

Hydrogen-bond networks in tris(4-hydroxyphenyl)methane and its 1:1 molecular complex with 4,4'-bipyridine

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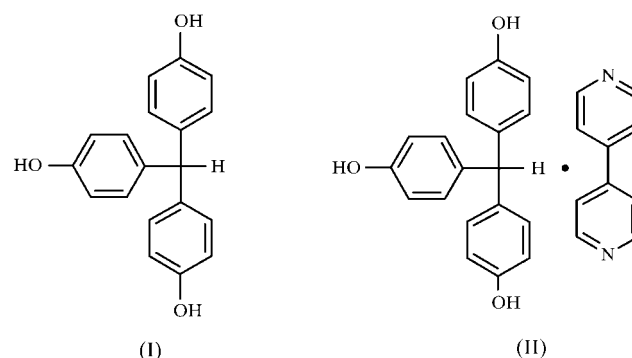
In tris(4-hydroxyphenyl)methane (or 4,4',4''-methanetriyltriphenol), C₁₉H₁₆O₃, molecules are connected by O—H···O hydrogen bonds [O···O = 2.662 (2) and 2.648 (2) Å] into two-dimensional square networks that are twofold interpenetrated. In tris(4-hydroxyphenyl)methane–4,4'-bipyridine (1/1), C₁₉H₁₆O₃·C₁₀H₈N₂, trisphenol molecules form rectangular networks *via* O—H···O [O···O = 2.694 (3) Å] and C—H···O [C···O = 3.384 (3) Å] hydrogen bonds. Bipyridine molecules hydrogen bonded to phenol moieties [O···N = 2.622 (3) and 2.764 (3) Å] fill the voids to complete the structure.

Comment

The crystal structures of 1,1,1-tris(4-hydroxyphenyl)ethane and its adducts with many nitrogen bases have been reported (Ferguson *et al.*, 1997; Bényei *et al.*, 1998; Zakaria *et al.*, 2002*a,b*). These structures contain sheets and open networks of O—H···O, O—H···N and N⁺—H···O[−] hydrogen bonds, with up to tenfold interpenetration of giant hexagons in 1,1,1-tris(4-hydroxyphenyl)ethane–4,4'-bipyridine (2/3) (Bényei *et al.*, 1998). Molecules with C₃ symmetry are important in the crystal engineering (Desiraju, 1989; Moberg, 1998) of supramolecular architectures, in host–guest systems and in the design of non-linear optical materials. In this context, we have determined the crystal structure of tris(4-hydroxyphenyl)methane, (I). Cocrystallization of (I) with 4,4'-bipyridine in a 2:3 stoichiometry gave the 1:1 adduct, (II).

The crystal structure of (I) contains one molecule of tris(4-hydroxyphenyl)methane in the asymmetric unit (Fig. 1). The phenol groups act as donors and acceptors of hydrogen bonds, such that each molecule is bonded to six others through O—

H···O hydrogen bonds (Table 2). Hydroxy atom O1 acts as a hydrogen-bond donor to atom O2 at $(x - \frac{1}{2}, y - \frac{1}{2}, z)$, thus generating chains of molecules running parallel to [110], and atom O3 acts as a hydrogen-bond donor to atom O1 at $(1 + x, y, 1 + z)$, thus generating chains of molecules parallel to [101]. The intersection of these two linear motifs generates two-dimensional square networks parallel to the $(\bar{1}11)$ plane (Fig. 2), which are identical to the square nets observed in the crystal structure of 1,1,1-tris(4-hydroxyphenyl)ethane (Ferguson *et al.*, 1997), with which the present compound is isomorphous [after appropriate cell transformation of the 1,1,1-tris(4-hydroxyphenyl)ethane cell from *Ia* to *Cc*]. The third hydroxy group (O2) acts as a hydrogen-bond donor to atom O3 at $(x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{3}{2})$, thus generating an identical square network parallel to the $(11\bar{1})$ plane. These two square networks interpenetrate in the structure at an angle of $\sim 160^\circ$, being connected *via* the O2—H2···O3 hydrogen bond (Fig. 3).



The crystal structure of (II) contains one molecule of (I) and one molecule of 4,4'-bipyridine in the asymmetric unit (Fig. 4). One of the hydroxy groups of the molecule of (I) acts as a hydrogen-bond donor to a *d*-glide-related O atom, and the other two hydroxy groups act as hydrogen-bond donors to 4,4'-bipyridine molecules. Each molecule of (I) is connected to

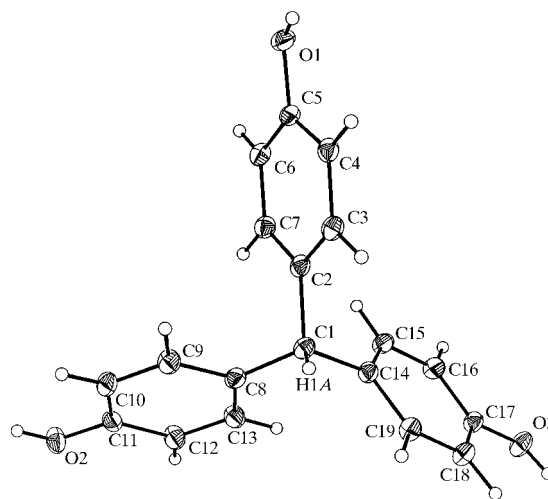


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms.

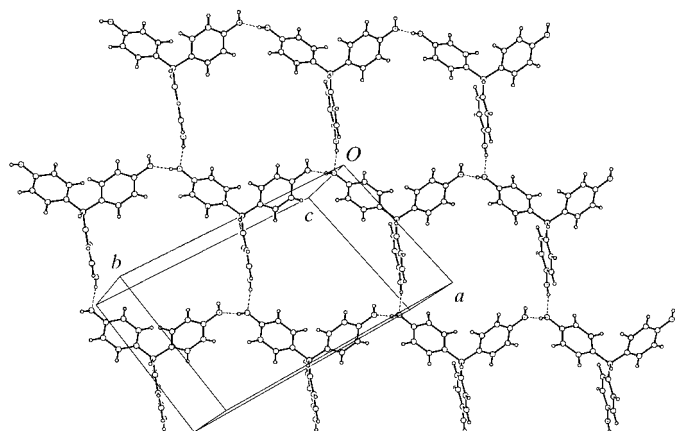


Figure 2
A view of the crystal structure of (I), showing the two-dimensional square network.

two others, thus forming zigzag chains *via* O—H···O hydrogen bonds (Table 4). Atom O2 acts as a hydrogen-bond donor to atom O1 in the molecule at $(\frac{3}{4} - x, \frac{1}{4} + y, -\frac{1}{4} + z)$, thus generating a zigzag chain parallel to [011] and produced by the *d*-glide plane. The zigzag chain related by the twofold rotation axis runs parallel to [0 $\bar{1}$ 1]. Atom C15 acts as a hydrogen-bond

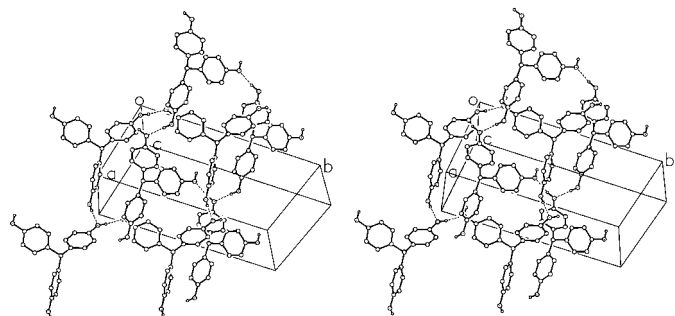


Figure 3
A stereoview of (I), showing the concatenation of two square nets. H atoms bonded to C atoms have been omitted for clarity.

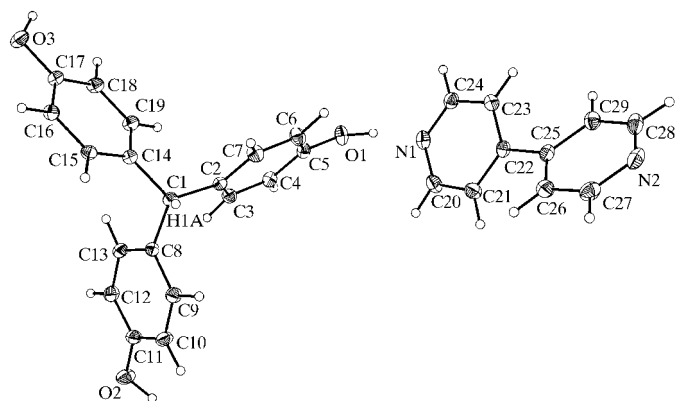


Figure 4
A view of the molecular components of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms.

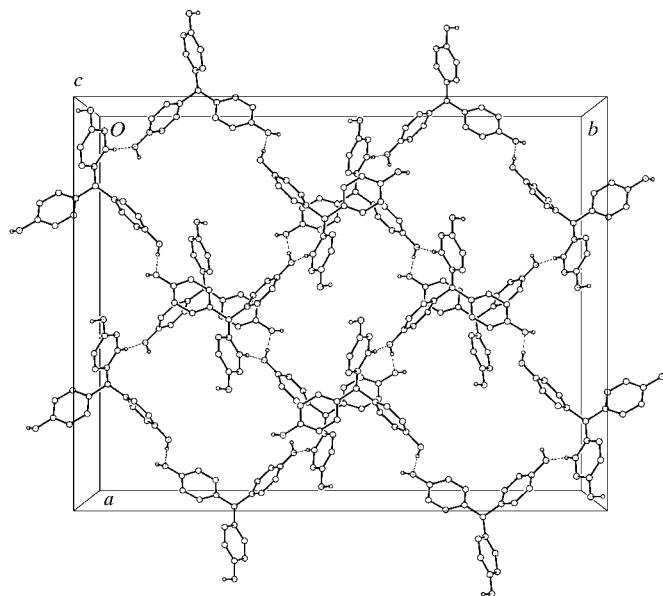


Figure 5
A view of the crystal structure of (II), showing the rectangular voids in the *ab* plane. H atoms bonded to C atoms, except that involved in hydrogen bonding (C15), have been omitted for clarity.

donor to atom O2 of the *d*-glide-related molecule at $(-\frac{1}{4} + x, \frac{5}{4} - y, -\frac{1}{4} + z)$, resulting in a zigzag chain parallel to $[\bar{1}01]$. The net result of the O—H···O and C—H···O hydrogen-bonded chains is a rectangular grid parallel to the *ab* plane, with voids of 9.6×12.5 Å (Fig. 5). This two-dimensional network is not flat but has undulated layers, with molecules of (I) occupying a thickness approximately equal to the length of the *c* axis. Atoms O1 and O3 act as hydrogen-bond donors to atoms N1 and N2, respectively. Thus, each rectangular network is connected to two others by a bipyrindine molecule parallel to [001]. The threading of two bipyrindine molecules through a rectangular void is shown as a stereoview in Fig. 6. The crystal structure of (II) can be compared with the 2:1 adduct of 1,1,1-tris(4-hydroxyphenyl)ethane and bis(4-pyridyl)ethane (Zakaria *et al.*, 2002*a*), in which the supramolecular structure consists of continuously interwoven bilayers.

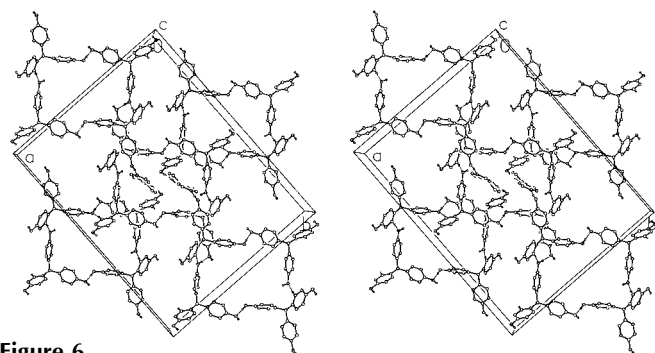


Figure 6
A stereoview of the crystal structure of (II), showing two bipyrindine linkers connecting the hydrogen-bonded networks of (I) and passing through the rectangular void of a third network. H atoms bonded to C atoms, except that involved in hydrogen bonding (C15), have been omitted for clarity.

The conformations of the trisphenol molecules in the two crystal structures are different (Tables 1 and 3); the torsion angles about the C1—C_{aryl} bond are similar in (II), whereas they are very different in (I). In (II), the dihedral angle between the planes of the bipyridine rings is -32.2 (3)°.

Experimental

Tris(4-hydroxyphenyl)methane was prepared according to the procedure of Kolasa *et al.* (2000). A mixture of 4-hydroxybenzaldehyde (1.0 g, 8 mmol) and phenol (2.6 g, 28 mmol) in 1,4-dioxane (15 ml) and water (15 ml) at 273 K was treated dropwise with concentrated H₂SO₄ (10 ml). The reaction mixture was allowed to warm to room temperature and was stirred for 6 h before being neutralized with NaHCO₃ solution and extracted with ether. The ether layer was washed with water and brine, dried with MgSO₄, and concentrated *in vacuo* to yield (I). The product was purified by column chromatography to yield pure (I), which was crystallized from methanol (m.p. 513 K). Crystals of the 1:1 molecular complex, (II) (m.p. 470 K), of (I) and 4,4'-bipyridine were obtained upon cocrystallization of the components in a 2:3 ratio from acetonitrile.

Compound (I)

Crystal data

C ₁₉ H ₁₆ O ₃	$D_x = 1.242 \text{ Mg m}^{-3}$
$M_r = 292.32$	Mo $K\alpha$ radiation
Monoclinic, <i>Cc</i>	Cell parameters from 1475 reflections
$a = 12.326$ (3) Å	$\theta = 3.7\text{--}29.7^\circ$
$b = 18.573$ (4) Å	$\mu = 0.08 \text{ mm}^{-1}$
$c = 7.4961$ (15) Å	$T = 100$ (1) K
$\beta = 114.36$ (3)°	Needle, brown
$V = 1563.4$ (7) Å ³	$0.40 \times 0.35 \times 0.20 \text{ mm}$
$Z = 4$	

Data collection

Kuma KM-4 CCD diffractometer	$R_{\text{int}} = 0.031$
ω scans	$\theta_{\text{max}} = 29.7^\circ$
7459 measured reflections	$h = -16 \rightarrow 16$
2056 independent reflections	$k = -25 \rightarrow 14$
1844 reflections with $I > 2\sigma(I)$	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0573P)^2 + 0.0272P]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.101$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.22$	$\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$
2056 reflections	$\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
263 parameters	
All H-atom parameters refined	

Table 1

Selected torsion angles (°) for (I).

H1A—C1—C2—C3	26.9 (13)	H1A—C1—C8—C9	61.2 (14)
H1A—C1—C14—C19	16.9 (14)		

Table 2

Hydrogen-bonding geometry (Å, °) for (I).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O1—H1 ⁱ ⋯O2 ⁱ	0.87 (2)	1.81 (3)	2.662 (2)	168 (3)
O2—H2 ⁱⁱ ⋯O3 ⁱⁱ	0.88 (2)	1.81 (2)	2.662 (2)	163 (2)
O3—H3 ⁱⁱⁱ ⋯O1 ⁱⁱⁱ	0.86 (3)	1.81 (3)	2.648 (2)	166 (3)

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

Compound (II)

Crystal data

C ₁₉ H ₁₆ O ₃ ·C ₁₀ H ₈ N ₂	Mo $K\alpha$ radiation
$M_r = 448.50$	Cell parameters from 2377 reflections
Orthorhombic, <i>Fdd2</i>	$\theta = 3.5\text{--}29.9^\circ$
$a = 26.483$ (5) Å	$\mu = 0.08 \text{ mm}^{-1}$
$b = 34.102$ (7) Å	$T = 100$ (1) K
$c = 10.483$ (2) Å	Needle, brown
$V = 9468$ (3) Å ³	$0.45 \times 0.40 \times 0.25 \text{ mm}$
$Z = 16$	
$D_x = 1.259 \text{ Mg m}^{-3}$	

Data collection

Kuma KM-4 CCD diffractometer	$R_{\text{int}} = 0.043$
ω scans	$\theta_{\text{max}} = 29.9^\circ$
22 391 measured reflections	$h = -36 \rightarrow 34$
3352 independent reflections	$k = -46 \rightarrow 45$
2951 reflections with $I > 2\sigma(I)$	$l = -14 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.043$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.095$	$(\Delta/\sigma)_{\text{max}} = 0.069$
$S = 1.12$	$\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$
3352 reflections	$\Delta\rho_{\text{min}} = -0.18 \text{ e \AA}^{-3}$
404 parameters	Extinction correction: <i>SHELXL97</i>
All H-atom parameters refined	Extinction coefficient: 0.00029 (7)

Table 3

Selected torsion angles (°) for (II).

C23—C22—C25—C29	-32.2 (3)	H1A—C1—C14—C15	-34.6 (12)
H1A—C1—C2—C7	-33.0 (14)	H1A—C1—C8—C9	-40.7 (14)

Table 4

Hydrogen-bonding geometry (Å, °) for (II).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
C15—H15A ⁱ ⋯O2 ^{iv}	0.97 (3)	2.42 (3)	3.384 (3)	175 (2)
O2—H2 ^v ⋯O1 ^v	0.92 (4)	1.78 (4)	2.694 (3)	174 (3)
O1—H1 ^{vi} ⋯N1	1.04 (3)	1.60 (3)	2.622 (3)	169 (3)
O3—H3 ^{vii} ⋯N2 ^{vi}	0.97 (3)	1.80 (3)	2.764 (3)	174 (3)

Symmetry codes: (iv) $x - \frac{1}{4}, \frac{3}{4} - y, z - \frac{1}{4}$; (v) $\frac{3}{4} - x, \frac{1}{4} + y, z - \frac{1}{4}$; (vi) $x - \frac{1}{4}, \frac{3}{4} - y, \frac{3}{4} + z$.

Both structures are non-centrosymmetric. However, because the anomalous dispersion effects were insignificant, Friedel opposite reflections were merged. The Flack (1983) parameters are thus indeterminate. Refined C—H distances of 0.93 (3)—1.02 (3) and 0.94 (2)—1.03 (3) Å, and O—H distances of 0.84 (3)—0.90 (3) and 0.92 (4)—1.04 (3) Å were obtained for (I) and (II), respectively.

For both compounds, data collection: *KM-4 Software* (Kuma, 1999); cell refinement: *KM-4 Software*; data reduction: *CrysAlis* (Kuma, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); 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: JZ1567). Services for accessing these data are described at the back of the journal.

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