

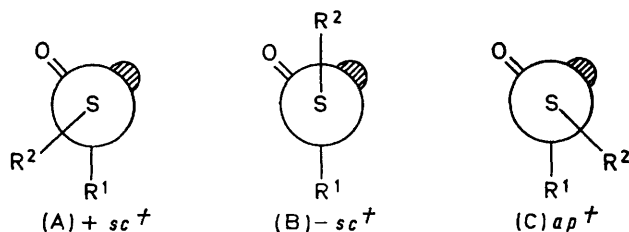
## Dipole Moments and Conformation of Thiosulphinates

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The conformation of some *S*-alkyl and -aryl thiosulphinates has been evaluated from the electric dipole moments measured in benzene solution. The synclinal conformation (A) here observed is the same as for sulphinates. From comparison with disulphides and their *S*-oxides, it appears that the stereochemistry of all these compounds is controlled by the *gauche* interaction of the two C-S bonds.

THE conformation of thiosulphinates, *viz.* (A), (B), or (C), may be of interest from two points of view. The first concerns the comparison with the oxygen analogues, *i.e.* sulphinates. These have a purely formal analogy to carboxylates, but their arrangement is completely different. The planarity of the whole CO<sub>2</sub> group arises from the *sp*<sup>2</sup> hybridization of carbon, and the conformation at the C-O bond is synperiplanar with respect



to the carbonyl oxygen and the R<sup>2</sup> group (corresponding to a dihedral angle R<sup>1</sup>-C-O-R<sup>2</sup> of 180°). On the other hand the pyramidal *sp*<sup>3</sup> configuration of sulphur in the SO<sub>2</sub> group is associated with a synclinal † conformation<sup>1</sup>

† For the notation +*sc*, -*sc*, and *ap* see ref. 2. They represent the mutual position of the S=O and S-R<sup>2</sup> bonds. The angle τ, defined as the dihedral angle R<sup>1</sup>-S-S-R<sup>2</sup>, was used for comparison of different types of compounds.

<sup>1</sup> O. Exner, P. Dembech, and P. Vivarelli, *J. Chem. Soc. (B)*, 1970, 278.

similar to (A), *i.e.* with a dihedral angle R<sup>1</sup>-S-O-R<sup>2</sup> of *ca.* 60°. It is known that the conformations of carboxylates and their sulphur analogues, *viz.* thiocarboxylates, are the same.<sup>3</sup> Our aim was to investigate whether this holds also for sulphinates and thiosulphinates. The non-planar arrangement of the R-SO-S group was proven by resolution into enantiomers.<sup>4</sup>

The second point of interest is the comparison of various derivatives containing two linked sulphur atoms in different oxidation states. This may reveal whether the presence of oxygen has a pronounced effect on conformation.

The experimental approach was that used previously;<sup>1,3</sup> experimental dipole moments, plotted as μ<sup>2</sup>, were compared graphically with calculated values.<sup>5</sup>

### RESULTS AND DISCUSSION

The results are collected in the Table. Since measurements of this class of compounds have not been pre-

<sup>2</sup> Information Bulletin No. 35, IUPAC Nomenclature of Organic Chemistry, Zürich, 1969.

<sup>3</sup> O. Exner, V. Jehlička, and J. Firl, *Coll. Czech. Chem. Comm.*, 1971, **36**, 2936.

<sup>4</sup> J. L. Kice and G. B. Large, *J. Amer. Chem. Soc.*, 1968, **90**, 4069.

<sup>5</sup> O. Exner and V. Jehlička, *Coll. Czech. Chem. Comm.*, 1965, **30**, 639.

viously reported, we may only state that our values seem to be reasonably consistent, although the differences between similar compounds (I)—(III) are somewhat

Polarization data and dipole moments of various thiosulphinates in benzene at 25°

Compound	$R_{11}^{20}/$ $\text{cm}^3$ <sup>a</sup>	$\infty P_2/$ $\text{cm}^3$	$\mu_{15\%}/$ $\text{D}$ <sup>b</sup>	$\mu_{15\%}/$ $\text{D}$ <sup>b</sup>	$\mu_{\text{calc.}}/$ $\text{D}$
(I) MeSOSMe	27.5	232.3	3.15	3.13	2.98
(II) MeSOSPh	47.6	179.4	2.52	2.47	3.06
(III) PhSOSPh	67.5	290.2	3.27	3.22	3.20
(IV) 4-ClC <sub>6</sub> H <sub>4</sub> SOSPh	72.5	219.4	2.64	2.58	2.70
(V) PhSOSC <sub>6</sub> H <sub>4</sub> Cl-4	72.5	295.0	3.26	3.22	3.89

<sup>a</sup> Calculated using Vogel's atomic and group increments (A. I. Vogel, *J. Chem. Soc.*, 1948, 1833) and the value of 16.18 cm<sup>3</sup> for the functional group SO-S. The latter was derived from the previously reported (ref. 1) increment of 10.02 cm<sup>3</sup> for SO-O group. Conjugation in Ph-S or Ph-SO has been accounted for by increments 0.4 or 0.25 cm<sup>3</sup>, respectively, as previously reported (ref. 1). <sup>b</sup> Correction for the atomic polarization, 5 or 15% of the  $R_D$  value, respectively.

larger than usual. Compounds (I)—(IV) have dipole moments close to those of structurally similar sulphinates.<sup>1</sup>

The expected dipole moments for various conformations were calculated by vector addition of bond moments, the same values being used as previously.<sup>1</sup> The S-S bond moment was taken as zero in the first approximation, although the two atoms are different in character and the assumption of a small moment would improve the agreement with experiment. The bond angles used were  $R^1-S-O = R^1-S-S = \angle O=S-S = 106^\circ$  and  $S-S-R^2 = 102^\circ$ .

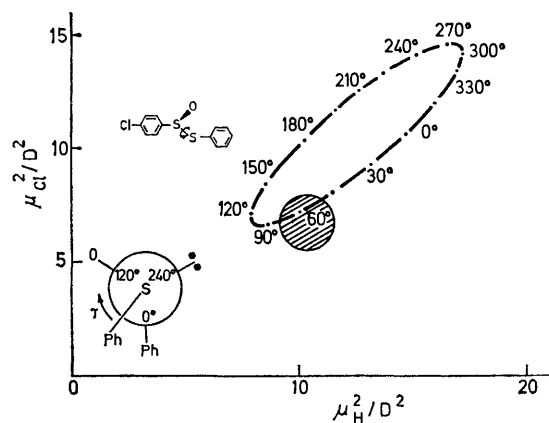
Two particular problems in computation may be mentioned. It has been argued that the moment of the lone electron pair must be given a value, at least in unsymmetrical compounds.<sup>6</sup> This view is substantiated inasmuch as realistic values of bond moments cannot be obtained without this correction. However, when the only task is to obtain reasonable computed moments for the whole molecule, the problem is purely a formal one. *E.g.* the lone pair moment of sulphides is included in the C-S bond moment and enters implicitly all computations on divalent sulphur derivatives. In polyvalent derivatives the formal S=O bond moment is derived by comparing sulphoxides and sulphides, but really it represents the difference between the S=O and lone pair moments. Therefore, while the whole set of bond moments is consistent, the individual values cannot have any physical meaning. In this paper we used this formal framework, whereas the lone pair moment is not explicitly considered.

The second problem concerns the mesomeric moments. This concept, criticized as to its physical meaning,<sup>7</sup> can be conveniently employed as a formal correction, ac-

\* The reliability of our conclusions may be estimated by probability calculus, the result depending on *a priori* assumptions.<sup>9</sup> *E.g.* considering only the three possibilities (A)—(C), we obtain quite low probabilities (38—90%) that conformation (A) is the right one, for individual compounds. However, on the assumption that all the derivatives have the same conformation, the probability rises to 96%. The standard error<sup>9</sup> in the calculation of dipole moments was estimated to be 0.3 D.

counting for the difference between aromatic and aliphatic derivatives. Consequently, in this paper we use a mesomeric moment<sup>1</sup> of 0.55 D for the system Ph-SO.

Compounds (III) and (IV) offer the possibility of graphical comparison.<sup>5</sup> Their dipole moments, calculated for various values of the dihedral angle  $\tau$ , are plotted as  $\mu^2$  (Figure) and compared with experiment (hatched circle). By changing the angle  $\tau$ , an ellipse is produced in the graph, and the experimental point coincides with  $\tau = 60^\circ$ , as in (A). This result cannot be significantly confirmed by the pair of compounds (III) and (V) since two points always coincide. In addition agreement with experiment is worse and



Squared dipole moment ( $\mu_{\text{H}}^2$ ) of phenyl benzenethiosulphinate (III) vs. the squared dipole moment ( $\mu_{\text{Cl}}^2$ ) of the corresponding 4-chloro-derivative (IV). The hatched circle and the dots refer to the experimental and calculated dipole moments, respectively.

would require some correction, *e.g.* a small S-S moment. This situation is not unexpected on the basis of the observed behaviour of aryl carboxylates and sulphinates.<sup>8</sup> In these cases substitution of the aryl ring gave even worse results. Hence, we preferred to calculate the dipole moments of all compounds (I)—(V) for  $\tau = 60^\circ$  (last column in the Table) and to compare them with the experimental ones. The average difference of 0.31 D is satisfactory.\*

That conformation (A) was found for sulphinates<sup>1</sup> and thiosulphinates together with the results for esters and thioesters,<sup>3</sup> suggests that the substitution of oxygen by sulphur is irrelevant. This is in agreement with the principle of *gauche* interaction of polar bonds<sup>10</sup> which seems to control the conformation of functional groups containing heteroatoms. We have compared various compounds containing two linked sulphur atoms in

<sup>6</sup> L. K. Yuldasheva, R. P. Arshinova, and S. G. Vulfson, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1969, 555.

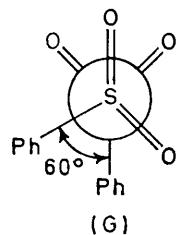
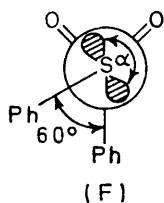
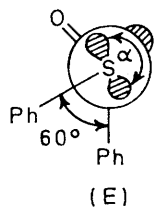
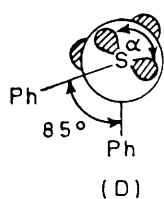
<sup>7</sup> V. Všetěčka and O. Exner, *Coll. Czech. Chem. Comm.*, in the press.

<sup>8</sup> O. Exner, Z. Fidlerová, and V. Jehlička, *Coll. Czech. Chem. Comm.*, 1968, **33**, 2019.

<sup>9</sup> O. Exner, *Coll. Czech. Chem. Comm.*, 1970, **35**, 187.

<sup>10</sup> S. Wolfe, A. Rauk, L. M. Tel, and G. I. Csizmadia, *J. Chem. Soc. (B)*, 1971, 136.

different states of oxidation, *i.e.* as S, SO, or SO<sub>2</sub>. For aromatic derivatives the angle  $\tau$  is 85° in disulphides<sup>11</sup> (D) and *ca.* 60° in thiosulphinates (E) and thiosulphonates<sup>12</sup> (F). On the basis of the measured dipole moments<sup>13</sup> a similar conformation (G) seems probable for 1,2-disulphones (different to that observed in the crystalline state<sup>14</sup>), whereas the 1,2-disulphoxides and sulphonyl-sulphoxides are still poorly characterized compounds. In terms of the principle of *gauche* interaction<sup>10</sup> it may be stated that the interaction of the two C-S bonds is predominant, although there are other polar bonds present, particularly in (F).<sup>\*</sup> Hence, the principle of *gauche* interaction should be completed by distinguishing among types of polar bonds. If it is assumed that the interaction of bonds of parallel polarity is more important, the conformations (E)–(G) can be understood. An alternative explanation in



terms of the lone-pair repulsion may be advanced.<sup>15</sup> In order to explain form (E) in particular, one must

<sup>\*</sup> Moreover, structure (F) violates the so-called Edward-Lemieux principle<sup>10</sup> which disfavors structures with a polar bond between two electron pairs.

<sup>11</sup> M. J. Aroney, R. J. W. Le Fèvre, R. K. Pierens, and H. L. K. The, *Austral. J. Chem.*, 1968, **21**, 281.

<sup>12</sup> O. Exner, D. N. Harpp, and J. G. Gleason, *Canad. J. Chem.*, 1972, **50**, 548.

<sup>13</sup> A. L. McClellan, 'Tables of Experimental Dipole Moments,' Freeman, San Francisco, 1963.

<sup>14</sup> C. T. Kiers and A. Vos, *Rec. Trav. chim.*, 1972, **91**, 126.

<sup>15</sup> N. L. Owen and N. Sheppard, *Proc. Chem. Soc.*, 1963, 264.

<sup>16</sup> D. La Verne Small, J. H. Bailey, and C. J. Cavallito, *J. Amer. Chem. Soc.*, 1947, **69**, 1710.

suppose that sulphur is hybridized such that the *s* character is concentrated in the lone pairs and the angle  $\alpha$  between them is larger than 120°. In addition, different hybridization could account for the different values of  $\tau$  in (D) and (E). In conclusion, these compounds do not allow a clear decision between the two theories,<sup>10,15</sup> both of which can be applied when some additional assumptions are made.

#### EXPERIMENTAL

**Materials.**—Methyl methanethiosulphinate (I) has been obtained by controlled oxidation of the corresponding disulphide with perbenzoic acid in chloroform. The product was purified by repeated fractional distillation, b.p. 39–40° at 0.2 mmHg (lit.,<sup>16</sup> b.p. 64° at 0.5 mmHg). Phenyl benzenesulphinate (III),<sup>17</sup> phenyl 4-chlorobenzenesulphinate (IV),<sup>18</sup> and 4-chlorophenyl benzenesulphinate (V)<sup>18</sup> were prepared by condensation of the appropriate sulphonyl chlorides with thiophenols in dry diethyl ether in the presence of pyridine.<sup>17,18</sup> Phenyl methanesulphinate (II) was synthesized by this procedure. The crude material was distilled under vacuum, collecting the fraction with b.p. 68–70° at 0.2 mmHg (Found: C, 50.4; H, 4.7; S, 37.3. C<sub>7</sub>H<sub>8</sub>OS<sub>2</sub> requires C, 48.8; H, 4.7; S, 37.2%). The purity of compounds (I)–(V) was controlled by titration of S=O group following Barnard's method.<sup>19</sup>

Dimethyl disulphide,<sup>20</sup> methanesulphonyl chloride,<sup>21</sup> benzenesulphonyl chloride,<sup>22</sup> 4-chlorobenzenesulphonyl chloride,<sup>18</sup> and 4-chlorothiophenol<sup>23</sup> were obtained by the usual methods.

**Physical Measurements.**—The physical measurements were carried out in benzene solution at 25° as previously described.<sup>1,5,8</sup>

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<sup>17</sup> H. J. Backer and H. Kloosterziel, *Rec. Trav. chim.*, 1954, **73**, 129.

<sup>18</sup> U. Marangelli, G. Modena, and P. E. Todesco, *Gazzetta*, 1960, **90**, 681.

<sup>19</sup> D. Barnhard and R. Cole, *Analyt. chim. Acta*, 1959, **20**, 540.

<sup>20</sup> F. Arndt, *Ber.*, 1921, **54**, 2236.

<sup>21</sup> I. B. Douglass and B. S. Farah, *Org. Synth.*, 1960, **40**, 62.

<sup>22</sup> I. B. Douglass and B. S. Farah, *J. Org. Chem.*, 1958, **23**, 330.

<sup>23</sup> H. J. Backer and N. D. Dijkstra, *Rec. Trav. chim.*, 1933, **52**, 701.