471. *Molecular Polarisability. The Conformations of* cyclo*Heptanone and of Certain Other Cyclic Ketones.*

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Assumptions previously made in elucidating the structures of *cyclo*pentanone, *cyclo*hexanone, and (±)-camphor from molar Kerr constant data are now justified by the determination of the molecular anisotropies ($10^3\,{}_\infty\delta_2^{\,2}$) at infinite dilution in carbon tetrachloride. The values found are $31{\cdot}1_3$, $11{\cdot}6_0$, and $39{\cdot}8_4$ respectively, and for *cyclo*heptanone $27{\cdot}0_8$. ${}_\infty({}_mK_2)$ of *cyclo*heptanone is $156{\cdot}8 \times 10^{-12}$ in carbon tetrachloride at 25°; The structure of this ketone is discussed.

Stereostructures for *cyclo*pentanone, *cyclo*hexanone, and camphor were specified by Le Fèvre and Le Fèvre[1] in 1956. The supporting evidence in each case depended effectively on agreement between the values of b_1, b_2, and b_3 (the three tensor components defining the polarisability ellipsoid of a molecule) derived from the experimental molar

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

Kerr constant, and those computed from a knowledge of the constituent link polarisabilities and stereochemistry of the appropriate 5- or 6-ring structure. In the deduction of b_1, b_2, and b_3 from the expression ${}_mK_{\text{expt.}} = 2\pi N(\theta_1 + \theta_2)/9$ (for expansions of θ_1, θ_2, etc., and definitions of other symbols, see ref. 2), however, there was no information on light scattering then available by means of which the small term θ_1 could be separated from the comparatively large θ_2, and accordingly an estimate of θ_1 was made for each substance.

The introduction by Le Fèvre and Purnachandra Rao [2] of a procedure whereby the molecular anisotropy, δ_2^2, of a solute can be determined at infinite dilution has changed the situation; θ_1 is easily accessible from δ_2^2, and a complete analysis of the results in ref. 1 is now possible. The present paper deals with this matter and also extends the investigation to *cyclo*heptanone.

EXPERIMENTAL

Materials.—*cyclo*Heptanone (L. Light and Co. Ltd.) was dried (Na_2SO_4) and distilled, b. p. 180°/760 mm. Other solutes were those used by Le Fèvre and Le Fèvre.[1] Carbon tetrachloride (" sulphur free ") was stored over calcium chloride, after fractionation through a 1 metre column packed with glass helices.

TABLE 1. *Depolarisation factors of solutions in carbon tetrachloride.**

cyclo*Pentanone*, $D = -0{\cdot}5435$ †

10^5f_2 ...	1677	3407	6270	9043	11,850	14,997
$10^2\Delta_{12}$...	4·662	5·659	7·503	9·095	10·98	13·25

whence $\Delta\Delta = 0{\cdot}6216f_2 + 0{\cdot}171f_2^2$
and ${}_\infty\delta_2^2 = 31{\cdot}13 \times 10^{-3}$

cyclo*Hexanone*, $D = -0{\cdot}6565$ †

10^5f_2	2582	5283	8057	10,418	13,366
$10^2\Delta_{12}$	4·050	4·621	4·990	5·594	6·124

whence $\Delta\Delta = 0{\cdot}2139f_2 - 0{\cdot}116f_2^2$
and ${}_\infty\delta_2^2 = 11{\cdot}60 \times 10^{-3}$

cyclo*Heptanone*, $D = -0{\cdot}7111$ †

10^5f_2 ...	2672	4848	7062	9481	12,131
$10^2\Delta_{12}$ ...	5·005	6·251	7·421	8·799	10·52

whence $\Delta\Delta = 0{\cdot}5460f_2 + 0{\cdot}272f_2^2$
and $\delta_2^2 = 27{\cdot}08 \times 10^{-3}$

(±)-*Camphor*, $D = 0{\cdot}9714$ †

10^5f_2	2589	4203	5664	7018	8518
$10^2\Delta_{12}$	5·653	6·912	8·110	9·201	10·48

whence $\Delta\Delta = 0{\cdot}8297f_2 - 0{\cdot}1025f_2^2$
and ${}_\infty\delta_2^2 = 39{\cdot}84 \times 10^{-3}$

* $\Delta_1 = 0{\cdot}0346$ (from ref. 2).
† D is a density factor given by $d_{12} = d_1 + Df_2$.

TABLE 2. *Kerr effects, dielectric polarisations, etc., for solutions of* cyclo*heptanone in carbon tetrachloride.**

10^5w_2	$10^7\Delta B$	ε^{25}	d_4^{25}	10^5w_2	$10^7\Delta B$	$10^4\Delta n$
674	0·097	2·3402	1·57766	2007	0·259	4
1024	0·141	2·3990	1·57409	2362	0·304	5
1227	0·163	2·4331	1·57201	3253	0·419	7
1444	0·196	2·4696	1·56980	4228	0·542	9

whence $10^7\Delta B = 13{\cdot}51w_2 - 17{\cdot}7w_2^2$, and $\delta = 193{\cdot}0$; $\sum\Delta n/\sum w_2 = \sum 0{\cdot}0211$, and $\gamma = 0{\cdot}014_5$
$\sum\Delta\varepsilon/\sum w_2 = 16{\cdot}80$; $\sum\Delta d/\sum w_2 = -1{\cdot}020_8$, and $\beta = -0{\cdot}644_2$.
Therefore ${}_\infty({}_mK_2) = 156{\cdot}8 \times 10^{-12}$ and ${}_\infty P_2 = 233{\cdot}4$ c.c.

* For $w_2 = 0$, $B_1 = 0{\cdot}070 \times 10^{-7}$, $n_D^{25} = 1{\cdot}5475$, $\varepsilon_1^{25} = 2{\cdot}2270$, $d_4^{52} = 1{\cdot}58454$.

Apparatus and Methods.—Details have been given for depolarisation factors,[2] dielectric constants,[3] electric double refractions,[4,5] and extrapolation procedures and calculations.[2,4,5,6,7] Solutions were made up by weight and concentrations expressed as molar fractions for the depolarisation observations and as weight fractions for the others. Measurements are set out in Tables 1 and 2, in which symbols have the following meanings: f molar fraction, Δ depolarisation factor, δ_2^2 molecular anisotropy, w weight fraction, ε dielectric constant, d density, $\Delta\Delta$, ΔB, and Δn the differences respectively of depolarisation factors, Kerr constants, and refractive indexes between solution and pure solvent. Suffixes 1, 2, or 12 indicate, in order, solvent,

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[2] Le Fèvre and Purnachandra Rao, *J.*, 1957, 3644.
[3] Buckingham, Chau, Freeman, Le Fèvre, Narayana Rao, and Tardif, *J.*, 1956, 1405.
[4] Le Fèvre and Le Fèvre, *Rev. Pure and Appl. Chem.*, 1955, **5**, 261.
[5] Le Fèvre and Le Fèvre, *J.*, 1953, 4041.
[6] Le Fèvre, " Dipole Moments," Methuen, London, 3rd Edn., 1953.
[7] Harris, Le Fèvre, and Sullivan, *J.*, 1953, 1622.

solute, or solution; δ *without a suffix* denotes the constant in the equation for the Kerr effect of a solution, $B_{12} = B_1(1 + \delta w_2)$ and (cf. ref. 4, p. 283) is to be distinguished from $\delta_2{}^2$ which is the " molecular anisotropy " of a solute; θ_1 and θ_2 are the " anisotropy " and " dipole " terms contained in the molar Kerr constant, ${}_{\mathrm{m}}K$; their suffixes have no reference to the components of a mixture. Polarisations, total, or electronic or distortion, molecular refractions, and dipole moments are represented conventionally by P or ${}_{\mathrm{E}}P$ or ${}_{\mathrm{D}}P$, R, and μ. Extrapolated values for solutes at infinite dilution are shown thus: ${}_{\infty}P_2$, ${}_{\infty}({}_{\mathrm{m}}K_2)$, ${}_{\infty}\delta_2{}^2$, etc.

DISCUSSION

Dipole Moment of cyclo*Heptanone.*—The observed total polarisation (233·4 c.c.) at infinite dilution in carbon tetrachloride at 25° in conjunction with a distortion polarisation of 34·0 c.c. (*i.e.*, $1{\cdot}05R_{\mathrm{D}}$) corresponds to a dipole moment of $3{\cdot}1_2$D. Such a result is in good agreement with the only value ($3{\cdot}1_0$ D) previously recorded.[8] The polarity of *cyclo*heptanone is thus[1] 0·1 D greater than that of *cyclo*pentanone and 0·02 D less than that of *cyclo*hexanone, which among the cyclanones so far examined[8] exhibits the maximum moment.

Anisotropy Terms.—These have been calculated (see Table 3) by the equation

$$\theta_1 = ({}_{\infty}\delta_2{}^2)(b_1 + b_2 + b_3)^2 Q/45kT$$

where $Q = {}_{\mathrm{D}}P/{}_{\mathrm{E}}P$, and T = absolute temperature; $(b_1 + b_2 + b_3)$ is obtained from the electronic polarisation as $9({}_{\mathrm{E}}P)/4\pi N$. Le Fèvre and Le Fèvre,[1] lacking the depolarisation data now available, adopted 1×10^{-35} as an approximation for θ_1 for *cyclo*pentanone, *cyclo*hexanone, and camphor. It is now clear that only in the last-named case was the assumed magnitude seriously incorrect; even so the effect on the estimations of b_1 and $(b_2 + b_3)$ is slight.

TABLE 3. *Calculation of anisotropy terms* (θ_1) *for four cyclic ketones.*

	$10^3\,{}_{\infty}\delta_2{}^2$	${}_{\mathrm{D}}P$ (c.c.) *	${}_{\mathrm{E}}P$ (c.c.)	$10^{35}\theta_1$
*cyclo*Pentanone	31·13	24·48	22·79 †	1·31
*cyclo*Hexanone	11·60	29·26	27·25 †	0·70
*cyclo*Heptanone	27·08	33·98	31·62 †	2·22
(±)-Camphor	39·84	46·20	43·74 †	6·40

* ${}_{\mathrm{D}}P = 1{\cdot}05R_{\mathrm{D}}$. † Calc. from refractivities given by Vogel.[9] † Cf. Wetterfors.[10]

Polarisability Ellipsoids.—Information requisite for the evaluation of these is in Table 4. The semi-axes obtained are in the three right-hand columns.

TABLE 4. *Calculation of semi-axes of the molecular polarisability ellipsoids for four cyclic ketones.*

	$10^{35}(\theta_1 + \theta_2)$	$10^{23}(b_1 + b_2 + b_3)$	μ (D)	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$
*cyclo*Pentanone	35·11 *	2·694 *	3·02 *	0·99	1·03	$0{\cdot}67_5$
*cyclo*Hexanone	43·80 *	3·221 *	3·14 *	$1{\cdot}18_5$	1·12	$0{\cdot}91_5$
*cyclo*Heptanone	37·29 †	3·760 †	3·12 †		See text	
(±)-Camphor	27·36 *	5·201 *	3·09 *	1·79	2·13	$1{\cdot}28_5$

* From ref. 1. † From present measurements.

For camphor, b_1 emerges as $1{\cdot}79 \times 10^{-23}$ and $(b_2 + b_3)$ as $3{\cdot}41_5 \times 10^{-23}$, in good accord with the earlier[1] estimates (involving a speculative θ_1) of $1{\cdot}80 \times 10^{-23}$ and $3{\cdot}40 \times 10^{-23}$ c.c. respectively.

On pp. 3552 and 3556 of ref. 1 equations are given for the three semi-axes of *cyclo*pentanone and *cyclo*hexanone in terms of the polarisabilities of the corresponding hydrocarbons, of the C–H link, and of the C=O bond. Regarding the last, only approximate magnitudes of the longitudinal, transverse, and " vertical " (see p. 300 of ref. 4) polarisabilities were available in 1956. However, consequent upon the determination of ${}_{\infty}\delta_2{}^2$ for acetone by Le Fèvre and Purnachandra Rao,[2] and the re-evaluation of the molecular

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[8] Günthard and Gäumann, *Helv. Chim. Acta*, 1951, **34**, 39.

[9] Vogel, *J.*, 1938, 1323.

[10] Wetterfors, *Z. Physik*, 1922, **8**, 229.

polarisability ellipsoid for this ketone, $b_L^{C=O}$, $b_T^{C=O}$, and $b_V^{C=O}$ can now be computed as $0{\cdot}230_5$, $0{\cdot}140_5$, and $0{\cdot}046 \times 10^{-23}$ c.c. respectively. (The calculation is based on the trigonal structure of acetone reported by Allen, Bowen, Sutton, and Bastiansen.[11])

Insertion of these bond semi-axes into the equations mentioned a few lines above yields the following results:

	cyclo*Pentanone*		cyclo*Hexanone*	
	Calc.	Obs.	Calc.	Obs.
$10^{23}b_1$	0·99	0·99	1·18	$1{\cdot}11_5$
$10^{23}b_2$	0·98	1·03	1·13	1·12
$10^{23}b_3$	0·73	$0{\cdot}67_5$	0·94	$0{\cdot}91_5$

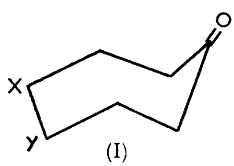
There is the possibility that the C=O group in acetone may not be electrically identical with those of the *cyclic* ketones. However, the agreement between prediction and measurement for *cyclo*hexanone indicates that any such variation cannot be large, while the greater deviation between $b_{3\text{ calc.}}$ and $b_{3\text{ obs.}}$ for *cyclo*pentanone could arise from the fact that the 5-ring is slightly less non-planar than previously calculated by Le Fèvre and Le Fèvre.[1] This matter will be considered elsewhere.

Conformation of cyclo*Heptanone.*—A 7-membered ring cannot have a regular structure. There are however in the case of *cyclo*heptanone two factors which must limit the number of possible configurations. These are (*a*) the mutual repulsions between the links attached to neighbouring carbon atoms, and (*b*) the tendency within the molecule to retain as tetrahedral the C–C–C angles.

If, therefore, one denotes as C_1 the carbon atom which is part of the C=O dipole, and as $C_2 \cdots C_7$ the remaining carbon atoms in the *cyclo*heptanone ring, it is reasonable to assume that $C_2 \cdots C_7$ with their associated bonds will lie in relation to one another as closely as is possible to those relative positions in which they lie in the " chair " form of *cyclo*hexane.

The number of possible stereoforms of *cyclo*heptanone is then given by the number of ways in which C_1 can be interpolated into a " chair " $C_2 \cdots C_7$ ring system with the minimum relative disturbance of adjacent C–H dipoles. This can be illustrated by Catalin models.

The representation commonly written (I) can be criticised because the pairs of C–H links at X and Y are not " staggered." Mirror-image forms being ignored, there appear to be two conformations derivable from (I) which satisfy the requirements (*a*) and (*b*). The first of these (*A*) is obtained by placing the C=O group at either X or Y, the second (*B*) by twisting XY anticlockwise, about a line through the mid-point of XY and the carbonyl carbon atom, and allowing consequential rotational readjustments of other carbon atoms to occur. The models so generated can be described as follows: in *A*, carbon atoms C_2, C_4, and C_6 and C_3, C_5, and C_7 lie in two parallel planes; in *B*, if carbon atoms 1, 2, and 7 define a basal plane, the heights of the remaining carbon atoms above this plane are in the order $4 < 5 < 3 \leqslant 6$.



(I)

For *A*, $\mu_{\text{resultant}}$ acts along one of the principal axes, and in the expression

$$\theta = [(\mu_1^2 - \mu_2^2)(b_1 - b_2) + (\mu_2^2 - \mu_3^2)(b_2 - b_3) + (\mu_3^2 - \mu_1^2)(b_3 - b_1)]/45k^2T^2$$

$\mu_{\text{resultant}} = \mu_1$ and $\mu_2 = \mu_3 = 0$. Accordingly, following the usual procedure, we should extract $b_1 = 1{\cdot}34_5$, $b_2 = 1{\cdot}45$, and $b_3 = 0{\cdot}97 \times 10^{-23}$ from our measurements, while the corresponding quantities computed from link polarisabilities would be 1·38, 1·32, and $1{\cdot}06_5 \times 10^{-23}$ respectively. The disagreement between the found and calculated values of b_2 and (particularly) b_3 indicate that structure *A* is incorrect. In fact, if $\mu_{\text{resultant}}$ lies along a principal axis, the smallest predictable b_3 would be $1{\cdot}01 \times 10^{-23}$, corresponding to a completely planar configuration for the molecule—an idea not seriously advanced.

For *B*, because the precise position of C_1 with reference to the C_2, C_4, C_6 and C_3, C_5, C_7 planes is not known, the magnitudes of μ_1, μ_2, and μ_3 cannot be calculated, and accordingly

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[11] Allen, Bowen, Sutton, and Bastiansen, *Trans. Faraday Soc.*, 1952, **48**, 991.

it is not possible to evaluate b_1, b_2, and b_3 from the experimental observations and to confirm by computation. The results for *cyclo*heptanone exclude a structure of type *A*, but cannot give a complete interpretation of one of type *B*. They will therefore have to be left in terms of θ_1 and θ_2 until further information concerning the molecule is forthcoming from other sources. It is perhaps relevant, and a point favouring *B*, that of structures *A* and *B* only the latter has C–H bonds on carbon atoms 3 and 6 appropriately directed for bridging by $>$NR to give the skeleton of the tropinones.

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