# ORGANIC COMPOUNDS

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## Piperazine–4,4′-Sulfonyldiphenol (1/2): a Self-Assembled Channel Structure

PAMELA I. COUPAR,[a] GEORGE FERGUSON[b] AND CHRISTOPHER GLIDEWELL[a]

[a]*School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland, and* [b]*Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada, N1G 2W1. E-mail: cg@st-andrews.ac.uk*

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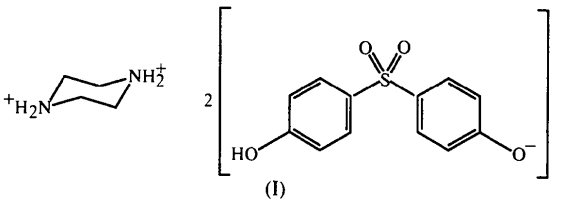
### Abstract

Interaction of piperazine with 4,4′-sulfonyldiphenol at ambient temperature in methanol yields the salt, piperazine-1,4-diium bis(4,4′-sulfonyldiphenolate), $C_4H_{12}N_2^{2+}.2C_{12}H_9O_4S^-$, in which pairs of phenolate anions form cyclic dimers. The cations act as multiple hydrogen-bond donors, of both the N—H···O and C—H···O types, which tie these dimers into stacks enclosing channels 4.3 Å in diameter.

### Comment

Hydrogen bonds of types O—H···O, O—H···N and N—H···O are among the most robust and versatile synthons in crystal engineering (Subramanian & Zaworotko, 1994; Desiraju, 1995). Polyphenols are excellent building blocks for crystal-engineering purposes as they exhibit higher acidity than alcohols and thus a greater propensity to form strong hydrogen bonds, while their frameworks have well defined structures with only limited conformational flexibility; among such phenols, 4,4′-sulfonyldiphenol, $SO_2(C_6H_4OH)_2$, has the added advantage of being able to act as an acceptor of hydrogen bonds, using the sulfonyl O atoms, as well as a donor, as demonstrated by its own crystal structure (Glidewell & Ferguson, 1996) and that of its adduct with hexamethylenetetramine (Coupar, Ferguson & Glidewell, 1996*b*). Piperazine is a similarly versatile building block in that it can act not only as an acceptor of hydrogen bonds, but also as a donor, forming N—H···O hydrogen bonds in its adduct with phenol (Loehlin, Etter, Gendreau & Cervasio, 1994) and N—H···$\pi$(arene) hydrogen bonds in the adduct with 4,4′-thiodiphenol, $S(C_6H_4OH)_2$ (Coupar, Ferguson & Glidewell, 1996*a*). We report here the structure of the 1:2 adduct formed between piperazine and 4,4′-sulfonyldiphenol, *i.e* (I).



(I)

Single-crystal X-ray diffraction showed unambiguously that adduct (I) is in fact a salt, $[piperazineH_2]^{2+}.2[HOC_6H_4SO_2C_6H_4O]^-$, in which each molecule of the bisphenol has transferred a single proton to the piperazine (Fig. 1). In addition to the explicit location of all the H atoms in difference maps, other metrical evidence in support of these proton transfers includes the difference between the C14—O14 and C24—O24 bond lengths, and the elongation of the piperazine C—N bond lengths compared with those in unprotonated piperazine, for example 1.460 (3) and 1.462 (3) Å in the 1:1 adduct, (II), formed with 4,4′-thiodiphenol, $S(C_6H_4OH)_2$ (Coupar, Ferguson & Glidewell, 1996*a*). Pairs of the resulting phenolate anions form centrosymmetric cyclic dimers in which the components are connected by short O—H···$O^-$ hydrogen bonds (Table 3); these dimers are themselves joined by the centrosymmetric $[piperazineH_2]^{2+}$ cations to form a continuous three-dimensional network (Fig. 2). The two axial N—H bonds of the cation form short N—H···$O^-$ hydrogen bonds to the deprotonated O atoms in a pair of phenolate dimers, while the two equatorial N—H bonds each form bifurcated N—H···O hydrogen bonds to sulfonyl O atoms in two different phenolate dimers. In addition, there are weak C—H···$O^-$ hydrogen bonds formed by two of the equatorial C—H bonds in the piperazine acting as donors towards deprotonated phenolate O atoms, which are therefore bis-acceptors. Overall, each $[piperazineH_2]^{2+}$ cation acts as a hydrogen-bond donor to no fewer than eight O atoms in six different phenolate dimers.

The hydrogen bonding in the cyclic phenolate dimers is characterized by the graph set $R_2^2(24)$ (Etter, 1990;

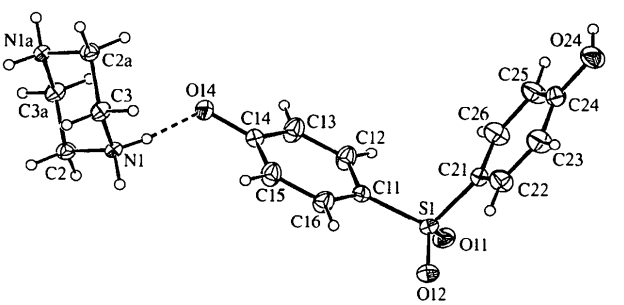



Fig. 1. A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

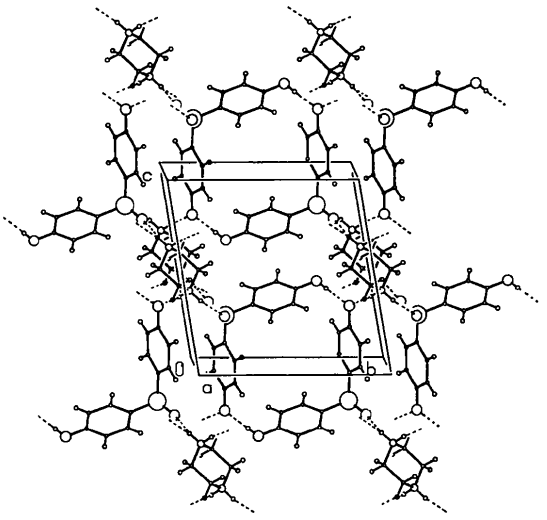


Fig. 2. A view of the crystal structure viewed along the [100] direction, showing the hydrogen-bond network.

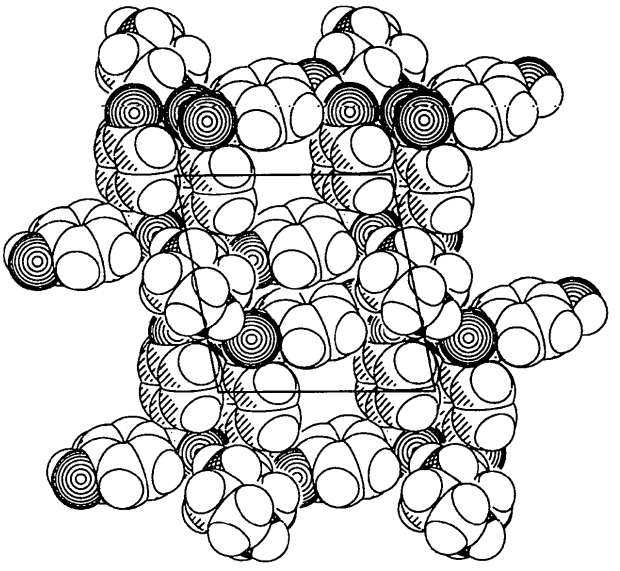


Fig. 3. A space-filling view of the crystal structure showing the channels parallel to the [100] direction.

Bernstein, Davis, Shimoni & Chang, 1995), while the bifurcated hydrogen bonds formed by the equatorial N—H bonds form chains characterized by the graph set $C_1^2(4)$; these motifs organize the phenolate dimers into stacks generated by the unit translation along the short *a* axis. Finally, the N—H···O hydrogen bonds formed by the axial N—H bonds serve to tie neighbouring stacks together, forming a continuous array with the channel axes all parallel to the [100] direction; this cross-linking motif has graph set $C_3^2(19)$, where the chain direction is parallel to the [111] direction. Each stack encloses a linear channel which is lined with arene rings and is therefore expected to be hydrophobic (Fig. 3). These channels have a volume of 82.2 Å$^3$ per unit cell, just over 11% of the total cell volume, with a cross-sectional area of 14.5 Å$^2$ and a diameter of 4.3 Å, *i.e.* of molecular dimensions. Careful analysis using the *SQUEEZE* option in *PLATON* (Spek, 1995*a*) showed that the channels did not contain any trace of methanol.

When the preparation was repeated using acetonitrile as solvent instead of methanol, another adduct, (III), was obtained having composition piperazine–sulfonyldiphenol–$CH_3CN$ (1/2/1). The powder X-ray diffractograms of (I) and (III) were virtually identical, suggesting that the framework structure of (I) is retained in the acetonitrile solvate (III). Although single crystals of (III) diffracted very poorly at ambient temperature, a data set was collected which confirmed the retention of the framework and showed an ill-defined elongated portion of electron density consistent with the presence of $CH_3CN$ molecules lying in the channels and being disordered about inversion centres. No coordinates were derived for the '$CH_3CN$' atoms. Low-temperature studies on (III) are planned.

Although aqueous solution p$K_a$ values are not quantitatively applicable to reactions in non-aqueous media, nevertheless, in terms of the aqueous solution p$K_a$ values for piperazine [p$K_1$ 5.68 and p$K_2$ 9.82 (Long, 1961)] and those for typical phenols [*ca* 10 (Long, 1961)], the double protonation of piperazine observed in (I) is unexpected. The driving force for the proton transfers is undoubtedly the cohesive energy of the resulting solid, made up of the ionic lattice energy and the hydrogen-bonding energy, itself enhanced by the ionic nature of the components (Aakeröy & Seddon, 1993). The major structural differences between (I) and the sheet structure of (II) (Coupar, Ferguson & Glidewell, 1996*a*) provide a good illustration of the mismatch strategies adopted when the numbers of hydrogen-bond donors and acceptors in a system differ (Hunter, 1991; Hanton, Hunter & Purvis, 1992; Glidewell & Ferguson, 1994). In (I), the excess of acceptors is accommodated by formation of C—H···O and bifurcated N—H···O hydrogen bonds, while in (II), the deficit of conventional acceptors is accommodated by formation of N—H···$\pi$(arene) hydrogen bonds.

This rationale indicates that the use of moderately basic polyamines with polyphenols or other hydrogen-bond donors, which themselves also contain an excess of hydrogen-bond acceptor sites, should constitute an effective strategy for the self-assembly of three-dimensional organic arrays stabilized by both hydrogen bonding and ionic lattice energy. Appropriate design of the components should lead to channels or pores of predictable size.

## Experimental

Crystallization at ambient temperature of methanol solutions containing 4,4′-sulfonyldiphenol and piperazine, with piper-

azine:bisphenol molar ratios in the range 1:1 to 1:2, yielded the same analytically pure phase of (I) having the composition piperazine–4,4′-sulfonyldiphenol (1/2). Analysis for (I): found C 57.3, H 5.2, N 4.8%; $C_{28}H_{30}N_2O_8S_2$ requires C 57.3, H 5.2, N 4.8%. Similar preparations using acetonitrile solutions with molar ratios again in the range 1:1 to 1:2 yielded analytically pure (III) of composition piperazine–4,4′-sulfonyldiphenol–acetonitrile (1/2/1). Analysis for (III): found C 57.7, H 5.2, N 6.4%; $C_{30}H_{33}N_3O_8S_2$ requires C 57.4, H 5.3, N 6.7%.

*Crystal data*

$C_4H_{12}N_2^{2+}.2C_{12}H_9O_4S^-$
$M_r$ = 586.66
Triclinic
$P\bar{1}$
$a$ = 5.6703 (5) Å
$b$ = 11.4012 (12) Å
$c$ = 11.6108 (13) Å
$\alpha$ = 100.619 (13)°
$\beta$ = 92.757 (7)°
$\gamma$ = 96.479 (8)°
$V$ = 731.22 (13) Å$^3$
$Z$ = 1
$D_x$ = 1.332 Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda$ = 0.7107 Å
Cell parameters from 25 reflections
$\theta$ = 10.35–20.52°
$\mu$ = 0.233 mm$^{-1}$
$T$ = 294 (1) K
Block
0.42 × 0.40 × 0.29 mm
Colorless

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3165 measured reflections
3165 independent reflections
2005 observed reflections [$I > 2\sigma(I)$]

$\theta_{max}$ = 26.9°
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 14$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity decay: 4.8%

*Refinement*

Refinement on $F^2$
$R(F)$ = 0.0531
$wR(F^2)$ = 0.1416
$S$ = 0.981
3165 reflections
182 parameters
H atoms riding (C—H 0.93 and 0.97, N—H 0.90 and O—H 0.82 Å)

$w = 1/[\sigma^2(F_o^2) + (0.0789P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.456 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.253 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 (Å²)*

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

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| S1 | 0.07376 (12) | 0.21301 (6) | 0.22491 (5) | 0.0332 (2) |
| O11 | 0.3226 (3) | 0.2010 (2) | 0.2425 (2) | 0.0417 (5) |
| O12 | −0.0953 (4) | 0.1398 (2) | 0.2791 (2) | 0.0448 (5) |
| O14 | −0.1826 (4) | 0.1347 (2) | −0.2818 (2) | 0.0431 (5) |
| O24 | −0.0528 (4) | 0.7193 (2) | 0.3898 (2) | 0.0563 (6) |
| C11 | −0.0015 (4) | 0.1857 (2) | 0.0740 (2) | 0.0307 (6) |
| C12 | 0.1632 (5) | 0.2198 (3) | −0.0011 (2) | 0.0472 (7) |
| C13 | 0.1023 (5) | 0.2032 (3) | −0.1199 (2) | 0.0494 (8) |
| C14 | −0.1241 (5) | 0.1500 (2) | −0.1668 (2) | 0.0337 (6) |
| C15 | −0.2844 (5) | 0.1152 (3) | −0.0898 (2) | 0.0462 (7) |
| C16 | −0.2255 (5) | 0.1332 (3) | 0.0294 (2) | 0.0448 (7) |
| C21 | 0.0381 (5) | 0.3643 (2) | 0.2767 (2) | 0.0330 (6) |
| C22 | −0.1554 (5) | 0.3951 (3) | 0.3379 (3) | 0.0470 (7) |
| C23 | −0.1809 (6) | 0.5139 (3) | 0.3758 (3) | 0.0515 (8) |
| C24 | −0.0179 (5) | 0.6038 (2) | 0.3523 (2) | 0.0400 (6) |
| C25 | 0.1763 (6) | 0.5732 (3) | 0.2918 (3) | 0.0551 (8) |
| C26 | 0.2059 (6) | 0.4539 (3) | 0.2553 (3) | 0.0504 (8) |
| N1 | −0.5003 (4) | −0.0353 (2) | −0.3886 (2) | 0.0295 (5) |
| C2 | −0.3893 (5) | −0.1046 (2) | −0.4873 (2) | 0.0345 (6) |
| C3 | −0.6986 (4) | 0.0225 (2) | −0.4317 (2) | 0.0343 (6) |

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

| | | | |
|---|---|---|---|
| S1—O11 | 1.442 (2) | O24—C24 | 1.348 (3) |
| S1—O12 | 1.443 (2) | N1—C2 | 1.477 (3) |
| S1—C11 | 1.746 (2) | N1—C3 | 1.477 (3) |
| S1—C21 | 1.757 (3) | C2—C3$^i$ | 1.508 (3) |
| O14—C14 | 1.335 (3) | | |
| O11—S1—O12 | 118.03 (11) | C11—S1—C21 | 105.93 (11) |
| O11—S1—C11 | 108.17 (12) | C2—N1—C3 | 111.0 (2) |
| O11—S1—C21 | 107.59 (12) | N1—C2—C3$^i$ | 109.6 (2) |
| O12—S1—C11 | 108.71 (12) | N1—C3—C2$^i$ | 110.2 (2) |
| O12—S1—C21 | 107.78 (12) | | |
| O11—S1—C11—C16 | 147.6 (2) | O12—S1—C21—C26 | 168.4 (2) |
| O12—S1—C11—C16 | 18.3 (3) | C11—S1—C21—C26 | −75.4 (2) |
| C21—S1—C11—C16 | −97.3 (2) | O11—S1—C21—C22 | −140.1 (2) |
| O11—S1—C11—C12 | −34.1 (3) | O12—S1—C21—C22 | −11.9 (3) |
| O12—S1—C11—C12 | −163.4 (2) | C11—S1—C21—C22 | 104.3 (2) |
| C21—S1—C11—C12 | 81.0 (2) | C3—N1—C2—C3$^i$ | 58.0 (3) |
| O11—S1—C21—C26 | 40.1 (2) | C2—N1—C3—C2$^i$ | −58.4 (3) |

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

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O24—H24···O14$^i$ | 0.82 | 1.75 | 2.560 (3) | 170 |
| N1—H1$A$···O14 | 0.90 | 1.68 | 2.579 (3) | 173 |
| N1—H1$B$···O11$^{ii}$ | 0.90 | 2.37 | 2.985 (3) | 126 |
| N1—H1$B$···O12$^{iii}$ | 0.90 | 2.21 | 2.918 (3) | 136 |

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $-x, -y, -z$; (iii) $-1-x, -y, -z$.

Data collection: *CAD-4/PC Software* (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*. Program(s) used to refine structure: *NRCVAX*94 and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*94, *PLATON* (Spek, 1995*a*), *PLUTON* (Spek 1995*b*) and *ORTEP*II (Johnson, 1976). 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: AB1418). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

PAMELA I. COUPAR,[a] GEORGE FERGUSON[b] AND CHRISTOPHER GLIDEWELL[a]

[a]*School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland, and* [b]*Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1. E-mail: cg@st-andrews.ac.uk*

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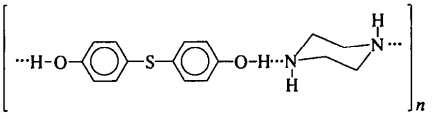
## Abstract

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