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Two independent $C_2^2(20)$ chains in the hydrogen-bonded structure of 4,4'-biphenol–4,4'-bipyridyl (1/1)

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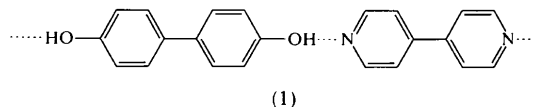
Abstract

In the 1:1 adduct of 4,4'-biphenol and 4,4'-bipyridyl, $C_{12}H_{10}O_2 \cdot C_{10}H_8N_2$, the molecules are linked by O—H \cdots N hydrogen bonds [O \cdots N range 2.700 (2)–2.736 (2) Å and O—H \cdots N range 163–170°] into two types of $C_2^2(20)$ chain running parallel to the [10 $\bar{1}$] and [21 $\bar{2}$] directions.

Comment

In hydrogen-bonded adducts formed by the combination of double donors of hydrogen bonds, such as bisphenols, with an equal number of double acceptors, such as diamines, the predominant mode of aggregation is expected to be the formation of chains, with the two molecular components alternating along the chain (Coupar *et al.*, 1997; Ferguson, Coupar & Glidewell, 1997). This simple model is complicated by the subsequent coiling of the chains, when this is permitted by the conformational flexibility of the molecular components, and single (Ferguson *et al.*, 1999), double (Coupar *et al.*, 1997) and triple (Coupar *et al.*, 1997; Lavender *et al.*, 1999) helices are all formed rather readily by such means. It has been suggested (Ferguson, Bell *et al.*, 1997) that where the molecular components are flexible, the coiling is likely to be dominated by the soft (Braga *et al.*, 1995) hydrogen bonds, but where the molecular components have little or no conformational flexibility, then uncoiled and essentially linear chains may result. In 4,4'-bipyridyl, the sole conformational degree of freedom is rotation about the central C—C bond, and this has no effect on the relative positions of the N acceptor sites; in 4,4'-biphenol, rotation about the central C—C bond again has no effect on the relative positions of the O atoms, so that the only conformational degrees of freedom are the rotations of the hydroxyl groups about the adjacent C—O bonds. We report here the structural characterization of the 1:1 adduct $C_{12}H_{10}O_2 \cdot C_{10}H_8N_2$,

(1), formed between 4,4'-biphenol and 4,4'-bipyridyl, where simple uncoiled chains are both expected and observed.



Compound (1) crystallizes in space group $P\bar{1}$ with $Z = 4$ and $Z' = 2$. The asymmetric unit (Fig. 1) consists of one 4,4'-biphenol and two 4,4'-bipyridyl molecules, all in general positions, together with one half of each of two further 4,4'-biphenol molecules both lying across independent centres of inversion. All of the molecular components are neutral, and there is no evidence from difference maps for any transfer of protons from O to N. The five independent molecular components are linked by four types of O—H \cdots N hydrogen bond (Table 2) into two distinct types of nearly linear chains (Fig. 2). One type of chain involves only the 4,4'-biphenol molecule containing O34 and O44 and lying in a general position, while the other involves the two centrosymmetric molecules, containing O14 and O24, respectively (Figs. 1 and 2). The 4,4'-biphenol in the general position combines with just one of the two independent 4,4'-bipyridyl molecules, that containing N74 and N84, to generate by translation a $C_2^2(20)$ chain running parallel to the [10 $\bar{1}$] direction. Atoms O34 and O44 at (x, y, z) act as donors to N74 and N84 at (x, y, z) and $(x - 1, y, z)$, respectively (Fig. 2 and Table 2). Two chains of this type run through each unit cell; one chain lies in the domain $0.52 < y < 0.97$, and the second, antiparallel chain, related to the first by the action of centres of inversion, lies in the domain $0.03 < y < 0.48$.

The second type of chain involves both of the centrosymmetric 4,4'-biphenol molecules, together with the 4,4'-bipyridyl molecule containing N54 and N64: these molecular units combine to form another $C_2^2(20)$ chain running parallel to the [21 $\bar{2}$] direction (Fig. 2). The centrosymmetric 4,4'-biphenol units containing O14 and O24 are centred at $(0,0,1)$ and $(1, \frac{1}{2}, 0)$, respectively. Atoms O14 and O24 at (x, y, z) are donors to N54 and N64, respectively, also at (x, y, z) , while the symmetry-related O $\bar{1}4$ and O $\bar{2}4$ in the same biphenol units are donors to N54 and N64 in the 4,4'-bipyridyl units at $(-x, -y, 2 - z)$ and $(2 - x, 1 - y, -z)$, respectively. As with the [10 $\bar{1}$] chains, there are two antiparallel [21 $\bar{2}$] chains running through each unit cell.

Despite their different directions, and despite the fact that one type of chain is generated by translation and the other by inversions, the overall conformations of the two types of chain are rather similar, and both types of chain are nearly linear. This is shown particularly clearly in the projection of the structure down the [010] direction onto the ac face (Fig. 3). This projection, where the directions of the [10 $\bar{1}$] and [21 $\bar{2}$] chains appear identical,

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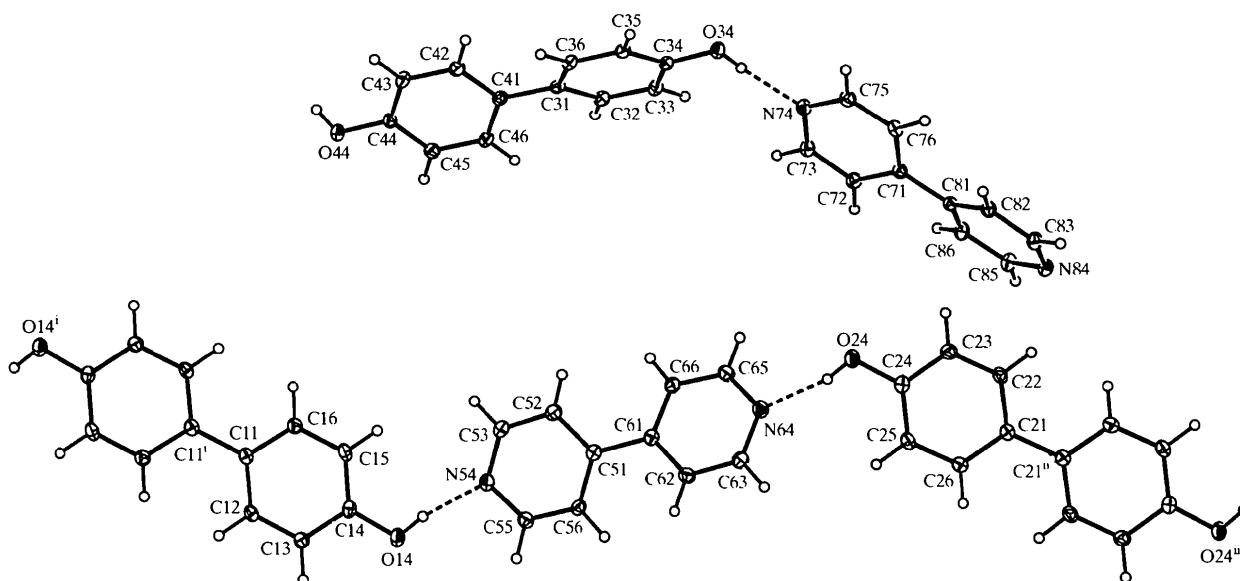


Fig. 1. The molecular components of compound (1) showing the atom-labelling scheme [symmetry codes: (i) $-x, -y, 2-z$; (ii) $2-x, 1-y, -z$]. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as spheres of arbitrary radii.

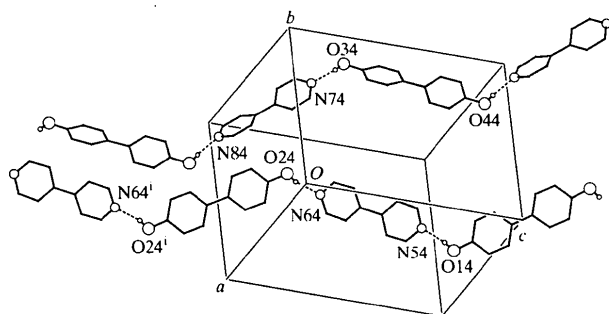


Fig. 2. Part of the crystal structure of (1), showing one $[10\bar{1}]$ chain and one $[21\bar{2}]$ chain. For the sake of clarity, H atoms bonded to C atoms have been omitted [symmetry code: (i) $2-x, 1-y, -z$].

demonstrates the essentially linear grain of the structure: the chains running across the face diagonal in this projection are an antiparallel pair of $[10\bar{1}]$ chains, and $[21\bar{2}]$ and $[10\bar{1}]$ chains alternate thereafter across the projection. Despite the number of independent aryl rings in the structure of (1), there are no aromatic $\pi \cdots \pi$ stacking interactions, nor are there any soft $C-H \cdots O$ hydrogen bonds.

The simple uncoiled chains in compound (1) may be compared with the chains formed in adducts of 4,4'-bipyridyl with other simple bis-phenols. With 2,2'-biphenol, the 1:1 adduct contains triple helices (Lavender *et al.*, 1999), with 4,4'-sulfonyldiphenol, $O_2S(C_6H_4OH)_2$, a single helix is formed, but neighbouring helices are linked by means of $C-H \cdots O$ hydrogen bonds (Ferguson *et al.*, 1999), and with 4,4'-thiodiphenol, $S(C_6H_4OH)_2$, rather than a 1:1 adduct, a 3:2 adduct is formed in which there are finite centrosymmetric strings (Lough *et al.*, 1999).

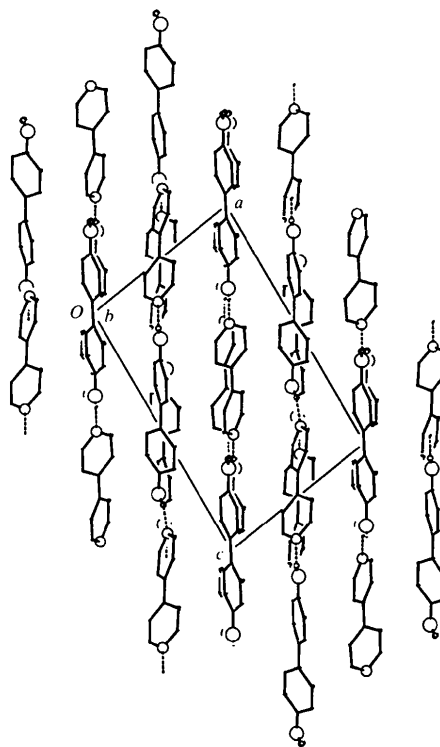


Fig. 3. Projection of the crystal structure of (1) down the $[010]$ direction onto the ac face, showing the almost linear chains. For the sake of clarity, H atoms bonded to C atoms have been omitted.

Within the molecular components of (1), the 4,4'-biphenol units containing O14 and O24 necessarily contain parallel aromatic rings: in the remaining 4,4'-biphenol unit, containing O34 and O44, the interplanar

dihedral angle is 25.1(1)°. In the two independent 4,4'-bipyridyl units, containing N54 and N74, the corresponding dihedral angles are 21.0(1) and 22.7(1)°, respectively. The exocyclic C—C—O bond angles in the biphenol units all show the usual dependence on the location of the substituent on O (Table 1); the C—N—C angles in the bipyridyl units are all significantly less than 120°. Other bond lengths and angles are typical of their types.

Examination of the structure with *PLATON* (Spek, 1999) showed that there are no solvent-accessible voids in the crystal lattice. There are, however, two small voids each of volume *ca* 8.7 Å³ located at ±(0.448, 0.775, 0.780) and between them representing *ca* 1% of the total cell volume. It may be speculated that the unexpected structure of (1), with two different types of chain, may result from the attempt by the system to minimize its void space in seeking a thermodynamic minimum.

Experimental

Equimolar quantities of 4,4'-biphenol and 4,4'-bipyridyl were dissolved separately in a mixture of methanol and acetone (1:2 *v/v*). The solutions were mixed and set aside to crystallize, producing analytically pure compound (1). Analysis, found: C 77.6, H 5.5, N 8.2%; C₂₂H₁₈N₂O₂ 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

C₁₂H₁₀O₂·C₁₀H₈N₂
M_r = 342.38
 Triclinic
P $\bar{1}$
a = 10.1188 (4) Å
b = 11.5242 (4) Å
c = 15.7404 (5) Å
 α = 92.957 (2)°
 β = 97.931 (2)°
 γ = 105.392 (2)°
V = 1745.25 (11) Å³
Z = 4
D_x = 1.303 Mg m⁻³
D_m not measured

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans with κ offsets
 Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
T_{min} = 0.971, *T_{max}* = 0.982
 29 886 measured reflections
 7983 independent reflections

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 7983 reflections
 θ = 3.06–27.49°
 μ = 0.084 mm⁻¹
T = 100 (1) K
 Block
 0.35 × 0.25 × 0.22 mm
 Colourless

5116 reflections with *I* > 2σ(*I*)
R_{int} = 0.063
 θ_{\max} = 27.49°
h = 0 → 13
k = -14 → 14
l = -20 → 20
 Intensity decay: negligible

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.044
wR(*F*²) = 0.115
S = 0.953
 7983 reflections
 474 parameters
 H atoms constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0637P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.001

$\Delta\rho_{\max} = 0.377 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.217 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick, 1997a)
 Extinction coefficient: 0.0046 (12)
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

O14—C14	1.360 (2)	N64—C63	1.342 (2)
O24—C24	1.365 (2)	N64—C65	1.339 (2)
O34—C34	1.367 (2)	N74—C73	1.339 (2)
O44—C44	1.364 (2)	N74—C75	1.345 (2)
N54—C53	1.341 (2)	N84—C83	1.339 (2)
N54—C55	1.338 (2)	N84—C85	1.342 (2)
O14—C14—C13	117.98 (14)	O44—C44—C43	122.65 (14)
O14—C14—C15	123.66 (13)	O44—C44—C45	118.20 (14)
O24—C24—C23	117.47 (14)	C53—N54—C55	116.51 (12)
O24—C24—C25	123.67 (13)	C63—N64—C65	116.55 (13)
O34—C34—C33	123.81 (14)	C73—N74—C75	116.89 (14)
O34—C34—C35	116.95 (14)	C83—N84—C85	116.47 (14)

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

D—H...A	D—H	H...A	D...A	D—H...A
O14—H14...N54	0.84	1.89	2.724 (2)	169
O24—H24...N64	0.84	1.89	2.711 (2)	165
O34—H34...N74	0.84	1.88	2.700 (2)	163
O44—H44...N84	0.84	1.91	2.736 (2)	170

Symmetry code: (i) *x* - 1, *y*, *z*.

Compound (1) crystallized in the triclinic system; space group *P* $\bar{1}$ was assumed and confirmed by the analysis. H atoms were treated as riding with C—H = 0.95 and O—H = 0.84 Å.

Data collection: *KappaCCD Server Software* (Nonius, 1997). Cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997). Data reduction: *DENZO-SMN*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997b). Program(s) used to refine structure: *NRCVAX96* (Gabe *et al.*, 1989) and *SHELXL97* (Sheldrick, 1997a). Molecular graphics: *NRCVAX96*, *ORTEPII* (Johnson, 1976) and *PLATON* (Spek, 1999). Software used to prepare material for publication: *NRCVAX96*, *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the University of Toronto using a Nonius KappaCCD diffractometer purchased with funds from NSERC Canada. RMG thanks EPSRC (UK) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1325). Services for accessing these data are described at the back of the journal.

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2,2'-Biphenol–1,4-diazabicyclo[2.2.2]octane (2/1), a three-dimensional framework built from O—H···O, O—H···N, N—H···O and C—H···π(arene) hydrogen bonds

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Abstract

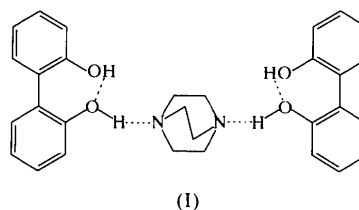
In the 2:1 adduct of 2,2'-biphenol and 1,4-diazabicyclo[2.2.2]octane, 2C₁₂H₁₀O₂·C₆H₁₂N₂, there are eight molecules of the biphenol and four molecules of the amine in the asymmetric unit, and several of these components exhibit orientational disorder even at 100 K. Each biphenol unit contains an intramolecular O—H···O hydrogen bond [O···O range for the ordered components 2.594 (6) to 2.668 (5) Å]. Each of the amines is hydrogen bonded to two biphenol units [O···N range for the ordered components 2.521 (7) to 2.594 (6) Å], so forming four independent three-molecule aggregates. These aggregates are further linked by an extensive

series of C—H···π(arene) interactions into a continuous three-dimensional framework.

Comment

The bis-tertiary amine 1,4-diazabicyclo[2.2.2]octane, (DABCO), is a strong acceptor of hydrogen bonds which readily forms adducts with phenols and bis-phenols. With simple mono-phenols, which can act as donors forming just one hydrogen bond per molecule, 1:2 adducts (DABCO)·2(phenol) are formed whose structures are built from finite three-molecule aggregates, which are held together by two O—H···N hydrogen bonds (Mak *et al.*, 1984; Takama *et al.*, 1988). Rather similar adducts can be formed with tertiary alcohols (Yasui *et al.*, 1989). In 1:1 adducts, bis-phenols which can act as double donors of hydrogen bonds form continuous chains with DABCO (Mak *et al.*, 1984; Ferguson, Coupar & Glidewell, 1997; Ferguson *et al.*, 1998), and where the bis-phenol has little or no conformational flexibility, the resulting chains are essentially rigid with no coiling (Mak *et al.*, 1984; Ferguson *et al.*, 1998). It has been suggested (Ferguson, Bell *et al.*, 1997) that chain-coiling controlled largely by the soft (Braga *et al.*, 1995) hydrogen bonds is likely to occur where one or other of the components in such a chain exhibits conformational flexibility.

In 2,2'-biphenol, HOC₆H₄—C₆H₄OH, there is no real restriction to rotation about the central C—C bond, so that a wide range of conformations is accessible. In the crystal structure of the pure substance, intramolecular O—H···O hydrogen bonds are present (Byrne *et al.*, 1998), but in its hydrate (Chen *et al.*, 1996) and in its adducts with 4,4'-bipyridyl (Lavender *et al.*, 1999) and hexamethylenetetramine (MacLean *et al.*, 1999), 2,2'-biphenol forms only intermolecular hydrogen bonds. We have therefore sought to prepare, and structurally characterize, a 1:1 adduct of 2,2'-biphenol with DABCO, in the expectation of observing highly coiled chains. In the event, co-crystallization of the two molecular components in various proportions consistently yielded the 2:1 adduct 2C₁₂H₁₀O₂·C₆H₁₂N₂, (I), whose structure consists of finite aggregates, but which is nonetheless crystallographically interesting.



The diffraction intensities for compound (I) pointed strongly towards the centrosymmetric space group *P4/m*. However, repeated and robust attempts at structure solution in *P4/m* were all dismally unsuccessful, but the structure was solved very easily in the

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