

Conformational Analysis. XII. The Structure of Gaseous 1,3-Dichloropropane, $(\text{CH}_2\text{Cl})_2\text{CH}_2$, as Determined by Electron Diffraction and Compared with Molecular Mechanics Calculations

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Gaseous 1,3-dichloropropane has been studied at a nozzle temperature of 38 °C. Three conformers *GG*, *AG* and *AA* were detected. Results are presented with error limits (2σ). The following values for bond lengths (r_g) and bond angles (\angle_α) are average parameters for the conformers: $r(\text{C}-\text{H})=1.124(12)$ Å, $r(\text{C}-\text{C})=1.531(8)$ Å, $r(\text{C}-\text{Cl})=1.798(6)$ Å, $\angle\text{CCC}=112.9^\circ$ (1.0), $\angle\text{CCCl}=111.6^\circ$ (0.2). By symmetry *AA* has a staggered conformation, while *AG* and *GG* have torsion angles close to staggered values. The composition at 38 °C is: 73 % (4) of *GG*, 24 % (4) of *AG*, and less than 10 % of *AA*.

An average torsional force constant for the conformers and vibrational frequencies corresponding to the torsional modes have been estimated by combining information from electron diffraction and vibrational spectroscopy. It has been shown that the experimental assignment of low frequencies is most probably wrong.

The conformational energies of the title compound have been compared with the experimentally determined conformational energies of several 1,3-dihalopropanes as well as 1,2,3-trihalopropanes.

This work is part of a systematic conformational study of halogenated propanes by electron diffraction. The title compound is referred to as DCP. Results for 1,3-dibromopropane (DBP) have recently been published.¹ A series of investigations related to these studies are listed in Ref. 2.

Classically the possible number of staggered conformers in DXP is *nine*, as indicated in Fig. 1 of Ref. 1. The four conformers which are distinguishable by vibrational spectroscopy, are characterized as follows:

Conformer	Pointgroup	Symmetry number
XCCCX[<i>AA</i>]	C_{2v}	2
X XCCC[<i>AG</i>]	C_1	1
X CCC[<i>GG</i>]	C_2	2
X CCC[<i>GG</i> (1:3)]	C_s	1
X X		

The classical multiplicities¹ of the conformers are 1[*AA*], 4[*AG*], 2[*GG*], and 2[*GG*(1:3)]. The numbering of atoms in *GG* is shown in Fig. 1.

Sheppard *et al.*^{3,4} studied 1,3-dihalopropanes and based on infrared spectra they concluded that DCP crystallized in the *GG* conformation at low temperatures. An extended vibrational spectral study of DCP as liquid, in solution, and in the crystalline state has been published by Klæboe *et al.*⁵ They found that the conformers *GG*, *AG*, and *AA* were present in the liquid.

CALCULATION OF STRUCTURAL PARAMETERS, CONFORMATIONAL ENERGIES, TORSIONAL BARRIERS, AND TORSIONAL FORCE CONSTANTS

The semi-empirical energy model corresponds to simple molecular-mechanics calculations, including atom-atom potentials and valence force constants, as described in Ref. 6. Energy parameters were taken from the work of Abraham and Parry.⁷ The diagonal force constants in Table 5 were used.

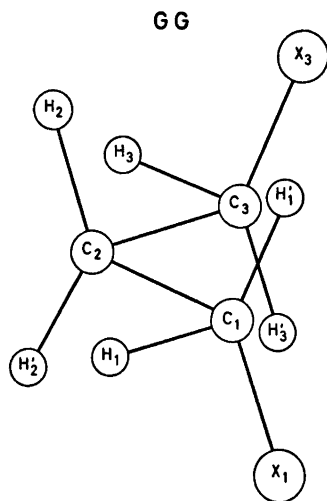


Fig. 1. The numbering of atoms in the GG conformer of 1,3-dichloropropane.

The parameter values in Table 1 correspond to the minima found by minimizing the energy. GG and AG have nearly staggered conforma-

tions, while AA is exactly staggered and GG(1:3) is far from staggered.

According to the calculated conformational energies of Table 2, AA is the energetically most stable conformer. Zero-point vibrational energies for the conformers have not been included.

Torsional barriers between the conformers are shown in Table 3. Each energy value has been obtained by adjusting all geometry variables except for the values of ϕ_{1-2} being 60 and 180°, and ϕ_{2-3} being ± 60 and $\pm 180^\circ$. Such values of the torsion angles correspond to (1:2) eclipsed conformations.

The barrier for the transition *anti-gauche* in propyl chloride⁸ is 2.78 kcal/mol,* while the *gauche-gauche* barrier corresponds to 2.96 kcal/mol. The calculated barrier for the transition AA-AG in DCP is 3.9 kcal/mol, and the fact that this barrier is higher than those in propyl chloride seems reasonable. However, the calculated barrier of 6.5 kcal/mol, corre-

* 1 kcal = 4.184 kJ.

Table 1. Calculated structural parameters in the stable conformers of 1,3-dichloropropane.

Parameter r (Å), \angle (°)	"Normal" value	AA	AG	GG	GG(1:3)
$r(\text{C}-\text{H})$	1.094	1.095	1.095	1.095	1.095
$r(\text{C}-\text{C})$	1.513	1.523	1.526	1.529	1.530
$r(\text{C}-\text{X})$	1.760	1.765	1.766	1.767	1.767
$\angle \text{CCC}$	110.0	110.2	112.3	114.3	114.1
$\angle \text{CCX}$	109.47	110.6	111.0	111.3	112.6
$\angle \text{C}_1\text{C}_2\text{H}$	109.47	109.7	109.8	109.9	109.4
$\angle \text{C}_2\text{C}_1\text{H}$	109.47	109.4	109.1	108.8	108.9
$\angle \phi_{1-2}$	- ^a	0.0	+112.5	+113.3	-100.7
$\angle \phi_{2-3}$	- ^a	0.0	+4.1	+113.3	+100.7

^a Values (ϕ_{1-2} , ϕ_{2-3}) for exactly staggered conformations are: AA (0°, 0°), AG (120°, 0°), GG (120°, 120°), and (-120°, 120°) for GG(1:3).

Table 2. Conformational energies (kcal/mol) for 1,3-dichloropropane.

Type of energy	AA	AG	GG	GG(1:3)
E (bonded)	0.188	0.594	1.103	2.579
E (van der Waals)	1.508	1.764	1.860	1.865
E (polar: X...H)	-5.973	-6.185	-6.313	-5.865
E (polar: X...X)	1.450	1.617	1.858	2.320
E (total) - E (AA)	0.0	0.62	1.33	3.72

Table 3. Torsional barriers (kcal/mol) between conformers of 1,3-dichloropropane.

ϕ_{1-2} ϕ_{2-3}	0°	60°	120°	180°
180°	6.5	14.0	8.7	26.4
120°	0.6(AG)	4.2	1.3(GG)	8.7
60°	3.9	8.2	4.2	14.0
0°	0.0(AA)	3.9	0.6(AG)	6.5
-60°	3.9	8.5	4.6	14.0
-120°	0.6(AG)	4.6	3.7[GG(1:3)]	8.7
-180°	6.5	14.0	8.7	26.4

sponding to the transition *AG-AG*, seems unreasonably high.

Clearly *AA*, *AG* and *GG* correspond to well defined minima of the potential energy, while the conformer *GG(1:3)* corresponds to a rather shallow minimum. The barrier height is less than 1 kcal/mol for the transition *GG(1:3) - AG*.

The torsional force constants of Table 4 were calculated at the conformational minima. It

is noteworthy that the magnitude of the interaction constant ($F_{\phi\phi'}$) is quite small for all three conformers.

CALCULATION OF VIBRATIONAL QUANTITIES

Valence force constants, except for the torsional part, were taken from works of Schachtschneider⁹ and Snyder.¹⁰ The final force-constant values used in this work are shown in Table 5. An average torsional force constant has been adjusted to fit the experimental intensities. The normal-coordinate program described by Gwinn¹¹ was used in computing vibrational frequencies. The fit between observed spectroscopic frequencies¹² and those calculated is shown in Table 6. If the torsional modes are not included, the average relative deviation between observed and calculated frequencies is *ca.* 2%. Keeping in mind that the non-torsional force constants were not adjusted, the fit is very good for non-torsional

Table 4. Calculated torsional force constants (F_{ϕ}) in conformers of 1,3-dichloropropane. The values were numerically computed according to the definitions given.

[mdyn Å (rad) ⁻²]	<i>AA</i>	<i>AG</i>	<i>GG</i>
$F_{\phi}(1-2) = \partial^2 E / \partial \phi_{1-2}^2$	0.125	0.167	0.168
$F_{\phi}(2-3) = \partial^2 E / \partial \phi_{2-3}^2$	0.125	0.126	0.168
$F_{\phi\phi'} = \partial^2 E / \partial \phi_{1-2} \partial \phi_{2-3}$	-0.010	-0.043	-0.062

Table 5. Valence force constants for 1,3-dichloropropane.

Stretch (mdyn/Å)	Bend [mdyn Å (rad) ⁻²]
C-C: 4.57	CCC: 0.90
C-X: 3.18	CCH: 0.68 (in C-CH ₂ X)
C-H: 4.85 (in C-CH ₂ X)	CCH: 0.67 (in >CH ₂)
C-H: 4.55 (in >CH ₂)	CCX: 1.17
	HCH: 0.45 (in C-CH ₂ X)
Stretch/bend (mdyn/rad)	HCH: 0.55 (in >CH ₂)
C-X/CCX: 0.73 (C-X common)	HCX: 0.79
C-X/HCX: 0.33 (C-X common)	
C-C/CCC: 0.35 (C-X common)	Stretch/stretch (mdyn/Å)
C-C/CCX: 0.29 (C-C common)	C-C/C-X: 0.730 (C-C common)
C-C/CCH: 0.26 (C-C common)	C-C/C-C: 0.064 (C-C common)
Bend/bend [mdyn Å (rad) ⁻²]	Torsion [mdyn Å (rad) ⁻²]
CCC/CCH: -0.124 (C-C common)	$F_{\phi} = 0.17$ (all conformers;
CCH/HCX: 0.105 (in C-CH ₂ X)	$F_{\phi} = F_{\phi}(1-2) = F_{\phi}(2-3)$ and
HCX/HCX: 0.097 (in C-CH ₂ X)	$F_{\phi\phi'} = 0$).

Table 6. Vibrational frequencies (cm^{-1}) in 1,3-dichloropropane. Observed values are given in parentheses.¹²

Approximate mode	GG	AG	AA
Asym. torsion (ω_1)	60(190)	114	148
Sym. torsion (ω_2)	145(180)	89	116
CCX-bend (ω_3)	225(348)	259	143
CCX-bend (ω_4)	387(362)	285	386
CCC-bend	466(457)	442(431)	307(372)
Asym. C-X	656(641)	668(656)	685(697)
Sym. C-X	680(679)	736(727)	783(780)
CH ₂ -rock	839(861)	829(793)	807(793)
CH ₂ -rock	888(867)	901	897
CH ₂ -rock	992(967)	986	1017
Sym. C-C	1034(1001)	1049(1034)	1061(1034)
Asym. C-C	1034(1077)	1026	1012(1064)
CH ₂ -twist	1139(1150)	1143	1127(1135)
CH ₂ -twist	1154(1194)	1155	1165
CH ₂ -twist	1249(1280)	1254	1259
CH ₂ -wag	1276(1258)	1282	1285(1270)
CH ₂ -wag	1297(1316)	1312	1328
CH ₂ -wag	1388(1357)	1373(1352)	1357(1352)
CH ₂ -scissor	1436(1421)	1437	1435
CH ₂ -scissor	1440(1443)	1439	1438
CH ₂ -scissor	1479(1455)	1482	1485
C-H stretch	2860(2868)	2860	2861
C-H stretch	2915(2918)	2914(2925)	2914(2925)
C-H stretch	2959(2941)	2960(2953)	2960(2953)
C-H stretch	2960(2967)	2960(2953)	2960(2953)
C-H stretch	2998(3001)	2999	2999
C-H stretch	3000(3001)	2999	2999

Table 7. Mean amplitudes of vibration (u) and K values for the GG conformer of 1,3-dichloropropane, at 38 °C. The range of values have been indicated [$u(\text{C-H})$: 0.078–92].

Type of dist. (r)	r (Å)	u (Å)	K (Å)
C-H	1.095	0.078-92	0.017-25
C-C	1.529	0.0518	0.0050
C-X (X=Cl)	1.767	0.0530	0.0158
C ₂ ...X ₁	2.725	0.0712	0.0094
C ₃ ...H ₁ '	2.163	0.1080	0.0162
C ₁ ...C ₃	2.569	0.0698	0.0042
C ₁ ...H ₂	2.149	0.1079	0.0123
X ₁ ...H ₁ '	2.353	0.1087	0.0291
H...H	1.76-8	0.127-8	0.021-35
X ₁ ...X ₃	4.218	0.2745	0.0001
C ₁ ...X ₃ (<i>gauche</i>)	3.268	0.1556	0.0065
X ₁ ...H ₂ (<i>anti</i>)	3.678	0.1041	0.0109
X ₁ ...H ₂ ' (<i>gauche</i>)	2.863	0.1659	0.0122
X ₁ ...H ₃ '	2.824	0.2498	0.0199
X ₁ ...H ₃	4.179	0.1799	0.0850

modes, except for the observed value¹² $\omega_3 = 348 \text{ cm}^{-1}$ which was assigned¹² to the lowest CCX-bending mode within the GG conformer. The calculated value is 225 cm^{-1} . The force constants would have to be changed drastically in order to fit this assignment. In Table 1 of Ref. 12 several values in the range 215–221 cm^{-1} have been assigned as CCX-bending modes. Could not a reassignment remove the large discrepancy on this point?

Mean amplitudes of vibration (u) and perpendicular amplitude correction coefficients (K) were computed as described in Ref. 13. K and u values for internuclear distances are found in Table 7. Some of these quantities are quite sensitive to the values of the torsional force constants. In Table 8 are shown values of vibrational quantities corresponding to different values of the average diagonal torsional force constant. The force constant $F_\phi = 0.17 \text{ mdyn } \text{Å} (\text{rad})^{-2}$ corresponds to the best value as estimated from the electron diffraction data.

Table 8. Vibrational quantities in 1,3-dichloropropane. (Torsional interaction force constant $F_{\phi\phi'} = 0$.)

Torsional force constant			
$F_{\phi}(1-2) = F_{\phi}(2-3) = F_{\phi}[\text{mdyn } \text{Å} (\text{rad})^{-2}]$	0.13	0.17	0.27
Mean amplitudes, u (Å) at 38 °C, for the $X_1 \cdots X_3$ distance in			
conformer <i>AA</i>	0.101	0.101	0.101
conformer <i>AG</i>	0.164	0.160	0.144
conformer <i>GG</i>	0.289	0.275	0.222
Torsional frequencies (cm^{-1}) for the conformer <i>GG</i>			
asym. mode (ω_1)	57	60	76
sym. mode (ω_2)	139	145	174

EXPERIMENTAL AND DATA REDUCTION

A commercial sample of DCP was obtained from FLUKA. The purity of the sample which was used was better than 99 %.

Electron-density photographs were made at a nozzle temperature of 38 °C in the Balzer¹⁴ apparatus¹⁵ under conditions summarized below.

Nozzle-to-plate distance (mm)	579.7	189.7
Electron wave length (Å)	0.05852	0.05857
Number of plates	4	5
Range of data, in s (Å ⁻¹)	1.25–13.25	6.0–39.5
Data interval, Δs (Å ⁻¹)	0.125	0.25
Uncertainty in s -scale (%)	0.14	0.14

The electron wave length was determined by calibration against ZnO, and benzene. The data were reduced in the usual way¹⁶ 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. 2. The intensities have been modified by $s/|f_{\text{Cl}}^2|$.

Scattering amplitudes were calculated by the partial-wave method¹⁷ using Hartree-Fock atomic potentials.¹⁸

The radial distribution (RD) curve, obtained by Fourier transformation¹⁶ of the final experimental intensity, is presented in Fig. 3.

STRUCTURE ANALYSIS

Radial distribution (RD) curves for the conformers and the final experimental curve are shown in Fig. 4. The conformers *GG* and *AG* are clearly present in considerable amounts,

and *GG* is the most abundant conformer. The small peak in the experimental RD curve at *ca.* 5.5 Å might correspond to a small contribution from the conformer *AA*. Approximate composition parameters (α) were estimated from the RD curves: $\alpha(\textit{GG}) \approx 70\%$, $\alpha(\textit{AG}) \approx 25\%$, and $\alpha(\textit{AA}) \approx 5\%$.

According to the calculated energy values in Table 2, *GG*(1:3) is *ca.* 4 kcal/mol less stable than *AA*. If the semi-empirical results are

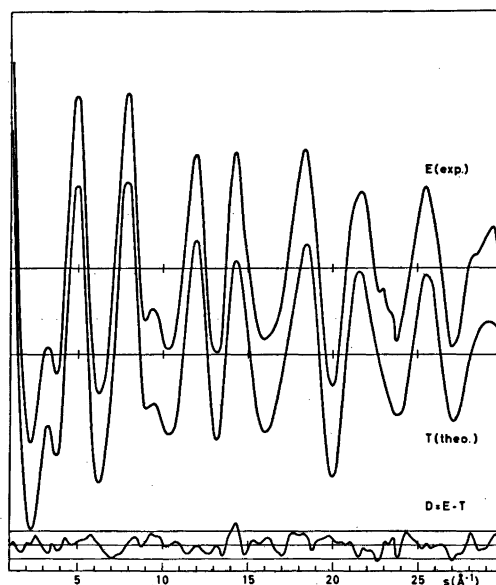


Fig. 2. Experimental (E) and theoretical (T) intensity curves for 1,3-dichloropropane at 38 °C, and $D = E - T$, corresponding to the final least-squares parameters. The straight lines give the experimental uncertainties (± 3 times experimental standard deviation).

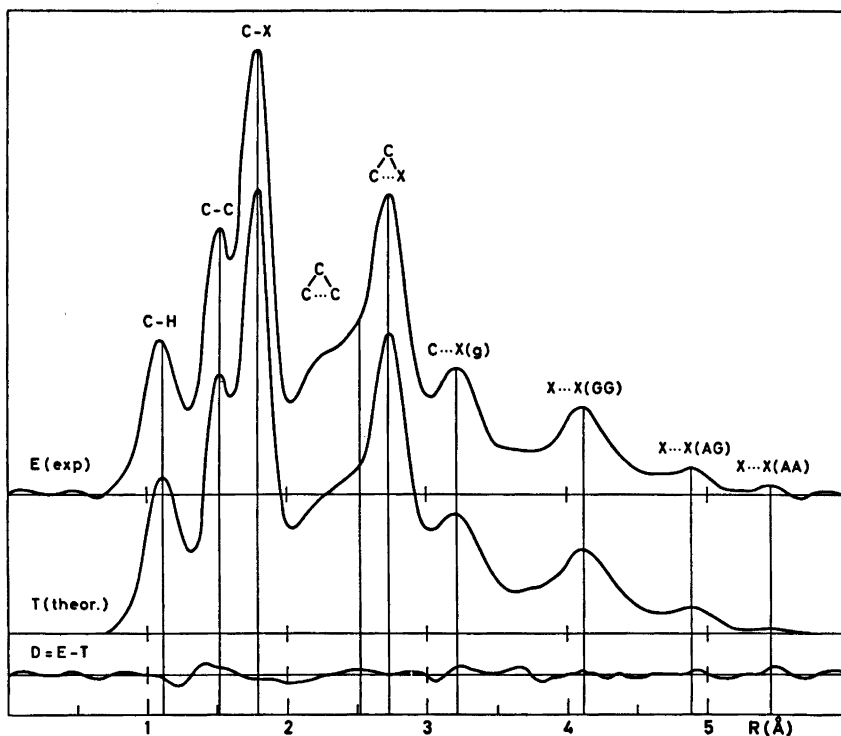


Fig. 3. Experimental (E) and theoretical (T) radial distribution curves for 1,3-dichloropropane at 38°C, and $D = E - T$. The curves were calculated from the intensities in Fig. 2 with an artificial damping constant of 0.002 \AA^2 .

approximately correct, the percentage of $GG(1:3)$ has to be very small ($< 1\%$).

Least-squares refinements

In calculating theoretical intensities for the least-squares refinements,¹⁶ 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 explained in Ref. 16. Models for the conformers were constructed as explained in Ref. 1. The models were defined in terms of the following average parameters: $r(C-H)$, $r(C-C)$, $r(C-X)$, $\angle CCC$, $\angle CCX$, $\angle C_2CH$, $\angle CC_2H$, ϕ_{1-2} , ϕ_{2-3} , and $\angle(HC_1H)'$ which is the projection of the HC_1H' angle on a plane perpendicular to the C_2-C_1 axes. Also adjusted were the composition parameters $\alpha(GG)$ and $\alpha(AG)$ with $\alpha(AA) = 100 - \alpha(GG) - \alpha(AG)$. Non-bonded distances were computed as dependant parameters, re-

stricted under the constraints of geometrically consistent r_α parameters.^{18,20}

Determination of the torsional force constant

The torsional modes of vibration contribute substantially to the mean amplitudes of several internuclear distances in a molecule like DCP. Since a reasonable force field was known, except for the torsional part, torsional force constants can be adjusted to fit the electron diffraction data. Determination of all torsional force constants is not possible. However, an average value (F_ϕ) for the conformers, assuming $F_\phi(1-2) = F_\phi(2-3) = F_\phi$, were estimated as follows. K and u values were computed for several values of F_ϕ and then included in the least-squares refinements. The structure and composition parameters were adjusted for each new value of F_ϕ . The best fit between theoretical

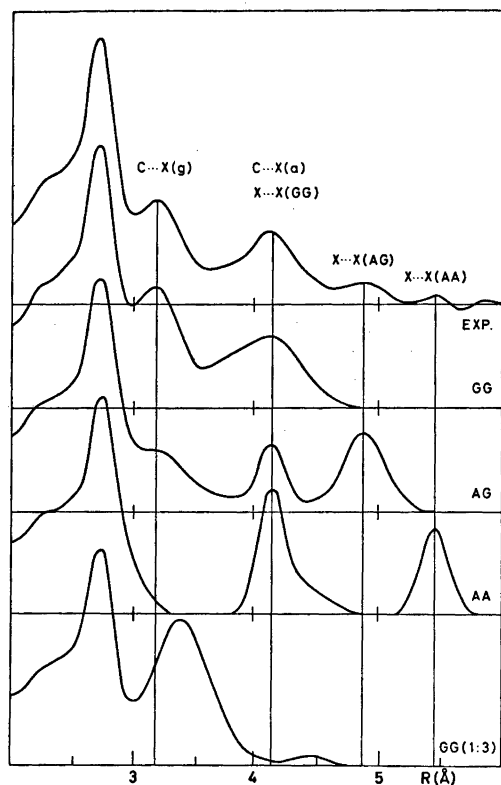


Fig. 4. Radial distribution curves for conformers of 1,3-dichloropropane at 38 °C. Theoretical curves for the conformers *GG*, *AG*, *AA* and *GG(1:3)* are shown together with the final experimental curve. (Damping constant equal to 0.002 Å².)

and experimental intensities was obtained for $F_\phi = 0.17$ m dyn Å (rad)⁻², with error limits of ca. 30%. The error limits are subjective to a certain degree and do not allow for systematic²¹ errors. The average experimental F_ϕ value (0.17) is in excellent agreement with the calculated F_ϕ value (0.168) of the *GG* conformer. The calculated average F_ϕ value (0.146) for the *AG* conformer also agrees with the experimental value. The calculated F_ϕ value (0.125) for the *AA* conformer is indirectly supported by the good agreement found for *GG* and *AG*.

In spite of the fact that the torsional interaction constant $F_{\phi\phi'}$ has not been determined in this work, the calculated values of Table 4 are indirectly supported by the agreement found for the diagonal force constants.

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FINAL RESULTS

Parameters from the final least-squares refinements¹⁶ and standard deviations (σ) corrected for correlation in the experimental data²² are given. In the final refinements, intensities beyond $s = 30.0$ Å⁻¹ were not included. Using a diagonal weight matrix, all intensities were given equal weight.

Bond lengths and bond angles are found in Table 9. The uncertainty in the s -scale (0.14%) has been included in the standard deviations for bond lengths.

Composition parameters and torsion angles are found in Table 10. The three torsion angles $\phi_{1-2}(AG)$, $\phi_{2-3}(AG)$, and $\phi_{1-2}(GG) = \phi_{2-3}(GG)$ were not refined independently. However, a common deviation parameter (ϕ_0) was refined. The relationship between ϕ_0 and the torsion angles are given in Table 10. The value of ϕ_0

Table 9. Average bond lengths and bond angles in the conformers of 1,3-dichloropropane. Standard deviations are given in parenthesis (X = Cl).

Bond lengths (r_a in Å)	Bond angle ($\angle \alpha$ in deg.)
$r(C-H) = 1.118(6)$	$\angle CCC = 112.9(0.5)$
	$\angle CCX = 111.6(0.1)$
	$\angle C_1C_2H = 108.8(-)^a$
$r(C-C) = 1.529(4)$	$\angle C_2C_1H = 109.9(-)^a$
	$\angle HC_1X = 107.8(0.1)^b$
	$\angle HC_2H = 108.3(0.1)^b$
$r(C-X) = 1.796(3)$	$\angle HC_2H = 108.0(0.7)^b$
	$\angle (HC_1H')^* = 120.0^c$

^a Calculated value for *GG* (Table 1). ^b Dependent parameter. ^c Assumed value.

Table 10. Composition parameters (α) and torsion angles (ϕ) for 1,3-dichloropropane, with standard deviations in parentheses.

Conformer	<i>GG</i>	<i>AG</i>	<i>AA</i>
α (in %)	73(2)	24(2)	3(3) ^a
ϕ_{1-2} (in deg.)	114.2(0.6) ^b	114.2(0.6) ^c	0(-) ^d
ϕ_{2-3} (in deg.)	114.2(0.6) ^b	5.8(0.6) ^c	0(-) ^d

^a $\alpha(AA) = 100 - \alpha(GG) - \alpha(AG)$. ^b $\phi_{1-2} = \phi_{2-3} = 120 - \phi_0$. ^c $\phi_{1-2} = 120 - \phi_0$ and $\phi_{2-3} = \phi_0$. ϕ_0 was refined. ^d Assumed value.

is a measure of the deviation from staggered conformations, and the value 5.8° for this parameter is significantly different from 0° . Moreover, calculated values of torsion angles in Table 1 agree with experimental values of Table 10.

An attempt to refine the torsion angles of GG and AG independently led to the same value of $\phi(GG)$, however, unreasonable values for $\phi_{1-2}(AG)$ and $\phi_{2-3}(AG)$ were obtained with standard deviations six times as large as those reported in Table 10.

As final u and K values are reported those of Table 7 corresponding to the value 0.17 mdyne Å (rad)⁻² for the torsional force constant. These u values are consistent with the electron-diffraction data.

The following parameter correlation coefficients (ρ) had $|\rho| > 0.4$: $\rho(C-C/\angle CCX) = -0.56$, $\rho(\phi_0/\angle CCC) = -0.79$, $\rho[\alpha(AG)/\alpha(GG)] = -0.77$.

DISCUSSION

The percentages α^* and α of two conformers in equilibrium in the gas phase are related to the expression for the equilibrium constant, as given in eqn. (1):

$$\alpha^*/\alpha = q(M^*/M)\exp(-\Delta E^m/RT) \quad (1)$$

If Q^{vib} is the vibrational partition function of a conformer referred to the potential-energy minimum of that conformer, then $q = (Q^*/Q)^{\text{vib}}$. $\Delta E^m = E^* - E$ is the potential-energy difference between the two conformers. The difference ΔE^m is measured between energy minima. The vibrational energy is included in the quantity Q^{vib} . R and T have their usual meanings. The classical multiplicities¹ of the conformers are: $M(AA) = 1$, $M(AG) = 4$, and $M(GG) = 2$.

If the quantities Q^{vib} are known, then ΔE^m may be computed from eqn. (1). Conversely, if the quantity ΔE^m is known the q value may be calculated. In eqn. (1) it is assumed that the classical rotational partition functions of the conformers are equal, and that is very nearly true for the conformers AA , AG and GG .

According to the semi-empirical energy model, AA is the conformer of lowest minimum energy, while GG and AG are 1.3 and 0.6 kcal/mol less stable than AA , respectively. If the values $\Delta E^m(AA-GG) = 1.3$ kcal/mol and $\Delta E^m(AG-GG) = -0.7$ kcal/mol are accepted then

the quantities $q(AA/GG)$ and $q(AG/GG)$ have to be quite different from 1.0. On the other hand, if the conformers have equal Q^{vib} values then $\Delta E^m(AA-GG) = +1.5$ kcal/mol and $\Delta E^m(AG-GG) = +1.1$ kcal/mol, with GG the energetically most stable conformer.

The conformational force fields have to be very different in order that $\Delta E^m(AG-GG) = -0.7$ kcal/mol. The value of $q(AG/GG)$ would then have to be equal to 0.05. A complete set of reliable experimental vibrational frequencies for each conformer does not exist. However, most probably, the conformational difference in force fields are due to different torsional force constants. If the calculated torsional force constants of Table 4 and the remaining force field of Table 5 are used then $q(AG/GG) = 1.2$ as calculated from the vibrational frequencies. Using equal force constants for the conformers the quantity $q(AG/GG) = 1.1$. Thus it seems quite improbable that any reasonable combination of torsional force constants could lead to the very low value 0.05 for $q(AG/GG)$.

As the q values remain unknown at present, the values $q(AA/GG) = q(AG/GG) = 1$ are assumed. The best estimates for the conformational energies are then: $\Delta E^m(AG-GG) = 1.1 \pm 0.2$ kcal/mol, and $\Delta E^m(AA-GG) \geq 1.5$ kcal/mol. The last value has to be very uncertain. The percentage of AA was 3% with a formal standard deviation of 3% which means that only a lower limit of $\Delta E^m(AA-GG)$ can be estimated.

The conformational energy of $GG(1:3)$ remains unknown. However, according to the calculated values of Table 2 this conformer is 3.7 kcal/mol less stable than AA , and 2.4 kcal/mol less stable than GG . The fact that the fit between calculated and experimental intensities is good does not exclude a small percentage of $GG(1:3)$ at the present temperature.

Experimentally determined conformational energies for 1,3-dihalopropanes and 1,2,3-trihalopropanes have been summarized below. The energy values relative to the most stable GG conformer are given in kcal/mol.

1,3-Dihalopropanes	X = Cl	X = Br
		(Ref. 1)
AA : XCCCX	1.5	1.6

AG: $\begin{array}{c} \text{X} \\ \text{XCCC} \end{array}$	1.1	0.9
GG: $\begin{array}{c} \text{X} \\ \text{CCC} \\ \text{X} \end{array}$	0	0
1,2,3-Trihalopropanes	X = Cl (Ref. 23)	X = Br (Ref. 6)
AG: $\begin{array}{c} \text{XX} \\ \text{XCCC} \end{array}$	0.7	1.5
GG: $\begin{array}{c} \text{XX} \\ \text{CCC} \\ \text{X} \end{array}$	0	0

For 1,3-dichloro-2,2-dimethylpropane²⁴ the energy values are 0, 1.1, and 1.3 kcal/mol for the conformers GG, AG, and AA, respectively. In calculating these values it was assumed that conformers of the same molecule have equal vibrational partition functions ($q = 1$). All molecules were studied by electron diffraction, and further details about the conformational equilibria in the gas phase are found in Refs. 1, 6, 23, and 24.

In conclusion, it has been established that for all of these halopropanes, the near-staggered GG conformer with nearly parallel C₁-X and C₃-H bonds are more stable than any other conformer in the gas phase.

The extra stability of this type of GG conformation awaits a theoretical explanation, which can hardly be obtained quantitatively by simple molecular mechanics calculations, nor by any straightforward modification of such calculations.

The average torsional force constants for 1,3-dihalopropanes (X = Cl, Br) are 0.17 (Cl) and 0.24 (Br)¹ mdyne Å (rad)⁻², and for 1,2,3-trihalopropanes (X = Cl, Br) the values are 0.25 (Cl)²⁵ and 0.30 (Br)⁶ mdyne Å (rad)⁻². The value 0.17 mdyne Å (rad)⁻², as determined in this work, also is reasonable compared to the larger values for the remaining compounds. The final adjustment of force constants for these compounds ought to take into account the information derived from electron-diffraction data.

REFERENCES

- Farup, P. E. and Stølevik, R. *Acta Chem. Scand. A* 28 (1974) 680.
- Fernholt, L. and Stølevik, R. *Acta Chem. Scand. A* 29 (1975) 651.
- Brown, J. K. and Sheppard, N. *Proc. R. Soc. London A* 231 (1955) 555.
- Dempster, A. B., Price, K. and Sheppard, N. *Spectrochim. Acta Part A* 25 (1969) 1381.
- Thorbjørnsrud, J., Ellestad, O. H., Klæboe, P. and Torgrimsen, T. *J. Mol. Struct.* 15 (1973) 61.
- Stølevik, R. *Acta Chem. Scand. A* 28 (1974) 299.
- Abraham, R. J. and Parry, K. J. *J. Chem. Soc. B* (1970) 539.
- Radcliffe, K. and Wood, J. L. *Trans. Faraday Soc.* 62 (1966) 1678.
- Schachtschneider, J. H. and Snyder, R. G. *Vibrational Analyses of Polyatomic Molecules, IV*. Project No. 31450, Technical Report No. 122-63 of Shell Development Company.
- Snyder, R. G. *J. Mol. Spectrosc.* 28 (1960) 273.
- Gwinn, W. D. *J. Chem. Phys.* 55 (1971) 477.
- Thorbjørnsrud, J., Ellestad, O. H., Klæboe, P. and Torgrimsen, T. *J. Mol. Struct.* 15 (1973) 61.
- Stølevik, R., Seip, H. M. and Cyvin, S. J. *Chem. Phys. Lett.* 15 (1972) 263.
- Zeil, W., Haase, J. and Wegmann, L. *Z. Instrumentenk.* 74 (1966) 84.
- Bastiansen, O., Graber, R. and Wegmann, L. *Balzer's High Vacuum Report* 25 (1969) 1.
- Andersen, B., Seip, H. M., Strand, T. G. and Stølevik, R. *Acta Chem. Scand.* 23 (1969) 3224.
- Peacher, J. and Willis, J. C. *J. Chem. Phys.* 46 (1967) 4809.
- Strand, T. G. and Bonham, R. A. *J. Chem. Phys.* 40 (1964) 1668.
- Morino, Y., Kuchitsu, K. and Oka, T. *J. Chem. Phys.* 36 (1962) 1108.
- Kuchitsu, K. *J. Chem. Phys.* 49 (1968) 4456.
- Fernholt, L. and Stølevik, R. *Acta Chem. Scand. A* 28 (1974) 935.
- Seip, H. M. and Stølevik, R. In Cyvin, S. J., Ed., *Molecular Structures and Vibrations*, Elsevier, Amsterdam 1972.
- Farup, P. E. and Stølevik, R. *Acta Chem. Scand. A* 28 (1974) 871.
- Stølevik, R. *Acta Chem. Scand. A* 28 (1974) 455.

Received March 10, 1976.