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## Key indicators

Single-crystal X-ray study  
T = 296 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$   
R factor = 0.032  
wR factor = 0.088  
Data-to-parameter ratio = 15.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

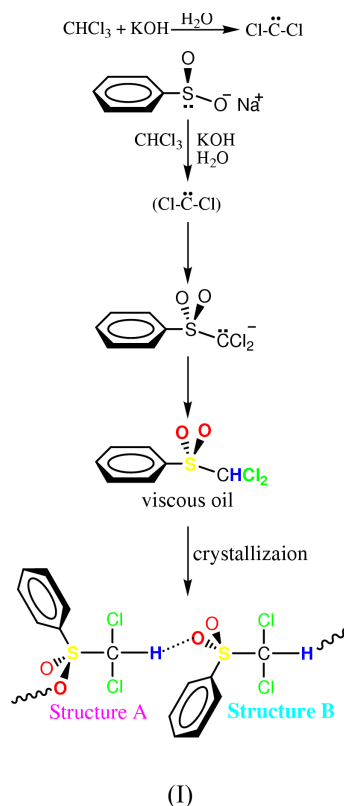
## Dichloromethyl phenyl sulfone

The unequivocal structure of dichloromethyl phenyl sulfone,  $\text{C}_7\text{H}_6\text{Cl}_2\text{O}_2\text{S}$ , (I), via X-ray analysis is reported for the first time. Prepared from the reaction of sodium benzenesulfinate with chloroform in KOH, (I) exhibited a sharp melting point, 331.5–332.0 K. Several different melting points have been reported. We find that (I) crystallizes as two chemically identical molecules in the asymmetric unit, but with a number of small geometric differences between the two molecules. Intermolecular  $\text{Cl}_2\text{C}-\text{H}\cdots\text{O}-\text{S}(\text{O})-\text{Ph}$  hydrogen bonding between the two geometrically different molecules produces infinite molecular chains, which may induce the small geometric differences exhibited in the two molecules of (I).

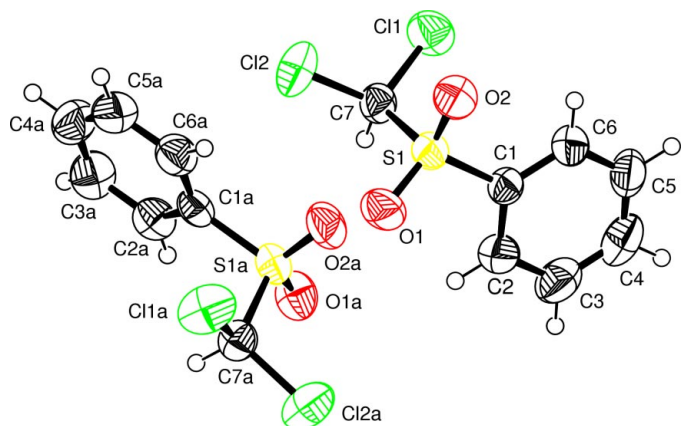
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## Comment

We first encountered 'problems' with dichloromethyl phenyl sulfone, (I), during its synthesis from the reaction of sodium benzenesulfinate with  $\text{CHCl}_3$  in aqueous KOH (Chan-Yu-King, 1986), illustrated in the Scheme.



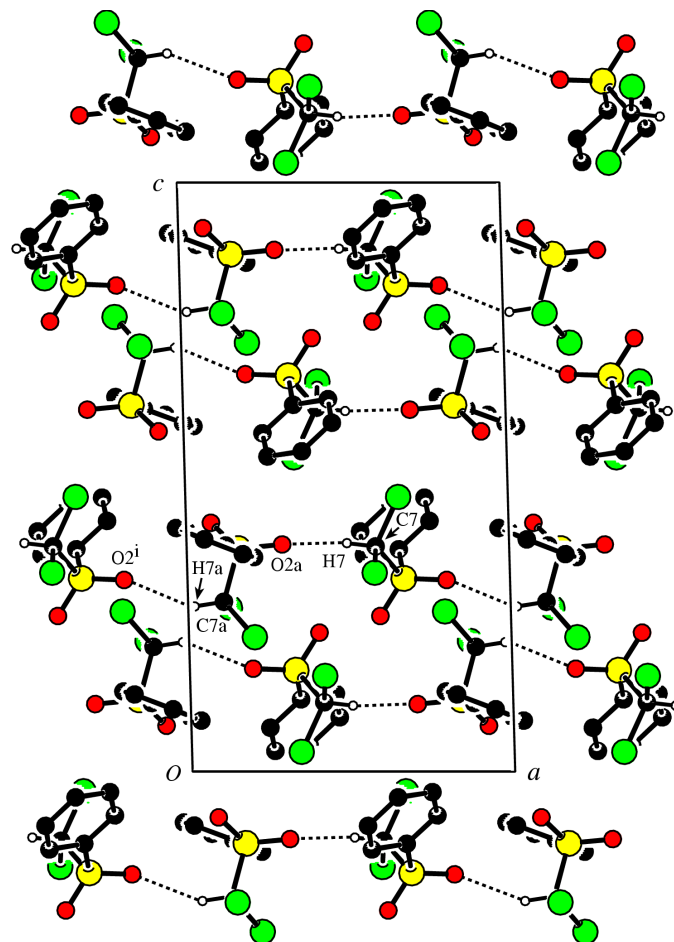
Depending on the mode of isolation, it remained as a viscous oil or its crystals exhibited various melting points: 302–303, 316–317, and 331.0–331.5 K. The  $^1\text{H}$ , as well as the  $^{13}\text{C}$ ,



**Figure 1**  
The molecular structure and atom-numbering scheme for (I), with displacement ellipsoids at the 50% probability level. Both molecules in the asymmetric unit are shown.

NMR spectra of the oil and the highest-melting crystals were virtually identical and very well fit the pattern expected from dichloromethyl phenyl sulfone. Several different melting points were also reported in the literature: 354.5–356.0 K (Middelbos *et al.*, 1971), 352–354 K (Grossert *et al.*, 1984), 332–333 K (Galvagni *et al.*, 1990), 329 K (Otto, 1889), and 328 and 329 K (Bohme & Gran, 1953). Questions arose, therefore, as to the true identity of this compound and its true melting point. To this end, an X-ray crystal structure analysis of our product, which melted sharply at 331.5–332.0 K, was undertaken to ascertain its structure.

The molecular structure with atom labels is shown in Fig. 1. There is no question that the compound is dichloromethyl phenyl sulfone. Two crystallographically distinct molecules of (I) in the asymmetric unit are chemically identical but are slightly different geometrically, as shown by the parameters compared in Table 1. The geometrical differences between the two crystallographically distinct molecules are reflected mainly in their corresponding torsion angles, and may be associated with their packing. Indeed, an examination of close intermolecular contacts reveals intermolecular hydrogen bonding involving the acidic  $\alpha$ -H atom and an O atom of the sulfonyl group,  $\text{Cl}_2\text{C}-\text{H}\cdots\text{O}-\text{S}(\text{O})-\text{Ph}$ , leading to infinite molecular chains parallel to the  $a$  axis, shown in the packing diagram (Fig. 2). The chains consist exclusively of the two geometrically different molecules, alternately hydrogen bonded to each other *via* the  $\text{Cl}_2\text{C}-\text{H}$  group of one molecule with the  $\text{O}-\text{S}(\text{O})-\text{Ph}$  of a geometrically different molecule, the  $\text{Cl}_2\text{C}-\text{H}$  of the latter molecule with the  $\text{O}-\text{S}(\text{O})-\text{Ph}$  of another molecule of the first type, and so on. The two hydrogen bonds per molecule making up the chain are also significantly different from each other, as shown by the data in Table 2. We propose that this difference in hydrogen-bonding parameters exhibited by the two hydrogen-bonded molecules of (I) may cause it to exist as two crystallographically distinct molecules in the asymmetric unit. The dichloromethyl group of (I), like the related  $\alpha$ -bromoisopropyl group in 2-bromo-2-propyl phenyl sulfone, did not exhibit the rotational disorder



**Figure 2**  
The molecular packing and hydrogen bonding in (I), viewed down the  $b$  axis. Phenyl H atoms have been omitted for clarity. [Symmetry code: (i)  $x-1, y, z$ .]

displayed by the  $\alpha$ -bromo- and  $\alpha$ -chloroisopropyl groups in the corresponding crystalline mesityl sulfones (*cf.* Meyers *et al.*, 2001; Robinson, Parady *et al.*, 2001; Chan-Yu-King *et al.*, 2001) and a related  $\alpha$ -bromo ketone (Robinson, Sandrock *et al.*, 2001).

These results confirm that 331.5–332.0 K is the correct melting point of (I). The substantially higher melting points reported by Middelbos *et al.* (1971) and Grossert *et al.* (1984), noted above, are virtually identical to that of benzenesulfonic acid, which would be formed on acidification of residual sodium benzenesulfinate, the major reactant in the Middelbos synthesis and possible side product in the Grossert method. However, the viscous oil that did not crystallize, which formed in one of our syntheses, as well as the product which melted sharply at 302–303 K and the one that melted at 316–317 K, may also be compound (I), but at different stages of hydrogen-bonded chain formation or with different types of hydrogen bonding, or even without hydrogen bonding. The tendency of (I) to lose crystallinity in the X-ray beam indeed may reflect a breakdown of the hydrogen bonding in the crystal.

## Experimental

Compound (I) was prepared by treating sodium benzenesulfinate with  $\text{CHCl}_3$  in an aqueous solution of KOH, as reported previously (Middelbos *et al.*, 1971). The mixture was heated at *ca* 343 K for 12 h to provide two layers, which were separated. The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$ , the extracts were added to the original organic layer, and the combined solution was dried (anhydrous  $\text{MgSO}_4$ ) and evaporated in vacuo to a colorless viscous oil (42% yield). Crystallization was not effected either by scratching the container side-walls, or by keeping the oil in the freezer ( $\ll 273$  K) for 24 h. However, NMR ( $\text{CDCl}_3$ ) showed this product was pure;  $^1\text{H}$ :  $\delta$  6.28 (*s*, 1H), 7.40–7.80 (*m*, 3H), 8.05 (*dd*,  $J = 8$  Hz, 2 Hz, 2H);  $^{13}\text{C}$ :  $\delta$  79.8, 129.2, 131.1, 132.1, 135.5. Some of this viscous oil was removed and added to hexane, and the mixture was heated to boiling. The hexane solution was removed from the viscous oil on the bottom and put in the freezer for 12 h. White crystals separated and were filtered off and dried by evaporation: m.p. 302–303 K. Some of these crystals were removed and added to the oil that did not dissolve in the hexane; the oil slowly crystallized at room temperature, yielding white crystals, also m.p. 302–303 K. The original viscous oil was similarly seeded and slowly crystallized at room temperature; these crystals also melted at 302–303 K. After standing at room temperature for 5 d, they were removed; m.p. 330–331 K. A variety of melting points have been reported for (I), and are discussed above. Middelbos *et al.* (1971) reported recrystallizing their product from ethanol. Ethanolic solutions of our viscous oil failed to form any solids in the freezer, even from very concentrated solution. Addition of a small amount of water to the ethanolic solution at room temperature caused the separation of an oil; when carried out with the solution immersed in an ice bath, the addition of water caused the formation of white microcrystals, m.p. 315–317 K (vacuum dried at 303–313 K for 15 min, m.p. 317–318 K), which did not change even after the crystals were dried *in vacuo* for 15 h at room temperature. But, after standing for 5 d, these same crystals exhibited m.p. 331–331.5 K, as we originally found from crystallization in hexane solution kept in the freezer. In several cases, the melt from these crystals in the melting point capillary was allowed to cool. No recrystallization occurred even down to 312 K. When the capillary was removed from the bath, no crystallization occurred until the tube was tapped gently on a hard surface. This recrystallized material again had m.p. 331–331.5 K. The procedure was repeated with identical results.

### Crystal data

$\text{C}_7\text{H}_6\text{Cl}_2\text{O}_2\text{S}$	$D_x = 1.604 \text{ Mg m}^{-3}$
$M_r = 225.09$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 10.353$ (3) Å	$\theta = 13.7$ – $16.2^\circ$
$b = 9.5269$ (10) Å	$\mu = 0.87 \text{ mm}^{-1}$
$c = 18.9124$ (18) Å	$T = 296 \text{ K}$
$\beta = 91.541$ (14) $^\circ$	Prism, colorless
$V = 1864.6$ (7) Å $^3$	$0.41 \times 0.35 \times 0.30 \text{ mm}$
$Z = 8$	

### Data collection

Rigaku AFC-5S diffractometer	$R_{\text{int}} = 0.018$
$\omega$ scans	$\theta_{\text{max}} = 25.1^\circ$
Absorption correction: $\psi$ scan (North <i>et al.</i> , 1968)	$h = 0 \rightarrow 12$
$T_{\text{min}} = 0.723$ , $T_{\text{max}} = 0.769$	$k = 0 \rightarrow 11$
3501 measured reflections	$l = -22 \rightarrow 22$
3305 independent reflections	3 standard reflections
2137 reflections with $I > 2\sigma(I)$	every 100 reflections
	intensity decay: 0.9%

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0253P)^2 + 0.876P]$
$R[F^2 > 2\sigma(F^2)] = 0.032$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.088$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.21 \text{ e \AA}^{-3}$
3305 reflections	$\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$
218 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.0119 (5)

**Table 1**

Selected geometric parameters (Å,  $^\circ$ ).

C1–C7	1.753 (3)	S1–O2	1.430 (2)
C1a–C7a	1.745 (3)	S1a–O2a	1.429 (2)
C2–C7	1.746 (3)	S1–C1	1.754 (3)
C2a–C7a	1.749 (3)	S1a–C1a	1.752 (3)
S1–O1	1.425 (2)	S1–C7	1.824 (3)
S1a–O1a	1.428 (2)	S1a–C7a	1.816 (3)
O1–S1–O2	119.83 (14)	O2a–S1a–C7a	108.09 (15)
O1a–S1a–O2a	119.20 (14)	C1–S1–C7	102.10 (13)
O1–S1–C1	110.07 (14)	C1a–S1a–C7a	103.49 (14)
O1a–S1a–C1a	109.97 (14)	C2–C7–C1	111.72 (17)
O2–S1–C1	109.68 (14)	C2a–C7a–C1a	111.32 (17)
O2a–S1a–C1a	109.47 (15)	C2–C7–S1	108.24 (16)
O1–S1–C7	105.14 (14)	C2a–C7a–S1a	108.26 (16)
O1a–S1a–C7a	105.37 (14)	C11–C7–S1	111.31 (16)
O2–S1–C7	108.45 (14)	C1a–C7a–S1a	110.25 (17)
O1–S1–C1–C2	24.6 (3)	O1–S1–C7–C2	61.40 (19)
O1a–S1a–C1a–C2a	19.7 (3)	O1a–S1a–C7a–C2a	58.43 (19)
O2–S1–C1–C2	158.5 (2)	O2–S1–C7–C2	–67.91 (18)
O2a–S1a–C1a–C2a	152.4 (2)	O2a–S1a–C7a–C2a	–70.04 (19)
C7–S1–C1–C2	–86.6 (3)	C1–S1–C7–C2	176.34 (16)
C7a–S1a–C1a–C2a	–92.5 (2)	C1a–S1a–C7a–C2a	173.91 (16)
O1–S1–C1–C6	–155.9 (2)	O1–S1–C7–C1	–175.45 (16)
O1a–S1a–C1a–C6a	–160.5 (2)	O1a–S1a–C7a–C1a	–179.58 (16)
O2–S1–C1–C6	–22.1 (3)	O2–S1–C7–C1	55.2 (2)
O2a–S1a–C1a–C6a	–27.7 (3)	O2a–S1a–C7a–C1a	51.9 (2)
C7–S1–C1–C6	92.8 (3)	C1–S1–C7–C1	–60.51 (19)
C7a–S1a–C1a–C6a	87.3 (3)	C1a–S1a–C7a–C1a	–64.10 (19)

**Table 2**

Hydrogen-bonding geometry (Å,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C7–H7 $\cdots$ O2a	0.98	2.18	3.151 (4)	172
C7a–H7a $\cdots$ O2 <sup>i</sup>	0.98	2.42	3.305 (4)	149

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

Compound (I) loses crystallinity very slowly in air, the edges of the crystal faces becoming slightly rounded after weeks of exposure. In the X-ray beam the loss of crystallinity begins almost immediately. A thin coating of epoxy and a faster data collection rate allowed reasonably good data to be collected. All H atoms were refined as riding.

Data collection: *MSC/AFD Diffractometer Control Software* (Molecular Structure Corporation, 1996); cell refinement: *MSC/AFD Diffractometer Control Software*; data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SIR92* (Burla *et al.*, 1989); program(s) used to refine structure: *LS* in *TEXSAN* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2000); software used to prepare material for publication: *TEXSAN*, *SHELXL97* and *PLATON*.

This paper is dedicated to Dr James W. Neckers on the occasion of his 100th birthday.

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