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Highly Porous Hydrogen-Bond Networks from a Triptycene-Based Catechol

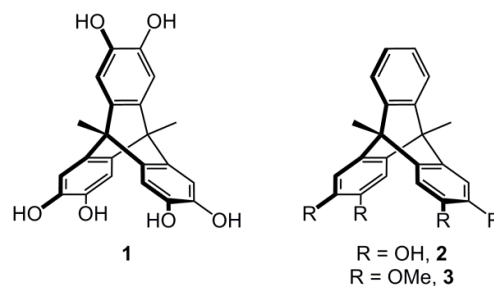
Sam Greatorex and Malcolm A. Halcrow*

Solvate crystals of 9,10-dimethyl-2,3,6,7,14,15-hexa(hydroxy)-triptycene (**1**) form a variety of 3D hydrogen-bonded topologies, including *bcu*, *acs*, *bsn* and an apparently new 7-connected net. Several of these networks contain 1D or 2D arrays of solvent-filled channels, amounting to up to 60 % solvent-accessible void space.

Triptycene derivatives are finding increasing use as scaffolds for supramolecular architectures,¹⁻⁶ in polynucleating ligands for transition ions⁷⁻¹² and for polymeric materials.¹³⁻¹⁵ Diamino-substituted phenylene residues in triptycenes are readily converted by Schiff base condensations into extended arenes,¹⁶ annelated heterocycles^{11,12} or polydentate metal-binding domains.⁸⁻¹⁰ Alternatively, catechol functions in triptycene derivatives have been used as components in hydrogen-bonded supramolecular assemblies, or incorporated into larger crown ether receptors¹⁻⁵ or microporous polymer materials.¹³⁻¹⁵ Many of these studies make use of the rigid three-fold conformation of the triptycene moiety, which pre-disposes them to form cyclic or porous structures in molecular assemblies¹⁻⁶ or extended solids.^{7,8,13,14,16}

Following our interest in redox-active molecular architectures with *bis*- and *tris*-catechol components,^{17,18} we identified 9,10-dimethyl-2,3,6,7,14,15-hexa(hydroxy)triptycene (**1**) and 9,10-dimethyl-2,3,6,7-tetra(hydroxy)triptycene (**2**; Scheme 1)⁶ as potentially useful components in supramolecular assembly structures. We report here that solvate crystals of **1** adopt a number of novel hydrogen bonded network structures with substantial solvent-supported void space†. Crystal structures of solvates of **2**, and of 9,10-dimethyl-2,3,6,7-tetra(methoxy)triptycene (**3**, ESI†), are also briefly described.

Recrystallisation of **1** from alcohol solvents using diethyl ether as antisolvent yields crystals of **1**·2Et₂O‡. These adopt



Scheme 1 The triptycene derivatives discussed in this work.

the tetragonal space group *I4₁cd*, with half a molecule of **1** per asymmetric unit spanning a crystallographic *C*₂ symmetry axis. Each molecule donates four, and accepts four, O–H...O hydrogen bonds from nearest neighbour molecules of **1** (Fig. 1), as well as hydrogen bonding to two solvent sites. Thus, each molecule of **1** is eight-connected to a distorted cubic array of neighbour molecules, forming a CsCl (*bcu*) topology net that is distorted by the elongated *c* axis of the tetragonal crystal (ESI†).^{20,21}

The triptycene molecules in **1**·2Et₂O‡ form chequerboard layers in the [001] plane, with each molecule oriented at right angles to its four nearest neighbours within the layer. This arrangement affords a 2D network of interconnected channels along the {110} vectors, of approximate dimensions 4.2 x 4.5 Å (Fig. 2). The channels contain the diethyl ether molecules, which are disordered but well defined in the Fourier map (ESI†). Taken in isolation, the network of **1** has a void volume of 2568.3 Å³ per unit cell, or 46.6 % of the cell volume.

Three other solvates of **1** were also obtained, from vapour-diffusion crystallisations using the alternative antisolvent pentane. The solvate **1**·3.4thf adopts a trigonal space group *P3c1*, and is topologically very different from **1**·2Et₂O. The [1·3thf] moieties in the asymmetric unit of **1**·3.4thf occupy general crystallographic sites, but show only small deviations from local *C*₃ symmetry down the centre of the triptycene framework. All the molecules of **1** in **1**·3.4thf are co-aligned,

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† Electronic Supplementary Information (ESI) available: full experimental details of the crystallographic data collection and refinements; powder diffraction data; and additional crystallographic Figures and Tables showing the hydrogen bonding in the crystals. CCDC 1440046-1440052. See DOI: 10.1039/x0xx00000x

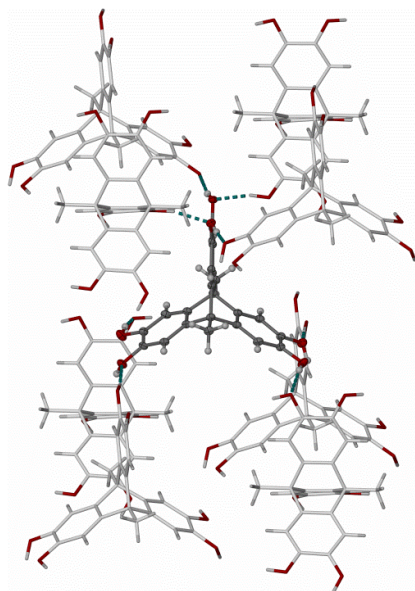


Fig. 1 Packing diagram of **1**·2Et₂O, showing each molecule of **1** hydrogen bonding to an approximately cubic array of eight nearest neighbours. The diethyl ether solvent molecules are not shown, for clarity. Colour code: C, dark grey or white; H, pale grey; O, red.

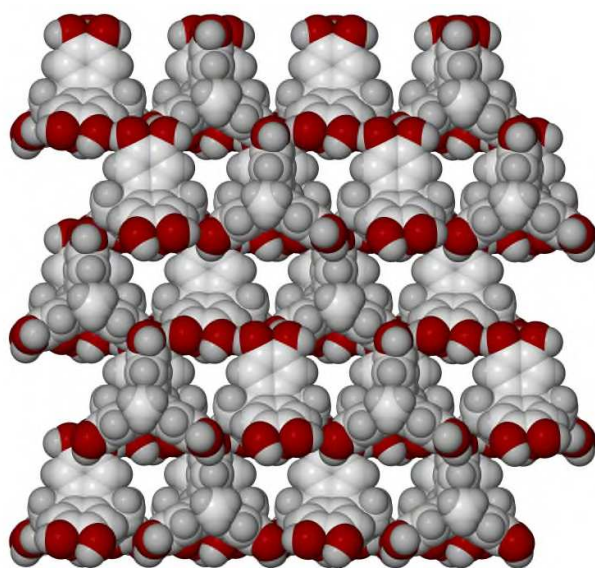


Fig. 2 Space-filling packing diagram of the molecules of **1** in **1**·2Et₂O, showing the channels in the lattice. The view is parallel to the (110) crystal vector, with the *c* axis vertical. An identical series of channels, interconnecting with these ones, occurs at right angles along $(\bar{1}10)$. Colour code: C, white; H, pale grey; O, red.

and hydrogen bond to a trigonal prismatic array of six nearest neighbours in a $4^9.6^6$ (**acs**) net topology (ESI[†]).^{20,21} This leads to *C*₃-symmetric Y-shaped channels parallel to (001), with each arm of the channels being occupied by a resolved, hydrogen-bonded thf molecule (Fig. 3). There is additional void space at the centre of the channels which is occupied by unresolved 0.4-equiv thf according to a *SQUEEZE* analysis.²² Omitting the solvent molecules, the volume of void space in this topology of **1** is 3089 Å³ or 59.6 % of the unit cell, which is substantially higher than for **1**·2Et₂O. The chiral space group adopted by

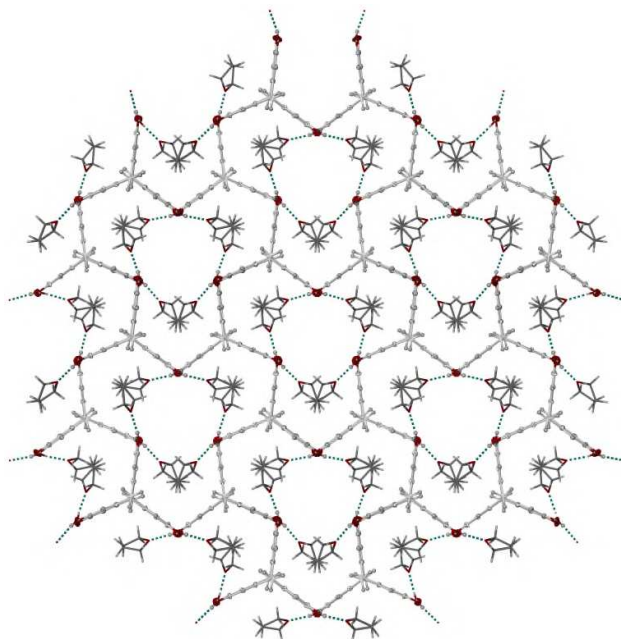


Fig. 3 Packing diagrams of **1**·3.4thf, showing the solvent-filled channels in the lattice. The views are parallel to the (001) crystal vector, with the *a* axis horizontal. Top: view showing the resolved thf sites, with atomic displacement ellipsoids at the 50 % probability level (for **1**) or with arbitrary atomic radii (thf). Bottom: space-filling plot showing the molecules of **1** only. Colour code: C (**1**), white; C (solvent), dark grey; H, pale grey; O, red.

1·3.4thf reflects the asymmetry of the **acs** net, although the absolute chirality of the light atom crystal could not be determined during the structure analysis.

The topology of **1**·2.15CHCl₃ (monoclinic, *C2/c*) is different again, although all the molecules of **1** are also co-aligned along (001). Each molecule of **1** in this lattice is now connected by O–H...O hydrogen bonding to seven nearest neighbours. The resultant hydrogen bond network is an apparently new variant of the class of uninodal 7-connected topologies based on

pillared stacks of 4^4 nets (ESI[†]).²³ In contrast to **1**·3.4thf, whose solvent channels are lined by six-membered molecular circuits of **1** (Fig. 3), **1**·2.15CHCl₃ contains two smaller channel motifs formed from two- and four-membered circuits of **1** (Fig. 4). The smaller channels (*ca.* 4.5 x 6.1 Å) are occupied by disordered, but well defined, molecules of chloroform which do not participate in hydrogen bonding. The contents of the larger channels (5.5 x 14.2 Å) were not resolved, but are probably additional chloroform according to *SQUEEZE*.²² The

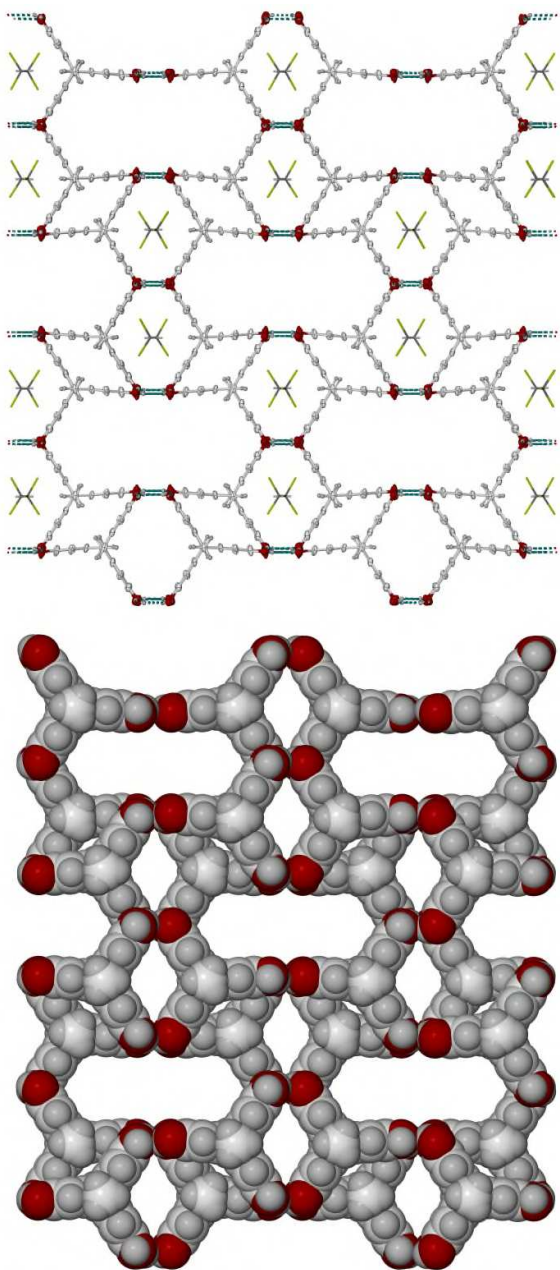


Fig. 4 Packing diagrams of **1**·2.15CHCl₃, showing the solvent-filled channels in the lattice. The views are parallel to the (001) crystal vector, with the *a* axis horizontal. Top: view showing the resolved chloroform sites, with atomic displacement ellipsoids at the 50 % probability level (for **1**) or with arbitrary atomic radii (CHCl₃). Bottom: space-filling plot showing the molecules of **1** only. Colour code: C (**1**), white; C (solvent), dark grey; H, pale grey; O, yellow; O, red.

combined volume of the channels in this network of **1** is 2837 Å³ per unit cell, or 49.8 % of the material.

Unlike the other solvates of **1**, the molecules in **1**·EtOAc (triclinic, $P\bar{1}$) do not form a porous hydrogen-bonded network. Its hydrogen bonding topology is complicated by a disordered hydroxyl group, which donates half-occupied hydrogen bonds to two different acceptors in the lattice. There are three ordered connections between nearest neighbour molecules, which form a 2D puckered 6^3 topology in the $[\bar{1}11]$ plane. The disordered OH group is involved in three additional half-occupied connections, two of them *via* the solvent molecule which accepts two hydrogen bonds from different molecules. If all these connections are considered, the resultant hydrogen bond network corresponds to a $4^8.5^4.6^3$ (**bsn**) 3D net topology, which has racemic helical character (ESI[†]).^{20,21}

Bulk samples of **1**·2Et₂O, **1**·3.4thf and **1**·2.15CHCl₃ are phase-pure and isostructural with the crystalline material by X-ray powder diffraction (ESI[†]). The powder patterns retain their form upon exposure to air at room temperature for 60-80 mins, with slow peak broadening over time indicating gradual loss of crystallinity. However, upon annealing at 370 K for 30 mins all three materials transform to a new phase (**1'**), which was not structurally characterized but is assigned as solvent free **1**. In contrast, microcrystalline samples of **1** crystallized from ethyl acetate/pentane contain predominantly **1'** by powder diffraction, instead of the crystallographic **1**·EtOAc phase. It is unclear whether this reflects the true composition of the sample, or rapid conversion of **1**·EtOAc into **1'** following solvent loss inside the diffractometer.

Two solvates of **2** were also obtained during this study, neither of which is porous. The asymmetric unit of $2 \cdot \frac{1}{2} \text{Et}_2\text{O} \cdot \frac{1}{2} \text{H}_2\text{O} \ddagger$ contains two formula units. It forms a 2D bilayer hydrogen bond network parallel to $[10\bar{2}]$, whose topology depends on the unique water molecule which is disordered between two- and three-connected sites. The crystallographically ordered connections between molecules of **2** afford a binodal five-connected topology, which becomes trinodal if the part-occupied connections to the water are also considered (ESI[†]). In contrast, **2**·dioxane contains just one molecular environment linked to six nearest neighbours, two of them *via* the bridging solvent molecule. The direct contacts between molecules of **2** form a four-connected $6^5.8$ (**dmp**) hydrogen bonded net²¹ which is modified by additional, solvent-bridged diagonal connections between adjacent six-membered rings (ESI[†]). The structure of **3**, an intermediate in the synthesis of **2**, is also shown in the ESI[†].

Conclusions

It has previously been noted that triptycene derivatives are useful scaffolds to support porosity in molecular assemblies or crystalline networks.^{6-8,14-16} These results, in conjunction with another recent study,⁶ highlight that **1** is an attractive and synthetically accessible precursor towards that end. Our current work aims to use **1** as a component in more robust

metal-organic assemblies and frameworks, with potential to combine porosity and redox-active properties.²⁴

Experimental

Compounds **1**, **2** and **3** were prepared by the literature procedures.^{1,4} Other experimental details are in the ESI†.

Acknowledgements

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Notes and references

‡ The structures of $1 \cdot 2\text{Et}_2\text{O}$ and $2 \cdot \frac{1}{2}\text{Et}_2\text{O} \cdot \frac{1}{2}\text{H}_2\text{O}$ have been communicated before.¹⁹ However their supramolecular topologies, and the pore structure of $1 \cdot 2\text{Et}_2\text{O}$, were not discussed in this earlier report, and the published structures were not deposited with the CCDC.

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