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Chemical Analysis by X-Ray Crystallography—Structure of Dimethyl Sulphone

By D. A. Langs,† J. V. Silverton,*‡ and (in part) W. M. Bright

(*Chemistry Department, Georgetown University, Washington, D.C.* 20007)

Summary The crystal and molecular structure of dimethyl sulphone have been determined by *X*-ray diffraction techniques: the *R*-factor is 4% and bond lengths are given to *ca.* 0·005 Å.

The reaction products of an apparently unsuccessful attempt to prepare a copper complex using dimethyl sulphoxide as a solvent were set aside in a stoppered vial for several months. One of us (D.A.L.) noticed near the top of the vial slightly yellow prismatic crystals which appeared to have sublimed from the reaction products. Since volatile, solid products had not been expected, we attempted to determine the formula of the crystals using "Crystal Data Determinative Tables."[1] The substance is orthorhombic, with possible space groups: *Amma* (D_{2h}^{17}), $A2_1ma$ (C_{1v}^{12}) and $Ama2(C_{2v}^{16})$, cell dimensions: $a = 7{\cdot}36$, $b = 7{\cdot}36$, $c = 8{\cdot}00$ Å (all with probable error 0·01Å), but was not listed in "Crystal Data." A literature search did not produce identification and, since there was insufficient material for chemical analysis (three crystals about 0·5 mm in cross section) and, given the relatively high symmetry, the substance was apparently fairly simple, we attempted to solve the crystal structure. No knowledge of the formula was possible since we did not wish to risk losing any of the crystals in a density determination. 277 independent observable reflections were measured, using the moving counter–moving crystal method out to a 2θ angle of 60° with Mo-K_α *X*-radiation. The number of observations represents 88% of those possible at the 2θ limit. The cut-off limit for observations was twice the standard deviation based on counting statistics. The crystal used was sealed in a thin Pyrex capillary.

A Patterson map was interpreted in terms of three independent atoms, all in special positions of the space group *Amma*. One of the atoms had about twice the electron density of the others. Interatomic distances indicated that the molecule was probably dimethyl sulphone. The heavy atoms refined by diagonal least-squares to an *R*-factor of 10% on this assumption and a difference map then gave hydrogen atom positions in agreement with the formula assignment. Inclusion of the hydrogen atoms reduced the *R*-factor to 7%.

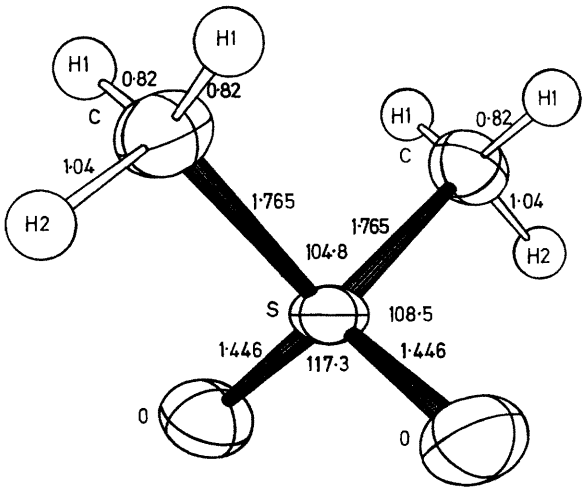

FIGURE. *Bond lengths and angles.*[2] *E.s.d.'s*: *lengths*: S–O, S–C, C–H(1), C–H(2); 0·003, 0·005, 0·05, 0·03 Å, *respectively*; *angles*: O–S–O, C–S–C, O–S–C; 0·2, 0·2, 0·1°, *respectively*. *All* O–S–C *angles are required to be equal by symmetry.*

Two cycles of full-matrix least-squares refinement gave an *R*-factor of 4·0% and the co-ordinates and thermal parameters given in the Table. The refinement appears to confirm the choice of space group. The bond lengths and angles are given in the Figure. There are no heavy atom intermolecular contacts less than 3·5 Å and the bond

† Present address: School of Chemistry, University of Sydney, Sydney, N.S.W. 2006, Australia.
‡ Present address: Laboratory of Chemistry, National Heart and Lung Institute, NIH, Bethesda, Maryland 20014.

lengths are in good agreement with previous electron diffraction[2] results, although estimated standard deviations in this study are lower than those previously quoted.

crystals, from the Aldrich Chemical Company, melting point range 2°, were unsuitable for crystallography, but a simple sublimation technique gave satisfactory crystals.

Positional and thermal parameters

[Fractional co-ordinates and thermal parameters are multiplied by 10^5. E.s.d.'s are given in parentheses and the absence of a standard deviation indicates that the value was required by symmetry and not refined. Temperature factor: $\exp(\beta_{11}h^2 + \beta_{12}hk + \beta_{13}hl + \beta_{22}k^2 + \beta_{23}kl + \beta_{33}l^2)$]

	x	y	z	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
S	25000	0	14856(18)	1914(36	0	0	1501(30)	0	802(20)
O	25000	16802(36)	5497(30)	3141(90)	0	0	2334(71)	854(54)	1627(58)
C	5957(79)	0	28264(56)	2268(120)	0	710(89)	1956(103)	0	1493(84)
H(1)	−5671(619)	0	20903(529)	Isotropic temperature factor B = 6·0 assigned					
H(2)	4799(455)	9191(358)	33928(314)						

For final confirmation of the formula we obtained some dimethyl sulphone and measured cell dimension data in agreement with the previous results. As received, the

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[1] J. D. M. Donnay, G. Donnay, E. G. Cox, O. Kennard, and M. V. King, "Crystal Data Determinative Tables," 2nd edn., A.C.A. Monograph No. 3, 1963.
[2] M. Lister and L. E. Sutton, *Trans. Faraday Soc.*, 1939, **35**, 495; R. W. Allen and L. E. Sutton, *Acta Cryst.*, 1950, **3**, 46.
[3] After application of 'riding motion' corrections following W. Busing and H. A. Levy, *Acta Cryst.*, 1964, **17**, 142, S–O becomes 1·473 Å and S–C 1·781 Å.