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https://doi.org/10.1039/c6ce00966b

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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, in polynucleating ligands for transition ions and for polymeric materials. Diamino-substituted phenylene residues in triptycenes are readily converted by Schiff base condensations into extended arenes, annelated heterocycles or polydentate metal-binding domains. Alternatively, catechol functions in triptycene derivatives have been used as components in hydrogen-bonded supramolecular assemblies, or incorporated into larger crown ether receptors or microporous polymer materials. Many of these studies make use of the rigid three-fold conformation of the triptycene moiety, which predisposes them to form cyclic or porous structures in molecular assemblies or extended solids.

Following our interest in redox-active molecular architectures with bis- and tris-catechol components, 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) 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 were also obtained, from vapour-diffusion crystallisations using the alternative antisolvent pentane. The solvate [1·3thf] moieties in the asymmetric unit of 1·3thf occupy general crystallographic sites, but show only small deviations from local C3 symmetry down the centre of the triptycene framework. All the molecules of 1 in 1·3.4thf are co-aligned,
and hydrogen bond to a trigonal prismatic array of six nearest neighbours in a $4^{9.66}_{\text{acs}}$ net topology (ESI†). 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. 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 $\text{acs}$ 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, $C2/c$) 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 nets (ESI†). In contrast to 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. The 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 ̅T) 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 6⁵ topology in the [1 1 1] 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 4⁸.5⁶.6³ (bsn) 3D net topology, which has racemic helical character (ESI†).

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 2-½Et₂O-½H₂O‡ contains two formula units. It forms a 2D bilayer hydrogen bond network parallel to [0 1 0], 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 6⁵.8 (dmp) hydrogen bonded net 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. These results, in conjunction with another recent study, 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.\textsuperscript{24}

Experimental

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

Acknowledgements

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

Notes and references

† The structures of 1·2Et$_2$O and 2·½Et$_2$O·½H$_2$O have been communicated before.\textsuperscript{19} However their supramolecular topologies, and the pore structure of 1·2Et$_2$O, were not discussed in this earlier report, and the published structures were not deposited with the CCDC.