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Self-assembled triple helices in the hydrogen-bonded structure of 2,2′-biphenol–4,4′-bipyridyl (1/1)†

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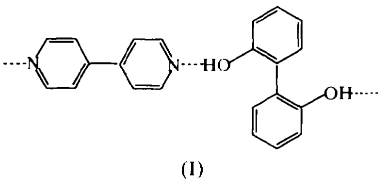
Abstract

In the hydrogen-bonded structure of the title compound, $C_{12}H_{10}O_2 \cdot C_{10}H_8N_2$, the molecular components are linked by O—H···N hydrogen bonds having O···N distances of 2.793 (3) and 2.750 (3) Å into $C_2^2(16)$ chains which are coiled round 2_1 screw axes forming triple helices.

Comment

When bis-phenols form hydrogen-bonded adducts with di-tertiary amines, the supramolecular structures are generally based upon chains of alternating bis-donors and bis-acceptors of hydrogen bonds. When the molecular components have only very limited torsional flexibility, the chains are generally simple and uncoiled, while the presence of torsional degrees of freedom in the molecular components often permits the chains to coil (Coupar *et al.*, 1997; Ferguson, Bell *et al.*, 1997; Ferguson, Coupar & Glidewell, 1997). In 4,4′-biphenol, the distance between the two hydroxyl O atoms, and their mutual orientation, is independent of any rotation about the central C—C bond. Hence, when this phenol forms a hydrogen-bonded adduct with the rigid diamine 1,4-diazabicyclo[2.2.2]octane, the supramolecular structure consists of long, non-folded chains (Ferguson *et al.*, 1998). However, in the isomeric 2,2′-biphenol the essentially free rotation about the central C—C bond allows a range of inter-oxygen distances, and in most of its non-planar conformations this phenol will introduce bends into any chain of which it is a component. Hence, chains resulting from adduct formation are expected to be folded (Ferguson, Bell *et al.*, 1997). Here we report the structure of the 1:1 adduct, (I), formed between 2,2′-biphenol and 4,4′-bipyridyl in which the chains are coiled into triple helices.



(I)

Compound (I) crystallizes in the centrosymmetric space group $P2_1/n$ with one molecule of each component in the asymmetric unit (Fig. 1). The components are linked into continuous chains by means of O—H···N hydrogen bonds, but there is no evidence of any proton transfer from the phenol to the diamine. Within the asymmetric unit, atom O1 acts as a hydrogen-bond donor to N34 (Table 2). In addition, atom O2 at (x, y, z) acts as a donor to N44 at ($0.5 - x$, $-1.5 + y$, $0.5 - z$), while O2 at ($0.5 - x$, $-1.5 + y$, $0.5 - z$) acts in turn as donor to N44 at (x, $-3 + y$, z). The resulting chain, generated by the 2_1 screw axis at (0.25, y, 0.25), thus has a repeat period of three unit cells and so there are three identical but independent chains generated by this single screw axis. These chains are thus coiled together to form a triple helix (Fig. 2). Four such triple helices, two of each hand, run through each unit cell.

Such self-assembled multiple helices are not unprecedented in hydrogen-bonded adducts between phenols and poly-aza acceptors. Thus in adducts with hexamethylenetetramine, $(CH_2)_6N_4$, the bis-phenol 4,4′-isopropylidenediphenol, $Me_2C(C_6H_4OH)_2$, forms double helices and the tris-phenol 1,1,1-tris(4-hydroxyphenyl)ethane, $CH_3C(C_6H_4OH)_3$, forms triple helices (Coupar *et al.*, 1997). On the other hand, the molecular components of compound (I) probably represent the simplest building blocks hitherto reported as capable of generating a multiple-helical structure by self-assembly.

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† IUPAC name: 2,2′-biphenyldiol–4,4′-bipyridyl (1/1).

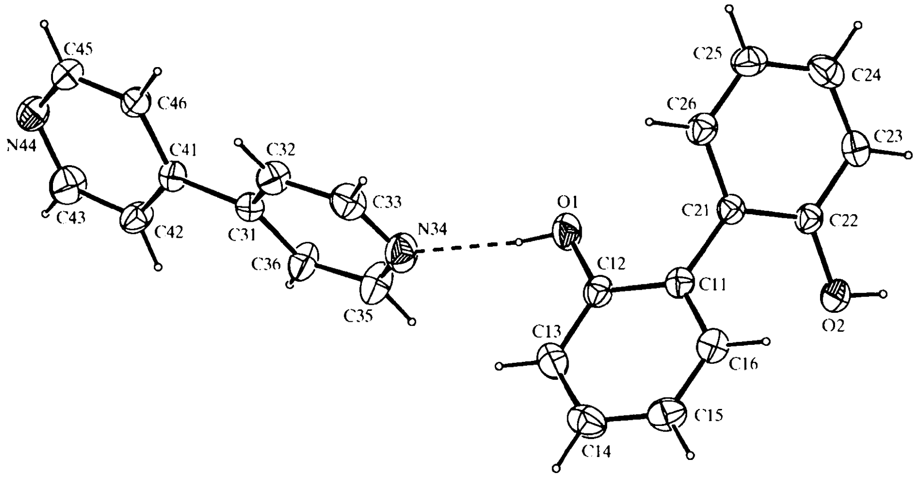

Fig. 1. A view of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

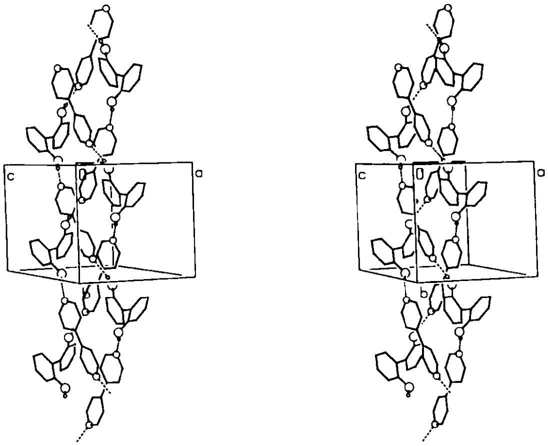

Fig. 2. Stereoview of part of the crystal structure, showing one of the triple helices.

The two independent O—H···N hydrogen bonds are quite short for their type, and both approach linearity (Table 2). The hydrogen-bonding motifs may be described in terms of graph-set notation (Bernstein *et al.*, 1995): $N_1 = DD$, $N_2 = C_2^2(16)$.

The highest possible molecular symmetries for 2,2′-biphenol and 4,4′-bipyridyl are C_{2h} (2/*m*) and D_{2h} (*mmm*), respectively. In compound (I), each molecular component exhibits approximate, but non-crystallographic C_2 symmetry. The dihedral angle between the two heteroaryl rings in the bipyridyl component is 21.4 (1)°, but the key to the chain-coiling is the dihedral angle between the two rings in the biphenol component, 55.4 (1)°. Each occurrence of the biphenol component introduces a significant bend into the chain, permitting the observed coiling.

In the biphenol component, the O—C—C angles exhibit the usual difference between large angles *cisoid* to the hydroxyl hydrogen and small angles *transoid* to this hydrogen, and in the bipyridyl component the C—N—C angles are much less than 120° (Table 1). The other bond lengths and angles are all typical of their types (Allen *et al.*, 1987).

Experimental

Equimolar quantities of 2,2′-biphenol and 4,4′-bipyridyl were separately dissolved in methanol. The solutions were mixed and the mixture set aside to crystallize, providing compound (I). Analysis: found C 77.1, H 5.4, N 8.2%; $C_{22}H_{18}N_2O_2$ requires C 77.2, H 5.3, N 8.2%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

$C_{12}H_{10}O_2 \cdot C_{10}H_8N_2$
$M_r = 342.38$
Monoclinic
$P2_1/n$
$a = 10.8952\,(17)$ Å
$b = 9.9647\,(10)$ Å
$c = 16.288\,(4)$ Å
$\beta = 93.982\,(12)°$
$V = 1764.1\,(5)$ Å^3
$Z = 4$
$D_x = 1.289$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8.62–18.82°$
$\mu = 0.084$ mm^{-1}
$T = 294\,(1)$ K
Plate
0.40 × 0.38 × 0.10 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3385 measured reflections
3274 independent reflections
1653 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.017$
$\theta_{\rm max} = 25.43°$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 19$
3 standard reflections
frequency: 120 min
intensity variation: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.104$
$S = 0.905$
3274 reflections
238 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0574P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.182$ e Å^{-3}
$\Delta\rho_{min} = -0.172$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.0069 (10)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C12	1.359 (2)	C11—C21	1.497 (2)
O2—C22	1.356 (2)	C31—C41	1.480 (2)
O1—C12—C11	118.11 (16)	O2—C22—C23	121.90 (17)
O1—C12—C13	121.69 (18)	C33—N34—C35	116.02 (18)
O2—C22—C21	117.91 (16)	C43—N44—C45	116.02 (17)
C16—C11—C21—C26	−124.4 (2)	C36—C31—C41—C42	21.2 (3)
C12—C11—C21—C26	55.6 (2)	C32—C31—C41—C42	−162.8 (2)
C16—C11—C21—C22	55.2 (2)	C36—C31—C41—C46	−156.7 (2)
C12—C11—C21—C22	−124.8 (2)	C32—C31—C41—C46	19.3 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N34	0.82	1.98	2.793 (3)	172
O2—H2···N44'	0.82	1.96	2.750 (3)	161

Symmetry code: (i) $\frac{1}{2} - x, y - \frac{3}{2}, \frac{1}{2} - z$.

Compound (I) crystallized in the monoclinic system. From the systematic absences, the space group was $P2_1/n$. H atoms were treated as riding atoms (C—H 0.93 and O—H 0.82 Å).

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* (*CAD*-4-*PC Software*; Enraf–Nonius, 1992). Data reduction: *DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1998). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*97 and *WordPerfect* macro *PREP*8 (Ferguson, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1245). Services for accessing these data are described at the back of the journal.

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Paroxetine hydrochloride hemihydrate

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Abstract

The structure of the title compound {systematic name: (3*S*-*trans*)-3-[(1,3-benzodioxol-5-yloxy)methyl]-4-(4-fluorophenyl)piperidinium chloride hemihydrate, $C_{19}H_{21}FNO_3^+ \cdot Cl^- \cdot 0.5H_2O$}, comprises two piperidinium cations (*A* and *B*), two chloride anions, and one water molecule in the asymmetric unit. A piperidinium proton of cation *A* is hydrogen bonded to the water molecule. The second proton points in the direction of one chloride anion, as does a piperidinium proton of cation *B*. One water proton points in the direction of another chloride anion.

Comment

Paroxetine hydrochloride hemihydrate is a serotonin (5-HT) uptake inhibitor and is of therapeutic use as an antidepressant (Barnes *et al.*, 1988). There is increased interest in the use of paroxetine as an alternative to the benzodiazepines in the treatment of generalized anxiety disorder (Rocca *et al.*, 1997). Paroxetine hydrochloride hemihydrate, (I), can be dehydrated, although the hemihydrate is more stable (Buxton *et al.*, 1988). Recently, a variety of 'anhydrates' have been reported