Conformational Analysis. XIV. The Structure of Gaseous 1,3-Dichlorohexafluoropropane, $(CF_2Cl)_2CF_2$, as Determined by Electron Diffraction and Compared with Molecular Mechanics Calculations

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Gaseous 1,3-dichlorohexafluoropropane has been studied at a nozzle temperature of 20 °C. Three conformers *AA*, *AG* and *GG* were detected. Results are presented with error limits (2σ). The following values for bond lengths (r_g) and bond angles ($\angle$) are average parameters for the conformers: r(C – F) = 1.337 (4) Å, r(C – C) = 1.560 (6) Å, r(C – Cl) = 1.755 (6) Å, $\angle$CCC = 114.3° (2.0), $\angle$CCCl = 109.9° (0.8), $\angle$C2C1F = 108.9 (0.8), $\angle$FC2F = 106.6 (2.0). *AA* has an all staggered conformation, while *AG* and *GG* have torsion angles close to the staggered values. The conformational composition is: 53 % (6) of *AA*, 39 % (8) of *AG* and less than *ca.* 10 % of *GG*.

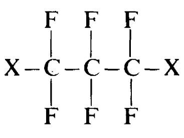
A normal coordinate analysis has been carried out, and calculated values of the vibrational amplitudes were included in the structural analysis.

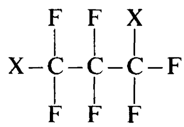
The diffraction data are consistent with the results obtained from molecular – mechanics calculations.

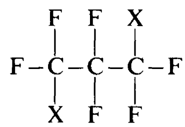
The results have been compared with those obtained for $(CH_2Cl)_2CH_2$.

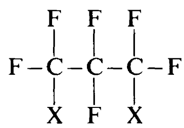
This work is part of a systematic conformational study of halogenated propanes. Classically the number of staggered conformers in $(CF_2X)_2CF_2$ is nine. Four conformers are distinguishable by vibrational spectroscopy.

Assuming all-staggered conformations, the distinguishable forms are characterized as follows (X = Cl):

AA: 

AG: 

GG: 

GG(1:3): 

The conformer *GG (1:3)* possesses one parallel (1:3) X···X interaction and therefore the conformational energy of this conformer is significantly higher than the energies of the other conformers. The classical multiplicities are 1, 4, 2, and 2 for *AA*, *AG*, *GG*, and *GG(1:3)*, respectively.

CALCULATIONS

Calculation of conformational energies, structural parameters, torsional barriers and force constants. The energy model is a molecular – mechanics calculation which includes atom-atom potentials and valence force constants, as described in Ref. 1. Energy parameters were taken from the work of Abraham *et al.*[2] The polar terms were not included in this work. The diagonal force constants in Table 3 were used.

The parameter values in Table 1 correspond to the minima found by minimizing the energy function. Clearly *AG* and *GG* have nearly (1:2) staggered conformations while *AA* is exactly staggered and *GG(1:3)* is far from staggered. According to the energy values of Table 1, *AA* is the energetically most stable conformer. Zero-point vibrational energies for the conformers have not been included here.

Torsional barriers are shown in Table 2. Each energy value has been obtained gy adjusting bond lengths and bond angles. At the minima the values of the torsion angles were also adjusted (see Table 1). The value $\phi_{1-2}=60°$ and values of ϕ_{2-3} equal to $\pm 60°$ correspond to (1:2) *eclipsed* transition forms. All conformers correspond to well – defined minima of the energy function. The lowest barriers correspond to transitions involving the conformer *AG*: 5.4 kcal/mol ($AG \rightarrow AA$), 5.7 kcal/mol ($GG \rightarrow AG$) and 4.1 kcal/mol ($GG(1:3) \rightarrow AG$).

Torsional force constants were calculated at the conformational minima. The values were numerically computed according to the definitions given below:

(mdyn Å (rad)$^{-2}$)	*AA*	*AG*	*GG*
$F_\phi(1-2)=\partial^2E/\partial\phi^2_{1-2}$	0.24	0.28	0.27
$F_\phi(2-3)=\partial^2E/\partial\phi^2_{2-3}$	0.24	0.24	0.27
$F_{\phi\phi'}=\partial^2E/\partial\phi_{1-2}\partial\phi_{2-3}$	−0.09	−0.15	−0.19

The symbol F_ϕ represents the diagonal force constant while $F_{\phi\phi'}$ represents the non-diagonal interaction term.

Values of the diagonal force constants were also calculated according to the formula in Ref. 3. The values estimated in this way were: $F_\phi(1-2)=F_\phi(2-3)=0.27$ for *AA*, $F_\phi(1-2)=0.27$ and $F_\phi(2-3)=0.29$ for *AG*, and $F_\phi(1-2)=F_\phi(2-3)=0.29$ for *GG* in units of mdyn Å (rad)$^{-2}$. The agreement with values based on molecular – mechanics calculations is good.

Calculation of vibrational quantities. Only an approximate force field is needed in order to compute vibrational amplitudes for the internuclear distances. For the compound studied here spectroscopic force constants were not available. However, valence force constants of F_3C-CF_3,[4] Cl_2CF_2,[5] $CH_3-CF_2-CH_3$[6] and $CH_2Cl-CH_2-CH_2Cl$[7] were available. Based on the information from these four compounds, values of the valence force

Table 1. Calculated conformational energy parameters for 1,3-dichlorohexafluoropropane.

Conformer	*AA*	*AG*	*GG*	*GG(1:3)*
ΔE (kcal/mol)[a]	0	1.06	2.01	3.55
ϕ_{1-2}(°)[b]	0(0)	+114.5(120)	+118.6(120)	−109.2(−120)
ϕ_{2-3}(°)[b]	0(0)	+3.5(0)	+118.6(120)	+109.2(+120)
∠CCC(°)[c]	112.5	114.9	117.4	117.4
r(CC)[d] (Å)	1.535	1.538	1.541	1.543

[a] Conformational energy $\Delta E=E-E(AA)$. [b] Torsion angles. Values corresponding to exactly (1:2) staggered conformation are given in parentheses. [c] Reference value 110.0°. [d] Reference value 1.513 Å.

Table 2. Torsional barriers (kcal/mol) between conformers of 1,3-dichlorohexafluoropropane. All values are relative to $E_{AA}=0$.

ϕ_{1-2} / ϕ_{2-3}	0°	60°	120°	180°
180°	8.5	22.8	11.2	∞
120°	1.1(*AG*)	7.7	2.0(*GG*)	11.2
60°	6.5	17.5	7.7	22.8
0°	0(*AA*)	6.5	1.1(*AG*)	8.5
−60°	6.5	17.5	7.6	22.8
−120°	1.1(*AG*)	7.6	*3.5 GG(1:3)*	11.2
−180°	8.5	22.8	11.2	∞

constants were selected. The torsional part of the force field could not be obtained in this way.

In previous works on halogenated propanes (Conformational Analysis I–XIII)[8] an average diagonal force constant for the torsional part of the force field was adjusted to fit theelectron diffraction data. The data for the title compound contain less information for this purpose than the data of previously mentioned compounds. The vibrational amplitude u(Cl...Cl) for the most abundant conformer *AA* (54 %) is essentially independent of the torsional force constant value. The value of u(Cl...Cl) for the conformer *GG* depends strongly on the torsional force constant value. However, *GG* is present in too small an amount (*ca.* 7 %) to give significant information about the force constant values of that conformer. The presence of *AG* (39 %) and the value of u(X···X) could, in principle, provide information about the torsional force constants of that conformer. Based on these considerations and similar arguments for the remaining u-values, it was decided to include only an average torsional force constant ($\bar{F}_\phi$) for the conformers. The value selected for $\bar{F}_\phi$ was 0.27 mdyn Å (rad)$^{-2}$ as calculated from the formula in Ref. 3. For the partial force constants F^*(FF), F^*(CF), F^*(XF), and F^*(CX) the values 0.021, 0.065, 0.048 and 0.110 in units of mdyn Å(rad)$^{-2}$ were used. The value of $\bar{F}_\phi$ was not adjusted, however, the torsional frequency values calculated with $\bar{F}_\phi$ equal to 0.18, 0.27 and 0.36 mdyn Å(rad)$^{-1}$ are given below.

Table 3. Valence force constants for 1,3-dichlorohexafluoropropane (X=Cl). Symbol in parentheses indicates atom or bond which is common for the interaction term.

Stretch (mdyn/Å)		Bend[mdyn Å(rad)$^{-2}$]	
C–F	5.68	FCX	1.40
C–X	3.30	FCF	1.69
C–C	4.57	CCX	1.17
		CCC	0.90
Stretch/bend (mdyn/rad)		CCF	0.79
CC/CCC	0.39(CC)		
CC/CCX	0.29(CC)		
CC/CCF	0.19(CC)	Stretch/stretch (mdyn/Å)	
CC/FCF	−0.19(C)	CF/CF	0.99(C)
CC/FCX	−0.20(C)	CF/CX	0.81(C)
CX/CCX	0.55(CX)	CC/CX	0.35(C)
CX/FCX	0.32(CX)	CC/CF	0.51(C)
CX/FCF	−0.21(C)		
CF/FCF	0.28(CF)		
CF/CCF	0.29(CF)	Torsion [mdyn Å(rad)$^{-2}$]	
CF/CCF	−0.29(C)	$F_\phi = 0.27$ (all conformers)	
CF/XCF	0.31(CF)	$F_\phi = F_\phi(1-2) = F_\phi(2-3)$	
CF/XCF	−0.15(C)	$F_{\phi\phi'}$0 (interaction term)	
CF/CCC	−0.22(C)		

Table 4. Calculated mean amplitudes of vibration (u). The range of u values and corresponding internuclear distances (r) are given including values for the conformers *AA*, *AG* and *GG*. (X=Cl).

Type of dist.	r (Å)	u (Å)
C–F	1.336	0.046
C–C	1.559	0.051
C–X	1.754	0.052
F···F	2.14–2.19	0.056
C···F	2.36	0.070
F···X	2.54	0.062
C···C	2.62	0.071
C···X	2.71	0.067
X···F(g)	2.88–2.97	0.129–0.134
X···F(a)	3.89	0.068
C···F(g)	2.85–2.96	0.125
C···F(a)	3.75	0.071
F···F(g)	2.61–2.87	0.121–0.122
F···F(a)	3.50	0.069
C···X(g)	3.34	0.135
C···X(a)	4.15	0.070
$F_1 \cdots F_3$(gg)	2.55–2.66	0.192–0.193
$F_1 \cdots F_3$(gg)	3.25–3.44	0.188
$F_1 \cdots F_3$(ag)	4.07–4.22	0.121–0.124
$F_1 \cdots F_3$(aa)	4.72	0.088
$X_1 \cdots F_3$(gg)	2.91	0.209
$X_1 \cdots F_3$(gg)	3.92	0.207
$X_1 \cdots F_3$(ag)	4.50–4.56	0.126–0.127
$X_1 \cdots F_3$(aa)	5.06	0.091
$X_1 \cdots X_3$(gg)	3.95	0.230
$X_1 \cdots X_3$(ag)	4.87	0.141
$X_1 \cdots X_3$(aa)	5.41	0.094

A normal coordinate analysis[9] was carried out for each of the conformers. Calculated values of the torsional frequencies in cm^{-1} are as follows:

	($\bar{F}_\phi = 0.18$)	($\bar{F} = 0.27$)	($\bar{F}_\phi = 0.36$)
AA:	54–60	66–72	76–82
AG:	50–62	61–74	70–82
GG:	46–66	55–79	63–89

The lowest values of remaining frequencies are 103, 104 and 106 cm^{-1} for *GG*, *AG* and *AA*, respectively, and essentially independent of the torsional force constant value. The highest values are 1257, 1266, and 1271 cm^{-1} for *AA*, *AG* and *GG*, respectively. The final force constant values used in this work are shown in Table 3. Mean amplitudes of vibration (u) were computed[10] and their values are given in Table 4.

EXPERIMENTAL AND DATA REDUCTION

A commercial sample of the compound was used. The purity was *ca.* 99 %. Electron density photographs were made at a nozzle temperature of 20 °C in the Balzer apparatus[11,12] under conditions summarized below.

Nozzle-to-plate distance (mm)	500.12	250.12
Electron wave length (Å)	0.05845	0.05850
Number of plates	4	5
Range of data in s ($Å^{-1}$)	1.25 – 15.50	2.25 – 30.50
Data interval Δs ($Å^{-1}$)	0.125	0.250
Uncertainty in s-scale(%)	0.14	0.14

The electron wave length was determined by calibration against TlCl and benzene.[13] The data were reduced in the usual way[14] 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 final experimental intensity curve is shown in Fig. 1. The intensities have been modified by $s|f'_{Cl}|f'_{C}|^{-1}$. Scattering amplitudes (f') were calculated by the partial-wave method[15] using Hartree-Fock atomic potentials.[16] The radial distribution (RD) curve[14] is shown in Fig. 2.

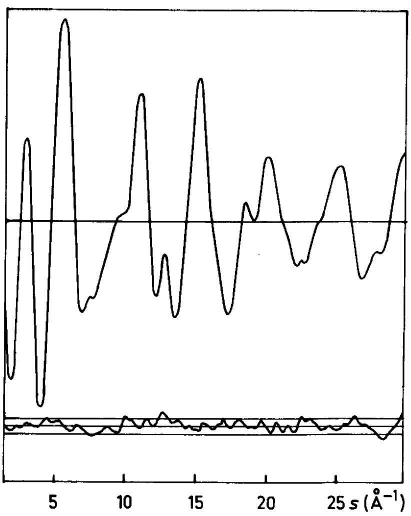


Fig. 1. Experimental intensity curve and difference curve between experimental and theoretical intensities. The straight lines give the experimental uncertainties as ±3 times the average standard deviations.

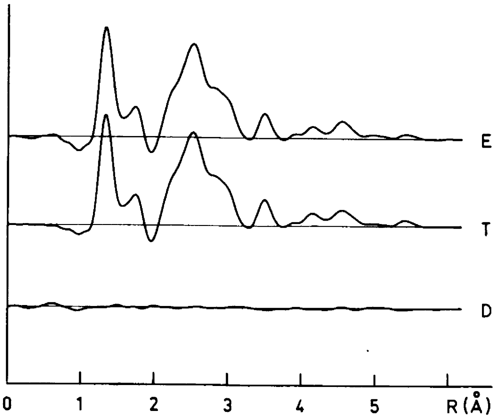


Fig. 2. Experimental (E) and theoretical (T) RD curves computed with an artificial damping constant of 0.002 $Å^2$. D = E − T.

STRUCTURE ANALYSIS

Radial distribution (RD) curves are shown in Fig. 2 and the final intensity curve in Fig. 1. Both conformers, *AA*, and *AG*, contribute to the RD-curve peaks at 2.5 – 3.2, 3,5, 3.8 – 4.2 and 4.6 Å, while only *AA* contributes to the peak at 5.4 Å and mainly *AG* contributes to the peak at 5.0 Å. The longest internuclear distance is $X_1 \cdots X_3$ (*AA*) at 5.41 Å. Internuclear distances are found in Table 4. The conformers *AA* and *AG* are clearly present in considerable amounts.

According to the energy values in Table 1, *GG(1:3)* is 3.6 kcal/mol less stable than *AA*, corresponding to a percentage of *GG(1:3)* less than 1 %. A small percentage of *GG* has to be expected at the experimental temperature.

In calculating the intensities for the least-squares refinements[14] it was decided not to include a contribution from the *GG(1:3)* conformer. The least-squares program is a modified version of the program described in Ref. 14. Models for the conformers were constructed in terms of the following average conformational parameters:

r(C – F), r(C – C), r(C – X), ∠CCC, ∠CCX, ∠C2C1F, ∠FC2F, ϕ_{1-2}, ϕ_{2-3} and ∠(FC1F)* which is the projection of the FC1F angle on a plane perpendicular to the C2 – C1 axes. Also adjusted were the composition parameters $\alpha(AA)$ and $\alpha(AG)$ with $\alpha(GG) = 100 - \alpha(AA) - \alpha(AG)$. Nonbonded distances were computed as dependent parameters restricted by the constraints of the conformational models.

It is assumed that: the $C-CF_2X$ groups are equivalent and possess C_s symmetry, the $C-CF_2-C$ group possesses C_{2v} symmetry, all C−F bonds have equal length, and thus the conformers have identical structures except for the values of the torsion angles ϕ_{1-2} and ϕ_{2-3} which define the rotation around the C−C bonds.

The expected conformational differences in structural parameters as derived by molecular-mechanics calculations are found in Table 1.

RESULTS

Parameters from the final least-squares refinements and standard deviations (σ) corrected for correlation in the experimental data[17] are given below. In the final refinements, intensities beyond $s=29.75$ Å^{-1} were not included. Using a diagonal weight matrix, all intensities between $s=3.0$ Å^{-1} and $s=28.0$ Å^{-1} were given equal weight. The remaining intensities were given reduced weight.

Calculated mean amplitudes of vibration were included in the analysis as fixed parameters.

The following average values were obtained for the independent bond lengths, r_g(Å), and bond angles, ∠(in deg), of the conformers (X=Cl):

$r_g(C-F)=1.337$ (2)	∠CCC = 114.3(1.0)
	∠CCX = 109.9 (0.4)
$r_g(C-C)=1.560$ (3)	∠C2C1F = 108.9 (0.4)
	∠FC2F = 106.6 (1.0)
$r_g(C-X)=1.755$ (3)	∠(FC1F)* = 120.0 (assumed)

The uncertainty in the s-scale (0.14 %) has been included in the standard deviations for bond lengths.

The values of the *dependent* bond angles are: ∠C1C2F = 108.9°(0.4), ∠FC1F = 110.2°(0.5) and ∠XC1F = 109.6°(0.5).

The torsion angles were not refined independently. However, a relationship between a deviation parameter (ϕ_0) and the torsion angles was introduced as suggested by the molecular−mechanics calculations. For the *AG* conformer it was assumed that $\phi_{1-2}=120°-\phi_0$ and $\phi_{2-3}=0.5\ \phi_0$. The parameter ϕ_0 was refined and the value obtained was $\phi_0=7.2°$ with $\sigma=2.4°$. For *AA* and *GG* exactly (1:2) staggered conformations were assumed.

Composition parameters (α) and torsion angles (ϕ) for the conformers are given below:

Conformer	*AA*	*AG*	*GG*
α (in %)	53(3)	39(4)	7(3)
ϕ_{1-2} (in deg.)	0	112.8(2.4)	120
ϕ_{2-3} (in deg.)	0	3.6(1.2)	120

For the conformer *AG* these values agree with those in Table 1. The differences are not statistically significant.

The following correlation coefficients (ρ) had absolute values greater than 0.5: $\rho(2,6)=-0.54$, $\rho(4,8)=-0.57$, $\rho(8,11)=-0.58$, $\rho(8,12)=0.60$, $\rho(4,12)=-0.52$, $\rho(11,12)=-0.76$.

The numbering of parameters is: $r(C-C)=2$, ∠C2C1F = 6, $\phi_0=8$, $\alpha(AA)=11$ and $\alpha(AG)=12$.

DISCUSSION

Assuming equal values of the vibrational partition functions[7] for the conformers, the values of the conformational energies are:
$E(AG)-E(AA)=1.0\pm0.2$ kcal/mol and
$E(GG)-E(AA)\geq1.0$ kcal/mol. The percentage of *GG* being 7 % ($\sigma=3$ %), only a rough lower limit of the difference $E(GG)-E(AA)$ can be estimated. With $\alpha(GG)=7$ % the value of $E(GG)-E(AA)$ is 1.6 kcal/mol.

The conformational energy of *GG(1:3)* was not determined experimentally at the present temperature. However, according to the energy values of Table 1, *AG* is 1.1 kcal/mol less stable than *AA* and *GG* is 2.0 kcal/mol less stable than *AA*, in agreement with the experimental values above. According to the values in Table 1 *GG(1:3)* is 3.6 kcal/mol less stable than *AA*. The fact, that *GG(1:3)* was not included in the conformational analysis, seems justified.

Clearly the values of the vibrational amplitudes (u-values) fit the experimental data well. The average torsional force constant value 0.27 mdyn Å(rad)$^{-1}$ derived from the formula in Ref. 3, and in agreement with the values based on molecular−mechanics calculations, is also consistent with the experimental data. Although the torsional interaction terms $F_{\phi\phi'}$ were not determined in this work, the values of $F_{\phi\phi'}$ derived from molecular−mechanics calculations seem reasonable.

In conclusion, it has been established that the values of the conformational energy parameters, the torsional force constants, and the structural parameters derived from molecular−mechanics calculations agree with the experimentally determined values.

The experimental results for $(CF_2X)_2CF_2$ and $(CH_2X)_2CH_2$ [7] are compared below. Standard deviations are shown in parentheses (σ).

X=Cl	$(CF_2X)_2CF_2$	$(CH_2X)_2CH_2$
Nozzle temperature (°C)	20	38
Percentage of conformers (*AA*, *AG*, *GG*)	53,39,7	3,24,73
r_g(C−C) in Å	1.560(3)	1.531(4)
∠CCC in deg.	114.3(1.0)	112.9(0.5)
r_g(C−X) in Å	1.755(3)	1.798(3)
∠CCX in deg.	109.9(0.4)	111.6(0.1)
$\bar{F}_\phi$ (average torsional force constant) in mdyn Å(rad)$^{-2}$	0.27	0.17

The conformational distributions of the two compounds at room temperature are clearly different. The difference in the C−C and C−X bond lengths as well as the difference in the CCX bond angles, are statistically significant. The difference in the CCC bond angles is expected, but hardly statistically significant.

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