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Neutron powder diffraction studies of dimethyl sulfoxide

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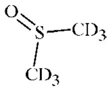
The crystal structure of perdeuterodimethyl sulfoxide, $(CD_3)_2SO$, has been refined at 2 and 100 K, and characterized as a function of temperature up to 275 K against high-resolution neutron powder diffraction data. The structure determined previously by Thomas, Shoemaker & Eriks [*Acta Cryst.* (1966), **21**, 12–20] ($T = 278$ K) is shown to remain down to 2 K. At 2 K, the S—O bond distance is 1.495 (2) Å. The fact that the molecule is distorted from ideal C_s point symmetry may be explained by the short D···O contacts of the respective methyl groups.

Comment

The coordination chemistry of sulfoxides boasts an extensive literature covering structural, spectroscopic and quantum chemical studies [see, for example, Calligaris (2004) and references therein]. However, in this recent review on metal sulfoxide complexes, it is noted that the reference value for the S—O bond length in pure dimethyl sulfoxide (DMSO) dates back to limited X-ray single-crystal studies by Thomas *et al.* (1966) and Viswamitara & Kannan (1966). The present study, using modern high-resolution neutron powder diffraction techniques, aims to provide a more accurate reference structure at low temperature.


(I)

The asymmetric unit of perdeuterodimethyl sulfoxide, (I), at 2 K is presented in Fig. 1, and plots of the Rietveld refinement results at 2 and 100 K are shown in Figs. 2 and 3, respectively. The molecular dimensions derived at both temperatures are unexceptional. The S—O bond length of 1.495 (2) Å (2 K) is in excellent agreement with the average value of 1.492 (2) Å reported by Calligaris (2004) for uncoordinated sulfoxides. [Calligaris also notes a recent unpublished study by Geremia at 164 K, quoting a distance of 1.480 (2) Å, or 1.499 Å on correction for thermal motion effects.] The deviations from ideal C_s point symmetry of the molecule are small but significant. For example, at 2 K, the methyl groups are eclipsed and rotated only 2.75 (13)° (C1) and 1.50 (13)° (C2) away from the ideal orientation. No significant differences are observed in S—C bond distances at this temperature.

Fig. 4 gives a representation of the packing in this structure. The molecules are arranged in layers parallel to the *ab* plane, with the S—O bond dipoles directed into each sheet. The coupling between molecules within a sheet is indicated by the selected intermolecular distances given in Table 1. Each D atom of atom C1 makes a short D···O contact, whereas there

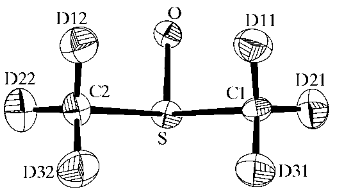


Figure 1
The asymmetric unit of (I) at 2 K, with displacement ellipsoids drawn at the 50% probability level.

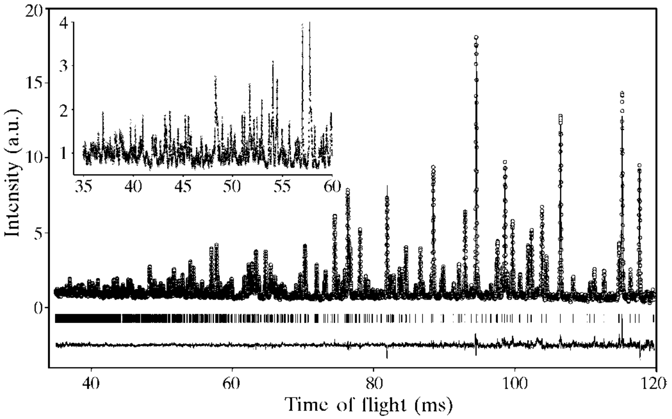


Figure 2
The final Rietveld plot of (I) at 2 K, showing the calculated (line), observed (o) and difference (lower) profiles. Vertical bar markers indicate calculated Bragg peak positions. The equivalent *d*-spacing range corresponds to 0.7–2.4 Å (0.7–1.2 Å inset).

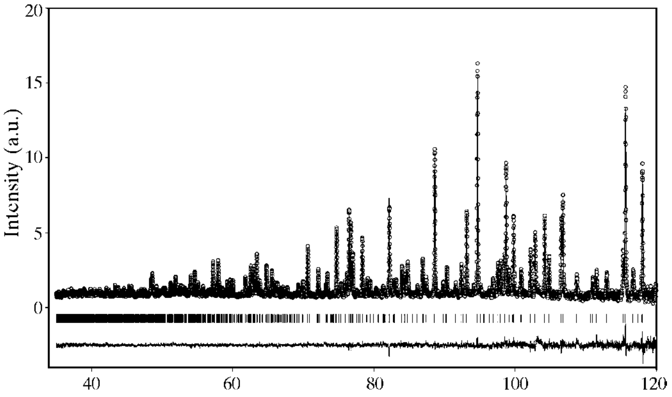


Figure 3
The final Rietveld plot of (I) at 100 K, showing the calculated (line), observed (o) and difference (lower) profiles. Vertical bar markers indicate calculated Bragg peak positions.

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is only one D···O contact associated with the C2 methyl group. This contrast in short contacts is reflected by the smaller displacement parameters observed for atom C1 compared with those of C2 and accounts in large part for the observed deviations from ideal molecular symmetry, which are seen to increase with temperature. At 100 K, significant differences are observed in the S—C bond lengths, which are 1.828 (3) and 1.788 (3) Å for atoms C1 and C2, respectively. This difference reflects the anisotropic environment of the molecule in the crystal, which is also observed in the thermal expansion.

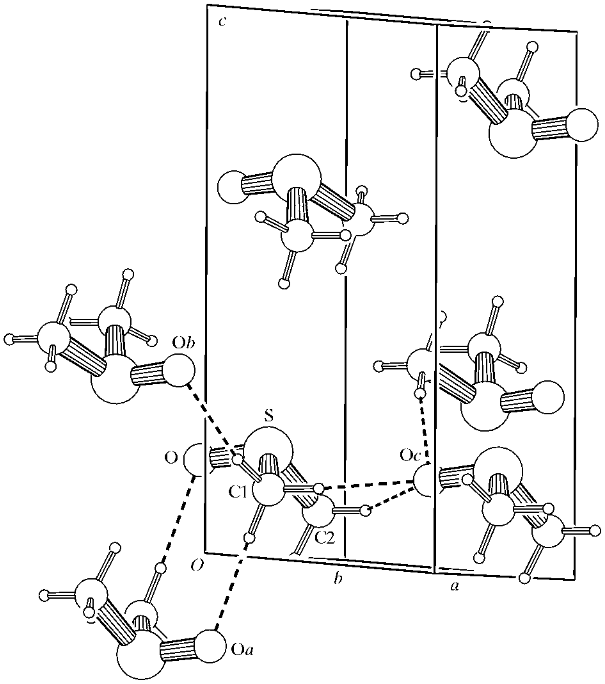

Figure 4
A packing diagram showing selected intermolecular contacts (see also Table 1). [Symmetry codes: (*a*) $-x, -y, -z$; (*b*) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (*c*) $1 + x, y, z$.]

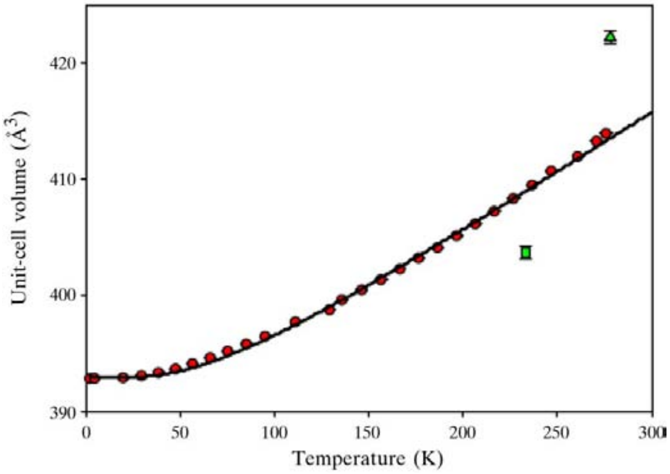

Figure 5
The variation in unit-cell volume (circles) and Debye fit (see *Comment*) with temperature on heating for (I). Values from the previous single-crystal studies of Thomas *et al.* (1966) (triangle) and Viswamitara & Kannan (1966) (square) are shown for comparison.

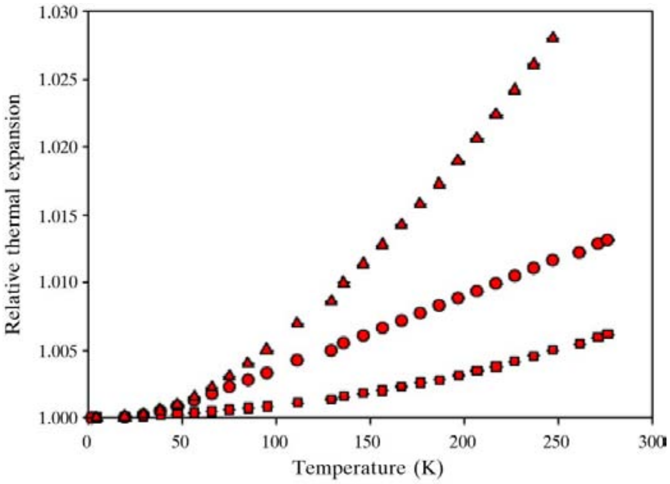

Figure 6
The thermal expansion of the *a* (circle), *b* (square) and *c* (triangle) lattice parameters relative to their values at 2 K.

The variation of unit-cell volume as a function of temperature is shown in Fig. 5. The data are well fitted using a Debye model (Sayetat *et al.*, 1998) with the refined parameters $V_{0\rm K}$ = 392.936 (1) Å^3 and θ_D = 251.8 (4) K. The relative thermal expansion along each of the unit-cell axes is shown in Fig. 6. The expansion along *c* is markedly greater than for *a* and *b*, reflecting the stronger intermolecular contacts within the layers of molecules in this plane.

Experimental

Deuterated DMSO melts at 291 K. A 99.99% deuterated sample supplied by Sigma Chemical Ltd was hand ground at liquid nitrogen temperatures. A sample (approximately 2 g) of the fine powder obtained was then sealed in a 11 mm-diameter vanadium sample can. The sample was loaded into a standard vanadium tailed 'orange' cryostat (Brochier, 1977) and the sample was annealed at 100 K for 2 h. Data were recorded at 100 K for a period of 112 µA h (*ca* 3 h). The sample was then cooled to 2 K and measurements made for a period of 150 µA h (*ca* 4 h). The sample was heated to 10 K and then up to 275 K in 10 K steps, recording data for 9 µA h (5 min) following a temperature equilibration period of 2 min. Data were recorded using the high-resolution powder diffractometer (HRPD) at the ISIS Facility, Rutherford Appleton Laboratory, England, at backscattering $\langle 2\theta \rangle$ = 168° over the time-of-flight range 30–130 ms corresponding to a *d*-spacing range of some 0.6–2.6 Å.

Compound (I) at 2 K

Crystal data

C_2D_6OS
M_r = 84.17
Monoclinic, $P2_1/c$
a = 5.2213 (1) Å
b = 6.7525 (1) Å
c = 11.2121 (1) Å
β = 94.8460 (3)°
V = 393.88 (1) Å^3
Z = 4
D_x = 1.418 Mg m^{-3}
Time-of-flight neutron radiation
λ = 1.24–5.36 Å
T = 2.0 K
White
Specimen shape: cylinder
25 × 11 mm
Particle morphology: irregular powder

Data collection

HRPD diffractometer
Specimen mounting: standard cylindrical vanadium sample holder

Refinement

$R_\mathrm{p} = 0.0366$
$R_\mathrm{wp} = 0.0419$
$R_\mathrm{exp} = 0.0304$
$S = 1.38$
Excluded region(s): none
GSAS TOF profile function number 2
93 parameters
All D-atom parameters refined
$(\Delta/\sigma)_\mathrm{max} = 0.04$
$\Delta\rho_\mathrm{max} = 0.10$ fm Å^{-3}
$\Delta\rho_\mathrm{min} = -0.10$ fm Å^{-3}
Preferred orientation correction: none

Compound (I) at 100 K

Crystal data

C_2D_6OS
$M_r = 84.17$
Monoclinic, $P2_1/c$
$a = 5.2390$ (1) Å
$b = 6.7581$ (1) Å
$c = 11.2696$ (1) Å
$\beta = 94.8053$ (3)°
$V = 397.60$ (1) Å^3
$Z = 4$
$D_x = 1.406$ Mg m^{-3}
Time-of-flight neutron radiation
$\lambda = 1.24$–5.36 Å
$T = 100.0$ K
White
Specimen shape: cylinder
25 × 11 mm
Particle morphology: irregular powder

Data collection

HRPD diffractometer
Specimen mounting: standard cylindrical vanadium sample holder

Table 1
Contact distances (Å) for DMSO.

	2 K	100 K
D11$\cdots$O$^\mathrm{i}$	2.3453 (15)	2.3715 (18)
D21$\cdots$O$^\mathrm{ii}$	2.3035 (14)	2.3101 (17)
D31$\cdots$O$^\mathrm{iii}$	2.3025 (12)	2.3097 (16)
D32$\cdots$O$^\mathrm{iii}$	2.5167 (14)	2.5184 (16)

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

Refinement

$R_\mathrm{p} = 0.0377$
$R_\mathrm{wp} = 0.0403$
$R_\mathrm{exp} = 0.0342$
$S = 1.17$
Excluded region(s): none
GSAS TOF Profile function number 2
93 parameters
All D-atom parameters refined
$(\Delta/\sigma)_\mathrm{max} = 0.04$
$\Delta\rho_\mathrm{max} = 0.14$ fm Å^{-3}
$\Delta\rho_\mathrm{min} = -0.17$ fm Å^{-3}
Preferred orientation correction: none

For both compounds, data collection: ISIS instrument control program (ICP, Rutherford Appleton Laboratory, England); cell refinement: *GSAS* (Larson & von Dreele, 1994); data reduction: standard HRPD normalization routines (Ibberson *et al.*, 1992); program(s) used to refine structure: *GSAS*; molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); 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: FA1152). Services for accessing these data are described at the back of the journal.

References

Brochier, D. (1977). ILL Technical Report 77/74. Institut Laue–Langevin, BP 156 – 38042 Grenoble Cedex 9, France.
Calligaris, M. (2004). *Coord. Chem. Rev.* **248**, 351–375.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Ibberson, R. M., David, W. I. F. & Knight, K. S. (1992). Report RAL-92-031. Rutherford Appleton Laboratory, Didcot, Oxfordshire, England.
Larson, A. C. & von Dreele, R. B. (1994). *GSAS.* LANSCE, Los Alamos National Laboratory, New Mexico, USA.
Sayetat, F., Fertey, P. & Kessler, M. (1998). *J. Appl. Cryst.* **31**, 121–127.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Thomas, R., Shoemaker, C. B. & Eriks, K. (1966). *Acta Cryst.* **21**, 12–20.
Viswamitara, M. A. & Kannan, K. K. (1966). *Nature* (*London*), **209**, 1016–1017.