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Conformational Analysis. XVII. The Structure of 1,1-Dichloropropane $Cl_2CH\text{-}CH_2\text{-}CH_3$ as Determined by Electron Diffraction and Compared with Molecular-mechanics Calculations

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Gaseous 1,1-dichloropropane was studied at a nozzle temperature of 25 °C. Two conformers, *AG* and *GG*, were detected with 66±3% of *AG*. The following values for bond lengths (r_g) and bond angles (∠) are conformational averages: r(C–C) =1.522(6) Å, r(C–Cl)=1.781(6) Å, ∠CCC= 113.3(14)°, ∠CCCl=110.7(4)°, ∠ClCCl=109.3(4)°. The results have been presented with error limits (2σ). A normal-coordinate calculation gave the value 130 cm^{-1} for the C–$CHCl_2$ torsional mode within both conformers. The ED results agree with those from molecular-mechanics calculations.

This work is part of a conformational study of halogenated alkanes by gas-phase electron diffraction and molecular-mechanics calculations. The two 1:2 staggered conformers are *AG* and *GG* as indicated in Table 1. The multiplicity of *AG* is two corresponding to enantiomeric forms.

CALCULATIONS

Calculations of conformational energies and torsional barriers. Molecular-mechanics calculations were carried out using non-bonded potential functions in the Morse formulation.[1] The potential parameters are found in Ref. 2. The electrostatic terms of the potential have been calculated with the following charges (q) on the atoms: q(Cl)= –0.12, $g(C_1)$ =0.039, $q(H_1)$=0.050, $q(C_2)$= –0.009, $q(H_2)$= 0.029, $q(C_3)$= –0.011 and $q(H_3)$=0.028 in e-units. The charges were derived as suggested by Sanderson,[3] but reduced by a factor of 1.6.[4] The diagonal force constants of Ref. 4 were used for bond lengths and bond angles. An intrinsic torsional potential with threefold symmetry and a barrier height of 11.1 kJ/mol was included.

Calculated results are given in Table 1. Each energy value has been obtained by adjusting bond lengths and bond angles. At the energy minima the torsional angles were also adjusted. Energy minima are represented by the numbers 0 and 1.7 for *GG* and *AG*, respectively. Thus *GG* is energetically the most stable form. The energy minima, represented by the central number in each block of Table 1, are surrounded by torsional barriers, represented by the remaining eight numbers in each block, corresponding to forms with one or both terminal groups eclipsing the central CH_2 group. *AG* has approximately a staggered conformation while *GG* is exactly staggered. Each conformer corresponds to well-defined minima of the potential energy function.

The CH_3-torsional barriers are 12.1 and 12.9 kJ/mol for *GG* and *AG*, respectively. The lowest barrier for a conformational transition is 14.2 for the transition between enantiomeric forms of *AG*. For the transition *GG*→*AG* the lowest barrier is 23.4 kJ/mol.

Conformational differences between parameter values of bond angles are small. The largest value was 1.8° for ∠CCC. All conformational differences between bond lengths were negligible.

If the charges on the atoms are neglected the difference in energy $\Delta E = E(AG) - E(GG)$ is reduced to 0.8 kJ/mol.

MM calculations were also carried out on 1-

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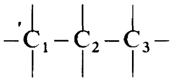
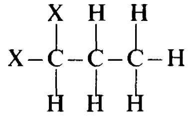
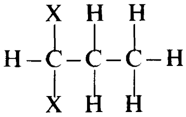
Table 1. Conformational energies and structural parameters, for 1,1-dichloropropane obtained by molecular-mechanics calculations.

X=Cl	*AG*	*GG*
Conformer  $-\overset{\vert}{\underset{\vert}{C_1}}-\overset{\vert}{\underset{\vert}{C_2}}-\overset{\vert}{\underset{\vert}{C_3}}-$	 $X-\overset{X}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$	 $H-\overset{X}{\underset{X}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$
Symmetry	C_1	C_s
Energies[a] in kJ/mol	46.9 14.6 32.2 23.4 1.7 16.3 46.9 14.6 32.2	46.9 12.1 46.9 23.4 0[b] 23.4 36.9 12.1 46.9
Torsional angle deviations from staggered form		
$\Delta\phi(1-2)$ in deg.	+6.2	0
$\Delta\phi(2-3)$ in deg.	−2.9	0
Valence angles in deg.		
∠CCC	113.4	115.2
∠CCX	110.2	110.8

[a] Horisontal variation corresponds to 60° change in $\phi(1-2)$. Vertical variation corresponds to 60° change in $\phi(2-3)$. [b] All energy values are relative to this value.

Table 2. Calculated mean amplitudes of vibration (u). The range of u values and the corresponding internuclear distances (r) are given. T=298 K.

Type of distance (X=Cl)	r(Å)	u(Å) × 10^3
C−H	1.108	78−79
C−X	1.781	52
C−C	1.522	51−52
X···X	2.87	68
X···H	2.35	107
C···H	2.16	107−108
X···C	2.72	67
H···H	1.78	127−128
C···C	2.55	70−71
C···H(g)	2.73−2.83	152−172
C···H(a)	3.48−3.51	105−106
H···H(g)	2.44−2.52	166−181
H···H(a)	3.05−3.06	130
X···C(g)	3.15−3.25	132−138
X···C(a)	4.09	70
X···H(g)	2.83−2.94	150−155
X···H(a)	3.67−3.68	102
H···H(aa)	4.31	144
H···H(ag)	3.82	174
H···H(ga)	3.72	177
H···H(gg″)	2.48	236
H···H(gg)	3.12	250
X···H(ga)	4.19−4.20	166−167
X···H(ag)	4.36−4.48	157−162
X···H(aa)	4.87	122
X···H(gg)	3.56−3.61	263−254
X···H(gg″)	2.81−2.92	231−242

chloropropane.[4] A conformational energy difference of 1.5 kJ/mol in favour of *gauche* was obtained, in agreement with the observed[5] value 1.3±0.8 kJ/mol. Also in this case the energy difference was reduced to about half when charges on the atoms were neglected.

Calculation of vibrational quantities. A normal-coordinate analysis[6] was carried out for each of the conformers, and mean amplitudes of vibration (u- and K-values) were computed.[7] Internuclear distances and their u-values are given in Table 2. The force constants, except for the torsional part, were taken from Ref. 8. The torsional force constants (F_ϕ) were computed from the formula given in Ref. 9. The values of $F_\phi(C_1-C_2)$ are 0.31 and 0.24 mdyn Å

Table 3. Calculated values of the torsional frequencies in cm^{-1}. Variation with the torsional force constant $F_\phi(C_1-C_2)$. The value of $F_\phi(C_2-C_3)$ was 0.086 m dyn Å(rad)$^{-2}$.

$F_\phi(C_1-C_2)$ m dyn Å(rad)$^{-2}$	0.22(*GG*) 0.17(*AG*)	0.31(*GG*) 0.24(*AG*)	0.40(*GG*) 0.31(*AG*)
GG	114	131	144
	204	205	205
AG	112	130	145
	202	202	202

(rad)$^{-2}$ for *GG* and *AG*, respectively. For $F_\phi(C_2-C_3)$ the value 0.086 mdyn Å (rad)$^{-2}$ was obtained for both conformers. The variation of the torsional frequencies with the value of $F_\phi(C_1-C_2)$ is shown in Table 3. Clearly the torsional modes are well separated with about 200−205 cm^{-1} corresponding to the methyl torsion and the lower mode corresponding to $C-CHX_2$ torsion at about 130 cm^{-1}.

Both of the torsional modes within the *GG* conformer belong to the species A″. In the low-frequency region below 300 cm^{-1} are found two additional modes corresponding to 214(A′) and 294(A′) for *GG*, but 243 and 286 cm^{-1} for *AG*.

EXPERIMENTAL

The compound was provided by K&K-laboratories and purified by gas chromatography. The sample used for ED had a purity in excess of 98%. ED-diagrams were recorded with the Balzers apparatus[10,11] at a nozzle temperature of 25 °C. Two sets of plates were obtained:

	Set 1	Set 2
Number of plates	6	6
Nozzle-to-plate distance (mm)	500.1	250.1
Electron wavelength (Å)	0.05859	0.05859

The electron wavelength was determined by calibration against benzene.[12] The data were treated in the usual way[13] to yield an intensity curve for each plate. Average curves for each set of distances were formed. A composite curve was then made by connecting the two average curves after scaling. The intensities have been calculated by the partial-wave method[14] using Hartree-Fock atomic potentials.[15]

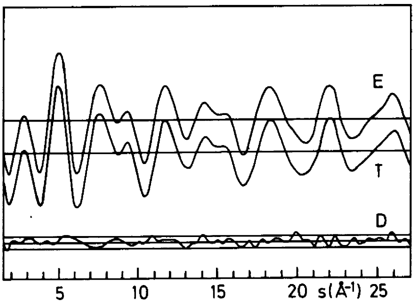


Fig. 1. Experimental (*E*) and theoretical (*T*) intensity curves for 1,1-dichloropropane and $D=E-T$ corresponding to the final least-square parameters. The straight lines show the experimental uncertainties (±3 times the experimental standard deviation).

RESULTS AND DISCUSSION

Final intensity curves and radial distribution curves (RD) are shown in Figs. 1 and 2. RD-curves for the individual conformers together with the experimental RD-curve are shown in Fig. 3. Clearly both of the conformers are present, *AG* being the most abudant conformer. The peak at 4.1 Å corresponds to the internuclear distance Cl···C (*anti*) only found in *AG*, while the peak at 3.2 Å corresponds to Cl···C (*gauche*) also found in *GG*. All distances are listed in Table 2.

It was assumed that the groups of atoms possess symmetry as follows: C_s for X_2HC-C, C_{2v} for $C-CH_2-C$, and C_{3v} for $C-CH_3$. All C−H bonds have equal lengths and the two C−C bonds also have equal lengths. Thus the conformers have identical structures except for the values of the torsional angles around the C_1-C_2 and C_2-C_3

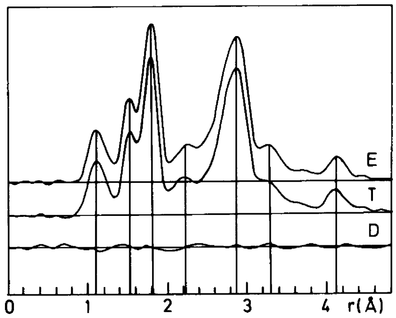


Fig. 2. Experimental (*E*) and theoretical (*T*) radial distribution curves for 1,1-dichloropropane and $D=E-T$. The damping constant was 0.002 Å^2.

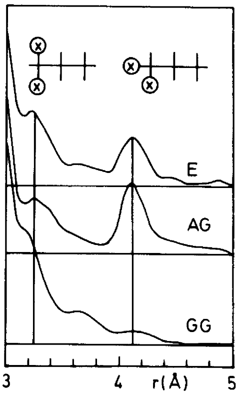


Fig. 3. Radial distribution curves for conformers of 1,1-dichloropropane are shown together with the final experimental curve. Only the conformational sensitive part is shown. Damping constant was 0.002 Å^2.

bonds. For *GG* the torsional angles were restricted at values corresponding to exactly staggered form. The torsional angles of *AG* were defined in the following way: $\phi(1-2)=126.2°+\phi_0$ and $\phi(2-3)=-(2.9°+\phi_0)$. If $\phi_0=0°$ the torsional angles have values corresponding to those in Table 1. The parameter ϕ_0 was refined together with the parameters r(C−H), r(C−C), r(C−X), ∠CCX, ∠CCC, $\alpha(GG)$ and ∠(XCX)* which is the projection of the XCX angle on a plane perpendicular to the C_1-C_2 axis. Parameters from the final least-squares refinements and standard deviations(σ) corrected for correlation[16] are given in Table 4. The uncertainty in the s-scale (0.14 %) has been included in the σ values for bond lengths. Non-bonded distances were computed as dependent parameters restricted under the constrains of r_α parameters.[17,18]

Table 4. Structural parameters and conformational composition for 1,1-dichloropropane. Standard deviations (σ) apply to the last digit given (X=Cl).

Bond lengths (r_g) in Å and bond angles ($\angle_\alpha$) in deg.

C−H	1.108(5)	∠CCC	113.3(7)
C−C	1.522(3)		
C−X	1.781(3)	∠CCX	110.7(2)
∠XCX	109.3(2)	∠HCX	107.7(3)
∠HC$_2$H	107.6(−)^a	∠C$_2$CH	109.9(−)^a
∠HC$_3$H	108.9(4)	∠CC$_2$H	108.6(3)

Torsional angle deviations from staggered form

	AG	*GG*
$\Delta\phi(1-2)$ in deg.	+10.0(12)^c	0^b
$\Delta\phi(2-3)$ in deg.	−6.7(12)^c	0^b
Composition(%)	66(3)	34(3)

^{a}Assumed value from MM-calculations. ^{b}Exactly staggered form was assumed. ^{c} $\phi_0=3.8(12)°$ and ∠(XCX)* =121.5(5)°, see text.

Four u-values corresponding to the isolated peaks on the RD curve were refined with the following result: u(C−H)=0.078(5), u(C−C)=0.052(3), u(C−Cl)=0.049(2) and u(C...C(a))=0.072(6) Å. The values are in reasonable agreement with those shown in Table 2. The remaining u values were included in the refinements as fixed parameters taken from Table 2.

The following parameter-correlation coefficients(ρ) had absolute values greater than 0.4:$\rho(2,5)=-0.48$, $\rho(3,6)=-0.46$, $\rho(4,7)=-0.57$ and $\rho(5,6=+0.90$, with the parameters numbered as follows: 2,3,4,5,6,7 for r(C−C), r(C−X), ∠CCC, ∠CCX, ∠(XCX)*, ϕ_0, respectively.

Comparing the structural parameter values of Tables 1 and 4 shows that the predictions based on MM calculations are confirmed by the experimental findings.

Assuming equal vibrational and rotational partition functions for the conformers, the value of the energy difference $\Delta E=E(AG)-E(GG)$ is zero as computed from the composition in Table 4. If, however, the ratio $Q(GG)/Q(AG)=0.83$ between vibrational partition functions(Q) is included as determined by the calculated frequencies, then $\Delta E=0.5$ kJ/mol. The values of the rotational partition functions were very nearly equal. Including error limits ($\pm 2\sigma$) $\Delta E=0.4\pm0.8$ kJ/mol is presented as the final value. From the MM calculations (Table 1) $\Delta E=1.7$ was obtained. Both values indicate that *GG* is the energetically most stable conformer.

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