Molecular Structure of 2,2-Dichloropropane as Determined by a Combined Use of the Electron-diffraction Data and the Spectroscopic Moments of Inertia

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The molecular structure of 2,2-dichloropropane has been determined by the joint analysis of the electron-diffraction data and the moments of inertia obtained by Matsumura and Takeo by means of microwave spectroscopy. Under the assumptions that r_g(C–H) is in the range of 1.100—1.110 Å and that φ_α(HCH) is larger than 107.0°, the structure parameter values have been determined (with the limits of error in parentheses) to be as follows: r_g(C–Cl), 1.799(3) Å; r_g(C–C), 1.523(4) Å; r_g(Cl···Cl), 2.910(1) Å; r_g(C···Cl), 2.702(1) Å; φ_{av}(ClCCl), 108.3(3)°, and φ_{av}(CCC), 113.0(4)°. The r_g-structure determined in the present study is in perfect conformity with the r_0-structure determined by Matsumura and Takeo. The C–Cl and C–C distances are shorter than the corresponding distances in 2-chloropropane.

Since Lide and Jen first pointed out the systematic elongation of C–Cl bonds in a series of molecules (methyl, ethyl, isopropyl, and *t*-butyl chlorides),[1] the environment effect on bond lengths in the halogen derivatives of alkanes has been the subject of many studies. A similar systematic elongation of the C–F bonds observed for the fluorine derivatives of alkanes may be involved in studies of the environment effect.[2] Recently, Matsumura and his collaborators have carried out extensive microwave studies of the chlorine and fluorine derivatives of methane.[3] From their results and those for halogenated ethanes and propanes quoted in the literature, they have systematized changes in the carbon-halogen bond lengths with the number of halogen atoms and methyl groups attached to the carbon atom in question. However, the comparisons of the bond lengths so far reported are, in most cases, based upon the r_s distances determined by microwave spectroscopy.[4]

In the present authors' opinion, the r_g distances are preferable to the r_s distances for comparing bond lengths, as was mentioned in the preceding paper on 2-chloropropane.[5] However, high-precision data on the r_g-structures of halogenated alkanes are rather few. The present paper will report the structure of 2,2-dichloropropane as determined by a combined use of the electron-diffraction data obtained by the present study and the moments of inertia obtained by Matsumura and Takeo by microwave spectroscopy,[6] as part of a series of studies of the molecular structures of chlorinated alkanes.

Experimental

A guaranteed reagent purchased from Nakarai Chemicals, Ltd., was used without further purification. Diffraction photographs were taken at room temperature, 20 °C, on the unit eqipped with an r^3-sector[7] under the following experimental conditions: camera lengths, 244.3 and 109.3 mm; accelerating voltage, 42 kV; beam current, 0.15 μA; exposure times, about 70 s for the short camera length and about 50 s for the long camera length; sample pressure, 50 Torr.[8] The wavelength, or the scale factor, was determined by reference to the pattern of carbon disulfide taken under the same experimental conditions. The covered s ranges were 3—19 Å^{-1} and 6—40 Å^{-1} for the long and short camera distances respectively. Two plates from the long camera distance and five plates from the short camera distance were selected for analysis.

Analysis of the Diffraction Data

The reduction of the observed total intensities to the molecular intensities[9] and the determination of the parameter values by the least-squares method were carried out following our usual procedure.[10] The following assumptions were set up with respect to the molecular geometry: (1) C_{2v} symmetry for the molecule as a whole, (2) local C_{3v} symmetry for the methyl tops, (3) zero tilt angles for the methyl tops, *i.e.*, the C_3 axes of the methyl tops coincident with the C–C bond axes, (4) staggered conformation about the C–C bonds with HCCCH in plane, as was assumed for 2-chloropropane. The mean amplitudes were fixed at values calculated using the Urey-Bradley force field proposed by Green and Harrison.[11] The calculated mean amplitudes for the main distances are shown in Table 1.

TABLE 1. CALCULATED MEAN AMPLITUDES AT 20 °C (in Å units)

Distance	Calculated mean amplitude	
C–Cl	0.0631	
C–C	0.0519	
C–H	0.0784	
Cl···Cl	0.0851	
C···Cl	0.0769	
Cl:::H_{gauche}	0.1833	H in CCC plane
	0.2113	H out of CCC plane
Cl:::H_{trans}	0.1061	
C···C	0.0788	

Starting with the r_0-structure reported by Matsumura and Takeo,[6] four distances, Cl···Cl, C–Cl, C···Cl, and C–C, were adjusted by fixing the r_a(C–H) and φ_α(HCH) at plausible values.[4,12] Since the contributions to the molecular intensities are small from the distances

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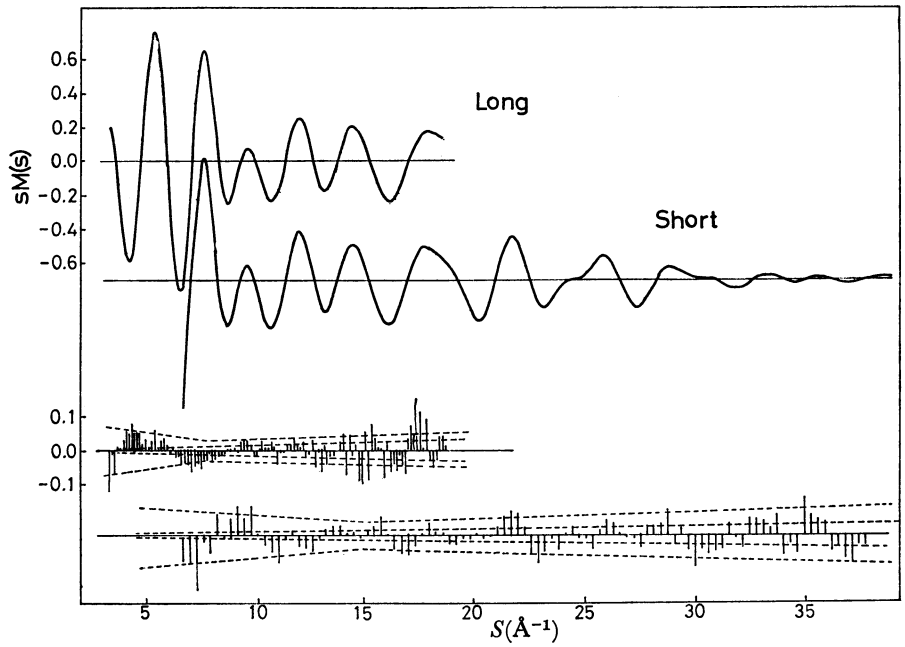

Fig. 1. The best fit theoretical molecular intensity curves, $sM(s)$, and the differences, $sM(s)^{obsd}-sM(s)^{calcd}$, for typical data from the long and the short camera distances. In the afferences, the inner broken lines indicate the limit of detection in photometry and the outer broken lines the estimated limit of errors in the observed intensities; see Ref. 5. The ordinate for the differences is taken twice as large as that for the intensity curves.

TABLE 2. RESULTS OF ELECTRON DIFFRACTION (distance in Å; angle in degree units)[a]

Distance	r_g	r_α^0 [b]
Cl···Cl	2.903(7)	2.902
C–Cl	1.797(4)	1.792
C···Cl	2.702(4)	2.700
C–C	1.519(6)	1.515
Index of resolution	0.98—1.04	

a) The values in parentheses indicate the limits of error, which were estimated from the random errors and the error in the scale factor. The uncertainty included in the scale factor is ±0.10% in the distances. The r_a(C–H) and the φ_α(HCH) were assumed to be 1.110 Å and 108.5° respectively. b) As to the conversion of r_g to r_α^0, see text. The uncertainties in the r_α^0 values are equivalent to those in the r_g values.

involving H atoms, the influence of the assumed distances on the results is insignificant; the converged values vary only by one-thousandth angstrom or less as long as the φ_α(HCH) and the r_a(C–H) values are limited within reasonable ranges (see Ref. 12 and also the next section). The final results are listed in Table 2, while the best-fit theoretical intensity curves and the residuals for the observed intensities for typical plates are shown in Fig. 1. The residuals are depicted on a double scale. The inner broken lines on the residuals indicate the limit of detection in photometry, while the outer ones indicate the boundary of the distribution of the residuals in the molecular intensities observed by a normal technique.[13]

Joint Analysis

The moments of inertia of $(CH_3)_2C^{35}Cl_2$ and $(CH_3)_2C^{35}Cl^{37}Cl$ in the ground state have been reported by Matsumura and Takeo.[6] Since the $^{35}Cl^{37}Cl$ species does not provide additional information,[5] only the moments of inertia of $(CH_3)_2C^{35}Cl_2$ were used for the joint analysis in the present study. These effective moments of inertia, $I^{(eff)}$, were corrected for the vibrational effect and converted into the moments of inertia, $I^{(z)}$, for the zero-point average structure.[14] The corrections, ΔI, were calculated by using the force constants given by Green and Harrison.[11] The barrier to the hindered rotation about the C–C axis was estimated to be about 3.4 kcal/mol.[11] In general, somewhat different ΔI values are obtained by using either one of two alternatives, the small-amplitude[14] or the large-amplitude treatment[15] for the methyl torsion. The

TABLE 3. EFFECTIVE MOMENTS OF INERTIA, THE VIBRATIONAL CORRECTION, AND THE MOMENTS OF INERTIA FOR THE ZERO-POINT AVERAGE STRUCTURE OF $(CH_3)_2C^{35}Cl_2$ (in amu Å² units)[a]

	$I^{(eff)}$ [b]	ΔI	$I^{(z)}$ [c]
a	138.056	0.108	138.164
b	205.617	0.112	205.729
c	234.154	0.044	234.198

a) The corrections were calculated by the small-amplitude treatment. See text. b) Calculated from the observed rotational constants by using, as the conversion factor, 505376 MHz amu Å². c) $I^{(z)} = I^{(eff)} + \Delta I$.

barrier to the hindered rotation of this molecule is almost the same as that of 2-chloropropane.[5] Therefore, the differencc in the r_z(C–H) value or in the φ_z(HCH) value of the 2,2-dichloropropane obtained by the two treatments is practically the same as that in the case of 2-chloropropane.[5] In the present analysis, the small-amplitude treatment was adopted; the ΔI and $I^{(z)}$ values thus obtained are listed in Table 3, together with $I^{(eff)}$. The ΔI and the $I^{(z)}$ values to be obtained by the large-amplitude treatment can be estimated by referring to the results of 2-chloropropane.[5] In either treatment, the same r_g values are finally yielded. The r_g distances determined by the electron diffraction were converted into the r_α^0 distances by correcting them for the anharmonic term, the centrifugal stretching, and the perpendicular vibration. The r_α^0 values thus obtained are also entered in Table 2. The Morse asymmetry constants, a_3, were assumed to be 2.0, 2.1, and 2.0 Å^{-1} for the C–Cl, C–C, and C–H distances respectively, and zero for all the non-bonded atom pairs.

The structure of 2,2-dichloropropane is defined by the six parameters, r(C–C), r(Cl···Cl), r(C···Cl), r(C–H), and ∠HCH, under the same assumptions with respect to the geometry as those employed in the analysis of the electron-diffraction data. In determining these six parameter values, the three moments of inertia can be used in addition to the two r_α^0 values for the bonded distances determined by the electron diffraction. Obviously these five experimental values are not sufficient for determining the six parameters of this molecule. Thus, a reasonable assumption as to the ranges of r(C–H) and ∠HCH was used and the skeletal parameters were determined with smaller uncertainties than those of the electron-diffraction results.

The analysis was done through the following steps. For the bonded distances, r(C–C) and r(C–Cl), the results obtained by the electron diffraction are illustrated in a two-dimensional space, as is shown in Fig. 2, where the axes are scaled in r_α^0 derived from r_g. In Fig. 2, the O point indicates the best-fit values determined by the electron diffraction, while the ellipse shows the boundary of the total limits of error, which were estimated from the random errors obtained by the least-squares refinement and the error included in the scale factor. The straight line S shows the direction of change in r(C–C) and r(C–Cl) with a change in the scale factor. For any pair of the C–C and C–Cl distances, the three moments of inertia give the relation among the other four parameters. When the A, B, C, and D points are chosen on the S line in Fig. 2, the relations can be represented by the corresponding parallel straight lines in the r(C–H)–∠HCH space, as is shown in Fig. 3. The relations may be described numerically as follows; (1) for any pair of r(C–C) and r(C–Cl), a variation of ±0.005 Å in r(C–H) is equivalent to variations of ±0.22° in ∠HCH, ∓0.0004 Å in r(Cl···Cl) (or ∓0.02° in ∠ClCCl), without any change in the C···Cl distance, and (2) an increase of 0.01% in both r(C–C) and

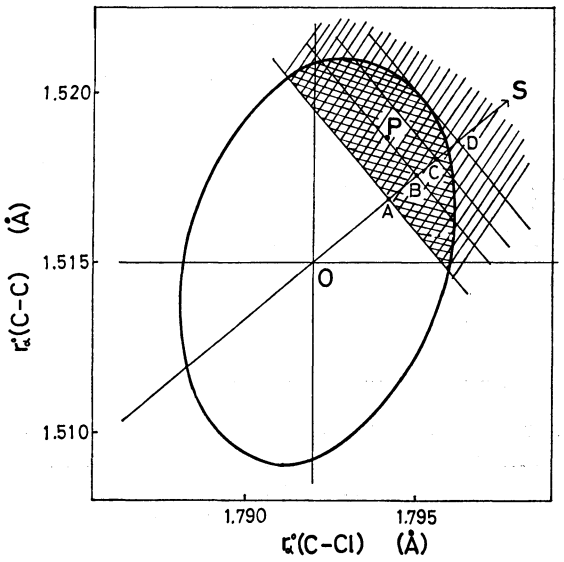

Fig. 2. The allowed range of the r_α^0(C–Cl) and r_α^0(C–C) distances. The shading indicates the range allowed by the spectroscopic moments of inertia under the conditions that the r_α^0(C–H) is in the range of 1.075—1.085 Å and the φ_α(HCH) is larger than 107.0°. The cross-shaded area is the range allowed by both electron diffraction results and the spectroscopic moments of inertia under the same conditions. The O point shows the best fit values which were obtained by converting the r_g values determined by electron diffraction into the r_α^0 values and the P point is the center of the cross-shaded area. The limits of error in the r_α^0 values are taken to be identical to those in the experimental r_g values. See text about other details.

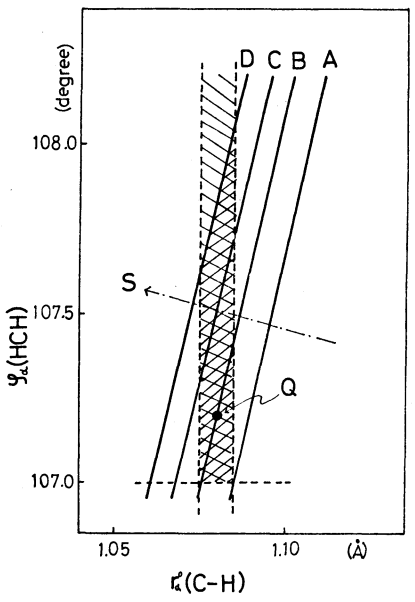

Fig. 3. The correlation diagram of the r_α^0(C–H) and the φ_α(HCH) which satisfy the three observed $I^{(z)}$. The region assumed for the r_α^0(C–H) and the φ_α(HCH) is indicated by shading. The pararell lines, A, B, C, and D, corresponds to the A, B, C, and D points in Fig. 2 respectively. The S line with an arrow indicates the direction of an increase in the scale factor. The upper boundary limited by the D line is determined by the electron diffraction results. The cross-shaded area then corresponds to that in Fig. 2. The Q point indicates the final representative values which are compatible with the P point in Fig. 2.

r(C–Cl) is equivalent to either changes of +0.11° in ∠HCH and +0.0003 Å in r(C···Cl), or changes of −0.0025 Å in r(C–H), +0.0004 Å in r(C···Cl), and +0.0002 Å in r(Cl···Cl).

Here, we put restrictions on the allowed ranges of the r(C–H) and ∠HCH. In various molecules which are about the size of the present one, the r_g(C–H) have been found in the ranges of 1.100—1.110 Å, which corresponds to the range of 1.075—1.085 Å in r_α^0(C–H), and the φ_α(HCH) have been found to be larger than 107.0°. Thus, the r_α^0(C–H) and φ_α^0(HCH) values of the present molecule were assumed to be in the ranges of values mentioned above. This region is indicated by shading in Fig. 3. It may be seen that line A in Fig. 3 is a limiting case in which the line is scarcely in contact with the region allowed by the restrictions for r(C–H) and ∠HCH. Accordingly, the A point in Fig. 2 represents the lower limit of the allowed region with respect to the scale factor. When the r(C–C) and the r(C–Cl) change along a line perpendicular to the S line, changes in the moments of inertia due to a change in the r(C–C) are almost cancelled by those due to a change in the r(C–Cl); consequently, the calculated values of the moments of inertia do not change practically. Thus, the relation between r(C–H) and ∠HCH shown by the A, B, C, and D lines in Fig. 3 holds well for any pair of the C–C and C–Cl distances on the lines perpendicular to the S line through the A, B, C, and D points in Fig. 2 respectively. In Fig. 2, the line through the A point, which corresponds to the A line in Fig. 3, is, then, the lower boundary in the r(C–C)–r(C–Cl) space. The shaded area in Fig. 2 is the region thus limited.

The upper boundary in the r(C–C)–r(C–Cl) space is formed by the error-ellipse of the electron-diffraction results. The line tangent to the ellipse and perpendicular to the S line in Fig. 2 passes through the D point. Then, the D line in Fig. 3 becomes the corresponding upper boundary in the r(C–H)–∠HCH space. The allowed regions thus determined are shown as the cross-shaded area in Figs. 2 and 3. In this procedure, the allowed ranges of the r(Cl···Cl) and the r(C···Cl) are concurrently determined, since the areas in Figs. 2 and 3 also define the ranges of these parameters, though implicitly.

The values of r(C–Cl) and r(C–C) at the approximate center, P, of the cross-shaded area in Fig. 2 were taken as the final ones. The final values for the other four parameters were chosen at the middle point of the ranges of the parameters which are compatible with the values of r(C–C) and r(C–Cl) given by the P point. The final values for r(C–H) and ∠HCH thus determined are represented by the Q point in Fig. 3. The results are summarized in Table 4. In the table, the allowed ranges for the parameters are given by the farthest separations from the respective final value in the allowed region, such as the cross-shaded area in Fig. 2. The allowed ranges for the skeletal parameters are narrower than those for the r_α^0 values determined by the electron diffraction alone. (*cf.* Table 2). This is because we assumed the C–H distance and the HCH angle to be within the limited ranges of values. The uncertainties included in the $I^{(z)}$ values are estimated to be 0.01 amu Å².[16] The corresponding variations in the parameter-values are only ±0.0007 Å for the C–H distance and ±0.03° for the HCH angle, and negligible for the other distances. Therefore, the uncertainties in the $I^{(z)}$ values do not affect the final allowed ranges.

TABLE 4. RESULTS OF THE COMBINED ANALYSIS[a]

	r_{av} or φ_{av}	Allowed range	r_g[c]
C–Cl	1.794	±0.003	1.799
C–C	1.519	±0.004	1.523
Cl···Cl	2.908	±0.001	2.910
C···Cl	2.700	±0.001	2.702
C–H	[1.080[b]	±0.005	1.101]
ClCCl[d]	108.3	±0.3	
CCC[d]	113.0	±0.4	
HCH	[107.2[b]	+0.9 −0.2]	
CCCl[d]	108.9	±0.4	

a) Distances in Å units, and angles in degree units. The r_{av}(C–H) and the φ_{av}(HCH) were assumed to be in the range of 1.075—1.085 Å and larger than 107.0° respectively; they are indicated by brackets. See text. b) The values obtained by the large-amplitude treatment would be 1.090 Å for the r_{av}(C–H) and 107.4° for the φ_{av}(HCH). c) The limits of error in the r_g values are equivalent to the allowed ranges of the r_{av}. d) Calculated from the distance-parameters.

Discussion

The r_0-structure determined by Matsumura and Takeo[6] is reproduced in the third column of Table 5 and compared with the result obtained by the present study in the second column of the table. The r_g(C–C) and r_g(C–Cl) values differ slightly from the r_0 values. However, if the difference in their physical meanings is taken into account,[17] such differences between r_g and r_0 as are shown in the table may be said to be reasonable. Thus, except for the structure of the methyl top, the two results are in good agreement with each other.

A comparison with the structure of 2-chloropropane

TABLE 5. COMPARISON OF THE STRUCTURES OF 2,2-DICHLOROPROPANE DETERMINED BY THE PRESENT AND THE MICROWAVE STUDIES, AND THE STRUCTURE OF 2-CHLOROPROPANE (in Å and degree units)

	2,2-Dichloropropane		2-Chloropropane
	r_g or φ_{av} (Present study)	r_0 (Matsumura *et al.*)[a]	r_g or φ_{av} (Iijima *et al.*)[b]
C–Cl	1.799(3)	1.793(5)	1.812(1)
C–C	1.523(4)	1.522 (assumed)	1.527(1)
ClCCl	108.3(0.3)	108.2(0.5)	
CCC	113.0(0.4)	113.0(0.5)	112.7(0.4)
CCCl[c]	108.9(0.4)	108.9	109.0(0.2)

a) Ref. 6. b) Ref. 5. c) Calculated from the other parameter values.

reported previously, which is also shown in Table 5, shows that the C–C and C–Cl distances are shorter in 2,2-dichloropropane than those in 2-chloropropane. An increase in the number of Cl atoms results in the shortenings of the C–C and C–Cl bonds. In spite of the contraction of the C_2CCl_2 frame of 2,2-dichloropropane, the valence angles, CCC and CCCl, are the same as those in 2-chloropropane, while the ClCCl angle is much smaller than the tetrahedral angle. Probably, the repulsive interactions between the two methyl tops and between the methyl top and the chlorine atom overcome the interaction between the two chlorine atoms.

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. The authors also wish to thank Dr. Chi Matsumura of the National Chemical Laboratory for Industry for permitting them to use his results prior to publication.

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12) In practice, the ranges of the r_a(C–H) and the φ_α(HCH) adopted were 1.08—1.10 Å and 108—110° respectively. See the section on joint analysis in the text.

13) A few points fall outside the expected limits of error. In the present analyses, all the observed values were employed. However, they do not affect the results. See Ref. 5.

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