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2,3,6,7,10,11-Hexahydroxytriphenylene tetrahydrate: a new form of an important starting material for supramolecular chemistry and covalent organic frameworks

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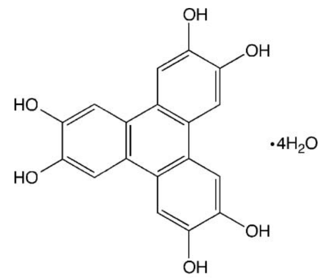
In the title compound, $C_{18}H_{12}O_6{\cdot}4H_2O$, the 2,3,6,7,10,11-hexahydroxytriphenylene molecule is located on a twofold axis and two water molecules occupy general positions. The compound forms (4,4) two-dimensional nets *via* hydrogen bonds between neighbouring hexahydroxytriphenylene molecules, somewhat similar to the cyclopentanone solvates but distinctively different from the monohydrate form. Hydrogen bonds to water molecules connect these layers to form a complicated three-dimensional net, supported also by strong π–π stacking.

Comment

2,3,6,7,10,11-Hexahydroxytriphenylene has emerged as an important starting material for making discrete supramolecular units (Fyfe *et al.*, 2000; Waldvogel *et al.*, 2000; Bomkamp *et al.*, 2007) and so-called covalent organic frameworks based on $B(Ph)(O)_2$ trigonal secondary building units (Cote *et al.*, 2005; El-Kaderi *et al.*, 2007). After recovering hexahydroxytriphenylene from unsuccessful reactions we found a new hydrate, 2,3,6,7,10,11-hexahydroxytriphenylene tetrahydrate, (I), different from the other three crystal forms reported for this compound, *viz.* the monohydrate, (II) [$P2_1/c$, a = 11.127 (2) Å, b = 12.797 (3) Å, c = 11.081 (2) Å and β = 119.32 (3)°; Andresen *et al.*, 2000], the cyclopentanone trisolvate, (III) [$P2_1$, a = 7.986 (3) Å, b = 10.161 (2) Å, c = 18.554 (2) Å and β = 99.84 (1)°; Toda *et al.*, 2000] and the cyclopentanone tetrasolvate monohydrate, (IV) [$P2_1/c$, a = 7.603 (7) Å, b = 20.937 (3) Å, c = 22.245 (3) Å and β = 91.85 (3)°; Toda *et al.*, 2000].

This new hydrate, (I), seems to be relatively stable, as the crystal structure presented here was obtained several months after the initial preparation. However, the anisotropy of the solvent water O atoms may indicate that these water molecules are partially lost from the structure and therefore are less well defined.



(I)

Tetrahydrate (I) has a C_2-symmetric hexahydroxytriphenylene unit very similar to those in the three previously reported structures (Fig. 1). As there is some indication that radical species may form (Grange *et al.*, 2010), special attention was paid to the C—O distances in order to rule out a semiquinone molecule. However, all these bond lengths in (I) are consistent with a C—O single bond (Table 1).

A more intricate question is the hydrogen-bond networks in (I)–(IV). Diols of rigid hydrocarbon skeletons are known to form three-dimensional networks of different topologies (Wells, 1954; Wallentin *et al.*, 2009), but hydrated species may be less straightforward to interpret in this way and the large number of hydroxy groups in the case of (I) will add to the complexity.

Analysing the four structures, we find that in the cyclopentanone trisolvate, (III), each hexahydroxytriphenylene molecule forms hydrogen bonds to four other units, forming a (4,4) two-dimensional net, with the cyclopentanones hydrogen bonded and protruding from the network. The situation in (IV) is similar, but with an even thicker layer of cyclopentanones in between the aromatic networks. In the monohydrate,

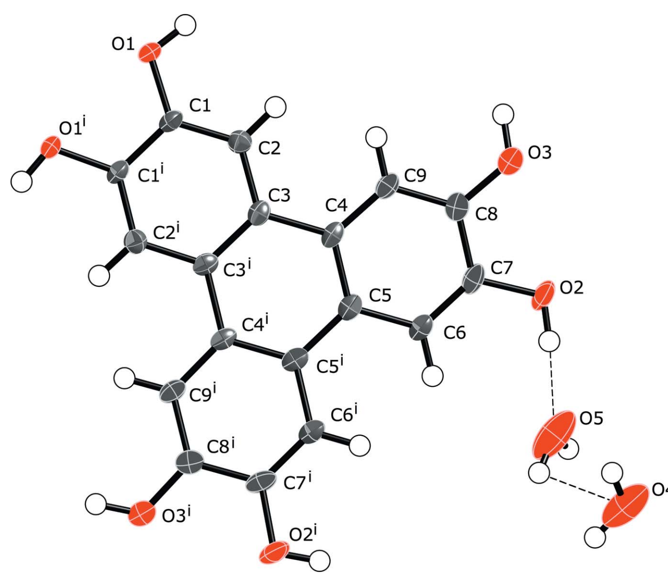


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines. [Symmetry code: (i) $-x + 1$, y, $-z + \frac{3}{2}$.]

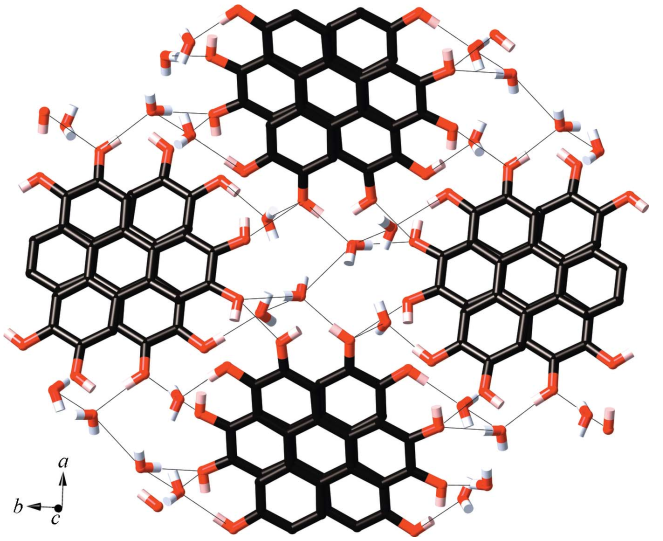


Figure 2
The two-dimensional network of (I), built from hexahydroxytriphenylene units hydrogen bonding to their neighbours (red in the electronic version of the paper), and the three-dimensional structure, built up by free water molecules hydrogen bonding to other water molecules or to hexahydroxytriphenylene molecules. Hydrogen bonds are shown as thin black lines.

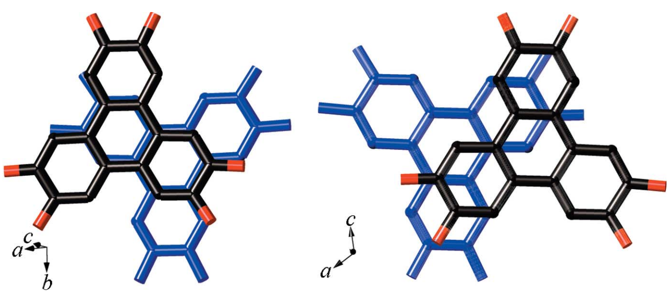


Figure 3
A comparison of the π–π stacking in (I) (left) and (II) (right).

(II), each hexahydroxytriphenylene molecule forms hydrogen bonds to six other hexahydroxytriphenylenes, giving an intricate double layer of two (4,4) nets where every vertex is connected to two other vertices in a neighbouring net. The water molecules further hydrogen bond these layers to form a complicated three-dimensional net.

In the tetrahydrate reported here, the (4,4) two-dimensional net from (III) and (IV) is reproduced but, instead of hydrocarbon rings separating layers of hexahydroxytriphenylene molecules, this less dense two-dimensional net is further crosslinked by water molecules to form a complex three-dimensional net (Fig. 2). The interpretation of this net in terms of topology would result in a network with at least four different types of vertices, and we do not see any advantage in this type of interpretation in this case. There is also substantial π–π stacking, seemingly more than in the monohydrate, (II) (Fig. 3). Pertinent measurements for these π–π interactions (refer to Fig. 3) are: centroid–centroid distances of 3.447 and 3.650 Å, and offset angles of 18 and 26°. The closest contact distances are C9$\cdots$C4 of 3.293 (4) Å and C9$\cdots$C4 of 3.381 (4) Å.

Experimental

2,3,6,7,10,11-Hexamethoxytriphenylene was prepared according to the literature method of Zniber *et al.* (2002). Other chemicals were purchased from Aldrich and used as received. The syntheses and ^{1}H NMR and mass spectrometric analyses were carried out at Chalmers University of Technology. The X-ray data collection and structure solution were carried out at the University of Eastern Finland.

Hexahydroxytriphenylene has been reported as colourless (Andresen *et al.*, 2000; Toda *et al.*, 2000), grey (Zniber *et al.*, 2002) or brown (Bhalla *et al.*, 2009). Recent reports of the synthesis of hexahydroxytriphenylene using anaerobic conditions lead one to conclude that the darker preparations are contaminated by oxidized forms of the molecule (Percec *et al.*, 2009). The structure of (I) reported herein was obtained independently from one white and one black crystal, with no dramatic crystal quality differences between the two samples.

For the preparation of 2,3,6,7,10,11-hexahydroxytriphenylene monohydrate, 2,3,6,7,10,11-hexamethoxytriphenylene (1 g, 2.45 mmol) was added to a solution of glacial acetic acid and hydroiodic acid (aqueous, 57 wt.%; 50:50 *v*/*v*, 50 ml) and the resulting solution heated under reflux overnight. A red suspension formed and was filtered off. The product was purified by crystallization with the addition of water and was obtained as black crystals (yield 500 mg, 60%). ^{1}H NMR and mass spectrometric characterizations of the product were concordant with the literature (Zniber *et al.*, 2002). The crystals which formed were characterized by X-ray diffraction as having the published 2,3,6,7,10,11-hexahydroxyterphenylene monohydrate crystal structure [Cambridge Structural Database (CSD; Allen, 2002) entry XEFSIK; Andresen *et al.*, 2000].

For the preparation of 2,3,6,7,10,11-hexahydroxytriphenylene tetrahydrate, (I), 2,3,6,7,10,11-hexahydroxytriphenylene monohydrate (100 mg, 2.9 mmol) and sodium borohydride (10 mg) were added to water (20 ml) and the resulting mixture heated under reflux overnight. The solution was then allowed to evaporate slowly and colourless crystals of (I) suitable for single-crystal X-ray diffraction were obtained.

Crystal data

$C_{18}H_{12}O_6 \cdot 4H_2O$
$M_r = 396.34$
Orthorhombic, *Pbcn*
$a = 14.2694$ (8) Å
$b = 16.5639$ (8) Å
$c = 7.2237$ (4) Å
$V = 1707.37$ (16) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.13$ mm^{-1}
$T = 100$ K
0.14 × 0.07 × 0.05 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008*a*)
$T_{min} = 0.982$, $T_{max} = 0.994$
19113 measured reflections
1567 independent reflections
928 reflections with $I > 2\sigma(I)$
$R_{int} = 0.083$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.130$
$S = 1.02$
1567 reflections
127 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

The hexahydroxyphenylene molecule is located on a twofold axis. The water and hydroxy H atoms were located in a difference Fourier map but constrained to ride on their parent atoms, with $U_{iso}(H) = 1.5U_{eq}(O)$. The remaining H atoms were positioned geometrically

Table 1
Selected bond lengths (Å).

O1—C1	1.366 (3)	O3—C8	1.338 (3)
O2—C7	1.372 (3)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2^{i}	0.86	1.92	2.781 (2)	176
O2—H2···O5	0.88	1.81	2.675 (3)	170
O3—H3···O4^{i}	0.90	1.75	2.649 (3)	170
O4—H4A···O4^{ii}	0.84	2.34	2.930 (5)	128
O4—H4B···O1^{iii}	0.84	2.08	2.914 (3)	176
O5—H5A···O3^{iv}	0.87	1.96	2.787 (3)	159
O5—H5B···O4	0.87	2.38	2.761 (3)	107

Symmetry codes: (i) $-x+\frac{3}{2}, y-\frac{1}{2}, z$; (ii) $-x+1, -y+1, -z+1$; (iii) $x, -y, z-\frac{1}{2}$; (iv) $-x+\frac{3}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$.

and were also constrained to ride on their parent atoms, with C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C). The highest peak is located 0.60 Å from atom H3 and the deepest hole is located 0.95 Å from atom O5.

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008*b*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008*b*); molecular graphics: *CrystalMaker* (Palmer, 2010); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3069). Services for accessing these data are described at the back of the journal.

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