

Table 7. Dependence of  $r(\text{C}=\text{O})$  on environment of acceptor group

Acceptor type	'Single' acceptor†		'Double' acceptor†		'Triple' acceptor†	
	$N$ ‡	$\mu$	$N$	$\mu$	$N$	$\mu$
Carboxyl	168	1.209 (1)	45	1.221 (3)	1	1.233 (-)
Ketone	54	1.234 (2)	16	1.241 (3)	0	—
Amide	479	1.229 (1)	113	1.238 (1)	4	1.252 (4)
Carboxylate	98	1.242 (1)	176	1.248 (1)	19	1.253 (1)

(b) Spearman rank correlation coefficients of  $r(\text{C}=\text{O})$  and  $r(\text{H}\cdots\text{O})$ 

Acceptor type	'Single' acceptor	'Double' acceptor	'Triple' acceptor
Carboxyl	-0.344§	-0.476§	—
Ketone	-0.639§	-0.432§	—
Amide	-0.141§	-0.335§	-0.470
Carboxylate	-0.086	-0.119§	-0.304§

\* If a C=O group is involved in two crystallographically independent N-H...O=C hydrogen bonds, both will normally be in the data set on which our survey is based. In constructing Table 7(a), duplicate occurrences of the same C=O group were eliminated, i.e. each crystallographically independent C=O group was counted once, and only once.

† Defined in text.

‡  $N$  = number of observations in sample,  $\mu$  = sample mean.

§ Significantly different from zero at or above 95% confidence level (one-tailed test).

gen bonds. Corresponding figures for amides, ketones and carboxyls are 20, 23 and 21%, respectively. This is consistent with our conclusion that carboxylates form stronger hydrogen bonds than amides, ketones and carboxyls.

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## Studies of Bonding at S in the Solid State. The Structure of 1-(Methylsulfonyl)-2-(phenylthio)ethane at 86 K

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### Abstract

Structure data for a variety of crystalline molecules containing S in different oxidation states show that sulfides represent a structural discontinuity relative to the corresponding sulfoxides and sulfones. The

apparent anomalous behavior of sulfides seems to be general, but is different in aromatic and aliphatic compounds. Simple models for bonding cannot predict the observed anomalies. The trend in C–S–C angles, with a minimum for the sulfoxides, was observed previously in gaseous molecules. The observa-

tions on bonding at S in the solid state have been further verified in a low-temperature X-ray study of 1-(methylsulfonyl)-2-(phenylthio)ethane,  $C_9H_{12}O_2S_2$ ,  $M_r = 216.32$ , orthorhombic, space group  $P2_12_12_1$ ,  $a = 5.312(1)$ ,  $b = 8.599(1)$ ,  $c = 22.262(3) \text{ \AA}$ ,  $V = 1016.9(3) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 1.413 \text{ Mg m}^{-3}$ ,  $\lambda(\text{Mo } K\alpha) = 0.71073 \text{ \AA}$ ,  $\mu = 0.468 \text{ mm}^{-1}$ ,  $F(000) = 456$ , final  $R = 0.025$  for 1691 observed reflections. The present study also provides new data on the angular distortions in benzene rings caused by a thio S substituent. The crystal structure features two  $O \cdots H-C$  contacts significantly shorter than the normal van der Waals distance. Similar short contacts have been found in related structures.

### Introduction

The present work is part of a crystallographic investigation of small S-containing molecules with the general formula  $R_1-X_1-CH_2-CH_2-X_2-R_2$ . A major motive for these studies is to acquire precise experimental models of the bonding at S and its dependence on oxidation state and electronic properties of the terminal R groups. For some of the compounds more detailed studies of the charge-density distribution are in progress. So far the following structures have been analyzed:

$R_1$	$X_1$	$X_2$	$R_2$
Me	SO	SO	Me
Me	SO	SO <sub>2</sub>	Me
Me	SO <sub>2</sub>	SO <sub>2</sub>	Me
Me	SO <sub>2</sub>	SO <sub>2</sub>	Ph
Ph	SO <sub>2</sub>	SO <sub>2</sub>	Ph

In the following we present the results from a low-temperature X-ray study of 1-(methylsulfonyl)-2-(phenylthio)ethane (MSO<sub>2</sub>PS), with  $R_1 = \text{Me}$ ,  $R_2 = \text{Ph}$ ,  $X_1 = \text{SO}_2$  and  $X_2 = \text{S}$ . MSO<sub>2</sub>PS is the first member in the series with a thio group and thus provides new information on the bonding properties of divalent S relative to higher valency states.

### Experimental

Single crystals of MSO<sub>2</sub>PS from ether prismatic along **a** with well-developed faces (100), (010) and (001), size  $\sim 0.63 \times 0.25 \times 0.07 \text{ mm}$ , m.p.  $324.0\text{--}325.0 \text{ K}$ . Cell dimensions and crystal orientation determined from Mo  $K\alpha_1$  peaks of 18 reflections ( $2\theta: 50\text{--}60^\circ$ ) centered at beginning and end of data collection, changes in parameters  $< 2\sigma$ . Intensities of 1753  $hkl$  reflections ( $h 0 \rightarrow 7$ ,  $k 0 \rightarrow 12$ ,  $l 0 \rightarrow 31$ ) excluding extinctions measured without attenuators to a limit in  $(\sin \theta)/\lambda$  of  $0.704 \text{ \AA}^{-1}$  with Nb-filtered Mo  $K\alpha$  radiation on a diffractometer controlled by the Vanderbilt disk-oriented program system (Lenhart, 1975).  $\omega/2\theta$  scan mode, scan speed  $2^\circ \text{ min}^{-1}$  in  $2\theta$ , basic scan width  $2\theta(\bar{\alpha}) - 0.85$  to  $2\theta(\bar{\alpha}) + 0.95^\circ$ , backgrounds measured

for 20 s at each limit of the scan. Intensities below  $2\theta \sim 13^\circ$  remeasured semi-manually with reduced low-angle scans to minimize errors caused by the Nb K absorption edge. A set of three standard intensities measured at intervals of 60 reflections. Data scaled with a polynomial fit to the average standard curve and corrected for coincidence loss. The recovery constant with this crystal was estimated to  $8.0 \times 10^{-8} \text{ counts}^{-1}$  from a comparison with other data sets collected on this diffractometer. Intensities corrected for absorption, factors in the range 1.031 to 1.118 calculated with a modified version of the program *ABSOR* (Templeton & Templeton, 1973). Standard deviations calculated as:  $\sigma(F^2) = \sigma(I)(Lp)^{-1}(\text{scale})$  and  $\sigma^2(I) = \sigma_{\text{count}}^2 + (SI_{\text{net}})^2$ , value of  $S$  estimated to 0.015. Intensities of five reflections were corrected for superposition in background or scan range by the  $\beta$  peak of a higher-order reflection. Eight reflections were deleted at this stage: six at  $2\theta < 10^\circ$  with the Nb K edge within the range of their peak scans and two because of irregular peak shapes. Another 54 reflections with  $F^2 < \sigma(F^2)$  were weighted zero. The two S atoms of the asymmetric unit were located from Patterson maps and positions for C and O atoms found by the difference Fourier technique. Following initial isotropic refinement of C, O and S, H atoms were added with positions from a  $\Delta F$  map. Anisotropic temperature factors were assigned to C, O and S but not to H. Quantity  $\sum w(|F_o| - k|F_c|)^2$  with  $w = 1/\sigma^2(F_o)$  minimized by full-matrix least squares, 166 variables.  $R = 0.025$ ,  $wR = 0.026$ ,  $R(F^2) = 0.035$ ,  $S = 1.63$ ,  $(\Delta/\sigma)_{\text{max}} = 0.002$ . Final difference electron density within  $-0.22$  and  $+0.31 \text{ e \AA}^{-3}$ , all extrema exceeding  $\sim 0.19 \text{ e \AA}^{-3}$  in magnitude correspond to bonding features. Scattering factors those of Doyle & Turner (1968) except for H (Stewart, Davidson & Simpson, 1965); anomalous-dispersion values for S from Cromer & Liberman (1970). A set of local programs was used for analyses and reduction of the data (Svinning & Mo, 1978), programs for structure solution and refinement from *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), drawings of molecules made by *ORTEP* (Johnson, 1976). Final atomic parameters are given in Table 1.\*

### Results and discussion

#### The molecular structure

Both end groups of MSO<sub>2</sub>PS are oriented *gauche* as shown in Fig. 1.

\* Tables of structure factors, positional and thermal parameters for H and anisotropic thermal parameters for the non-H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39138 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates and equivalent isotropic thermal parameters for non-H atoms

Coordinates are  $\times 10^5$  for S and  $\times 10^4$  for C and O. Thermal parameters,  $U_{eq}(\text{\AA}^2 \times 10^4)$ , are calculated from  $U_{eq} = \frac{1}{3} \sum_{ij} U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$ , where  $U_{ij}$  are defined by  $T(\theta) = \exp[-2\pi^2(U_{11}a^*h^2 + \dots + 2U_{12}a^*b^*hk + \dots)]$ . E.s.d.'s are given in parentheses.

	x	y	z	$U_{eq}$
S(1)	30326 (9)	-22637 (5)	22586 (2)	107 (2)
S(2)	8310 (10)	15253 (5)	10402 (2)	158 (2)
C(1)	2698 (4)	-1212 (2)	2930 (1)	164 (9)
C(2)	1386 (4)	-1155 (2)	1712 (1)	126 (8)
C(3)	2519 (3)	455 (2)	1613 (1)	131 (8)
C(4)	1483 (4)	490 (2)	369 (1)	127 (8)
C(5)	-230 (4)	702 (2)	-99 (1)	156 (9)
C(6)	168 (4)	-29 (2)	-649 (1)	171 (9)
C(7)	2226 (4)	-990 (2)	-734 (1)	166 (8)
C(8)	3934 (4)	-1200 (2)	-267 (1)	156 (8)
C(9)	3584 (4)	-452 (2)	283 (1)	143 (8)
O(1)	1773 (3)	-3746 (1)	2320 (1)	178 (6)
O(2)	5677 (2)	-2295 (2)	2098 (1)	168 (6)

Bond lengths and angles are given in Table 2. At 86 K thermal parameters of the atoms are small to moderate (Table 1). Thermal motion in the phenyl end does not fit a rigid-body model and no corrections were applied. It is noted that the shortest bond of the ring, 1.383 (3) Å after the least-squares refinement, is between the atoms with the largest values of  $U_{eq}$ , C(6) and C(7). Corrections of terminal bonds in the methylsulfonyl end are very small. The largest shifts according to the minimum-correction formalism (Busing & Levy, 1964) are in the S-O bonds, 0.001 Å.

### S bonding

In previous analyses of S-containing structures we have examined the results in the light of the Walsh-Bent rehybridization theory (Walsh, 1947; Bent, 1961). This theory states in a qualitative sense that if a group or atom  $X$  (which can also be an unshared electron pair  $E$ ) bonded to a central atom  $A$  is replaced by a more electronegative group  $X'$ , then the  $p$  character of the remaining  $\sigma$ -bonds involving  $A$  will decrease. The expected effect is successively shorter bonds and larger bond angles at  $A$ .

A second popular model for bonding, applicable to bond-angle variations also in tetrahedral and related molecules, is the valence-shell electron-pair

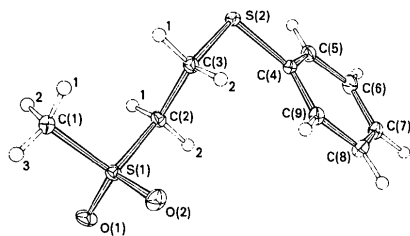


Fig. 1. Molecular conformation of  $\text{MSO}_2\text{PS}$  and the labeling of atoms. Numbering of H atoms is given only where necessary.

Table 2. Bond lengths (Å) and angles ( $^\circ$ ) with e.s.d.'s

Values including 'minimum' thermal correction are in square brackets.

S(1)-C(1)	1.757 (2)	C(4)-C(5)	1.394 (3)
S(1)-C(2)	1.776 (2)	C(5)-C(6)	1.393 (3)
S(1)-O(1)	1.446 (1)[1.447]	C(6)-C(7)	1.383 (3)
S(1)-O(2)	1.450 (1)[1.451]	C(7)-C(8)	1.391 (3)
S(2)-C(3)	1.810 (2)	C(8)-C(9)	1.396 (3)
S(2)-C(4)	1.774 (2)	C(9)-C(4)	1.392 (3)
C(2)-C(3)	1.525 (3)		
C(1)S(1)C(2)	104.9 (1)	S(2)C(4)C(5)	115.8 (1)
C(1)S(1)O(1)	109.0 (1)	S(2)C(4)C(9)	124.3 (1)
C(1)S(1)O(2)	108.5 (1)	C(4)C(5)C(6)	119.9 (2)
C(2)S(1)O(1)	108.1 (1)	C(5)C(6)C(7)	120.7 (2)
C(2)S(1)O(2)	108.5 (1)	C(6)C(7)C(8)	119.4 (2)
O(1)S(1)O(2)	117.1 (1)	C(7)C(8)C(9)	120.6 (2)
S(1)C(2)C(3)	113.1 (1)	C(8)C(9)C(4)	119.6 (2)
C(2)C(3)S(2)	111.6 (1)	C(9)C(4)C(5)	119.8 (2)
C(3)S(2)C(4)	104.0 (1)		

### Bonds and angles involving H

	Number	Range	Mean	$\sigma_{ave}$
C-H(ali)	7	0.89-1.00	0.94	0.3
C-H(aro)	5	0.91-1.01	0.96	0.2
SCH	7	103-111	107	1.3
CCH	4	110-112	111	1.3
CC H(phenyl)	10	116-124	120	1.3
HCH	5	107-114	110	2.0

repulsion (VSEPR) model (Gillespie, 1972). The VSEPR model assumes that the geometry at a central atom is determined mainly by the number of electron pairs in its valence shell and their angular space requirements. According to Gillespie (1972) the electron-pair repulsions generally decrease in magnitude in the order lone-pair: lone-pair > lone-pair: bond-pair > bond-pair: bond-pair. The inference also from this model, therefore, is increasing bond angles  $X-A-X$  in the series  $AX_2E_2$ ,  $AX_3E$ ,  $AX_4$ .

Our results for sulfoxides,  $\text{SOX}_2E$ , and sulfones,  $\text{SO}_2X_2$ , where  $X$  is an organic group, corroborate the predictions of both theories (Mo & Berg, 1982), as do the results from experimental (e.g. Chu, 1975; Ammon, Fallon & Plastas, 1976) and theoretical studies (e.g. Rohmer & Roos, 1975; Müller, Schweig & Vermeer, 1975) of other sulfoxide and sulfone structures.

The structure parameters for the sulfide moiety,  $\text{SX}_2E_2$ , in  $\text{MSO}_2\text{PS}$  are in disagreement with the bonding models, however. Hargittai & Baranyi (1977) have noted the same peculiar trend in  $X-S-X$  angles, i.e.  $\text{SX}_2E_2 > \text{SOX}_2E$ , in the series of gaseous species  $\text{SX}_2E_2$ ,  $\text{SOX}_2E$ ,  $\text{SO}_2X_2$ , where  $X = \text{F}$  or  $\text{Cl}$ . These authors also point out, however, that the original VSEPR model is not well suited for such systems since it does not take into account the relative angular space requirements of double bonds and lone pairs.

In order to quantify this apparent anomaly in crystalline molecules we have compiled in Table 3 bond lengths and angles at S for some well refined sulfides, sulfoxides and sulfones. Parameters involving aro-

Table 3. Structure parameters for some sulfides, sulfoxides and sulfones

Bond lengths are in Å and angles in degrees, e.s.d.'s in parentheses. For each group of compounds, mean values are given with the weighted sample error in square brackets.

Compound	Reference	Non-terminal C-C	S-C(aro)	Non-terminal S-C(ali)	Terminal S-C(ali)	C-S-C(aro)	C-S-C(ali)
D,L-Alanyl-L,D-methionine	(a)	1.508 (5)		1.811 (4)	1.792 (7)		99.1 (2)
L-Methionyl-L-methionine	(b)	1.515 (5)		1.816 (3)	1.803 (5)		99.8 (2)
		1.523 (4)		1.813 (3)	1.794 (6)		99.9 (2)
Tetrakis(phenylthio)ethylene	(c)		1.770 (3) 1.767 (3)			103.2 (1) 103.6 (1)	
S-Carboxymethyl-L-cysteine	(d)			1.804 (3) 1.807 (3)			100.3 (2)
Hexakis(methylthio)benzene	(e)		1.778 (2) 1.778 (2) 1.779 (2)		1.805 (4) 1.795 (3) 1.794 (4)	103.8 (2) 102.4 (1) 101.8 (1)	
3,3'-Thiodipropionic acid	(f)			1.818 (2)			100.3 (2)
1-(Methylsulfonyl)-2-(phenylthio)ethane <sup>LT</sup>	(g)		1.774 (2)	1.810 (2)		104.0 (1)	
Range		0.015	0.012	0.014	0.013	2.2	1.2
Mean value with error*		1.517 [4]	1.776 [2]	1.811 [2]	1.797 [2]	103.0 [4]	99.9 [2]
(+)-Methyl <i>p</i> -tolyl sulfoxide	(h)		1.804 (3-6) <sup>T</sup>		1.809 (3-6) <sup>T</sup>	97.6 (3)	
<i>o</i> -Carboxyphenyl methyl sulfoxide	(i)		1.800 (3)		1.788 (5)	97.8 (2)	
(-)- <i>o</i> -Carboxyphenyl methyl sulfoxide	(j)		1.800 (5)		1.782 (6)	98.8 (2)	
<i>meso</i> -Ethane-1,2-bis(methyl sulfoxide) <sup>†</sup>	(k)	1.516 (2)		1.802 (2)	1.788 (2) <sup>T</sup>		97.0 (1)
<i>meso</i> -Ethane-1,2-bis(phenyl sulfoxide) <sup>†</sup>	(l)	1.507 (3)	1.798 (3)	1.814 (4)		98.5 (1)	
S-Carboxymethyl-L-cysteine sulfoxide	(m)			1.810 (3) 1.801 (3)			94.5 (1)
2-(Methylsulfinyl)-1-phenylethanol	(n)			1.813 (2)	1.786 (3)		96.8 (1)
Range		0.009	0.006	0.013	0.027	1.2	2.5
Mean value with error*		1.513 [4]	1.800 [1]	1.807 [3]	1.789 [3]	98.4 [2]	96.1 [8]
S-Carboxymethyl-L-cysteine sulfone	(o)			1.772 (5) 1.788 (5)			103.8 (2)
Ethane-1,2-bis(phenyl)sulfone <sup>HO†</sup>	(p)	1.519 (2)	1.762 (2)	1.786 (2)		104.7 (1)	
1-(Methylsulfonyl)-2-(phenylsulfonyl)ethane <sup>HO</sup>	(q)	1.525 (3)		1.783 (2)	1.759 (3)		103.9 (1)
			1.768 (2)	1.782 (2)		105.5 (1)	
Ethane-1,2-bis(methyl)sulfone <sup>HO†</sup>	(r)	1.515 (1)		1.779 (2)	1.758 (2) <sup>T</sup>		104.7 (1)
1-(Methylsulfonyl)-2-(phenylthio)ethane <sup>LT</sup>	(g)			1.776 (2) <sup>T</sup>	1.757 (2) <sup>T</sup>		104.9 (1)
Range		0.010	0.006	0.016	0.002	0.8	1.1
Mean value with error*		1.517 [2]	1.765 [3]	1.781 [2]	1.758 [1]	105.1 [4]	104.5 [3]

LT: Data collected at 86 K. HO: High-order refinement: (p) 0.72-0.923 Å<sup>-1</sup>; (q) 0.65-0.807 Å<sup>-1</sup>; (r) 0.70-1.00 Å<sup>-1</sup>. T: Thermal correction applied.

References: (a) Stenkamp & Jensen (1974); (b) Stenkamp & Jensen (1975); (c) Collins & Davis (1978); (d) Mighell, Hubbard, Harris, Staffa & Zervos (1979); (e) Peach & Burschka (1982); (f) Prout & Hernández-Cassou (1982); (g) this work; (h) de la Camp & Hope (1970); (i) Dahlén (1973); (j) Dahlén (1974); (k) Svinning, Mo & Bruun (1976); (l) Pelizzi, Michelon & Bonivento (1976); (m) Staffa, Zervos, Mighell & Hubbard (1976); (n) Hoyos Guerrero, Martínez-Carrera & García-Blanco (1983); (o) Hubbard, Mighell, Staffa, Zervos & Konopelski (1976); (p) Mo, Berg, Thorkildsen & Gaasdal (1979); (q) Mo & Gaasdal (1980); (r) Mo & Berg (1982); (s) Haagensen (1978).

\* Mean value ( $\bar{x}_m$ ) and weighted sample error ( $\sigma$ ) calculated as:  $\bar{x}_m = \sum_{i=1}^N (x_i/\sigma_i^2) / \sum_{i=1}^N (1/\sigma_i^2)$ ;  $\sigma = [\sum_{i=1}^N ((x_i - \bar{x}_m)^2/\sigma_i^2) / (N-1) \sum_{i=1}^N (1/\sigma_i^2)]^{1/2}$ .

† Alternative names for these compounds are 1,2-bis(methylsulfinyl)ethane and 1,2-bis(phenylsulfinyl)ethane for the sulfoxides, and 1,2-bis(methylsulfonyl)ethane and 1,2-bis(phenylsulfonyl)ethane for the sulfones.

matic (aro) and aliphatic (ali) C atoms are listed separately in the table; we have also made a distinction between terminal and non-terminal S-C(ali) bonds. Within each group of compounds the former type of bond is the shorter. The terminal aliphatic group in all the structures is methyl, for which neglect of thermal-vibration shortening may be serious. For the sulfides and sulfoxides, therefore, the difference, about 0.015 Å, could be a thermal effect. Results from

thermal corrections applied to two of the sulfoxides are ambiguous on this point, however. Among the sulfones terminal S-C(ali) bonds are significantly shorter also after thermal correction, cf. ethane-1,2-bis(methyl)sulfone (room temperature) and MSO<sub>2</sub>PS (low temperature). Bond shortening due to asphericity of the charge density should be essentially corrected for in the high-order refinements of three of the sulfones in the table, among them also ethane-1,2-

bis(methyl)sulfone. High-order refinements with low-temperature data need be carried out to explore further the nature of the remaining discrepancy between terminal and non-terminal S-C(al) bonds.

Bond angles C-S-C are also listed separately according to whether the sequence contains one aromatic C atom or both C aliphatic. There seems to be a real difference between the two categories among the sulfides, the data for the sulfoxides being less conclusive. In the sulfone group no clear distinction is apparent.

The tabulated mean values show that the S-C(al) bonds (non-terminal) are very similar in the sulfides and sulfoxides, 1.811 and 1.807 Å, respectively, and longer than in the sulfones, 1.781 Å.\* Bond angles C-S-C(al) in the sulfides are larger than in the sulfoxides, the order being sulfone > sulfide > sulfoxide. The similarity of sulfide and sulfoxide C-S distances is also evident in the published data for thiirene and thiirane rings and some oxygenated derivatives (Ammon *et al.*, 1976). This result contrasts the very large contraction of C-S bonds in dioxides *vs* oxides, which was discussed by Ammon *et al.* (1976), about 0.075 and 0.090 Å for the thiirene and thiirane series, respectively. In the latter series the magnitudes of C-S-C angles are ranked sulfide > sulfone > sulfoxide, which is the same as observed by Hargittai & Baranyi (1977) in gaseous  $SX_2E_2$ ,  $SOX_2E$ ,  $SO_2X_2$ , with  $X = F$  or  $Cl$ .

In the aromatic systems the C-S distances in sulfides and sulfones are comparable, 1.776 and 1.765 Å, respectively, both shorter than 1.800 Å in the sulfoxides. Bond angles are in decreasing order sulfone > sulfide > sulfoxide. The same trends are found in thioxanthene derivatives (Chu, 1975) where both C atoms bonded to S belong to aromatic rings.

Table 3 clearly shows that the sulfides represent a structural discontinuity from point of view of the simple models for bonding. The observed trend in C-S-C angles has been tentatively explained by incorporating in the VSEPR model the total angular space requirements of all bond and lone-pair orbitals about S (Schmiedekamp, Cruickshank, Skaarup, Pulay, Hargittai & Boggs, 1979). Based also on *ab initio* MO-LCAO-SCF calculations of  $SX_2E_2$ ,  $SOX_2E$  and  $SO_2X_2$ , where  $X = H$  or  $F$ ,† these authors were led to propose: (1) that the single lone pair in a sulfoxide is significantly larger than either lone pair in the corresponding sulfide, and (2) that S-O bonds are nearly as space-filling as lone pairs. As a result, less space is allotted to the  $X$  atoms in the sulfoxide than in either sulfide or sulfone, and this is reflected in the relative magnitudes of the parent  $X-S-X$  angles. The calculations by Schmiedekamp *et al.* (1979) which included 3*d* orbitals on S gave the following param-

eters for the energy-optimized geometries of  $SH_2$ ,  $SOH_2$  and  $SO_2H_2$ , S-H bonds: 1.335, 1.361 and 1.346 Å, and H-S-H angles: 93.6, 89.2 and 97.7°. Similar trends are found for the S-C(ar) bonds and C-S-C(ar) angles, *cf.* Table 3.

Bonding to the strongly electronegative O in the oxygenated species will increase the effective nuclear charge on S. This is one prerequisite for contraction of the 3*d* orbitals on S necessary for their contribution on bonding. Schmiedekamp *et al.* (1979) observed that bonds and angles involving O in  $SOH_2$  and  $SO_2H_2$  improved significantly when the calculations included 3*d* orbitals. According to Roos and coworkers (Rohmer & Roos, 1975; and references cited therein) the S 3*d* population and the gross atomic charge on S increase in roughly linear proportion in the series thiirane, thiirane monoxide and thiirane dioxide. In their *ab initio* MO-LCAO-SCF calculations in the thiirane series these authors obtained excellent agreement with experimental data only when 3*d* orbitals were included. But they also point out that the magnitude of the bond-length variations can be explained largely by the variation in the donor-acceptor strength of the fragment  $Y$  ( $Y = S, SO, SO_2$ ). In view of the differences in the organic fragments, their arguments are not directly applicable to the structures under discussion.

The significance of 3*d* orbitals for S bonding is a controversial subject. In many calculations on sulfides, sulfoxides and sulfones, their role has been described more as polarization functions of the *s* and *p* orbitals (Clark, 1970). It is possible that calculations with larger basis sets involving only *s* and *p* functions could reproduce molecular quantities equally well. In this context, it is interesting to note that Manne (1967) in MO-LCAO-SCF calculations of the electronic structure of some S and Cl oxyanions excluding *d* orbitals obtained generally very good agreement with spectroscopic measurements. For a better understanding of bonding at S, highly precise experimental and theoretical studies of geometry, deformation density and other electronic properties related to the charge-density distribution must be conducted on series of simple systems containing S, SO or  $SO_2$ , respectively.

### The phenyl ring

Substitution of the H atoms in a benzene ring is known to induce distortions from the regular  $D_{6h}$  symmetry of the ring (Domenicano, Vacigo & Coulson, 1975*a, b*). Norrestam & Schepper (1979, 1981) have recently developed models for predicting the distortions of multi-substituted benzenes in terms of the calculated (Hehre, Radom & Pople, 1972)  $\sigma$ - and  $\pi$ -electron-donating properties of the individual substituents. Our results for  $MSO_2PS$  indicate that a thio S group has little perturbing effect on the ring

\* Errors in the mean values are given in Table 3.

†  $SO_2F_2$  not included.

Table 4. Endocyclic valency angles ( $^{\circ}$ ) with e.s.d.'s for some thio S-substituted benzenes

Compound	Reference*	$\alpha$ (ipso)	$\beta$ (ortho)	$\gamma$ (meta)	$\delta$ (para)
1-(Methylsulfonyl)-2-(phenylthio)ethane	(g)	119.8 (2)	119.9 (2)	120.7 (2)	119.4 (2)
Tetrakis(phenylthio)ethylene†	(c)	119.8 (2)	119.6 (2)	120.6 (2)	119.3 (3)
		119.4 (3)	119.8 (3)	120.4 (3)	119.3 (3)
		119.4 (3)	120.6 (3)	119.8 (3)	120.0 (3)
		119.9 (3)	120.3 (3)	119.9 (3)	120.3 (3)
tert-Butylimido-A <sup>4</sup> -thio(phenylthio)methyl p-tolyl sulfone	(s)	119.5 (7)	120.2 (7)	119.9 (9)	120.3 (9)
		119.7 (8)	120.5 (8)	119.9 (9)	120.3 (9)
Range		0.4	1.0	1.2	1.0
Mean value with error‡		119.7 [1]	119.9 [1]	120.5 [1]	119.5 [2]

\* References are given in Table 3.

† Crystal structure has two independent phenyl rings.

‡ See footnote of Table 3 for calculation of mean and error values.

geometry. Table 4 gives endocyclic bond angles in four thio S-substituted benzene rings. Mean deviations from  $120^{\circ}$  are small; unfortunately there is a fairly large scatter among the values for some of the angles. The largest mean deviations are in the  $\gamma$  (meta) and  $\delta$  (para) angles,  $+0.5$  and  $-0.5^{\circ}$ , respectively. These values are practically unchanged when the less precise angles of reference (s) are excluded. Domenicano *et al.* (1975*b*) give  $\Delta\alpha = -0.25^{\circ}$ . The angular deviations in MSO<sub>2</sub>PS are:  $\Delta\alpha \sim \Delta\beta = -0.2$ ,  $\Delta\gamma = +0.7$  and  $\Delta\delta = -0.6^{\circ}$ ; the e.s.d. in these C–C–C angles is  $0.2^{\circ}$ .

### Packing of the molecules

The aromatic rings of the molecules form strings of columns, molecules in adjacent columns being

tilted in the opposite sense with respect to the column axis (Fig. 2). The resulting herringbone pattern is commonly found in crystalline structures with planar rings. Within each column there are three C···C inter-ring distances in the normal van der Waals range, 3.525 (3)–3.564 (3) Å. The closest contacts between adjacent columns are: C(8)···H(8<sup>v</sup>),\* 2.75, C(9)···H(8<sup>v</sup>), 2.78 and C(4)···H(5<sup>vi</sup>), 2.89 Å. All contacts with H have been calculated with C–H lengths normalized to 1.09 Å. There are also two C···C contacts connecting ring atoms C(6) and C(7) with methyl C(1<sup>xii</sup>), both at 3.525 (3) Å.

The O atoms interact with several aliphatic C atoms; the three shortest distances range from 3.232 (3) to 3.363 (2) Å with mean value 3.300 Å. There are four O···H distances  $\leq 2.49$  Å; O(2)···H(21<sup>ii</sup>), at 2.31, and O(2)···H(11<sup>viii</sup>), at 2.42 Å, shown in Fig. 2 as broken lines, are significantly shorter than a normal van der Waals O···H distance. Similar and even shorter O···H–C contacts have been found in other crystalline members of this family of compounds (Mo & Berg, 1982).

For the low-temperature work we used an Enraf–Nonius gas-flow cryostat, substantially modified by Professor H. Hope. Financial support through Grant D.22.52.005 from Norges Almenvitenskapelige Forskningsråd (NAVF) is gratefully acknowledged.

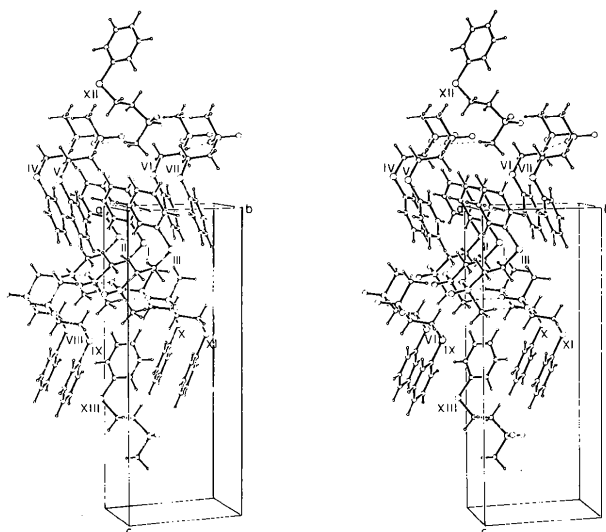


Fig. 2. Stereodrawing of the molecular packing. Two short O···H contacts are shown as broken lines, O(2)···H(21<sup>ii</sup>), 2.31 and O(2)···H(11<sup>viii</sup>), 2.42 Å. Numbering of molecules corresponds to the following symmetry code: (i)  $x, y, z$ ; (ii)  $1+x, y, z$ ; (iii)  $-1+x, y, z$ ; (iv)  $\frac{1}{2}+x, -\frac{1}{2}-y, -z$ ; (v)  $-\frac{1}{2}+x, -\frac{1}{2}-y, -z$ ; (vi)  $\frac{1}{2}+x, \frac{1}{2}-y, -z$ ; (vii)  $-\frac{1}{2}+x, \frac{1}{2}-y, -z$ ; (viii)  $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$ ; (ix)  $-x, -\frac{1}{2}+y, \frac{1}{2}-z$ ; (x)  $1-x, \frac{1}{2}+y, \frac{1}{2}-z$ ; (xi)  $-x, \frac{1}{2}+y, \frac{1}{2}-z$ ; (xii)  $\frac{1}{2}-x, -y, -\frac{1}{2}+z$ ; (xiii)  $\frac{1}{2}-x, -y, \frac{1}{2}+z$ .

\* The symmetry code is given in the legend of Fig. 2.

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## Structure and Conformational Analysis of Methyl $\alpha$ -Thiomaltoside,\* $C_{13}H_{24}O_{10}S$

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### Abstract

This paper deals with the crystal and molecular structure of methyl  $\alpha$ -thiomaltoside, which is the first structure ever reported for a thio-disaccharide system. The crystal structure of the title compound has been established by direct methods from 4777 independent reflections and refined to a final  $R$  value of 0.042. The crystal belongs to the monoclinic system, space group  $P2_1$ , and has a unit cell of dimensions  $a = 14.196$  (4),  $b = 4.846$  (1),  $c = 12.410$  (3) Å,  $\beta = 110.12$  (10)°, with  $Z = 2$ ,  $V = 801.1$  Å<sup>3</sup>;  $M_r = 372.4$ ,  $D_m = 1.54$  (1),  $D_x = 1.543$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu(\text{Mo } K\alpha) = 0.17$  mm<sup>-1</sup>,  $F(000) = 396$ , room temperature. The two glucose residues have the <sup>4</sup>C<sub>1</sub> conformation and are  $\alpha(1 \rightarrow 4)$  linked. The structural features at the glycosidic bridge are: C(1)–S(1) = 1.826 (1), C(4')–S(1) = 1.828 (1) Å, C(1)–S(1)–C(4') = 100.3 (1)°. Comparison with other sulphur-containing molecular segments has been performed. The conformational angles  $\varphi = \text{O}(5)–\text{C}(1)–\text{S}(1)–\text{C}(4')$

and  $\psi = \text{C}(1)–\text{S}(1)–\text{C}(4')–\text{C}(5')$  at the glycosidic linkage have the values 89 and  $-116.8^\circ$  respectively. The observed conformational behaviour has been analysed with the aid of a conformational analysis investigation. The primary hydroxyl group in the non-reducing residue is in the *gt* conformation, whereas a *gg* orientation is observed for the corresponding hydroxyl in the reducing residue. There is no intramolecular hydrogen bond, and the structure is maintained by an extensive network of hydrogen bonds.

### Introduction

The understanding of the structural basis for the action of glycanases and, more generally, of proteins continues to be of interest (Pincus & Scheraga, 1981; Warshel, 1981). In the field of polyosidase–oligosaccharide complexes, 1-thioglycosides have appeared to be good substrate analogues (Monod, 1956; Boos, Schaedel & Wallenfelds, 1967; Rafestin, Obrenovitch, Oblin & Monsigny, 1974; Steers, Cuatrecasas & Pollard, 1971; Claeysens, Kersters-Hilderson, Van Wauve & De Brugue, 1970). This potentiality is also

\* Methyl 4-S- $\alpha$ -D-glucopyranosyl-4-thio- $\alpha$ -D-glucopyranoside.  
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