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The Molecular Structure of *n*-Butyl Chloride and *sec*-Butyl Chloride. II. Hindered Rotation[1a]

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The electron diffraction data for *n*-butyl chloride and *sec*-butyl chloride have been analyzed in terms of a distribution of internal rotational isomers. It was assumed that *cis* isomers were not present because the temperature at which the data were obtained was about 300°K. It was found in the case of *n*-butyl chloride that the data were compatible with an isomer distribution of 11% TT, 11% TG, 37% GT, 17% GG′ and 24% GG″ where the first T or G refers to the chlorine end of the molecule and the second to the methyl end. The GG″ form is the most completely coiled of all the isomers. *Sec*-butyl chloride is a substituted ethane-like molecule and the data were compatible with a minimum of about 50% of the molecules in a configuration in which the methyl group at one end was simultaneously *gauche* to the chlorine atom and *trans* to the other methyl group at the other end of the molecule. The data seem to indicate that the *gauche* form is stabilized when the opposing groups are methyl or methylene opposite chlorine and that the *trans* form is stabilized when methyl or methylene is *trans* to a methyl group. The results may also suggest that the methyl-chlorine stability forces are non-bonded in character.

It is of particular interest to investigate the shape of molecules in the gas phase since the information derived from such investigations may shed some insight into the problem of understanding the causes of hindered rotation in molecules. The investigation of this problem in molecules as large as the butyl halides can, at this time, probably be carried out most easily by use of the electron diffraction method since a definitive microwave study of molecules of this size would be a somewhat difficult job.

Perhaps the most important reason for studying *n*-butyl chloride is to determine the distribution of internal rotational isomers. In this molecule an ethane-like situation exists about two bonds and it is therefore possible to determine whether or not the adjacent barriers are independent as the results for the *n*-pentane and other larger *n*-hydrocarbons would suggest.[2a,2b]

In the case of *sec*-butyl chloride, an ethane-like situation exists about one bond where a methyl group can be either *gauche* (G) or *trans* (T) to a chlorine atom or another methyl group. The results of this competition can be compared with the findings of Morino and Kuchitsu in *n*-propyl chloride where the *gauche* form is found to be more stable than the *trans*.[3] It should be emphasized at the outset that the factors affecting *gauche–trans* stability may very well be due to a different class of phenomena than those influencing the eclipsed and staggered conformations found in ethane. In fact, this view has been put forward as early as 1940 by Pitzer.[2b] The energy differences affecting *gauche–trans* stability are less than 900 calories in most cases so that such effects may be due to some form of nonbonded interaction.[4]

In every case studied so far, the energy differences are significantly less than the ethane value. In this work rotational isomers containing only *gauche* and *trans* forms (staggered) are assumed to exist.

Procedure

The experimental data were obtained and analyzed as described in the previous paper.[5] The temperature at which the experiment was performed was 298°K. The long (21.35 cm.) camera distance data were particularly useful since all of the information on hindered rotation is contained in this region ($10 \leq q \leq 50$). The experimental intensity curves and smooth backgrounds are shown in Figs. 1 and 2 for the *n*-butyl and *sec*-butyl chloride, respectively. In Figs. 3 and 4, the possible rotational isomers for the two molecules are depicted.

For *n*-butyl chloride and *sec*-butyl chloride, the experimental data can be analyzed for the percentages of the various rotational isomers by first calculating reduced molecular intensity curves for the pure rotational isomers given in Figs. 3 and 4 using the data found in ref. 5 and then obtaining the coefficients of each isomer in the linear combination which best fits the experimental data according to the least squares criterion. This process must, of course, be incorporated in a self-consistent procedure since the background function used to obtain the experimental reduced intensity function is slightly dependent on the particular rotational isomer distribution which is used. The coefficients of the linear combination give the fraction of the molecules present in a particular isomeric form. It is, of course, important to note that these results depend to some extent on the assumption that the bond lengths are the same in all the rotational isomers. In the case of *n*-butyl chloride and *sec*-butyl chloride, only four and two parameters, respectively, are needed to characterize the distribution of the isomers present since the requirement of normalization of the coefficients will eliminate one unknown in each case.

It should be noted that angles of 60° and 180° are assumed for the *gauche* and *trans* forms in order to calculate the intensity functions for the rotational isomers. It may turn out, however, that in the analysis of the radial distribution curve for the longer non-bonded interactions some adjustment of the *gauche* angle will be necessary. The terminal methyl groups were assumed to be in a staggered conformation throughout the analysis.

Results

In Table I, the results for the analysis of these two molecules are summarized. Comparisons with previous results on *n*-butane and *n*-propyl chloride are also given. In Figs. 5 and 6, points on the experimental reduced intensity curve $M(q)$ represented by black dots are compared with the intensity curves for the various pure rotational isomers. In Figs. 7 and 8, the variation in the fractions of rotational isomers present is shown by theoretical background calculations.[6] This is simply

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[3] Y. Morino and K. Kuchitsu, *J. Chem. Phys.*, **28**, 175 (1958).

[4] L. S. Bartell, *ibid.*, **32**, 827 (1960).

[5] T. Ukaji and R. A. Bonham, *J. Am. Chem. Soc.*, **84**, 3627 (1962).

[6] See for instance, Y. Morino and E. Hirota, *J. Chem. Phys.*, **28**, 185 (1958).

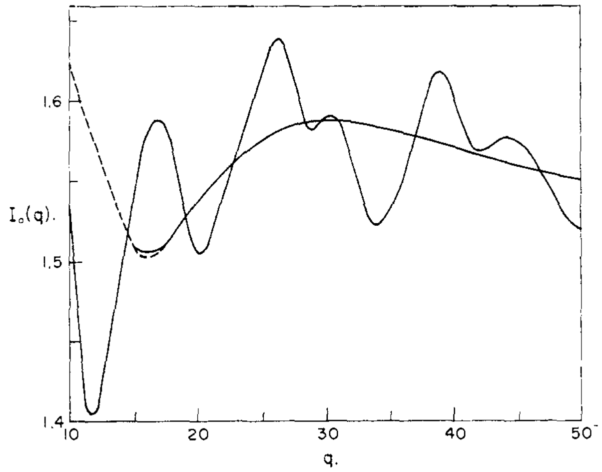

Fig. 1.—Experimental long camera distance intensity curve for *n*-butyl chloride showing the background function (smooth solid line) used in calculating the radial distribution curve.

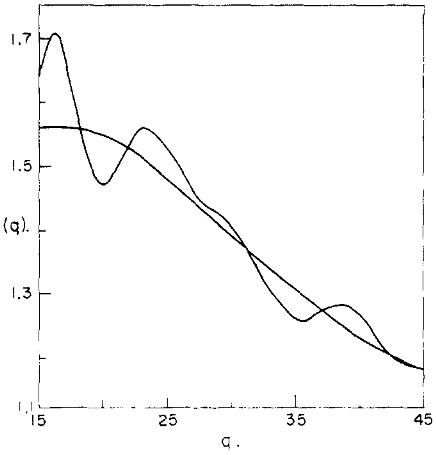

Fig. 2.—Experimental long camera distance intensity curve for *sec*-butyl chloride showing the background function (smooth solid line) used in calculating the radial distribution curve.

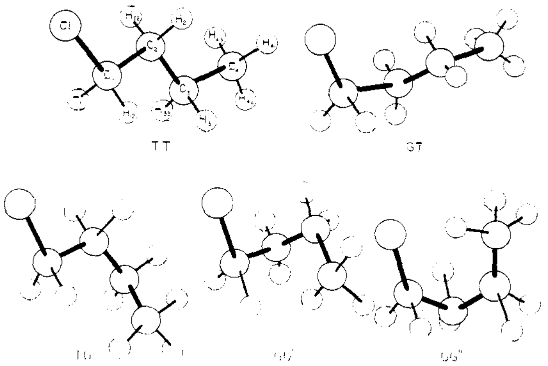

Fig. 3.—Structural models of assumed rotational isomers for *n*-butyl chloride. *Gauche* angles were assumed to be ±60° and *trans* angles were assumed to be 180°.

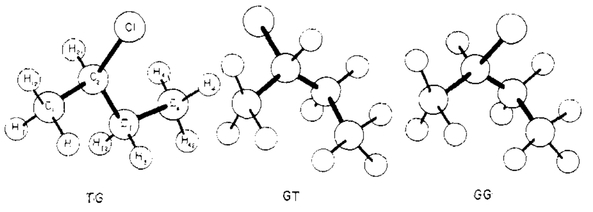

Fig. 4.—Structural models of assumed rotational isomers for *sec*-butyl chloride. Only the staggered ethane-like configurations have been assumed to exist.

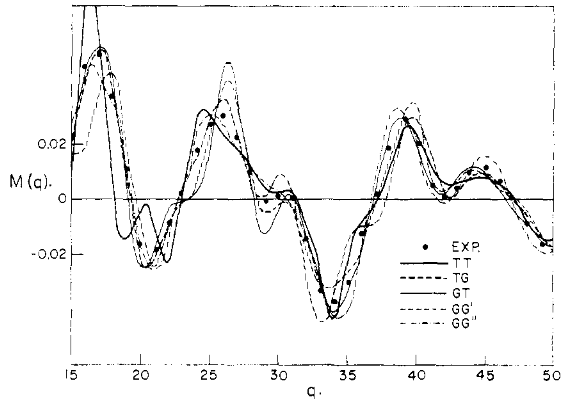

Fig. 5.—Comparison between the experimental reduced intensity function (dots) for *n*-butyl chloride and the reduced intensity functions for the various pure rotational isomers.

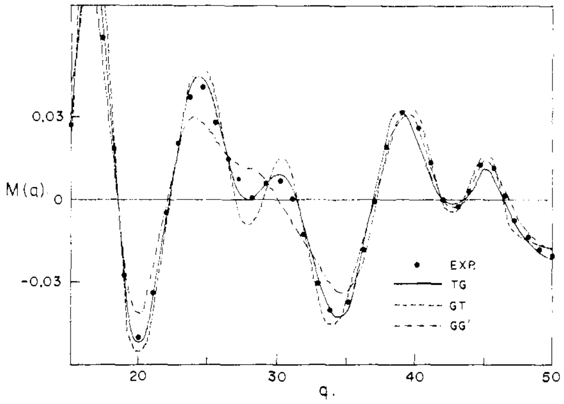

Fig. 6.—Comparison between the experimental reduced intensity function (dots) for *sec*-butyl chloride and the reduced intensity functions for the various pure rotational isomers.

a means to show the correlation between theory and experiment in a more sensitive manner than the usual comparison of calculated and experimental $M(q)$ curves. Figure 9 shows the sensitivity of the large r part of the radial distribution function to variations in the percentages of the various rotational isomers present.

The isomer fractions in Table I were calculated from a least squares fit of the experimental reduced intensity curve by a linear combination of pure isomeric forms. The standard deviation of the complete fit in each case was less than 2%. The uncertainties in the fractions of each isomeric form have been estimated at ±10% as there is probably at least a 1 to 5% error in the experimental points which were used in the fit.

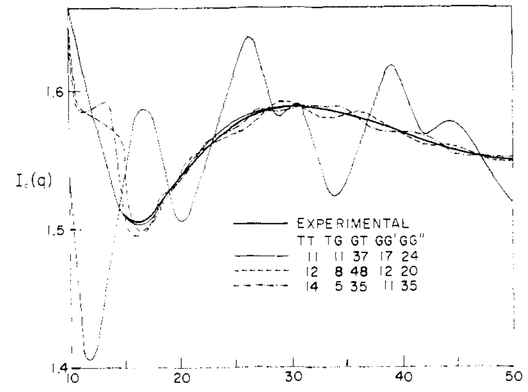

Fig. 7.—Background variation of several different combinations of internal rotational isomers for *n*-butyl chloride. Note the smooth, heavy, solid line is the experimental background line.

It is also possible to estimate the change in free energy ΔF_0 for the reaction *trans* $\rightleftarrows$ *gauche* from the electron diffraction results. By using Boltzmann statistics, the ratio of the *gauche* to *trans* concentrations can be related to the change in free energy by the relation

$$n_g/n_t = 2\exp[-\Delta F_0/RT] \qquad (1)$$

where n_g is the fraction of *gauche* form present and n_t is the fraction of *trans* form present.[7] Spectroscopic studies depend on a knowledge of certain partition functions in order to calculate ΔH for the above reaction from temperature studies of line intensities.[8] The electron diffraction technique measures the molecular fractions directly so that an estimate of ΔF_0 can be obtained by a study at a single temperature without the use of a partition function. An estimate of ΔH and hence perhaps ΔS can then be obtained by temperature studies utilizing either electron diffraction or spectroscopic techniques.[9]

If expression 1 is used to estimate *trans–gauche* energy differences, the *trans* form at the methyl end of *n*-butyl chloride appears to be more stable by 415 cal./mole than the *gauche* form and the *gauche* form at the chlorine end appears to be more stable by 318 cal./mole over the *trans* form at the same end of the molecule. If the temperature is assumed to be uncertain by 10%[10] and allowance is made for the assumptions employed in the calculation of the percentages of the various rotational isomers, uncertainties of the order of 150 cal./mole would be associated with the above results. For *sec*-butyl chloride, the results lead to an estimated energy difference between the Cl-*gauche*, methyl-*trans* and the other two isomers present, of 415 cal./mole. It was assumed that the other two isomers were present in equal concentrations. Taking this into account, the estimated errors would be −200 cal./mole and +300 cal./mole. The estimate of a larger positive error comes about because the GT form by itself is in very good agreement with experiment (see Fig. 6), and it is felt that the least squares results give an estimate of the minimum percentage of this form present. The main reason for the over-all larger error estimate is that the two forms TG and GG were assumed to be present in equal concentrations. Qualitatively, it would seem that there should be a bigger difference between the fractions of these two forms present. A crude estimate of this difference using the results found for *n*-butane,[7] and *n*-propyl chloride[3] suggests that the difference might be as large as 20%. The results for the *gauche* C—C non-bonded distance in both molecules suggests an angle of approximately 64° for the *gauche* isomers. Although this is of the same magnitude and in the same direction as the angle in *n*-butane, the experimental uncertainty is too great to dwell on the significance of these values.

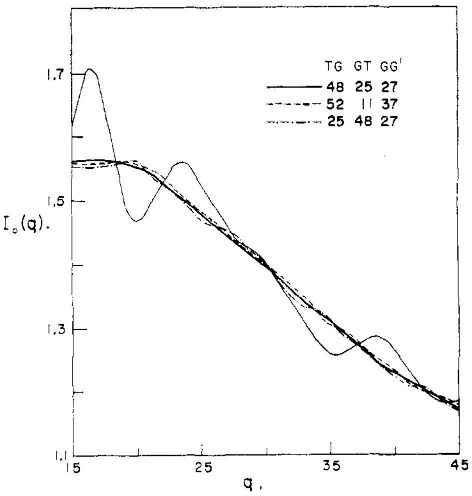

Fig. 8.—Background variation of several different combinations of internal rotational isomers for *sec*-butyl chloride.

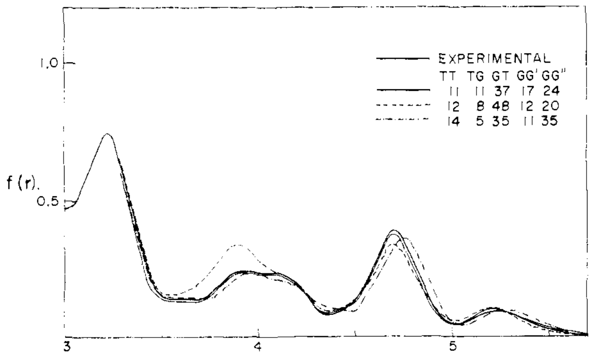

Fig. 9.—Sensitivity of the large *r* part of the radial distribution curve for *n*-butyl chloride to variations in the rotational isomer distribution. Note heavier solid line is the experimental radial distribution curve.

Conclusions.—The information obtained by this investigation is in qualitative agreement with the results found in previous investigations.[2a,3,7]

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(7) R. A. Bonham and L. S. Bartell, *J. Am. Chem. Soc.*, **81**, 3491 (1959).

(8) G. J. Szasz, *J. Chem. Phys.*, **23**, 2449 (1955).

(9) We wish to thank Professor L. S. Bartell for pointing out this fact.

(10) The work of Professor K. Hedberg with PCl_3 indicates that there is little if any change in the vibrational temperature of the molecule on expansion into the vacuum chamber. K. Hedberg and M. Iwasaki, *J. Chem. Phys.*, **36**, 589 (1962).

TABLE I

ANALYSIS OF PARAMETERS DEPENDENT ON HINDERED ROTATION AND COMPARISON WITH OTHER MOLECULES

$r_g(0)$, Å.	*n*-Butyl chloride	*sec*-Butyl chloride	*n*-Butane[a]	*n*-Propyl[b] chloride
C—C (*gauche*)	3.073 ± 0.020[c]	3.075 ± 0.020	3.072 ± 0.015	. . .
C—C (*trans*)	3.902 ± .020	3.904 ± .020	3.900 ± 0.008	. . .
C—Cl (*gauche*)	3.251 ± .020	3.261 ± .020	. . . .	. . .
C—Cl (closest)	2.682 ± .030	. . . .	. . . .	. . .
C—Cl (*trans*)	4.711 ± 0.020	4.083 ± .025	. . . .	. . .
l_{ij}, Å.				
C—C (*gauche*)	0.108 ± 0.020	0.098 ± 0.020	0.109 ± 0.016	. . .
C—C (*trans*)	.075[d]	.075[d]	0.083 ± 0.014	. . .
C—Cl (*gauche*)	.097 ± 0.020	.098 ± 0.020	. . . .	0.114
C—Cl (closest)	.115[d]	. . . .	. . . .	. . .
C—Cl (*trans*)	.095[d]	.090[d]	. . . .	0.068
% of Isomers (First symbol refers to chlorine)				
TT	11	. .	60	. .
TG	11	25	40	20
GT	37	48	. .	80
GG′	17	27	. .	. .
GG″	24	. .	. .	. .

[a] See ref. 7. [b] See ref. 3. [c] Since the overlapping of peaks in the region of the radial distribution curve from which these parameters have been obtained is quite severe, the precisions have been given as three times the standard deviation defined in ref. 5. [d] Estimated values compatible with the experimental data.

A more quantitative comparison, however, does reveal some interesting differences. The available evidence from analysis of *n*-hydrocarbons[2] would seem to indicate that there is no significant coupling between the barrier to rotation about one C–C bond and the barrier about an adjacent C–C bond. The results for *n*-butyl chloride may suggest such a coupling or else some sort of non-bonded interaction between the terminal groups in the molecule. The uncoupled model would predict on the basis of the *n*-butane and *n*-propyl chloride results the following percentages of the various rotational isomers: TT = 12, GT = 48, TG = 8 and GG (all forms) = 32. The results found indicate an extra stability of the GG forms due to the presence of the completely coiled CG″ form in a high concentration (24%). This form is sterically prohibited in the case of *n*-pentane as H–H distances of less than 1.5 Å. in length would result unless the molecules were badly distorted. The extra stability of the GG forms can also be seen in the estimated energy differences between isomers. The ratio of *trans* stability in *n*-butane and *gauche* stability in *n*-propyl chloride is 1.62 while the ratio in *n*-butyl chloride is 1.30.

The added GG stability might be explained in terms of forces transferred along the bond path of the molecule, but the non-coupling evidence in the *n*-hydrocarbons and the stability of the GG″ form in *n*-butyl chloride suggest that the forces governing *trans–gauche* stability are of a non-bonded character. In fact, Szasz has suggested that it may be possible to describe the *gauche* stabilization in *n*-propyl chloride in terms of a non-bonded electrostatic effect.[8] Also as has been pointed out earlier, Bartell[4] has shown that non-bonded repulsions can be used to calculate a reasonable value for the *trans–gauche* energy difference in *n*-butane.[3] It is important, however, to point out that these semi-empirical attempts to explain barriers have failed badly in attempts to explain the barrier in ethane.

The results for *sec*-butyl chloride clearly indicate that a methyl group shows a greater attraction for a chlorine atom than for another methyl group. The approximate energy difference between *gauche* and *trans* forms in *n*-propyl chloride is qualitatively the same as that found in *sec*-butyl chloride. Work is presently underway to determine the structure of isobutyl chloride where one chlorine atom can be simultaneously *gauche* to two methyl groups. The value of the energy difference between the *trans* and *gauche* forms in this case might give some indication as to the nature of the forces involved.

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