Coupar, P. I., Ferguson, G. & Glidewell, C. (1996*b*). *Acta Cryst.* Submitted.
Desiraju, G. R. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2311–2327.
Enraf–Nonius (1992). *CAD-4/PC Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Glidewell, C. & Ferguson, G. (1994). *Acta Cryst.* C**50**, 1362–1366.
Glidewell, C. & Ferguson, G. (1996). *Acta Cryst.* C**52**, 2528–2530.
Hanton, L. R., Hunter, C. A. & Purvis, D. H. (1992). *J. Chem. Soc. Chem. Commun.* pp. 1134–1136.
Hunter, C. A. (1991). *J. Chem. Soc. Chem. Commun.* pp. 749–751.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Loehlin, J. H., Etter, M. C., Gendreau, C. & Cervasio, E. (1994). *Chem. Mater.* **6**, 1218–1221.
Long, C. (1961). *Biochemists Handbook*, pp. 45–52. London: E. & F. N. Spon.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Spek, A. L. (1995*a*). *PLATON. Molecular Geometry Program*. Version of July 1994. University of Utrecht, The Netherlands.
Spek, A. L. (1995*b*). *PLUTON. Molecular Graphics Program*. Version of July 1994. University of Utrecht, The Netherlands.
Subramanian, S. & Zaworotko, M. J. (1994). *Coord. Chem. Rev.* **137**, 357–401.

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# N—H···π(arene) Hydrogen Bonding in 4,4′-Thiodiphenol–Piperazine (1/1)

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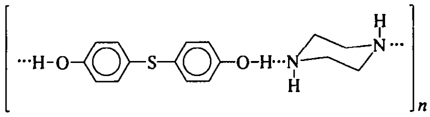
## Abstract

In the 1:1 adduct formed between 4,4′-thiodiphenol [$S(C_6H_4OH)_2$] and piperazine ($C_4H_{10}N_2$), the components are linked into chains by O—H···N hydrogen bonds, with an O···N distance of 2.725 (3) Å. These chains are themselves cross-linked into sheets by N—H···π(arene) hydrogen bonds.

## Comment

Piperazine ($C_4H_{10}N_2$) is a potentially valuable building block in crystal engineering. It contains two hydrogen-bond acceptor sites and the two N—H bonds are potential hydrogen-bond donors. In addition, there is some structural flexibility available due to both the variable conformation of the ring and the axial/equatorial arrangement of the hydrogen-bond donor and acceptor sites. The behaviour of piperazine may also act as a pointer to that of other polyaza macrocycles of the $(CH_2CH_2N)_n$ type. Despite these possibilities, very few examples of the use of piperazine in host–guest chemistry have been reported. In the chain-forming 1:1 adduct with ferrocene-1,1′-diylbis(diphenylmethanol), piperazine adopts a chair conformation having one N—H bond axial and the other equatorial; piperazine, however, acts only as an acceptor of hydrogen bonds (O—H···N) and the N—H bonds play no part in the hydrogen-bonding scheme (Glidewell, Ferguson, Lough & Zakaria, 1994). In contrast, in the 2:1 adduct with phenol, $2C_6H_5OH.C_4H_{10}N_2$, which also forms chains, both N—H bonds are axial in the piperazine units, which have chair conformations, and act as both donors and acceptors of hydrogen bonds, forming N—H···O and O—H···N hydrogen bonds with phenol units (Loehlin, Etter, Gendreau & Cervasio, 1994). As part of a wider study of adduct formation by bisphenols and trisphenols with polyaza acceptors, we have now studied the interaction of bisphenols of type $X(C_6H_4OH)_2$ ($X$ = O, S, $SO_2$, CO, $CMe_2$) with piperazine. These bisphenols form adducts with phenol:piperazine ratios of either 1:1 ($X$ = O, S, CO) or 2:1 ($X$ = $SO_2$, CO, $CMe_2$), and we report here the structure of a representative 1:1 adduct having $X$ = S, namely, 4,4′-thiodiphenol–piperazine (1/1), (I), in which the hydrogen-bonding behaviour of the piperazine turns out to be different from that observed in the adducts mentioned above.



(I)

The bisphenol components of compound (I) lie on twofold rotation axes and the piperazine units lie on inversion centres, thus adopting a chair conformation; the N—H bonds are axial and the nitrogen lone pairs are equatorial (Fig. 1). The bisphenol and piperazine units are linked by O—H···N hydrogen bonds into chains which extend along the **c** direction (Table 3 and Fig. 2); two such chains run through each unit cell, with chain axes $(0,0,z)$ and $(\frac{1}{2},\frac{1}{2},z)$. The N···O distance (Table 3) is, as expected, less than the values of 2.821 (3) and 2.867 (3) Å observed for the two independent O···N distances in the ferrocenediol adduct (Glidewell, Ferguson, Lough & Zakaria, 1994). These values all lie between the values of 2.682 (3) and 3.075 (4) Å observed for the O—H···N and N—H···O hydrogen bonds, respectively, in the phenol adduct (Loehlin, Etter, Gendreau & Cervasio, 1994). The chains in (I) formed by the O—H···N hydrogen bonds are themselves cross-linked by N—H···π(arene) interactions. The N—H bond of

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the piperazine unit at ($x$, $y$, $z$) acts as a hydrogen-bond donor to the C1–C6 arene ring at ($x$, $-1+y$, $z$), while the symmetry-related N—H bond in the same piperazine unit acts as donor to the bisphenol at ($-x$, $1-y$, $-z$). These interactions thus serve to connect the chains into sheets parallel to the *bc* plane. The shortest H···C and N···C distances are those to the C3 and C4 atoms (Table 3). The H···C distances to the other C atoms of this ring are C1 3.06, C2 2.88, C5 2.83 and C6 3.02 Å. All of the H···C values are towards the lower end of the range of N—H···π(arene) hydrogen bonds recognized in a study of salts of organic cations with the tetraphenylborate anion, in which these short contacts were held to be a result of a positive hydrogen-bonding tendency rather than a passive response to packing requirements (Bakshi *et al.*, 1994; Knop, Cameron, Bakshi, Linden & Roe, 1994).

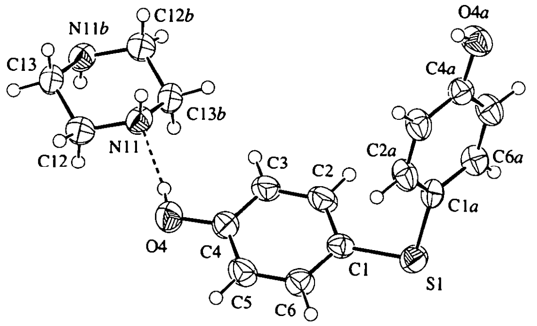

Fig. 1. A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The suffix '*a*' corresponds to symmetry code (i) and '*b*' to symmetry code (ii) as given in Table 2.

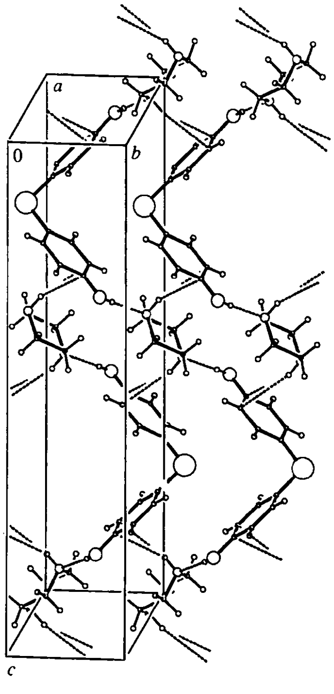

Fig. 2. A view of part of the crystal structure showing the zigzag chains extending in the **c** direction. Hydrogen bonds and N—H···π(arene) interactions are shown as dotted lines.

Within the molecular fragments, the interatomic distances are unexceptional; the skeletal conformation adopted by the bisphenol fragment is very far from $C_{2v}$ symmetry.

## Experimental

A sample of compound (I) was prepared by dissolving separately in methanol equimolar quantities of piperazine (0.43 g, 5.0 mmol in 50 ml) and 4,4′-thiodiphenol (1.09 g, 5.0 mmol in 50 ml), mixing the solutions and allowing the resulting solution to crystallize. Analysis found: C 63.4, H 6.8, N 9.4%; $C_{16}H_{20}N_2O_2S$ requires: C 63.1, H 6.6, N 9.2%. Crystals suitable for single-crystal diffraction were selected directly from the prepared sample.

*Crystal data*

$C_4H_{10}N_2.C_{12}H_{10}O_2S$
$M_r = 304.40$
Monoclinic
$C2/c$
$a = 11.628$ (2) Å
$b = 5.5524$ (6) Å
$c = 23.931$ (3) Å
$\beta = 96.82$ (2)°
$V = 1534.1$ (3) Å$^3$
$Z = 4$
$D_x = 1.318$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 9.57$–$19.56$°
$\mu = 0.217$ mm$^{-1}$
$T = 294$ (1) K
Needle
0.35 × 0.15 × 0.08 mm
Colourless

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1727 measured reflections
1658 independent reflections
824 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.027$
$\theta_{\rm max} = 26.9$°
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 30$
3 standard reflections frequency: 60 min intensity decay: none

*Refinement*

Refinement on $F^2$
$R(F) = 0.0543$
$wR(F^2) = 0.1155$
$S = 0.937$
1658 reflections
98 parameters
H atoms riding (*SHELXL*93 defaults; C—H 0.93 and 0.97, N—H 0.86 and O—H 0.82 Å)
$w = 1/[\sigma^2(F_o^2) + (0.041P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.184$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.193$ e Å$^{-3}$
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0085 (10)
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 (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.

## References

Bakshi, P. K., Linden, A., Vincent, B. R., Roe, S. P., Adhikesavalu, D., Cameron, T. S. & Knop, O. (1994). *Can. J. Chem.* **72**, 1273–1293.

Enraf–Nonius (1992). *CAD*-4-*PC*. Version 1.1. Enraf–Nonius, Delft, The Netherlands

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Glidewell, C., Ferguson, G., Lough, A. J. & Zakaria, C. M. (1994). *J. Chem. Soc. Dalton Trans.* pp. 1971–1982.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Knop, O., Cameron, T. S., Bakshi, P. K., Linden, A. & Roe, S. P. (1994). *Can. J. Chem.* **72**, 1870–1881.

Loehlin, J. H., Etter, M. C., Gendreau, C. & Cervasio, E. (1994). *Chem. Mater.* **6**, 1218–1221.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Spek, A. L. (1995*a*). *PLATON. Molecular Geometry Program.* Version of July 1995. University of Utrecht, The Netherlands.

Spek, A. L. (1995*b*). *PLUTON. Molecular Graphics Program.* Version of July 1995. University of Utrecht, The Netherlands.

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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,