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Greatorex, S and Halcrow, MA orcid.org/0000-0001-7491-9034 (2016) Highly Porous Hydrogen-Bond Networks from a Triptycene-Based Catechol. CrystEngComm, 18 (25). pp. 4695-4698.

https://doi.org/10.1039/c6ce00966b

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

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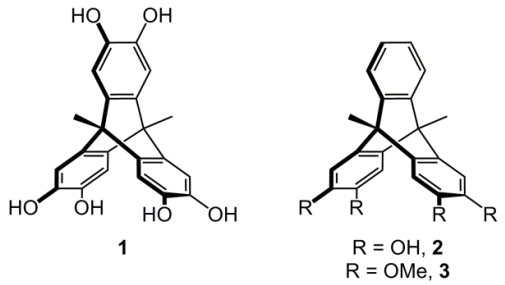
Solvate crystals of 9,10-dimethyl-2,3,6,7,14,15-hexa(hydroxy)-triptycene (1) form a variety of 3D hydrogen-bonded topologies, including bcu, acs, bsn and an apparently new 7-connected net. Several of these networks contain 1D or 2D arrays of solvent-filled channels, amounting to up to 60 % solvent-accessible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

Triptycene derivatives are finding increasing use as scaffolds for supramolecular architectures,[1-6] in polynucleating ligands for transition ions[7-12] 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 receptors[1-5] 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 assemblies[1-6] 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**·2Et$_2$O‡. These adopt



Scheme 1 The triptycene derivatives discussed in this work.

the tetragonal space group $I4_1cd$, 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**·2Et$_2$O‡ 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 Å^3 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**·2Et$_2$O. 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

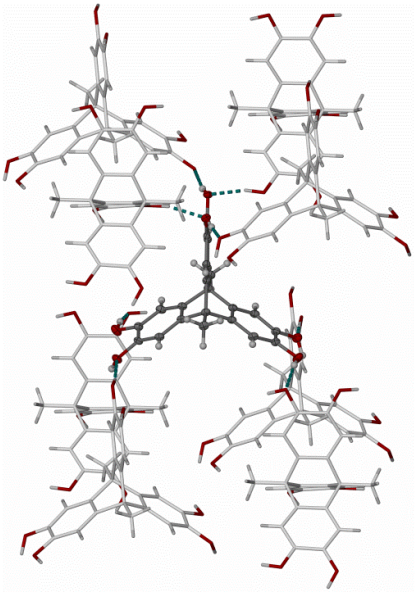

Fig. 1 Packing diagram of **1**·2Et$_2$O, showing each molecule of **1** hydrogen bonding to an approximately cubic array of eight nearest neighbours. The diethyl ether solvent molecules are not shown, for clarity. Colour code: C, dark grey or white; H, pale grey; O, red.

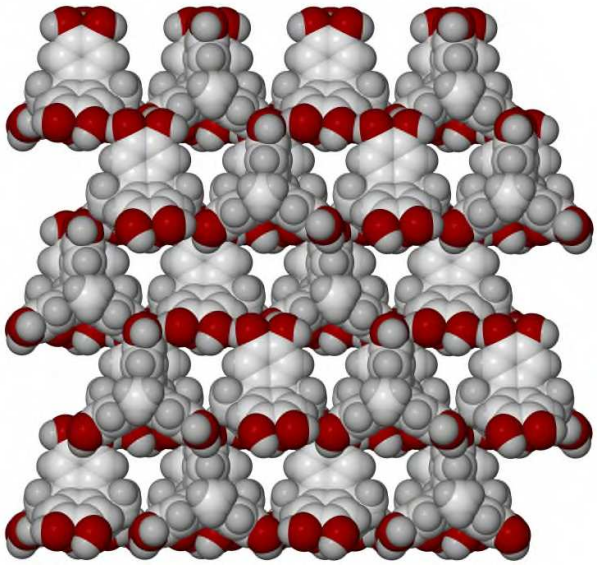

Fig. 2 Space-filling packing diagram of the molecules of **1** in **1**·2Et$_2$O, showing the channels in the lattice. The view is parallel to the (110) crystal vector, with the *c* axis vertical. An identical series of channels, interconnecting with these ones, occurs at right angles along ($\bar{1}$10). Colour code: C, white; H, pale grey; O, red.

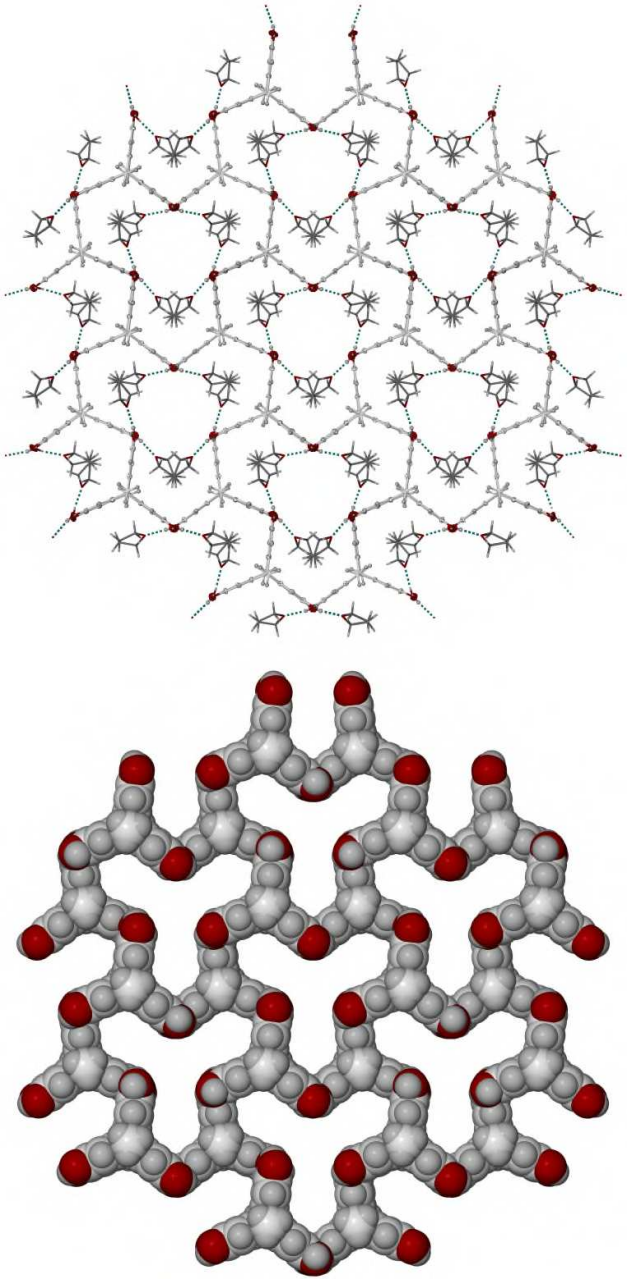

Fig. 3 Packing diagrams of **1**·3.4thf, showing the solvent-filled channels in the lattice. The views are parallel to the (001) crystal vector, with the *a* axis horizontal. Top: view showing the resolved thf sites, with atomic displacement ellipsoids at the 50 % probability level (for **1**) or with 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.

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 Å^3 or 59.6 % of the unit cell, which is substantially higher than for **1**·2Et$_2$O. The chiral space group adopted by **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**·2.15CHCl$_3$ (monoclinic, *C*2/*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**·2.15$CHCl_3$ 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 combined volume of the channels in this network of **1** is 2837 $Å^3$ per unit cell, or 49.8 % of the material.

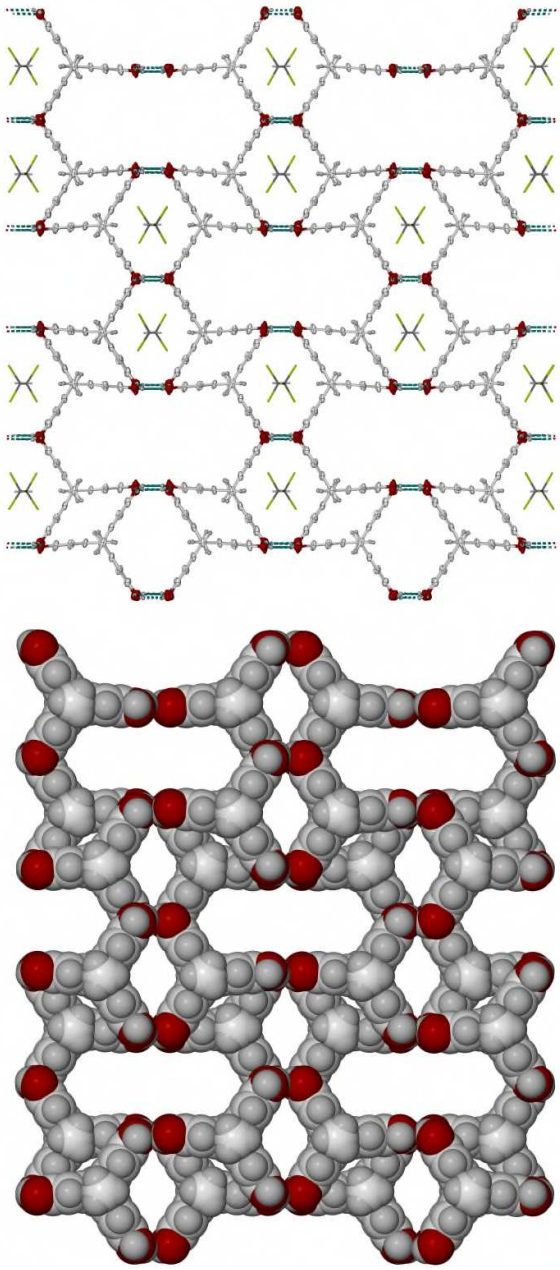

Fig. 4 Packing diagrams of **1**·2.15$CHCl_3$, showing the solvent-filled channels in the lattice. The views are parallel to the (001) crystal vector, with the *a* axis horizontal. Top: view showing the resolved chloroform sites, with atomic displacement ellipsoids at the 50 % probability level (for **1**) or with arbitrary atomic radii ($CHCl_3$). Bottom: space-filling plot showing the molecules of **1** only. Colour code: C (**1**), white; C (solvent), dark grey; H, pale grey; C;, yellow; O, red.

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**·2Et_2O, **1**·3.4thf and **1**·2.15$CHCl_3$ 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**·½Et_2O·½H_2O‡ 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 net[21] 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

This work was funded by the EPSRC (DTG studentship to SG).

Notes and references

‡ The structures of **1**·2Et_2O and **2**·½Et_2O·½H_2O have been communicated before.[19] However their supramolecular topologies, and the pore structure of **1**·2Et_2O, were not discussed in this earlier report, and the published structures were not deposited with the CCDC.

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