

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° θ shell, only 33% of the data could be observed. Preliminary scans in the 20–25° θ 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 (AFIX147 option in SHELXL93; Sheldrick, 1993).

For both compounds, data collection: CAD-4/PC Software (Enraf–Nonius, 1992); cell refinement: SET4 and CELDIM (Enraf–Nonius, 1992); data reduction: DATRD2 in NRCVAX94 (Gabe, Le Page, Charland, Lee & White, 1989); program(s) used to solve structures: SHELXS86 (Sheldrick, 1985); program(s) used to refine structures: NRCVAX94 and SHELXL93; molecular graphics: ORTEPII (Johnson, 1976), NRCVAX94, PLATON and PLUTON (Spek 1995b); software used to prepare material for publication: NRCVAX94, SHELXL93 and WordPerfect macro PREPCIF.

GF thanks NSERC (Canada) for research grants.

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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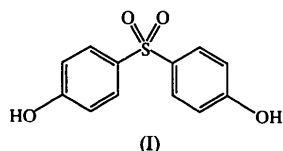
Abstract

In the structure of 4,4'-sulfonyldiphenol, O₂S(C₆H₄OH)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 $C(2)R_4^1(26)$ in 4,4'-biphenol and $C_3^3(6)R_4^1(28)$ 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, SO₂ 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, O₂S(C₆H₄OH)₂, (I).

Compound (I) (Fig. 1) crystallizes with the rare combination of space group *Aba2* and $Z' = 1$ [$Z' =$



Z/n , where n is the order of the group (Brock & Dunitz, 1994)]. Each of the hydroxy groups acts as a hydrogen-bond donor and each of the sulfonyl O atoms as a hydrogen-bond acceptor (Table 3), hence each molecule is hydrogen bonded to four others and a square net results. Atom O1 of the molecule at (x, y, z) acts as donor to the sulfonyl atom O11 in the molecule at $(\frac{1}{2} + x, \frac{1}{2} - y, z)$ giving a chain parallel to the a direction, generated by the a glide plane, for which the graph-set descriptor (Etter, 1990; Bernstein, Davis, Shimoni & Chang, 1995) is C(8). A second chain motif runs parallel to the c direction, also with graph set C(8): atom O2 in the molecule at (x, y, z) acts as donor to the sulfonyl atom O12 in the molecule at $(x, y, -1 + z)$. The combined effect of these two chain-forming motifs is to generate square nets with graph-set descriptor

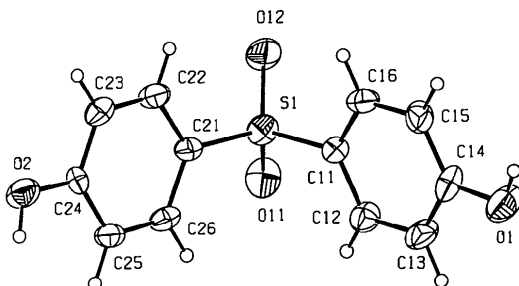


Fig. 1. A view of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

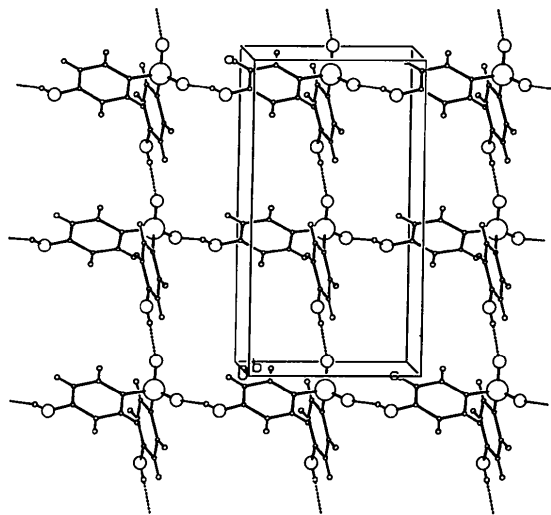


Fig. 2. A view of the crystal structure showing the formation of one net.

$R_4^4(32)$ (Fig. 2). The quasi-tetrahedral disposition of the hydrogen-bond donors and acceptors in (I), allied to the action of the a glide plane in generating these nets, causes them to be puckered rather than planar.

These square nets (Fig. 2) encompass only two molecules of (I) per unit cell; the unit-cell contents, with $Z = 8$, therefore requires the occurrence of four such nets. The action of the 2_1 screw axis parallel to the c direction generates a second net which is interwoven with the first, to form a bilayer, with molecules of one net occupying the voids enclosed by the $R_4^4(32)$ rings of the other (Fig. 3); thus the molecule at $(\frac{1}{2} - x, y, \frac{1}{2} + z)$ effectively fills the void in the $R_4^4(32)$ ring illustrated in Fig. 2. This pair of interwoven nets, which lies almost entirely within one half of the unit cell with $0 < y < \frac{1}{2}$, is then repeated by the action of the A -face centring to generate another interwoven pair of nets lying in the other half of the cell with $\frac{1}{2} < y < 1.0$. Such an arrangement is readily accommodated by the large b dimension of the unit cell. There are no short contacts between an interwoven bilayer and its two neighbouring bilayers.

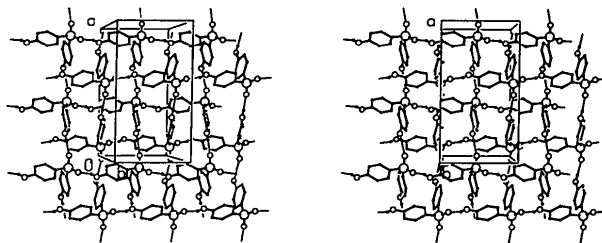


Fig. 3. Stereoview of the structure, showing the interpenetration of two nets.

Although the molecules are not subject to any crystallographically imposed symmetry, the conformation adopted by the heavy-atom skeleton is close to the optimum C_{2v} : the aryl rings $C1n$ and $C2n$ ($n = 1-6$) make angles with the $C11-S1-C21$ plane of $86.5(3)$ and $80.3(2)^\circ$, respectively. The $C-S$ bond lengths are below the lower quartile value (1.756 \AA) for such bonds in aryl sulfones (Allen *et al.*, 1987); the other bond lengths are unexceptional. Examination of the structure with *PLATON* (Spek, 1995a) showed that there were no solvent-accessible voids in the crystal lattice.

Experimental

Compound (I) was obtained from Aldrich; crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in methanol.

Crystal data

$C_{12}H_{10}O_4S$
 $M_r = 250.26$

Mo $K\alpha$ radiation
 $\lambda = 0.7107 \text{ \AA}$

Orthorhombic

Aba2

a = 15.048 (2) Å

b = 19.295 (3) Å

c = 8.1684 (10) Å

V = 2371.6 (6) Å³

Z = 8

D_x = 1.402 Mg m⁻³D_m not measured

Cell parameters from 25

reflections

θ = 8.7–17.0°

μ = 0.272 mm⁻¹

T = 294 (1) K

Plate

0.33 × 0.21 × 0.17 mm

Colourless

O11—S1—O12	118.0 (3)	O12—S1—C11	108.6 (3)
O11—S1—C11	107.2 (2)	O12—S1—C21	108.0 (3)
O11—S1—C21	109.0 (3)	C11—S1—C21	105.4 (3)
O12—S1—C11—C12	-152.1 (5)	O12—S1—C21—C22	-18.6 (5)
O11—S1—C11—C12	-23.6 (7)	O11—S1—C21—C22	-147.8 (4)
C21—S1—C11—C12	92.4 (6)	C11—S1—C21—C22	97.4 (5)

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

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1...O11 ⁱ	0.82	1.93	2.746 (5)	178
O2—H2...O12 ⁱⁱ	0.82	1.92	2.708 (6)	162

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

Compound (I) crystallized in the orthorhombic system. From the manner in which the data were collected (with $a < b < c$), the systematic absences allowed the space group to be either *C2cb* or *Cmca*. Both possibilities were examined and *C2cb* shown to be correct. The *C2cb* system was transformed to the equivalent standard *Aba2* system before the final refinement.

Data collection: *CAD-4/PC Software* (Enraf–Nonius, 1992). Cell refinement: *SET4* and *CELDIM* (Enraf–Nonius, 1992). Data reduction: *DATRD2* in *NRCVAX94* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SOLVER* in *NRCVAX94*. Program(s) used to refine structure: *NRCVAX94* and *SHELXL93* (Sheldrick, 1993). Molecular graphics: *NRCVAX94*, *ORTEPII* (Johnson, 1976) in *PLATON* (Spek, 1995a), and *PLUTON* (Spek 1995b). Software used to prepare material for publication: *NRCVAX94*, *SHELXL93* and *WordPerfect* macro *PREPCIF*.

GF thanks NSERC (Canada) for research grants.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1406). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Data collection

Enraf–Nonius CAD-4 diffractometer

θ/2θ scans

Absorption correction:

numerical, by Gaussian integration from crystal shape

T_{min} = 0.946, T_{max} = 0.958

2708 measured reflections

1386 independent reflections

565 observed reflections

[I > 2σ(I)]

R_{int} = 0.027θ_{max} = 26.87°

h = 0 → 19

k = -24 → 24

l = 0 → 10

3 standard reflections

frequency: 60 min

intensity decay: 3.0%

Refinement

Refinement on F²R[F² > 2σ(F²)] = 0.0468wR(F²) = 0.0874

S = 0.905

1386 reflections

156 parameters

H atoms riding (C—H 0.93,

O—H 0.82 Å)

w = 1/[σ²(F_o²) + (0.0310P)²]where P = (F_o² + 2F_c²)/3(Δ/σ)_{max} < 0.001Δρ_{max} = 0.217 e Å⁻³Δρ_{min} = -0.265 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)

Absolute configuration:

Flack (1983) parameter

= -0.05 (18)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U _{eq}
S1	0.07269 (9)	0.13582 (8)	0.0000 (3)	0.0554 (4)
O1	0.3105 (2)	0.3743 (2)	-0.0554 (8)	0.087 (2)
O2	0.1319 (3)	-0.0021 (2)	-0.6277 (6)	0.0685 (15)
O11	-0.0170 (2)	0.1625 (2)	0.0109 (8)	0.0739 (12)
O12	0.1032 (3)	0.0904 (2)	0.1284 (5)	0.0713 (15)
C11	0.1438 (3)	0.2068 (2)	-0.0106 (10)	0.0443 (14)
C12	0.1121 (3)	0.2696 (3)	-0.0668 (8)	0.055 (2)
C13	0.1689 (4)	0.3250 (3)	-0.0806 (8)	0.066 (2)
C14	0.2570 (4)	0.3181 (3)	-0.0372 (8)	0.060 (2)
C15	0.2893 (3)	0.2553 (3)	0.0177 (11)	0.064 (2)
C16	0.2320 (4)	0.2004 (2)	0.0314 (9)	0.059 (2)
C21	0.0852 (4)	0.0929 (3)	-0.1852 (8)	0.044 (2)
C22	0.1414 (4)	0.0361 (3)	-0.1988 (9)	0.057 (2)
C23	0.1558 (5)	0.0053 (3)	-0.3460 (9)	0.059 (2)
C24	0.1143 (3)	0.0306 (3)	-0.4827 (10)	0.0454 (15)
C25	0.0586 (3)	0.0869 (3)	-0.4750 (9)	0.050 (2)
C26	0.0442 (3)	0.1170 (3)	-0.3255 (8)	0.048 (2)

Table 2. Selected geometric parameters (Å, °)

S1—O11	1.448 (3)	S1—C21	1.735 (7)
S1—O12	1.442 (5)	O1—C14	1.359 (5)
S1—C11	1.741 (5)	O2—C24	1.368 (8)