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Molecular Structure of 2-Chloropropane, as Determined by a Combined Use of the Electron Diffraction Data and the Spectroscopic Moments of Inertia*

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The gas-phase molecular structure of 2-chloropropane, $(CH_3)_2CHCl$, has been investigated by means of electron diffraction and by a joint analysis of the diffraction results and the spectroscopic moments of inertia. The structure parameters, distances in r_g and angles in φ_{av}, were determined (with parenthesized limits of error) to be as follows; C–Cl 1.812(1) Å, C–C 1.527(1) Å, C···Cl 2.720(2) Å, C–H 1.104(4) Å, ∠CCC 112.7(4)° and ∠HCH 108.5(8)°. The CCH_{sec} angle was assumed to be 109.8(20)°. The present results, together with the data for other molecules, confirmed a systematic elongation of the C–Cl r_g-distance in the series of methyl, ethyl, isopropyl, and *t*-butyl chlorides.

The systematic elongation of the C–Cl distances in the series of chloroalkanes (*viz.*, methyl, ethyl, isopropyl, and *t*-butyl chlorides) was first pointed out by Lide and Jen.[1] In the corresponding series of fluorides, a similar trend has also been observed.[2,3] These notable appearances of the environment effect on structure parameters are worth careful investigation, perhaps next after the environment effect on carbon-carbon bonds.[4]

For the series of chlorides mentioned above, the r_s-structures were determined by means of microwave spectroscopy. For *t*-butyl chloride, Hilderbrandt and Wieser obtained the r_z- and r_g-structure by an electron-diffraction investigation and a joint analysis of both the diffraction data and the spectroscopic moments of inertia.[5,6] For the other three molecules of the series, there has so far been no high-precision study by gas-electron diffraction. The present paper will report the structure determination of isopropyl chloride, or 2-chloropropane, by means of a joint analysis of the diffraction data and the spectroscopic moments of inertia. A similar study for the structures of ethyl chloride and methyl chloride will be reported in succeeding papers.[7,8]

A brief comment must be added to clarify why we are not content with the r_s-structures which are already available. The r_s-structure is the only existing structural information which can be obtained by making the optimal use of the experimental values of the ground-state rotational constants, without any knowledge of the molecular force field. It is widely accepted that the r_s-structure is useful, not only qualitatively, but, to a considerable extent, quantitatively as well.

In some favorable cases, the r_s-structure can be a good estimate of the r_e-structure. Watson[10] showed that the $I_s=(1/2)(I_e+I_0)$ relation holds for linear, planar, and symmetric top molecules. It is, then, possible to derive the r_e-structure from the r_s-structure and the observed ground-state rotational constants. The relation is theoretically approximate, but it is sufficiently good for molecules which do not contain light atoms, *e.g.*, hydrogen. For the molecules which contain hydrogen atoms, it seems that much is still left to be investigated about the physical nature of the r_s-structure.

In several recent determinations of accurate r_g-distances which were obtained by the combined use of spectroscopic and diffraction information, it was found, contrary to one's expectation, that the differences between r_g and r_s are not necessarily the same for similar bonded distances in different molecules.[11] The C–C distance of *t*-butyl chloride is one such case, the r_g-value being smaller than the r_s-value. This suggests that the r_s-structure (r_0-structure, too) may not be suitable for critical comparison and quantitative discussion of structural parameters.

TABLE 1. THE r_s- AND r_g-DISTANCES OF C–Cl AND C–C BONDS IN THE SERIES OF CHLORIDES (in Å units)[a]

		C–Cl	C–C	Reference
CH_3Cl	r_s	1.781(1)	—	12
	r_g	1.783(2)	—	8
CH_3CH_2Cl	r_s	1.788(2)	1.520(3)	13
	r_g	1.797(3)	1.526(4)	7
$(CH_3)_2CHCl$	r_s	1.798 (+8, −4)	1.520 (+4, −6)	14, 15
	r_g	1.812(1)	1.527(1)	b)
$(CH_3)_3CCl$	r_s	1.803(2)	1.530(2)	1
	r_g	1.830(5)	1.528(3)	5

a) The uncertainties to be attached to the last significant digit are shown in the parentheses. b) This work.

In the series of chlorides shown in Table 1, the documented r_s-values of C–Cl distances can not clearly establish the longer C–Cl of *t*-butyl chloride as compared with that of isopropyl chloride, if the quoted uncertainties are taken into consideration. In the present study, the uncertainties have been reduced by the use of joint analysis, and the difference in C–Cl distances has been clarified in terms of the r_g-structure, as is summarized in Table 1. The C–C r_g distances are nearly constant in this series of molecules, contrary to the difference observed in the r_s-structure.

Experimental

A guaranteed reagent of the Tokyo Kasei Co., Ltd., was used without further purification. The diffraction photographs were taken at room temperature on a unit with an

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* 1Å=100 pm is used throughout this paper.

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r^3-sector,[16] under the following conditions: camera length, 109.3 mm; accelerating voltage, 40 kV; beam current, 0.2 μA; exposure time, 1 min; and sample pressure, 60 Torr (1 Torr= 133.322 Pa). The total range of s covered was from 7 to 38 Å^{-1}.

Five sets of plates were taken during a week, each set containing six plates obtained in a sequence of exposures. The first set, like the last, was of the diffraction patterns of carbon disulfide, by which the scale factor was calibrated. The scale factors yielded by the two sets of carbon disulfide patterns agreed with each other within 0.1%. The relative stability of the accelerating voltage was monitored by a digital voltmeter and found to be within 0.05% during the term of a week. The nozzle setting was kept untouched so that the camera length was kept constant. Six plates of 2-chloropropane were selected from eighteen plates and analyzed by the least-squares method.

Analysis of the Diffraction Data

The procedure used to analyze the diffraction data of this molecule was much like that for 2-fluoropropane previously reported.[3] Four distances, C–C, C–Cl, C–H, and C···Cl, were adjusted by the least-squares method for molecular intensity. The remaining eighteen distances were fixed initially at the r_s-values by Tobiason and Schwendeman[14] and finally at values consistent with the converged values of the four adjusted distances, the r_s-values being still used for the parameters which could not be deduced from the four converged values. All the mean amplitudes were fixed at the values calculated by Cyvin and Cyvin.[17] The other details followed the routine procedure described in Ref. 18. The results of the least-squares adjustment are listed in Table 2.

TABLE 2. RESULTS OF THE LEAST-SQUARES ANALYSIS OF THE DIFFRACTION DATA FOR 2-CHLOROPROPANE$^{a)}$
(in Å units)

	C–C	C–Cl	C–H	C···Cl
r_a	1.523_1	1.807_6	1.098_5	2.715_2
$\sigma_1^{b)}$	0.001_6	0.001_6	0.002_9	0.001_9
σ_2	0.001_3	0.000_7	0.001_6	0.000_8
$\varepsilon^{c)}$	0.004_3	0.004_4	0.007_3	0.005_4
r_g	1.525	1.809	1.104	2.717

a) Index of resolution: 0.95—1.00 b) For the definitions of σ_1 and σ_2, see Ref. 19. c) Limits of error estimated from $2.5\sigma_1$ and the systematic error originating in the uncertainty of the scale factor.

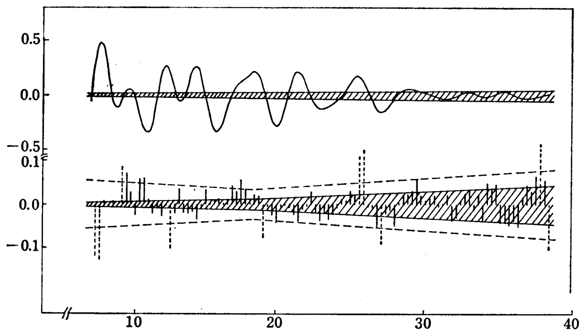

Fig. 1. The best-fit theoretical molecular intensity and the residuals of 2-chloropropane. See text.

The best-fit calculated molecular intensity and the residuals of the observed are shown in Fig. 1.[20] The residuals are shown in an enlarged scale, four times as great as that of $sM(s)$ curve. The narrower boundaries with shading correspond to ±2 of the last digit of the digital voltmeter, that is, the limits of detection in the photometry. The outer boundaries (shown by the broken lines) are the estimated limits of error in the intensity measurement; they indicate the normally expected range of scattering in the intensity data. Some of the points exceeded the boundary, more or less for accidental reasons. These points were zero-weighted in the final refinement and are shown by vertical broken lines in Fig. 1. The shifts of the converged values of the parameters caused by the use of the modified weight were within the standard deviations, which were reduced to about two thirds of the standard deviations in the unmodified case.

Joint Analysis

The effective moments of inertia, as determined by Tobiason and Schwendeman,[14] were corrected for the vibrational effect and converted into $I^{(z)}$, the moments of inertia for the zero-point average structure.[4] The corrections were calculated by the use of the force constants obtained by Cyvin and Cyvin.[17] Since the barrier to the methyl torsion has been reported to be greater than 3.45 kcal/mol,[14] the torsional motions were treated as small amplitude vibrations. The r_g distances of the C–C, C–Cl, and C···Cl atom-pairs determined by electron diffraction were converted into r_α^0 distances[21] by correcting for the anharmonic term, the centrifugal stretching, and the perpendicular vibration. The Morse parameter, a_3, was assumed to be 2.0 Å^{-1} for C–C and C–Cl distances and zero for the non-bonded C···Cl distance. The numerical values of these vibrational corrections are summarized in Table 3.

TABLE 3. MOMENTS OF INERTIA, VIBRATIONAL CORRECTION, AND $r_\alpha{}^0$-DISTANCES OF 2-CHLOROPROPANE$^{a)}$

	$I^{(\mathrm{eff})\ b)}$	$\Delta I^{c)}$	$I^{(z)}$ (in amu Å^2)
a	62.639	0.073	62.712
b	110.566	0.084	110.650
c	157.557	0.063	157.620

	$r_g - r_\alpha{}^0$	$r_\alpha{}^{0\ d)}$ (in Å)
C–C	0.0030	1.522_1
C–Cl	0.0034	1.805_8
C···Cl	0.0021	2.715_1

a) Similar tables for isotopic species are omitted. b) Calculated from the rotational constants[14] by means of the conversion factor of 505376 Mc amu Å^2. c) Vibrational correction for $I^{(\mathrm{eff})}$. $I^{(z)}=I^{(\mathrm{eff})}+\Delta I$. d) See Ref. 6 for the definition.

The uncertainty of $I^{(z)}$ was assumed to be 0.01 amu Å^2, while that of r_α^0 was taken to be equivalent to the limits of error of the r_a values. The zero-point average structure (r_{av}-structure)[21] was determined by a joint analysis of the r_α^0 by diffraction and of $I^{(z)}$ by spectroscopy. $(CH_3)_2CH^{35}Cl$, $-^{37}Cl$, $-D^{35}Cl$, and $(CH_3)(CD_3)$-$CD^{35}Cl$ (the C's are all ^{12}C) were selected for the structure analysis in the present work.

It has been our experience that the moments of inertia of the isotopic species of such heavy atoms as ^{13}C and ^{37}Cl can not give additional information independent of that of the parent species. This comes about for two reasons. First, the range of parameters which can account for the $I^{(z)}$ of both the parent species and the isotopic species is usually rather wide. Thus, the use of $I^{(z)}$ for the isotopic species is of no help in reducing the range of parameters already limited by the results of electron diffraction, if the uncertainties of $I^{(z)}$, which are of the order of 0.01 amu Å^2, are taken into consideration. Secondly, the border between the acceptable region and the unacceptable region of the parameters is very vulnerable to the estimated isotope effects in structure parameters and to the amount of the uncertainty of $I^{(z)}$, for which no quantitative method of estimation has been established.[22]

The deuterated species, on the other hand, can provide independent information. In this case, however, the isotope effect on the structure parameters becomes important. For the bonded distances, the isotope effect may be estimated fairly well by assuming a Morse-type anharmonic potential and using a diatomic approximation.[23] For the bond angles, usually almost nothing is known about the anharmonicity.

It seems to be a sound approach to the problem to let the isotope effects in the bond angles be adjustable and to determine the values from the $I^{(z)}$ of the deuterated species, as has already been attempted in some of the previous studies.[24–26] Fortunately, the deuterated species are very effective in reducing the allowed range of parameters, even if additional freedom is introduced by adjustable isotope effects. Moreover, the discrepancy between the calculated and observed values of $I^{(z)}$ develops markedly with small changes in the parameters, so that the final conclusion for the structure is not sensitive to the estimated amount of the uncertainty in $I^{(z)}$.

Therefore, in the present study, the structure parameters were first determined chiefly by the use of the $I^{(z)}$ of the parent species. The $I^{(z)}$ of the ^{37}Cl species were calculated by the same parameter values only in order to confirm that they were consistent with the observed values. The allowable ranges of the parameters are naturally very wide at this stage, covering an area bounded only by the limits of error in the results of electron diffraction. They were then reduced by the use of the deuterated species. The isotope effects in $\angle ClCD_s$, $\angle DCD$ in the methyl tops and $\angle CCC$ in the D-4 species were adjusted, while the isotope effect in the C–H bond was assumed to be the value calculated by the diatomic approximation, with an estimated uncertainty of ±0.0015 Å.[27]

The local C_{3v} symmetry was assumed for the methyl tops. The tilting angle was assumed to be zero. The methyl C–H distance and the secondary C–H distance were assumed to be equivalent in their r_g values. Therefore, their difference in r_{av}-structure was fixed at the calculated value, 0.007_5 Å. A pertinent piece of information from the microwave study is that one of the methyl C–H bonds lies on the CCC plane in the trans position to the C–C bond.[14] There are still seven independent structure parameters left,—— C–C, C–Cl, C···Cl, $\angle CCC$, C–H, and $\angle HCH$ in the methyl top and $\angle CCH_s$. For the C–C, C–Cl, and C···Cl distances, the most probable values and the uncertainties by which the parameters may vary have been determined by electron diffraction. Therefore, three more parameters can be determined by the three moments of inertia of the parent species. By considering that the $I^{(z)}$ values are least sensitive to a change in $\angle CCH_s$, it was assumed at the value in the r_s-structure, 109.8°, with an estimated uncertainty of ±2°.

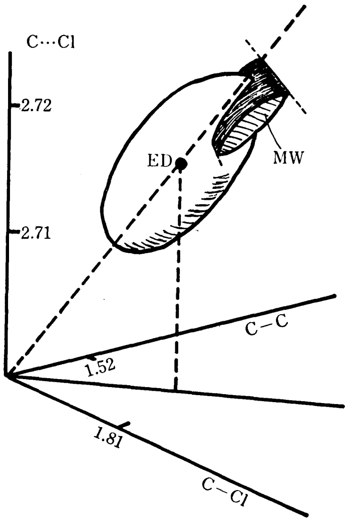

Fig. 2. The allowable range of structure parameters shown in the three-dimensional parameter space. The limits of error of electron diffraction is shown by a boundary like a rugby ball. The region compatible with spectroscopic moments of inertia is shown by the shaded portion of the space, which extends to both sides more than depicted.

The range of parameters compatible with the $I^{(z)}$ of the deuterated species as well as the parent species is shown schematically in Fig. 2; it is denoted as MW, with shading. The most probable values can be determined by the portion of the MW region which is inside the error boundary of electron diffraction. Figure 3 shows the section of Fig. 2 by means of a plane defined by the C···Cl axis and a straight line connecting the origin and the ED point. In the sections parallel to that shown in Fig. 3, the situation is more or less similar.

The results obtained are summarized in Table 4. Uncertainties originating from the several different factors are also shown: ε_1, the half-width of the variation in the parameter value corresponding to the allowed region; ε_2, the uncertainty originating in the uncertainty of $I^{(z)}$, ±0.01 amu Å^2, although the correlations among the parameters are not shown; ε_3, the uncertainty due to the assumed $\angle CCH_s$, ±2°; and ε_4, that due to the

Table 4. Zero-point average structure of 2-chloropropane[a)]
(in Å and degrees units)

	r_{av}, ϕ_{av}	ε_1	ε_2	ε_3	ε_4	ε_0
C–Cl	1.808_4	0.001	—	—	—	0.001
C–C	1.524_2	0.001	—	—	—	0.001
C···Cl	2.718_2	0.002	—	—	—	0.002
(∠CCCl	109.00)					
∠CCC	112.7_1	0.20	0.09	0.27	—	0.4
$C-H_{Me}$	1.093[b)]	0.002	0.001	0.003	—	0.004
∠HCH	108.4_7[b)]	0.55	0.12	0.57	—	0.8
$\delta(CCD_{sec})$[c)]	0.24[d)]	0.03	0.1	—	—	0.1
δ(DCD)	0.26	0.17	0.1	—	0.07	0.2
δ(CCC)	0.0	0.0	0.03	—	0.01	0.03

r_g: C–Cl 1.812, C–C 1.527, C···Cl 2.720, C–H 1.104 Å.

a) ε_1 through ε_4 are uncertainties from various sources. ε_0 is the total estimate of uncertainty. See text.

b) The effect of methyl torsion is eliminated by adding 0.010 Å to C–H and 0.17° to ∠HCH. See text.

c) $\delta(CCD_{see})$, $\angle CCD_{sec}-\angle CCH_{sec}$; δ(DCD), ∠DCD−∠HCH; δ(CCC), $\angle CCC(D_4)-\angle CCC(H)$.

d) This amount is equivalent to −0.5° in $\delta(ClCD_{sec})$.

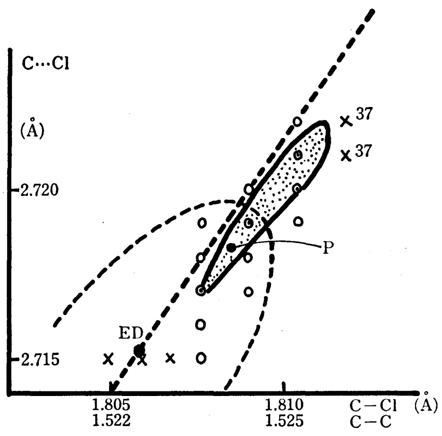

Fig. 3. A section of Fig. 2. See text.

× ; Points not compatible with $I^{(z)}$ of the D_s-species.

$\times^{37}$; Points not compatible with $I^{(z)}$ of ^{37}Cl species.

○ ; Points compatible with $I^{(z)}$ of D_s-species, but not with those of D-4 species.

⊙ and the area shown with dots; Points compatible with $I^{(z)}$ of D_s and D-4 species as well as those of the parent species.

uncertainty of the assumed isotope effect in the C–H(D) distance, ±0.0015 Å. The total estimates of uncertainty are then shown in the last column as ε_0.

The parameters of the structure of methyl tops, C–H and HCH, apparently decrease upon averaging over the torsional motion. For comparative purposes, however, it is desirable to get structure parameters which correspond to that of the large-amplitude treatment,[24)] or a structure in which the average over the torsional motion is excluded. In the values listed in Table 4, the averaging effect of the torsional motion is eliminated by adding 0.010 Å to the determined C–H distance and 0.17° to the HCH angle. Thes corrections were evaluated from the differences between the present results and those of the large-amplitude treatment.[28)] They were also in good agreement with the estimates by a simple model-calculation that the apparent shrinking of the C–H distance is due only to the perpendicular amplitude of the torsional mode and that the decrease in the HCH angle is caused by a slight bending of the shrunken C–H bonds, so that all the hydrogen atoms may lie on the same plane as that in the torsional-equilibrium configuration.

Discussion

The skeletal structure has already been discussed in the introductory part, where it was compared with the structures of other normal alkyl chlorides. The structure of the methyl top of this molecule is much like that of acetone, including a positive isotope effect in the DCD angle, which was interpreted as being due to the repulsive interaction between two methyl tops.[29)] The isotope effect in the CCC angle was −0.3° in D-6 acetone, while it is zero in the present case. This is not in perfect conformity with the picture of the repulsive interaction, although the amount of δ(CCC) is expected to be smaller in the present species, for which only one of the two methyl tops is deuterated.

The positive isotope effect in $\angle CCD_s$, obtained as 0.24°, corresponds to a negative one in the $ClCD_s$ angle, −0.5°. This may be manifestation of the anharmonicity due to a repulsive interaction between the chlorine and the secondary hydrogen.

In the present study, the anharmonicity in non-bonded C···Cl was neglected in obtaining r_α^0 from r_g. If the Morse-type parameter, a_3, had a non-zero value, the ellipse shown in Fig. 3 by the broken curve would be shifted parallel to the C···Cl axis downwards or upwards, according to whether it has a positive value or a negative one. The overlapping area and, therefore, the structure parameters would be almost the same for a negative value within 0—2 Å^{-1}. However, for a positive a_3, the overlapping area would decrease rapidly, and the consistency between the diffraction results and the spectroscopic moments of inertia would diminish. A possibility of a non-bonded anharmonicity which could be expressed by a Morse-type potential with a negative a_3 value has also been found in recent studies of $CHCl_3$[30)] and $CHBr_3$[31)] molecules.

TABLE 5. COMPARISON BETWEEN r_s AND r_{av} STRUCTURE OF 2-CHLOROPROPANE[a)]
(in Å and degrees units)

	I	II	III
C–Cl	1.797	1.797—1.807	1.808
C–C	1.520	1.505—1.523	1.524
C–H_{Me}	1.092 1.099[b)]	1.091—1.099	1.093
C–H_s	1.091	1.091—1.117	1.093
CCCl	109.5		109.0
CCC	112.8	112.5—114.6	112.7
HCH($\alpha\beta,\beta\gamma$)	109.1	108.9—109.2	108.5
HCH(α,γ)	108.3		108.5
CCH_β	110.0	110.0—111.9	110.4
H_sCCl	105.2	103.5—105.4	106.1
CCH_s	109.8		(109.8)[c)]

a) I: the complete r_s-structure; Ref. 14. II: the range of variation in the r_s-structure; Ref. 15. III: the r_{av}-structure of the present study. b) According to Ref. 15. c) Assumed.

Tobiason and Schwendeman determined the complete r_s-structure for this molecule by the use of the species isotopically substituted for all non-equivalent atoms.[14)] It is compared in Table 5 with the r_{av}-structure determined in the present study. There also are shown the ranges in the variation of the r_s-values reported by Schwendeman.[15)] These variations are what would be caused by different analytical methods as well as by an insufficient number of isotopic species. It may be noted that the complete r_s-structure is in fair agreement with the r_{av}-structure except for the C–Cl distance, and that the maximum deviation of an incomplete r_s-value from the r_{av}-value may be about 2° in bond-angles. It seems, then, appropriate to assume an uncertainty of $\pm 2°$ when some bond angle in the r_s-structure are used as complementary information in determining the r_{av}-structure.

The numerical computations were performed on a FACOM 230-75 of the Hokkaido University Computing Center and on a FACOM 270-20 in the laboratory of Professor Kimio Ohno, to whom the authors' thanks are due.

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20) The numerical data of the total intensity and the background, together with the elements of the correlation matrix, are deposited with the Chemical Society of Japan (Document No. 7718).

21) For the definitions of $r_\alpha{}^0$ and r_{av}, see Ref. 6.

22) The major terms of the vibrational correction to the rotational constants are of the $1/\omega$ type, where ω is the frequency of normal vibrations.[24)] The discrepancy between the true ω and the value calculated by the use of an available set of force constants may be estimated to be less than 10% of ω. In the present study, the uncertainty of the correction was, then, estimated to be about 10% of the amount of the correction itself, rounded out to the order of 0.01 amu Å^2.

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27) Estimated from an uncertainty of ± 0.5 Å^{-1} in a_3.

28) In the present study, the vibrational correction was also calculated by the large-amplitude treatment. Then the process of eliminating the effect of the torsional motion might seem to be meaningless. However, it is intended that the step discussed here shall be applied to other molecules for which the torsional barrier is high, and the analysis may be performed solely by the small-amplitude treatment. The values of the vibrational correction for the parent species in the large-amplitude treatment are: ΔI_a 0.161, ΔI_b 0.213, and ΔI_c 0.149 amu Å^2.

29) The methyl structure of acetone: r_{av}(C–H) 1.091(3) Å, ϕ_{av}(HCH) 108.5(5)°, and δ(DCD) 0.17(20)°. See Ref. 25.

30) H. Kunimi and M. Kimura, to be published.

31) K. Tamagawa and M. Kimura, to be published.