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# Hydrogen-Bonded Chains in 4,4′-Dihydroxybenzophenone–4,4′-Bipyridyl (1/1) and Chains of Rings in 1,3,5-Trihydroxybenzene–4,4′-Bipyridyl (2/3)

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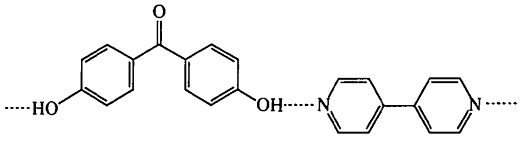
## Abstract

In the 1:1 adduct of 4,4′-dihydroxybenzophenone and 4,4′-bipyridyl, $[OC(C_6H_4OH)_2].(NC_5H_4–C_5H_4N)$, the components are linked into chains by O—H···N hydrogen bonds. In the 2:3 adduct formed between 1,3,5-trihydroxybenzene and 4,4′-bipyridyl, $2[C_6H_3(OH)_3].3(NC_5H_4–C_5H_4N)$, pairs of molecules of each component are linked by O—H···N hydrogen bonds into macrocyclic rings, which are themselves linked by further 4,4′-bipyridyl molecules into chains of rings; these chains are cross-linked by C—H···O hydrogen bonds.

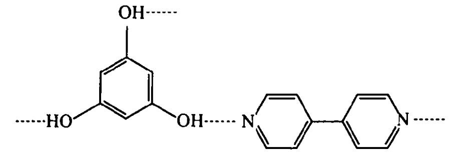
## Comment

4,4′-Bipyridyl forms an adduct of 1:1 stoichiometry with the diol ferrocene-1,1′-diylbis(diphenylmethanol), $Fe(C_5H_4CPh_2OH)_2$, but despite the exact numerical match in this system between the number of hydroxy groups, hydrogen-bond donors and N atoms acting as hydrogen-bond acceptors, only one half of the 4,4′-bipyridyl molecules in the adduct participate in the hydrogen-bonding scheme (Glidewell, Ferguson, Lough & Zakaria, 1994). In view of this unexpected behaviour, we have now investigated the behaviour of 4,4′-bipyridyl with some bis-phenols and tris-phenols; since phenols are somewhat more acidic than tertiary alcohols, they can be expected to be more effective hydrogen-bond donors towards 4,4′-bipyridyl. The adducts thus formed illustrate the versatility of the O—H···N synthon in crystal engineering (Subramanian & Zaworotko, 1994; Desiraju, 1995).

Co-crystallization of bis-phenols of the type $X(C_6H_4OH)_2$ with 4,4′-bipyridyl in methanol solution yielded analytically pure adducts of 1:1 stoichiometry for $X$ = O, S, $SO_2$ and CO; with each of the tris-phenols $CH_3C(C_6H_4OH)_3$ and 1,3,5-trihydroxybenzene, adducts having 2:3 tris-phenol:bipyridyl stoichiometry were obtained. Few of these adducts yield crystals suitable for single-crystal X-ray diffraction, but we have obtained such crystals for two representative adducts, 4,4′-dihydroxybenzophenone–4,4′-bipyridyl (1/1), (I), and 1,3,5-trihydroxybenzene–4,4′-bipyridyl (2/3), (II), and we report here their structures.



(I)



(II)

The structure of compound (I) (Fig. 1) is dominated by the formation of simple chains consisting of alternate bis-phenol and 4,4′-bipyridyl units joined together by O—H···N hydrogen bonds (Fig. 2), as expected when the two components employ two hydrogen-bond donors and acceptors respectively. Atom O1 in the asymmetric unit at ($x$, $y$, $z$) acts as hydrogen-bond donor to atom N34 within the same unit, while atom O2 in this unit acts as donor to atom N44 in the bipyridyl molecule at $(-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$. Repetition of these hydrogen bonds generates chains running parallel to the direction $[\bar{1}01]$, in which the chain-forming motif has graph set $C_2^2(21)$ (Bernstein, Davis, Shimoni & Chang, 1995). The chains are arranged within the unit cell such that pairs of bipyridyl rings related by centres of inversion and lying in adjacent chains form stacks parallel to the [010] direction, but none of the individual C···C or C···N distances is significantly shorter than the sum of van der Waals radii. In addition to the involvement of atoms O1 and O2 as donors of hydrogen bonds, the carbonyl O atom, O3, is potentially an acceptor of hydrogen bonds and, in the absence of other donors, C—H···O hydrogen-bond formation may be expected (Hunter, 1991).

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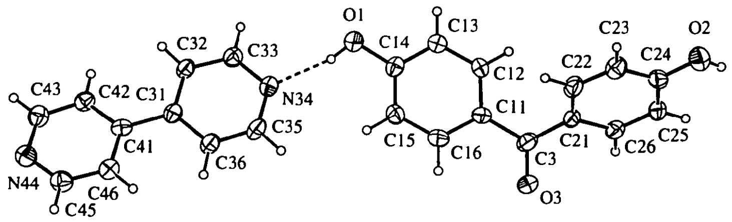

Fig. 1. A view of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

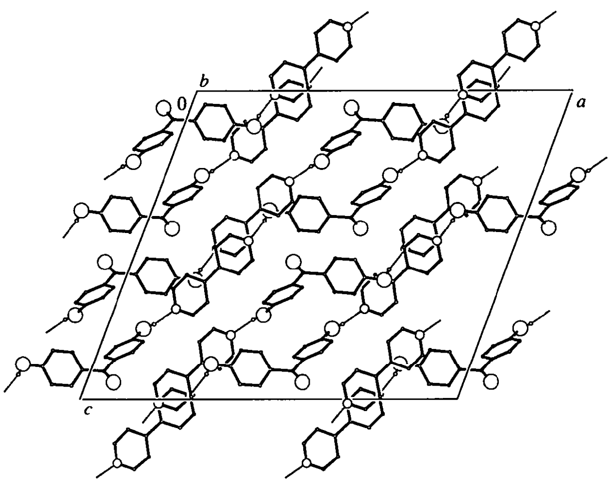

Fig. 2. A view of the crystal structure of (I). H atoms bonded to C atoms are omitted for clarity.

Atom O3 does, in fact, form one such bond with the C42—H42 bond in the bipyridyl molecule at ($\frac{1}{2}$ + *x*, $-\frac{1}{2}$ + *y*, *z*) as donor; this motif generates a further chain, characterized by the graph set $C^2_2(15)$ and running in the direction $[\bar{1}10]$. Examination of the structure with *PLATON* (Spek, 1995*a*) showed that while there were no solvent-accessible voids in the crystal lattice; there were four small symmetry-related voids each of 13 Å$^3$, each too small to accommodate any solvent molecule.

In the structure of adduct (II), the asymmetric unit contains two molecules of 1,3,5-trihydroxybenzene and three of 4,4′-bipyridyl. Within the asymmetric unit there are five independent O—H···N hydrogen bonds involving atoms O11, O13, O15, O21 and O23 as the hydrogen-bond donors (Fig. 3 and Table 6), while the remaining O—H group in this unit, O25—H25, acts as donor to the remaining N atom, N84, in the aggregate at (−1 + *x*, *y*, 1 + *z*). The overall structural motif is therefore that of macrocycles, built up from two molecules each of the two components, linked together by the third independent bipyridyl unit into chains parallel to the $[10\bar{1}]$ direction, to give a 'chain of rings' (Bernstein, Davis, Shimoni & Chang, 1995). The hydrogen-bonding motif defining the macrocycles has the graph set $R^4_4(30)$, while the chain-forming motif, of which there are two independent branches running through the two bipyridyl units in the macrocycle, has graph set $C^4_4(30)$, so that the overall graph set for this chain of rings is $C^4_4(30)[R^4_4(30)]$ (Bernstein, Davis, Shimoni & Chang, 1995). In addition to the O—H···N hydrogen bonds, the structure of adduct (II) also exhibits a number of C—H···O hydrogen bonds (Table 6). The C63—H63 bond in one of the macrocycle bipyridyl units, at (*x*, *y*, *z*), acts as donor to O23 in the tris-phenol unit at (−*x*, 2 − *y*, 1 − *z*); hydrogen bonds of this type cross-link the chains in the *ac* plane. There are also two independent C—H···O interactions forming cross-links in the [010] direction: the C16—H16 bond at (*x*, *y*, *z*) acts as donor to O13 at ($-\frac{1}{2}$ − *x*, $-\frac{1}{2}$ + *y*, −*z*), and the C24—H24 bond at (*x*, *y*, *z*) acts as donor towards O21 at ($-\frac{1}{2}$ − *x*, $\frac{1}{2}$ + *y*, 1 − *z*). The effect of these weak, but cooperative C—H···O hydrogen bonds is to link all the chains of rings into a continuous three-dimensional network.

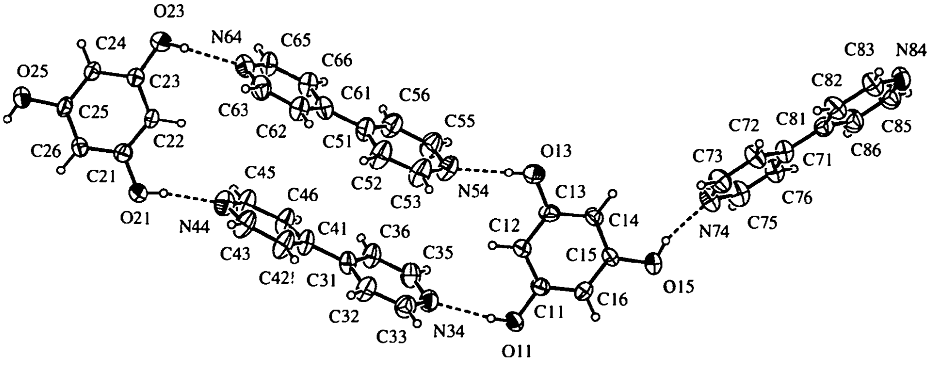

Fig. 3. A view of (II) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

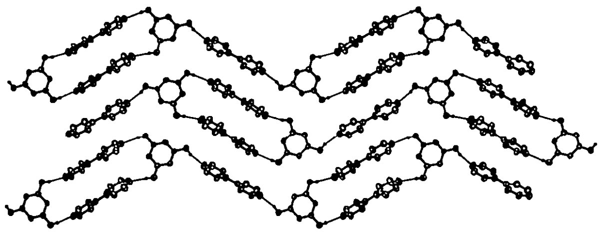

Fig. 4. Part of the crystal structure of (II) showing the extended zigzag hydrogen-bonded chains and the stacking of the bipyridyl molecules. For clarity, only the hydroxy H atoms are shown.

The zigzag chains are stacked by the action of the $2_1$ screw axis such that alternate chains in the [010] direction have the spacer bipyridyl units and the ring-forming bipyridyl units stacked in register to give a continuous stacking of roughly parallel bipyridyl units (Fig. 4). However, as in adduct (I), none of the inter-ring C···C or C···N distances, either across the macrocycle or between different chains, is significantly less than the sum of the van der Waals radii.

In adduct (I) the bis-phenol component could, in principle, adopt a skeletal conformation having $C_{2v}$ symmetry, or any subgroup of $C_{2v}$; in the event this component, although having no symmetry crystallographically imposed, adopts a conformation close to $C_2$ symmetry, as shown by the torsion angles O3—C3—C*n*1—C*n*2 and O3—C3—C*n*1—C*n*6 (*n* = 1, 2; Table 2). The dihedral angle between the two rings of the bipyridyl component is 12.7 (2)°. In adduct (II), the dihedral angles between the two rings of each of the three independent bipyridyl units are 9.1 (5), 5.8 (5) and 1.7 (5)° for the molecules containing N34, N54 and N74, respectively. The bond distances are all typical. Examination of the structure with *PLATON* showed that there were no solvent accessible voids in the crystal lattice.

## Experimental

Samples of adducts (I) and (II) were prepared by co-crystallizing the phenol and bipyridyl from methanol solutions. In each system, the same adduct, as judged from both elemental analysis and powder X-ray diffraction, was obtained from all starting compositions with phenol:bipyridyl molar ratios within the range 2:1 to 1:2. Elemental analysis of (I): found C 74.2, H 5.1, N 7.6%; $C_{23}H_{18}N_2O_3$ requires C 74.6, H 4.9, N 7.6%. Elemental analysis of (II): found C 69.9, H 5.1, N 11.9%; $C_{42}H_{36}N_6O_6$ requires C 70.0, H 5.0, N 11.7%. Other 1:1 adducts were formed by the bis-phenols $X(C_6H_4OH)_2$, with $X$ = O (III), S (IV) and $SO_2$ (V), and by the tris-phenol $CH_3C(C_6H_4OH)_3$ (VI). Elemental analyses: (III) found C 74.1, H 4.9, N 8.0%; $C_{22}H_{18}N_2O_3$ requires C 73.7, H 5.1, N 7.8%; (IV) found C 70.9, H 4.9, N 7.7%; $C_{22}H_{18}N_2O_2S$ requires C 70.6, H 4.8, N 7.5%; (V) found C 63.9, H 4.7, N 6.5%; $C_{22}H_{18}N_2O_4S$ requires C 64.7, H 4.9, N 6.9%; (VI) found C 77.9, H 5.6, N 8.0%; $C_{70}H_{60}N_6O_6$ requires C 77.8, H 5.6, N 7.8%. Crystals of adducts (I) and (II) suitable for single-crystal X-ray diffraction were selected directly from the analytical samples.

### Compound (I)

*Crystal data*

$C_{13}H_{10}O_3.C_{10}H_8N_2$
$M_r$ = 370.39
Monoclinic
$C2/c$
$a$ = 25.559 (2) Å
$b$ = 7.0926 (7) Å
$c$ = 22.138 (2) Å
$\beta$ = 110.792 (8)°
$V$ = 3751.9 (6) Å$^3$
$Z$ = 8
$D_x$ = 1.311 Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda$ = 0.7107 Å
Cell parameters from 25 reflections
$\theta$ = 8.83–12.87°
$\mu$ = 0.088 mm$^{-1}$
$T$ = 294 (1) K
Block
0.35 × 0.35 × 0.31 mm
Colourless

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3376 measured reflections
3292 independent reflections
1398 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int}$ = 0.018
$\theta_{\rm max}$ = 25°
$h = -30 \rightarrow 28$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 26$
3 standard reflections
frequency: 120 min
intensity decay: 2.4%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.0706$
$wR(F^2) = 0.1513$
$S$ = 0.951
3292 reflections
255 parameters
H atoms riding (C—H 0.93, O—H 0.82 Å)
$w = 1/[\sigma^2(F_o^2) + (0.0467P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.167 e Å$^{-3}$
$\Delta\rho_{\rm min}$ = −0.173 e Å$^{-3}$
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$) for (I)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| O1 | 0.68746 (10) | 0.1980 (5) | 0.11420 (13) | 0.0604 (9) |
| O2 | 0.40228 (12) | 0.9010 (5) | 0.2275 (2) | 0.0684 (9) |
| O3 | 0.42771 (11) | 0.2269 (5) | 0.05463 (14) | 0.0789 (11) |
| C3 | 0.4643 (2) | 0.3291 (8) | 0.0905 (2) | 0.0590 (13) |
| C11 | 0.5232 (2) | 0.3041 (7) | 0.0953 (2) | 0.0522 (12) |
| C12 | 0.5672 (2) | 0.3343 (6) | 0.1526 (2) | 0.0543 (13) |
| C13 | 0.6217 (2) | 0.2973 (6) | 0.1585 (2) | 0.0534 (12) |
| C14 | 0.6332 (2) | 0.2327 (6) | 0.1062 (2) | 0.0454 (11) |
| C15 | 0.5901 (2) | 0.2023 (7) | 0.0479 (2) | 0.0588 (13) |
| C16 | 0.5356 (2) | 0.2352 (7) | 0.0435 (2) | 0.0661 (15) |
| C21 | 0.4499 (2) | 0.4791 (8) | 0.1286 (2) | 0.0510 (12) |
| C22 | 0.4750 (2) | 0.6552 (8) | 0.1381 (2) | 0.0617 (14) |
| C23 | 0.4580 (2) | 0.7956 (7) | 0.1700 (2) | 0.0602 (13) |
| C24 | 0.4170 (2) | 0.7598 (7) | 0.1953 (2) | 0.0517 (12) |
| C25 | 0.3918 (2) | 0.5853 (7) | 0.1865 (2) | 0.0563 (13) |
| C26 | 0.4078 (2) | 0.4489 (7) | 0.1536 (2) | 0.0576 (13) |
| C31 | 0.7618 (2) | −0.0762 (6) | −0.0729 (2) | 0.0449 (11) |
| C32 | 0.7925 (2) | −0.0480 (6) | −0.0084 (2) | 0.0496 (12) |
| C33 | 0.7664 (2) | 0.0164 (6) | 0.0323 (2) | 0.0513 (12) |
| N34 | 0.71218 (14) | 0.0562 (5) | 0.0137 (2) | 0.0524 (10) |
| C35 | 0.6827 (2) | 0.0302 (7) | −0.0487 (2) | 0.0588 (13) |

| | | | | |
|---|---|---|---|---|
| C36 | 0.7054 (2) | −0.0349 (6) | −0.0925 (2) | 0.0535 (12) |
| C41 | 0.7878 (2) | −0.1491 (6) | −0.1190 (2) | 0.0439 (11) |
| C42 | 0.8410 (2) | −0.2255 (6) | −0.0980 (2) | 0.0499 (12) |
| C43 | 0.8632 (2) | −0.2873 (6) | −0.1428 (2) | 0.0571 (12) |
| N44 | 0.8360 (2) | −0.2816 (5) | −0.2071 (2) | 0.0575 (10) |
| C45 | 0.7851 (2) | −0.2084 (7) | −0.2267 (2) | 0.0618 (13) |
| C46 | 0.7594 (2) | −0.1427 (7) | −0.1858 (2) | 0.0588 (13) |

Table 2. *Selected geometric parameters (Å, °) for (I)*

| | | | |
|---|---|---|---|
| O1—C14 | 1.357 (4) | C3—C11 | 1.481 (5) |
| O2—C24 | 1.358 (5) | C3—C21 | 1.483 (6) |
| O3—C3 | 1.226 (5) | | |
| O3—C3—C11 | 119.9 (4) | C11—C3—C21 | 119.7 (4) |
| O3—C3—C21 | 120.4 (4) | | |
| O3—C3—C11—C12 | −145.8 (5) | O3—C3—C21—C26 | 35.8 (6) |
| O3—C3—C11—C16 | 29.1 (7) | C32—C31—C41—C42 | 12.4 (6) |
| O3—C3—C21—C22 | −141.0 (4) | C36—C31—C41—C46 | 13.3 (6) |

Table 3. *Hydrogen-bonding geometry (Å, °) for (I)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1···N34 | 0.82 | 1.91 | 2.713 (4) | 166 |
| O2—H2···N44$^{i}$ | 0.82 | 1.92 | 2.724 (4) | 169 |
| C42—H42···O3$^{ii}$ | 0.93 | 2.42 | 3.336 (5) | 171 |

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

## Compound (II)

### *Crystal data*

$2C_6H_6O_3.3C_{10}H_8N_2$
$M_r = 720.77$
Monoclinic
$P2_1/a$
$a = 16.716$ (5) Å
$b = 13.765$ (5) Å
$c = 17.782$ (3) Å
$\beta = 117.18$ (2)°
$V = 3639.9$ (17) Å$^3$
$Z = 4$
$D_x = 1.315$ Mg m$^{-3}$
$D_m$ not measured

Mo *Kα* radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 6.45–12.43°$
$\mu = 0.090$ mm$^{-1}$
$T = 294$ (1) K
Plate
0.41 × 0.41 × 0.14 mm
Colourless

### *Data collection*

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3505 measured reflections
3361 independent reflections
1093 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.039$
$\theta_{\rm max} = 20°$
$h = -16 \rightarrow 14$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity decay: 6.1%

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.0769$
$wR(F^2) = 0.1875$
$S = 0.905$
3361 reflections
493 parameters
H atoms riding (C—H 0.93, O—H 0.82 Å)
$w = 1/[\sigma^2(F_o^2) + (0.0610P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.007$
$\Delta\rho_{\rm max} = 0.194$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.177$ e Å$^{-3}$
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$) for (II)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | *x* | *y* | *z* | $U_{\rm eq}$ |
|---|---|---|---|---|
| O11 | 0.1543 (5) | 0.3013 (4) | 0.0540 (4) | 0.065 (2) |
| O13 | 0.2211 (5) | 0.6392 (5) | 0.0497 (5) | 0.091 (2) |
| O15 | 0.3119 (5) | 0.4063 (4) | −0.0922 (5) | 0.081 (2) |
| C11 | 0.1914 (6) | 0.3767 (7) | 0.0289 (6) | 0.057 (2) |
| C12 | 0.1861 (6) | 0.4698 (7) | 0.0543 (5) | 0.058 (2) |
| C13 | 0.2254 (6) | 0.5450 (8) | 0.0292 (6) | 0.061 (2) |
| C14 | 0.2682 (6) | 0.5270 (7) | −0.0211 (5) | 0.059 (2) |
| C15 | 0.2705 (6) | 0.4306 (8) | −0.0445 (6) | 0.057 (2) |
| C16 | 0.2313 (6) | 0.3568 (7) | −0.0214 (5) | 0.058 (2) |
| O21 | −0.1831 (5) | 0.6781 (4) | 0.4834 (5) | 0.086 (2) |
| O23 | −0.1653 (5) | 1.0163 (4) | 0.4281 (5) | 0.076 (2) |
| O25 | −0.3010 (5) | 0.9201 (4) | 0.5944 (5) | 0.078 (2) |
| C21 | −0.1992 (6) | 0.7732 (8) | 0.4923 (6) | 0.059 (2) |
| C22 | −0.1700 (5) | 0.8453 (7) | 0.4556 (5) | 0.055 (2) |
| C23 | −0.1883 (6) | 0.9416 (8) | 0.4647 (6) | 0.056 (2) |
| C24 | −0.2308 (5) | 0.9648 (7) | 0.5126 (5) | 0.057 (2) |
| C25 | −0.2597 (6) | 0.8901 (8) | 0.5473 (6) | 0.058 (2) |
| C26 | −0.2436 (6) | 0.7952 (7) | 0.5387 (5) | 0.058 (2) |
| C31 | 0.0197 (7) | 0.4748 (7) | 0.2562 (6) | 0.066 (2) |
| C32 | 0.0972 (7) | 0.4216 (7) | 0.2954 (6) | 0.080 (3) |
| C33 | 0.1304 (6) | 0.3728 (7) | 0.2490 (5) | 0.078 (3) |
| N34 | 0.0915 (5) | 0.3703 (6) | 0.1651 (5) | 0.073 (2) |
| C35 | 0.0166 (6) | 0.4224 (6) | 0.1285 (6) | 0.078 (3) |
| C36 | −0.0217 (6) | 0.4749 (7) | 0.1690 (6) | 0.075 (2) |
| C41 | −0.0205 (7) | 0.5299 (7) | 0.3010 (7) | 0.076 (3) |
| C42 | 0.0236 (7) | 0.5414 (7) | 0.3873 (6) | 0.095 (3) |
| C43 | −0.0144 (6) | 0.5960 (7) | 0.4281 (6) | 0.097 (3) |
| N44 | −0.0947 (6) | 0.6369 (6) | 0.3917 (5) | 0.086 (2) |
| C45 | −0.1364 (7) | 0.6220 (7) | 0.3092 (5) | 0.089 (3) |
| C46 | −0.1027 (7) | 0.5711 (7) | 0.2645 (6) | 0.088 (3) |
| C51 | 0.0480 (7) | 0.7767 (8) | 0.2245 (7) | 0.080 (3) |
| C52 | 0.1233 (7) | 0.7251 (8) | 0.2671 (7) | 0.101 (3) |
| C53 | 0.1637 (7) | 0.6759 (8) | 0.2272 (6) | 0.103 (3) |
| N54 | 0.1344 (6) | 0.6708 (6) | 0.1443 (5) | 0.090 (2) |
| C55 | 0.0576 (6) | 0.7169 (7) | 0.1029 (6) | 0.094 (3) |
| C56 | 0.0134 (7) | 0.7698 (7) | 0.1383 (6) | 0.090 (3) |
| C61 | 0.0053 (7) | 0.8335 (7) | 0.2645 (7) | 0.068 (2) |
| C62 | 0.0444 (6) | 0.8474 (7) | 0.3515 (6) | 0.078 (3) |
| C63 | 0.0037 (6) | 0.9028 (7) | 0.3886 (6) | 0.078 (3) |
| N64 | −0.0759 (5) | 0.9448 (6) | 0.3445 (5) | 0.074 (2) |
| C65 | −0.1136 (6) | 0.9340 (7) | 0.2608 (5) | 0.073 (2) |
| C66 | −0.0757 (6) | 0.8792 (7) | 0.2187 (6) | 0.076 (3) |
| C71 | 0.4990 (7) | 0.6419 (7) | −0.2068 (7) | 0.069 (2) |
| C72 | 0.5271 (7) | 0.6463 (7) | −0.1205 (6) | 0.079 (3) |
| C73 | 0.4775 (6) | 0.5948 (7) | −0.0902 (6) | 0.084 (3) |
| N74 | 0.4036 (5) | 0.5437 (6) | −0.1345 (5) | 0.077 (2) |
| C75 | 0.3777 (7) | 0.5421 (7) | −0.2172 (5) | 0.084 (3) |
| C76 | 0.4235 (7) | 0.5881 (7) | −0.2531 (6) | 0.077 (3) |
| C81 | 0.5495 (7) | 0.6918 (7) | −0.2448 (7) | 0.067 (2) |
| C82 | 0.6267 (6) | 0.7436 (7) | −0.2001 (6) | 0.078 (3) |
| C83 | 0.6708 (6) | 0.7897 (7) | −0.2403 (5) | 0.081 (3) |
| N84 | 0.6437 (6) | 0.7872 (6) | −0.3231 (5) | 0.081 (2) |
| C85 | 0.5681 (6) | 0.7383 (7) | −0.3660 (6) | 0.089 (3) |
| C86 | 0.5194 (7) | 0.6891 (7) | −0.3321 (6) | 0.088 (3) |

Table 5. *Selected geometric parameters (Å, °) for (II)*

| | | | |
|---|---|---|---|
| O11—C11 | 1.383 (10) | O21—C21 | 1.361 (10) |
| O13—C13 | 1.357 (10) | O23—C23 | 1.363 (10) |
| O15—C15 | 1.359 (9) | O25—C25 | 1.370 (9) |
| C36—C31—C41—C46 | 9.9 (14) | C52—C51—C61—C62 | 6.8 (15) |
| C32—C31—C41—C42 | 8.0 (14) | C72—C71—C81—C82 | 1.2 (13) |
| C56—C51—C61—C66 | 4.2 (15) | C76—C71—C81—C86 | 2.6 (13) |

Table 6. *Hydrogen-bonding geometry (Å, °) for (II)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O11—H11···N34 | 0.82 | 2.03 | 2.794 (9) | 154 |
| O13—H13···N54 | 0.82 | 1.95 | 2.708 (10) | 154 |
| O15—H15···N74 | 0.82 | 1.96 | 2.747 (10) | 159 |
| O21—H21···N44 | 0.82 | 1.94 | 2.714 (10) | 158 |

| | | | | |
|---|---|---|---|---|
| O23—H23···N64 | 0.82 | 2.02 | 2.728 (10) | 145 |
| O25—H25···N84$^{i}$ | 0.82 | 1.97 | 2.756 (10) | 159 |
| C12—H12···N34 | 0.93 | 2.63 | 3.332 (13) | 133 |
| C16—H16···O13$^{ii}$ | 0.93 | 2.30 | 3.197 (12) | 162 |
| C24—H24···O21$^{iii}$ | 0.93 | 2.39 | 3.285 (12) | 160 |
| C63—H63···O23$^{iv}$ | 0.93 | 2.52 | 3.334 (13) | 147 |

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

All the crystals shattered easily on attempts to cut them to suitable size. Several crystals of (II) were examined and none diffracted strongly. The best one was chosen for the analysis and in the 2–20° $\theta$ shell, only 33% of the data could be observed. Preliminary scans in the 20–25° $\theta$ shell gave no observable data and data collection was terminated. We attribute the relatively high $R$ factors [0.071 for (I), 0.07 for (II)] to the very poor quality of even the best crystals, the poor diffraction at room temperature and to decay in the X-ray beam. $\Delta\rho$ maps in the planes normal to the C—O bonds in the expected locus of the hydroxy H atoms were used to locate all hydroxy H atoms. Their coordinates were then refined using a riding model (*AFIX*147 option in *SHELXL*93; Sheldrick, 1993).

For both compounds, data collection: *CAD-4/PC Software* (Enraf–Nonius, 1992); cell refinement: *SET*4 and *CELDIM* (Enraf–Nonius, 1992); data reduction: *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *NRCVAX*94 and *SHELXL*93; molecular graphics: *ORTEP*II (Johnson, 1976), *NRCVAX*94, *PLATON* and *PLUTON* (Spek 1995*b*); software used to prepare material for publication: *NRCVAX*94, *SHELXL*93 and *WordPerfect* macro *PREPCIF*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1404). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Interpenetrating Square Nets in the Hydrogen-Bonded Structure of 4,4′-Sulfonyldiphenol

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## Abstract

In the structure of 4,4′-sulfonyldiphenol, $O_2S(C_6H_4OH)_2$, the molecules are linked into square nets by O—H···O═S hydrogen bonds with O···O distances of 2.746 (5) and 2.708 (6) Å; pairs of nets are interwoven but there are no significant interactions between adjacent bilayers.

## Comment

In the structures of simple unfunctionalized bis-phenols such as 4,4′-biphenol (Jackisch *et al.*, 1990) and 4,4′-isopropylidenediphenol (Goldberg, Stein, Tanaka & Toda, 1991), the hydroxy groups act as both donors and acceptors of hydrogen bonds. In this way, each molecule is hydrogen bonded to four others and in both structures this leads to the formation of sheets characterized by the graph sets $C(2)R_4^4(26)$ in 4,4′-biphenol and $C_3^3(6)R_4^4(28)$ in 4,4′-isopropylidenediphenol (Etter, 1990; Bernstein, Davis, Shimoni & Chang, 1995). By contrast, functionalized bis-phenols of the type $X(C_6H_4OH)_2$, where $X$ is a potential acceptor of hydrogen bonds such as O, S, $SO_2$ or CO, offer the possibility of O—H···$X$ hydrogen bonding rather than hydrogen bonding which involves simply the hydroxy groups. If the spacer function $X$ were to act as a double acceptor of hydrogen bonds so that each molecule is hydrogen bonded to four others, then four-connected nets, either planar or tetrahedral, could occur. Given the intramolecular distance between hydrogen-bond donors and acceptors in such cases (*ca* 6.0–6.8 Å), a single network whether planar or tetrahedral would probably lead to a structure with a high proportion of void space, and hence unstably low density. As in previously observed examples of such networks (Duchamp & Marsh, 1969; Ermer, 1988; Ermer & Eling, 1988), multiple interpenetrating networks are likely. Here we report such a network in the structure of 4,4′-sulfonyldiphenol, $O_2S(C_6H_4OH)_2$, (I).

Compound (I) (Fig. 1) crystallizes with the rare combination of space group *Aba*2 and $Z' = 1$ [$Z'$ =

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