Molecular Polarisability. The Molar Kerr Constant and Conformation of Diphenyl Ether as a Solute in Benzene

By R. J. W. LE FÈVRE, A. SUNDARAM and K. M. S. SUNDARAM

(Received August 14, 1961)

Attention has recently[1] been drawn to the problem of assigning a space-formula to diphenyl ether. Both in conversations at Princeton and in Ref. 1, p. 30, Professor K. Higasi has indicated that the Sydney group might provide helpful evidence on the matter. Accordingly we have measured the molar Kerr constant of diphenyl ether at infinite dilution in benzene and now desire to record and discuss our results.

Experimental and Computational Methods.— For brevity we omit details of apparatus and

---

[1] K. Higasi, "Dielectric Relaxation and Molecular Structure", *Monograph Series of the Research Institute of Applied Electricity*, No. 9, Hokkaido University, Sapporo, Japan, 1961.

technique since they are described in detail elsewhere[2,3]. Dielectric constants, ε, densities, d, refractive indexes, n, and Kerr constants, B, of solutions containing weight fractions, w, of diphenyl ether in benzene at 25° are listed in Table I; the n's and B's were measured with Na-light. Suffixes 1, 2, and 12 indicate respectively a property of the solvent, solute, or solution; the prefix Δ denotes a difference between solution and solvent, e. g. $\Delta\varepsilon=\varepsilon_{12}-\varepsilon_1$, $\Delta d=d_{12}-d_1$, $\Delta n=n_{12}-n_1$, and $\Delta B=B_{12}-B_1$. The symbols α, β, γ, and δ are from the equations, $\varepsilon_{12}=\varepsilon_1(1+\alpha w_2)$, $d_{12}=d_1((1+\beta w_2)$, $n_{12}=n_1(1+\gamma w_2)$, and $B_{12}=B_1(1+\delta w_2)$, which are assumed to apply at low w_2's and to be usable whenever Δ(property) appears rectilinear with w_2; γ' refers to the square of the refractive index, $n^2{}_{12}=n^2{}_1(1+\gamma' w_2)$. Molar Kerr constants, total polarisations, etc., extrapolated to infinite dilution are written ${}_\infty({}_\mathrm{m}K_2)$, ${}_\infty P_2$, etc.; calculations of these are via specific quantities, e. g. ${}_\mathrm{S}K_2$, p_2, and r_2, which when $w_2=0$ are given by relations 1, 2, and 3:

$${}_\infty({}_\mathrm{S}K_2)={}_\mathrm{S}K_1(1-\beta+\gamma+\delta-H\gamma-J\alpha\varepsilon_1) \quad (1)$$

where ${}_\mathrm{S}K_1=6\lambda n_1 B_1/(n^2{}_1+2)^2(\varepsilon_1+2)^2 d_1$

$$H=4n^2{}_1/(n^2{}_1+2)$$

and $J=2/(\varepsilon_1+2)$;

$${}_\infty p_2=p_1(1-\beta)+3\alpha\varepsilon_1/d_1(\varepsilon_1+2)^2 \quad (2)$$

where $p_1=(\varepsilon_1-1)/d_1(\varepsilon_1+2)$;

$${}_\infty r_2=r_1(1-\beta)+3\gamma' n^2{}_1/d_1(n^2{}_1+2)^2 \quad (3)$$

where $r_1=(n^2{}_1-1)/d_1(n^2{}_1+2)$

Derivations of Eqs. 1, 2, and 3 may be found in Refs. 2 and 3. Benzene used as solvent was purified as described in Ref. 3, p. 45.

Observations and Quantities Deduced Therefrom.—These are set out in Table I. When $w_2=0$ (i. e. for the pure solvent) the following apply at 25°: $n_1=1.4973$, $n^2{}_1=2.24191$, $\varepsilon_1=2.2725$, $d_1=0.87378$, and $B=0.410\times10^{-7}$.

TABLE I. DIPHENYL ETHER IN BENZENE AT 25°

$10^5 w_2$	1035	2249	3432	6853	10985	14557	18137
$10^4\Delta n$	7	15	22	46	74	102	131
$10^4\Delta n^2$	20	44	64	135	218	301	387
$10^4\Delta\varepsilon$	114	240	372	737	1165	1551	1805
$10^5\Delta d$	173	373	575	1168	1892	2515	3157
$10^{11}\Delta B$	61	132	210	410	681	870	1120

whence $\sum\Delta n/\sum w_2=0.069$

$\sum\Delta n^2/\sum w_2=0.204$

$\sum\Delta\varepsilon/\sum w_2=1.04_6$

$\Delta d=0.1672w_2+0.0340w^2{}_2$

$\sum\Delta B/\sum w_2=0.606\times10^{-7}$

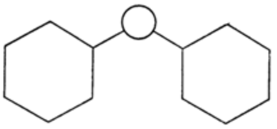
From these data we have: ${}_\infty P_2=80.29$ cc., $R_\mathrm{D}=52.68$ cc., ${}_\mathrm{D}P=1.05R_\mathrm{D}=55.31$ cc., $\mu=1.10_5$D., and ${}_\infty({}_\mathrm{m}K_2)=22.4\times10^{-12}$.

Wesson[4] lists two earlier determinations of the dipole moment of diphenyl ether in benzene (viz. 1.02 and 1.13 D.) with neither of which is the new value of 1.10_5 D. in serious disharmony. The Kerr effect of diphenyl ether has never been examined before, either as a pure liquid or as a solute.

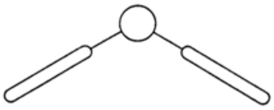
Discussion.—The molar Kerr constant of a substance depends upon the principal axes, b_1, b_2, and b_3, of the appropriate polarisability ellipsoid, together with the direction of action of the resultant dipole moment and its magnitude. For a given molecular model, these axes can be calculated from the longitudinal, transverse, and "vertical" polarisabilities of the constituent bonds and groups. (Examples of such operations are given in Refs. 2 or 5.) In the present case only the C–O link[6] and the phenyl-group[7] are concerned:

			C–O	C_6H_5
Longitudinal polarisability		$b_\mathrm{L}\times10^{23}$	0.081	1.056
Transverse	〃	$b_\mathrm{T}\times10^{23}$	0.039	1.056
"Vertical"	〃	$b_\mathrm{V}\times10^{23}$	0.039	0.671

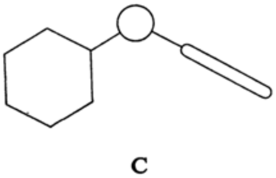
Four models will now be considered, A, B, C and D; only the first three are illustrated here:



A



B



C

---

[2] C. G. Le Fèvre and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1953, 4041; 1954, 1577; *Rev. Pure and Appl. Chem.*, 5, 261 (1955); Chap. XXXVI in Physical Method of "Organic Chemistry", Ed. Weissberger, Interscience Pub., New York, London, 3rd edn., Vol. 1, p. 2459.

[3] R. J. W. Le Fèvre, "Dipole Moments", Methuen, London, 3rd edn. (1953), Chap. II.

[4] L. G. Wesson, "Tables of Electric Dipole Moments", Technology Press, Massachusetts Institute of Technology (1948).

[5] R. J. W. Le Fèvre, "Applications in Chemistry of Properties Involving Molecular Polarisability", Liversidge Research Lecture, *J. Proc. Roy. Soc. N. S. W.*, 95, 1 (1961).

[6] C. G. Le Fèvre and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1956, 3549.

[7] M. Aroney and R. J. W. Le Fèvre, ibid., 1960, 3600.

TABLE II. PRINCIPAL POLARISABILITIES AND MOLAR KERR CONSTANTS CALCULATED FOR MODELS A TO D

Model*	$10^{23}b_1$	$10^{23}b_3$	$10^{23}b_3$	$10^{12}{}_{\mathrm{m}}K_2$ calcd.
A	2.212	2.253	1.420	+84.1
B	1.635	2.060	2.190	−54.1
C	1.836_5	2.243_5	1.805	−16.6
D	2.003	2.246	1.636	+22.6

* The direction in which b_1 is measured bisects the C_1-O-$C_{1'}$ angle, that for b_2 is parallel to the $C_1 \cdots\cdots C_{1'}$ line, and that for b_3 is perpendicular to the C_1-O-$C_{1'}$ triangle.

The molecule is planar in A; in B both phenyl-rings are at 90° to the plane of A; C is Morino's conformation[1] with one ring as in A and one as in B; D is generated from A by twisting each phenyl group by 37° about its O-C_1-C_4 line. In all cases $\mu_{\text{resultant}}$ is taken as acting along the bisector of the C-O-C angle, which—following Higasi[1]—is adopted as 120°. Calculations are summarised in Table II.

Since the molar Kerr constant obtained by experiment is 22.4×10^{-12}, it appears that neither A nor B nor C *alone* represents the diphenyl ether molecule in benzene. It is of course possible to devise mixtures of A and B, or of A with B and C, for which the expected ${}_{\mathrm{m}}K$ would equal that observed, yet there seems to be no recorded evidence against the view that the ether exists as a *single* form, in which case one of type D is indicated.

The angle of twist of 37° was selected by trial and error and is advanced as an "order of magnitude" estimate only (because the data for C-O and phenyl are drawn from paraldehyde[6] and benzene[7] respectively and may not be quite appropriate for diphenyl ether, in which some conjugation effects must also be present). Nevertheless it is interesting that Higasi (Ref. 1, p. 26) calculates that the twist angles for the configuration of minimum energy are 32.5°, and later in the same work (pp. 112—113) explicitly mentions the possibility of a form such as D, which *inter alia* would satisfy Katayama's X-ray study of *o, o′*-diiododiphenyl ether (in which the I······I distance was found to be 5.28±0.07 Å) if the twist angles in this substituted molecule had the values 17.5°.

Finally it is relevant to mention that, via the Kerr effect, Aroney and Le Fèvre[7] concluded that the phenyls in triphenylamine were twisted 65∼70° from the positions in which the three-fold axis of symmetry is parallel to the planes of the Ar-rings, while via electron diffraction, Sasaki, Kimura, and Kubo[8] found angles of 47±5°. By similar arguments to those used with NPh_3, Aroney and Le Fèvre[7] have deduced angles of ca. 45° for triphenylmethane, and unpublished measurements and calculations for benzophenone suggest that twists of about 45° are satisfactory for this molecule also.

Grateful acknowledgement is made to the University of Sydney of the award of an H. B. and F. M. Gritton Research Scholarship to K. M. S. and of the F. A. Q. Stephens Research Fellewship to A. S.

Chemistry School
University of Sydney
N. S. W., Australia

---

[8] Y. Sasaki, K. Kimura and M. Kubo, *J. Chem. Phys.*, 11, 477 (1959).