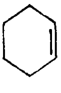
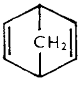
89. *Molecular Polarisability. The Conformations of Five Cyclic Olefins.*

By C.-Y. Chen, R. J. W. Le Fèvre, and K. M. S. Sundaram.

Molar Kerr constants and apparent dipole moments for the five hydrocarbons (I) to (V) in carbon tetrachloride are recorded and discussed in terms of possible non-planar conformations.

The measurements and calculations here reported concern hydrocarbons (I) to (V) for which no geometrically specified stereo-structures appear yet to have been established by experiment. In qualitative terms, Barton, Cookson, Klyne, and Shoppee [1] have described (I) as a puckered or " half-chair " form, for the atoms in which Corey and Sneen [2] have published co-ordinates based on C–C and C=C distances of 1·55 and 1·34 Å, respectively; (II) of necessity must contain a "boat" C_6 skeleton; a number of choices exist for (III)—(V), some of which may be eliminated by considerations involving the anisotropies of polarisability of the C–C and C=C bonds.


(I)



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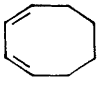
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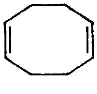
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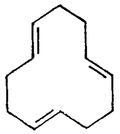
(V)

Experimental

Materials.—*Cyclohexene* (B.D.H. product) was washed several times with aqueous ferrous sulphate until no further oxidation was apparent; the peroxide-free compound was then dried quickly over magnesium perchlorate and distilled, the fraction boiling at 83·0—83·4°/760 mm. being collected and stored under nitrogen; n_{D}^{25} 1·4436, d_4^{25} 0·8062, ε^{25} (relatively to benzene, $\varepsilon = 2{\cdot}2725$) $2{\cdot}219_8$, whence $R_{\mathrm{D}} = 27{\cdot}04$ and ${}_{\mathrm{T}}P = 29{\cdot}45$ c.c., for the undiluted liquid. Bicyclo-(2,2,1)heptadiene (II) was a gift from the Shell Development Co. (Modesto, Calif., U.S.A.); it was distilled after drying over magnesium sulphate, b. p. 82—83°/760 mm., n_{D}^{20} 1·4700. Specimens of 1,3-cyclo-octadiene (III), b. p. 143°/760 mm., n_{D}^{20} 1·4933, 1,5-cyclo-octadiene (IV), b. p. 151°/760 mm., n_{D}^{20} 1·4942, and 1,5,9-cyclododecatriene (V), b. p. 95°/13 mm., n_{D}^{20} 1·5072 (from Cities Service Research and Development Co., Sixty Wall Tower, New York) were presented to us by Dr. N. A. Gibson of this Department.

Measurements.—Apparatus, procedures, notation, and methods of calculation have been

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[1] Barton, Cookson, Klyne, and Shoppee, *Chem. and Ind.*, 1954, 21.

[2] Corey and Sheen, *J. Amer. Chem. Soc.*, 1955, **77**, 2505.

those described in refs. 3—5. Observed increments, from solvent to solutions containing weight-fractions w_2 of solute, in refractive index n, density d, dielectric constant ε, and Kerr constant B, are listed in Table 1; quantities calculated therefrom are in Table 2. For carbon tetrachloride as solvent, when $w_2 = 0$, $\varepsilon^{25} = 2{\cdot}2270$, $d_4^{25} = 1{\cdot}58454$, $n_D^{25} = 1{\cdot}4575$, and $10^7 B_D^{25} = 0{\cdot}070$.

TABLE 1.

Incremental refractive indexes, dielectric constants, etc., for solutions in carbon tetrachloride at 25°.

Solute: *Cyclohexene*

10^5w_2	$10^4\Delta n$	$10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
379	—	−574	—	—
718	—	−1073	—	—
1203	—	−1785	—	—
1415	−0·3	−2097	—	—
2031	—	—	73	—
2037	−0·6	−2999	—	—
2367	−0·7	−3482	—	—
2523	−0·7	−3705	—	—
2887	—	—	—	15
2968	—	—	107	—
3087	−1	−4511	—	—
3808	—	—	137	—
4559	—	—	—	21
4776	—	—	—	21
4899	—	—	175	—
5211	—	—	—	23
6769	—	—	—	27

whence $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}003$; $\Sigma\Delta n^2/\Sigma w_2 = -0{\cdot}009$; $\Sigma\Delta d/\Sigma w_2 = -1{\cdot}473$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}359$; $\Sigma\Delta B/\Sigma w_2 = 0{\cdot}442 \times 10^{-7}$

Solute: 2,5-*Bicycloheptadiene*

10^5w_2	$10^4\Delta n$	$10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
4596	12	−5264	97	15
6267	15	−7058	125	21
7740	20	−8657	147	23
8293	23	−9233	150	25
10,555	26	−11,577	175	30
12,215	32	−13,433	195	33
16,462	37	−17,704	221	40
18,628	44	−19,346	235	43
22,881	52	−23,087	240	52

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}024$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}071$; $\Delta d = -1{\cdot}2134w_2 + 0{\cdot}921w_2^2$; $\Delta\varepsilon = 0{\cdot}232w_2 - 0{\cdot}5699w_2^2$; $10^7\Delta B = 0{\cdot}3496w_2 - 0{\cdot}5904w_2^2$

Solute: 1,3-*Cyclo-octadiene*

10^5w_2	$10^4\Delta n$	$10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
911	6	−1164	61	5
1143	7	−1467	74	7
1271	9	−1645	85	8
1322	10	−1699	89	9
1492	11	−1930	100	10
1620	12	−2107	108	11
1744	13	−2232	117	12

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}072$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}212$; $\Sigma\Delta d/\Sigma w_2 = -1{\cdot}2884$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}667$; $\Sigma\Delta B/\Sigma w_2 = 0{\cdot}652 \times 10^{-7}$

Solute: 1,5-*Cyclo-octadiene*

10^5w_2	$10^4\Delta n$	$10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
1326	10	−1612	32	5
2877	22	−3488	71	10
3706	28	−4484	91	12
4712	36	−5665	114	17
5411	41	−6472	130	19
6756	52	−8004	157	23

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}076$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}223$; $-\Delta d = 1{\cdot}2357w_2 - 0{\cdot}7428w_2^2$; $\Sigma\varepsilon = 0{\cdot}258w_2 - 0{\cdot}365w_2^2$; $\Sigma\Delta B/\Sigma w_2 = 0{\cdot}347 \times 10^{-7}$

Solute: 1,5,9-*Cyclododecatriene*

10^5w_2	$10^4\Delta n$	$10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
732	6	−922	27	2
945	8	−1189	35	3
1131	9	−1419	42	4
1245	10	−1563	46	5
1311	11	−1652	50	5
1399	12	−1760	53	6
1454	13	−1826	55	6

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}084$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}248$; $\Sigma\Delta d/\Sigma w_2 = -1{\cdot}2573$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}375$; $\Sigma\Delta B/\Sigma w_2 = 0{\cdot}377 \times 10^{-7}$

TABLE 2.

Polarisations, apparent moments, molar Kerr constants, etc., calculated from Table 1.

Solute	$\alpha\varepsilon_1$	$-\beta$	$\gamma' n_1^2$	$_\infty P_2$ (c.c.)	R_D (c.c.)	μ (D) *	γ	δ	$10^{12}\,_\infty(_mK_2)$
Cyclohexene	0·359	0·9296	−0·075	32·2	27·2	0·42	−0·002	6·32	4·97
2,5-Bicycloheptadiene	0·232	0·7657	0·071	32·0	28·7	0·31	0·017	4·99	4·60
1,3-Cyclo-octadiene	0·667	0·8131	0·212	43·6	36·3	0·52	0·049	9·31	8·72
1,5-Cyclo-octadiene	0·258	0·7798	0·223	38·2	35·8	0·17	0·052	4·96	5·32
1,5,9,-Cyclododecatriene	0·375	0·7935	0·248	59·8	54·6	0·35	0·058	5·38	8·42

* Calc. with $_DP$ taken as $1{\cdot}05R_D$.

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[3] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.* (*Australia*), 1955, **5**, 261; Ch. XXXVI in "Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ., London, 3rd edn., Vol. 1, p. 2549.

[4] Le Fèvre, "Dipole Moments," Methuen, London, 3rd edn., 1953, Ch. 2.

[5] Le Fèvre and Sundaram, *J.*, 1962, 1494.

DISCUSSION

Apparent Dipole Moments.—The moment of cyclohexene given in Table 2 is slightly smaller than has been reported previously (0·63 D in carbon tetrachloride or 0·75 D in hexene,[6] and 0·61 D as a gas [7]). Smyth,[8] noting that Kubo's observations [7] lead to a negative value for the atomic polarisation, comments that 0·6 D may be too high. From the total polarisation (29·45 c.c.) and molecular refraction (27·04 c.c.) now found for the pure liquid, a polarity of 0·34 D is indicated; autoxidation occurs readily, and after exposure to air specimens give higher polarisations than those quoted.

Conformations of Solutes.—Possible models of the molecules concerned are placed within an arbitrary set of *XYZ* axes and the principal polarisabilities computed by the method described in ref. 9. Bond polarisabilities (in 10^{-23} c.c. units) required are: [3]

	b_L	b_T	b_V
C–H	0·064	0·064	0·064
C–C	0·099	0·027	0·027
C=C	0·280	0·073	0·077

The molar Kerr constants to be expected for each conformation are then evaluated and compared with the $_{m}K$ from experiment.

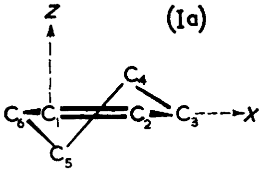
For cyclohexene we consider two models (Ia) and (Ib); in both, carbon atoms 6, 1, 2, 3 are in one plane, the *X* axes are from C(1) to C(2), and the *Z* axes are perpendicular to the 6, 1, 2, 3 plane. In (Ia) the CCC angles at the various C atoms are [2] at C(1) and C(2), 122° 30′, at C(3) and C(6), 111° 12′, at C(4) and C(5), 107° 43′, and the C · · · · C distances are for C=C, 1·34 Å, and for C–C, 1·55 Å; in (Ib) the corresponding quantities are 116°, 109° 28′, 112°, 1·34 and 1·54 Å, respectively. Co-ordinates for C(1) to C(6) are therefore:

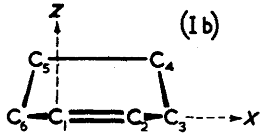
for model (Ia)

C(1)	(0, 0, 0)	C(4)	(1·315, 2·524, 0·430)
C(2)	(1·340, 0, 0)	C(5)	(0·025, 2·524, −0·430)
C(3)	(2·173, 1·307, 0)	C(6)	(−0·833, 1·307, 0)

for model (Ib)

C(1)	(0, 0, 0)	C(4)	(1·440, 2·236, 1·147)
C(2)	(1·340, 0, 0)	C(5)	(−0·100, 2·236, 1·147)
C(3)	(2·015, 1·384, 0)	C(6)	(−0·675, 1·384, 0)


(Ia)


(Ib)

Calculations of molar Kerr constants are summarised as Table 3. The observed $_{m}K$ being $4{\cdot}97 \times 10^{-12}$, conformation (Ia) is to be preferred. The fact that the measured $_{m}K$ exceeds the greater of those calculated may indicate that a flatter structure than (Ia) would be more appropriate (*e.g.*, we find that a planar form, based on the bond lengths used above for (Ib) and with angles at C(1) and C(2) of 116°, at C(4) and C(5) of 112°, and at C(3) and C(4) of 132° 5′, gives a calc. $_{m}K$ of $7{\cdot}2 \times 10^{-12}$).

For bicyclo(2,2,1)heptadiene we consider structure (IIa), a " Barton " model [10] of which showed angles as follows: a = 109°, b = 92°, angle between planes I and II = 114°, and

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[6] Puchalik, *Acta Phys. Polon.*, 1935, **4**, 145.

[7] Kubo, *Sci. Papers Inst. Phys. Chem. Res., Tokyo*, 1937, **32**, 26.

[8] Smyth, " Dielectric Behavior and Structure," McGraw-Hill, New York, Toronto, London, 1955, p. 263.

[9] Eckert and Le Fèvre, *J.*, 1962, 1081.

[10] Barton, *Chem. and Ind.*, 1956, 1136.

TABLE 3.

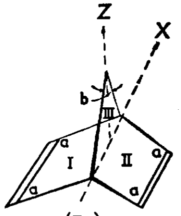
Principal polarisabilities, moment components, etc., calculated for models (Ia) and (b).

Model		Direction cosines with X	Y	Z	Moment components	$10^{12}(_{\rm m}K)$ (calc.
(Ia)	$b_1 = 1{\cdot}194$	0·997	0	−0·072	$\mu_1 = 0$	+3·6
	$b_2 = 1{\cdot}039$	0	1	0	$\mu_2 = \mu_{\rm res.}$ *	
	$b_3 = 0{\cdot}884$	0·072	0	0·997	$\mu_3 = 0$	
(Ib)	$b_1 = 1{\cdot}190$	1	0	0	$\mu_1 = 0$	+1·9 †
	$b_2 = 1{\cdot}030$	0	0·852	−0·524	$\mu_2 = +0{\cdot}358$	
	$b_3 = 0{\cdot}897$	0	+0·524	0·852	$\mu_3 = +0{\cdot}220$	

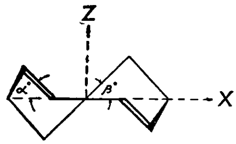
* Since $2b_2 - b_1 - b_3 = 0$, the magnitude of μ_2 does not affect $_{\rm m}K$ calc. † Were $\mu = 0{\cdot}6$ D the $_{\rm m}K$ calc. would be $0{\cdot}5 \times 10^{-12}$.

that between I and III = 123°; the axis *OX* is parallel to the double bonds and *OZ* bisects the methylene angle *b*. The direction of action of the resultant moment is taken as *OZ*. The computed polarisability semi-axes for (IIa) emerge as $b_1 = 1{\cdot}340_3$ (along *OX*), $b_2 = 1{\cdot}001_5$ (along *OY*) and $b_3 = 0{\cdot}974_6$ (along *OZ*); therefore $10^{35}\theta_1 = 1{\cdot}48_2$ $10^{35}\theta_2 = -0{\cdot}48_4$, and $10^{12}{}_{\rm m}K$ calc. = 4·2. The approach of $_{\rm m}K$ calc. to that found ($4{\cdot}6 \times 10^{-12}$) is satisfactory when the uncertainty of estimations of small moments is considered: had μ been measured as $0{\cdot}27_5$ D instead of 0·31 D the two $_{\rm m}K$'s would have been equal.

With 1,3-cyclo-octadiene (III) we note that, despite the positions of the double bonds, no marked exaltation of molecular refraction is apparent ($R_{\rm D}$ obs. = 36·3 c.c., calc. from bond refractions given by Vogel *et al.*[11] $R_{\rm D}$ = 36·2 c.c.). Were (III) a flat structure, its polarisability semi-axes would be: $b_1 = 1{\cdot}499$ (along the bisector of the angle between the two C=C bonds), $b_2 = 1{\cdot}499$, and $b_3 = 1{\cdot}084$ (perpendicular to the ring-plane); with $\mu = 0{\cdot}52$ D acting along b_1, we have $10^{35}\theta_1 = 2{\cdot}046$ and $10^{35}\theta_2 = 1{\cdot}473$, whence $_{\rm m}K$ calc. = $14{\cdot}8 \times 10^{-12}$. This is larger than the $_{\rm m}K$ obs. By making the model non-planar, prediction and experiment can be brought together; *e.g.*, if the two double bonds and their three associated single bonds are kept flat and the remaining single bonds arranged as specified above in cyclohexene, we have $b_1 = 1{\cdot}516$, $b_2 = 1{\cdot}449$, and $b_3 = 1{\cdot}119$; then with $\mu = 0{\cdot}52$ D $10^{35}\theta_1 = 1{\cdot}610$, $10^{35}\theta_2 = 0{\cdot}933$, and $_{\rm m}K$ calc. = $10{\cdot}7 \times 10^{-12}$, which also exceeds the value from experiment. Furthermore, Leybold models show that the above two structures are highly strained. Since the absence of exaltation suggests that the C=C–C=C unit is not coplanar, forms such as (IIIa) should be envisaged. When $\alpha = 30°$ and $\beta = 40°$ the following values emerge: $b_1 = 1{\cdot}454$ (along the *Y* axis) $b_2 = 1{\cdot}422$ (along the *X* axis), and $b_3 = 1{\cdot}200$; with $\mu_1 = 0{\cdot}52$ D acting on the *Y* axis, $10^{35}\theta_1$ is 0·682, $10^{35}\theta_2$ is 1·015, and $_{\rm m}K$ calc. = $7{\cdot}14 \times 10^{-12}$. Small modification in α and β would lead to an $_{\rm m}K$ calc. = $8{\cdot}72 \times 10^{-12}$, but these have not been evaluated as the small value observed is itself uncertain.



(IIa)



(IIIa)

For 1,5-cyclo-octadiene, we first consider five models. If in (IV) as written, *XYZ* axes are placed with *X* and *Y* in the plane of the paper, with *Y* parallel to the C=C links, and *Z* at 90° to *X* and *Y*, the models may be described as follows: (IVa), with all bonds lying in the *XY* plane; (IVb), with the two double bonds in the *XY* plane but with the other

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[11] Vogel, Cresswell, Jeffrey, and Leicester, *J.*, 1952, 514.

bonds disposed spherically symmetrically; (IVc), with b_{XX} as in (IVb) but with bonds arranged so that $b_{YY} = b_{ZZ}$; (IVd), with the double bonds twisted oppositely by 20° about the X axis and the other bonds situated symmetrically, and (IVe), as (IVd) but with a twist angle of 30°. These structures should be non-polar; they are unlikely to be rigid, so that the small apparent moment (0·17 D) given in Table 2 does not make them unreasonable; their corresponding polarisability semi-axes, anisotropy terms, and molar Kerr constants are:

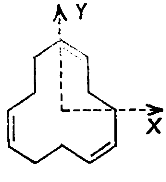
Model	b_{XX}	b_{YY}	b_{ZZ}	$10^{35}\theta_1$	$10^{12}({}_{\mathrm{m}}K)_{\mathrm{calc.}}$
(IVa)	1·364	1·634	1·084	2·70	$11{\cdot}3_5$
(IVb)	1·220	1·634	1·228	2·00	8·41
(IVc)	1·220	1·431	1·431	0·588	2·47
(IVd)	1·220	1·586	1·276	1·39	5·85
(IVe)	1·220	1·532	1·330	0·983	3·76

Thus a conformation near to that specified as (IVd), and between (IVd) and (IVe), seems to fit the present observations. The further alternative non-polar form, with the double bonds in one plane and the CH_2–CH_2 bonds in another parallel to the first, should show a resultant moment resembling that of (II) and acting along b_{ZZ}. However, with $\mu = 0{\cdot}17$ D we find $b_1 = 1{\cdot}562$ (parallel to the C=C bonds), $b_2 = 1{\cdot}252$ (at 90° to the double bonds, but in their plane), $b_3 = 1{\cdot}268$, $10^{35}\theta_1 = 1{\cdot}086$, $10^{35}\theta_2 = -0{\cdot}110$, and ${}_{\mathrm{m}}K$ calc. $= 4{\cdot}10 \times 10^{-12}$; this is less than the experimental value for ${}_{\mathrm{m}}K$, and, were a larger moment presumed, would be more so. An additional objection to the last model is that in it the methylene C–H links are not staggered.

In 1,5,9-cyclododecatriene, let the arbitrary XYZ axes be placed with X and Y in the plane of (V); a flat model will be symmetrical about the Z axis, and therefore non-polar; b_{ZZ} and $b_{XX} = b_{YY}$ by calculation are 1·626 and 2·249, respectively, whence $10^{35}\theta_1$ becomes 4·47 and the predicted ${}_{\mathrm{m}}K = 18{\cdot}8 \times 10^{-12}$. This is too large. Next, we suppose that only the three C=C bonds remain in the XY plane and that all the other bonds are disposed spherically symmetrically; then μ is again zero, $b_{XX} = b_{YY} = 2{\cdot}141$, $b_{ZZ} = 1{\cdot}842$, and $10^{35}\theta_1 = 1{\cdot}06$; ${}_{\mathrm{m}}K$ calc. is $4{\cdot}46 \times 10^{-12}$, which is less than that observed. Finally we assume a structure (Va) in which an XY plane is defined by C(3)C(7)C(11), and in which the double bonds are inclined at $\alpha°$ to this plane (Va) can be viewed as corresponding to three cyclohexene-like portions united as a 3-bladed propellor). Then, for $\alpha = 10$ or 15°, we have (for a non-polar molecule):

$\alpha°$	$b_1 = b_2$	b_3	$10^{35}(\theta)$	$10^{12}({}_{\mathrm{m}}K)_{\mathrm{calc.}}$
10	2·190	1·750	2·301	9·68
15	2·173	1·784	1·798	7·56

The ${}_{\mathrm{m}}K$ as measured is between these values. A scale model of (Va) is somewhat flexible, and it is therefore unlikely that in fact all six C–H moments associated with the three olefinic bonds are cancelled vectorially. We suspect, but cannot prove, that the apparent moment observed is too high; even so, were it real, it would need to act at 40—50° to the XY plane in the above versions of (Va) to lead to the observed ${}_{\mathrm{m}}K$; such a disposition is not unreasonable; alternatively, a smaller real moment of 0·16—0·17 D could act at 90° to the XY plane and also give an ${}_{\mathrm{m}}K$ calc. of $8{\cdot}4 \times 10^{-12}$.



(Va)

Conclusions.—For none of these hydrocarbons is a planar conformation reconcilable with the observed molar Kerr constants. Non-planar models, more satisfactory in this respect, can be specified. These are: (Ia) for cyclohexene, (IIa) for bicycloheptadiene, (IIIa) for 1,3-cyclo-octadiene, (IVd) for 1,5-cyclo-octadiene, and (Va) for 1,5,9-cyclododecatriene.

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