

Chemistry of Sulphines. Part XXIV.¹ Dipole Moments of Sulphines

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Dipole moments have been measured for *p,p'*-disubstituted diphenyl sulphines (I), fused aromatic sulphines (II), adamantanethione *S*-oxide, and dichloro sulphine in benzene at 25°. The group dipole moment of the CSO system is 3.84 D directed towards the sulphine oxygen at an angle of 20° with the C–S bond. The CSO function in the aromatic diphenyl sulphines (I) and in fluorene-9-thione *S*-oxide (IIa) has a positive mesomeric moment in contrast with the carbonyl group in the corresponding ketones. The mesomeric PhCSO moment was calculated as 0.28 D. The CSO group moment was used to calculate PhĈCl and the C–Cl group moment in the isomeric chloro phenyl sulphines (Va and b). The latter data were used to calculate ClĈCl in dichloro sulphine (IV). Vector addition of group moments in the fused xanthione *S*-oxide (IIb) reveals that zwitterionic structures play an important role. These structures are not encountered in the folded thioxanthione *S*-oxide (IIc). The configuration of the sulphoxide-sulphine (IIId) was determined as *anti* by means of vector addition of group moments.

SULPHINES (thione *S*-oxides) are a class of heterocumulenes which are readily available by oxidation of the corresponding thiocarbonyl compounds.² Dipole moments have been used by King and Durst³ to assign the geometry of the isomeric chloro phenyl sulphines and by us⁴ to differentiate between *Z*- and *E*-mesityl phenylthio sulphines. This paper deals with the dipole moments of *p,p'*-disubstituted diphenyl sulphines (I), fused aromatic sulphines (II), adamantanethione *S*-oxide (III), and the chloro sulphines (IV) and (Va and b). The aim of this

EXPERIMENTAL

The dipole moments were determined according to Guggenheim's procedure⁵ by using equation (1). [Basic

$$\frac{(\epsilon_{12} - n_{12})^2}{(\epsilon_{12} + 2)(n_{12}^2 + 2)} = \frac{4\pi N\mu^2 \cdot C_2}{27kT} \quad (1)$$

data are given in Supplementary Publication No. SUP 21071 (4 pp.).†]

Benzene (Merck) which was used as solvent, was distilled over sodium before use. The dielectric constants were measured with a dipolemeter type DM 01 (Wissenschaftlich-Technische Werkstätte, Weilheim), using thermostatted gold-plated brass cells of either type DFL 1 (40 ml) or DFL 2 (8 ml). The refractive indices were measured with a thermostatted Abbé refractometer (Bellingham and Stanley). The dipole moments were calculated from the slope of the plot of the left hand term of equation (1) against C_2 (mol ml⁻¹).

The group dipole moment used in this paper are taken from refs. 6 and 7 unless stated otherwise.

The sulphines (Ia–d),^{2,8} (IIa–c),² (III),⁹ and (IV)¹⁰ were all prepared as described previously. The isomeric sulphines (Ie and f) were obtained by peroxy-acid oxidation of the corresponding thiobenzophenone. The isomers, obtained as a 1:1 mixture (72%), were separated by fractional crystallization from ether–pentane, (Ie), m.p. 117–120°; (If), m.p. 88–95° [contaminated with 15% of (Ie)]. The dipole moment given for (If) is corrected for this impurity. The geometry of the two isomers was established by n.m.r. using substituent constants.⁸ The aromatic protons gave A₂B₂ spectra: (Ie) δ 7.70 (*o*-H, *syn*), 7.24 (*m*-H, *syn*), 7.52 (*o*-H, *anti*), and 8.24 (*m*-H, *anti*); (If) δ 7.98 (*o*-H, *syn*), 8.28 (*m*-H, *syn*), 7.27 (*o*-H, *anti*), and 7.27 (*m*-H, *anti*). The prefix *syn* stands for protons *syn* to the CSO system. The magnitude of the dipole moments of the respective isomers supports the assignment of configuration.

⁴ B. Zwanenburg, L. Thijs, and J. Strating, *Rec. Trav. chim.*, 1971, **90**, 614.

⁵ H. Bradford Thompson, *J. Chem. Educ.*, 1966, **43**, 66; E. A. Guggenheim, *Trans. Faraday Soc.*, 1949, **45**, 714.

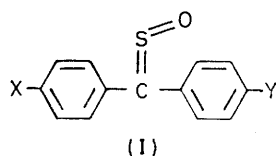
⁶ C. W. N. Cumper, *Tetrahedron*, 1969, **25**, 3131.

⁷ A. G. McClellan, 'Tables of Experimental Dipole Moments,' Freeman, London, 1963.

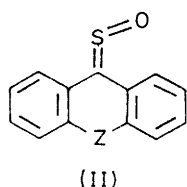
⁸ B. Zwanenburg, L. Thijs, and A. Tangerman, *Tetrahedron*, 1971, **27**, 1731.

⁹ B. Zwanenburg, A. Wagenaar, L. Thijs, and J. Strating, *J.C.S. Perkin I*, 1973, 73.

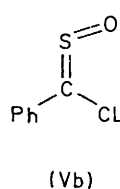
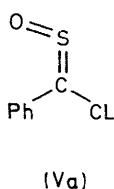
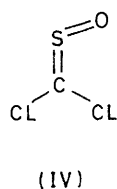
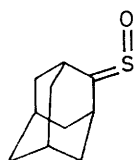
¹⁰ B. Zwanenburg, L. Thijs, and J. Strating, *Tetrahedron Letters*, 1969, 4461.



- a; X = Y = H
 b; X = Y = Cl
 c; X = Y = Me
 d; X = Y = OMe
 e; X = NO₂, Y = Me
 b; X = Me, Y = NO₂



- a; Z = -
 b; Z = O
 c; Z = S
 d; Z = SO
 e; Z = SO₂



study was to determine the magnitude and the direction of the group moment of the CSO system and the use of this group moment in the calculation of the dipole moments of different types of sulphines.

† For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1973, Index issue. Items less than 10 pp. are supplied as full-size copies.

¹ Part XXIII, B. Zwanenburg and A. Wagenaar, *Tetrahedron Letters*, 1973, 5009.

² B. Zwanenburg, L. Thijs, and J. Strating, *Rec. Trav. chim.*, 1967, **86**, 577; B. Zwanenburg and J. Strating, *Quart. Reports Sulfur Chem.*, 1970, **5**, 79.

³ J. F. King and T. Durst, *J. Amer. Chem. Soc.*, 1963, **85**, 2676.

The dipole moments are listed in the Table.

Dipole moments in benzene at 25°					
$\mu(D) \pm 0.05$		$\mu(D) \pm 0.05$		$\mu(D) \pm 0.05$	
(Ia)	3.62	(If)	5.68	(IIe)	4.18
(Ib)	2.40	(IIa)	3.15	(III)	3.84
(Ic)	3.96	(IIb)	3.50	(IV)	2.04
(Id)	4.31	(IIc)	3.08	(Va)	2.63
(Ie)	3.34	(IId)	2.61	(Vb)	3.97

DISCUSSION

The mesomeric moment of a functional group is defined as the algebraic difference between the dipole moments of a molecule having that functional group attached to a benzene nucleus and a molecule in which that group is linked to a saturated hydrocarbon chain.^{11a} Subtraction of the moment of the aliphatic sulphine (III) * from that of the aromatic diphenyl sulphine (Ia) gives a small mesomeric moment of +0.22 D. The mesomeric moment of the CSO group in the fused aromatic fluorene S-oxide (IIa) amounts to +0.69 D. These positive values indicate that in the aromatic sulphines some charge is withdrawn from the CSO function. This can be explained by invoking a contribution from the resonance structure A (Figure 1) which gains in importance when

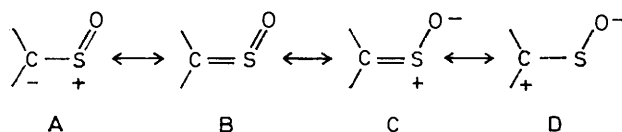


FIGURE 1

the negative charge on the sulphine carbon atom can be delocalized over the aromatic π system, and this is even more the case when the aromatic nuclei are forced into the CSO plane as is the case for fluorene S-oxide. Hückel² and SCF-MO-CNDO¹² calculations have shown that the carbon atom of the sulphine group is indeed slightly negative. It should be noted that the situation for the sulphines is reversed from that encountered for the corresponding ketones. The mesomeric moment of the CO group in benzophenone is -0.28 D^{11a} and in fluorene -0.62 D.⁷

The mesomeric interaction between the benzene and CSO π systems in diphenyl sulphine (Ia) is small, probably due to twist between the two systems. Hence, the mesomeric interactions between the CSO system and the substituents in the benzene ring in the diphenyl sulphines (Ib-f) will be very small and therefore can be neglected.† Consequently, in the substituted diphenyl sulphines

* Adamantanethione S-oxide was accepted as the aliphatic reference compound with some reservation in view of the abnormal polarisability encountered in 1-substituted adamantanones (L. W. Deady, M. Kendall, R. D. Topsom, and R. A. Y. Jones, *J.C.S. Perkin II*, 1973, 416). However, simple aliphatic sulphines such as dimethyl sulphine are too unstable to permit the determination of a dipole moment (W. A. Sheppard and J. Diekmann, *J. Amer. Chem. Soc.*, 1964, **86**, 1891).

† This treatment was also used for substituted benzophenones.¹³

‡ Since the methoxy-group has no linear moment, sulphine (Id) cannot be used in a simple manner to evaluate α and ω .

§ For comparison the group vector of the sulphoxide function as derived from substituted diphenyl sulphoxides is 4.02 D directed towards the sulphoxide oxygen at an angle of 33° with the bisectrix of the angle between the two phenyl rings.¹⁴

(Ib-f) the dipole moment of diphenyl sulphine (3.62 D) represents the group moment of the CSO system including mesomeric interactions. For the moments of the substituents the values of the corresponding monosubstituted benzenes (PhCl 1.59; PhMe 0.43; PhNO₂ 3.99 D) were taken. Vector addition of the group moments in the substituted diphenyl sulphines (Ib and c) and (Ie and f) ‡ results in four equations with two unknowns, *viz.* the angles α and ω (see Figure 2a). For example, for sulphine (Ib) equation (2) is found. By

$$\mu_{\text{exp}}^2 = \mu_{\text{CSO}}^2 + (2\mu_{\text{Cl}} \cos \frac{1}{2}\omega)^2 + 2\mu_{\text{CSO}}(2\mu_{\text{Cl}} \cos \frac{1}{2}\omega) \cos (180 - \alpha) \quad (2)$$

simultaneous solution of the four equations for ω a value of $130 \pm 1^\circ$ was found and for α $21 \pm 1^\circ$. The value of ω agrees well with that found for benzophenones ($131^\circ 20'$).¹³

The dipole vector of (Ia) (3.62 D) is composed of the aliphatic group vector of the CSO group (3.84 D) and the mesomeric contribution *c* (Figure 2b) of the two phenyl rings whose vector is directed along the bisectrix of ω . By the equation $(3.84)^2 = (3.62)^2 + c^2 + 2(3.62)c \cos \alpha$ the magnitude of the mesomeric contribution *c* is calculated as 0.235 D. With this value the mesomeric group moment of PhCSO (mesomeric vector *d* along the Ph-sulphine carbon bond) can be derived (0.28 D) as also the angle α' of the real group moment of the CSO function (3.84 D) with the C-S bond (20°).§

Using the CSO group moment of 3.84 D and an angle α' of 20° , the mesomeric PhCSO moment of 0.28 D, and $\widehat{\text{PhCS}} 115^\circ$ [similar to $\widehat{\text{PhCS}}$ in the diphenyl sulphines (I)]

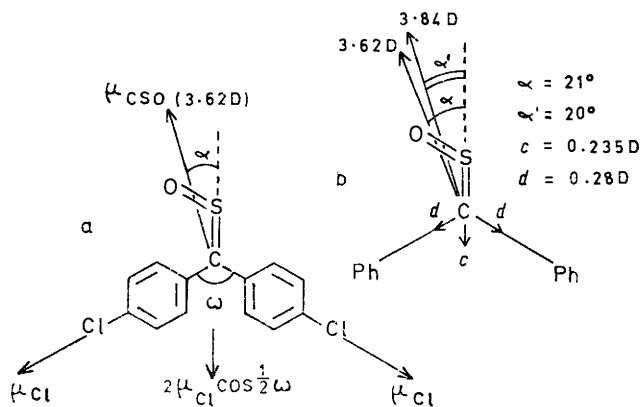


FIGURE 2

for the isomeric chloro phenyl sulphines (Va and b), two vector equations can be set up with two unknowns, *viz.* the C-Cl group moment and $\widehat{\text{PhCCl}}$. The best fit was obtained for $\mu(\text{C-Cl}) = 2.10 \pm 0.15$ D and $\widehat{\text{PhCCl}} = 130 \pm 3^\circ$. Thus, the C-Cl group moment is close to the

¹¹ J. W. Smith, 'Electric Dipole Moments,' Butterworths, London, 1955 (a) pp. 202-205; (b) p. 194.

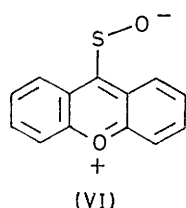
¹² J. P. Snyder, *J. Org. Chem.*, 1973, **38**, 3965.

¹³ G. Pfister-Guillouzo, M. Grimaud, and J. Deschamps, *Bull. Soc. chim. France*, 1969, 1203.

¹⁴ H. Lumbruso and G. Montaudo, *Bull. Soc. chim. France*, 1964, 2119.

aliphatic C-Cl moment (1.90—2.10 D^{11b}) and much higher than the aromatic C-Cl moment (1.59 D⁶), indicating that mesomeric interactions of the chlorine with the CSO system are negligible. For dichloro sulphine (IV) (μ 2.04 D) a value of $120 \pm 4^\circ$ for $\widehat{\text{ClCCl}}$ was calculated using the C-Cl moment of 2.10 ± 0.15 D and the CSO moment of 3.84 D with an angle α' of 20° . For comparison the $\widehat{\text{ClCCl}}$ angle in phosgene has been found to be 112.5° .¹⁵

X-Ray studies¹⁶ reveal that heterocyclic compounds derived by replacing the 9- and 10-carbon atom of anthracene by atoms A and B are planar if both A and B are



either C or O, but folded if at least one of A and B is S. Therefore we propose the dihedral angle θ between the two aromatic rings for (IIb) will be close to 180° and that the molecules (IIc—e) are folded with θ ca. 130° .

The dipole moment of xanthione S-oxide (IIb) (3.50 D) is considerably higher than calculated (2.37 D) by vector addition of fluorenethione S-oxide (3.15 D at an angle α'' with the C-S bond) and dibenzofuran^{14,17} (0.88 D). The angle α'' can be derived analogously to α' (Figure 2b) and is 23.5° . To account for the difference in experimental and calculated moments the contribution of zwitterionic structures as (VI) must be invoked, as has been suggested¹⁸ for xanthone and xanthione. This resonance structure where negative charge is donated to the CSO function is the opposite of that suggested for diphenyl sulphine (Ia) and fluorenethione S-oxide (IIa) where negative charge is withdrawn from the CSO group. Probably the CSO group has ambident character. In the fused folded sulphines (IIc—e) the interactions between the CSO function and the fusing element will be small because the CSO system is bent out of the plane of the phenyl rings. Therefore the bond moments for twisted systems may be used¹⁹ for these compounds: $\mu(\text{Ph}_2\text{CSO}) = 3.62$ D at an angle of 21° with the C-S bond; $\mu(\text{Ph}_2\text{S}) = 1.55$ D; $\mu(\text{Ph}_2\text{SO}) = 4.02$ D¹⁴ at

an angle of 33° with the bisectrix of the two phenyl rings; $\mu(\text{Ph}_2\text{SO}_2) = 5.05$ D.⁶ From these data and the experimental moment (4.18 D) for the sulphone-sulphine (IIe) an interacting angle between $\mu(\text{CSO})$ and $\mu(\text{SO}_2)$ of 125° is obtained from a vector diagram. Similarly, an interacting angle of 122.5° between $\mu(\text{CSO})$ and $\mu(\text{S})$ for the sulphide-sulphine (IIc) is found. Since this angle is very close to that found for the sulphone-sulphine (IIe) contributions of zwitterionic structures as (VI) are negligible. The same conclusion for this sulphine was drawn from n.m.r. analysis.⁸

For the sulphoxide-sulphine (IIId) two configurations are possible, *syn*-(S=O axial) and *anti*-(S=O equatorial) (Figure 3). From the observed dipole moment of 2.61 D and the group moments $\mu(\text{CSO})$ and $\mu(\text{SO})$ an interacting angle of 140° for the group vectors is calculated.

In view of the results obtained for the sulphide-sulphine (IIc) and the sulphone-sulphine (IIe) where $\mu(\text{S})$ and $\mu(\text{SO}_2)$ are directed along the bisectrix, a good estimate for the angle between $\mu(\text{CSO})$ and the bisectrix b (Figure 3) in this sulphoxide-sulphine (IIId) will be 125° . Taking into account the angle β of 33° between $\mu(\text{SO})$ and the bisectrix b , the value of 140° between the interacting

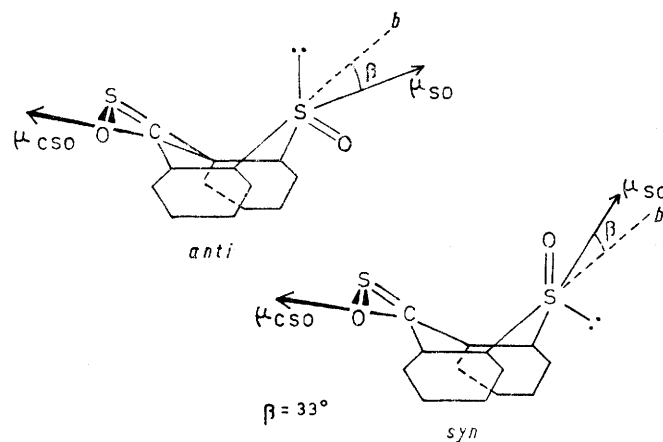


FIGURE 3

vectors $\mu(\text{CSO})$ and $\mu(\text{SO})$ is only compatible with the *anti*-configuration. It should be noted that we were previously unable to assign the geometry of this sulphoxide-sulphine.

[3/1854 Received, 6th September, 1973]

¹⁵ P. W. Allen and L. E. Sutton, *Acta Cryst.*, 1950, **3**, 46.

¹⁶ S. Hosoya, *Acta Cryst.*, 1963, **16**, 310.

¹⁷ E. Bretscher, *Helv. Chim. Acta*, 1929, **2**, 257.

¹⁸ E. Bergmann and A. Weizmann, *Chem. Rev.*, 1941, **29**, 562.

¹⁹ M. J. Aroney, R. J. W. Le Fèvre, and J. D. Saxby, *J. Chem. Soc.*, 1965, 571.