Dipole Moments and Dielectric Relaxation Times of Some Dialkyl and Diaryl Disulphides and Diphenyl Disulphone

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Dielectric relaxation times τ and electric dipole moments μ(loss) of nine dialkyl and diaryl disulphides and of diphenyl disulphone have been measured as solutes in benzene at 20° using a standing wave method at frequencies 1·140, 3·040, and 8·540 GHz. In each case the data are well described by a Debye curve and μ(loss) is generally close to the 'static' dipole moment. The τ values and the observed Debye behaviour are explained in terms of an overall molecular relaxation process with little apparent contribution from intramolecular rotations about the S–S bond.

DIALKYL DISULPHIDES and diaryl disulphides and disulphones are known to have a skew configuration in solution.[1–4] The possibility of rotational freedom about the S–S link in disulphides was investigated by dielectric relaxation techniques [5–7] but the results were not conclusive. Nelson and Smyth [5] made dielectric loss measurements on solutions of diphenyl disulphide in benzene at 9·64 and 22·54 GHz. From the relatively low estimate of τ (13 ps) and non-zero value of α (0·3) for the Cole–Cole distribution parameter, they proposed that a significant degree of intramolecular relaxation takes place about S–S. Measurements on this compound and on four other disulphides made by Le Fèvre *et al.*[6] indicated Debye behaviour (and, by inference, a high barrier to rotation about the S–S bond) but only two frequencies (3·109 and 9·400 GHz) were available. Hufnagel's earlier measurements [7] at 19·15 and 42·25 GHz on diphenyl disulphide deviated slightly from a Debye curve. No dielectric loss data have previously been recorded for disulphones. In view of the limitations of earlier work [8] and the discrepancies which have been noted when dielectric loss is determined by different techniques, we have carried out measurements on dimethyl, di-t-butyl, diphenyl, bis-*p*-chlorophenyl, di-β-naphthyl, dibenzoyl, and bis-*o*-, -*m*-, and -*p*-nitrophenyl disulphides, and diphenyl disulphone as solutes in benzene at 20° using a highly reliable standing wave method at frequencies of 1·140, 3·040, and 8·540 GHz.

EXPERIMENTAL

Apparatus.—Dielectric constants (ε') and loss factors (ε'') of dilute solutions in benzene (at 20°) were obtained at 1·140, 3·040, and 8·540 GHz using a Central Research Laboratory, Red Wing, Minnesota, dielectrometer fitted with machined copper cells suitable for liquid samples. This instrument employs the standing wave method of Roberts and von Hippel [9] and has been described previously.[10] From these data are calculated incremental loss tangents ($\Delta\tan\delta$), and the slope (ψ) of the plot of the tan δ increments against weight fraction of solute (w_2) can be derived at each frequency.

Materials.—The disulphides were commercial samples which had been purified to give m.p.s or b.p.s in accord with literature values. Diphenyl disulphone was kindly provided by Dr. K. E. Calderbank. AnalaR grade benzene was dried over sodium, half-frozen, and the solid separated, melted, and stored over sodium wire.

RESULTS

The ψ values, dipole moments μ(loss), and dielectric relaxation times τ are listed in Table 1.† The latter two parameters were calculated from the Debye curve of best fit (with the aid of an I.B.M. 7040 computer) using the Debye equation in the form set out by Le Fèvre and Sullivan.[11] The dipole moment obtained in this way has been designated μ(loss) to distinguish it from the moment value obtained using kHz frequencies, μ(static).

DISCUSSION

The loss moments of Table 1 are in reasonable accord with the corresponding 'static' moments which have been recorded for dimethyl disulphide (1·87 D),[6] di-t-butyl disulphide (1·84 D),[6] diphenyl disulphide (1·79 D),[6] bis-*p*-chlorophenyl disulphide (0·4$_5$ D),[6] di-β-naphthyl disulphide (1·97 D),[6] bis-*o*-nitrophenyl disulphide (5·37 D),[12] bis-*m*-nitrophenyl disulphide (4·44 D),[12] bis-*p*-nitrophenyl disulphide (3·63 D),[12] and diphenyl disulphone (3·93 [13] and 4·04 D [3]). Each of these μ(static) values were obtained assuming that the distortion polarisation $_{\mathrm{D}}P$ is 1·05 times the molecular D line refractivity R_{D} except in the case of diphenyl disulphone for which $_{\mathrm{D}}P$ had been taken as equal to R_{D}. The loss moment for dibenzoyl disulphide (0·65 D) is lower than μ(static) estimates of 1·1 [14] and 1·1—1·4 D [13] (calculated on the

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† Experimental data (dielectric constants ε', loss factors ε'', and incremental loss tangents $\Delta\tan\delta$ of solutions in benzene at 20°) are deposited as Supplementary Publication No. SUP 21295 (6 pp). For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue.

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basis of ${}_{\mathrm{D}}P = R_{\mathrm{D}}$) and 1·16 D (now found, taking ${}_{\mathrm{D}}P = 1{\cdot}05\ R_{\mathrm{D}}$), but for this molecule the orientation polarisation, ${}_{\mathrm{O}}P$, and hence μ(static) are relatively small quantities and sensitively vary with the ${}_{\mathrm{D}}P : R_{\mathrm{D}}$ ratio assumed. The dielectric relaxation times now determined for dimethyl, di-t-butyl, diphenyl, bis-*p*-chlorophenyl, and di-β-naphthyl disulphides are in general agreement with the earlier results of Le Fèvre *et al.*[6] The most significant difference is observed with di-β-naphthyl disulphide for which an increase of *ca.* 20% in ψ is now found in the 3·0—3·1 GHz region and this results in a change in τ from 33 to 39 ps.

TABLE 1

Values of $\psi(=\Sigma\Delta\tan\delta/\Sigma w_2)$, dipole moments μ(loss), and dielectric relaxation times τ of solutes in benzene at 20°

Solute	ψ(1·140 GHz)	ψ(3·040 GHz)	ψ(8·540 GHz)	μ(loss)/D *	τ/ps ‡
Dimethyl disulphide	$0{\cdot}042_6$	0·107	0·301	1·85 ± 0·02	4·0
Di-t-butyl disulphide	$0{\cdot}049_8$	0·134	0·333	1·85 ± 0·02	7·9
Diphenyl disulphide	$0{\cdot}084_7$	0·213	0·357	1·77 ± 0·02	17·0
Bis-*p*-chlorophenyl disulphide	$0{\cdot}004_4$	$0{\cdot}008_7$	$0{\cdot}011_5$	0·37 ± 0·04	23
Di-β-naphthyl disulphide	0·155	0·291	0·233	1·95 ± 0·02	39
Dibenzoyl disulphide	$0{\cdot}013_5$	$0{\cdot}029_9$	$0{\cdot}035_1$	0·65 † ± 0·03	26
Bis-*o*-nitrophenyl disulphide	1·47	2·21	1·38	5·28 ± 0·02	53
Bis-*m*-nitrophenyl disulphide	0·584	1·25	1·36	4·34 ± 0·02	28
Bis-*p*-nitrophenyl disulphide	0·597	1·08	0·889	3·78 ± 0·02	39
Diphenyl disulphone	0·411	0·998	1·31	3·92 ± 0·02	23

* 1 D = $3{\cdot}336 \times 10^{-30}$C m. † Measurement of the ' static ' moment yielded μ = 1·16 D, from ${}_{\infty}P_2 = 109{\cdot}7\ \mathrm{cm}^3$, $R_{\mathrm{D}} = 78{\cdot}1\ \mathrm{cm}^3$ and ${}_{\mathrm{D}}P = 1{\cdot}05\ R_{\mathrm{D}}$. ‡ Uncertainty <1 ps.

TABLE 2

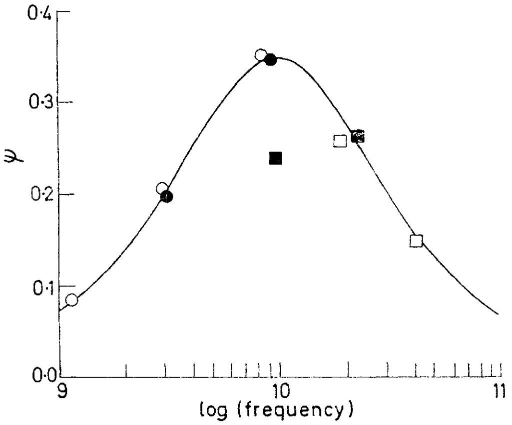
ψ Frequency data for diphenyl disulphide in benzene at 20—25°

Frequency (GHz)	1·140	3·040	3·109	8·540	9·400	9·64	19·15	22·54	42·25
ψ	$0{\cdot}084_7$ [a]	0·213 [a]	0·195 [b]	0·357 [a]	0·349 [b]	0·24 [c]	0·258 [d]	0·263 [c]	0·147 [d]

[a] Present work. [b] From ref. 6. [c] From ref. 5. [d] From ref. 7.

The dielectric loss data for all the disulphides are found, in each instance, to fit very closely a Debye curve corresponding to a single relaxation time. This can best be explained in terms of a predominant overall molecular relaxation process with relatively little contribution from intramolecular relaxation mechanisms arising from rotations about the S–S bond. We note that for the two dialkyl disulphides examined the frequencies employed in the measurements are lower than the respective $f_{\max.}$ values, and absorptions from intramolecular rotations, which would occur at higher frequencies, cannot be excluded. However, with the larger diaryl disulphides, the frequency range includes $f_{\max.}$ and extends into the region in which rapid intramolecular relaxation absorptions would be apparent. For diphenyl disulphide in benzene, a thorough description of the dielectric absorption is now possible by combining present measurements with others already in the literature; the data, converted to ψ values, are given in Table 2. If the one observation at 9·64 GHz[5] is ignored, a Debye curve with μ = 1·77 D and τ = 17·0 ps fits all eight points with less than 6% variation between $\psi_{\mathrm{calc.}}$ and $\psi_{\mathrm{obs.}}$ (the curve is shown in the Figure). This may be interpreted to indicate either a greatly predominant overall molecular relaxation or alternatively an exclusively intramolecular mechanism. The latter possibility is unlikely in view of the magnitude of τ(diphenyl disulphide); *cf.* diphenyl sulphide for which Di Carlo and Smyth[15] have deduced relaxation times of 16 and 4 ps associated with the overall and the internal rotations, respectively.

The relaxation times of the six disulphides R_2S_2 (R = Me, $\mathrm{Bu^t}$, Ph, $p\text{-ClC}_6H_4$, Bz, and $\beta\text{-C}_{10}H_7$) show a regular increase consistent with the increasing bulk of the R groups. The isomeric bisnitrophenyl disulphides, however, have a large variation in their τ values. Those of the *m*- and *p*-nitro-isomers are somewhat greater than τ of bis-*p*-chlorophenyl disulphide and this is in part a consequence of the larger size of the nitro-group.



Dielectric absorption for diphenyl disulphide in benzene: ○, this work; ●, ref. 6; □, ref. 7; ■, ref. 5

Another significant factor is specific benzene solvation[16] of the highly polar C_{ar}–NO_2 groups (predominantly through dipole-induced dipole interactions); this would have a greater effect on the *p*-nitro-group which is more exposed than a nitro-group in the *meta*-position. Fairhall and Ritchie[12] have proven that the solute structure

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of bis-*o*-nitrophenyl disulphide differs markedly from that of the other isomeric forms because of intramolecular interactions involving the *o*-nitro-groups. Such differences in solute shape should be reflected in the increased τ value of the *o*-nitro-compound. It is significant that τ for bis-*p*-chlorophenyl disulphide (23 ps) is intermediate between the values 17 and 26 ps found when R is phenyl and benzoyl respectively. Since bis-*p*-chlorophenyl disulphide has a very small electric moment (0·37 D), intramolecular relaxation involving rotation about S–S of the highly polar chlorophenyl group would contribute appreciably to the dielectric absorption and lead to gross departures from Debye behaviour. This is contrary to observation and supports the notion of an overall molecular process. A similar effect is observed for dibenzoyl disulphide suggesting that rotations about the C–S bonds are also hindered possibly through repulsive interactions between the carbonyl groups and sulphur lone pairs. Kessler and Rundel[17] have observed a temperature dependence of n.m.r. spectra of substituted diphenyl disulphides (though not for dialkyl disulphides to −95°); they estimated free energies of activation for rotations about S–S of the order of 15 kcal mol^{-1}. Hordvik[18] has pointed out that the non-cyclic disulphides show a stereochemical preference for the skew configuration partly because of lone pair repulsions, which are minimal when the dihedral angle of the CSSC group is 90°, and partly as a result of π-bonding (involving overlap between lone pair orbitals and empty sulphur *d* orbitals) which is most pronounced for this molecular geometry. Such factors result in shortening of the S–S bond (compared with that in cyclic, five-membered disulphides in which the S_2 group valencies approach a planar *cis*-arrangement) and they contribute to the relative rigidity of the R_2S_2 system. In the case of diphenyl disulphone the sulphur lone pairs are no longer present but this is still conformationally similar to the disulphides R_2S_2 (from dipole moment evidence) and it conforms also to a Debye type of absorption. The relaxation time of diphenyl disulphone is 6 ps greater than that of diphenyl disulphide consistent with the additional bulk of the molecule. It appears then that the steric and electrostatic interactions between the two SO_2 groupings stabilise the skew configuration for this molecule and result in greatly hindered rotation about the S–S bond.

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