

## THE CONFORMERS OF 2-BROMOCYCLOHEXANONE

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**Abstract**—The infrared and ultraviolet carbonyl absorptions of 2-bromocyclohexanone have been examined in a variety of solvents. The data are consistent with an equilibrium *axial*-2-bromocyclohexanone  $\rightleftharpoons$  *equatorial*-2-bromocyclohexanone for which the equilibrium constant varies as a function of solvent over the range 0.3–1.0. The earlier and apparently contradictory data in the literature have been re-examined and are considered to be consistent with this conclusion.

CONFORMATIONAL analysis of 2-bromocyclohexanone (I) suggests that either the axial or the equatorial conformation would be possible for the 2-bromine substituent. Accordingly, an equilibrium mixture of *axial*-(Ia) and *equatorial*-2-bromocyclohexanone (Ie) might be expected to exist. A simpler situation could occur if one conformation for the bromine (axial or equatorial) were much preferred and I would then be essentially conformationally pure. The following data were interpreted by Corey<sup>1</sup> as evidence that 2-bromocyclohexanone (I) had almost exclusively the axial conformation for the bromine. First, the main infra-red carbonyl absorption maximum of I (carbon tetrachloride solution) was only slightly displaced from that of cyclohexanone (II), a fact which indicated the presence of the axial conformer.<sup>2</sup> A shoulder on the main absorption band which occurred at 14 cm<sup>-1</sup> higher frequency relative to II was assigned<sup>2</sup> to the conformer which had the bromine equatorial, but the slight intensity of the shoulder was considered to indicate that only a "small amount" of the *equatorial* isomer Ie was present. Second, support for the conclusions drawn from the infrared spectra was obtained when a theoretical value for the "minimum" energy difference between the two conformations was calculated. The magnitude of this energy difference predicted an equilibrium mixture that contained "at least 97 per cent" of *axial*-2-bromocyclohexanone.

The dipole moment of I in heptane, benzene and dioxane solution was determined by Kumler and Huitric.<sup>3</sup> In the light of Corey's work, and especially the energy calculations, the experimentally determined moment of I in all solvents would be expected to be virtually identical with the theoretical dipole moment calculated for Ia. It was found, however, that the dipole moment of I increased with increasing dielectric character of the solvent employed for the measurement and was of such a magnitude in each medium as to indicate far less than the estimated<sup>1</sup> 97 per cent of Ia to be present. These data might have been interpreted as consistent with an equilibrium mixture of Ia and Ie which was influenced by the solvent but, because of Corey's work, Kumler and Huitric preferred to consider that a third isomer, a "flexible form" whose conformation was intermediate between Ia and Ie, was present.

<sup>1</sup> E. J. Corey *J. Amer. Chem. Soc.* **75**, 2301 (1953).

<sup>2</sup> R. N. Jones, D. A. Ramsay, F. Herling and K. Dobriner *Ibid.* **74**, 2828 (1952).

<sup>3</sup> W. D. Kumler and A. C. Huitric *Ibid.* **78**, 3369 (1956).

The two investigations which have ascribed very different conformational situations for 2-bromocyclohexanone (I) employed different physical quantities to describe the system I. To correlate the earlier data and to provide a starting point for the present study it was necessary to choose the most reasonable individual bond moments for the carbon-bromine and carbon-oxygen dipoles of I and to determine the dipole angles of Ia and Ic as precisely as possible. These two sets of constants were necessary for the calculations of the theoretical dipole moments of Ia and Ic and of the energy difference between the two conformers. Corey deliberately chose physical constants which would yield a minimum energy difference,<sup>1</sup> and it should be noted that estimates of the individual bond moments and of the dipole angles as well as a simple method by which the geometry of I could be calculated were not then available. Kumler and Huitric<sup>3</sup> assigned the individual bond moments from consideration of related studies, but apparently calculated dipole angles for Ia and Ic on the basis of a geometrically inadequate model.

A more accurate representation of the structure of I than was used by the previous workers is now available, for Corey and Sneed<sup>4</sup> have determined by vector analysis the exact geometry of "cyclohexylidene" (chair form). With a simple correction to replace the exocyclic methylene carbon by oxygen, this geometry allowed exact calculation of the molecular geometry of cyclohexanone (II) and thus of the system I.\* The dipole angles ( $\chi$ ) of  $109^{\circ}51'$  and  $51^{\circ}54'$  and the dihedral angles ( $\phi$ ) of  $102^{\circ}13'$  and  $16^{\circ}17'$  were determined for Ia and Ic, respectively.<sup>5</sup> The geometry of the two conformations is summarized in Figure 1.

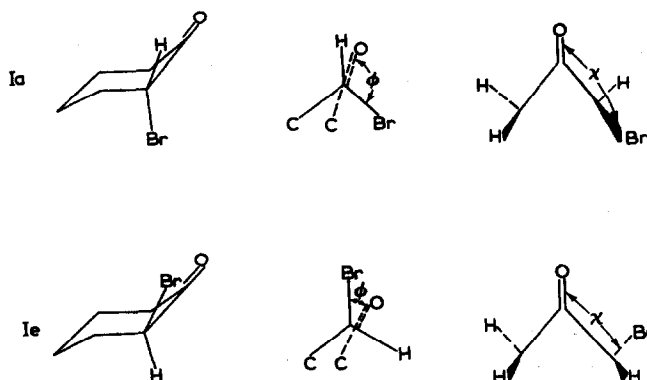


FIG. 1.

The dipole moments determined for cyclohexyl bromide and cyclohexanone (II) were  $2.1 D^6$  and  $2.9 D^7$ , respectively. As evidenced by work with other compounds wherein rigid models were employed to describe a molecule,<sup>8</sup> the values determined

\* Since the necessary data are not available, the model here assumed does not take into account the probable slight spreading of the angles by dipole-dipole repulsions.

<sup>1</sup> E. J. Corey and R. A. Sneed *J. Amer. Chem. Soc.* **77**, 2505 (1955).

<sup>2</sup> R. C. Cookson *J. Chem. Soc.* 282 (1954) estimated dihedral angles of  $105^{\circ}$  and  $15^{\circ}$  with no indication as to the methods employed to obtain these values.

<sup>3</sup> O. Hassel and E. Naeshagen *Z. Physik. Chem. B* **15**, 373 (1932).

<sup>4</sup> R. J. W. LeFevre *Dipole Moments* p. 63. John Wiley, New York (1953).

<sup>5</sup> P. Bender, D. L. Flowers and H. L. Goering *J. Amer. Chem. Soc.* **77**, 3463 (1955).

for the simple cases will not describe the existing individual bond moments of the carbon-halogen and carbon-oxygen dipoles of a molecule such as I because inductive interaction between adjacent dipoles operates to lower the actual bond moment of each dipole. The adjusted values of 1.91 D ( $\mu_{\text{C-Br}}$ ) and 2.83 D ( $\mu_{\text{C=O}}$ ) were selected by Kumler and Huitric by analogy with other data<sup>8</sup> as the best values for the case at hand and the present study employs these bond moments for each conformer also.\* Table 1 summarizes the physical quantities which are to be utilized in the present discussion and compares them with the values of the two previous investigations.

*Theoretical energy calculations.* The total energy difference between Ia and Ie is the net result of a steric and an electrostatic energy unique to each conformer. Equation (1) was employed by Corey<sup>1</sup> to calculate the electrostatic energies,  $E_e$ , of Ia and Ie, and this equation was originally derived for two (magnetic) dipoles interacting in

$$E_e = \frac{\mu_{\text{C-Br}}\mu_{\text{C=O}}}{r^3} (\cos \chi - 3 \cos \alpha_1 \cos \alpha_2) \quad (1)$$

a field of constant force (vacuum, dielectric constant unity).<sup>9</sup> However, in a molecule in a liquid phase the effective dielectric constant D in the vicinity of the dipoles is certainly not unity. Thus the electrostatic energies calculated from equation (1) must be divided by the dielectric constant of the medium through which the dipoles interact.† Although no way is available to precisely calculate this term an approximation to a similar situation was suggested by Kirkwood and Westheimer.<sup>10</sup> A molecule which contained interacting charges was considered to outline a sphere inside which the charges were placed and the effective dielectric constant within this sphere was proposed to have the value 2, this value being considered more reasonable than unity. The sphere was then considered to be surrounded by a medium having a dielectric constant equal to that of the solvent. This approximation enabled the cited authors to obtain calculated values for dissociation constants of various substituted organic acids which were in good agreement with experiment, and their success would seem to justify the use of this concept of a local dielectric constant for the present study. If the value 2 is taken to represent the dielectric constant of the medium within the molecule, and if this molecule is placed in a bulk medium of dielectric constant 2 (heptane solution), then the electrostatic energies calculated for Ia and Ie may be more reasonably expected to approximate the real situation.

The steric energy difference of Ia and Ie is difficult to assess for there are few pertinent data which permit calculation of this term. Corey<sup>1</sup> estimated 0.4 kcal/mole for this difference, the energy of Ia being more positive, and this value was retained for the present calculations.

Employing the physical quantities developed in the present study for system I (Table 1) and equation (1) divided by the dielectric constant 2, the difference in electrostatic energy between Ia and Ie in heptane solution was calculated to be 1.93

\* Since Ia and Ie have quite different dipole angles, the mutual inductance of the adjacent dipoles may be slightly different for each conformer. As a result, the actual individual bond moments of Ia may be larger and those of Ie are possibly smaller.<sup>8</sup> Further refinement of these constants is not readily accomplished and would in any event provide only a minor change in the calculated dipole moments of each conformer.

† This relationship follows from classical electrostatics which shows that the interaction energy of charges in a medium is equal to the energy in vacuum divided by the dielectric constant of the medium.

<sup>9</sup> J. H. Jeans *Mathematical Theory of Electricity and Magnetism* (5th Ed.) p. 377. The University Press, Cambridge (1933).

<sup>10</sup> J. G. Kirkwood and F. H. Westheimer *J. Chem. Phys.* 6, 506, 513 (1938).

TABLE 1

Conformer	Dipole angles	$\mu_{C-Br}$	$\mu_{C=O}$	Investigation
Ia	109°51'	1.91 D	2.83 D	This study
Ie	51°54'			
Ia	125°	1.91 D	2.83 D	Kumler and Huitric <sup>8</sup>
Ie	55°			
Ia	134°	1.2 D	2.5 D	Corey <sup>1</sup>
Ie	50°			

kcal/mole, the Ia conformer being the more stable. The steric energy of 0.4 kcal/mole which destabilizes Ia provided a total energy difference of 1.53 kcal/mole; this energy difference indicates an equilibrium mixture comprised of 93 per cent Ia and 7 per cent Ie for heptane solution at 25°. The dipole moment data<sup>8</sup> are consistent with an equilibrium mixture in heptane solution which contains 68 per cent Ia and 32 per cent Ie (Table 2). In view of the approximations required for the energy calculations, the

TABLE 2.—CARBONYL ABSORPTION DATA OF I AND II IN VARIOUS SOLVENTS

No.	Solvent	$\lambda_{max} \text{ cm}^{-1}$			Molar- rity I and II	Optical densities		% I as Ia infrared	% I as Ia dipole moments <sup>a</sup>
		Ie	Ia	II		Ia	II		
1	Homogeneous	1749	1732	1724	—	—	—	c. 50 <sup>b</sup>	—
2	Carbon tetrachloride	1742	1730	1730	0.126	0.330	0.447	74	
3	Chloroform	1736	1721	1711	0.120	0.348	0.500	68	
4	Carbon disulfide	1738	1726	1726	0.137	0.348	0.509	68	
5	Benzene	1741	1729	1724	0.127	0.300	0.491	60	60
6	Dioxane	1740	1728	1719	0.119	0.259	0.457	57	51
7	Dimethyl sulfoxide	1743	1729	1717	0.133	0.260	0.494	53	
8	<i>n</i> -Heptane	1741	1728	1732	0.122	0.232	0.516	45 <sup>b</sup>	68
9	Cyclohexane	1743	1728	1737	0.130	0.297	0.544	55 <sup>b</sup>	

<sup>a</sup> Calculated with the theoretical dipole moments  $\mu_{Ia} = 2.82$  D,  $\mu_{Ie} = 4.34$  D, obtained employing the constants of the present study (Table 1), and the equation<sup>17</sup>  $\mu_{observed}^2 = N_a \mu_{Ia}^2 \pm N_e \mu_{Ie}^2$

<sup>b</sup> See text for discussion concerning these apparently anomalous values.

agreement with the dipole moment studies is reasonable. Of more significance is the qualitative conclusion to be derived from these calculations that an equilibrium mixture of Ia and Ie may be expected to exist in which the minor conformer is present to the extent of *at least* several per cent.

For interconvertible isomers of different electrostatic energies, the composition of their equilibrium mixture is influenced by the solvent in which the measurement is made.<sup>11</sup> For the system I, conformer Ie has the higher electrostatic energy. Accordingly the position of the predicted Ia  $\rightleftharpoons$  Ie equilibrium would be expected to be displaced to the right in solvents of higher dielectric constant than heptane. This shift

<sup>11</sup> K. Kozima, K. Sakashita and S. Maeda *J. Amer. Chem. Soc.* 76, 1965 (1954); A. Tulinskie, A. DiGiacomo and C. P. Smyth *Ibid.* 75, 3552 (1953).

is exactly what has been found from the dipole moment study of I in various solvents<sup>3</sup> and from the spectral studies of the present investigation.

*Spectral studies.* The infrared and ultraviolet absorption curves of I and II were examined in various solvents, and these spectral studies suggest an observable equilibrium.\* The infrared data obtained for each solvent allowed an estimation of the position of the equilibrium for the particular medium and the ratio of *axial* to *equatorial* conformer was obviously influenced by the solvent.

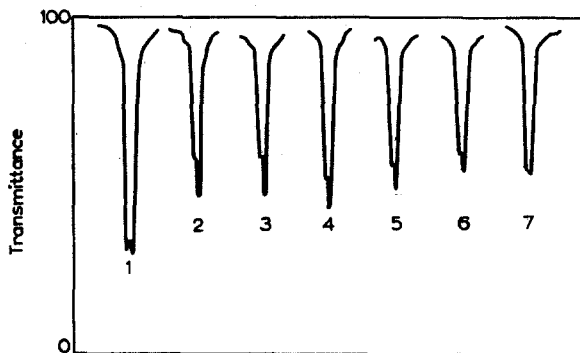


Fig. 2. Carbonyl absorption bands of 2-bromocyclohexanone in various solvents. The band numbers correspond to those described in Table 2.

The infrared carbonyl absorptions of 2-bromocyclohexanone (I) and cyclohexanone (II) in the solvents chloroform, carbon disulfide, carbon tetrachloride, *n*-heptane, cyclohexane, benzene, dioxane, and dimethyl sulfoxide were compared at similar molar concentrations and the curve of I in each of these solvents was composed of two maxima which could not be completely resolved, as is shown in Fig. 2. The absorption band which was displaced to a higher frequency from the maximum of cyclohexanone was assigned to Ie and the absorption band which was at a similar frequency to that of II was assigned to Ia.<sup>2</sup> Table 2 records the carbonyl frequencies.

Analysis of the infrared spectra to determine the amounts of Ia and Ie present in the various solutions was complicated by the fact that the conformers cannot be obtained in pure form and the absorption curves of Ia and Ie were not cleanly separable. However, an *axial*  $\alpha$ -bromoketosteroid has an integrated carbonyl absorption intensity virtually identical with the similar area calculated for the parent ketosteroid.<sup>2</sup> This relationship suggested that the ratio of extinction coefficients of the Ia and II maxima would serve to estimate the per cent of Ia present in the various solutions, and this simplifying approximation was employed for the present study. The amount of Ie present was taken to be the difference between 100 per cent and the estimated per cent of Ia. An alternative method of curve resolution is to reflect the side of the principle band (extinction coefficient plotted against frequency) away from the interfering band about its axis and to graphically integrate separately the symmetrical band

\* Certain aliphatic  $\alpha$ -halocarbonyl compounds exist as a mixture of rotational isomers and the presence of these isomers has been confirmed from the infrared spectra. L. J. Bellamy, L. C. Thomas and R. L. Williams [*J. Chem. Soc.* 3704 (1956)], studied the infrared spectra of some  $\omega$ -chloroacetophenones at different temperatures, and each of these compounds had two carbonyl absorption bands which were not completely resolvable. From the manner in which the relative intensities of the maxima were influenced by temperature, assignment of each of the carbonyl absorption bands to a particular rotational isomer was possible.

and the absorption outside the symmetrical band.<sup>13</sup> This procedure is carried out with difficulty with spectra obtained on the Baird instrument because the areas are so small. This admittedly inaccurate method was also applied in the present case, and the areas of the curves so obtained (assuming the same inherent integrated band intensities) indicated, for example, 80 per cent and 73 per cent Ia in chloroform and benzene, respectively. Since the equatorial band is probably in fact of lower inherent intensity,<sup>3</sup> these would be minimum values, and they certainly are in as good agreement with the more accurate values found from the extinction coefficients as can be expected.

For the solvents carbon tetrachloride, chloroform, carbon disulfide, benzene and dioxane, the carbonyl absorption curve had a main band (Ia isomer) with a shoulder on the higher frequency side (Ie isomer) and the amounts of Ia present in these solutions varied in a regular manner from 74–57 per cent (Table 2). Dimethyl sulfoxide ( $D \approx 45$ ) solutions of I afforded an absorption curve having two non-resolvable bands of nearly equal intensity. The amount of Ia present was estimated to be 50 per cent from the ratio of the extinction coefficients of Ia and II, and the shift in equilibrium composition of the mixture was in the direction consistent with this more polar solvent acting to stabilize the conformer which has the higher electrostatic energy, Ie.

The carbonyl bands in the infrared spectra of I in *cyclohexane* and *n*-heptane showed two maxima of equal intensity which as before were not completely resolvable. From the non-polar character of these hydrocarbon solvents, one would expect the equilibrium mixture to be similar to that obtained for benzene. A reason for the apparent anomaly was evident when the molecular weight of I was determined in *cyclohexane* solution at the concentration employed for the infrared study. The experimental value was 2.7 times greater than the value for the monomeric I, and a slight decrease of this association was observed when the determination was repeated with a more dilute solution. The infrared band attributed to Ie likewise decreased in intensity relative to the Ia band upon dilution. *Cyclohexanone* (II) was also associated at the concentrations employed for the infrared study, and this compound afforded a significantly lower value for the experimentally determined molecular weight in a more dilute solution. Such association phenomena under similar circumstances are well known; for example, acetic anhydride is complexed in *cyclohexane*.<sup>13</sup> The low melting point of *n*-heptane prevented molecular weight determinations from being conveniently performed with it as solvent, but the similarity of *n*-heptane and *cyclohexane* and the virtually identical contour of the infrared carbonyl absorption curves of I obtained in the two solvents strongly suggest that I is also associated in *n*-heptane solutions. The amounts of Ia estimated from the infrared spectra would be lower than the values expected from the dielectric constants of these hydrocarbon solvents, for the association phenomena would be expected to create areas of high dielectric constant in the immediate vicinity of the carbonyl groups and, as a result, the equilibrium  $Ia \rightleftharpoons Ie$  would be displaced to the right.\* No such effect was noticed in the

\* *A priori* a reasonable alternative would be that one band was due to the associated form and the other to the unassociated form. This possibility was excluded on the basis that neither *cis*- nor *trans*-2-bromo-4-*t*-butylcyclohexanone (unpublished results), compounds which are constrained to essentially one conformation<sup>14,15</sup> but presumably still capable of carbonyl association, exhibits an analogous change in their respective carbonyl absorptions with change of solvent from carbon tetrachloride to *n*-heptane.

<sup>13</sup> R. N. Jones, W. F. Forbes and W. A. Mueller *Canad. J. Chem.* **35**, 504 (1957).

<sup>14</sup> D. C. Jones *J. Chem. Soc.* 1193 (1928).

<sup>15</sup> S. Winstein and N. J. Holness *J. Amer. Chem. Soc.* **77**, 5562 (1955).

<sup>16</sup> E. L. Eliel and R. S. Ro *Chem. & Ind. (Rev.)* 251 (1956).

dipole moment study of I in heptane solution, presumably because these measurements were performed at lower (typical) concentrations where the association would be negligible. The ultraviolet absorption of I in *n*-heptane solution (see later) was obtained with a more dilute solution than was necessary for the infrared study and no association of I at this concentration ( $10^{-3}$  M) was evident.

The experimentally determined molecular weight of I in benzene at the concentration employed for the infrared study was identical with the calculated value. Since the absorption curves of I in carbon tetrachloride, chloroform, carbon disulfide, benzene and dioxane formed a progressive series, no association of I in these media was indicated. Freezing point determinations of I and II in dimethyl sulfoxide also established that no association occurred in this solvent, the experimental and the actual molecular weights being identical. Consequently the shift in the equilibrium in this case was attributed to the high dielectric character of the dimethyl sulfoxide medium. The infrared absorption of pure I (no solvent) had two bands of nearly equal intensity and the contour of the curve was similar to, though more completely resolved than, that afforded by I in *cyclohexane*, *n*-heptane, and dimethyl sulfoxide. The estimated 50 per cent Ia composition, here again, is probably the result of association. This conclusion is supported by the fact that a simple ketone, acetone, is significantly dimerized even in the vapor phase.<sup>16</sup>

Table 2 records the estimated amounts of Ia present in the particular solvents employed for the infrared and the dipole moment studies. It is seen that the infrared analyses of the benzene and dioxane solutions of I, although of approximate nature in view of the difficulties, afforded values in reasonable agreement with those now calculated from the dipole moment data.

The ultraviolet absorption curves of I and II in carbon tetrachloride, *n*-heptane and 95 per cent ethanol were examined and the individual absorption maxima and intensities are summarized in Table 3. For each solvent I had its absorption maximum at longer wave length than the parent compound, the displacement of ca. 22  $m\mu$  indicating the presence of the *axial* conformer.<sup>17</sup> This does not contradict the infrared studies for the ultraviolet extinction coefficient of an equatorial  $\alpha$ -bromoketosteroid in all solvents is appreciably lower than that of an axial  $\alpha$ -bromoketosteroid, and, indeed, approximates that of the parent ketone at all wave lengths.<sup>17</sup> The amounts of Ie estimated to be present from the dipole moment and infrared studies are thus too small to be detected by a separate maximum in the ultraviolet spectra, but the maxima do show a skewing which is not inconsistent with the presence of comparable amounts of Ie and Ia in 95 per cent ethanol and somewhat less Ie in the other solvents. The difference between the intensity of the absorption maximum of an *axial*  $\alpha$ -bromoketosteroid and the parent compound has been found to be at least 0.5 log  $\epsilon$  units for ethanol solutions.<sup>5</sup> In the present study the difference in log  $\epsilon$  of I and II was of this magnitude for the non-polar solvents but was appreciably lower for the 95 per cent ethanol medium (Table 3). This smaller difference in absorption intensity between I and II in the more polar solvent is consistent with a shift of the position of the equilibrium toward Ie as a consequence of the relatively high dielectric character of 95 per cent ethanol.

It would seem that the conclusions drawn by each previous investigator differ

<sup>16</sup> R. E. Pennington and K. A. Kobe *J. Amer. Chem. Soc.* **79**, 300 (1957).

<sup>17</sup> S. Mizushima *Structure of Molecules and Internal Rotation* p. 34. Academic Press, New York (1954).

primarily in degree because if the experimental data only are considered the qualitative conclusions from each study are in fact in agreement: (1) The infrared spectrum of I established the presence of both the *equatorial*- and the *axial*-2-bromocyclohexanone in carbon tetrachloride solution and (2) the dipole moment study can be most simply interpreted as the result of an equilibrium mixture of Ia and Ib the composition of which was affected by solvent. The spectral studies herein reported are hence consistent with all of the experimental data of the earlier work. The proposed modifications to describe the geometry of I and to account for the effect of the

TABLE 3.—ULTRAVIOLET ABSORPTION DATA FOR I AND II IN VARIOUS SOLVENTS

Solvent	$\lambda_{\max}$ m $\mu$		log $\epsilon$		(I-II)	
	I	II	I	II	$\lambda_{\max}$	log $\epsilon$
Carbon tetrachloride	312	290	2.02	1.41	+22	0.61
<i>n</i> -Heptane	312	291	1.98	1.18	+21	0.80
95 per cent ethanol	307	282	1.37	1.15	+25	0.22

solvent upon the electrostatic energies of the two conformers have served to effect a more complete correlation of the dipole moment studies and the calculated theoretical energy difference between the two conformers. An equilibrium ratio of *equatorial*- to *axial*-2-bromocyclohexanone which varies with solvent from 0.3 to 1.0 appears to be entirely consistent with all the data.

Consideration of a third conformer, the "flexible form",<sup>18</sup> would seem unnecessary for all the data may now be satisfactorily interpreted employing the simpler situation of the two conformers which are securely identified from other systems. Although a strict proof of the non-existence of the flexible form in the present system has not been obtained it would seem improbable that the flexible form would fit the observed facts, especially the spectral data.

Various alkylated 2-bromocyclohexanones have been studied by Corey and co-workers.<sup>19</sup> Their data also appear to be consistent with the conclusions drawn in the present work. It is of interest that these investigators concluded that 2-bromo-6,6-dimethylcyclohexanone existed as an equilibrium mixture of *axial* and *equatorial* conformers on the basis that two distinct carbonyl infrared absorption maxima were observed<sup>19a</sup> and the separation of 23 cm<sup>-1</sup> for these bands apparently allowed easy resolution. In the present study the two infrared maxima of the homogeneous sample of I were 17 cm<sup>-1</sup> apart while in various solvents the separation of the bands was only 12–15 cm<sup>-1</sup> (Table 2). Fig. 2 shows that the resolution of the two maxima, although incomplete in the latter cases, was better for the homogeneous sample.

#### EXPERIMENTAL

**2-Bromocyclohexanone (I).** The procedure used was a modification of that described for the preparation of 2-chlorocyclohexanone.<sup>20</sup> Cyclohexanone, 10 g, and 30

<sup>18</sup> C. G. LeFevre and R. S. W. LeFevre *J. Chem. Soc.* 3549 (1956); W. Kwestroo, F. A. Meijer and E. Haviga *Rec. Trav. Chim. Pays. Bas.* 73, 717 (1954).

<sup>19</sup> (a) E. J. Corey, T. H. Copie and W. A. Wozniak *J. Amer. Chem. Soc.* 77, 5415 (1955); (b) E. J. Corey *Ibid.* 75, 3297 (1953); (c) E. J. Corey *Ibid.* 76, 175 (1954).



ml of water were placed in a three-necked flask equipped with a stirrer and a dropping funnel. Bromine, 16 g, was added dropwise to the stirred heterogeneous mixture during 1 hour, and a water-ice bath (5°) was employed to cool the reaction. When addition was completed, stirring was continued until the reaction mixture was colorless (30–60 min), the cooling bath being allowed to warm during this period. The crude product was isolated<sup>20</sup> and was distilled through a 2 ft column of the Podbielniak type to give 12 g (65 per cent) of I, b.p. 83° (6 mm),  $n_D^{20}$  1.5096; reported<sup>1</sup>  $n_D^{27}$  1.5093. Pure I could be stored protected from light at 0° for at least several weeks. *cyclo*Hexane and benzene solutions of I showed no evidence of decomposition (pink color) until after several days standing exposed to light at room temperature. Dimethyl sulfoxide solutions of I evidenced decomposition after 5–10 hr at room temperature.

*Infrared studies.* The spectra were obtained employing a Baird Double Beam Infrared spectrophotometer, AB Model. The concentrations of I and II in all solvents were as like as possible (ca. 0.12 M). The stability of pure I (no solvent) to infrared light was established when 3 identical and superimposable spectra were recorded for the sample at 5 min intervals, the cell with the sample being retained in the beam's path during the interim periods. For this reason and the fact that decomposition of various solutions of I was slow at room temperature, the spectra of I in solution are considered to be uncomplicated with impurities. Samples of I were subjected to simple vacuum distillation just before use. Commercial *cyclo*hexanone (II) was purified by distillation,  $n_D^{25}$  1.4475; reported<sup>21</sup>  $n_D^{15}$  1.4520.

*n*-Heptane and spectral-grade *cyclo*hexane were chromatographed on silica gel and the eluates were distilled from phosphorous pentoxide. Dioxane was purified in the usual way.<sup>22</sup> Thiophene-free benzene was dried by azeotropic distillation. The solvents carbon disulfide, chloroform, carbon tetrachloride were those designated "spectral-grade". Dimethyl sulfoxide, commercial grade, was purified by distillation, b.p. 76° (16 mm), m.p. 18.0–18.4°.

The amount of Ia in each solvent was calculated from the ratio of the optical density of Ia to the optical density of II at the same concentration and Beer's Law was assumed to hold for these calculations over the limited range necessary. The optical densities are recorded in Table 2.

*Ultraviolet studies.* The solvents carbon tetrachloride and *n*-heptane were those cited above and the spectra were recorded employing a Beckman Spectrophotometer with Spectracord attachment. The concentrations of I were  $2.55 \times 10^{-3}$  M in *n*-heptane,  $2.35 \times 10^{-3}$  M in carbon tetrachloride,  $2.70 \times 10^{-3}$  M in 95 per cent ethanol; and the corresponding concentrations of II were  $3.03 \times 10^{-2}$  M,  $2.78 \times 10^{-3}$  M, and  $2.40 \times 10^{-2}$  M.

*Melting point determinations.* The *cyclo*hexane used for the spectral studies was not of sufficient purity for ordinary freezing point determinations. The impurities present formed solid solutions, a continuous lowering of temperature being observed with determination of the freezing point of the solvent itself. Accordingly, a modified Rast method was employed. The solution, placed in a simple freezing point apparatus, was cooled to afford crystallization. The bath temperature was allowed to rise and the

<sup>20</sup> M. S. Newman, M. D. Earbman and H. Hipsher *Organic Synthesis Coll.* Vol. III, p. 188. John Wiley, New York (1955).

<sup>21</sup> E. H. Huntress and S. P. Mulliken *Identification of Pure Organic Compounds* p. 382. John Wiley, New York (1946).

<sup>22</sup> L. Fieser *Experiments in Organic Chemistry* p. 369. D. C. Heath and Co. New York (1941).

temperature of the solution was recorded as a function of time. The plot of the data afforded a smooth curve and the point of intersection of the line drawn through the first portion of the curve (melting of the solid suspended in the solution) with the line drawn through the second portion of the curve (warming of the clear solution) was taken as the melting point. Two or three determinations were performed for each solution and excellent reproducibility of the melting points was obtained. That I did not decompose during the experiments was concluded from the fact that pure I could be recovered quantitatively from these solutions. The data are recorded in Table 4.

TABLE 4

Compound	Molal concentration <sup>b</sup>	Observed depression	Molecular weight exp./calcd. value
	Solvent—cyclohexane, $K_f = 20.3^\circ$ .		
I	0.155	1.1790°	2.7
I	0.016	0.1315°	2.4
II	0.154	0.6563°	4.8
II	0.017	0.1313°	2.6
<i>n</i> -heptane	0.153	3.034°	1.02
	Solvent—benzene, $K_f = 5.12^\circ$ .		
I	0.154	0.798°	1.0
	Solvent—dimethyl sulfoxide, $K_f = 2.04^\circ$ .		
benzene	0.113	0.232°	1.00
II	0.111	0.222°	1.03
	Solvent—dimethyl sulfoxide, $K_f = 4.12^\circ$ .		
benzene	0.114	0.469°	1.00
I	0.114	0.464°	1.01

<sup>a</sup> Calculated from the heat of fusion, R. A. Ruehrwein and H. M. Huffman *J. Amer. Chem. Soc.* **65**, 1620 (1943).

<sup>b</sup> Molal concentrations here correspond closely to (molar) concentrations employed for infrared studies.

<sup>c</sup> Two different samples of solvent were employed and the melting point depression was determined using benzene as the standard compound.

**Molecular geometry.** II was placed in the co-ordinate system as used for "cyclohexylidene", and the co-ordinates of the ring carbons and hydrogens of II were assigned the values obtained earlier for the hydrocarbon.<sup>4</sup> The co-ordinates of the carbon having the exocyclic substituent were  $-0.732, 0, +0.258$ , and thus a line drawn from the origin to the carbonyl carbon of II described an angle with the *xy*-plane of  $19^\circ 25'$  and was  $0.778 \text{ \AA}$  in length. Since the carbonyl carbon-oxygen bond (length  $1.22 \text{ \AA}$ ) is simply an extension of this line, the oxygen atom was  $1.998 \text{ \AA}$  from the origin and had co-ordinates relative to the attached carbon of  $-1.151, 0, +0.406$ .

This model of II was used to calculate the dipolar angles involving the carbonyl group and the axial and equatorial 2-substituents. The method is indicated for the equatorial substituent. The co-ordinates of the equatorial hydrogen were  $-0.538, +0.808$  and  $+0.481^4$  relative to the attached carbon. Thus a triangle may be constructed, the three corners of which are the origin and the co-ordinates given above for the oxygen and hydrogen. The oxygen-hydrogen distance in the triangle was thus  $1.017 \text{ \AA}$  and knowing the three sides of the triangle, the desired angle between C=O

and (e) C—H was calculated to be  $51^{\circ}54'$ . The axial hydrogen, in a similar manner, afforded a dipole angle of  $109^{\circ}51'$ .

*Calculation of electrostatic energy of Ia and Ie.* The modified equation (2) was employed for heptane solution:

$$E_e = \frac{\mu_{\text{C-Br}}\mu_{\text{C=O}}}{2r^2} (\cos \chi - 3 \cos \alpha_1 \cos \alpha_2) \quad (2)$$

The quantities

$$r = [a^2 \sin^2 \theta_1 + b^2 \sin^2 \theta_2 - 2ab \sin \theta_1 \sin \theta_2 \cos \phi + (c_0 - a \cos \theta_1 - b \cos \theta_2)^2]^{\frac{1}{2}},$$

$$\cos \alpha_1 = (a^2 + r^2 - c_0^2 - b^2 + 2c_0 b \cos \theta_2)/2ar,$$

$$\cos \alpha_2 = (b^2 + r^2 - c_0^2 - a^2 + 2c_0 a \cos \theta_1)/2br,$$

$$\cos \chi = \sin \theta_1 \sin \theta_2 \cos \phi - \cos \theta_1 \cos \theta_2$$

are those described.<sup>23</sup> In particular, the dipole angles  $\chi$  obtained by the vector analyses of Ia and Ie afford the dihedral angles ( $\phi$ )  $16^{\circ}17'$  for Ie and  $102^{\circ}13'$  for Ia. The bond lengths  $a = \text{C=O} = 1.22 \text{ \AA}$ ,  $b = \text{C-Br} = 1.91 \text{ \AA}$ ,  $c_0 = \text{C-C} = 1.54 \text{ \AA}$ , and the bond angles  $\theta_1 = \text{C-C=O} = 120^{\circ}$ ,  $\theta_2 = \text{C-C-Br} = 109^{\circ}28'$  were employed and the individual bond moments were assigned as  $\mu_{\text{C-Br}} = 1.91 \text{ D}$ ,  $\mu_{\text{C=O}} = 2.83 \text{ D}$ . The electrostatic energies of Ia and Ie were found to be  $-1.71$  and  $+0.22 \text{ kcal/mole}$ , respectively.

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<sup>23</sup> C. P. Smyth, R. W. Dornte and E. B. Wilson, Jr. *J. Amer. Chem. Soc.* **53**, 4242 (1931).