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Ladder and Hexagonal Hydrogen-bond Networks from a Self-complementary H-shaped Tecton

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Self-assembly of the H-shaped tecton 1,4-di[bis (4′-hydroxyphenyl)methyl]benzene 1 via O—H···O hydrogen bonds leads to a ladder or hexagonal network depending on the included solvent molecule. MeOH and EtOH solvates of 1 have isostructural hexagonal networks whereas inclusion of MeCN or dioxane results in a ladder structure. The ladder rung distance is modularly expanded from 11 to 20 Å in the cocrystal of 1 with 4,4′-bipyridine. The novel H-tecton adds to the library of T- and Y-shaped and tetrahedral organic nodes for network construction.

Keywords: Ladder; Hexagonal; Hydrogen bond; Network; Crystal engineering; Crystal structure prediction

INTRODUCTION

Crystal engineering of network architectures from molecular building blocks, or tectons [1–7], is a popular research activity in supramolecular chemistry because of the diverse networks that can be synthesized and their potential utility in materials science. The use of ligand- and metal-center libraries to assemble 1D ladder, 2D brick wall and 3D frame coordination polymer structures from T-shaped nodes (Scheme 1) is by now well illustrated [8–14]. Organic T-tectons, however, have been reported only recently and fewer examples of all-organic networks [15–20] are known compared to metal–organic structures. One of the challenges in organic network synthesis is to graft a 90°bond angle at the T-node whereas this geometry is quite common in metal centers (e.g. trigonal bipyramidal, octahedral, square planar). Hexagonal networks are commonplace for Y-shaped organic molecules because trigonal tectons with a 120°bond angle are easily available, as in, for example, trimesic acid, cyclohexanetricarboxylic acid, triphenoxytriazine, cyclotriphosphazene and guanidinium. [21–30]. In continuation of our interest in the design of organic T-tectons for self-assembly to various tiling patterns [17–19], we report here a novel H-shaped building block, 1,4-di[bis(4′-hydroxyphenyl)methyl]benzene **1**, and its octamethyl derivative **2**. These H-shaped molecules crystallize as 1D ladder and 2D hexagon network structures via O—H···O hydrogen bonds. Although there are numerous examples of T- [10] and Y-shaped [21–30] molecules, and L- [8] and V-shaped [4] ligands are also known, there is to our knowledge only one report on crystal engineering with an H-shaped molecule [31–32]. The selection of building block **1** as H-tecton is justified (Scheme 2) because: (1) the molecule crystallizes from several common solvents; (2) the conformationally flexible, strong hydrogen-bonding phenol OH groups are the “sticky groups”; (3) the rigid aromatic rings not only give the requisite H-shape but also can participate in attractive edge-to-face, π–π stacking and other stabilizing motifs; and (4) the facile synthesis of **1** affords ready access to several derivatives.

EXPERIMENTAL

Synthesis [33]

A mixture of terephthalaldehyde (500 mg, 3.7 mmol) and phenol (1.8 mL, 14.9 mmol) in glacial acetic acid (10 mL) was treated dropwise with concentrated HCl (10 mL). The reaction mixture was stirred at room temperature for 24 h. The mixture was poured into crushed ice and the precipitate was filtered and

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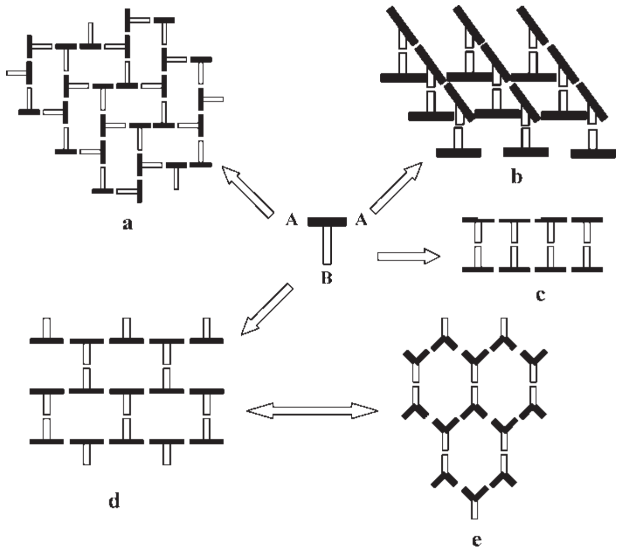
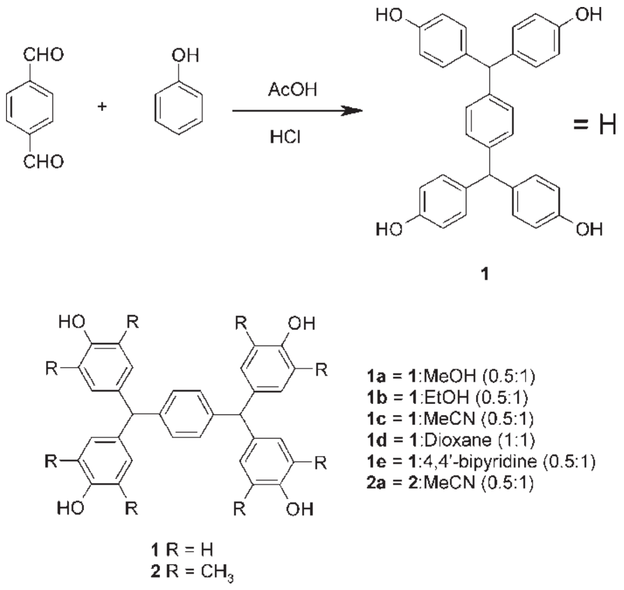


SCHEME 1 Some typical three-connected networks from a T-node. (a) parquet floor; (b) bilayer; (c) ladder; (d) brick wall; (e) honeycomb.

washed with cold water. The dried compound **1** was purified by column chromatography using ethyl acetate–*n*-hexane (1:4) to yield 884 mg (50%) of the pure product. Compound **2** was prepared using the same procedure with 2,6-dimethylphenol in 50% yield. **1**: ^{1}H NMR (DMSO-d_6) δ 5.28 (2H, s), 6.65 (8H, d, 8.5 Hz), 6.86 (8H, d, 8.5 Hz), 6.98 (4H, s), 9.19 (4H, s). IR (KBr pellets): 3503, 3016, 2920, 1608, 1504, 1417, 891 cm^{-1}, mp 275°C. **2**: ^{1}H NMR (DMSO-d_6) δ 2.08 (24H, s), 5.15 (2H, s), 6.59 (8H, s), 6.95 (4H, s), 8.00 (4H, s). IR (KBr pellets): 3290, 3016, 2924, 1597, 1510, 854, 833, 636 cm^{-1}, mp 261 °C.



SCHEME 2 Synthesis and crystalline derivatives of H-tectons **1** and **2**.

X-ray Crystallography

X-ray intensity data for **1a**, **1b** and **2a** were collected on a Nonius Kappa CCD detector and data for **1c–e** were collected on a Bruker SMART APEX CCD area detector using graphite-monochromated Mo Kα radiation. Crystal structures were solved by direct methods using SHELXS-97 [34] and refined by full-matrix least-squares refinement on F^2 with anisotropic displacement parameters for non-H atoms using SHELXL-97 [34]. All H atoms were refined isotropically. Table I gives the pertinent crystallographic data for the inclusion compounds and hydrogen-bond geometry is listed in Table II.

Thermal Analysis

Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC 822e module and thermogravimetric analysis (TGA) on a Mettler Toledo TGA/SDTA 851e module. Crystals taken from the mother liquor were blotted dry on filter paper and placed in open alumina pans for TGA and in crimped but vented aluminum sample pans for DSC. The sample size in each case was 5–7 mg. The temperature range was typically 30–300 °C and the heating rate was 10 °C/min. The samples were purged with a stream of nitrogen flowing at 150 mL/min for DSC and 50 mL/min for TG.

RESULTS AND DISCUSSION

All solvates and clathrates were obtained by crystallization of **1** and **2** from a minimum amount of the appropriate solvent. Cocrystals of **2** with 4,4′-bipyridine were obtained upon crystallizing stoichiometric amounts of the two components from MeCN. These solids were characterized by NMR and IR spectroscopy, and their structures determined by single-crystal X-ray diffraction. The stoichiometry of each solvate was estimated by TGA and confirmed by X-ray analysis. Crystallization of **1** from MeOH afforded single crystals of the 0.5:1 solvate (**1a**). The X-ray structure was solved and refined in the orthorhombic space group *Pbca*. Molecules of **1** form a hexagonal network parallel to the (2 1 0) plane through phenol O—H···O (1.74 Å, 168.3°, neutron-normalized geometry) hydrogen bonds with cavities of 17 × 22 Å (Fig. 1a). These voids are filled through the interpenetration of two such networks that are inclined at an angle of 81°, leading to the triply interpenetrated crystal structure (Fig. 1b) [35–36]. MeOH molecules serve as bridges in connecting the hexagonal networks via O—H···O (1.64 Å, 172.9°1.76 Å, 170.2°) hydrogen bonds. Crystallization of **1** from EtOH also afforded single crystals of

TABLE I Crystallographic data for the compounds in the study

	1a	**1b**	**1c**	**1d**	**1e**	**2a**
Empirical formula	$(C_{32}H_{26}O_4)_{0.5}\cdot(CH_4O)$	$(C_{32}H_{26}O_4)_{0.5}\cdot(C_2H_6O)$	$(C_{32}H_{26}O_4)_{0.5}\cdot(C_2H_3N)$	$(C_{32}H_{26}O_4)\cdot(C_4H_8O_2)$	$(C_{32}H_{26}O_4)_{0.5}\cdot(C_{10}H_8N_2)$	$(C_{40}H_{42}O_4)_{0.5}\cdot(C_2H_3N)$
Formula wt.	538.61	566.66	556.64	562.63	786.90	668.84
Host:guest	0.5:1	0.5:1	0.5:1	1:1	0.5:1	0.5:1
Crystal system	Orthorhombic	Orthorhombic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	*Pbca*	*Pbca*	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
T (K)	153(2)	153(2)	100(2)	100(2)	100(2)	153(2)
a (Å)	14.975(3)	15.617(3)	8.3782(6)	7.7824(6)	7.5019(15)	12.167(2)
b (Å)	8.7282(17)	8.5810(17)	11.3411(8)	11.3108(9)	10.300(2)	8.1210(16)
c (Å)	21.887(4)	22.385(5)	15.8113(11)	16.5601(13)	14.545(3)	19.304(4)
α (°)	90	90	73.9340(10)	103.4840(10)	99.31(3)	90
β (°)	90	90	87.5710(10	90.3910(10)	97.00(3)	102.80(3)
γ (°)	90	90	88.7050(10)	91.3160(10)	105.73(3)	90
Z	4	4	2	2	1	2
V (Å^3)	2860.8(10)	2999.8(10)	1442.29(18)	1417.04(19)	1051.1(4)	1860.0(6)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
D_{calc} (g/cm^3)	1.251	1.153	1.187	1.319	0.996	1.419
F [000]	1144	1104	544	596	332	858
μ (mm^{-1})	0.085	0.076	0.077	0.089	0.064	0.092
2θ (°)	6.56–54.96	6.36–54.96	3.74–49.42	3.70–52.74	2.88–56.86	6.08–55.00
Index ranges	$-19 \le h \le 19$ $-11 \le k \le 11$ $-27 \le l \le 27$	$-20 \le h \le 20$ $-11 \le \mathrm{k} \le 11$ $-28 \le 1 \le 28$	$-9 \le h \le 9$ $-13 \le k \le 13$ $-18 \le l \le 18$	$-9 \le h \le 9$ $-14 \le k \le 14$ $-20 \le l \le 20$	$-10 \le h \le 9$ $-13 \le k \le 13$ $-18 \le l \le 18$	$-15 \le h \le 15$ $-10 \le k \le 8$ $-25 \le l \le 24$
Reflections collected	5570	6285	13317	25758	12383	7268
Unique reflections	3259	3422	4915	5782	4957	4253
Observed reflections	2286	2430	4181	5220	3485	2748
$R_{(int)}$	0.0223	0.0275	0.0237	0.0216	0.0196	0.0326
R_1 [$F_o > 4\sigma(F_o)$]	0.0449	0.0486	0.0445	0.0458	0.0537	0.0489
wR_2	0.1111	0.1548	0.1085	0.1275	0.1634	0.1357
Goodness-of-fit	1.049	1.059	1.022	1.038	1.040	1.092

TABLE II Neutron-normalized hydrogen-bond data

Compound	D—H···A	D···A (Å)	H···A (Å)	D—H···A (°)
1a	O—H···O	2.734(2)	1.76	170.2
	O—H···O	2.709(2)	1.74	168.3
	O—H···O	2.622(2)	1.64	172.9
1b	O—H···O	2.711(2)	1.73	171.8
	O—H···O	2.661(9)	1.68	179.7
	O—H···O	2.761(8)	1.83	156.5
1c	O—H···N	2.838(2)	1.88	165.5
	O—H···O	2.766(2)	1.82	159.6
	O—H···O	2.768(2)	1.81	164.2
	O—H···N	2.791(3)	1.83	163.8
1d	O—H···O	2.667(2)	1.72	161.6
	O—H···O	2.760(2)	1.87	149.2
	O—H···O	2.711(2)	1.77	159.5
	O—H···O	2.756(2)	1.79	165.3
1e	O—H···N	2.703(3)	1.73	168.4
	O—H···N	2.729(2)	1.76	168.2
2a	O—H···O	2.750(2)	1.91	141.8
	O—H···N	2.896(2)	1.99	151.2

the 0.5:1 solvate (**1b**). The structure of **1b** is similar to that of **1a** showing recurrence of a (6,3) hydrogen-bond network in alcohol solvates. Disordered EtOH molecules connect the otherwise identical triply interpenetrated hexagonal network of **1** via phenol O—H···O hydrogen bonds (1.68 Å, 179.7°1.83 Å, 156.5°). The honeycomb network of **1a** may be compared with hexagonal nets derived from 4,4′-bipyrazole [37] and anthracene-bis(resorcinol) [31], and the inclined interpenetration in these structures is similar to 1,3,5-cyclohexanetricarboxylic acid hydrate (1:1) [28].

Crystallization of **1** from MeCN afforded solvate **1c** (0.5:1). The crystal structure was solved and refined in space group $P\bar{1}$ with two half molecules of **1** and two molecules of MeCN in the asymmetric unit. The H-shaped molecule **1** aggregates via phenol O—H···O (1.82 Å, 159.6°1.81 Å, 164.2°) hydrogen bonds to produce 1D ladders [32,38–40,41–42] with cavities of 6 × 11 Å along [102] and [10-2], shown in Fig. 2a. MeCN molecules are hydrogen bonded to the ladder rungs (O—H···N: 1.88 Å, 165.5°1.83 Å, 163.8°Fig. 2b). Crystallization of **1** from dioxane (1:1, **1d**) also afforded the ladder structure (Fig. 3a) with one molecule of dioxane connecting rungs of adjacent ladders via O—H···O (1.72 Å, 161.6°1.77 Å, 159.5°) hydrogen bonds. Parallel interpenetration of the resulting 2D networks of **1** and dioxane (Fig. 3b) gives the doubly interpenetrated structure (Fig. 3c).

These structures show the role of the included solvent in guiding the final network architecture of **1**. Solvents that function as hydrogen-bond acceptors only, such as MeCN and dioxane, give 1D ladder structures whereas solvents with acceptor and donor groups, such as MeOH and EtOH, give 2D honeycomb grids. A similar solvent-dependent supramolecular isomerism is observed for 4,4′-(fluorene-9,9-diyl)diphenol host [43]. The MeCN solvate of this diphenol has a helical structure but the EtOH clathrate is layered. This difference in the topology of the network, (4,3) ladder *vs.* (6,3) honeycomb, depending on the solvent of crystallization is related to the conformation of the phenol OH groups in crystal structures of **1**, as shown in Fig. 6.

Crystallization of octamethyl H-tecton **2** from MeCN afforded 0.5:1 solvate **2a**, with a structure similar to **1c** (Fig. 4a). Here also, the H-shaped molecule **2** aggregates to form ladders via O—H···O (1.91 Å, 141.8°) hydrogen bonds. The cavities in these ladders are occupied by two solvent molecules that are bonded via O—H···N (1.99 Å, 151.2°) hydrogen bonds (Fig. 4b). The fact that parent structures **1c** and **1d** and octamethyl derivative **2a** have the same 1D network means that the crystal structure can tolerate a small molecular perturbation but the final crystal architecture depends more on the included solvent in the crystal lattice. Therefore, modular extension of the architecture to extended ladders or hexagons by incorporating linear spacer groups should be possible in such a system. Indeed, crystallization of

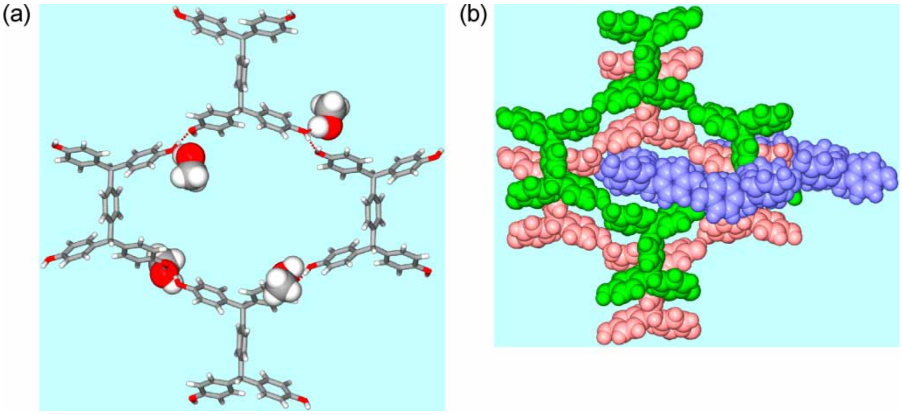


FIGURE 1 Hexagonal network in crystal structure **1a**. MeOH molecules are shown as large spheres for clarity. (b) Threefold inclined interpenetrated network. MeOH molecules connecting the networks are not shown for clarity.

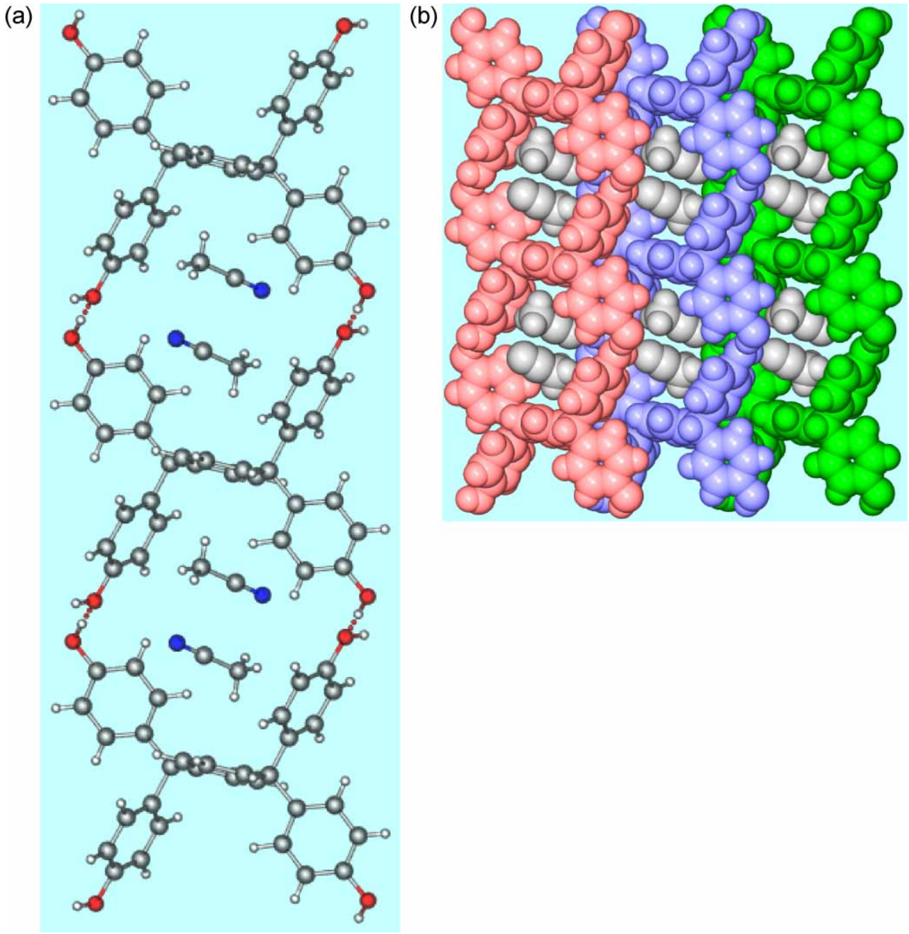


FIGURE 2 Hydrogen-bonded ladders in crystal structure **1c** with included MeCN molecules in rectangular cavities. (b) Stacked arrangement of hydrogen-bonded ladders.

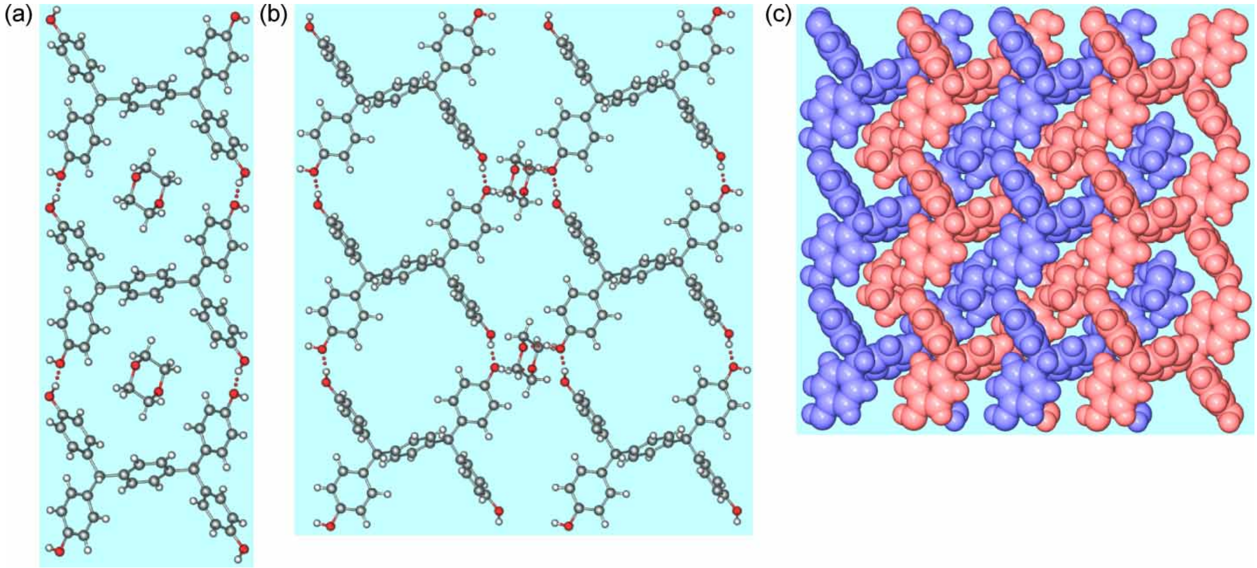


FIGURE 3 Ladder network in **1d** with included dioxane molecules in rectangular cavities. (b) 2D hydrogen-bond network of host and guest molecules. (c) Twofold parallel interpenetration in crystal structure **1d**.

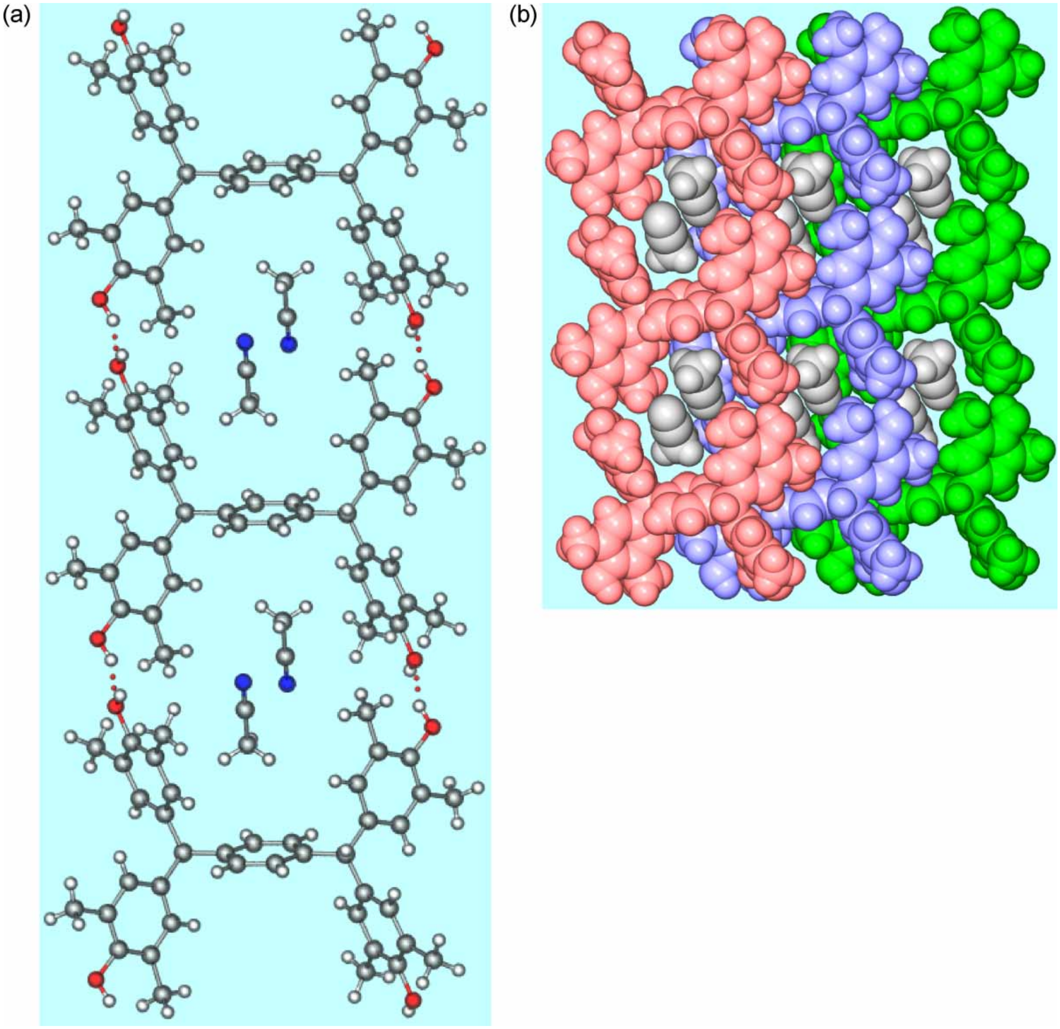


FIGURE 4 Hydrogen-bonded ladder in crystal structure **2a** and included MeCN molecules in rectangular cavities. (b) The stacking of hydrogen-bonded ladders is similar to that in Fig. 2.

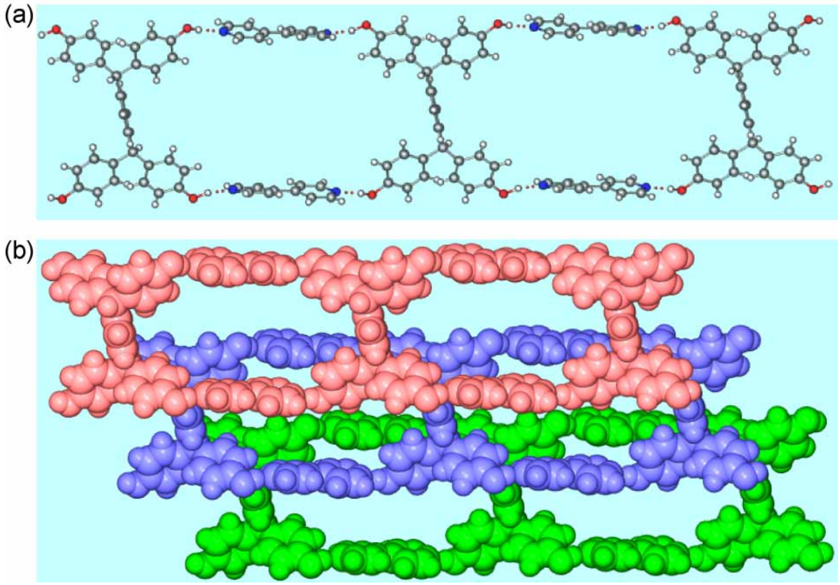


FIGURE 5 Hydrogen-bonded ladders in crystal structure **1e** with rectangular cavities of 6 × 20 Å. No solvent is included in the crystal. (b) Stacking of hydrogen-bonded ladders.

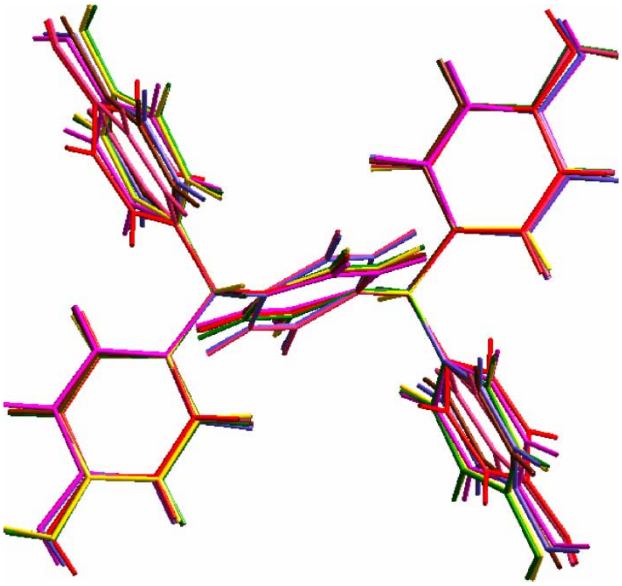
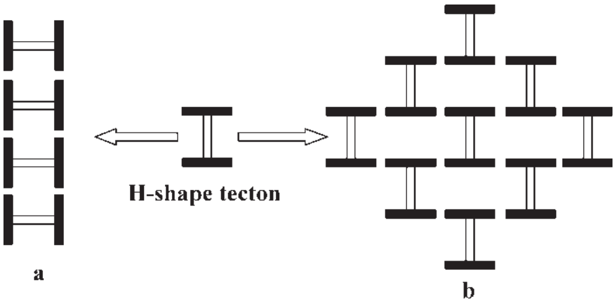


FIGURE 6 Overlay diagram of seven molecules of **1** to show the rigid H-tecton and conformationally flexible phenol OH groups. Green = **1a**, Yellow = **1b**, Magenta, Brown = **1c**, Blue, Pink = **1d**, Red = **1e**. **1c** and **1d** have two symmetry-independent molecules in the crystal structure.

1 and 4,4′-bipyridine from MeCN afforded the 1:2 cocrystal **1e**. The crystal structure of this complex shows the formation of a non-interpenetrated and non-solvated ladder network (Fig. 5a). The linear bipyridine spacer expands the ladder-rung distance from 11 Å in **1c** to 20 Å in **1e**. These elongated ladders stack with offset parallel to the (3 1 4) plane (Fig. 5b). Ladder networks in this study are similar to ladder networks generated from anthracene-bis(hydroquinone), another H-shaped tecton [32].

Figure 6 shows the overlay diagram of molecule **1** in five crystal structures. The H-tecton can propagate to a 1D ladder or 2D brick wall (topologically identical to the hexagon) network depending on how the hydrogen-bonded molecules are arranged (Scheme 3). 1D extension requires that the OH group is oriented inwards whereas a 2D grid results when the OH groups are divergent. The overlay diagram shows that the rigid aromatic H-core overlaps with little variation whereas the flexible phenol OH groups adopt different conformations leading to supramolecular diversity in the final architecture. Despite small variations in the inclination of the aromatic connectors, there are no significant herringbone T-motif or π–π stacking interactions in crystal structures of **1**.

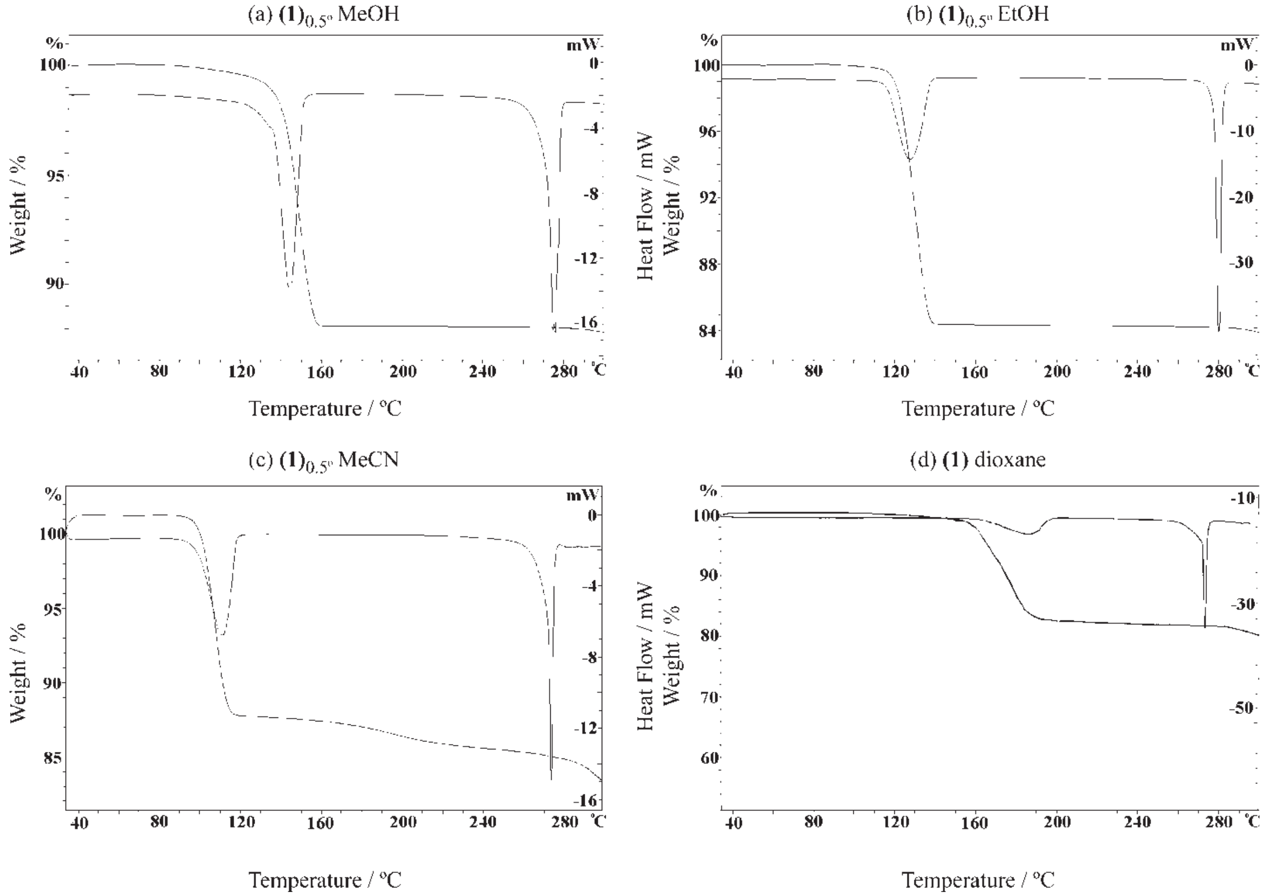


SCHEME 3 Supramolecular networks from an H-tecton: (a) ladder; (b) brick wall.

In addition to X-ray diffraction, thermal analysis is an important tool for the characterization of inclusion compounds [44]. TGA is used to obtain an accurate host:guest ratio and DSC gives information about guest release onset temperature, polymorphic phase changes, melting transition and enthalpy change. DSC and TG were performed on **1a–d** to measure the thermal stability of these solvates (Fig. 7). In all cases, weight loss occurred in a single step well above the boiling point of the pure solvent (MeCN 100–120°C, dioxane 170–190°C, MeOH/EtOH 120–140°C). MeOH, EtOH and dioxane escape from the crystal lattice at a higher temperature compared to MeCN. The robust incorporation of the first three guest molecules in the host lattice compared to MeCN may be ascribed to strong host···guest hydrogen bonds. MeOH and EtOH act as both acceptor and donor groups through two O—H···O hydrogen bonds and dioxane accepts two O—H···O hydrogen bonds, whereas MeCN forms only one O—H···N hydrogen bond with the host framework. The observed weight loss of solvent in TGA measurements is in good agreement with the host:guest stoichiometry calculated from the X-ray structure. DSC traces of these solvates exhibit two endotherms corresponding to guest loss followed by melting of the host at 275 °C. Relevant thermal data are summarized in Table III.

CONCLUSIONS

Hydrogen-bond networks of a novel tetraphenol H-tecton are described in this article. An advantage with the H-shaped tecton, a molecular surrogate of the T-dimer, is that a smaller number of self-assembly motifs are possible compared to the T-tecton. For example, the parquet grid motif is not possible from an H-building block. Self-assembly of a T-node via two A···A and one B···B recognition leads to ladder and brick wall networks whereas two A···B and one A···A recognition leads to the parquet floor (Scheme 1). Only the former self-assembly route is observed in an H-tecton (Scheme 3). One of the continuing challenges in crystal engineering is that it is still not possible to predict the crystal structure from the molecular structure [45–46]. In the present context, one of the several tiling patterns of Scheme 1 may be obtained from a T-molecule but the specific network that will result, its interpenetration mode and guest inclusion behavior are difficult to know beforehand in organic solids. H-tectons offer



(a) $(\mathbf{1})_{0.5}\cdot$MeOH

(b) $(\mathbf{1})_{0.5}\cdot$EtOH

(c) $(\mathbf{1})_{0.5}\cdot$MeCN

(d) (**1**) dioxane

FIGURE 7 TGA and DSC traces for inclusion compounds (a) **1a**, (b) **1b**, (c) **1c** and (d) **1d**.

TABLE III Thermal analysis (TGA and DSC) data for some inclusion compounds in this study

Inclusion complex	Observed weight loss from TG (%)	Calculated weight loss from host: guest ratio in X-ray	Guest release T_{on} (°C)	Boiling point of guest (°C)	ΔH (J g^{-1}) (for guest release)
$(\mathbf{1})_{0.5}\cdot$MeOH, **1a**	11.9	11.9 (0.5:1)	136	64–66	218.36
$(\mathbf{1})_{0.5}\cdot$EtOH, **1b**	15.5	16.3 (0.5:1)	116	77–79	193.28
$(\mathbf{1})_{0.5}\cdot$MeCN, **1c**	13.6	14.7 (0.5:1)	99	81–82	150.05
$(\mathbf{1})\cdot$dioxane, **1d**	18.6	18.6 (1:1)	169	100–102	105.81

a simplification in crystal design strategies by reducing the number of possible networks with only a marginal increase in molecular structure complexity. The trade-off is, on balance, favorable for the supramolecular chemist, as we show by the crystallization of **1** and **2**, to predictable ladder and honeycomb networks depending on guest inclusion. Further studies with different solvent and spacer molecules to build supramolecular hydrogen-bond networks with H-tecton are in progress.

Supporting Information

Crystallographic data are available in CIF format for **1a–e** and **2a** from the authors.

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