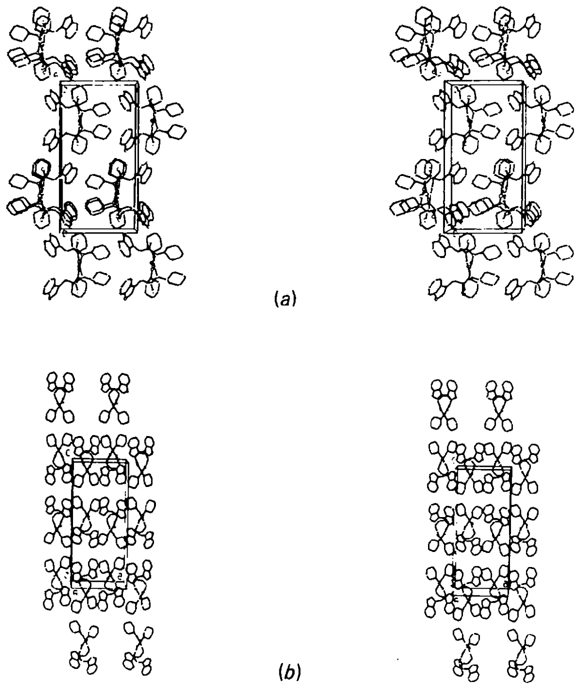

Fig. 2. Stereoscopic drawings of (*a*) (I) viewed along *a* axis, *b* axis vertical, *c* axis horizontal; and (*b*) (II) viewed along *a* axis, *c* axis vertical, *b* axis horizontal.

Fig. 2 shows the molecular packing of (I) and (II). In (I), the molecules related by *a*-glide symmetry form a molecular column with hexagonally arranged indole and cyclohexyl rings, and elongate parallel to the *a* axis. On the other hand, *A* and *B* in (II) form double layers consisting of indole and cyclohexyl rings perpendicular to the *c* axis. These layers in both crystals are stabilized by hydrogen-bond formation and van der Waals contacts with neighboring layers. Any specific interactions between the indole ring and the imide or urea group, which could account for the different spectral properties in their solution states, could not be observed in either crystal. The π-electron properties of the indole ring in (I) and (II) may be responsible for the difference, and are at present under consideration by molecular orbital methods.

References

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–73. Birmingham: Kynoch Press.

KENNARD, O. (1968). *International Tables for X-ray Crystallography*, Vol. III, p. 276. Birmingham: Kynoch Press.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

The Universal Crystallographic Computing System (1979). The Computation Center, Osaka Univ.

Acta Cryst. (1983). C**39**, 1297–1300

The Structure of Acetone Diethyl Sulfone,* $C_7H_{16}O_4S_2$, at 293 K and at 138 K

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Abstract. $M_r = 228\cdot3$, monoclinic, $P2/c$, $a = 17\cdot945\,(7)$, $b = 6\cdot229\,(1)$, $c = 19\cdot435\,(13)$ Å, $\beta = 90\cdot55\,(2)°$, $V = 2172\cdot3$ Å^3, $Z = 8$, $D_x = 1\cdot396$, $D_m = 1\cdot389$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1\cdot54178$ Å, $\mu = 43\cdot2$ cm^{-1}, $F(000) = 976$, $R = 0\cdot067$ for 4460 diffractometer data ($2\theta_{\max} = 150°$), $T = 293$ K; $a = 17\cdot811\,(10)$, $b = 6\cdot121\,(2)$, $c = 19\cdot272\,(9)$ Å, $\beta = 90\cdot67\,(4)°$, $V = 2100\cdot9$ Å^3, $Z = 8$, $R = 0\cdot052$ for 4155 diffractometer data ($2\theta_{\max} = 150°$), $T = 138$ K. There is no significant difference between the room-temperature structure and the low-temperature structure. There are three different types of molecules in the unit cell. Two of these possess a twofold symmetry and their midpoints occupy special positions at ($x = 0$, $z = \frac{1}{4}$) and at ($x = \frac{1}{2}$, $z = \frac{1}{4}$). The center of the third molecule lies very close to ($x = \frac{1}{4}$, $z = 0$). Such packing gave rise to very strong pseudo orthorhombic symmetry for the crystal structure. Three molecules in the asymmetric unit are quite similar. The average S—C(ethyl) distance of 1·775 (1) Å is significantly shorter than the average of the other S—C bonds [1·829 (1) Å] in the molecule. The angular disposition of bonds around the S atoms in the present structure differs from those observed in other sulfones.

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* 2,2-Bis(ethylsulfonyl)propane.

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Introduction. Acetone diethyl sulfone, commonly known as sulfanol, had been used in the past as a soporific drug. One of us (AKR) has been studying the ESR spectra of γ-irradiated sulfanol in single-crystal form in the temperature range 77–300 K and has found distinctly different spectral results at 77 K and at room temperature.

The ESR study of irradiated sulfones and polysulfones gives compelling evidence (Ayscough, Ivin & O'Donnell, 1965; Roy, 1966) that in these cases the weaker C—S bonds are preferentially broken in the irradiation process rather than C—C or C—H bonds. Preliminary analysis of the γ-irradiated sulfanol $[(CH_3)_2C(SO_2C_2H_5)_2]$ ESR spectra at 77 K (A. K. Roy, unpublished work) strongly indicates the presence of the $(CH_3)_2\dot{C}(SO_2C_2H_5)$ radical; no other detectable ESR signal from any other type of radical is found at 77 K. But as the temperature of the system is slowly raised it is found that above 173 K changes take place in the nature of the ESR spectra. The spectrum is dominated by a strong singlet plus some additional minor lines. The strong singlet could be attributed to the $C_2H_5\dot{S}O_2$ radical but the minor lines could not be identified properly in the absence of crystallographic data of sulfanol. The crystal structure analysis of sulfanol both at room temperature and at an available low temperature (138 K) was undertaken to help explain the spectral results.

Experimental. Colorless, prismatic crystals from dioxane at room temperature; separate crystals for data collection at 138 K (0·77 × 0·58 × 0·10 mm) and at 293 K (0·74 × 0·33 × 0·26 mm); all X-ray measurements on a Nonius CAD-4 automatic diffractometer fitted with a liquid-nitrogen low-temperature set-up; systematic absences: $h0l$, $l = 2n + 1$; cell parameters by least squares fit of $\pm 2\theta$ of 24 reflections (2θ range 18–42°) at low temperature and of 12 reflections (2θ range 20–40°) at room temperature, using Cu $K\alpha_1$ ($\lambda = 1{\cdot}54041$ Å); density at room temperature by flotation (mixture of carbon tetrachloride and hexane); intensity data of all unique reflections with $2\theta \leq 150°$ (at 293 K $-19 \leq h \leq 19$, $0 \leq k \leq 7$, $0 \leq l \leq 24$; at 138 K $-22 \leq h \leq 22$, $0 \leq k \leq 7$, $0 \leq l \leq 24$) (Cu $K\bar{\alpha}$, Ni filter, $\lambda = 1{\cdot}54178$ Å) using θ–2θ scan technique with variable scan width and variable horizontal aperture; maximum variation of monitor intensity 2% at low temperature and 4% at room temperature; at 138 K, data measured 4155, observed 4003 $[I > 2\sigma(I)]$; at 293 K, data measured 4460, observed 3969; absorption correction by a Gaussian method (Coppens, Leiserowitz & Rabinovich, 1965); individual structure amplitude given an experimental weight, $w_F = 1/\sigma_F^2$ [σ_F from counting statistics (Ealick, van der Helm & Weinheimer, 1975)].

Structure determined by a combination of direct methods, Patterson analyses and difference Fourier syntheses; refinement by block-diagonal least squares $[\sum w(\Delta F)^2$ minimized]; H atoms from a difference Fourier map; final refinement with anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for H atoms; refinement discontinued when (Δ/σ)max. $<0{\cdot}3$; for low-temperature structure, final $R = 0{\cdot}043$ for observed data, $R = 0{\cdot}052$ for all data, $S = 2{\cdot}4$; for room-temperature structure, final $R = 0{\cdot}048$ for observed data, $R = 0{\cdot}067$ for all data, $S = 2{\cdot}1$; analyses of $\sum w\Delta F^2$ *versus* $\sin\theta$ consistent; $\Delta\rho$ in final difference map $\pm 0{\cdot}4$ e Å^{-3}; scattering factors for S, C and O atoms and anomalous-dispersion factors for S atoms from *International Tables for X-ray Crystallography* (1974); hydrogen scattering factors from Stewart, Davidson & Simpson (1965); structure factor, least-squares refinement and Fourier calculations were performed using the NRC system of programs (Ahmed, 1966).

Discussion. The final atomic parameters are listed in Table 1.* The atom-numbering scheme is shown in a perspective drawing of a single molecule of sulfanol in Fig. 1.

There are three different types of molecules (designated molecule A, B and C respectively) in the unit cell. Two of these possess twofold symmetry and their mid-points occupy special positions at ($x = 0$, $z = \frac{1}{4}$) and at ($x = \frac{1}{2}$, $z = \frac{1}{4}$) respectively. Molecule A (Fig. 1) is slightly asymmetric and occupies a general position. However, its center lies very close to ($x = \frac{1}{4}$, $z = 0$). Such molecular orientation has led to a strong pseudo orthorhombic symmetry in the crystal structure, a fact reflected both in the cell parameters and in the intensity data (particularly in the $h0l$ data).

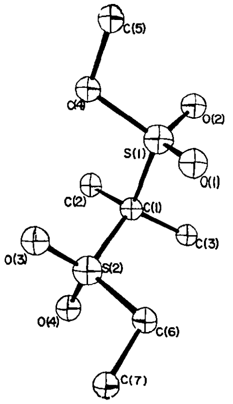

Fig. 1. Single molecule of sulfanol showing the atom-numbering scheme.

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* Lists of hydrogen parameters, distances and angles, anisotropic thermal parameters for nonhydrogen atoms, and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38613 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters and equivalent isotropic temperature factors* (Å²) *of the non-hydrogen atoms*

Upper values correspond to the low-temperature structure and lower values to the room-temperature structure

$$U_{eq} = 1/(6\pi^2)\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	$x(\times 10^5)$	$y(\times 10^4)$	$z(\times 10^5)$	$U_{eq}.(\times 10^4)$
Molecule *A*				
S(1)	17524 (2)	9838·9 (9)	4559 (2)	175 (3)
	17488 (3)	9818·6 (13)	4440 (3)	472 (4)
S(2)	32604 (2)	10088·7 (9)	−2640 (2)	162 (3)
	32504 (3)	10097·9 (12)	−2715 (3)	444 (4)
O(1)	20624 (10)	7914 (3)	7864 (9)	216 (8)
	20546 (11)	7949 (4)	7746 (11)	542 (12)
O(2)	12815 (10)	11238 (3)	8656 (10)	271 (9)
	12745 (13)	11177 (4)	8443 (13)	692 (16)
O(3)	29048 (10)	8709 (3)	−7775 (9)	253 (9)
	28994 (13)	8794 (4)	−7919 (11)	673 (15)
O(4)	37823 (10)	11721 (3)	−5050 (10)	270 (9)
	37720 (14)	11694 (4)	−4906 (14)	712 (15)
C(1)	25307 (13)	11596 (4)	1890 (11)	170 (10)
	25231 (15)	11551 (4)	1834 (14)	441 (14)
C(2)	22460 (15)	13342 (4)	−3186 (14)	256 (13)
	22458 (22)	13294 (6)	−3106 (19)	653 (21)
C(3)	28579 (15)	12597 (4)	8561 (13)	222 (12)
	28442 (19)	12519 (5)	8481 (16)	574 (18)
C(4)	12319 (14)	9004 (4)	−2930 (13)	252 (12)
	12416 (19)	8970 (7)	−2988 (19)	662 (21)
C(5)	5885 (15)	7537 (5)	−599 (15)	318 (14)
	6088 (22)	7527 (8)	−817 (25)	822 (27)
C(6)	37359 (14)	8443 (4)	3566 (13)	209 (11)
	37117 (18)	8413 (6)	3297 (16)	562 (17)
C(7)	43313 (15)	7068 (4)	20 (15)	275 (13)
	43096 (19)	7122 (6)	−160 (23)	713 (23)
Molecule *B*				
S(1)	7126 (2)	6926·7 (9)	29495 (2)	164 (3)
	7108 (3)	6961·4 (12)	29417 (3)	449 (4)
O(1)	3385 (10)	8590 (3)	33474 (9)	226 (8)
	3412 (11)	8577 (4)	33390 (11)	604 (14)
O(2)	11726 (10)	5374 (3)	33261 (10)	270 (9)
	11689 (14)	5448 (4)	33069 (14)	714 (16)
C(1)	0	5290 (5)	25000	169 (15)
	0	5351 (6)	25000	465 (21)
C(2)	3762 (15)	3900 (4)	19404 (14)	260 (13)
	3714 (23)	3989 (6)	19416 (20)	726 (23)
C(4)	12752 (14)	8202 (4)	23128 (13)	212 (11)
	12615 (16)	8238 (6)	23117 (16)	560 (18)
C(5)	18447 (15)	9704 (4)	26683 (15)	283 (13)
	18297 (19)	9694 (7)	26536 (23)	746 (24)
Molecule *C*				
S(1)	41856 (2)	7038·6 (9)	22406 (2)	160 (3)
	41942 (3)	6965·3 (12)	22395 (3)	442 (4)
O(1)	44358 (10)	5398 (3)	17562 (9)	208 (8)
	44451 (11)	5352 (43)	17653 (10)	567 (12)
O(2)	36355 (10)	8602 (3)	19992 (9)	236 (9)
	36498 (13)	8482 (4)	19979 (13)	640 (14)
C(1)	50000	8680 (5)	25000	163 (14)
	50000	8592 (6)	25000	427 (20)
C(2)	48019 (15)	10073 (4)	31326 (14)	220 (12)
	48023 (19)	9960 (5)	31250 (19)	603 (20)
C(4)	38219 (14)	5736 (4)	29856 (11)	201 (11)
	38273 (18)	5692 (5)	29788 (15)	537 (17)
C(5)	31544 (15)	4310 (4)	27646 (14)	260 (12)
	31720 (19)	4294 (7)	27686 (20)	689 (22)

The molecular backbone forms a planar chain consisting of atoms S(1), S(2), O(2), O(4) and C(1). The bond lengths and bond angles are listed in Table 2. For the symmetric molecules (molecules *B* and *C*), only the unique lengths and angles are given. A comparison of the low-temperature and room-temperature results shows that there is no significant difference between the two. The discussion in the text is limited to the results of the low-temperature structure.

Dimensionally, the three molecules are almost identical. One noticeable difference between the asymmetric molecule (*A*) and the symmetric ones (*B*, *C*) is in the angle S(1)—C(1)—S(2): 112·5 (1)° in molecule *A*, 113·5 (1)° in *B*, and 113·4 (1)° in molecule *C*. The corresponding S—S distances in the three molecules are 3·041 (1), 3·057 (1) and 3·058 (1) Å respectively. The eight independent S—O distances in the structure are virtually equivalent. Individual distances are within 2σ of the mean value of 1·444 (1) Å which is in fair

Table 2. *Bond lengths* (Å) *and angles* (°)

Upper values correspond to low-temperature and lower values to room-temperature structures.

	Molecule *A*	Molecule *B*	Molecule *C*
S(1)–O(1)	1·446 (2)	1·442 (2)	1·445 (2)
	1·436 (2)	1·435 (3)	1·439 (2)
S(1)–O(2)	1·441 (2)	1·445 (2)	1·443 (2)
	1·435 (3)	1·434 (3)	1·435 (2)
S(2)–O(3)	1·442 (2)		
	1·438 (3)		
S(2)–O(4)	1·445 (2)		
	1·433 (3)		
S(1)–C(1)	1·833 (2)	1·827 (2)	1·829 (2)
	1·834 (3)	1·830 (3)	1·833 (2)
S(2)–C(1)	1·825 (2)		
	1·824 (3)		
S(1)–C(4)	1·781 (3)	1·774 (3)	1·772 (2)
	1·779 (4)	1·769 (3)	1·774 (3)
S(2)–C(6)	1·772 (3)		
	1·770 (3)		
C(1)–C(2)	1·531 (3)	1·534 (3)	1·532 (3)
	1·529 (4)	1·535 (5)	1·528 (4)
C(1)–C(3)	1·533 (3)		
	1·533 (4)		
C(4)–C(5)	1·528 (4)	1·525 (4)	1·531 (4)
	1·512 (6)	1·514 (5)	1·516 (5)
C(6)–C(7)	1·522 (4)		
	1·504 (5)		
O(1)–S(1)–O(2)	117·7 (1)	117·4 (1)	117·8 (1)
	117·5 (1)	117·4 (1)	117·8 (1)
O(1)–S(1)–C(1)	108·4 (1)	108·4 (1)	108·0 (1)
	108·3 (1)	108·2 (1)	108·2 (1)
O(1)–S(1)–C(4)	108·4 (1)	109·0 (1)	109·2 (1)
	108·2 (2)	108·8 (1)	109·1 (1)
O(2)–S(1)–C(1)	104·6 (1)	105·3 (1)	104·9 (1)
	104·9 (1)	105·4 (1)	105·0 (1)
O(2)–S(1)–C(4)	108·3 (1)	108·4 (1)	107·9 (1)
	108·3 (2)	108·4 (2)	107·6 (1)
C(1)–S(1)–C(4)	109·2 (1)	107·9 (1)	108·8 (1)
	109·5 (1)	108·2 (1)	108·8 (1)
O(3)–S(2)–O(4)	117·6 (1)		
	117·8 (2)		
O(3)–S(2)–C(1)	108·4 (1)		
	108·1 (1)		
O(3)–S(2)–C(6)	109·4 (1)		
	109·2 (2)		
O(4)–S(2)–C(1)	105·6 (1)		
	105·8 (1)		
O(4)–S(2)–C(6)	107·8 (1)		
	107·7 (2)		
C(1)–S(2)–C(6)	107·6 (1)		
	107·9 (1)		
S(1)–C(1)–S(2)*	112·5 (1)	113·5 (1)	113·4 (1)
	112·9 (2)	113·5 (1)	112·9 (1)
S(1)–C(1)–C(2)	110·1 (2)	109·3 (1)	109·5 (1)
	110·4 (2)	109·2 (2)	109·8 (2)
S(1)–C(1)–C(3)*	106·3 (2)	106·1 (1)	106·1 (1)
	106·2 (2)	106·1 (2)	106·1 (1)
S(2)–C(1)–C(2)	106·2 (2)		
	106·1 (2)		
S(2)–C(1)–C(3)	109·7 (2)		
	109·8 (2)		
C(2)–C(1)–C(3)*	112·1 (2)	112·6 (1)	112·4 (1)
	111·6 (3)	112·9 (2)	112·2 (2)
S(1)–C(4)–C(5)	108·4 (2)	109·4 (2)	108·7 (2)
	109·3 (3)	110·1 (2)	109·4 (2)
S(2)–C(6)–C(7)	110·0 (2)		
	110·7 (2)		

* In molecule *B* and molecule *C*, atoms S(2) and C(3) refer to twofold-symmetry-related S(1) and C(2).

agreement with S—O distances observed in other sulfone structures (Sime & Woodhouse, 1974*a,b*; Kiers & Vos, 1972). S—C distances in sulfanol fall into two distinct categories. S—C(ethyl) distances [average of four bonds, 1·775 (1) Å] are significantly shorter than the S—C(central) distances [average of four bonds, 1·829 (1) Å]. This difference may be due in part to the fact that both the S and C(central) atoms are fully substituted. Extension of bonds between two quaternary atoms with partially eclipsed substituents has been reported (Birnbaum, 1972; Lindner, Ketschke, Hafner & Ude, 1980; Destro, Pilati & Simonetta, 1980; Poling & van der Helm, 1976). However, the S—C(ethyl) distance of 1·775 Å is much shorter than the expected S—C(sp^3) distance. In fact, this distance compares well with an average S—C(sp^2) distance of about 1·78 Å observed in a series of diphenyl sulfone structures (Sime & Woodhouse, 1974*a,b*). On the other hand, short S—C(sp^3) distances in the range 1·74–1·78 Å have been observed in 1-methylsulfonyl-2-methylsulfoxyethane (Berg, Bruun & Mo, 1978) and in other related structures (Hummelink, 1974; Svinning, Mo & Bruun, 1976).

The angular disposition of the bonds about the S atoms deviates significantly from that of a regular tetrahedron with a large O—S—O angle [average in three molecules is 117·6 (1)°]. But unlike in other sulfones (Laur, 1971; Sime & Woodhouse, 1974*a,b*), where the four O—S—C angles invariably have an intermediate value (range 107–108°) and C—S—C angle the smallest value (range 104–105°), in sulfanol the angles O(2)—S(1)—C(1) and O(4)—S(2)—C(1) have the smallest values [average 105·1 (1)°], whereas the average C—S—C angle of 108·2 (1)° falls in the intermediate range. This deviation seems to be related to the conformation of the sulfone group which is different in sulfanol compared to other known sulfones. In sulfanol, atoms O(2) and O(4) lie in the plane of the central chain formed by the atoms C(1), S(1) and S(2), while in most other sulfones the O atoms lie away from the central plane as in 1-methylsulfonyl-2-methylsulfoxyethane (Berg, Bruun & Mo, 1978), in diphenyl sulfone (Kiers & Vos, 1972) and in a series of diphenyl sulfone derivatives (Sime & Woodhouse, 1974*a,b*).

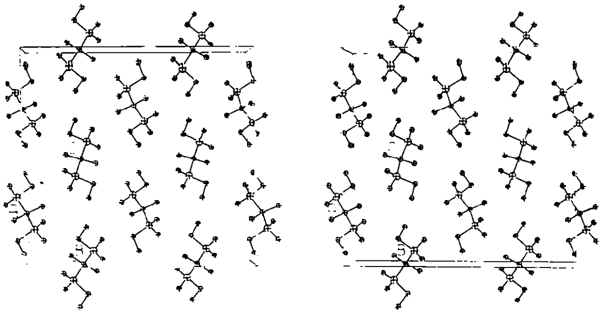

Fig. 2. A stereoview of the crystal structure of sulfanol.

C—H distances in the present structure vary between 0·89 and 1·1 Å. Fig. 2 shows the contents of one unit cell. The packing is fairly compact, but there are no unusually short intermolecular contacts.

The presence of two distinct types of S—C bonds in sulfanol may explain some of the results of the ESR spectra of γ-irradiated sulfanol. If irradiation causes scission of a S—C bond it is most likely that it would be one of the S—C(central) bonds which are weaker than the S—C(ethyl) bonds, and one would expect radicals of the type $(CH_3)_2\dot{C}(SO_2C_2H_5)$ and $C_2H_5SO_2$ to be trapped in the irradiated crystals. In the ESR study $(CH_3)_2\dot{C}(SO_2C_2H_5)$ has definitely been identified at 77 K, but $C_2H_5SO_2$ has not been detected at this temperature, although the latter radical appears at higher temperature. The crystal structure of sulfanol at 138 K is essentially identical to that at 293 K. The change in appearance of the ESR spectrum with temperature should therefore have another cause rather than a structural one. A likely mechanism would be that the $C_2H_5\dot{S}O_2$ radical is not observed at 77 K because of ionization into $C_2H_5SO_2^+ + e$, while at room temperature this process does not occur or that by electron recapture the spectrum of the $C_2H_5\dot{S}O_2$ radical is observed while also the $(CH_3)_2\dot{C}(C_2H_5SO_2)$ radical further dissociates.

References

Ahmed, F. R. (1966). *SFLS*, Fourier program, *NRC*-10. National Research Council, Ottawa, Canada.

Ayscough, P. B., Ivin, K. J. & O'Donnell, J. H. (1965). *Trans. Faraday Soc.* **61**, 1110–1115.

Berg, O., Bruun, T. & Mo, F. (1978). *Acta Chem. Scand. Ser. A*, **32**, 163–168.

Birnbaum, G. I. (1972). *Acta Cryst.* B**28**, 1248–1254.

Coppens, P., Lieserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.

Destro, R., Pilati, T. & Simonetta, M. (1980). *Acta Cryst.* B**36**, 2500–2503.

Ealick, S. E., van der Helm, D. & Weinheimer, A. J. (1975). *Acta Cryst.* B**31**, 1618–1626.

Hummelink, T. H. (1974). *J. Cryst. Mol. Struct.* **4**, 87–96.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72, 149. Birmingham: Kynoch Press.

Kiers, C. Th. & Vos, A. (1972). *Recl Trav. Chim. Pays-Bas*, **91**, 126–132.

Laur, P. H. (1971). *Sulfur in Organic and Inorganic Chemistry*, Vol. III, p. 227. New York: Dekker.

Lindner, H. J., Ketschke, B., Hafner, K. & Ude, W. (1980). *Acta Cryst.* B**36**, 758–759.

Poling, M. & van der Helm, D. (1976). *Acta Cryst.* B**32**, 3349–3351.

Roy, A. K. (1966). PhD Thesis, Univ. of Leeds, England.

Sime, J. G. & Woodhouse, D. I. (1974*a*). *J. Cryst. Mol. Struct.* **4**, 269–285.

Sime, J. G. & Woodhouse, D. I. (1974*b*). *J. Cryst. Mol. Struct.* **4**, 287–303.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Svinning, T., Mo, F. & Bruun, T. (1976). *Acta Cryst.* B**32**, 759–763.