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The Molecular Structure of Ethyl Chloride 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 ethyl chloride has been determined by a joint analysis of the electron-diffraction data and the moments of inertia obtained by Schwendeman and Jacobs by means of microwave spectroscopy. In the analysis, a staggered conformation with C_s symmetry for the molecule and a local C_{3v} symmetry about the C–C axis for the methyl group were assumed. Under the further assumptions that $\varphi_{av}(\mathrm{HCH})_{\mathrm{CH_3}}$ is 109.2±2° and $\varphi_{av}(\mathrm{CCH})_{\mathrm{CH_3}}$ is in the range of 113.6—109.6°, the following parameter values were determined: r_g(C–C), 1.528(4) Å; r_g(C–Cl), 1.802(3) Å; r_g(C···Cl), 2.746(5) Å; $r_g(\mathrm{C{-}H})_{\mathrm{CH_3}}$, 1.103(4) Å; $\varphi_{av}(\mathrm{HCH})_{\mathrm{CH_3}}$, 110.0(1.6)°; and φ_{av}(CCCl), 110.7(0.3)°. The r_g and r_s distances for the C–Cl and C–C bonds of various chlorinated alkanes were plotted against the difference between the numbers of methyl groups and chlorine atoms, $\Delta n = n(\mathrm{CH_3}) - n(\mathrm{Cl})$. In general, as the number of chlorine atoms increases, both distances become shorter, though the r_g distances are longer than the r_s distances by 0.01—0.03 Å.

In order to examine the environment effect on the bond lengths in the halogen derivatives of alkanes, precise structural determinations of chlorinated alkanes have been initiated[1)] and in the preceding paper the structure of 2,2-dichloropropane has been reported.[2)] As one of this series of studies, the results for ethyl chloride will be reported in the present paper.

Several microwave studies of this molecule can be found in the literature.[3–6)] Among them, Schwendeman and Jacobs studied the widest variety of isotopic species and determined the r_s-structure.[6)] Their data on the moments of inertia contain information necessary for our purpose, and the r_s-structure will serve for comparison with the r_g-structure determined by the present study.

According to them and also to Lide,[5)] the barrier to the hindered rotation is about 3.6 kcal/mol, a value which is very close to those for propane,[7)] 2-chloropropane,[8)] and 2,2-dichloropropane.[9)] This means that the torsional motion may be regarded as a small amplitude vibration in evaluating the vibrational correction of the present molecule as of the other molecules mentioned above; this correction is necessary to convert the r_g values determined by the electron diffraction and the observed moments of inertia, $I^{(\mathrm{eff})}$, into the values in the zero-point average structure, r_α^0 or $I^{(z)}$.[10)] In this study, therefore, the vibrational correction has been carried out by the small-amplitude treatment[11)] after the manner adopted in previous papers.[1,2)]

Experimental

The sample of ethyl chloride was a guaranteed reagent purchased from Nakarai Chemicals, Ltd., and was used without further purification. Diffraction photographs were taken with a unit in our laboratory at room temperature, 20 °C. The other experimental conditions were as follows: camera length, 109 mm; accelerating voltage, 42 kV; beam current, 0.1 μA; sample pressure, 50 Torr,[12)] and exposure time, 110 s. The covered s range was 6—40 Å^{-1}.[12)] The wavelength, or the scale factor, was determined by reference to the diffraction pattern of carbon disulfide taken under the same experimental conditions. Three plates were selected for analysis.

Analysis of Electron-diffraction Data

The observed total intensities[13)] were reduced to the molecular intensities, $sM(s)$, following our usual procedure.[14)] The molecular intensities thus obtained were used for the refinement of the molecular parameter values by means of the least-squares method.[14)] In the refinement, the following assumptions were made as to the molecular geometry: (1) a staggered conformation with C_s symmetry for the molecule as a whole; (2) a local C_{3v} symmetry for the methyl group; (3) a zero tilt angle for the methyl group, and (4) r_a(C–H) distances equal to 1.105 Å, $\varphi_\alpha(\mathrm{CCH})_{\mathrm{CH_3}}=111.6°$, $\varphi_\alpha(\mathrm{HCH})_{\mathrm{CH_3}}=109.2°$, and $\varphi_\alpha(\mathrm{HCH})_{\mathrm{CH_2}}=108.5°$. These assumed values were taken from the r_s-structure determined by Schwendeman and Jacobs.[6)] The values left to be determined are, then, the bonded C–Cl and C–C distances and the non-bonded C···Cl distance. All the mean amplitudes were fixed at values calculated using the force field proposed by Dempster and Zerbi.[15)] The calculated mean amplitudes for the main distances are listed in Table 1. 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 non-bonded atom pairs, in the estimation of the asymmetry parameters, κ. As long as the distances and

Table 1. Calculated mean amplitudes at 20 °C (in Å units)

Distance	Calculated mean amplitude
C–Cl	0.0533
C–C	0.0510
C–H	0.0784
C···Cl	0.0799
Cl···H	0.1068
Cl:::H_{trans}	0.1062
Cl:::H_{gauche}	0.1813

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Table 2. Results of electron diffraction (in Å units)[a)]

	r_g [b)]	r_α^0 [c)]
C···Cl	2.739(11)	2.733
C–Cl	1.798(5)	1.795
C–C	1.523(8)	1.520
Index of resolution	0.93—1.04	

a) The geometry of the methyl group was assumed at the values determined by microwave spectroscopy. See text. b) The values in parentheses indicate the limits of error, which were estimated from the random errors obtained in the least-squares adjustment and the systematic errors included in the scale factor, which was ±0.06 % in distances. c) r_α^0 were derived from r_g; see text. The errors are regarded to be the same as those for r_g.

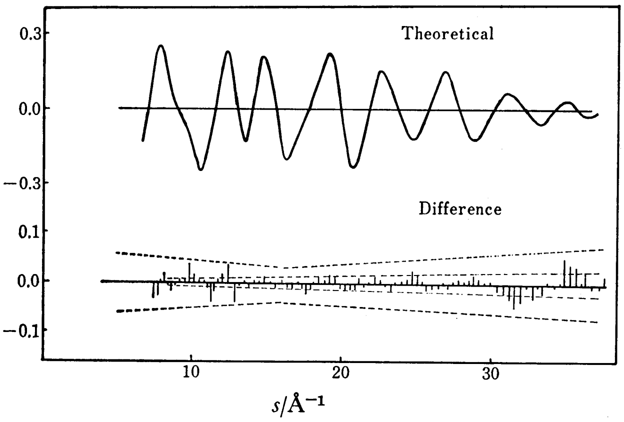

Fig. 1. The theoretical molecular intensity curve, $sM(s)$, for the best fit parameters, and the difference, $sM(s)^{\text{obsd}}$–$sM(s)^{\text{calcd}}$. In the difference, the inner broken lines indicate the limit of detection in photometry, and the outer broken lines the estimated limit of errors in the observed intensities; see Ref. 1. The ordinate for the difference curve is enlarged twice as large as that of the intensity curve.

angles in the methyl group are assumed to be within the ranges of plausible values (see the next section), the converged C–Cl, C–C, and C···Cl values change by only one or two thousandths Å, a value which is much smaller than the limits of error.

The results of the least-squares analyses are listed in Table 2. Figure 1 shows the theoretical molecular intensity curve for the best-fit parameters and the difference between the theoretical and observed intensities.

Joint Analysis

The r_g values obtained by the electron-diffraction were converted into the r_α^0 values using the parallel and perpendicular mean amplitudes calculated at 293 and 0 K, the centrifugal stretching, and the assumed Morse asymmetry constants. The r_α^0 values thus obtained are also entered in Table 1.

The moments of inertia have been determined by Schwendeman and Jacobs for seven isotopic species, including the parent $CH_3CH_2{}^{35}Cl$ species.[6)] Among them, the ^{37}Cl-species and ^{13}C-species do not provide additional information useful for our purpose,[1)] and the species containing a partially deuterated methyl group would not be helpful for the determination of the molecular structure because they have no local C_{3v} symmetry in the r_z-structure and so only increase the number of parameters to be determined. Thus, we made use of the moments of inertia of only two species, $CH_3CH_2{}^{35}Cl$ and $CH_3CD_2{}^{35}Cl$. The observed moments of inertia, $I^{(\text{eff})}$, were corrected for the harmonic vibrations by means of the small-amplitude treatment and were converted into the zero-point moments of inertia, $I^{(z)}$. The results are listed in Table 3.[16)]

Table 3. Observed and corrected moments of inertia and the vibrational corrections (in amu Å^2 units)[a)]

		$I^{(\text{eff})}$	ΔI	$I^{(z)}$
$CH_3CH_2{}^{35}Cl$	a	16.121	0.020	16.141
	b	91.992	0.139	92.131
	c	101.843	0.084	101.927
$CH_3CD_2{}^{35}Cl$	a	20.935	0.021	20.956
	b	94.414	0.124	94.538
	c	105.902	0.083	105.985

a) The conversion factor: 505376 MHz amu Å^2. b) $I^{(z)}=I^{(\text{eff})}+\Delta I$. c) The uncertainties included in ΔI, and accordingly in $I^{(z)}$ also, are estimated to be about 10% of the corrections themselves; see Ref. 1. The joint analysis was, therefore, carried out by assuming the uncertainties in $I^{(z)}$ to be ±0.01 amu Å^2.

The isotope effect for the C–H distance, $\delta(\text{C–D})=r_z(\text{C–D})-r_z(\text{C–H})$, was estimated and assumed to be -0.0007 ± 0.0014 Å.[17)] However, the $\varphi_z(\text{DCD})$ and the $\varphi_z(\text{CCD})$ values were added in parameters because no appropriate method of estimation has been found. Taking all the $r_g(\text{C–H})$ distances to be equivalent, the difference between the $r_z(\text{C–H})_{\text{CH}_3}$ and $r_z(\text{C–H})_{\text{CH}_2}$ distances was estimated to be 0.007 Å by converting the r_g values into the corresponding r_z values. Thus the number of parameters to be adjusted becomes nine (see Table 5 below), while the available data are two bonded distances determined by the electron diffraction and the six moments of inertia. The C···Cl distance obtained by the electron diffraction was not used, for the r_α^0 value derived from the r_g value might not be accurate enough; anharmonicity for a non-bonded atom-pair is still ambiguous. Therefore, the value of $\varphi_z(\text{HCH})_{\text{CH}_3}$ was assumed to be 109.2±2° by referring to the reported r_s-structure[6)] (see also Table 5).[18)] The eight parameters to be determined are r(C–C), r(C–Cl), r(C···Cl), $r(\text{C–H})_{\text{CH}_3}$, $\angle\text{HCH}_{\text{CH}_2}$, δ(DCD) $(=\angle\text{DCD}_{\text{CD}_2}-\angle\text{HCH}_{\text{CH}_2})$, $\angle\text{CCH}_{\text{CH}_3}$, and δ(CCD) $(=\angle\text{CCD}_{\text{CD}_2}-\angle\text{CCH}_{\text{CH}_2})$.

However, in fitting the eight parameters to the eight observed quantities, the allowed ranges for r(C–C) and r(C–Cl) could never be smaller than the limits of error of the electron-diffraction results, and the values of the other parameters may include both unreasonably large and small values. Therefore, the reported r_s-structure[6)] was again used in order to restrict the $\varphi_z(\text{CCH})_{\text{CH}_3}$ so that it was in the range of 111.6±2.0°.[18)]

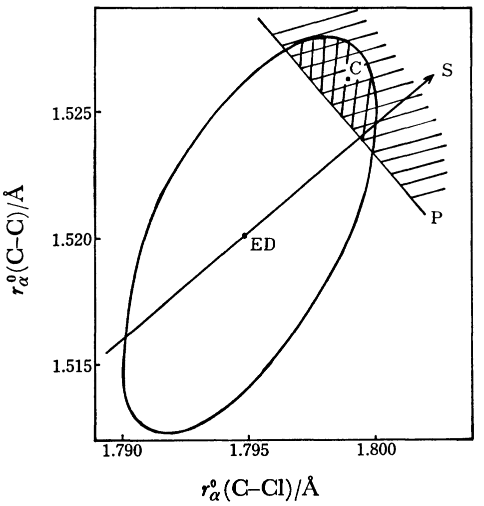

Fig. 2. The diagram of the allowable range of the C–Cl and C–C distances. The ED point indicates the best values determined by electron diffraction. The shaded area is allowed by the moments of inertia when the isotope effect, δ(C–D), is taken as −0.0007 Å and the C point indicates the final values. See text for the details. The cross-shaded area is allowed by both the electron diffraction data and the moments of inertia.

Figure 2 shows the r(C–C) and r(C–Cl) values allowed by the electron-diffraction data and the six moments of inertia under the assumptions and the restriction mentioned above. In this figure, the ED point represents the best values determined by electron diffraction, while the ellipse shows the total limits of error estimated from both the random error obtained by the least-squares adjustment and the systematic error included in the scale factor. The straight line, S, indicates the direction of change in the distances with the change in the scale factor. On the other hand, the shading in Fig. 2 indicates the area obtained by projecting the region allowed by the six moments of inertia onto the r(C–C)-r(C–Cl) plane. The P line perpendicular to the S line represents a lower bondary of the allowed region on the r(C–C)-r(C–Cl) plane, when δ(C–D) is taken to be −0.0007 Å. Thus, the cross-shaded area is the region of the r(C–C) and r(C–Cl) values allowed by both the electron-diffraction data and the moments of inertia. The final r_{av}(C–C) and r_{av}(C–Cl) values, represented by the point C in Fig. 2, were taken at the center of a rectangle which contained the allowable region and had its sides parallel to S and P. With these r_{av}(C–C) and r_{av}(C–Cl) values, and on the assumptions that $\varphi_{av}(HCH)_{CH_2}$= 109.2°, that δ(C–D) = −0.0007 Å, and that $\varphi_{av}(CCH)_{CH_3}$ was in the range of 113.6—109.6°, the final values for the other parameters were determined; with these values the six moments of inertia were satisfied best. The results are listed in the 2nd column of Table 4.

The errors listed in Table 4 were estimated as follows: ε_1 are the limits of the allowable parameter values explored with the C–C and the C–Cl values in the allowed region shown in Fig. 2; ε_2 are the limits of error due to the uncertainty included in ΔI, ±0.01 amu Å^2;[19] ε_3 were estimated by considering that the assumed $\varphi_z(HCH)_{CH_2}$ included an uncertainty of ±2°; ε_4 and ε_4' were estimated from the uncertainty included in the isotope effect for the C–H distance. As was mentioned before, the uncertainty in the δ(C–D) was estimated to be ±0.0014 Å. A change in the δ(C–D) causes the P line to shift parallel to itself in Fig. 2 and, consequently, influences the limits of error in two manners. The first influence appears as the shift of the C point, while the second one brings about a change in the width of the allowed region on the C–Cl *vs.* C–C map. A decrease in the δ(C–D) makes the P line shift in the direction of the scale factor decrease. Therefore, in order to estimate errors, it is necessary to estimate only the

TABLE 4. RESULTS OF THE JOINT ANALYSIS (in Å and degree units)

	r_{av} or φ_{av}	ε_1	ε_2	ε_3	ε_4	ε_4'	ε_0
C–C	1.5262	+0.0018 −0.0022	—	—	−0.002	±0.002	±0.004
C–Cl	1.7990	+0.0010 −0.0025	—	—	−0.001	±0.001	±0.003
C···Cl	2.7399	+0.0028 −0.0011	±0.0002	±0.0025	−0.002	±0.002	±0.005
C–H$_{CH_3}$[a]	1.082	+0.001 −0.001	±0.001	±0.003	+0.001	±0.001	±0.004
HCH$_{CH_3}$	109.8	+0.35 −0.35	±0.2	±1.5	−0.4	±0.4	±1.6
CCH$_{CH_2}$	110.6	+3.0 −0.0	±0.2	±1.0	+2.0	—	±3.0
HCH$_{CH_2}$	[109.2][c]						
δ(C–D)[b]	[−0.0007][c]						
δ(DCD)[b]	0.2	+0.05 −0.05	±0.1	±0.8	+0.1	—	±0.9
δ(CCD)[b]	0.8	+0.2 −1.0	±0.1	±0.3	+0.4	—	±1.1

a) $r_z(C-H)_{CH_3} - r_z(C-H)_{CH_2} = -0.007$ Å. b) $\delta(C-D) = r_z(C-D) - r_z(C-H)$; $\delta(DCD) = \varphi_z(DCD) - \varphi_z(HCH)$; $\delta(CCD) = \varphi_z(CCD) - \varphi_z(CCH)$. c) These values were assumed. The errors associated with the assumptions are estimated as ε_3, ε_4, and ε_4'. See text.

TABLE 5. FINAL PARAMETER VALUES
(in Å and degree units)

	r_{av} or φ_{av}	r_g	r_s[a]
C–C	1.526(4)	1.528(4)	1.520(3)
C–Cl	1.799(3)	1.802(3)	1.788(2)
C···Cl	2.740(5)	2.746(5)[d]	(2.730)[f]
C–H_{CH_3}	1.091(4)[b,c]	1.103(4)	1.091(10)
HCH_{CH_3}	110.0(1.6)[c]		108.5(0.5)
CCH_{CH_3}	110.6(3.0)		111.6(0.5)
δ(DCD)[e]	0.2(0.9)		
δ(CCD)[e]	0.8(1.0)		
CCCl	110.7(0.3)[f]		111.0(0.1)
HCH_{CH_2}	[109.2][g]		109.2(0.5)
δ(C–D)	[−0.0007][g,h]		

a) Ref. 6. b) $r_z(C\text{–}H)_{CH_3} - r_z(C\text{–}H)_{CH_2} = -0.007$ Å. c) 0.009 Å and 0.2° were added to the values in Table 3 in order to convert them into the values for the torsionless molecule. d) Converted from r_{av} assuming the asymmetry constant to be zero. e) $\delta(DCD) = \varphi_z(DCD)_{CD_3} - \varphi_z(HCH)_{CH_3}$; $\delta(CCD) = \varphi_z(CCD)_{CD_3} - \varphi_z(CCH)_{CH_3}$. f) Calculated from the other parameter values. g) These values were assumed in the joint analysis. See text. h) $\delta(C\text{–}D) = r_z(C\text{–}D)_{CD_3} - r_z(C\text{–}H)_{CH_3} = -0.0007 \pm 0.0014$ Å.

influence of the decrease in the δ(C–D). ε_4 and ε_4' are uncertainties related to the shift of the C point and the increase in the allowed region respectively, when $\delta(C\text{–}D) = -0.0007 - 0.0014$ Å. A similar effect of the uncertainty of $\angle HCH_{CH_3}$ to the allowed region on the C–C *vs.* C–Cl was negligibly small. In order to assign the total errors, it seems safe to adopt as great error as possible in the present case. Therefore, as for ε_1 we adopted a greater value, irrespective of its sign, while for ε_4 we ignored the fact that it is applicable only in the specified direction. Then the total errors, ε_0, were estimated by considering all these errors to be independent of one another: they are listed in the last column of Table 4. Table 5 shows the final values for r_{av} and φ_{av}, their limits of error, and the r_g values derived from the r_{av}. In order to compare the C–H distances and HCH angles in various molecules, it is desirable to list these parameters in the state in which the torsional motions are eliminated.[20] Therefore, Table 5 gives the r_{av}(C–H) and the φ_{av}(HCH) for the torsionless state. They were obtained by adding 0.009 Å and 0.2° respectively to the r_{av} and φ_{av} obtained by the small-amplitude treatment.[1]

Discussion

We adopted the value of 2.746 Å as the final r_g(C···Cl) distance, the value of 2.739 Å obtained by the electron-diffraction being consistent with it within the limits of error. In deriving the r_g value from the r_{av} value, the Morse asymmetry constant a_3 for this non-bonded distance was assumed to be zero. However, the possibility of a_3 having a negative value has been pointed out in the study of 2-chloropropane[1] and also in the recent studies of $CHBr_3$, CH_2Br_2[21] and $CHCl_3$.[22] In the present case, a negative a_3 brings the r_g(C···Cl) obtained by the joint analysis closer to the diffraction value, although the large uncertainty of the latter makes it difficult to place any significance on the closeness of the two values. A similar situation was also found in the Cl···Cl distance of 2,2-dichloropropane.[2]

In the present analysis, we had to assume the symmetry of the methyl group. As a result, only the average values of the C–H distances and the HCH angles were determined for the structure of the methyl group. According to the microwave study by Zeil *et al.*, the r_s-structure of the methyl top does not have C_{3v} local symmetry.[23] However, since the method of using these r_s data in the determination of the r_g or r_{av} structure has not been established, the precise structure of the methyl group of this molecule in terms of r_g or r_{av} is left unsolved. Similar situations are probably more or less present for other molecules as well. This seems to pose a problem for the future.

The last column of Table 5 shows the r_s values reported by Schwendeman and Jacobs.[6] It should be

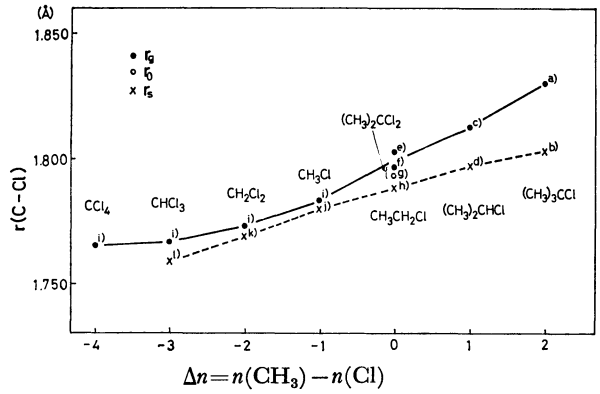

Fig. 3. The r_g(C–Cl) and r_s(C–Cl) distances of chlorinated alkanes plotted against $\Delta n = n(CH_3) - n(Cl)$: a) Ref. 25; b) Ref. 26; c) Ref. 1; d) Ref. 8; e) the present study; f) Ref. 2; g) r_0 value, Ref. 24; h) Ref. 6; i) preliminary results in our laboratory, which are almost the same as those reported so far; j) Ref. 12; k) Ref. 28; l) Ref. 29.

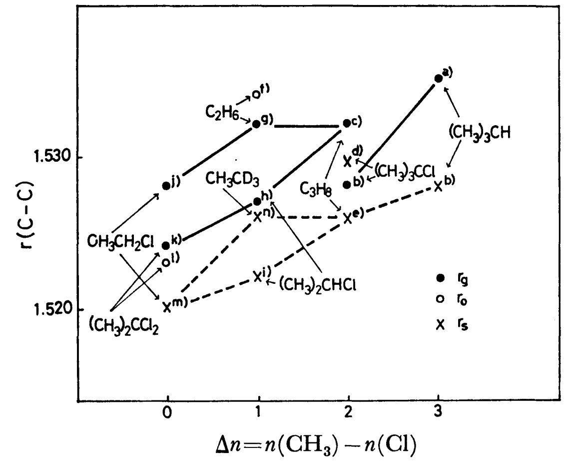

Fig. 4. The r_g(C–C) and r_s(C–C) distances of chlorinated alkanes plotted against $\Delta n = n(CH_3) - n(Cl)$; a) Ref. 30; b) Ref. 25; c) Ref. 31; d) Ref. 26; e) Ref. 32; f) Ref. 33; g) Ref. 34; h) Ref. 1; i) Ref. 8; j) the present study; k) Ref. 2; l) Ref. 24; m) Ref. 23; n) Ref. 35.

noted that the r_s distances are all shorter than the corresponding r_g distances.

Matsumura and his co-workers showed that the C–Cl and C–C r_s distances for various chlorinated alkanes exhibit systematic changes against the difference between the numbers of methyl groups and chlorine atoms attached to the carbon atom, $\Delta n = n(CH_3) - n(Cl)$.[24] Their results are reproduced in Figs. 3 and 4, together with the plotting of the r_g values. As may be seen in Fig. 3, the C–Cl distances become shorter as Δn decreases; if Δn is the same, the C–Cl distances are also the same. For the C–C distances in Fig. 4, the situation is a little more complicated. For compounds consisting of the same number of carbon atoms, the one with more chlorine atoms has a shorter C–C distance, while compounds with the same number of chlorine atoms have nearly the same C–C distance. The r_g distances show a similar tendency, but generally they are longer than the corresponding r_s distances. An exception is found in the C–C distance of *t*-butyl chloride, in which the r_s value could be unusual, for the central carbon is very close to the center of gravity of the molecule.

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

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