

# Chloromethyl-cyclopropane. Molecular Structure and Conformation in the Gas Phase as Determined by Electron Diffraction and Compared to Molecular Mechanics Calculation

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A gas phase electron diffraction study of chloromethyl-cyclopropane indicates that at 45 °C there is predominantly *gauche* conformer. The structure results in terms of  $r_a$  distances and  $\angle_a$  angles are as follows:  $r(\langle C-C \rangle) = 1.519(3)$  Å ( $\langle \rangle$  denoting average),  $r(C-Cl) = 1.798(5)$  Å,  $r(\langle C-H \rangle) = 1.087(9)$  Å,  $\angle C-C-C(\text{exocyclic}) = 117.2(9)^\circ$ ,  $\angle C-C-Cl = 112.6(7)^\circ$ ,  $\angle C-C-H(\text{ring}) = 116.0(1.5)^\circ$ ,  $\angle C-C-H(\text{CH}_2\text{Cl}) = 110.3(3.2)^\circ$ ,  $\tau_g$  (*gauche* torsional angle relative to  $0^\circ$  for C-Cl bond eclipsing cyclopropane ring) =  $116.0(3.8)^\circ$ . Uncertainties are given as  $2\sigma$ , where  $\sigma$  includes uncertainties due to correlation among observations, electron wavelength and other parameters used in the data reduction. A molecular mechanics calculation agrees to the conformational result of the electron diffraction study. A normal coordinate analysis based on a valence force field was made, and some frequencies were suggested reassigned.

Conformational behaviour when a cyclopropane ring has a vinyl or another double bond containing substituent, has to some extent been investigated in gas phase by electron diffraction (ED).<sup>1-4</sup> However, studies of such molecules with saturated substitution seem to be fewer.<sup>5</sup> The simplest example of rotational conformation of a saturated group connected to a cyclopropane ring is a  $\text{CH}_2\text{X}$  group. Both bromomethyl- and chloromethyl-cyclopropane have been studied in the gas phase by microwave (MW) spectroscopy<sup>6-8</sup> and by infrared and Raman spectroscopy.<sup>9-11</sup> From one of the MW studies of chloromethyl-cyclopropane,<sup>7</sup> it was concluded that two conformers coexisted. The other MW investigation<sup>8</sup> and the infrared and

Raman data of Ref. 9 were interpreted as showing practically only *gauche* conformer. In a more recent

work<sup>10</sup> it was concluded that the amount of *gauche* conformer was 95 % in the liquid phase.

Methyl-cyclopropane has been studied by ED.<sup>13</sup> It was not expected as possible to obtain reliable information, neither about deviations between the skeletal structure of methyl-cyclopropane and chloromethyl-cyclopropane, nor about differences within the ring bond lengths.<sup>14</sup> Therefore, the main objective of this investigation is to study the conformation of the molecule.

## EXPERIMENTAL AND DATA REDUCTION

A commercial sample of chloromethyl-cyclopropane (>98 %) was obtained from Aldrich Chemical Company. Data were recorded with the Balzer Eldigraph KDG-2 apparatus<sup>15,16</sup> at a nozzle temperature of 45 °C. Nozzle-to-plate distances of 50.0 and 25.0 cm were used. The electron wavelength was calibrated against benzene.<sup>17</sup> Electron diffraction photographs were recorded on Kodak Electron Image plates. Optical densities were measured by a single-beam densitometer. For the 50 and 25 cm data, 4 and 3 plates, respectively, were selected for analysis. The data were reduced using standard data reduction programs for the Norwegian ED group.<sup>18</sup>

A calculated background<sup>19</sup> was subtracted from the experimental data. This was done for each plate to yield data  $I_m(s)$  corresponding to the formula

$$I_m(s) = k \sum_{i \neq j} n_{ij} |f'_i(s)| |f'_j(s)| \cos[\eta_i(s) - \eta_j(s)] \exp(-\frac{1}{2} l_{ij}^2 s^2) \sin(r_{ij}s) (r_{ij}s)^{-1}$$

$f'_i$ 's are modified electron scattering amplitudes,  $\eta_i$ 's the phases of the scattered waves  $r_{ij}$  and  $l_{ij}$  the interatomic distances  $r_a$  and the root-mean-square

amplitudes of vibration, and  $n_{ij}$  the multiplicity of these distances.

Data for each camera distance were combined to one average curve.<sup>18</sup> The least square refinements were based on curves in the form  $sI_m(s)$ . Least square calculations were made by a modified version of a program originally written by L. Hedberg, who also wrote the original versions of the programs used to calculate backgrounds and radial distribution (RD) curves. Calculation of vibrational quanti-

ties used in the analysis were made by a program written by R. L. Hilderbrandt. The electron scattering amplitudes and phase shifts<sup>18</sup> were calculated analytically by a program originally written by A. C. Yates. For these calculations Hartree-Fock potentials were used<sup>20</sup> for C and Cl while molecular bonded potentials were used for H.<sup>21</sup> The molecular mechanics calculations were made by a program written by S. Rustad, R. Stølevik and H. M. Seip.

Table 1. Chloromethyl-cyclopropane. Results from the normal coordinate analysis. Observed frequencies are taken from Ref. 9.

Frequency Obs.	Calc.	Approx. description	Potential energy distribution
<i>gauche</i> conformer			
3085	3105	asym. str. CH <sub>2</sub> (ring)	C-H <sub>ring</sub> (100)
—	3103	asym. str. CH <sub>2</sub> (ring)	C-H <sub>ring</sub> (100)
3077	3077	str. CH	C-H <sub>3</sub> (87)
3031	3039	sym. str. CH <sub>2</sub> (ring)	C-H <sub>ring</sub> (86)
3009	3019	sym. str. CH <sub>2</sub> (ring)	C-H <sub>ring</sub> (99)
2996	2984	asym. str. CH <sub>2</sub> (Cl)	C-H <sub>Cl</sub> (100)
2956	2962	sym. str. CH <sub>2</sub> (Cl)	C-H <sub>Cl</sub> (98)
1460	1483	sci. CH <sub>2</sub> (ring)	H-C-H <sub>ring</sub> (48) C-C-H <sub>ring</sub> (46) C-C <sub>ring</sub> (26)
1447	1449	sci. CH <sub>2</sub> (Cl)	H-C-H <sub>Cl</sub> (63) C-C-H <sub>Cl</sub> (15)
1433	1433	sci. CH <sub>2</sub> (ring)	H-C-H <sub>ring</sub> (65) C-C-H <sub>ring</sub> (15)
1375	1366	bend CH	C-C-H <sub>3</sub> (34) C-C-H <sub>ring</sub> (22) C-C-H <sub>2</sub> Cl (20)
1293	1233	str. C-CH <sub>2</sub> Cl	C-CH <sub>2</sub> Cl (25) C-C-H <sub>Cl</sub> (19)
1281	1296	wag CH <sub>2</sub> (Cl)	C-C-H <sub>Cl</sub> (54) Cl-C-H (42)
1268	1262	tw. CH <sub>2</sub> (Cl)	C-C-H <sub>Cl</sub> (40) C-CH <sub>2</sub> Cl (28)
1197	1144	def. ring	C-C <sub>ring</sub> (29) C-C-H <sub>ring</sub> (17) C-CH <sub>2</sub> Cl (17)
1168	1189	asym. rock CH <sub>2</sub> (ring)	C-C-H <sub>ring</sub> (99)
1117	915	asym. tw. CH <sub>2</sub> (ring)	C-C-H <sub>ring</sub> (52)
1051	1038	asym. wag CH <sub>2</sub> (ring)	C-C-H <sub>ring</sub> (72)
1022	1005	sym. wag CH <sub>2</sub> (ring)	C-C-H <sub>ring</sub> (69)
973	970	sym. rock CH <sub>2</sub> (ring)	C-C <sub>ring</sub> (35) C-C-H <sub>ring</sub> (43) Cl-C-H (23)
918	924	def. ring	C-C <sub>ring</sub> (75) C-C-H <sub>ring</sub> (17)
882	882	rock CH <sub>2</sub> (Cl)	C-C-H <sub>ring</sub> (60) Cl-C-H (28)
834	805	def. ring	C-C <sub>ring</sub> (44) C-C-H <sub>ring</sub> (17)
796	796	bend CH	C-C-H <sub>3</sub> (54) tors. ring (14) C-C-H <sub>ring</sub> (16)
773	736	sym. tw. CH <sub>2</sub> (ring)	C-C-H <sub>ring</sub> (103) tors. ring (24)
700	700	str. C-Cl	C-Cl (62)
399	412	bend C-C-C	C-C-C (70)
343	328	bend C-C-C	C-C-C (43) C-Cl (23)
213	215	bend C-C-Cl	C-C-Cl (42) C-C-C (31)
100	99	tors. C-CH <sub>2</sub> Cl	tors. C-CH <sub>2</sub> Cl (82)
<i>syn</i> conformer			
—	689	str. C-Cl	C-Cl (43) C-C <sub>ring</sub> (39)
462	457	bend C-C-C	C-C-C (34) C-Cl (37)
—	331	bend C-C-C	C-C-C (71) tors. ring (23)
—	164	bend C-C-Cl	C-C-Cl (53) C-C-C (33)
—	108	tors. C-CH <sub>2</sub> Cl	C-CH <sub>2</sub> Cl (71) tors. ring (24)

## NORMAL COORDINATE ANALYSIS

The present conformational study was expected to be sensitive to the values of the vibrational quantities, which therefore should be calculated as accurately as possible. A valence force field was used. The force field was combined from two sources. For the cyclopropane ring, the force field in Ref. 22 was used. For the  $\text{CH}_2\text{Cl}$  group part of a force field for 3-chloro-propene was used. This force field has shown good transferability,<sup>23</sup> partly because great care was taken to develop the force field with as few and as local interaction force constants as possible.

As a start it was decided to use  $\text{C}-\text{C}_2-\text{H}_3$  bend and interaction force constants equal to those of the ring  $\text{CH}_2$  groups. The force constants for-exocyclic  $\text{C}-\text{C}-\text{C}$  bends and  $\text{C}-\text{C}-\text{C}/\text{C}-\text{C}-\text{C}$  interaction was first taken from Ref. 24. The torsional force constants were fitted to the observed *gauche* torsional frequency,<sup>9,10</sup>  $100\text{ cm}^{-1}$ . By using this force field, the normal coordinate calculation for *gauche* conformer gave most frequencies in good agreement with observed ones.<sup>9,10</sup> However, the approximate description according to the present calculation is partly different from earlier interpretations.<sup>9,10</sup> In Table 1 are given calculated frequencies and the description suggested from the present calculation. The calculated frequencies in

Table 1 are the result of a force field with slight modifications for  $\text{C}-\text{C}-\text{C}$ ,  $\text{C}-\text{C}-\text{C}/\text{C}-\text{C}-\text{C}$  and  $\text{C}-\text{C}_2-\text{H}_3$  force constants. The force constants associated with the  $\text{CH}-\text{CH}_2\text{Cl}$  part of the molecule are given in Table 2.

The frequencies observed at 1293, 1168, 973 and 796 are described differently from the interpretations of Refs. 9 and 10. The present interpretation is strengthened by the fact that ring  $\text{CH}_2$  twist and rock and  $\text{CH}$  bend frequencies are now quite close to the corresponding frequencies in bromocyclopropane<sup>25</sup> and cyclopropane.<sup>22</sup> It should be pointed out that, by varying the force constants within reasonable limits, the present calculation can definitely not give as low a  $\text{C}-\text{CH}_2\text{Cl}$  frequency as  $970\text{ cm}^{-1}$ .

The present calculation shows good transferability of the force field used for the  $\text{CH}_2\text{Cl}$  group. However, there is an interesting similarity to 3-chloro-1-propene not associated with the  $\text{CH}_2\text{Cl}$  part of the molecule. The value obtained for  $\text{C}-\text{C}_2-\text{H}_3$  bend force constants is very close to the value of the  $=\overset{\text{C}}{\underset{\text{H}}{\text{C}}}$  force constant in 3-chloro-1-propene,  $0.52\text{ mdyn \AA rad}^{-2}$ . If the double bond in 3-chloro-1-propene is regarded as a bent bond, the low  $\text{C}-\text{C}_2-\text{H}_3$  bend in chloromethyl-cyclopropane corresponds to the out-of-plane  $=\text{C}-\text{H}$  bend in 3-chloro-1-propene, observed at  $590\text{ cm}^{-1}$ .<sup>26</sup> By giving double masses to the terminal  $=\text{CH}_2$  group in 3-chloro-1-propene, the  $\text{CH}_2=\text{CH}$  group is made equally heavy as the  $\text{C}_3\text{H}_5$  group in chloromethyl-cyclopropane. Such a calculation gives a  $=\text{C}-\text{H}$  out-of-plane frequency of  $870\text{ cm}^{-1}$ , while the in-plane  $=\text{C}-\text{H}$  bend is still close to  $1300\text{ cm}^{-1}$ . This corresponds quite well to 796 and  $1375\text{ cm}^{-1}$  for similar bend frequencies in chloromethyl-cyclopropane.

As to the present interpretation, the calculated frequencies of the *gauche* conformer deviates by  $19\text{ cm}^{-1}$  as an average from the ones observed in Ref. 9. It is likely that the *gauche* vibrational quantities are calculated as good approximations to the actual values. However, for the *syn* conformer ( $\text{C}-\text{Cl}$  bond eclipsing the ring) there is more uncertainty associated with the vibrational quantities, especially since there is no observed torsional frequency. All force constants used for *syn* conformer were directly transferred from the *gauche* conformer. However, the effect of variation in *syn* torsional force constants was estimated by a calculation according to the method of partial force constants

Table 2. Chloromethyl-cyclopropane. Valence force constants used for the  $\text{CH}-\text{CH}_2\text{Cl}$  part of the molecule.

Type of force constant	Value <sup>a</sup>
$\text{C}_2-\text{C}_3$	4.96
$\text{C}-\text{Cl}$	2.66
$\text{C}_3-\text{H}$	4.82
$\text{C}_2-\text{H}_3$	5.13
$\text{C}-\text{C}-\text{Cl}$	1.01
$\text{C}_2-\text{C}_3-\text{H}$	0.77
$\text{Cl}-\text{C}-\text{H}$	0.64
$\text{H}-\text{C}_3-\text{H}$	0.52
$\text{C}-\text{C}_2-\text{H}_3^b$	0.51
$\text{C}-\text{C}-\text{C}^b$	0.95
$\tau(\text{C}-\text{CH}_2\text{Cl})^b$	0.11
$\text{C}_3-\text{H}/\text{C}_3-\text{H}$	0.07
$\text{C}_2-\text{C}_3/\text{C}_2-\text{C}_3-\text{H}$	0.43
$\text{C}_2-\text{C}_3-\text{H}/\text{C}_2-\text{C}_3-\text{H}$	-0.04
$\text{Cl}-\text{C}-\text{H}/\text{C}_2-\text{C}_3-\text{H}$	0.08
$\text{C}-\text{C}-\text{C}/\text{C}-\text{C}-\text{C}^b$	0.20

<sup>a</sup>In  $\text{mdyn \AA}^{-1}$  and  $\text{mdyn \AA rad}^{-2}$ . <sup>b</sup>Force constants fitted to observations.

Table 3. Chloromethyl-cyclopropane. Vibrational amplitudes, calculated and refined, at temperature 45 °C.

Type of distance	$r^{a,b,c}$	$l^a$		
		Calc. <sup>b</sup>	Refined <sup>d</sup>	Parameter No.
C-H	1.09	0.77	0.071(5)	12
C-C <sub>ring</sub>	1.59	0.049	0.052	} (3)
C-CH <sub>2</sub> Cl	1.59	0.051	0.054	
C-Cl	1.80	0.052	0.043(3)	14
C <sub>1</sub> ...C <sub>3</sub>	2.59	0.079		
C <sub>2</sub> ...Cl	2.76	0.079	0.079(7)	15
C <sub>1</sub> ...Cl	3.50(3.00)	0.172(0.156)	0.179(33)	16
C <sub>4</sub> ...Cl	4.09(3.16)	0.094(0.156)	0.096(10)	17

<sup>a</sup>In Å. <sup>b</sup>Values in parentheses for *syn* conformer. <sup>c</sup> $r_a$  distances correspond to independent parameters in Table 6. <sup>d</sup>Error estimates as described in text.

developed for acyclic halopropanes<sup>27</sup> and by comparison to 3-chloro-1-propene.<sup>23</sup> Thus, apart from the *gauche* value of 0.11; 0.05 and 0.20 mdyne Å rad<sup>-2</sup> were used for calculating *syn* vibrational quantities. However, the influence on the vibrational quantities associated with the conformational dependent distances C<sub>1</sub>...Cl and C<sub>4</sub>...Cl (see Fig. 2) is small; Calculated root-mean-square amplitudes of vibration are given in Table 3.

In Table 1 are included the lower frequencies calculated for *syn* conformer.

In liquid phase there was observed a band at 462 cm<sup>-1</sup> which was assigned as belonging to the *syn* conformer.<sup>9</sup> The present normal coordinate calculation supports this by a calculated *syn* frequency of 457 cm<sup>-1</sup>. Contrary to the calculation in Ref. 9, the present potential energy distribution shows considerable contribution from C-Cl stretch to the corresponding normal coordinate. This frequency may be expected to be one of the strongest in the *syn* conformer spectrum. Therefore, even at low concentration of *syn* conformer this frequency may show up as a weak band.

## MOLECULAR MECHANICS CALCULATION

The molecular mechanics (MM) calculations were based on use of non-bonded potential functions described as Morse curves.<sup>28</sup> The intrinsic torsional barrier was determined by a similar MM calculation for methyl-cyclopropane, where the energy barrier was fitted to an observed value of 2.90 kcal mol<sup>-1</sup>.<sup>29,30</sup> Other parameters were identical to those used for MM calculations of a series of haloalkanes.<sup>31,32</sup>

The MM calculations were made with complete geometry relaxation. Two well-defined minima were found. The energetically most stable conformer was found to be *gauche*. The ED observable quantities, *gauche* torsional angle  $\tau_g$  and *syn* torsional amplitude  $\langle \tau_s^2 \rangle^{\frac{1}{2}}$ , and other results from the MM calculations are given in Table 4.

The MM calculated energies do not include zero-point vibrational energy. This was included in the calculation of conformational composition ( $\alpha_g$ ,  $\alpha_s$ ,  $g$  and  $s$  denoting *gauche* and *syn* respectively) by calculating the vibrational partition functions,  $Q^{\text{vib}}$ , with respect to the potential energy minima. The conformational composition in the gas phase is described by

$$\frac{\alpha_g}{\alpha_s} = 2 \left( \frac{Q_g}{Q_s} \right)^{\text{rot}} \left( \frac{Q_g}{Q_s} \right)^{\text{vib}} \times \exp(-\Delta E/RT) = 2q \exp(-\Delta E/RT)$$

Table 4. Chloromethyl-cyclopropane. Results obtained from molecular mechanics calculation.<sup>a</sup>

Conformer	<i>gauche</i>	<i>syn</i>
$-\Delta E$ (kJ mol <sup>-1</sup> ) <sup>b</sup>	0.0	6.9(6.6) <sup>c</sup>
Barriere towards <i>gauche</i> <sup>b</sup>	15.9	17.1
Torsional angle in energy minimum	117.1	0.0
$\tau$ and $\langle \tau_s^2 \rangle^{\frac{1}{2}}$	117.5	11.0
Torsional force constant (mdyn Å rad <sup>-2</sup> )	0.11	0.13
$\angle$ C-C-Cl	109.2	113.9
$\angle$ C-C-C	118.0	119.9

<sup>a</sup>For meaning of symbols, see text. <sup>b</sup>Used following charges: C<sub>ring</sub> -0.016, C<sub>3</sub> 0.005, H<sub>ring</sub> 0.018, H<sub>4,5</sub> 0.041, Cl -0.141. <sup>c</sup>Calculated by using zero charge on all atoms.

where  $\Delta E$  is the difference between minima of *gauche* and *syn* conformer. The rotational partition functions were calculated from the MM obtained geometries. The value of  $(Q_g/Q_s)^{\text{vib}}$  is somewhat dependent on the unknown *syn* torsional frequency. By using the same limits for force constants as described for calculation of vibrational quantities, the value of  $q$  varied from 0.7 to 1.0. If this variation is used as the only error estimate, the MM calculations give a contribution of  $94 \pm 3\%$  *gauche* conformer.

The torsional force constants were also calculated directly from the MM results. As can be seen from Tables 2 and 4, the MM calculated *gauche* torsional force constant is in excellent agreement with the value obtained from observations.

## STRUCTURE AND CONFORMATION

In Fig. 2 is shown the RD curve calculated from the experimental intensity curve in Fig. 1 as

$$D(r) = \frac{2}{\pi} \Delta s \sum_{s_{\min}}^{s_{\max}} (|f'_{\text{Cl}}| |f'_c|)^{-1} s I_m(s) \exp(-Bs) \sin rs$$

The main interatomic distances (for atomic numbering see Fig. 2) for the *gauche* conformer are indicated on the figure. The torsion dependent  $\text{C}\cdots\text{Cl}$  distance of a possible *syn* conformer will be located at 3.1 Å. It is obvious from the experimental RD curve that the amount of *syn* conformer is very small, if any at all.

For the least square refinements a unit weight matrix was used. The molecular geometry was calculated using the geometry consistent  $r_a$  parameters,<sup>32</sup>  $r_a = r_a - \frac{l^2}{r} + K$ . After a preliminary test only *gauche* and *syn* conformers were considered. Some restrictions had to be made on the molecular geometry. Experience from 1-butene<sup>34</sup> and 3-chloro-1-propene<sup>12</sup> indicates that MM calculations will give quite reliable angle differences between conformers. Except for the torsion angle, the most pronounced parameter difference between *gauche* and *syn* conformers are the C–C–Cl angle and the exocyclic C–C–C angles. The *syn* C–C–Cl and C–C–C angles are MM calculated to be respectively 4.7 and 1.9° larger than the *gauche* ones. The differences were kept constant at these values during the least square refinements. However, as the refinements showed a quite large *gauche* C–C–

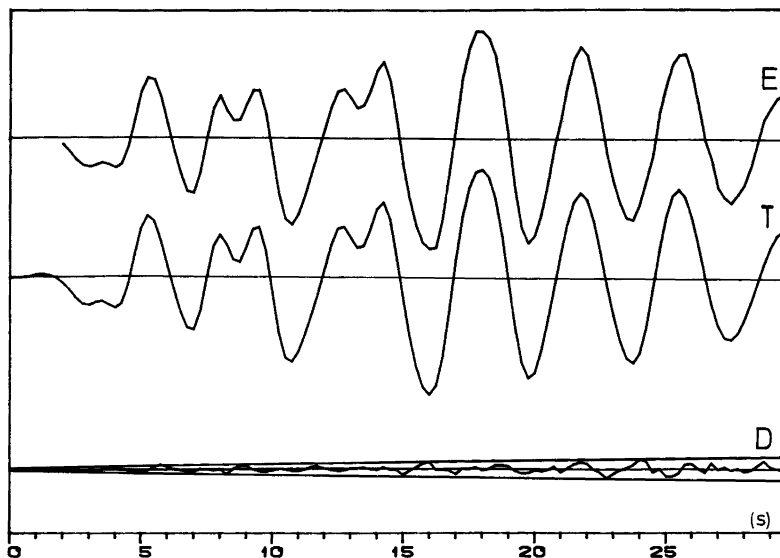


Fig. 1. Chloromethyl-cyclopropane. Intensity curves in the form  $sI_m(s)$ . Experimental curve (E) is the composite curve for all plates and camera distances. Theoretical curve (T) was calculated from parameters in Tables 3 and 6. Difference curve (D) is  $E - T$ . All curves are on the same scale.  $\Delta s = 0.25$ . The straight lines give the experimental uncertainties as three times the standard deviation.

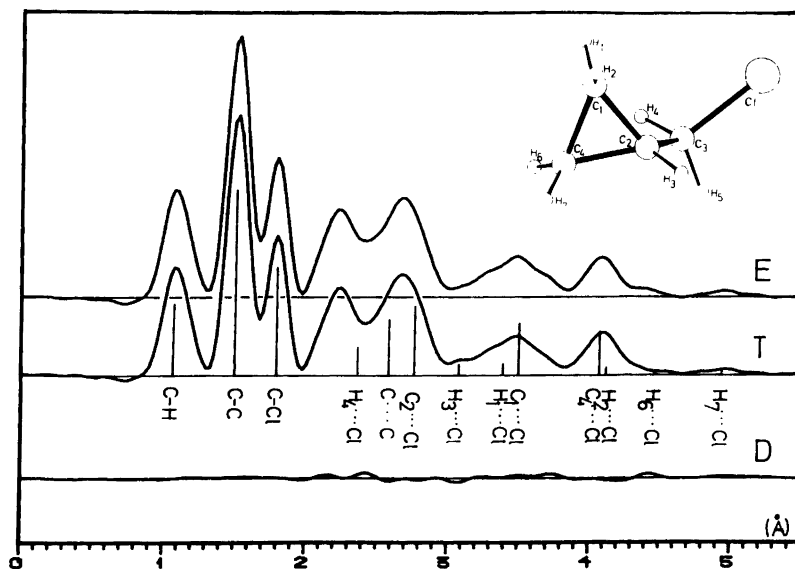


Fig. 2. Chloromethyl-cyclopropane. Radial distribution curves as fourier transforms of the intensity curves in Fig. 1, using  $B=0.0015 \text{ \AA}^2$  and theoretical data for unobserved area  $0 < s < 2.0$ . The vertical lines show the most important distances, height being proportional to weight of distance. All curves are on the same scale.

Cl angle, the difference was reduced to  $2.0^\circ$ . In addition only the torsion angle was different for the two conformers.

All C–C bond lengths within the ring were assumed to be equal. Also all ring C–C–H angles were refined to an average value  $C_s$  symmetry was assumed for the  $\text{CH}_2\text{Cl}$  group. These assumptions seemed to be justified by the MM calculations, since the variation within the parameters refined as averages were very small. In addition all C–H distances were assumed to have the same length.

The difference  $\Delta C-C = r(\text{C}-\text{CH}_2\text{Cl}) - r(\text{C}-\text{C}_{\text{ring}})$  could not be determined directly from the ED data. A refinement where all the vibrational amplitudes were kept at their calculated values gave an unreasonably large value  $\Delta C-C = 0.05 \pm 0.02 \text{ \AA}$ . Though  $\Delta C-C$  was systematically varied, it was not possible to judge from  $R$ -factors or RD curves whether the actual difference was positive or negative. However, when the MW results for rotational constants,  $B_0$ , for  $\text{C}_3\text{H}_5\text{CH}_2^{35}\text{Cl}$  were taken into consideration,<sup>8</sup> the best fit to  $B_0$  was obtained for  $\Delta C-C = 0.00 \text{ \AA}$ . The  $r_z$  parameters were converted to a  $r_z$  structure<sup>33</sup> according to the formula

$$r_z = r_z(0) = r_z(T) - \frac{3}{2}a(\langle l(T)^2 \rangle - \langle l(0)^2 \rangle) + K(T) - K(0),$$

where 0 and T denote parameter value at 0 K and actual temperature,  $a$  is the Morse anharmonicity parameters whose values were taken from diatomic molecules.<sup>35</sup> Corrections for vibration–rotation interaction were made<sup>33</sup> and resulting  $B_0$  values can be compared to MW observations from Table 5.

$\Delta C-C$  strongly correlated to other geometry parameters, (correlation coefficients  $\rho(1/2) = -.9$ ,  $\rho(2/8) = -.5$  and  $\rho(2/9) = -.4$ ). A variation of  $\Delta C-C = 0.02$  changes the exocyclic C–C–C and the C–C–Cl angles by  $0.5$  and  $0.8^\circ$ , respectively. However, a larger absolute value than  $0.02 \text{ \AA}$  for  $\Delta C-C$  seems unreasonable. Thus, the influence on other parameters from keeping  $\Delta C-C = 0.00$  for further refinements, was not very large. After

Table 5. Chloromethyl-cyclopropane. Calculated rotational constants (in MHz) and values obtained from microwave experiment of Ref. 8.

Constant	$\text{C}_3\text{H}_5\text{CH}_2^{35}\text{Cl}$		$\text{C}_3\text{H}_5\text{CH}_2^{37}\text{Cl}$	
	ED	MW	ED	MW
A	11747	11746	11731	11692
B	2018	2047	1968	1998
C	1867	1887	1823	1843

Table 6. Chloromethyl-cyclopropane. Final structural results from analysis of electron diffraction data at 45 °C.

No.	Parameter type	Parameter value ( $r_a, \angle_a$ ) <sup>a</sup>
1	$\langle C-C_{ring} \rangle$	1.519(3)
2	$\Delta C-C^b$	0.00 <sup>e</sup>
3	C-Cl	1.798(5)
4	$\langle C-H \rangle$	1.087(9)
5	C <sub>2</sub> -C <sub>3</sub> -H	110.3(3.2)
6	pCl-C-H <sup>e</sup>	120. <sup>d</sup>
7	C-C-H <sub>ring</sub>	116.0(1.5)
8	C-C-Cl	112.6(7)
9	C-C-C	117.2(9)
10	$\tau_g$	116.0(3.8)
11	$\alpha_g$	96(9)
	R	7.9

<sup>a</sup>In Å and deg. <sup>b</sup>Defined in text. <sup>c</sup>Angle between projections of C<sub>3</sub>-Cl and C<sub>3</sub>-H on plane perpendicular to the C-CH<sub>2</sub>Cl bond. <sup>d</sup>Assumed. <sup>e</sup>For choice of value, see text.

The value of syn torsional amplitude influences the obtained composition quite strongly. Allowing  $\tau_s^2$ <sup>‡</sup> to take the value 40°, gave as result 85 % *gauche* conformer. However, such a model did not improve the fit to the experimental data. Because of the quite strong influence of the value of  $\langle \tau_s^2 \rangle$ <sup>‡</sup> on the conformational composition, it was decided to introduce pseudo-conformers in *syn* position. Instead of one *syn* conformer, whose ED observable position is determined by  $\langle \tau_s^2 \rangle$ <sup>‡</sup>, several pseudo-conformers at equally distributed torsional angles were used. Vibrational amplitudes were calculated without contribution from the torsional movement. A *gauche* contribution as low as 85 % could not be obtained for this model. In the final model were used 4 *syn* pseudo-conformers distributed according to the potential energy function resulting from the MM calculations. The torsional angles and distribution within the *syn* pseudo-conformers thus obtained were: 5° (56 %), 15° (32 %), 25° (9 %) and 35° (3 %).

## RESULTS

The molecular structure of the *gauche* conformer, which is essentially the only conformer present, is given in Table 6. The error estimates are obtained

introducing a constant value for  $\Delta C-C$ , root-mean-square amplitudes associated with bonded distances and C...Cl distances of the *gauche* conformer were allowed to refine.

Table 7. Chloromethyl-cyclopropane. Parameter value comparison to some related molecules.<sup>b</sup>

Molecule	Method	$\langle C-C_{ring} \rangle$	$\Delta C-C$	$\langle C-C \rangle$ <sup>c</sup>	$\angle C-C-C$	$\angle C-C-Cl$	C-Cl	$\tau_g$	Ref.
Methyl cyclopropane	<i>ab</i>								
	<i>initio</i>	1.518	-.018	1.513	115.6	-	-	-	14
	MW	(1.514) <sup>a</sup>	.008	1.516	118.9	-	-	-	30
	ED	1.509(2)	.008	1.511	118.4	-	-	-	13
Bromomethyl-cyclopropane	MW	(1.514) <sup>a</sup>	.008	1.516	117.7	-	-	-	6
Chloromethyl cyclopropane	MW	(1.514) <sup>a</sup>	(.008) <sup>a</sup>	-	(115.8) <sup>a</sup>	(109.5) <sup>a</sup>	1.791(2)	120.2(5)	8
	ED	-	-	1.519(3)	117.2(9)	112.6(7)	1.798(5)	116.0(3.8)	this work
3-chloro-1-propene	ED	-	-	1.494(2)	-	110.7(4)	1.791(1)	-	12
3-chloro-2-methyl-1-propene	ED	-	-	1.499(1)	-	113.0(2)	1.790(1)	-	23
1-chloro-propane	ED	-	-	1.53(2)	-	111.(2.)	1.77(2)	-	41
Ethylchloride	ED	-	-	1.526(4)	-	110.7(3)	1.802(3)	-	42
1,3-dichloro-propane	ED	-	-	1.529(4)	-	111.6(1)	1.796(3)	-	39

<sup>a</sup> Assumed value. <sup>b</sup> Error estimates are not directly comparable throughout the table. <sup>c</sup> For acyclic molecules this is the C-CH<sub>2</sub>Cl bond length.

from least square standard deviation,  $\sigma_0$ , as  $2\sigma = 2[(c_1\sigma_0)^2 + c_2r^2]^{\frac{1}{2}}$ , where  $c_1$  includes correction for correlation among observations;<sup>36</sup>  $c_1=2$  when  $r < 2 \text{ \AA}$ ,  $=1.5$  when  $2 < r < 3 \text{ \AA}$  and  $=1$  when  $r > 3 \text{ \AA}$ .  $c_2$  includes corrections for uncertainty in the electron wavelength and other parameters used in data reduction;  $c_2=0.001$  for distances and amplitudes of vibration. For angles and conformational composition  $c_1=1.5$  and  $c_2=0$ .<sup>36</sup> The correlation coefficients for which  $|\rho| > 5$  are:  $\rho(4/10)=.6$ ,  $\rho(5/8)=-.5$ ,  $\rho(8/9)=.5$ ,  $\rho(8/10)=.6$ ,  $\rho(9/10)=.7$ ,  $\rho(11/16)=.7$  and  $\rho(11/17)=.6$ .

Based on the parameters described in Table 3 (refined  $l$ 's) and 6, and use of the *syn* pseudo-conformer model, the amount of *gauche* conformer was found to be  $96 \pm 9\%$ . The RD curve obtained from this model is shown in Fig. 2.

## DISCUSSION

The ED data support the conclusions from the MW<sup>8</sup> and the infrared and Raman<sup>9</sup> studies that gaseous phase chloromethyl-cyclopropane exists predominantly as *gauche* conformer. The result is also very close to the conclusion from liquid data in Ref. 10, 95% *gauche*. 96% *gauche* conformer is in excellent agreement with the MM calculation, where non-bonded potential values corresponding to  $sp^3$  hybridized carbon atoms were used. Since the cyclopropane ring may be regarded as having pseudo  $\pi$ -orbitals,<sup>37</sup> a comparison to 3-chloro-1-propene, which is found to exist as ca. 80% *gauche* conformer, is of interest.<sup>12,26,38</sup> It was found that MM calculations for 3-chloro-1-propene, using the same non-bonded potentials, gave as result only *gauche* conformer. Also the observed *gauche* torsional angle is close to the MM calculated one.

In Table 7 some of the geometrical parameters of chloromethyl-cyclopropane are listed together with those of related molecules. The present study did not give any additional information about the relative length of the C–C bonds. However, there is an indication that the C–C distances are longer than in methyl-cyclopropane. If the ring bonds were fixed at the same length as found in the ED study of methyl-cyclopropane, the exocyclic C–C bond refined to an unreasonably large value. Although distances found by MW and ED studies are not directly comparable, it can be said that there is good agreement between the partial  $r_0$  structure of bromomethyl-cyclopropane (where the C–CH<sub>2</sub>Br distance was fitted to observed data) and the result

of this study. The C–Cl bond length is close to what have been found for other molecules having terminal CH<sub>2</sub>Cl groups.

Due to large uncertainties, it is difficult to establish definite conclusions about the effect of the cyclopropane ring on conformation and bond lengths. The conformational composition seems to be as expected for a saturated system. However, although not observed, it may be that the pseudo  $\pi$ -system of the ring slightly affects the exocyclic bond lengths, while at the same time the apparent *syn* stabilizing effect observed in 3-chloro-1-propene is not provided by this system. Theoretical calculations<sup>40</sup> have shown that both vinyl-like and non-vinyl-like properties of the cyclopropane ring may be explained by the Walsh orbital model.<sup>37</sup>

The refined non-bonded vibrational amplitudes (Table 3) did not show much deviation from calculated ones. Thus, it is probable that also the other calculated amplitudes were good approximations to the experimental ones. The deviations in bonded vibrational amplitudes had no observable effect on other parameters.

With the small amount of *syn* conformer present, it was not considered worthwhile to study the conformational composition at a higher temperature. Using the MM results, only 10% *syn* conformer would be expected at 200 °C.

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