678. *Molecular Polarisability. Conformational Equilibria in 2-Chloro- and 2-Bromo-cyclohexanones*

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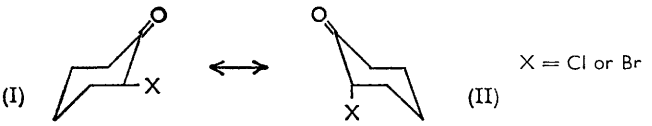
The conformational equilibria in 2-chloro- and 2-bromo-cyclohexanones have been investigated further by measurements of molecular anisotropies and p.m.r. spectra of these compounds alone and in various solvents (n-hexane, carbon tetrachloride, benzene, dioxan). *cis*- and *trans*-2-Chloro-4-t-butylcyclohexanone are used as conformationally homogeneous models for the p.m.r. study of 2-chlorocyclohexanone. The conclusions reached are in good agreement with those from previous investigations.

The conformations of 2-chloro- and 2-bromo-cyclohexanones have been much studied in recent years.[1-5] The early conclusion [1] that the halogen atom of each of these compounds was mainly held axially was questioned [2] on the basis of dipole moment measurements. It is now generally accepted that the available data concerning the conformations

[1] E. J. Corey, *J. Amer. Chem. Soc.*, 1953, **75**, 2301.
[2] W. D. Kumler and A. C. Huitric, *J. Amer. Chem. Soc.*, 1956, **78**, 3369.
[3] (*a*) J. Allinger and N. L. Allinger, *Tetrahedron*, 1958, **2**, 64; (*b*) N. L. Allinger, J. Allinger, and N. A. LeBel, *J. Amer. Chem. Soc.*, 1960, **82**, 2926; (*c*) N. L. Allinger, J. Allinger, L. A. Freiberg, R. F. Czaja, and N. A. LeBel, *ibid.*, p. 5876, and references therein.
[4] K. Kozima and E. Hirano, *J. Amer. Chem. Soc.*, 1961, **83**, 4300.
[5] E. W. Garbisch, jun., *J. Amer. Chem. Soc.*, 1964, **86**, 1780.

of the 2-halogenocyclohexanones can be explained in terms of equilibria between the conformers (I) and (II), in which the amount of the equatorial form (I) varies with the



polarity of the solvent used. Since these two conformers are likely to differ greatly both in polarity and in polarisability, the measurement of their molar Kerr constants as solutes in different solvents should provide useful information about the equilibria. P.m.r. spectroscopy has already been applied to the conformational analysis of 2-bromocyclohexanone;[5] in this Paper, we report extensions of such a study, and a similar investigation on 2-chlorocyclohexanone. However, only the proton spin coupling parameter approach is employed, to minimise the effect of all possible intermolecular interactions.

Experimental

Materials.—2-Chlorocyclohexanone,[6] *cis*- and *trans*-2-chloro-4-t-butylcyclohexanone,[3c] and 2-bromocyclohexanone [3a] were prepared by reported procedures, freshly distilled samples being used for all measurements. Benzene and carbon tetrachloride, as solvents, were given the standard pretreatment (ref. 7 page 45), dioxan was purified according to Vogel,[8] and n-hexane was of spectroscopic grade, carefully dried over sodium.

Apparatus, Procedures, etc.—These were as in ref. 9, wherein symbols used here are defined. Fuller descriptions of apparatus, derivations of equations, etc., may be found in refs. 7 and 10. P.m.r. spectra were determined, at room temperature, on a Varian A-60 analytical spectrometer with tetramethylsilane as internal reference. The coupling constants were reproducible to 0·1—0·2 c./sec.

Measurements and Results.—Observed quantities (other than p.m.r. data given separately in

Table 1

Dielectric constants, birefringences, etc., for solutions of 2-chloro- and 2-bromocyclohexanone in different solvents

2-Chlorocyclohexanone in n-hexane

10^5w_2 ...	1370	1574	2003	2551	3162
$10^7\Delta B$ ...	0·0528	0·0635	0·0798	0·0995	0·1231

whence $\Sigma\Delta B/\Sigma w_2 = 3·928$

2-Bromocyclohexanone in n-hexane

10^5w_2 ...	964	1268	2146	2612	2992
$10^7\Delta B$ ...	0·0160	0·0236	0·0394	0·0457	0·0525

whence $\Sigma\Delta B/\Sigma w_2 = 1·775$

2-Chlorocyclohexanone in carbon tetrachloride

10^5w_2 ...	298	570	623	892	997
$-10^4\Delta$	10	19	29	43	49
$\Delta\varepsilon$	0·0544	0·1057	0·1166	0·1696	0·1910
$10^7\Delta B$ ...	0·0324	0·0735	0·0790	0·1104	0·1204

whence $\Sigma\Delta B/\Sigma w_2 = 12·30$, $\Sigma\Delta\varepsilon/\Sigma w_2 = 18·86$, $\Sigma\Delta d/\Sigma w_2 = -0·4435$

2-Bromocyclohexanone in carbon tetrachloride

10^5w_2 ...	409	620	728	980	1477
$-10^4\Delta d$	11	17	20	26	40
$\Delta\varepsilon$	0·0508	0·0768	0·0903	0·1216	0·1831
$10^7\Delta B$ ...	0·0194	0·0304	0·0345	0·0459	—

whence $\Sigma\Delta B/\Sigma w_2 = 4·757$, $\Sigma\Delta\varepsilon/\Sigma w_2 = 12·40$, $\Sigma\Delta d/\Sigma w_2 = -0·2705$

2-Chlorocyclohexanone in benzene

10^5w_2 ...	500	877	1014	1159	1583
$10^7\Delta B$ ...	0·0758	0·1218	0·1495	0·1755	0·2303

whence $\Sigma\Delta B/\Sigma w_2 = 14·67$

2-Bromocyclohexanone in benzene

10^5w_2 ...	1072	1213	1604	2095	2985
$10^7\Delta B$ ...	0·0751	0·0877	0·1145	0·1515	0·2137

whence $\Sigma\Delta B/\Sigma w_2 = 7·164$

2-Chlorocyclohexanone in dioxan

10^5w_2 ...	458	595	829	950	1071
$10^7\Delta B$ ...	0·0632	0·0841	0·1182	0·1350	0·1493

whence $\Sigma\Delta B/\Sigma w_2 = 14·09$

2-Bromocyclohexanone in dioxan

10^5w_2 ...	547	986	1275	1460	2287
$10^7\Delta B$ ...	0·0420	0·0763	0·0926	0·1089	0·1731

whence $\Sigma\Delta B/\Sigma w_2 = 7·52$

[6] *Org. Synth.*, Coll. Vol. III, 1955, p. 188.
[7] R. J. W. Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953.
[8] A. I. Vogel, " Practical Organic Chemistry," 3rd edn., Longmans, London, 1959, p. 177.
[9] R. J. W. Le Fèvre and K. M. S. Sundaram, *J.*, 1962, 1494.
[10] C. G. Le Fèvre and R. J. W. Le Fèvre, (*a*) *Rev. Pure Appl. Chem.* (*Australia*), 1955, **5**, 261; (*b*) Ch. XXXVI in " Physical Methods of Organic Chemistry," ed. Weissberger, Interscience, New York, 3rd edn., Vol. 1, p. 2459.

a later section) against standard headings are in Table 1; from them are calculated the polarisations, refractions, apparent dipole moments, molar Kerr constants, etc., shown in Table 2. For the pure solvents, numerical values of various properties at 25° are:

Solvent	n_1	ε_1	d_1	10^7B
n-Hexane *	1·3723	1·8889	0·6549	0·047
Carbon tetrachloride	1·4575	2·2270	1·5845	0·070
Benzene	1·4973	2·2725	0·8738	0·410
Dioxan	1·4202	2·2090	1·0280	0·068

* n_1, ε_1, and d_1 taken as for pure n-hexane; B measured during present work.

TABLE 2

Polarisations, apparent dipole moments, and molar Kerr constants * of 2-chloro- and 2-bromo-cyclohexanones in various solvents

Solvent	$\alpha\varepsilon_1$	β	γ †	δ	$_\infty P$ (c.c.)	μ (D)	$10^{12}{}_mK_2$
2-Chlorocyclohexanone							
n-Hexane	6·375	0·4377	0·1097	83·57	272·25	3·45	163·36
Carbon tetrachloride	18·16	−0·2799	0·0245	175·7	296·07	3·58	166·88
Benzene	11·40	0·2432	−0·0153	35·78	319·82	3·78	298·87
Dioxan	13·98	0·1148	0·0618	207·16	339·67	3·91	310·21
2-Bromocyclohexanone							
n-Hexane	4·60	0·5787	0·1135	37·77	263·49	3·37	96·51
Carbon tetrachloride	12·40	−0·1707	−0·0530	67·96	270·60	3·43	61·30
Benzene	7·383	0·40	0·0132	17·47	281·86	3·50	195·70
Dioxan	9·080	0·4332	0·0640	110·59	302·07	3·64	219·72

* Except for those relating to solutions in carbon tetrachloride, the values of $\alpha\varepsilon_1$ and βd were recalculated from Kumler and Huitric's data [2] and results in n-heptane are used as those in n-hexane; the values for $\alpha\varepsilon_1$ in benzene and dioxan were checked by measuring one solution in each solvent in this laboratory and finding the agreement with ref. 2 satisfactory. † Values for γn_1 are taken as $(n_{\text{pure solute}} - n_{\text{solvent}})$ for all $_\infty({}_mK_2)$ calculations; such a simplification should not introduce any significant error.

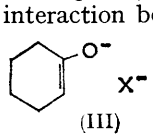
DISCUSSION

Following the vector analytical approach of Corey and Sneen,[11] and adopting their geometric parameters, the partial molecular co-ordinates for the 2-halogenocyclohexanones emerge as those given beside Figure 1.

We take the moment [3a] of the C=O and C–X bonds as 2·84 and 1·91 D, and bond polarisabilities [12] as follows:

	C–H	C–C	C=O	C–Cl	C–Br
$10^{24}b_L$	0·64	0·99	2·30	3·18	4·65
b_T	0·64	0·27	1·40	2·20	3·10
b_V	0·64	0·27	0·46	2·20	3·10

[The bond polarisabilities from the methyl halides are used here for the C–X links in 2-halogenocyclohexanones because in the equatorial conformer (I) the dipole–dipole interaction between the carbonyl and the C–X groups will tend to decrease the polarisability of the C–X link.[13] Although participation of the valence-bond structure (III) [3c] in the ground state of the axial conformer (II) may increase the polarisability of the C–X, the molar Kerr constants calculated for (II), using bond polarisabilities from isopropyl [13] and t-butyl halides, are quite small (between +2 and -3×10^{-12}) irrespective of whether X = Cl or Br; therefore, we are confident that such a choice is justified.]


(III)

The calculated dipole moments and molar Kerr constants for the conformers (I) and (II)

[11] E. J. Corey and R. A. Sneen, *J. Amer. Chem. Soc.*, 1955, **77**, 2505.
[12] R. J. W. Le Fèvre, *J. Proc. Roy. Soc. New South Wales*, 1961, **95**, 1.
[13] Unpublished results.

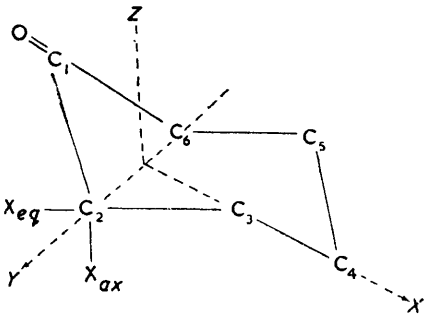


FIGURE 1. Partial molecular geometry of 2-halogenocyclohexanone

C_1 (−0·732, 0, 0·258), C_2 (0, 1·340, 0), C_3 (1·430, 1·270, 0·554), C_4 (2·130, 0, 0), C_5 (1·430, −1·270, 0·554), C_6 (0, −1·340, 0), O (−1·895, 0, 0·668); X_{eq} * (a) X = Cl (−0·869, 1·301, 0·777), (b) X = Br (−0·958, 1·435, 0·856); X_{ax}: * (a) X = Cl (0·045, 0·318, −1·728), (b) X = Br (0·050, 0·351, −1·904).

* All relative to C_2 and based on bond lengths of C–Cl and C–Br of 1·76 and 1·94 Å, respectively.

then appear as in Table 3. The values from experiment recorded in Table 2 correspond to percentage contributions from the conformer (I), computed by the equation

$$\% \text{ contribution of (I)} = \frac{[({}_mK_2)_{obs.} - ({}_mK_2)_{calc.} \text{ for (II)}]}{[({}_mK_2)_{calc.} \text{ for (I)} - ({}_mK_2)_{calc.} \text{ for (II)}]},$$

in the two 2-halogenocyclohexanones, as given in Table 4.

TABLE 3

Calculated polarisability semi-axes, dipole moments, molar Kerr constants, and the relevent direction cosines

Compound	$10^{24}b_i$ (calc.)	Direction cosines with X	Y	Z	μ (D) (calc.)	$10^{12}{}_mK_2$ (calc.)
2-Chlorocyclohexanone (I)	b_1 = 14·26	0·751	−0·628	−0·204	4·29	382·4
	b_2 = 13·40	0·630	0·774	−0·063		
	b_3 = 10·70	0·197	−0·082	0·977		
2-Chlorocyclohexanone (II)	b_1 = 13·64	0·969	−0·099	−0·227	2·81	37·6
	b_2 = 13·21	−0·119	0·990	−0·073		
	b_3 = 11·48	0·218	0·098	0·971		
2-Bromocyclohexanone (I)	b_1 = 14·32	0·700	0·710	−0·073	4·29	451·4
	b_2 = 15·68	−0·681	0·694	0·233		
	b_3 = 11·63	0·217	−0·113	0·970		
2-Bromocyclohexanone (II)	b_1 = 14·60	0·928	0·193	−0·320	2·81	1·9
	b_2 = 14·15	−0·246	0·960	−0·134		
	b_3 = 12·85	0·281	0·203	0·938		

TABLE 4 *

Percentage equatorial 2-chloro(or 2-bromo)cyclohexanone in various solvents at 25°

Solvent	From dipole moment	From i.r. (by temp. variation)	From u.v.	From equil. of 4-t-butyl derivatives	From $({}_mK_2)_{obs.}$
n-Hexane †	24(15)	27(—)	37(—)	—(—)	37(21)
Carbon tetrachloride	—(—)	—(26)	—(—)	43(—)	38(13)
Benzene	44(24)	—(40)	—(—)	63(—)	76(43)
Dioxan	63(38)	—(43)	63(—)	72(—)	79(48)

* All data, except those from molar Kerr constants, are taken from refs. 3*b* and *c*. † The i.r. and u.v. measurements were in " iso-octane."

Since all the molar Kerr constant measurements were carried out at high dilution, the figures given in Table 4 should closely approach those appropriate for infinite dilutions. In all cases, except that of 2-bromocyclohexanone in n-hexane, the contribution from the more polar conformer (I) is solvent-dependent and increases in the order n-hexane ≤ carbon tetrachloride < benzene ≤ dioxan; the amount of (I) present in the equilibrium mixtures, estimated from the molar Kerr constants observed, agree with previous work [3b,c] within experimental error. It has already been proved [3a] that 2-bromocyclohexanone associates strongly in hydrocarbons; the higher molar Kerr constant observed, and therefore greater participation of the conformer (I) in n-hexane as compared with that in carbon tetrachloride, is not unexpected. However, such a difference may be quite small, as revealed in our p.m.r. spectral study to be discussed later. It is interesting to

note that the percentage of (I) in the equilibria calculated from dipole moment measurements is consistently lower than values derived from other methods. A possible reason is that the moments, based on those of *cis*-2-chloro(or 2-bromo)-4-t-butylcyclohexanone and its *trans*-isomer, taken as 4·29 (4·27) and 3·17 (3·20) D for (I) and (II), respectively,[3b,c]

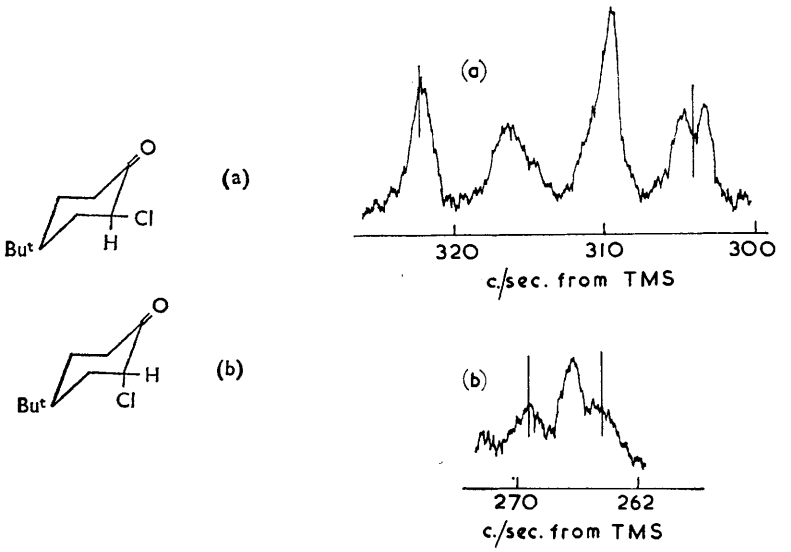


FIGURE 2. Proton spin coupling parameters for the 2-protons in *cis*- and *trans*-2-chloro-4-t-butylcyclohexanones

$J(H_\alpha,H_{\beta ax}) + J(H_\alpha H_{\beta eq}) =$ (a) 18·0; (b) 5·5 c./sec.

are too large; we have found that 4-t-butylcyclohexanone exhibits a moment of 3·2 D in carbon tetrachloride compared with the 3·0 D shown by cyclohexanone. The result of using larger moments for the conformers (I) and (II) is to increase the apparent contribution from (II) in these equilibria at the expense of (I).*

Proton Magnetic Resonance Spectra.—In conjunction with polarisation and polarisability measurements, we have also recorded the p.m.r. spectra of 2-chloro- and 2-bromo-cyclohexanones in a number of solvents and as neat liquids. Although both the shielding parameter and the nuclear spin coupling approach to the conformational analysis of 2-bromocyclohexanone have been demonstrated by Garbisch,[5] only the nuclear spin parameters are used in this study because these are not sensitive to intermolecular interactions such as association, preferential orientation, etc., which would affect the shielding parameters.

cis- and *trans*-2-Chloro-4-t-butylcyclohexanone were taken as conformationally homogenous models from which are extracted $J_{(I)Cl}$ and $J_{(II)Cl}$ (these notations have the same meaning as in ref. 5). The values, determined in *ca.* 15% w./w. solutions, are shown

* An alternative explanation has been provided by one of the referees of this Paper. "If the 2-halogenocyclohexanones associate, the moment of the associated form will probably be lower than that of the monomer, for either (I) or (II), so the amount of (I) calculated from the results, assuming that only monomers need be considered, is going to be low compared with that calculated by methods which are not so affected by the association. In brief, association to a less polar form will give the appearance of a smaller amount of the more polar monomer. This seems the simplest explanation, or at least a vital part of the explanation of the discrepancy between the electric dipole moment results and those from the other methods." Nevertheless, Allinger and Allinger pointed out [3a] that association phenomena, which would be expected to stabilise the more polar conformer (I), are relatively unimportant for 2-bromocyclohexanone as a solute in carbon tetrachloride, benzene, dioxan, etc., at moderate concentrations. It is, therefore, our belief that the referee has alluded to only one of the several factors probably involved in the equilibria of 2-halogenocyclohexanones.

in Figure 2. Together with $J_{(I)Br} = 18{\cdot}2$ c./sec. and $J_{(II)Br} = 5{\cdot}7$ c./sec. from ref. 5, they provide the basis for estimating the percentage contribution from the conformer (I) in various solvents for the two corresponding 2-halogenocyclohexanones.

Some slight perturbation and splitting are observed for the 2-proton resonances of *cis*- and *trans*-2-chloro-4-t-butylcyclohexanone as in the bromo-analogues;[5] possibly, they arise from the same sort of interactions as found in the bromo-compounds. The similarity between $J_{(I)Cl}$,$J_{(II)Cl}$ and $J_{(I)Br}$,$J_{(II)Br}$ seems to indicate that the chlorine and the bromine atoms in 2-halogeno-4-t-butylcyclohexanones have approximately the same electro-

TABLE 5

J_0 for 2-chloro(2-bromo)cyclohexanones as solutes or undiluted, and the percentage of (I) in the equilibria

Solvent	J_0 (c./sec.)	% of (I)	Solvent	J_0 (c./sec.)	% of (I)
n-Hexane	10·8(8·7)	42(24)	Dioxan	13·8(11·5)	67(46)
Carbon tetrachloride ...	10·8(8·2)	42(20)	Undiluted	14·0(11·7)	68(48)
Benzene	13·6(10·5)	65(38)			

TABLE 6

Values of J_0 and the percentage contribution from the equatorial conformer (I) as a function of the mole percentages of 2-chlorocyclohexanone in carbon tetrachloride

Mole % of 2-chlorocyclohexanone	2	5	10	25	33	50	100
J_0 (c./sec.)	10·3	10·3	11·5	12·6	13·1	13·4	14·0
Mole % of (I)	38	38	48	57	61	63	68

negativity [14] provided that there are no distortions of the normal chair forms of these molecules. Such argument is, further, supported by the dipole moments [3b,c] reported in benzene at 25°: X = Cl (I) 4·29 D, (II) 3·17 D; X = Br (I) 4·27 D, (II) 3·20 D. Furthermore, the axial 2-proton of *trans*-2-chloro-4-5-butylcyclohexanone resonates at a lower magnetic field than the equatorial 2-proton, consistently with the shielding effect of the carbonyl group,[15] and the axial proton shows a J_{ae} of 5·4 c./sec., thus adding to the evidence put forward by Williams and Bhacca [16] that J_{ae} is usually much larger than J_{ea} or J_{ee} (which is normally very close to J_{ea}).

In Table 5, are summarised the observed separations between the terminal lines of the C_2-proton resonances (J_0) for 2-chloro(2-bromo)-cyclohexanones as solutes in different solvents and alone. The percentage contributions (N_1) from the conformer (I) are computed by means of the relationship:

$$N_1 = (J_0 - J_{(II)})/(J_{(I)} - J_{(II)})$$

The concentration of the solutions used is *ca.* 5% molar.

Comparing Tables 3 and 5, it can be seen that the conclusion reached, regarding the mobile equilibria in 2-halogenocyclohexanones, by p.m.r. spectroscopy is in excellent agreement with those obtained by other physicochemical methods. Here, the abnormality of 2-bromocyclohexanone in n-hexane is, again, revealed; within experimental error, 2-chlorocyclohexanone does not seem to behave in the same way; this fact is also clearly indicated by the polarisability data. To complete our study on the 2-halogenocyclohexanones, we record the values of J_0 and the percentage contribution from the equatorial conformer (I) of 2-chlorocyclohexanone as a function of the mole percentages in carbon tetrachloride as Table 6. Table 6 demonstrates once more that the contribution from the more polar conformer (I) increases as the dielectric constant of the solvent increases, and

[14] K. L. Williamson, *J. Amer. Chem. Soc.*, 1963, **85**, 516.
[15] K. M. Wellman and F. G. Bordwell, *Tetrahedron Letters*, 1963, 1703.
[16] D. H. Williams and N. S. Bhacca, *J. Amer. Chem. Soc.*, 1964, **86**, 2742.

that the use of solutions of molar fraction of 5% or less to approximate to infinite dilution, as in the present work, is justified.

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