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Conformational Analysis. XIII. The Structure of Gaseous 1,1,2,3,3-Pentachloropropane, $(CHCl_2)_2CHCl$, as Determined by Electron Diffraction and Compared with Molecular Mechanics Calculations

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1,1,2,3,3-Pentachloropropane has been studied at a nozzle temperature of 83 °C. One conformer, which contains no parallel (1:3) Cl···Cl interaction, was detected. 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) = 1.523(18) Å, r(C−Cl) = 1.776(4) Å, ∠CCC = 113.8°(1.6), $\angle C_2C_1X$ = 111.8°(1.0), $\angle C_1C_2X$ = 109.8°(1.2). The conformer has torsion angles close to staggered values. An average torsional force constant was estimated by combining information from vibrational spectroscopy and electron diffraction. Vibrational frequencies, u and K values, have been computed.

The diffraction data are consistent with the results obtained from molecular-mechanics calculations, which predict *ca.* 95 % of the stable conformer.

According to the molecular-mechanics calculations the lowest rotational barriers, involving transitions between enantiomeric forms of the stable conformer, are 7 − 9 kcal/mol.*

The results are compared with those of 1,1,2,2,3,3-hexachloropropane.

Six energetically different conformers have to be considered as shown in Table 1. The conformers *2*, *3*, and *4* exist as enantiomeric pairs.

From IR spectra and coupling constants derived from NMR spectra Dempster *et al.*[1] concluded that *PCP* (1,1,2,3,3-pentachloropropane exists in conformation *4* in the liquid phase. Conformer *4* is the only one which does not possess parallel (1:3) Cl···Cl interactions.

* 1 kcal = 4.184 kJ.

CALCULATIONS OF CONFORMATIONAL ENERGIES, GEOMETRIES, TORSIONAL BARRIERS, AND FORCE CONSTANTS

The energy model corresponds to molecular-mechanics calculations, including atom-atom potentials [2] and valence force constants as described in Ref. 3, and applied in subsequent

Table 1. Staggered conformers of 1,1,2,3,3-pentachloropropane ($C_1C_2C_3$).

	Conformer		ϕ°_{12} (deg.)	ϕ°_{23} (deg.)	Symmetry
1	XHX HCCCH XXX		0	0	C_s
2	XHX XCCCH HXX	XHX HCCCX XXH	120 0	0 120	C_1
3	HHX XCCCH XXX	XHH HCCCX XXX	−120 0	0 120	C_1
4	XHH XCCCX HXX	HHX XCCCX XXH	120 −120	120 −120	C_1
5	XHX XCCCX HXH		120	−120	C_s
6	HHH XCCCX XXX		−120	120	C_s

Table 2. Calculated conformational energy parameters for 1,1,2,3,3-pentachloropropane.

Conformer	*1*	*2*	*3*	*4*	*5*	*6*
ΔE (kcal/mol) [a]	6.9	2.5	3.3	0	4.7	3.2
Composition (%) [b]	0	3	1	95	0	1
ϕ_{1-2}(°) [c]	0.7	115.8	−139.0	115.2	−129.3	−136.8
ϕ_{2-3}(°) [c]	−0.7	−20.7	2.8	123.5	129.3	136.8
∠CCC (°)	120.4	117.1	116.7	112.9	113.8	113.9
$F_\phi(1-2)$ [d]	0.55	0.36	0.39	0.31	0.42	0.34
$F_\phi(2-3)$ [d]	0.55	0.45	0.30	0.37	0.42	0.34
$F_{\phi\phi'}$ [e]	−0.08	−0.07	−0.21	−0.08	−0.31	−0.20

[a] Conformational energy $\Delta E = E - E(4)$. [b] Assuming equal vibrational partition functions and 83 °C. [c] Torsion angles (see also Table 1). [d] Diagonal torsional force constants in m dyn Å (rad)$^{-2}$. [e] Non-diagonal element.

papers (conformational analysis I–XI). In minimizing the energy the geometry was constrained as explained below. Results corresponding to energy minima are shown in Table 2, and further details are given elsewhere.[4] The deviations from exact staggered forms are found by comparing ϕ values in Tables 1 and 2.

Dempster *et al.*[5] have determined the rotational barrier for the transition *4* (120, 120°) → *4* (−120, −120°). The experimental NMR value is $\Delta H^* = 6.7 \pm 1.0$ kcal/mol. In the same paper [5] the authors propose a mechanism which can be indicated as follows (approximate values of the torsion angles are given): *4*(120, 120°) → transition state (180, 180°)* → *4* (−120, −120°). However, the calculated barrier heights are shown in Table 3. The proposed mechanism corresponds to a barrier height of 15.5 kcal/mol. The following mechanism: *4* (120, 120°) → (180, 120°)* → *6* (240, 120°) → (240, 180°)* → *4* (240, 240°)≡*4* (−120, −120°) includes two barrier heights of 8.4 kcal/mol, which is comparable with the experimental value. Our mechanism includes conform *6* having one parallel (1:3) Cl···Cl interaction, while the first mechanism was proposed in order to avoid the parallel (1:3) Cl···Cl interaction.[5] Although the calculated barrier heights are uncertain values the error is hardly as large as 7 kcal/mol.

CALCULATION OF VIBRATIONAL QUANTITIES

Valence force constants, except for the torsional part were taken from works of Schachtschneider [6] and Snyder.[7] The final force-constant values used in this work are found in Ref. 4. An average torsional force constant has been adjusted to fit the diffraction data as described below. The normal-coordinate program described by Gwinn [8] was used in computing vibrational frequencies. The fit between observed [1] and calculated [4] frequencies

Table 3. Torsional barriers (kcal/mol) within 1,1,2,3,3-pentachloropropane. The energy values have been obtained by adjusting all geometry variables except for the ϕ-values being ±60, ±180°. The exact values of ϕ corresponding to conformational minima are found in Table 2.

ϕ_{1-2} / ϕ_{2-3}	−120°	−60°	0°	60°	120°	180°
180°	8.4	21.4	8.4	18.4	8.6	15.5
120°	3.2(*6*)	13.0	3.3(*3*)	7.7	0(*4*)	8.4
60°	13.0	36.3	16.5	33.9	14.3	21.4
0°	3.3(*3*)	16.5	6.9(*1*)	10.0	2.5(*2*)	8.4
−60°	7.7	33.9	10.0	29.7	8.6	18.4
−120°	0(*4*)	14.3	2.5(*2*)	8.6	4.7(*5*)	8.6

Table 4. Mean amplitudes of vibration (u in Å) calculated for Cl···Cl internuclear distances with $F_\phi = 0.27$, 0.43, and 0.54 mdyn Å (rad)$^{-2}$ at 83 °C.

Distance (r)	r(Å)	0.27	0.43	0.54
$X_1 \cdots X_2$ (*a:anti*)	4.36	0.0724	0.0723	0.0722
$X_1 \cdots X_2$ (*g:gauche*)	3.28	0.158	0.145	0.141
$X_2 \cdots X_3$ (*g:gauche*)	3.26	0.160	0.148	0.143
$X_2 \cdots X_3$ (*g:gauche*)	3.32	0.160	0.147	0.143
$X_1 \cdots X_3$ (*a a*)	5.10	0.102	0.101	0.101
$X_1 \cdots X_3$ (*a g*)	4.75	0.168	0.156	0.152
$X_1 \cdots X_3$ (*a g*)	4.92	0.153	0.142	0.139
$X_1 \cdots X_3$ (*g g*)	4.03	0.255	0.218	0.204

is satisfactory for calculating mean amplitudes of vibration. However, the important frequencies below 562 cm^{-1} have not been observed.[1]

Mean amplitudes of vibration (u) and perpendicular amplitude correction coefficients (K) were computed as described in Ref. 9 Some of these quantities are sensitive to the values of the torsional force constants.[4] The average torsional force constant $F_\phi = F_\phi(1-2) = F_\phi(2-3)$ corresponding to the best value as estimated from the diffraction data, was used. The values of the torsional frequencies calculated with $F_\phi = 0.43$ mdyn Å (rad)$^{-2}$ and $F_{\phi\phi'} = 0$ are 74 and 82 cm^{-1}, while the lowest non-torsional frequencies are 99, 154, 170, 203, 275, 322, 344, 418 and 568 cm^{-1}. Final u- and K values for all internuclear distances are found in Ref. 4. Only the most important u values for Cl···Cl distances are shown in Table 4.

EXPERIMENTAL AND DATA REDUCTION

A commercial sample of PCP was obtained. The purity was better than 99 %.

Electron-density photographs were made at a nozzle temperature of 83 °C in the Balzer[10] apparatus[11] under conditions summarized below.

Nozzle-to-plate distance (mm)	500	250.0
Electron wave length (Å)	0.05852	0.05853
Number of plates	3	4
Range of data, in s (Å^{-1})	1.25 – 15.625	2.25 – 30.50
Data interval Δs (Å^{-1})	0.125	0.250
Uncertainty in s-scale (%)	0.14	0.14

The electron wavelength was determined by calibration against ZnO and benzene.[20] The data were reduced in the usual way [12] 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 intensity curve is shown in Fig. 1. The intensities have been modified by $s/|f'_{Cl}|^{-2}$. Scattering amplitudes (f') were calculated by the partial-wave method [13] using Hartree-Fock atomic potentials.[14] The radial distribution (RD) curve [12] is shown in Fig. 2.

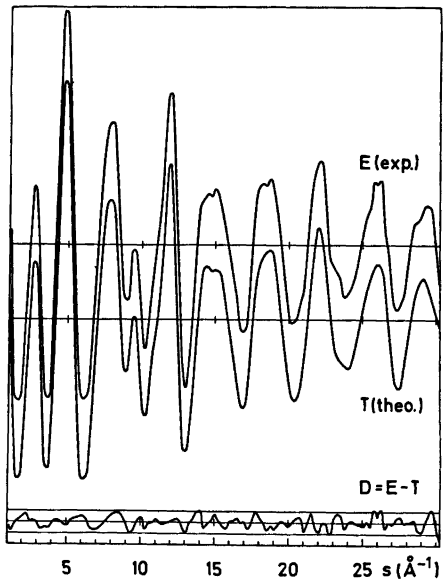

Fig. 1. Experimental (E) and theoretical (T) intensity curves for 1,1,2,3,3-pentachloropropane, and D = E – T, corresponding to final least-squares parameters. The straight lines give the experimental uncertainties as ±3 times the standard deviations.

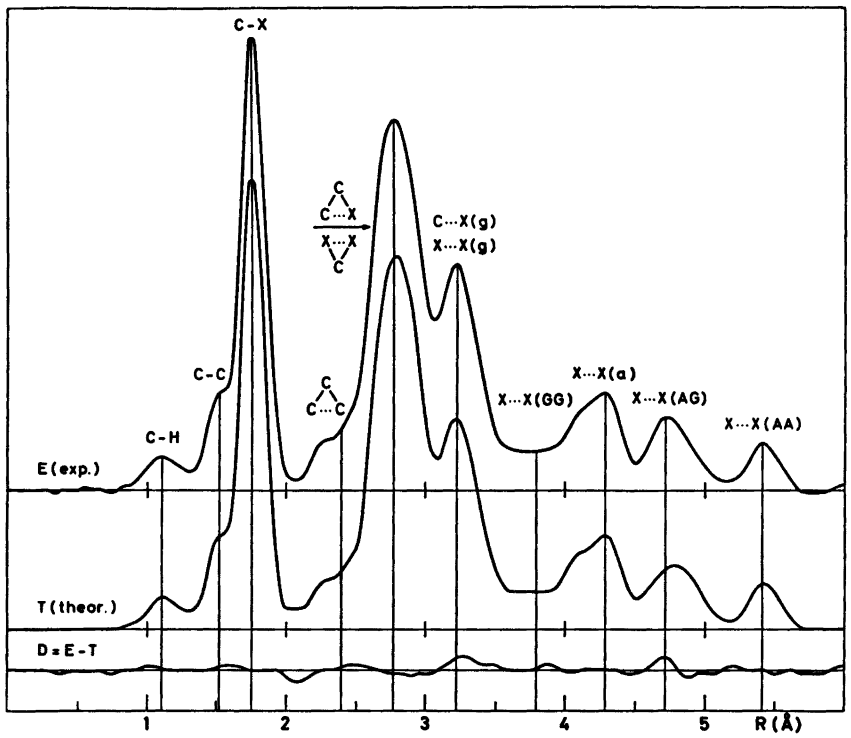

Fig. 2. Experimental (E) and theoretical (T) RD curves for 1,1,2,3,3-pentachloropropane at 83 °C. The curves were computed from the intensities in Fig. 1 with an artificial damping constant of 0.002 Å^2.

STRUCTURE ANALYSIS

According to the calculated energies, 95 % of conformer *4* is expected in the conformational mixture at 83 °C. It was assumed that only intensities corresponding to conformer *4* had to be included in the least-squares analysis.[12] It was assumed that the group $C_1-C_2(XH)-C_3$ and the two $C-CHX_2$ groups possess C_s symmetry, all C–H bonds have equal lengths, all C–X bonds have equal lengths, and the C–C bonds have equal lengths. The geometrical model is then defined in terms of the following average parameters: r(C–H), r(C–C) r(C–X), ∠CCC, $\angle C_2C_1H$, $\angle C_1C_2H$, $\angle C_2C_1X$, $\angle C_1C_2X$, the torsion angles ϕ_{2-1} and ϕ_{2-3} and $\angle(XC_1X)^*$ which is the projection of the angle XC_1X on a plane perpendicular to the C_2-C_1 axes. Non-bonded distances were computed as dependent parameters, restricted under the constraints of geometrically consistent r_α parameters,[15,16] by including vibrational correction terms $D = r_\alpha - r_a$ for all distances.

The following parameter correlation coefficients (ϱ) had values of $|\varrho|$ greater than 0.4: $\varrho[\angle C_2C_1X/r(C-C)] = -0.75$, $\varrho(\phi_{1-2}/\angle C_2C_1X) = 0.42$, $\varrho[\angle(XC_1X)^*/r(C-C)] = -0.64$, $\varrho[\angle(XC_1X)^*/\angle C_2C_1X] = 0.93$, and $\varrho[\angle(XC_1X)^*/\phi_{1-2}] = 0.45$.

Determination of the torsional force constant

In previous papers (Conf. anal. I–XII) it has been shown that information about the torsional force constants can be obtained from the diffraction data. Assuming the harmonic force field, two diagnol elements $F_\phi(1-2)$, $F_\phi(2-3)$, and the non-diagnol element $F_{\phi\phi'}$ have to be determined (see Table 2). Determination of all three elements is not possible from diffraction data alone. However, an

Table 5. Structure parameters for conformer *4* of 1,1,2,3,3-pentachloropropane. Bond lengths (r_a) in Å, bond angles ($\angle_\alpha$) and torsion angles (ϕ) in deg. Standard deviations in parenthesis.

r(C−X)	1.774(2)	∠CCC	113.8(0.8)
r(C−C)	1.521(9)	$\angle C_3C_1X$	111.8(0.5)
r(C−H)	1.115(−)[a]	$\angle C_1C_2X$	109.8(0.6)
ϕ_{1-2}	112.3(0.9)	$\angle C_2C_1H$	109.4(−)[c]
ϕ_{2-3}	123.8(1.1)	$\angle C_1C_3H$	107.3(−)[c]
$\angle HC_1X$	106.6(0.6)[b]	$\angle(XC_1X)^*$	123.3(0.8)[d]
$\angle HC_2X$	108.3(1.8)[b]	$\angle XC_1X$	109.5(0.2)[b]

[a] Estimated from the RD curve in Fig. 2. [b] Dependent angle. [c] Values from molecular-mechanics calculations. [d] Defined in text above.

average value $F_\phi = F_\phi(1-2) = F_\phi(2-3)$ for conformer *4* was estimated. The best fit between theoretical and experimental intensities was obtained for $F_\phi = 0.43$ mdyn Å (rad)$^{-2}$, with error limits [17] of *ca.* 20 %. The estimated value is not considered significantly different from those calculated for conformer *4* in Table 2. The calculated $F_{\phi\phi'}$ value of Table 2 is indirectly supported by the agreement found for the diagonal elements.

RESULTS

Structural parameters from the final least-squares refinements and standard deviations corrected for correlation in the experimental data [18] are given in Table 5. In the final refinements all intensities were given equal weight. Calculated vibrational parameters, u and K values, were included. The agreement between intensity curves in Fig. 1 shows that the calculated values of the vibrational parameters [4] are reasonable.

The structure parameters obtained for conformer *4* by molecular-mechanics calculations are: ∠CCC = 112.9°, $\angle C_2C_1X = 112.4°$, $\angle C_1C_2X = 111.0°$, $\angle(XC_1X)^* = 121.6°$, $\phi_{1-2} = 115.2°$, and $\phi_{2-3} = 123.5°$. The agreement with experimental values in Table 5 is fair. Both sets of values show that $\angle C_2C_1X > \angle C_1C_2X$, $\angle(XC_1X)^* > 120°$, $\phi_{1-2} < 120°$ (staggered), and $\phi_{2-3} > 120°$ (staggered).

DISCUSSION

The lack of agreement between theoretical and experimental RD curves at *ca.* 4.75 Å might be an indication that more than one conformer ought to be included in the analysis. Intensity contributions from conformer *2*, and later on conformers *3* and *6*, corresponding to 2, 5, 10, and 20 % did not lead to a better fit. The diffraction data are thus consistent with the results obtained from the molecular-mechanics calculations.

The results for *PCP* are compared with those of *HCP* (1,1,2,2,3,3-hexachloropropane).[19] Both molecules exist in the gas phase as conformers without parallel (1:3) Cl···Cl interactions. The results are given in Table 6.

Since the parameters $r(C_1-X)$ and $r(C_2-X)$ were treated as one independent variable within *PCP*, 1.776 Å is an average value approximately equal to $[4r(C_1-X)+r(C_2-X)]/5$. This

Table 6. The results for *PCB* compared with those for *HCP*.

Parameter		X H H XC(1)C(2)C(3)X H X X	X X H XC(1)C(2)C(3)X H X X
$r_g(C_1-X)$	(Å)	(1.776)	1.780(5)
$\angle_\alpha C_2C_1X$	(°)	111.8(0.5)	111.4(0.4)
$\angle_\alpha C_1C_2X$	(°)	109.8(0.6)	108.8(0.4)
$r_g(C_2-X)$	(Å)	(1.776)	1.752(9)
$\angle_\alpha$CCC	(°)	113.8(0.8)	108.0(1.0)
r_g(C−C)	(Å)	1.523(9)	1.558(8)
ϕ_{1-2}	(°)	112.3(0.9)	116.2(0.7)
ϕ_{2-3}	(°)	123.8(1.1)	116.2(0.7)
$\angle(XC_1X)^*$	(°)	123.3(0.8)	120.5(0.8)
F_ϕ [mdyn Å (rad)$^{2-}$]		0.43	0.86

relation [4] is based on the assumption that the vibrational parameters for the two bond types are equal. Substituting $r(C_1-X)=1.780$ Å from *HCP* in the above relation, the value $r(C_2-X)=1.760$ Å was obtained with $\sigma=0.022$ Å. The values of $r(C_2-X)$ within *PCP* and *HCP* thus are not significantly different. Statistically the parameters $r(C-C)$ and $\angle CCC$ are significantly different within the two compounds, and both conformers have torsion angles close to staggered values, but significantly different from 120° (staggered). The two conformers have nearly equal values of the C_2C_1X angles as well as the C_1C_2X angles. The main conclusion of this comparison must be that the effect of having one heavy Cl atom at the centre of *PCP*, as compared with two symmetrically substituted Cl atoms at the centre of *HCP*, is of little importance to the values of structural parameters within the terminal groups. However, the effect on the $r(C-C)$ and $\angle CCC$ values is pronounced. The values of the torsional force constants are very different for the two conformers, while both molecules exist in nearly staggered conformations.

According to the molecular-mechanics calculations the lowest rotational barriers, involving transitions between enantiomeric forms of the stable conformers, are 7 – 9 kcal/mol within *PCP* and 14 – 15 kcal/mol within *HCP*. The ratio between these values is roughly equal to the ratio between the experimentally estimated torsional force constants.

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