due also to Mr. B. S. Borie for X-ray diffraction measurements. We are especially grateful to Professor V. Schomaker for several illuminating discussions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

An Electron Diffraction Investigation of the Molecular Structures of 1,1,1-Trichloroethane, 2,2-Dichloropropane and 2-Chloro-2-methylpropane[1]

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An electron diffraction investigation of the molecular structures of 1,1,1-trichloroethane, 2,2-dichloropropane and *t*-butyl chloride has yielded the following results: 1,1,1-trichloroethane, C–Cl = $1.77_5 \pm 0.02$ Å., C–C = 1.50 to 1.58 Å. (assumed), ∠C–C–Cl = 110 ± 1.5°; 2,2-dichloropropane, C–Cl = $1.77_6 \pm 0.02$ Å., C–C = 1.54 ± 0.04 Å., ∠Cl–C–Cl = 109.5 ± 2°, ∠C–C–Cl = 109 ± 3°; *t*-butyl chloride, C–Cl = 1.80 ± 0.04 Å., C–C = 1.54 ± 0.03 Å., ∠C–C–Cl = 107.5 ± 1.5°.

Introduction

One of the important applications of electron diffraction has been the study of the effects produced in the configuration of a molecule when certain groups or atoms therein are replaced by other groups or atoms. The purpose of the present investigation was to determine whether any structural differences result from the substitution of methyl groups for chlorine atoms in the series: 1,1,1-trichloroethane, 2,2-dichloropropane and 2-chloro-2-methylpropane (*t*-butyl chloride). It was also hoped that accurate values could be obtained for the bond distances and angles in these compounds so that comparisons with distances and angles in other compounds would be possible. Of these compounds, the first and third have been previously investigated by Beach and Stevenson.[2,3] The diffraction patterns obtained by Beach and Stevenson did not extend to as large a scattering angle as is generally obtained with the apparatus available in this Laboratory. Since the outer part of the diffraction pattern is often the most valuable in structure determinations, repetition of their work was considered worthwhile in the hope that a more precise determination would result. Furthermore, their determinations were made without allowance for the displacements of atoms caused by intramolecular vibration. In the case of a molecule such as *t*-butyl chloride with a large number of hydrogen atoms, vibration factors assume considerable importance and the study of this compound cannot be considered complete without an investigation of their effects.

When this investigation was undertaken there was no report in the literature of a structural investigation of 2,2-dichloropropane. When the work was near its completion, however, mention was made in a review article[4] of an unpublished diffraction investigation of this compound by J. O'Gorman and V. Schomaker. The authors have been informed by Dr. Schomaker that the values given in the review article were based upon an incomplete study.

Experimental

Commercial samples of 1,1,1-trichloroethane and *t*-butyl chloride were purified by washing with appropriate reagents followed by rectification in all-glass columns. The sample of 2,2-dichloropropane was prepared from acetone and phosphorus pentachloride following in most essentials the method outlined by Smyth and Turkevich.[5] The refractive indices of the samples used were as follows: 1,1,1-trichloroethane, $n^{20}\text{D}$ 1.4380; 2,2-dichloropropane, $n^{20}\text{D}$ 1.4148; *t*-butyl chloride, $n^{20}\text{D}$ 1.3852.

The electron diffraction photographs were prepared using an apparatus built by Professor H. J. Yearian of the Department of Physics of Purdue University. The wave length of the electrons as determined from the transmission patterns of zinc oxide was about 0.055 Å. and the camera distance was about 11 cm. The diffraction patterns extend to approximately $q = 90$ for each compound and are represented by curves VIS in Figs. 2, 4 and 6. The q_0 values are given in Tables I, II and III.

Interpretation.—In interpreting the photographs both the visual correlation method[6] and the radial distribution method[7] were employed. The intensity curves used in the visual correlation were calculated from the equation

$$I(q) = \sum_i \sum_j \frac{Z_i Z_j}{r_{ij}} \exp\left(-b_{ij}q^2\right) \sin \frac{(\pi q r_{ij})}{(10)}$$

The summations were performed from punched cards[7,8] by an I.B.M. tabulating machine. In the calculation of all intensity curves the bonded C–H distance (1.09 Å.) and the short non-bonded C–H distance (2.16 Å.) were damped by the factors $b = 0.00018$ and $b = 0.00035$, respectively. These values have been found by Schomaker[9,10] to account adequately for the distribution of these distances due to vibration in several similar compounds. The values of b_{ij} assigned to other distances will be discussed separately for each compound. The radial distribution functions were calculated from the equation[7]

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[1] Contains material from the doctoral thesis of J. W. Coutts, Research Corporation Fellow in Chemistry, Purdue University, 1949–1950.

[2] J. Y. Beach and D. P. Stevenson, THIS JOURNAL, **60**, 475 (1938).

[3] J. Y. Beach and D. P. Stevenson, *ibid.*, **61**, 2643 (1939).

[4] P. W. Allen and L. E. Sutton, *Acta Crystallographica*, **3**, 46 (1950).

[5] C. P. Smyth and A. Turkevich, THIS JOURNAL, **62**, 2468 (1940).

[6] L. O. Brockway, *Revs. Mod. Phys.*, **8**, 231 (1936).

[7] P. A. Shaffer, V. Schomaker and L. Pauling, *J. Chem. Phys.*, **14**, 659 (1946).

[8] P. A. Shaffer, V. Schomaker and L. Pauling, *ibid.*, **14**, 648 (1946).

[9] V. Schomaker and P. Shaffer, THIS JOURNAL, **69**, 1555 (1947).

[10] W. N. Lipscomb and V. Schomaker, *J. Chem. Phys.*, **14**, 475 (1946).

$$rD(r) = \sum_{q=1,2\ldots}^{q\,\max} I(q) \exp(-bq^2) \sin\left(\frac{\pi}{10} qr\right)$$

The values of $I(q)$ were read from the visual curve at integral values of q. Intensity values for the inner portions of the patterns which do not appear on the visual curve were read from theoretical intensity curves. The factor b was chosen so that $\exp(-bq^2_{\max}) = 0.1$.

1,1,1-Trichloroethane.—The intensity curves were not affected appreciably either quantitatively or qualitatively by the omission of the terms involving non-bonded H atoms. Therefore these terms were omitted from the summation. Application of a small damping factor to the non-bonded C–Cl distances, which was found necessary for the other two compounds, caused no appreciable change in the appearance of the trichloroethane curves. These distances were therefore included without damping, *i.e.*, $b = 0$.

The range over which the shape parameters ($\alpha = \angle$ C–C–Cl and C–Cl/C–C) were varied is shown in Fig. 1; C–C was fixed at 1.54 in all models and C_{3v} symmetry was assumed.

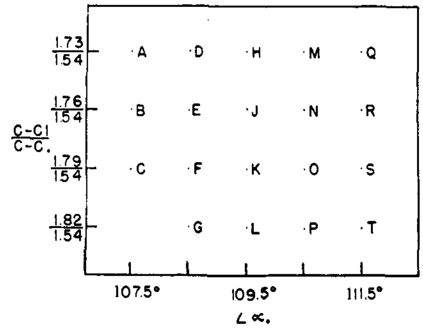

Fig. 1.—Parameter chart for 1,1,1-trichloroethane.

The features of the visual curve (curve VIS in Fig. 2) which proved to be the most sensitive to parameter changes lie between $q = 35$ and $q = 70$. The seventh minimum is not as deep as the sixth and eighth. Although it is difficult to estimate the heights of the sixth and seventh maxima relative to each other they are both less intense than the fifth and eighth maxima. The ninth maximum is a weak, unresolved peak, with the ninth minimum being shallow compared to the eighth and tenth.

The curves plotted in Fig. 2 will serve to illustrate the criteria which were used in selecting the acceptable models. Curves for models A, B and C are very similar qualitatively and were eliminated because the ninth maximum appears too strong relative to the eighth and tenth and because the seventh maximum appears too intense relative to the sixth and eighth. Curves D and G are representative of models having the angle α equal to 108.5° and show the effects which result from increasing the C–Cl distance. These curves are incompatible with the visual curve because of the relative heights of the sixth, seventh and eighth maxima. Curves H and L, representing models with $\alpha = 109.5°$, are in good general agreement with the visual curve; J and K are also acceptable. Of the models with $\alpha = 110.5°$, M can be eliminated because of the fact that the ninth and tenth minima are of equal depth. The unresolved nature of the ninth maximum is considered to be one of the most characteristic features of the pattern, and curves showing the ninth minimum as deep as or deeper than the tenth can be eliminated with confidence. As the C–Cl distance is increased the ninth minimum becomes more shallow as shown by curve P and models N, O and P are acceptable. Increasing α to 111.5° causes the ninth minimum to become still deeper and all models with this value of α can be rejected. Model T has been plotted as the model at this angle which is closest to being acceptable. It will be noted from the above discussion and from the curves plotted in Fig. 2 that the changes occurring in the qualitative appearance of the curves as the C–Cl/C–C ratio is increased are rather slight. This is not surprising in view of the small contribution of the C–C terms to the intensity summation. Several models were calculated with C–Cl/C–C ratios outside the parameter range of Fig. 1 and it was found that in order to eliminate such models it was necessary to consider C–Cl distances considerably above 1.82 Å. or below 1.73 Å. On this account it was considered impractical to try to evaluate the C–C distance. In view of the many compounds in which the C–C distance is known to be very close to 1.54 Å. the parameter field was restricted to those models with q/q_0 ratios giving a C–C distance between the limits 1.50 and 1.58 Å.

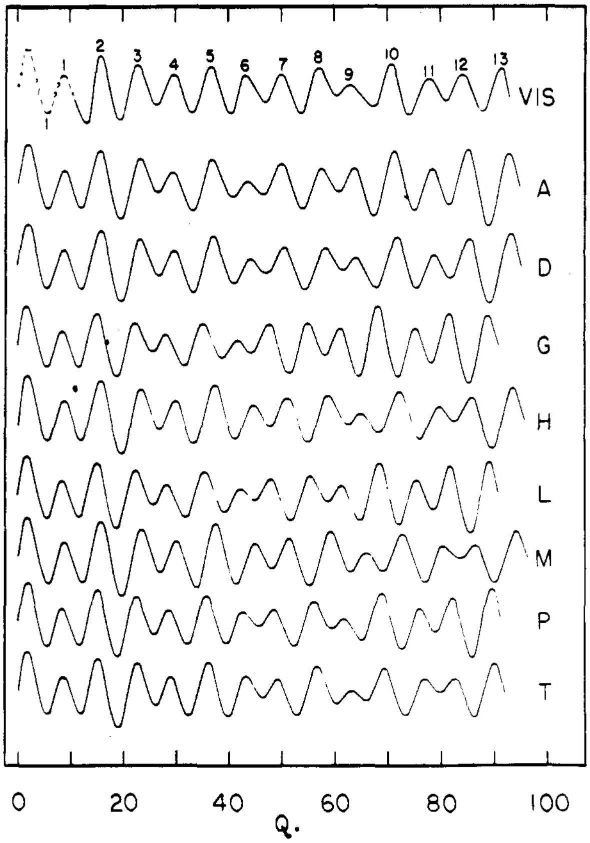

Fig. 2.—Observed and calculated intensity curves for 1,1,1-trichloroethane.

The q/q_0 ratios for models J and O are listed in Table I. The values for features which were difficult to measure reliably are enclosed in parentheses and were omitted in calculating the mean q/q_0 ratios.

Since all the acceptable models have $\alpha = 109.5°$ or 110.5° the best model has been chosen as one with $\alpha = 110°$. The C–Cl and Cl–Cl distances obtained for the various acceptable models were as follows: H, 1.772, 2.888; J, 1.771, 2.887; K, 1.770, 2.888; L, 1.771, 2.890; N, 1.778, 2.889; O, 1.783, 2.888; P, 1.782, 2.888. The non-bonded C–Cl distance in these models varies from 2.68 to 2.74 Å.

The final choice of parameters with their estimated limits of uncertainty are: C–Cl = $1.77_5 \pm 0.02$ Å., C–C = 1.50–1.58 Å. (assumed) and ∠C–C–Cl = 110 ± 1.5°. The Cl–C–Cl angle is 109 ± 1.5°. These results are in good agreement with those obtained from the main peaks of the radial distribution curve at 2.88 Å. and 1.77 Å.

2,2-Dichloropropane.—All models used for calculation of the theoretical intensity curves were assumed to have the symmetry of the C_{2v} point group. The methyl groups were assumed to be oriented with their equilibrium positions

TABLE I

1,1,1-TRICHLOROETHANE

Feature			q/q_0	
Max.	Min.	q_0	Model J	Model O
	2	13.43	(0.901)	(0.894)
2		15.95	(.991)	(.978)
	3	19.61	.999	.984
3		22.79	1.018	1.009
	4	26.58	1.005	0.993
4		29.67	1.001	.991
	5	33.26	0.998	.986
5		36.67	1.009	.998
	6	40.43	1.012	.994
6		43.39	1.019	1.009
	7	47.05	1.005	0.997
7		50.10	1.004	.996
	8	53.70	1.006	.998
8		56.95	(1.017)	(1.008)
	9	60.38	(1.017)	(1.014)
9		63.25	(1.013)	(1.006)
	10	67.58	0.994	0.983
10		70.57	1.009	.996
	11	74.10	1.011	1.001
11		77.83	1.007	1.001
	12	80.95	1.004	0.994
12		84.00	1.005	.995
	13	88.04	1.005	.993
13		91.29	1.011	1.001
		Mean q/q_0	1.006	0.996
		Mean deviation	0.005	0.005

such that the hydrogen atoms were as far as possible from the chlorine atoms. The bonded C–H distances were taken as 1.09 Å. and tetrahedral angles were assumed in the methyl groups.

The choice of vibration factors to be applied to the Cl–H and C–H distances which change upon rotation of the methyl group about the C–C bond became part of the experimental investigation. It was expected that the vibration factors to be applied to these distances would be large. If there were no rotation of the methyl group about the C–C bond, a minimum value of b of the order of 0.00035 would still be needed to account for the distribution of distances due to the vibration of the H atoms. Any rotation of the group makes necessary an increased value of b to account for the increased distribution of distances about the equilibrium position.

For a preliminary investigation of the effects of these vibration factors it was found convenient to omit completely the rotation-dependent distances, *i.e.*, b was made infinitely great. Several models over a wide parameter range were calculated in this manner but it was found impossible to obtain agreement between the calculated and visual curves. The curves which appeared closest to fitting the visual curve were then altered by reducing the vibration factor to its assumed minimum value of 0.00035. No curves with this value of b were compatible with the visual curve. Correlation between the two assumed extremes of b was not possible without application of damping factors to other distances.

With the rotation-dependent distances still omitted a damping factor was applied to the non-bonded C–Cl distance to allow for vibrations of the carbon and chlorine atoms attached to the central carbon atom. Such a factor should necessarily be small since the amplitude of vibration of the carbon atoms will be less than that of the hydrogen atoms. The chlorine atoms will be subject to even smaller amplitudes of vibration and hence the Cl–Cl distance should not require a damping factor. Furthermore, it turned out that the Cl–Cl distance in most of the acceptable models was almost the same as the heavily damped Cl–H distance so that the vibration factor applied to the latter will effectively include any slight factor which should possibly be applied to the Cl–Cl distance. No factor was applied to non-bonded C–C distance since its effective weight in the summation is very small. It was found that the use of a factor b of the order of 0.0001 in damping the non-bonded C–Cl distance was very effective in bringing the theoretical curves into agreement with the visual curve.

Several curves were then calculated with various combinations of the factors b_1 (non-bonded C–Cl) and b_2 (non-bonded Cl–H). Because of the complexity of the problem it was assumed that the same vibration factor applied to each of the non-bonded Cl–H distances. The relatively unimportant rotation-dependent C–H distances were omitted completely. The factors b_1 and b_2 fortunately affected the curves in such a way that it was possible to find optimum combinations of the two. A further simplifying assumption made in choosing b_1 and b_2 was that a satisfactory combination should give good results for both 2,2-dichloropropane and *t*-butyl chloride. The factors which give the best results were $b_1 = 0.00006$ and $b_2 = 0.0008$. It is not claimed that these factors necessarily represent the correct values; the problem was already one of four parameters without the evaluation of vibration factors. It can only be asserted that they were chosen after a careful consideration of their effects on several curves. Further, in the selection of acceptable models allowances were made in doubtful cases for the effects which would be produced by a reasonable variation in b_1 and b_2.

The features of the visual curve (see Fig. 4) which are most sensitive to changes in parameters and vibration factors are the sixth and seventh maxima. These broad peaks are not symmetrical but show a measurable maximum of intensity on their inner side and gradually taper off in intensity toward the outside. The seventh maximum is broader than the sixth. Neither of these peaks showed any doublet character. The outer region of the pattern showed a small maximum ($q = 77$) partially resolved from a larger maximum at $q = 84$ with a measurable minimum between the two.

The calculated curves were very sensitive to changes in the angle β (Cl–C–Cl), with the great majority of acceptable models being found at $\beta = 109.5°$. Although occasional acceptable models were found with $\beta = 110.5°$ or $108.5°$ none was found with β greater or less than these values. It is believed that enough models of this type were calculated to ensure that qualitative agreement is impossible for values of β differing from 109.5° by more than 1.5°. Figure 3 represents the parameter range studied for $\beta = 109.5°$. The range covered for other values of β was by no means as complete.

The curves of Fig. 4 will illustrate the principal criteria used in the selection of acceptable models. Firstly, curves showing partial resolution of the seventh maximum into a doublet have been rejected unless the degree of resolution is such that a reasonable variation of vibration factors may be expected to bring the curve into agreement with the visual curve. See, for example, curves P and V which were considered acceptable on this basis. Curve AA was rejected since any combination of b_1 and b_2 which tends to improve the appearance of the seventh maximum confers pronounced asymmetry of the wrong type on the sixth maximum (*i.e.*, it causes a more gradual slope toward the inside than the outside). Similarly, curves showing pronounced resolution of the sixth maximum (*e.g.*, X and E) were rejected, while curves similar to S were accepted as borderline cases in view of the changes which might result from changes in vibration factors. Model B, for which the seventh maximum is insufficiently asymmetric and the sixth broader than the seventh, has also been eliminated; other models with α ($\angle$ CCC) = 105.5° give curves showing greater discrepancies. Curves showing asymmetry of the wrong type in the seventh maximum (see curves H and AD) were rejected since it may be safely predicted that the changes in vibration factors required to reverse the asymmetry of the seventh maximum would bring about the appearance of a shoulder on the side of the sixth maximum.

The effects of changing the angle β are illustrated by curves U-1 ($\beta = 107.5°$) and U-2 ($\beta = 111.5°$); the other parameters correspond to those of model U. These effects were found to be of the same general nature for all values of α in the parameter range studied.

The range of acceptable models is indicated in Fig. 3. Selecting the middle of this range gives the best value of α as 110.5°. It has already been pointed out that the best value of β is 109.5°. The q/q_0 ratios for two of the best models (M and U) are listed in Table II. The bonded C–Cl distances calculated from the q/q_0 ratios for all acceptable

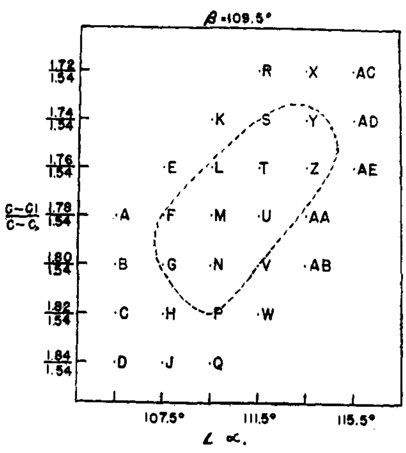

Fig. 3.—Parameter chart for 2,2-dichloropropane.

models, range from 1.771 to 1.784 Å. and the average value for all acceptable models is 1.776 Å. Similarly, the non-bonded C–Cl distances range from 2.692 to 2.720 Å. and the non-bonded Cl–Cl distances range from 2.887 to 2.914 Å.

TABLE II

2,2-DICHLOROPROPANE

Feature Max.	Feature Min.	q_0	q/q_0 Model M	q/q_0 Model U
	2	13.30	(0.917)	(0.917)
2		16.20	(0.994)	(0.994)
	3	20.15	(0.990)	(0.985)
3		23.30	1.004	1.004
	4	26.96	0.996	0.996
4		30.14	0.993	0.990
	5	33.93	0.988	0.985
5		37.62	1.000	1.002
	6	41.86	0.998	0.998
6		46.00	(1.002)	(1.004)
	7	52.20	(1.004)	(1.004)
7		56.53	(1.019)	(1.011)
	8	65.57	0.991	0.995
8		69.39	1.000	1.003
	9	73.47	0.999	1.003
9		77.03	1.000	1.004
	10	80.83	(0.983)	(0.985)
10		83.62	0.994	0.994
	11	87.79	0.993	0.993
11		90.65	1.006	1.006
		Mean q/q_0	0.997	0.998
		Mean deviation	0.004	0.005

The final values for the parameters and other important distances and angles are listed below. In setting the ranges of uncertainty a somewhat greater latitude has been placed on α and β than is indicated by the range of acceptable models. This arises from making an additional allowance for possible uncertainties caused by choice of vibration factors. In summary, the accepted values are: C–Cl (bonded) = 1.77_6 ± 0.02 Å.; C–C (bonded) = 1.54 ± 0.04 Å.; C–Cl (non-bonded) = 2.71 ± 0.03 Å.; Cl–Cl (non-bonded) = 2.90 ± 0.03 Å.; ∠C–C–C (α) = 110.5 ± 5°; ∠Cl–C–Cl (β) = 109.5 ± 2°; ∠Cl–C–C = 109.2 ± 3°.

The values for the bonded and non-bonded C–Cl distances are in excellent agreement with those taken from the main peaks of the radial distribution curve at 1.78 Å. and 2.71 Å.

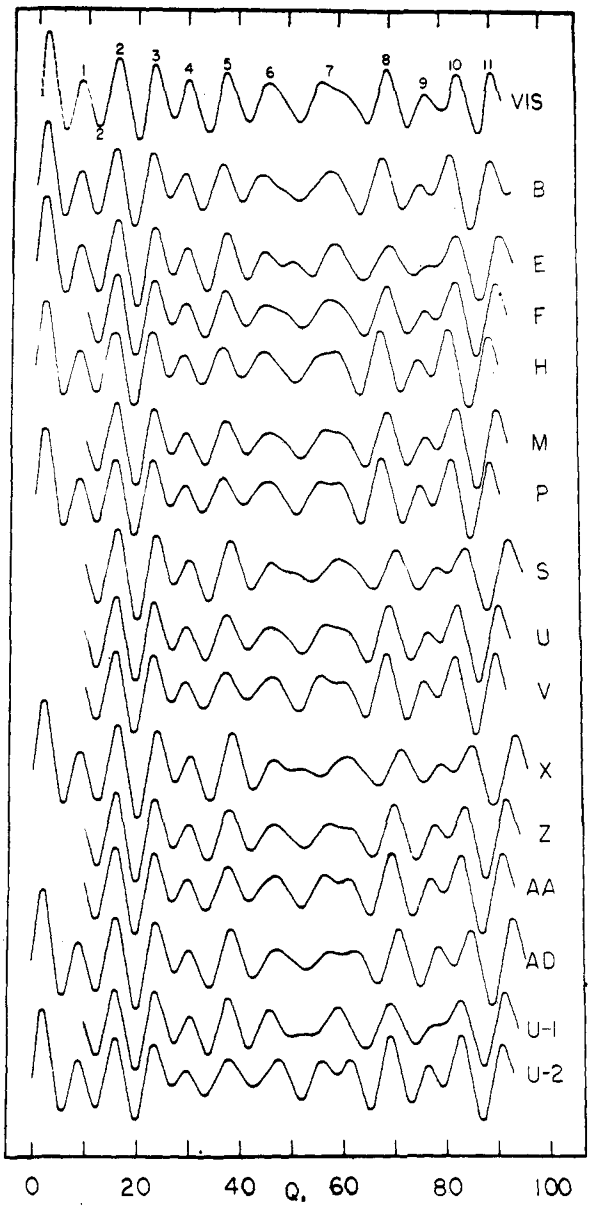

Fig. 4.—Observed and calculated intensity curves for 2,2-dichloropropane.

***t*-Butyl Chloride.**—This molecule was assumed to have the symmetry of the C_{3v}. point group, with the methyl groups oriented so that the hydrogen atoms were as far as possible from the chlorine atom. The vibration factors were the same as those used for 2,2-dichloropropane; in addition, the non-bonded C–C distances were modified by a vibration factor equal to that used for the C–Cl distances, *viz.*, 0.00006. The longest non-bonded Cl–H distance and the longest non-bonded C–H distance were omitted. Many additional models were calculated with different vibration factors in order to note their effects. The range of parameters studied is shown in Fig. 5 where α is the angle Cl–C–C.

The features of the pattern which proved to be of particular value in choosing among models may be seen from curve VIS in Fig. 6. The fifth maximum appeared more intense than those on either side of it, with the sixth minimum being more shallow than the fifth or seventh. The seventh maximum is particularly sensitive to parameter changes. It appears as a very broad peak, falling off in intensity toward its outer edge. It shows little, if any, detectable doublet character but has a measurable maximum of intensity on its inner side. The ninth maximum is also asymmetric, increasing in intensity toward the outside. This peak has a point of inflection or weak shoulder on its inner side.

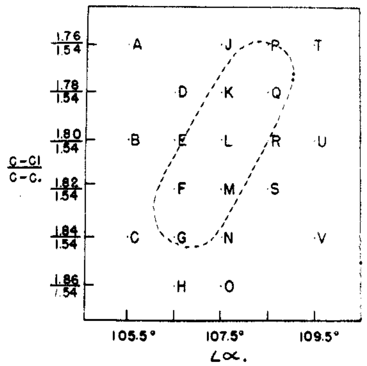

Fig. 5.—Parameter chart for *t*-butyl chloride.

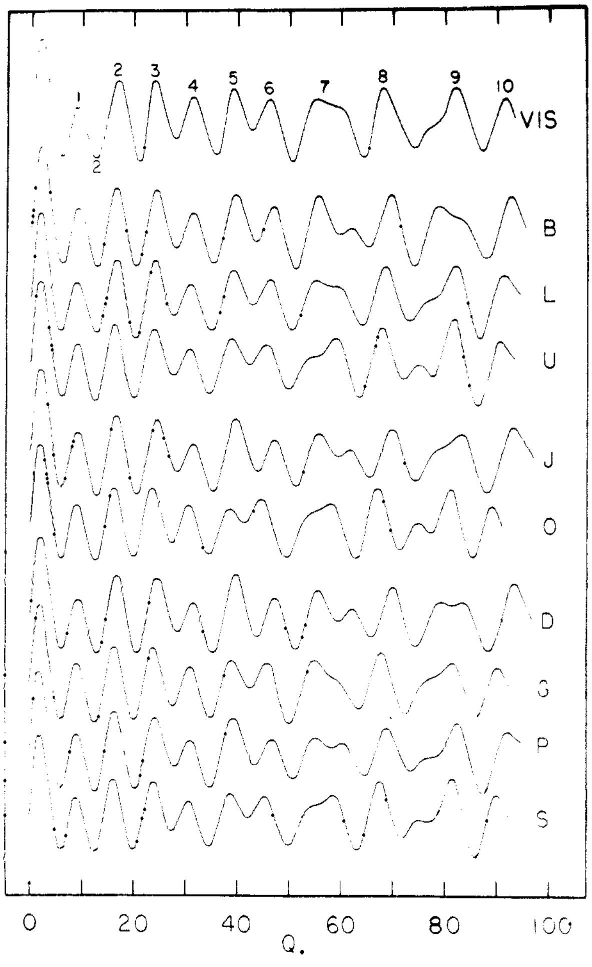

Fig. 6.—Observed and calculated intensity curves for *t*-butyl chloride.

Several curves representative of the different areas of the studied parameter range are shown in Fig. 6. Curves B, L, U and J, L, O illustrate the general changes occurring upon crossing the parameter field horizontally or vertically. It is evident from curves B, L and U that increasing the angle α causes a reversal in the asymmetry of the seventh and ninth maxima, with curve L being in best agreement with the visual curve. Models B, E and U were rejected. R was accepted as a borderline case after making due allowances for possible effects resulting from alterations in vibration factors.

In going from curve J through O the sixth maximum increases in intensity relative to the fifth, the seventh maximum reverses the nature of its asymmetry and the shoulder moves down the side of the ninth maximum and becomes resolved into a small but definite maximum. These variations, like those observed in changing α, combine to give the best agreement with the visual curve in the vicinity of model L. Model J was rejected on account of the pronounced resolution of the seventh maximum, while N and O were rejected because of the inversion in the relative intensities of the fifth and sixth maxima and the reversed asymmetry of the seventh maximum. Models K and M were accepted.

Models G and P lie at the extreme ends of the diagonal field of acceptable models. Although curves showing resolution of the seventh maximum of the degree occurring in curve P were not accepted in the case of the curves for 2,2-dichloropropane they are more difficult to eliminate for the present compound for two reasons: the appearance of the seventh maximum is more shelf-like than in the dichloropropane pattern, and the effects of vibration factors in this compound are in general greater than for dichloropropane.

Models D and S have been shown in Fig. 6 in addition to those already mentioned so that the appearance of any curve of the parameter field may be readily judged by interpolation. The range of acceptable models is indicated in Fig. 5 and the q/q_0 ratios for model L are listed in Table III; also listed are the ratios for two models which lie at the edges of the acceptable range.

Table III

Tertiary Butyl Chloride

Feature Max.	Feature Min.	q_0	q/q_0 Model L	q/q_0 Model P	q/q_0 Model G
2		17.12	(0.981)	(0.958)	(0.975)
	3	20.82	(0.976)	(0.985)	(0.965)
3		24.10	1.000	1.000	0.984
	4	27.69	1.004	1.018	1.004
4		31.32	0.993	0.996	0.996
	5	35.62	0.983	0.982	0.982
5		39.02	1.008	1.015	1.007
	6	42.68	1.007	1.022	0.998
6		46.19	1.004	1.015	.995
	7	50.39	1.002	1.010	.996
7		55.13	(1.001)	(1.003)	(1.011)
	8	63.95	0.999	1.014	0.996
8		67.89	1.004	1.017	1.002
	9	74.23	0.986	0.995	0.979
9		81.77	1.003	1.011	0.997
	10	86.29	1.002	1.013	1.001
10		91.29	1.000	1.011	0.990
Mean q/q_0			1.000	1.009	0.995
Mean deviation			0.005	0.009	0.006
C–Cl (bonded)			1.800	1.776	1.831
C–C (bonded)			1.540	1.554	1.532
C–Cl (non-bonded)			2.700	2.704	2.696

The imposition of vibration factors has a quantitative as well as qualitative effect on the curves. In the case of *t*-butyl chloride this effect is considerable because of the large number of distances affected by vibration factors. In order to test the effects of variations of these factors a number of different curves were calculated for model L. It was found that the use of either extreme value of b_2, *i.e.*, $b_2 = 0$ or $b_2 = \infty$, causes an appreciable drift in q/q_0's with increasing q. In the former case the q/q_0 ratios increase with increasing q, while in the latter case the drift is in the opposite direction. It was also found that the largest changes in q/q_0 ratio occur upon the initial introduction of vibration factors of the order of 0.0001 or 0.0010 and in going from a factor of such size to an infinite factor. Therefore, provided reasonable vibration factors are used at all and provided important distances are not omitted completely the quantitative results are not greatly affected by changes in factors over the usual range. Another point noted was that the curves calculated with the values of b_1 and b_2 which were considered to give the best qualitative agreement also gave the least mean deviation of those studied.

From the parameter chart it is evident that the best model is very closely represented by model L. The best values of the structural parameters have been derived, therefore, from model L and the limits of uncertainty have been imposed after a consideration of the extreme values of the various parameters at which acceptable models have been found, with the necessary allowances for possible errors in experimental measurements.

The final values with their estimated limits of uncertainty are: C–Cl (bonded) = 1.80 ± 0.04 Å.; C–C (bonded) = 1.54 ± 0.03 Å.; ∠Cl–C–C = 107.5 ± 1.5°. Other values of interest are: ∠C–C–C = 111.5 ± 1.5°; C–Cl (non-bonded) = 2.70 ± 0.02 Å.; C–C (non-bonded) = 2.54 ± 0.03 Å. The values for the non-bonded C–Cl, the bonded C–C and the bonded C–Cl are in good agreement with the respective values from the main peaks of the radial distribution curve, at 2.69, 1.53 and 1.81 Å.

Discussion

The results of this study give the same value for the C–Cl distances in 1,1,1-trichloroethane and in in 2,2-dichloropropane, *viz.*, 1.77_5 Å. However, the corresponding bond in *t*-butyl chloride appears to be significantly longer, *i.e.*, 1.80 Å. The limits of uncertainty of these distances are such that one cannot insist that the bond length in *t*-butyl chloride is longer than in the other two compounds but it seems quite likely that the difference is real. It is interesting to note that in the analogous series of chlorosilanes the Si–Cl bond has been found[11] to be longer in trimethylsilicon chloride than in the other two members.

Another significant difference between *t*-butyl chloride and the other two compounds is in the Cl–C–C angle which changes from 110° and about 109° in 1,1,1-trichloroethane and 2,2-dichloropropane, respectively, to 107.5° in *t*-butyl chloride. Schomaker[12] has given a value of 110 ± 2° for this angle in ethyl chloride while Beach and Stevenson[3] reported a value of 110 ± 3° in isopropyl chloride. Thus the angle is significantly different from tetrahedral only in the case of *t*-butyl chloride.

A comparison of important non-bonded distances in the three compounds, *e.g.*, Cl–Cl and C–Cl shows that these distances are very nearly the same in all three compounds. It is possible that these distances may represent the closest possible distance of approach of these atoms and that this may be an important factor in determining the configuration of the molecules.

It is believed that the results given in this study for 1,1,1-trichloroethane and *t*-butyl chloride are more reliable than those reported by Beach and Stevenson. The outermost feature of their trichloroethane pattern was at q = 57 and in the *t*-butyl chloride pattern at q = 46. In the present investigation the patterns for both compounds extended to q = 91. It is of significance that the features which were found to be of special value in choosing the acceptable models lay beyond the outermost edge of Beach and Stevenson's patterns or at their extreme edge where it is difficult to estimate the relative intensities or shapes of features. The larger value obtained in this study for the C–Cl distance in 1,1,1-trichloroethane (1.77_5 *vs.* 1.76 Å.) is partly due to the fact that our best model has been selected at a slightly different C–C–Cl angle and partly due to a difference in scale of the photographs obtained in the two studies. The value for the C–Cl distance in *t*-butyl chloride as found in this investigation is 0.02 Å. greater than that reported previously. The discrepancy is partly due to the fact that Beach and Stevenson did not consider vibration factors and partly because their patterns did not permit rejection of a tetrahedral model which gave a short C–Cl distance.

It cannot be claimed that the vibration factors used in this study necessarily represent the correct values. However, they have been chosen after a careful consideration of the effects of their variation over large ranges in many curves and in two compounds. It is believed that they are at least of the correct order of magnitude and that they should therefore be useful in the investigation of other related compounds.

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[11] R. L. Livingston and L. O. Brockway, THIS JOURNAL, **68**, 719 (1946).

[12] V. Schomaker, reported by Allen and Sutton, ref. 4.