Conformational Analysis. VII. The Molecular Structure and Torsional Oscillations of Gaseous Octachloropropane (C₃Cl₈) 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 (2σ). The following values for bond lengths (r) and bond angles (∠) were obtained: \( r(C=Cl) = 1.657(30) \), \( r(1-6, \text{in } -CCl_3) = 1.764(12) \), \( r(C-Cl, \text{in } >CCl_3) = 1.812(40) \), \( ∠CCC = 119.0^\circ(40) \), \( ∠CCCI (\text{in } -CCl_3) = 110.4^\circ(1.0) \), and \( ∠CCCI (\text{in } >CCl_3) = 104.5^\circ(1.0) \). Non-bonded internuclear distances were computed as dependent quantities, restricted under the constraints of geometrically consistent r parameters.

It is noteworthy that the two energetically unfavourable parallel (1:3) Cl-Cl interactions did not lead to a twist of the -CCl₃ groups. The -CCl₃ groups are staggered (C₃v symmetry) relative to the >CCl₃ group. However, the values of the parameters \( r(C-Cl) \) and ∠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:

(BrCH₂-CHBr-CH₂Br), (BrH₄C-CH₂-CH₃Br), (CiH₄C-CHCl-CH₂Cl). Also molecules with CH₂X (X = Cl or H) groups bonded to the central C atom of a C-C-C skeleton have been studied: [C(CH₃Cl)₄], [(CH₃)₂C(CH₄Cl)₂], [(CH₃)₂C(CH₂Cl)₂], [(CH₃)₄C(CH₂Cl)₂].

General information relevant to this investigation and to the electron diffraction method 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. With heavily chlorinated propanes most of the staggered conformers are unstable because of parallel (1:3) Cl-Cl interaction 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 it is known that the C-C bond length is longer (1.564 ± 0.014 Å)
than that of ethane and propane, while the structural parameters of the CCl₃ groups in hexachloroethane are normal, (C–Cl = 1.769 ± 0.003 Å and ∠CCC = 110.0 ± 0.5°). From this information and a feeling that the results obtained for octachloropropane would be relevant for other heavily substituted molecules, 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 (Vₙ, a, b, c, and d) were taken from the work of Abraham and Parry. 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 (τ) was not adjusted. (τ = 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 Cᵥv, corresponding to staggered –CX₃ groups (ϕ = 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 –CX₃ group eclipsing the >CX₄ group, and the other –CX₃ 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 –CX₃ 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 numerically computed according to their definitions (Fϕ = ∂²E/∂ϕ² and Fϕϕ = ∂²E/∂ϕ∂ϕ′) at the minimum of potential energy. For small deviations from a staggered conformation (|ϕ| < 20°) the potential minimum is close to a paraboloid:

\[ E = \frac{1}{2} F_ϕ (ϕ_{1-2}^2 + ϕ_{2-3}^2) + F_{ϕϕ} (ϕ_{1-2} ϕ_{2-3}) + E_{\text{min}} \]

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–C (1.513)</td>
<td>(110.0) = 120.0</td>
</tr>
<tr>
<td>C–X (1.760)</td>
<td>(109.5) = 113.7 (in –CX₃)</td>
</tr>
<tr>
<td>C–C (1.760)</td>
<td>(109.5) = 107.9 (in &gt;CX₄)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Torsion angles (°)</th>
<th>[mdyn Å (rad)⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ϕ(1–2) = ϕ(2–3) = 0.0 (staggered, Cᵥv symmetry)</td>
<td></td>
</tr>
<tr>
<td>Torsional force constants</td>
<td></td>
</tr>
<tr>
<td>Fₖ(1–2) = Fₖ(2–3) = 0.69 and Fₖₖ(1–2, 2–3) = −0.49</td>
<td></td>
</tr>
</tbody>
</table>

a “Normal” values of the parameters are shown in parentheses. For the XCX angles 109.47° were used as “normal” values. b ϕ = 60° in the expression \( V_ϕ = (V_ϕ/2)\sum_1^k \cos(3(ϕ_{k–1}^– ϕ_{k})) \), 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 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 was used in computing vibrational frequencies. The molecular model possessed $C_{1v}$ symmetry, and according to Herzberg the assignment of frequencies is: $A_i(9)$, $A_s(5)$, $B_i(7)$, and $B_s(6)$.

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 ($F_\phi^\Gamma$) 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 $F_\phi^\Gamma$, 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 valid:

$u^2 = (a_1/\omega_1)^2 + (a_2/\omega_2)^2 + u_0^2$ and $K = (b_1/\omega_1)^2 + (b_2/\omega_2)^2 + K_\phi$. (The relations follow from the general formulas for $u$ and $K$ if the conditions above are fulfilled.) The quantities $a$, $b$, $u_0$, and $K_\phi$ are approximately independent of the values of $\omega_1$ and $\omega_2$.

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

<table>
<thead>
<tr>
<th>Stretch (mdyn Å⁻¹)</th>
<th>Bend [mdyn Å (rad)⁻²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C−C 4.39</td>
<td>CCX 1.17</td>
</tr>
<tr>
<td>C−X 2.76</td>
<td>XCX 1.13</td>
</tr>
<tr>
<td></td>
<td>CCC 0.90</td>
</tr>
</tbody>
</table>

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:

CCX/CCX = +0.041 (dihedral angle between CCC and CCX is 180°)

CCX/CCX = −0.024 (dihedral angle between CCC and CCX is 80°)

CCX/CCX = −0.090 (dihedral angle between CCX angles is 180°)

CCX/CCX = +0.070 (dihedral angle between CCX angles is 60°)

Torsion [mdynÅ (rad)⁻²]: $F_\phi = 0.36^d$ ($F_\phi^\Gamma = 0$)

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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 $\phi_{i−1}$ (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. $^d$ 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.) $X=Cl$.

<table>
<thead>
<tr>
<th>$A_2$</th>
<th>48, Torsion (3)$^a$</th>
<th>$A_3$</th>
<th>272, XCC(3) + CCX(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_2$</td>
<td>62, Torsion (3 + 2)$^b$</td>
<td>$B_3$</td>
<td>313, CXX(2 + 3) + C$-X$(2)$^d$</td>
</tr>
<tr>
<td>$A_1$</td>
<td>77, CXX(3)$^c$</td>
<td>$A_1$</td>
<td>353,$^c$ XCC(2) + CCC + C - X(2)</td>
</tr>
<tr>
<td>$B_2$</td>
<td>133, CXX(3 + 2)</td>
<td>$B_2$</td>
<td>389, XCC(3)</td>
</tr>
<tr>
<td>$A_1$</td>
<td>166, CXX(3 + 2)</td>
<td>$A_1$</td>
<td>419, C - X(2 + 3) + XCC(3)</td>
</tr>
<tr>
<td>$B_2$</td>
<td>177, CXX(3 + 2)</td>
<td>$B_1$</td>
<td>646, C - X(3) + CXX(2)</td>
</tr>
<tr>
<td>$A_1$</td>
<td>188, XCC(3) + CCX(3)</td>
<td>$A_1$</td>
<td>738, C - X(2 + 3)</td>
</tr>
<tr>
<td>$B_2$</td>
<td>202, CXX(3) + XCC(3)</td>
<td>$B_2$</td>
<td>743, C - X(2 + 3)</td>
</tr>
<tr>
<td>$A_1$</td>
<td>208, CXX(3 + 2) + XCC(3)</td>
<td>$B_1$</td>
<td>796, C - X(3 + 2)</td>
</tr>
<tr>
<td>$A_2$</td>
<td>221, XCC(2 + 3)</td>
<td>$A_2$</td>
<td>812, C - X(3)</td>
</tr>
<tr>
<td>$B_2$</td>
<td>242, XCC(3)</td>
<td>$B_2$</td>
<td>866, C - X(3 + 2)</td>
</tr>
<tr>
<td>$A_1$</td>
<td>283, XCC(3)</td>
<td>$A_1$</td>
<td>898, C - X(3) + C - C</td>
</tr>
<tr>
<td>$A_2$</td>
<td>265, XCC(3 + 2)</td>
<td>$B_1$</td>
<td>1175, C - C + C - X(3)</td>
</tr>
</tbody>
</table>

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 $\text{-CX}_2$ groups. $^b$ (3 + 2) means large displacements in $\text{-CX}_3$ groups and smaller displacements in the group $\text{>CX}_2$. $^c$ CCX (or CCC, XCC) means bending of this type of bond angle. $^d$ $\text{C-X}$ (or $\text{C-C}$) means stretching of this kind of bond. $^e$ The combination XCC(2) + CCC + C - X(2) thus means; large deformation of the XCC angle in the group $\text{>CX}_3$ + bending of the angle CCC + stretching of the C - X bonds in the $\text{>CX}_2$ 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 $F_{\phi\phi'}$, $\omega_1(A_1)$ 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 $\omega_1(A_1)$ 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.

<table>
<thead>
<tr>
<th>Dist. Type</th>
<th>Dist. (Å)$^a$</th>
<th>$u$-value (Å)</th>
<th>$K$-value (Å)</th>
<th>$D$-value (Å)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C - C</td>
<td>(1.66)</td>
<td>0.0567</td>
<td>0.0042</td>
<td>-0.0022</td>
</tr>
<tr>
<td>C$-X_2$</td>
<td>(1.81)</td>
<td>0.0622</td>
<td>0.0071</td>
<td>-0.0049</td>
</tr>
<tr>
<td>C$-X_1$</td>
<td>(1.76)</td>
<td>0.0599</td>
<td>0.0134</td>
<td>-0.0114</td>
</tr>
<tr>
<td>C$-X_1'$</td>
<td>(1.76)</td>
<td>0.0599</td>
<td>0.0134</td>
<td>-0.0114</td>
</tr>
<tr>
<td>C$_1$...C$_3$</td>
<td>(2.83)</td>
<td>0.0803</td>
<td>0.0024</td>
<td>-0.0001</td>
</tr>
<tr>
<td>C$_1$...X$_1'$</td>
<td>(2.81)</td>
<td>0.0777</td>
<td>0.0103</td>
<td>-0.0082</td>
</tr>
<tr>
<td>C$_1$...X$_1$</td>
<td>(2.81)</td>
<td>0.0777</td>
<td>0.0107</td>
<td>-0.0085</td>
</tr>
<tr>
<td>C$_1$...X$_2$</td>
<td>(2.72)</td>
<td>0.0803</td>
<td>0.0059</td>
<td>-0.0035</td>
</tr>
<tr>
<td>X$_1$...X$_1''$</td>
<td>(2.55)</td>
<td>0.0733</td>
<td>0.0191</td>
<td>-0.0167</td>
</tr>
<tr>
<td>X$_1$...X$_1'$</td>
<td>(2.85)</td>
<td>0.0833</td>
<td>0.0186</td>
<td>-0.0172</td>
</tr>
<tr>
<td>X$_1''$...X$_1'$</td>
<td>(2.97)</td>
<td>0.0791</td>
<td>0.0083</td>
<td>-0.0062</td>
</tr>
<tr>
<td>C$_1$...X$_1''(a)$</td>
<td>(4.35)</td>
<td>0.0826</td>
<td>0.0040</td>
<td>-0.0024</td>
</tr>
<tr>
<td>C$_1$...X$_1'(g)$</td>
<td>(3.46)</td>
<td>0.1508</td>
<td>0.0071</td>
<td>-0.0005</td>
</tr>
<tr>
<td>X$_1''$...X$_1'(g)$</td>
<td>(3.24)</td>
<td>0.1608</td>
<td>0.0103</td>
<td>-0.0024</td>
</tr>
<tr>
<td>X$_1''$...X$_1'(a)$</td>
<td>(4.35)</td>
<td>0.0835</td>
<td>0.0073</td>
<td>-0.0057</td>
</tr>
<tr>
<td>X$_1''$...X$_1''(AA)$</td>
<td>(5.58)</td>
<td>0.1196</td>
<td>0.0044</td>
<td>-0.0018</td>
</tr>
<tr>
<td>X$_1''$...X$_1''(AG)$</td>
<td>(5.06)</td>
<td>0.1547</td>
<td>0.0045</td>
<td>+0.0004</td>
</tr>
<tr>
<td>X$_1''$...X$_1''(GG)$</td>
<td>(4.24)</td>
<td>0.2496</td>
<td>0.0054</td>
<td>+0.0093</td>
</tr>
<tr>
<td>X$_1''$...X$_1''(GG)$</td>
<td>(3.14)</td>
<td>0.2564</td>
<td>0.0176</td>
<td>+0.0033</td>
</tr>
</tbody>
</table>

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

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

\[
\begin{align*}
F_\phi \text{ [mdyn Å (rad)^{-2}]} & \quad 0.18 & \quad 0.36 & \quad 0.68 \\
\text{Torsional frequencies (cm}^{-1}) & \quad 38(A_2) & \quad 48(A_2) & \quad 65(A_2) \\
& \quad 50(B_2) & \quad 62(B_2) & \quad 82(B_2) \\
\text{\( u \)-Values (Å) for X⋯X distances} & \quad X_1⋯X_2 (gauche) & 0.178 & 0.161 & 0.144 \\
& \quad X_1⋯X_2 (anti) & 0.084 & 0.084 & 0.083 \\
& \quad X_1⋯X_2 (A\text{A}) & 0.120 & 0.120 & 0.120 \\
& \quad X_1⋯X_2' (AG) & 0.165 & 0.155 & 0.145 \\
& \quad X_1'⋯X_2'' (GG) & 0.293 & 0.250 & 0.209 \\
& \quad X_1'′⋯X_2''' (GG) & 0.276 & 0.256 & 0.238 \\
\end{align*}
\]

c. 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\(^{-1}\).

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) \( \geq 480.4 \) \( \leq 200.5 \)
- Electron wavelength (Å) \( \geq 0.06458 \) \( \leq 0.06458 \)
- Number of plates 4
- Range of data, in \( s (\text{Å}^{-1}) \) \( \geq 1.50 – 19.75 \) \( \leq 7.25 – 44.50 \)
- Data interval, \( \Delta s (\text{Å}^{-1}) \) \( \geq 0.125 \) \( \leq 0.250 \)
- Estimated uncertainty in the \( s \)-scale \( \geq 0.14 \% \) \( \leq 0.14 \% \)

The electron wavelength was determined by calibration against gold and corrected by an experiment with \( \text{CO}_2 \) 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.

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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}.

Fig. 3. Experimental (E) and theoretical (T) intensity curves for octachloropropane at ca. 180 °C, corresponding to the final least-squares parameters. Curve D represents E - T, and the straight lines give the experimental uncertainty (± 3 x experimental standard deviation).

Fig. 4. Radial distribution curves for octachloropropane at 180 °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 dumping constant equal to 0.0020 Å⁻¹.

The final experimental intensity curve is shown in Fig. 3. The intensities have been modified by $s/|C|^2$. The scattering amplitudes were calculated by the partial-wave method using Hartree-Fock atomic potentials.

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 –CCI groups are nearly staggered relative to the >CCI group.

A. LEAST-SQUARES REFINEMENTS

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

1. the plane of the CX$_3$ 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 $C_{3}$ symmetry.

Models were refined in terms of the following structural parameters: bond lengths, $\tau$(C–C), $\tau$(C–X, in CX$_3$), and $\tau$(C–X, in CX$_3$); bond angles: $\angle$CCC, $\angle$CCX (in C–CX$_3$), and $\angle$CCX (in >CX$_3$); torsion angles of the –CX$_3$ groups relative to the <CX$_3$ 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$_2$ 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)–X$_1$) = +\tau and $\tau_2 = \tau$(C(3)–X$_2$) = –\tau. For $\tau = 0^\circ$ the C–CX$_3$ groups possess $C_{3v}$ symmetry. Starting with $C_{3v}$ symmetry and a given value for $\angle$C$_2$C$_3$X ($\angle$C$_2$C$_3$X = $\angle$C$_2$C$_3$X), a negative value of $\tau$ leads to a decrease in the values of $\angle$C$_2$C$_3$X$_1$ and $\angle$C$_2$C$_3$X$_2$, while the value of $\angle$C$_2$C$_3$X$_1$ increases. Negative values of $\tau$ thus lead to longer X$_1$···X$_2$ and X$_1$···X$_3$ internuclear distances.

For $\tau = 0^\circ$ the two different CCX angles of the C–CX$_3$ groups were not refined independently. The angle C$_1$C$_1$X$_1$ (C$_1$C$_1$X$_1$) 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 $r_a$ parameters.

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

\[ (\frac{Q}{Q_{\text{min}}}^{1/2}) \]

Fig. 5. The quantity $R^* = (Q/Q_{\text{min}})^{1/2}$ as a function of the diagonal torsional force constant $F_\phi$. $Q = V_P V$: 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 \( (\omega(A_2) = 48 \text{ cm}^{-1}) \) alone contributes more than 60% to the \( u \) value of \( X_1'\cdots X_2'' \).

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 \( (Q = \text{VPY}) \) was obtained. In each least-squares run all geometry variables of a staggered model \( (\phi_{1-2} = \phi_{2-3} = 0^\circ) \) 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 \( (Q/Q_{\text{min}})^{1/4} \) 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: \( F_{\phi} = 0.30^{+2.14}_{-0.07} \) 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 \( (433 \text{ K}) \) 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: \( u^2 \approx A(T/F_{\phi}) + u_0^2 \) and \( K \approx A' \times (T/F_{\phi}) + K_0 + A + A' \times u_0^2 \) and \( K_0 \) are not dependent on \( F_{\phi}'s \). \( A \) 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 \( (dT/T) \) is approximately equal to the relative error \( (dS/F_{\phi}) \) in \( F_{\phi} \).

(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 \( ^{13} \) 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 \( s = 34.0 \text{ Å}^{-2} \) were not included in the final refinements.

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

Non-bonded distances were restricted under the geometrical constraints of \( r_\sigma \) parameters, by including correction terms \( D = r_\sigma - r_\sigma \) \( (D = u^2/r-K) \) 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 \( 0^\circ \) (staggered model) with a

Table 6. Structural parameters in octachloropropane ($X = \text{Cl}$).

<table>
<thead>
<tr>
<th>Bond lengths ($r_a$) (Å)</th>
<th>Bond angles ($\angle_a$) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r(\text{C} - \text{C})$ = 1.655(15)</td>
<td>$\angle \text{CCC} = 119.0(2.0)$</td>
</tr>
<tr>
<td>$r(\text{C} - \text{X}, \text{in } \text{CX}_3)$ = 1.762(6)</td>
<td>$\angle \text{CCX} (\text{in } - \text{CX}_4) = 110.4(0.5)$</td>
</tr>
<tr>
<td>$r(\text{C} - \text{X}, \text{in } \text{CX}_3)$ = 1.810(20)</td>
<td>$\angle \text{CCX} (\text{in } &gt; \text{CX}_4) = 104.5(0.5)$</td>
</tr>
</tbody>
</table>

Standard deviations are given in parentheses. The uncertainty (0.14 %) in the $a$-scale has been included in the standard deviations for bond distances. An experiment with CO$_2$ gave a correction of +0.1 % in the $a$-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 $r_a$ 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 ($\tau = 0^\circ$), were refined simultaneously.

The tilt-angle parameter ($\tau$) was then introduced and refined, while the torsion angles were fixed at staggered values. ($\phi = 0^\circ$) The molecular model then possessed $C_{2v}$ symmetry. The remaining structural parameters were refined simultaneously. The value of $\tau$ found in this way was $-0.7^\circ$ 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 $C_{2v}$.

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 $r_a$ parameters, the calculated peak at ca. 5.5 Å, corresponding to the $X_1\cdots X_4$ 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 $X_1\cdots X_4$ distance. (The harmonic contribution to the shrinkage of $X_1\cdots X_4$ 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 $q$), $X = \text{Cl}$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
<th>(5)</th>
<th>(6)</th>
<th>(7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r(\text{C} - \text{C})$</td>
<td>1</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r(\text{C} - \text{X})$ in CX$_3$</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\angle \text{CCC}$</td>
<td>-51</td>
<td>91</td>
<td>-84</td>
<td>100</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\angle \text{CCX}$ in - CX$_4$</td>
<td>-51</td>
<td>91</td>
<td>-84</td>
<td>100</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\tau(\text{tilt})$</td>
<td>-45</td>
<td>-83</td>
<td>86</td>
<td>89</td>
<td>-1</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>$u(\text{C} - \text{X})$</td>
<td>36</td>
<td>72</td>
<td>-72</td>
<td>77</td>
<td>-2</td>
<td>84</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Two kinds of parameter correlation ($q$) matrixes are presented. The $q$ 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 damping constant equal to 0.0010 Å².

Parameters 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–CCl₃ group are found in the ranges 1.76–1.77 Å and 110–111°, respectively. The structural parameters C–Cl and $\angle_{\text{CCl}}$ of the C–CCl₃ 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 –CCl₃ 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 cannot 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 CCC(4)—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.

Acknowledgements. We are grateful to Cand. real. A. Almenningen for recording the diffraction photographs, and to Prof. N. Sheppard who initiated this investigation through his stimulating lecture here in Oslo several years ago. Computer programs made available by Dr. H. M. Seip, Prof. W. D. Gwinn, and Cand. real. S. Rustad have been extensively used in this work. Financial support from Norges almenviten-
skappelige forskningsråd is gratefully acknowledged.

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Received June 10, 1974.