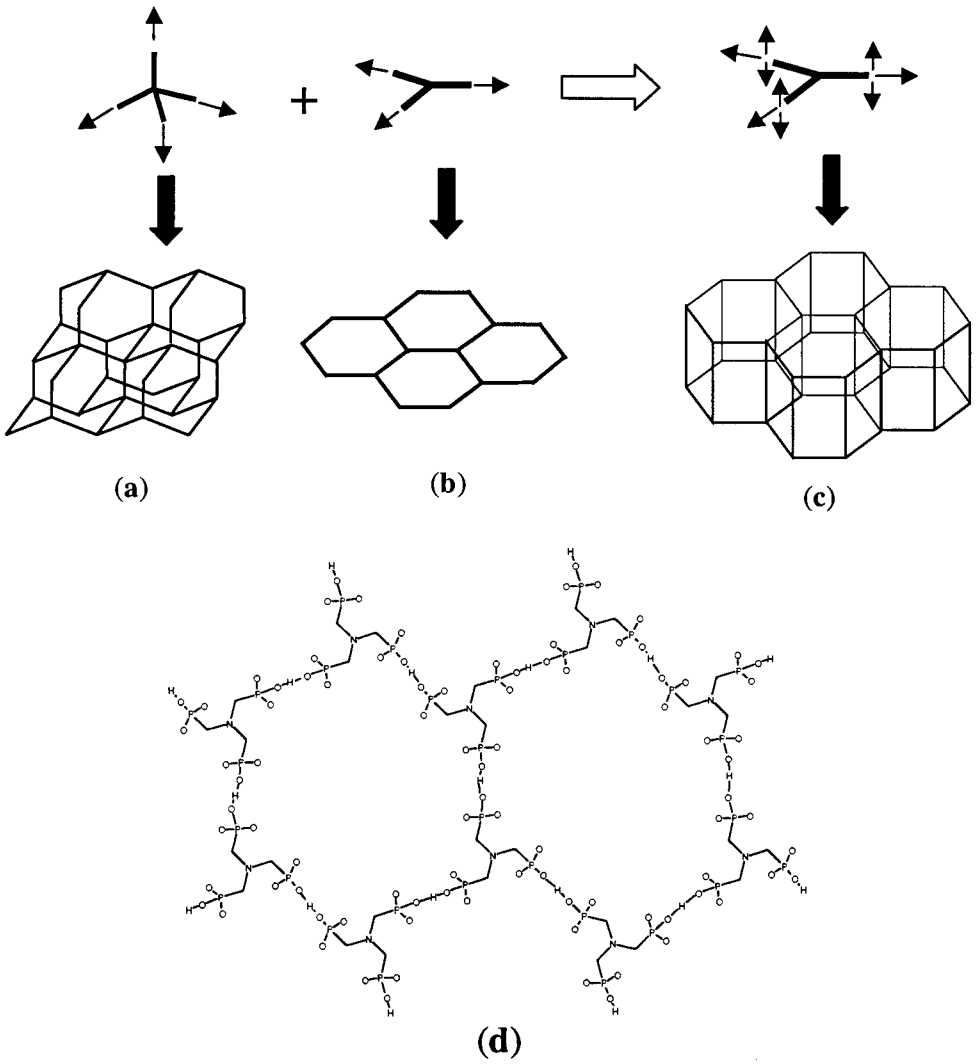
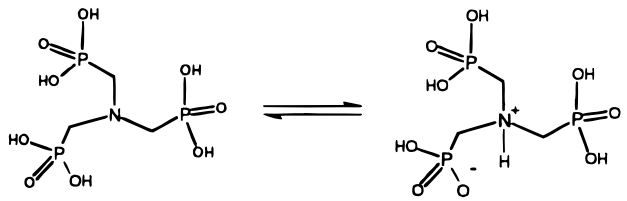


Figure 1. Schematic diagram of three-dimensional (a) and two-dimensional (b) structures formed by self-assembly of tetrahedral and trigonal molecular building blocks. Self-assembly of trigonal molecular building blocks with tetrahedrally shaped functional groups may lead to the formation of three-dimensional open hexagonal networks (c). A hexagonal structure formed by very strong symmetrical ionic hydrogen bonds of nitrilotri-(methylphosphonate). Note that the oxygen atoms perpendicular to the plane of the hexagonal layer can lock the neighboring layers through strong hydrogen bonds to form a 3D network.

molecular symmetry with tetrahedrally shaped functional groups in an organic molecular building block (Figure 1a−c).

In general, planar molecular building blocks with trigonal symmetry and complementary in-plane directional forces form two-dimensional hexagonal networks (e.g., 1,3,5-benzenetricarboxylic acid, Figure 1b).[7] We can construct a three-dimensional hexagonal network if we could identify trigonal molecular building blocks that can form directional interactions in all three dimensions as shown in Figure 1c. In fact, nonplanar nitrilotri(methylphosphonic acid), **1H$_6$**, is capable of forming such three-dimensional hydrogen-bonding interactions using three of its tetrahedrally shaped phosphonic acid groups. However, acid **1H$_6$** exists as a zwitter ion in its pure form and reveals a complex three-dimensional structure with no predictable structure patterns involving five of its acidic protons.[8]



1H$_6$

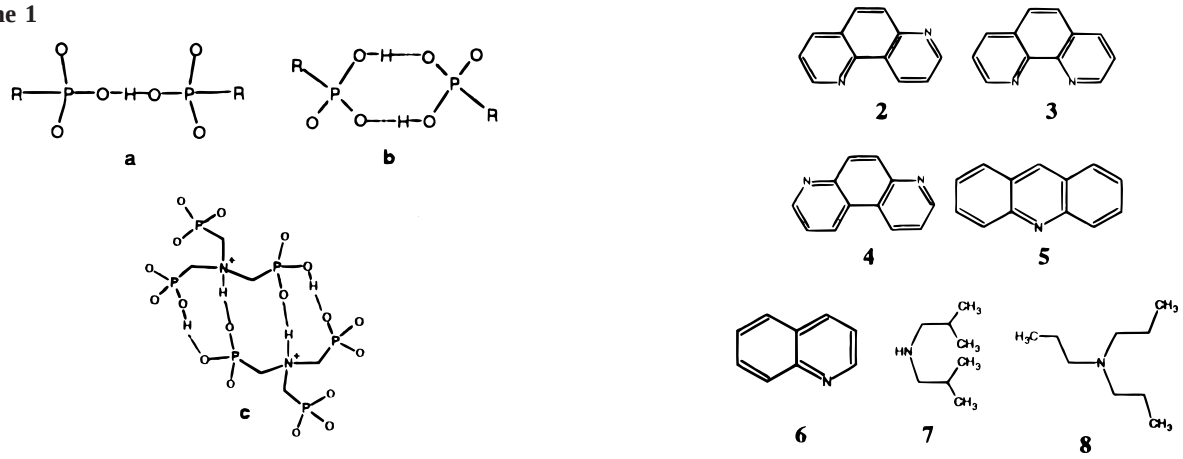
Our recent studies on phosphonic acids clearly demonstrate that deprotonation of the organo phosphonic acids with amines results in very strong and predictable structural aggregates through symmetrical O···H···O hydrogen bonds or hydrogen-

(5) Although there are a number of 3D hydrogen bonded networks in the Cambridge Structural Database, the only reliable and predictable 3D open networks continue to be diamonoid networks based on molecular building blocks with T_d symmetry and complementary intermolecular interactions. In this article, we tried to devise a new strategy of constructing generic 3D hexagonal open networks using a novel self-complementary molecular building block. However, see the following references and ref 6 for some very interesting 3D networks and open networks based on hydrogen bonding: (a) Brunet, P.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1997**, *119*, 2737−2738. (b) Bhyrappa, P.; Wilson, S. R.; Suslick, K. S. *J. Am. Chem. Soc.* **1997**, *119*, 8492−8502. (c) Ung, A. T.; Gizachew, D.; Bishop, R.; Scudder, M. L.; Dance, I. G.; Craig, D. C. *J. Am. Chem. Soc.* **1995**, *117*, 8745−8756. (d) Endo, K.; Sawaki, T.; Koyanagi, M.; Kobayashi, K.; Masuda, H.; Aoyama, Y. *J. Am. Chem. Soc.* **1995**, *117*, 8341−8352. (e) Martin, J. D.; Leafblad, B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3318−3320. (f) Aakeroy, C. B.; Beatty, A. M.; Leinen, D. S. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1815−1819. (g) Kumar, R. K.; Balasubramanian, S.; Goldberg, I. *Chem. Commun.* **1998**, 1435−1436. (h) Kepert, C. J.; Hesek, D.; Beer, P. D.; Rosseinsky, M. J. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3158−3160. (i) Ranford, J. D.; Vittal, J. J.; Wu, D.; Yang, X. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3498−3501.

Table 1. Crystallographic Data for Molecular Complexes **9**−**16**

property	**9** $1H_5$·**2H**·$2H_2O$	**10** $1H_5$·**3H**	**11** (**1**·**5H**)·(**5**)$_{0.5}$	**12** 1·**8H**	**13** 1·**6H**	**14** (**1**·(**2H**)$_2$)·$3H_2O$	**15** (**1**·(**4H**)$_2$)·$5H_2O$	(**16** 1·(**7H**)$_2$)
color	orange-red	colorless	yellow	colorless	colorless	orange-red	pale pink	colorless
mp/°C	>300	255	240	200	169	240	>125−129	215
formula	$C_{15}H_{24}N_3O_{11}P_3$	$C_{15}H_{20}N_3O_9P_3$	$C_{22}H_{25}N_3O_9P_3$	$C_{12}H_{33}N_2O_9P_3$	$C_{12}H_{18}N_2O_9P_3$	$C_{27}H_{34}N_5O_{12}P_3$	$C_{27}H_{38}N_5O_{14}P_3$	$C_{19}H_{50}N_3O_9P_3$
M	515.28	479.25	567.86	442.31	427.19	713.50	749.53	557.53
crystal system	triclinic	triclinic	triclinic	monoclinic	orthorhombic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$Pccn$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
A/Å	7.1731(9)	8.1519(5)	10.1587(7)	9.022(2)	26.284(2)	7.4491(4)	6.955(2)	10.7547(8)
B/Å	11.566(1)	11.2550(7)	11.0566(8)	16.150(4)	8.4774(7)	13.7121(8)	11.543(3)	11.3487(8)
C/Å	13.807(2)	11.3742(7)	11.7805(8)	14.251(4)	15.344(1)	15.1279(9)	21.051(5)	12.8909(9)
α	70.627(2)	72.239(1)	84.166(1)	90	90	86.543(1)	93.338(4)	85.094(1)
β	84.071(2)	74.563(1)	75.208(1)	94.525(5)°.	90	89.146(1)	95.348(4)	73.287(1)
γ	81.720(2)	85.809(1)	70.257(1)	90	90	76.255(2)	105.497(4)	76.390(2)
Z	2	2	2	4	8	2	2	2
V/Å^3	1067.4(2)	958.0(1)	1203.9(2)	2069.9(9)	3419.0(8)	1498.2(1)	1615.3(6)	1464.3(2)
D_c/ g cm^{-3}	1.603	1.661	1.566	1.419	1.660	1.582	1.541	1.264
no. of mesd reflcns	4840	6116	5465	9100	14714	9758	10178	9580
no. of unique reflcns	3036	4230	3423	2967	2466	6831	7163	6733
R	0.044	0.053	0.053	0.092	0.077	0.035	0.068	0.038
$wR2$	0.096	0.138	0.144	0.217	0.199	0.010	0.150	0.096

Scheme 1



bonded dimers (Scheme 1).[9] Indeed, strong symmetrical hydrogen bonds (motif **a**) will have stabilization energies greater than up to 10 times of those normally occurring hydrogen bonds.[10] Therefore, it occurred to us that we can synthesize very stable hydrogen-bonded open hexagonal networks by selective deprotonation of triphosphonic acids (Figure 1d). We found that monodeprotonation of acid $\mathbf{1H_6}$ using certain amines leads to the formation of predictable three-dimensional hexagonal networks. Further, double deprotonation of the acid $\mathbf{1H_6}$ results in the formation of only one-dimensional chain structures as strong multiple hydrogen bonds between the deprotonated acids control the network structure. To understand the conditions required to induce self-complementary three-dimensional hydrogen-bonding motifs in acid $\mathbf{1H_6}$ we have systematically studied the 1:1 and 1:2 (i.e., ($\mathbf{1H_5}$ or $\mathbf{1H_4}$)−ammonium salts) molecular complexes of acid $\mathbf{1H_6}$ using amines **2**−**8**. The molecular complexes of phenanthrolines exhibit interesting absorption properties depending upon the relative positioning of N atoms and the hydrogen-bonding environment and serve as model compounds for studying the design of thermally stable colorants.[11]

Experimental Section

Synthesis. All of the chemicals were purchased from either Aldrich or Fluka and were used without further purification. The acid $\mathbf{1H_6}$ was reacted with amines **2**−**8** either in 1:1 or 1:2 molar ratio in ethanol, ethanol−water, or DMSO−water solvent mixtures.

Single crystals of 1:1 molecular complexes **9** ($\mathbf{1H_5}$·**2H**·$2H_2O$) and **10** ($\mathbf{1H_5}$·**3H**) were obtained by slow evaporation of an ethanol−water solvent mixture containing acid $\mathbf{1H_6}$ (0.300 g, 1 mmol) and corresponding phenanthrolines **2** (0.180 g, 1 mmol) and **3** (0.180 g, 1 mmol). The 1:1 molecular complexes **11** ((**1**·**5H**)·(**5**)$_{0.5}$) and **12** (**1**·**8H**) were obtained by reacting acid $\mathbf{1H_6}$ (0.300 g, 1 mmol) with acridine (**5**, 0.180 g, 1 mmol) and tripropylamine (**8**, 0.143 g, 1 mmol) in DMSO−water solution mixture and in ethanol, respectively. The 1:1 molecular complex **13** (**1**·**6**H) between quinoline (**6**, 0.129 g, 1 mmol) and acid $\mathbf{1H_6}$ (0.300 g, 1 mmol) was obtained from DMSO−water solution mixture. The 1:2 molecular complexes **14** ((**1**·(**2H**)$_2$)·$3H_2O$), **15** ((**1**·(**4H**)$_2$)·$5H_2O$), and **16** (1·(**7H**)$_2$) were obtained by reacting acid $\mathbf{1H_6}$ (0.150 g, 0.5 mmol) with the amines **2** (0.180 g, 1 mmol), **4** (0.180 g, 1 mmol), and **7** (0.130 g, 1 mmol) in ethanol−water mixture, respectively.

Our efforts to crystallize the 1:1 complexes of acid $\mathbf{1H_6}$ with simple aromatic and alkyl amines (e.g., dimethylamine, pyridine) to form 3D hydrogen bonded hexagonal networks in the presence of certain aromatic additives/templates (e.g., anthracene) were not successful so far.

X-ray Crystallography: Data ($4 < \theta < 56$) on complexes **9**−**16** were collected on a Bruker-AXS CCD area detector-equipped diffractometer with Mo Kα ($\lambda = 0.71073$ Å) radiation at 110 K using a stream of nitrogen gas. The crystal structures of **9**−**16** were solved by direct methods using the SHELXTL package.[12] All the non-hydrogen atoms were anisotropically refined and aromatic, methylene hydrogen atoms were calculated ($d_{CH} = 0.95$ Å) and fixed with thermal parameters based

(6) Gong, B.; Zheng, C.; Skrzypczak-Jankun, E.; Yan, Y.; Zhang, J. *J. Am. Chem. Soc.* **1998**, *120*, 11194−11195 and references therein.

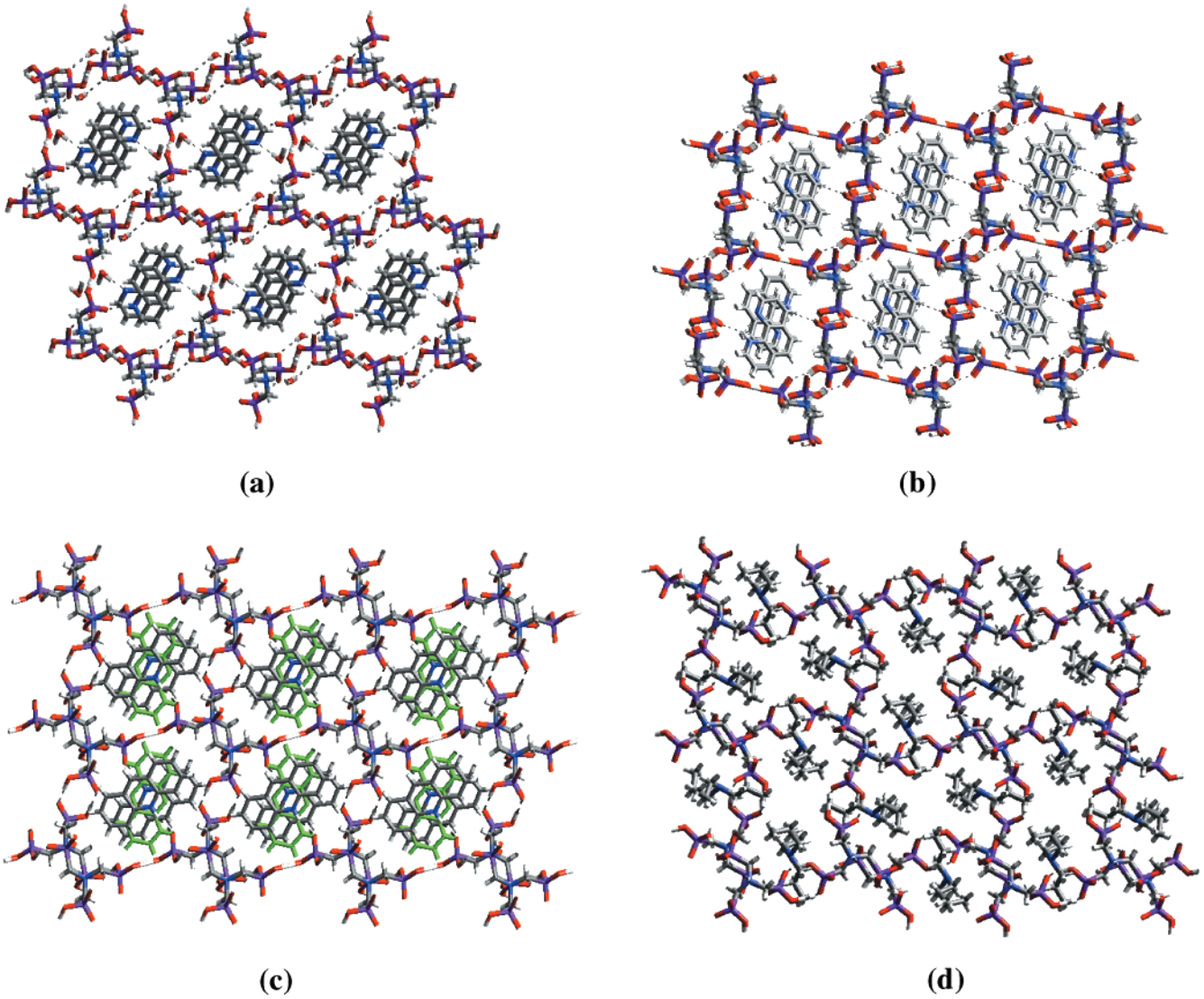


Figure 2. Packing diagrams of three-dimensional hexagonal structures of molecular complexes **9** (a), **10** (b), **11** (c), and **12** (d). The neutral acridine, **5**, encapsulated in the cavities of **11** is shown in green. The hexagonal 3D networks of **12** are squashed and part of the tripropylamine occupies the molecular cavities running perpendicular to hexagonal cavities.

upon the C atoms to which they are bonded. All the water, OH, and NH protons were determined via difference Fourier maps. The neutral acridine, **5**, included in complex **10** is disordered as the asymmetric unit contains only a half molecule. Also, one of the three phosphonic acid groups in acid $\mathbf{1H_6}$ of complex **13** was disordered and the site occupancy factors (0.5) for O atoms were refined by identifying reasonable temperature factors. The crystallographic details of complexes **9**−**16** are summarized in Table 1. X-ray powder diffraction spectra of complex **9** were recorded using a Seifert-Scintag PAD V diffractometer after heating at 160 and 300 °C.

Spectroscopy: The solution-state and solid-state spectra of phenanthrolines, **2**−**4**, and complexes **8** and **9** were recorded using a Cary 219 spectrophotometer. The solid-state UV/vis absorption spectra of the materials were recorded by making a Nujol mull of finely ground single crystals and mounting the mulls on a quartz glass plate or on a Whatman filter paper. The solution-state spectra of phenanthrolines and corresponding monoprotonated forms were recorded in MeOH.

The TGA was recorded using a Dupont Instruments 951 Theromogravimetric Analyzer under N_2 atmosphere.

Results and Discussion

3D Hexagonal Networks − Hydrogen Bond Donor:Acceptor Ratio and Template Effects. Complexes **9**−**12** are interesting 3D hexagonal structures with monoprotonated cations and clathrated guest molecules occupying the open cavities (Figure 2a−d). Four acidic protons of $\mathbf{1H_5}$ in complexes **9**−**12** are shared over three phosphonic acid groups. Each phosphonic acid group in **9** bears 2, 1.5, and 0.5 proton(s), respectively, while in **10** the protons are distributed as 1.5, 1.5, and 1 proton(s) per phosphonic acid group. The proton distribution ratio among phosphonic acids in **11**−**13** is 2:1:1. The H atom positions in **9**−**16** were identified via difference Fourier maps (except in the disordered phosphonic acid group in **13**) and further confirmed by the careful observation of P−O bond lengths and concerned hydrogen-bonding distances.

(7) Herbstein, F. H. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vogtle, F., Lehn, J.-M., Eds.; Pergamon: Oxford, 1996; Vol. 6, pp 61−82.
(8) Daly, J. J.; Wheatley, P. J. *J. Chem. Soc. A* **1967**, 212−221.
(9) Sharma, C. V. K.; Clearfield, A. *J. Am. Chem. Soc.* In press.
(10) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: New York, 1991.
(11) (a) Schmidt, M. U. In *Crystal Engineering: From Molecules and Crystals to Materials*; Braga, D., Orpen, G., Eds.; NATO ASI series; Kluwer: Dordecht, The Netherlands, 1999; pp 309−326. (b) Lincke, G. *Dyes Pigments* **2000**, *44*, 101−122.
(12) Sheldrick, G. M. SHELXTL, Crystallographic Software Package. SHELXTL, Version 5.1, Bruker-AXS, Wisconsin, 1998.

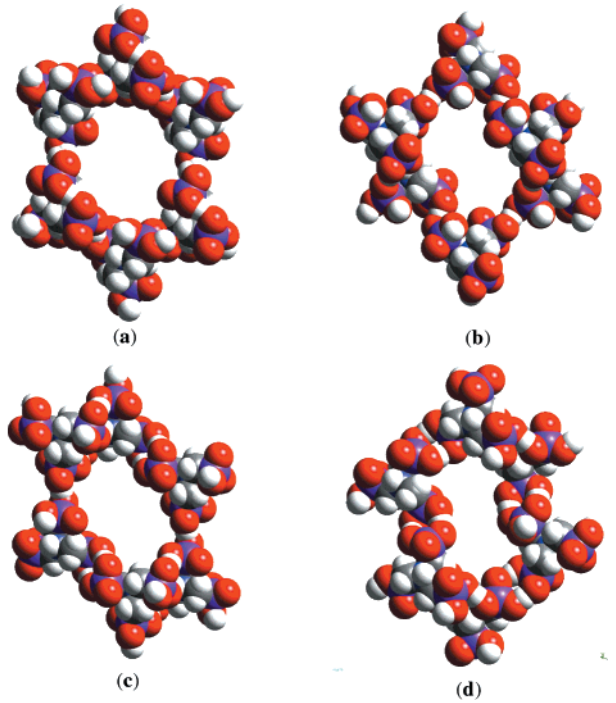


Figure 3. Hexagons in complexes **9**−**12** are shown in space-filling model to highlight the hydrogen bonding patterns, internal cavity dimensions, and the shape: (a) **9**, motif a, 9.7 × 12.0 Å^2; (b) **10**, motifs a and c, 8.2 × 12.7 Å^2; (c) **11**, motifs a−c, 8.3 × 12.3 Å^2; and (d) **12**, motifs b and c, 6.7 × 12.3 Å^2.

The three-dimensional hexagonal network in **9** is exclusively stabilized by very short symmetrical hydrogen bonds (motif **a**). The 2D layer structure has a hydrogen-bonding pattern identical with the hexagonal network shown in Figure 1d (O···O, 2.452(4), 2.461(4), 2.476(4) Å). The internal dimensions of the hexagonal cavities are ca. 9.7 × 12.0 Å^2 (Figure 3a). These hexagons are further linked through symmetrical hydrogen bonds in the third dimension resulting in a very rigid three-dimensional cooperative hydrogen-bonded network with hydrophilic cavities along the walls of the supramolecular hexagon (O···O, 2.464(3), 2.455(3) Å, Figure 4a). The two hydration water molecules occupy these cavities and form hydrogen bonds with phosphonic acids (O−H···O, 2.723(3), 2.839(3) Å), the unprotonated amine of **2** (O−H···N, 3.129(6) Å), and the protonated amine of acid **1** (N^+−H···O, 2.691(4) Å) to strengthen the 3D network.

Interestingly, complex **10** is not solvated with water like **9** and yet forms a three-dimensional hexagonal structure with a combination of strong symmetrical hydrogen bonds and hydrogen-bonded dimers (Figures 2b and 3b). In effect, four symmetrical hydrogen bonds (motif **a**) and two dimers (motif **c**) stabilize each hexagon in the network (O···O, 2.413(2), 2.426(2), 2.565(2) Å; N···O, 2.640(2) Å; internal dimensions of the hexagonal cavities, 8.2 × 12.7 Å^2). These hexagons are in turn linked through robust hydrogen bonds in the third dimension (motifs **a** and **b**, O···O 2.511(2), 2.480(2) Å, Figure 4b) resulting in a distorted 3D hexagonal network.

The phenanthrolinium cations in the cavities of **9** and **10** are stacked with a mean interplanar and centroid−centroid distances of 3.52 Å, 3.61 Å and 3.33 Å, 3.99 Å, respectively. The electrostatic interactions between the stacked phenanthrolinium cations in **9** and **10** are well optimized with the protonated amine moiety overlapping with the unprotonated amine moiety (Figure 5a,b).

Unlike complexes **9** and **10**, the hexagonal network of complex **11** is stabilized by all hydrogen-bonding motifs **a**−**c** as shown in Figures 2c and 3c (O···O, 2.443(3) (**a**), 2.574(3) (**b**), 2.512(3) Å; N···O, 2.654(3) Å (**c**), internal dimensions of the hexagon are 8.3 × 12.3 Å^2). The hexagons are held together through rigid hydrogen-bonded dimers in the third dimension as shown in Figure 4c (O···O, 2.590(3) Å). More importantly, complex **11** encapsulates half a molecule of neutral acridine (disordered) as a guest in the open hexagonal networks. The neutral acridines stack with the protonated acridines in such a way that every third molecule in the stacked column is a neutral acridine (i.e., ...AABAABAAB..., Figure 5c). The interplanar, centroid−centroid distances between the two protonated acridines and between the protonated and neutral acridines are 3.27 Å, 3.76 Å and 3.28 Å and 3.4 Å, respectively. The stacking distances between acridines are significantly shorter as compared to phenanthrolines and this explains why the hexagonal cavities of **11** were able to accommodate an additional neutral guest molecule in the open cavity. Also, the neutral acridines stack with protonated acridines at an angle not only to optimize the electrostatic interactions but also to effectively fill in the void space of the open networks (Figures 3c and 5c). These results indicate that the shape of the cations and the solvated guest molecules play an important role (templating effect) in determining the type(s) of hydrogen bonding motif(s) in a hexagonal network (Figure 3).

The presence of a 3D hexagonal network in complex **12** is very striking because of the fact that a tertiary alkylamine was used to deprotonate the acid **1H$_6$** unlike in the previous three complexes. The hexagonal network of **12** is stabilized by hydrogen bonding motifs **b** and **c** (O···O, 2.445(6), 2.515(7), 2.527(7) Å; N···O, 2.681(7) Å; cavity internal dimensions, 6.7 × 12.3 Å^2) and is significantly distorted as compared to **9**−**11** (Figures 2 and 3). Interestingly, tripropylamine, **9**, not only occupies the hexagonal molecular cavities but also partially fills the molecular cavities running perpendicular to the hexagonal open networks (Figure 2d). The hydrogen-bonding pattern of the hexagonal motif's side-walls is shown in Figure 4d (O···O, 2.481(7) Å).

The only exception to the formation of 3D open hexagonal networks in this study is complex **13**. Monodeprotonation of acid **1H$_6$** using quinoline, **6**, leads to the formation of a complex two-dimensional hydrogen-bonding network as shown in Figure 6. Also, the hydrogen-bonding motifs of **13** have no resemblance to motifs **a**−**c** and because of the disorder in one of the three phosphonic acids, some of the hydrogen-bonding contacts were not well-defined. Structural features of this complex emphasize the fact that the size of the cation/guest/template in the open networks and the nature of its intermolecular interactions play a critical role in determining the 3D hexagonal network formation. The quinolinium cations placed between the hydrogen-bonded layers form both stacking (with interplanar and centroid−centroid distances of 3.65 Å and 3.85 Å) and herringbone interactions as shown in Figure 7. The sandwiched herringbone geometry adopted by **6H** is in corroboration with the well-established empirical rules on the nature of stacking interactions in simple aromatic hydrocarbons.[13] Further, **6H** cannot effectively fill the void space, if the open networks (with internal dimensions ca. 8.5 × 12. 5 Å^2) were formed due to its smaller size.

Double Deprotonation of Acid 1H$_6$: Loss of 3D Self-Complementarity. Double deprotonation of acid **1H$_6$** using two

(13) (a) Desiraju, G. R.; Gavezzotti, A. *Acta Crytallogr.* **1989**, *B45*, 473−482. (b). Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525−5534.

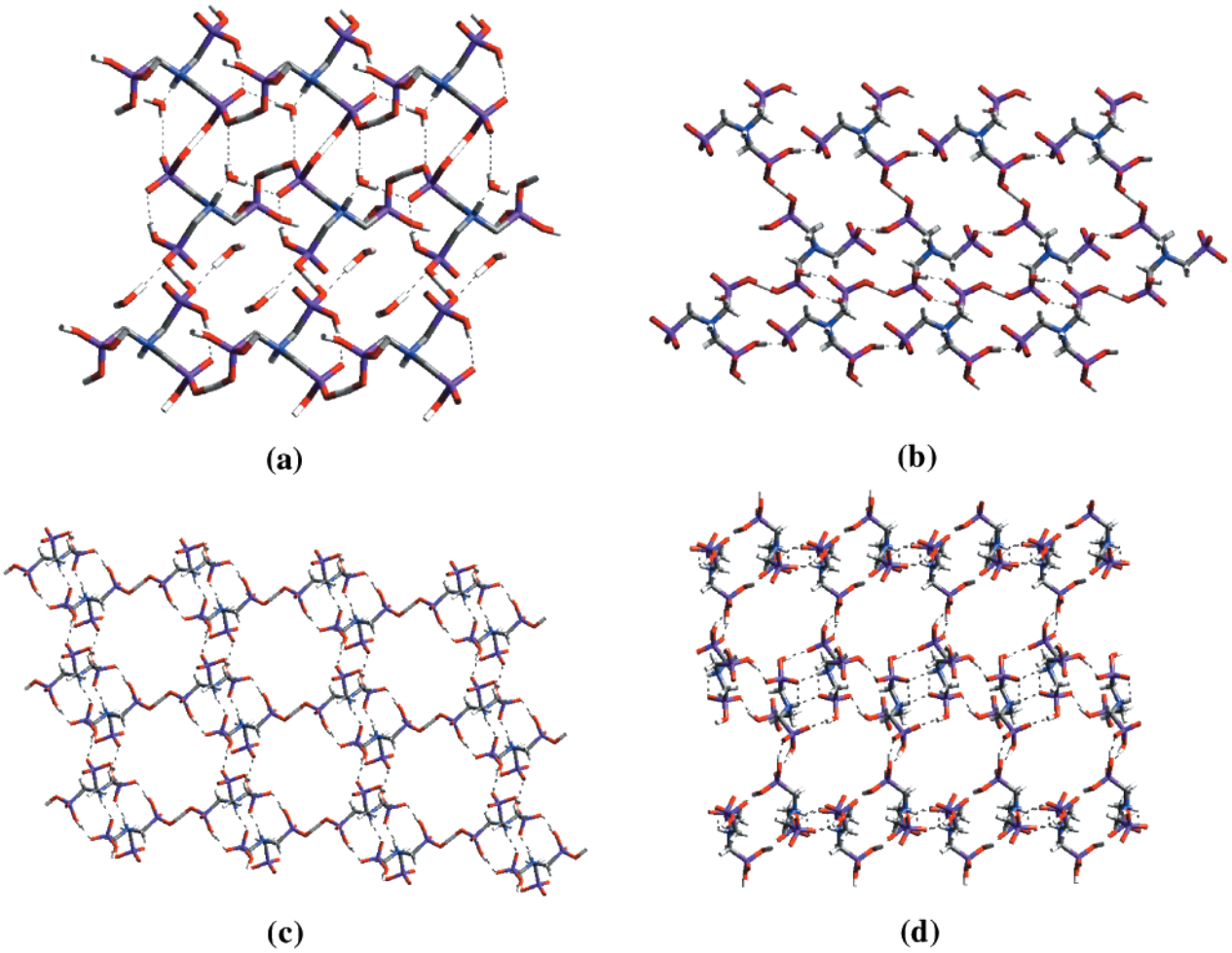


Figure 4. The sidewalls of the hydrogen bond hexagonal grids of **9** (a), **10** (b), **11** (c), and **12** (d). Two water molecules occupy the hydrophilic cavities of **8**. Acid moieties in **10** are further linked through motif **c** and are not shown here. Also, notice the presence of molecular cavities in some of these networks.

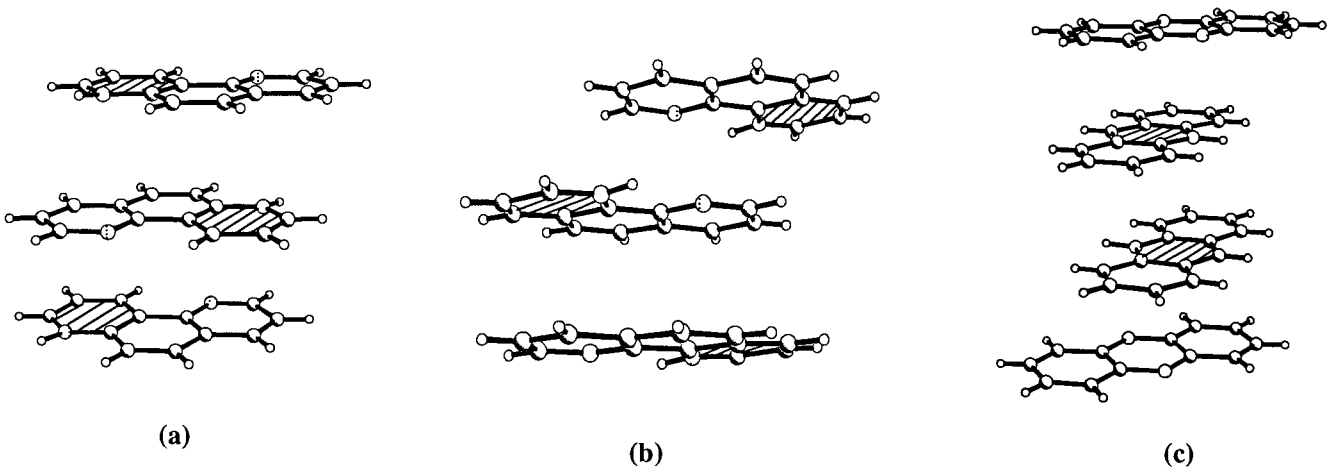


Figure 5. The stacking nature of phenanthrolines in the open cavities of **9** (a), **10** (b), and **11** (c). The protonated moiety of the amine (hatched) stacks with the unprotonated amine moiety of the phenanthrolines to optimize electrostatic interactions. Complex **11** accommodates an addition of neutral acridine, **5**, in the open cavities by forming shorter stacking interactions. Every third molecule in the sacked column is a neutral disordered acridine.

moles of amine effectively leaves one proton each on three of the phosphonic acid groups. Consequently, the three-dimensional complementary hydrogen-bonding ability of the anion $1H_4$ is lost and **14**−**16** form only one-dimensional hydrogen bonded chains.

Anion $\mathbf{1H_4}$ in **14** self-assembles to form a one-dimensional hydrogen-bonded chain as shown in Figure 8a (O···O, 2.548-(2), 2.575(2), 2.636(2) Å). The 1D chains are in turn hydrogen bonded with three solvated water molecules to form a bilayer structure with alternating cationic and anionic frameworks (Figure 9a). Complex **15** also forms a bilayer-type structure like **14** but is solvated with five water molecules and forms a corrugated sheet structure. The one-dimensional chain structure (O···O, 2.467(4), 2.585(4) Å) and the packing diagram of **14**

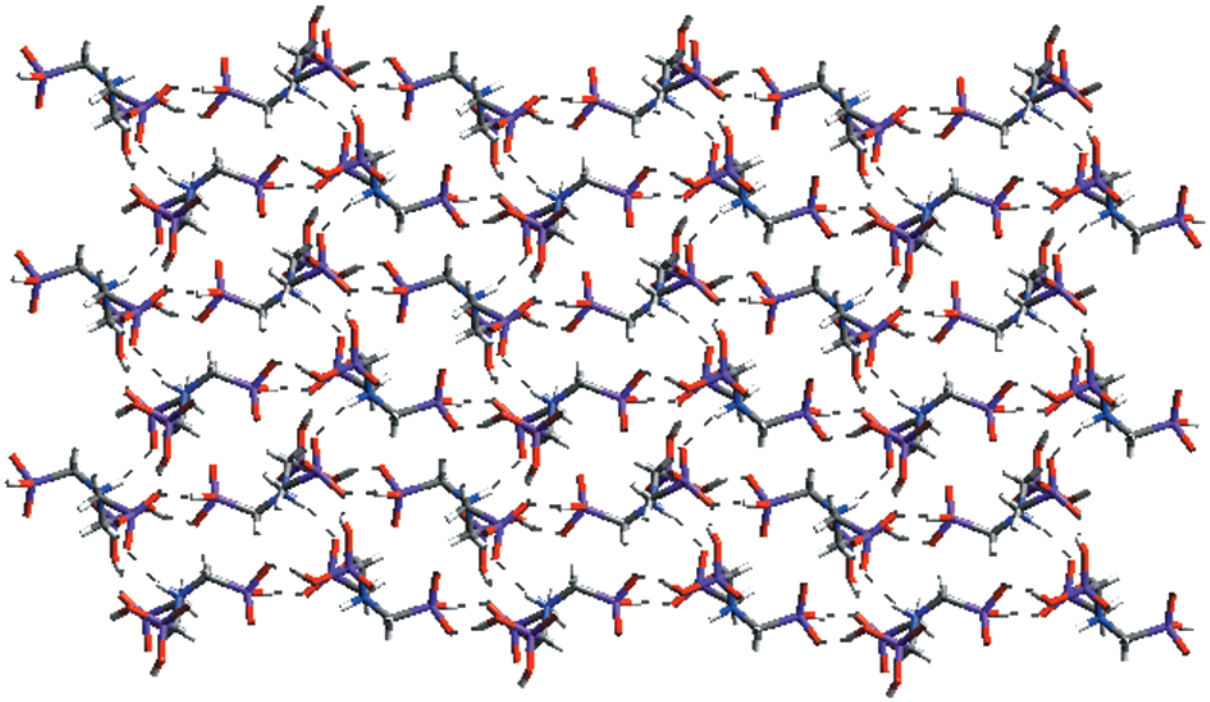


Figure 6. The two-dimensional hydrogen bonding network observed in complex **13**. One of the phosphonic acid groups is disordered. For clarity the disordered O atoms are not shown.

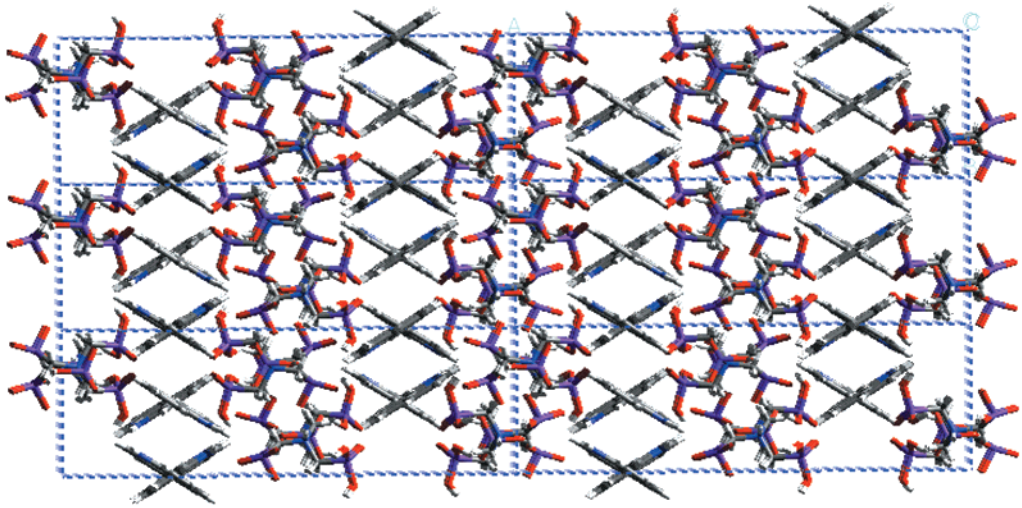


Figure 7. The packing diagram of complex **13** showing the sandwiched herringbone type of interactions among **6H**.

are shown in Figures 8b and 9b, respectively. Probably, the hydration ability of complexes **13** and **14** may be understood from the fact that double deprotonation of the acid $\mathbf{1H_6}$ causes an imbalance in the proton donor:acceptor ratio (i.e., greater number of good proton acceptors than proton donors) and the water molecules with more proton donors avoid such an imbalance.[14]

The one-dimensional chain structure of **16** is stabilized exclusively by motifs **b** and **c** as shown in Figure 8c (O···O, 2.504(2), 2.550(2), 2.515(2) Å; N···O, 2.590(2) Å). Interestingly, this complex is not solvated with water molecules such as **14** and **15** probably due to the presence of an NH proton in the secondary amine unlike in the previous two complexes. The hydrogen-bonded one-dimensional chains are surrounded by protonated alkylamines with their hydrophilic moieties pointing toward the chain (N···O, 2.697(2), 2.815(2), 2.745(2), 2.708(2) Å) and the hydrophobic alkyl moieties pointing outward as shown in the packing diagram of **16** (Figure 9c).

The crystal structures of complexes **9**−**16** clearly indicate that the hydrogen bond donor:acceptor ratio and hierarchical hydrogen-bonding strengths in anions $\mathbf{1H_5}$ and $\mathbf{1H_4}$ primarily determine the formation of a three-dimensional self-complementary hexagonal network. However, the template effects also play a role in determining 3D hexagonal open network formation. It is to be mentioned here that one cannot form an open network without the aid of a template(s), however strong the bonds (coordination/covalent) between the molecular building blocks may be. Therefore, it is not surprising that no 3D open porous hexagonal structures of $\mathbf{1H_5}$ will be formed in the absence of templating effects.

Thermal Stability and Coloration Properties. The thermal stability and coloration properties of the open 3D hexagonal networks presented here are of significant interest. The melting

(14) Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1991**, 426−428.

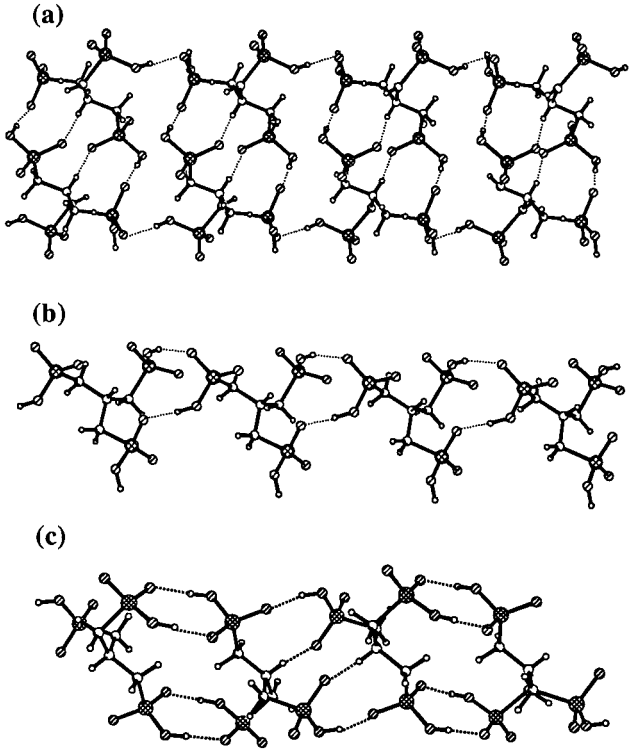


Figure 8. The One-dimensional hydrogen bonding structural motifs observed in doubly deprotonated acids of $\mathbf{1H_6}$ in complexes **14** (a), **15** (b), and **16** (c) illustrating the variations in hydrogen bonding patterns.

points of complexes **9**−**16** are listed in Table 1. Of the four open hexagonal networks discussed here (i.e., **9**−**12**), the structural and chemical properties of **9** are particularly interesting for a variety of reasons. Complex **9** is solvated with two water molecules and yet forms the open hexagonal network with a relatively high melting point. The thermal gravimetric analysis (TGA) of **9** indicates two stepwise losses of water molecules at 150.0 and 250.0 °C. The remaining compound can be heated to 325 °C without any additional weight loss. The high melting point of **9** can be correlated to its hydrogen-bonding motifs. While **9** is exclusively stabilized by very robust symmetrical hydrogen-bonding patterns (motif **a**), **10**−**12** are stabilized by the combination of hydrogen-bonding motifs **a**−**c** (Figure 3). The X-ray diffraction pattern of **9** recorded after the loss of first and second water molecules (i.e., around 160 and 260 °C) clearly indicated the loss of crystallinity only after the dissociation of a second water molecule at 260 °C. The powder diffraction spectra at this temperature reveal broad peaks. The loss of crystallinity may not necessarily represent the total collapse of the anionic hydrogen-bonding network. Therefore, we do not know whether the hexagonal framework of this compound remains intact or readjusts after the loss of water molecules. However, as discussed below, 1,7-phenathroline continues to exist in the protonated form even after heating to 300 °C.

More interestingly, the proton transfer influences the absorption properties of **9** but has no effect on the analogous complex **10**. 1,7-Phenanthroline (mp 80 °C) changes its color from pale yellow (λ 368 nm, and 384 nm) to deep orange-red upon protonation. The solid-state UV/vis spectra of **9** indicate two peaks at 358 (s) and 388 nm (w) and a broad absorption band between 400 and 550 nm (Figure 10a).[15] The UV/vis spectra of **9** recorded after heating at 160 and 300 °C also indicate a charge-transfer band in the region 400−550 nm. However, the absorption properties in the region of 300−400 nm are significantly altered (Figure 10b). These results may suggest that amine **2** remains in the protonated form even at higher temperatures (i.e., the proton transfer is irreversible) and the stacking geometry of **2H** inside the hexagonal cavities may vary after the loss of water molecules. The structural features of **9** bring out a new concept that we can control the absorption properties of colorants/pigments and enhance their thermal stability by encapsulating different structural forms (conjugation modes) of molecules into suitable rigid three-dimensional host matrices by optimizing hydrogen-bonding properties.[11]

Conclusions. Our present studies clearly demonstrate that monodeprotonation of the acid $\mathbf{1H_6}$ leads to the formation of predictable and prototypal three-dimensionally hydrogen-bonded hexagonal networks. Indeed, current crystal engineering strategies for designing organic three-dimensional open networks are more or less limited to diamondoid-type structures only as molecular building blocks with T_d symmetry and complementary intermolecular interactions (tectons) are known for such structures.[5,6,16] For the first time we proved here that one can also target the design of a three-dimensionally connected hexagonal open network by using organic molecular building blocks and achieve such a goal by combining trigonal molecular symmetry with tetrahedrally shaped terminal functional groups (Figures 1 and 2).

The engineering strategy presented for the design of an open 3D hexagonal networks is generic. A variety of amines (e.g., **2**−**5**, **8**) can be used to deprotonate the acid to form open networks provided that the cations/neutral molecules can effectively fill in the resultant void space. Any one or a combination of hydrogen-bonding motifs shown in Scheme 1 form the 3D hexagonal networks reported here. Consequently, the open networks can adjust to some extent to fine-tune the internal dimensions of the cavity to well-accommodate the cation/template based on its size, shape, and functionality (Figure 3). This fact is transparent from the hydrogen-bonding motifs and crystal structures observed for complexes **9**−**12.** However, if the size of the cation/guest is too small as compared to the free volume of the hexagonal cavities, they cannot efficiently fill the empty space of hexagonal networks. In such cases, the flexibility in hydrogen-bonding patterns may not be of much help in attaining close-packed structures and no open structure will be formed. For this reason, quinoline, **6**, owing to its smaller size does not form an open structure in **13**. Indeed, acridine, **5**, is also incapable of efficiently filling void space of open 3D hexagonal networks, but the inclusion of a neutral acridine as a guest and manipulation in stacking interactions alleviates the close-packing requirements through template effects (Figure 2c and 5c).

Interestingly, the hexagonal networks presented here *cannot interweave to fill the void space because of their unique three-dimensional connectivity, so the only possible way to eschew the void space in these systems is through template effects*. One may be able to exploit the self-assembled systems of $\mathbf{1H_5}$ for generating porosity by using smaller amines and templating agents.

Although phosphonic acids are well-known to form robust ionic hydrogen bonds, they have not yet been exploited for

(15) The UV/vis spectra of neutral and protonated forms of **2** in MeOH: 326 (s), 356 (m), 366 nm (m), **2**; 320 (s), 345 (m), 400−500 nm (broad), **2H**. The protonation of **3** (324 (s), 384 nm (w)) and **4** (302 (s), 336 (s), 388 nm (w)) has no effect on their absorption spectra.

(16) (a) Wuest, J. D. In *Mesomolecules: From Molecules to Materials*; Mendenhall, G. D., Greenberg, A., Liebman, J. F., Eds.; Chapman & Hall, New York, 1995. (b) Zaworotko, M. J. *Chem. Soc. Rev.* **1994**, *23*, 283−288. (c) Ermer, O. *J. Am. Chem. Soc.* **1988**, *110*, 3747−3754.

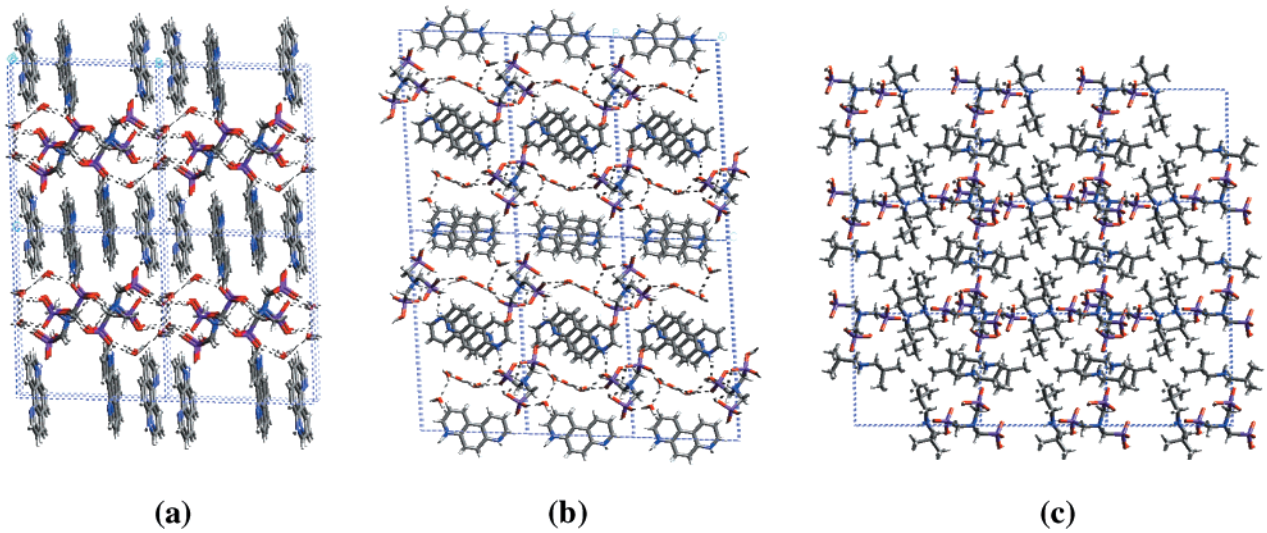


Figure 9. The crystal packing diagrams of doubly deprotanted acid $\mathbf{1H_6}$ complexes **14**, **15**, and **16**. **14** and **15** are solvated with three and five water molecules and form two-dimensional layered structures. **15** forms a hydrogen-bonded chain that is surrounded by diisopropylamines with their hydrophilic moieties pointing inward and the hydrophobic moieties pointing outward.

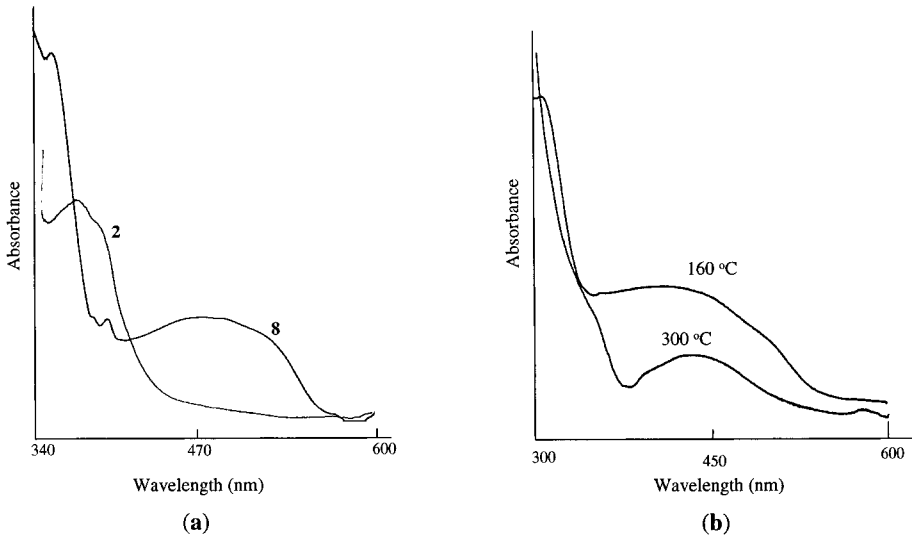


Figure 10. (a) The solid-state UV/vis spectra of 1,7-phenanthroline **2** and its complex **9**. The charge-transfer band in the region of 400−500 nm is due to protonation. (b) The charge-transfer band of **9** remained intact even after heating at 160 and 300 °C.

rational design of organic solids.[17,18] Probably for the first time we successfully employed the phosphonic acid group synthons for crystal engineering purposes, and the triphosphonic acid system reported here may represent a fundamental example for the design of 3D hexagonal structures such as its two-dimensional analogue 1,3,5-benzenetricarboxylic acid (trimesic acid). The logical extension to our results would be the synthesis of a variety of triphosphonic acids (e.g. 1,3,5-benzene triphosphonic acid) and deprotonation of such acids using a variety of amines/templates to form the open 3D hexagonal structures.

The structural features of complexes **9** and **10** may shed light on the design of novel materials where the thermal stability, proton transfer, and absorption properties can be exploited for the design of heat-stable colorants or sensor materials. Our results also propose a novel route for synthesizing heat-stable colorants with tunable absorption properties.

Acknowledgment. The authors would like to acknowledge the support received from NSF (Grant CHE-98 07975) for the purchase of a Bruker-AXS SMART CCD area detector and Grant No. DMR-9707151 for financial support of this study. We also thank Ms. Amellia J. Hessheimer, an undergraduate research scholar, for her assistance in crystallizing some of the complexes reported here.

Supporting Information Available: Crystallographic data of **9**−**16** (crystallographic information, atomic coordinates, bond lengths and angles, temperature factors, ORTEP diagrams), solution/solid-state UV/vis spectra of **2**−**4** and **9**, TGA of **9**, and X-ray powder diffraction spectra of **9** recorded after heating at 160 and 260 °C (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA9935512

(17) Indeed, organophosphonic acids are widely used in the design of advanced inorganic solids and thin films, but their potential in the context of organic solids design has not been exploited. For example, see: (a) Clearfield, A. Metal phosphonate chemistry. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; John Wiley & Sons: New York, 1998; Vol. 47, pp 371−510. (b) Mallouk, T. E.; Gavin, J. A. *Acc. Chem. Res.* **1998**, *31*, 219−227.

(18) (a) Hilderbrand, R. L., Ed. *The Role of Phosphonates in Living Systems*; CRC Press Inc.: Boca Ration, FL, 1983. (b) Chirizia, R.; Herlinger, A. W.; Cheng, Y. D.; Ferraro, J. R.; Rickert, P. G.; Horwitz, E. P. *Solvent Extr. Ion Exch.* **1998**, *16*, 505−526.