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

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

	x	*y*	*z*	U_{eq}
S1	0	1.1724 (2)	−1/4	0.0477 (4)
O4	−0.1981 (2)	0.4853 (4)	−0.09741 (9)	0.0564 (6)
C1	−0.0579 (2)	0.9657 (5)	−0.20374 (10)	0.0379 (7)
C2	0.0110 (2)	0.7937 (5)	−0.17464 (11)	0.0487 (8)
C3	−0.0335 (2)	0.6309 (5)	−0.13966 (11)	0.0488 (8)
C4	−0.1497 (2)	0.6389 (5)	−0.13227 (11)	0.0405 (7)
C5	−0.2192 (2)	0.8122 (6)	−0.16056 (11)	0.0495 (8)
C6	−0.1734 (2)	0.9732 (5)	−0.19615 (11)	0.0456 (8)
N11	−0.0560 (2)	0.1351 (4)	−0.04841 (9)	0.0443 (6)
C12	−0.1213 (3)	0.0416 (5)	−0.00462 (13)	0.0544 (9)
C13	−0.0648 (2)	−0.1766 (5)	0.02595 (12)	0.0507 (8)

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

S1—C1	1.781 (3)	N11—C13^{i}	1.462 (3)
O4—C4	1.361 (3)	C12—C13	1.524 (4)
N11—C12	1.460 (3)		
C1^{ii}—S1—C1	99.8 (2)		
C1^{ii}—S1—C1—C2	56.9 (2)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···N11	0.82	1.92	2.725 (3)	168
N11—H11···C3^{iii}	0.90	2.71	3.579 (4)	163
N11—H11···C4^{iii}	0.90	2.69	3.505 (4)	152

Symmetry code: (iii) $x, y - 1, z$.

Examination of the structure with *PLATON* (Spek, 1995*a*) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *CAD*-4-*PC* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* in *CAD*-4-*PC*. Data reduction: *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SOLVER* in *NRCVAX*94. Program(s) used to refine structure: *NRCVAX*94 and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*94, *ORTEP*II (Johnson, 1976) in *PLATON* and *PLUTON* (Spek, 1995*b*). Software used to prepare material for publication: *NRCVAX*94, *SHELXL*93 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: CF1131). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two- and Three-Dimensional Hydrogen-Bonding Networks in the Structures of 4,4′-Dihydroxybenzophenone and 4,4′-Thiodiphenol

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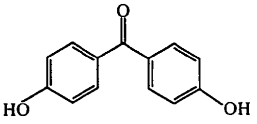
Abstract

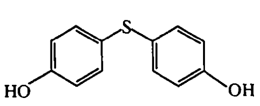
The two independent molecules in the structure of 4,4′-dihydroxybenzophenone, $OC(C_6H_4OH)_2$, are joined by O—H···O hydrogen bonds involving only hydroxy groups into chains each consisting of a single type of molecule, with O···O distances of 2.791 (4) and 2.785 (4) Å in the two types of chain; the chains are then linked into sheets by hydrogen bonds using carbonyl-O atoms as acceptors [O···O 2.627 (4) and 2.624 (4) Å]. In the structure of 4,4′-thiodiphenol, $S(C_6H_4OH)_2$, the molecules are linked into chains *via* centrosymmetric $(OH)_2$ motifs [O···O 2.755 (3) and 2.808 (3) Å] which are cross-linked by further O—H···O hydrogen bonds [O···O 2.710 (3) Å] to give a three-dimensional network.

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, in the structure of 4,4′-sulfonyldiphenol the hydroxy groups act as donors only while the sulfonyl-O atoms are the acceptors (Glidewell & Ferguson, 1996*b*); again, each molecule is hydrogen bonded to four others, forming planar nets characterized by the graph set $R_4^4(32)$ with, in addition, pairs of such nets interwoven to form bilayers. Here we report the structures of two more functionalized bis-phenols, 4,4′-dihydroxybenzophenone (4,4′-carbonyldiphenol), $OC(C_6H_4OH)_2$, (I), and 4,4′-thiodiphenol, $S(C_6H_4OH)_2$, (II), in each of which the hydrogen-bonding scheme is dominated by interactions involving the hydroxy groups as both donors and acceptors of hydrogen bonds; compounds (I) and (II) form continuous hydrogen-bonded networks which are two- and three-dimensional, respectively.



(I)



(II)

In the structure of (I), there are two independent molecules in the asymmetric unit, labelled *A* and *B*, both with approximate C_2 symmetry (Tables 1 and 3, Figs. 1 and 2); in addition, there is orientational disorder with two further sites occupied by some 13% of the molecules, labelled *C* and *D* (see *Experimental* section). The minor components (molecules *C* and *D*) occupy much the same volume elements as the major components (molecules *A* and *B*), rather as the major and minor components occupy similar volume elements in 1,3-adamantanedicarboxylic acid (Glidewell & Ferguson, 1996*a*). The following structural description refers to the major components *A* and *B* (see *Experimental* section).

Molecules of types *A* and *B* form independent antiparallel chains linked by O—H···O hydrogen bonds involving only hydroxy groups (Fig. 2). In one chain, atom O1*A* in the molecule at (x, y, z) acts as donor to atom O2*A* in the molecule at ($-x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$), giving chains around the 2_1 screw axis with the O—H···O hydrogen bonds all lying in the direction [0$\bar{1}$0]. In the other chain, atom O1*B* at (x, y, z) acts as donor to O2*B* at ($-1 - x$, $\frac{1}{2} + y$, $-\frac{1}{2} - z$) giving similar chains but with the O—H···O hydrogen bonds all in the direction [010]. In each of the chains, the hydrogen-bonding motif has graph set *C*(12) (Etter, 1990; Bernstein *et al.*, 1995). This chain formation utilizes only a single hydroxy-H atom per bis-phenol molecule so that the bonds O2*n*—H2*n* (*n* = *A*, *B*) are still available as hydrogen-bond donors. These O2*n*—H2*n* bonds in fact act as donors to the carbonyl-O atoms of molecules in adjacent chains; atom O2*A* acts as donor to carbonyl-O atom O3*B* within the same asymmetric unit while atom O2*B* at (x, y, z) acts as donor to atom O3*A* at ($x - 1$, y, $z - 1$). These inter-chain O—H···O═C hydrogen bonds give rise to cross-linking chains, running in the direction [101], again with alternate chains having antiparallel O—H···O hydrogen bonds and characterized by the graph set $C_2^2(16)$.

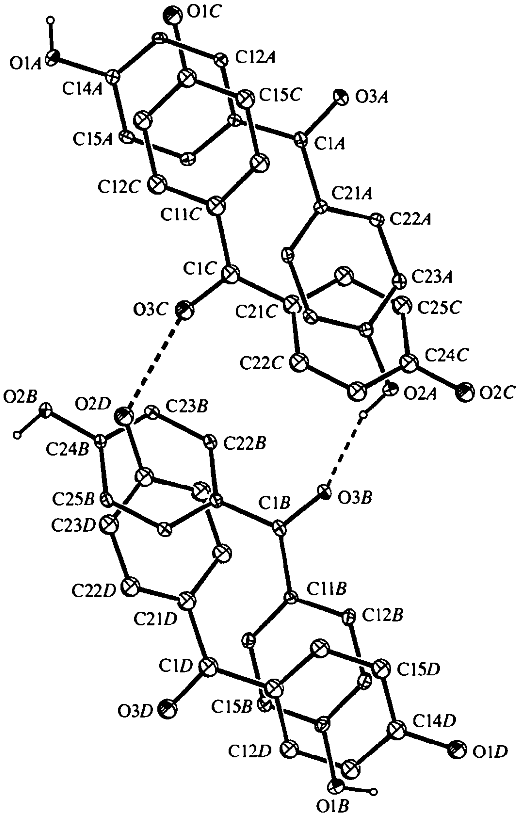


Fig. 1. A view showing how the *A*–*B* and *C*–*D* hydrogen-bonded pairs of molecules in (I) are disordered and with an indication of the atomic numbering scheme. Aromatic ring C atoms are numbered as C*n*1*m*–C*n*6*m* (*n* = 1, 2; *m* = *A*, *B*, *C*, *D*). For clarity, displacement ellipsoids are drawn at the 10% probability level. Intra-asymmetric unit hydrogen bonds are indicated by dashed lines.

The combined effect of the *C*(12) chains parallel to the **b** direction and the $C_2^2(16)$ chains parallel to [101] is the generation of sheets (Fig. 2) whose network contains rings of two sizes, characterized by the graph sets $R_4^4(40)$ and $R_4^4(20)$. Examination of the structure with *PLATON* (Spek, 1995*a*) showed no solvent-accessible void space anywhere within the structure. In particular, there is no free space within the $R_4^4(40)$ and $R_4^4(20)$ rings as these are lined by twelve and four C—H bonds, respectively (Fig. 2).

It is noteworthy that the two O—H···O hydrogen bonds with carbonyl-O atoms as acceptors have O···O distances very much shorter than those with hydroxy-O atoms as acceptors (Table 4). This is either a consequence of higher electron density at the carbonyl-O atoms arising from the contribution of canonical forms of type $R_2C^+—O^-$, or results from intermolecular packing effects which prevent the O—H···O(hydro-

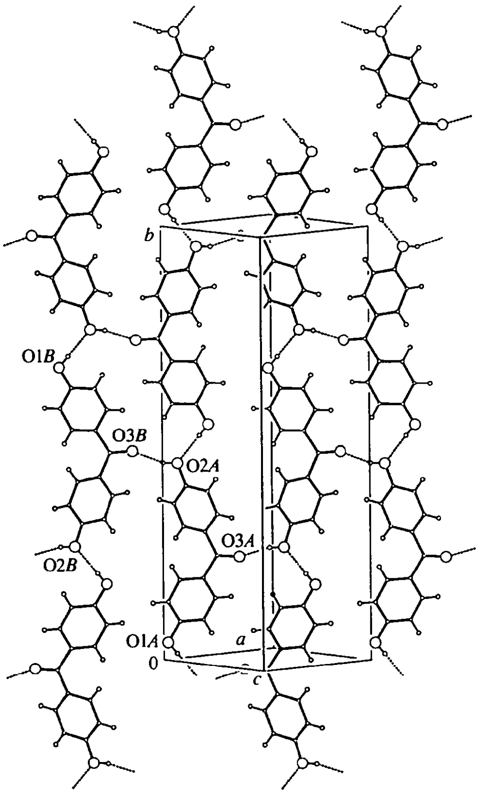


Fig. 2. A view of the sheets of hydrogen-bonded *A*–*B* molecules in (I); the diagram for the *C*–*D* molecules is very similar.

xy) distances from becoming any shorter [the shortest non-hydrogen-bonded intermolecular O···H interactions are O2*A*···H13*A* (at $-x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$) 2.74 Å and O2*B*···H13*B* (at $-1 - x$, $y - \frac{1}{2}$, $-\frac{1}{2} - z$) 2.76 Å]. This pattern of long and short O···O distances in the hydrogen bonds involving *A* and *B* is precisely repeated in the O···O contacts between *C* and *D* (Table 4). Although the hydroxy-H atoms in *C* and *D* could not be located because of their very small contribution to the total X-ray scattering, the O···O distances suggest a pattern of hydrogen bonding for *C* and *D* identical to that found for *A* and *B*.

Compound (II) has both the hydroxy-H atoms disordered over two equally populated sites; both H-atom sites associated with atom O1 and one of the O2 sites are involved in the hydrogen bonding. Atom O1 in the molecule at (x, y, z) (Fig. 3) acts as donor, *via* H1*A*, to the corresponding atom O1 in the molecule at ($1 - x$, $-y$, $1 - z$), so generating a cyclic centrosymmetric $(OH)_2$ motif having graph set $R_2^2(4)$; this motif is unknown in simple organic alcohols (Brock & Duncan, 1994) but occurs rather frequently in ferrocenyl alcohols (Glidewell, Klar, Lightfoot, Zakaria & Ferguson, 1996). Similarly, atom O2 in the molecule at (x, y, z) forms, *via* H2*A*, another $R_2^2(4)$ $(OH)_2$ motif with atom O2 in the molecule at ($2 - x$, $1 - y$, $1 - z$), and these two $(OH)_2$ motifs together generate a $C_2^2(24)$ chain running in the direction [110] (Fig. 4). The action of the 2_1 screw axes is to generate similar chains along $[1\bar{1}0]$. Thus, normal to [001] there is a series of $C_2^2(24)$ chains, alternate members of which run along [110] and $[1\bar{1}0]$, and which are inclined at an angle of 29.59 (1)° to one another. The cross-links between these chains employ the other H-atom site, H1*B*, associated with O1. Atom O1 at (x, y, z) acts, *via* H1*B*, as donor to atom O2 at ($\frac{3}{2} - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$) and this interaction, together with the (O2—H2*A*)$_2$ units described earlier, give rise to $C_4^4(8)$ chains parallel to the **c** direction. These $C_4^4(8)$ chains then serve to cross-link the chains normal to [001] into a continuous three-dimensional network. The other H-atom site associated with atom O2, H2*B*, plays no part in the hydrogen-bonding scheme.

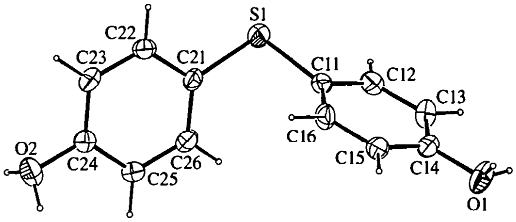


Fig. 3. A view of (II) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

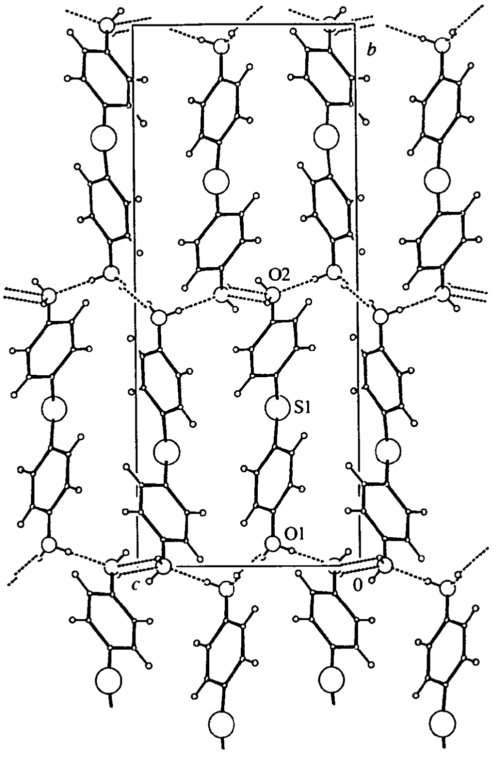


Fig. 4. A view of part of the hydrogen-bonding network in the crystal structure of (II).

The O···O distances within the hydrogen bonds of (II) (Table 4) are comparable with those in (I) which are associated with hydroxy-only interactions. As in (I), the molecular conformation of (II) is close to C_2 symmetry (Table 3). The bond lengths are unexceptional: examination of the structure with *PLATON* showed that there were no solvent-accessible voids in the crystal lattice.

Both (I) and (II) form structures in which the hydroxy groups are dominant in the development of the hydrogen-bonding scheme; in this respect they differ markedly from the chemically rather analogous 4,4′-sulfonyldiphenol where the sole hydrogen bonds are of the O—H···O═S type. The structure of (I), in forming a two-dimensional hydrogen-bonded array, is thus more closely related to those of the unfunctionalized 4,4′-biphenol and 4,4′-isopropylidenediphenol than to the interwoven bilayer structure of 4,4′-sulfonyldiphenol; the behaviour of (II) mimics that of 4,4′-biphenol and 4,4′-isopropylidenediphenol in that the central sulfide functionality is not employed in the hydrogen-bonding scheme.

Experimental

Compounds (I) and (II) were obtained from Aldrich; crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of solutions in methanol.

Compound (I)

Crystal data

$C_{13}H_{10}O_3$
$M_r = 214.21$
Monoclinic
$P2_1/c$
$a = 9.450(2)$ Å
$b = 24.456(3)$ Å
$c = 9.484(2)$ Å
$\beta = 103.607(13)°$
$V = 2130.3(7)$ Å^3
$Z = 8$
$D_x = 1.336$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 8.7–17.6°$
$\mu = 0.095$ mm^{-1}
$T = 294(1)$ K
Block
0.40 × 0.38 × 0.33 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4877 measured reflections
4612 independent reflections
1444 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.021$
$\theta_{\rm max} = 27°$
$h = -12 \rightarrow 11$
$k = 0 \rightarrow 31$
$l = 0 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: no decay, variation 0.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0700$
$wR(F^2) = 0.2188$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.245$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.311$ e Å^{-3}

$S = 0.917$
4612 reflections
295 parameters
H atoms riding (C—H 0.93, O—H 0.82 Å)
$w = 1/[\sigma^2(F_o^2) + (0.0910P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

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*A*	−0.1193 (3)	0.04702 (11)	0.1720 (4)	0.0618 (10)
O2*A*	−0.0571 (4)	0.45885 (10)	0.2109 (3)	0.0581 (10)
O3*A*	0.2427 (3)	0.24405 (13)	0.4931 (3)	0.0635 (10)
C1*A*	0.1329 (3)	0.24711 (14)	0.3899 (3)	0.0396 (11)
C11*A*	0.0665 (3)	0.19509 (8)	0.3254 (3)	0.0347 (11)
C12*A*	0.1501 (2)	0.14777 (11)	0.3506 (3)	0.0418 (11)
C13*A*	0.0889 (3)	0.09773 (9)	0.3000 (3)	0.0387 (12)
C14*A*	−0.0560 (3)	0.09502 (8)	0.2242 (3)	0.0441 (12)
C15*A*	−0.1396 (2)	0.14234 (11)	0.1990 (3)	0.0461 (12)
C16*A*	−0.0784 (3)	0.19238 (9)	0.2496 (3)	0.0425 (12)
C21*A*	0.0746 (3)	0.30144 (8)	0.3383 (3)	0.0353 (10)
C22*A*	0.0940 (3)	0.34386 (10)	0.4386 (2)	0.0431 (12)
C23*A*	0.0490 (3)	0.39647 (9)	0.3937 (3)	0.0450 (13)
C24*A*	−0.0153 (3)	0.40667 (8)	0.2486 (3)	0.0421 (12)
C25*A*	−0.0347 (3)	0.36425 (10)	0.1484 (2)	0.0439 (12)
C26*A*	0.0103 (3)	0.31164 (9)	0.1932 (2)	0.0365 (11)
O1*B*	−0.6110 (4)	0.67980 (12)	−0.3596 (4)	0.0688 (12)
O2*B*	−0.5618 (4)	0.26707 (11)	−0.2682 (3)	0.0609 (10)
O3*B*	−0.2534 (3)	0.48484 (12)	−0.0251 (3)	0.0627 (10)
C1*B*	−0.3637 (4)	0.48116 (14)	−0.1267 (3)	0.0448 (12)
C11*B*	−0.4291 (3)	0.53204 (8)	−0.1987 (3)	0.0366 (11)
C12*B*	−0.3432 (2)	0.57883 (11)	−0.1782 (3)	0.0441 (12)
C13*B*	−0.4024 (3)	0.62874 (9)	−0.2324 (3)	0.0471 (13)
C14*B*	−0.5476 (3)	0.63187 (8)	−0.3070 (3)	0.0466 (12)
C15*B*	−0.6335 (2)	0.58509 (11)	−0.3275 (3)	0.0453 (12)
C16*B*	−0.5743 (3)	0.53517 (9)	−0.2734 (3)	0.0430 (12)
C21*B*	−0.4236 (3)	0.42579 (8)	−0.1688 (3)	0.0389 (11)
C22*B*	−0.4014 (3)	0.38560 (10)	0.0622 (2)	0.0419 (11)
C23*B*	−0.4492 (3)	0.33250 (9)	−0.0976 (3)	0.0457 (13)
C24*B*	−0.5191 (3)	0.31958 (8)	−0.2396 (3)	0.0374 (11)
C25*B*	−0.5413 (3)	0.35976 (10)	−0.3462 (2)	0.0409 (11)
C26*B*	−0.4936 (3)	0.41287 (9)	−0.3108 (2)	0.0421 (12)
O1*C*	0.1109 (19)	0.0914 (6)	0.369 (2)	0.067 (2)
O2*C*	0.0610 (17)	0.5047 (5)	0.286 (2)	0.067 (2)
O3*C*	−0.2606 (15)	0.2864 (6)	0.0514 (16)	0.067 (2)
C1*C*	−0.1428 (14)	0.2908 (4)	0.1460 (13)	0.067 (2)
C11*C*	−0.0744 (13)	0.2384 (5)	0.2056 (11)	0.067 (2)
C12*C*	−0.1559 (13)	0.1906 (5)	0.182 (2)	0.067 (2)
C13*C*	−0.0935 (16)	0.1412 (5)	0.237 (2)	0.067 (2)
C14*C*	0.0505 (15)	0.1397 (5)	0.3156 (15)	0.067 (2)
C15*C*	0.1320 (14)	0.1876 (6)	0.339 (2)	0.067 (2)
C16*C*	0.0696 (14)	0.2369 (5)	0.284 (2)	0.067 (2)
C21*C*	−0.0883 (11)	0.3471 (4)	0.1848 (14)	0.067 (2)
C22*C*	−0.1054 (18)	0.3866 (5)	0.0767 (13)	0.067 (2)
C23*C*	−0.0551 (19)	0.4395 (5)	0.1110 (16)	0.067 (2)
C24*C*	0.0122 (13)	0.4528 (5)	0.2535 (17)	0.067 (2)
C25*C*	0.029 (2)	0.4133 (6)	0.3615 (14)	0.067 (2)
C26*C*	−0.021 (2)	0.3605 (5)	0.3272 (13)	0.067 (2)
O1*D*	−0.3759 (18)	0.7275 (6)	−0.1775 (18)	0.067 (2)
O2*D*	−0.4483 (17)	0.3174 (6)	−0.186 (2)	0.067 (2)
O3*D*	−0.7552 (15)	0.5301 (6)	−0.4813 (16)	0.067 (2)
C1*D*	−0.6418 (13)	0.5276 (4)	−0.3819 (13)	0.067 (2)
C11*D*	−0.5708 (13)	0.5803 (5)	−0.3276 (11)	0.067 (2)
C12*D*	−0.6503 (14)	0.6285 (5)	−0.354 (2)	0.067 (2)
C13*D*	−0.5851 (16)	0.6780 (5)	−0.304 (2)	0.067 (2)
C14*D*	−0.4404 (15)	0.6792 (5)	−0.2270 (14)	0.067 (2)
C15*D*	−0.3609 (14)	0.6309 (6)	−0.201 (2)	0.067 (2)
C16*D*	−0.4261 (14)	0.5815 (5)	−0.251 (2)	0.067 (2)
C21*D*	−0.5904 (10)	0.4724 (4)	−0.3291 (13)	0.067 (2)
C22*D*	−0.6115 (18)	0.4289 (5)	−0.4262 (13)	0.067 (2)
C23*D*	−0.564 (2)	0.3768 (5)	−0.3785 (16)	0.067 (2)

C24*D*	−0.4952 (13)	0.3682 (5)	−0.2337 (16)	0.067 (2)
C25*D*	−0.4741 (19)	0.4117 (6)	−0.1366 (14)	0.067 (2)
C26*D*	−0.5217 (19)	0.4638 (5)	−0.1843 (13)	0.067 (2)

The *A* and *B* molecules have 0.869 (3) occupancy and those of the *C* and *D* molecules have 0.131 (3) occupancy.

Compound (II)

Crystal data

$C_{12}H_{10}O_2S$
$M_r = 218.26$
Monoclinic
$P2_1/n$
$a = 5.5808$ (8) Å
$b = 21.128$ (3) Å
$c = 8.8006$ (12) Å
$\beta = 93.192$ (10)°
$V = 1036.1$ (2) Å^3
$Z = 4$
$D_x = 1.399$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 9.30$–18.60°
$\mu = 0.286$ mm^{-1}
$T = 294$ (1) K
Plate
0.33 × 0.31 × 0.08 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: Gaussian by integration from crystal shape
$T_{\min} = 0.9240$, $T_{\max} = 0.9776$
2370 measured reflections
2236 independent reflections

775 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.026$
$\theta_{\max} = 27°$
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 26$
$l = 0 \rightarrow 11$
3 standard reflections
frequency: 120 min
intensity decay: no decay, variation 0.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0472$
$wR(F^2) = 0.1044$
$S = 0.825$
2236 reflections
138 parameters
H atoms riding [*SHELXL*93 (Sheldrick, 1993) defaults, C—H 0.93, O—H 0.82 Å]

$w = 1/[\sigma^2(F_o^2) + (0.0370P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.241$ e Å^{-3}
$\Delta\rho_{\min} = -0.230$ 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 2. *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*	$U_{\rm eq}$
S1	0.10327 (15)	0.29058 (4)	0.36646 (13)	0.0612 (4)
O1	0.5863 (4)	0.04138 (9)	0.3951 (3)	0.0655 (8)
O2	0.8143 (4)	0.49949 (10)	0.3856 (2)	0.0551 (7)
C11	0.2679 (5)	0.21882 (14)	0.3813 (4)	0.0389 (9)
C12	0.1731 (5)	0.17071 (15)	0.4652 (4)	0.0457 (9)
C13	0.2767 (6)	0.11133 (14)	0.4682 (4)	0.0467 (9)
C14	0.4799 (6)	0.10030 (15)	0.3917 (4)	0.0409 (9)
C15	0.5797 (5)	0.14836 (14)	0.3104 (4)	0.0443 (9)
C16	0.4717 (5)	0.20701 (14)	0.3044 (4)	0.0449 (9)
C21	0.3263 (5)	0.35069 (14)	0.3744 (4)	0.0393 (9)
C22	0.2933 (5)	0.40177 (15)	0.2780 (4)	0.0439 (9)
C23	0.4523 (6)	0.45232 (14)	0.2844 (4)	0.0461 (10)
C24	0.6492 (5)	0.45055 (14)	0.3850 (4)	0.0384 (9)
C25	0.6834 (5)	0.40010 (14)	0.4824 (4)	0.0430 (9)
C26	0.5207 (6)	0.35070 (15)	0.4781 (4)	0.0475 (9)

Table 3. *Selected geometric parameters (Å, °) for molecules (IA), (IB), (IC), (ID) and (II)*

	(I*A*)^a	(I*B*)^b	(I*C*)^c	(I*D*)^d	(II)^e
O1*n*—C14*n*	1.357 (3)	1.357 (3)	1.357 (6)	1.361 (6)	1.379 (3)
O2*n*—C24*n*	1.359 (3)	1.354 (3)	1.359 (6)	1.361 (6)	1.385 (3)
O3*n*—C1*n*	1.250 (4)	1.245 (4)	1.259 (8)	1.251 (8)	
*X*1*n*—C11*n*	1.485 (4)	1.483 (4)	1.484 (6)	1.487 (6)	1.774 (3)
*X*1*n*—C12*n*	1.477 (4)	1.485 (4)	1.485 (6)	1.483 (6)	1.777 (3)
O3*n*—C1*n*—C11*n*	117.6 (3)	118.6 (3)	115.4 (3)	117.2 (7)	
O3*n*—C1*n*—C21*n*	119.3 (3)	118.1 (3)	116.9 (3)	116.9 (3)	
C11*n*—*X*1*n*—C21*n*	123.0 (3)	123.4 (3)	127.6 (3)	125.9 (3)	104.4 (1)
*X*1*n*—C11*n*—C12*n*	118.3 (2)	117.4 (2)	119.3 (5)	119.5 (5)	117.2 (2)
*X*1*n*—C11*n*—C16*n*	121.6 (2)	122.4 (2)	120.7 (5)	120.5 (5)	123.8 (3)
*X*1*n*—C21*n*—C22*n*	117.8 (2)	117.8 (2)	119.2 (5)	119.3 (5)	117.8 (2)
*X*1*n*—C21*n*—C26*n*	122.1 (2)	122.1 (2)	120.8 (5)	120.7 (5)	123.3 (3)
O3*n*—C1*n*—C11*n*—C12	−18.9 (2)	17.7 (3)	−14.7 (10)	19.1 (10)	
O3*n*—C1*n*—C21*n*—C22	−29.6 (3)	28.4 (3)	−37.6 (9)	33.6 (9)	
C21*n*—*X*1*n*—C11*n*—C12	161.6 (2)	−162.7 (2)	165.4 (9)	−161.0 (10)	142.3 (3)
C11*n*—*X*1*n*—C21*n*—C22	149.9 (2)	−151.1 (2)	142.3 (9)	−146.4 (8)	139.3 (3)

In the atom labels, (*a*) *n* = *A*, *X* = C; (*b*) *n* = *B*, *X* = C; (*c*) *n* = *C*, *X* = C; (*d*) *n* = *D*, *X* = C; (*e*) *n* = null, *X* = S.

Table 4. *Hydrogen-bonding geometry (Å, °) for (I) and (II)*

D	H	*A*	*D*—*H*	H···*A*	*D*···*A*	*D*—H···*A*
(I)						
O1*A*	H1*A*	O2*A*$^{\rm i}$	0.82	1.97	2.791 (4)	175
O2*A*	H2*A*	O3*B*	0.82	1.85	2.627 (4)	159
O1*B*	H1*B*	O2*B*$^{\rm ii}$	0.82	1.97	2.785 (4)	176
O2*B*	H2*B*	O3*A*$^{\rm iii}$	0.82	1.82	2.624 (4)	165
O1*C*	–	O2*C*$^{\rm i}$	–	–	2.86 (3)	–
O2*C*	–	O3*D*$^{\rm iv}$	–	–	2.54 (2)	–
O1*D*	–	O2*D*$^{\rm ii}$	–	–	2.87 (3)	–
O2*D*	–	O3*C*	–	–	2.63 (2)	–
(II)						
O1	H1*A*	O1$^{\rm v}$	0.82	1.98	2.755 (3)	158
O1	H1*B*	O2$^{\rm vi}$	0.82	1.90	2.710 (3)	169
O2	H2*A*	O2$^{\rm vii}$	0.82	2.20	2.808 (3)	131

Symmetry codes: (i) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (ii) $-1-x, \frac{1}{2}+y, -\frac{1}{2}-z$; (iii) $x-1, y, z-1$; (iv) $1+x, y, 1+z$; (v) $1-x, -y, 1-z$; (vi) $\frac{3}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (vii) $2-x, 1-y, 1-z$.

Crystals of (I) did not diffract strongly [only 31.3% of the data could be labelled as 'observed' with $I > 2\sigma(I)$] and it soon became apparent that there was appreciable disorder in the structure. While the two independent molecules of the structure were located fairly straightforwardly, refinement gave nonsensical molecular geometry (*e.g.* puckered aromatic rings) and difference maps were not clean. From careful examination of difference map sections [with the COFOUR option in *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989)] of the residual electron density in the planes of the aromatic rings (and above and below these rings), it became clear that the two main (*A* and *B*) molecules had intermingled with the minor components (*C* and *D*) in different orientations. The *A*–*B* and *C*–*D* dimeric units occupied essentially the same volume elements and had similar modes of intermolecular hydrogen bonding. We were then able to derive approximate coordinates for all the atoms of the minor components and we estimated the disorder ratio to be 0.85/0.15 from peak heights. For the final *SHELXL*93 (Sheldrick, 1993) refinement with constraints and restraints, all the aromatic rings were constrained to be planar hexagons with C—C 1.39 Å and the exocyclic C and O atoms were restrained to lie in the aromatic ring planes by means of the FLAT instruction. Soft DFIX restraints were applied to the C—O and exocyclic C—C distances. The non-H atoms of the major (*A*,*B*) component were allowed anisotropic vibration parameters and the atoms of the minor component were held to a common isotropic displacement parameter. The (*A*,*B*)/(*C*,*D*) occupancy ratio refined to 0.869 (3)/0.131(3). The various O···O intermolecular contacts are consistent with only one hydrogen-bonding scheme for each of the *A*,*B* and *C*,*D* systems; the hydroxy-H atoms of the *A*,*B* system could be seen in difference map sections and were allowed for in the refinement by means of the appropriate *SHELXL* AFIX-147 instructions. No allowance was made for the hydroxy-H atoms of the minor component.

Compound (II) crystallized in the monoclinic system; space group $P2_1/n$ from the systematic absences. Difference maps calculated in planes normal to the relevant C—O bonds with the COFOUR option in *NRCVAX* showed clearly that the hydroxy-H atoms were equally disordered over two sites. These were allowed for in the *SHELXL*93 refinement by use of the AFIX-147 option.

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) for (I); *SOLVER* in *NRCVAX*94 for (II). For both compounds, program(s) used to refine structures: *NRCVAX*94 and *SHELXL*93 (Sheldrick, 1993); molecular graphics: *NRCVAX*94, *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1995*a*), *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, least-squares-planes data, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1407). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4,7-Bis(2-thiophenoyl)-1-thia-4,7-diazacyclononane

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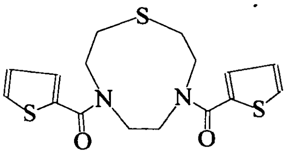
Abstract

The title compound, $C_{16}H_{18}N_2O_2S_3$, has two thiophenoyl arms linked to the N atoms of the central 1-thia-4,7-diazacyclononane ring. The resulting amide groups are close to planar. One of the thiophene rings shows disorder.

Comment

The structures of the Cu^{II} (Wasielewski & Mattes, 1990) and Pd^{II} (Chak, McAuley & Whitcome, 1994) complexes of 4,7-bis(pyridylmethyl)-1-thia-4,7-diazacyclononane have been determined. Here we report the structure of a closely related ligand, (1), where the pendant arms are thiophenoyl rather than pyridylmethyl.



(1)

The torsion angles C3—N4—C41—C42 and C8—N7—C71—C72 of 7.2 (4) and 9.8 (4)°, respectively, indicate that the amide units are almost planar: this is due to the partial double-bond character between C41/N4 and C71/N7. The N4—C41/N7—C71 and C41=O41/C71=O71 bond lengths of