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3-Chloro-2-methyl-1-propene. Molecular Structure and Conformation in the Gas phase as Determined by Electron Diffraction and Molecular Mechanics Calculation

S.H. SCHEI

Department of Chemistry, University of Trondheim, NLHT Rosenborg, N-7000 Trondheim, Norway

A gas phase electron diffraction study of 3-chloro-2-methyl-1-propene shows that at 20 °C there is 87(7) % of the *gauche* conformer with average torsional angle 115.6 (2.8)° relative to 0° for the *syn* form, which was assumed to be the minor contributing conformer having an r.m.s. torsional amplitude of 12(8)°. The *gauche* structural results in terms of r_a distances and $\angle_\alpha$ angles were found to be; r(C=C)=1.340(6) Å, r(C–CH_2Cl)=1.492(4) Å, r(C–Cl)=1.791(5) Å, $\angle$C=C–CH_2Cl=121.5(1.2)°, ($\angle$C=C–CH_2Cl–$\angle$C=C–CH_3= −0.5°, constraint from molecular mechanics calculation), $\angle$C–C–Cl=112.8(.4)°. Uncertainties are given as 2σ,where σ includes uncertainty due to correlation among observations and parameters used in the data reduction. The molecular mechanics calculations agreed well with the electron diffraction conformational result.

It has been found by both vibrational spectroscopy and electron diffraction (ED) studies, that 2-halosubstitution of 3-chloro-1-propene (hereafter denoted CP) changes the conformational composition considerably from that of CP itself.[1–4]

However, vibrational spectroscopy study of the corresponding methylsubstituted molecule, 3-chloro-2-methyl-1-propene (hereafter denoted CMP) showed that the conformational composition in that case, as for CP, was strongly dominated by the *gauche* form (Fig. 1) and only two conformers were found,[6] in contrast to an earlier vibrational spectroscopy study of CMP[7] which was interpreted as showing three confor-

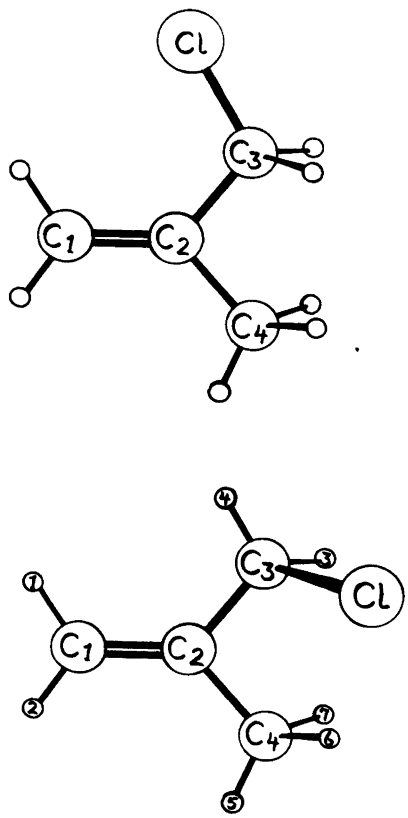

Fig. 1. 3-Chloro-2-methyl-1-propene. *Syn* (upper) and *gauche* (lower) conformers with numbering of the atoms. H-atoms are shown with numbers only.

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mers. The Raman band intensities[6] as a function of temperature in liquid phase gave an energetical preference of 2.5±0.5 kJ mol^{-1} for the *gauche* form, corresponding to about 15 % of the syn conformer at 20 °C. *Syn* was favoured as the second conformer in agreement with the results for other 3-substituted propenes.[5,8–13]

Based on the indications that the second conformer must be *syn*, the ED investigation of CMP was initiated. Contrary to the case of CP, an ED study of CMP will hardly be able to discern between small amounts of *syn* or *anti* (torsional angle 180° relative to *syn*) forms, due to their similar distribution of the C···Cl distances. However, the *gauche* + *syn* presumption should make it possible to obtain both quantitative conformational and structural information about CMP in gas phase.

EXPERIMENTAL AND DATA REDUCTION

A commercial sample of CMP (>97 %) was obtained from Fluka AG. Data were recorded with the Balzers Eldigraph KDG-2[14,15] at a nozzle temperature of 20 °C on Kodak Electron Image plates. The electron wavelength was calibrated against benzene.[16] Optical densities were measured by the Joyce Loebl densitometer. Four plates were selected for analysis from each of the two nozzle-to-plate distances, 50 and 25 cm. The data were reduced in the usual way.[17,18] The least squares refinements were based on one average curve from each camera distance in the form $sI_m(s)$. Fig. 2 shows the composite $sI_m(s)$ curve.

STRUCTURE AND CONFORMATIONAL ANALYSIS

Molecular mechanics calculations. The molecular mechanics (MM) calculations were based on the use of non-bonded potential functions described as Morse curves.[19] The parameters used in these calculations are the same as those used for other chloro-containing molecules.[20,21] The MM calculations were made with complete geometry relaxation, except that the carbon skeleton was restricted to planarity. Well-defined minima were found for *gauche* and *syn* positions, the *gauche* conformer being 2.8 kJ mol^{-1} lower in energy than the *syn* form. The *anti* energy

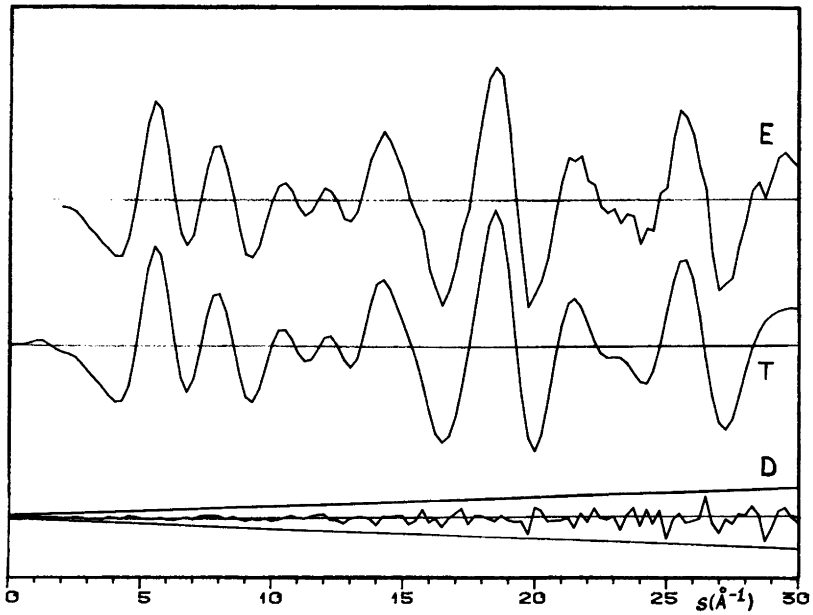

Fig. 2. 3-Chloro-2-methyl-1-propene. Intensity curves in the form sI_m (*s*). Experimental curve (E) is the composite of all plates and distances. Theoretical curve (T) was calculated from parameters in Tables 3 and 4. Difference curve (D) is E−T. All curves are on the same scale. The straight lines show the experimental uncertainties as three times the standard deviation. Δs=0.25 Å^{-1}.

maximum was calculated 15 kJ mol^{-1} above the *gauche* minimum. Results from the calculations are given in Table 1. If the charges on the atoms (Table 1) were neglected, the *syn* minus *gauche* energy difference was reduced to 2.0 kJ mol^{-1}.

The conformational composition resulting from the MM calculations was calculated by inclusion of values for the vibrational and rotational partition functions according to the MM results.[18] Thus, the MM calculations (Table 1) suggest 18 % *syn* conformer at 20 °C.

Vibrational quantities. Normal coordinate calculations based on a valence force field have been made for $CH_2=C(CH_3)-CH_2X$, X=Br, C≡N.[22] A corresponding force field was used for CMP. No refinement of force constants was made. The force constants listed in Table 2 reproduced the *gauche* frequences[6] to an average deviation of 16 cm^{-1}. Root mean square amplitudes of vibration (*l*) are given in Table 3.

Analysis of electron diffraction data. The experimental radial distribution (RD) curve is shown in Fig. 3. The main distances of CMP can be located directly from the figure. It is obvious that the dominating conformer is *gauche*.

A unit weight matrix was used in the least squares refinements. The calculations were made by use of geometry consistent r_a distances.[23]

The *gauche* conformer has symmetry C_1. The lack of symmetry combined with the two C–C distances and the two C=C–C angles of the same magnitude, made geometrical constraints necessary. Studies of other 3-substituted propenes have indicated that relative angle values calculated by the MM method are quite good. Therefore, $\Delta\angle C=C-C = \angle C=C-C_3-\angle C=C-C_4$ was kept at the MM calculated value. $\Delta r(C-C)=r(C_2-C_4)-r(C_2-C_3)$ was estimated to be 0.009 Å from the distances found in propene[24] and CP.[5]

C–C–H angles for the CH_3 and CH_2Cl groups were set equal to the values found in isobutene[25] and CP,[5] respectively. Local C_{3v} and C_s symme-

Table 1. 3-Chloro-2-methyl-1-propene, results obtained from molecular mechanics calculation.[a]

	gauche	*syn*
Energy (kJ mol^{-1})	0.0	2.8
Torsional angle in energy minimum (deg.)	110.0	0.0
Torsional force constant (mdyn Å rad^{-2})	0.09	0.03
Valence angles (deg.)		
∠C=C–C_3	122.5	124.0
∠C=C–C_4	122.0	121.1
∠C–C–Cl	112.5	114.4

[a] The following charges (*q*) were used on the atoms: $q(Cl)=-0.14$, $q(C_{1-2})=-0.01$, $q(C_3)=0.01$, $q(C_4)=-0.02$, $q(H_{1-2})=0.02$, $q(H_{3-4})=0.04$, $q(H_{5-7})=0.02$ in e-units.

Table 2. 3-Chloro-2-methyl-1-propene, the valence force field used in the calculation of vibrational quantities. Force constants are given in mdyn $Å^{-1}$ (stretch) and mdyn Å rad^{-2} (bend, torsion) for *gauche/syn* conformer.

Type	Coordinate	Value
str.	C=C	9.14
	C–C	4.24
	C–Cl	2.66
	=C–H	5.00
	C_3–H	4.82
	C_4–H	4.71
bend	C=C–C_3	0.97/1.83
	C=C–C_4	0.97
	C–C–C	0.73
	C–C–Cl	1.01/1.52
	C=C–H	0.52
	H–C_1–H	0.39
	C–C_3–H	0.76
	H–C_3–H	0.53
	C–C_4–H	0.65
	H–C_4–H	0.54
	Cl–C–H	0.63
tors	C=C	0.49
	C_2–C_3	0.14/0.03
	C_2–C_4	0.08
o.o.p.	$=CH_2$	0.21
	$=CC_2$	0.35
str./str.	C–C/C–C	0.78
	C_3–H/C_3–H	0.08
	C_4–H/C_4–H	0.05
str./bend	C=C/C=C–H	0.40
	C=C/C–C–C	−0.43
	C–C/C–C–C	0.32
	C–C/C–C_3–H	0.36/0.41
	C–C/C–C_4–H	0.35
bend/bend	C–C_3–H/C–C_3–H	−0.16/−0.20
	C–C_4–H/C–C_4–H	−0.01
	Cl–C–H/C–C_3–H	0.07/0.11
	C=C_3–C/C–C–Cl	– /0.52
tors./o.o.p.	C=C/=CC_2	−0.06/–

Table 3. 3-chloro-2-methyl-1-propene. Calculated and refined root mean square amplitudes of vibration (in Å) for bonded distances, C···C, C···Cl and Cl···H distances. Values are given as *gauche/syn*.

No.	Distance	r_a	$l_{calc.}$	$l_{ref.}$[a]	
17	C–H	1.10	0.077		
18	C=C	1.34	0.042		
19	C–C	1.50	0.052		
20	C–Cl	1.79	0.052	0.055(5)	
21	C_1···Cl	3.72/3.03	0.116/0.100	0.117(11)	
22	C_2···Cl	2.73	0.078/0.073	0.063(6)	
23	C_4···Cl	3.29/4.10	0.154/0.073	0.138(15)	
24	C_1···C_3	2.47	0.066	0.066	}
25	C_1···C_4	2.47	0.066	0.066	}(11)
26	C_3···C_4	2.56	0.068	0.068	}
27	Cl···H_3	2.37	0.115		
28	Cl···H_6	2.92/4.37	0.251/0.196		
29	Cl···H_7	3.69/4.48	0.284/0.196		
30	Cl···H_1	3.93/2.57	0.201/0.173		
31	Cl···H_5	4.24/4.87	0.180/0.122		
32	Cl···H_2	4.60/4.10	0.148/0.126		

[a] For type of uncertainty, see text and Ref. 18.

tries were assumed for the CH_3 and CH_2Cl groups.

Since there is only a small amount of the *syn* conformer present, the determination of this amount may be relatively sensitive to the choice of *syn* geometry compared to *gauche* geometry. For similar molecules *syn* minus *gauche* angle values calculated by the MM method seem to reflect trends[26] found by experimental methods. Accordingly, MM calculated differences (*syn* – *gauche*) for both the C=C–C and the C–C–Cl angles were used. It was not possible to release the constraints mentioned earlier. For example, an attempt to refine both ∠C=C–C_3 and ∠C=C–C_4 showed large standard deviation, and the correlation coefficient between those parameters was 0.99. The effect of the constraints was tested by systematic variations of the actual parameters. The constraints in the *gauche* conformer had, within reasonable limits, no influence upon the conformational composition. However, when the *syn* and *gauche* conformers were restricted to have equal geometries, exept for the torsional amplitude $\langle(\Delta\tau_s)^2\rangle^{1/2}$ and the average torsional angle τ_g, then α_s (amount of *syn* conformer) was found to increase 5 %.

In a series of refinements the *syn* conformer was represented by several pseudo-conformers.[18] Then the corresponding *l*-values were calculated without contribution from torsional movement. Refinement of the relative amount of pseudo-conformers gave no change in the total amount of *syn* conformers. The pseudo-conformers were in some refinements kept at distributions corresponding to various potentials. Even this gave only negligible changes in the total α_s.

Different sets of calculated vibrational quantities were used. The best fit between experimental and theoretical data was obtained with a *gauche* torsional force constant f_τ=0.14 mdyn Å rad^{-2}.

As expected, refinements including *anti* instead of *syn* conformer resulted in a nearly equally good fit between theoretical and experimental data. For reasons mentioned earlier, this possibility was disregarded.

Table 4. 3-chloro-2-methyl-1-propene. Final results from the least squares refinements of electron diffraction data at 20 °C. Values are given as *gauche/syn* (r_a in Å, $\angle_\alpha$ in degrees, α and *R*-factor in %).

No.	Parameter	$r_a/\angle_\alpha$
1	r(C=C)	1.340(6)[a]
2	$r(C_2–C_3)$	1.492(4)
3	Δr(C–C)[b]	0.009[c]
4	r(C–Cl)	1.791(5)
5	r(=C–H)	1.098(9)
6	Δr(C–H)[b]	0.009[c]
7	∠C=C–C_3	121.5(12)/123.0[d]
8	$\Delta\angle$C=C–C[b]	−0.5[d]/−2.9[d]
9	∠C–C–Cl	112.8(0.4)/114.7[d]
10	∠C=C–H	119.2(3.9)
11	∠C–C_3–H	112.5[c]
12	∠C–C_4–H	111.0[c]
13	*p*Cl–C–H[e]	120.5[d]
14	τ_g	115.6(2.8)
15	$\langle(\Delta\tau_s)^2\rangle^{1/2}$	12(8)
16	α_g	87(7)
	R^{lc}/R^{sc}[f]	6.7/12.3

[a] For type of error limit, see text and Ref. 18. [b] Defined in text. [c] For choice of value, see text. [d] Value or relative value taken from molecular mechanics calculation. [e] Angle between projections of C–Cl and C_3–H on plane perpendicular to C_2–C_3 bond. [f] lc and sc denotes long and short camera distances, respectively.

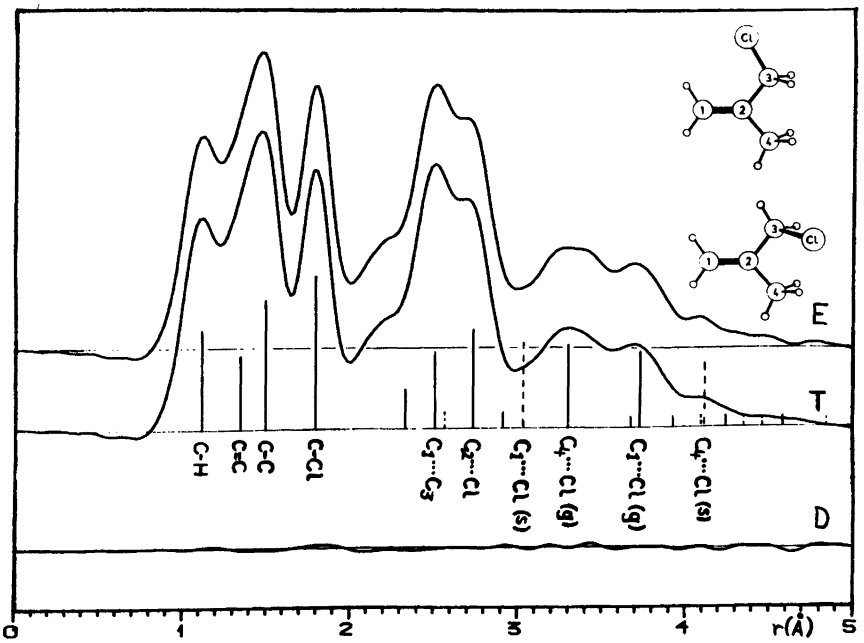

Fig. 3. 3-Chloro-2-methyl-1-propene. Radial distribution curves as Fourier transforms of the intensity curves in Fig. 2, using a modification function $(f_{Cl}(s)\cdot f_C(s))^{-1}$, theoretical data for unobserved area $s < 2.0$ Å^{-1} and damping $B=0.002$ Å^2. The vertical lines show the most important distances, height being proportional to the weight of the distance. The unlabelled lines refer to Cl···H distances. Dotted vertical lines refer to *syn* conformer, but their heights are not scaled to the conformational amount. All curves are on the same scale.

RESULTS AND DISCUSSION

Geometrical, vibrational and conformational results as found from the ED study are given in Tables 3 and 4. The uncertainties are given as 2σ, where σ includes uncertainty due to correlation among observations and uncertainty in the parameters used in the data reduction.[18]

Correlation coefficients for which $|\rho| > 0.5$ are: $\rho(1/7) = -0.56$, $\rho(1/11) = 0.70$, $\rho(2/7) = -0.52$, $\rho(2/15) = 0.52$, $\rho(4/15) = 0.78$, $\rho(5/14) = 0.63$, $\rho(5/15) = 0.99$, $\rho(7/14) = -0.78$, $\rho(7/23) = 0.88$, where parameter numbers are given in Tables 3 and 4.

Figs. 2 and 3 show the theoretically calculated intensity and RD curves, respectively.

87(7) % *gauche* conformer in the gaseous phase indicates no noticable change in conformational composition when passing from liquid[6] (80–85 % depending on the value of the partition functions) to gas. The agreement with the MM calculation (82 %) is better than can generally be expected for this type of molecule. It is interesting to note that the *syn* amount of CMP is not much different from the amount of the most symmetric form in 1-chloro-2-methylpropane (*ca.* 20 %).[27]

The determination of the conformational composition was slightly dependent upon f_τ^g, and introduction of *syn* minus *gauche* angle differences. However, the values chosen for these quantities are reasonable according to existing information on these kinds of molecules.[26] α_g was also slightly influenced by the refinement of a few l_{ij}-values. This dependecy is well covered by the error limit. Further confidence in the result is given by the fact that refined l_{ij}'s show small deviations from calculated values, with one exception. The vibrational amplitude for the distance Cl···C_2 is significantly lower than the calculated value (Table 3). Comparison with similar molecules [18,28–30] shows that the calculated value is quite close to what is normally calculated for a Cl···C distance over one angle.

Table 5. Geometrical parameters of 3-chloro-2-methyl-1-propene compared with related molecules.[a]

Molecule	Ref.	C=C	=C−CH_2Cl	C−Cl	C=C−C_3	C−C−Cl	τ_g
CH_2=C(CH_3)−CH_2Cl(r_a)	This work	1.340	1.492	1.791	121.5	112.8	115.6
CH_2=CH−CH_2Cl(r_a)	5	1.337	1.494	1.792	122.5	110.7	123.5
CH_2=C(CH_2Cl)−CH_2Cl(r_a)	31	1.331	1.502	1.799	121	111.5	115
CH_2=CCl−CH_2Cl(r_a)	2	1.334	1.504	1.776	127.6	110.2	108.9
CH_2−CH_2−CH−CH_2Cl(r_a)	18	–	–	1.798	–	112.6	116.0
CH_3−CH(CH_3)−CH_2Cl(r_g)	27	–	–	1.804	–	112	126
CH_2=C(CH_3)−CH_3(r_g)	25	1.342	–	–	122.0	–	–

[a] Uncertainties are not given, since they are not comparable among the different works.

For chloromethyl-cyclopropane[18] the corresponding $l_{Cl\cdots C}$ was refined close to a value calculated from a related force field. The discrepancy between calculated and refined value in the present case does not seem to have an obvious explanation, but similar differences have also been observed in other molecules.

The f_τ^g which reproduces the *gauche* torsional frequency in gas phase (84 cm^{-1})[6] is 0.08 mdyn Å rad^{-2}, the MM calculation gave 0.09 and the best fit to the ED data was obtained for f_τ^g=0.14 mdyn Å rad^{-2}. The latter gives a torsional frequency of 104 cm^{-1}, close to the observation in liquid phase.[6] The f_τ^g found from ED experiment is 1.5 times larger than f_τ^g calculated by MM, as was the case also for 2,3-dichloro-1-propene and CP. Thus, the relative f_τ^g calculated by MM seems to exhibit some reliability. This is comforting, since the torsional frequencies still are unobserved for many related molecules.

The *gauche* torsional angle is 8° smaller than what was found in CP.[5] The MM calculations suggest a value 6° lower than the ED result, similar to the relative MM and ED results for CP and 2,3-dichloro-1-propene.[20] Thus, the trend in the MM calculations is quite good.

There are very good agreements between C=C−C and C−C−Cl angles as calculated by MM and experimentally found from ED. A difference of 1° is better than one can except from a simple method as MM.

The geometrical parameters for CMP are compared to those of related molecules in Table 5. The results for CMP fit very nicely into the trends established by these molecules.

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