Dipole Moments and Molecular Conformation of Aryl Diarylmethyl Sulphides

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The electric dipole moments of $X^1C_6H_4(X^2C_6H_4)CHSC_6H_4Y$ ($X^1 = X^2$ = H, *p*-Cl, or *p*-Me, Y = *m*- or *p*-Cl or *p*-Me) have been measured in benzene solution. From the value found for $\widehat{CSC}$ (114°) it is suggested that there is some mixing between the 3*s* orbital and the two 3*p* orbitals of the sulphur atom involved in the C–S bonds. It has been shown that there is free internal rotation about the bond between sulphur and the *sp*^{3} carbon atoms.

DIPHENYL SULPHIDE has been widely studied by physical techniques.[1] The results show that its molecular configuration is mainly determined by steric interactions between the two phenyl groups and by the conjugation between these and the sulphur atom. The sulphur atom may act as either an electron donor or acceptor, and it can be predicted that substitution of a benzene ring by a non-aromatic group should change both the basicity of sulphur and the conformation of the remaining phenyl group. The compounds $PhSMMe_3$ (M = C, Si, Ge, Sn, or Pb) have been investigated previously[2] with the aim of studying these effects.

This paper reports electric dipole moment measurements on some aryl diarylmethyl sulphides, $X^1C_6H_4$-$(X^2C_6H_4)CHSC_6H_4Y$ ($X^1 = X^2$ = H, *p*-Me or *p*-Cl, Y = *m*- or *p*-Cl or *p*-Me).† The information on the structure in non-polar solvents so obtained, apart from its intrinsic interest, can be used in the interpretation of data on the charge transfer complexes formed between these compounds and molecular iodine.[4]

Physical data and observed dipole moments

Compound	ε_1	*a*	V_1/cm^3 g^{-1}	*b*	$n_1{}^2$	*c*	R_D/cm^3	$P_{2\infty}$/cm^3	μ/D
Ph_2CHSPh	2·2732	1·200	1·1444	−0·300	2·2435	0·361	87·3	129·4	1·47
p-$MeC_6H_4PhCHSPh$	2·2728	1·187	1·1444	−0·266	2·2436	0·333	93·1	146·1	1·61
$Ph_2CHSC_6H_4Cl$-*p*	2·2725	1·100	1·1443	−0·360	2·2435	0·340	91·4	137·2	1·50
p-$ClC_6H_4PhCHSPh$	2·2730	1·812	1·1440	−0·317	2·2436	0·283	91·9	182·1	2·10
(*p*-$ClC_6H_4)_2CHSPh$	2·2730	1·598	1·1442	−0·340	2·2435	0·263	98·3	186·1	2·07
$Ph_2CHSC_6H_4Cl$-*m*	2·2728	1·711	1·1445	−0·310	2·2438	0·288	92·8	176·9	2·03
$Ph_2CHSC_6H_4Me$-*p*	2·2725	1·437	1·1445	−0·228	2·2436	0·291	93·9	157·5	1·76
(*p*-$ClC_6H_4)_2CHSC_6H_4Cl$-*p*	2·2725	1·068	1·1440	−0·296	2·2435	0·140	104·3	172·0	1·82

EXPERIMENTAL

Materials.—Aryl diarylmethyl sulphides were prepared in 70% yield from the appropriately substituted diphenylmethanols and benzenethiols in acetic acid–sulphuric acid.[5] They were recrystallized twice from ethanol, and the purity was checked by n.m.r. spectroscopy and elemental analysis. *p*-Chlorophenyl bis-*p*-chlorophenylmethyl sulphide has m.p. 80°; other m.p.s are reported in ref. 4. Benzene (Erba RP grade) was used without further purification as the solvent for all physical measurements.

Physical Measurements.—These were performed as before,[6] at 25 ± 0·1°. The uncertainty in the observed dipole moments is estimated to be ±0·02 D. The Table collects the observed dipole moments and the parameters used in calculating them.

RESULTS AND DISCUSSION

Theoretical Dipole Moments.—These were calculated by assuming that $\mu(\overset{+\!\longrightarrow}{\text{C–Cl}}) = 1{\cdot}59$ D (the value observed

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† One of us (A. C.) has reported[3] a study of substituent effects on the polarographic reduction of most of the molecules examined here.

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for chlorobenzene in benzene),[7] $\overset{+\!\!\longrightarrow}{\mu(\text{Ph–S})} = 1{\cdot}3$ D, deduced from the observed moment for Ph_2S (1·55 D),[8] using $\widehat{CSC} = 109°$,[9] and $\overset{\longleftarrow\!\!+}{\mu(\text{C–Me})} = 0{\cdot}4$ D.[7]

Basicity and Atomic Orbitals of Sulphur.—To obtain information on the basicity of sulphur in the compounds under study we calculated the Ph_2CH–S group moment and the angle θ that this forms with the vector $\overset{+\!\!\longrightarrow}{\mu(\text{Ph–S})}$. Taking into account the fact that the moments $\overset{\longleftarrow\!\!+}{\mu(C_{al}\text{–H})}$ and $\overset{\longleftarrow\!\!+}{\mu(C_{ar}\text{–H})}$ are nearly the same [10] and that the observed dipole moment of diphenylmethane is very small,[11] it may be assumed, to a good approximation, that $\theta = \widehat{CSC}$. For this calculation, equations (1) and (2) were used. Here $\mu(\text{I})$ and $\mu(\text{II})$ are the observed

$$\mu^2(\text{I}) = \mu_x^{\,2} + \mu_y^{\,2} + 2\mu_x\mu_y \cos\theta \qquad (1)$$

$$\mu^2(\text{II}) = \mu_x'^{\,2} + \mu_y^{\,2} + 2\mu_x'\mu_y \cos(180° - \theta) \qquad (2)$$

moments for Ph_2CHSPh and $Ph_2CHS(p\text{-}ClC_6H_4)$, respectively; μ_x and μ_x' the group moments $\overset{+\!\!\longrightarrow}{\mu(\text{Ph–S})}$ (1·3 D) and $\overset{\longleftarrow\!\!+}{\mu(p\text{-}ClC_6H_4\text{–S})}$ (0·3 D) respectively, and μ_y the unknown moment $\overset{+\!\!\longrightarrow}{\mu(Ph_2CH\text{–S})}$. Solution of the two equations gives $\overset{+\!\!\longrightarrow}{\mu(Ph_2CH\text{–S})}$ 1·4 D and θ 114 ± 3°.* The fact that this group moment value is higher than that for $\overset{+\!\!\longrightarrow}{\mu(\text{Me–S})}$ calculated from the observed moment for dimethyl sulphide (1·1 and 1·2 D for $\widehat{CSC}$ 99 and 105°,[12] respectively, and $\mu_{obs} = 1{\cdot}45$ D [13]) may be due to various factors. The most important of these is the assumption that $\overset{+\!\!\longrightarrow}{\mu(\text{Ph–S})}$ is 1·3 D which is higher than would be expected for these molecules. In fact, due to the effect of the diphenylmethyl group, the isolated phenyl group may rotate out of the CSC plane.† This causes a decrease in the mesomeric moment $\overset{\longleftarrow\!\!+}{\mu(\text{Ph–S})}$ derived from inclusion of electrons from the $3p$ orbital of sulphur in the π system of the phenyl group. Thus the basicity of sulphur increases in these compounds compared with thioanisole in which the phenyl ring is in the CSC plane and favours conjugation between the sulphur lone pair and the π system.

The basicity is also influenced by an increase in the $\widehat{CSC}$ angle. In fact, if the sulphur electrons of the C–S bond are purely of the p type, this angle should be 90° or a little more than 90°. A significantly higher value indicates some mixing of $3s$ electrons with p orbitals giving rise to atomic orbitals with greater overlap and a larger $\widehat{CSC}$ angle.[16] The lone pair hybrid, having directional character, might then be responsible for the sulphur basicity, as an alternative to that derived from invoking the pure p lone pair.

Molecular Conformation.—There are two possibilities for the configuration of the present molecules: (i) a rigid structure is present; (ii) a structure with free internal rotation occurs.

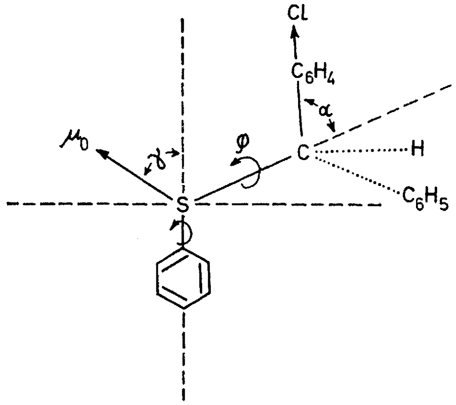

FIGURE 1 Molecular diagram used in the vector analysis of $(p\text{-}ClC_6H_4)_2CHSPh$ and $p\text{-}ClC_6H_4PhCHSPh$

(i) *Rigid structure.* In this case, assuming that the chlorine atoms of the diphenylmethyl group, given their position, do not interact with the isolated phenyl group, the molecular geometry of $p\text{-}ClC_6H_4PhSPh$ and $(p\text{-}ClC_6H_4)_2CHSPh$ must be very similar. Vector analysis of these compounds was carried out by using equation (3)

$$\mu_{obs}^{\,2} = \mu_0^{\,2} + \mu_1^{\,2} + 2\mu_0\mu_1 \cos\alpha \cos(\gamma + 66°) + 2\mu_0\mu_1 \sin\alpha \cos\phi \cos(\gamma - 24°) \qquad (3)$$

where μ_{obs} is the observed dipole moment of $p\text{-}ClC_6H_4PhCHSPh$ or $(p\text{-}ClC_6H_4)_2CHSPh$; μ_0 the moment observed for Ph_2CHSPh; μ_1 is $\overset{+\!\!\longrightarrow}{\mu(\text{C–Cl})}$ and the vector sum of the two $\overset{+\!\!\longrightarrow}{\mu(\text{C–Cl})}$, respectively, for the mono- and di-chloro-derivatives; α is the complement of the angle $\widehat{SC_{sp^3}Cl}$ for the monochloro-derivative (Figure 1); and

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* These values give μ_{calc} 1·75 for $Ph_2CHCC_6H_4Me\text{-}p$ compared with μ_{obs} 1·76 D.

† From quantum mechanical calculations it was found that twisting around the C–S bond takes place more easily than bending of the valency angle $\widehat{CSC}$.[14] Also the conjugation energy between the sulphur atom and the phenyl ring in PhSH is $\leqslant 0{\cdot}5$ kcal mol^{-1}.[15]

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ϕ the complement of the angle between the S–C_{sp^3} bond and the vector sum of the two $\mu(\overrightarrow{\text{C–Cl}})$ for the dichloro-derivative. For the remaining symbols see Figure 1. Using the values for $\mu(\overrightarrow{\text{Ph}_2\text{CH–S}})$ and θ found above, and 116° for the angle $C_{sp^2}\widehat{C_{sp^3}}C_{sp^3}$,* the conformations of Figure 2 were obtained. Because these are very different a rigid structure may be excluded.

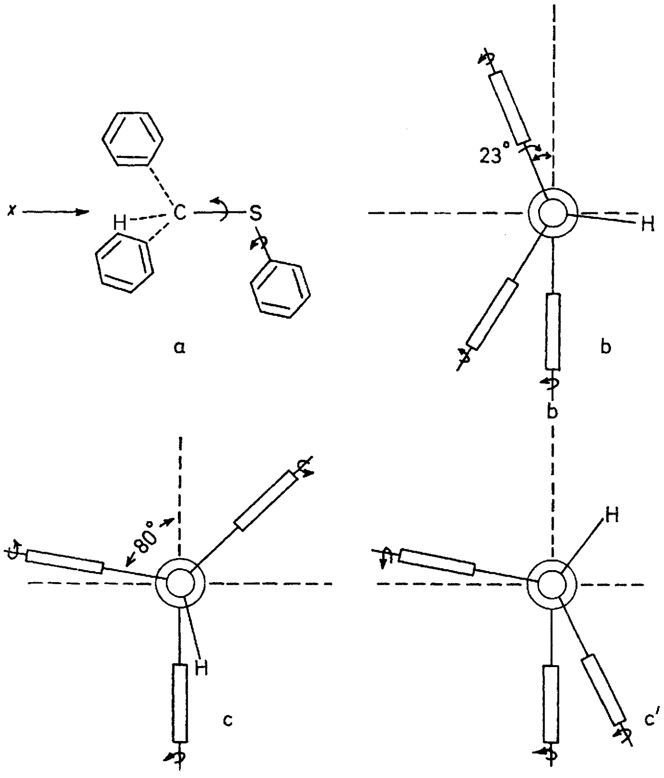

FIGURE 2 Rigid structures for Ph_2CHSPh: a, viewed along *x*; b, from vector analysis of $(p\text{-}ClC_6H_4)_2CHSPh$; and c, c′, from vector analysis of $p\text{-}ClC_6H_4PhCHSPh$

(ii) *Free internal rotation.* For this situation the calculation of theoretical dipole moment $(\mu_R^2)^{\frac{1}{2}}$ was performed according to equation (4) [19] where μ_0 is the

$$\mu_R^2 = \mu_0^2 + \Sigma\mu_k^2 \qquad (4)$$

vector sum of all components of rotating moments along their axes of rotation; $\Sigma\mu_k^2$ is the sum of the squares of the rotating moments perpendicular to their axes of rotation. The following values were obtained: for $p\text{-}ClC_6H_4PhCHSPh$ μ_{calc} 2·0 D (μ_{obs} 2·10) and for $(p\text{-}ClC_6H_4)_2CHSPh$ μ_{calc} 2·0 D (μ_{obs} 2·07). The fact that the calculated moments compare very favourably with the observed values, suggests that free internal rotation is possible. This is also the preferred situation, a rigid structure being excluded. Unfortunately, both possibilities (i) and (ii) are in agreement with the trend in equilibrium constants for the complexes formed between molecular iodine and MeSPh (12·1), $PhCH_2SPh$ (9·7), Ph_2CHSPh (5·2), and Ph_3CSPh (3·2 l mol^{-1}), found for cyclohexane solution at 25·0°.[4]

The results obtained may appear strange at first sight. In fact, a value of $\widehat{\text{CSC}} \gg 90°$ should indicate steric hindrance between the diphenylmethyl and the phenyl group. It is noteworthy, nevertheless, that for PhSMe also, for which $\widehat{\text{SCS}} > 90°$ is expected, it was suggested [20] that steric interference between the phenyl and methyl groups does not occur.

The remaining compounds, the moments of which we report mainly because they are not available in the literature, do not give much further information. The fact that the moment of $p\text{-}MeC_6H_4PhCHSPh$ (1·61 D) is greater than that of Ph_2CHSPh (1·47 D) excludes the possibility of a rigid structure having the methine hydrogen atom *cis* to the phenyl group, even if this situation is preferred on steric grounds. This conclusion may also be deduced from a comparison of the dipole moments of Ph_2CHSPh, $(p\text{-}ClC_6H_4)_2CHSPh$, and $(p\text{-}ClC_6H_4)_2CHSC_6H_4Cl\text{-}p$.

Finally, in regard to the conformation of the phenyl group, no information may be obtained from the present data because the dipole moment observed for $Ph_2CHSC_6H_4Cl\text{-}m$ is compatible with the existence of more than one conformation.

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* This value was deduced from the observed moments for $(p\text{-}NO_2C_6H_4)_2CH_2$ (4·68 D) [17] and $PhNO_2$ (4·00 D).[18]

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