

## Hydrogen-bonded molecular ladders in 1,4-bis(4-chlorophenylsulfonyl)-2,5- dimethylbenzene

James L. Wardell,<sup>a</sup> John N. Low<sup>b</sup> and Christopher  
Glidewell<sup>c\*</sup>

<sup>a</sup>Department of Chemistry, University of Aberdeen, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, <sup>b</sup>Department of Applied Physics and Electronic and Mechanical Engineering, University of Dundee, Nethergate, Dundee DD1 4HN, Scotland, and <sup>c</sup>School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland  
Correspondence e-mail: cg@st-andrews.ac.uk

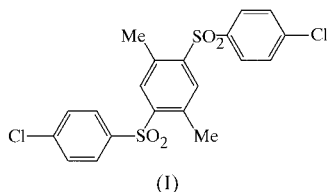
Received 5 April 2000

Accepted 18 April 2000

In the title compound, C<sub>20</sub>H<sub>16</sub>Cl<sub>2</sub>O<sub>4</sub>S<sub>2</sub>, the molecules lie across centres of inversion. A single type of intermolecular C—H···O hydrogen bond, with a C···O distance of 3.254 (3) Å and a C—H···O angle of 132°, links the molecules into ladders whose uprights form C(6) chains and whose rungs enclose centrosymmetric R<sub>2</sub><sup>2</sup>(22) rings.

### Comment

In molecular solids which contain an excess of hard hydrogen-bond acceptors over hard hydrogen-bond donors (Braga *et al.*, 1995), it is to be expected that C—H bonds, particularly those in aromatic systems, will participate as donors in hydrogen bonds of the types C—H···O or C—H···N (Hanton *et al.*, 1992). Aromatic sulfones are particularly effective in C—H···O hydrogen-bond formation between aromatic C—H bonds acting as hydrogen-bond donors and sulfone S=O bonds acting as acceptors (Glidewell *et al.*, 1995; Meehan *et al.*, 1997; Ferguson *et al.*, 1999). In particular, the bis(sulfones) (PhSO<sub>2</sub>)<sub>2</sub>CH<sub>2</sub> (Glidewell *et al.*, 1995) and (4-MeOC<sub>6</sub>H<sub>4</sub>-SO<sub>2</sub>)<sub>2</sub>CH<sub>2</sub> (Meehan *et al.*, 1997) form one-dimensional chains and a three-dimensional framework, respectively, as a result of

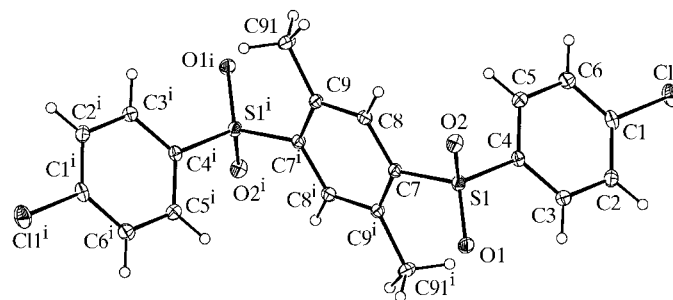


such hydrogen-bond formation. As an example of a bis(sulfone) in which a further aromatic nucleus has been incorporated between the two sulfone groups, we now report the structure of the title compound, (I), wherein the molecules are linked into a molecular ladder by C—H···O hydrogen bonds.

Compound (I) crystallizes in the space group  $P\bar{1}$  with  $Z = 1$ ; hence the molecules lie across centres of inversion and, for the sake of convenience, the reference molecule has been placed across the inversion centre at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . The molecular conformation of (I) (Fig. 1) is dominated by the near coplanarity of the O—S—C—C fragments (Table 1). As commonly observed in diaryl sulfones (Ferguson *et al.*, 1999), there is an electrostatic attraction between the S=O bond, which is polarized in the sense S<sup>+</sup>—O<sup>-</sup>, and an *ortho* C—H bond in the adjacent ring, polarized in the sense C<sup>-</sup>—H<sup>+</sup>. In the most common arrangement, as also found here, each O atom of the sulfone unit interacts with a different ring, so that the local symmetry around the S atom is close to C<sub>2</sub>.

Both of the S1—C7—C9<sup>i</sup> and C7<sup>i</sup>—C9—C9<sup>i</sup> bond angles [symmetry code: (i) 1 - x, 1 - y, 1 - z] are significantly greater than 120° (Table 1). This type of angular distortion has been observed in several diaryl sulfones where there is a methyl group adjacent to the SO<sub>2</sub> unit (Jeyakanthan *et al.*, 1998), and it may plausibly be interpreted as arising from repulsive interactions between the methyl group and the adjacent sulfone unit. The O—S—O bond angle is much larger than tetrahedral. All the bond lengths are typical of their types (Allen *et al.*, 1987).

There is a single type of intermolecular hydrogen bond (Table 2) linking the molecules. Atom C2 at (x, y, z), a component of the molecule centred at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , acts as hydrogen-bond donor to O2 at (x, y - 1, z), which is a component of the molecule centred at  $(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$ ; repetition of this hydrogen bond generates a C(6) chain running parallel to [010] and generated by translation (Fig. 2). The symmetry-related C2 atom in the original  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  molecule is at (1 - x, 1 - y, 1 - z), and this acts as donor to O2 at (1 - x, 2 - y, 1 - z), which is a component of the molecule centred at  $(\frac{1}{2}, \frac{3}{2}, \frac{1}{2})$ ; hence, another C(6) chain is generated, running antiparallel to the first. The overall supramolecular structure (Fig. 2) thus takes the form of a molecular ladder, in which the uprights are formed by a pair of antiparallel C(6) chains, while the rungs are provided by the central aryl rings of successive molecules. Between the rungs are R<sub>2</sub><sup>2</sup>(22) rings centred at  $(\frac{1}{2}, n, \frac{1}{2})$  (n = zero or integer), but the aromatic and methyl H atoms preclude the presence of any void space. A single ladder runs through each unit cell, and there are no significant interactions between

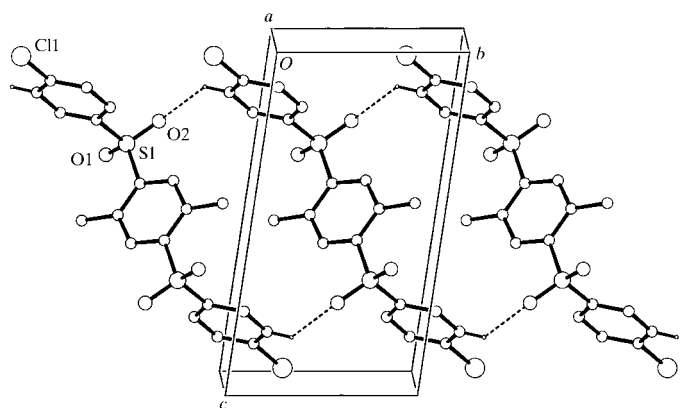


**Figure 1**

The molecule of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of an arbitrary radius [symmetry code: (i) 1 - x, 1 - y, 1 - z].

neighbouring ladders; in particular, there are no aromatic  $\pi \cdots \pi$  stacking interactions.

It is notable that the intermolecular hydrogen bonding does not involve the central aryl ring. By contrast, in each of  $(\text{PhSO}_2)_2\text{CH}_2$  (Glidewell *et al.*, 1995) and  $(4\text{-MeOC}_6\text{H}_4\text{SO}_2)_2\text{CH}_2$  (Meehan *et al.*, 1997), both of the C—H bonds of the central methylene unit are engaged in hydrogen-bond formation. It is thus of interest to consider some related compounds retrieved from the Cambridge Structural Database (CSD; Allen & Kennard, 1993). In  $(\text{PhSO}_2\text{CH}_2)_2$  (FAHNOR; Hauback & Mo, 1990), although the molecules could lie across centres of inversion, as in (I), they do not in



**Figure 2**

Part of the crystal structure of (I) showing the formation of a molecular ladder. For the sake of clarity, the atom labels are applied to the unit at  $(x, y - 1, z)$  and H atoms not involved in the supramolecular structure have been omitted.

fact do so; the molecules are again linked into molecular ladders, but the C—H $\cdots$ O hydrogen bonds forming the uprights use only H atoms from the central  $-\text{CH}_2-\text{CH}_2-$  unit. The ladders are linked into a two-dimensional array by further C—H $\cdots$ O hydrogen bonds involving the aromatic rings. For neither the *Z* isomer of  $\text{PhSO}_2\text{CH}=\text{CHSO}_2\text{Ph}$  (DEBYIS; De Lucchi *et al.*, 1985) nor the centrosymmetric *E* isomer (DEBYOY; De Lucchi *et al.*, 1985) are there any H-atom coordinates in the CSD; nonetheless, it is clear from the short intermolecular C $\cdots$ O distances that the intermolecular aggregation is dominated by the aromatic C—H bonds rather than those in the alkene fragment. The factors which determine the involvement of aromatic *versus* other C—H bonds in these systems are as yet not fully clear. However, it may be expected that aliphatic C—H bonds adjacent to  $\text{SO}_2$  units are more acidic than is typical for aliphatic C—H bonds, and thus more like aromatic C—H bonds in their hydrogen-bonding behaviour.

## Experimental

A sample of 2,5-bis(4-chlorophenylthio)-1,4-dimethylbenzene (Grant *et al.*, 1987) was oxidized using sodium periodate in  $\text{CH}_2\text{Cl}_2$  to yield (I). Crystals suitable for single-crystal X-ray diffraction were grown from an ethanol solution (m.p. 506–508 K).

## Crystal data

$\text{C}_{20}\text{H}_{16}\text{Cl}_2\text{O}_4\text{S}_2$   
 $M_r = 455.35$   
 Triclinic,  $P\bar{1}$   
 $a = 5.4859$  (2) Å  
 $b = 6.9595$  (4) Å  
 $c = 12.5211$  (7) Å  
 $\alpha = 98.6245$  (17)°  
 $\beta = 93.561$  (4)°  
 $\gamma = 92.174$  (3)°  
 $V = 471.18$  (4) Å<sup>3</sup>

$Z = 1$   
 $D_x = 1.605$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 2112 reflections  
 $\theta = 1.65\text{--}27.45^\circ$   
 $\mu = 0.592$  mm<sup>-1</sup>  
 $T = 150$  (2) K  
 Plate, colourless  
 $0.10 \times 0.10 \times 0.03$  mm

## Data collection

Nonius KappaCCD diffractometer  
 $\varphi$  and  $\omega$  scans with  $\kappa$  offsets  
 Absorption correction: multi-scan (SORTAV; Blessing, 1995, 1997)  
 $T_{\min} = 0.943$ ,  $T_{\max} = 0.985$   
 5965 measured reflections  
 2112 independent reflections

1689 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.039$   
 $\theta_{\max} = 27.45^\circ$   
 $h = -7 \rightarrow 7$   
 $k = -9 \rightarrow 8$   
 $l = -16 \rightarrow 16$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.039$   
 $wR(F^2) = 0.104$   
 $S = 1.073$   
 2112 reflections  
 128 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0411P)^2 + 0.1338P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.39$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.53$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

S1—O1	1.4322 (14)	S1—C7	1.782 (2)
S1—O2	1.4416 (14)	Cl1—C1	1.738 (2)
S1—C4	1.772 (2)		
O1—S1—O2	118.67 (9)	C8—C7—C9 <sup>i</sup>	121.76 (18)
O1—S1—C4	108.12 (9)	C8—C7—S1	115.96 (15)
O2—S1—C4	107.72 (9)	C9 <sup>i</sup> —C7—S1	122.24 (14)
O1—S1—C7	110.17 (9)	C8—C9—C7 <sup>i</sup>	115.95 (17)
O2—S1—C7	107.60 (9)	C7 <sup>i</sup> —C9—C91	124.97 (18)
C4—S1—C7	103.49 (9)	C8—C9—C91	119.06 (18)
O1—S1—C4—C3	−4.3 (2)	O2—S1—C7—C8	17.70 (17)

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

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
C2—H2 $\cdots$ O2 <sup>ii</sup>	0.95	2.54	3.254 (3)	132

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

Compound (I) crystallized in the triclinic system; space group  $P\bar{1}$  was assumed and confirmed by the analysis. H atoms were treated as riding, with C—H 0.95 (aromatic) and 0.98 Å (methyl). Examination of the structure with PLATON (Spek, 1999) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, using a Nonius KappaCCD diffractometer. The authors thank the staff for all their help and advice.

---

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1006). Services for accessing these data are described at the back of the journal.

---

## References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–37.
- Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
- Braga, D., Grepioni, F., Biradha, K., Pedireddi, V. R. & Desiraju, G. R. (1995). *J. Am. Chem. Soc.* **117**, 3156–3166.
- De Lucchi, O., Pasquato, L., Modena, G. & Valle, G. (1985). *Z. Kristallogr.* **170**, 267–274.
- Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
- Ferguson, G., Glidewell, C., Gregson, R. M. & Lavender, E. S. (1999). *Acta Cryst.* **B55**, 573–590.
- Glidewell, C., Lightfoot, P. & Patterson, I. L. J. (1995). *Acta Cryst.* **C51**, 1648–1651.
- Grant, D. W., Hogg, D. R. & Wardell, J. L. (1987). *J. Chem. Res. (S)*, pp. 392–393.
- Hanton, L. R., Hunter, C. A. & Purvis, D. H. (1992). *J. Chem. Soc. Chem. Commun.* pp. 1134–1136.
- Hauback, B. C. & Mo, F. (1990). *Z. Kristallogr.* **191**, 195–207.
- Jeyakanthan, J., Velmurugan, D., Panneerselvam, K., Soriano-Garcia, M., Perumal, S. & Chandrasekaran, R. (1998). *Acta Cryst.* **C54**, 630–633.
- Meehan, P. R., Gregson, R. M., Glidewell, C. & Ferguson, G. (1997). *Acta Cryst.* **C53**, 1975–1978.
- Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (1999). *PLATON*. Version of January 1999. University of Utrecht, The Netherlands.