686. *Molecular Polarisability. The* C–C, C–O, C=O, C–Cl, C–Br, *and* C–I *Link Polarisabilities, and the Conformations of* cyclo*Pentane, of* cyclo*Hexyl Chloride, Bromide, and Iodide, and of* cyclo*Pentanone,* cyclo*Hexanone,* cyclo*Hexane-*1 : 4*-dione, Camphor, Paraldehyde, and Tetrahydrofuran.*

By (Mrs.) C. G. Le Fèvre and R. J. W. Le Fèvre.

A study of the electric double refraction of solutions of *cyclo*pentane and *cyclo*hexane, of various of their ketonic and halogeno-derivatives, and of paraldehyde, tetrahydrofuran, and (±)-camphor leads to the following conclusions: (*a*) the longitudinal and transverse polarisabilities of the C–C link are respectively $0{\cdot}097_9 \times 10^{-23}$ and $0{\cdot}027_2 \times 10^{-23}$ in *cyclo*pentane and $0{\cdot}098_6 \times 10^{-23}$ and $0{\cdot}027_4 \times 10^{-23}$ in *cyclo*hexane; corresponding values for other bonds are b_L^{C-Cl} 0·382, b_T^{C-Cl} 0·185, b_L^{C-Br} 0·530, b_T^{C-Br} 0·270, b_L^{C-I} 0·807, b_T^{C-I} 0·418, $b_L^{C=O}$ 0·236, $b_T^{C=O}$ 0·139, $b_V^{C=O}$ 0·025, b_L^{C-O} 0·081, and b_T^{C-O} 0·039 (all $\times 10^{-23}$ c.c.).

These data are applied in conformational analysis. *cyclo*Pentane appears non-planar with two carbon atoms differently out of the plane of the remaining three. The same skeleton is satisfactory for *cyclo*pentanone, the *cyclo*pentyl halides, and tetrahydrofuran. Preliminary calculations show it to be applicable to camphor. *cyclo*Hexanone has a chair structure. The halogen atoms in *cyclo*hexyl chloride, bromide, and iodide are predominantly equatorial. Solutions of *cyclo*hexane-1 : 4-dione may contain 20% of a boat form in which the CO groups are part of the basal plane of four carbon atoms. Infrared spectra confirm the absence of enolisation in the diketone.

New determinations of the polarisations at infinite dilution in carbon tetrachloride of twelve substances are listed; apparent moments, on the assumption ${}_DP = 1{\cdot}05R_D$, are also given, and compared with results in the literature.

The work recorded in this paper originated as an attempt to ascertain by experiment the polarisability ellipsoid of the C–C link. For reasons already set out [1-6] the longitudinal and the transverse polarisability (b_L^{C-C} and b_T^{C-C} respectively) of this bond cannot be reliably derived from measurements on the simpler non-polar paraffins, and the suitability of *cyclo*hexane as an alternative seemed therefore worth exploration. The project in its development involved the determination of the molar Kerr constants at infinite dilution, ${}_\infty({}_mK_2)$, of some fourteen substances, mainly halogeno- and keto-derivatives of *cyclo*pentane and *cyclo*hexane, and provided evidence on the conformations of several of these.

For brevity, neither definitions of symbols to be used nor expansions of quantities such as θ_1, θ_2, θ_3, etc., will be repeated here—they are given in full in a recent review,[2] and with less detail in refs. 1 and 3—9. Computations of molecular-polarisability ellipsoids from bond ellipsoids have also been illustrated frequently by us [1-9] and therefore need not be explained again.

The C–C *Link in* cyclo*Hexane.*—The observed ${}_\infty({}_mK_2)$ for this hydrocarbon in carbon tetrachloride is $0{\cdot}98_7 \times 10^{-12}$—a value so small that we feel justified in assuming the

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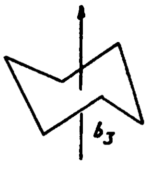
[1] Le Fèvre and Le Fèvre, *Chem. and Ind.*, 1955, 1121.
[2] *Idem, Rev. Pure Appl. Chem.*, 1955, **5**, 261.
[3] Le Fèvre, Le Fèvre, and Rao, *J.*, 1956, 708.
[4] Le Fèvre and Le Fèvre, *Chem. and Ind.*, 1955, 506.
[5] Le Fèvre, Presidential Address to Section B, A.N.Z.A.A.S., Melbourne, 1955, *Austr. J. Sci.*, 1956, **18**, 39.
[6] Le Fèvre and Le Fèvre, *J.*, 1954, 1577.
[7] *Idem, J.*, 1953, 4041.
[8] *Idem, J.*, 1955, 1641.
[9] *Idem, J.*, 1955, 2750.

absence or insignificance of a distortion term (the θ_3 of ref. 3) and in calculating the polarisability semiaxes of the molecule directly from the relations (1) and (2):

$$_{\infty}({}_{m}K_2) = 2\pi N\theta_1/9 \qquad (1)$$

$$_{\mathrm{E}}P = 4\pi N(b_1 + b_2 + b_3)/9 \qquad (2)$$

For reasons summarised by Hazebroek and Oosterhoff [10] *cyclo*hexane may be taken as existing at ordinary temperatures very largely as chair molecules (I), in which six hydrogen atoms are disposed [11] in an "equatorial" belt, and the six others alternately upwards and downwards so that their C–H bond directions are parallel to the axis running perpendicularly through the planes of carbon atoms 1, 3, and 5, or 2, 4, and 6. The symmetry of model (I) permits the simplification in equations (1) and (2) that $b_1 = b_2$; ${}_{\mathrm{E}}P$ and ${}_{\mathrm{D}}P$ are known respectively from the data of Vogel [12] and Le Fèvre and Narayana Rao; [13] semiaxes therefore follow as $b_1 = b_2 = 1{\cdot}11_7 \times 10^{-23}$ and $b_3 = 0{\cdot}97_5 \times 10^{-23}$.



(I)

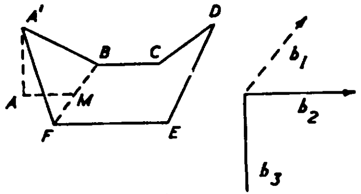
These molecular polarisabilities can be rewritten in terms of four link polarisabilities $b_{\mathrm{L}}^{\mathrm{C-C}}$, $b_{\mathrm{T}}^{\mathrm{C-C}}$, $b_{\mathrm{L}}^{\mathrm{C-H}}$, and $b_{\mathrm{T}}^{\mathrm{C-H}}$, the last two of which are known.[1] Appropriate expressions follow. In order to find out what effect a small content of boat forms (II) would have upon the magnitudes of $b_{\mathrm{L}}^{\mathrm{C-C}}$ and $b_{\mathrm{T}}^{\mathrm{C-C}}$, relations based on configuration (II) are also included.
The calculated tensor components are:

(a) *For the chair form of* cyclo*hexane*:

$$\begin{aligned} b_1 = b_2 = {} & 2b_{\mathrm{L}}^{\mathrm{C-C}} \cos^2 19^\circ\, 28' \,(2\cos^2 60^\circ + 1) + 2b_{\mathrm{T}}^{\mathrm{C-C}} (2\cos^2 30^\circ \\ & + 2\sin^2 19^\circ\, 28' \,.\, \cos^2 60^\circ + \sin^2 19^\circ\, 28') + 6b_{\mathrm{T}}^{\mathrm{C-H}} + 2b_{\mathrm{L}}^{\mathrm{C-H}} \cos^2 19^\circ\, 28' \\ & + 2b_{\mathrm{T}}^{\mathrm{C-H}} \sin^2 19^\circ\, 28' + 4b_{\mathrm{L}}^{\mathrm{C-H}} \cos^2 19^\circ\, 28' \\ & + 4b_{\mathrm{T}}^{\mathrm{C-H}} \sin^2 19^\circ\, 28' \,.\, \cos^2 60^\circ + 4b_{\mathrm{T}}^{\mathrm{C-H}} \cos^2 30^\circ \end{aligned}$$

$$\begin{aligned} b_3 = {} & 6b_{\mathrm{L}}^{\mathrm{C-C}} \sin^2 19^\circ\, 28' + 6b_{\mathrm{T}}^{\mathrm{C-C}} \cos^2 19^\circ\, 28' + 6b_{\mathrm{L}}^{\mathrm{C-H}} \\ & + 6b_{\mathrm{L}}^{\mathrm{C-H}} [\cos^2 (\pi - 109^\circ\, 28')] + 6b_{\mathrm{T}}^{\mathrm{C-H}} \sin^2 (\pi - 109^\circ\, 28') \end{aligned}$$

(b) *For the boat form of* cyclo*hexane*:



(II)

(b_1 acts along FB, b_2 along FE)

$$\begin{aligned} b_1 = {} & 2b_{\mathrm{T}}^{\mathrm{C-C}} + 4b_{\mathrm{L}}^{\mathrm{C-C}} \cos^2 A'FM + 4b_{\mathrm{T}}^{\mathrm{C-C}} \sin^2 A'FM + 4b_{\mathrm{T}}^{\mathrm{C-C}} \sin^2 A'FA \,.\, \cos^2 AFM \\ & + 4[b_{\mathrm{L}}^{\mathrm{C-H}} \sin^2 (109^\circ\, 28'/2) + b_{\mathrm{T}}^{\mathrm{C-H}} \cos^2 (109^\circ\, 28'/2)] + 8b_{\mathrm{T}}^{\mathrm{C-H}} \end{aligned}$$

$$\begin{aligned} b_2 = {} & 2b_{\mathrm{L}}^{\mathrm{C-C}} + 4b_{\mathrm{L}}^{\mathrm{C-C}} \cos^2 A'FA \,.\, \cos^2 (\pi - AFE) + 4b_{\mathrm{T}}^{\mathrm{C-C}} \sin^2 (\pi - AFE) \\ & + 4b_{\mathrm{T}}^{\mathrm{C-C}} \sin^2 A'FA \,.\, \cos^2 (\pi - AFE) + 8(b_{\mathrm{L}}^{\mathrm{C-H}} \cos^2 109^\circ\, 28' \\ & + b_{\mathrm{T}}^{\mathrm{C-H}} \sin^2 109^\circ\, 28') + 2b_{\mathrm{L}}^{\mathrm{C-H}} + 2b_{\mathrm{L}}^{\mathrm{C-H}} \cos^2 (90^\circ - 19^\circ\, 28') \\ & + 2b_{\mathrm{T}}^{\mathrm{C-H}} \sin^2 (90^\circ - 19^\circ\, 28') \end{aligned}$$

$$\begin{aligned} b_3 = {} & 2b_{\mathrm{T}}^{\mathrm{C-C}} + 4b_{\mathrm{L}}^{\mathrm{C-C}} \sin^2 A'FA + 4b_{\mathrm{T}}^{\mathrm{C-C}} \cos^2 A'FA + 4(b_{\mathrm{L}}^{\mathrm{C-H}} \cos^2 19^\circ\, 28' \\ & + b_{\mathrm{T}}^{\mathrm{C-H}} \sin^2 19^\circ\, 28') \cos^2 60^\circ + 4b_{\mathrm{T}}^{\mathrm{C-H}} \sin^2 60^\circ + 4b_{\mathrm{L}}^{\mathrm{C-H}} \cos^2 19^\circ\, 28' \\ & + 4b_{\mathrm{T}}^{\mathrm{C-H}} \sin^2 19^\circ\, 28' + 2b_{\mathrm{T}}^{\mathrm{C-H}} + 2b_{\mathrm{L}}^{\mathrm{C-H}} \cos^2 19^\circ\, 28' + 2b_{\mathrm{T}}^{\mathrm{C-H}} \sin^2 19^\circ\, 28' \end{aligned}$$

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[10] Hazebroek and Oosterhoff, *Discuss. Faraday Soc.*, 1951, **10**, 87.
[11] Hassel, *Quart. Rev.*, 1953, **7**, 221.
[12] Vogel, (*a*) *J.*, 1938, 1323; (*b*) 1948, 1809.
[13] Le Fèvre and Rao, *Austral. J. Chem.*, 1955, **8**, 39.

where A is the projection of A' in the $BCEF$ plane and M the mid-point of BF, and $\cos A'FA = 7^{\frac{1}{2}}/3$, $\cos AFE = -1/7^{\frac{1}{2}}$, and $\cos AFM = (6/7)^{\frac{1}{2}}$.

Accordingly, from (a) we obtain $b_L^{C-C} = 0{\cdot}098_6 \times 10^{-23}$ and $b_T^{C-C} = 0{\cdot}027_4 \times 10^{-23}$, yielding a b_L/b_T ratio of 3·60. Were *cyclo*hexane to contain a low proportion of " boat " forms (Hazebrock and Oosterhoff's paper indicates a possibility of a few units percent.) these figures would scarcely be altered, since from (b), for 100% "boat" forms, b_L^{C-C} and b_T^{C-C} emerge as $0{\cdot}10_9$ and $0{\cdot}02_2 \times 10^{-23}$ respectively.

The present result is thus close to that deduced by Bunn and Daubeny,[14] *viz.*, $b_L^{C-C}/b_T^{C-C} = 3{\cdot}67$, from the refractive indices and density of crystalline hexatriacontane, and differs markedly from estimates, around 90, drawn in the earlier literature from measurements on ethane (cf. refs. 1—5).

The Conformation of cyclo*Pentane.*—An examination of *cyclo*pentane yielded ${}_{\infty}({}_mK_2) = 0{\cdot}75 \times 10^{-12}$. By setting up the equations appropriate for a *flat* molecule, *viz.*:

$$b_1 = b_2 = b_L^{C-C} + 2b_L^{C-C}(\cos^2 72^\circ + \cos^2 36^\circ) + 2b_T^{C-C}(\cos^2 18^\circ + \cos^2 54^\circ) + 10b_L^{C-H}$$
$$b_3 = 5b_T^{C-C} + 10b_L^{C-H}$$

(noting that $b_L^{C-H} = b_T^{C-H} = b_V^{C-H}$), we obtained a b_L^{C-C}/b_T^{C-C} ratio of 2·52. So marked a change (from 3·60 to 2·52) in this ratio in passing from *cyclo*hexane to *cyclo*pentane seemed *a priori* unlikely. An obvious cause of the discrepancy lay in the configuration adopted: had it been taken as non-planar a larger b_L^{C-C}/b_T^{C-C} ratio would have resulted. Electron-diffraction studies of decafluoro*cyclo*pentane,[15] and spectroscopic measurements [16] and entropy considerations [17-19] with *cyclo*pentane itself, had in fact already raised the possibility that the 5-carbon ring was not flat.

Previous workers [15-19] do not uniformly propose a single structure. *E.g.*, Bastiansen, Hassel, and Lund [15] say that " we have not been able to demonstrate that the five-membered ring must necessarily be non-planar, but it seems rather probable that a deviation from a planar carbon ring is present." They suggest a form in which $C_{(1)}$ is below and $C_{(3)}$ above a plane containing $C_{(2)}$, $C_{(4)}$, and $C_{(5)}$. They remark that " A definitive solution of the problem cannot be given at present based on the electron diffraction method . . . other models may be just as probable." Tschamler and Voetter [16] speak of a slight departure from planarity with *cyclo*pentane but do not specify it. American authors [17-19] favour a C_S configuration with one carbon out of the plane of the other four but do not exclude a form C_2 similar to that discussed by Bastiansen *et al.*

The C_S model is attractive, since it is commonly assumed to occur in natural polycyclic systems (*e.g.*, chloro-, bromo-, and cyano-camphor,[20] in calciferol 4-iodo-5-nitrobenzoate,[21] in ring D of cholesteryl iodide,[22] etc.).

The situation has been assessed by Barker and Stephens [23] thus: planar structures are stabilised by forces tending to retention of tetrahedral angles but repulsions between hydrogens of neighbouring methylene groups are at a maximum in flat models. Repulsions produce torsional forces around the C–C bonds which (cf. Miller and Inskeep [24]) act to pucker the ring. Barker and Stephens consider this puckering to be small so that, with a few exceptions, (spectroscopic) selection rules for a planar ring can be followed. At the outset there was therefore no evidence enabling us to choose between the C_S and the C_2 configuration for *cyclo*pentane, although we slightly preferred the latter since it appeared to offer the better mutual accommodation for the hydrogen atoms.

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[14] Bunn and Daubeny, *Trans. Faraday Soc.*, 1954, **50**, 1173.
[15] Bastiansen, Hassel, and Lund, *Acta Chem. Scand.*, 1949, **3**, 297.
[16] Tschamler and Voetter, *Monatsh.*, 1952, **83**, 302, 835, 1228.
[17] Aston, Schumann, Fink, and Doty, *J. Amer. Chem. Soc.*, 1941, **63**, 2039.
[18] Kilpatrick, Pitzer, and Spitzer, *ibid.*, 1947, **69**, 2483.
[19] Aston, Fink, and Schumann, *ibid.*, 1943, **65**, 341.
[20] Wiebenga and Krom, *Rec. Trav. chim.*, 1946, **65**, 663.
[21] Crowfoot and Dunitz, *Nature*, 1948, **162**, 608.
[22] Carlisle and Crowfoot, *Proc. Roy. Soc.*, 1945, *A*, **184**, 64.
[23] Barker and Stephens, *J.*, 1954, 4550.
[24] Miller and Inskeep, *J. Chem. Phys.*, 1950, **18**, 1519.

A different approach was then made. The molar Kerr constants of *cyclo*pentyl chloride, bromide, and iodide, of *cyclo*pentanone, and of tetrahydrofuran were ascertained as follows :

	$10^{12}\ _{\infty}({}_mK_2)$		$10^{12}\ _{\infty}({}_mK_2)$
*cyclo*Pentyl chloride	59·3	*cyclo*Pentanone	147·6
,, bromide	96·8	Tetrahydrofuran	$-2{\cdot}4$
,, iodide	153·4		

At first glance the most significant of these results is that of tetrahydrofuran which in no circumstances could be planar and have a negative Kerr constant. In fact, if we may anticipate knowledge of the polarisabilities of the C–O link, a planar configuration should, by adopting the C–O–C angle reported by Allen and Sutton,[25] have ${}_mK$ nearly $+30 \times 10^{-12}$.

For the quantitative analysis of these data we have made three assumptions : that the b_L^{C-C}/b_T^{C-C} ratio should be the same in 5- as in 6-membered rings, that the *cyclo*pentane skeleton persists unaltered in derivatives of this hydrocarbon, and that with polar solutes θ_1 may be neglected, so that $_{\infty}({}_mK_2) \sim 2\pi N\theta_2/9$ (numerical data justifying the last approximation have been given earlier [6,9]). Then, when the molecular resultant moment μ lies along b_1 we may write :

$$\theta_2 = \mu^2(2b_1 - b_2 - b_3)/45k^2T^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

whence the quantity $(2b_1 - b_2 - b_3)$ is directly obtainable. Now if b_1', b_2', and b_3' are the polarisabilities of *cyclo*pentane such that b_1' is in the direction of $\mu_{\text{resultant}}$ in *cyclo*pentanone, *i.e.*, along *MA* in (V), then, writing b^{cp} to refer to *cyclo*pentanone, we have :

$$b_1^{\text{cp}} = b_1' + b_L^{C=O} - 2b_L^{C-H}$$
$$b_2^{\text{cp}} = b_2' + b_T^{C=O} - 2b_L^{C-H}$$
$$b_3^{\text{cp}} = b_3' + b_V^{C=O} - 2b_L^{C-H}$$

whence

$$\begin{aligned} 2b_1 - b_2 - b_3 &= 2b_1' - b_2' - b_3' + 2b_L^{C=O} - b_T^{C=O} - b_V^{C=O} \\ &= 2b_1' - b_1' - b_3' + 3b_L^{C=O} - b_{\text{Tot}}^{C=O} \end{aligned}$$

(where $b_{\text{Tot}}^{C=O}$ signifies the total of the longitudinal and two transverse polarisabilities of the C=O bond—it can be calculated from link refractivities).

Similarly for the *cyclo*pentyl halides the molecular semi-axes are :

$$b_1 = b_1' \cos^2 109^\circ\,28'/2 + b_3' \sin^2 109^\circ\,28'/2 + b_L^{C-Hal} - b_L^{C-H}$$
$$b_2 = b_2' + b_T^{C-Hal} - b_L^{C-H}$$
$$b_3 = b_3' \cos^2 109^\circ\,28'/2 + b_1' \sin^2 109^\circ\,28'/2 + b_T^{C-Hal} - b_L^{C-H}$$

Using a b_L^{C-C}/b_T^{C-C} ratio of 3·6, we next proceeded to calculate for *cyclo*pentane itself values b_1', b_2', and b_3' for its tensor ellipsoid. These, in addition to yielding the observed ${}_mK$ for *cyclo*pentane, had other requirements imposed on them : (1) They had to represent the three principal polarisabilities of a stereochemical conformation which might reasonably be expected to exist. (2) They had, when substituted into the expression for $2b_1 - b_2 - b_3$ for *cyclo*pentanone, to yield a value for this term from which $({}_mK)_{\text{calc.}}$ for the compound could be derived and found to be in accordance with $({}_mK)_{\text{expt.}}$. (3) They had, when inserted into $2b_1 - b_2 - b_3$ for *cyclo*pentyl halides, to give figures for b_L^{C-Hal} and b_T^{C-Hal} which when used in calculating ${}_mK$ for the *cyclo*hexyl halides produced results in agreement with $({}_mK)_{\text{expt.}}$. (4) They had to represent the principal polarisabilities of a stereochemical structure on which, with appropriate modifications, we could explain the negativity of ${}_mK$ for tetrahydrofuran.

As already stated, there appeared to be two possible conformations, (III*a* and *b*) in which respectively four and three carbon atoms lie in one plane. Only the second of these (III*b*), by the criterion outlined above, satisfied all our results. Its generation can be credibly viewed as follows : initially let the five carbons be disposed as in *cyclo*hexane

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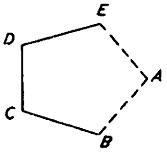
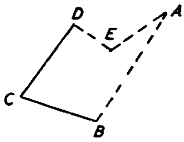
[25] Allan and Sutton, *Acta Cryst.*, 1950, **3**, 46.

(see IV), with tetrahedral angles at E, A, and B; then D and C would be separated by a distance 2 × (C–C bond length) sin (109° 28′/2), whereas in fact [18, 25] the distance is 1·54 Å. With a model it is found that this distance can be achieved by altering the angles at A, B, and E by a concertina-like movement thus retaining as much staggering as possible



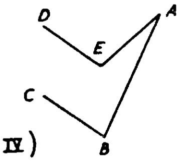
(IIIa)

Four carbons in one plane.



(IIIb)

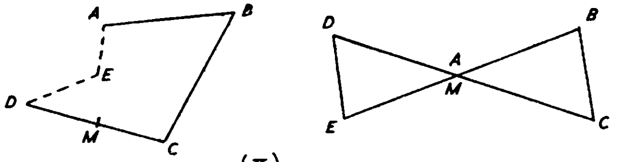
Three carbons in one plane.



(IV)

of all the adjacent C–H links; it becomes also obvious that C and D cannot both lie in the same plane as B and E.

We think that ideally the correct (single) conformation should be that which affords uniform mutual repulsion of C–H bonds; however, being unable to calculate this, *a priori*, by trial and error we have evolved the structure (V). This is applicable to all the 5-membered rings studied in this paper. With reference to (V) it is specified as follows: If X, M, and Y are the midpoints of DE, CD, and BC respectively, then A, X, M, and Y lie on one plane. The projections of B, C, D, and E on this plane are at B', C', D', and E', where $BB' = CC' = DD' = EE' = 0{\cdot}32$ Å. The angles at A, C, and D are, in order, 111°, 108°, and 108°, and the C–C distance 1·54 Å. Then AB and AE lie at an angle R to the horizontal ($AXMY$ plane), where $R = 12°\ 1'$; and CD, BC, and DE lie at an angle S to the horizontal



(V)

Conformation proposed for *cyclo*pentane.

where $S = 24°\ 36'$. Angle P is the projection of $\angle BCD$ on $B'CD'$ in the horizontal plane minus 90°, $\angle P = 35°\ 40'$; $\angle Q$ is $B'AE'/2 = 54°\ 38'$ where $B'AE'$ is the projection of $\angle BAE$ in the horizontal plane.

Appropriate expressions for the semiaxes of the polarisability ellipsoid are (b_1 along XY, b_2 along MA):

$$\begin{aligned}
b_1 = {} & b_{\mathrm{L}}^{\mathrm{C-C}} \cos^2 24°\ 36' + b_{\mathrm{T}}^{\mathrm{C-C}} \sin^2 24°\ 36' \qquad \text{(for } C\text{–}D\text{)} \\
& + 2b_{\mathrm{L}}^{\mathrm{C-C}} \cos^2 12°\ 1' \,.\, \sin^2 Q + 2b_{\mathrm{T}}^{\mathrm{C-C}} \cos^2 Q + 2b_{\mathrm{V}}^{\mathrm{C-C}} \sin^2 12°\ 1' \,.\, \sin^2 Q \\
& \qquad \text{(for } A\text{–}B \text{ and } A\text{–}E\text{)} \\
& + 2b_{\mathrm{L}}^{\mathrm{C-C}} \cos^2 24°\ 36' \,.\, \sin^2 P + 2b_{\mathrm{V}}^{\mathrm{C-C}} \sin^2 24°\ 36' \,.\, \sin^2 P + 2b_{\mathrm{T}}^{\mathrm{C-C}} \cos^2 P \\
& \qquad \text{(for } B\text{–}C \text{ and } D\text{–}E\text{)} \\
& + 10b_{\mathrm{L}}^{\mathrm{C-H}}
\end{aligned}$$

$$\begin{aligned}
b_2 = {} & b_{\mathrm{T}}^{\mathrm{C-C}} \qquad \text{(for } C\text{–}D\text{)} \\
& + 2b_{\mathrm{L}}^{\mathrm{C-C}} \cos^2 12°\ 1' \,.\, \cos^2 Q + 2b_{\mathrm{T}}^{\mathrm{C-C}} \sin^2 Q + 2b_{\mathrm{V}}^{\mathrm{C-C}} \sin^2 12°\ 1' \,.\, \cos^2 Q \\
& \qquad \text{(for } A\text{–}B \text{ and } A\text{–}E\text{)} \\
& + 2b_{\mathrm{L}}^{\mathrm{C-C}} \cos^2 24°\ 36' \,.\, \cos^2 P + 2b_{\mathrm{V}}^{\mathrm{C-C}} \sin^2 24°\ 36' \,.\, \cos^2 P + 2b_{\mathrm{T}}^{\mathrm{C-C}} \sin^2 P \\
& \qquad \text{(for } B\text{–}C \text{ and } D\text{–}E\text{)} \\
& + 10b_{\mathrm{L}}^{\mathrm{C-H}}
\end{aligned}$$

$$\begin{aligned}
b_3 = {} & 2b_{\mathrm{L}}^{\mathrm{C-C}} \sin^2 12°\ 1' + 2b_{\mathrm{V}}^{\mathrm{C-C}} \cos^2 12°\ 1' \qquad \text{(for } A\text{–}B \text{ and } A\text{–}E\text{)} \\
& + 2b_{\mathrm{L}}^{\mathrm{C-C}} \sin^2 24°\ 36' + 2b_{\mathrm{T}}^{\mathrm{C-C}} \cos^2 24°\ 36' \qquad \text{(for } B\text{–}C \text{ and } D\text{–}E\text{)} \\
& + b_{\mathrm{L}}^{\mathrm{C-C}} \sin^2 24°\ 36' + b_{\mathrm{T}}^{\mathrm{C-C}} \cos^2 24°\ 36' \qquad \text{(for } C\text{–}D\text{)} \\
& + 10b_{\mathrm{L}}^{\mathrm{C-H}}
\end{aligned}$$

From refractivity data, $b_{\mathrm{Tot}}^{\mathrm{C-C}}$ appears as $0{\cdot}153_3$ and $0{\cdot}152_3 \times 10^{-23}$ respectively in *cyclo*hexane and *cyclo*pentane. Accordingly, with a $b_{\mathrm{L}}^{\mathrm{C-C}}/b_{\mathrm{T}}^{\mathrm{C-C}}$ ratio of 3·60, $b_{\mathrm{T}}^{\mathrm{C-C}} = 0{\cdot}097_9 \times 10^{-23}$ and $b_{\mathrm{T}}^{\mathrm{C-C}} = 0{\cdot}027_2 \times 10^{-23}$ for the C–C bond in 5-membered rings. Therefore, for *cyclo*pentane we have :

$$10^{23}b_1 = 0{\cdot}962,\ 10^{23}b_2 = 0{\cdot}891,\ 10^{23}b_3 = 0{\cdot}814,$$
$$10^{35}\theta_1 = 0{\cdot}178, \text{ and } {}_{\infty}({}_mK)_{\mathrm{calc.}} = 0{\cdot}74_9 \times 10^{-12}.$$

The last figure compares well with ${}_{\infty}({}_mK)_{\mathrm{expt.}} = 0{\cdot}75 \times 10^{-12}$.

Verification of Proposed cyclo*Pentane Structure.*—The argument concerning *cyclo*pentanone will be set out first. For acetone, according to Allen and Sutton's list,[25] the C–C–O angle is 123°; using b^{ac} to refer to acetone, we may write :

$$b_1^{\mathrm{ac}} = b_{\mathrm{L}}^{\mathrm{C=O}} + 2b_{\mathrm{L}}^{\mathrm{C-C}}\cos^2 57° + 2b_{\mathrm{T}}^{\mathrm{C-C}}\sin^2 57° + 6b_{\mathrm{L}}^{\mathrm{C-H}}$$
$$b_2^{\mathrm{ac}} = b_{\mathrm{T}}^{\mathrm{C=O}} + 2b_{\mathrm{L}}^{\mathrm{C-C}}\sin^2 57° + 2b_{\mathrm{T}}^{\mathrm{C-C}}\cos^2 57° + 6b_{\mathrm{L}}^{\mathrm{C-H}}$$
$$b_3^{\mathrm{ac}} = b_{\mathrm{V}}^{\mathrm{C=O}} + 2b_{\mathrm{T}}^{\mathrm{C-C}} + 6b_{\mathrm{L}}^{\mathrm{C-H}}$$

We [7] found ${}_{\infty}({}_mK_2)^{\mathrm{ac}}$ to be 101×10^{-12}, whence $\theta_1 + \theta_2 = 24{\cdot}0 \times 10^{-35}$. As a near approximation let $\theta_1 = 1 \times 10^{-35}$, then $\theta_2 = 2{\cdot}3 \times 10^{-34}$. By use of equation (3), and with $b_{\mathrm{Tot}}^{\mathrm{C=O}}$ in acetone $= 0{\cdot}394 \times 10^{-23}$, $b_{\mathrm{L}}^{\mathrm{C=O}}$ emerges as $0{\cdot}230 \times 10^{-23}$. If now in the expressions giving b_1, b_2, and b_3 for *cyclo*pentanone, as set out above, we write the values previously calculated for b_1, b_2, and b_3 of *cyclo*pentane, and adopt $b_{\mathrm{L}}^{\mathrm{C=O}} = 0{\cdot}230 \times 10^{-12}$, then θ_2^{cp} may be computed as $33{\cdot}8 \times 10^{-35}$, which is in good agreement with $(\theta_1 + \theta_2)_{\mathrm{expt.}} = 35{\cdot}11 \times 10^{-35}$; or, if we transform to molar Kerr constants and assume $\theta_1^{\mathrm{cp}} = 1 \times 10^{-35}$, we have $({}_mK)_{\mathrm{calc.}} = 146{\cdot}3 \times 10^{-12}$ against $({}_mK)_{\mathrm{expt.}} = 147{\cdot}6 \times 10^{-12}$.

No precise stereostructure for *cyclo*pentanone seems to have been given before. Erlandsson,[26] from the micro-wave spectrum of this ketone, recently concluded that the carbon ring is non-planar.

Another test involves *cyclo*pentyl chloride, bromide, and iodide. From the measured ${}_{\infty}({}_mK_2)$'s and moments of these substances, by neglecting θ_1 because the μ's involved are not small, and by using equation (3) we obtained $2b_1 - b_2 - b_3$, whence, using configuration (V), $b_{\mathrm{L}}^{\mathrm{C-Hal}}$ and $b_{\mathrm{T}}^{\mathrm{C-Hal}}$ were deduced as follows :

	C–Cl	C–Br	C–I
$10^{23}b_{\mathrm{L}}$	0·382	0·530	0·807
$10^{23}b_{\mathrm{T}}$	0·185	0·270	0·418

We assumed that the last quantities were likely to be the same in 5- as in 6-membered rings. By insertion in the expression for b_1, b_2, and b_3 for the " equatorial " and the " axial " conformations of each of the *cyclo*hexyl halides, θ_1 and θ_2 and hence the ${}_mK$'s were computed.

The relations applicable are (where b^{ch} refer to *cyclo*hexanone) :

For the " equatorial " halides :

$$b_1 = b_{\mathrm{L}}^{\mathrm{C-Hal}} + b_1^{\mathrm{ch}}\cos^2 19°\,28' + b_3^{\mathrm{ch}}\sin^2 19°\,28' - b_{\mathrm{L}}^{\mathrm{C-H}}$$
$$b_2 = b_{\mathrm{T}}^{\mathrm{C-Hal}} + b_2^{\mathrm{ch}} - b_{\mathrm{L}}^{\mathrm{C-H}}$$
$$b_3 = b_{\mathrm{T}}^{\mathrm{C-Hal}} + b_3^{\mathrm{ch}}\cos^2 19°\,28' + b_1^{\mathrm{ch}}\sin^2 19°\,28' - b_{\mathrm{L}}^{\mathrm{C-H}}$$

For the " axial " halides :

$$b_1 = b_{\mathrm{L}}^{\mathrm{C-Hal}} + b_3^{\mathrm{ch}} - b_{\mathrm{L}}^{\mathrm{C-H}}$$
$$b_2 = b_3 = b_{\mathrm{L}}^{\mathrm{C-Hal}} + b_1^{\mathrm{ch}} - b_{\mathrm{L}}^{\mathrm{C-H}}$$

The results expressed as molar Kerr constants are :

*cyclo*Hexyl halide	$10^{12}\ {}_mk_{\mathrm{calc.}}$ Equatorial confn.	$10^{12}\ {}_mK_{\mathrm{calc.}}$ Axial confn.	$10^{12}\ {}_mK_{\mathrm{expt.}}$
Chloride	130	42	122
Bromide	179	82	181
Iodide	246	152	249

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[26] Erlandsson, *J. Chem. Phys.*, 1954, **22**, 563.

The equatorial conformations of these halides are thus unambiguously indicated. Such would not be the case had the molecular ellipsoid for *cyclo*pentane been seriously in error. The conclusion is in harmony with other work reviewed by Hassel.[11]

The Conformation of Tetrahydrofuran.—It next became of interest to know whether the model for *cyclo*pentane was applicable to other 5-membered ring molecules. Tetrahydrofuran was therefore considered, the following dimensions (Allen and Sutton [25]) being used: C–O distance 1·43 Å; C–C distance 1·54 Å; angle C–O–C 111° ± 2°. On the basis of form (V) let the oxygen atom lie at position A and the carbon atoms be at B, C, D, and E; take the mid-points of DE, CD, and BC respectively as X, M, and Y, and regard the $AXMY$ plane as horizontal, and denote the projections of B, C, D, and E on to this plane as B', C', D', and E' where $BB' = CC' = DD' = 0{\cdot}32$ Å. The angles at A, C, and D are 111° ± 2° while those corresponding to R, S, P, and Q in *cyclo*pentane emerge, in order, as 12° 57′, 24° 36′, 43° 2′, and 55°. Then, putting b_1 along the direction of $\mu_{\text{resultant}}$, *i.e.*, along MA, and b_2 along XY, we have (writing b^{tf} to refer to tetrahydrofuran):

$$\begin{aligned}
b_1^{\text{tf}} = {} & b_{\text{T}}^{\text{C–C}} \qquad \text{(for } C\text{–}D\text{)} \\
& + 2b_{\text{L}}^{\text{C–O}} \cos^2 12^\circ\, 57' \,.\, \cos^2 Q + 2b_{\text{T}}^{\text{C–O}} \sin^2 Q + 2b_{\text{T}}^{\text{C–O}} \sin 12^\circ\, 57' \,.\, \cos^2 Q \\
& \qquad \text{(for } A\text{–}B \text{ and } A\text{–}E\text{)} \\
& + 2b_{\text{L}}^{\text{C–C}} \cos^2 24^\circ\, 36' \,.\, \cos^2 P + 2b_{\text{T}}^{\text{C–C}} \sin^2 24^\circ\, 36' \,.\, \cos^2 P + 2b_{\text{T}}^{\text{C–C}} \sin^2 P \\
& \qquad \text{(for } B\text{–}C \text{ and } D\text{–}E\text{)} \\
& + 8b_{\text{L}}^{\text{C–H}}
\end{aligned}$$

$$\begin{aligned}
b_2^{\text{tf}} = {} & b_{\text{L}}^{\text{C–C}} \cos^2 24^\circ\, 36' + b_{\text{T}}^{\text{C–C}} \sin^2 24^\circ\, 36' \qquad \text{(for } C\text{–}D\text{)} \\
& + 2b_{\text{L}}^{\text{C–O}} \cos^2 12^\circ\, 57' \,.\, \sin^2 Q + 2b_{\text{T}}^{\text{C–O}} \cos^2 Q + 2b_{\text{T}}^{\text{C–O}} \sin^2 12^\circ\, 57' \,.\, \sin^2 Q \\
& \qquad \text{(for } A\text{–}B \text{ and } A\text{–}E\text{)} \\
& + 2b_{\text{L}}^{\text{C–C}} \cos^2 24^\circ\, 36' \,.\, \sin^2 P + 2b_{\text{T}}^{\text{C–C}} \sin^2 24^\circ\, 36' \,.\, \sin^2 P + 2b_{\text{T}}^{\text{C–C}} \cos^2 P \\
& \qquad \text{(for } B\text{–}C \text{ and } C\text{–}E\text{)} \\
& + 8b_{\text{L}}^{\text{C–H}}
\end{aligned}$$

$$\begin{aligned}
b_3^{\text{tf}} = {} & 2b_{\text{L}}^{\text{C–O}} \sin^2 12^\circ\, 57' + 2b_{\text{T}}^{\text{C–O}} \cos^2 12^\circ\, 57' \qquad \text{(for } A\text{–}B \text{ and } A\text{–}E\text{)} \\
& + 2b_{\text{L}}^{\text{C–C}} \sin^2 24^\circ\, 36' + 2b_{\text{T}}^{\text{C–C}} \cos^2 24^\circ\, 36' \qquad \text{(for } B\text{–}C \text{ and } D\text{–}E\text{)} \\
& + b_{\text{L}}^{\text{C–C}} \sin^2 24^\circ\, 36' + b_{\text{T}}^{\text{C–C}} \cos^2 24^\circ\, 36' \qquad \text{(for } C\text{–}D\text{)} \\
& + 8b_{\text{L}}^{\text{C–H}}
\end{aligned}$$

Adopting the same $b_{\text{L}}^{\text{C–C}}$ and $b_{\text{T}}^{\text{C–C}}$ values as for *cyclo*pentane, and using a $b_{\text{L}}^{\text{C–O}}/b_{\text{T}}^{\text{C–O}}$ ratio of 2·08 (derived from ${}_mK$ for paraldehyde as discussed below), together with $\mu_{\text{expt.}} = 1{\cdot}81$ D, yields:

$$10^{23}b_1 = 0{\cdot}759, \qquad 10^{23}b_2 = 0{\cdot}836, \qquad 10^{23}b_3 = 0{\cdot}706$$

whence

$$\theta_1 + \theta_2 = -0{\cdot}54 \times 10^{-35}$$

and ${}_mK_{\text{calc.}} = -2{\cdot}27 \times 10^{-12}$, compared with ${}_\infty({}_mK_2)_{\text{expt.}} = -2{\cdot}4 \times 10^{-12}$.

Agreement between prediction and measurement is satisfactory. It may be remarked that the alternative model, analogous to the C_S form of *cyclo*pentane, requires for a negative Kerr constant a considerable interplanar angle; although such folding may be forced in rigid polycyclic molecules, *e.g.*, cantharidin, it is quite credible that it cannot be held in single, and therefore more flexible, ring systems. It is relevant that Tschamler and Voetter,[16] from Raman and infrared spectral data, could only conclude that tetrahydrofuran had pseudo-symmetry $\text{D}_{5\text{h}}$, *i.e.*, that the ring was not completely flat (a similarly qualitative opinion had been reported by Beach [27] in 1941); on the other hand, tetrahydrothiophen was recognised [16] as probably having symmetry C_2, *i.e.*, symmetry of the type here allotted to tetrahydrofuran.

Derivation of $b_{\text{L}}^{\text{C–O}}$ *and* $b_{\text{T}}^{\text{C–O}}$.—In paraldehyde it is considered that the three methyl

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[27] Beach, quoted as " private communication " by Aston *et al.*, *J. Amer. Chem. Soc.*, **1941**, **63**, 2030.

groups are disposed equatorially.[28-33] Allen and Sutton [25] list C–O and C–C separations of 1·43 and 1·54 Å. The molecular skeleton, by analogy with trioxan,[34, 35] and by relationship with dioxan,[36, 37] is a "staggered" or chair structure. On these premises, putting b_1 in the direction of $\mu_{\text{resultant}}$, we may write:

$$b_1 = 6b_L^{C-O}\sin^2 19^\circ\,28' + 6b_T^{C-O}\cos^2 19^\circ\,28' + 3b_L^{C-H} + 3[b_L^{C-C}\cos^2(90 - 19^\circ\,28')] + 3b_T^{C-C}\cos^2 19^\circ\,28' + 9b_L^{C-H}$$

and $$b_2 = b_3 = 2b_L^{C-O}\cos^2 19^\circ\,28' . (2\cos^2 60^\circ + 1) + 2b_T^{C-O}(2\cos^2 30^\circ + 2\sin^2 19^\circ\,28' . \cos^2 60^\circ + \sin^2 19^\circ\,28') + 12b_L^{C-H} + b_L^{C-C}\cos^2 19^\circ\,28' + b_T^{C-C}\sin^2 19^\circ\,28' + 2(b_L^{C-C}\cos^2 19^\circ\,28' . \cos 60^\circ + b_T^{C-C}\sin 19^\circ\,28' . \cos 60^\circ + b_T^{C-C}\cos 30^\circ)$$

In carbon tetrachloride, $_\infty(_mK_2)$ for paraldehyde is now found to be $-57·0 \times 10^{-12}$, whence, with $_EP = 31·70$ c.c. and $\mu = 1·98$ D, $10^{23}b_1 = 1·162$ and $10^{23}b_2 = 10^{23}b_3 = 1·292$. Solution of the above equations then gives:

$$10^{23}b_L^{C-O} = 0·081,\ 10^{23}b_T^{C-O} = 0·039, \text{ and } b_L^{C-O}/b_T^{C-O} = 2·08$$

In these calculations we have assumed the "chair" angles to be tetrahedral. Small deviations from this value do not appreciably affect the b_L^{C-O}/b_T^{C-O} ratio. Further, if expressions for b_1, b_2, and b_3 be set up for a paraldehyde structure in which the methyl groups are axially disposed, then computation along the lines just set out produces a b_L^{C-O}/b_T^{C-O} ratio of approximately 1 : 2. Such a result, which is highly unlikely, can be regarded as further evidence for the equatorial disposition of the three methyl groups.

Conformation of cyclo*Hexanone.*—Results already mentioned in this paper allow *a priori* calculations to be made of $_\infty(_mK_2)$ for *cyclo*hexanone in its boat and chair conformations; $b_L^{C=O} = 0·230 \times 10^{-23}$ is derived from acetone. We have for the chair form:

$$b_1^{ch} = b_1^{ch}\sin^2(109^\circ\,28'/2) + b_3^{ch}\cos^2(109^\circ\,28'/2) + b_L^{C=O} - 2b_L^{C-H}$$
$$b_2^{ch} = b_2^{ch} + b_T^{C=O} - 2b_L^{C-H}$$
$$b_3^{ch} = b_3^{ch}\sin^2(109^\circ\,28'/2) + b_1^{ch}\cos^2(109^\circ\,28'/2) + b_V^{C=O} - 2b_L^{C-H}$$

and for the boat form:

$$b_1^{ch} = b_L^{C=O} + b_2^{ch}\cos^2(109^\circ\,28'/2) + b_3^{ch}\sin^2(109^\circ\,28'/2) - 2b_L^{C-H}$$
$$b_2^{ch} = b_T^{C=O} + b_1^{ch} - 2b_L^{C-H}$$
$$b_3^{ch} = b_V^{C=O} + b_2^{ch}\sin^2(109^\circ\,28'/2) + b_3^{ch}\cos^2(109^\circ\,28'/2) - 2b_L^{C-H}]$$

From these equations we deduce molar Kerr constants for the two forms as follow:

$$\text{Chair, } {}_mK_{\text{calc.}} = 178 \times 10^{-12} \qquad \text{Boat, } {}_mK_{\text{calc.}} = 54 \times 10^{-12}$$

The observed $_\infty(_mK_2)$ being 183×10^{-12}, we conclude that *cyclo*hexanone under our conditions exists in the chair form.

Conformation of cyclo*Hexane*-1 : 4-*dione.*—This substance has been studied in benzene, because of its sparing solubility in carbon tetrachloride; its $_\infty(_mK_2)$ is $-41·2 \times 10^{-12}$.

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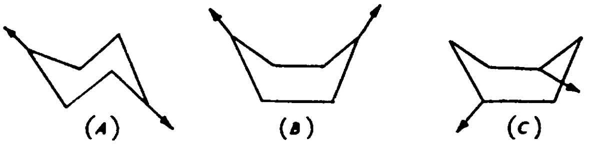
[28] Ackerman and Mayer, *J. Chem. Phys.*, 1936, **4**, 377.
[29] Brockway and Carpenter, *J. Amer. Chem. Soc.*, 1936, **58**, 1270.
[30] Gerding *et al.*, *Rec. Trav. chim.*, 1939, **58**, 604, 614; 1941, **60**, 258.
[31] Calderbank and Le Fèvre, *J.*, 1949, 199.
[32] Le Fèvre, Mulley, and Smythe, *J.*, 1950, 290.
[33] Saksena, *Proc. Indian Acad. Sci.*, 1940, **12**, *A*, 321.
[34] Moerman, *Rec. Trav. chim.*, 1937, **56**, 161.
[35] Moerman and Wiebenga, *Z. Krist.*, 1937, **97**, 323.
[36] Hassel and Viervoll, *Acta Chem. Scand.*, 1947, **1**, 149.
[37] Brockway and Sutton, *J. Amer. Chem. Soc.*, 1935, **57**, 473.

Older evidence [38] for non-enolisation has now been supplemented by infrared spectral data (see Experimental section) which confirm this conclusion. In the absence of enol forms, negativity of ${}_mK$ must be due to the presence of one or more boat conformations.

Accordingly we set up the expressions for b_1, b_2, and b_3, of the three possible configurations indicated in (VI).


(*A*) (*B*) (*C*)

(VI)

For the chair form *A* we have:

$$b_1 = 2b_L^{C=O} + b_1^{ch}\sin^2(109^\circ\,28'/2) + b_3^{ch}\cos^2(109^\circ\,28'/2) - 4b_L^{C-H}$$
$$b_2 = 2b_T^{C=O} + b_1^{ch} - 4b_L^{C-H}$$
$$b_3 = 2b_V^{C=O} + b_1^{ch}\cos^2(109^\circ\,28'/2) + b_3^{ch}\sin^2(109^\circ\,28'/2) - 4b_L^{C-H}$$

For the boat form *B* we have :

$$b_1 = b_3^{ch} - 4b_L^{C-H} + 2b_L^{C=O}\sin^2(109^\circ\,28'/2) + 2b_V^{C=O}\cos^2(109^\circ\,28'/2)$$
$$b_2 = b_2^{ch} - 4b_L^{C-H} + 2b_L^{C=O}\cos^2(109^\circ\,28'/2) + 2b_V^{C=O}\sin^2(109^\circ\,28'/2)$$
$$b_3 = b_1^{ch} - 4b_L^{C-H} + 2b_T^{C=O}$$

(In this computation and those following, polarisabilities written as b_1^{ch}, b_2^{ch}, and b_3^{ch} are those appropriate for the boat conformation.) For the boat form *C* we must first refer to (VII). Let *ABCDEF* be the skeleton structure of this form ($AB = l$); the C=O links at *C* and *F* lie in the *ABCD* and the *ADEF* plane respectively. *A'* lies on *AD* and is the projection of *A* perpendicular to *BF*. Then $AFA' = 19^\circ\,28'$. Because μ at *F* bisects the angle *AFE*, $\angle A'FK = 109^\circ\,28'/2 - 19^\circ\,28'$; therefore μ at *F* makes an angle $109^\circ\,28'/2$ with *DA*; $FA' = l\cos 19^\circ\,28'$, and $FA'' = l\sin 109^\circ\,28'/2$ (where *A''* is the projection of *A'* on to *BF*); then $\angle FA'A'' = 60^\circ$, and $\angle FA'B = 120^\circ$.

Accordingly, taking b_1 along $\mu_{\text{resultant}}$ we have :

$$b_1 = b_3^{ch} + 2b_L^{C=O}\sin^2 109^\circ\,28' \,.\, \cos^2 60^\circ + 2b_V^{C=O}\sin^2 60^\circ + 2b_T^{C=O}\cos^2(109^\circ\,28'/2)\cos^2 60^\circ - 4b_L^{C-H}$$
$$b_2 = 2b_L^{C=O}\cos^2(90^\circ - \phi) + 2b_V^{C=O}\sin^2(90^\circ - \phi) + b_1^{ch}\cos^2\omega + b_2^{ch}\sin^2\omega - 4b_L^{C-H}$$

where $\cos^2\omega = \cos^2(109^\circ\,28'/2)\cos^2(90^\circ - \phi)$,

and $\cos\phi = \sin(109^\circ\,28'/2)\,.\,\cos 60^\circ = 65^\circ\,54'$

$$b_3 = 2b_T^{C=O} + b_1^{ch}\sin^2\omega + b_2^{ch}\cos^2\omega - 4b_L^{C-H}$$

Resultant moments are calculated for models (*A*), (*B*), and (*C*) by using $\mu^{C=O} = 3{\cdot}14$ D (as in *cyclo*hexanone). In order to avoid an accumulated error in $b_L^{C=O}$, we redetermined this value directly from ${}_mK$ for *cyclo*hexanone, following the procedure previously discussed for obtaining b_L^{C-Hal} and b_T^{C-Hal} from *cyclo*pentyl halides. We thus found $b_L^{C=O} = 0{\cdot}236 \times 10^{-23}$ and $b_V^{C=O} + b_T^{C=O} = 0{\cdot}164 \times 10^{-23}$. Substituting for $b_L^{C=O}$ in the expanded $\theta_1 + \theta_2$ term gives $b_V^{C=O} = 0{\cdot}025 \times 10^{-23}$ and $b_T^{C=O} = 0{\cdot}139 \times 10^{-23}$. These values and $\mu_{\text{resultant}}$ for (*B*) and (*C*) can only be regarded as near estimates because of their mode of derivation.

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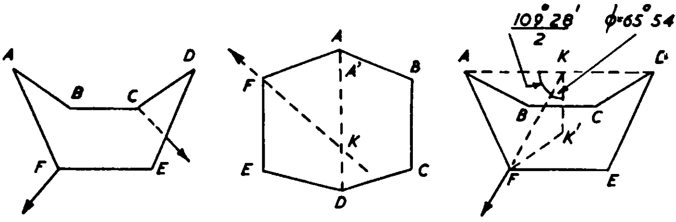
[38] Le Fèvre and Le Fèvre, *J.*, 1935, 1696.

Our final calculations in comparison with experiment are:

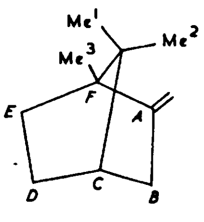
Configuration	$10^{12}\ ({}_mK)_{\text{calc.}}$	$10^{12}\ ({}_mK)_{\text{expt.}}$
(*A*)	7·6	−41·2
(*B*)	16·8	
(*C*)	−233	

The results are in conformity with a 20% mixture of (*C*) and 80% of (*A*). Incidentally, the observed dipole moment, 1·2 D, can reasonably be shown to correspond with 21% of (*C*) and 79% of (*A*). Such excellent agreement between two different methods we regard as fortuitous.

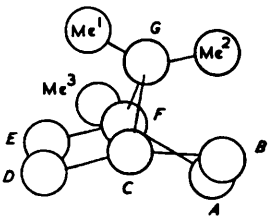
It is interesting that in conformation (*C*) the two C=O dipoles are situated in those positions that allow maximum staggering of the adjacent C–H bonds in the molecule. Conformation (*B*) does not permit this. Our conclusions thus support ideas that in saturated cyclic hydrocarbons mutual repulsions between C–H links are the dominant factors determining configuration. Although form (*C*) is not that discussed[38] by us in 1935, the fact remains that *cyclo*hexane-1 : 4-dione is still the only example of a monocyclic *cyclo*hexane derivative whose existence in a boat conformation has been detected by experiment (cf. Hassel[11]).



(VII)



(VIII)



(IX)

Conformation of Camphor.—Bredt's classical formula for this ketone, (VIII), contains two fused non-planar 5-rings. It is therefore of interest to explore the applicability of our *cyclo*pentane conformation to such a case.

${}_\infty({}_mK_2)$ of (±)-camphor is 115×10^{-12}. Let θ_1 be approx. 1×10^{-35}, then $\theta_2 = 2{\cdot}64 \times 10^{-34}$; and since $\mu = 3{\cdot}1_1$ D, $2b_1 - b_2 - b_3 = 0{\cdot}208 \times 10^{-23}$. Because $b_1 + b_2 + b_3 = 5{\cdot}201 \times 10^{-23}$ (from refractivity), b_1 emerges as $1{\cdot}80_3 \times 10^{-23}$ and $(b_2 + b_3)$ as $3{\cdot}39_8 \times 10^{-23}$. Since b_1 lies along $\mu_{\text{resultant}}$ we can write (using b^{cam} to refer to camphor, and b^{sk} to refer to the carbon skeleton):

$$b_1^{\text{cam}} = b_1^{\text{sk}} + \tfrac{16}{3} b_{\text{Tot}}^{\text{C–H}} + b_{\text{L}}^{\text{C=O}}$$

$$(b_2 + b_3)^{\text{cam}} = (b_2 + b_3)^{\text{sk}} + \tfrac{32}{3} b_{\text{Tot}}^{\text{C–H}} + b_{\text{T}}^{\text{C=O}} + b_{\text{V}}^{\text{C=O}}$$

If we adopt $b_{\text{L}}^{\text{C=O}} = 0{\cdot}230 \times 10^{-23}$, as in *cyclo*pentanone, and $b_{\text{Tot}}^{\text{C=O}} = 0{\cdot}432 \times 10^{-23}$ (obtained from $b_1 + b_2 + b_3$ for camphor, *viz.*, $5{\cdot}201 \times 10^{-23}$. This, equals $8b_{\text{Tot}}^{\text{C–C}}$, as in 5-membered rings, plus $3b_{\text{Tot}}^{\text{C–C}}$ as in propane, plus $16b_{\text{Tot}}^{\text{C–H}}$, plus $b_{\text{Tot}}^{\text{C=O}}$) then $b_1^{\text{sk}} = 1{\cdot}57_3 \times 10^{-23}$ and $(b_2 + b_3)^{\text{sk}} = 3{\cdot}19_6 \times 10^{-23}$.

We shall now attempt, so far as available data make possible, to compute the ellipsoid of the skeleton. In Model (IX) let the C=O dipole act at *A*, the *gem.*-dimethyl group lie at *G*, and the other methyl group at *F*. Let *M*, *X*, *Y*, and *Z* be the mid-points of *CG*, *BC*, *GF*, and *EF*. In the five-membered ring *ABCGF* b_1' and b_2' lie along *MA* and *XY* respectively, and for the ring *CDEFG* b_1'' and b_2'' lie along *DY* and *ZM* respectively. Carbon atoms *B* and *E* must of necessity be situated in space above what in (VIII) would be the *ABDE* plane. The effect of this on the 6-membered ring *ABCDEF* is to permit staggering of adjacent C–H links at *D* and *E*—an advantage not associated with (VIII). Information concerning the C–C–C angles at *G* and *F* is not available : we assume them to be tetrahedral. From a model it is seen that *DY*, and *AM* and *XY* and *ZM* are roughly perpendicular to one another. We may therefore regard the carbon atoms *A*—*G* as comprising two 5-membered rings *ABCGF* and *CDEFG*, where b_1' is perpendicular to b_1'', so that, if in computing the molecular polarisability of the skeleton we, in effect, superimpose b_1'', b_2'', b_3'' appropriately on b_1', b_2', and b_3', we obtain a nearly isotropic whole. However, in so doing, we have used the *FG* and the *GC* link twice, and have not taken into consideration the bonds *F*–Me³, *G*–Me¹, and *G*–Me². The contributions of *G*–Me¹ and *G*–Me² compensate for the double use of *FG* and *GC*, and accordingly, as a near estimate, it seems that it is only the anisotropy of polarisability of the C–C link *F*–Me³ which could result in the camphor skeleton's becoming non-isotropic; in other words, we conclude that approximately $b_1^{\text{sk}} = b_2^{\text{sk}} = b_3^{\text{sk}}$, or $2b_1^{\text{sk}} \sim (b_2 + b_3)^{\text{sk}}$. This is in agreement with the values $2b_1^{\text{sk}} = 3{\cdot}14_6 \times 10^{-23}$ and $(b_2 + b_3)^{\text{sk}} = 3{\cdot}19_6 \times 10^{-23}$ obtained from our experimental ${}_{\infty}({}_mK_2)$ for camphor.

EXPERIMENTAL

Materials.—The solutes were redistilled or recrystallised, as necessary, before use and had the b. p.s or m. p.s recorded for pure samples in Beilstein's " Handbuch." The authors thank Mr. D. G. Pettit for preparing *cyclo*hexane-1 : 4-dione. Solvents were purified as noted in ref. 6.

Infrared Spectrum of cyclo*Hexane*-1 : 4-*dione.*—This was kindly recorded, for a Nujol mull down to 650 cm.⁻¹ and for a solution (w_2 = 0·0533) in benzene down to 1250 cm.⁻¹, by Mr. R. L. Werner (N.S.W. University of Technology). Absorption frequencies in cm.⁻¹ noted (other than those due to Nujol or benzene) were :

For the mull : 1710 (s and broad), 1404 (w), 1342 (w), 1325 (w), 1310 (m), 1295 (w), 1260 (vw), 1200 (vw), 1167 (w), 1142 (m), 1086 (w), 1062 (w), 964 (m), 925 (m), 872 (w), 803 (s);

For the solution : 1727 (s), 1417 (m), 1394 (w), 1330 (w shoulder), 1306 (m), 1290 (w, shoulder), 1258 (m).

(s = strong, m = medium, w = weak, v = very.)

The majority of these bands can be assigned straightforwardly to various C–H and skeletal motions. We follow Ramsay and Sutherland [39] in attributing the feature at 803 cm.⁻¹ to C–C stretching (802 cm.⁻¹ in the Raman spectrum of liquid *cyclo*hexane [39]). Absorptions at 1404 (mull) or 1417 cm.⁻¹ (solution) recall the observation by Francis [40] that CH_2 groups adjacent to carbonyl display deformational frequencies *ca.* 1410 cm.⁻¹, *i.e.*, lower than the " normal " 1453 cm.⁻¹ found in, *e.g.*, *cyclo*hexane. For our purposes, however, the important point is that no sign was detected of OH absorption in the 3400—3600 cm.⁻¹ region. Apart from the C–H bands, the spectra of both Nujol and benzene were unaffected by the dione down to the point where $\nu_{\text{C=O}}$ became apparent.

TABLE 1. *Solvent constants.*

Temp.	10^7B_D	n_D	d_4^t	ε_1	H	J	$10^{14}\,{}_sK_1$
			Carbon tetrachloride				
20°	0·072	1·4604	1·5940	2·2360	2·064	0·4721	0·761
25	0·070	1·4575	1·5845	2·2270	2·060	0·4731	0·749
			Benzene				
25	0·410	1·4973	0·8738	2·2725	2·114	0·4681	7·56

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[39] Ramsay and Sutherland, *Proc. Roy. Soc.*, 1947, *A*, 190, 245.

[40] Francis, *J. Chem. Phys.*, 1951, **19**, 942.

TABLE 2. *Weight fractions, Kerr constants, refractive indexes, and dielectric constants of solutions at 25°.*

*cyclo*Hexane in carbon tetrachloride

10^5w_2	$10^7\Delta B$	n_D	d	ε
1574	$-0{\cdot}000_5$	1·4567	1·55992	—
2618	—	1·4556	1·54280	—
3083	−0·001	—	1·53426	2·2188
3202	−0·001	1·4553	—	2·2185
4596	—	1·4546	—	2·2134
5343	−0·002	—	—	—
7036	−0·003	—	1·47413	2·1956
12,239	−0·005	—	—	—

whence $10^7\Delta B = -0{\cdot}0349w^2 - 0{\cdot}053w_2^2$
$\Sigma\Delta n/\Sigma w_2 = -0{\cdot}065_1$
$\Sigma\Delta d/\Sigma w_2 = 1{\cdot}586_5$
$\Sigma\Delta\varepsilon/\Sigma w_2 = -0{\cdot}034_4$

*cyclo*Hexyl bromide in carbon tetrachloride

1646	0·168	—	—	—
2170	0·229	—	—	—
2189	0·249	1·4586	1·5782	2·3651
2567	0·274	1·4590	1·5770	2·3858
5241	0·582	1·4604	1·5692	2·5483

whence $10^7\Delta B = 10{\cdot}48w_2 + 12{\cdot}0w_2^2$
$\Sigma\Delta n/\Sigma w_2 = 0{\cdot}055$
$\Sigma\Delta d/\Sigma w_2 = -0{\cdot}291_1$
$\Sigma\Delta\varepsilon/\Sigma w_2 = 6{\cdot}18_4$

*cyclo*Hexanone in carbon tetrachloride

887	0·164	—	2·4018	1·5753
949	0·169	—	—	1·5751
1301	0·235	—	—	—
1771	0·322	—	—	1·5666
2159	0·382	1·4573	—	1·5622
2392	—	1·4572	2·6913	—
3128	0·563	1·4571	2·8319	1·5531
3734	—	1·4570	2·9491	—

whence $10^7\Delta B = 18{\cdot}0_7w_2 - 4{\cdot}0w_2^2$
$\Sigma\Delta n/w_2 = -0{\cdot}012$
$\Sigma\Delta d/\Sigma w_2 = -1{\cdot}014$
$\Sigma\Delta\varepsilon/\Sigma w_2 = 19{\cdot}39$

*cyclo*Pentyl chloride in carbon tetrachloride

1516·5	0·083	1·4575	1·57122	2·3459
1781	0·097	—	1·56858	2·3708
1843	0·101	—	—	—
2730	0·150	1·4572	1·56054	2·4293
2753	0·151	1·4572	—	—
3550	0·195	1·4571	—	—
4901	0·270	1·4570	1·54183	2·6178

whence $10^7\Delta B = 5{\cdot}45w_2 + 1{\cdot}1w_2^2$
$\Sigma\Delta n/\Sigma w_2 = -0{\cdot}011$
$\Sigma\Delta d/\Sigma w_2 = -0{\cdot}878_3$
$\Sigma\Delta\varepsilon/\Sigma w_2 = 7{\cdot}831$

*cyclo*Pentyl iodide in carbon tetrachloride

1431	0·120	—	—	2·2949
1648	0·138	1·4595	1·58654	2·3012
2473	0·211	1·4597	1·58789	2·3383
2479	0·211	1·4598	—	—
2614	0·229	1·4603	—	—
3191	0·287	1·4604	—	—
6962	—	—	—	2·5431
7361	—	1·4638	1·59400	2·5588

whence $10^7\Delta B = 7{\cdot}64_1w_2 + 40{\cdot}6w_2^2$
$\Sigma\Delta n/\Sigma w_2 = 0{\cdot}093_6$
$\Sigma\Delta d/\Sigma w_2 = 0{\cdot}1298$
$\Sigma\Delta\varepsilon/\Sigma w_2 = 4{\cdot}53_5$

*cyclo*Hexyl chloride in carbon tetrachloride

10^5w_2	$10^7\Delta B$	n_D	d	ε
584	0·043	—	—	—
771	0·068	—	—	—
1657	0·166	—	1·5696	2·3565
2388	0·216	—	—	—
3167	0·302	1·4576	1·5562	2·4738
4984	0·479	1·4578	1·5431	2·6151
9586	0·873	—	—	—

whence $10^7\Sigma B = 9{\cdot}71w_2 - 6{\cdot}1w_2^2$
$\Sigma\Delta n/\Sigma w_2 = 0{\cdot}0049$
$\Sigma\Delta d/\Sigma w_2 = -0{\cdot}862_6$
$\Sigma\Delta\varepsilon/\Sigma w_2 = 7{\cdot}79_4$

*cyclo*Hexyl iodide in carbon tetrachloride

906	0·100	1·4585	1·58467	2·2710
928	0·102	1·4587	—	—
1054	0·117	1·4588	—	—
1590	0·174	1·4594	—	—
1923	0·212	1·4596	1·58478	2·3183
1445	0·266	1·4601	1·58486	2·3440

whence $10^7\Delta B = 11{\cdot}17w_2 - 10{\cdot}96w_2^2$
$\Sigma\Delta n/\Sigma w_2 = 0{\cdot}114_2$
$\Sigma\Delta d/\Sigma w_2 = 0{\cdot}0131$
$\Sigma\Delta\varepsilon/\Sigma w_2 = 4{\cdot}78_4$

*cyclo*Pentane in carbon tetrachloride

5678	−0·004	1·4503	1·48664	2·1948
7155	−0·005	—	—	—
9289	−0·006	—	—	—
11,697	−0·007	1·4426	1·39543	2·1641
12,889	−0·007	—	—	—
18,979	−0·009	1·4334	1·30270	2·1327

whence $10^7\Delta B = -0{\cdot}077w_2 + 0{\cdot}16w_2^2$
$\Sigma\Delta n/\Sigma w_2 = -0{\cdot}127$
$\Delta d = -1{\cdot}827w_2 + 1{\cdot}8w_2^2$
$\Delta\varepsilon = 0{\cdot}600w_2 + 0{\cdot}54w_2^2$

*cyclo*Pentyl bromide in carbon tetrachloride

658	0·051	—	—	—
911	0·063	1·4578	1·5825	2·2819
2191	0·139	—	—	—
2231	0·155	1·4581	1·5797	2·3617
3080	0·218	1·4588	1·5780	2·4155
4592	0·345	—	—	—

whence $10^7\Delta B = 6{\cdot}19_5w_2 + 28{\cdot}2w_2^2$
$\Sigma\Delta n/\Sigma w_2 = 0{\cdot}035$
$\Sigma\Delta d/\Sigma w_2 = -0{\cdot}2137$
$\Sigma\Delta\varepsilon/\Sigma w_2 = 6{\cdot}07_7$

*cyclo*Pentanone in carbon tetrachloride

403	0·075	—	—	—
477	0·080	—	—	—
533	0·091	—	—	—
559	0·099	—	$1{\cdot}5789_5$	2·3473
607	0·105	—	—	—
768	0·134	—	—	—
889	0·156	—	—	—
1073	0·190	1·4572	$1{\cdot}5738_5$	2·4508
1118	0·198	—	1·5734	2·4566
1228	0·218	—	—	—
1336	0·238	—	—	—
1886	—	1·4571	1·5658	2·6204
3219	—	1·4569	—	—

whence $10^7\Delta B = 16{\cdot}9_8w_2 + 64w_2^2$
$\Sigma\Delta n/\Sigma w_2 = -0{\cdot}021$
$\Sigma\Delta d/\Sigma w_2 = -0{\cdot}992_2$
$\Sigma\Delta\varepsilon/\Sigma w_2 = 20{\cdot}86$

TABLE 2. (*Continued.*)

Tetrahydrofuran in carbon tetrachloride

10^5w_2	$10^7\Delta B$	n_D	d	ε
1336	−0·002	1·4571	1·56878	2·3406
2943	−0·005	—	—	—
4443	—	1·4565	1·53316	2·6048
5118	$-0{\cdot}007_5$	—	—	—
5656	−0·008	1·4545	1·51930	2·7067
6235	$-0{\cdot}009_5$	—	—	—
10,103	−0·015	—	—	—

$$\text{whence } 10^7\Delta B = -\,0{\cdot}152_1w_2 + 0{\cdot}42_4w_2^2$$
$$\Sigma\Delta n/\Sigma w_2 = -\,0{\cdot}038_5$$
$$\Sigma\Delta d/\Sigma w_2 = -\,1{\cdot}158$$
$$\Sigma\Delta\varepsilon/\Sigma w_2 = 8{\cdot}49_2$$

(±)-*Camphor in carbon tetrachloride*

10^5w_2	$10^7\Delta B$	n_D	d	ε
482	0·034	—	—	—
1086	0·081	1·4580	—	—
1134	0·091	1·4581	—	—
1432	—	1·4582	1·5702	2·4020
2274	0·186	1·4585	1·5624	2·5044
2945	0·245	1·4588	1·5562	2·5863
4709	—	1·4597	1·5390	2·7987

$$\text{whence } 10^7\Delta B = 7{\cdot}36w_2 + 33w_2^2$$

*cyclo*Hexane-1 : 4-dione in benzene

10^5w_2	418	649	924	1123	1315	2048	3227	3849
$10^7\Delta B$	−0·010	−0·013	−0·013	−0·018	−0·034	−0·038	−0·067	−0·072

$$\text{whence } 10^7\Delta B = -\,2{\cdot}01_4w_2 + 2{\cdot}1w_2^2$$

Paraldehyde in carbon tetrachloride at 20°

10^5w_2	1918	2902	4400	5004	9488	9654	10,833	14,561
$10^7\Delta B$	−0·097	−0·090	−0·170	−0·205	−0·494	−0·473	−0·574	−0·757

$$\text{whence } \Delta B = -\,3{\cdot}99w_2 - 9{\cdot}4w_2^2$$

TABLE 3. *Calculation of molar Kerr constants at infinite dilution at 25°.*

Solute	$\alpha\varepsilon_1$	β	γ	δ	$10^{12}\,{}_\infty({}_mK_2)$
*cyclo*Hexane	$-0{\cdot}034_4$	−1·001	−0·045	−0·499	$0{\cdot}98_7$
*cyclo*Hexyl chloride	$7{\cdot}79_4$	−0·544	0·003	138·7	121·3
,, bromide	$6{\cdot}18_4$	−0·184	0·038	149·7	180·7
,, iodide	$4{\cdot}78_4$	$0{\cdot}008_3$	0·078	159·5	248·8
*cyclo*Hexanone	19·39	−0·640	−0·008	258·1	184·2
*cyclo*Hexane-1 : 4-dione *	$1{\cdot}45_7$ †	0·239 †	−0·010 †	$-4{\cdot}91_2$	$-41{\cdot}2_2$
*cyclo*Pentane	−0·600	$-1{\cdot}15_5$	−0·087	−1·10	$0{\cdot}75_1$
*cyclo*Pentyl chloride	$7{\cdot}83_1$	−0·554	−0·007	77·86	$59{\cdot}3_1$
,, bromide	$6{\cdot}07_7$	−0·135	0·024	$88{\cdot}50_0$	$96{\cdot}8_2$
,, iodide	$4{\cdot}53_5$	$0{\cdot}081_9$	0·064	109·2	158·4
*cyclo*Pentanone	$20{\cdot}8_6$	−0·626	−0·014	242·6	147·6
Tetrahydrofuran	$8{\cdot}49_2$	−0·731	−0·026	$-2{\cdot}17_1$	$-2{\cdot}39_2$
Paraldehyde	6·21 ‡	−0·605 ‡	−0·062 ‡	$-55{\cdot}4_2$ ¶	$-57{\cdot}0_2$
(±)-Camphor	$12{\cdot}1_8$	−0·612	0·032	105·1	$115{\cdot}0_5$

* Solvent : benzene; in other cases, carbon tetrachloride.

† Recalc. from Le Fèvre and Le Fèvre.[38] ‡ From Le Fèvre, Mulley, and Smythe.[32]

¶ Measured at 20°.

TABLE 4. *Values of* $\theta_1 + \theta_2$ *and* b_{Tot}.

	$10^{35}(\theta_1 + \theta_2)$	R_∞ (c.c.)	$10^{23}(b_1 + b_2 + b_3)$	Source from which R_∞ is calculated
*cyclo*Hexane	$0{\cdot}23_5$	27·15	3·209	12*a*
*cyclo*Hexyl chloride	28·85	32·26	3·813	12*b*
,, bromide	42·97	34·71	4·103	12*b*
,, iodide	59·17	39·70	4·692	12*b*
*cyclo*Hexanone	43·80	27·25	3·221	12*a*
*cyclo*Hexane-1 : 4-dione	−9·80	27·31	3·228	*x*
*cyclo*Pentane	0·179	22·57	2·667	12*a*
*cyclo*Pentyl chloride	14·10	27·33	3·230	12*b*
,, bromide	$23{\cdot}02_5$	30·21	3·571	12*b*
,, iodide	37·66	35·15	4·155	12*b*
*cyclo*Pentanone	35·11	22·79	2·694	12*a*
Tetrahydrofuran	−0·569	19·38	2·291	*y*
Paraldehyde	−13·56	31·70	3·746	*z*
(±)-Camphor	27·36	44·01 *	5·201	*z*

* *I.e.*, R_D calc. from bond refractions. Refs. : *x*, Clarke, *J.*, 1912, **101**, 1788. *y*, Böhme and Schurhoff, *Chem. Ber.*, 1951, **84**, 41. *z*, Vogel, Cresswell, Jeffery, and Leicester, *J.*, 1952, 514.

TABLE 5. *Polarisations at 25° and estimations of dipole moment.*

Solute	${}_\infty P_2$ (c.c.)	R_D (c.c.)	μ (D) *
*cyclo*Hexane	27·8	27·7	0
*cyclo*Hexyl chloride	131·5	33·0	2·18
,, bromide	142·2	35·6	$2{\cdot}2_6$
,, iodide	144·7	$41{\cdot}0_5$	$2{\cdot}2_3$
*cyclo*Hexanone	231·1	27·87	3·14
*cyclo*Hexane-1 : 4-dione †	59·8 ‡	27·7	$1{\cdot}2_3$
*cyclo*Pentane	23·2	23·1	0
*cyclo*Pentyl chloride	116·6	27·96	$2{\cdot}0_6$
,, bromide	126·9	30·99	$2{\cdot}1_5$
,, iodide	127·2	36·38	$2{\cdot}0_9$
*cyclo*Pentanone	211·0	23·31	$3{\cdot}0_2$
Tetrahydrofuran	87·8	19·87	$1{\cdot}8_1$
(±)-Camphor	241·4	44·0	$3{\cdot}0_9$

* Calc. by assuming ${}_DP = 1{\cdot}05R_D$. † Solvent : benzene. In other cases, carbon tetrachloride.
‡ Recalc. from ref. 38.

TABLE 6. *Previously recorded dipole moments.*

*cyclo*Hexane	B. 25°. 28 c.c. 0 (1)
*cyclo*Hexyl chloride	B. 25°. 143 c.c. 2·3 (1)
	B. 60°. ${}_0P = 91$ c.c. 2·07 (2)
	B. 18°. ${}_0P = 94$ c.c. 2·10 (3)
*cyclo*Hexyl bromide	B. 25°. 150 c.c. 2·3 (1)
	B. 60°. ${}_0P = 95$ c.c. 2·11 (2)
,, iodide	B. 60°. ${}_0P = 83$ c.c. 1·98 (2)
*cyclo*Hexanone	B. No exptl. details. 2·75 (4)
	B. 25°. 202 c.c. 2·9 (1)
	B. 25°. 211·8 c.c. 3·01 (5)
	D. 25°. 202·2 c.c. 2·90 (6)
	B. 19°. Dielectric loss method. 3·02 (7)
	B. 18·5°. ,, ,, 2·90 (8)
	B. 20°. 225·4 c.c. 3·08 (9)
	CH. 20°. 219·7 c.c. 3·04 (9)
	CT. 20°. 232·8 c.c. 3·14 (9)
*cyclo*Pentane	liq. 20°. $\varepsilon = 1{\cdot}965$. $n_D^2 = 1{\cdot}984$. 0 (10)
*cyclo*Pentyl chloride	B. 25°. 117·2 c.c. 2·08 (11)
,, bromide	B. 25°. 130·0 c.c. 2·20 (11)
,, iodide	B. 25°. 122·8 c.c. 2·06 (11)
*cyclo*Pentanone	B. 22°. ${}_0P = 192 \pm 4$ c.c. $3{\cdot}00 \pm 0{\cdot}03$ (12)
	B. 25°. 197·0 c.c. 2·93 (5)
	B. 20°. 196·3 c.c. 2·86 (9)
	CH. 20°. 187·2 c.c. 2·81 (9)
	CT. 20°. 201·3 c.c. 2·93 (9)
Tetrahydrofuran	B. 25°. ${}_0P = 60{\cdot}9$ c.c. 1·71 (13)
	D. 25°. ${}_0P = 67{\cdot}8$ c.c. 1·81 (13)
	B. 20°. No pol^{ns}. given. 1·68 (14)
Camphor	B. 22°. ${}_0P = 190 \pm 4$ c.c. $2{\cdot}95 \pm 0{\cdot}03$ (12)
	B. 22°. ${}_0P = 181 \pm 3$ c.c. $2{\cdot}94 \pm 0{\cdot}03$ (15)
	B. 20°. 242 c.c. 3·05 (16)
	Hp. Temp. variation of dielectric absn. 2·98 (7)
	Hp. Wave-length variation of dielectric absn. 2·97 7)
	B. 20°. *ca.* 235 c.c. 2·90—2·91 (17)
	B. 25°. 241·4 c.c. 3·10 (18)

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Measurements.—These were made by the methods described earlier,[7] when the symbols used here were defined and the extrapolation procedure was explained. The observations recorded in Table 2 are for 20° or 25°, at which the appropriate data for the two solvents involved are listed in Table 1. The calculations of ${}_\infty({}_mK_2)$ are in Table 3. Other necessary quantities follow as Table 4.

Polarisations and Dipole Moments.—Incidental to determination of $_{\infty}({}_mK_2)$ is the provision of data from which $_{\infty}P_2$ may be calculated; by using the approximation that $_{\text{D}}P = 1{\cdot}05R_{\text{D}}$, apparent moments for the solutes now under examination have been calculated (see Table 5).

It is seen that the moments of the bromides exceed those of the chlorides. Such is not always the case: $\mu_{\text{CH}_3\text{Cl}}$ is greater [41] than $\mu_{\text{CH}_3\text{Br}}$, and the same is true of ethyl chloride and bromide.[42] However, with increase in size of the alkyl radical the relation is reversed, the polarities of *n*-propyl and *n*-butyl chloride being less than those of the corresponding bromides.[41]

Except with *cyclo*-pentanone and -hexanone, carbon tetrachloride has not hitherto been used as solvent. Recorded determinations, mostly in benzene, display some variability among themselves, but, even so, change of medium does not appear to cause marked effects. Comparison with previous measurements is best made *via* figures for $_{\infty}P_2$ (when these are accessible) since the μ's quoted by other workers depend on the particular convention adopted to estimate distortion polarisations. Table 6 briefly summarises the literature. The code of the M.I.T Tables [43] is used to indicate solvent and temperature (B = benzene, CH = *cyclo*-hexane, CT = carbon tetrachloride, D = dioxan, Hp = heptane). Polarisations (total in most cases, orientation $_{\text{O}}P$ in some) are shown as c.c.; they are followed by the moment actually given in the reference cited in parentheses.

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