

Conformational Analysis. X. The Molecular Structure, Torsional Oscillations, and Conformational Equilibria of Gaseous 1,1,2,2,3,3-Hexachloropropane ($\text{CHCl}_2\text{CCl}_2\text{CHCl}_2$) as Determined by Electron Diffraction and Compared with Semi-empirical (Molecular Mechanics) Calculations

LIV FERNHOLT and REIDAR STØLEVIK

Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

Gaseous 1,1,2,2,3,3-hexachloropropane has been studied at a nozzle temperature of 112 °C. The abundant conformer (*GG*) is the one without parallel (1:3) $\text{Cl}\cdots\text{Cl}$ interactions. According to semi-empirical calculations the remaining conformers [*AG*, *GG*(1:3), and *AA*] are from 3.6 to 6.0 kcal/mol less stable than *GG*.

Structural parameters in the *GG* conformer are presented with error limits (2σ). The following values for bond lengths (r_e) and bond angles ($\angle\alpha$) were obtained. Within the $\text{C}-\text{CHCl}_2$ groups: $r(\text{C}-\text{C})=1.558(16)$ Å, $r(\text{C}-\text{Cl})=1.780(10)$ Å, $\angle\text{CCCl}=111.4^\circ(0.8)$; within the $>\text{CCl}_2$ group: $r(\text{C}-\text{Cl})=1.752(18)$ Å, $\angle\text{CCCl}=108.8^\circ(0.4)$, and $\angle\text{CCC}=108.0^\circ(2.0)$. The deviations from a strictly all-staggered (1:2) conformation are quite small.

The torsional force constant has been estimated from the electron-diffraction data, and the values of the fundamental torsional frequencies have been limited to the range 85–117 cm^{-1} , with 99 cm^{-1} (A) and 103 cm^{-1} (B) as the most probable values.

To a large extent the structural parameters predicted by the molecular-mechanics calculations reasonably agree with the experimental results.

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: $\text{BrH}_2\text{C}-\text{CHBr}-\text{CH}_2\text{Br}$,¹ $\text{BrH}_2\text{C}-\text{CH}_2-\text{CH}_2\text{Br}$,² $\text{ClH}_2\text{C}-\text{CHCl}-\text{CH}_2\text{Cl}$,³ $\text{Cl}_2\text{C}-\text{CCl}_2-\text{CCl}_3$,⁴ $\text{Cl}_2\text{HC}-\text{CCl}_2-\text{CCl}_3$,⁵ and $\text{Cl}_2\text{HC}-$

CH_2-CCl_3 .⁶ Also molecules with $-\text{CH}_2\text{X}$ (X:Cl or H) groups bonded to the central C atom of a C-C-C skeleton were studied: $\text{C}(\text{CH}_2\text{Cl})_4$,⁷ $(\text{CH}_3)_2\text{C}(\text{CH}_2\text{Cl})_2$,⁸ and $\text{CH}_3-\text{C}(\text{CH}_2\text{Cl})_3$.⁹

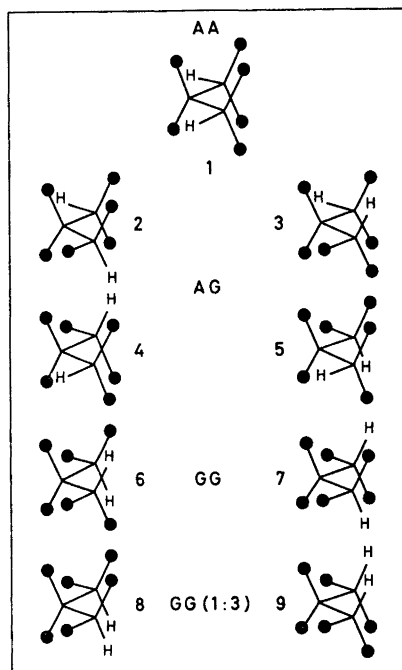


Fig. 1. The staggered conformers in $\text{CHX}_2\text{CX}_2\text{CHX}_2$.

General information¹⁰ relevant to this investigation and to the electron-diffraction method¹¹ is found in Refs. 10 and 11.

The compound will be referred to as H6. The number of all-staggered (1:2) conformers in H6 is nine, as indicated in Fig. 1. There are four spectroscopically distinguishable conformers, *AA*, *AG*, *GG*, and *GG(1:3)*, with classical multiplicities² 1, 4, 2, and 2, respectively. The symbols *A* (*anti*) and *G* (*gauche*), used in conformational names, thus indicate whether the hydrogen atoms are *anti* or *gauche* relative to the CCC plane. The symbols (*A* and *G*) are also used in order to indicate *anti/gauche* relations of a Z'...Z'' distance (Z: H, Cl) in a Z'-C-C-C-Z'' fragment, while lower case letters (*a* and *g*) indicate whether a Z'...Z'' distance (Z: C, H, Cl) is *anti* or *gauche* in a Z'-C-C-Z'' fragment (see Table 7).

Chlorinated propanes were extensively studied by Sheppard *et al.* using NMR and vibrational spectroscopy. The principal results obtained from such studies in the liquid phase are found in Refs. 12, 13, and 14. In heavily chlorinated propanes many staggered conformers have parallel C-Cl bonds on the same side of the carbon skeleton. Conformers which possess parallel (1:3) Cl...Cl interactions, are energetically less stable than conformers without such interactions.¹² *GG* (Fig. 2) is therefore expected to be the most stable conformer of H6.

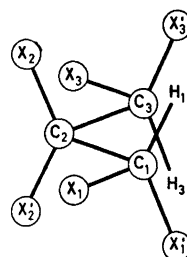


Fig. 2. The numbering of atoms in the *GG* conformer (No. 6 in Fig. 1).

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

The semi-empirical energy model corresponds to simple molecular-mechanics calculations, including atom-atom potentials and valence force constants as described in Ref. 1.

Energy parameters (*a*, *b*, *c*, *d*, and V_0) were taken from the paper by Abraham and Parry,¹⁵ and the diagonal force constants of Table 5 were used. In minimizing the energy, the geometry was constrained as described in Sect. V-A.

The values of the structural parameters are shown in Table 1. According to these results

Table 1. Calculated structural parameters for the stable conformers of $\text{CHX}_2\text{CX}_2\text{CHX}_2$, (X = Cl). The projection of the XCX' angle (in $\text{C}-\text{CHX}_2$) on a plane perpendicular to the C-C axis was assumed to be 120° .

Parameter (normal value)	<i>GG</i>	<i>AG</i>	<i>AA</i>	<i>GG(1:3)</i>
C-X (1.760 Å) in $-\text{CHX}_2$	1.776	1.775	1.772	1.777
C-X (1.760 Å) in $>\text{CX}_2$	1.788	1.785	1.781	1.788
C-C (1.513 Å)	1.561	1.568	1.569	1.569
C-H (1.094 Å)	1.094	1.094	1.096	1.094
$\angle\text{CCC}$ (110.0°)	110.6	115.5	121.1	112.7
$\angle\text{CCX}$ (109.47°) in $-\text{CHX}_2$	113.2	114.2	114.6	114.8
$\angle\text{CCX}$ (109.47°) in $>\text{CX}_2$	109.9	109.1	107.9	109.7
$\angle\text{CCH}$ (109.47°)	109.6	108.9	108.9	107.4
Torsion angles				
$\phi_{1-2}(60^\circ)^a$	-118.1	+123.7	± 0.6	+128.4
	(-120.0) ^b	(+120.0) ^b	(0) ^b	(+120.0) ^b
$\phi_{2-3}(60^\circ)^a$	-118.1	-10.3	± 0.0	-128.4
	(-120.0) ^b	(0) ^b	(0) ^b	(-120.0) ^b

^a $\phi_0 = 60^\circ$ in eqn. (1) in Ref. 1. ^b Torsion angles of the all-staggered (1:2) conformers *GG* (No. 6), *AG* (No. 2), *AA* (No. 1), and *GG(1:3)* (No. 8); see also Fig. 1.

Table 2. Calculated conformational energies (kcal/mol) for $\text{CHX}_2\text{CX}_2\text{CHX}_2$, ($\text{X}=\text{Cl}$).

Type of energy ^a	<i>GG</i>	<i>AG</i>	<i>AA</i>	<i>GG(1:3)</i>
<i>E</i> (bonded)	4.74	7.67	10.64	8.09
<i>E</i> (van der Waals)	5.66	5.94	4.90	6.72
<i>E</i> (polar: Cl···H)	-6.22	-6.11	-6.02	-5.74
<i>E</i> (polar: Cl···Cl)	24.42	24.74	25.06	24.74
<i>E</i> (total)	28.56	32.24	34.59	33.81
<i>E</i> (total) - <i>E</i> (<i>GG</i>) = ΔE^m	0 (min.)	3.66	6.01	5.23

^a Details about the energy expression are found in Ref. 1. The zero-point vibrational energies of the conformers are not included.

Table 3. Calculated conformational energies and torsional barriers in $\text{CHX}_2\text{CX}_2\text{CHX}_2$, ($\text{X}=\text{Cl}$). Details about the conformational minima are given in Tables 1 and 2. The energy values here are relative to the *GG* value. See also Fig. 1 and explanations in the text.

ϕ_{2-3} (°)	ϕ_{1-2} (°) -180 180	-120	-60	0	60	120
		180	25.3	14.1	29.3	13.9
-180	14.1	<i>GG(1:3)</i> 5.2	15.3	<i>AG</i> 3.7	15.0	<i>GG</i> 0.0
60	29.3	15.3	42.1	17.5	41.9	15.0
0	13.9	<i>AG</i> 3.7	17.5	<i>AA</i> 6.0	17.5	<i>AG</i> 3.7
-60	29.3	15.0	41.9	17.5	42.1	15.3
-120	14.1	<i>GG</i> 0.0	15.0	<i>AG</i> 3.7	15.3	<i>GG(1:3)</i> 5.2

the value of $\angle\text{CCC}$ is very large for *AA* and quite small for *GG*. The greatest deviation from staggered torsion angles is found in the conformer *AG* (ca. 10°), while *GG* is nearly staggered, and *AA* is exactly staggered. It is noteworthy that the resulting conformational symmetries are equal to those of the staggered conformers (*AA*: C_{2v} , *AG*: C_1 , *GG*: C_2 , and *GG(1:3)*: C_s).

Conformational energies are found in Table 2. According to the present energy model, *GG* is the conformer of lowest energy. The destabilizing effects of parallel (1:3) Cl···Cl interactions are clearly demonstrated.

Torsional barriers may be estimated from the energy values in Table 3. Each energy value in Table 3 corresponds to a conformer having all structural parameters adjusted; except for one or two torsion angles (ϕ), corresponding to *eclipsed* conformers, being kept at constant

values ($\phi: \pm 60, \pm 180^\circ$). The actual values of the geometry variables are not shown in Table 3, however, the values of the torsion angles ϕ_{1-2} and ϕ_{2-3} are approximately those given in parenthesis. Clearly, the stable conformers correspond to well-defined minima of the potential-energy function. The lowest barrier is as high as ca. 9 kcal/mol [*GG(1:3)*→*GG*].

Torsional force constants were computed according to their definitions (Table 4). Derivatives were calculated numerically at the potential-energy minima. Except for *GG*, the interaction constants ($F_{\phi\phi'}$) are quite large in magnitude.

III. CALCULATION OF VIBRATIONAL QUANTITIES

Valence force constants, except for the torsional part of the force field, were taken from

Table 4. Calculated torsional force constants for $\text{CHX}_2\text{CX}_2\text{CHX}_2$, ($\text{X} = \text{Cl}$).

Type of force constant [in mdyne $\text{\AA}(\text{rad})^{-2}$]	<i>GG</i>	<i>AG</i>	<i>AA</i>	<i>GG(1:3)</i>
$F_\phi(1-2)^a = \partial^2 E / \partial \phi_{1-2}^2$	0.49	0.51	0.45	0.53
$F_\phi(2-3)^a = \partial^2 E / \partial \phi_{2-3}^2$	0.49	0.50	0.45	0.53
$F_{\phi\phi}^b = \partial^2 E / \partial \phi_{1-2} \partial \phi_{2-3}$	-0.08	-0.28	-0.39	-0.31

^a Diagonal force constant. ^b Interaction force constant (non-diagonal element).

Table 5. Valence force constants for $\text{CHX}_2\text{CX}_2\text{CHX}_2$, ($\text{X} = \text{Cl}$).

Stretch (mdyne \AA^{-1})	Bend [mdyne $\text{\AA}(\text{rad})^{-2}$]
C-C: 4.39	CCC: 0.94
	CCX: 1.08
C-X: 3.35	CCH: 0.69
	XCX: 1.13
C-H: 4.89	XCH: 0.83
Stretch/stretch (mdyne \AA^{-1} ; C is common)	
C-X/C-X: 0.49, C-X/C-C: 0.73, C-C/C-C: 0.064	
Stretch/bend [mdyne $(\text{rad})^{-1}$]	
C-C is common; C-C/CCX: 0.19, C-C/CCH: 0.25, C-C/CCC: 0.35	
C-X is common; C-X/CCX: 0.55, C-X/XCH: 0.33, C-X/XCX: 0.40	
Bend/bend [mdyne $\text{\AA}(\text{rad})^{-2}$], bond angles on the same C atom	
C-X is common; XCX/CCX: -0.13	
C-C is common; CCC/CCH: -0.12	
C-H is common; HCX/HCX: 0.09, CCH/HCX: 0.10	
C-C is common, but bond angles on adjacent C atoms	
CCH/CCX: 0.04 (HCCX anti), CCH/CCX: -0.04 (HCCX gauche)	
CCC/CCX: 0.04 (CCCX anti), CCC/CCX: -0.03 (CCCX gauche)	
CCX/CCX: -0.09 (XCCX anti), CCX/CCX: 0.07 (XCCX gauche)	
Torsion ^a [mdyne $\text{\AA}(\text{rad})^{-2}$] for the <i>GG</i> conformer	
$F_\phi(1-2) = F_\phi(2-3) = 0.86^b$ and $F_{\phi\phi}(1-2; 2-3) = 0$	

^a The torsional force constants were defined as follows: each fragment of type $\text{A}'-\text{C}_1-\text{C}_2-\text{A}''$ ($\text{A}: \text{C}, \text{Cl}, \text{H}$) were assigned an equal torsional force constant. The total force constant (F_ϕ) for the torsion coordinate ϕ_{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 of the torsion fragments. ^b This value was estimated from the electron-diffraction data as described in Sect. V-B.

the work ¹⁶ by Schachtschneider and Snyder. Certain compromises between force constant values had to be made. The final values selected for H6 are given in Table 5. The diagonal torsional force constants were adjusted (Sect. V-B).

The normal-coordinate program described by Gwinn ¹⁷ was used in computing vibrational frequencies (Table 6) for the *GG* conformer of

H6. The molecular model possessed C_2 symmetry [A(14) and B(13)].

Mean amplitudes of vibration (u) and vibrational correction terms, $D = r_\alpha - r_a = (u^2/r) - K$, were calculated according to the formulas derived in Ref. 18. Their values are found in Table 7.

According to the semi-empirical model (Table 4), the value of the torsional interaction

Table 6. Fundamental frequencies (ω) in the *GG* conformer of $\text{CHX}_2\text{CH}_2\text{CHX}_2$, ($\text{X}=\text{Cl}$ and ω in cm^{-1}).

The force constants in Table 5 and the Cartesian coordinates (C_2 sym.) in Table 9 were used. Species (A and B) and approximate interpretations of modes are given: C-H, C-C, and C-X indicate stretching of these types of bonds, while CCC, CCH, CCX, XCX, and HCX indicate bending of these types of bond angles.

90 (A: CCX), 99 (A: torsion ++), ^a 103 (B: torsion +-), ^a
157 (B: CCX), 163 (A: CCX), 172 (B: CCX),
193 (A: CCX+XCX), 253 (A: XCX in $>\text{CX}_2$), 274 (B: XCX),
344 (A: XCX), 345 (B: CCX+XCX), 365 (A: CCX+XCX),
561 (B: CCX+C-X), 643 (A: C-X in $>\text{CX}_2$), 728 (B: C-X),
776 (B: C-X), 787 (A: C-X), 834 (A: CCC+C-X),
885 (B: C-X in $>\text{CX}_2$), 982 (A: C-C), 1169 (B: C-C+CCH),
1257 (A: CCH), 1265 (B: CCH+C-C), 1487 (A: HCX),
1490 (B: HCX), 2933 (A: C-H), 2993 (B: C-H)

^a The deformations in torsion angles ($\Delta\phi$) are approximately: $\text{A}(\Delta\phi_{1-2} \approx +\Delta\phi_{2-3})$ and $\text{B}(\Delta\phi_{1-2} \approx -\Delta\phi_{2-3})$.

Table 7. Mean amplitudes of vibration (u) and vibrational correction terms ($-D$) for the *GG* conformer of $\text{CHX}_2\text{CX}_2\text{CHX}_2$ at 112 °C. ($\text{X}=\text{Cl}$, see Fig. 2). The force constants in Table 5 and the Cartesian coordinates in Table 9 were used in calculating these quantities. The correction term corresponds to $r_a - r_\alpha = K - (u^2/r) = -D$.

Type of dist. (r)	r (Å)	u (Å)	$K - (u^2/r)$
C-X' (in- CHX_2)	(1.78)	0.0537	0.00615
C-X (in- CHX_2)	(1.78)	0.0538	0.00722
C-X (in CX_2)	(1.76)	0.0548	0.00295
C-C	(1.57)	0.0542	0.00171
C-H	(1.09)	0.0778	0.01023
$C_2 \cdots H_1$	(2.19)	0.1090	0.00413
$C_2 \cdots X_1$	(2.74)	0.0758	0.00522
$C_2 \cdots X_1'$	(2.74)	0.0758	0.00394
$C_1 \cdots C_3$	(2.57)	0.0787	0.00008
$C_1 \cdots X$	(2.72)	0.0746	0.00156
$X_1 \cdots H_1$	(2.37)	0.1057	0.00973
$X_1' \cdots H_1$	(2.37)	0.1057	0.00779
$X_1 \cdots X_1'$	(2.90)	0.0739	0.00851
$X_2 \cdots X_2'$	(2.88)	0.0721	0.00294
$H_1 \cdots H_3$ (GG)	(3.12)	0.1977	-0.00196
$C_1 \cdots H_3$ (g)	(2.79)	0.1544	-0.00170
$H_1 \cdots X_2'$ (a)	(3.69)	0.1043	0.00410
$H_1 \cdots X_3$ (g)	(2.91)	0.1468	0.00022
$H_1 \cdots X_3'$ (GG)	(2.66)	0.2233	-0.00796
$C_1 \cdots X_3'$ (g)	(3.12)	0.1372	-0.00159
$C_1 \cdots X_3$ (a)	(4.15)	0.0772	0.00179
$X_1 \cdots X_2$ (g)	(3.22)	0.1370	0.00019
$X_1 \cdots X_2'$ (g)	(3.22)	0.1425	-0.00079
$X_1' \cdots X_2'$ (g)	(3.22)	0.1359	-0.00056
$X_1' \cdots X_2$ (a)	(4.32)	0.0754	0.00242
$X_1 \cdots X_3$ (AA)	(5.47)	0.1073	-0.00032
$X_1 \cdots X_3'$ (AG)	(4.74)	0.1472	-0.00177
$X_1' \cdots X_3'$ (GG)	(3.87)	0.1942	-0.00580

Table 8. Vibrational quantities in the *GG* conformer of $\text{CHX}_2\text{CX}_2\text{CHX}_2$, calculated with different values of the torsional force constant (F_ϕ). ($\text{X}=\text{Cl}$). See also explanations given in Tables 5, 6, 7 and 9.

F_ϕ [mdyn Å(rad) ⁻²]	0.63	0.86 ^a	1.17
$u(\text{X} \cdots \text{X})$	u (in Å units) ^b at 112 °C		
$X_1' \cdots X_3'$ (GG)	0.2113	0.1942	0.1805
$X_1 \cdots X_3'$ (AG)	0.1518	0.1472	0.1434
$X_1 \cdots X_2$ (g)	0.1424	0.1370	0.1326
$X_1 \cdots X_2'$ (g)	0.1479	0.1425	0.1381
$X_1' \cdots X_2'$ (g)	0.1417	0.1359	0.1310
Low frequencies	ω (in cm^{-1} units) ^c		
Torsion (A)	85	99	112
Torsion (B)	90	103	117
Bending (A)	91	90	91
(B)	153	157	162
(A)	160	163	166
(B)	171	172	173
(A)	193	193	194
(A)	251	253	255
(B)	271	274	279
(A)	341	344	347
(B)	342	345	348
(A)	362	365	369
(B)	558	561	565

^a The best value as determined in Sect. V-B.
^b Mean amplitude of vibration (u). ^c All frequency values calculated with $F_\phi = 0.86$ are found in Table 6.

Table 9. Cartesian coordinates (x, y, z) of atoms in the GG conformer of $\text{CHX}_2\text{CX}_2\text{CHX}_2$.

Atom (X = Cl)	x (Å) ^a	y (Å) ^a	z (Å) ^a
C_2	0 ^b	0 ^b	0 ^b
C_1	1.2829	0.9072	0
X_1	2.7334	-0.1184	0
H_1	1.2829	1.5365	0.8900
X_1'	1.2829	1.9328	-1.4504
C_3	-1.2829	0.9072	0
X_3	-2.7334	-0.1184	0
H_3	-1.2829	1.5365	-0.8900
X_3'	-1.2829	1.9328	1.4504
X_2	0	-1.0165	1.4378
X_2'	0	-1.0165	-1.4378

^a See Fig. 2. These values of the Cartesian coordinates were used in the calculations of all vibrational quantities (staggered model). ^b The origin of the coordinate system is on the atom C_2 .

constant ($F_{\phi\phi'}$) for GG is much smaller in magnitude than the diagonal element (F_{ϕ}). All vibrational quantities were calculated with $F_{\phi\phi'}$ equal to zero. Although the values of the torsional frequencies depend on the value of $F_{\phi\phi'}$ it has been shown⁴ that the u and K values are much less dependent on the value of $F_{\phi\phi'}$.

Some of the vibrational quantities are quite sensitive to the value of the torsional element F_{ϕ} . In Table 8 are shown low vibrational frequencies and mean amplitudes of vibrational corresponding to values of F_{ϕ} in the range 0.63–1.17 mdyn Å (rad)⁻².

Values of the Cartesian coordinates, which were used in calculations of all vibrational quantities, are found in Table 9.

IV. EXPERIMENTAL AND DATA REDUCTION

H6 was obtained from "K & K" laboratories. The purity of the sample which was used, was better than 98 %.

Electron-diffraction photographs were made at a nozzle temperature of 112 °C in the Oslo apparatus¹⁹ under conditions summarized below.

Nozzle-to-plate distance (mm)	480.7	200.8
Electron wave length (Å)	0.06460	0.06460
Number of plates	4	6

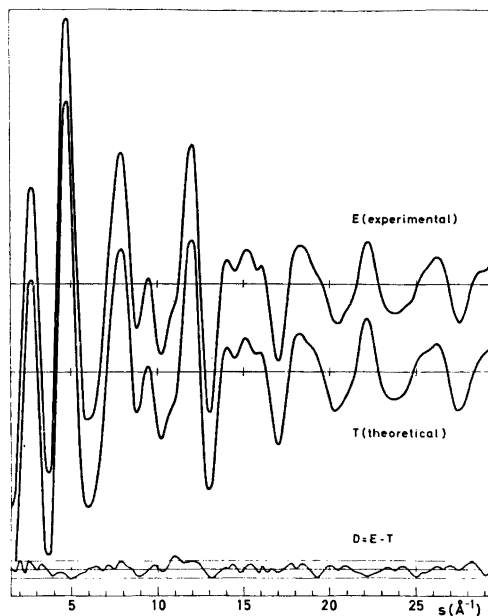


Fig. 3. Experimental (E) and theoretical (T) intensity curves, and $D = E - T$, corresponding to the final least-squares parameters. The straight lines give the experimental uncertainties (± 3 times experimental standard deviation).

Range of data, in s (Å ⁻¹)	1.500–19.375	7.25–43.25
Data interval, Δs (Å ⁻¹)	0.125	0.250
Estimated uncertainty in s -scale (%)	0.14	0.14

The electron wave length was determined by calibration against gold and corrected by an experiment with CO_2 giving a correction of +0.1 % in the s -scale. The data were reduced in the usual way²⁰ to yield an intensity curve for each plate.

Average curves for each set of distances were formed. A composite curve was then made by connecting the two average curves after scaling. The final experimental curve is shown in Fig. 3. The intensities were modified²⁰ by $s/f_{\text{Cl}}'^{-2}$. The scattering amplitudes were calculated by the partial-wave method,²¹ using Hartree-Fock atomic potentials.²²

The radial-distribution curve obtained by Fourier²⁰ transformation of the final experimental intensity curve is shown in Fig. 4.

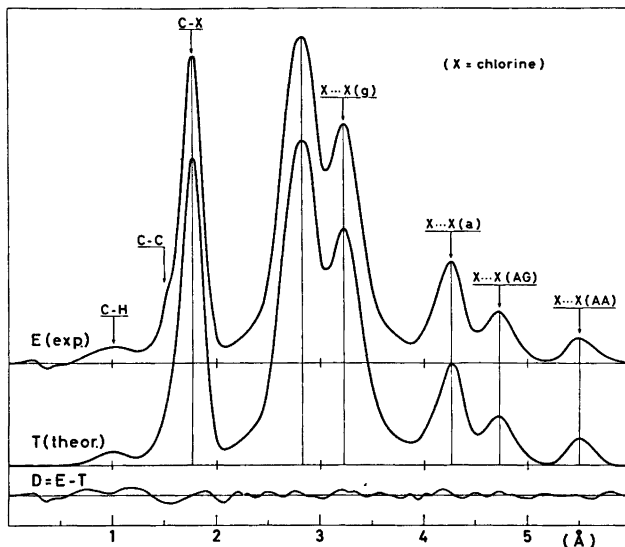


Fig. 4. Experimental (E) and theoretical (T) radial distribution curves, and $D = E - T$. The curves were calculated from the intensity curves in Fig. 3. with an artificial damping constant of 0.0020 \AA^2 . Some of the peaks corresponding to non-bonded internuclear distances have been indicated; see also Tables 12 and 7.

V. STRUCTURE ANALYSIS

From the experimental RD-curve (Fig. 4) several conclusions can be reached before starting the least-squares refinements. The fact that the peak marked $X \cdots X(AA)$ is present in the experimental curve, shows that the abundant conformer at 112°C has to be either GG or $GG(1:3)$. Only these two conformers possess the very long (*ca.* 5.5 \AA) internuclear distance of the type $X \cdots X(AA)$, which corresponds to $X_1 \cdots X_3$ in Fig. 2 (see also Fig. 1).

According to the calculated energy values in Table 2, $GG(1:3)$ is *ca.* 5 kcal/mol less stable than GG . If the semi-empirical results are approximately correct, the percentages of other conformers than GG have to be very small ($< 1\%$).

A. Least-squares refinements

In calculating theoretical intensities for the least-squares refinements,²⁰ it was decided not to consider contributions from other conformers than GG .

Several assumptions about bond lengths and bond angles were made in constructing the molecular model, as summarized below (see

Fig. 2):

- (1) the $>CX_2$ group possess C_{2v} symmetry,
- (2) the $C-CHX_2$ groups are equal and possess C_s symmetry.

Models were adjusted in terms of the following structural parameters: $r(C-H)$, $r(C-C)$, $r(C_2-X)$, $r(C_1-X) = r(C_3-X)$, $\angle CCC$, $\angle CCH$, $\angle CC_2X$, $\angle CC_1X = \angle CC_3X$, $\angle(XC_1X') = \angle(XC_3X')$, and the torsion angles ϕ_{1-2} and ϕ_{2-3} . $\angle(XC_1X')$ is the projection of the XC_1C' angle on a plane perpendicular to the C_1-C_2 axis. For the strictly all-staggered (1:2) AA conformation (Fig. 1) the torsion angles ϕ_{1-2} and ϕ_{2-3} are both zero degrees. The atoms $H-C-C-C-H$ are then coplanar. For the strictly all-staggered (1:2) GG conformation in Fig. 2, the value is -120° for both ϕ_{1-2} and ϕ_{2-3} , corresponding to a planar arrangement of the atoms $X_1-C_1-C_2-C_3-X_3$.

Non-bonded internuclear distances were computed as dependent quantities, restricted under the constraints of geometrically consistent r_α parameters.^{23,24} The bonds $C-X$ and $C-X'$ in the $-CHX_2$ group are not vibrationally identical, (Table 7), however, this fact was allowed for when D values ($D = r_\alpha - r_a = (u^2/r) - K$) were assigned to the internuclear distances.

B. Determination of torsional force constants

Assuming $F_\phi(1-2) = F_\phi(2-3) = F_\phi$ and $F_{\phi\phi'} = 0$, the value of F_ϕ was estimated from the electron-diffraction data as follows: u and K values for different values of F_ϕ were calculated (Sect. III) and then included in the least-squares refinements. The value of F_ϕ which lead to a minimum in the error sum (VPV), was 0.86 mdyn Å (rad)⁻², within error limits of ca. 30 %. The error limits are subjective to a certain degree, and do not allow for systematic errors.

VI. FINAL RESULTS

Parameters from the least-squares refinements and their standard deviations (σ) corrected for correlation²⁵ in the experimental data, are given in Table 10. The final parameters correspond to refinements with equal weights for all intensities. Data beyond $s = 29.5 \text{ \AA}^{-1}$ were not included in these refinements.

Parameter-correlation coefficients (ρ) are shown in Table 11.

The deviation of torsion angles from a strictly all-staggered (1:2) *GG* conformation is small (3.8°), but statistically significant ($\sigma = 0.7^\circ$).

Table 10. Structural parameters in the *GG* conformer of $\text{CHX}_2\text{CX}_2\text{CHX}_2$, (X = Cl). Standard deviations are shown in parentheses. The uncertainty (0.14 %) in the s -scale has been included in the standard deviations for bond lengths. An experiment with CO_2 gave a correction of +0.1 % in the s -scale. The bond lengths are therefore 0.1 % longer than the least-squares estimates.

Bond lengths (Å) ^a (r_α -values)	Bond angles (°) ^a ($\angle\alpha$ -values)
$r(\text{C}-\text{C}) = 1.556(8)$	$\angle\text{CCC} = 108.0(1.0)$
$r(\text{C}-\text{X}) = 1.778(5)$ in $-\text{CHX}_2$	$\angle\text{CCX} = 111.4(0.4)$ in $\text{C}-\text{CHX}_2$
$r(\text{C}-\text{X}) = 1.750(9)$ in $>\text{CX}_2$	$\angle\text{CCX} = 108.8(0.2)$ in $>\text{CX}_2$
$r(\text{C}-\text{H}) = 1.02(4)$	$\angle\text{CCH} = 105.2(4.1)$
$\phi_{1-2} = \phi_{2-3} = -116.2^\circ(0.7)^\text{b}$	$\angle(\text{XCX}')^\text{c} = 120.5(0.8)$

^a The geometrical assumptions were explained in Sect. V-A. ^b The torsion angles of the *GG* conformer were refined assuming $\phi_{1-2} = \phi_{2-3}$ as suggested by the results in Table 1. $\phi_{1-2} = \phi_{2-3}$ corresponds to C_2 symmetry. ^c The projection of the XCX' angle in $\text{C}-\text{CHX}_2$ on a plane perpendicular to the C-C axis of that group.

Table 11. Parameter correlation ($\rho \times 100$).

Parameter ^a	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	
$r(\text{C}_1-\text{X})$	(1)	100											
$r(\text{C}_2-\text{X})$	(2)	-85	100										
$r(\text{C}-\text{C})$	(3)	-1	-8	100									
$r(\text{C}-\text{H})$	(4)	-6	9	-7	100								
$\angle\text{CCC}$	(5)	-70	78	-7	9	100							
$\angle\text{C}_2\text{CX}$	(6)	25	-29	-72	19	-23	100						
$\angle\text{CC}_2\text{X}$	(7)	-24	26	7	-18	1	-52	100					
$\angle\text{CCH}$	(8)	27	32	-53	29	-20	63	-40	100				
ϕ^b	(9)	17	-24	-3	-1	-49	30	17	-3	100			
$\angle(\text{XCX}')^\text{c}$	(10)	-74	63	-37	16	61	20	19	-5	6	100		
$u(\text{C}-\text{X})^\text{d}$	(11)	-41	46	-41	10	33	21	3	6	-6	45	100	
Scale ^e	(12)	31	-27	-51	8	-33	63	-30	33	18	-2	30	100

^a The geometrical assumptions were explained in Sect. V-A. ^b Torsion angles: $\phi_{1-2} = \phi$ and $\phi_{2-3} = \phi$. ^c The projection of the XCX' angle in $\text{C}-\text{CHX}_2$ on a plane perpendicular to the C-C axis of that group. ^d All $u(\text{C}-\text{X})$ values were refined as one parameter. ^e Scale factor between experimental and theoretical intensities.

The fit obtained between theoretical and experimental curves (Figs. 3 and 4) using u and K values calculated with the force constants of Table 5 is quite satisfactory. Moreover, it is important that the large number of u values do not have to be adjusted as individual parameters. However, it ought to be kept in mind that all torsion dependent u and K values have been adjusted *simultaneously* by adjusting the diagonal torsional force constant (Sect. V-B). The vibrationally consistent set of u values in Table 7, which combine information from both vibrational spectroscopy and electron diffraction, are considered the final ones for H6.

The u values of the C—Cl bonds were refined, together with the structural parameters, as one variable. The average value obtained (0.054 Å) is in excellent agreement with the calculated values in Table 7.

VII. DISCUSSION

It has been shown that the abundant conformer, in the gas phase, at 112 °C, is GG . Although the percentages of AA , AG , and $GG(1:3)$ were not determined, it is unlikely that the sum of contributions from these conformers is greater than 10 %. The conformational energies predicted by the semiempirical model (Table 2) are thus consistent with the experimental finding. Moreover, if the calculated energies are approximately correct, the contributions from other conformers than GG are negligible at 112 °C.

The value of the torsional force constant calculated in Sect. II (Table 4) is too low compared with the experimentally estimated value (Sect. V-B). However, the structural parameter values calculated for the GG conformer (Table 1) agree quite well with the corresponding experimental values (Table 10). The largest discrepancies are found for $r(\text{C—H})$ and $\angle\text{CCH}$, however, these parameters are experimentally very uncertain. Although adjustments within the non-torsional force constants and the "normal" reference parameters could remove most of the remaining discrepancies, it was felt that results from additional molecules ought to be included before such corrections were considered.

According to the semi-empirical calculations, all stable conformers of H6 are nearly staggered (Table 1), however, some bond angles are proba-

Table 12. Comparison of structural parameters in 1,1,2,2,3,3-hexachloropropane (H6) and octachloropropane (O8).

$\begin{array}{c} \text{H} \quad \text{X} \quad \text{X} \\ \quad \quad \\ \text{X}-\text{C}-\text{C}-\text{C}-\text{X} \\ \quad \quad \\ \text{X} \quad \text{X} \quad \text{H} \end{array}$	$\begin{array}{c} \text{X} \quad \text{X} \quad \text{X} \\ \quad \quad \\ \text{X}-\text{C}-\text{C}-\text{C}-\text{X} \\ \quad \quad \\ \text{X} \quad \text{X} \quad \text{X} \end{array}$		
H6	O8		
$\begin{array}{c} \text{X} \\ \\ \text{C}-\text{C}-\text{C} \\ \\ \text{X} \end{array}$			
Bond lengths and bond angles in the group ^{a,b}	GG conformer of H6 ^c (see Fig. 2)	All-staggered (1:2) conformer of O8 ^d	Difference (H6—O8)
$r_a(\text{C—C})$ (Å)	1.556(8)	1.655(15)	−0.099
$r_a(\text{C—X})$ (Å)	1.750(9)	1.810(20)	−0.060
$\angle_\alpha\text{CCC}$ (°)	108.0(1.0)	119.0(2.0)	−11.0
$\angle_\alpha\text{CCX}$ (°)	108.8(0.2)	104.5(0.5)	+ 4.3

^a C_{2v} symmetry was assumed for this group.

^b Standard deviations are given in parentheses.

^c The remaining structural parameters are found in Table 10. ^d Further details about O8 are found in Ref. 4.

bly quite different within the conformers. The most dramatic difference is expected for the value of $\angle\text{CCC}$, which is quite small in GG , while the value in AA is *ca.* 10° greater. Such a large $\angle\text{CCC}$ value, (121°) for AA is consistent with the *experimental* result obtained for octachloropropane (O8). In O8 the experimental value is 119° ($\sigma = 2^\circ$). The AA conformer of H6 and the all-staggered (1:2) conformer of O8 both have parallel C—Cl bonds on both sides of the carbon skeleton.

The structural parameters of the $\begin{array}{c} \text{X} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{X} \end{array} < \text{C} < \text{C}$ group in H6 and O8 have been compared in Table 12. The differences in parameter values between the two molecules are highly significant. The values in Table 12 clearly demonstrate the steric effects of having parallel C—Cl bonds on both sides of the carbon skeleton. It is noteworthy that the deviations from all-staggered (1:2) conformations, are small in both molecules.

Observed vibrational frequencies for H6 were not available, however, the force constants used

in this work are consistent with the electron-diffraction data. Moreover, the diagonal element of the torsional force field in the *GG* conformer have been estimated, (Sect. V-B), and the values of the fundamental torsional frequencies [$\omega_\phi(A)$ and $\omega_\phi(B)$] have been limited to the range 85–117 cm^{-1} . The most probable values are 99 and 103 cm^{-1} for $\omega/(A)$ and $\omega/(B)$, respectively (Table 8). For the *GG* conformer the lowest fundamental is the “CCX bending” frequency at *ca.* 90 $\text{cm}^{-1}(A)$.

Acknowledgements. We are grateful to Cand. real. Arne Almenningen for recording the diffraction photographs. 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 almenvitenskapelige forskningsråd is gratefully acknowledged.

REFERENCES

1. Stølevik, R. *Acta Chem. Scand. A* 28 (1974) 299.
2. Farup, P. E. and Stølevik, R. *Acta Chem. Scand. A* 28 (1974) 680.
3. Farup, P. E. and Stølevik, R. *Acta Chem. Scand. A* 28 (1974) 871.
4. Fernholt, L. and Stølevik, R. *Acta Chem. Scand. A* 28 (1974) 935.
5. Johnsen, J. P. and Stølevik, R. *Acta Chem. Scand. A* 29 (1975) 201.
6. Johnsen, J. P. and Stølevik, R. *Acta Chem. Scand. A* 29 (1975) 457.
7. Stølevik, R. *Acta Chem. Scand. A* 28 (1974) 327.
8. Stølevik, R. *Acta Chem. Scand. A* 28 (1974) 455.
9. Stølevik, R. *Acta Chem. Scand. A* 28 (1974) 612.
10. Bastiansen, O., Seip, H. M. and Boggs, J. E. *Perspect. Struct. Chem.* 4 (1971) 60.
11. Seip, H. M. In Sim, G. A. and Sutton, L. E., Eds., *Molecular Structure by Diffraction Methods*, Specialist Periodical Reports, The Chemical Society, London 1973, Vol. 1, Part 1, Chapter 1.
12. Dempster, A. B., Price, K. and Sheppard, N. *Spectrochim. Acta A* 25 (1969) 1381.
13. Dempster, A. B., Price, K. and Sheppard, N. *Spectrochim. Acta A* 27 (1971) 1563.
14. Dempster, A. B., Price, K. and Sheppard, N. *Spectrochim. Acta A* 27 (1971) 1579.
15. Abraham, R. J. and Parry, K. J. *J. Chem. Soc. B* (1970) 539.
16. Schachtschneider, J. H. and Snyder, R. G. *Vibrational Analysis of Polyatomic Molecules. IV.* (Force constants for the halo-paraffins). Project No. 31450, Technical Report No. 122-63 of Shell Development Company.
17. Gwinn, W. D. *J. Chem. Phys.* 55 (1971) 477.
18. Stølevik, R., Seip, H. M. and Cyvin, S. J. *Chem. Phys. Lett.* 15 (1972) 263.
19. Bastiansen, O., Hassel, O. and Risberg, E. *Acta Chem. Scand.* 9 (1955) 232.
20. Andersen, B., Seip, H. M., Strand, T. G. and Stølevik, R. *Acta Chem. Scand.* 23 (1969) 3224.
21. Peacher, J. and Willis, J. C. *J. Chem. Phys.* 46 (1967) 4809.
22. Strand, T. G. and Bonham, R. A. *J. Chem. Phys.* 40 (1964) 1686.
23. Morino, Y., Kuchitsu, K. and Oka, T. *J. Chem. Phys.* 36 (1962) 1108.
24. Kuchitsu, K. *J. Chem. Phys.* 49 (1968) 4456.
25. Seip, H. M. and Stølevik, R. In Cyvin, S. J., Ed., *Molecular Structures and Vibrations*, Elsevier, Amsterdam 1972.

Received February 10, 1975.