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# Conformational Analysis. VII. The Molecular Structure and Torsional Oscillations of Gaseous Octachloropropane ($C_3Cl_8$) as Determined by Electron Diffraction and Compared with Semi-empirical (Molecular Mechanics) Calculations

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Gaseous octachloropropane has been studied by electron diffraction at a nozzle temperature of 160 °C. Results are presented with error limits ($2\sigma$). The following values for bond lengths ($r_g$) and bond angles ($\angle_\alpha$) were obtained: $r$(C–C) = 1.657(30) Å, $r$(C–Cl, in $-CCl_3$) = 1.764(12) Å, $r$(C–Cl, in $>CCl_2$) = 1.812(40) Å, $\angle$CCC = 119.0°(4.0), $\angle$CCCl (in $-CCl_3$) = 110.4°(1.0), and $\angle$CCCl (in $>CCl_2$) = 104.5°(1.0). Non-bonded internuclear distances were computed as dependent quantities, restricted under the constraints of geometrically consistent $r_\alpha$ parameters.

It is noteworthy that the two energetically unfavourable parallel (1:3) Cl···Cl interactions did not lead to a twist of the $-CCl_3$ groups. The $-CCl_3$ groups are staggered ($C_{2v}$ symmetry) relative to the $>CCl_2$ group. However, the values of the parameters $r$(C–C) and $\angle$CCC are quite different from those in propane itself.

To a large extent the values of the structural parameters predicted by the semi-empirical model, reasonably agree with the experimental findings.

It has been demonstrated that the diagonal torsional force constant can be estimated from the electron-diffraction data, if the remainder of the force field is approximately known. The most probable values of the two torsional frequencies are expected in the range 45 – 65 $cm^{-1}$. The torsional force constant predicted by the semiempirical model does not agree with the experimental finding, which is 0.36 mdyn Å $(rad)^{-2}$ for the diagonal element.

## I. INTRODUCTION

This work is part of a systematic conformational study of halogenated propanes by electron diffraction in the gas phase. Results for the following molecules have recently been published: $(BrCH_2-CHBr-CH_2Br)$,[1] $(BrH_2C-CH_2-CH_2Br)$,[2] $(ClH_2C-CHCl-CH_2Cl)$.[3] Also molecules with $CH_2X$ (X = Cl or H) groups bonded to the central C atom of a C–C–C skeleton have been studied: $[C(CH_2Cl)_4]$,[4] $[(CH_3)_2C(CH_2Cl)_2]$,[5] $[(CH_3)C(CH_2Cl)_3]$.[6]

General information [7] relevant to this investigation and to the electron diffraction method [8] is found in Refs. 7 and 8.

For heavily chlorinated propanes very few conformers are found compared to the number of theoretically possible conformers with all-staggered (1:2) interactions.[9,10] With heavily chlorinated propanes most of the staggered conformers are unstable because of parallel (1:3) Cl···Cl interaction [9,10] which give rise to parallel C–Cl bonds on the same side of the carbon skeleton. In octachloropropane itself there are two parallel (1:3) Cl···Cl interactions. The repulsion between the Cl atoms has to be considerable. It is, however, a fact that the molecule exists, and at least one conformer must be stable. The present study is concerned with the details in structural and vibrational parameters of the stable conformer in the gas phase. Due to the strong repulsion between the large Cl atoms, some of the structural parameters of octachloropropane have to be quite different from those in propane itself.

For hexachloroethane [11] it is known that the C–C bond length is longer (1.564 ± 0.014 Å)

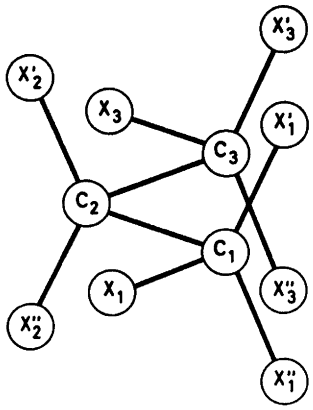


*Fig. 1.* Numbering of atoms in octachloropropane (X = Cl).

than that of ethane and propane, while the structural parameters of the $CCl_3$ groups in hexachloroethane are normal, (C − Cl = 1.769 ± 0.003 Å and ∠CCCl = 110.0 ± 0.5°).[11] From this information and a feeling that the results obtained for octachloropropane would be relevant for other heavily substituted molecules [9,10] an investigation seemed desirable.

## II. SEMI-EMPIRICAL CALCULATIONS OF STRUCTURAL PARAMETERS, TORSIONAL FORCE CONSTANTS, AND TORSIONAL BARRIERS

Molecular mechanics calculations including atom-atom potentials and force constants were carried out as described in Ref. 1. Energy parameter ($V_0$, $a$, $b$, $c$, and $d$) were taken from the work of Abraham and Parry.[12] The diagonal valence force constants in Table 2 were used. "Normal" values of the geometry parameters are given in Table 1 together with the results of these calculations. In minimizing the energy, the geometrical model was constrained as described in Sect. V-A. The value of the tilt angle ($\tau$) was not adjusted. ($\tau = 0°$). The remaining structure parameters, including two *independent* torsion angles, were adjusted simultaneously.

According to this energy model, only *one* stable conformer can exist. The symmetry of that conformer is $C_{2v}$, corresponding to staggered $-CX_3$ groups ($\phi = 0°$) with two parallel (1:3) Cl···Cl interactions. The C − C bond lengths and the CCC bond angle are considerably increased compared to propane itself.

The barrier obtained with one $-CX_3$ group eclipsing the $>CX_2$ group, and the other $-CX_3$ group fixed in the staggered position, is *ca.* 19 kcal/mol. This type of conformation corresponds to a *col* (saddle point) in the potential energy. A true potential *maximum* corresponds to both $-CX_3$ groups being eclipsed. The energy value obtained for this maximum is too large to have any physical meaning.

The values of the torsional force constants in Table 1 were numer.cally computed according to their definitions ($F_\phi = \partial^2 E/\partial\phi^2$ and $F_{\phi\phi'} = \partial^2 E/\partial\phi\partial\phi'$) at the minimum of potential energy. For small deviations from a staggered conformation ($|\phi| < 20°$) the potential minimum is close to a paraboloid:

$$E = \tfrac{1}{2}F_\phi(\phi_{1-2}^2 + \phi_{2-3}^2) + F_{\phi\phi'}\phi_{1-2}\phi_{2-3} + E_{\min}.$$

*Table 1.* Results of semi-empirical calculations for octachloropropane (X = Cl).

| Bond lengths (Å) | Bond angles (°) |
|---|---|
| C − C (1.513)[a] = 1.594 | ∠CCC (110.0) = 120.0 |
| C − X (1.760) = 1.778 (in $-CX_3$) | ∠CCX (109.5) = 113.7 (in $-CX_3$) |
| C − X (1.760) = 1.801 (in $>CX_2$) | ∠CCX (109.5) = 107.9 (in $>CX_2$) |

Torsion angles[b] (°)

$\phi(1-2) = \phi(2-3) = 0.0$ (staggered, $C_{2v}$ symmetry)

Torsional force constants [mdyn Å (rad)$^{-2}$]

$F_\phi(1-2) = F_\phi(2-3) = 0.69$ and $F_{\phi\phi'}(1-2, 2-3) = -0.49$

[a] "Normal" values of the parameters are shown in parentheses. For the XCX angles 109.47° were used as "normal" values. [b] $\phi_0 = 60°$ in the expression $V_\phi = (V_0/2)\sum_k\{1 + \cos[3(\phi_{k-2} - \phi_0)]\}$, with $k = 1$ and 3.

## III. CALCULATION OF VIBRATIONAL QUANTITIES

Valence force constants, except for the torsional part of the force field, were taken from the work [13] of Schachtschneider and Snyder. Certain compromises between force-constant values had to be made. The final values selected for octachloropropane are given in Table 2. The diagonal torsional force constant was adjusted (see Sect. V-B).

The normal-coordinate program described by Gwinn [14] was used in computing vibrational frequencies. The molecular model possessed $C_{2v}$ symmetry, and according to Herzberg [15] the assignment of frequencies is: $A_1(9)$, $A_2(5)$, $B_1(7)$, and $B_2(6)$.

Mean amplitudes of vibration ($u$) and vibrational correction terms ($K$ and $D$) were calculated as explained in Ref. 16. Their values are found in Table 4.

Some of these quantities are quite sensitive to the value of the diagonal torsional force constant, which have been adjusted to fit the experimental intensities (Sect. V-B). In Table 5 are shown torsional frequencies and mean amplitudes of vibration corresponding to different values of the diagonal torsional force constant $F_\phi$, with the torsional interaction constant ($F_{\phi\phi'}$) fixed at zero value.

According to the semi-empirical calculations (Table 1), the value of the torsional interaction constant is negative and comparable in magnitude to the value of the diagonal element ($F_\phi$). Although the values of the torsional frequencies depend on the value of $F_{\phi\phi'}$, it will be shown that the $u$ and $K$ values are less dependent on the value of the interaction constant.

For *high* temperatures and *low* values of the torsional frequencies ($\omega_1$ and $\omega_2$) the following relations are approximately valide:
$u^2 \simeq (a_1/\omega_1)^2 + (a_2/\omega_2)^2 + u_0^2$ and $K \simeq (b_1/\omega_1)^2 + (b_2/\omega_2)^2 + K_0$. (The relations follow from the general formulas [16] for $u$ and $K$ if the conditions above are fulfilled.) The quantities $a$, $b$, $u_0$, and $K_0$ are approximately independent of the values of $\omega_1$ and $\omega_2$.

*Table 2.* Valence force constants for octachloropropane (X = Cl).

| Stretch (mdyn Å$^{-1}$) | | Bend [mdyn Å (rad)$^{-2}$] | |
|---|---|---|---|
| C – C | 4.39 | CCX | 1.17 |
| C – X | 2.76 | XCX | 1.13 |
| | | CCC | 0.90 |

Stretch/stretch (mdyn Å$^{-1}$), C is common

C – C/C – X = 0.73; C – C/C – C = 0.064; and C – X/C – X = 0.496

Stretch/bend [mdyn (rad)$^{-1}$]

C – C is common: C – C/CCX = 0.29; C – C/CCC = 0.35
C – X is common: C – X/CCX = 0.55; C – X/XCX = 0.41
C is common: C – X/XCX = 0.38

Bend/bend [mdyn Å (rad)$^{-2}$]

C – X is common: XCX/XCX = – 0.13, CCX/XCX = – 0.12
C is common: CCX/XCX = – 0.06
C – C is common:
CCC/CCX = + 0.041 (dihedral angle between CCC and CCX is 180°)
CCC/CCX = – 0.024 (dihedral angle between CCC and CCX is 60°)
CCX/CCX = – 0.090 (dihedral angle between CCX angles is 180°)
CCX/CCX = + 0.070 (dihedral angle between CCX angles is 60°)

Torsion[a] [mdynÅ (rad)$^{-2}$]: $F_\phi = 0.36$[b] ($F_{\phi\phi'} = 0$)

[a] The torsional force constants have been defined in the following way: each fragment of type A′ – $C_1$ – $C_2$ – A″ (A = C or Cl) has been assigned an equal torsional force constant. The total force constant ($F_\phi$) for the torsional coordinate $\phi_{i-2}$ (i = 1,3) is thus the sum of *nine* equal contributions. The input to Gwinn's normal-coordinate program demands a separate specification for each torsion fragment. [b] This value was estimated from the electron diffraction data as described in Sect. V-B.

*Table 3.* Fundamental vibrational frequencies $\omega$ ($cm^{-1}$), in octachloropropane. ($C_{2v}$ sym.) X = Cl.

| | | | |
|---|---|---|---|
| $A_2$ | 48, Torsion (3)[a] | $A_2$ | 272, XCX(3)+CCX(3) |
| $B_2$ | 62, Torsion (3+2)[b] | $B_2$ | 313, CCX(2+3)+C−X(2)[d] |
| $A_1$ | 77, CCX (3)[c] | $A_1$ | 353,[e] XCX(2)+CCC+C−X(2) |
| $B_2$ | 133, CCX(3+2) | $B_1$ | 389, XCX(3) |
| $A_2$ | 166, CCX(2+3) | $A_1$ | 419, C−X(2+3)+XCX(3) |
| $B_1$ | 177, CCX(2+3) | $B_1$ | 646, C−X(3)+CCX(2) |
| $A_1$ | 188, XCX(3)+CCX(3) | $A_1$ | 738, C−X(2+3) |
| $B_1$ | 202, CCX(3)+XCX(3) | $B_2$ | 743, C−X(2+3) |
| $A_2$ | 208, CCX(3+2)+XCX(3) | $B_1$ | 796, C−X(3+2) |
| $A_1$ | 221, XCX(2+3) | $A_2$ | 812, C−X(3) |
| $B_2$ | 242, XCX(3) | $B_2$ | 866, C−X(3+2) |
| $B_1$ | 263, XCX(3) | $A_1$ | 869, C−C+C−X(3) |
| $A_1$ | 265, XCX(3+2) | $A_1$ | 898, C−X(3)+C−C |
| | | $B_1$ | 1175, C−C+C−X(3) |

The value of $\omega(cm^{-1})$ and the species which $\omega$ belongs to have been given. In addition, an *approximate* interpretation of the modes have been suggested. [a] (3) means that large displacements are mainly found in $-CX_3$ groups. [b] (3+2) means large displacements in $-CX_3$ groups and smaller displacements in the group $>CX_2$. [c] CCX(or CCC, XCX) means bending of this type of bond angle. [d] C−X (or C−C) means stretching of this kind of bond. [e] the combination XCX(2)+CCC+C−X(2) thus means: large deformation of the XCX angle in the group $>CX_2$+bending of the angle CCC+stretching of the C−X bonds in the $>CX_2$ group. The largest contribution is always mentioned first.

The torsional frequencies, calculated for different values of $F_{\phi\phi'}$, with $F_\phi = 0.36$ mdyn Å $(rad)^{-2}$, have been shown in Fig. 2. For large negative values of $F_{\phi\phi'}$, $\omega_1(A_2)$ is greater than $\omega_2(B_2)$, while $\omega_1(A_2)$ is smaller than $\omega_2(B_2)$ if the value of $F_{\phi\phi'}$ is greater than *ca.* −0.18 mdyn Å $(rad)^{-2}$. Starting with zero value for $F_{\phi\phi'}$, a negative value of $F_{\phi\phi'}$ of *ca.* −0.26 mdyn Å $(rad)^{-2}$ leads to the effect that $\omega_1(A_2)$ is decreased by *ca.* 11 % and $\omega_2(B_2)$ is increased by

*Table 4.* Mean amplitudes of vibration ($u$) and vibrational correction terms ($K$ and $D$) for octachloropropane at 160 °C, X = Cl.

| Dist. Type | Dist. (Å)[a] | $u$-value (Å) | $K$-value (Å) | $D$-value (Å)[b] |
|---|---|---|---|---|
| C−C | (1.66) | 0.0567 | 0.0042 | −0.0022 |
| $C_2-X_2$ | (1.81) | 0.0622 | 0.0071 | −0.0049 |
| $C_1-X_1$ | (1.76) | 0.0599 | 0.0134 | −0.0114 |
| $C_1-X_1'$ | (1.76) | 0.0599 | 0.0134 | −0.0114 |
| $C_1\cdots C_3$ | (2.83) | 0.0803 | 0.0024 | −0.0001 |
| $C_2\cdots X_1'$ | (2.81) | 0.0777 | 0.0103 | −0.0082 |
| $C_2\cdots X_1$ | (2.81) | 0.0777 | 0.0107 | −0.0085 |
| $C_1\cdots X_2$ | (2.72) | 0.0803 | 0.0059 | −0.0035 |
| $X_1'\cdots X_1''$ | (2.85) | 0.0733 | 0.0191 | −0.0167 |
| $X_1\cdots X_1'$ | (2.85) | 0.0833 | 0.0196 | −0.0172 |
| $X_2'\cdots X_2''$ | (2.97) | 0.0791 | 0.0083 | −0.0062 |
| $C_1\cdots X_3$(a) | (4.35) | 0.0826 | 0.0040 | −0.0024 |
| $C_1\cdots X_3'$(g) | (3.46) | 0.1508 | 0.0071 | −0.0005 |
| $X_1\cdots X_2'$(g) | (3.24) | 0.1608 | 0.0103 | −0.0024 |
| $X_1'\cdots X_2'$(g) | (3.24) | 0.1601 | 0.0100 | −0.0021 |
| $X_1'\cdots X_2''$(a) | (4.35) | 0.0835 | 0.0073 | −0.0057 |
| $X_1\cdots X_3$(AA) | (5.58) | 0.1196 | 0.0044 | −0.0018 |
| $X_1\cdots X_3'$(AG) | (5.06) | 0.1547 | 0.0043 | +0.0004 |
| $X_1'\cdots X_3''$(GG) | (4.24) | 0.2496 | 0.0054 | +0.0093 |
| $X_1'\cdots X_3'$(GG) | (3.14) | 0.2564 | 0.0176 | +0.0033 |

The force constants in Table 2 were used. [a] $C_{2v}$ symmetry was assumed, and $\tau$(tilt) = 0°. [b] $D = R_\alpha - R_a = u^2/R - K$.

*Table 5.* Vibrational quantities in octachloropropane; torsional frequencies and $u$ values (at 160 °C), X = Cl. See also Tables 2, 3, and 4.

| $F_\phi$ [mdyn Å (rad)$^{-2}$] | 0.18 | 0.36 | 0.68 |
|---|---|---|---|
| Torsional frequencies (cm$^{-1}$) | | | |
| | 38($A_2$) | 48($A_2$) | 65($A_2$) |
| | 50($B_2$) | 62($B_2$) | 82($B_2$) |
| $u$-Values (Å) for X···X distances | | | |
| $X_1 \cdots X_2$ (*gauche*) | 0.178 | 0.161 | 0.144 |
| $X_1 \cdots X_2$ (*anti*) | 0.084 | 0.084 | 0.083 |
| $X_1 \cdots X_3$(AA) | 0.120 | 0.120 | 0.120 |
| $X_1 \cdots X_3'$(AG) | 0.165 | 0.155 | 0.145 |
| $X_1' \cdots X_3''$(GG) | 0.293 | 0.250 | 0.209 |
| $X_1' \cdots X_3'$(GG) | 0.276 | 0.256 | 0.238 |

*ca.* 13 %. According to the semi-empirical calculations (Table 1) such a large negative value of $F_{\phi\phi'}$ is not unlikely. Unfortunately, the formulas above for the $u$ and $K$ values are not sensitive to such changes in the $\omega$ values. The decrease in $\omega_1$ will increase the value of the $\omega_1^{-2}$ term, but that change will be approximately compensated by the decrease in the $\omega_2^{-2}$ term, due to the increase in $\omega_2$. The effect is thus *ca.* 5 %, or less, for typical $u$ values.

A change in the *diagonal* force constant ($F_\phi$) on the other hand, will increase or decrease the values of $\omega_1$ and $\omega_2$ simultaneously (see Table 5).

It is thereby demonstrated that the value of $F_{\phi\phi'}$ is not critical in computing $u$ and $K$ values. However, the absolute value of the difference between the torsional frequencies is *decreased* for large negative values of $F_{\phi\phi'}$ (Fig. 2).

The most probable values of the torsional frequencies are thus expected in the range 45 – 65 cm$^{-1}$.

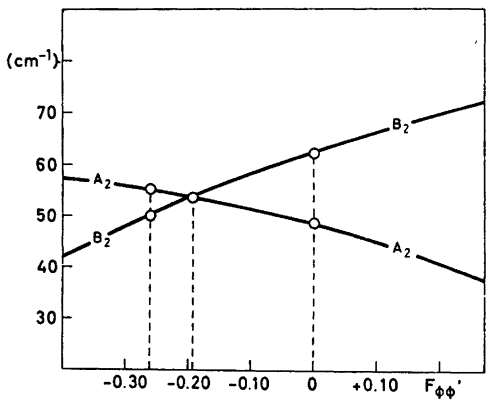


*Fig. 2.* Torsional frequencies (cm$^{-1}$) in octachloropropane calculated for different values of the interaction-force constant $F_{\phi\phi'}$. The remainder of the force constants are found in Table 2. $F_{\phi\phi'}$ in mdyn Å (rad)$^{-2}$.

## IV. EXPERIMENTAL AND DATA REDUCTION

Octachloropropane was obtained from "K & K" laboratories. The commercial sample was purified by recrystallization. The final melting point was 159 – 160 °C.

Electron diffraction photographs were made at a nozzle temperature of 160 °C in the Oslo apparatus,[17] under conditions summarized below.

| | | |
|---|---|---|
| Nozzle-to-plate distance (mm) | 480.4 | 200.5 |
| Electron wavelength (Å) | 0.06458 | 0.06458 |
| Number of plates | 4 | 4 |
| Range of data, in $s$ (Å$^{-1}$) | 1.50 – 19.75 | 7.25 – 44.50 |
| Data interval, $\Delta s$ (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 +0.10 % in the $s$-scale. The data were reduced in the usual way [18] 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.

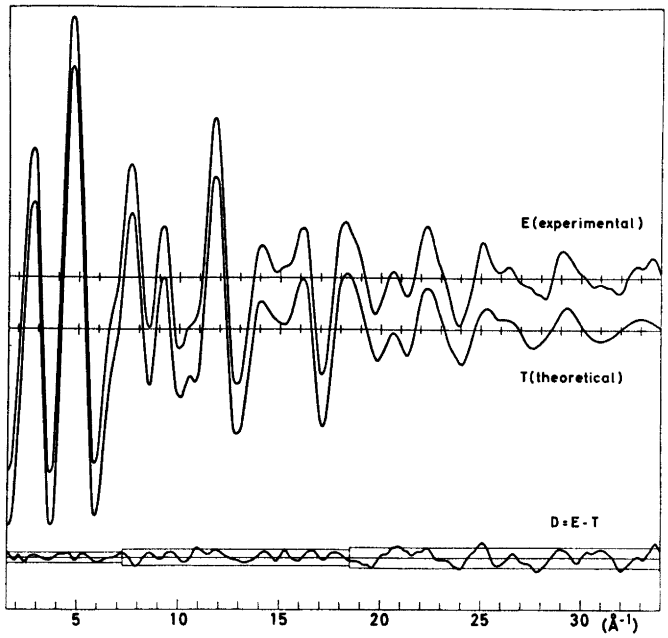


*Fig. 3.* Experimental (E) and theoretical (T) intensity curves for octachloropropane at *ca.* 160 °C, corresponding to the final least-squares parameters. Curve D represents E − T, and the straight lines give the experimental uncertainty ( ± 3 × experimental standard deviation).

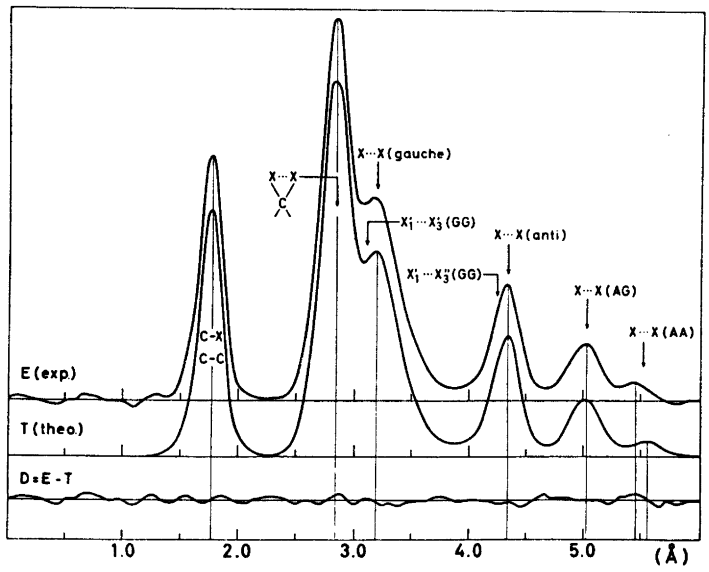


*Fig. 4.* Radial distribution curves for octachloropropane at 160 °C. Experimental (E) and theoretical (T) radial distribution curves, and difference curve (D). The RD curves were calculated from the intensities of Fig. 3 using an artificial demping constant equal to 0.0020 Å².

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 method [19] using Hartree-Fock atomic potentials.[20]

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

## V. STRUCTURE ANALYSIS

From the experimental RD curve (Fig. 4), before refinements had been started, two important conclusions were reached: (1) the C–C bond lengths have to be very long; (2) the stable conformation of the molecule possesses an internuclear Cl···Cl distance *ca.* 5.5 Å long (X···X(AA) in Fig. 4). Such a long Cl···Cl distance is only possible if both $-CCl_3$ groups are nearly staggered relative to the $>CCl_2$ group.

### A. Least-squares refinements

The geometrical model for the molecule was constructed with the following assumptions:

(1) the plane of the $CX_2$ group (X = Cl) is perpendicular to the plane of the C atoms and bisects the CCC angle;

(2) the two $C-CX_3$ groups are equal;

(3) the $CX_3$ groups possess $C_{3v}$ symmetry, while the $C-CX_3$ groups possess $C_s$ symmetry.

Models were refined in terms of the following structural parameters; *bond lengths:* $r$(C–C), $r$(C–X, in $CX_3$), and r(C–X, in $CX_2$); *bond angles:* ∠CCC, ∠CCX (in $C-CX_3$), and ∠CCX (in $>CX_2$); *torsion angles of the $-CX_3$ groups relative to the $<CX_2$ group:* $\phi_{1-2}=\phi(C_1-C_2)$ and $\phi_{2-3}=\phi(C_2-C_3)$; *and a tilt angle ($\tau$) within the $C-CX_3$ groups.*

The values of the $\phi$ angles are both *zero* when the atoms $X_1-C_1-C_2-C_3-X_3$ are coplanar, corresponding to a *staggered* model.

The tilt angle ($\tau$) was defined as a rotation of the $CX_3$ group around an axis through the C atom of that group, the axis being perpendicular to the CCC plane. The two $CX_3$ groups were assigned tilt angles as follows: $\tau_1=\tau(C(1)\text{-}X_3)=+\tau$ and $\tau_3=\tau[C(3)X_3]=-\tau$. For $\tau=0°$ the $C-CX_3$ groups posses $C_{3v}$ symmetry. Starting with $C_{3v}$ symmetry and a given value for $\angle C_2CX$ ($\angle C_2C_1X=\angle C_2C_3X$), a *negative* value of $\tau$ leads to a *decrease* in the values of $\angle C_2C_1X_1$ and $\angle C_2C_3X_3$, while the value of $\angle C_2C_1X_1'$ ($=\angle C_2C_1X_1''=\angle C_2C_3X_3'=\angle C_2C_3X_3''$) *increases*. Negative values of $\tau$ thus lead to *longer* $X_1'\cdots X_3'$ and $X_1''\cdots X_3''$ internuclear distances.

For $\tau\neq 0°$ the two different CCX angles of the $C-CX_3$ groups were not refined independently. The angle $C_2C_1X_1$ ($=C_2C_3X_3$) was chosen as the *independent* parameter.

The angles, $\phi$ and $\tau$, were never refined simultaneously. If $\tau$ was refined, then the value of $\phi$ was fixed at zero degrees, and *vice versa.*

Non-bonded internuclear distances were computed as dependent quantities, restricted under the constraints of geometrically consistent $r_\alpha$ parameters.[21,22]

### B. Determination of torsional force constants

Mean amplitudes of vibration ($u$) and perpendicular amplitude correction coefficients ($K$) are easily calculated if a reasonable force field is known for the molecule (see Sect. III). The

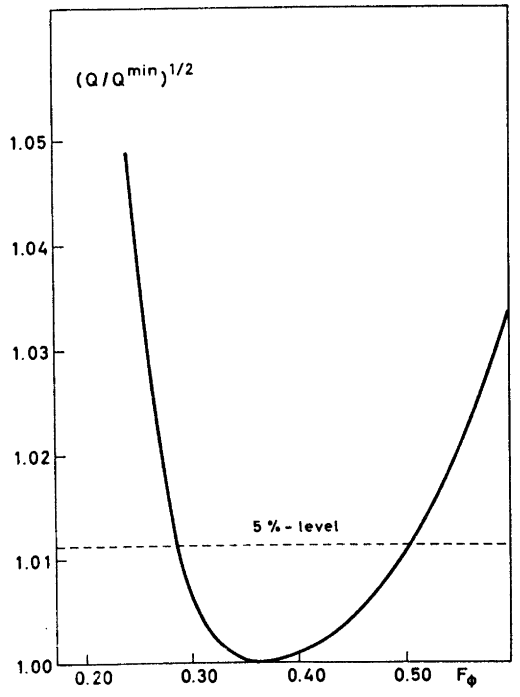


*Fig. 5.* The quantity $R^* = (Q/Q^{min})^{\frac{1}{2}}$ as a function of the diagonal torsional force constant $F_\phi$. $Q=\mathbf{V'PV}$: the error sum. V is the residual (experimental intensity minus calculated intensity).

values of the torsional force constants [$F_\phi(1-2)=F_\phi(2-3)=F_\phi$ and $F_{\phi\phi'}(1-2;2-3)$] for octachloropropane had not been determined prior to this investigation. However, the diagonal part of the torsional force field ($F_\phi$) can be determined from the electron-diffraction data. Torsional modes contribute substantially to the $u$ and $K$ values of several internuclear distances in a molecule like octachloropropane. Such $u$ values are those listed in Table 5. One torsional mode ($\omega(A_2)=48$ cm$^{-1}$) alone contributes more than 60 % to the $u$ value of $X_1'\cdots X_3''$.

The value of $F_\phi$ was determined as follows: $u$ and $K$ values for different values of $F_\phi$ were calculated, and then included in the least-squares refinements. The value of $F_\phi$ which leads to a minimum in the error sum ($Q=$ **V'PV**) was obtained. In each least-squares run all geometry variables of a staggered model ($\phi_{1-2}=\phi_{2-3}=0°$) were refined. In adjusting the $F_\phi$ value, it is important that as many as possible of the geometry parameters are refined simultaneously. The quantity $(Q/Q^{\min})^{\frac{1}{2}}$ as a function of $F_\phi$ is shown in Fig. 5. The 5 %-significance level, according to Hamiltons $R$-factor test, is also give. The most probable value of $F_\phi$ and the error limits corresponding to the 5 % significance level are: $F_\phi=0.36^{+0.14}_{-0.07}$ mdyn Å (rad)$^{-2}$. The error limits need a few comments:

(1) The error limits do not allow for *systematic* errors within the remainder of the force field. However, the non-torsional part of the force field seems to be quite acceptable. Moreover, the value of the torsional interaction force constant ($F_{\phi\phi'}$) has not been adjusted (see Sect. II).

(2) The nozzle temperature (433 K) was used in calculating vibrational quantities. The relevant temperature for the expanding gas is lower than 433 K. The correct vibrational temperature is not known, however, the *systematic* error introduced in the determination of the torsional force constant may be estimated, as follows. For *high* temperature ($T$) and *low* $F_\phi$ values the following expressions are approximately valid: $u^2\simeq A(T/F_\phi)+u_0^2$ and $K\simeq A'\times(T/F_\phi)+K_0$. $A$, $A'$, $u_0^2$, and $K_0$ are not dependent on $F$'s. $A$ and $A'$ are temperature-independent quantities. Although $u_0^2$ and $K_0$ are temperature-dependent quantities, the present approximative analysis will not take this into consideration. It then follows that the relative error ($\Delta F_\phi/F_\phi$) in $F_\phi$ is approximately equal to the relative error ($\Delta T/T$) in $T$. If the fall in temperature is as large as *ca.* 40 K, then the value of $F_\phi$, as determined here, is *ca.* 10 % too high. A systematic error in the $F_\phi$ value is propagated to the value of the torsional frequencies ($\omega_\phi$), and approximately, $(\Delta\omega_\phi/\omega_\phi)=\frac{1}{2}(\Delta F_\phi/F_\phi)$.

(3) Also the drawing of a background may introduce a *systematic* error in the $F_\phi$ value. After a background correction has been introduced, a new adjustment of the $F_\phi$ value ought to be carried out. However, this type of error is not considered as critical. The errors of type (1) and (2) could be critical.

Until the low torsional frequencies have been directly observed, the value of the interaction constant ($F_{\phi\phi'}$) remains unknown. According to the semi-empirical energy model, the value has to be negative (Sect. II).

## VI. FINAL RESULTS

Parameters from the least-squares refinements and standard deviations ($\sigma$) corrected for correlation [23] in the experimental data are given.

According to the experimental uncertainties (see Fig. 3) the diagonal weights of the intensities in the least-squares refinements ought to be smaller for larger $s$ values. Two diagonal weight schemes, one with constant weight, and one with variable weights corresponding to the experimental uncertainties, were tried. The parameters obtained were practically identical in the two cases. The final parameters correspond to refinements with equal weights for all intensities. However, the data beyond $s=$ 34.0 Å$^{-1}$ were not included in the final refinements.

The final structure parameters are found in Table 6, and parameter-correlation coefficients ($\varrho$) are found in Table 7.

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

Initially the torsion-angle parameter ($\phi$) was refined with $\phi_{1-2}=\phi_{2-3}=\phi$, corresponding to a molecular model possessing $C_2$ symmetry. Refinements of that parameter, before and after background corrections, always yielded values very close to 0° (staggered model) with a

*Table 6.* Structural parameters in octachloropropane (X = Cl).

| Bond lengths ($r_a$) (Å) | Bond angles ($\angle_\alpha$) (°) |
|---|---|
| $r$(C−C) = 1.655(15) | ∠CCC = 119.0(2.0) |
| $r$(C−X, in $CX_3$) = 1.762(6) | ∠CCX (in $-CX_3$) = 110.4(0.5) |
| $r$(C−X, in $CX_2$) = 1.810(20) | ∠CCX (in $>CX_2$) = 104.5(0.5) |

Standard deviations are given in parentheses. The uncertainty (0.14 %) in the $s$-scale has been included in the standard deviations for bond distances. 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 obtained by the least-squares refinements. Bond angles are those of the self-consistent $r_\alpha$ structure. The values correspond to a molecular model with $C_{2v}$ symmetry and a tilt angle of zero.

standard deviation ($\sigma$) larger than the parameter itself. The remaining structure parameters, except for the tilt angle ($\tau = 0°$), were refined simultaneously.

The tilt-angle parameter ($\tau$) was then introduced and refined, while the torsion angles were fixed at staggered values. ($\phi = 0°$) The molecular model then possessed $C_{2v}$ symmetry. The remaining structural parameters were refined simultaneously. The value of $\tau$ found in this way was −0.7° with a standard deviation of 0.8°. Clearly the value of $\tau$ is not significantly different from 0°.

In conclusion, no significant deviations from a molecular model with $C_{2v}$ symmetry were detected. Moreover, the local symmetry of the $C-CX_3$ group is not significantly different from $C_{3v}$.

C−Cl and C−C bonds contribute to the peak in the RD curve at *ca.* 1.5−2.0 Å. Although the contribution from the C−C bond distances is not resolved, the effect of introducing C−C bond lengths different from the most probable value (*ca.* 1.66 Å) is demonstrated in Fig. 6. The two theoretical RD curves correspond to intensity curves obtained by adjusting all structure parameters, except for the C−C bond lengths and the $\phi$ angles.

Except for the region at *ca.* 5.5 Å, the fit between theoretical and experimental radial distribution curves (Fig. 4) is satisfactory. Although the non-bonded distances were restricted under the constraints of $r_\alpha$ parameters, the calculated peak at *ca.* 5.5 Å, corresponding to the $X_1 \cdots X_3$ distance, does not fit the experimental curve well enough. Only harmonic contributions to the vibrational shrinkage corrections were considered in this work, however, the anharmonicity involved could lead to an additional shrinkage for the $X_1 \cdots X_3$ distance. (The harmonic contribution to the shrinkage of $X_1 \cdots X_3$ is *ca.* 0.02 Å).

The fit obtained between theoretical and experimental intensities (Fig. 3), using the $u$ and $K$ values calculated with the force constants of Table 2, is generally quite satisfactory. It is important that the large number of $u$ values do not have to be adjusted as *individual* param-

*Table 7.* Parameter correlation coefficients (100 $\varrho$), X = Cl.

| Parameter | | (1) | (2) | (3) | (4) | (5) | (6) | (7) |
|---|---|---|---|---|---|---|---|---|
| r(C−C) | (1) | 100 | (−13)[a] | (−57) | (−45) | (−16) | (−43) | (−70) |
| r(C−X) in $CX_3$ | (2) | 1[a] | 100 | (−48) | (71) | (14) | (−60) | (−31) |
| ∠CCC | (3) | −51 | −72 | 100 | (−9) | (−34) | (−71) | (69) |
| ∠CCX in $-CX_3$ | (4) | 17 | 91 | −84 | 100 | (7) | (−42) | (20) |
| ∠CCX in $<CX_2$ | (5) | −18 | 4 | 3 | −10 | 100 | (−21) | (10) |
| $r$(C−X) in $CX_2$ | (6) | −45 | −83 | 86 | 89 | −1 | 100 | (49) |
| $\tau$(tilt) | (7) | −43 | −48 | 84 | −67 | 33 | 62 | 100 |
| $u$(C−X)[b] | (8) | 36 | 72 | −72 | 77 | −2 | 84 | −52 |

[a] Two kinds of parameter correlation ($\varrho$) matrixes are presented. The $\varrho$ values in parentheses correspond to a refinement with no $u$ values refined; [b] only *one* $u$-value parameter of this kind (C−X) was refined.

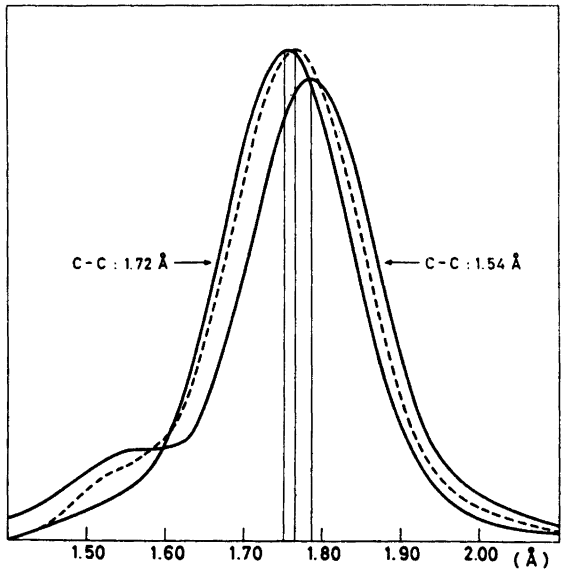


*Fig. 6.* Radial distributions for octachloropropane. The experimental (– – –) RD curve and two theoretical RD curves (C–C = 1.54 Å and 1.72 Å) are shown. The curves were calculated with an artificial demping constant equal to 0.0010 Å$^2$.

eters in the least-squares refinements. However, it ought to be kept in mind that the torsion-dependent $u$ and $K$ values have been adjusted simultaneously by adjusting the torsional force constant $F_\phi$ (Sect. V-B). The $u$ values of Table 4, which combine information from both vibrational spectroscopy and electron diffraction, are considered the final ones for octachloropropane. The vibrationally consistent set of $u$ values in Table 4 is considered more reliable than the individual $u$ values obtained by direct least-squares refinements in the usual way. Direct refinements of $u$ values were also carried out. The results of such refinements were generally not significantly different from the values of Table 4. Only one $u$ value [$u$(C–Cl) = 0.045 Å, $\sigma$ = 0.006 Å], obtained in this way, was significantly different from the value (*ca.* 0.060 Å) of Table 4. Most probably the low value for $u$(C–Cl) is caused by an error in the blackness correction. It is, however, unlikely that such an error is critical for determination of the remaining $u$ values.

## VII. DISCUSSION

Typical C–Cl bond lengths and CCCl bond angles of a C–$CCl_3$ group are found in the ranges 1.76 – 1.77 Å and 110 – 111°, respectively. The structural parameters C–Cl and ∠CCCl of the C–$CCl_3$ groups in octachloropropane are thus quite normal. The C–C bond lengths and the CCC angle are very different from those in propane itself. It is also noteworthy, that the very unfavourable parallel (1:3) Cl···Cl interactions, did not lead to a detectable twist of the –$CCl_3$ groups.

To a large extent the values of the structural parameters, predicted by the semi-empirical model (Table 1), reasonably agree with the experimental findings. Although adjustments in the non-torsional force constants and the "normal" parameters would remove most of the discrepancies, it was felt that results from additional molecules ought to be included, before such corrections were considered. However, the very large diagonal element predicted for the torsional force field ($F_\phi$) would not be much changed by such corrections. The most probable value of $F_\phi$ (0.36 mdyn Å (rad)$^{-2}$) as determined from the electron diffraction data (Sect. V-B), is significantly smaller than the value (0.69) predicted by the semi-empirical model (Sect. II).

It has been demonstrated that the diagonal element of the torsional force field may be

estimated from the gas electron diffraction data. Although the torsional interaction-force constant can not be obtained in this way, the most probable values of the two torsional frequencies have been limited to the range 45 – 65 $cm^{-1}$. It seems that the very low CCCl($A_1$)-bending frequency of 77 $cm^{-1}$ is not unlikely. Perhaps more interesting for the vibrational spectroscopy is the finding that three of the fundamental frequencies of gaseous octachloropropane have to be expected at values less than 100 $cm^{-1}$.

The fundamental vibrational frequencies of octachloropropane have not been observed, but the force constants used in this analysis are consistent with the electron diffraction data. It is, however, not unlikely that the true values of the valence force constants are quite different from those in Table 2. The very long C – C bond lengths and the large CCC angle may be indicative of large anharmonic terms in the force field, resulting in too long C – C bond lengths, as only harmonic contributions to the vibrational corrections were considered in this work.

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