

Hexahydroxybenzene–2,2′-bipyridine
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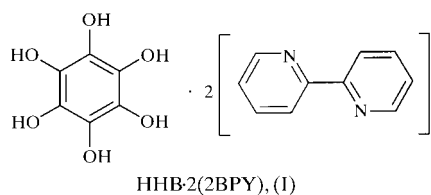
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2,2′-Bipyridine (2BPY) and hexahydroxybenzene (HHB) crystallize in a 2:1 ratio as a neutral molecular adduct, $C_6H_6O_6 \cdot 2C_{10}H_8N_2$, in space group $P\bar{1}$ with $Z = 1$ and with the HHB molecule lying on an inversion centre. HHB, of which this is the first single-crystal X-ray structure determination, forms $O-H \cdots O$ hydrogen-bonded chains parallel to the a axis, with $O \cdots O$ distances of 2.761 (1) and 2.782 (1) Å. $O-H \cdots N$ hydrogen bonds to the 2BPY molecules crosslink these chains, with $O \cdots N$ distances of 2.707 (1) and 2.735 (1) Å.

Comment

In order to investigate a variety of molecular interactions in the solid state, in particular $N-H \cdots O$ and $O-H \cdots N$ hydrogen bonds, we attempted to produce cocrystals of 2,2′-bipyridine (2BPY) and tetrahydroxybenzoquinone (THBQ), but during the crystallization process THBQ was reduced to hexahydroxybenzene (HHB). The resulting cocrystal, (I), comprised a neutral molecular adduct of 2BPY and HHB in a 2:1 ratio in space group $P\bar{1}$ with $Z = 1$, with the HHB molecule residing on an inversion centre.



Reduction of quinone to hydroquinone is a reaction commonly found in organic textbooks (March, 1985; Vollhardt & Schore, 1994). The addition of hydroxyl groups to the ring weakens the carbonyl bond in quinone derivatives, as can be seen in the X-ray diffraction-determined bond lengths in quinone ($C=O = 1.222$ Å; Allen *et al.*, 1992), 2,5-dihydroxybenzoquinone ($C=O = 1.232$ Å; Cowan *et al.*, 2001a) and THBQ ($C=O = 1.235$ Å; Cowan *et al.*, 2001b). This weakening of the carbonyl bond facilitates reduction by stabilizing

the reaction intermediates (Vollhardt & Schore, 1994). Indeed, HHB is synthesized from THBQ (Fatiadi & Sager, 1975), but under acidic conditions. We are unsure how this reaction has taken place under the essentially neutral conditions of the present crystallization.

IR absorption spectra were recorded for the crystal of (I), for THBQ, and for a 2:1 mixture of 2BPY and THBQ. The spectra of THBQ and of the THBQ/2BPY mixture show a significant carbonyl peak at 1600 cm^{-1} , while the spectrum for (I) shows no significant peak in this region. The freshly prepared KBr disc of (I) was colourless, but it turned pale pink a few hours after preparation, which is evidence of moisture- and air-induced oxidation of HHB to TBHQ, as observed by Fatiadi & Sager (1975) in pure HHB crystals. THBQ is highly coloured and a trace amount can cause intense coloration. After recollection of the spectrum on the reprepared discoloured disc of (I), no significant difference was observed.

The HHB molecular refinement behaves normally and there is no evidence in the s.u.'s of the bond lengths or in unusual anisotropic displacement parameters of rotational disorder that could disguise THBQ as HHB (Fig. 1). The molecular geometry of HHB is as expected, although there are no examples in the Cambridge Structural Database (CSD; Allen & Kennard, 1993) for comparison. All the C–C bond distances are identical to within three s.u.'s [1.399 (2), 1.401 (1) and 1.399 (2) Å] and there are only slight differences in the C–O bond distances [1.379 (1), 1.382 (1) and 1.376 (2) Å]. The average C–C–O angles of the hydroxy groups to the benzene ring are 118.1° *trans* to the H atom and 121.9° *cis* to the H atom. This asymmetry is common in phenol molecules in the CSD and is due to the asymmetry of the hydroxyl group. The 2BPY moiety can be neutral, or singly or doubly protonated. In (I), it is unprotonated and in an almost planar *trans* conformation [$N1-C10-C20-N2 = 171.15(10)^\circ$], with an angle of $8.73(6)^\circ$ between the two pyridyl rings.

The HHB molecules, which occupy centrosymmetric unit-cell corner sites, form columns of parallel rings in the b direction and hydrogen-bonded chains in the a direction

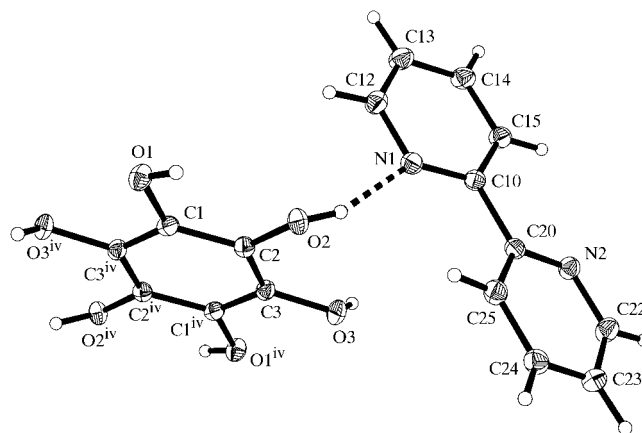


Figure 1

The molecular structure of (I) with 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii and the dashed line indicates a hydrogen bond [symmetry code: (iv) $-x, 1-y, -z$].

[O1 \cdots O2ⁱ = 2.761 (1) Å; symmetry code: (i) 1 - x, 1 - y, -z]. The 2BPY molecules, which stack in pairs with a mean separation of 3.46 Å, lie approximately parallel to the *bc* plane and these stacks form zigzag columns in the *a* direction, with a separation between 2BPY 'dimers' of 3.50 Å. A dimer of 2BPY molecules is hydrogen bonded to the same HHB molecule, with O \cdots N distances of 2.707 (1) (O2 \cdots N1) and 2.735 (1) Å [O3 \cdots N2ⁱⁱ; symmetry code: (ii) -x, -y, 1 - z] linking the HHB columns to the 2BPY dimers (Fig. 2). The 2BPY and HHB molecules in (I) are also linked by two weak C \cdots O hydrogen bonds [C15 \cdots O3ⁱⁱⁱ 3.333 (1) Å and C14 \cdots O3ⁱⁱⁱ 3.432 (1) Å; symmetry code: (iii) x, y - 1, z; details are given in Table 1].

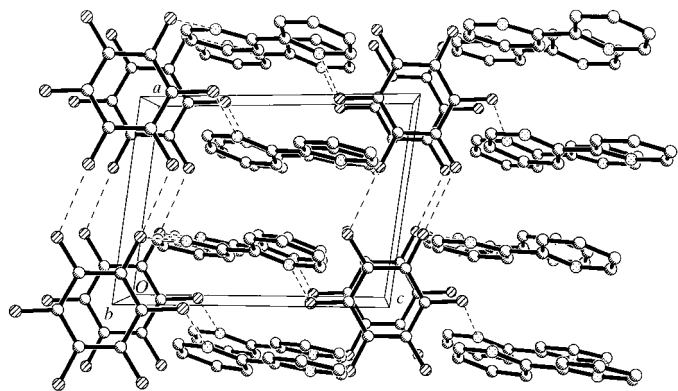


Figure 2

The packing diagram for (I) viewed along the *b* axis; H atoms have been omitted for clarity and the dashed lines indicate hydrogen bonds. The chains of HHB molecules and zigzag stacks of 2BPY molecules parallel to the *a* axis are evident.

Experimental

A solution of 2,2'-bipyridine in methanol (0.5 ml, 0.2 mol) was poured slowly into a narrow test-tube containing an aqueous solution of tetrahydroxybenzoquinone (approximately 0.5 ml, 0.2 mol) to produce an interface. Pale-yellow plate-shaped crystals of (I) suitable for X-ray analysis were produced by slow mixing of the solutions. IR spectra of the starting materials and product were recorded using KBr discs on a Perkin-Elmer 580B IR spectrometer.

Crystal data

C ₆ H ₆ O ₆ ·2C ₁₀ H ₈ N ₂	Z = 1
<i>M_r</i> = 486.48	<i>D_x</i> = 1.464 Mg m ⁻³
Triclinic, <i>P</i> 1̄	Mo <i>K</i> α radiation
<i>a</i> = 7.2913 (5) Å	Cell parameters from 991 reflections
<i>b</i> = 7.9434 (5) Å	θ = 10.3–30.8°
<i>c</i> = 9.9197 (7) Å	μ = 0.11 mm ⁻¹
α = 76.584 (4)°	<i>T</i> = 100 (2) K
β = 80.959 (4)°	Plate, pale yellow
γ = 86.321 (4)°	0.36 × 0.32 × 0.12 mm
<i>V</i> = 551.68 (6) Å ³	

Data collection

Bruker SMART CCD area-detector diffractometer	<i>R</i> _{int} = 0.034
ω scans	θ _{max} = 29°
6594 measured reflections	<i>h</i> = -9 → 9
2850 independent reflections	<i>k</i> = -10 → 10
2536 reflections with <i>I</i> > 2σ(<i>I</i>)	<i>l</i> = -13 → 13

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0568P)^2 + 0.196P]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.112$	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.06	$\Delta\rho$ _{max} = 0.40 e Å ⁻³
2850 reflections	$\Delta\rho$ _{min} = -0.20 e Å ⁻³
207 parameters	All H-atom parameters refined

Table 1

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H \cdots <i>A</i>	<i>D</i> –H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> –H \cdots <i>A</i>
O1–H1 \cdots O2 ⁱ	0.86 (2)	1.98 (2)	2.761 (1)	151 (2)
O1–H1 \cdots O2	0.86 (2)	2.37 (2)	2.782 (1)	110 (2)
O2–H2 \cdots N1	0.88 (2)	1.86 (2)	2.707 (1)	162 (2)
O3–H3 \cdots N2 ⁱⁱ	0.89 (2)	1.86 (2)	2.735 (1)	168 (2)
C14–H14 \cdots O3 ⁱⁱⁱ	0.99 (2)	2.51 (2)	3.432 (1)	154 (14)
C15–H15 \cdots O3 ⁱⁱ	0.96 (2)	2.47 (2)	3.333 (1)	149 (14)

Symmetry codes: (i) 1 - x, 1 - y, -z; (ii) -x, -y, 1 - z; (iii) x, y - 1, z.

All H atoms were located in difference Fourier maps and refined with isotropic displacement parameters [C–H = 0.96 (2)–0.99 (2) Å]; the C–H and O–H distances all refined to within standard ranges and there were no anomalous values of *U*_{iso}. The ten highest peaks in the residual electron density all lie in the centres of aromatic bonds. There is no indication of disorder in the O–H hydrogen bonds.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1065). Services for accessing these data are described at the back of the journal.

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