Conformational Analysis. II. The Molecular Structure, Torsional Oscillations, and Conformational Equilibria of Gaseous Tetrakis-(chloromethyl)methane, $C(CH_2Cl)_4$, as Determined by Electron Diffraction and Compared with Semiempirical Calculations

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Gaseous $C(CH_2Cl)_4$ has been studied by electron diffraction at a temperature of 105°C. Only two conformers named **D** (with D_{2d} symmetry) and **S** (with S_4 symmetry) were detected, see Fig. 1. The two conformers are present in equal amounts. Results are presented with error limits (2σ). The following values for distances (r_a) and angles $(\angle_\alpha)$ are appropriate for the structure of both conformers: $C-H = 1.127(18)$ Å, $C-C = 1.539(8)$ Å, $C-Cl = 1.792(6)$ Å, $\angle CCX = 113.5°(0.8)$, $\angle CCH = 108.°(2.0)$.

Non-bonded distances were computed as dependent quantities restricted under the constraints of geometrically consistent r_α parameters.

The carbon-atom framework of both conformers shows small, but significant, deviations from a tetrahedral arrangement, in agreement with semiempirical calculations. The torsion angles of conformer **S** are significantly different from exact staggered values; also predicted by the semiempirical calculations.

Torsional force constants and frequencies for both conformers have been determined by combining information from electron diffraction and vibrational spectroscopy.

The conformational energies have been estimated. Conformer **D** has a higher minimum energy than **S**, but the probability of **D** is considerably increased by a lower vibrational energy and a larger vibrational entropy than **S** (see Table 15). Conformers of low symmetry $(C_1, C_2, \text{ and } C_s)$ are not present in detectable amounts, as predicted by the semiempirical calculations, too.

INTRODUCTION

$C(CH_2X)_4(X = F,Cl,Br,I)$ compounds will be referred to in general as TMX and $C(CH_2Cl)_4$

as TMCL. The number of possible staggered conformers in TMX is 81, but only six are spectroscopically distinguishable, as indicated in Table 1. All conformers, except two, have one or more parallel (1:3) $X\cdots X$ interactions. The two exceptions are shown in Fig. 1, and these conformers will be referred to as **D** (possessing D_{2d} symmetry) and **S** (possessing S_4 symmetry), respectively.

The problem of molecular structure and conformational equilibria of $C(CH_2X)_4$ have engaged several chemists since the first investigation appeared in 1932. The idea about conformational equilibria was not available to the first investigators, and the methods of structural chemistry have been further developed since then.[1,2]

In 1932 Wagner et al.[3] carried out the first X-ray investigation on TMX (X = Cl, Br,I) and concluded that the molecules possessed C_{2h} symmetry. De Laszlo[4] in 1934 carried out the first electron-diffraction study on TMX (X = Br,I) and found the X atoms to be in one plane, a finding which is quite close to the arrangement in one of the conformers, the one with D_{2d} symmetry. Hassel et al.,[5] in 1937, using both X-ray and electron-diffraction methods proved that their data were not consistent with C_{2h} symmetry for the molecules (X = Cl,Br,I). Hassel also concluded that no simple arrangement of atoms agreed with their electron-diffraction data, and further, that large internal motion is present in these molecules.

Table 1. Characterisation of the six spectroscopically distinguishable staggered conformers of $C(CH_2X)_4$. The symbols A(*anti*) and G(*gauche*) have been used to characterize $C-X$ bonds (*anti* or *gauche* to the CCC framework) of a $X-CCC-X'$ fragment, while small letters a(*anti*) or g(*gauche*) have been used for $C-X$ bonds (*anti* or *gauche* to the CCC framework) of a $C-C-C-X$ fragment. The type of $X\cdots X$ distance corresponding to a (1:3) $X\cdots X$ *parallel interaction* has been specified as GG(1:3). All staggered conformers possess four $C\cdots X(a)$ and eight $C\cdots X(g)$ distances.

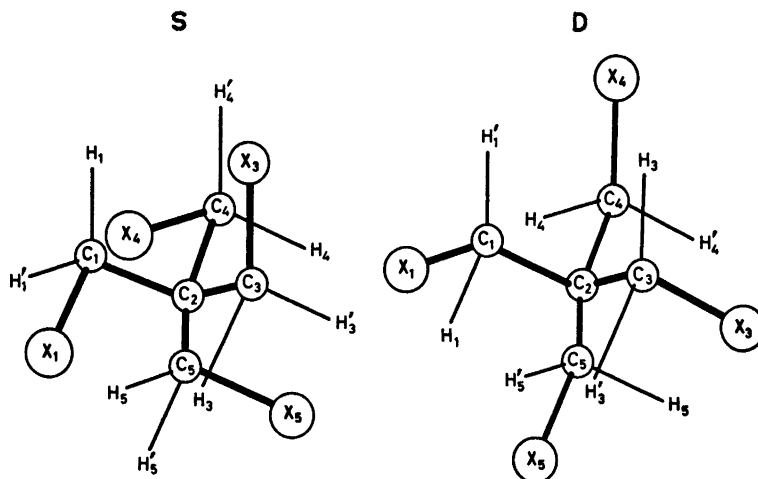| Classical statistical weight	Point group and (symmetry number)	Type of $X\cdots X$ distances			
		GG	AG	AA	GG(1:3)
3	$D_{2d}(4)$	4	0	2	0
24	$C_1(1)$	2	2	1	1
12	$C_2(2)$	1	2	1	2
12	$C_s(1)$	0	2	1	3
24	$C_1(1)$	1	4	0	1
6	$S_4(2)$	2	4	0	0

Fig. 1. Numbering of atoms in the two conformers **D** and **S** of $C(CH_2X)_4$. The conformer **D** has D_{2d} symmetry: three C_2 (mutually perpendicular), one S_4 (coincident with one C_2), two σ_d (through S_4). The **S** conformer has S_4 symmetry: one S_4 coincident with one C_2.

In the period 1939−1966 several investigations took place, including spectroscopic studies [6,8,10] and measurements of dipole moments,[7,8,9] however, the conformational equilibrium was not quantitatively described before the present work.

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

The method of classical mechanics was used. The semiempirical calculations were carried out as described in Ref. 11. Energy parameters were taken from the work of Abraham and Parry,[12] and the valence force constants in Table 5 were used. The "normal" values of the geometry parameters are given in Table 2. In minimizing the energy, the geometry was constrained in the same way as described in sect. V−A, except that all torsion angles were adjusted as independent variables.

The conformational geometries derived from the semiempirical energy model are presented in Table 2. Calculated structure parameters are in reasonable agreement with the corresponding

Table 2. Calculated geometries for conformers of $C(CH_2Cl)_4$.

Type of parameter	"Normal" value	Conformer D	Conformer S
C−H(Å)	1.094	1.093	1.093
C−C (Å)	1.513	1.544	1.543
C−X (Å)	1.780	1.790	1.790
$C_1C_2C_3{}^a$(°)	109.47	106.8	111.7
CCX (°)	109.47	113.7	113.7
CCH (°)	109.47	110.2	110.1
ϕ_{1-2} (°)	$(60)^b$	0.0	126.3
ϕ_{3-2} (°)	$(60)^b$	0.0	126.3
ϕ_{4-2} (°)	$(60)^b$	0.0	−126.3
ϕ_{5-2} (°)	$(60)^b$	0.0	−126.3

^{a} In imimizing the energy, the geometry was constrained in the same way as described in sect. V-A.

^{b} $\phi_0 = 60°$, and $V_\phi = \dfrac{V_0}{2} \sum_k \{1 + \cos[3(\phi_{k-2} - \phi_0)]\}$ with $k = 1,3,4,5$.

Table 3. Calculated conformational energies in $C(CH_2Cl)_4$. In minimizing the energy, the geometry was constrained in the same way as described in sect. V-A.

Type of energy (in kcal/mol)	Conformer D	Conformer S	Difference (D − S)
E (bonded)	4.26	4.06	+0.20
E (van der Waals)	4.90	4.68	+0.22
E (polar: X···H)	−17.20	−17.36	+0.16
E (polar: X···X)	10.75	10.58	+0.17
E (total)	2.71	1.96	+0.75

experimental values of Tables 9−11. The value of ϕ_s, $126.3° − 120° = +6.3°$, for the conformer S has the right sign and magnitude, the experimental value being $+4.1°$. It is also noteworthy that there are no deviations from staggered geometry in the conformer D. Moreover, the deviations from a tetrahedral carbon framework seem significant. The deviation parameters (θ_c) are $−2.7°$ $(106.8 − 109.47°)$ and $+2.2°$ $(111.7 − 109.47°)$ for the conformers D and S, respectively. These values are in excellent agreement with the experimental values $−2.4°$ and $+2.4°$, respectively, (sect. VI).
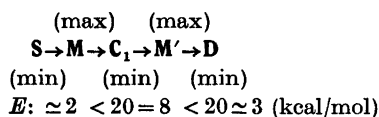
In Table 3 are the results for conformational energies. According to the present energy model, conformer S is 0.75 kcal/mol more stable than conformer D.

The conformers with *one* parallel (1:3) X···X interaction, corresponding to C_1 symmetry in Table 1, have their torsion angles displaced from staggered values. The energy of these conformers is thereby considerably lowered. However, the lowest energy obtained was still more than 5 kcal/mol higher than the value for the conformer D. The calculations also lead to the conclusion that the *eclipsed* conformer of lowest energy is about 5 kcal/mol less stable than conformer D.

Some of the torsional barriers have to be very high, and probably all of them are too high to be detected by electron diffraction. Nevertheless, NMR studies might lead to some information. Therefore, it is of interest to estimate the value of the *lowest* barrier height when a conformation S is changed into D by rotations of −CH_2X groups around the C−C bonds. If high barriers are to be avoided, then conformational minima, corresponding to conformers of low

symmetry (C_1), are always reached before **S** is changed into **D** by rotations around $C-C$ bonds. The conformers **S** and **D** are thus separated by double-maxima as indicated below:

$$\begin{array}{ccc} \text{(max)} & \text{(max)} & \\ \mathbf{S} \to \mathbf{M} \to & \mathbf{C_1} \to \mathbf{M'} \to \mathbf{D} & \\ \text{(min)} & \text{(min)} & \text{(min)} \end{array}$$

E: $\simeq 2 < 20 = 8 < 20 \simeq 3$ (kcal/mol)

Valence force constants may be *numerically* computed from the semiempirical energy model.[11] The general expression for a quadratic force constant is:

$$F_q = \partial^2 E / \partial q^2 \text{ or } F_{qq'} = \partial^2 E / \partial q \partial q'$$

(q: internal coordinate). Torsional force constants (F_ϕ and $F_{\phi\phi'}$) are given in Table 4, together with second order derivatives of the energy under the constraints corresponding approximately to the torsional modes of vibrations.

Table 4. Calculated torsional force constants for conformers of $C(CH_2Cl)_4$.

(mdyn Å (rad)$^{-2}$)	Conformer **D**	Conformer **S**
F_ϕ(diagonal)^a	0.28	0.30
$F_{\phi\phi'}$ (AA)^b	-0.012	$-$
$F_{\phi\phi'}$ (AG)^b	$-$	-0.050
$F_{\phi\phi'}$(GG)^b	-0.087	-0.043
$F(+ + + +)^c$	0.40	1.43
$F(+ + - -)^c$	1.77	0.71
$F(+ - 00)^c$	0.58^d	$-$
$F(+ - + -)^c$	$-$	0.73^d

^{a} $F_\phi(1-2) = F_\phi(3-2) = F_\phi(4-2) = F_\phi(5-2) = F_\phi$.
^{b} in the conformer **D** are two different kinds of $F_{\phi\phi}$ interaction constants (AA and GG) corresponding to XCCCX fragments having their X$\cdots$X distances AA or GG, respectively; in the **S** conformer are constants of type AG as well as GG. ^{c} $F(+ + + +)$, $F(+ + - -)$, $F(+ - 00)$, and $F(+ - + -)$ are second order derivatives of the energy with respect to ϕ, under the constraints of the torsional modes (approximately), as follows:
$(+ + + +)$; $\Delta\phi_{1-2} = \Delta\phi_{3-2} = \Delta\phi_{4-2} = \Delta\phi_{5-2} = \Delta\phi$
$(+ + - -)$; $\Delta\phi_{1-2} = \Delta\phi_{3-2} = \Delta\phi$ and $= \Delta\phi_{4-2} = \Delta\phi_{5-2} = -\Delta\phi$
$(+ - 00)$; $\Delta\phi_{1-2} = \Delta\phi_{3-2} = \Delta\phi$ and $\Delta\phi_{4-2} = \Delta\phi_{5-2} = 0$
$(+ - + -)$; $\Delta\phi_{1-2} = \Delta\phi_{4-2} = \Delta\phi$ and $\Delta\phi_{3-2} = \Delta\phi_{5-2} = -\Delta\phi$
^{d} Degenerate mode belonging to species E.

III. CALCULATION OF VIBRATIONAL QUANTITIES

Valence force constants, except for the torsional part, were taken from the extensive work of Schachtschneider[13] and Snyder.[14] The final force constant values used are shown in Table 5.

The normal coordinate program described by Gwinn[15] was used in computing vibrational frequencies.

Mean amplitudes of vibration corresponding to three different values of the torsional force constants were calculated as described in Ref.[16] In Table 6 are given u and K values[16] for internuclear distances. Some of these quantities are quite sensitive to the values of torsional force constants,[11] which have been adjusted to fit the experimental intensities, as described in sect. V $-$ B.

Several other vibrational quantities in a molecule like TMCL also vary with the torsional force constants. To illustrate this point, some of these quantities have been calculated using different values of the torsional force constants, and the results are found in Table 7 and Table 8.

IV. EXPERIMENTAL AND DATA REDUCTION

The compound was made following the synthesis of Mooradian *et al.*[17] After it was recrystallized from CH_3OH and sublimation of the crystals had been carried out, the compound melted at $96 - 97°C$.

Electron-diffraction photographs were made at a nozzle temperature of 105°C in the Oslo apparatus,[18] under conditions summarized below:

Nozzle-to-plate distance (mm)	480.68	200.63
Electron wavelength (Å)	0.06458	0.06458
Number of plates:	5	5
Range of data, in s(Å^{-1})	$1.375 - 19.875$	$7.50 - 35.25$
Data interval, Δs (Å^{-1})	0.125	0.250
Estimated uncertainty in the s-scale (%)	0.14	0.14

The electron wavelength was determined by calibration against gold, and corrected by an experiment with CO_2 giving a correction of

Table 5. Valence force constants for $C(CH_2Cl)_4$.
The torsional force constants have been defined in the following way: each fragment $A-C-C-C$ ($A=H$, X see Fig. 1) has been assigned an equal torsional force constant. The total force constant for the torsional coordinate ϕ_{i-2} ($i=1,3,4,5$) is thus the sum of *nine* equal contributions, one from each fragment $A-C_i-C_2-C$. The input to Gwinn's normal coordinate program [15] demands a separate specification for each torsional fragment.

Stretch (mdyn/Å)   Bend (mdyn Å $(rad)^{-2}$)

$C-C=4.534$	$HCH=0.460$	$CCX=0.980$
$C-H=4.850$	$HCX=0.860$	$CCC=1.086$
$C-X=3.140$	$CCH=0.677$	

Stretch/Stretch (mdyn $Å^{-1}$)
(C common): $C-C/C-X=0.730$, $C-C/C-C=0.101$, $C-H/C-H=0.059$

Stretch/Bend (mdyn $(rad)^{-1}$)
(C−C common): $C-C/CCC=0.417$, $C-C/CCX=0.075$, $C-C/CCH=0.260$
(C−X common) $C-X/HCX=0.330$, $C-X/CCX=0.550$

Bend/Bend (combination of two angles with the central C atom common, $-$mdyn Å $(rad)^{-2}$)
(C−X common): $HCX/HCX=0.161$, (C−H common): $HCC/HCX=0.089$
(C−C common): $HCC/HCC=-0.014$, (C common): $HCC/HCX=0.030$

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: $CCC/CCX=-0.024$, $HCC/CCC=-0.058$

Torsion (mdyn Å $(rad)^{-2}$), see also sect. V-B
$F_\phi(S)=0.88$; for conformer **S**
$F_\phi(D)=0.36$; for conformer **D**

Table 6. Calculated u and (K) values (Å) for internuclear distances in $C(CH_2Cl)_4$ at 105°C. The valence force field given in Table 5 was used, and staggered conformers with tetrahedral C-atom arrangement were assumed. The torsional force constant (F_ϕ) is defined in Table 5.

Distance type	R (Å)	$F_\phi=0.36$	$F_\phi=0.62$	$F_\phi=0.88$
$C-H$	(1.127)	0.078 (0.0217)	0.078 (0.0185)	0.078 (0.0171)
$C-C$	(1.539)	0.053 (0.0045)	0.052 (0.0040)	0.052 (0.0037)
$C-X$	(1.792)	0.055 (0.0152)	0.055 (0.0114)	0.055 (0.0097)
$C_1 \cdots C_3$	(2.51)	0.075 (0.0041)	0.074 (0.0035)	0.073 (0.0033)
$C_1 \cdots C_4$	(2.51)	0.075 (0.0045)	0.074 (0.0039)	0.073 (0.0036)
$C \cdots X$	(2.78)	0.076 (0.0108)	0.076 (0.0084)	0.076 (0.0073)
$C \cdots H$	(2.16)	0.110 (0.0145)	0.109 (0.0120)	0.109(0.0109)
$X \cdots H$	(2.39)	0.109 (0.0243)	0.109 (0.0182)	0.109 (0.0156)
$H \cdots H$	(1.85)	0.127 (0.0291)	0.126 (0.0237)	0.125 (0.0213)
$X \cdots X(GG)$	(3.90)	0.247 (0.0073)	0.209 (0.0064)	0.189 (0.0060)
$X \cdots X(AG)$	(4.83)	0.165 (0.0069)	0.154 (0.0052)	0.148 (0.0044)
$X \cdots X(AA)$	(5.56)	0.103 (0.0052)	0.103 (0.0037)	0.103 (0.0030)
$C \cdots X(g)$	(3.16)	0.150 (0.0087)	0.139 (0.0066)	0.133 (0.0059)
$C \cdots X(a)$	(4.11)	0.075 (0.0068)	0.075 (0.0052)	0.075 (0.0045)
$X \cdots H(GG)$	(2.69)	0.239 (0.0167)	0.224 (0.0130)	0.216 (0.0115)
$X \cdots H(AG)$	(4.19)	0.170 (0.0111)	0.162 (0.0092)	0.157 (0.0083)
$X \cdots H(AG)$	(4.42)	0.162 (0.0106)	0.157 (0.0082)	0.153 (0.0071)
$X \cdots H(GG)$	(3.53)	0.225 (0.0122)	0.200 (0.0102)	0.185 (0.0093)
$X \cdots H(AA)$	(4.95)	0.124 (0.0100)	0.124 (0.0078)	0.124 (0.0068)
$C \cdots H(g)$	(2.74)	0.157 (0.0109)	0.151 (0.0089)	0.147 (0.0080)
$C \cdots H(a)$	(3.48)	0.105 (0.0107)	0.105 (0.0092)	0.105 (0.0084)

Table 7. Calculated frequencies in the range $60-325$ cm^{-1} for conformers of $C(CH_2Cl)_4$ The torsional force constant (F_ϕ) is defined in Table 5. Frequencies corresponding to torsional oscillations are indicated by (ϕ), and degenerate frequencies (belonging to species E) by d.

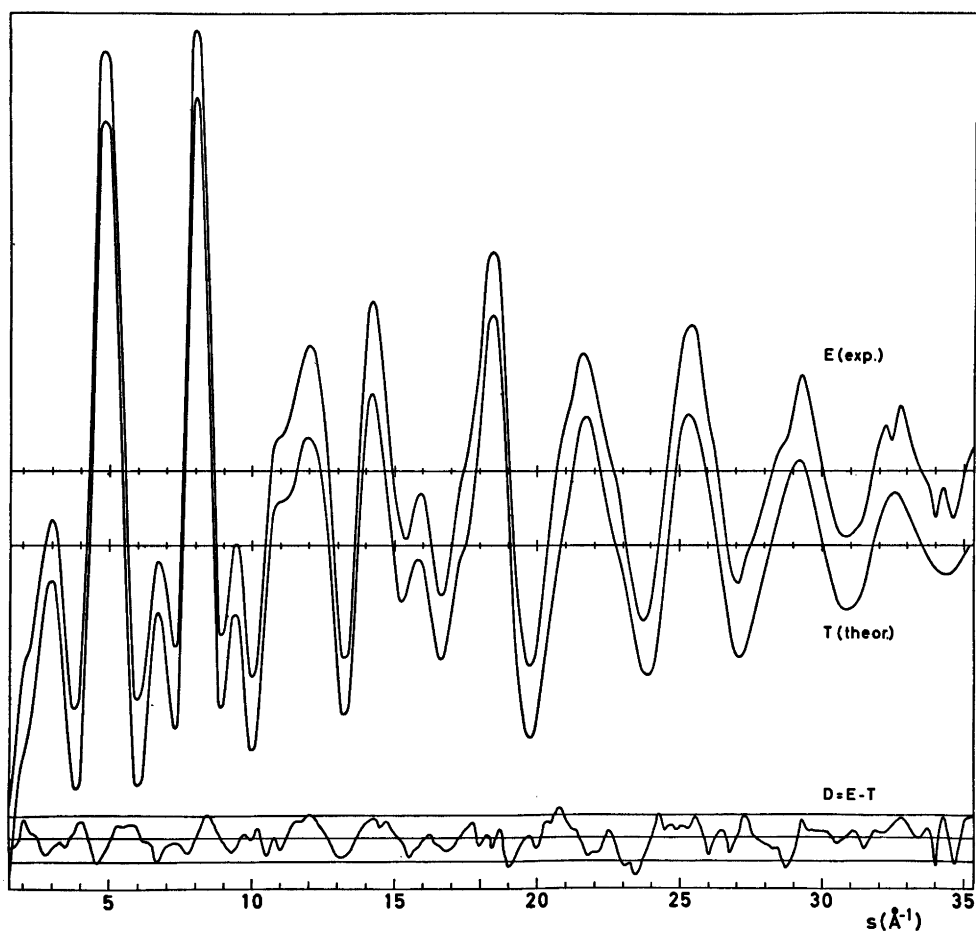| $F_\phi = 0.36$		$F_\phi = 0.62$		$F_\phi = 0.88$	
D	**S**	**D**	**S**	**D**	**S**
66 (ϕ)	67 (ϕ)	79 (ϕ)	82 (ϕ)	88 (ϕ)	91 (ϕ)
82 $(\phi)^d$	80 (ϕ)	89	89	90	91
88	90	100 $(\phi)^d$	90 (ϕ)	112 $(\phi)^d$	110 (ϕ)
151	110 $(\phi)^d$	155	122 $(\phi)^d$	158	129 $(\phi)^d$
217^d	195	229^d	197	240^d	199
236 (ϕ)	220^d	302 (ϕ)	254^d	323 (ϕ)	280^d

Fig. 2. 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 give the experimental uncertainty ($\pm 3 \times$ experimental standard deviation).

Table 8. Ratios between vibrational partition functions for conformers of $C(CH_2Cl)_4$ at 105°C. The ratio is defined as $(Q_D/Q_S)^{vib}$, and Q^{vib} is the vibrational partition function, referred to energy *minimum* for the conformer. The difference in vibrational energy is thus included in these ratios. F_ϕ is the torsional force constant as defined in Table 5. $(Q_D/Q_S)^{vib}$ is also a function of temperature, and the values at 205°C and 305°C are 37.5 and 29.8, respectively, with $F_\phi(S) = 0.88$ and $F_\phi(D) = 0.36$ mdyn Å $(rad)^{-2}$. If $F_\phi(S) = F_\phi(D)$ the ratio does *not* vary with temperature.

$F_\phi(S)$	$F_\phi(D)$	(0.36)	(0.62)	(0.88)
(0.36)		1.046	0.114	0.019
(0.62)		9.55	1.046	0.177
(0.88)		56.5	6.17	1.046

+ 0.10 % in the *s*-scale. The data were reduced in the usual way [19] 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 $s/|f'_{Cl}|^2$. The scattering amplitudes were calculated by the partial wave method [20] using Hartree-Fock atomic potentials.[21]

Contributions to the theoretical intensities from H···H distances, the H atoms bonded to different carbon atoms, were not included.

The radial distribution curve obtained by Fourier transformation of the final experimental intensity is presented in Fig. 3.

V. STRUCTURE ANALYSIS AND REFINEMENTS

The calculated conformational energies suggest that only two spectroscopically distinguishable conformers, **D** and **S**, are present in detectable amounts at 105°C. From the areas under the two peaks (see Fig. 3) corresponding to the distances X···X(AG) and X···X(AA) it was
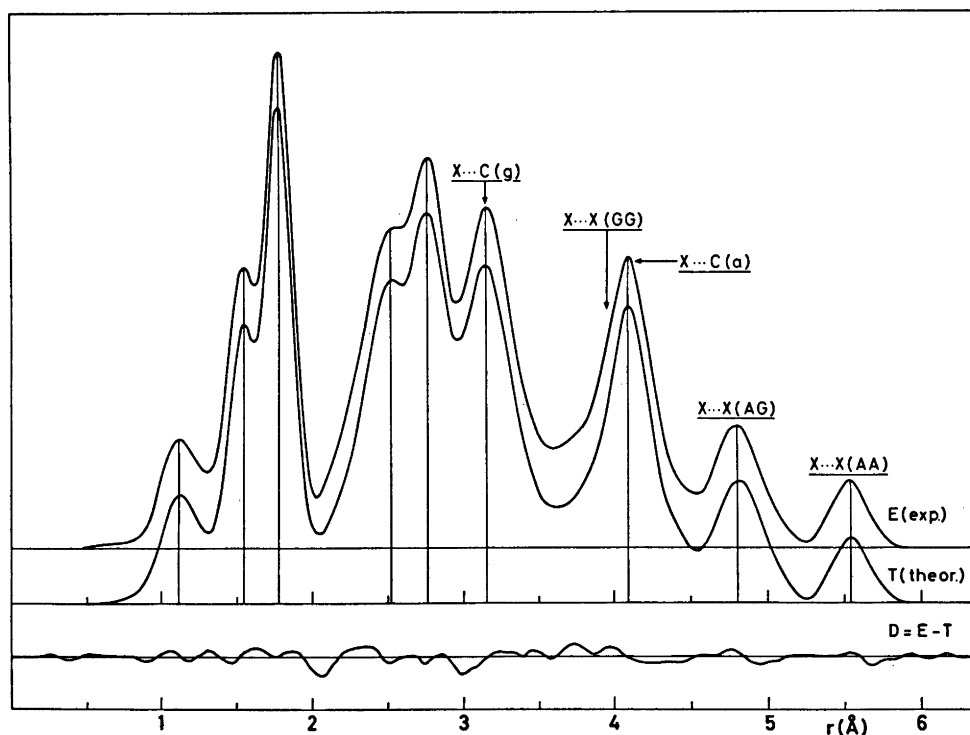

Fig. 3. Experimental (E) and theoretical (T) radial distribution curves and difference curve (D). The RD curves were calculated from the intensity curves of Fig. 2 with an artificial damping constant 0.0020 Å².

easily concluded, that **D** and **S** have to be present in nearly equal amounts.

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. 19. 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 C-atom framework possess D_{2d}, symmetry, with $\angle C_1C_2C_3 = \angle C_4C_2C_5 = 109.47° - \theta_c$ for the **D** conformer and $\angle C_1C_2C_3 = \angle C_4C_2C_5 = 109.47° + \theta_c$ for the **S** conformer; (2) all four $C-CH_2X$ groups are equal; (3) each of the $C-CH_2X$ groups possess C_s symmetry, and the projection of the angle HCH′ on a plane perpendicular to the $C-C$ axis is 120°; (4) the conformers **D** and **S** have identical structures except for the $C-C$ torsion angles and the CCC angles.

Models were defined in terms of the following average parameters: $C-H$, $C-C$, $C-X$, $\angle CCX$, $\angle CCH$ and θ_c. The torsion angles of the **S** conformer were defined as follows:

$$\phi_{1-2} = \phi_{3-2} = 120° + \phi_s \quad \text{and}$$
$$\phi_{4-2} = \phi_{5-2} = -120° - \phi_s.$$

The deviation angle ϕ_s was refined. All torsion angles for the **D** conformer are equal to 0°. The exact staggered conformers thus have torsional angles: 120, 120, −120, −120° for **S**, and 0, 0, 0, 0° for **D**.

Also adjusted was the composition parameter, the relative amount of conformer **S**. Nonbonded distances were computed as dependent parameters, restricted under the constraints of geometrically consistent r_α parameters.[22,23]

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 had to be corrected, however, none of the important conclusions about the structure and composition were changed thereby.

All important parameters could be simultaneously refined. The combination of all geometry variables, the u values for bond distances and for non-bonded distances of the kinds $C\cdots C$, $X\cdots X$, and $X\cdots C$, the composition parameter, and a scale factor refined to give convergence
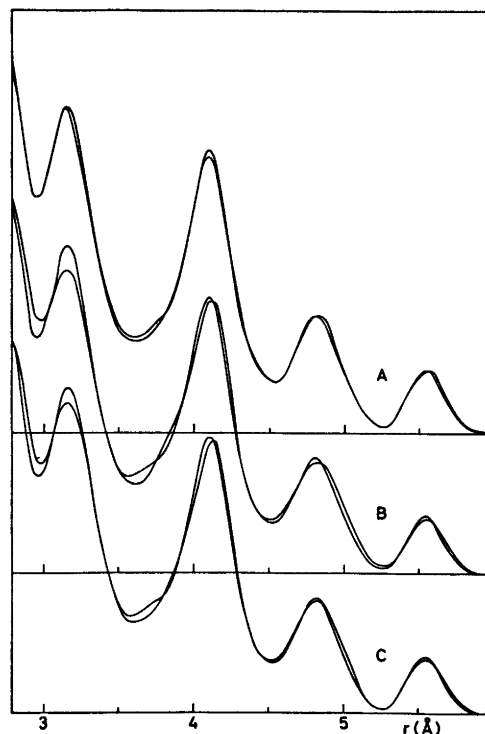

Fig. 4. Three different theoretical RD curves are shown together with the experimental curve. (A) corresponds to final parameters, and several u values have been refined. (B) corresponds to $F_\phi(D) = F_\phi(S) = 0.53$ mdyn Å $(rad)^{-2}$, and computed u values. (C) corresponds to $F_\phi(D) = 0.36$ mdyn Å $(rad)^{-2}$ and $F_\phi(S) = 0.88$ mdyn Å $(rad)^{-2}$, and computed u values. A damping constant of 0.0020 Å² was used.

and reasonable parameter values.

B. Determination of torsional force constants. The torsional modes of vibration contribute substantially to the mean amlplitudes of several distances in a molecule like TMCL. Therefore, since a reasonable force field is known, except for the torsional part, the torsional force constants can be adjusted to fit the electron-diffraction data.[11] The following procedure was used: First an average torsional force constant $(\bar{F}_\phi)$, common to both conformers **D** and **S**, was determined. Parallel and perpendicular 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** = 862) was obtained for $\bar{F}_\phi = 0.53$ mdyn Å $(rad)^{-2}$. The best fit obtained in this

way was good, but not quite satisfactory. The discrepancies between theoretical and experimental RD curves indicated that the torsional force constant of conformer **D** ought to be smaller than the one for conformer **S**, see Fig. 4. The two conformers were then assigned different values, $F_\phi(D)$ and $F_\phi(S)$. The combination of force constants that lead to minimum in the error sum was determined by a systematic iteration procedure, and the best fit was obtained with $F_\phi(D) = 0.36$ and $F_\phi(S) = 0.88$ mdyn Å(rad)$^{-2}$. The new value of $V'PV$ [19] is only 5 % less than the value obtained with $F_\phi(D) = F_\phi(S) = \bar{F}$, however the theoretical RD curve [19] corresponding to u values computed with the new set of torsional force constants, was clearly improved compared to the one with $F_\phi(D) = F_\phi(S) = 0.53$ mdyn Å (rad)$^{-2}$; see Fig. 4.

Interaction constants of the type $F_{\phi\phi'}$ have not been determined, but values computed from the energy model are shown in Table 4. Although the absolute values of these interaction constants are small, the effect on torsional frequencies are not negligible. The influence on u and K values are, however, very small.

As already pointed out in a previous paper,[11] it is difficult to estimate uncertainties in the F_ϕ values. However, the most probable torsional force constants and their estimated *minimum* error limits are:

For conformer **D**:

$$F_\phi(D) = 0.36 {\scriptstyle \begin{array}{c}+0.17\\-0.06\end{array}} \text{ mdyn Å (rad)}^{-2}$$

For conformer **S**:

$$F_\phi(S) = 0.88 {\scriptstyle \begin{array}{c}+0.10\\-0.25\end{array}} \text{ mdyn Å (rad)}^{-2}$$

Not all combinations of F_ϕ values are equally probable. Certain combinations of the extreme of the permissible ranges are less likely than others. All combinations of values for $F_\phi(D)$ and $F_\phi(S)$ within a triangle having corners (0.30, 0.92), (0.44, 0.94), and (0.53, 0.53) are very probable.

The adjustement of F_ϕ values is not a simple and straightforward matter. One has to refine all relevant geometry parameters simultaneously in each least-squares run. If that is not done, the F_ϕ values obtained 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 the error limits do not allow for systematic errors in the remainder of the force field.

VI. FINAL RESULTS

Results from the least-squares refinements, and standard deviations (σ) corrected for correlation in the experimental data,[24] are given. All intensities were given equal weights in the final refinements.

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

Table 9. Bond lengths (Å) for $C(CH_2Cl)_4$. 0.14 % uncertainty in the wavelength has been included in the σ values. An experiment with CO_2 gave a correction of $+0.1$ % in the s-scale, therefore the bond lengths given are 0.1 % longer than those obtained directly by refinements. Parameter correlation: $\varrho(C-X, CCX) = -0.51$.

Bond	r_a	σ
C – H	1.127	0.009
C – C	1.539	0.004
C – Cl	1.792	0.003

Table 10. Bond angles for $C(CH_2Cl)_4$.

Angle	$\angle_\alpha(°)$	σ
$\angle CCX$	113.5	0.4
$\angle CCH$	108.0	1.0
$\angle C_1C_2C_3(D)$	106.1	0.9[a]
$\angle C_1C_2C_3(S)$	111.9	0.9[a]
$\angle XCH$	108.2[b]	1.0
$\angle HCH$	110.9[b]	1.0
$\angle C_1C_2C_4(D)$	111.2[b]	0.9
$\angle C_1C_2C_4(S)$	108.3[b]	0.9

[a] It was assumed that the carbon-atom framework in both conformers possessed D_{2d} symmetry. For the conformer **D** $\angle C_1C_2C_3 = \angle C_4C_2C_5 = 109.47° - \theta_c$, and for the conformer **S** $\angle C_1C_2C_3 = \angle C_4C_2C_5 = 109.47° + \theta_c$. The parameter θ_c was refined, and the value obtained was $+2.4°$ with a standard deviation of 0.9°. Parameter correlation: $\varrho(u_g(C\cdots X), CCX) = 0.58$, $\varrho(u_a(C\cdots X), CCX) = -0.52$. [b] These angles were computed as dependent quantities.

Table 11. Torsion angles [$\angle_\alpha$ values (°)] for the conformers **S** and **D** in $C(CH_2Cl)_4$. The torsion angles of the **S** conformer were confined as follows: $\phi_{1-2} = \phi_{3-2} = 120° + \phi_s$ and $\phi_{4-2} = \phi_{5-2} = -120° - \phi_s$, and the deviation angle ϕ_s was refined. (The torsion angles of the **D** conformer are equal to zero by definition.) The value obtained for ϕ_s was $+4.1°$ with a standard deviation of 0.8°. Parameter correlation: $\varrho(\phi_s, \theta_c) = 0.80$.

Conformer	ϕ_{1-2}	ϕ_{3-2}	ϕ_{4-2}	ϕ_{5-2}
S	$+124.1(0.8)$	$+124.1(0.8)$	$-124.(0.8)$	$-124.1(0.8)$
D	(0)	(0)	(0)	(0)

Table 12. Cartesian coordinates (Å) for conformers of $C(CH_2Cl)_4$ (see Fig. 1). The coordinates have been calculated using the final structure parameters, and the numbering of atoms is found in Fig. 1. The principal axes' moments of inertia are (amu Å²): $I_A = I_B = 657.94$ and $I_C = 1193.77$ for conformer **D**, $I_A = 629.03$ and $I_B = I_C = 940.31$ for conformer **S**.

	(x)	(y)	(z)
Conformer D (D_{2d})			
C_2	0	0	0
C_1	1.2299	0.9251	0
X_1	2.7888	0.0413	0
H_1'	1.1860	1.5627	0.9283
H_1	1.1860	1.5627	-0.9283
C_3	-1.2299	0.9251	0
X_3	-2.7888	0.0413	0
H_3'	-1.1860	1.5627	-0.9283
H_3	-1.1860	1.5627	0.9283
C_4	0	-0.9251	1.2299
X_4	0	-0.0413	2.7888
H_4	0.9283	-1.5627	1.1860
H_4'	-0.9283	-1.5627	1.1860
C_5	0	-0.9251	-1.2299
X_5	0	-0.0413	-2.7888
H_5	0.9283	-1.5627	-1.1860
H_5'	0.9283	-1.5627	-1.1860
Conformer S (S_4)			
C_2	0	0	0
C_1	1.2751	0.8617	0
X_1	1.3512	2.0252	-1.3608
H_1'	2.1623	0.1709	-0.0767
H_1	1.3015	1.4446	0.9642
C_3	-1.2751	0.8617	0
X_3	-1.3512	2.0252	1.3608
H_3'	-2.1623	0.1709	0.0767
H_3	-1.3015	1.4446	-0.9642
C_4	0	-0.8617	1.2751
X_4	1.3608	-2.0252	1.3512
H_4	-0.9642	-1.4446	1.3015
H_4'	0.0767	-0.1709	2.1623
C_5	0	-0.8617	-1.2751
X_5	-1.3608	-2.0252	-1.3512
H_5	0.9642	-1.4446	-1.3015
H_5'	-0.0767	-0.1709	-2.1623

values, corresponding to final torsional force constants, are shown in Table 6.

Parameter correlation coefficients with absolute values larger than 0.50 are included in Tables 9 – 13.

Bond lengths corresponding to r_a values [19] are given in Table 9, and bond angles in Table 10. The torsion angles of the conformer **S** have been adjusted and the values are found in Table 11. The torsion angles of conformer **D** have been kept constant at values also shown in Table 11.

Cartesian coordinate for the conformers are found in Table 12.

Several u values have been refined and compared to those computed using the final torsional force constants (see Table 13). Both sets of u values are experimental, but the calculated values combine information from spectroscopy as well as from electron diffraction. Some u values get very small contributions from the torsional modes of vibration. Such u values are those corresponding to bond distances, distances over *one* bond angle, distances $X \cdots X(AA)$, and the distance $X \cdots C(a)$. The fact that these u values are generally in good agreement with those refined directly, is important. The valence force field used for TMCL thus seems reasonable. The value of $u(C-X)$, determined directly by leastsquares refinements, is significantly different from the spectroscopic value, probably due to an error in blackness correction. It is, however, unlikely that other u values are significantly disturbed by this type of error. The average deviation between the two sets of u values is less than 8 %, while the average, $\langle \sigma/u \rangle$, relative uncertainty of the refined u values is 8.5 %.

The relative amounts of the conformers **D** and **S** were easily determined. The composition parameter $\alpha_S(\alpha_D = 100 - \alpha_S)$ was introduced, and

Table 13. Mean amplitudes (u) of vibration for $C(CH_2Cl)_4$ at 105°C.

Type of distance	Distance (Å)	Calculated u value[a] (Å)	Refined u value[b] (Å)	σ (Å)
C−H	(1.127)	0.078	0.077	0.010
C−C	(1.539)	0.052	0.053	0.005
C−X	(1.792)	0.055	0.045	0.003
C···C	(2.51)	0.074	0.094	0.015
X···C$_2$	(2.78)	0.076	0.076	0.006
X$_1$···H$_1$	(2.40)	0.109	0.105	0.018
X···C(g) in D	(3.16)	0.150	0.137	0.017
X···C(g) in S	(3.1−3.2)	0.133	0.120[c]	(−)[c]
X···C(a)	(4.11)	0.075	0.079	0.006
X···X(AG) in S	(4.83)	0.148	0.136	0.006
X···X(GG) in D	(3.98)	0.247	0.305	0.030
X···X(GG) in S	(3.81)	0.189	0.247[c]	(−)[c]
X···X(AA) in D	(5.56)	0.103	0.100	0.009

[a] The u values correspond to the valence force field of Table 5 with torsional force constants $F_\phi(D) = 0.36$ and $F_\phi(S) = 0.88$ mdyn Å (rad)$^{-2}$. [b] Values obtained by least-squares refinements. [c] Refined together with the previous u value as *one* parameter. Parameter correlation: $\varrho[u(C\cdots C), \alpha_s] = 0.59$, $\varrho[u(C\cdots C), u(C-X)] = -0.63$, $\varrho[u_g(C\cdots X), u_a(C\cdots X)] = -0.64$, $\varrho[u_{GG}(X\cdots X), \alpha_s] = -0.54$.

Table 14. Calculations of ΔE^m using three different sets of torsional force constants. F_ϕ: torsional force constant, see Table 5 for definition of F_ϕ. The energy differences were calculated from eqn. (1) using the experimental equilibrium constant of 1.0, and the symmetry numbers $4(D_{2d})$ and $2(S_4)$.

	I	II	III
$F_\phi(D)$, mdyn Å (rad)$^{-2}$	0.36	0.51	0.62
$F_\phi(S)$, mdyn Å (rad)$^{-2}$	0.88	0.74	0.62
$(Q_D/Q_S)^{vib}_{T=378\ K}$	56.5	5.53	1.05
$\Delta E^m = E_D^m - E_S^m$, kcal/mol	+2.50	+0.75	−0.52

Table 15. Values of thermodynamic quantities relevant to the equilibrium between conformers (**S D**) of $C(CH_2Cl)_4$. Differences are always **D** minus **S**. Quantities being dependent on temperature have been marked by the suffix T. ($\Delta H_T = \Delta E_T$ for the gas equilibrium $S \rightleftharpoons D$).

$(T = 378\ K)$ $\Delta G_T = \Delta E_T - T\Delta S_T = -RT \ln K_p$ $(K_p = 1.0, \Delta G_T = 0)$

$\Delta E^m = +2.5$ kcal/mol

$\Delta E_T^{vib} = -1.5^a$ kcal/mol

$\Delta E_T = \Delta E^m + \Delta E_T^{vib} = +1.0$ kcal/mol

$\Delta S_\sigma = -R \ln (\sigma_D/\sigma_S) = -R \ln 2$

$\Delta S_T^{vib} = +4.0^b$ cal/(deg mol)

$\Delta S_T = \Delta S_\sigma + \Delta S_T^{vib} = +2.6$ cal/(deg mol)

[a] The difference in zero-point vibrational energy, $\Delta E_0^{vib} = \frac{1}{2}Nhc(\sum \omega_D - \sum \omega_S)$, is -2.0 kcal/mol. $\Delta E_T^{vib} = RT^2 d \ln q^{vib}/dT$ with $q^{vib} = (Q_D/Q_S)_T^{vib}$ and the vibrational partition function Q^{vib} referred to the *minimum* of potential energy for the conformer; see also Table 14. [b] Calculated according to the standard expression for the contribution of entropy associated with vibrational degrees of freedom: $\Delta S_T^{vib} = R \ln q^{vib} + RT d(\ln q^{vib})/dT$. [m] Difference between potential energy *minima* for the conformers.

the value obtained from least-squares refinements was $\alpha_S = 50$ % ($\sigma = 1$ %).

VII. DISCUSSION

Following standard statistical thermodynamics,[25,26] the relative amounts α_D and α_S for the two conformers ($S \rightleftharpoons D$) in equilibrium in the gas phase, are related to the theoretical expression for the equilibrium constant, as given in eqn. 1:

$$\alpha_D/\alpha_S = (\sigma_D/\sigma_S)^{-1}(Q_D/Q_S)^{vib}\exp(-\Delta E^m/RT) \quad (1)$$

(The *classical* rotational partition functions for the two conformers are very nearly equal.) Q^{vib} is the vibrational partition function, referred to the *minimum* of potential energy, for a conformer. $\Delta E^m = E_D^m - E_S^m$ is the difference in potential energy between the two conformers, and the difference is measured between energy *minima*. The difference in zero-point vibrational energy is thus included in the ratio between the vibrational energy partition functions. σ is the symmetry number of a conformer.[26] R and T have their usual thermodynamic meanings.

The difference in free energy (ΔG) between the two conformers is zero at 105°C. If the vibrational partition functions for the conformers are known, then ΔE^m may be estimated from eqn. (1). The *ratio* between the partition functions depends on the *difference* in torsional force constants as demonstrated in Table 8. Calculations of ΔE^m using three different sets of torsional force constants are summarized in Table 14. The combination I (0.36, 0.88) corresponds to the torsional force constants determined from the electron diffraction data. The combination II (0.51, 0.74) lead to the value of ΔE^m (0.75 kcal/mol) predicted by the semiempirical energy model. Both experiment and semiempirical calculations thus indicate that conformer **D** is *less* stable than conformer **S**, but the ΔE^m values do not agree. The possibility III ($F_\phi(D) = F_\phi(S)$) seems to be unlikely.

The fact that the two conformers are present in equal amounts is thereby given a reasonable explanation: the lower minimum energy of conformer **S** is compensated by the lower *vibrational* energy and larger vibrational entropy of conformer **D**. (The relative amount of **D**

ought to be increased by an increase in temperature.)

Values of thermodynamic functions, relevant to the equilibrium between the conformers, $S \rightleftharpoons D$, have been summarized in Table 15.

Although T, ΔE_T, and ΔS_T are rather uncertain quantities, the values of Table 15 may serve as a warning. Because of lack of spectroscopic information it has been quite common practice to assume equal vibrational partition functions for different conformers. For conformers with torsional oscillations of low frequencies that approximation has to be questioned. If the thermodynamic quantities are computed assuming *equal* torsional force constants, quite different values for ΔE_T and ΔS_T are obtained. However, more important is the consequence that the temperature dependency of ΔE_T and ΔS_T is lost. The study of conformational equilibria at several temperatures [27] is a promising approach. The usual practice has been to obtain ΔS and ΔE from the effect of temperature on composition by use of the relation $\Delta G_T = \Delta E - T\Delta S$ assuming ΔE and ΔS temperature *independent* quantities. The formula may still be used, if the temperature dependency of ΔE and ΔS is taken into consideration. Nevertheless, the most direct relation between composition, temperature, and fundamental thermodynamic quantities is eqn. (1). All information about ΔE_T^{vib} and ΔS_T^{vib} may be derived from the function $(Q_D/Q_S)_T^{vib}$, which is directly related to the difference in force fields of the conformers.

The thermodynamic quantities relevant to the equilibrium between the abundant conformers of TMCL have been estimated. However, electron diffraction data at increased temperatures, together with observed vibrational frequencies in the range $50-300$ cm^{-1} are needed to determine more accurately the thermodynamic quantities. P. Klæboe and coworkers at this university are investigating TMCL by IR and Raman, and electron-diffraction data in the range $150-200$°C have been recorded. B. Pedersen and coworkers, also at this university, have started on a NMR investigation of TMCL and related compounds.

The conformers **D** and **S** ought to have zero electric dipole moments as suggested by their geometry. The observed moment, however, is

0.43 Debye for TMCL.[9] In their paper [9] Thompson and Sweeney discuss the origin for this non-zero moment. At least two possible explanations exist: (1) the moment is induced by the torsional oscillations, or (2) conformers of low symmetry (C_1 in Table 1) are present in detectable amounts. The second possibility seems to be ruled out by the values of conformational energies obtained from the semi-empirical calculations. The electron-diffraction data at 105°C exclude relative amounts of C_1 conformers larger than $5-6$ %.

Finally, have the results (structure parameters, conformational energy, and torsional force constants) predicted by the semiempirical energy model been confirmed by the experimental findings? Considering the experimental uncertainties, the calculated structure parameters (Table 2) agree with the experimental (Tables 9 $-$ 11) values. The calculated torsional force constants (Table 4) do not agree with those determined from the electron-diffraction data. (sect. V $-$ B) Both experimental and calculated values for $\Delta E^m = E_D^m - E_S^m$, 2.5 and 0.75 kcal/mol, respectively, indicate that conformer **D** is less stable than conformer **S**. Considering the large uncertainty involved, the two values are not significantly different.

REFERENCES

1. Bastiansen, O., Seip, H. M. and Boggs, J. E. In Dunitz, J. D. and Ibers, J. A., Eds., *Perspectives in Structural Chemistry*, Wiley, New York 1971, Vol. IV.
2. Seip, H. M. In Sim, G. A. and Sutton, L. E. Eds., *Molecular Structure by Diffraction Methods* Specialist Periodical Reports, The Chemical Society, London 1973, Vol. 1, Part 1, Chapter 1.
3. Wagner, G. and Dengel, G. *Z. Phys. Chem. B 16* (1932) 382.
4. De Laszlo, H. *C. R. Acad. Sci. 198* (1934) 2235.
5. Hassel, O. and Strømme, L. C. *Z. Phys. Chem. B 38* (1937) 349.
6. Ballaus, O. and Wagner, J. *Z. Phys. Chem. B 45* (1939) 165.
7. Mortimer, C. T., Speeding, H. and Springale, *J. Chem. Soc.* (1957) 188.
8. Lumbroso, H. and Lauranson, D. *Bull. Soc. Chim. Fr.* (1959) 513.
9. Thompson, H. B. and Sweeney, C. C. *J. Phys. Chem. 64* (1960) 221.
10. Geiseler, G. and Ratz, L. *Z. Naturforsch. 21* (1966) 1889.
11. Stølevik, R. *Acta Chem. Scand. A 28* (1974) 299.
12. Abraham, R. J. and Parry, K. J. *J. Chem. Soc. B* (1970) 539.
13. Schachtschneider, J. H. and Snyder, R. G. *Vibrational Analysis of Polyatomic Molecules. IV* (Force constants for the haloparaffins). Project No. 31450, Technical Report No. 122 $-$ 63 of Shell Development Company.
14. Snyder, R. G. and Schachtschneider, J. H. *Spectrochim. Acta 21* (1965) 169.
15. Gwinn, W. D. *J. Chem. Phys. 55* (1971) 477.
16. Stølevik, R., Seip, H. M. and Cyvin, S. J. *Chem. Phys. Letters 15* (1972) 263.
17. Mooradian, A. and Cloke, J. B. *J. Amer. Chem. Soc. 39* (1945) 942.
18. Bastiansen, O., Hassel, O. and Risberg, E. *Acta Chem. Scand. 9* (1955) 232.
19. Andersen, B., Seip, H. M., Strand, T. G. and Stølevik, R. *Acta Chem. Scand. 23* (1969) 3224.
20. Peacher, J. and Willis, J. C. *J. Chem. Phys. 46* (1967) 4809.
21. Strand, T. G. and Bonham, R. A. *J. Chem. Phys. 40* (1964) 1686.
22. Morino, Y., Kuchitsu, K., and Oka, T. *J. Chem. Phys. 36* (1962) 1108.
23. Kuchitsu, K. *J. Chem. Phys. 49* (1968) 4456.
24. Seip, H. M. and Stølevik, R. In Cyvin, S. J., Ed., *Molecular Structures and Vibrations*, Elsevier, Amsterdam 1972.
25. Glasstone, S. *Theoretical Chemistry*, Van Nostrand, London.
26. Herzberg, G. *Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand, Princeton.
27. Almenningen, A., Bastiansen, O., Fernholt, L. and Hedberg, K. *Acta Chem. Scand. 25* (1971) 1946.