

Neutron powder diffraction study of
perdeuterodimethyl sulfone

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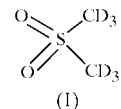
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The crystal structure of perdeuterodimethyl sulfone, $(\text{CD}_3)_2\text{SO}_2$ or $\text{C}_2\text{D}_6\text{O}_2\text{S}$, has been refined at 4.5 K against high-resolution neutron powder diffraction data. The structure determined previously by Sands [*Z. Kristallogr.* (1963), **119**, 245–251] at ambient temperature is shown to remain down to liquid helium temperature, and at 4.5 K the S–C and S–O bond distances are 1.441 (2) and 1.760 (2) Å, respectively. The molecules are distorted tetrahedra with C_{2v} point symmetry (crystallographic symmetry $m2m$ for S and m for C, O and one D atom) and are linked through a network of weak hydrogen bonds in the *C*-centred orthorhombic structure.

Comment

Dimethyl sulfone is a member of a family of compounds with the general formula Y_2XZ_2 ($\text{Y} = \text{H, F}$ or CH_3 ; $\text{X} = \text{O, S}$ or Se ; $\text{Z} = \text{O}$ or S) in which the molecules may be characterized in terms of distorted tetrahedra with C_{2v} symmetry. In view of recent interest in sulfone reactivity and chemical bonding (Dobado *et al.*, 1999), and structural analyses of coordinated sulfone ligands compared with the free molecules (Dikarev *et al.*, 2003), it is surprising that the fully refined low-temperature structure of dimethyl sulfone, (I), has not been reported. The heavy-atom structure of (I) has been known for some time (Sands, 1963), determined from single-crystal X-ray diffraction data at ambient temperature. The structure is orthorhombic (space group $Cmcm$), with bond lengths determined to a precision of some 0.02 Å and bond angles to 1°. A more recent investigation (Langs *et al.*, 1970) reports the structure, including H-atom positions, in space group $Amma$, and although there are inconsistencies in the reported coordinates according to the Cambridge Structural Database (CSD, Version 5.28 of January 2007; Allen, 2002), the structure is essentially in agreement with that proposed by Sands. Dimethyl sulfone has a relatively high melting point (382 K) in comparison with the sulfonyl halides, such as Cl_2SO_2 and F_2SO_2 , which are similar in structure and molecular weight, and early reports had suggested properties associated with plastic crystalline behaviour. Heat capacity measurements

(Clever & Westrum, 1970) found no corroborative evidence supporting plastic behaviour in (I) or associated structural phase transitions between 5 K and the melting point. The present study, using modern high-resolution neutron powder diffraction techniques, aims to provide a more accurate reference structure at low temperature.



The molecular structure of (I) at 4.5 K is presented in Fig. 1 and plots of the Rietveld refinement results are shown in Fig. 2. The derived molecular dimensions are given in Table 1 and in general there is good agreement with results from density functional theory calculations (Dobado *et al.*, 1999), molecular mechanics calculations (Allinger & Fan, 1993) and electron diffraction (Hargittai & Hargittai, 1974). The main exception is the O–S–O bond angle, which is some 2° smaller in the crystal structure, although good agreement is maintained for the C–S–C bond angle. The S–C bond length is also shorter by some 0.2 Å in the 4.5 K structure, which is a small but still significant discrepancy.

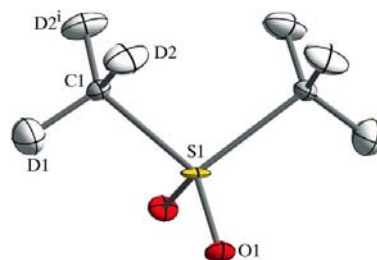


Figure 1

The molecular structure of (I) at 4.5 K, showing the atom-numbering scheme for the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level. Unlabelled atoms are related to labelled atoms by the symmetry operator $(-x, y, z)$.

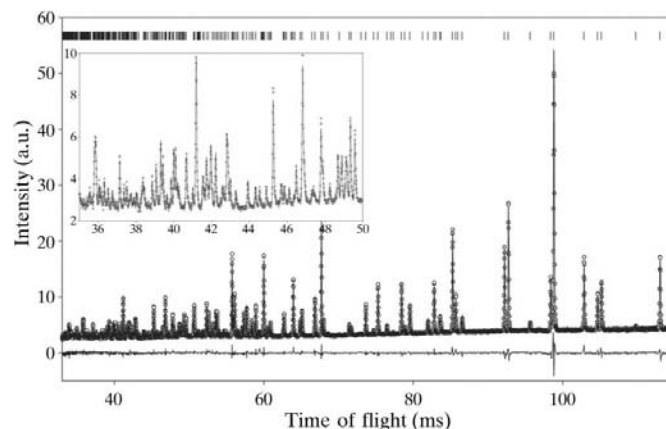


Figure 2

The final Rietveld plot of (I) at 4.5 K, showing the calculated (line), observed (open circles) and difference (lower) profiles. Vertical bar markers indicate calculated Bragg peak positions. The equivalent d -spacing range corresponds to 0.68–2.38 Å (0.73–1.04 Å inset).

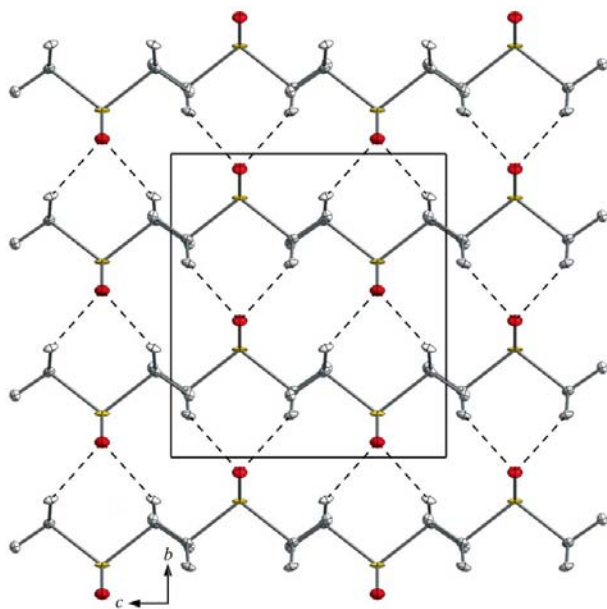


Figure 3
The hydrogen bonding (dashed lines) in the crystal structure of (I), viewed along the crystallographic *a* direction.

The difference in molecular conformation between the crystal and gas-phase structures is presumably a consequence of weak hydrogen bonding in the former. The effect of these nonbonded interactions was also reported by Machida *et al.* (1979) following analysis of the vibrational spectra recorded on both normal and perdeuterodimethyl sulfone. Fig. 3 shows the hydrogen bonding in (I) at 4.5 K and geometric details are given in Table 2. The C–S–C plane of each molecule is aligned parallel to the crystallographic *c* axis and these sheets are crosslinked by hydrogen bonds. Similar behaviour has been reported in the corresponding selenone structure (Dikarev *et al.*, 2003), which also shows hydrogen bonding in the solid state.

In the crystal structure, the S atom lies on a site of symmetry *m2m*, and the C and O atoms, along with one D atom, lie on mirror planes.

Experimental

(CD₃)₂SO₂ (1 g) (99 atom% D; Sigma Aldrich Chemical Ltd) was sealed in an 8 mm diameter vanadium sample can and loaded into a standard vanadium-tailed 'orange' cryostat (Brochier, 1977). Data were recorded using the high-resolution powder diffractometer (HRPD) at the ISIS Facility, Rutherford Appleton Laboratory, UK, at backscattering $2\theta = 168^\circ$ over the time-of-flight range 30–130 ms, corresponding to a *d*-spacing range of some 0.6–2.6 Å. The sample has a waxy appearance and data were recorded at 293 K for a brief period of 15 μAh (*ca* 25 min) to check first the crystallinity of the powder. [Refined lattice constants at 293 K are *a* = 7.3276 (1) Å, *b* = 8.0182 (1) Å, *c* = 7.3457 (1) Å and *V* = 431.60 (1) Å³.] The sample was then cooled to 4.5 K and measurements made for a period of 200 μAh (*ca* 6 h).

Crystal data

C₂D₆O₂S
M_r = 100.15
Orthorhombic, *Cmcm*
a = 7.12899 (2) Å
b = 7.93194 (3) Å
c = 7.17658 (2) Å
V = 405.81 (1) Å³

Z = 4
Time-of-flight neutron radiation
T = 4.5 K
Specimen shape: cylinder
25 × 8 mm
Particle morphology: irregular powder, white

Data collection

HRPD diffractometer, ISIS, RAL, UK
Specimen mounting: standard cylindrical vanadium sample holder

Scan method: time-of-flight, 30–130 ms

Refinement

R_p = 0.027
R_{wp} = 0.037
R_{exp} = 0.019
R_B = 0.073
S = 1.98
Wavelength of incident radiation: 1.24–5.36 Å

Excluded region(s): none
Profile function: *GSAS TOF* profile function number 3
370 reflections
48 parameters
Preferred orientation correction: none

Table 1

Selected geometric parameters (Å, °).

C1–D1	1.0796 (13)	D1–D2	1.7928 (13)
C1–D2	1.0959 (8)	O1–S1	1.4405 (19)
C1–S1	1.760 (2)	O1–O1 ⁱⁱ	2.4551 (15)
D1–C1–D2	110.98 (9)	C1–S1–C1 ⁱⁱ	103.69 (16)
D1–C1–S1	107.33 (12)	C1–S1–O1	108.86 (4)
D2–C1–D2 ⁱ	109.79 (12)	C1 ⁱⁱ –S1–O1	108.86 (4)
D2–C1–S1	108.84 (9)	O1–S1–O1 ⁱⁱ	116.9 (2)

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

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C1–D1...O1 ⁱⁱⁱ	1.08 (1)	2.70 (1)	3.6395 (14)	146 (1)
C1–D2...O1 ^{iv}	1.10 (1)	2.47 (1)	3.4485 (13)	148 (1)

Symmetry codes: (iii) $-x, -y, -z + 1$; (iv) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

The diffraction data were analysed using the Rietveld method implemented in the *GSAS* program suite (Larson & Von Dreele, 1994). The peak shape was modelled using the type 3 time-of-flight profile function comprising the convolution of back-to-back exponentials with a pseudo-Voigt function. The background was modelled using a shifted Chebyshev function comprising ten terms. The structure was refined without the use of constraints and using anisotropic displacement parameters for all atoms. Parameters for the starting model were taken from the ambient-temperature structure reported by Sands (1963), including estimated positions for the D atoms assuming a C–D bond length of 1.095 Å.

Data collection: ISIS instrument control program (ICP); cell refinement: *GSAS* (Larson & Von Dreele, 1994); data reduction: standard HRPD normalization routines; program(s) used to refine structure: *GSAS*; molecular graphics: *DIAMOND* (Brandenburg & Putz, 2004); software used to prepare material for publication: *GSAS*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3079). Services for accessing these data are described at the back of the journal.

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