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Host–guest complexes of 3,5-dinitrobenzonitrile: channels and sandwich supramolecular architectures☆

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Abstract—Host–guest type complexes of 3,5-dinitrobenzonitrile, **1**, with some hydrocarbons like benzene, naphthalene, *p*-xylene, *o*-xylene, and aza donor molecules (acridine, phenazine and phenothiazine) have been reported. In all the complexes, **1** forms a host network, yielding channels (in three-dimensional arrangement), which are filled by guest molecules, except in the complex of **1** with *p*-xylene. In this complex, although a host–guest type network is observed, the molecules of **1** and *p*-xylene are arranged in such a manner that the hydrocarbon is embedded between the layers of **1**, like in inorganic clay structures. All the complexes have been characterized by single crystal X-ray diffraction methods.

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1. Introduction

In the new era of crystal engineering of supramolecular assemblies, attention is directed towards the synthesis of functional solids with novel tailor-made properties.[1–3] In this direction, noncovalent bonds and dative bonds have been well utilized, because of their directional nature, to create a variety of supramolecular architectures.[4–7] Among the numerous assemblies, host–guest type systems gained special attention for possible applications in the areas of catalysis, separation technology, biomimetics, etc.[8–10] Early success of the synthesis was obtained with carboxylic acid compounds.[11,12] For instance, trimesic acid is a well-known representative example for a class of organic host-structures,[11d–f] while a molecular adduct of trithiocyanuric acid and 4,4′-bipyridyl is one of the binary component hosts, accommodating different types of guest molecules ranging from benzene to anthracene.[13] Other pseudo host–guest type systems, that we reported were adducts of 3,5-dinitrobenzoic acid, and its 4-methyl and 4-chloro derivatives, with anthracene.[14] In these complexes, the acid molecules form a hexagonal ensemble with cavities, which are being occupied by anthracene molecules (see Fig. 1).

The cavities, however, failed to align in a three-dimensional arrangement to yield channels, thus, true host–guest systems could not be obtained. Further, cavity structures were obtained in the presence of hydrocarbon moieties only, while replacement of the anthracene with aza-molecules like acridine, phenazine, 4,4′-bipyridine, etc. gave different assemblies possessing molecular tapes.[15] Nevertheless, aza-molecules could be incorporated as guests upon replacement of the acid group on 3,5-dinitrobenzoic acid with an amide group.[16a] But, surprisingly, hydrocarbons failed to form host–guest systems with the 3,5-dinitrobenzamide.[16b] Thus, both the acid and its amide were able to form only the guest–specific host lattices. In addition, it is understood that, the host-network is created by both strong (O–H···O, N–H···O) and weak (C–H···O) hydrogen bonds.

Hence, we aimed to explore the feasibility of construction of host lattices entirely through weak hydrogen bonds, as such assemblies are not well known in the literature, and also with the hope of creating a universal host rather than one

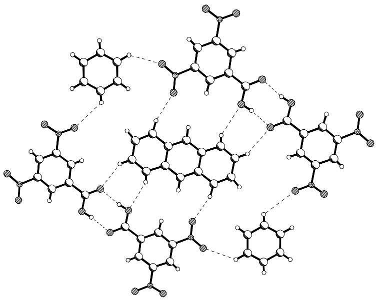

Figure 1. Host–guest complex of 3,5-dinitrobenzoic acid with anthracene in the presence of benzene.

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Keywords: 3,5-Dinitrobenzonitrile; Host–guest complexes; Channel structures; Layered structures.

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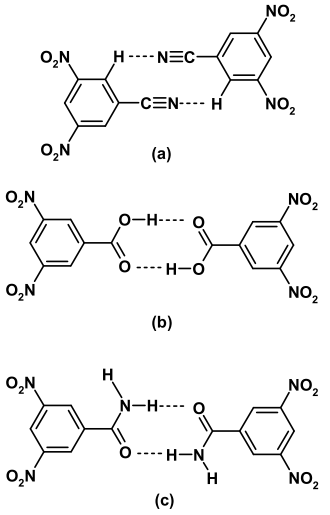

Figure 2. Hydrogen bonding arrangement between the adjacent molecules of (a) 3,5-dinitrobenzonitrile (b) 3,5-dinitrobenzoic acid and (c) 3,5-dinitrobenzamide.

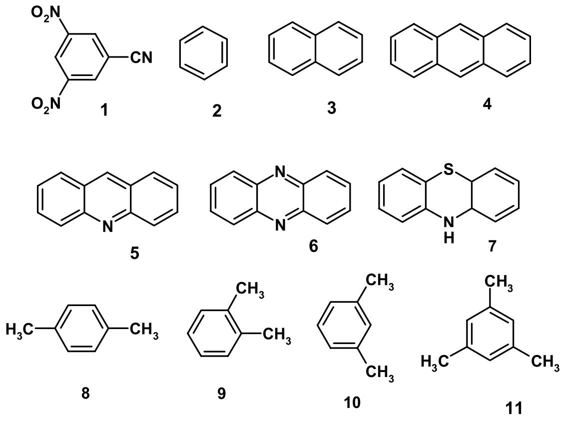

Chart 1.

that is guest specific, utilizing the flexible nature of the weak hydrogen bonds.[17] For this purpose, in our search for a potential molecular entity that provides a topologically similar hydrogen bonding network as that of 3,5-dinitrobenzoic acid and the corresponding amide, we have come across 3,5-dinitrobenzonitrile, **1**, the crystal structure of which was determined by us recently,[18] having the required features. The association of two neighbouring molecules of **1** is shown in Figure 2a along with the similar arrangements for acid and amide analogues in Figure 2b and c, respectively.

Since the topology of the hydrogen bond arrangement is identical, we believed that 3,5-dinitrobenzonitrile, **1** would yield host networks with appropriate guest molecules. Further evidence in this regard is obtained with the reported crystal structure of adduct of **1** and anthracene.[19] Hence, our endeavour started with the crystallization of **1** with benzene, naphthalene, acridine, phenazine, phenothiazine, -*o*, -*m* and -*p* xylenes, mesitylene, etc. Structural aspects of some of these co-crystals, as listed in Chart 1, will be discussed in this article, in a detailed manner.

2. Results and discussion

Crystallization of **1** from a benzene solution gave single crystals, which are quite unstable at ambient conditions suggesting that a solvated complex resulted. Characterization of the single crystals by X-ray diffraction studies reveals a 1:1 molar ratio complex of **1** and benzene. This complex forms channels in its three-dimensional structure along a crystallographic axis. The three-dimensional structure and the arrangement of molecules around the void space are shown in Figure 3a and b, respectively.

The molecules of **1** form a hexagonal network in such a manner that in each hexagon, dimers of **1** (held together by centrosymmetric cyclic C–H···N hydrogen bonds) are connected together by acyclic C–H···O hydrogen bonds (Fig. 3b). The H···N distance in the cyclic pattern is 2.64 Å with the C–H···N angle of 146°, whereas the H···O distance in the acyclic C–H···O hydrogen bonds is 2.94 Å. Other characteristics of the hydrogen bonds are given in Table 1. Thus, a cavity of dimensions 7×15 Å^2 is created

Reactants	**Solvent**	**Product and Composition**	
1 + 2	**benzene**	**2a**	**1:1**
1 + 5	**methanol**	**5a**	**2:1**
1 + 6	**methanol**	**6a**	**2:1**
1 + 7	**methanol**	**7a**	**2:1**
1 + 8	**methanol**	**8a**	**1:1**

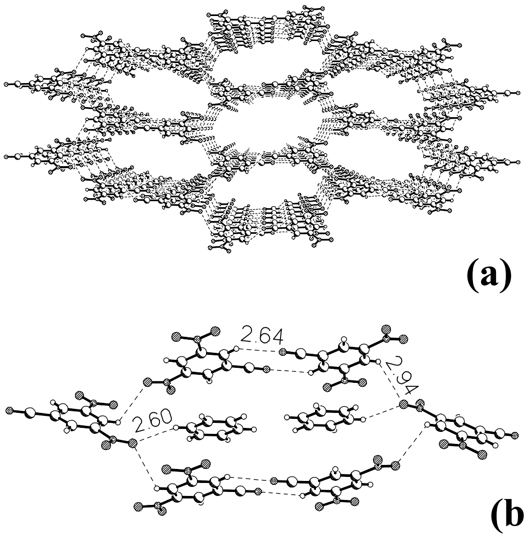

Figure 3. (a) Representation of channels observed in the three-dimensional arrangement of the adduct, **2a**, formed between 3,5-dinitrobenzonitrile, **1** with benzene. (b) Hexagonal arrangement of molecules of **1**, forming a cavity of dimension, (7×15 Å^2).

Table 1. Characteristics of hydrogen bonds[a] distances, Å and angles ° observed in the molecular adducts, **2a**, **5a**, **6a** and **8a**

Hydrogen bonds (donor–H···acceptor)	**2a**			**5a**			**6a**			**8a**		
C–H···O	2.47	3.24	130.0	2.52	3.47	166.2	2.48	3.41	162.7	2.60	3.45	162.9
	2.60	3.46	157.1	2.53	3.35	138.5	2.55	3.37	137.0	2.74	3.44	137.9
	2.61	3.33	125.2	2.59	3.42	139.9	2.57	3.43	142.4	2.78	3.31	120.9
	2.64	3.43	149.5	2.85	3.75	160.6	2.80	3.57	139.6	2.81	3.63	145.0
	2.87	3.42	120.0	2.87	3.63	139.9	2.82	3.72	159.2	2.82	3.57	140.1
	2.94	3.42	113.6							2.85	3.43	125.3
										2.89	3.72	146.6
										2.90	3.75	168.4
										2.90	3.53	124.8
C–H···N	2.64	3.42	145.8	2.45	3.33	158.6	2.48	3.34	161.5	2.65	3.44	143.4
	2.81	3.44	123.9	2.93	3.76	144.1	2.86	3.68	144.1	2.88	3.66	143.5
	2.87	3.60	131.9							2.91	3.58	129.9

[a] In each complex, the three numbers correspond to H···acceptor, donor···acceptor and angle.

and benzene molecules fit in these cavities, interacting with the host network through the formation of C–H···O hydrogen bonds. These hydrogen bonds were formed between the aromatic hydrogens of benzene and $-NO_2$ groups of **1**, with an H···O distance of 2.60 Å (Table 1). Thus, adduct **2a**, as anticipated, gave a host–guest channel structure, entirely made up of weak hydrogen bonds, C–H···N and C–H···O.

Further, a close look at Figure 3b shows that molecules having dimensions equivalent to that of two or three fused benzene moieties can also form similar complexes, replacing the benzene molecules. Hence, we attempted to co-crystallize **1** with naphthalene, **3**. However, the crystals of the adduct of **1** were highly unstable as well as of poor quality to carry out any further analysis. Instead, we obtained stable and good quality single crystals with acridine, **5**, and phenazine, **6**, in a 2:1 ratio. The two-complexes have been labeled as **5a** and **6a**, respectively.

Analysis of X-ray diffraction data of **5a** and **6a** reveal that these two are isomorphous to complex **2a**, with similar unit cell dimensions and crystallizing in the same space group, $P2_1/c$. Further, **2a**, **5a** and **6a** are also iso-structural with the formation of channel structures in the three-dimensional arrangement, similar to the one shown in Figure 3a for **2a**; the only difference being that the channels are occupied by single molecules[20] of either acridine or phenazine molecules in **5a** and **6a** as shown in Figure 4a and b, respectively. In each hexagon the molecules of **1** exist as dimers by forming a centrosymmetric 10-membered ring pattern through C–H···N hydrogen bonds (H···N, 2.45 and 2.48 Å for **5a** and **6a**, respectively, Table 1). Such adjacent dimers are further held together by C–H···O hydrogen bonds (**5a**, H···O, 2.87 and **6a**, 2.80 Å) leading to the formation of cavities (Fig. 4).

A noteworthy and unique nature of the adducts **2a**, **5a** and **6a** is the retention of the host lattice by **1**, irrespective of the nature of the functional groups present on the guest molecules, unlike in the corresponding acid and amide analogues. This is further reflected in the formation of an iso-structural complex between **1** and phenothiazine as confirmed by single crystal[21] as well as X-ray powder diffraction techniques. The powder X-ray diffraction patterns are shown in Figure 5.

The patterns shown in Figure 5, were obtained from the ground mixtures of **1** with **5**, **6** and **7**. It is evident that the intense peak at 25.5°, as well as other minor peaks in Figure 5c match with similar peaks shown in Figure 5a and b. Hence, it could be concluded that **1** and **7** also forms a complex, which is iso-structural to that of **5a** and **6a**. 3,5-dinitrobenzonitrile, **1**, however, forms a different host–guest structure, in an intercalated manner (see Fig. 6a), with *p*-xylene and *o*-xylene.

Crystallization of **1** from *o*-, *m*-, and *p*-xylenes as well as mesitylene gave colorless, block-like single crystals from only *o*-xylene[22] and *p*-xylene, which are also unstable like **2a**, but, *m*-xylene and mesitylene yielded only parent crystals of **1**. The crystals obtained from *p*-xylene have been labeled as **8a**. Structure determination reveals that **8a** crystallizes in a 1:1 ratio of **1** and *p*-xylene, with two molecules of each in the asymmetric unit. The two symmetry independent molecules of **1** are labeled as A and B, while the *p*-xylene molecules are labeled as C and D.

In adduct **8a**, *p*-xylene and **1** form a stacked sheet structure, in the three-dimensional arrangement, shown in Figure 6b,

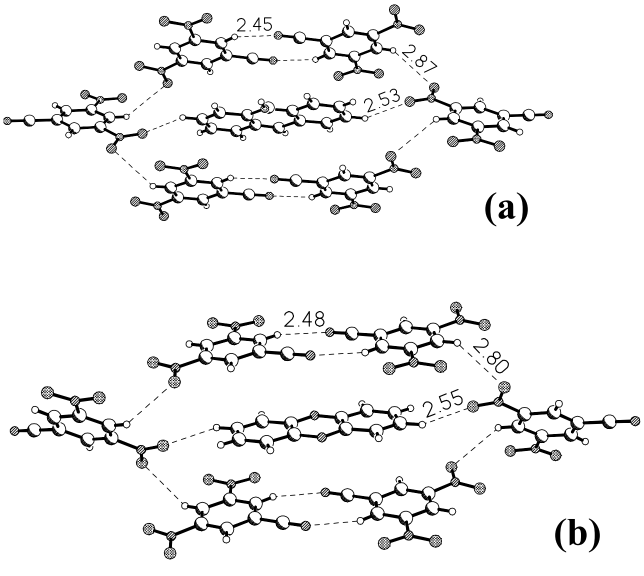

Figure 4. Arrangement of molecules in the adducts (a) **5a** and (b) **6a**, in an hexagonal manner creating voids, which are occupied by guest molecules.

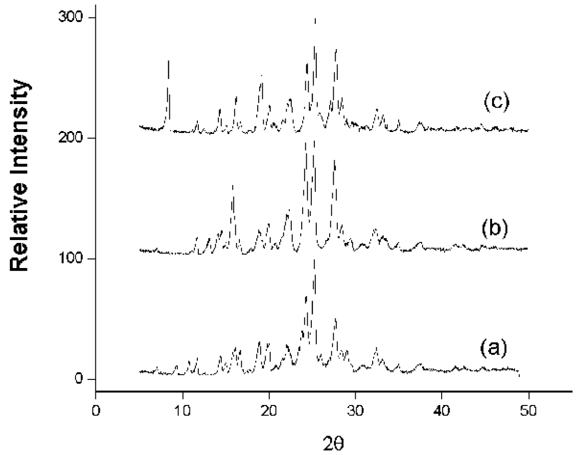

Figure 5. Powder X-ray diffraction patterns of ground mixture of complexes of **1** with (a) acridine (b) phenazine and (c) phenothiazine.

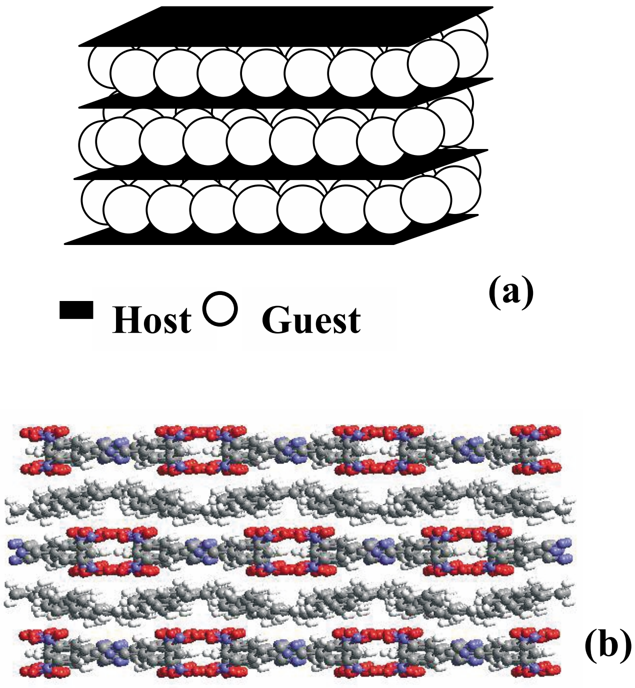

Figure 6. (a) Schematic represenatation of intercalated host–guest complexes. (b) Three-dimensional arrangement of 3,5-dinitrobenzonitrile, **1** and *p*-xylene molecules in the alternate layers in the crystal structure of adduct, **8a**.

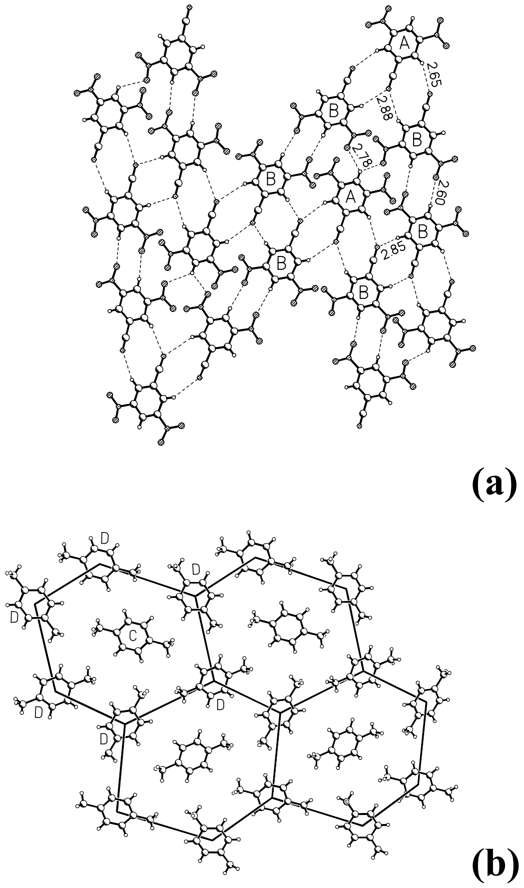

Figure 7. (a) Interaction among the molecules of **1** within a two-dimensional sheet in the complex, **8a**. (b) Two-dimensional sheet arrangement of *p*-xylene molecules constituting a hexagonal arrangement.

such that *p*-xylene molecules are embedded between the layers of **1**, with a close resemblance to inorganic clay structures.[23]

Within the layers of **1**, the molecules are arranged in such a way that interaction between the symmetry independent molecules (A–B) and symmetry dependent molecules (B–B) constitute zig-zag molecular tapes. There is no interaction of the type A–A. This arrangement is shown in Figure 7a. In each tape, molecules A and B are held together by C–H···N hydrogen bond dimers with H···N distances of 2.65 and 2.88 Å (Table 1). However, symmetry dependent molecules (B) form centrosymmetric cyclic C–H···O hydrogen-bonded coupling with an H···O distance of 2.60 Å. Such adjacent tapes are further connected to each other forming a centrosymmetric cyclic coupling consisting of C–H···N hydrogen bonds, (H···N, 2.85 Å, Table 1). However, in the *p*-xylene layers, the two symmetry independent molecules arrange such that each of six molecules of a particular symmetry (say D) form a hexagonal network around the other molecules (say C), as shown in Figure 7b. This network is stabilized by typical H···H van der Waals interactions, generally known for hydrocarbons.[24]

2.1. Hexagonal versus intercalated host–guest complexation

A comparison of **2a**, **5a**, **6a** and **8a** reveals that the dimensions of the guest molecules (benzene, phenazine and acridine) in adducts, **2a**, **5a** and **6a** is approximately 9 Å.[25] Thus, those molecules could fit into the channels with average dimensions 14×7 $Å^2$ formed by the hexagonal arrangement of host molecules. However, *p*-xylene with the dimension of ~7 Å appears to be too small to remain in the channels of 14 Å as a single molecule like acridine and phenazine in **5a** and **6a**, respectively, and at the same time it will become big to occupy as two molecules like benzene in **2a**. Hence *p*-xylene failed to yield an iso-structural complex. In general, if the dimension of the guest molecules is inappropriate to the void space that is being created by the hexagonal arrangement of host molecules, the result is often the formation of a different type of assembly. Nevertheless, still, **1** is able to form a host–guest type complex with *p*-xylene, perhaps, due to the flexibility of the weak C–H···N hydrogen bonds for the reorganization to be commensurate with the dimensions of guest molecules. Thus, it may be concluded that 3,5-dinitrobenzonitrile, **1**, would yield host–guest type complexes, possessing hexagonal channels with the guests of dimension ~9 Å, otherwise, it may form intercalated channel structures. However, if the incoming substrate possesses strong donor/acceptor groups, naturally, **1** would yield different types of molecular adducts.[18]

In conclusion, we have reported host–guest complexes of 3,5-dinitrobenzonitrile, **1**, with various hydrocarbons, as well as aza molecules in which **1** acts as a host lattice accommodating different types of guest molecules. It is also observed that depending upon the dimensions of the guest molecules, different types of host networks are created to yield either hexagonal channels or intercalated channels. These variations appear to be the result of involvement of only weak hydrogen bonds in the formation of either host-network or host–guest interactions. Thus, these examples have demonstrated the utility of the weak hydrogen bonds such as C–H···N, C–H···O, etc. for the creation of flexible supramolecular assemblies, which may have potential applications in the areas of catalysis, separation technology, etc. due to the formation of structures with void space.

3. Experimental

3.1. Synthesis of 2a, 5a, 6a and 8a

All the chemicals were obtained from commercial suppliers (Sigma-Aldrich) and used without further purification. HPLC grade solvents were used for the crystallization experiments. Synthesis of co-crystals was carried out by dissolving the reactants in the appropriate solvents, either at room temperature or by warming on a water bath, and subsequently cooling by a slow-evaporation method. In a typical experiment, 96.5 mg (5 mmol) of 3,5-dinitrobenzonitrile and 45.1 mg of phenazine (2.5 mmol) were dissolved in a boiling methanol solution and then subsequently cooled to room temperature. Yellow colored stable and plate-like single crystals of good quality were obtained over a period of 3 days and were used for X-ray diffraction studies. However, in the case of adducts of hydrocarbons like benzene, *p*-xylene, the obtained complexes were found to be unstable upon removing from the mother liquor. Crystallographic studies on these crystals were carried out following special procedures as described in Section 3.2.

3.2. X-ray crystallography

Good-quality single crystals carefully chosen using a Leica microscope equipped with CCD camera were used to collect X-ray intensity data on a Bruker diffractometer (APEX CCD area detector). The data collection were carried out at 133 K for **2a** and **8a**, whereas for **5a** and **6a** were carried out at room temperature (293 K). The unstable crystals **2a** and **8a** were smeared in paraffin oil as soon as removed from the mother liquor, to protect from decomposition during the data collection period. The data were processed using Bruker suite of programmes (SAINT).[26] Structure determination and refinements were carried out using SHELXTL package.[27] All the intermolecular interactions were computed using PLATON prorgramme.[28] Full details of crystallographic information are deposited at Crystallographic Data Centre as supplementary publication (**2a**, CCDC 219919; **5a**, CCDC 219920; **6a**, 219921; **8a**, 219922). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB12 1EZ, UK [fax: +44-1223-336033 or email: deposit@ccdc.cam.ac.uk].

3.2.1. Crystal data for 2a. ($C_7H_3N_3O_4$): (C_6H_6), fw=271.23, monoclinic, $P2_1/c$, a=6.836(2) Å, b=7.229(2) Å, c=25.840(1) Å, β=92.44°(1), V=1275.8(5) Å^3, Z=4, D_{calc}=1.412 g cm^{-3}, $F(000)$=560, λ(Mo Kα)=0.71073, T=133 K, reflections collected/unique 5167/1806 (R_{int}=0.0362), final GooF=1.210, R_1=0.0592, wR_2=0.1428, 217 parameters, μ=0.108 mm^{-1}, R indices based on 1633 reflections with $I>2\sigma(I)$ (refinement on F^2), absorption corrections applied.

3.2.2. Crystal data for 5a. ($C_7H_3N_3O_4$): ($C_{13}H_9N_1$), fw=283.23, monoclinic, $P2_1/c$, a=6.979(1) Å, b=7.277(1) Å, c=24.807(4) Å, β=90.48°(3), V=1259.8(3) Å^3, Z=4, D_{calc}=1.493 g cm^{-3}, $F(000)$=582, λ(Mo Kα)=0.71073, T=133 K, reflections collected/unique 5201/1803 (R_{int}=0.0212), Final GooF=1.038, R_1=0.0368, wR_2=0.1034, 232 parameters, μ=0.114 mm^{-1}, R indices based on 1482 reflections with $I>2\sigma(I)$ (refinement on F^2), absorption corrections applied.

3.2.3. Crystal data for 6a. 2($C_7H_3N_3O_4$): ($C_{12}H_8N_2$), fw=283.23, monoclinic, $P2_1/c$, a=6.873(1) Å, b=7.308(1) Å, c=24.871(5) Å, β=90.68°(1), V=1249.1(4) Å^3, Z=4, D_{calc}=1.506 g cm^{-3}, $F(000)$=580, λ(Mo Kα)=0.71073, T=293 K, reflections collected/unique 5094/1787 (R_{int}=0.0176), Final GooF=1.046, R_1=0.0390, wR_2=0.1036, 219 parameters, μ=0.116 mm^{-1}, R indices based on 1546 reflections with $I>2\sigma(I)$ (refinement on F^2), absorption corrections applied.

3.2.4. Crystal data for 8a. ($C_7H_3N_3O_4$): (C_8H_{10}), fw=897.85, monoclinic, $C2/c$, a=16.628(5) Å, b= 13.530(4) Å, c=21.080(6) Å, β=112.95°(1), V=4367.0(2) Å^3, Z=4, D_{calc}=1.366 g cm^{-3}, $F(000)$=1872, λ(Mo Kα)=0.71073, T=133 K, reflections collected/unique 9077/3131 (R_{int}=0.0264), Final GooF=1.128, R_1=0.0491, wR_2=0.1137, 378 parameters, μ=0.102 mm^{-1}, R indices based on 2560 reflections with $I>2\sigma(I)$ (refinement on F^2), absorption corrections applied.

4. Supplementary Material

A total of 44 pages, X-ray data with details of refinement procedures (cif files), ORTEP diagrams, lists of bond parameters (bong lengths and angles), structure factors of molecular complexes **2a**, **5a**, **6a** and **8a**.

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References and notes

1. (a) Desiraju, G. R. *Crystal engineering: the design of organic solids*; Elsevier: Amsterdam, 1989. (b) Lehn, J. M. *Supramolecular chemistry: concepts and perspectives*; VCH: Weinheim, 1995. (c) Steed, J. W.; Atwood, J. L. *Supramolecular chemistry*; Wiley: Chichester, 2000.
2. (a) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311–2327. (b) Desiraju, G. R. *Nature* **2001**, *412*, 397–400. (c) Desiraju, G. R. *Nature* **2003**, *423*, 485. (d) MacDonald, J. C.; Whitesides, G. M. *Chem. Rev.* **1994**, *94*, 2383–2420.
3. (a) Whitesides, G. M.; Simanek, E. E.; Mathias, J. P.; Seto, C. T.; Chin, D. N.; Mammen, M.; Gordon, D. M. *Acc. Chem. Res.* **1995**, *28*, 37–44. (b) Zimmerman, S. C.; Corbin, P. S. *Struct. Bond.* **2000**, *96*, 63–94. (c) Timmerman, P.; Prins, L. J.; Reinhoudt, D. N. *Angew. Chem., Int. Ed.* **2001**, *40*, 2382–2426. (d) Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120–126. (e) Huang, K.-S.; Britton, O.; Bryn, S. R.; Etter, M. C. *J. Mater. Chem.* **1997**, *7*, 713–720. (f) Kudava, S. S.; Blaser, D.; Boese, R.; Desiraju, G. R. *J. Org. Chem.* **2001**, *66*, 1621–1626.
4. (a) Pedireddi, V. R.; Chatterjee, S.; Ranganathan, A.; Rao, C. N. R. *Tetrahedron* **1998**, *54*, 9457–9474. (b) Pedireddi, V. R.; PrakashaReddy, J. *Tetrahedron Lett.* **2002**, *43*, 4927–4930. (c) Pedireddi, V. R.; Belhekar, D. *Tetrahedron* **2002**, *58*, 2937–2941. (d) Pedireddi, V. R.; Ranganathan, A.; Rao, C. N. R. *J. Am. Chem. Soc.* **1999**, *121*, 1752–1753. (e) Pedireddi, V. R. *Cryst. Growth. Des.* **2001**, *1*, 383–385. (f) Pedireddi, V. R.; Chatterjee, S.; Ranganathan, A.; Rao, C. N. R. *J. Mol. Struct.* **2000**, *520*, 107–115.
5. (a) Nangia, A. *Curr. Opin. Solid State Mater. Sci.* **2001**, *5*, 115–122. (b) Vishweshwar, P.; Nangia, A.; Lynch, V. M. *J. Org. Chem.* **2002**, *67*, 556–565. (c) Ranganathan, D.; Lakshmi, C.; Karle, I. L. *J. Am. Chem. Soc.* **1999**, *121*, 6103–6107. (d) Bong, D. T.; Clark, T. D.; Granja, J. R.; Ghadiri, M. R. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 988–1011. (e) Zerkowski, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994**, *116*, 4298–4304. (f) Aakeroy, C. B.; Beatty, A. M.; Helfrich, B. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 3240–3242. (g) Batchelor, E.; Klinowski, J.; Jones, W. *J. Mater. Chem.* **2000**, *10*, 839–848.
6. (a) Hollingsworth, M. D.; Brown, M. E.; Dubley, M.; Chaung, H.; Peterson, M. L.; Hillier, A. C. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 965–969. (b) Hollingsworth, M. D.; Brown, M. E.; Santasiero, B. D.; Huffman, J. C.; Goss, C. R. *Chem. Mater.* **1994**, *6*, 1227–1244. (c) Biradha, K.; Dennis, D.; Mackinnon, V. A.; Sharma, C. V. K.; Zaworotko, M. *J. Am. Chem. Soc.* **1998**, *120*, 11894–11903. (d) Holman, K. T.; Martin, S. M.; Parker, D. P.; Ward, M. D. *J. Am. Chem. Soc.* **2001**, *123*, 4421–4431. (e) Steiner, T. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 48–76. (f) Zaman, B.; Tomura, M.; Yamashita, Y. *J. Org. Chem.* **2001**, *66*, 5987–5995. (g) Shan, N.; Bond, A. D.; Jones, W. *Cryst. Eng* **2002**, *5*, 9–24.
7. (a) Romero, F. M.; Ziessel, R.; Dupontgervais, A.; Vandorsselaer, A. *Chem. Commun.* **1996**, 551–554. (b) Fujita, M.; Sasaki, O.; Mitsuhashi, T.; Fujita, T.; Yazaki, J.; Yamaguchi, K.; Ogura, K. *Chem. Commun.* **1996**, 1535–1536. (c) Zaworotko, M. J.; Kravtsov, V.; Moulton, B.; Abourahma, H. *J. Am. Chem. Soc.* **2002**, *124*, 9990–9991. (d) Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474–484.
8. (a) Seo, J. S.; Whang, D.-M.; Lee, H.-Y.; Jun, S. I.; Oh, J.-H.; Jeon, Y.-J.; Kim, K.-M. *Nature* **2000**, *404*, 982–986. (b) Sawaki, T.; Aoyama, Y. *J. Am. Chem. Soc.* **1999**, *121*, 4793–4798. (c) Aoyama, Y. *Top. Curr. Chem.* **1998**, *198*, 131–161.
9. (a) Li, H.; Eddaoudi, M.; O' Keefee, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276–279. (b) Choi, H. J.; Lee, T. S.; Suh, M. P. *Angew. Chem., Int. Ed.* **1999**, *38*, 1405–1408.
10. (a) Tanev, P. T.; Pinnavaia, T. J. *Science* **1996**, *271*, 1267–1269. (b) Hamilton, A. D.; van Engen, D. *J. Am. Chem. Soc.* **1987**, *109*, 5035–5036. (c) Seneque, O.; Rager, M.-N.; Giorgi, M.; Reinaud, O. *J. Am. Chem. Soc.* **2000**, *122*, 6183–6189.
11. (a) Pedireddi, V. R.; Arora, K. K. *J. Org. Chem.* **2003**, *68*, in press. (b) Ermer, O.; Neudorfl, J. *Chem. Eur. J.* **2001**, *7*, 4961–4980. (c) Sharma, C. V. K.; Zaworotko, M. J. *Chem. Commun.* **1996**, 2655–2656. (d) Duchamp, D. J.; Marsh, R. E. *Acta Crystallogr. Sect. B* **1969**, *25*, 5–19. (e) Melendez, R. E.; Sharma, C. V. K.; Zaworotko, M. J.; Bauer, C.; Rogers, R. D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2213–2215. (f) Kolotuchin, S. V.; Fenlon, E. E.; Wilson, S. R.; Loweth, C. J.; Zimmerman, S. C. *Angew Chem., Int. Ed. Engl.* **1995**, *34*, 2654–2656. (g) Evans, O. R.; Lin, W. *Chem. Mater.* **2001**, *13*, 3009–3017.
12. (a) Braga, D.; Maini, L.; Paganelli, F.; Tagliavini, E.; Casolari, S.; Grepioni, F. *J. Organomet. Chem.* **2001**, *637*, 609–615. (b) Holy, P.; Zavada, J.; Cisarova, I.; Podlaha, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 381–383. (c) Howard, J. A. K.; Perepichka, D. F.; Bryce, M. R.; Batsanov, A. S.; Cuello, A. O.; Gray, M.; Rotello, V. M. *J. Org. Chem.* **2001**, *66*, 4517–4524. (d) Goodman, M.; Del Valle, J. R. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 1600–1602. (e) Barthelet, K.; Marrot, J.; Riou, D.; Ferey, G. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 281–284. (f) Ermer, O.; Neudorfl, J. *Helv. Chim. Acta* **2001**, *84*, 1268–1313.
13. Pedireddi, V. R.; Chatterjee, S.; Ranganathan, A.; Rao, C. N. R. *J. Am. Chem. Soc.* **1997**, *119*, 10867–10868.
14. (a) Pedireddi, V. R.; Jones, W.; Chorlton, A. P.; Docherty, R. *Chem. Commun.* **1996**, 987–988. (b) Pedireddi, V. R.; Jones, W.; Chorlton, A. P.; Docherty, R. *Tetrahedron Lett.* **1998**, *39*, 5409–5412.
15. (a) Pedireddi, V. R.; Jones, W.; Chorlton, A. P.; Docherty, R. *Chem. Commun.* **1996**, 997–998. (b) Pedireddi, V. R.; Chatterjee, S.; Ranganathan, A. *Tetrahedron Lett.* **1998**, *39*, 9831–9834.
16. (a) Pedireddi, V. R.; PrakashaReddy, J. *Tetrahedron Lett.* **2003**, *44*, 6679–6681. (b) Pedireddi, V. R.; PrakashaReddy, J. Unpublished results.
17. Desiraju, G. R.; Steiner, T. The weak hydrogen bond in structural chemistry and biology; Oxford University Press: New York, 1999.
18. Pedireddi, V. R.; PrakashaReddy, J.; Arora, K. K. *Tetrahedron Lett.* **2003**, *44*, 4857–4860.
19. Bock, H.; Ziemer, K.; Nather, C.; Schodel, H.; Kleine, M.; Sievert, M. *Z. Naturforsch. Teil B* **1996**, *51*, 1538–1554.
20. Occupation of cavities by single molecules of acridine and

phenazine, indeed, suggests dense-packing of channels in **5a** and **6a** than in **2a**, which is also reflected in the calculated densities of crystal lattices (**2a**, 1.412; **5a**, 1.493 and **6a**, 1.506 g cm^{-3}).

21. Unit cell dimensions of **1** and **7** are a=7.060(1), b=7.112(9), c=24.850(4), α=90.00, β=90.20(1), γ=90.00°, V=1248.0(3) Å^3. Since these parameters are very similar to those for **2a**, **5a** and **6a**, and also the iso-structurality among them is established through powder X-ray diffraction methods, crystal structure determination is not carried out.
22. Single crystals of *o*-xylene adduct of **1** are extremely unstable that we were able to collect data sufficient for unit cell determination only. Unit cell parameters are a=13.86(1), b=16.63(9), c=25.65(2), α=71.82(8), β=82.94(4), γ=66.13(4)°, V=5135(6) Å^3. These unit cell parameters are closely similar to that of **8a**, suggesting iso-structurality with **8a**.
23. (a) Zhang, Z.; Hicks, R. W.; Pauly, T. R.; Pinnavaia, *J. Am. Chem. Soc.* **2002**, *124*, 1592–1593. (b) Jones, W.; Theocharis, C. R. *Chem. Commun.* **1984**, 369–370. (c) Jones, W.; Bond, A. D.; Benevelli, F. *J. Mater. Chem.* **2002**, *12*, 324–332.
24. (a) Desiraju, G. R.; Gavezzotti, A. *Acta. Crystallogr. Sect. B* **1988**, *44*, 427–434. (b) Desiraju, G. R.; Gavezzotti, A. *Acta. Crystallogr. Sect. B* **1989**, *45*, 473–482.
25. The dimension of a benzene molecule is ≈4.5 Å. However, taking into account of two molecules present in the channels, the dimension of the guest is considered to be 9 Å.
26. Siemens, SMART System, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 1995.
27. Sheldrick, G. M. *SHELXTL-PLUS*: *Program for Crystal Structure Solution and Refinement*; University of Gottingen: Gottingen, Germany, 1997.
28. Spek, A. L. *PLATON*: *Molecular Geometry Program*; University of Utrecht, The Netherlands, 1995.