853. *Molecular Polarisability. Electric Dipole Moments and Molar Kerr Constants of Two Sulphoxides and Three Sulphones as Solutes.*

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Dipole moments and molar Kerr constants are reported for Me_2SO, Me_2SO_2, $[CH_2]_4SO_2$, Ph_2SO, and Ph_2SO_2, as solutes. Polarisability specifications of dimethyl sulphone have been estimated and used to deduce that (*a*) the five-membered ring of tetrahydrothiophen dioxide is probably planar, (*b*) the benzene rings in diphenyl sulphone are approximately perpendicular to the C–S–C plane, and (*c*) the observed molar Kerr constant of diphenyl sulphoxide can be reconciled with that calculated for a configuration analogous to that found for diphenyl sulphone.

That average polarisabilities of structures related as R_2S, R_2SO, and R_2SO_2 are usually very similar is shown by the corresponding molecular refractions; *e.g.*, for Me_2S, Me_2SO, Me_2SO_2, Ph_2S, Ph_2SO, and Ph_2SO_2 the R_D's are 19·0, 20·1, 20·1, 60·0, 61·4, and 62·2 c.c., respectively. Evidently the semi-axes of the molecular polarisability ellipsoids for a given sulphide–sulphoxide–sulphone series are either the same or vary in ways such that their means remain constant. As the dipole moments of the six molecules just cited differ markedly (being, in order, 1·56, 4·03, 4·26, 1·50, 4·08, and 4·71 D), information on the anisotropic polarisabilities of the species should be provided by measurements of their molar Kerr constants. No ${}_mK$'s of sulphoxides or sulphones have been hitherto recorded.

Experimental

Materials, Apparatus, etc.—The solutes were prepared and/or purified to give: dimethyl sulphone, m. p. 108°; dimethyl sulphoxide, b. p. 94—96°/20 mm.; diphenyl sulphone, m. p. 125—126°; diphenyl sulphoxide, m. p. 71°; tetrahydrothiophen dioxide, m. p. *ca.* 23°.

Apparatus, techniques, symbols, and methods of calculation have been described before.[1-3]

[1] Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953.
[2] Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.
[3] Le Fèvre and Le Fèvre, (*a*) *Rev. Pure Appl. Chem.* (*Australia*), 1955, **5**, 261; (*b*) Chapter XXXVI in " Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ., Inc., New York, London, 3rd edn., Vol. I, p. 2459.

TABLE 1.

Incremental Kerr constants, dielectric constants, densities, and refractive indexes for solutions at 25°.

Dimethyl sulphone in benzene

10^5w_2	172	478	492	507	530	637	668
$10^7\Delta B$ ...	−0·014	−0·044	−0·042	−0·045	−0·044	−0·055	−0·060

whence $\sum 10^7\Delta B/\sum w_2 = -8{\cdot}73$.

10^5w_2	277	346	422	431	627	690
ε^{25}	2·3313	2·3452	2·3601	2·3629	2·3994	2·4213

whence $\sum\Delta\varepsilon/\sum w_2 = 21{\cdot}0$.

10^5w_2	372	454	516	530	540	682	736	759	774
$10^4\Delta n$	—	—	—	—	—	—	−2	−2	−2
d_4^{25}	0·87487	0·87512	0·87526	0·87530	0·87536	0·87576	0·87588	0·87597	0·87597

whence $\sum\Delta n/\sum w_2 = -0{\cdot}026$; $\sum\Delta d/\sum w_2 = 0{\cdot}288$.

Dimethyl sulphoxide in carbon tetrachloride

10^5w_2	192	288	604	896	909	1138
$10^7\Delta B$ ...	0·031	0·059	0·113	0·164	0·170	0·204

whence $\sum 10^7\Delta B/\sum w_2 = 18{\cdot}4$.

10^5w_2	330	498	514	626	856	1285	1289
ε^{25}	2·3579	2·4279	2·4309	2·4724	2·5704	2·7506	2·7502
d_4^{25}	—	1·58114	—	—	1·57881	—	1·57584

10^5w_2	1452	1480	1512	1631	2007	2470
ε^{25}	2·8219	2·8215	—	—	—	—
d_4^{25}	—	1·57520	1·57431	1·57401	1·57224	1·56906

where $\sum\Delta\varepsilon/\sum w_2 = 40{\cdot}3$; $\sum\Delta d/\sum w_2 = -0{\cdot}652$.

10^5w_2	2686	2847	3333
$10^4\Delta n$	15	15	20

where $\sum\Delta n/\sum w_2 = 0{\cdot}056$.

Diphenyl sulphone in benzene

10^5w_2	103	228	287	411	418	489	660	860	1060	1268	2257
$10^7\Delta B$	−0·024	−0·058	−0·069	−0·100	−0·097	−0·130	−0·172	−0·232	−0·259	−0·335	−0·577

whence $\sum 10^7\Delta B/\sum w_2 = -25{\cdot}5$.

10^5w_2	213	474	877	888	894	940	966	1270	1514	1906	2305
ε^{25} ...	—	2·3338	—	2·3894	2·3864	2·3904	2·3925	2·4370	2·4631	—	—
d_4^{25} ...	0·87440	0·87508	0·87638	0·87635	0·87623	—	—	0·87743	—	0·87919	0·88036
$10^4\Delta n$	—	—	—	—	—	—	—	—	—	15	19

whence $\sum\Delta\varepsilon/\sum w_2 = 12{\cdot}7$; $\sum\Delta d/\sum w_2 = 0{\cdot}285$; $\sum\Delta n/\sum w_2 = 0{\cdot}081$.

Diphenyl sulphoxide in carbon tetrachloride

10^5w_2	343	414	462	659	990
$10^7\Delta B$	−0·027	−0·025	−0·033	−0·049	−0·068

whence $\sum 10^7\Delta B/\sum w_2 = -7{\cdot}15$.

10^5w_2	278	347	533	621	825
$10^4\Delta n$	7	9	14	16	21

whence $\sum\Delta n/\sum w_2 = 0{\cdot}257$.

10^5w_2	186	236	328	365	497	551
ε^{25}	2·2582	2·2665	2·2815	2·2880	2·3096	2·3195

whence $\sum\Delta\varepsilon/\sum w_2 = 16{\cdot}7$.

10^5w_2	475	492	825	1282	1351
d_4^{25}	1·58256	1·58235	1·58084	1·57896	1·57873

whence $\sum\Delta d/\sum w_2 = -0{\cdot}435$.

Tetrahydrothiophen dioxide in benzene

10^5w_2	618	827	848	1271	1526	1878	2496	2717
$10^7\Delta B$	0·051	0·089	—	0·112	0·140	0·176	0·217	—
$10^4\Delta n$	—	—	—	—	—	2	3	4
d_4^{25}	—	—	0·87641	0·87778	0·87858	0·87972	0·88167	0·88234

whence $\sum 10^7\Delta B/\sum w_2 = 9{\cdot}11$; $\sum\Delta n/\sum w_2 = 0{\cdot}013$; $\sum\Delta d/\sum w_2 = 0{\cdot}315$.

10^5w_2	164	283	395	992	1803	2611
ε^{25}	2·3057	2·3304	2·3546	2·4737	2·6362	2·7973

whence $\sum\Delta\varepsilon/\sum w_2 = 20{\cdot}2$.

TABLE 2.

Dielectric polarisations, dipole moments, and molar Kerr constants (from observations on solutions at 25°).

Solute	Solvent	$\alpha\varepsilon_1$	β	γ	δ	${}_\infty P_2$ (c.c.)	R_λ (c.c.)	μ (D) *	$10^{12}{}_\infty({}_mK_2)$
Me_2SO_2	C_6H_6	21·0	0·330	−0·018	−21·3	393	20·08 †	4·26	−217
Me_2SO	CCl_4	40·3	−0·411	0·038	263	354	20·06 †	4·03	+144
Ph_2SO_2	C_6H_6	12·7	0·326	0·054	−62·2	571	62·2 ‡	4·97	−1115
Ph_2SO	CCl_4	16·7	−0·275	0·176	−102	405	61·4 §	4·08	−165
$[CH_2]_4SO_2$	C_6H_6	20·2	0·361	0·009	22·2	482	26·5 §	4·71	+121

* Calc. by assuming ${}_DP = 1{\cdot}05R_\lambda$. † For He light, λ 5876 Å (Price and Gillis, *J. Amer. Chem. Soc.*, 1953, **75**, 4750). ‡ For Na light, λ 5893 Å (Baliah and Shanmuganathan, *Trans. Faraday Soc.*, 1959, **55**, 232). § For Na light (present work).

Observations are recorded in Table 1 and results summarised in Table 2. The quantities $\Delta\varepsilon$, Δd, Δn, and ΔB are the differences between the dielectric constants, densities, refractive indexes, and Kerr constants, respectively, of the solvents and of solutions containing weight fractions w_2 of solute. The following data apply at 25° to the two solvents involved:

	ε_1	d_1	$(n_1)_D$	10^7B_1
Benzene	2·2725	0·87378	1·4973	0·410
Carbon tetrachloride	2·2270	1·58454	1·4575	0·070

Previous Measurements.—The following dipole moments (in D) have been recorded (solvent or state given in parentheses; B = benzene; G = gaseous state): dimethyl sulphone,[4] 4·41 (G),[5] 4·25 (B); diphenyl sulphone,[6] 5·05 (B),[7] 5·14 (B),[8] 5·02 (B),[9] 5·12 (B),[10] 4·93 (B); diphenyl sulphoxide,[11] 4·08 (B),[6] 4·17 (B),[12] 4·00 (B),[8] 4·05 (B); tetrahydrothiophen dioxide,[13] 4·69 (B),[14] 4·81 (B).

DISCUSSION

Dimethyl Sulphone.—The molecular symmetry is such that the principal axes can be located as shown in Fig. 1 with b_1 and b_2 in the C–S–C plane and b_3 normal to this plane. It follows that $\mu_1 = \mu_{obs}$, $\mu_2 = \mu_3 = 0$, so that the molar Kerr constant can be expressed in terms of the optical polarisabilities b_1, b_2, and b_3 by the relations:

$$ {}_mK_2 = 2\pi\boldsymbol{N}(\theta_1 + \theta_2)/9, \qquad (1)$$

$$ \theta_1 = {}_DP[(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2]/45\boldsymbol{k}T_E P, $$

and

$$ \theta_2 = \mu^2_{obs}\,(2b_1 - b_2 - b_3)/45\boldsymbol{k}^2T^2, $$

where θ_1 and θ_2 are the anisotropy and dipole terms, respectively, ${}_DP$ is the distortion polarisation, and ${}_EP$ is the electronic polarisation.

Price and Gillis[15] give the molecular refraction of dimethyl sulphone as $R_{5876} = 20{\cdot}08$ c.c., from which, if we assume that ${}_EP = 0{\cdot}90$, $R_{5876} = 18{\cdot}1$ c.c. (cf. 18·26 c.c. calculated by Coop and Sutton[4]), we obtain a second equation in b_1, b_2, and b_3:

$$ {}_EP = 4\pi\boldsymbol{N}(b_1 + b_2 + b_3)/9. \qquad (2)$$

[4] Coop and Sutton, *Trans. Faraday Soc.*, 1939, **35**, 505.
[5] Lumbroso and Passerini, *Bull. Soc. chim. France*, 1955, 1179.
[6] De Vries and Rodebush, *J. Amer. Chem. Soc.*, 1931, **53**, 2888.
[7] Bergmann and Tschudnovsky, *Ber.*, 1932, **65**, 457.
[8] Gur'yanova, *Zhur. fiz. Khim.*, 1950, **24**, 479.
[9] Baliah and Shanmuganathan, *Trans. Faraday Soc.*, 1959, **55**, 232.
[10] Gomel, Lumbroso, Marziano, and Passerini, *Bull. Soc. chim. France*, 1959, 1908.
[11] Bergmann, Engel, and Sandor, *Z. phys. Chem.*, 1930, *B*, **10**, 397.
[12] Hampson, Farmer, and Sutton, *Proc. Roy. Soc.*, 1933, *A*, **143**, 147.
[13] Longster and Walker, *Trans. Faraday Soc.*, 1953, **49**, 228.
[14] Cumper and Vogel, *J.*, 1959, 3521.
[15] Price and Gillis, *J. Amer. Chem. Soc.*, 1953, **75**, 4750.

As no light-scattering data exist from which $\sum(b_i - b_j)^2$, and thence the θ_1 term, can be evaluated, an exact solution for the polarisability semi-axes is not possible. However, μ is very large, so that θ_2 which is proportional to μ^2 is great and, from the sign of the observed molar Kerr constant, is negative; $|\theta_1|$ must then be insignificantly small compared with $|\theta_2|$. From equation (1), $\theta_1 + \theta_2 = -51{\cdot}6 \times 10^{-35}$ and if we neglect the θ_1 term we are able to evaluate $(2b_1 - b_2 - b_3)$ which in combination with equation (2) yields a solution for b_1 of $0{\cdot}64_5$ (Note: in the following text polarisabilities are expressed as 10^{-23} c.c. units). The estimate of b_1 is insensitive to changes in the value assumed for θ_1, *e.g.*, if $|\theta_1| = 20\%$ of $|\theta_2|$, then $b_1 = 0{\cdot}63$.

Tetrahydrothiophen Dioxide.—For this molecule the b_1, which we locate along the bisector of the angle OSO (the assumed dipole moment direction), can be expressed in terms of the following components:

$$b_1([CH_2]_4SO_2) = b_1(Me_2SO_2) + 2b_L^{C-H} + b_T^{C-O} + 2b_L^{C-C}\cos^2\theta + 2b_T^{C-C}\sin^2\theta,$$

where θ is the angle between each C–C link (α), in Fig. 2, and the b_1 direction. The bond angles in the five-membered ring are uncertain: ∠CSC for dimethyl sulphone is quoted

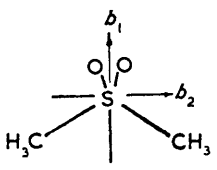

FIG. 1.

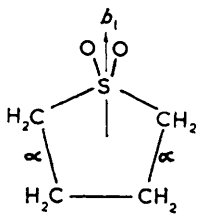

FIG. 2.

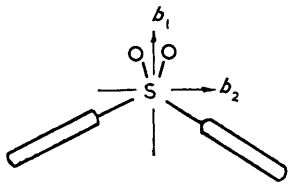

FIG. 3.

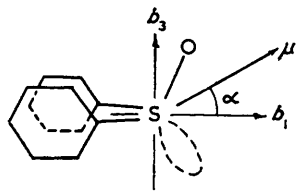

FIG. 4.

as 115° ± 15° (ref. 16, M139) and as 98° for β-isoprene sulphone (ref. 16, M184). If we consider a structure in which the ring is assumed to be planar with each bond angle 108°, then b_1 (calc.) would be 0·99 ($b_L^{C-O} = 0{\cdot}099$, $b_T^{C-O} = b_V^{C-O} = 0{\cdot}027$; $b_L^{C-H} = b_T^{C-H} = b_V^{C-H} = 0{\cdot}064$). The observed ${}_\infty({}_mK_2)$ is $+121 \times 10^{-12}$ from which $\theta_1 + \theta_2$ equals $28{\cdot}8 \times 10^{-35}$ and if $\theta_2 \gg \theta_1$ then $(2b_1 - b_2 - b_3) = ca.\ 0{\cdot}10$. From ${}_EP([CH_2]_4SO_2) = 25{\cdot}1_5$ c.c {$= {}_EP(Me_2SO_2) + 2{}_EP^{C-H} + 3{}_EP^{C-C}$},[17] we obtain $(b_1 + b_2 + b_3)$ as 2·99; b_1 thence becomes 1·03, in fair agreement with the estimate for a planar ring configuration.

Molecular Conformations of Diphenyl Sulphone.—Two structures have been examined: (I) in which the benzene ring planes are normal to the C–S–C plane (see Fig. 3), and (II) in which the benzene rings have been rotated 90° from their positions in (I). Each structure has two planes of symmetry so that the principal axes directions are as shown in Fig. 3; μ_1 in each case equals 4·97 D (the observed dipole moment from Table 2); $\mu_2 = \mu_3 = 0$. The bond angle CSC is taken as 100° (ref. 16, M230). Bond and group polarisability specifications are as follows: $b_1(Ph) = b_2(Ph) = 1{\cdot}056$, $b_3(Ph) = 0{\cdot}672$; $b_1(C_2SO_2) = 0{\cdot}26$, $b_2(C_2SO_2) = b_3(C_2SO_2) = 0{\cdot}37$ (the last three are the dimethyl sulphone semi-axes less six C–H contributions, the assumption being made that $b_2 = b_3$ for this group).

Baliah and Shanmuganathan [9] give the molecular (D line) refraction of diphenyl sulphone as 62·2 c.c. from which ${}_EP(Ph_2SO_2)$ follows as 56·0 c.c. (which is 0·90 R_D). The calculated electronic polarisation is 55·2 c.c. [${}_EP(Ph_2SO_2)$ (calc.) $= {}_EP(Me_2SO_2) - 6{}_EP(C-H) + 2{}_EP(Ph)$; the C–H bond and Ph group values are from ref. 17]. The difference ${}_EP_{exp} - {}_EP_{calc}$ is equal to an exaltation of polarisability Δb of 0·10 which in the subsequent calculations we treat as an increment of $\Delta b/2$ on each of the polarisability

[16] Sutton *et al.*, " Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Special Publ.* No. 11, 1958.
[17] Le Fèvre and Steel, *Chem. and Ind.*, 1961, 670.

semi-axes b_1(Ph). The calculated values for structures (I) and (II) for diphenyl sulphone are:

Structure	b_1 (calc.)	b_2 (calc.)	b_3 (calc.)	$10^{12}{}_mK$ (calc.)
(I)	1·96	2·23	2·48	−1066
(II)	2·41	2·54	1·71	+809

The observed $_\infty(_mK_2)$ is -1115×10^{-12} in reasonable agreement with that predicted for structure (I). Toussaint [18] in 1945 had concluded from an *X*-ray crystal analysis of di-*p*-bromophenyl sulphone that the benzene ring planes are approximately perpendicular to the Br–S–Br plane.

Dimethyl Sulphoxide and Diphenyl Sulphoxide.—Specification of the molecular polarisability semi-axes for dimethyl sulphoxide is not possible from the data available. For this we require: a third equation in b_1, b_2, and b_3, the location of b_1 and b_3 in the plane of symmetry, and the direction of action of the permanent dipole moment with respect to the principal axes b_1 and b_3. Price and Gillis [15] have shown that the molecular refractions (He line) of molecules R_2X (X = S, SO, or SO_2) are almost equal, from which we infer that $\sum b^{S-O}$ is approximately equal to $\sum b$ for a lone-pair of electrons; however, we are unable as yet to estimate the anisotropy of polarisability for electrons occupying non-bonding orbitals.

In the case of diphenyl sulphoxide the magnitude and the location of the polarisability semi-axes for any conformation will be governed in most part by the orientation of the phenyl groups within the molecule; so it is reasonable to assume that the polarisability specifications for any configuration of diphenyl sulphoxide will not differ significantly from those calculated for the analogous configuration of diphenyl sulphone.

Abrahams [19] has shown that for diphenyl sulphoxide in the solid state the benzene ring planes are approximately perpendicular to the C–S–C plane. If we accept this, then b_1, b_2, and b_3 must be *ca.* 1·96, 2·23, and 2·48, respectively [the semi-axes for structure (I) of diphenyl sulphone]. The dependence of $_mK$ (calc.) for diphenyl sulphoxide on α, the angle between the direction of action of μ_{res} and the b_1 axis in Fig. 4, is shown below:

α	0°	10°	20°	30°	37°	38°	39°	40°
$10^{12}{}_mK$ (calc.)	−715	−673	−546	−357	−196	−172	−147	−123

Agreement between the observed and calculated values is obtained provided $\alpha = ca.$ 38°. From ref. 16, M230, the angle OSO in di-*p*-bromophenyl sulphone is 131°, so that each S–O link is inclined 65·5° to the b_1 direction. Ref. 19 lists results for diphenyl sulphoxide from which the corresponding angle is calculable as 65°. If we regard $\mu(Ph_2SO)$(obs.) as the resultant of $\mu(Ph_2S)$ (1·50 D from ref. 20) and μ(SO), then the latter moment is 3·22 D and $\mu(Ph_2SO)$ (obs.) acts at 46° to b_1, *i.e.*, $\alpha = 46°$.

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[18] Toussaint, *Bull. Soc. chim. belges*, 1945, **54**, 319.
[19] Abrahams, *Acta Cryst.*, 1957, **10**, 417.
[20] Aroney, Le Fèvre, and Saxby, *J.*, 1963, 1167.