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Conformational Analysis. VIII. The Molecular Structure, Torsional Oscillations, and Conformational Equilibrium of Gaseous 1,1,2,2,3,3,3-Heptachloropropane ($CHCl_2—CCl_2—CCl_3$) as Determined by Electron Diffraction and Compared with Semi-empirical (Molecular Mechanics) Calculations

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Gaseous 1,1,2,2,3,3,3-heptachloropropane (HCP) has been studied by electron diffraction at a nozzle temperature of 80 °C. *Gauche* and *anti* conformers are possible for HCP. The conformer with the H atom *anti* to the CCC group was not present in detectable amounts, however, a small percentage (< 10 %) can not be ruled out. According to the semi-empirical calculations the percentage of *anti* should be less than 0.5 % at 80 °C.

Results are presented with error limits (2σ). The following values for bond lengths (r_g) and bond angles ($\angle_\alpha$) were obatined. Average parameters within the C—C—C group: r(C—C) = 1.603(12) Å and $\angle$CCC = 117.6°(3.8), average parameters within the $-CCl_3$ and $-CHCl_2$ groups: r(C—Cl) = 1.779(12) Å and $\angle$CCCl = 110.3°(1.2), average parameters within the $>CCl_2-$ group: r(C—Cl) = 1.767(28) Å and $\angle$CCCl = 108.3°(1.2). The deviations from an exact all-staggered (1:2) *gauche* conformation are statistically significant, but quite small [*ca.* 8°(2)].

It has been demonstrated, that for the *gauche* conformer an average torsional force constant can be estimated from the electron-diffraction data, if the remainder of the force field is approximately known. Within the experimental error limits, the values of the torsional force constants predicted by the energy model, agree with the experimental value.

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

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: $BrH_2C-CHBr-CH_2Br$,[1] $BrH_2C-CH_2-CH_2Br$,[2] $ClH_2C-CHCl-CH_2Cl$,[3] $Cl_3C-CCl_2-CCl_3$;[4] 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: $C(CH_2Cl)_4$,[5] $(CH_3)_2C(CH_2Cl)_2$,[6] and $(CH_3)C(CH_2Cl)_3$.[7]

General information [8] relevant to this investigation and to the electron-diffraction method [9] is found in Refs. 8 and 9.

Some of the symbols which are used in this paper need a few comments. HCP is used for the compound itself. Capital letters A/G combined as AA, AG and GG indicate *anti*/*gauche* relations of a Z···Y distance in a Z—C—C—C—Y fragment, while small letters a/g indicate *anti*/*gauche* Z···Y distance in a Z—C—C—Y fragment (see Table 7).

Chlorinated propanes have been extensively studied by Dempster, Price and Sheppard using IR and NMR spectroscopy. The principal results obtained from such studies in the liquid phase, are found in Refs. 10, 11, and 12. In heavily chlorinated propanes many staggered confor-

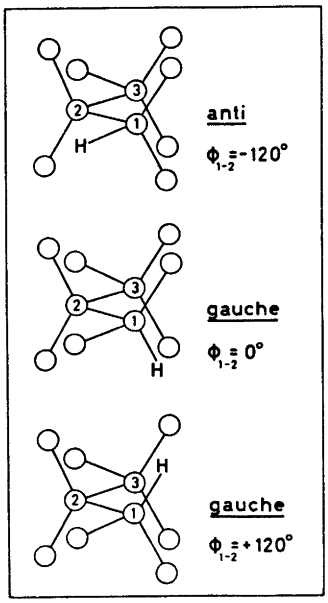

Fig. 1. The staggered conformers which are possible in 1,1,2,2,3,3,3-heptachloropropane. The two *gauche* forms are spectroscopically indistinguishable.

mers have parallel C—Cl bonds on the same side of the carbon skeleton [parallel (1:3) Cl···Cl interaction].[10] Conformers which possess parallel (1:3) Cl···Cl interactions, are energetically less stable than conformers without such interactions.[10]

Assuming all-staggered (1:2) conformations, only two spectroscopically distinguishable forms are possible for HCP. The conformers and their names are shown in Fig. 1. The two *gauche* forms are not spectroscopically distinguishable. If the torsion angles of a *gauche* conformer have to be specified, then the one with $\phi_{1-2}=\phi_{2-3}=0°$ in staggered positions will be mentioned. Both of the staggered conformers possess parallel (1:3) Cl···Cl interactions.

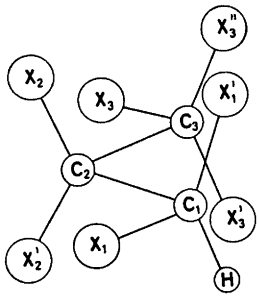

Fig. 2. The numbering of atoms in the *gauche* conformer of 1,1,2,2,3,3,3-heptachloropropane.

The liquid and crystal IR spectra, obtained near room temperature, show no indication of more than one conformer.[11] It is likely that the *gauche* conformer, which has one parallel (1:3) Cl···Cl interaction less than the *anti* conformer, is the most stable one energetically. It is also likely that the C—C bonds and the CCC angles in both conformers have unusual values, in accordance with the experimental findings for octachloropropane.[4] Most probably, *gauche* conformers have torsion angles somewhat different from staggered values.

II. CALCULATION OF CONFORMATIONAL ENERGIES, GEOMETRIES, BARRIERS AND TORSIONAL 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,[13] and the diagonal force constants of Table 5 were used. In minimizing the energy, the geometry was constrained in the same way as described in Sect. V-A.

The structural parameters of the conformers are presented in Table 1.

Conformational energies are found in Table 2. According to the present energy model, *gauche* is the conformer of lowest potential energy. The energy minimum of *gauche* is somewhat displaced from an exact staggered conformation, leading to a lower conformational energy. For *anti* the energy minimum corresponds to an exact staggered conformation with $\phi_{1-2}=-120°$ and $\phi_{2-3}=0°$.

Torsional barriers may be estimated from the energy values of 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) being kept at constant values. Eclipsed conformers correspond to values of ϕ being $\pm 60°$ or $\pm 180°$. The actual

Table 1. Calculated structural parameters in the stable conformers of 1,1,2,2,3,3,3-heptachloropropane. In minimizing the energy the geometry was constrained as described in Sect. V-A.

Type of parameter r(Å), ∠(°), X=Cl	Normal value	*gauche*	*anti*
Average parameters in the CCC group:			
r(C–C)	(1.513)	1.597	1.582
∠CCC	(110.0)	114.8	120.7
Average parameters in the $-CX_3$ and $-CHX_2$ groups:			
r(C–X)	(1.760)	1.779	1.776
∠CCX	(109.47)	113.6	113.9
r(C–H)	(1.094)	1.093	1.095
∠CCH	(109.47)	109.1	109.0
Average parameters in the $\angle CX_2$ group:			
r(C–X)	(1.760)	1.797	1.793
∠CCX	(109.47)	109.2	107.9
Torsion angles:			
$\angle\phi_{1-2}(-C_1-C_2)$	(60)[a]	+6.6[b]	−120.0
$\angle\phi_{2-3}(-C_2-C_3)$	(60)[a]	−7.2[b]	±0.0

[a] $\phi_0 = 60°$ in eqn. (1) in Ref. 1. [b] $\phi_{1-2} = \phi_{2-3} = 0°$ for exact staggered positions (Fig. 1). Conventional designation of ϕ values would be $\phi_{1-2} = \pm 60°$ *(gauche)* and $\phi_{1-2} = 180°$ *(anti)*.

Table 2. Calculated conformational energies in 1,1,2,2,3,3,3-heptachloropropane. Details about the energy expression are found in Ref. 1. The zero-point vibrational energies of the conformers are not included.

Type of energy (kcal/mol)	*gauche*	*anti*	Δ(g−a)
E(bonded)	9.2	12.3	−3.1
E(van der Waals)	7.5	6.7	+0.8
E(polar: Cl···H)	−3.8	−3.5	−0.3
E(polar: Cl···Cl)	32.4	33.0	−0.6
E(total)	45.3	48.5	−3.2

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. Details about the stable conformers are found in Table 1 and Table 2. The stable conformers correspond to well defined minima of the potential-energy surface. The lowest barrier is as high as 9.3 kcal/mol.

Table 3. Calculated conformational energies and torsional barriers in 1,1,2,2,3,3,3-heptachloropropane.

ϕ_{2-3} (°)	ϕ_{1-2} (°) −180 +180 −60	−120	0 +120	+60
−60 +60	44.8	18.7	16.9	28.5
0	14.5	*anti*= 3.2[a]	"*gauche*"= 1.4[a] min (=0)	9.3

[a] Details about the conformational minima are given in Tables 1 and 2. The energy values here are relative to the *gauche* value. See also explanations in the text.

Table 4. Calculated torsional force constants in conformers of 1,1,2,2,3,3,3-heptachloropropane.

(mdyn Å (rad)$^{-2}$)	*gauche*	*anti*
$F_\phi(1-2)^a = \delta^2E/\delta\phi_{1-2}^2$	0.57	0.47
$F_\phi(2-3)^a = \delta^2E/\delta\phi_{2-3}^2$	0.67	0.68
$F_{\phi\phi'}{}^b = \delta^2E/\delta\phi_{1-2}\delta\phi_{2-3}$	−0.35	−0.44

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

Torsional force constants were computed according to their definitions (Table 4). The derivatives were calculated numerically at the potential-energy minima.

III. CALCULATION OF VIBRATIONAL QUANTITIES

Infrared and Raman frequencies and schematic assignments for liquid and crystalline HCP have been published by Sheppard *et al.*[11] However, the low frequencies (< *ca.* 550 cm^{-1}), which are the most important ones for an electron-diffraction study, have not been published.

Therefore, valence force constants, except for the torsional part, were taken from the work of Schachtschneider and Snyder.[14] Certain compromises between force-constant values had to be made. The final values selected for HCP are given in Table 5.

Table 5. Valence force constants for 1,1,2,2,3,3,3-heptachloropropane (X=Cl).

Stretch (mdyn Å^{-1})		Bend (mdyn Å (rad)$^{-2}$)			
C—C	4.39	CCC	0.90	HCX	0.79
C—H	4.89	CCH	0.69	XCX	1.13
C—X	2.76	CCX	1.17	—	

Stretch/stretch (mdyn Å^{-1}), C common
C—X/C—X 0.49; C—X/C—C 0.73; C—C/C—C 0.064

Stretch/bend (mdyn (rad)$^{-1}$)
C—C common: C—C/CCX 0.29; C—C/CCC 0.35; C—C/CCH 0.25
C—X common; C—X/CCX 0.55; C—X/HCX 0.33; C—X/XCX 0.41
C common: C—X/XCX 0.38

Bend/bend (mdyn Å (rad)$^{-2}$)
C—X common: XCX/XCX −0.13; CCX/XCX −0.12
C common: CCX/XCX −0.06
C—H common: HCX/HCX 0.09; CCH/HCX 0.10
C—C common (dihedral angles in parenthesis)
CCC/CCX +0.04 (CCC/CCX 180°)
CCC/CCX −0.02 (CCC/CCX 60°)
CCX/CCX −0.09 (CCX/CCX 180°)
CCX/CCX +0.07 (CCX/CCX 60°)
CCX/CCH +0.07 (CCX/CCH 180°)
CCX/CCH −0.04 (CCX/CCH 60°)
CCH/CCC −0.06 (CCH/CCC 60°)
Torsion [a] (mdyn Å (rad)$^{-2}$)
$F_\phi(1-2)=F_\phi(2-3)=0.54$ (see Sect. V-B),[b] $F_{\phi\phi'}=0$

[a] The torsional force constants have been defined in the following way: each fragment of type A′—C_i—C_3—A″ (A=C, Cl, or H) has been assigned an equal torsional force constant. The total force constant (F_ϕ) for the torsional coordinate ϕ_{i-3} (i=1,3) is thus 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 6. Fundamental vibrational frequencies (cm^{-1}) in the *gauche* conformer of 1,1,2,2,3,3,3-heptachloropropane. The force constants in Table 5 and the cartesian coordinates in Table 8 were used in calculating these frequencies.

Torsional oscillations:[a]	67 and 77
Bending vibrations:[b]	93, 144, 169, 177, 192, 210, 228, 254, 266, 298, 331, 345, 408
C—Cl stretching:[c]	565, 653, 700, 774, 776, 845, 879
C—C stretching:[d]	904 and 1173
C—H deformation:[e]	1234 and 1255
C—H stretching:	2995

[a] The two modes are roughly described as follows: 67 cm^{-1} ($\Delta\phi_{1-3}=+\Delta\phi_{2-3}$) and 77 cm^{-1} ($\Delta\phi_{1-2}\simeq-\Delta\phi_{2-3}$), where $\Delta\phi$ represents the torsion-angle deformation. [b] Modes largely corresponding to mixed CCX, XCX, and CCC angle deformations. [c] Largely C—X stretching, but mixed with angle deformations. [d] Largely C—C stretching. [e] Deformations in CCH and HCX angles.

The normal-coordinate program described by Gwinn [15] was used in computing vibrational frequencies. Their values are shown in Table 6. The agreement between these values and those observed by Sheppard *et al.*[11] is quite good. The C—Cl stretching frequencies were assigned to observations between 578 and 872 cm^{-1}. The average relative deviation between observed and calculated values is less than 2 % for C—Cl stretching modes, while the average deviation for the remaining modes is *ca.* 5 %.

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 7.

According to the semi-empirical model (Table 4), the value of the torsional interaction constant ($F_{\phi\phi'}$) is negative and in magnitude comparable to the value of the diagonal elements. The values of the torsional frequencies depend on the value of $F_{\phi\phi'}$. However, it has been shown [4]

Table 7. Mean amplitudes of vibration (u) and vibrational correction terms, $K-(u^2/r)$, for the *gauche* conformer of 1,1,2,2,3,3,3-heptachloropropane at 80 °C. The force constants in Table 5 and the cartesian coordinates in Table 8 were used in calculating these quantities. The correction term corresponds to $r_a-r_\alpha=K-(u^2/r)= -D$.

Dist. type (X=Cl)	u-Value (Å)	$K-(u^2/r)$ (Å)	Dist. type (X=Cl)	u-Value (Å)	$K-(u^2/r)$ (Å)
C_1-C_2	0.0544	0.0020	$X_1'\cdots H$	0.1093	0.0115
C_2-C_3	0.0550	0.0013	$X_1\cdots H$	0.1093	0.0120
C_1-X_1'	0.0574	0.0087	$X_1\cdots X_1'$	0.0735	0.0129
C_1-X_1	0.0575	0.0085	$X_3'\cdots X_3''$	0.0757	0.0076
C_3-X_3'	0.0570	0.0056	$X_3\cdots X_3''$	0.0757	0.0086
C_3-X_3''	0.0570	0.0060	$X_3\cdots X_3'$	0.0757	0.0079
C_3-X_3	0.0570	0.0062	$X_2\cdots X_2'$	0.0743	0.0036
C_2-X_2	0.0590	0.0032	$C_1\cdots X_3'$(g)	0.1301	−0.0007
C_2-X_2'	0.0589	0.0032	$C_1\cdots X_3''$(g)	0.1301	−0.0008
C_1-H	0.0778	0.0124	$C_3\cdots X_3$(g)	0.1297	0.0004
$C_2\cdots H$	0.1099	0.0058	$C_1\cdots X_3$(a)	0.0765	0.0011
$C_2\cdots X_1'$	0.0725	0.0064	$C_3\cdots X_1$(a)	0.0766	0.0021
$C_2\cdots X_1$	0.0724	0.0063	$C_3\cdots H$(g)	0.1503	±0.0000
$C_2\cdots X_3'$	0.0728	0.0038	$X_1'\cdots X_2'$(a)	0.0759	0.0049
$C_2\cdots X_3''$	0.0727	0.0039	$X_3'\cdots X_2$(a)	0.0762	0.0020
$C_2\cdots X_3$	0.0725	0.0047	$X_3''\cdots X_2'$(a)	0.0762	0.0022
$C_1\cdots C_3$	0.0741	0.0002	$X_2\cdots H$ (a)	0.1044	0.0058
$C_1\cdots X_2$	0.0735	0.0026	$X_2'\cdots H$ (g)	0.1515	0.0015
$C_1\cdots X_2'$	0.0733	0.0025	$X_1'\cdots X_2$(g)	0.1383	0.0013
$C_3\cdots X_2$	0.0735	0.0018	$X_3'\cdots X_2'$(g)	0.1344	±0.0000
$C_3\cdots X_2'$	0.0736	0.0019	$X_3''\cdots X_2$(g)	0.1344	−0.0001
$X_1\cdots X_2$(g)	0.1414	0.0069	$X_1'\cdots X_3'$(GG)	0.1996	−0.0056
$X_1\cdots X_2'$(g)	0.1370	0.0071	$X_1'\cdots X_3''$(GG)	0.2193	−0.0051
$X_3\cdots X_2$(g)	0.1371	0.0004	$X_1'\cdots X_3$(AG)	0.1334	−0.0009
$X_3\cdots X_2'$(g)	0.1373	0.0003	$X_1\cdots X_3'$(AG)	0.1344	−0.0004
$X_3'\cdots H$(GG)	0.2159	−0.0040	$X_1\cdots X_3''$(AG)	0.1343	−0.0008
$X_3''\cdots H$(GG)	0.1954	−0.0032	$X_1\cdots X_3$(AA)	0.1130	0.0001
$X_3\cdots H$(AG)	0.1499	0.0001	—	—	—

Table 8. Cartesian coordinates (x,y,z) and the root-mean-square displacements of atoms in the *gauche* conformer of 1,1,2,2,3,3,3-heptachloropropane (at 80 °C).

x (Å) (see Fig. 2)[a]	y (Å)	z (Å)	Atom	$\langle\Delta x^2\rangle^{\frac{1}{2}}$ (in Å units)[b]	$\langle\Delta y^2\rangle^{\frac{1}{2}}$	$\langle\Delta z^2\rangle^{\frac{1}{2}}$
0	0	0	C_2	0.0422	0.0698	0.0632
1.3947	0.7843	0	C_1	0.0570	0.0550	0.0635
1.4619	1.4332	−0.9227	H	0.1543	0.1420	0.1272
1.5179	1.8071	1.4396	X_1'	0.1171	0.1017	0.1202
2.7401	−0.3663	0	X_1	0.0685	0.0866	0.1188
−1.3947	0.7843	0	C_3	0.0486	0.0486	0.0509
−1.5179	1.8071	−1.4396	X_3'	0.1005	0.0885	0.0739
−1.5179	1.8071	1.4396	X_3''	0.1175	0.0968	0.0741
−2.7401	−0.3663	0	X_3	0.0736	0.0707	0.1092
0	−1.0743	1.4062	X_2	0.0786	0.0872	0.0743
0	−1.0748	−1.4062	X_2'	0.0786	0.0846	0.0740

[a] These values of the cartesian coordinates were used in the calculations of all vibrational quantities (staggered model). [b] The r.m.s. quantities were computed according to formulas given in Ref. 16.

Table 9. Vibrational quantities in the *gauche* conformer of 1,1,2,2,3,3,3-heptachloropropane, calculated with different values of the average torsional force constant ($\bar{F}_\phi$). See also explanations given in the Tables 5, 6, 7, and 8. $\bar{F}_{\phi\phi'}$ was fixed at zero value.

$\bar{F}_\phi$(mdyn Å (rad)$^{-2}$)	0.36	0.54[a]	0.81
Mean amplitudes u(X···X), X=Cl	u (Å) at 80 °C		
X···X(*anti*)[b]	0.076	0.076	0.076
X···X(*gauche*)[b]	0.147	0.138	0.130
$X_1'\cdots X_3'$(GG)	0.225	0.200	0.180
$X_1'\cdots X_3''$(GG)	0.231	0.219	0.210
X···X (AG)[b]	0.140	0.134	0.129
X···X (AA)	0.113	0.113	0.113
Low frequencies[c]	ω cm^{-1})		
ω_1(torsion)	55	67	81
ω_2(»)	66	77	84
ω_3(bend)	89	92	101
ω_4(»)	140	144	151
ω_5(»)	167	169	171
ω_6(»)	177	177	178
ω_7(»)	192	192	193
ω_8(»)	210	210	211

[a] The best value as determined in Sect. V-B. [b] Average value for several X···X distances of this type. See also Table 7. [c] All frequencies, calculated with $\bar{F}_\phi = 0.54$, have been shown in Table 6.

that the u and K values are much less dependent on the $F_{\phi\phi'}$ value.

Values of the cartesian coordinates (x,y,z) and the vibrational quantities $\langle\Delta x^2\rangle^{\frac{1}{2}}$, $\langle\Delta y^2\rangle^{\frac{1}{2}}$, $\langle\Delta z^2\rangle^{\frac{1}{2}}$ have been given in Table 8. The coordinate values in Table 8 were used in all calculations involving vibrational quantities. The r.m.s. quantities were computed according to the formulas derived in Ref. 16.

According to the adjustments described in Sect. V-B, the most probable value of the average torsional force constant ($\bar{F}_\phi$) is expected in the range 0.36—0.81 mdyn Å (rad)$^{-2}$. In Table 9 are shown low vibrational frequencies and mean amplitudes of vibration corresponding to values of $\bar{F}_\phi$ in this range.

IV. EXPERIMENTAL AND DATA REDUCTION

HCP was obtained from "K&K" laboratories. The purity of the sample was better than 97 %.

Electron-diffraction photographs were made at a nozzle temperature of 80 °C in the Balzer [17] apparatus [18] under conditions summarized below.

Nozzle-to-plate distance (mm)	498.8	249.0
Electron wavelength (Å)	0.05856	0.05853
Number of plates	5	4
Range of data, in s(Å^{-1})	1.125—15.625	2.25—30.50
Data interval, Δs(Å^{-1})	0.125	0.25
Estimated uncertainty in s-scale (%)	0.14	0.14

The electron wavelength was determined by calibration against ZnO 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 way [19] to yield an intensity curve for each plate.

Average curves for each set of distances were formed. A composite curve was then made by connecting the two average curves after scaling. The final experimental curve is shown in Fig. 3. The intensities have been modified [19] by $s|f'_{Cl}|^{-2}$. The scattering amplitudes were calculated by the partial-wave method,[20] using Hartree-Fock atomic potentials.[21]

The radial-distribution curve obtained by Fourier [19] transformation of the final experimental intensity is shown in Fig. 4.

V. STRUCTURE ANALYSIS

From the RD curves in Fig. 5 it is obvious that *gauche* is the most abundant conformer. The relative amount of the *anti* conformer has to be very small. If the conformational energies predicted by the semi-empirical model are correct, the presence of the *anti* conformer can not be detected at 80 °C [$\alpha(anti) < 0.5$ %].

In calculating theoretical intensities, it was decided not to consider contributions from the *anti* conformer. (See also Sect. VII).

A. *Least-squares refinements.*[19] HCP represents a complicated structural problem. Several assumptions about bond lengths and bond angles

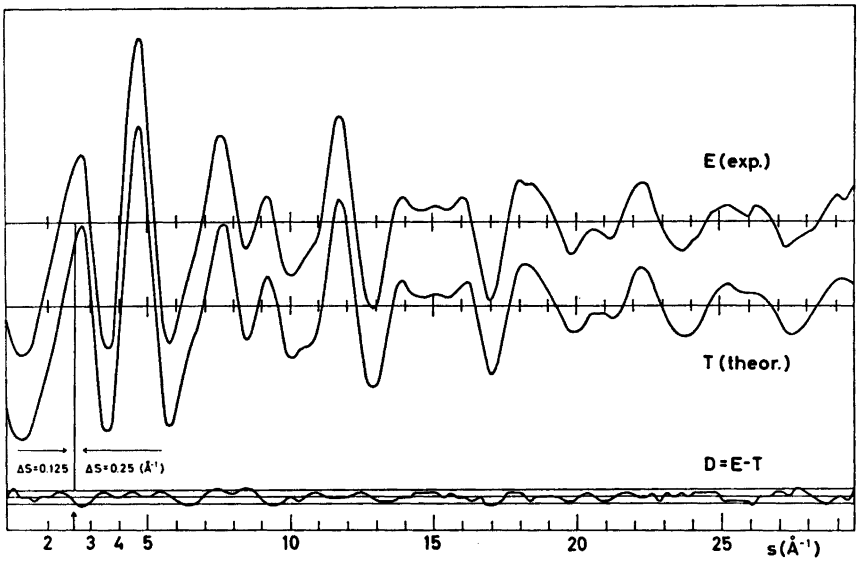

Fig. 3. Experimental (E) and theoretical (T) intensity curves for 1,1,2,2,3,3,3-heptachloropropane at 80 °C. The difference curve (D) is shown together with the experimental error limits of the intensities. All curves are on the same scale.

have to be made in constructing the molecular model to be used in the least-squares adjustments. The following assumptions were introduced (see Fig. 2).

(1) The plane of the CX_2 group is perpendicular to the plane of the C atoms and bisects the CCC angle,

(2) the $C-CX_3$ group possess C_{3v} symmetry,

(3) the $C-CHX_2$ group possess C_s symmetry, and the projection of the $X_1C_1X_1'$ angle on a plane perpendicular to the C_1-C_2 axis is 120,°

(4) the CCX angles in the $-CHX_2$ and $-CX_3$ groups are equal ($\angle CC_1X = \angle CC_3X$),

(5) all CCX angles of the $-CX_2-$ group are equal: $\angle CC_2X$,

(6) the C—X bond lengths of the $-CHX_2$ and $-CX_3$ groups are equal: $r(C_1-X)=r(C_3-X)$,

(7) the C—X bond lengths in the $-CX_2-$ group are equal: $r(C_2-X)$.

(8) the two C—C bond lengths are equal: $r(C-C)$.

Models were refined in terms of the following parameters: $r(C-C)$, $r(C_1-X)=r(C_3-X)$, $r(C_2-X)$, $r(C-H)$, $\angle CCC$, $\angle CC_1X=\angle CC_3X$, $\angle CC_2X$, and the torsion angles (ϕ_{1-2} and ϕ_{2-3}) of the *gauche* conformer (see Fig. 1). For the exact staggered conformation of *gauche* $\phi_{1-2}=\phi_{2-3}=0°$, corresponding to a coplanar 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.[22,23]

Several of the bond distances which have been assigned equal *lengths* in the least-squares adjustments, are not *vibrationally* identical, as shown in Table 7. This fact has been 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. 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 values of the torsional force constants $F_\phi(1-2)$, $F_\phi(2-3)$, and $F_{\phi\phi'}$ for HCP had not been experimentally determined prior to this investigation.

If the interaction constant ($F_{\phi\phi'}$) is not considered (see discussion in sect. III), then two elements, $F_\phi(1-2)$ and $F_\phi(2-3)$, of different values ought to be adjusted. It is clear that $F_\phi(1-2)<F_\phi(2-3)$. According to the semi-empirical model $F_\phi(2-3)$ is *ca.* 20 % (Table 4) greater than $F_\phi(1-2)$.

Unfortunately the electron-diffraction data for HCP do not contain enough information for an independent determination of $F_\phi(1-2)$ and

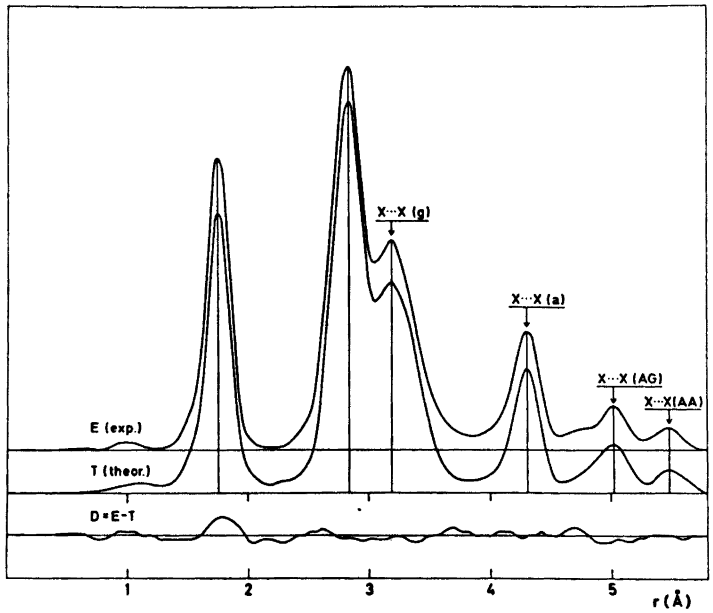

Fig. 4. Experimental (E) and theoretical (T) radial-distribution curves for 1,1,2,2,3,3,3-heptachloropropane at 80 °C and difference curve (D). The curves have been calculated by Fourier transformation of the intensities in Fig. 3, using an artificial damping constant equal to 0.0020 Å^2.

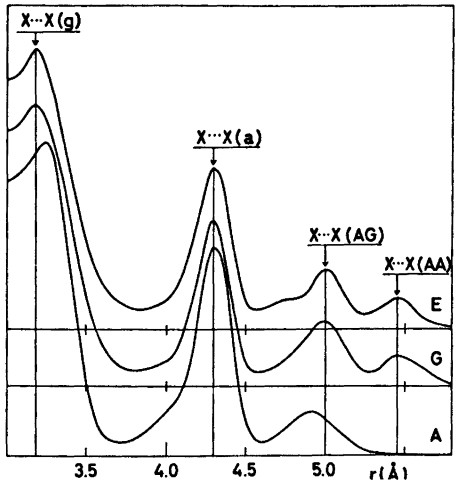

Fig. 5. Theoretical radial-distribution curves for the conformers *anti* (A) and *gauche* (G). The experimental curve (E) is also shown.

$F_\phi(2-3)$ simultaneously. It is, however, possible to estimate an average element $\bar{F}_\phi$ ($F_\phi(1-2)=F_\phi(2-3)=\bar{F}_\phi$).

The value of $\bar{F}_\phi$ was determined as follows: u and K values for different values of $\bar{F}_\phi$ were calculated and then included in the least-squarse refinements. The value of $\bar{F}\phi$ which lead to a minimum in the error sum (V'PV) was obtained. In each least-squares run all structural variables were refined simultaneously. The best value of $\bar{F}_\phi$ obtained in this way was: $\bar{F}_\phi = 0.54\ ^{+0.27}_{-0.18}$ mdyn Å (rad)$^{-2}$. The error limits are believed to be pessimistic; however, there is no objective way to estimate these limits. The most direct estimate, but subjective to a certain degree, is probably obtained by comparing experimental and calculated RD curves for a range of $\bar{F}_\phi$ values. Several types of *systematic* errors ought to be considered, as discussed in a previous paper.[4] The error limits here do not allow for systematic errors.

VI. FINAL RESULTS

Parameters from the least-squares refinements, and their standard deviations (σ) corrected for correlation [24] in the experimental data, are given in Table 10. The final parameters correspond to refinements with equal weights for all intensities. Data beyond $s=29.5$ Å^{-1} were not included in these refinements.

Table 10. Structural parameters in the *gauche* conformer of 1,1,2,2,3,3,3-heptachloropropane (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_a-values)	Bond angles (°)[a] ($\angle_\alpha$-values)
r(C−C)=1.601(8)	∠CCC=117.6(1.9)
Average parameters in the $-CX_3$ and $-CHX_2$ groups:	
r(C−X)=1.777(6)	∠CCX=110.3(0.6)
Average parameters in the $>CX_2$ groups:	
r(C−X)=1.765(14)	∠CCX=108.3(0.6)
r(C−H)=1.05(9)[b]	∠CCH=(109.47)[c]
Torsion angles (assuming $\phi_{2-3}=-\phi_{1-2}$):	
$\phi_{1-2}=+7.8°(1.1)$[d] and $\phi_{2-3}=-7.8°(1.1)$[d]	

[a] The geometrical assumptions have been explained in Sect. V-A. [b] See Fig. 4. [c] Assumed value. [d] Staggered values: $\phi_{1-2}=\phi_{2-3}=0°$, see Fig. 1.

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

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

The fit obtained between theoretical and experimental intensities, using the u and K values calculated with the force constants of Table 5 was generally quite satisfactory. It is important that the large number of u values do not have to be adjusted as individual parameters in the least-squares refinements. However, it ought to be kept in mind that the torsiondependent u and K values have been adjusted *simultaneously* by adjusting the diagonal torsional-force constants (Sect. V-B). The vibrationally consistent u values of Table 7, which combine information from both vibrational spectroscopy and electron diffraction, are considered more reliable than the individual u values obtained by direct least-squares refinements in the usual way.[19] The average relative standard deviation, $\langle\sigma/u\rangle$, of individually adjusted u values was *ca.* 10 %, while the average relative deviation between these u values and those of Table 7, $\langle|\Delta|/u\rangle$, was *ca.* 16 %. Only one u value, u(C−Cl)=0.037 Å and σ=0.004 Å, obtained by direct refinement, was significantly different from the value (*ca.* 0.058 Å) of Table 7. Most probably the low value of u(C−Cl) is caused by an error in the blackness correction. It is, however, unlikely that such an error is critical for the determination of the remaining u values.

In calculating the theoretical intensities of Fig. 3, the individually adjusted u-values were used. The theoretical intensities obtained with the u-values from Table 7 were only slightly different from those of Fig. 3.

VII. DISCUSSION

In comparing theoretical radial distribution curves with the experimental one, it was concluded that the smallest detectable amount of *anti* is *ca.* 10 % or more. The actual amount of *anti* could not be determined by least-squares refinements in this particular case. However, from the experimental data alone a small (< 10 %) of *anti* is not ruled out.

Assuming equal vibrational partition functions for the conformers *anti* and *gauche*, and the conformational energies of Table 2 (ΔE(a−g)=3.2 kcal/mol), then the percentage of *anti* should be less than 0.5 % at 80 °C. In order to get as much as *ca.* 10 % of the *anti* conformer at 80 °C, the value of ΔE(a−g) have to be *ca.* 1.1 kcal/mol. It is possible, but unlikely, that the calculated energy difference ΔE(a−g) (3.2 kcal/mol) is wrong by as much as *ca.* 2 kcal/mol. Therefore, in conclusion, the best estimate of the conformational energy difference is 3.2 kcal/mol in favour of *gauche*, as predicted by the semi-empirical model. This estimate is also consistent with the electron-diffraction data.

It seems natural to compare the structural parameters of HCP with those found in octachloropropane (OCP),[4] where *all* hydrogen positions in propane have been substituted with chlorine. The C−C bond lengths and the CCC bond angles of both molecules are very different from those in propane itself. The experimentally determined difference between the C−C bond

Table 11. Parameter correlation coefficients (100 ϱ).

		(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
r(C−C)[a]	(1)	100										
r(C_2−X)	(2)	−37	100									
r(C_1−X)	(3)	6	−84	100								
r(C−H)	(4)	−10	6	3	100							
∠CCC	(5)	5	−48	54	10	100						
∠CC_1X	(6)	−62	82	−67	11	−32	100					
∠CC_2X	(7)	9	7	−10	0	−62	−27	100				
∠CCH	(8)	−41	19	−14	45	12	34	−3	100			
ϕ[b]	(9)	3	2	1	3	−38	−21	70	−2	100		
k(scale)	(10)	−32	−37	−26	20	−6	38	−1	34	7	100	
u(C−X)[c]	(11)	−18	−6	19	10	13	−5	4	12	9	54	100

[a] The geometrical assumptions are given in Sect. V-A. [b] Torsion angles: $\phi_{1-2}=\phi$ and $\phi_{2-3}=-\phi$. [c] All u(C−X) values were refined as one parameter.

lengths [r_a(OCP)−r(HCP)=1.655 Å−1.601 Å] is 0.054 Å, and the difference between the CCC angles (∠CCC(OCP)−∠CCC(HCP)=119.0°−117.6°) is 1.4°. According to the semi-empirical calculations the *anti* conformer of HCP should have a CCC bond angle even larger than the one in OCP. No significant deviations from an all-staggered (1:2) conformation were observed for OCP, while the deviations from an all-staggered (1:2) *gauche* conformation for HCP are statistically significant, but quite small.

To a large extent the values of the structural parameters predicted by the semi-empirical model (Table 1), reasonably agree with the experimental findings. Within the experimental error limits for HCP, the predicted parameters r(C−C), <CCC, and the torsion angles agree with the observed values. Although adjustments in the non-torsional force constants and the "normal" reference parameters (Table 1) would remove most of the remaining discrepancies, it was felt that results from additional molecules ought to be included before such corrections were considered.

It has been demonstrated that the average diagonal element of the torsional force field may be estimated from the 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 55−85 cm^{-1} (Table 9). For octachloropropane [4] this range was 45−65 cm^{-1}. The average torsional force constants were 0.54 and 0.36 mdyn Å $(rad)^{-2}$ for HCP and OCP, respectively. Within the experimental error limits (Sect. V-B) the calculated (Table 4) force constants agree with the experimental average value for HCP.

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