Chemistry of Sulphines.   Part XXIV.[1]   A Study of Rotational Isomerism in meta-Disubstituted Diphenyl Sulphines in Apolar and Polar Solvents by Means of Chemical Shift Differences

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The deshielding of the ortho-protons 2- and 6-H syn to the CSO system in 3,3'-disubstituted diphenyl sulphines (substituents Cl, NO_2, OMe, Me) is determined (Δ_2 and Δ_6) and discussed in terms of an equilibrium between a more and a less polar rotamer.   This rotational equilibrium is strongly dependent on the polarity of the solvent.   The n.m.r. spectrum of bis-3-chlorophenyl sulphine (Ia) in carbon tetrachloride shows that the deshielding of the two ortho-protons 2- and 6-H is about the same, which means that both rotamers are about equally populated.   In acetone, however, only one proton (2-H) is shifted downfield, while the other proton (6-H) is incorporated in the multiplet of the other aromatic protons, indicating that the equilibrium is completely at the side of the more polar rotamer.   The change in the equilibrium of bis-3-nitrophenyl sulphine (Ib) in going from deuteriochloroform to the polar solvent acetone is still more pronounced.   While in deuteriochloroform the equilibrium is on the side of the less polar rotamer, the reverse is the case in acetone.   The changes in the equilibrium of bis-3-methoxy- (Ic) and bis-3-methyl-phenyl sulphine (Id) are much smaller in going from an apolar to a polar solvent.   The proportions of the rotamers are about the same in the apolar solvents carbon tetrachloride and hexadeuteriobenzene.   The results are treated in a quantitative manner by applying the additivity rules of substituent constants and solvent effects of Diehl.

SUBSTITUENTS attached to adjacent, single bonded, carbon atoms in a molecule give rise to rotational isomerism around the connecting bond. This phenomenon can, amongst others, be studied by analysis of coupling constants [2,3] of protons attached to these adjacent carbon atoms and of chemical shift differences, the latter particularly in cyclic molecules.[4] In this paper we present a study of rotational isomerism by making use of chemical shift differences which are the result of different anisotropic effects on protons in the respective rotamers.

Sulphines represent a group of heterocumulenic compounds which contain the rigid non-linear CSO function.[5] This nonlinearity will direct certain chemical and spectroscopic effects to one side of the molecule.[6] Therefore, these compounds may be well suited for the aim of this study.   In a previous report [6] we analysed

the spectra of para-disubstituted diphenyl sulphines and evaluated the substituent constants of CSO-containing groups. The present report deals with the analysis of proton chemical shifts of meta-disubstituted diphenyl sulphines (I), which, as will be shown, provide a means to study rotational isomerism in these types of sulphines.

a; X = Cl   c; X = OMe
b; X = NO₂   d; X = Me

(I)
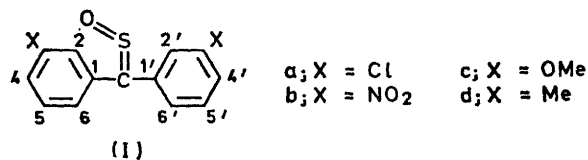
From aromatic sulphines such as diphenyl sulphine it is known [6] that the two ortho-protons syn to the CSO group are shifted downfield as a consequence of the

[1] Part XXIII, B. Zwanenburg, and A. Wagenaar, *Tetrahedron Letters*, 1973, 5009.
[2] R. J. Abraham, *J. Phys. Chem.*, 1969, **73**, 1192.
[3] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, 'Conformational Analysis,' Interscience, New York, 1965, p. 154.

[4] Ref. 3, p. 152.
[5] B. Zwanenburg and J. Strating, *Quart. Reports Sulfur Chem.*, 1970, **5**, 79.
[6] B. Zwanenburg, L. Thijs, and A. Tangerman, *Tetrahedron*, 1971, **27**, 1731.

anisotropic deshielding effect of the CSO system. Therefore, we would expect that in *meta*-disubstituted diphenyl sulphines (I) 2- and 6-H are also shifted downfield and that the respective chemical shifts can be calculated by applying Diehl's rule[7] for additivity of substituent constants. Thus, by taking $\delta(2\text{-H}) = 7\cdot26 - S_{o,\text{X}} - S_{o,Em}$ and $\delta(6\text{-H}) = 7\cdot26 - S_{p,\text{X}} - S_{o,Em}$, the values of $\delta(2\text{-H}) - \delta(6\text{-H})$ in carbon tetrachloride

E m   *E p*   *Z m*   *Z p*
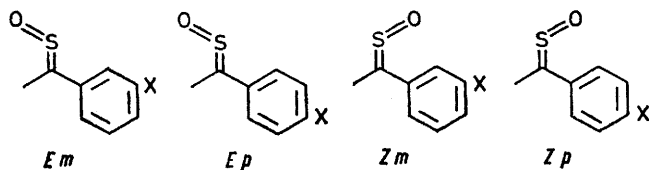
can be calculated and compared with those obtained experimentally (Table 1). These data clearly reveal

TABLE 1

Chemical shifts and deshielding effects

			Carbon tetrachloride			
			$\delta(2\text{-H}) - \delta(6\text{-H})$			
Compd.	$\delta(2\text{-H})$	$\delta(6\text{-H})$	Calc.	Exp.	Δ_2	Δ_6
(Ia)	7·79	7·75	0·11	0·04	−0·50	−0·57
(Ib) *	8·55	8·29	0·56	0·26	−0·27	−0·57
(Ic)	7·83	7·05	−0·06	0·78	−1·04	−0·20
(Id)	7·74	7·51	−0·02	0·23	−0·69	−0·44

δ Values recorded at 100 MHz, concentration 20 mg per 0·5 ml. * For (Ib): solvent $CDCl_3$.

that simple additivity rules for substituent effects cannot be applied for 2- and 6-H. The effect of the group *Em* on 2- and 6-H will now be taken as Δ_2 and Δ_6, respectively, which leads to the expressions (1) and (2).

$$\delta(2\text{-H}) = 7\cdot26 - S_{o,\text{X}} - \Delta_2 \qquad (1)$$

$$\delta(6\text{-H}) = 7\cdot26 - S_{p,\text{X}} - \Delta_6 \qquad (2)$$

The experimental values of Δ_2 and Δ_6 are listed in Table 1.

The Δ_2 and Δ_6 values which differ largely, particularly for (Ib—d), are the result of the pure inductive deshielding effect through bonds and the anisotropic deshielding effect through space of the CSO system on these protons. As the inductive deshielding effect must be the same for both protons, the difference in Δ_2 and Δ_6 reflects the difference in anisotropic deshielding effect of the CSO group on 2- and 6-H. Evidently, the average spatial position of 2- and 6-H with respect to the CSO group is not the same, which implies that the system can be described as an equilibrium between two rotational isomers P and Q (Figure 1). In rotamer P 2-H is situated in the deshielding region of the CSO group, whereas 6-H is most strongly affected in rotamer Q. The observed absorptions for 2- and

* $\delta_{\text{H},\alpha}$ stands for the chemical shift of benzene in solvent α, L' denotes the specific solvent effect of solvent α for the substituents as given in the indices.

6-H are time-averaged values resulting from rapid equilibration between the two rotamers. The position of phenyl ring B cannot be designated because 2'- and 6'-H do not show up sufficiently differently in the spectra for the reason that the anisotropic effect of the CSO system on these protons is negligible.

Since for bis-3-nitrophenyl sulphine (Ib) Δ_6 is much more negative than Δ_2 (Table 1), rotamer Q with the lower dipole moment is strongly favoured over rotamer P which has the higher dipole moment. In sulphine (Ia) there is only a small preference for the less polar rotamer Q. In sulphines (Ic and d) for which rotamer P is the less polar one, there is a strong preference for this rotamer as is indicated by the more negative value of Δ_2 compared with that of Δ_6. Thus, it may be concluded from the data in Table 1 that in all four sulphines
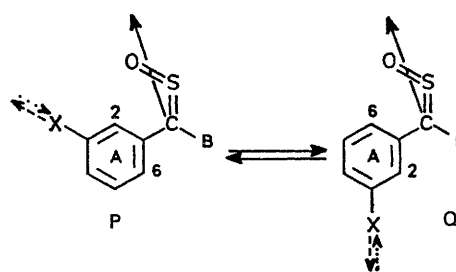

FIGURE 1 ━━▶ = Direction of the group dipole moment vector of the CSO system[1] (3·62 D), ----▶ = direction of the group dipole moment vector of X when X = Cl or NO_2, ----▶ = direction of the group dipole moment vector of X when X = Me. The group dipole moment vector of anisole is a rotating vector which makes an angle of 66·25° with the aryl C–O bond[8]

the less polar rotamer is favoured in the apolar solvent carbon tetrachloride [deuteriochloroform for (Ib)].

As rotamers P and Q differ in the relative orientation of the respective group dipole vectors and therefore will have different dipole moments, it may be expected that the rotamer ratio will depend on the polarity of the solvent. Such an effect has been observed for the rotamer equilibrium of halogeno-ethanes[2] and -cyclohexanes[9] in which cases the proportion of the more polar rotamer increases with increasing dielectric constant.[2]

To test the influence of the dielectric constant on the rotational equilibrium in question, the n.m.r. spectra of (Ia—d) were run in the polar solvent acetone and in the apolar solvent benzene.

By applying Diehl's rule[10] for the additivity of solvent effects the deshielding of 2- and 6-H (Δ_2 and Δ_6) in a solvent α can be calculated by comparison of the δ values of 2-H and 2'-H, and those of 6- and 6'-H, respectively. By means of equations (3) * and (4) * the desired expression (5) can be derived. In a similar manner equation (6) can be obtained.

[7] P. Diehl, *Helv. Chim. Acta*, 1961, **44**, 829.

[8] J. W. Smith, 'Electric Dipole Moments,' Butterworths, London, 1955, p. 96.

[9] R. J. Abraham and T. M. Siverns, *J.C.S. Perkin II*, 1972, 1587.

[10] P. Diehl, *Helv. Chim. Acta*, 1962, **45**, 568.

$$\delta(2\text{-H}) = \delta_{H,\alpha} - S_{o,X} - \Delta_2 - L'_{o,X,\alpha} - L'_{o,Em,\alpha} \quad (3)$$

$$\delta(2'\text{-H}) = \delta_{H,\alpha} - S_{o,X} - S_{o,Zm} - L'_{o,X,\alpha} - L'_{o,Zm,\alpha} \quad (4)$$

$$\delta(2\text{-H}) - \delta(2'\text{-H}) = -\Delta_2 + S_{o,Zm} - L'_{o,Em,\alpha} + L'_{o,Zm,\alpha} \quad (5)$$

$$\delta(6\text{-H}) - \delta(6'\text{-H}) = -\Delta_6 + S_{o,Zm} - L_{o',Em,\alpha} + L'_{o,Zm,\alpha} \quad (6)$$

The chemical shift differences in equations (5) and (6) can be evaluated by making the following assumptions: (i) $S_{o,Zm} = S_{o,Zp} = -0.06$ p.p.m.; (ii) $-L'_{o,Em} + L'_{o,Zm} = -L'_{o,Ep} + L'_{o,Zp}$; for benzene this amounts to $+0.47$ p.p.m., in acetone to -0.08 p.p.m. Insertion in equations (5) and (6) leads to (7) for benzene and to (8) for acetone. Assumption (i) is reasonable because

$$\delta(2\text{-H}) - \delta(2'\text{-H}) = -\Delta_2 + 0.41$$
$$\delta(6\text{-H}) - \delta(6'\text{-H}) = -\Delta_6 + 0.41 \quad (7)$$

$$\delta(2\text{-H}) - \delta(2'\text{-H}) = -\Delta_2 - 0.14$$
$$\delta(6\text{-H}) - \delta(6'\text{-H}) = -\Delta_6 - 0.14 \quad (8)$$

the predominant effect of substituent Zm will be exerted by the CSO group rather than by substituent X which is situated at a larger distance.

The values for $L'_{o,Ep}$ and $L'_{o,Zp}$ were determined from the spectra of *para*-disubstituted diphenyl sulphines in benzene and acetone (see Appendix). The expression $-L'_{o,Ep} + L'_{o,Zp}$ for all the substituents X used amounts to *ca.* $+0.47$ p.p.m. in benzene and to *ca.* -0.08 p.p.m. in acetone. These values were used to obtain equations (7) and (8). The Δ_2 and Δ_6 values thus obtained are listed in Table 2. The results show that Δ_2 and Δ_6 in

TABLE 2

Chemical shifts and deshielding effects

Compd.	$\delta(2\text{-H})$	$\delta(6\text{-H})$	$\delta(2'\text{-H})$	$\delta(6'\text{-H})$	Δ_2	Δ_6
			Benzene			
(Ia)	7·89	7·51	6·91	6·50	−0·57	−0·60
(Ib)	8·30	7·76	7·70	6·58	−0·19	−0·77
(Ic)	8·03	7·37	6·70	6·72	−0·92	−0·24
(Id)	7·90	7·73	6·91	6·91	−0·58	−0·41
			Acetone			
(Ia)	8·04	7·58	7·48	7·52	−0·70	−0·20
(Ib)	8·88	8·12	8·40	7·98	−0·62	−0·28
(Ic)	7·66	7·28	7·01	7·00	−0·79	−0·42
(Id)	7·69	7·59	7·28	7·28	−0·55	−0·45

δ Values recorded at 100 MHz, concentration 20 mg per 0·5 ml.

benzene are in the same range as those found in carbon tetrachloride which was to be expected for solvents of about equal dielectric constant. In acetone the Δ_2 and Δ_6 values are considerably different from those found in benzene and carbon tetrachloride.

In order to calculate the relative proportions of rotamers P and Q from Δ_2 and Δ_6 the anisotropic deshielding effects of the CSO system on protons 2- and 6-H, respectively, should be known. These values can be obtained from Δ_2 and Δ_6 by substraction of the inductive deshielding effect on 2- and 6-H. This inductive effect which is acting through bonds is the

same for 2- and 6-H. Its magnitude can be derived from a situation where either 2- or 6-H does not experience an anisotropic effect of the CSO system, hence when the conformational equilibrium has shifted completely to the side of one rotamer. In that case the inductive effect is represented by the Δ value of the proton furthest away from the CSO system. For sulphine (Ia) protons 2- and 6-H are shifted downfield with respect to the remaining aromatic protons for the solvents benzene and carbon tetrachloride, whereas in acetone only 2-H is observed downfield and 6-H is incorporated in the multiplet of the other aromatic protons (Figure 2).
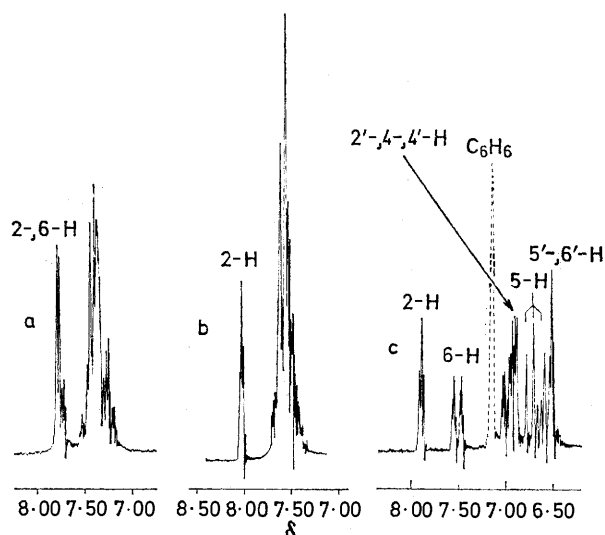

FIGURE 2 N.m.r. spectra of bis-3-chlorophenyl sulphine (Ia) at 100 MHz in: a, CCl₄; b, Me₂CO; c, C₆D₆

By following the shift of 6-H in carbon tetrachloride to which increasing amounts of acetone were added (*vide infra*) a gradual upfield shift is observed caused by a decrease in the anisotropic deshielding effect of the CSO system on this proton. When the ratio of carbon tetrachloride to acetone has reached 2 : 3 the spectral features are essentially those observed for acetone, implying that the anisotropic effect, at least in acetone, has become negligible and thus the Δ value of 6-H in acetone (-0.20 p.p.m.) may be taken as the inductive deshielding effect of the CSO group. The ratio of the Δ values corrected for this inductive effect now gives the relative proportions of the rotamers P and Q. For sulphines (Ia—d) in the three solvents studied, we also accepted the value of -0.20 p.p.m. as the correction for the inductive deshielding effect in these calculations, thus neglecting the minor differences due to the nature of the *meta*-substituent and the solvent change on this inductive effect. From the results listed in Table 3 the following conclusions may be drawn.

For sulphine (Ia) the rotamer populations of P and Q in benzene as well as in carbon tetrachloride are about equal, whereas in acetone the rotational equilibrium has completely shifted to the more polar rotamer P. For sulphine (Ib) rotamer Q is strongly favoured over P

in benzene and deuteriochloroform, while the reverse is the case in acetone. This means that the rotational equilibrium has shifted from the less polar rotamer Q

TABLE 3

Relative proportions of the rotamers P and Q

Solvent	CCl$_4$		C$_6$D$_6$		Me$_2$CO	
Compd.	P (%)	Q (%)	P (%)	Q (%)	P (%)	Q (%)
(Ia)	45	55	48	52	100	
(Ib)	16	84 [a]		100	84	16
(Ic)	100		95	5	73	27
(Id)	67	33	64	36	58	42

[a] Solvent CDCl$_3$.

to the more polar form P by going to a more polar solvent. For sulphines (Ic and d) the less polar rotamer P still predominates in acetone; however, the proportion
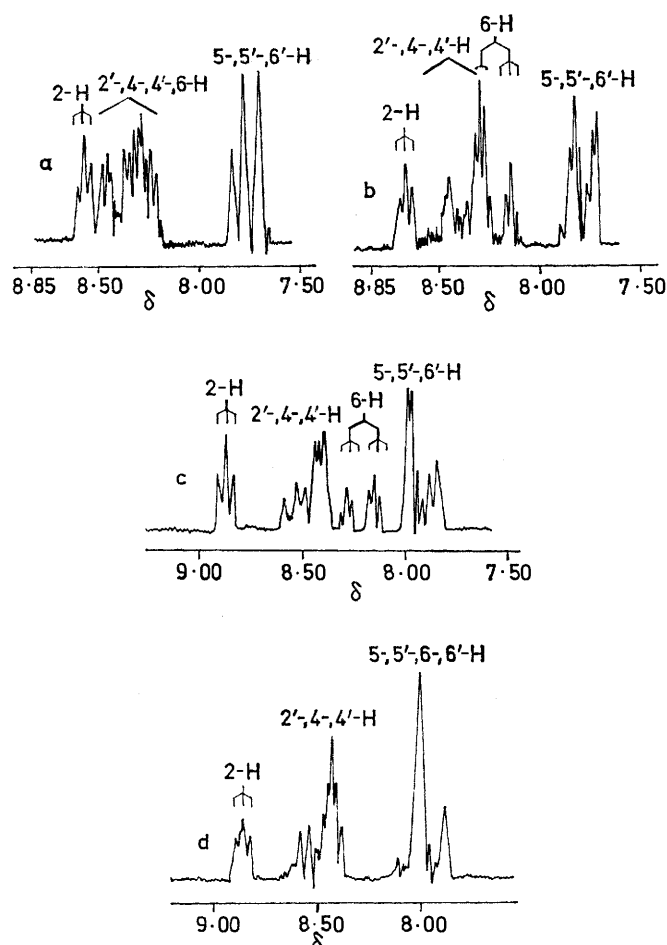

FIGURE 3 N.m.r. spectra of bis-3-nitrophenyl sulphine (Ib) at 60 MHz in: a, CDCl$_3$; b, CDCl$_3$–Me$_2$CO 6 : 1; c, CDCl$_3$–Me$_2$CO 1 : 1; d, Me$_2$SO

of Q becomes greater with increasing solvent polarity. It should be noted that the rotational equilibrium for

sulphines (Ic and d) is less sensitive for the change in solvent polarity than that for sulphines (Ia and b). This may be due to the relatively small contribution of the group vector of the substituents OMe and Me to the total dipole moment of these sulphines, which leads to a rather small change in dipole moment in going from rotamer P to Q.

Spectra of sulphines (Ia and b) were also run in different carbon tetrachloride–acetone and deuteriochloroform–acetone mixtures, clearly revealing that in both sulphines 2-H is shifted downfield while 6-H is shifted upfield with increasing ε. It appears that the spectrum of sulphine (Ia) in carbon tetrachloride–acetone = 2 : 3 (ε ca. 13) is the same as in acetone. It may be concluded that for a solvent with ε > 13 the rotational equilibrium for sulphine (Ia) is completely on the side of the more polar rotamer P. Spectra of sulphine (Ia) in butyl acetate (ε 5·01), dichloromethane (ε 9·08), pentan-2-one (ε 15·4), methanol (ε 32·6), acetonitrile (ε 35·1), and dimethyl sulphoxide (ε 46) convincingly show that in the first two solvents (ε < 13) 6-H is still somewhat deshielded, while the solvents with ε > 13 give the picture as found for acetone.

In Figure 3 the spectra of (Ib) in media of different ε are depicted. This nicely illustrates the effect of the solvent polarity on the 2- and 6-H absorptions. In dimethyl sulphoxide it appears that the rotamer equilibrium has completely shifted to the polar form P, since δ(6-H) is observed at about the same δ value as 6′-H.

EXPERIMENTAL

The n.m.r. spectra of sulphines (Ia—d) as solutes in CCl$_4$, CDCl$_3$, C$_6$D$_6$, and Me$_2$CO were recorded * with a Varian HA-100 spectrometer. Other spectra were run on a Varian A-60 spectrometer (60 MHz). Sample concentrations were 3—5% by weight. Tetramethylsilane was used as internal standard. 2- and 6-H absorb in most cases downfield with respect to the other aromatic protons and therefore their splitting pattern is almost first order (for an example see Figure 2c), unless the δ values of 2- and 6-H are almost the same (Figure 2a). In some cases where 6-H was obscured by other aromatic protons, the double resonance technique was used to determine its position (Figure 4) together with lanthanide induced shifts (2- and 6-H syn to the CSO system are shifted downfield to the greatest extent on complexation with lanthanides [11,12]) and changes in polarity of the solvent which produces large shifts only for 2- and 6-H. The positions of 2′- and 6′-H, necessary for evaluating equations (7) and (8), are difficult to determine, because first-order analyses are not sufficient. Therefore, the spectra were simulated with an iterative procedure (LAOCN III) † to get second-order analyses of the spectra. The δ values of the protons 2-, 2′-, 6-, and 6′-H compiled in Tables 1 and 2 are calculated with this procedure.

The values of δ$_{H,\alpha}$ (absorption of pure benzene, 5% by weight, in solvent α) which were necessary for the evalua-

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

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

tion of solvent effects were measured as 7·26, 7·17, and 7·35 for CCl_4, C_6D_6, and Me_2CO, respectively.
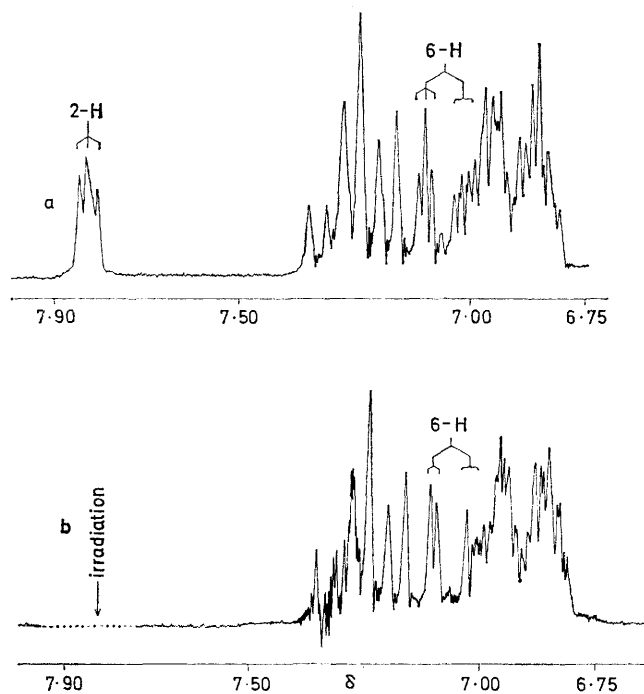

FIGURE 4 N.m.r. spectra of bis-3-methoxyphenyl sulphine (Ic) at 100 MHz: a, in CCl_4; b, double resonance spectrum in CCl_4 with irradiation at δ(2-H)

Sulphines (Ia—c) were prepared as described previously.[13] Sulphine (Id) was obtained by oxidation of the corresponding thione in 78% yield, m.p. 51·5—52·5°.

APPENDIX

To analyse the benzene and acetone solvent effects of the substituents Ep and Zp the n.m.r. spectra of para-disubstituted diphenyl sulphines were recorded in these solvents. The effective solvent effects were obtained according to Diehl's procedure [10] (Table 4). The substituent constants

TABLE 4

Effective solvent effects

	Acetone		Benzene	
Substituent	$L'_{o,Ep}$	$L'_{m,Ep}$	$L'_{o,Ep}$	$L'_{m,Ep}$
X = H	+0·05		−0·14	
X = Me	+0·05	−0·06	−0·27	+0·13
X = OMe	+0·05	−0·09	−0·30	+0·10
X = Cl	+0·10	−0·05	−0·14	+0·14
	$L'_{o,Zp}$	$L'_{m,Zp}$	$L'_{o,Zp}$	$L'_{m,Zp}$
X = H	−0·02		+0·30	
X = Me	−0·04	−0·05	+0·18	+0·27
X = OMe	+0·01	−0·10	+0·17	+0·19
X = Cl	−0·01	−0·05	+0·37	+0·30

$S_{o,X}$ and $S_{m,X}$ were taken from ref. 14, those of $S_{o,Ep}$, $S_{o,Zp}$, $S_{m,Ep}$, and $S_{m,Zp}$ from ref. 6, and the values of $L'_{o,X}$ and $L'_{m,X}$ from ref. 10. The data show that in benzene $L'_{o,Ep}$ is strongly negative, while $L'_{o,Zp}$ is strongly positive. This means that the ASIS effect on ortho-protons syn to the CSO group is negative and on ortho-protons anti to the CSO group positive. This ASIS effect has been used to assign the Z or E geometry to arylthio mesityl sulphines.[11] In acetone the solvent effects are reversed in sign and much smaller as those in benzene.

[13] A. Tangerman, L. Thijs, A. P. Anker, and B. Zwanenburg, J.C.S. Perkin II, 1973, 458.
[14] V. van Meurs, Rec. Trav. chim., 1968, 87, 145.