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Conformational Analysis. IX. The Molecular Structure, Torsional Oscillations, and Conformational Equilibrium of Gaseous 1,1,3,3,3-Pentachloropropane ($CHCl_2$—CH_2—CCl_3) as Determined by Electron Diffraction and Compared with Semi-empirical (Molecular Mechanics) Calculations

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Gaseous $CHCl_2-CH_2-CCl_3$ (PCP) has been studied by electron diffraction at a nozzle temperature of 80 °C. *Gauche* and *anti* conformers are possible for PCP. The conformer with the terminal H atom *anti* to the CCC group was not present in detectable amounts.

Results are presented with error limits (2σ). The following values for bond lengths (r_g) and bond angles ($\angle_\alpha$) were obtained: $r(C-C)=1.547(12)$ Å, $r(C-Cl)=1.774(4)$ Å, $\angle CCC=115.7°$ (2.8), and $\angle CCCl=109.9°$ (0.6). The deviations from an exact all-staggered (1:2) *gauche* conformation are large [$\phi_{1-2}=+14.1°$ (3.0) and $\phi_{2-3}=-22.5°$ (2.2); with $\phi_{1-2}=\phi_{2-3}=0°$ for the exact staggered form].

An average torsional force constant was estimated from the electron-diffraction data. Within the experimental error limits, the values of the diagonal torsional force constants predicted by the semi-empirical model, agree with the experimental value. The fundamental frequencies, 56 cm^{-1} and 77 cm^{-1}, corresponding to torsional oscillations in the *gauche* conformer, have been estimated.

Experimental and calculated results for $CHX_2-CH_2-CX_3$, $CHX_2-CX_2-CX_3$, and $CX_3-CX_2-CX_3$ (X = Cl) have been compared.

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] $Cl_3C-CCl_2-CHCl_2$,[4] $Cl_3C-CCl_2-CCl_3$.[5] Molecules with $-CH_2X$ groups (X = Cl or H) bonded to the central C atom of a C—C—C skeleton have also been investigated: $C(CH_2Cl)_4$,[6] $(CH_3)_2C(CH_2Cl)_2$,[7] and $(CH_3)C(CH_2Cl)_3$.[8]

General information [9] relevant to this investigation and to the electron diffraction method [10] is found in Refs. 9 and 10.

Chlorinated propanes were extensively studied by Sheppard *et al.* using vibrational and NMR spectroscopy. The principal results obtained by these methods, in the liquid phase, are found in Refs. 11, 12, and 13. Conformers which possess parallel C—Cl bonds on the same side of the carbon skeleton (parallel (1:3) Cl···Cl interaction), are energetically less stable than conformers without such interactions.[11]

Assuming all-staggered (1:2) conformations, only two spectroscopically distinguishable forms are possible for PCP. 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 ment. Both *anti* and *gauche* conformers involve parallel (1:3) Cl···Cl interactions, but the *gauche* ones have one such interaction less than the *anti* conformer.

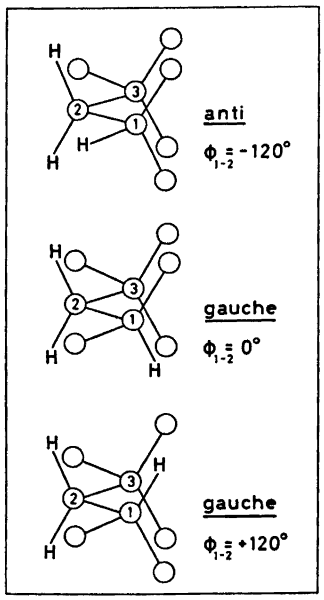

Fig. 1. The staggered conformers in $HCCl_2-CH_2-CCl_3$. The value of the torsion angle ϕ_{2-3} is 0° for exact staggered forms.

Based on vibrational and NMR spectra Sheppard *et al.*[12] concluded that only one type of conformer (*gauche*) is present in the liquid in any quantity.

Some symbols which are used in this paper need a few comments. PCP 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* relations in a Z–C–C–Y fragment. The symbols are then combined with the symbols for the internuclear Z···Y distance (see Table 7).

II. CALCULATION OF STRUCTURAL PARAMETERS, CONFORMATIONAL BARRIERS, TORSIONAL 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 Vo) were taken from the work of Abraham and Parry.[14] The diagonal valence force constants in Table 5 were used. In minimizing the energy, the geometrical model was constrained as described in Sect. V-A.

Table 1. Calculated structural parameters in the stable conformers of $C(1)HX_2-C(2)H_2-C(3)X_3$. The structural parameters were constrained as described in Sect. V-A.

Type of parameter r(Å), ∠(°), X=Cl	Normal value	*gauche*	*anti*
$r(C-C)^a$	(1.513)	1.543	1.552
$r(C-X)^b$	(1.760)	1.768	1.769
$r(C_2-H)$	(1.094)	1.096	1.096
$r(C_1-H)$	(1.094)	1.093	1.094
∠CCC	(110.0)	116.1	123.3
$\angle CCX^c$	(109.47)	111.1	112.1
$\angle C_2C_1H$	(109.47)	108.6	106.8
$\angle C_1C_2H$	(109.47)	110.4	108.9
$\angle\phi_{1-2}(-C_1-C_2-)$	$(60)^d$	+32.3	−102.0
$\angle\phi_{2-3}(-C_2-C_3-)$	$(60)^d$	+1.9	+17.0

[a] Average C–C parameter. [b] Average C–X parameter for $-CHX_2$ and $-CX_3$. [c] Average ∠CCX parameter for $C-CHX_2$ and $C-CX_3$. [d] $\phi = 60°$ corresponds $V_\phi = 0$; see Ref. 1.

Table 2. Calculated conformational energies in $C(1)HX_2-C(2)H_2-C(3)X_3$, X=Cl. The energy expression was explained in Ref. 1. Zero-point energies for the conformers are not included.

Type of energy (kcal/mol)	*gauche*	*anti*	Δ(g-a)
E(bonded)	3.76	7.87	−4.11
E(van der Waals)	3.42	3.30	+0.12
E(polar: Cl···H)	−10.80	−9.89	−0.91
E(polar: Cl···Cl)	10.36	11.79	−1.43
E(total)	6.74	13.07	−6.33

The structural parameters in Table 1 correspond to the minima found by minimizing the energy. It is clear that large deviations from all-staggered (1:2) conformations are likely for both *gauche* and *anti*. Moreover, the ∠CCC values of the conformers are quite different.

The calculated conformational energies which are given in Table 2, show that *gauche* is energetically more stable than *anti* by as much as 6.33 kcal/mol.

Torsional barriers may be estimated from the energy values in Table 3. The details about the three minima have been shown in Tables 1 and

Table 3. Calculated conformational energies and torsional barriers in $C(1)HX_2-C(2)H_2-C(3)X_3$, X = Cl. Approximative values of the torsion angles are those in parentheses (ϕ_{1-2} and ϕ_{2-3}; see also Fig. 1). All energy values are relative to the *gauche* minimum.

ϕ_{2-3}	ϕ_{1-2} $-180°$ $-60°$ $+180°$	$-120°$	$0°$ $+120°$	$+60°$
$+60°$ $-60°$	29.7	11.3	8.1	11.3
		"anti"	*"gauche"*	
$0°$	10.3	7.4[a] min: 6.33	3.6[b] min: 0	0.7

[a] Energy of the exact staggered *anti* form ($\phi_{1-2}=-120°$ and $\phi_{2-3}=0°$). Details about the *minimum* are given in Tables 1 and 2. [b] Energy of the exact staggered *gauche* forms ($\phi_{1-2}=\phi_{2-3}=0°$). Details about the *gauche* minimum are given in Tables 1 and 2. See also explanation in text.

2. All energy values are relative to the *gauche* minima. The values of the torsion angles (ϕ_{1-2} and ϕ_{2-3}) are approximately those given in parentheses. Each energy value was obtained by adjusting all geometry variables except for values of ϕ being $-180°$, $-60°$, $+60°$, and $+180°$. The energy value 8.1 kcal/mol thus corresponds to a form with $\phi_{2-3}=+60°$ (or $-60°$), while the value of ϕ_{1-2} is approximately equal to 0°. The actual values of the remaining structural variables are not shown in Table 3 in order to save space.

Between the two *gauche* minima is a low barrier of *ca.* 0.7 kcal/mol, corresponding to values of ϕ_{1-2} and ϕ_{2-3} being $+60°$ and 0°, respectively. The barrier separating *anti* and *gauche* minima is considerably higher.

Table 4. Calculated torsional force constants in Conformers of $C(1)HX_2-C(2)H_2-C(3)X_3$, X = Cl. These values were *numerically* computed according to the definitions given.

(mdyn Å (rad)$^{-2}$)	*gauche*	*anti*
$F_\phi(1-2)=\partial^2E/\partial\phi_{1-2}{}^2$	0.20	0.38
$F_\phi(2-3)=\partial^2E/\partial\phi_{2-3}{}^2$	0.27	0.44
$F_{\phi\phi'}=\partial^2E/\partial\phi_{1-2}\partial\phi_{2-3}$	-0.07	0.02

The *exact* all-staggered (1:2) forms clearly do not correspond to minima of the energy function. (7.4[a] and 3.6[b] in Table 3).

The torsional force constants of Table 4 were calculated at the conformational minima. It is noteworthy that the magnitude of the interaction constant ($F_{\phi\phi'}$) is quite small for both conformers.

III. CALCULATION OF VIBRATIONAL QUANTITIES

Vibrational frequencies for PCP (liquid) have been published by Sheppard *et al.*[12] However, the low frequencies (< ca. 570 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.[15] Certain compromises between force constant values had to be made. The final values selected for PCP are given in Table 5.

According to the semi-empirical model (Table 4) the value of the torsional interaction constant ($F_{\phi\phi'}$) is much smaller in magnitude than the diagonal element. $F_{\phi\phi'}$ has been given zero value in this work.

According to the semi-empirical model, a low barrier (0.7 kcal/mol) separates the two *gauche* conformers. If the calculated value of this barrier is correct, then the usual approximation assuming small vibrational amplitudes (SVA) is not valid, in calculating mean amplitudes of vibration for the *gauche* conformer. It is, however, possible that the calculated value is too low. With a barrier value of *ca.* 1.5 kcal/mol, or higher, the SVA approximation is valid at 60 °C. It was decided to apply the SVA approximation. The validity of that approximation then has to be judged by the final results (see Sect. VII).

The normal-coordinate program described by Gwinn [16] 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.*[12] is quite satisfactory. The average relative deviation between observed and calculated values is *ca.* 3 % for C–Cl stretching modes.

Mean amplitudes of vibration (u) and vibrational correction terms (K and D) for the

Table 5. Valence force constants for $C(1)HX_2-C(2)H_2-C(3)X_3$, X = Cl.

Stretch (mdyn Å^{-1})

C–C: 4.39
C–H: 4.89
C–X: 2.76

Bend (mdyn Å(rad)$^{-2}$)

CCC: 0.90
CCH: 0.69
CCX: 1.17
HCX: 0.79
XCX: 1.13
HCH: 0.54

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

C–X/CCX: 0.55 (C–X common)
C–X/HCX: 0.33 (C–X common)
C–C/CCX: 0.29 (C–C common)
C–C/CCC: 0.35 (C–C common)
C–C/CCH: 0.26 (C–C common)
C–X/XCX: 0.41 (C–X) common)
C–X/XCX: 0.38 (C common)

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
C–H/C–H: 0.06

Bend/bend (mdyn Å(rad)$^{-2}$)

HCX/HCX: 0.09 (C–H common)
XCX/XCX: −0.13 (C–X common)
CCX/XCX: −0.12 (C–X common)
CCX/XCX: −0.06 (C common)
CCH/HCX: 0.10 (C–H common)
CCH/CCC: −0.12 (C–C common)

Bend/bend (C–C common and dihedral angle *anti* or *gauche*)

CCC/CCX: 0.04 (*anti*) and −0.02 (*gauche*)
CCH/CCC: – (*anti*) and −0.06 (*gauche*)
CCH/CCH: 0.10 (*anti*) and −0.03 (*gauche*)

Torsion [a] (mdyn Å(rad)$^{-2}$)

$F_\phi(1-2) = F_\phi(2-3) = \bar{F}_\phi{}^b = 0.32_{-0.16}{}^{+0.18}$ ($F_{\phi\phi'} = 0$)

[a] The torsional force constants were defined as follows: each fragment $A'-C_i-C_2-A''$ (A = C, Cl, H) has been 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. Gwinn's normal-coordinate program [16] demands a separate specification for each torsion fragment. [b] This value was derived from the electron-diffraction data as described in Sect. V-B.

Table 6. Fundamental vibrational frequencies, ω(cm^{-1}), in the *gauche* conformer of $C(1)HX_2-C(2)H_2-C(3)X_3$, (X = Cl). The force constants of Table 5 were used. Experimental (average of liquid IR and Raman) values from Ref. 12 are shown in parentheses.

Torsion: 56 ($\Delta\phi_{1-2} \simeq +\Delta\phi_{2-3}$)[a] and 77 ($\Delta\phi_{1-2} \simeq -\Delta\phi_{2-3}$)[a]

Bend[b] (CCX, XCX, CCC): 110, 197, 214, 252, 262, 313, 369, 394, 478
C–X (stretch)[c]: 566, 640, 702, 758, 855 (577, 640, 716, 734, 831)
CH_2-rock: 998 (971)
CH_2-twist: 1197 (1204)
CH_2-wag: 1421 (1347)
C–C (stretch):[d] 1007, 1083, (1026, 1069)
Def.[e] (CCH, HCX): 1229, 1320 (–)[f]
Def.[e] (HCH): 1475 (1419)
C–H (stretch): 2991, 2997, 3001 (2943, 2982, 3003)

[a] Deformations in torsional angles ($\Delta\phi$) have been indicated. [b] Modes involving deformations in angles as indicated, mixed with a certain amount of C–X stretching. [c] Modes involving C–X stretching mixed with bending of CCX, HCX, and CCC angles. [d] Modes involving C–C stretching mixed with deformations of CCH angles. [e] Modes involving deformations of angles as indicated. [f] Experimental values in this range are: 1218, 1248, 1300.

Table 7. Mean amplitudes of vibration (u) and vibrational correction terms, $K-(u^2/r)$, for $C(1)HX_2-C(2)H_2-C(3)X_3$ at 60 °C. The force constants in Table 5 and the Cartesian coordinates in Table 9 were used in calculating these quantities. The correction terms correspond 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	0.0523	0.0038	$X_1'\cdots H_1$	0.1090	0.0176
C_2-C_3	0.0529	0.0024	$X_1\cdots H_1$	0.1090	0.0139
C_1-X_1'	0.0572	0.0128	$X_1\cdots X_1'$	0.0718	0.0177
C_1-X_1	0.0571	0.0094	$X_3'-X_3''$	0.0740	0.0081
C_3-X_3'	0.0563	0.0073	$X_3\cdots X_3''$	0.0740	0.0084
C_3-X_3''	0.0563	0.0082	$X_3\cdots X_3'$	0.0740	0.0068
C_3-X_3	0.0563	0.0076	$H_2\cdots H_2'$	0.1292	0.0109
C_2-H_2	0.0778	0.0110	$C_1\cdots X_3'$(g)	0.1323	−0.0001
C_2-H_2'	0.0778	0.0111	$C_1\cdots X_3''$(g)	0.1299	−0.0010
C_1-H_1	0.0778	0.0152	$C_3\cdots X_1'$(g)	0.1329	0.0026
$C_2\cdots H_1$	0.1089	0.0101	$C_1\cdots X_3$(a)	0.0792	0.0010
$C_2\cdots X_1'$	0.0702	0.0112	$C_3\cdots X_1$(a)	0.0756	0.0020
$C_2\cdots X_1$	0.0701	0.0072	$C_3\cdots H_1$(g)	0.1541	0.0022
$C_2\cdots X_3'$	0.0705	0.0048	$X_1'\cdots H_2'$(a)	0.1053	0.0133
$C_2\cdots X_3''$	0.0704	0.0054	$X_3'\cdots H_2$(a)	0.1052	0.0061
$C_2\cdots X_3$	0.0704	0.0056	$X_3''\cdots H_2'$(a)	0.1081	0.0068
$C_1\cdots C_3$	0.0716	0.0011	$H_2\cdots H_1$(a)	0.1275	0.0136
$C_1\cdots H_2$	0.1074	0.0075	$H_2'\cdots H_1$(g)	0.1647	0.0085
$C_1\cdots H_2'$	0.1068	0.0074	$X_1'\cdots H_2$(g)	0.1561	0.0080
$C_3\cdots H_2$	0.1071	0.0109	$X_3'\cdots H_2'$(g)	0.1448	0.0036
$C_3\cdots H_2'$	0.1070	0.0112	$X_3''\cdots H_2$(g)	0.1539	0.0036
$X_1\cdots H_2$(g)	0.1515	0.0054	$X_1'\cdots X_3'$(GG)	0.2342	−0.0093
$X_1\cdots H_2'$(g)	0.1518	0.0053	$X_1'\cdots X_3''$(GG)	0.2343	−0.0042
$X_3\cdots H_2$(g)	0.1468	0.0045	$X_1'\cdots X_3$(AG)	0.1230	−0.0008
$X_3\cdots H_2'$(g)	0.1521	0.0050	$X_1\cdots X_3'$(AG)	0.1542	−0.0022
$X_3'\cdots H_1$(GG)	0.2187	0.0004	$X_1\cdots X_3''$(AG)	0.1278	−0.0021
$X_3''\cdots H_1$(GG)	0.2035	−0.0041	$X_1\cdots X_3$(AA)	0.1165	0.0005
$X_3\cdots H_1$(AG)	0.1703	−0.0004	–	–	–

internuclear distances were calculated according to the formulas in Ref. 17. Their values are found in Table 7.

According to the adjustments described in Sect. V-B, the most probable value of the average torsional force constant ($\overline{F}_\phi$) is expected in the range 0.16 − 0.50 mdyn Å(rad)$^{-2}$. In Table 8 are shown low frequencies and important mean amplitudes of vibration corresponding to values of $\overline{F}_\phi$ in that range.

Values of the Cartesian coordinates (x,y,z) have been given in Table 9. The coordinate values in Table 9 were used in all calculations of vibrational quantities. The location of the Cartesian-coordinate system should be clear from the x, y, and z values in Table 9 (origin at the atom C_2).

IV EXPERIMENTAL AND DATA REDUCTION

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

Electron-diffraction photographs were made at a nozzle temperature of 60 °C in the Oslo apparatus [18] under conditions summarized below.

Nozzle-to-plate distance (mm)	481.8	201.8
Electron wavelength (Å)	0.06452	0.06452
Number of plates	6	6
Range of data, in s (Å^{-1})	1.375 − 19.375	7.25 − 43.25
Data interval, ΔS (Å^{-1})	0.125	0.25
Estimated uncertainty in s-scale %)	0.14	0.14

Table 8. Vibrational quantities in the *gauche* conformer of $C(1)HX_2-C(2)H_2-C(3)X_3$, (X = Cl), calculated for different values of the average torsional force constant ($\overline{F}_\phi$) at 60 °C.

$\overline{F}_\phi$ (mdyn Å(rad)$^{-2}$)	0.16[a]	0.32	0.50[a]
$u(X\cdots X)$[b] values (Å)			
$X_1\cdots X_3$ (AA)	0.125	0.117	0.113
$X_1'\cdots X_3$ (AG)	0.137	0.123	0.117
$X_1\cdots X_3'$ (AG)	0.171	0.154	0.147
$X_1\cdots X_3''$(AG)	0.144	0.128	0.121
$X_1'\cdots X_3''$ (GG)	0.277	0.234	0.215
$X_1\cdots X_3$ (GG)	0.303	0.234	0.204
$u(C\cdots X)$[b] values (Å)			
$C_1\cdots X_3$ (a)	0.083	0.079	0.078
$C_3\cdots X_1$ (a)	0.077	0.076	0.075
$C_1\cdots X_3'$ (g)	0.148	0.136	0.131
$C_1\cdots X_3''$ (g)	0.152	0.130	0.120
$C_3\cdots X_1'$ (g)	0.155	0.133	0.124
Frequencies,[c] ω (cm^{-1})			
Torsion (++)	40	56	69
Torsion (+−)	62	77	85
Bend (CCX/XCX/CCC)	107	110	113
	197	198	197
	213	214	215
	250	252	254
	260	262	264
	311	313	316
	356	369	377
	394	394	394
	452	478	499

[a] Except for these values, the force fields in Table 5 were used. [b] Mean amplitudes of vibration for torsion dependent X···X and C···X distances. See also Table 7. [c] Low vibrational frequencies (<500 cm^{-1}). See also Table 6.

Table 9. Cartesian coordinates from atoms in the *gauche* conformer of $C(1)HX_2-C(2)H_2-C(3)X_3$. These coordinate values were used in the calculations of all vibrational quantities (non-staggered model).

x (Å)	y (Å)	z (Å)	Atom[a] (X = Cl)
0	0	0	C_2
1.3137	0.8089	0	C_1
1.2493	1.6209	−0.7581	H_1
1.5757	1.5153	1.5903	X_1'
2.6629	−0.2504	−0.3931	X_1
−1.3137	0.8089	0	C_3
−1.1358	2.2299	−1.0226	X_3'
−1.6965	1.3192	1.6401	X_3''
−2.6251	−0.1890	−0.6175	X_3
0	−0.7106	0.8628	H_2
0	−0.7106	−0.8628	H_2'

[a] *Cf.* Fig. 2.

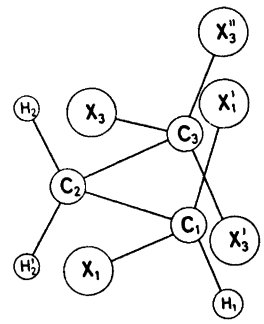

Fig. 2. Numbering of atoms (X = Cl) in the *gauche* conformer ($\phi_{1-2}=\phi_{2-3}=0°$) of $HCX_2-CH_2-CX_3$.

The electron wavelength 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 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 $s|f_{Cl'}|^{-2}$. Scattering amplitudes were calculated by the partial-wave method,[20] using Hartree-Fock atomic potentials.[21]

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

V. STRUCTURE ANALYSIS

The presence of the large peak in the experimental RD-curve (Fig. 4) at 5.0 − 5.5 Å shows that *gauche* is the predominating conformer.

According to the semi-empirical model, the conformational energy difference between *gauche* and *anti* is 6.3 kcal/mol in favour of *gauche*. If this value is approximately correct, then *anti* can not be present in detectable amounts at *ca.* 60 °C. Therefore, the *anti* conformer has not been included in the structural analysis. The validity of this assumption has to be judged by the final results (see also Sect. VII).

A. *Least-squares refinements.*[19] Several assumptions about bond lengths and bond angles had to be made in constructing the molecular model for the least-squares refinements. The following assumptions were introduced: (see Fig. 2; X = Cl)

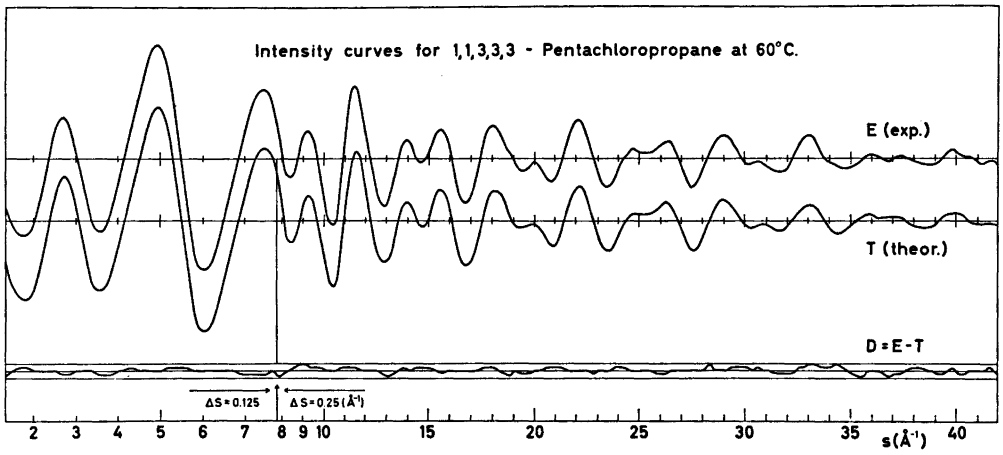

Fig. 3. Experimental (E) and theoretical (T) intensity curves, and D = E − T, corresponding to the final least-squares parameters. The straight lines give the experimental uncertainties (± 3 × experimental standard deviation).

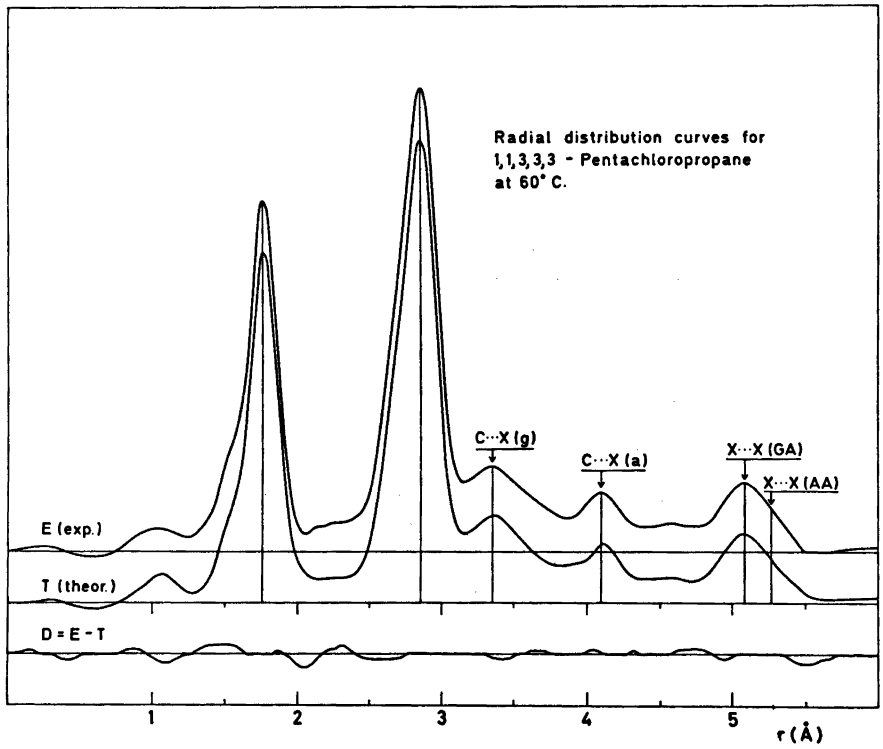

Fig. 4. Experimental (E) and theoretical (T) radial distribution curves, and D = E − T. The curves were calculated from the intensity curves in Fig. 3 with an artificial damping constant of 0.0020 Å^2. Some of the peaks corresponding to non-bonded internuclear distances have been indicated; see also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

(1) the plane of the CH_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) all CCX angles are equal, (5) all CCH angles of the $>CH_2$ group are equal: $\angle CC_2H$, (6) all C–X bond lengths are equal: $r(C-X)$, (7) the C–H bond lengths in the $>CH_2$ group are equal: $r(C_2-H)$, (8) the two C–C bond lengths are equal: $r(C-C)$.

Models were refined in terms of the following parameters: $r(C-C)$, $r(C-X)$, $r(C_1-H)$, $r(C_2-H)$, $\angle CCC$, $\angle CCX$, $\angle CC_2H$, $\angle C_2CH$, and the torsion angles (ϕ_{1-2} and ϕ_{2-3}) of the *gauche* conformer (see Fig. 1). For the exact all-staggered (1:2) conformation of *gauche* $\phi_{1-2}=\phi_{2-3}=0°$, corresponding to a coplanar arrangement of the atoms $X_1-C_1-C_2-C_3-X_3$ (Fig. 2).

Non-bonded internuclear distances were computed under the constraints of geometrically consistent r_α parameters.[22,23]

Several of the bond distances which have been assigned equal *lengths* 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 included for 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 (Sect. III). The values of the torsional force constants $F_\phi(1-2)$, $F_\phi(2-3)$, and $F_{\phi\phi'}$ had not been experimentally determined previous to this investigation.

If the value of the interaction constant ($F_{\phi\phi'}$) is assumed to be zero (see Table 4), then two elements, $F_\phi(1-2)$ and $F_\phi(2-3)$, of different values ought to be adjusted. According to the semi-empirical model (Table 4) the two diagonal constants have approximately equal value, ($F_\phi(2-3)$ being a little greater than $F_\phi(1-2)$.

Unfortunately, the electron-diffraction data for PCP do not contain enough information for an independent determination of both $F_\phi(1-2)$ and $F_\phi(2-3)$. It is, however, possible to estimate an average element $\overline{F}_\phi$, with $F_\phi(1-2)=F_\phi(2-3)=\overline{F}_\phi$.

The value of $\overline{F}_\phi$ was determined as follows: u and K values for different values of $\overline{F}_\phi$ were calculated and then included in the least-squares refinements. The value of $\overline{F}_\phi$ which lead to a minimum in the error sum (**VPV**)[19] was obtained. In each least-squares run all structural parameters, except for $r(C-H)$ and $\angle CCH$, were refined simultaneously. The best value of $\overline{F}_\phi$ obtained in this way was: $\overline{F}_\phi=0.32\ {}_{-0.16}{}^{+0.18}$ mdyn Å(rad)$^{-2}$. The error limits are believed to be pessimistic, however, there is no straight forward way to estimate these limits. The most direct estimate, but subjective to a certain degree, is obtained by comparing experimental and calculated RD curves for a range of $\overline{F}_\phi$ values. Several types of systematic errors ought to be considered, as discussed in a previous paper.[5] The error limits here do not allow for systematic errors.

VI. FINAL RESULTS

Parameters from the least-squares refinements,[19] 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 [19] for all intensities.

Table 10. Structural parameters in the *gauche* conformer of $C(1)HX_2-C(2)H_2-C(3)X_3$ (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)
$r(C-C)=1.545(6)$	$\angle CCC=115.7(1.4)$
$r(C-X)=1.772(2)$	$\angle CCX=109.9(0.3)$
$r(C-H)=1.05(-)^b$	$\angle CCH=109.47)^c$
Torsion angles	
$\phi_{1-2}=+14.1°$ (1.5)[d] and $\phi_{2-3}=-22.5°(1.2)^d$	

[a] The geometrical assumptions were explained in Sect. V-A. [b] Not refined; estimated from the RD curve in Fig. 4. [c] Assumed value; see Table 1. [d] Staggered values: $\phi_{1-2}=\phi_{2-3}=0°$; see Fig. 1.

Table 11. Correlation coefficients (100ϱ).

X = Cl[a]		(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
r(C−C)	(1)	100							
r(C−X)	(2)	−22	100						
∠CCC	(3)	−32	8	100					
∠CCX	(4)	−66	39	28	100				
ϕ_{1-2}	(5)	6	6	−22	−18	100			
ϕ_{2-3}	(6)	1	14	58	9	40	100		
u(C−X)[b]	(7)	−18	1	8	−3	4	−4	100	
scale[c]	(8)	−28	6	12	−15	13	−5	49	100

[a] The parameter assumptions are given in Sect. V-A. [b] All u(C−X) values were refined as one parameter; see also Table 7. [c] Scale-factor [19] between experimental and theoretical intensities.

Table 12. Refined and calculated mean amplitudes (u) of vibration for the *gauche* conformer of C(1)HX_2−C(2)H_2−C(3)X_3 at 60 °C. Standard deviations are given in parentheses.

Type of distance (r) (see Fig. 2; X = Cl)	r (Å) (see Fig. 4)	Refined u-value (Å)	Calculated[a] u-value (Å)
C−X (bond dist.)	(1.772)	0.044(2)	0.056
C···X (in CCX)	(2.71)	0.071(5)	0.070
X···X (in XCX)	(2.88)	0.065(2)	0.072
$C_1\cdots X_3'$ (g)	(2.99)	0.113(41)[b]	0.132
$C_1\cdots X_3''$(g)	(3.46)	0.112(41)[b]	0.130
$C_3\cdots X_1'$ (g)	(3.36)	0.114(41)[b]	0.133
$C_1\cdots X_3$ (a)	(4.10)	0.075(15)[b]	0.079
$C_3\cdots X_1$ (a)	(4.13)	0.071(15)[b]	0.076
$X_1'\cdots X_3'$ (GG)	(3.80)	0.197(24)	0.234
$X_1'\cdots X_3''$ (GG)	(3.27)	(0.234)(−)[c]	0.234
$X_1'\cdots X_3$ (AG)	(5.04)	0.143(20)[b]	0.123
$X_1\cdots X_3'$ (AG)	(4.56)	0.168(20)[b]	0.154
$X_1\cdots X_3''$ (AG)	(5.06)	0.146(20)[b]	0.128
$X_1\cdots X_3$ (AA)	(5.30)	(0.117(−)[c]	0.117

[a] Calculated in Sect. III. [b] Refined as one parameter. [c] Not refined.

Non-bonded internuclear distances were restricted under the geometrical constraints of r_α parameters,[22,23] by including correction terms $D = r_\alpha - r_a$, with $D = (u^2/r) - K$, for all distances (Sect. III)

The r(C−H) and ∠CCH parameters did not refine to reasonable values. All r(C−H) values were fixed at 1.05 Å as suggested by the C−H peak in the experimental RD curve (Fig. 4). All values of ∠CCH were fixed at 109.47° (see Table 1).

Parameter-correlation [19] coefficients (ϱ) are shown in Table 11.

It is important that the great number of u values (Table 7) do not have to be adjusted as individual 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 (Sect. V-B).

For internuclear distances between heavy atoms, several mean amplitudes of vibration were refined as individual parameters [19] together with the geometry variables. These u values, and the corresponding values calculated in Sect. III, have been compared in Table 12. Generally the agreement between the two sets of u values is reasonable, but unfortunately the standard

Table 13. Comparison of results for $C(1)HX_2-C(2)H_2-C(3)X_3=PCP$, $C(1)HX_2-C(2)X_2-C(3)X_3=HCP$, and $C(1)X_3-C(2)X_2-C(3)X_3=OCP$ as determined by electron diffraction and semi-empirical calculations.

X: chlorine	Experimental values PCP	HCP[a]	OCP[b]	Calculated values PCP	HCP[a]	OCP[b]
r_a(C−C) in Å	1.545(6)	1.601(8)	1.655(15)	1.543	1.597	1.594
$\angle_\alpha$ CCC in deg.	115.7(1.4)	117.6(1.9)	119.0(2.0)	116.1	114.8	120.0
Deviations of torsion angles from all-staggered (1:2) form:						
$\Delta\phi_{1-2}$ in deg.	+14.1(1.5)	+7.8(1.1)	±0.0[c]	+32.3	+6.6	±0.0
$\Delta\phi_{2-3}$ in deg.	−22.5(1.2)	−7.8(1.1)	±0.0[c]	+1.9	−7.2	±0.0
Average torsional force constant, $\overline{F}_\phi=F_\phi(1-2)=F_\phi(2-3)$:[d]						
$\overline{F}_\phi$(mdyn Å(rad)$^{-2}$)	$0.32^{+0.18}_{-0.16}$	$0.54^{+0.27}_{-0.18}$	$0.36^{+0.14}_{-0.07}$	–	–	–
$F_\phi(1-2)$	–	–	–	0.20	0.57	0.69
$F_\phi(2-3)$	–	–	–	0.27	0.67	0.69
Fundamental frequencies (ω) corresponding to torsional oscillations of $-CHX_2$ and $-CX_3$ groups:						
$\omega(++)$[e] in cm^{-1}	56	67	48	–	–	–
$\omega(+-)$[e] in cm^{-1}	77	77	62	–	–	–

[a] Parameters for the *gauche* conformer; for further details see Ref. 4. [b] For further details see Ref. 5. [c] No deviation from an all-staggered (1:2) conformer detected. [d] The experimental values were determined as explained in Sect. V-B. [e] Deformations in the torsion angles have been indicated; see also Table 6.

deviations for the torsion-dependent u values are very large. However, since the refined u values for torsion-dependent distances are consistent with those calculated in Sect. III, it is likely that the approximation assuming small vibrational amplitudes is valid for the *gauche* conformer of PCP at 60 °C (see also discussion in Sect. III).

Except for the u(C−X) value, the u values in Table 7 were used in calculating the final theoretical functions shown in Figs. 3 and 4. The vibrationally consistent set of u values in Table 7, which combine information from both spectroscopy and electron diffraction, are considered the final ones for PCP.

VII. DISCUSSION

The agreement between the experimental data and the theoretical functions (Figs. 3 and 4) is quite satisfactory. It is thereby shown that *gauche* is the predominating conformer of PCP in the gas phase at 60 °C. Although the *anti* conformer was not included in the least-squares refinements, the percentage of *anti* (< 0.5 %) corresponding to the conformational energies in Table 2, is consistent with the electron-diffraction data. A few percent (< 10 %) of *anti* is, however, not ruled out by the experimental data alone. Our result agrees with the conclusion drawn by Sheppard *et al.*[12] who studied PCP in the liquid phase.

According to the semi-empirical model a low torsional barrier (*ca.* 0.7 kcal/mol) separates the two *gauche* conformers (Table 3). The approximation assuming small vibrational amplitudes was discussed in Sects. III and VI. In conclusion, the barrier between the *gauche* conformers is probably not as low as 0.7 kcal/mol, but the value of the barrier was not determined in this work.

It seems natural to compare the results obtained for PCP with the results for HCP-($HCCl_2-CCl_2-CCl_3$)[4] and OCP($CCl_3-CCl_2-CCl_3$).[5] Experimental and calculated results for PCP, HCP, and OCP are found in Table 13. The results of the semi-empirical model to a large extent reasonably agree with the experimental findings; however, some shortcomings

of the model are obvious from the parameter values in Table 13. Although adjustments in the non-torsional force constants and the "normal" reference parameters (Table 1) could remove most of the discrepancies, it was decided that results from additional molecules ought to be included, before such corrections were considered.

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