458. *Molecular Polarisability. Electric Double Refraction of Solutions containing Optically Active Solutes.*

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The possibility of measuring the electric double refraction of optically active compounds in dilute solution is examined by comparing results obtained for (±)-solutes with those for their (+)- or (−)-isomers. Molar Kerr constants are reported for inactive and active camphor, camphorquinone, diethyl tartrate, and *N*-benzoylamphetamine; at infinite dilution the values for each pair of isomers differ only by amounts which are within the range of experimental errors often experienced in such determinations.

OUR standard arrangement [1,2] for measuring the electric birefringence of a solution requires the latter to be traversed by a ray of light plane-polarised at 45° to a transverse electric field. The solution is placed between Nicol prisms, crossed for extinction before application of the field. Phase differences are determined with the compensator described by Szivessy and Dierkesmann.[3] Two difficulties can be foreseen if the solution possesses natural optical rotatory power: (*a*) the field-polarisation angle will vary continuously as the light passes through the field, and (*b*) extinction under zero-field conditions will no longer involve polariser–analyser settings of $\pm\pi/2$ as required by the formulæ given in ref. 3. Of these, (*a*) is the more serious since it implies that the doubly refracting solution is not in the fixed azimuths $\pm\pi/4$, as normally used with optically inactive media, and that the maximum Kerr effect (induced by a field-polarisation angle of 45°) cannot be displayed by the liquid under examination. Since these considerations threaten the applicability of electric birefringence measurements to stereostructural questions concerning optically active substances, and since the assessment of their effects from *a priori* theory is complex, the problem has been approached experimentally.

EXPERIMENTAL

General.—Apparatus, procedures, symbols, and methods of calculation are as described or defined in refs. 1, 2, and 4. Contexts should prevent confusion between α, our usual symbol for the dielectric constant increment of a solution, and the conventional symbol of rotatory power.

Solvents.—These have been freshly-distilled calcium chloride-dried carbon tetrachloride or sodium-dried benzene, to which the following physical constants apply:

	ε	d_4^{25}	n_D^{25}	10^7B
Carbon tetrachloride	2·2270	1·5845	1·4575	0·070
Benzene	2·2725	0·87378	1·4973	0·410

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[1] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.* (*Australia*), 1955, **5**, 261.
[2] Le Fèvre and Le Fèvre, (*a*) *J.*, 1953, 4041; (*b*) *J.*, 1954, 1577.
[3] Szivessy and Dierkesmann, *Ann. Physik*, 1931, **11**, 949; *Z. Instrumentenkunde*, 1932, **52**, 337.
[4] Le Fèvre, " Dipole Moments," Methuen, London, 3rd Edn., 1953.

TABLE 1. *Kerr effects, dielectric constants, etc., for solutions in carbon tetrachloride or benzene at 25°.*

(+)-*Camphor in carbon tetrachloride*

10^5w_2	502	626	700	899	1021	1111	1473	1586	1617	1816
ε^{25}............	2·2872	2·3036	2·3100	2·3340	2·3460	2·3599	2·4006	2·4145	2·4177	2·4411
d^{25}	1·57930	1·57837	1·57731	1·57618	1·57416	1·57313	1·56975	1·56861	1·56827	1·56659
Δn	0·0002	0·0002	0·0002	0·0004	0·0004	0·0005	—	0·0005	0·0007	0·0010

whence $\Delta\varepsilon = 12{\cdot}01_5w_2 - 13{\cdot}34w_2^2$, $\sum\Delta d/\sum w_2 = -1{\cdot}002$, $\sum\Delta n/\sum w_2 = 0{\cdot}042$

10^5w_2	122	164	220	350	422	624
$10^7\Delta B$	0·008	0·012	0·020	0·033	0·041	0·066

whence $10^7\Delta B = 7{\cdot}42w_2 + 530w_2^2$

(—)-*Camphorquinone in carbon tetrachloride*

10^5w_2	281	349	393	484	578	706	900
ε^{25}............	2·2909	2·3105	2·3226	2·3448	2·3568	2·3957	2·4412

whence $\sum\Delta\varepsilon/\sum w_2 = 23{\cdot}67$

10^5w_2	175	314	411	516	665	793	897
d^{25}	1·58329	1·58209	1·58133	1·58044	1·57950	1·57830	1·57794
Δn	0·0002	0·0002	0·0004	0·0004	0·0005	0·0006	0·0006

whence $\sum\Delta d/\sum w_2 = -0{\cdot}766$, $\sum\Delta n/\sum w_2 = 0{\cdot}077$

10^5w_2	29	58	84	151	293
$10^7\Delta B$	0·004	0·010	0·015	0·030	0·066

whence $10^7\Delta B = 16{\cdot}96w_2 + 1875w_2^2$

(±)-*Camphorquinone in carbon tetrachloride*

10^5w_2	163	290	467	763	908
$10^7\Delta B$	0·025	0·054	0·084	0·125	0·159

whence $\sum\Delta B/\sum w_2 = 17{\cdot}25 \times 10^{-7}$

Diethyl (+)-*tartrate in carbon tetrachloride*

10^5w_2	386	775	1057	1222	1689	2519
ε^{25}............	2·2653	2·3016	2·3315	2·3455	—	2·4618
d^{25}	1,58215	1·58043	1·57859	1·57743	1·57512	1·57056
Δn	—0·0002	—0·0003	—0·0004	—0·0004	—0·0005	—0·0008

whence $\sum\Delta\varepsilon/\sum w_2 = 9{\cdot}57$, $\sum\Delta d/\sum w_2 = -0{\cdot}562$, $\sum\Delta n/\sum w_2 = -0{\cdot}034$

10^5w_2	245	343	422	596	750
$10^7\Delta B$	0·004	0·003	0·005	0·005	0·009

whence $\sum\Delta B/\sum w_2 = 1{\cdot}11 \times 10^{-7}$

Diethyl (±)-*tartrate in carbon tetrachloride*

10^5w_2	208	412	559	803	966	2696
$10^7\Delta B$	0·003	0·005	0·006	0·009	0·010	0·026

whence $\sum\Delta B/\sum w_2 = 1{\cdot}04 \times 10^{-7}$

(—)-N-*Benzoylamphetamine in benzene*

10^5w_2	275	355	487	527	552	610
ε^{25}............	2·2915	2·2968	2·3043	2·3068	2·3108	2·3123

whence $\sum\Delta\varepsilon/\sum w_2 = 6{\cdot}68$

10^5w_2	156	232	302	324	374	425	555	575
d^{25}	0·87420	0·87434	—	0·87440	0·87998	—	0·87482	0·87490
Δn	—	—	0·0002	0·0002	0·0004	0·0003	0·0006	0·0007

whence $\sum\Delta d/\sum w_2 = 0{\cdot}201$, $\sum\Delta n/\sum W_2 = 0{\cdot}082$

10^5w_2	292	409	418	574	597
$10^7\Delta B$	—0·004	—0·005	—0·006	—0·009	—0·009

whence $\sum\Delta B/\sum w_2 = -1{\cdot}44 \times 10^{-7}$

(±)-N-*Benzoylamphetamine in benzene*

10^5w_2	298	335	469	534	558
$10^7\Delta B_1$ ...	—0·004	—0·005	—0·006	—0·009	—0·009

whence $\sum\Delta B/\sum w_2 = -1{\cdot}49 \times 10^{-7}$

Solutes.—These were recrystallised or redistilled just before use. (−)-Camphorquinone was prepared by oxidation [5] of (+)-camphor under reflux with selenium dioxide for 3—4 hr. Filtration, precipitation by neutralisation, and crystallisation from light petroleum yielded orange needles, $[\alpha]_D = -100{\cdot}3°$ (toluene). (±)-Camphorquinone resulted from a similar treatment of (±)-camphor. Diethyl (+)-tartrate, a commercial sample of high purity (from British Industrial Solvents), after distillation at 160—162°/12—15 mm., had $[\alpha]_D = +5{\cdot}0°$. Diethyl racemate was prepared by following the directions of Vogel.[6] (+)- and (±)-Amphetamine, obtained as oils from the hydrochlorides by treatment with alkali, proved to be insufficiently soluble in either benzene or carbon tetrachloride, and were therefore converted by the Schotten–Baumann reaction [6] into the corresponding *N*-benzoyl derivatives.

Measurements.—These are listed in Table 1, and calculated quantities, including dipole moments and molar Kerr constants at infinite dilution, in Table 2.

Previous determinations. Dipole moments in Debye (D) units have been recorded (for benzene solutions at 25°, unless otherwise stated) as follows (references in parentheses):

(±)-Camphor: 2·95, (7), 22°; 2·94, (8), 22°; 3·05, (9), 20°; 2·91 (10), 20°; 3·10 (11); 3·09, (12), in CCl_4. (±)-Camphorquinone: 4·46, (13), 4·78, (14), 35°. Diethyl (±)-tartrate: 3·16, (15), 38°; 3·10, (16); 3·45, (11). Diethyl (+)-tartrate: 3·46, (11).

No molar Kerr constants for the solutes of Tables 1 and 2 are in the literature; de Mallemann [17] mentions the electric birefringence of some solutions of camphor in hexane, and Schob [18] reports the Kerr constant *B* of liquid ethyl (+)-tartrate from 0° to 80°, but in neither case are the data relevant to the present inquiry.

TABLE 2. *Calculation of results.*

	$\alpha\varepsilon_1$	β	γ	δ	$_\infty P_2$ (c.c.)	R (c.c.)	(μ) (D) *	$10^{12}{}_\infty({}_mK_2)$
(+)-Camphor	12·02	−0·632	0·029	106	239·3	44·8	3·06	116
(±)-Camphor	12·18	−0·612	0·032	105	—	—	—	115 [6]
(−)-Camphorquinone	23·67	−0·484	0·053	242	461·4	46·6	4·49	289
(±)-Camphorquinone	—	—	—	246	—	—	—	294 †
Diethyl (+)-tartrate	9·58	−0·355	−0·023	15·9	260·2	45·7	3·22	19·7
Diethyl (±)-tartrate	—	—	—	14·8	—	—	—	18·0
(−)-*N*-Benzoylamphetamine	6·68	0·230	0·055	−3·5	363·2	72·8	3·74	−107
(±)-*N*-Benzoylamphetamine	—	—	—	−3·6	—	—	—	−110

* Calculated for distortion polarisation of $1{\cdot}05R_D$.

† Values of $\alpha\varepsilon_1$, β, and γ measured for optically active species were assumed to hold for the corresponding racemate within the limits of experimental error.[11]

DISCUSSION

The last column of Table 2 shows that standard procedures [1,2] for the extrapolation of observations can lead to values of molar Kerr constants at infinite dilution which, for each pair of optically active–inactive isomers, differ no more than repeated determinations on a single inactive solute sometimes do. The situation resembles that found by Le Fèvre and Maramba [11] for the total polarisations of such pairs, values of $_\infty P_2$ being the same, within the normal range of experimental error, although the rates of change with concentration of P_2 were not always identical. If the differences, ΔB, listed in Table 1, between the Kerr constants of the solutions and solvent, are plotted against w_2 for the four solute pairs

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[5] Evans, Ridgion, and Simonsen, *J.*, 1934, 137.

[6] Vogel, " Practical Organic Chemistry," Longmans, London, 3rd Edn., 1956.

[7] Donle and Volkert, *Z. phys. Chem.* (*Leipzig*), 1930, *B*, **8**, 60.

[8] Wolf, *Physikal. Z.*, 1930, **31**, 227.

[9] Higasi, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1932, **11**, 729.

[10] Sahney, Burucha, and Sarua, *J. Ind. Chem. Soc.*, 1948, **25**, 285.

[11] Le Fèvre and Maramba, *J.*, 1952, 235.

[12] Le Fèvre and Le Fèvre, *J.*, 1956, 3549.

[13] Le Fèvre, Maramba, and Werner, *J.*, 1953, 2496.

[14] Narasimhan, *Proc. Indian Acad. Sci.*, 1953, **37***A*, 551.

[15] Wolf, *Trans. Faraday Soc.*, 1930, **26**, 315.

[16] Wolf and Bodenheimer, *Z. physikal. Chem.*, 1931, *Bodenstein Festschrift*, 620.

[17] de Mallemann, *Ann. Physique*, 1924, **2**, 99; *Compt. rend.*, 1923, **176**, 380; **177**, 1028.

[18] Schob, *Compt. rend.*, 1934, **198**, 2232.

under examination, points for the inactive form are in no case superior to those for the active form; in two of the instances the divergence, making $\Delta B/w_2$ less positive for the $(\pm)$- than for the $(+)$- or $(-)$- variety, clearly increases with w_2.

Since, as Table 10 in ref. 2(*b*) illustrates, errors in $_{\infty}({}_{\rm m}K_2)$ are mostly due to those in δ (by which ΔB is related to w_2) it is obvious that when dealing with an optically active solute particular care must be taken with the value of ΔB for the stronger solutions, because in the process of fitting observed ΔB's by the method of least squares to the equation $(\Delta B)_{w_2} = aw_2 + bw_2^2$ the value of a, *i.e.* $b_1\delta$ for $w_2 = 0$, is sensitively affected by these larger ΔB's; even so, the technique here justified is practically simpler than that suggested by Ilberg,[19] namely, to place the Kerr cell within a solenoid and to nullify the optical rotation by a superposed Faraday effect.

The award of a C.S.I.R.O. Senior Postgraduate Studentship to J. M. E. is gratefully acknowledged.

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[*Received, October* 31*st*, 1960.]

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[19] Ilberg, *Physikal. Z.*, 1925, **26**, 901.