

Conformational Analysis. IV. The Molecular Structure, Torsional Oscillations, and Conformational Equilibria of Gaseous $(\text{CH}_3)\text{C}(\text{CH}_2\text{Cl})_3$, 1,1,1-Tris(chloromethyl)ethane, as Determined by Electron Diffraction and Compared with Semiempirical Calculations

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Gaseous 1,1,1-tris(chloromethyl)ethane has been studied by electron diffraction at a nozzle temperature of 88 °C. Three spectroscopically distinguishable conformers *CS*, *CI*, and *C3* were detected (see Fig. 1 and Table 1). Results are presented with error limits (2σ). The following values for bond lengths (r_a) and bond angles (\angle_a) are average parameters for the conformers: $r(\text{C}-\text{H}) = 1.100(14)$ Å, $r(\text{C}-\text{C}) = 1.532(6)$ Å, $r(\text{C}-\text{Cl}) = 1.792(6)$ Å, $\angle\text{CCCl} = 113.9^\circ(0.6)$, $\angle\text{CCH} = 110.2^\circ(1.4)$, $\angle\text{HCH} = 108.7^\circ(1.8)$, and $\angle\text{HCCl} = 106.8^\circ(1.6)$. A tetrahedral arrangement of carbon atoms was assumed. Non-bonded internuclear distances were computed as dependent quantities under the constraints of geometrically consistent r_a parameters. The conformers have torsion angles close to staggered values.

The composition at ca. 88 °C is: 45 % (6) of *CS*, 34 % (16) of *CI*, and 21 % (14) of *C3*. Conformers with C-Cl bonds parallel are not present in detectable amounts.

According to the semi-empirical calculations, *C3* is the conformer of lowest minimum energy. The large percentage of *CS* encountered can be explained if it is assumed that the force field of *CS* is quite different from that of *C3* and *CI*. This point has been discussed.

Torsional force constants and frequencies corresponding to the torsional modes of the $-\text{CH}_2\text{Cl}$ groups have been estimated by combining information from electron diffraction and vibrational spectroscopy.

The characteristic structure parameters of molecules of the type $(\text{CH}_3)_{4-n}\text{C}(\text{CH}_2\text{Cl})_n$ with $n=2, 3, 4$, have been compared in Table 10.

I. INTRODUCTION

The present electron-diffraction work is part of a systematic conformational study of halogenated propanes and related molecules. General¹ information² relevant to this investigation and to the electron-diffraction method³ is found in Refs. 1, 2, and 3. The compounds $\text{C}(\text{CH}_2\text{Cl})_4$ ⁴ and $(\text{CH}_3)_2\text{C}(\text{CH}_2\text{Cl})_2$ ⁵ have recently been investigated by electron diffraction.

Compounds of the type $(\text{CH}_3)\text{C}(\text{CH}_2\text{X})_3$ will be referred to as TEX, and the title compound as TECL. Classically the possible number of staggered conformers for TEX is 27 (3^3), but only *seven* are spectroscopically distinguishable as indicated in Fig. 1 and Table 1. Including *enantiomeric* conformers, there are 11 *physically* distinguishable staggered conformers.

The conformational names (Table 1) have been chosen to indicate the symmetries of the conformers. The conformers *CS*, *CI*, and *C3* are expected to be the most stable ones and the conformers *CI(1:3)**, *CI(1:3)***, and *CS(1:3)* less stable because of parallel $(1:3)\text{X}\cdots\text{X}$ interactions.¹ The conformational energy of *C3(1:3)* has to be very high because of the very unfavourable X-atom arrangement.

The spectroscopically distinguishable conformers may be assigned *multiplicities* (M) in two ways, as follows:

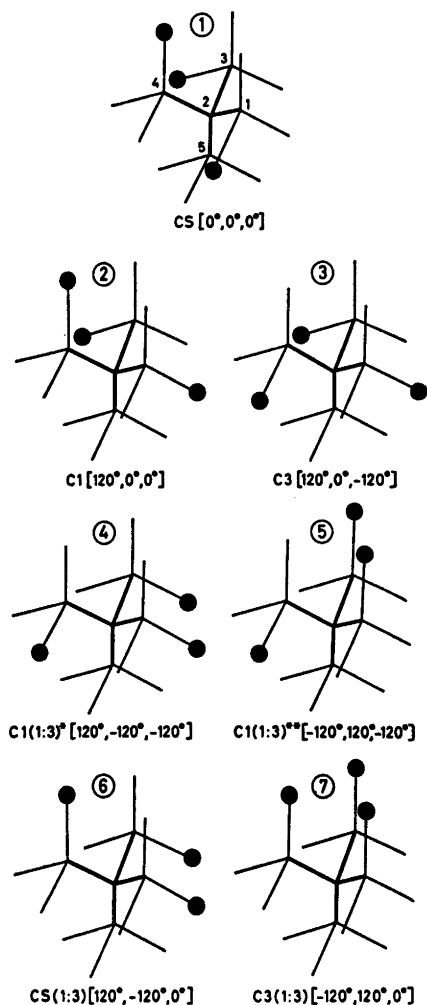


Fig. 1. Spectroscopically distinguishable staggered conformers of $(\text{CH}_3)\text{C}(\text{CH}_2\text{X})_3$. If a conformer has C-X bonds parallel, that is indicated in the name as (1:3). Numbers in brackets are values of the torsion angles ϕ_{1-2} , ϕ_{2-3} , and ϕ_{4-5} ($\phi_{5-2} = 0^\circ$).

(1) only distinguishable conformers (11) are considered (M_d in Table 1)

(2) all classically possible conformers (27) are considered (M_c in Table 1).

For two spectroscopically distinguishable conformers C and C*, having symmetry numbers σ and σ^* , it is noteworthy⁶ that $M_c^*/M_c = (M_d^*/M_d)(\sigma^*/\sigma)^{-1}$.

Acta Chem. Scand. A 28 (1974) No. 6

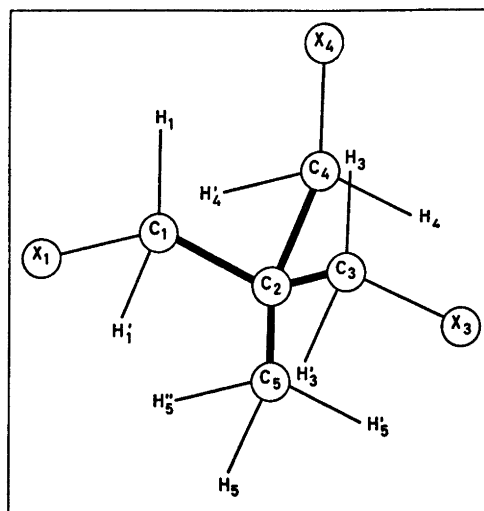


Fig. 2. Numbering of atoms in the conformer CS. The conventional name 1,1,1-tris(chloromethyl)ethane does not correspond to the numbering here.

II. CALCULATION OF CONFORMATION ENERGIES, GEOMETRIES, AND TORSIONAL FORCE CONSTANTS

The method of classical mechanics was used. The semiempirical energy calculations were carried out as described in Ref. 7. Energy parameters were taken from the work of Abraham and Parry,⁸ and the diagonal valence force constants in Table 6 of Ref. 4 were used. In minimizing the energy, the geometry was constrained in the same way as described in Sect. V-A, except that all torsional angles (ϕ) were adjusted as independent variables.

The conformational geometries derived from the semiempirical energy model are presented in Table 2 together with "normal" values⁷ of the geometry parameters.

In Table 3 are the results for conformational energies. According to the present energy model, C3 is the most stable conformer. Most of the staggered conformers, except for CS, C1, and C3, have high conformational energies due to parallel (1:3)X...X interactions (see Fig. 1). All conformers with parallel (1:3)X...X interactions have their torsion angles displaced from staggered values. The energy of these conformers is thereby considerably lowered, but the

Table 1. Characterisation of the seven spectroscopically distinguishable staggered conformers of $(\text{CH}_3)_3\text{C}(\text{CH}_2\text{X})_3$.

There are four $\text{X}\cdots\text{X}$ distances of different lengths: GG, AG, AA, and GG(1:3). 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. Lower case letters a(*anti*) and g(*gauche*) have been used to characterize the C–X bond (*anti* or *gauche* to the CCC framework) of a C–C–C–X fragment. The type of $\text{X}\cdots\text{X}$ distance corresponding to a *parallel* (1:3) $\text{X}\cdots\text{X}$ interaction (two C–X bonds parallel) has been specified as GG(1:3). All staggered conformers possess *three* C \cdots X(a) and *six* C \cdots X(g) distances.

	Name of conformer	Point group (symmetry number)	Multiplicities		Type of X \cdots X distances			
			M _d	M _c	GG	AG	AA	GG(:3)
(1)	CS	C _s (1)	1	3	2	0	1	0
(2)	CI	C ₁ (1)	2	6	1	2	0	0
(3)	C3	C ₃ (3)	2	2	0	3	0	0
(4)	CI(1:3)*	C ₁ (1)	2	6	0	1	1	1
(5)	CI(1:3)**	C ₁ (1)	2	6	1	1	0	1
(6)	CS(1:3)	C _s (1)	1	3	0	2	0	1
(7)	C3(1:3)	C _{3v} (3)	1	1	0	0	0	3

Table 2. Calculated conformational geometry for $(\text{CH}_3)_3\text{C}(\text{CH}_2\text{Cl})_3$. Distances in Å and angles in degrees.

Parameter (normal value)	CS	CI	C3
C–H (1.094)	1.093	1.093	1.093
C–C (1.513)	1.540	1.538	1.538
C–X (1.780)	1.790	1.790	1.789
CCC (109.47) ^a	(109.47) ^a	(109.47) ^a	(109.47) ^a
CCX (109.47)	113.9	113.5	113.4
CCH (109.47)	110.1	110.1	110.1
$\phi_{1-2}(-\text{CH}_2\text{X})^b$	-1.6	113.9	120.4
$\phi_{3-2}(-\text{CH}_2\text{X})$	+1.6	1.6	0.4
$\phi_{4-2}(-\text{CH}_2\text{X})$	0	1.0	-119.6
$\phi_{5-2}(-\text{CH}_3)$	0	-12.7	-15.0

^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. ^b $\phi_0 = 60^\circ$ in the expression $V_\phi = \frac{1}{2} V_0 \sum (1 + \cos(3\phi_{k-2} - \phi_0))$ with $k = 1, 3, 4, 5$.

Table 3. Conformational energies (kcal/mol) in $(\text{CH}_3)_3\text{C}(\text{CH}_2\text{Cl})_3$. Details about the energy expression are found in Ref. 7.

Type of energy	CS	CI	C3
<i>E</i> (bonded)	3.12	3.03	2.95
<i>E</i> (van der Waals)	5.02	4.66	4.71
<i>E</i> (polar, Cl \cdots H)	-14.93	-15.07	-15.33
<i>E</i> (polar, Cl \cdots Cl)	5.40	5.23	4.88
<i>E</i> (total)	-1.40	-2.16	-2.80
$\Delta E^m(\text{total}) = E - E(\text{C3})$	1.40	0.64	0.00

lowest energy obtained [for CS(1:3)] was still 4 kcal/mol higher than the energy for CS.

Some of the torsional barriers within TECL have to be very high, but the *lowest* torsional barriers separating the conformers CS, CI, and C3 are *ca.* 5–6 kcal/mol.

The staggered conformer C3(1:3)(-120°, 120°, 0°), with three C–X bonds parallel, corresponds to a *maximum* on the potential energy surface. If the C_{3v} symmetry is reduced to C₃ by a simultaneous change of the torsion angles ϕ_{1-2} , ϕ_{3-2} , and ϕ_{4-2} , then a conformation, C3(1:3)(-100°, 140°, 20°), corresponding to a *minimum* on the energy surface is obtained. That minimum is still several kcal/mol above the minima of the remaining conformers.

The results of the energy calculations therefore suggest that the three conformers CS, CI, and C3 ought to be present in detectable amounts at 88 °C.

Torsional force constants may be numerically

Table 4. Calculated torsional force constants for $(\text{CH}_3)\text{C}(\text{CH}_2\text{Cl})_3$.

mdyn Å (rad) ⁻²	CS	C1	C3
$F_\phi(-\text{CH}_2\text{X})^a$	0.28–0.32	0.25–0.28	0.26
$F_\phi(-\text{CH}_3)^b$	0.14	0.16	0.16
$-F_{\phi\phi'}(-\text{CH}_2\text{X}/-\text{CH}_2\text{X})^c$	0.01–0.12	0.05–0.11	0.06–0.07
$-F_{\phi\phi'}(-\text{CH}_2\text{X}/-\text{CH}_3)^c$	0.01–0.06	0.01–0.04	0.03–0.04

^a The range of values corresponding to $F_\phi(1-2)$, $F_\phi(3-2)$, and $F_\phi(4-2)$. ^b $F_\phi(-\text{CH}_3) = F_\phi(5-2)$.
^c All interaction force constants ($F_{\phi\phi'}$) are negative.

computed from the semiempirical energy model. The general expression for a quadratic force constant is:

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

Torsional force constants are given in Table 4. Experimental values are found in Sect. V-B.

III. CALCULATION OF VIBRATIONAL QUANTITIES

Valence force constants, except for the torsional part, were taken from the works of Schachtschneider⁹ and Snyder.¹⁰ The force constants for $(\text{CH}_3)_2\text{C}(\text{CH}_2\text{Cl})_2$ were also used for TECL, and their values are found in Table 6 of Ref. 4.

The normal coordinate program described by Gwinn¹¹ was applied in computing vibrational frequencies.

Mean amplitudes of vibration (u and K values) were computed as described in Ref. 12. For the molecules $(\text{CH}_2\text{Cl})_4\text{C}$ and $(\text{CH}_3)\text{C}(\text{CH}_2\text{Cl})_2$, mean amplitudes of vibration at 105 and 60 °C, respectively, have already been published.^{4,5} Therefore, only u values relevant for discussion and comparison with least-squares refined values are given here (Sect. VI). In Table 5 are shown some u values corresponding to different values of the torsional force constant $F_\phi(-\text{CH}_2\text{X})$.

If the torsional force constants estimated from the electron diffraction data are used, then the torsional oscillations of the $-\text{CH}_2\text{X}$ groups correspond to vibrational frequencies in the range 70–200 cm^{-1} . The lowest frequency (ca. 70 cm^{-1}) is expected for the conformer CS, while the conformers C1 and C3 may have frequencies as low as 100 cm^{-1} .

Table 5. Mean amplitudes of vibration, u (Å), for $(\text{CH}_3)\text{C}(\text{CH}_2\text{X})_3$ calculated at 88 °C using three different values of the torsional force constant $F_\phi(-\text{CH}_2\text{X})$; X = Cl.

$F_\phi(-\text{CH}_2\text{X})^a$	0.36	0.63	0.90
X...X(GG) ^b	0.242	0.204	0.186
X...X(AG) ^c	0.161	0.151	0.146
X...X(AA) ^d	0.101	0.100	0.100
C...X(<i>gauche</i>) ^e	0.146	0.136	0.131

^a Values of the valence force constants are found in Table 6 of Ref. 4. The value of $F_\phi(-\text{CH}_3)$ was 0.315 mdyn Å (rad)⁻². The torsional force constant F_ϕ were defined as follows: each fragment C–C–C–A (A = H or Cl) in a $-\text{C}-\text{CH}_2\text{Cl}$ group has been assigned an equal torsional force constant $f_\phi(-\text{CH}_2\text{X})$, while each fragment C–C–C–H in a $-\text{C}-\text{CH}_3$ group has been assigned an equal torsional force constant $f_\phi(-\text{CH}_3)$. The total force constant for the torsion coordinate ϕ_{i-2} ($i = 1, 3, 4$) is thus $F_\phi(i-2) = 9f_\phi(-\text{CH}_2\text{X})$ and $f_\phi(5-2) = 9f_\phi(-\text{CH}_3)$.
^b Present in the conformers CS and C1. ^c Present in the conformers C1 and C3. ^d Only present in conformer CS. ^e Present in all conformers.

The conformational analysis of a molecule like TECL would be greatly simplified if the lowest frequencies could be independently obtained by vibrational spectroscopy (see Sect. VII).

IV. EXPERIMENTAL AND DATA REDUCTION

The compound was obtained from "K & K" laboratories. The purity of the sample was better than 98 %.

Electron-diffraction photographs were made

at a nozzle temperature of 88 °C in the Oslo apparatus¹³ under conditions summarized below.

Nozzle-to-plate distance (mm)	480.74	200.60
Electron wavelength (Å)	0.06458	0.06458
Number of plates	4	4
Range of data, in s (Å ⁻¹)	1.50 – 19.875	7.25 – 44.25
Data interval, Δs (Å ⁻¹)	0.125	0.250
Estimated uncertainty in s -scale (%)	0.14	0.14

The electron wavelength was determined by calibration against gold and corrected by an experiment with CO₂ giving a correction of +0.1 % in the s -scale. The data were reduced in the usual way¹⁴ to yield an intensity 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 $s/|f'_{Cl}|^2$.

The scattering amplitudes were calculated by the partial wave method¹⁵ using Hartree-Fock atomic potentials.¹⁶

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

The radial distribution (RD) curve obtained by Fourier transformation¹⁴ of the final experimental intensity is presented in Fig. 4.

V. STRUCTURE ANALYSIS AND REFINEMENTS

From the experimental RD curve (Fig. 4) it was concluded that the conformers *CS*, *C1*, and *C3* are present, and approximate composition parameters (α) were estimated. [$\alpha(CS) \simeq \alpha(C1) + \alpha(C3) \simeq 50\%$]. The relative amounts of *C1* and *C3* can not easily be obtained from the RD curve alone. RD curves for the individual conformers are found 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. 14. 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 three C–CH₂X groups are equal; (3) each C–CH₂X group possesses *C_s* symmetry and the projection of $\angle HCH'$ on a plane perpendicular to the C–C axis is 120°;

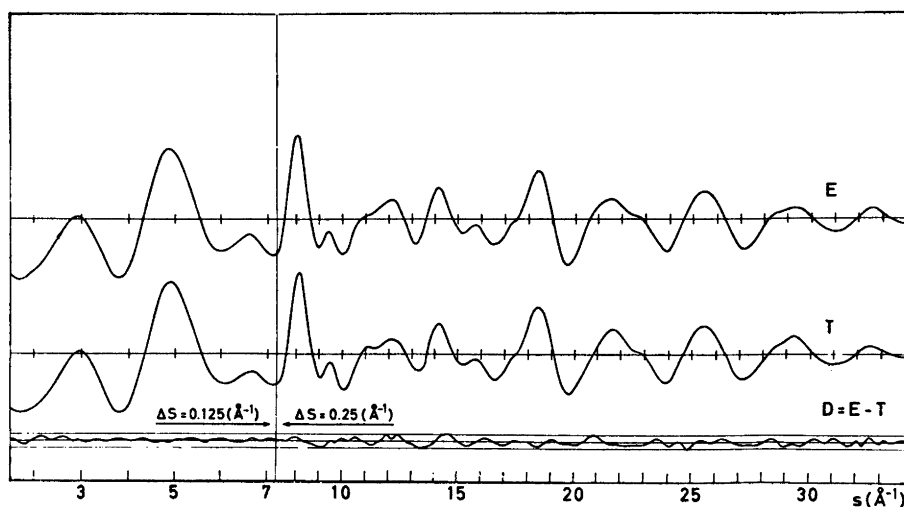


Fig. 3. Intensity curves for (CH₃)C(CH₂Cl)₃ at 88 °C. Experimental (E) and theoretical (T) intensity corresponding to the final least-squares parameters. Curve D represents E–T, and the straight lines give the experimental uncertainty ($\pm 3 \times$ experimental standard deviation).

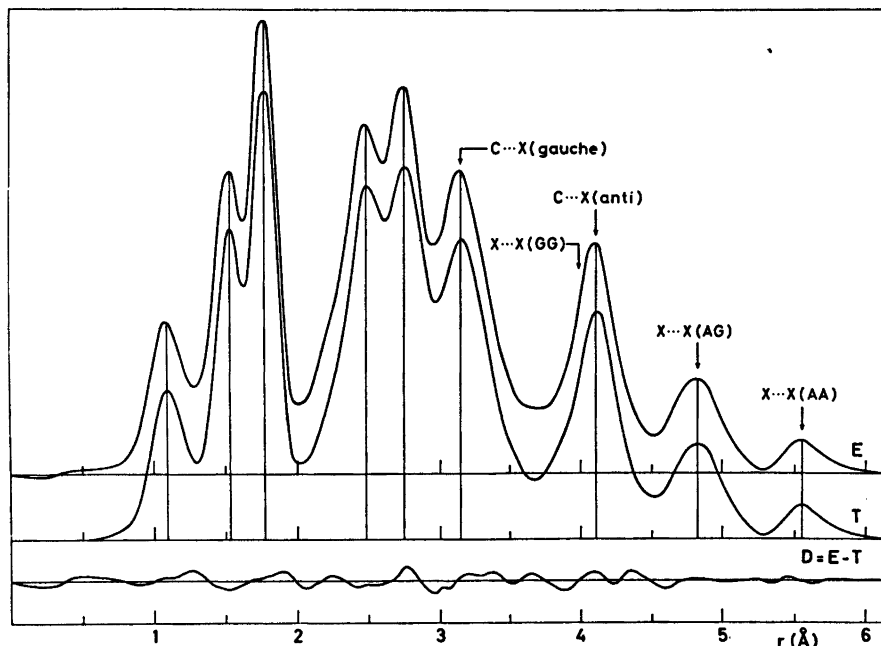


Fig. 4. Radial distribution curves for $(\text{CH}_3)\text{C}(\text{CH}_2\text{Cl})_3$ at 88°C . Experimental (E) and theoretical (T) radial distribution curves, and difference curve (D). The RD curves were calculated from the intensities of Fig. 3 with an artificial damping constant equal to 0.0020 \AA^2 .

(4) the $\text{C}-\text{CH}_3$ group possesses C_{3v} symmetry; (5) all $\text{C}-\text{H}$ bonds are equal; (6) all CCH angles are equal; (7) the conformers have identical structures except for the $\text{C}-\text{C}$ torsion angles (ϕ_{1-2} , ϕ_{2-3} , ϕ_{3-4} , and ϕ_{4-5}).

Models were defined in terms of the following average parameters: $\text{C}-\text{H}$, $\text{C}-\text{C}$, $\text{C}-\text{X}$, $\angle\text{CCX}$, $\angle\text{CCH}$, and the four ϕ angles. Also adjusted were the composition (%) parameters $\alpha(\text{CS})$ and $\alpha(\text{C1})$, with $\alpha(\text{C3}) = 100\% - \alpha(\text{CS}) - \alpha(\text{C1})$.

Corrections for the "Bastiansen-Morino" shrinkage¹⁷ 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.^{18,19}

B. Determination of torsional force constants. The torsional modes of vibration contribute substantially to the mean amplitudes of several internuclear distances in a molecule like TECL. 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 con-

stants from electron-diffraction data alone is not possible. Therefore, the theoretical values of Table 4 were used as a guide, and the following assumptions were made:

(1) all interaction constants $F_{\phi\phi'} = 0$; (2) in the conformer *CS*: $F_\phi(1-2) = F_\phi(2-3) = F_\phi(4-2) = F_\phi(\text{CS})$; (3) in the conformer *C1*: $F_\phi(1-2) = F_\phi(3-2) = F_\phi(4-2) = F_\phi(\text{C1})$; (4) in the conformer *C3*: $F_\phi(1-2) = F_\phi(3-2) = F_\phi(4-2) = F_\phi(\text{C3})$; (5) for all three⁴ conformers $F_\phi(5-2) = F_\phi(-\text{CH}_3) = 0.135 \text{ m dyn \AA (rad)}^{-2}$. Thus, three variables, $F_\phi(\text{CS})$, $F_\phi(\text{C1})$, and $F_\phi(\text{C3})$ were considered as independent variables. An average torsional constant ($F_\phi(\text{CS}) = F_\phi(\text{C1}) = F_\phi(\text{C3}) = \bar{F}_\phi$) equal to $0.63 \text{ m dyn \AA (rad)}^{-2}$ was tried. (That value of \bar{F}_ϕ was obtained for the molecules $\text{C}(\text{CH}_2\text{Cl})_4$ ⁴ and $(\text{CH}_3)_2\text{C}(\text{CH}_2\text{Cl})_2$ ⁵). Parallel and perpendicular amplitudes corresponding to $\bar{F}_\phi = 0.63$ were computed and included in the least-squares refinements. The structure and composition parameters were refined simultaneously. The fit obtained between theoretical and experimental intensities was practically as good as shown in Fig. 3. The discrepancies between

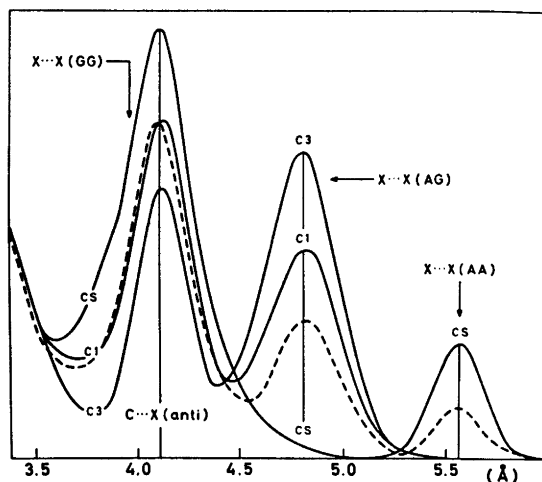


Fig. 5. Radial distribution curves for conformers of $(\text{CH}_3)\text{C}(\text{CH}_2\text{Cl})_3$. Experimental curve (---), and theoretical curves (—) for the conformers *CS*, *C1* and *C3*. An artificial damping constant equal to 0.0022 \AA^2 was used.

calculated u values for $\text{X}\cdots\text{X}$ distances of the type GG and AG (see Table 1) may be compared with the best least-squares estimates of Table 7. Although the individual least-squares estimates are quite uncertain, the discrepancies indicate that *C1* and *C3* may have greater average torsional force constants than *CS*.

Several combinations of F_ϕ values with $F_\phi(\text{CS}) < 0.63$ and $F_\phi(\text{C1}) = F_\phi(\text{C3}) > 0.63$ were then tried. Many combinations with $F_\phi(\text{CS})$ in the range 0.30–0.63 and $F_\phi(\text{C1})$ in the range 0.63–0.90 lead to a slight improvement, but

not significantly better than the fit obtained with $F_\phi(\text{CS}) = F_\phi(\text{C1}) = F_\phi(\text{C3}) = 0.63$. Although a definite conclusion could not be reached in this way, the most probable estimates for the F_ϕ values are presented as follows: $F_\phi(\text{CS})$ in the range 0.30–0.60, $F_\phi(\text{C1})$ and $F_\phi(\text{C3})$ in the range 0.70–0.90. The torsional force constants, $F_\phi(-\text{CH}_2\text{X})$, predicted by the semiempirical energy model are found in Table 4. Clearly, the calculated $F_\phi(-\text{CH}_2\text{X})$ values for the conformers *C1* and *C3* are too small, while the value (*ca.* 0.30) calculated for *CS* is not unlikely.

Table 6. Structure and composition parameters for $(\text{CH}_3)\text{C}(\text{CH}_2\text{Cl})_3$ at 88°C . Standard deviations are given in parentheses.

Parameter correlation: $|\rho| > 0.49$.

$\rho[\angle\text{CCX}/r(\text{C}-\text{C})] = -0.50$, $\rho[r(\text{C}-\text{C})/u(\text{X}_1\cdots\text{H}_1)] = -0.52$, $\rho[\alpha(\text{C1})/\alpha(\text{CS})] = -0.94$.

Bond ^a lengths (Å)	Bond ^b angles ($\angle\alpha$; deg.)	Composition parameters
$r_a(\text{C}-\text{H}) = 1.000(7)$	$\angle\text{CCCl} = 113.9(0.3)$	$\alpha(\text{CS}) = 45\% (3)$
$r_a(\text{C}-\text{C}) = 1.532(3)$	$\angle\text{CCH} = 110.2(0.7)$	$\alpha(\text{C1}) = 34\% (8)$
$r_a(\text{C}-\text{Cl}) = 1.792(3)$	$\angle\text{CCC} = (109.47)^c$	$\alpha(\text{C3}) = 21\% (7)^d$

^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 distance. ^b Bond angles are those of the self-consistent r_α structure. Dependent angles are: $\angle\text{HCH} = 108.7^\circ$ ($\sigma = 0.9^\circ$) and $\angle\text{HCCl} = 106.8^\circ$ ($\sigma = 0.5^\circ$). ^c Tetrahedral arrangement of C-atoms was assumed. ^d The parameters $\alpha(\text{CS})$ and $\alpha(\text{C1})$ were refined with $\alpha(\text{C3}) = 100\% - \alpha(\text{CS}) - \alpha(\text{C1})$.

VI. FINAL RESULTS

Parameters from the least-squares refinements¹⁴ and standard deviations (σ) corrected for correlation in the experimental data²⁰ are given. In the final refinements, intensities beyond $s=34.0 \text{ \AA}^{-1}$ were not included and, using a diagonal weight matrix, all intensities were given equal weights.

Non-bonded distances were restricted under the geometrical constraints of r_α parameters, by including correction terms $D=r_\alpha-r_a [D=(u^2/r)-K]$ for all distances.

Parameters correlation coefficients (ρ) are included in Tables 6–7. The structure and composition parameters are found in Table 6.

It is not possible to refine all torsion angles of the three conformers simultaneously as independent parameters. The results in Table 2 were used as a guide and the torsion angles were confined, as follows.

Conformer C1:

$$\phi_{1-2} = -\phi^\circ, \phi_{3-2} = +\phi^\circ, \text{ and } \phi_{4-2} = \phi_{5-2} = 0^\circ$$

Conformer C2:

$$\phi_{1-2} = 120^\circ - 4\phi^\circ, \phi_{3-2} = \phi_{4-2} = \phi^\circ, \text{ and } \phi_{5-2} = -8\phi^\circ$$

Conformer C3:

$$\phi_{1-2} = 120^\circ + \phi^\circ/4, \phi_{3-2} = \phi^\circ/4, \phi_{4-2} = -120^\circ + \phi^\circ/4, \text{ and } \phi_{5-2} = -9\phi^\circ$$

($\phi^\circ=0$ corresponds to staggered conformations.) The parameter ϕ° was refined, including as many as possible of the remaining least-squares parameters simultaneously. The absolute value of ϕ° was always found to be less than one standard deviation (σ) of that parameter ($\sigma=1^\circ$). The expected value of ϕ° according to Table 2 is $ca. +1.6^\circ$. Keeping in mind the assumptions involved, the theoretical value is in reasonable agreement with the experimental evidence.

Several mean amplitudes of vibration (u values) have been refined. In Table 7 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 relative deviation between the two

Table 7. Mean amplitudes (u) of vibration for $(\text{CH}_3)_3\text{C}(\text{CH}_2\text{Cl})_3$ at 88°C . Parameter correlation:

$|\rho| \geq 0.5$.

$$\rho[u(\text{AG})/u(\text{GG})] = -0.82, \rho[\alpha(\text{Cl})/u(\text{AG})] = -0.81, \rho[\alpha(\text{Cl})/u(\text{GG})] = -0.98,$$

$$\rho[\alpha(\text{CS})/u(\text{AA})] = +0.50, \rho[\alpha(\text{CS})/u(\text{AG})] = +0.66, \rho[\alpha(\text{CS})/u(\text{GG})] = +0.95.$$

The symbols AA, AG, and GG represent the three different kinds of $\text{X}\cdots\text{X}$ distances.

Type of distance	Dist. (\AA)	Calculated ^a u value (\AA)	Refined u value (\AA)	Standard deviation (\AA)
C–H	(1.10)	0.078	0.073	0.007
C–C	(1.53)	0.052	0.053	0.003
C–X	(1.79)	0.054	0.040	0.003
$\text{C}_2\cdots\text{X}$	(2.80)	0.074	0.071	0.003
$\text{C}\cdots\text{C}$	(2.50)	0.073	0.067	0.005
$\text{X}_1\cdots\text{H}_1$	(2.36)	0.108	0.103	0.008
$\text{C}\cdots\text{H}(\text{g})$	(2.74)	0.146	(0.146) ^b	–
$\text{C}\cdots\text{H}(\text{a})$	(3.46)	0.104	(0.104) ^b	–
$\text{C}\cdots\text{X}(\text{g})$	(3.16)	0.136	0.130	0.002
$\text{C}\cdots\text{X}(\text{a})$	(4.13)	0.074	0.074	0.003
$\text{X}\cdots\text{X}(\text{AA})$	(5.56)	0.100	0.101	0.014
$\text{X}\cdots\text{X}(\text{AG})$	(4.82)	0.151	0.130	0.019
$\text{X}\cdots\text{X}(\text{GG})$	(3.94)	0.204	0.280	0.071

^a Calculated with $\bar{F}_\phi=0.63 \text{ mdyn \AA (rad)}^{-2}$. ^b Not refined; calculated values were used.

sets of u values is ca. 7 % (u_{C-X} not included). The average relative uncertainty, $\langle \sigma/u \rangle$, of the refined u values is ca. 9 %. Since the calculated u values are reliable, then it is likely that the calculated K values are reliable to the same extent.

The u value for the bond C-X obtained by direct refinement is too small compared to the calculated value of 0.054 Å. The low value is most probably due to an error ⁵ in the blackness

Table 8. Cartesian coordinates (Å) for the conformers *CS*, *CI*, and *C3* of $(CH_3)_3C(CH_2X)_3$, X = Cl.

The coordinates have been calculated for staggered conformations, using the final bond angles ($\angle\alpha$) of Table 6 and r_g values for the bond lengths (see Table 10). The numbering of atoms in the conformer *CS* is shown in Fig. 2. The principal axes' moments of inertia are (amuÅ²):

$I_A = 331.98$, $I_B = 657.17$, and $I_C = 875.87$ for conformer *CS*

$I_A = 418.58$, $I_B = 603.80$, and $I_C = 842.64$ for conformer *CI*

$I_A = 521.35$, $I_B = 521.35$ and $I_C = 929.16$ for conformer *C3*

The coordinates for the conformer *CI* are equal to those of the conformer *CS*, with the following exceptions: X_1 ($x = 1.3724$, $y = 1.9749$, $z = -1.4204$) and H_1' ($x = 2.1636$, $y = 0.2586$, $z = 0$). The coordinates for the conformer *C3* are equal to those of the conformer *CI*, with the following exceptions: X_4 ($x = 1.4204$, $y = -1.9749$, $z = 1.3724$) and H_4 ($x = 0$, $y = -0.2586$, $z = 2.1636$).

<i>CS</i>	x	y	z
C ₁	1.2525	0.8857	0.0000
X ₁	2.7929	-0.0339	0.0000
H ₁	1.2645	1.5299	0.8989
H _{1'}	1.2645	1.5299	-0.8989
C ₂	0.0000	0.0000	0.0000
C ₃	-1.2525	0.8857	0.0000
X ₃	-2.7929	-0.0339	0.0000
H ₃	-1.2645	1.5299	0.8989
H _{3'}	-1.2645	1.5299	-0.8989
C ₄	0.0000	-0.8857	1.2525
X ₄	0.0000	0.0339	2.7929
H ₄	0.8989	-1.5299	1.2646
H _{4'}	-0.8989	-1.5299	1.2646
C ₅	0.0000	-0.8857	-1.2525
H ₅	0.0000	-0.2586	-2.1636
H _{5'}	-0.8989	-1.5299	-1.2646
H _{5''}	0.8989	-1.5299	-1.2646

correction,¹⁴ however, the remaining u values seem unaffected by that error.

Cartesian coordinates and principal axes' moments of inertia for the conformers are found in Table 8.

VII. DISCUSSION

The percentages α^* and α of two conformers (C=C*) in equilibrium in the gas phase, are related to the theoretical²¹ expression²² for the equilibrium constant, as given in eqn. (1):

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

with $M^*/M = (M_d^*/M_d)(\sigma^*/\sigma)^{-1} = M_c^*/M_c$

(see Table 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 included in the vibrational partition function. R and T have their usual thermodynamic meanings.

If the vibrational partition functions are known, then the quantity ΔE^m may be computed from eqn. (1). Conversely, if the quantity ΔE^m is known, then the ratios (q) between vibrational partition functions may be estimated from eqn. (1). Assuming the values of Table 3 for ΔE^m , q values have been computed and their values are found in Table 9.

If equal vibrational partition functions ($q=1$) are assumed, then eqn. (1) yield the values $\Delta E^m(q=1)$ of Table 9. According to the last set of ΔE^m values, the conformer *CS* is more stable than the conformers *CI* and *C3*. If the results from the semiempirical calculations were correct, then *C3* is the most stable conformer, and ca. 1.4 kcal/mol more stable than *CS*.

The great relative amount of the conformer *CS* encountered can be explained in at least two different ways: (1) the conformer *C3* has the lowest minimum energy as suggested by the semi-empirical calculations, but part of the force field for *CS* is quite different ($q \neq 1$) from that of *CI* and *C3*; (2) the force fields of the conformers are approximately equal ($q=1$) and *CS*

Table 9. Energy differences and ratios between vibrational partition functions for the conformers, *CS*, *C1*, and *C3* or $(\text{CH}_3)_2\text{C}(\text{CH}_2\text{Cl})_2$.

Difference or ratio	<i>CS</i> = <i>C1</i>	<i>CS</i> = <i>C3</i>	<i>C1</i> = <i>C3</i>
(1) $\Delta E^m(\text{CALC})^a$ in kcal/mol	+ 0.76	+ 1.40	+ 0.64
Ratio between vibrational partition functions (<i>q</i>)	7.6	10.0	1.3
(2) $\Delta E^m(q=1)$ in kcal/mol	- 0.70	- 0.25	+ 0.45
$\Delta E^m(q=1) - \Delta E^m(\text{CALC})$	- 1.46	- 1.65	- 0.19

^a Difference between conformational minima as predicted by the semiempirical energy model (Sect. II).

has the lowest minimum energy contrary to the results of semi-empirical calculations.

The experimental information available for TECL alone does not make a definite choice between the two alternatives possible. However, there is a certain evidence for the torsional force constants of *CS* being smaller than those of *C1* and *C3*.

The values [$\text{mdyn } \text{\AA} (\text{rad})^{-2}$] of the torsional force constants (F_ϕ) were confined as follows: $F_\phi(\text{CS}) = 0.63 - \Delta F_\phi$, and $F_\phi(\text{C1}) = 0.63 + \Delta F_\phi = F_\phi(\text{C3})$. The value of ΔF_ϕ which leads to the *q* values of Table 9 is 0.15, corresponding to $F_\phi(\text{CS}) = 0.48$ and $F_\phi(\text{C1}) = F_\phi(\text{C3}) \approx 0.78$. Such a difference between the torsional force constants is not contradicted by the experimentally determined mean amplitudes. The calculated values (Table 5) for $u[\text{X} \cdots \text{X}(\text{GG})]$ and $u[\text{X} \cdots \text{X}(\text{AG})]$ are 0.204 \AA and 0.150 \AA , respectively, if a force constant $F_\phi = 0.63$ is used for all three conformers. The best least-squares estimates (Table 7) are 0.280 \AA and 0.130 \AA . The calcu-

lated *u* value for $\text{X} \cdots \text{X}(\text{GG})$ is too small and the one for $\text{X} \cdots \text{X}(\text{AG})$ is too large compared to the least-squares estimates. The discrepancies between the two sets of *u* values are partly removed if $F_\phi(\text{CS}) = 0.48$ and $F_\phi(\text{C1}) = F_\phi(\text{C3}) = 0.78$. Unfortunately, the least-squares values are very uncertain quantities and no further conclusions about the value of ΔF_ϕ can reasonably be arrived at from *u* values alone. (If observed frequencies were available, then hopefully the difference between the force constants of the conformers could be determined.)

It is thereby demonstrated that a reasonable value of ΔF_ϕ could easily lead to *q* values as large as 7.6 and 10.0 in a molecule like TECL. In the molecules $\text{C}(\text{CH}_2\text{Cl})_4$ ⁵ and $(\text{CH}_3)_2\text{C}(\text{CH}_2\text{Cl})_2$ ¹⁴ similar situations were encountered. For $\text{C}(\text{CH}_2\text{Cl})_4$, a *q* value as large as 50, corresponding to a large difference in zero-point vibrational energy between the two abundant conformers, is possible.

The characteristic structure parameters for

Table 10. Structure parameters for molecules of the type $(\text{CH}_3)_{4-n}\text{C}(\text{CH}_2\text{X})_n$, *n* = 2, 3, and 4.

[X = Cl]	$(\text{CH}_3)_3\text{C}(\text{CH}_2\text{X})_2$	$(\text{CH}_3)_2\text{C}(\text{CH}_2\text{X})_3$	$\text{C}(\text{CH}_2\text{X})_4$	$\bar{M}(\text{calc.})^b$
$r_g(\text{C}-\text{H})^a$	1.107(4) ^c	1.106(7)	1.133(9)	(1.093-1.094)
$r_g(\text{C}-\text{C})$	1.533(2)	1.534(3)	1.541(4)	(1.534-1.544)
$r_g(\text{C}-\text{X})$	1.794(2)	1.794(3)	1.794(3)	(1.789-1.790)
$\angle_\alpha \text{CCX}$	114.3(0.2)	113.9(0.3)	113.5(0.4)	(113.3-113.9)
$\angle_\alpha \text{CCH}$	109.1(0.4)	110.2(0.7)	108.0(1.0)	(110.1-110.2)
$\angle_\alpha \text{CCC}$	(≈ 109.47) ^d	(≈ 109.47) ^d	(≈ 109.47) ^e	

^a $r_g = r_a + u^2/r$; the spectroscopic *u* values were used in computing the u^2/r term. ^b $\bar{M}(\text{calc.})$; represents the range of the (average) parameter as predicted by the semi-empirical calculations. ^c Standard deviations for the experimental parameters are found in parentheses. ^d Tetrahedral arrangements of C atoms were assumed. ^e Small, but significant, deviations from a tetrahedral arrangement of C atoms were detected.

molecules of the type $(\text{CH}_3)_{4-n}\text{C}(\text{CH}_2\text{Cl})_n$, with $n = 2, 3, 4$, have been compiled in Table 10. The parameters are average values for the molecules, but conformers of the same molecule may have unequal structure parameters as indicated by the semi-empirical calculations (see Table 2 and Refs. 4 and 5) Small, and in some cases experimentally significant, deviations from a tetrahedral arrangement of C atoms are likely. The abundant conformers of these molecules have torsion angles close to staggered values. Larger deviations ($10-20^\circ$) are only likely for $-\text{CH}_3$ groups. The values predicted by the semi-empirical model reasonably agree with the experimental values. Although small adjustments in the force constants and the "normal" parameter values (Table 2) would remove most of the discrepancies, it was felt that results from additional molecules ought to be included before such corrections were considered. Reasonable adjustments of this kind would change the values of the conformational energy differences very little.

Acknowledgements. I am grateful to Cand.real. A. Almennigen for recording the diffraction photographs, and to Prof. O. Bastiansen, Dr. A. Haaland, and Dr. H. M. Seip for helpful discussions. Computer programs made available by Dr. H. M. Seip, Cand.real. S. Rustad, and Prof. W. D. Gwinn have been extensively used in this work. Financial support from Norges almenvitenskapelige forskningsråd is gratefully acknowledged.

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Received February 25, 1974.