Chemistry of Sulphines. Part XXVII.[1] Conformational Analysis of Aryl- and Alkyl-thio, Aryl- and Alkyl-sulphinyl, and Aryl- and Alkyl-sulphonyl Sulphines by Means of Nuclear Magnetic Resonance Spectra and Dipole Moments

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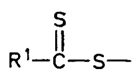
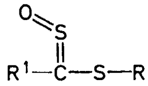
The preferred conformations of mesityl aryl- and alkyl-thio *E*- and *Z*-sulphines (II) and (III), mesityl aryl- and alkyl-sulphinyl *E*- and *Z*-sulphines (IV) and (V), and mesityl aryl- and alkyl-sulphonyl *E*- and *Z*-sulphines (VI) and (VII) have been determined by means of n.m.r. spectra (chemical shifts, ASIS, and LIS) and dipole moments. A comparison has been made with the corresponding 2,4,6-trimethyldithiobenzoates (I) which possess a linear *s-trans*-conformation. In none of the sulphines has such a linear conformation been found. Folded and gauche conformations dominate. The preferred conformations are in most cases rather rigid and are discussed in terms of electrostatic interactions of the sulphide, sulphoxide, or sulphone functions either with the sulphine oxygen in the *Z*-sulphines or with the sulphine lone pair in the *E*-isomers on the one hand and in terms of steric interactions on the other. In the crowded sulphines (IIe)—(VIIe), where R^2 = 2,4,6-$Me_3C_6H_2$, steric interactions between the *ortho*-methyl groups of both mesityl rings have been taken into account. In these sulphines the preferred conformations are sometimes different from those of the sulphines with R^2 = Ph. The sulphoxide *E*- and *Z*-sulphines exist as an equilibrium between two half-folded conformations. One conformation dominates the other. The thermodynamic parameters of these equilibria have been calculated. In the equilibrium of the sulphoxide *E*-sulphines remarkable effect on the equilibrium composition is observed upon addition of a shift reagent.

THE conformation of carboxylates, thiocarboxylates, and dithiocarboxylates has attracted considerable attention. Chiefly on the basis of dipole moment [2-5] and spectroscopic studies [6-8] it has been shown that all three types of compounds exist almost without exception in a remarkably rigid linear *s-trans*-conformation.

In previous Parts [9-11] the synthesis of a series of sulphines has been reported, *viz.* those derived from dithiocarboxylates by stepwise oxidation with peroxyacids. Since the CSO group is bent,[12,13] geometrical isomerism is possible; hence six types of sulphines arise and the aim of the present investigation is to establish the preferred conformations of these sulphines. The sulphines (II)—(VII) selected for the n.m.r. study are all derivatives of 2,4,6-trimethyldithiobenzoic acid.


$R^1-C(=S)-S-R^2$

(I)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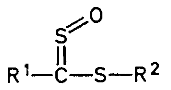
(II) (*E*)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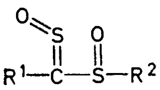
(III) (*Z*)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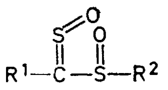
(IV) (*E*)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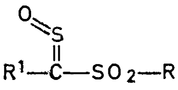
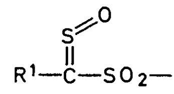
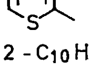
(V) (*Z*)


$R^1-C(=S{=}O)-SO_2-R^2$

(VI) (*E*)


$R^1-C(=S{=}O)-SO_2-R^2$

(VII) (*Z*)

R^1 = 2,4,6-$Me_3C_6H_2$
a; R^2 = Et
b; R^2 = Ph
c; R^2 = 
d; R^2 = 2-$C_{10}H_7$
e; R^2 = 2,4,6-$Me_3C_6H_2$

It was found [14] that the *ortho*-protons *syn* to the CSO system in diphenyl sulphines absorb at lower field by *ca.* 0·6 p.p.m. relative to the almost unperturbed *anti-ortho*-protons. The same deshielding has been observed for the *syn-ortho*-protons in phenyl phenylthio *E*-sulphine,[11] whereas in the *Z*-isomer all aromatic protons absorb at the same δ value. These observations have been explained [14] by assuming that *ortho*-protons *syn* to the CSO group turn around through the acetylene-like anisotropic deshielding cone [15] of the SO group of the

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[1] Part XXVI, A. Tangerman and B. Zwanenburg, *Tetrahedron Letters*, 1973, 5195.

[2] R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 1936, 1383.

[3] H. Lumbroso and P. J. W. Schuijl, *Compt. rend.*, 1967, *C*, **264**, 925.

[4] O. Exner, V. Jehlička, and A. Ohno, *Coll. Czech. Chem. Comm.*, 1971, **36**, 2157.

[5] O. Exner, V. Jehlička, and J. Firl, *Coll. Czech. Chem. Comm.*, 1971, **36**, 2936.

[6] J. E. Piercy and S. V. Subrahmanyan, *J. Chem. Phys.*, 1965, **42**, 1475.

[7] M. Ōki and H. Nakanishi, *Bull. Chem. Soc. Japan*, 1970, **43**, 2558.

[8] M. Ōki and H. Nakanishi, *Bull. Chem. Soc. Japan*, 1971, **44**, 3144.

[9] J. Strating, L. Thijs, and B. Zwanenburg, *Tetrahedron Letters*, 1966, 65.

[10] B. Zwanenburg, L. Thijs, and J. Strating, *Rec. Trav. chim.*, 1967, **86**, 577.

[11] B. Zwanenburg, L. Thijs, and J. Strating, *Rec. Trav. chim.*, 1971, **90**, 614.

[12] J. F. King and T. Durst, *J. Amer. Chem. Soc.*, 1963, **85**, 2676.

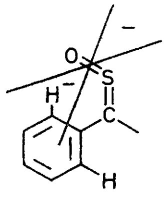
[13] B. Zwanenburg and J. Strating, *Quart. Rep. Sulfur Chem.*, 1970, **5**, 79.

[14] B. Zwanenburg, L. Thijs, and A. Tangerman, *Tetrahedron*, 1971, **27**, 1731.

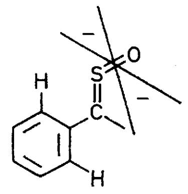
[15] C. H. Green and D. G. Hellier, *J.C.S. Perkin II*, 1972, 458.

sulphine system and that the *anti-ortho*-protons are unaffected by the CSO system.

From Tables 2, 3, and 9, it appears that in the sulphide, sulphoxide, and sulphone sulphines where R^2 is the non-anisotropic ethyl group, the protons of R^1 in the *E*-series (*syn*-protons) absorb at almost the same δ value as those in the *Z*-series (*anti*-protons). Hence, in the mesityl sulphines the *syn-ortho*-methyl protons are unaffected by the CSO system. This is due to the presence of a high rotational barrier about the mesityl–sulphine bond [16,17] in the *E*-series ($\Delta G^{\ddagger} > 20$ kcal mol^{-1}). Therefore, the mesityl–CSO part of the molecule can be considered as a rigid orthogonal system, with the consequence that the *ortho*-methyl groups in the *E*-series cannot rotate freely through the deshielding cone of the CSO system. In the *Z*-series there is also a high rotational barrier about the mesityl–sulphine bond [16,17] ($\Delta G^{\ddagger} > 19$ kcal mol^{-1}) indicating that the mesityl–CSO part may be regarded as a rigid orthogonal system in this case also. Furthermore, a comparison of the absorption data for the protons of R^1 in the sulphines with R^2 = Et shows that replacement of a sulphide by a sulphoxide or sulphone function has almost no effect on the chemical shift. In view of these facts, it may be concluded that the large differences in the absorption data for the protons of R^1 which are observed when the nonanisotropic ethyl group is replaced by the anisotropic aromatic group, can only be due to the anisotropic effect of this group transmitted through intramolecular shielding.

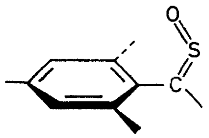


syn-protons

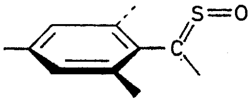


anti-protons

E-series



Z-series



In this paper the preferred conformation of the sulphines is deduced from an analysis of n.m.r. data in conjunction with dipole moment studies. When more than one conformation is present a fast exchange on the n.m.r. time scale must exist because only mean δ values are seen in the spectra.

RESULTS AND DISCUSSION

Aryl and Alkyl 2,4,6-Trimethyldithiobenzoates.—Although the preferred conformations of some dithiocarboxylates [3,5] have been determined the present compounds have not been investigated. In order to ensure that these dithiocarboxylates also have the *s-trans*-conformation the dipole moment of phenyl 2,4,6-trimethyldithiobenzoate (Ib) was measured in benzene at 25°. The moment, 1·81 D, is in accord with the anticipated value [5] for an exactly planar *s-trans*-conformation (1·78 D). The n.m.r. spectra which are collected in Table 1 substantiate the *s-trans*-conformation. Folded conformations cannot contribute in these dithiocarboxylates because no intramolecular shielding is observed.

TABLE 1

Chemical shifts of dithiocarboxylates (I)

	R^1			R^2
	δ(o-CH_3)	δ(p-CH_3)	δ(m-H)	δ
(Ia)	2·23	2·28	6·88	3·35 (CH_2), 1·40 (CH_3)
(Ib)	2·36	2·29	6·90	7·49 (C_6H_5)
(Ic)	2·33	2·29	6·89	7·20 (β-H), 7·20 (γ-H), 7·64 (δ-H)
(Id)	2·40	2·30	6·90	8·03 (α-H)
(Ie)	2·40	2·32	6·90	2·40 (o-CH_3), 2·35 (p-CH_3), 7·05 (m-H)

TABLE 2

Chemical shifts for sulphines (II) and (III)

	R^1			R^2
	δ(o-CH_3)	δ(p-CH_3)	δ(m-H)	δ
(IIa)	2·31	2·29	6·94	2·88 (CH_2), 1·35 (CH_3)
(IIb)	2·19	2·25	6·88	7·37 (C_6H_5)
(IIc)	2·18	2·25	6·88	7·10 (β-H), 6·98 (γ-H), 7·43 (δ-H)
(IId)	2·23	2·23	6·88	7·98 (α-H)
	(2·33) [a]	(2·29)	(6·98)	(8·13) (α-H)
(IIe)	2·34	2·27	6·94	2·54 (o-CH_3), 2·27 (p-CH_3), 7·00 (m-H)
	(2·42)	(2·32)	(7·02)	(2·59) (o-CH_3), (2·32) (p-CH_3), (7·06) (m-H)
(IIIa)	2·30	2·30	6·94	2·56 (CH_2), 1·18 (CH_3)
(IIIb)	2·23	2·15	6·71	7·18 (C_6H_5)
(IIIc)	2·27	2·18	6·75	7·00 (β-H), 6·81 (γ-H), 7·30 (δ-H)
(IIId)	2·25	2·06	6·65	7·79 (α-H)
	(2·28)	(2·07)	(6·67)	(7·71) (α-H)
(IIIe)	2·37	2·26	6·88	2·53 (o-CH_3), 2·26 (p-CH_3), 6·88 (m-H)
	(2·43)	(2·31)	(6·94)	(2·58) (o-CH_3), (2·31) (p-CH_3), (6·94) (m-H)

[a] Values in parentheses are δ values obtained at −60° in $CDCl_3$.

Mesityl Aryl- and Alkyl-thio Sulphines.—The chemical shifts of the respective protons of the sulphide *E*- and *Z*-sulphines (II) and (III) are listed in Table 2. These data reveal that the protons of R^1 in the sulphide *E*- and *Z*-sulphines (IIb—d) and (IIIb—d) where R^2 is aromatic, absorb at higher field than those in the sulphines where R^2 = Et. As argued before these upfield shifts must be attributed to the anisotropic effect of the aromatic ring R^2 by means of intramolecular shielding. This can only be envisaged as occurring in more or less folded conformations of the sulphide sulphines. Assuming such conformations it may be

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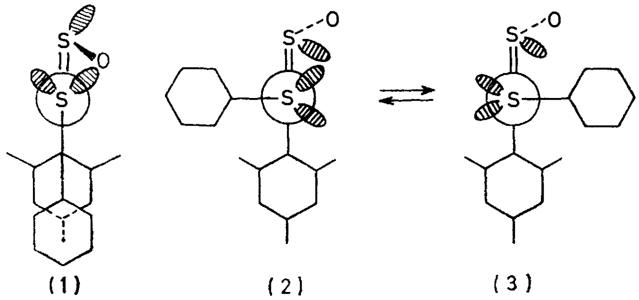
[16] A. Tangerman and B. Zwanenburg, *Tetrahedron Letters*, 1972, 5329.

[17] A. Tangerman and B. Zwanenburg, *J.C.S. Perkin II*, in the press.

expected that the mesityl ring will exert an intramolecular shielding on the protons of R^2. Indeed, the protons of R^2 in sulphines (IIa—d) and (IIIa—d) absorb at higher field than those in the corresponding dithiocarboxylates (Ia—d) which possess a linear *s-trans*-conformation. A closer examination of the data in Table 2 together with dipole moment studies allow a refinement of the description of the preferred conformations.

Comparison of the absorptions of the *meta*-protons and the *para*-methyl protons of R^1 and the aromatic protons of R^2 reveals that those of the *Z*-sulphines (IIIb—d) are at distinctly higher field than those of the corresponding *E*-sulphines. This observation can be accounted for by assuming for the *Z*-sulphines a preferred folded *s-cis*-conformation (1) (Scheme 1) in which the sulphine oxygen is situated between the lone pairs of the sulphenyl sulphur and the aromatic rings are placed approximately face-to-face. The upfield shifts of the protons of R^2 *e.g.* in sulphine (IIIb) [0·31 p.p.m., compared with the phenyl absorption in the corresponding dithiocarboxylate (Ib)], are in the order found for the phenyl absorptions of 1,8-diphenylnaphthalene in which the phenyl rings are face-to-face.[18] The *ortho*-methyl groups of R^1 in conformation (1) are outside the effective shielding region of R^2 and therefore will be only slightly affected. The magnitude of the shielding of the *meta*-protons and the *para*-methyl protons of R^1 by R^2 is in accord with the trend in the magnitude of the aromatic ring current of R^2, *viz.* naphthalene > benzene > thiophen.[19]



Scheme 1

Low temperature n.m.r. studies of the *Z*-sulphines (III) provide information about the rigidity of conformation (1). The absorption pattern of the *Z*-sulphines (IIIb—d) as listed in Table 2 for (IIId) remains almost unchanged between 32 and −60°, indicating that conformation (1) is rigid. Because of this rigidity dipole moments may also be used to establish the preferred conformation in the sulphide *Z*-sulphines. This treatment fully confirms the n.m.r. results because the experimental dipole moment of (IIIb) (5·19 D) is only compatible with the calculated moment for the folded *s-cis*-conformation (1) (4·95 D (see Appendix). Similarly, the experimental moments of mesityl ethylthio *Z*-sulphine (IIIa) (5·17 D), phenyl phenylthio *Z*-sulphine (4·95 D), and phenyl mesitylthio *Z*-sulphine (5·04 D) also point to this folded conformation.

In the sulphide *E*-sulphines (IIb—d), however, the protons of R^2 and the *meta*-protons and *para*-methyl protons of R^1 are shielded to a much lesser extent than the corresponding protons in the *Z*-isomers, indicating that face-to-face folded conformations such as (1) cannot adequately account for the n.m.r. spectra. The temperature effect on the spectrum of (IId) is small, suggesting that the variation in the preferred conformation in the temperature range (32 to −60°) is also small. Therefore, the dipole moment at 25° (in benzene) may be taken in good approximation as the dipole moment of the preferred conformation(s). Comparison of the experimental moment of (IIb) (3·52 D) with the moments computed for all possible conformations (see Appendix) leads to the conclusion that there are two enantiomeric gauche conformations (2) and (3) (Scheme 1) for the sulphide *E*-sulphines. The dipole moment of phenyl phenylthio *E*-sulphine (3·61 D) points to the same conclusion.

The sulphines (IIe) and (IIIe) in which R^1 as well as R^2 is mesityl form a special case. The protons of R^1 of mesityl mesitylthio *E*-sulphine (IIe) show the same features as those of the *E*-sulphines (IIb—d) (Table 2). Since the dipole moment of (IIe) (3·51 D) is also the same as that of (IIb), the same preferred gauche conformations (2) and (3) are suggested for (IIe). However, the spectral features of the protons of R^1 of the *Z*-isomer (IIIe) (Table 2) are considerably different from those of the *Z*-sulphines (IIIb—d) and almost identical with those of the *E*-isomer (IIe). Therefore, the folded conformation (1) is absent in (IIIe). Moreover, the dipole moment of (IIIe) (3·83 D) also differs from that of (IIIb) (5·19 D). From this dipole moment of (IIIe) the gauche conformations found for the sulphide *E*-sulphines were derived for the *Z*-isomer (IIIe). It is noteworthy that mesityl phenylthio *Z*-sulphine (IIIb) as well as phenyl mesitylthio *Z*-sulphine possesses the folded conformation (1), whereas in the case of (IIIe) gauche conformations are preferred. This conformational change is probably caused by a large steric interaction between the *ortho*-methyl groups in the respective mesityl substituents, which interaction will be diminished in the gauche conformations.

Mesityl Aryl- and Alkyl-sulphinyl Sulphines.—The spectral features of the sulphoxide *E*- and *Z*-sulphines (IV) and (V) are collected in Table 3.

Owing to the presence of the pyramidal asymmetric sulphoxide function the *ortho*-methyl groups as also the *meta*-protons of R^1 become diastereotopic,[11,16] provided rotation about the mesityl–sulphine bond is restricted. There is a striking difference in chemical shift between the *ortho*-methyl protons in the *E*- as well as in the *Z*-series when R^2 is aromatic. This difference cannot be due to the influence of the sulphoxide function on

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[18] H. O. House, R. W. Magin, and H. W. Thompson, *J. Org. Chem.*, 1963, **28**, 2403.

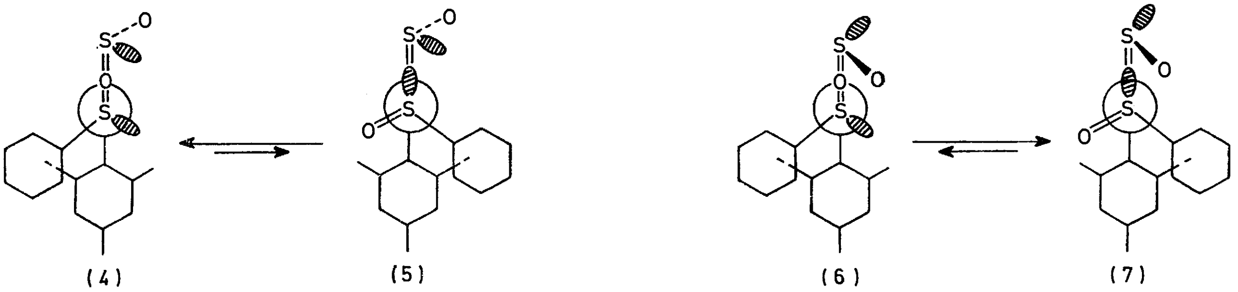
[19] J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High-resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959.

TABLE 3

Chemical shifts for sulphines (IV) and (V)

	R¹				R²
	δ(o-CH_3) (1)	δ(o-CH_3) (2)	δ(p-CH_3)	δ(m-H)	δ
(IVa)	2·37;	2·32	2·30	6·97	2·84 (CH_2), 1·37 (CH_3)
(IVb)	2·18;	1·63	2·24	6·88; 6·78	7·41 (o-H)
(IVc)	2·18;	1·87	2·26	6·89; 6·85	7·10 (β-H), 7·01 (γ-H), 7·67 (δ-H)
(IVd)	2·20;	1·55	2·24	6·88; 6·73	7·87 (α-H)
(IVe)	2·28;	1·79	2·23	6·88; 6·78	2·67 [o-CH_3(3)]; 1·89 [o-CH_3(4)], 2·25 (p-CH_3), 6·87; 6·72 (m-H)
(Va)	2·38;	2·38	2·31	6·97	3·52 (CH_2), 1·53 (CH_3)
(Vb)	2·41;	1·44	2·26	7·00; 6·82	7·81 (o-H)
(Vc)	2·38;	1·75	2·27	7·00; 6·88	7·66 (β-H), 7·14 (γ-H), 7·66 (δ-H)
(Vd)	2·44;	1·31	2·25	7·00; 6·75	8·23 (α-H)
(Ve)	1·95;	2·07	2·25	6·86; 6·84	2·29 (o-CH_3), 2·25 (p-CH_3), 6·78 (m-H)

the *ortho*-methyl protons of R¹ because, when R² is ethyl, the *ortho*-methyl protons of R¹ differ only slightly (see introductory remarks). The significant difference must be attributed to intramolecular shielding of one *ortho*-methyl by an aromatic R² group. Molecular models suggest that two types of conformation are possible in which such shielding is encountered, *viz.* (4) and (5) for the *E*-sulphines and (6) and (7) for the *Z*-sulphines (Scheme 2). Applying the corrected Johnson–Bovey isoshielding lines of benzene,[20] shielding values of 0·5—1 p.p.m. are calculated for the shielded *ortho*-methyl in these conformations, which values agree well with those obtained experimentally. In the sulphoxide *E*- and *Z*-sulphines the magnitude of the shielding of the high-field *ortho*-methyl group and the high-field *meta*-hydrogen by R² is in accord with the trend in the magnitude of the aromatic ring current of R².[19]



SCHEME 2

Table 4 records the temperature dependent spectra of the *ortho*-methyl protons of the sulphoxide *E*- and *Z*-sulphines (IVd) and (Vd). The absorption pattern of the *Z*-isomers undergoes only very small changes indicating that they exist, even at room temperature, in a rather rigid conformation. Hence, the dipole moment of the sulphoxide *Z*-sulphine (Vb) (3·88 D) may be considered as the moment of one conformation. This moment is compatible only with the calculated moment of conformation (7) (3·5—4·6 D) while for conformation (6) a dipole moment range of 6·7—7·1 D has been calculated (see Appendix). In the solid state the sulphoxide *Z*-sulphine (Vb) adopts a half-linear conformation as determined from an *X*-ray analysis.[21]

The sulphoxide *E*-sulphines give much larger shifts for the *ortho*-methyl protons on varying the temperature (Table 4) and are therefore conformationally less rigid than the *Z*-isomers. At room temperature both *ortho*-methyls are intramolecularly shielded, o-CH_3(2) to a larger extent than o-CH_3(1). At lower temperatures o-CH_3(1) becomes unshielded, while o-CH_3(2) is still more shielded. Probably at room temperature an equilibrium exists between the two conformations (4) and (5) with one predominating, an effect which becomes more pronounced at lower temperatures. The dipole moment for (IVb) (4·65 D) at 25° (in benzene) agrees well with this suggestion. The experimental moment is intermediate between the ranges calculated for conformations (4) (5·7—6·0 D) and (5) (2·9—3·9 D) (see Appendix).

TABLE 4

Chemical shifts for *ortho*-methyl protons of sulphines (IVd) and (Vd) at different temperatures

	(IVd) (*E*)		(Vd) (*Z*)	
	δ[o-CH_3(1)]	δ[o-CH_3(2)]	δ[o-CH_3(1)]	δ(o-CH_3(2)]
+60	2·16	1·60	2·43	1·34
+40	2·19	1·56	2·435	1·32
+20	2·22	1·52	2·44	1·30
0	2·25	1·48	2·45	1·28
−20	2·29	1·43	2·46	1·27
−40	2·34	1·39	2·47	1·26
−60	2·38	1·35	2·48	1·25

In order to gather more information about the suggested conformations for the sulphoxide *E*- and *Z*-sulphines, ASIS and LIS have been studied. The respective shifts of the *ortho*-methyl groups are compiled in Table 5. Figure 1 shows a plot of the LIS of the two *ortho*-methyl groups of (IVb) and (Vb) against [Eu(dpm)$_3$]/[substrate].

In these sulphoxide sulphines the shift reagent Eu(dpm)$_3$ has two possibilities for complexation, at the sulphine oxygen or at the sulphoxide oxygen. As shown previously [22] Eu(dpm)$_3$ complexes at the sulphine

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[20] C. W. Haigh and R. B. Mallion, *Org. Magnetic Resonance*, 1972, **4**, 203.

[21] Th. W. Hummelink, *J. Cryst. Mol. Struct.*, to be published.

[22] A. Tangerman and B. Zwanenburg, *Tetrahedron Letters*, 1973, 79.

oxygen atom in aromatic sulphines, sulphide sulphines, and sulphone sulphines. The shift data in Table 6 give more insight in the site of co-ordination in the sulphoxide sulphines. The LIS of the *ortho*-protons of R^2 in the sulphoxide *E*- and *Z*-sulphines (IVb) and (Vb) and in phenyl mesitylmethyl sulphoxide have almost the same value and are much larger than the LIS of the corresponding protons in the sulphide *E*- and *Z*-sulphines (IIb) and (IIIb), in which complexation with the sulphine oxygen does occur. These results clearly demonstrate that in the sulphoxide sulphines complexation of Eu(dpm)$_3$ preferably takes place at the sulphoxide oxygen atom and not at the sulphine oxygen atom.

TABLE 5

ASIS and LIS for *ortho*-methyl signals of sulphines (IV) and (V)

	E-series					*Z*-series			
	ASIS Δ(o-CH$_3$) [a]		LIS Δ(o-CH$_3$) [b]			ASIS Δ(o-CH$_3$) [a]		LIS Δ(o-CH$_3$) [b]	
(IVa)	0·30	0·14	1·06	1·74	(Va)	0·21	0·35	1·79	1·47
(IVb)	0·35	−0·12	1·00	1·83	(Vb)	0·11	0·18	2·66	1·57
(IVc)	0·30	−0·09	0·96	1·88	(Vc)	0·10	0·18	1·80	1·22
(IVd)	0·36	−0·14	1·06	1·96	(Vd)	0·09	0·21	1·89	1·08
(IVe)	0·23(1)	−0·14(2)	0·77(1)	1·54(2)	(Ve)			0·25(1)	1·92(2) [c]
	0·00(3)	0·24(4)	2·86(3)	0·65(4)				1·13(3)	0·15(4)

[a] Δ = δ(CDCl$_3$) − δ(C$_6$D$_6$). [b] Δ = δ[CDCl$_3$ + 0·3 equiv. Eu(dpm)$_3$] − δ(CDCl$_3$). [c] LIS values for (Ve) obtained at −43° [addition of 0·15 equiv. Eu(dpm)$_3$].

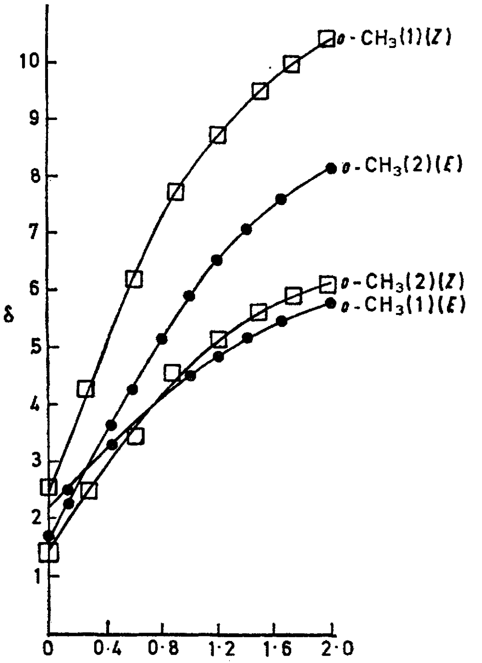

FIGURE 1 LIS of *ortho*-methyl groups of (IVb) (●) and (Vb) (□)

The shift data for the sulphoxide *Z*-sulphines (Vb—d) (Table 5, Figure 1) reveal that the low-field o-CH$_3$(1) give a much larger LIS than o-CH$_3$(2). This is compatible only with conformation (7) (Scheme 2), where the low-field *ortho*-methyl is closest to the site of complexation, the sulphoxide oxygen atom. For conformation (6) an almost equal LIS was expected for both *ortho*-methyl groups.

The LIS for the sulphoxide *E*-sulphines (IVb—d) indicate that the high-field o-CH$_3$(2) gives the largest shift. This can neither be explained by the predominant presence of conformation (5), where the low-field *ortho*-methyl should give the largest LIS, nor by that of conformation (4), where both *ortho*-methyls are situated at about the same distance from the sulphoxide function and therefore would give about the same LIS. As previously shown by us [23] and by other authors [24] complexation with a shift reagent may affect the equilibrium composition of conformers. The LIS results for the sulphoxide *E*-sulphines can only be explained by accepting such an effect on the conformational equilibrium of (4) and (5). Bearing in mind that a large difference in LIS between the two *ortho*-methyls is only understandable if Eu(dpm)$_3$ complexes with the sulphoxide oxygen in conformation (5), the observed LIS are explained as follows. In the uncomplexed state conformation (4) is preferred; however, complexation with Eu(dpm)$_3$ shifts the conformational equilibrium towards (5). Then the o-CH$_3$ which is at high-field in the uncomplexed state will give the largest LIS. Sulphoxide *E*-sulphines adopt conformation (4) in the solid state as determined from *X*-ray analysis of (IVb).[25]

TABLE 6

LIS for *ortho*-protons of compounds (IIb)—(Vb) and phenyl mesitylmethyl sulphoxide

	Δ(o-H)
(IIb)	0·80
(IIIb)	0·83
(IVb)	2·50
(Vb)	2·79
	2·53

Phenyl mesitylmethyl sulphoxide
Δ = δ[CDCl$_3$ + 0·3 equiv. Eu(dpm)$_3$] − δ(CDCl$_3$).

The ASIS results listed in Table 5 were analysed as follows. For benzene it is known [26,27] that complexation takes place at the positive end of a dipole in a

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[23] A. Tangerman and B. Zwanenburg, *Tetrahedron Letters*, 1973, 5195.

[24] W. G. Bentrude, H. W. Tan, and K. C. Yee, *J. Amer. Chem. Soc.*, 1972, **94**, 3264.

[25] Th. W. Hummelink, *J. Cryst. Mol. Struct.*, 1974, **4**, 87.

[26] P. Laszlo in ' Progress in N.M.R. Spectroscopy,' eds. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Pergamon, Oxford, vol. 3, 1967.

[27] T. Ledaal, *Tetrahedron Letters*, 1968, 1683.

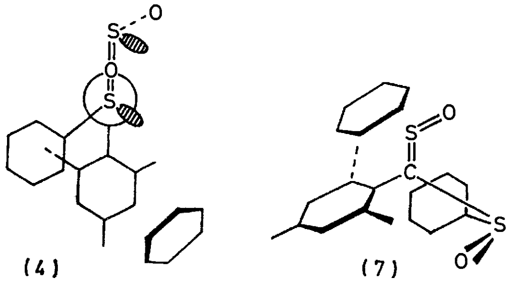
molecule. Because these sulphoxide sulphines possess both sulphoxide and sulphine dipoles, the following factors will govern the site of complexation of solvent benzene. First, benzene will complex *anti* to the CSO system; secondly, benzene will complex as far away as possible from the sulphoxide oxygen. Moreover, steric effects may influence the site of complexation. Thus the benzene–solute complexes presented in Scheme 3 are those adopted for the preferred conformations (4) and (7) of the sulphoxide *E*- and *Z*-sulphines, respectively. The low-field o-CH_3(1) in conformation (4) of the sulphoxide *E*-sulphines experiences a large positive ASIS, while that of o-CH_3(2), which is masked by the aromatic R^2 and therefore cannot be approached by solvent benzene, is negative. In conformation (5) the ASIS of the low-field o-CH_3(1) would be much smaller because the group is situated in the vicinity of the negative sulphoxide oxygen. In conformation (7) of the sulphoxide *Z*-sulphines both *ortho*-methyls give a positive ASIS. The ASIS of the low-field o-CH_3(1), which is in the vicinity of the sulphoxide oxygen, is smaller by about a factor of 2. In conformation (6), where both *ortho*-methyls are at the same distance from the sulphoxide oxygen, about the same value was expected for each group. In conclusion, the ASIS results agree well with the suggested preferred conformations (4) and (7) for the sulphoxide *E*- and *Z*-sulphines, respectively.

TABLE 7

Thermodynamic parameters for the equilibrium between conformations (4) and (5) in sulphoxide *E*-sulphines (IVb—e) and between conformations (6) and (7) in sulphoxide *Z*-sulphines (Vb—e)

	K^{20} [a]	ΔG^{20}/kcal mol^{-1}	ΔH/kcal mol^{-1}	ΔS/cal mol^{-1} K^{-1}	Mole fraction (4) 20°	Mole fraction (4) −60°
(IVb)	2·97	−0·63	−2·1	−5	0·75	0·91
(IVc)	2·43	−0·52	−2·2	−6	0·71	0·90
(IVd)	3·56	−0·74	−1·9	−4	0·78	0·92
(IVe)	3·36	−0·70	−1·5	−3	0·77	0·89 [b]
					Mole fraction (7)	
(Vb)	20·6	−1·76	−3·5	−6	0·95	1·0
(Vc)	16·5	−1·63	−3·6	−7	0·95	1·0
(Vd)	23·6	−1·84	−3·6	−6	0·96	1·0
(Ve)	1·30	−0·15	+3·1	+11	0·56	0·16 [c]

[a] For (IVb—d) $K = (4)/(5)$; for (IVe) $K = (4')/(5')$; for (Vb—d) $K = (7)/(6)$; for (Ve) $K = (7')/(6')$. [b] Mole fraction of conformation (4′). [c] Mole fraction of conformation (7′).



SCHEME 3

It should be noted that the *ortho*-protons of R^2 are situated at much lower field in the *Z*- than in the *E*-series (see Table 3). Molecular models clearly show that in the preferred conformation (7) for the sulphoxide *Z*-sulphines the *ortho*-protons of R^2 turn around through the deshielding cone of the SO part of the sulphine system.

Probably, the mesityl ethylsulphinyl *E*- and *Z*-sulphines (IVa) and (Va) possess the same preferred conformations as suggested for (IVb—d) and (Vb—d), respectively, because the *ortho*-methyl protons show the same ASIS and LIS features (Table 5). Moreover, the *E*-sulphine (IVa) has almost the same dipole moment (4·59 D) as (IVb) (4·65 D).

The equilibrium constant K of the equilibrium (5) $\rightleftharpoons$ (4) in the sulphoxide *E*-sulphines (IVb—d) can be calculated at different temperatures from the temperature dependent spectra of these sulphines. K is given by equation (1) where $\Delta\delta = \delta_u - \delta$ and

$$K = \Delta\delta/(\Delta\delta_{\text{max.}} - \Delta\delta) \qquad (1)$$

$\Delta\delta_{\text{max.}} = \delta_u - \delta_s$ and δ_u and δ_s are the δ values of the fully unshielded and the fully shielded *ortho*-methyl, respectively. The mole fraction of conformation (4) can be calculated from the chemical shift of o-CH_3(2) and the mole fraction of (5) from that of o-CH_3(1) (mole fraction $= \Delta\delta/\Delta\delta_{\text{max.}}$). δ_u and δ_s are the δ-values of the low- and high-field *ortho*-methyl, respectively, obtained at −60°, augmented or diminished, respectively, by 0·1 p.p.m. That the δ_u and δ_s values so obtained are correct is supported by the fact that the sum of the calculated mole fractions of (4) and (5) at different temperatures is *ca.* 1 ($\pm$0·04). Furthermore, plots of log K *versus* $10^3\ T^{-1}$, based on calculations for o-CH_3(2), are linear. The thermodynamic parameters ΔH, ΔS, and ΔG of the conformational equilibrium for these *E*-sulphines (Table 7) are calculated by means of equations (2) and (3). The

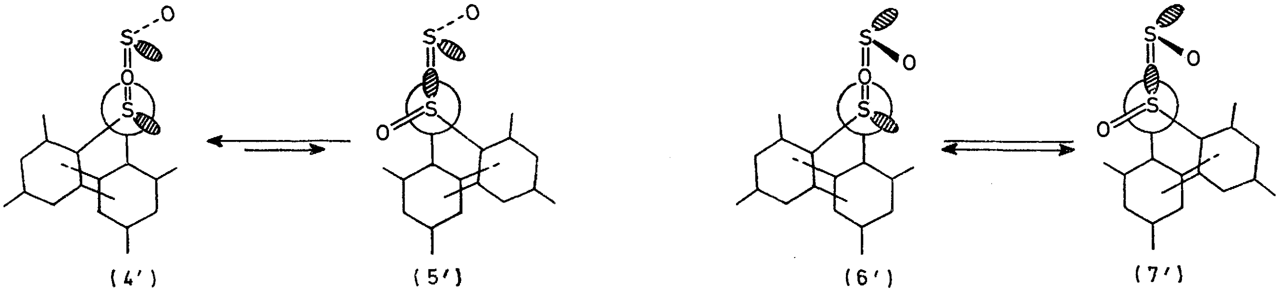
$$\log K = -\Delta H/2{\cdot}303RT + \Delta S/2{\cdot}303R \qquad (2)$$

$$\Delta G = -2{\cdot}303RT \log K \qquad (3)$$

data show that for the *E*-sulphines (IVb—d) conformation (4) is favoured over (5) by *ca.* 2 kcal mol^{-1} in enthalpy.

As already mentioned for the sulphoxide *Z*-sulphines (Vb—d), conformation (7) is rigid, the temperature effect being small (Table 4). Nevertheless, conformation (6) may be present to a very small extent because at higher temperatures the low-field o-CH_3(1) is still somewhat shielded compared with the situation at —60°. A *rough* estimate of the thermodynamic parameters of the equilibrium (6) $\rightleftharpoons$ (7) can be made by assuming that at —60° conformation (7) is the only one present, which means that at —60° $\delta[o\text{-}CH_3(1)]$ and $\delta[o\text{-}CH_3(2)]$ equal the δ_u and δ_s values, respectively, in equation (1). The obtained data (Table 7) reveal that conformation (7) is stabilized by *ca.* 3·5 kcal mol^{-1} in enthalpy over (6).

The n.m.r. spectra of the E- (IVe) as well as of the mesityl mesitylsulphinyl Z-sulphine (Ve) show four different *ortho*-methyl signals (the latter sulphine at lower temperatures), two for R^1 and two for R^2. This means that there are two rotational barriers in these molecules,[16,17] one about the R^1–sulphine bond ($\Delta G^{\ddagger}_c$ 25·9 and 21·3 kcal mol^{-1}, respectively) and the other about the R^2–sulphoxide bond ($\Delta G^{\ddagger}_c$ 17·9 and 14·4 kcal mol^{-1}, respectively). The ASIS and LIS * behaviour of the *ortho*-methyls of R^1 in the E-sulphine (IVe) (Table 5) is similar to that of the E-sulphines (IVb—d) which points to the predominant presence of conformation (4′) for (IVe) (Scheme 4), which resembles conformation (4) of (IVb—d). The ASIS and LIS of the *ortho*-methyls of R^2 (Table 5) are in good agreement with this preferred conformation (4′). The low-field o-CH_3(3) gives the largest LIS and the smallest ASIS, while the reverse is expected for the low-field *ortho*-methyl in conformation (5′). However, conformation (5′) must also be present to some extent, because the low-field o-CH_3(1) and o-CH_3(3) are still somewhat shielded at higher temperatures compared with the values at —60° (Table 8). The thermodynamic parameters of the conformational equilibrium in the sulphoxide E-sulphine (IVe), which are calculated as described for (IVb—d), are in the same range as those for (IVb—d) (Table 7). This observation agrees well with the finding that the dipole moment of (IVe) (4·81 D) is about the same as that of (IVb) (4·65 D).



Scheme 4

Table 8

Chemical shifts for *ortho*-methyl protons of mesityl mesitylsulphinyl E- and Z-sulphines at different temperatures

	(IVe) (E)				(Ve) (Z)			
T/°C	$\delta[o\text{-}CH_3(1)]$	$\delta[o\text{-}CH_3(2)]$	$\delta[o\text{-}CH_3(3)]$	$\delta[o\text{-}CH_3(4)]$	$\delta[o\text{-}CH_3(1)]$	$\delta[o\text{-}CH_3(2)]$	$\delta[o\text{-}CH_3(3)]$	$\delta[o\text{-}CH_3(4)]$
+60	2·24	1·82	2·64	1·92	1·88	2·12		
+40	2·265	1·80	2·66	1·90	1·92	2·09	2·29	
+20	2·29	1·775	2·68	1·875	1·98	2·03	Coalescence	
0	2·32	1·74	2·70	1·85	2·05	1·97	2·43	2·01
−20	2·355	1·71	2·72	1·82	2·16	1·88	2·57	1·95
−40	2·395	1·68	2·74	1·80	2·27	1·80	2·65	1·87
−60	2·43	1·655	2·76	1·78	2·37	1·71	2·75	1·78

Though the temperature effect in the sulphoxide Z-sulphines (Vb—d) is small (Table 4), a considerable effect was observed for the mesityl mesitylsulphinyl Z-sulphine (Ve) (Table 8). At room temperatures the *ortho*-methyls of R^1 are almost equally shielded which can be explained by the fact that for this Z-sulphine conformations (6′) and (7′) (Scheme 4) are present to approximately the same extent. At low temperature (—60°) the spectrum becomes almost identical with that of the E-isomer (IVe) and has the same LIS behaviour (Table 5). The high-field o-CH_3(2) of R^1 and the low-field o-CH_3(3) of R^2 give the largest LIS which can only be explained by assuming at lower temperatures a preferred conformation similar to (4′) for the E-isomer (IVe), *viz.* conformation (6′). The energy parameters of the equilibrium (6′) $\rightleftharpoons$ (7′) have been calculated for the Z-sulphine (Ve) (Table 7) using the δ_u and δ_s values for the E-isomer (IVe). The data show that for (Ve) conformation (7′) has become disfavoured by *ca.* 3 kcal mol^{-1} in enthalpy with respect to (6′) while for the Z-sulphines (Vb—d) conformation (7) is favoured over (6) by *ca.* 3·5 kcal mol^{-1}.

Mesityl Aryl- and Alkyl-sulphonyl Sulphines.—The n.m.r. data of the sulphone E- and Z-sulphines (VI) and (VII) are collected in Table 9.

In the sulphone E-sulphines (VIb—d) both *ortho*-methyls of R^1 are situated at high-field with respect to the unperturbed methyl groups of (VIa) and therefore are intramolecularly shielded by the aromatic R^2. As for the sulphoxide E- and Z-sulphines, the magnitude

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* For an explanation of the LIS results for (IVe) the same conformation change by complexation with Eu(dpm)$_3$ as given for the sulphoxide E-sulphines (IVb—d) should be assumed.

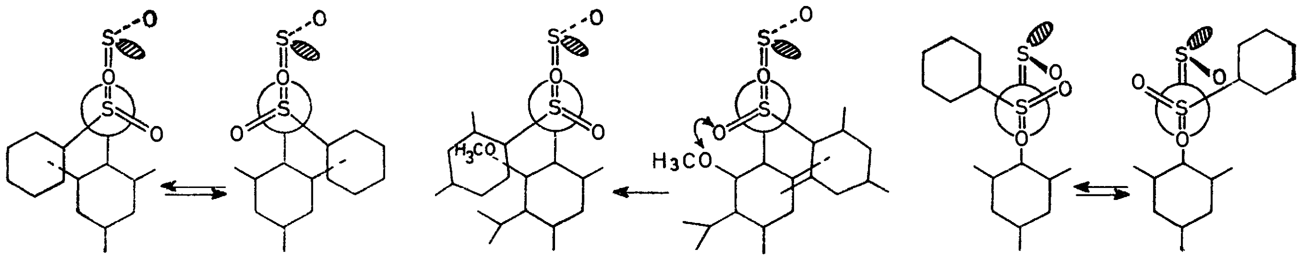
of the shielding values of the *ortho*-methyls by R^2 in the sulphone *E*-sulphines agrees well with the trend in the magnitude of the aromatic ring current of R^2. The δ values of the *ortho*-methyl signals are about intermediate between those of the high- and low-field *ortho*-methyl resonances of the sulphoxide sulphines (V) (Table 3). Therefore, an exchange between the two enantiomeric conformations (8) and (9) (Scheme 5) is suggested for the sulphone *E*-sulphines (VI). Similar conformations were also deduced from an *X*-ray analysis of (VIb).[21] From the fact that the spectral features remain almost the same at —60°, as shown for (VId) in Table 9, it may be concluded that no change in conformation occurs on varying the temperature. The calculated dipole moment for conformations (8) and (9) (5·1—5·9 D; see Appendix) is somewhat higher than the experimental moment of (VIb) (4·83 D). The dipole moment of phenyl phenylsulphonyl *E*-sulphine (4·73 D) indicates the same preferred conformations as for (VIb—d).

TABLE 9

Chemical shifts for sulphines (VI) and (VII)

	R^1			R^2
	δ(*o*-CH_3)	δ(*p*-CH_3)	δ(*m*-H)	δ
(VIa)	2·31	2·31	6·99	3·09 (CH_2), 1·40 (CH_3)
(VIb)	1·86	2·26	6·87	7·63 (*o*-H)
(VIc)	1·96	2·28	6·90	7·51 (β-H), 7·13 (γ-H) 7·78 (δ-H)
(VId)	1·82 (1·78) [a]	2·25 (2·27)	6·84 (6·88)	8·30 (8·36) (α-H)
(VIe)	1·90 (1·86) [a]	2·26 (2·30)	6·86 (6·91)	2·33 (2·30) (*o*-CH_3), 2·29 (2·34) (*p*-CH_3), 6·93 (6·98) (*m*-H)
(VIIa)	2·37	2·29	6·99	3·68 (CH_2), 1·50 (CH_3)
(VIIb)	2·21	2·29	6·96	8·14 (*o*-H)
(VIIc)	2·26	2·30	6·97	8·03 (β-H), 7·21 (γ-H), 7·80 (δ-H)
(VIId)	2·21 (2·19) [a]	2·30 (2·33)	6·97 (7·03)	8·75 (8·80) (α-H)
(VIIe)	2·14 (2·07) [a]	2·28 (2·32)	6·92 (6·98)	2·46 (2·38) (*o*-CH_3), 2·30 (2·32) (*p*-CH_3), 6·94 (6·98) (*m*-H)

[a] Values in parentheses are δ values obtained at —60°.



(8) (9) (8') (9') (10) (11)

SCHEME 5

A remarkable change in the conformational equilibrium of the sulphone *E*-sulphines was observed when one *ortho*-methyl was replaced by a methoxy-group. In this sulphone sulphine (Scheme 5) only the *ortho*-methoxy-group is intramolecularly shielded (δ 3·12, normal value in the corresponding sulphide *E*-sulphine 3·70) while the *ortho*-methyl group (δ 2·30) is not intramolecularly shielded. This means that conformation (8') (Scheme 5) is the only preferred one. Probably, conformation (9') is disfavoured by electrostatic repulsive interactions between one of the sulphone oxygens and the methoxy oxygen atom, which interactions are absent in conformation (8').

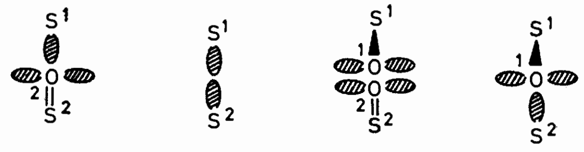
In the sulphone *Z*-sulphines (VIIb—d) *p*-CH_3 and *m*-H of R^1 (Table 9) absorb at about the same δ value as the corresponding protons in (VIIa) and are, therefore, not intramolecularly shielded. Thus, more linear conformations must be taken into account. Because the spectral features given in Table 9 for (VIId) remain almost unchanged at lower temperatures, it may be assumed that the sulphone *Z*-sulphines exist in rather rigid conformations. Therefore, the dipole moment for (VIIb) (4·68 D) may be used to determine the preferred conformations. Comparison of the experimental value with the calculated moments of all possible conformations (see Appendix) gives the two enantiomeric half-linear conformations (10) and (11) (Scheme 5) for the sulphone *Z*-sulphines. Compound (VIIb) adopts the same conformation in the solid state.[25]

The data in Table 9 also show that in the sulphone *Z*-sulphines (VIIb—d) the *ortho*-hydrogens of R^2 absorb at much lower field than the corresponding protons in the *E*-series, which has also been found to some extent for the sulphoxide sulphines and here also can be explained by the fact that in conformations (10) and (11) these protons turn around through the deshielding cone of the CSO system.

The spectral features of the protons of R^1 in the mesityl mesitylsulphonyl *E*- and *Z*-sulphines (VIe) and (VIIe) (Table 9) are the same as those of (VIb—d) and (VIIb—d), respectively, indicating that the preferred conformations are very similar to those suggested for (VIb—d) and (VIIb—d). Moreover, the dipole moment of (VIe) (4·88 D) is almost equal to that of (VIb) (4·83 D).

Conclusions.—In summary, the preferred conformations of the three types of sulphines in the *Z*-series vary from the folded *s-cis*-conformation (1) for the sulphide *Z*-sulphines to the half-folded conformation (7) for the sulphoxide *Z*-sulphines to the half-linear conformations (10) and (11) for the sulphone *Z*-sulphines. The preferred conformations in the *Z*-series are probably the result of a compromise between two effects: first, the electrostatic interactions of the sulphine oxygen atom either with the lone pairs on sulphur or with the sulphoxide and sulphone oxygen atoms; second, the interactions of R^2 either with the sulphine oxygen or with R^1. The change in conformational preference in the *Z*-series in going from the sulphide sulphines to the sulphoxide sulphines to the sulphone sulphines is probably the result of a smaller interaction between the sulphine oxygen and the lone pairs of the sulphenyl sulphur in the sulphide *Z*-sulphines than that of the sulphine oxygen and the sulphoxide or sulphone oxygen atoms in the sulphoxide and sulphone *Z*-sulphines. In the preferred conformations of the sulphoxide and sulphone *Z*-sulphines the sulphoxide and sulphone oxygen atoms tend to be as far away as possible from the sulphine oxygen atom.

The differences in the preferred conformations in the three types of sulphines in the *E*- are much smaller than in the *Z*-series. These are gauche conformations (2) and (3) for the sulphide *E*-sulphines, half-folded conformations (4) and (5) for the sulphoxide *E*-sulphines, and half-folded conformations (8) and (9) for the sulphone *E*-sulphines. In the *E*-sulphines there are in contrast with the *Z*-sulphines no interactions of the sulphide, sulphoxide, and sulphone functions with the sulphine oxygen atom but rather with the lone pair on the sulphine sulphur. Hence the spatial orientation of the sulphine oxygen in the *E*- and *Z*-sulphines is probably responsible for the differences in conformational behaviour of these geometrical isomers. This is most manifest from the preferred conformations in the sulphoxide *E*- and *Z*-sulphines. In the *Z*-isomer conformation (7) is favoured by *ca.* 3·5 kcal mol^{-1} in enthalpy over (6) while in the sulphoxide *E*-sulphines conformation (4), which resembles (6), is favoured over (5) by *ca.* 2 kcal mol^{-1} in enthalpy. The interaction of the essential lone pairs in the crucial area is pictured in Scheme 6 for the four conformations of these sulphoxide sulphines.



(4) (5) (6) (7)

SCHEME 6 S^1 = sulphine sulphur, S^2 = sulphoxide sulphur, O^1 = sulphine oxygen, O^2 = sulphoxide oxygen

The strongest interactions between lone pair orbitals are encountered in conformations (5) and (6) which make these conformations less favoured than (4) and (7), respectively, in which one lone pair orbital of a sulphur atom is situated between the two lone pair orbitals of an oxygen atom.

The situation is somewhat more complex for the sulphines in which R^2 is also a mesityl group. In some cases, as in conformation (1) of the sulphide *Z*-sulphines, large steric interactions between the *ortho*-methyl groups of both R^1 and R^2 result in a conformational change.

The most striking conclusion of this study is that in none of these sulphines is the linear *s-trans*-conformation preferred, whereas this stretched conformation is the only preferred one in the corresponding dithiocarboxylates (I).

EXPERIMENTAL

N.m.r. spectra were recorded with Varian A-60 or HA-100 spectrometers operating at 32° unless otherwise mentioned. Deuteriochloroform was used as solvent except in the ASIS experiments. Tetramethylsilane was used as an internal standard. Substrate concentrations were 30 mg per 0·5 ml. Dipole moments were determined according to Guggenheim's procedure.[28] Benzene (Merck) was distilled over sodium before use. Dielectric constants were measured with a type DM01 dipolemeter (Wissenschaftlich-Technische Werkstätte) using a thermostatted (25°) gold-plated brass cell (8 ml) of type DFL2. Refractive indices were measured with a thermostatted (25°) Abbé refractometer (Bellingham and Stanley).

Dithiocarboxylates were prepared according to Mayer *et al.*[29] All sulphines were prepared by stepwise oxidation of the corresponding dithiocarboxylates.[9–11] Sulphines (IIb)—(VIIb), and phenyl phenylthio *E*- and *Z*-sulphine, phenyl phenylsulphonyl *E*-sulphine,[11] (IIc)—(VIIc), (IId)—(VIId), (IIe)—(IVe), (VIe), and phenyl mesitylthio *Z*-sulphine [30] have been described previously.

Yields (%) and m.p.s (°) of other sulphines are as follows: (IIa), 57, oil; (IIIa), 34, 76—78; (IVa), 50, 85—86·5; (Va), 50, oil; (VIa), 60, 117—118; (VIIa), 61, 73·5—74; (Ve), 15, 139·5—141; (VIIe), 10, 198—200, 4,6-dimethyl-3-isopropyl-2-methoxyphenyl mesitylsulphonyl *E*-sulphine, 48, 151—153.

APPENDIX

The dipole moments of all possible conformations in the sulphide, sulphoxide, and sulphone *E*- and *Z*-sulphines have been computed by vector addition of the bond moments by means of a computer program. The calculation of the moments of the individual conformations may be performed very simply [31] by vector addition of the CSO moment and the moments of diphenyl sulphide, diphenyl sulphoxide, or diphenyl sulphone, respectively, provided that no electronic interaction occurs between the CSO group and the sulphide, sulphoxide, or sulphone function. This assumption is justified because no interaction has been found between the chlorine and the CSO function in some substituted chloro-sulphines.[32]

The following bond moments and bond angles were used: μ(CSO) = 3·84 D,[32] directed towards the sulphine oxygen at an angle of 20° with the C=S bond; $\mu(Ph_2S)$ = 1·30 D;[33] $\mu(Ph_2SO)$ = 4·07 D,[34] directed towards the sulphoxide oxygen at an angle of 33° with the bisectrix of the two phenyl rings; $\mu(Ph_2SO_2)$ = 5·05 D.[33] The small meso-

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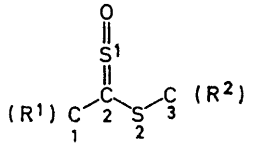
meric Ph–CSO moment (0·28 D),[32] which cannot play a role in these orthogonal mesityl sulphines, has been neglected in all cases. The following bond angles [see (VIII)] were employed: *E*-series, $\mathrm{C(1)\widehat{C(2)}S(1)} = 125$, $\mathrm{S(1)\widehat{C(2)}S(2)} = 115$, $\mathrm{C(1)\widehat{C(2)}S(2)} = 120°$; *Z*-series, $\mathrm{C(1)\widehat{C(2)}S(1)} = 115$, $\mathrm{S(1)\widehat{C(2)}S(2)} = 125$, $\mathrm{C(1)\widehat{C(2)}S(2)} = 120°$; sulphide sulphines, $\mathrm{C(2)\widehat{S(2)}C(3)} = 107°$;[33] sulphoxide sulphines, $\mathrm{C(2)\widehat{S(2)}C(3)} = 97$, $\mathrm{C(2)\widehat{S(2)}O} = 107°$; sulphone sulphines, $\mathrm{C(2)\widehat{S(2)}C(3)} = 107$, $\mathrm{C(2)\widehat{S(2)}O} = 107$, $\mathrm{O\widehat{S(2)}O} = 120°$. The bond angles have been derived from an *X*-ray study[21,25] of these sulphines. The calculated moments have been plotted in Figure 2 against α, the angle between the C(2)S(2)C(3) and the sulphine planes, starting with the linear *s-trans*-conformation (α = 0). In fact, this variation in α represents a rotation about the C(2)–S(2) bond. For the sulphide and sulphone sulphines the curves are symmetrical. This is not the case for the asymmetric sulphoxide sulphines, for which calculations have been performed for the enantiomers given in Scheme 2. The areas in which effective shielding of one *ortho*-methyl of R¹ is expected, as encountered in the sulphoxide *E*- and *Z*-sulphines and in the sulphone *E*-sulphines, are indicated in Figure 2 by a heavy line.



(VIII)

TABLE 10

Dipole moments (μ/D ± 0·05) in benzene at 25°

	(II)	(III)	(IV)	(V)	(VI)	(VII)
R¹ = Mesityl; R² = Ph	3·52	5·19	4·65	3·88	4·83	4·68
R¹ = R² = Mesityl	3·51	3·83	4·81		4·88	
R¹ = Ph; R² = Mesityl		5·04				
R¹ = Mesityl; R² = Et		5·17	4·59			
R¹ = R² = Ph	3·61	4·95			4·73	

The experimental dipole moments of the different types of sulphines are collected in Table 10.

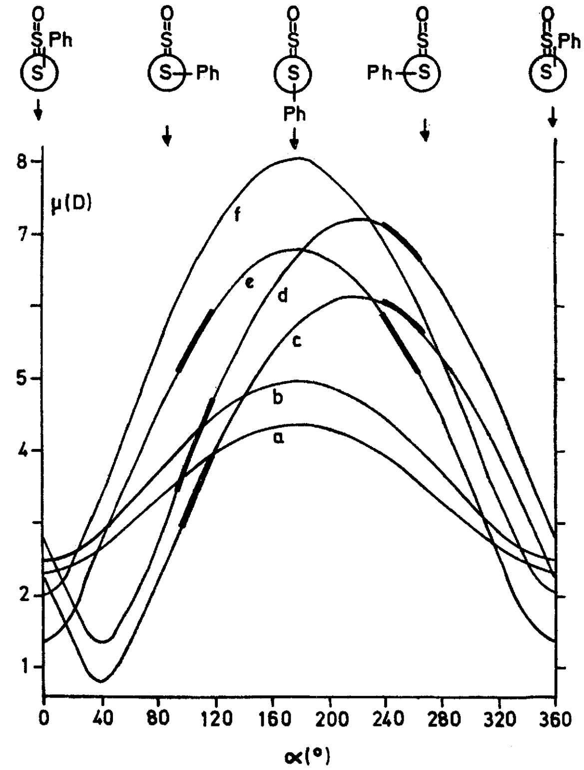


FIGURE 2 Variation of calculated dipole moments with α the angle between the C(2)S(2)C(3) plane and the sulphine plane for a, (II); b, (III); c, (IV); d, (V); e, (VI); f, (VII)

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