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Conformational Analysis. III. The Molecular Structure, Torsional Oscillations, and Conformational Equilibria of Gaseous $(CH_2Cl)_2C(CH_3)_2$, 1,3-Dichloro-2,2-dimethylpropane, as Determined by Electron Diffraction and Compared with Semiempirical Calculations

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Gaseous $(CH_2Cl)_2C(CH_3)_2$ has been studied by electron diffraction at a nozzle temperature of 60 °C. Three spectroscopically distinguishable conformers *GG*, *AG*, and *AA* (see Fig. 1) were detected. Results are presented with error limits (2σ). The following values for distances (r_a) and bond angles ($\angle\alpha$) are appropriate for the structure of all three conformers: $r(C-H) = 1.101(8)$ Å, $r(C-C) = 1.531(4)$ Å, $r(C-Cl) = 1.792(4)$ Å, $\angle CCCl = 114.3°(0.4)$, $\angle CCH = 109.1°(0.8)$. A tetrahedral carbon-atom framework was assumed. Non-bonded distances were computed as dependent quantities under the constraints of geometrically consistent r_α parameters.

By symmetry, *AA* has a staggered conformation. The conformations of *AG* and *GG* have torsion angles close to staggered values, but the deviations determined are not statistically significant.

The relative amounts of the conformers have been determined, and the composition at 60 °C is: 56 % (*4*) of *GG*, 37 % (*6*) of *AG*, and 7 % (*6*) of *AA*. The conformer with two parallel C—Cl bonds, *GG(1:3)*, is not present in detectable amounts.

Conformational energies have been estimated from the experimental composition. *AG* and *AA* have approximately equal *minimum* energy, while *GG* has about 1.6(±0.6) kcal/mol lower *minimum* energy. The difference in zero-pcint vibrational energy between *GG* and *AG*, due to unequal torsional force constants, may well as large as 1 kcal/mol, in favour of *AG*.

Valence force constants, corresponding to torsion of the $-CH_2Cl$ groups, have been estimated by combining information from electron diffraction and vibrational spectroscopy. Fundamental vibrational frequencies, which approximately correspond to torsional oscillations of the $-CH_2Cl$ groups, are expected in the range $80-170$ cm^{-1}.

Semiempirical calculations of conformational energies, torsional force constants, and geometries have been carried out. The calculated geometry is confirmed by the experimental findings, while the torsional force constants do not agree with those determined from electron diffraction. The greater stability of conformer *GG* is not predicted by the calculations, but no obvious correction in the standard energy parameters seems to be able to improve the theoretical results.

The *semi-empirical* energy model corresponds to simple *molecular mechanics caclulations*, involving atom-atom potentials and valence force constants.

I. INTRODUCTION

The present electron-diffraction work is part of a systematic conformational study of halogenated propanes and related molecules. General information [1,2] relevant to this investigation and to the electron-diffraction method [3] is found (reviewed) in Refs. 1, 2, and 3.

Compounds of the type $(CH_2X)_2C(CH_3)_2$ will be referred to as NDX(X = F, Cl, Br, I), and the title compound $(CH_2Cl)_2C(CH_3)_2$ as NDCL. Classically the possible number of staggered conformers in NDX is *nine*, as indicated in Fig. 1. The conformers *6* and *7* are *enantiomers* and thereby physically distinguishable, but neither spectroscopy nor electron diffraction can distin-

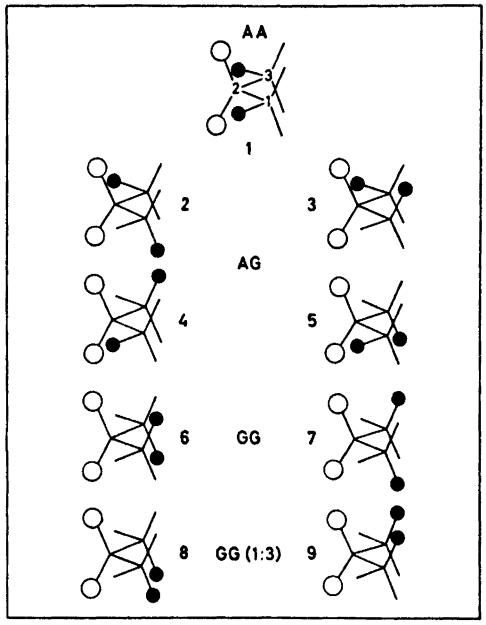

Fig. 1. Staggered conformers of 1,3-dihalo-2,2-dimethylpropane.

Table 1. Characterization of the four spectroscopically distinguishable staggered conformers of 1,3-dihalo-2,2-dimethylpropane. Classically there are *nine* possible staggered conformers. *Six* of the conformers are distinguishable, but only *four* are spectroscopically dinstinguishable (see Fig. 1).

Conformer	Point group	Symmetry number (σ)	M_c	M_d	$2(M_d/\sigma)$
AA	C_{2v}	2	1	1	1
AG	C_1	1	4	2	4
GG	C_2	2	2	2	2
GG(1:3)	C_s	1	2	1	2

guish between them. The conformers *8* and *9* are identical in *all* respects. The conformers *2* and *3* are enantiomers, while *4* and *5* are identical to *2* and *3*, respectively. In conclusion, there are *six* physically different conformers, but only *four* [*AA*, *AG*, *GG*, and *GG(1:3)*] are *spectroscopically* distinguishable, as indicated in Fig. 1 and Table 1.

The spectroscopically distinguishable conformers may be assigned multiplicities in two ways,

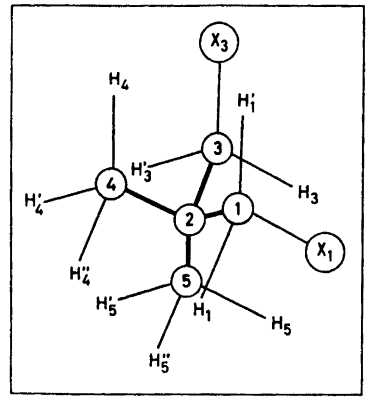

Fig. 2. Numbering of atoms in the conformer *GG*.

as follows: (1) only conformers being distinguishable (*six*) are considered (M_d in Table 1); (2) all classically possible conformers (*nine*) are included (M_c in Table 1). It is noteworthy [4] that $M_c^*/M_c = (M_d^*/M_d)(\sigma^*/\sigma)^{-1}$ for two spectroscopically distinguishable conformers, C and C*, having symmetry numbers σ and σ^*.

The total entropy difference ($\Delta S = S^* - S$) between two spectroscopically distinguishable conformers in the gas phase is:

$$\Delta S_T = \Delta S_T^{vib} + \Delta S^{rot} + \Delta S^{d}$$

ΔS_T^{vib} is the vibrational entropy difference and it is a function of temperature (T). ΔS^{rot} is the rotational entropy difference. If the classical rotational partition functions for the conformers are equal, then $\Delta S^{rot} = R \ln (\sigma^*/\sigma)^{-1}$. The term $\Delta S^{d} = R \ln (M_d^*/M_d)$. Using the relation between M_c, M_d and σ, the sum of ΔS^{rot} and ΔS^{d} is seen to be equal to $R \ln (M_c^*/M_c)$.

There are four X···X distances of different lengths: AA (*anti-anti*), AG (*anti-gauche*), GG (*gauche-gauche*), and GG(1:3) which corresponds to a parallell (1:3)X···X interaction. The symbols A (anti) and G (gauche) thus refer to the plane of the $C_1C_2C_3$ atoms (see Fig. 1).

II. CALCULATION OF CONFORMATIONAL ENERGIES, GEOMETRIES, BARRIERS, AND TORSIONAL FORCE CONSTANTS

The *semi-empirical* energy model corresponds to simple *molecular mechanics calculations*, involving atom-atom potentials and valence force

Table 2. Calculated conformational geometries for 1,3-dichloro-2,2-dimethylpropane. Distances in Å and angles in degrees.

Parameter (normal value)	*AA*	*AG*	*GG*	*GG(1:3)*
C–H(1.094)	1.093	1.094	1.093	1.093
C–C(1.513)	1.534	1.535	1.534	1.537
C–X(1.780)	1.789	1.789	1.789	1.791
$C_1C_2C_3$(109.47)[a]	108.0	109.3	110.5	109.8
CCX(109.47)	113.7	113.3	113.6	116.8
CCH(109.47)	110.2	110.1	110.1	109.8
$\phi_{1-2}(-CH_2X)$[b]	0	+117.4	+121.4	−106.9
$\phi_{3-2}(-CH_2X)$	0	+2.3	+121.4	+106.9
$\phi_{4-2}(-CH_3)$	0	+6.8	−6.7	0
$\phi_{5-2}(-CH_3)$	0	−11.4	−6.7	0

[a] In minimizing the energy, the geometry was constrained in the way described in sect. V-A, except for the torsion angles being adjusted as independent variables. Moreover, the CCC angles were adjusted too. The C-atom framework possesses D_{2d} symmetry with $\angle C_1C_2C_3 = \angle C_4C_2C_5$. [b] $\phi_0 = 60°$ in the expression $V_\phi = \frac{1}{2}V_0\sum_k[1+\cos(3\phi_{k-2}-\phi_0)]$ with $k = 1, 3, 4, 5$,

Table 3. Conformational energies (kcal/mol) for 1,3-dichloro-2,2-dimethylpropane. Details about the energy expression are found in Ref. 5.

Type of energy	*AA*	*AG*	*GG*	*GG(1:3)*
E (bonded)	2.14	2.06	2.13	4.64
E (van der Waals)	4.12	3.78	3.75	4.71
E (polar, Cl···H)	−11.59	−11.46	−11.17	−10.80
E (polar, Cl···Cl)	1.41	1.62	2.01	2.39
E (total)	−3.92	−4.00	−3.28	0.94
E (total) − E (total)$_{AG}$ = ΔE^m	0.08	0.00	0.72	4.94

constants, as described in Ref. 5. Energy parameters (V_0, a, b, c, d) were taken from the work of Abraham and Parry,[6] and diagonal valence force constants from Table 6 were used. "Normal" values [5] of the geometry parameters are given in Table 2.

The conformational geometries derived from the semi-empirical energy model are presented in Table 2. It is noteworthy that, except for *GG(1:3)*, the torsion angles of $-CH_2X$ groups are very nearly staggered for all conformers. Moreover, the deviations from a tetrahedral carbon framework are quite small in all conformers.

The conformational energies are found in Table 3. Contrary to the experimental findings, the conformers *AG* and *AA* are more stable than the conformer *GG*. The conformer [*GG(1:3)*] with two C–X bonds parallel has torsion angles displaced from staggered values. The energy of that conformer is thereby considerably lowered. However, the energy is nearly 5 kcal/mol higher than the energies for *AG* and *AA*.

Considering the conformers *GG*, *AG*, and *AA*, the conformational energy differences (ΔE^m) are largely determined by non-bonded (1:3) interactions. All three conformers (being nearly staggered) have non-bonded (1:2) distances (X···C and C···H) with equal multiplicities and almost equal lengths. The dominant (1:3) contributions are the polar X···H and X···X interactions.

Table 4. Conformational energy minima and torsional barriers in 1,3-dichloro-2,2-dimethylpropane (kcal/mol). Details about the conformational minima corresponding to the stable conformers *AA*, *AG*, *GG*, and *GG(1:3)* are found in Tables 2 and 3. See also explanations given in the text.

ϕ_{2-3}(°) \ ϕ_{1-2}(°)	0	60	120	180
180	6.33[s]	19.22[m]	9.93[s]	(∞)
120	0.00(AG)	6.53[s]	0.72(GG)	9.93[s]
60	6.12[s]	12.85[m]	6.53[s]	19.22[m]
0	0.08(AA)	6.12[s]	0.00(AG)	6.33[s]
−60	6.12[s]	13.14[m]	7.03[s]	19.22[m]
−120	0.00(AG)	7.03[s]	4.94[GG(1:3)]	9.93[s]
−180	6.33[s]	19.22[m]	9.93[s]	(∞)

[m] Corresponding to maximum. [s] Corresponding to "saddle-point".

In Table 4 are shown the conformational energy minima and torsional barriers between the conformers. Each energy value has been obtained by adjusting *all* geometry variables except for values of ϕ_{1-2} and ϕ_{3-2} being $\pm 60°$ and $\pm 180°$. (The latter values of ϕ_{1-2} and ϕ_{3-2} correspond to $-CH_2X$ groups *eclipsing* the C-atom framework.) The actual values of the geometry variables are not shown in Table 4; however, the values of ϕ_{1-2} and ϕ_{3-2} are approximately those in parenthesis (see also Table 2).

Table 5. Calculated torsional force constants for 1,3-dichloro-2,2-dimethylpropane.

(mdyn Å(rad)$^{-2}$)	*AA*	*AG*	*GG*
F ($-CH_2X$)	0.247[a]	0.22 − 4[b]	0.272[c]
F($-CH_3$)	0.135[d]	0.14 − 5[e]	0.130[f]
$-F_{\phi\phi'}$($-CH_2X$/ $-CH_2X$)[g]	0.011	0.062	0.096
$-F_{\phi\phi'}$($-CH_2X$/ $-CH_3$)[g]	0.062	0.01 − 6	0.01 − 6
$-F_{\phi\phi'}$($-CH_3$/ $-CH_3$)[g]	0.010	0.009	0.006

[a] $F_\phi(1-2)=F_\phi(3-2)$, [b] $F_\phi(1-2)\neq F_\phi(3-2)$, [c] $F_\phi(1-2)=F_\phi(3-2)$ [d] $F_\phi(4-2)=F_\phi(5-2)$, [e] $F_\phi(4-2)\neq F_\phi(5-2)$, [f] $F_\phi(4-2)=F_\phi(5-2)$ [g] All interaction force constants $F_{\phi\phi'}$ are negative. The ranges of force constants are indicated.

Torsional force constants may be numerically computed from the semiempirical energy model. The general expression for a quadratic force constant is:

$F_{qq'}=\partial^2 E/\partial q\partial q'$ (q: internal coordinate)

Torsional force constants are given in Table 5.

III. CALCULATION OF VIBRATIONAL QUANTITIES

Valence force constants, except for the torsional part, were taken from works of Schachtschneider [7] and Snyder.[8] The final force constant values used are shown in Table 6.

The normal-coordinate program described by Gwinn [9] was used in computing vibrational frequencies.

Mean amplitudes of vibration were computed as described in Ref. 10. In Table 7 are given u and K values for internuclear distances. Some of these quantities are quite sensitive to the values of torsional force constants, which have been adjusted to fit the experimental intensities, as described in sect. V-B. In Table 8 are shown some u values corresponding to different values of the torsional force constant $F_\phi(-CH_2X)$.

If the torsional force constants estimated from the electron-diffraction data are used, then the torsional oscillations of the $-CH_2X$ groups correspond to vibrational frequencies in the range 80 − 170 cm^{-1}.

IV. EXPERIMENTAL AND DATA REDUCTION

The compound was bought from "K & K" Laboratories. The purity of the sample was better than 97 %.

Electron-diffraction photographs were made at a nozzle temperature of 60°C in the Balzer [11] apparatus [12] under conditions summarized below.

Nozzle-to-plate distance (mm)	500.00	250.00
Electron wavelength (Å)	0.05843	0.05854
Number of plates:	4	5
Range of data, in s (Å^{-1})	1.25 − 15.25	2.25 − 30.50
Data interval, Δs (Å^{-1})	0.125	0.250
Estimated uncertainty in s-scale (%)	0.14	0.14

Table 6. Valence force constants for 1,3-dichloro-2,2-dimethylpropane.

Stretch (mdyn/Å)		Bend (mdyn Å/(rad)²)	
C–H(CH_2X)	4.850	CCH(CH_2X)	0.677
C–H(CH_3)	4.700	CCH(CH_3)	0.640
C–X	3.140	HCH(CH_2X)	0.412
C–C	4.534	HCH(CH_3)	0.500
		HCX	0.860
		CCC	1.086
		CCX	0.980

Stretch/Stretch (mdyn/Å)
C common: C–H/C–C = 0.73, C–C/C–C = 0.101, C–H/C–H = 0.059(CH_2X), C–H/C–H = 0.039(CH_3)

Stretch/Bend (mdyn/rad)
C–C common: C–C/CCC = 0.417, C–C/CCX = 0.075, C–C/CCH = 0.26
C–X common: C–X/HCX = 0.33, C–X/CCX = 0.55

Bend/Bend (mdyn Å/(rad)²); (combination of two angles with C atom common)
HCX/HCX(C–X common) = 0.161, HCC/HCX(C–H common) = 0.089, C–C common: HCC/HCC(CH_2X) = −0.014, HCC/HCC(CH_3) = −0.017; HCC/HCX (C common) = 0.030

Bend/Bend (combination of two angles with C–C common and dihedral angle *anti* or *gauche*)
anti: CCC/CCX = 0.046, HCC/CCC = 0.072
gauche: CCC/CCX = −0.024, HCC/HCC = −0.058

Torsion (mdyn Å/(rad)²)[a]
$F_\phi(-CH_2X)$ = 0.630 and $F_\phi(-CH_3)^b$ = 0.315

[a] The torsional force constants have been defined in the following way: each fragment C–C–C–A (A = H or Cl, see Fig. 2) in a —C(—)—CH_2Cl group has been assigned an equal torsional force constant $f_\phi(-CH_2X)$, while each fragment C–C–C–H in a —C(—)—CH_3 group has been assigned an equal torsional force constant $f_\phi(-CH_3)$. The total force constant for the torsion coordinate ϕ_{i-2} (i = 1, 3) is thus $F_\phi(i-2) = 9f_\phi(-CH_2X)$ and $F_\phi(j-2) = 9f_\phi(-CH)_3$ for j = 4,5. The input to Gwinn's normal coordinate program [9] demands a separate specification for each torsion fragment.
[b] These values were determined from the electron diffraction data, as described in sect. V-B.

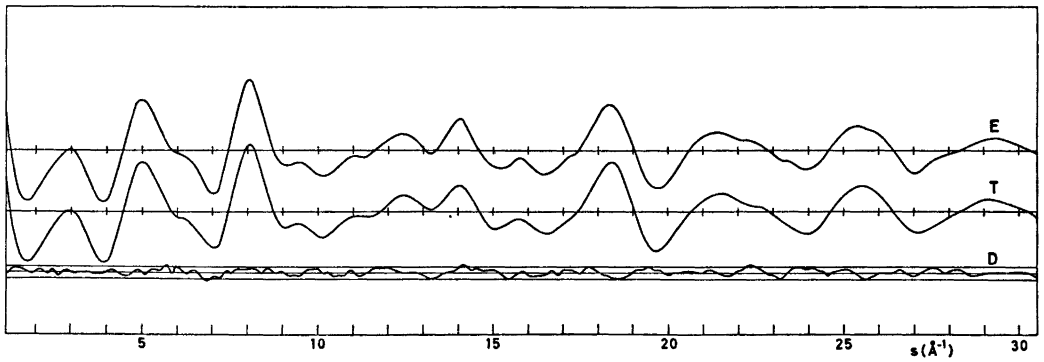

Fig. 3. Intensity curves for 1,3-dichloro-2,2-dimethylpropane at 60°C. Curve E shows the experimental intensity, and curve T the theoretical intensity corresponding to the final least-squares parameters. Curve D is the experimental minus theoretical, and the straight lines the give experimental uncertainty (± 3 × experimental standard deviation).

Table 7. Calculated u- and K-values (Å) in 1,3-dichloro-2,2-dimethylpropane at 60 °C.

Type of distance	Dist. (Å)	u value	K values AA	AG	GG
C – H(in CH_2X)	1.10	0.078	0.0166	0.0170	0.0173
C – H(in CH_3)	1.10	0.079	0.0227	0.0233	0.0234
C – C(C – CH_2X	1.53	0.052	0.0033	0.0032	0.0033
C – C(C – CH_3)	1.53	0.051	0.0041	0.0053	0.0053
$C_1 - X_1$	1.79	0.054	0.0087	0.0080	0.0075
$C_3 - X_3$	1.79	0.054	0.0087	0.0072	0.0075
$C_2 \cdots X$	2.80	0.072	0.0061	0.0043 – 6	0.0044
$C_2 \cdots H$	2.16	0.107 – 9[a]	0.010 – 4	0.011 – 6	0.010 – 6
C···C	2.50	0.071 – 2	0.003 – 4	0.003 – 6	0.003 – 6
X···H	2.36	0.108	0.014 – 5	0.013 – 5	0.013 – 4
H···H	1.80	0.127 – 8	0.020 – 33	0.021 – 32	0.022 – 32
C···X(a)	4.15	0.072	0.0031	0.0020 – 8	0.0029
C···X(g)	3.19	0.131	0.0042 – 9	0.003 – 4	0.003 – 4
C···H(g)	2.73	0.150	0.010 – 1	0.009 – 13	0.008 – 13
C···H(a)	3.46	0.103	0.007 – 11	0.008 – 13	0.007 – 14
X···X	5.59	0.095	0.0002	–	–
X···X	4.95	0.146	–	0.0005	–
X···X	3.96	0.197	–	–	0.0010
X···H(GG)	2.73	0.212 – 9	0.011	0.010 – 2	0.009 – 12
X···H(GG)	3.54	0.19 – 21	0.009	0.007 – 9	0.008
X···H(AG)	4.42	0.152 – 6	0.006	0.005 – 7	0.007
X···H(AG)	4.19	0.154 – 8	0.009	0.007 – 9	0.005 – 8
X···H(AA)	4.96	0.120	–	0.004 – 7	0.007
H···H(AG)	3.74	0.16 – 7	0.011 – 5	0.011 – 8	0.010 – 8
H···H(GG)	3.07	0.19 – 22	0.011 – 6	0.012 – 7	0.011 – 7
H···H(GG)	2.50	0.21 – 3	0.013 – 7	0.014 – 9	0.016 – 9
H···H(AA)	4.30	0.14 – 5	0.012 – 5	0.014 – 8	0.010 – 8

The torsional force constants $F_\phi(-CH_2X) = 0.630$ and $F_\phi(-CH_3) = 0.315$ mdyn Å $(rad)^{-2}$ were used, and the conformational geometries were *staggered*. For definition of F_ϕ, see Table 6.

[a] Range of values: 0.107 – 9 means 0.107 – 0.109.

Table 8. Mean amplitudes of vibration, u (Å), calculated at 60 °C using three different values of $F_\phi(-CH_2X)$.

$F_\phi(-CH_2X)$[a]	0.387[b]	0.630	0.855[c]
X···X(GG)	0.227	0.197	0.182
X···X(AG)	0.154	0.146	0.142
X···X(AA)	0.095	0.095	0.095
X···C(g)	0.139[b]	0.131[b]	0.127[b]

[a] For definition of F_ϕ, see Table 6. [b] Best value for conformer AG. [c] Best value for conformer GG.

The electron wavelength was determined by calibration against ZnO, and corrected by an experiment with CO_2 giving a correction of +0.1 % in the s-scale. The data were reduced 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 final experimental intensity curve is shown in Fig. 3. The intensities have been modified by $s/|f_C'||f_{Cl}'|$.

The scattering amplitudes were calculated by the partial wave method [14] using Hartree-Fock atomic potentials.[15]

The radial distribution curve obtained by Fourier transformation [13] of the final experimental intensity is presented in Fig. 4.

V. STRUCTURE ANALYSIS AND REFINEMENTS

The semiempirically calculated conformational energies (see sect. II) suggest that the conformer *GG(1:3)* is not present in detectable amounts at 60 °C. From the experimental RD curve (Fig. 4) it was easily concluded that the conformers AA, AG, and GG are present in

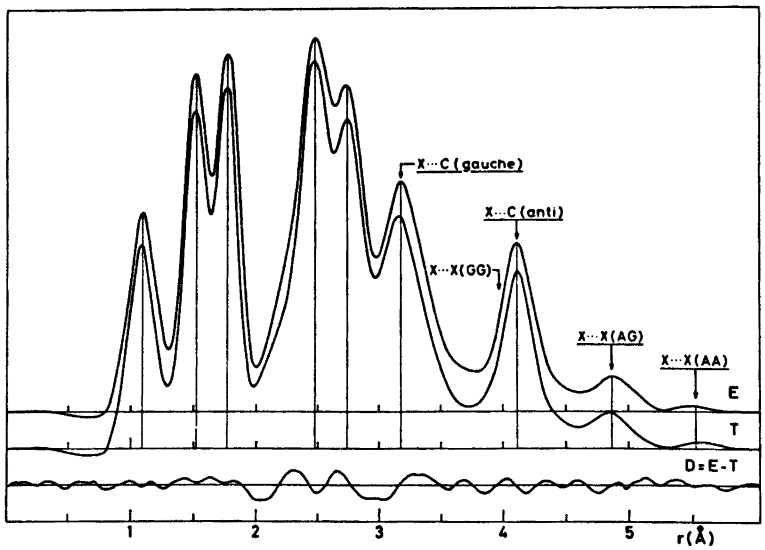

Fig. 4. Radial distribution curves for 1,3-dichloro-2,2-dimethylpropane at 60 °C. Experimental (E) and theoretical (T) radial distribution curves and difference curve (D). The RD curves were calculated from the intensity curves of Fig. 3 with an artificial damping constant 0.0020 Å².

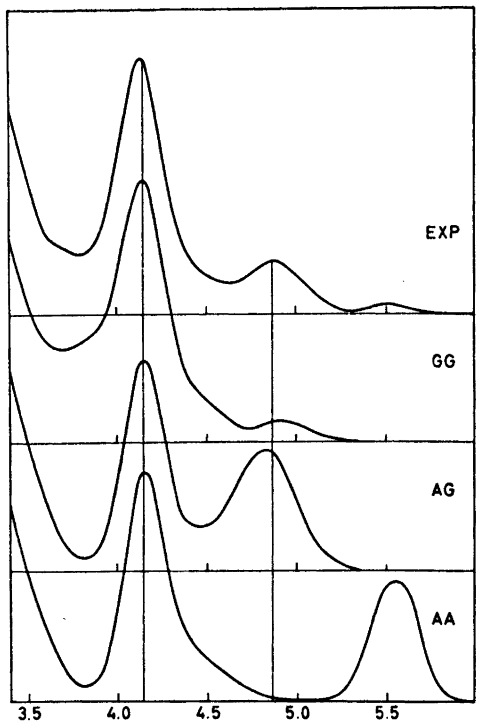

Fig. 5. Theoretical radial distribution curves for the conformers of 1,3-dichloro-2,2-dimethylpropane, and the experimental curve at 60°C. The artificial damping constant was 0.0020 Å².

detectable amounts, and *approximate* composition parameters were estimated. [α(GG) $\simeq$ 60 %, α(AG) $\simeq$ 40 %, and α(AA) < 10 %]. RD curves for the individual conformers are shown in Fig. 5.

A. Least-squares refinements. The least-squares program was written by H. M. Seip, and it is a modified version of the program explained in Ref. 13. Several conformers may be included in the refinements with the present version of the program.

Models for the conformers were constructed with the following geometrical assumptions: (1) the carbon atoms have a tetrahedral arrangement; (2) the two C–CH_2X groups are equal; (3) the two C–CH_3 groups are equal; (4) the C–CH_3 groups possess C_{3v} symmetry; (5) each C–CH_2X group possesses C_s symmetry and the projection of $\angle$HCH′ on a plane perpendicular to C–C is 120°; (6) the C–H bonds are equal; (7) $\angle$CCH in C–CH_2X and C–CH_3 are equal; (8) the conformers have identical structures except for the C–C torsion angles: ϕ_{1-2}, ϕ_{3-2}, ϕ_{4-2}, and ϕ_{5-2}.

Models were defined in terms of the following average parameters: C–H, C–C, C–X, $\angle$CCX, $\angle$CCH, and the four ϕ angles.

Also adjusted were the composition (%) parameters α(AG) and α(GG), with α(AA) = 100 % – α(AG) – α(GG).

Corrections for the Bastiansen-Morino shrinkage [16] effect on non-bonded distances have been included. Non-bonded distances were computed as dependent parameters, restricted under the constraints of geometrically consistent r_α parameters.[17,18]

In the first part of the structure analysis a number of refinements were carried out, in which selected combinations of parameters were allowed to vary, while others were held constant at plausible values. At some stages the background [13] had to be corrected; however, none of the important conclusions about structure and composition were changed thereby.

B. Determination of torsional force constants. The torsional modes of vibration contribute substantially to the mean amplitudes of several distances in a molecule like NDCl (see Table 8). Therefore, since a reasonable force field is known, except for the torsional part, torsional force constants can be adjusted to fit the electron-diffraction data. Determination of all torsional force constants from electron-diffraction data alone is *not* possible. Therefore, the theoretical values of Table 5 were used as a guide, and the following assumptions were made: (1) all interaction constants $F_{\phi\phi'}=0$; (2) in conformer *GG* $F_\phi(1-2)=F_\phi(3-2)=F_\phi(\mathrm{GG})$; (3) in conformer *AG* $F_\phi(1-2)=F_\phi(3-2)=F_\phi(\mathrm{AG})$; (4) in conformer *AA* $F_\phi(1-2)=F_\phi(3-2)=0.5\ [F_\phi(\mathrm{GG})+F_\phi(\mathrm{AG})]$; (5) for all conformers $F_\phi(4-2)=F_\phi(5-2=0.25\ [F_\phi(\mathrm{GG})+F_\phi(\mathrm{AG})]$. Thus two variables, $F_\phi(\mathrm{GG})$ and $F_\phi(\mathrm{AG})$, are considered for adjustment. The following procedure was used: Firstly, an average torsional force constant $[\bar{F}_\phi=F_\phi(\mathrm{GG})=F_\phi(\mathrm{AG})]$ common to all three conformers was determined. Parallel [10] and perpendicular [10] amplitudes for several values of $\bar{F}_\phi$ were computed and included in the least-squares refinements. The value of $\bar{F}_\phi$ which lead to minimum in the error sum (**V'PV**) was obtained for $\bar{F}_\phi=0.63$ mdyn Å (rad)$^{-2}$. The discrepancies between theoretical and experimental RD curves indicated that the torsional force constant $F_\phi(\mathrm{GG})$ is greater than $F_\phi(\mathrm{AG})$. The combination of force constants that lead to a minimum in the error sum (**V'PV**) was determined by a systematic iteration procedure, and the best fit was obtained with $F_\phi(\mathrm{GG})=0.855$ and $F_\phi(\mathrm{AG})=0.387$ mdyn Å (rad)$^{-2}$. The new value of **V'PV** is only 0.4 % less than the value obtained with $F_\phi(\mathrm{GG})=F_\phi(\mathrm{AG})=\bar{F}_\phi$.

Although the values of the individual, parameters $F_\phi(\mathrm{GG})$ and $F_\phi(\mathrm{AG})$ are very uncertain, the average parameter $\bar{F}_\phi$ is determined with less uncertainty. Keeping in mind the assumptions involved, the most probable parameter values [mdynÅ(rad)$^{-2}$] are as follows:

$F_\phi(\mathrm{GG})$ in the range $0.86-0.63$ ($\bar{F}_\phi=0.63$)
$F_\phi(\mathrm{AG})$ in the range $0.63-0.39$ ($\bar{F}_\phi=0.63$)
$F_\phi(-\mathrm{CH_3})\simeq 0.32$ (for all conformers)

The average value of $F_\phi(-\mathrm{CH_2X})$ is not significantly different from the one (0.62) determined for $(\mathrm{CH_2Cl})_4\mathrm{C}$.[19] For both molecules, it seems that the torsional force constants of the detectable conformers have quite different values; a conclusion not predicted by the results of semi-empirical calculations (Sect. II). In adjusting the F_ϕ parameters one has to refine all relevant geometry parameters simultaneously. If that is not done, the F_ϕ values may be quite biased. Moreover, the adjustments ought to be carried out after a reasonable background has been established. Finally, one should keep in mind that systematic errors in the remainder (sect. III) of the force field may be present.

VI. FINAL RESULTS

Results from the least-squares refinements and standard deviations (σ) corrected for correlation in the experimental data [20] are given. All intensities were given equal weights in the final refinements, using a diagonal weight matrix.

Non-bonded distances were restricted under the geometrical constraint of r_α parameters, by including correction terms $D=r_\alpha-r_a$ ($D=(u^2/r)-K$) for all distances. Calculated u and K values, corresponding to the final torsional force constant, are shown in Table 7.

The structure and composition parameters are given in Table 9.

The theoretical values for $\angle \mathrm{C_1C_2C_3}$ in Table 2 suggest that deviation from a tetrahedral arrangement of C atoms is small. Therefore the C atoms were assigned a tetrahedral framework in all refinements.

Torsion angles of the conformers *GG* and *AG* were confined (see also Table 2) as follows: $\phi_{1-2}=\phi_{3-2}=120°+\Delta\phi$ and $\phi_{4-2}=\phi_{5-2}=-5(\Delta\phi)$ *in the conformer GG*; $\phi_{1-2}=120°-\Delta\phi$, $\phi_{3-2}=\Delta\phi$, $\phi_{4-2}=5(\Delta\phi)$, and $\phi_{5-2}=-8(\Delta\phi)$ *in the conformer AG*. ($\Delta\phi=0°$ corresponds to both *GG* and *AG*

Table 9. Structure and composition parameters for 1,3-dichloro-2,2-dimethylpropane at 60 °C. Standard deviations are given in parentheses.

Bond[a] lengths (Å)	Bond[b] angles ∠α(°)	Composition parameters (%)
r_a(C−H) = 1.101(4)	∠CCCl = 114.3(0.2)	α(GG) = 56(2)
r_a(C−C) = 1.531(2)	∠CCH = 109.1(0.4)	α(AG) = 37(3)
r_a(C−Cl) = 1.792(2)	∠CCC = (109.47)[c]	α(AA) = 7(3)[d]

[a] An experiment with CO_2 gave a correction of 0.1 % in the s-scale. The bond lengths are therefore 0.1 % longer than those directly determined by least-squares refinements. The uncertainty (0.14 %) in the s-scale has been included in the standard deviations for bond distances. [b] The bond angles are those of the self-consistent r_α structure. Dependent angles are ∠HCH = 109.9° (σ = 0.5°) and ∠HCCl = 107.2° (σ = 0.3°). [c] Tetrahedral arrangement of C-atoms was assumed. [d] The parameters α(GG) and α(AG) were refined with α(AA) = 100 % − α(GG) − α(AG) and α[GG(1:3)] = 0 %.

Table 10. Mean amplitudes (u) of vibration for 1,3-dichloro-2,2-dimethylpropane at 60 °C.

Type of distance	Dist. (Å)	Calculated[a] u value (Å)	Refined u value (Å)	Standard deviation (σ)
C−H	(1.10)	0.078 − 9	0.075	0.004
C−C	(1.53)	0.051 − 2	0.055	0.003
C−X	(1.79)	0.054	0.052	0.003
C_2···X	(2.79)	0.072	(0.072)[c]	−
C···C	(2.50)	0.071 − 2	0.074	0.004
X···C(a)	(4.13)	0.072	0.077	0.003
X···C(g)	(3.17)	0.131	0.127	0.003
X···X(AA)	(5.57)	0.095	(0.095)[c]	−
X···X(AG)	(4.82)	0.146(0.154)[b]	0.154	0.017
X···X(GG)	(3.93)	0.197(0.182)[b]	0.213	0.019

[a] Calculated with $\bar{F}_\phi$ = 0.63 mdyn Å (rad)$^{-2}$, see also Table 7. [b] Values in parentheses calculated with F_ϕ(GG) = 0.855 and F_ϕ(AG) = 0.387, see also Table 8 for details. [c] Not refined; calculated values were used.

being *staggered*.) The parameter $\Delta\phi$ was refined, including as many as possible of the remaining least-squares parameters simultaneously. The values of the parameter $\Delta\phi$ were always found to be less than 1° (σ = 2°), indicating nearly staggered conformations for *GG* and *AG*. The same conclusion was reached by the semiempirical calculations. (Table 2)

Several mean amplitudes (u values) of vibration have been refined. In Table 10 their values are compared to those computed (sect. III). Both sets of u values are *experimental*, but the calculated values combine information from spectroscopy as well as from electron diffraction. The average deviation between the two sets of u values is less than 6 %, while the average relative, $\langle\sigma/u\rangle$, uncertainty of the refined u values is 6.5 %. In calculating the average deviation between the sets, only u values that have been refined were considered. The large number of mean amplitudes corresponding to non-bonded X···H and C···H distances could not be refined, but their values fit the experimental data well. It is thereby shown that *calculated* u values are reliable for NDCl. Since the u values are reliable, then it is likely that the calculated K values are reliable to the same extent.

Cartesian coordinates for the conformers *GG* and *AG* and principal axes' moments of inertia for the conformers *GG*, *AG*, and *AA* are found in Table 11.

Table 11. Cartesian coordinates (Å) for conformers of 1,3-dichloro-2,2-dimethylpropane (see Fig. 2). The coordinates have been calculated for staggered conformations, using the final structure parameters in Table 9 (r_a and $\angle\alpha$ values). The number of atoms in the conformer *GG* is shown in Fig. 2. The principal axes' moments of inertia are (amuÅ²):
$I_A = 251.58$, $I_B = 384.86$, and $I_C = 524.08$ *for conformer GG.*
$I_A = 182.08$, $I_B = 521.05$, and $I_C = 590.58$ *for conformer AG.*
$I_A = 112.53$, $I_B = 657.14$, and $I_C = 657.24$ *for conformer AA.*

Conformer GG[a] (corresponding to No. 7 in Fig. 1)				Conformer AG[a] (corresponding to No. 2 in Fig. 1)			
	x	*y*	*z*		*x*	*y*	*z*
C_1	0	0	0	C_1	0	0	0
C_2	1.2500	0.8839	0	C_2	1.2500	0.8839	0
X_1	1.3800	1.9762	−1.4147	X_1	1.3800	1.9762	−1.4147
H_1	2.1447	0.2422	0	H_1	2.1447	0.2422	0
H_1'	1.2435	1.5165	0.9011	H_1'	1.2435	1.5165	0.9011
C_3	−1.2500	0.8839	0	C_3	−1.2500	0.8839	0
X_3	−1.3800	1.9762	1.4147	X_3	−2.7947	−0.0244	0
H_3'	−2.1447	0.2422	0	H_3	−1.2435	1.5165	0.9011
H_3	−1.2435	1.5165	−0.9011	H_3'	−1.2435	1.5165	−0.9011
C_4	0	−0.8839	1.2500	C_4	0	−0.8839	1.2500
H_4	0	−0.2422	2.1447	H_4	0	−0.2422	2.1447
H_4''	0.9011	−1.5165	1.2435	H_4''	0.9011	−1.5165	1.2435
H_4'	−0.9011	−1.5165	1.2435	H_4'	−0.9011	−1.5165	1.2435
C_5	0	−0.8839	−1.2500	C_5	0	−0.8839	−1.2500
H_5	0	−0.2422	−2.1447	H_5	0	−0.2422	−2.1447
H_5'	−0.9011	−1.5165	−1.2435	H_5'	−0.9011	−1.5165	−1.2435
H_5''	+0.9011	−1.5165	−1.2435	H_5''	+0.9011	−1.5165	−1.2435

VII. DISCUSSION

Following standard statistical thermodynamics,[21,22] the percentages α^* and α of two conformers (C⇌C*) in equilibrium in the gas phase,[3] are related to the theoretical expression for the equilibrium constant, as given in eqn. (1):

$$\alpha^*/\alpha = (M_c^*/M_c)(Q^*/Q)^{vib} \exp(-\Delta E^m/RT) \quad (1)$$

(The *classical* rotational partition functions for the conformers are approximately equal.) Q^{vib} is the vibrational partition function of a conformer referred to the potential energy *minimum* of that conformer. $\Delta E^m = E^* - E$ is the potential-energy difference between the conformers, and the difference is measured between potential energy minima. The zero-point vibrational energy is thus included in the vibrational partition functions. R and T have their usual thermodynamic meanings, and M_c (Table 1) is the multiplicity of a conformer.

If the vibrational partition functions for the conformers are known, then the quantity ΔE^m may be estimated from eqn. (1). The ratios between the partition functions depend on the differences in force fields between the conformers.[19] Calculations of ΔE^m using two different sets of *torsional* force constants are summarized in Table 12. Both sets of results are equally probable as pointed out in sect. V-B. An approximate estimate of ΔE^m(GG − AG) is therefore -1.6 ± 0.6 kcal/mol.

If the value of ΔE^m (GG − AG) computed from the semiempirical energy model (+0.72 kcal/mol) is accepted, then the quantity q (Table 12) has to be 8.6 according to eqn. (1). Such a large value of q is possible, but only if some of the force constants of the conformer *GG* are much *smaller* than those of *AG*. The torsional force constants of the two conformers could well be different, but the experimental evidence of sect. V-B indicates a difference, if any significant difference at all, in the opposite direction.

Assuming equal vibrational partition functions for the conformers *AA* and *AG*, the quantity ΔE^m(AA − AG) is +0.2 kcal/mol, in agreement with the theoretical estimate (Table 3) of +0.08 kcal/mol.

Thus, the semi-empirical calculations correctly predict the energy difference between the

Table 12. Energy difference (ΔE^m) between the conformers GG and AG of 1,3-dichloro-2,2-dimethylpropane.

	I	II
$F_\phi(-CH_2X)^a$ in GG	0.630 mdyn Å (rad)$^{-2}$	0.855 mdyn Å (rad)$^{-2}$
$F_\phi(-CH_2X)^a$ in AG	0.630 ,, ,,	0.387 ,, ,,
$F_\phi(-CH_3)^a$ in AG and GG	0.315 ,, ,,	0.315 ,, ,,
$q=(Q(GG)/Q(AG))_T^{vib}$	1.04[b]	0.40[b]
$\Delta S_T^{vib}=S(GG)^{vib}-S(AG)^{vib}$	0.00[c] e.u.	−1.54[c] e.u.
$\Delta E^m=E(GG)^m-E(AG)^m$	−1.1[d] kcal/mol	−2.2[d] kcal/mol

[a] F_ϕ: torsional force constant. For definition of F_ϕ see Table 6. [b] $Q(GG)$ and $Q(AG)$: vibrational partition functions referred to the potential energy *minimum* of the conformers.

[c] Calculated according to the standard expression for contribution of entropy associated with vibrational degrees of freedom:

$\Delta S_T^{vib}=R \ln q+RT\, d(\ln q)/dT$.

[d] The force constants in column II lead to a difference (GG−AG) in zero-point vibrational energy of +0.96 kcal/mol. The energy differences were calculated according to eqn. (1) using the experimental equilibrium constant of 1.51.

conformers *AA* and *AG*, but the high conformational energy predicted for *GG* does not agree with the experiment. The conformer *GG(1:3)* has not been experimentally detected, but according to the energy differences in Table 3 that conformer should be present in negligible amounts at 60 °C.

Taking into consideration the symmetry numbers and multiplicities (Table 1) of the conformers, the *total entropy* differences may be expressed as follows:

$$\Delta S(GG-AG)=\Delta S_T^{vib}(GG-AG)-R \ln 2\simeq -2.2\pm 0.8 \text{ cal } K^{-1} \text{ mol}^{-1}$$

$$\Delta S(AA-AG)=\Delta S_T^{vib}(AA-AG)-R \ln 4$$

At present, no estimate of ΔS_T^{vib} (AA−AG) is available, however, the conformer *AA* most probably has a lower entropy than *AG*.

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