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1,3,5-Trihydroxybenzene–2,2'-Bipyridyl (1/2): a Hydrogen-Bonded Structure Based on a Stem-and-Leaves Motif

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Abstract

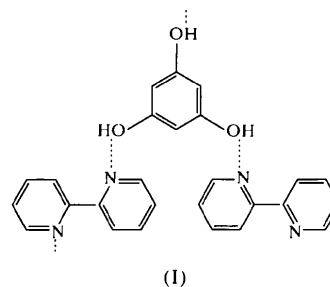
In the 1:2 adduct formed between 1,3,5-trihydroxybenzene (phloroglucinol) and 2,2'-bipyridyl, $C_6H_6O_3 \cdot 2C_{10}H_8N_2$, the triol molecules and half of the bipyridyl molecules are linked into chains by means of O—H...N hydrogen bonds, forming a stem, while the other half of the bipyridyl molecules are pendent from this stem, via O—H...N hydrogen bonds.

Comment

1,3,5-Trihydroxybenzene (phloroglucinol) forms a 2:3 hydrogen-bonded adduct with 4,4'-bipyridyl, with stoi-

chiometry $[C_6H_3(OH)_3]_2 \cdot [C_{10}H_8N_2]_3$ (Coupar *et al.*, 1996). In this adduct, each molecule of the triol component acts as a triple donor in O—H...N hydrogen bonds and each molecule of the bipyridyl acts as a double acceptor. Two molecules of each component are linked by hydrogen bonds to form $R_4^4(30)$ rings (Bernstein *et al.*, 1995), and these rings are linked by the third independent bipyridyl unit into a $C_4^4(30)[R_4^4(30)]$ chain-of-rings.

In contrast, cocrystallization of 1,3,5-trihydroxybenzene with 2,2'-bipyridyl yields the 1:2 adduct $C_6H_3(OH)_3 \cdot [C_{10}H_8N_2]_2$, (I). In adduct (I) (Fig. 1), the



triol molecules all act as triple donors in O—H...N hydrogen bonds, but the two independent bipyridyl units behave differently; half of the bipyridyl molecules act as double acceptors in O—H...N hydrogen bonds, forming a chain motif with the triol molecules, while the other half of the bipyridyl molecules act as single acceptors of O—H...N hydrogen bonds and are pendent from this chain, so forming a stem-and-

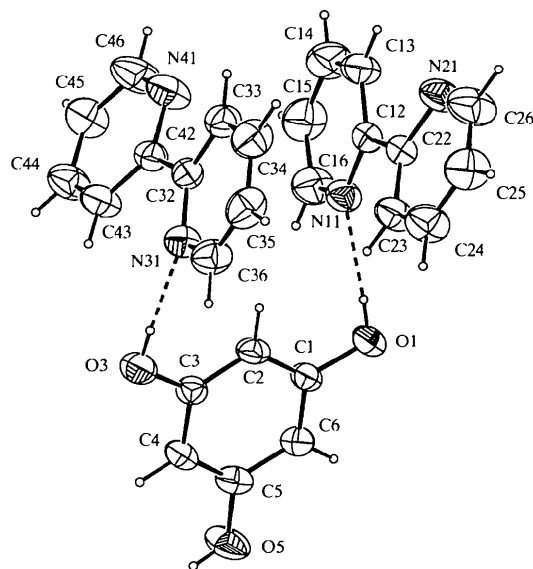


Fig. 1. The asymmetric unit of compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

leaves motif (Ferguson *et al.*, 1998). This connectivity in the 1:2 adduct, (I), is thus identical to that in the 1:2 adduct formed between 1,1,1-tris(4-hydroxyphenyl)ethane, CH₃C(C₆H₄OH)₃, and hexamethylenetetramine (HMTA), (CH₂)₆N₄, where half the HMTA molecules act as double acceptors within chains and half act as single acceptors pendent from the chains (Coupar *et al.*, 1997). However, whereas the chains in the CH₃C(C₆H₄OH)₃·(HMTA)₂ adduct are generated by the action of a 2₁ screw axis and are coiled to form triple helices, in compound (I), the chains are not coiled at all, but are generated by translation.

Atoms O1 and O3 act as donors to N11 and N31, respectively, within the asymmetric unit; atom O5 in the triol at (x, y, z) acts as donor to atom N21 in the bipyridyl at (x, 1+y, z), so generating a C₂(11) chain running parallel to the [010] direction. In addition to the hard (Braga *et al.*, 1995) O—H···N hydrogen bonds, there is a single soft C—H···N hydrogen bond involving the otherwise-unused N41 atom; the pyridyl C44 atom at (x, y, z) acts as donor to N41 in the unit at (−x, $\frac{1}{2} + y$, $-\frac{1}{2} - z$), and repetition of this motif provides a C(5) chain running parallel to [010], and generated by the action of the screw axis at (0, y, $-\frac{1}{4}$). This soft hydrogen bond thus reinforces the main chain-forming O—H···N hydrogen bonds. Four such [010] chains run through each unit cell, but there

are no hydrogen-bonding interactions between them. There are, however, some closely stacked and nearly parallel heteroaryl rings, whose interactions are likely to be weakly attractive (Hunter, 1994); thus, the N21-containing ring in the molecular aggregate at (x, y, z) is nearly parallel to, and only ca 3.6 Å distant from, the two N21-containing rings in the units at (x, y, z) and (x, $-\frac{1}{2} - y$, $\frac{1}{2} + z$). Propagation of these interactions by the symmetry operators thus generates two continuous stacks of alternating N21- and N31-containing rings running through the unit cell in the [001] direction.

The two independent molecules of 2,2'-bipyridyl in the structure of (I) are both close to the *trans*-planar conformation; the angle between the heteroaryl N11- and N21-containing rings is 15.0(1)°, and between the N31- and N41-containing rings, the angle is 14.7(1)°. In pure 2,2'-bipyridyl, the molecules lie across centres of inversion in P₂₁/c, so that the rings are strictly parallel (Merritt & Schroeder, 1956; Chisholm *et al.*, 1981). This conformational preference can most plausibly be ascribed to the mutual repulsion of the dipoles generated by the N atoms. The bipyridyl molecules show a similar sequence of bond lengths (Table 1) to that found in the pure compound (Chisholm *et al.*, 1981); the triol component shows a clear alternation of the values of the internal C—C—C bond angles.

Examination of the structure with *PLATON* (Spek, 1998) showed that there were no solvent-accessible voids in the crystal lattice.

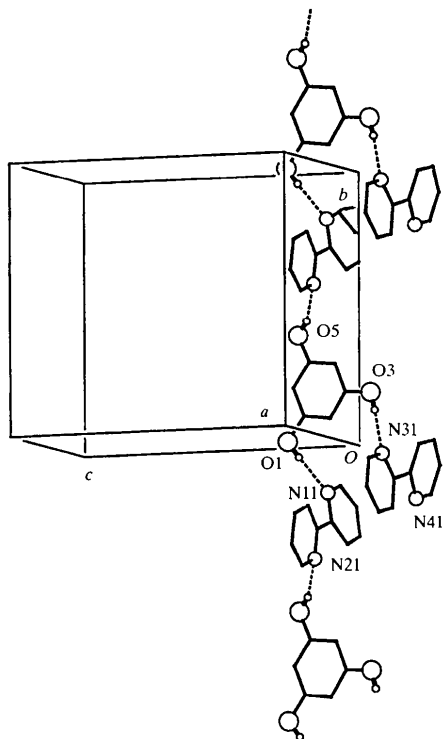


Fig. 2. A view of part of the crystal structure of (I), showing one of the chains parallel to [010].

Experimental

Equimolar quantities of 1,3,5-trihydroxybenzene and 2,2'-bipyridyl were separately dissolved in methanol. The solutions were mixed and the resulting mixture set aside to crystallize, producing analytically pure (I). Elemental analysis: found C 70.6, H 5.0, N 12.6%; C₂₆H₂₂N₄O₃ requires C 71.2, H 5.1, N 12.8%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

C₆H₆O₃·2C₁₀H₈N₂

M_r = 438.48

Monoclinic

P₂₁/c

a = 13.7975 (13) Å

b = 11.9811 (7) Å

c = 14.261 (2) Å

β = 110.516 (10)°

V = 2208.0 (4) Å³

Z = 4

D_x = 1.319 Mg m^{−3}

D_m not measured

Mo *K*α radiation

λ = 0.7107 Å

Cell parameters from 25

reflections

θ = 9.60–17.87°

μ = 0.089 mm^{−1}

T = 294 (1) K

Plate

0.40 × 0.40 × 0.14 mm

Colourless

Data collection

Enraf–Nonius CAD-4
diffractometer

R_{int} = 0.008

θ_{max} = 25.13°

$\theta/2\theta$ scans $h = -16 \rightarrow 15$
 Absorption correction: none $k = 0 \rightarrow 14$
 4131 measured reflections $l = 0 \rightarrow 17$
 3967 independent reflections 3 standard reflections
 2313 reflections with frequency: 120 min
 $I > 2\sigma(I)$ intensity decay: 6.1%

Refinement

Refinement on F^2 $\Delta\rho_{\max} = 0.151 \text{ e } \text{\AA}^{-3}$
 $R[F^2 > 2\sigma(F^2)] = 0.038$ $\Delta\rho_{\min} = -0.153 \text{ e } \text{\AA}^{-3}$
 $wR(F^2) = 0.098$ Extinction correction:
 $S = 0.992$ *SHELXL97*
 3967 reflections Extinction coefficient:
 302 parameters 0.0215 (12)
 H atoms constrained Scattering factors from
 $w = 1/[\sigma^2(F_o^2) + (0.0501P)^2]$ *International Tables for*
 where $P = (F_o^2 + 2F_c^2)/3$ *Crystallography* (Vol. C)
 $(\Delta/\sigma)_{\max} < 0.001$

Table 1. Selected geometric parameters (\AA , $^\circ$)

O1—C1	1.370 (2)	N21—C26	1.335 (3)
O3—C3	1.364 (2)	N31—C32	1.347 (2)
O5—C5	1.366 (2)	N31—C36	1.336 (2)
N11—C12	1.343 (2)	N41—C42	1.338 (2)
N11—C16	1.336 (2)	N41—C46	1.333 (3)
N21—C22	1.338 (2)		
C2—C1—C6	121.16 (16)	C1—C6—C5	118.69 (17)
C1—C2—C3	119.06 (15)	C12—N11—C16	117.65 (16)
C2—C3—C4	120.84 (16)	C22—N21—C26	117.06 (17)
C3—C4—C5	118.99 (16)	C32—N31—C36	117.53 (16)
C4—C5—C6	121.23 (16)	C42—N41—C46	117.16 (17)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1...N11	0.82	1.98	2.776 (2)	164
O3—H3...N31	0.82	2.02	2.834 (2)	175
O5—H5...N21 ⁱ	0.82	1.99	2.785 (2)	162
C44—H44...N41 ⁱⁱ	0.93	2.59	3.492 (3)	163

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

Compound (I) crystallized in the monoclinic system; space group $P2_1/c$ from the systematic absences. H atoms were treated as riding atoms (C—H 0.93 and O—H 0.82 \AA).

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992). Cell refinement: *SET4* and *CELDIM* in *CAD-4-PC Software*. Data reduction: *DATRD2* in *NRCVAX96* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *NRCVAX96* and *SHELXL97* (Sheldrick, 1997b). Molecular graphics: *NRCVAX96*, *ORTEPII* (Johnson, 1976) and *PLATON* (Spek, 1998). Software used to prepare material for publication: *NRCVAX96*, *SHELXL97* and *WordPerfect* macro *PRPCIF97* (Ferguson, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1206). Services for accessing these data are described at the back of the journal.

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Pairwise-Interlocked Chains in 4,4'-Sulfonyldiphenol–2,2'-Bipyridyl (1/1)

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Abstract

In the hydrogen-bonded structure of the title complex, $\text{O}_2\text{S}(\text{C}_6\text{H}_4\text{OH})_2 \cdot \text{C}_{10}\text{H}_8\text{N}_2$ or $\text{C}_{12}\text{H}_{10}\text{O}_4\text{S} \cdot \text{C}_{10}\text{H}_8\text{N}_2$, the bis-phenol molecules are linked into $C(8)$ chains by means of $\text{O—H} \cdots \text{O}=\text{S}$ hydrogen bonds, and the 2,2'-bipyridyl units, which act as single acceptors only, are pendent from these chains by means of $\text{O—H} \cdots \text{N}$ hydrogen bonds. Pairs of these chains, related by centres of inversion, are mutually interlocked *via* their pendent arms.