

# Conformational Analysis. XV. The Structure of 1,1,3,3-Tetrachloropropane (CHCl<sub>2</sub>)<sub>2</sub>CH<sub>2</sub> Determined by Electron Diffraction and Vibrational Spectroscopy and Compared with Molecular Mechanics Calculations

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Gaseous 1,1,3,3-tetrachloropropane was studied at a nozzle temperature of 62 °C. The experimental structural parameters agreed well with those calculated from molecular mechanics calculations.

Infrared spectra of the vapour, liquid and crystalline samples were recorded between 4000 and 40 cm<sup>-1</sup>. Raman spectra of the liquid, including polarization measurements, and of the amorphous and crystalline samples were obtained.

The compound existed as one predominant conformer (GG) in the vapour phase with the C–Cl bonds parallel to the C–H bonds on the same side of the carbon skeleton. From the vibrational spectra it can be concluded that no detectable amount of any additional conformers exists in the vapour, liquid, amorphous or crystalline states.

The fundamental frequencies were assigned and a simple normal coordinate analysis was carried out. A mechanism for the transition between enantiomeric forms of the GG conformer has been proposed.

1,1,3,3-Tetrachloropropane (hereafter called TCP) has previously been studied by means of Raman,<sup>1</sup> infrared<sup>2</sup> and NMR<sup>2</sup> spectroscopy. Dempster and coworkers<sup>2</sup> analyzed these data in terms of the nine possible conformers of which four are distinguishable by vibrational spectroscopic methods. The C–Cl stretching modes observed in the infrared and Raman spectra were interpreted<sup>2</sup> as two  $P_H$  and two  $P_X$  (according to the nomenclature

of Mizushima *et al.*<sup>3</sup>). Therefore, the conformer should be GG' or GG in the liquid and crystalline states, where the G notation describes *gauche* configuration between a C–H and the second nearest C–C bond (see the figures).

In our laboratories we have for a long time been interested in the conformers of halogenated propanes. As part of these investigations we decided to study TCP by means of gaseous electron diffraction, infrared and Raman spectroscopy in the vapour, liquid and crystalline states and to compare the results with molecular mechanics calculations.

## EXPERIMENTAL

The sample was kindly provided by Dr. P. Rademacher, Essen. It was prepared by adding HCl to propenal with subsequent chlorination first by PCl<sub>5</sub> and then by chlorine, according to well-known methods.<sup>5,6</sup> For electron diffraction a sample of ca. 98 % purity was employed, whereas a sample purified by gas chromatography was used for the vibrational spectra.

Electron diffraction diagrams were recorded with the Balzers apparatus<sup>7,8</sup> at a nozzle temperature of 62 °C. Two sets of plates were obtained: Set 1 (5 plates, electron wavelength 0.05856 Å, nozzle-to-plate distance 579.88 mm) and set 2 (5 plates, 0.05853 Å, 189.78 mm). The electron wavelength was determined from ZnO diagrams and benzene.<sup>9</sup> The data were treated in the usual way.<sup>10</sup> Scattering

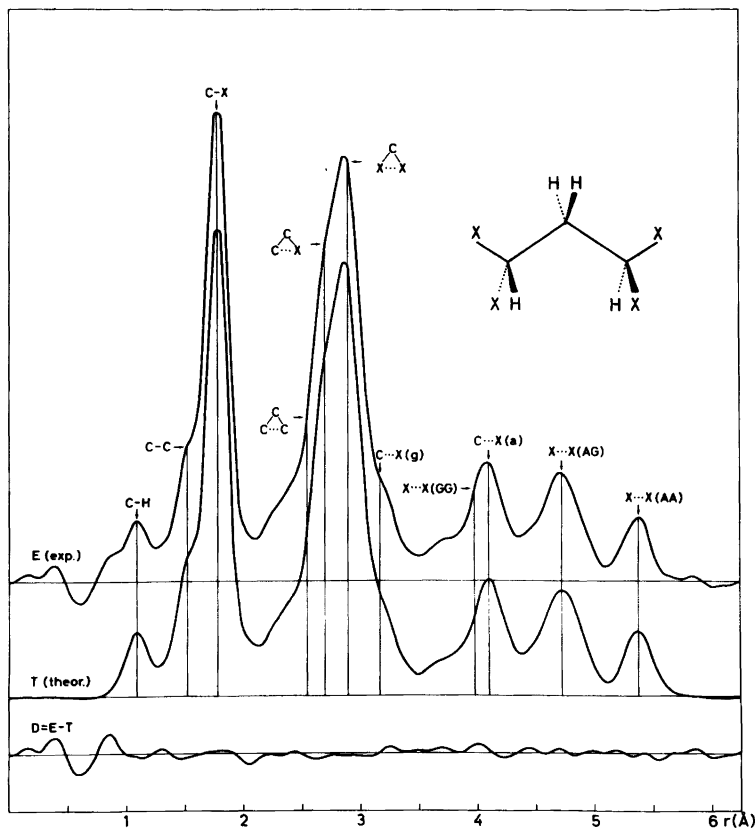


Fig. 1. Experimental (E) and theoretical (T) radial distribution curves for 1,1,3,3-tetrachloropropane at 335 K computed with an artificial damping constant of  $0.002 \text{ \AA}^2$ .  $D = E - T$ .

amplitudes were calculated as described previously.<sup>11</sup> Radial distribution functions (RD-curves) calculated by Fourier inversion of composite intensity curves are shown in Fig. 1.

The infrared spectra were recorded with Perkin-Elmer model 225 ( $4000-200 \text{ cm}^{-1}$ ) and Hitachi/Perkin-Elmer FIS-3 ( $400-90 \text{ cm}^{-1}$ ) spectrometers. Vapour cells, sealed liquid cells and cryostats, cooled with liquid nitrogen, had windows of KBr, CsI and polyethylene. Far IR spectra ( $500-40 \text{ cm}^{-1}$ ) of TCP in the vapour phase were recorded on an RIIC slow scan interferometer model 520, equipped with a 6 m light pipe gas cell.<sup>12</sup> Additional far IR spectra of the liquid ( $500-30 \text{ cm}^{-1}$ ) were recorded on a Bruker model 114 C fast scan interferometer.

The Raman spectra were recorded on a modified<sup>13</sup> Cary 81 spectrometer, excited by an argon ion laser (CRL 52 G).

## CALCULATIONS

*Calculations of conformational energies, structural parameters, torsional barriers and force constants.* Molecular mechanics calculations, which include atom-atom potentials and valence force constants, were carried out as described previously.<sup>14</sup> Potential parameters were taken from the work of Abraham and Parry.<sup>15</sup> Each energy value has been obtained by adjusting bond lengths and bond angles, and at the energy minima the values of the torsional angles were also adjusted. Conformational energies and rotational barriers predicted by these calculations are given in Table 1. All energies (expressed in kcal/mol) are relative to the energy (0) of the (GG) form. Energy minima are represented by the numbers 0, 2.6, 4.0 and 8.4 kcal/mol for the conformers GG, GG', AG, and AA, respectively. The corresponding energies of the exact 1:2-staggered

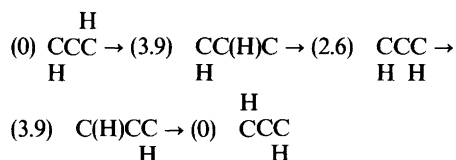
Table 1. Conformer energies for 1,1,3,3-tetrachloropropane obtained by Molecular Mechanics calculations.<sup>a</sup>

Type of conformer (staggered form) C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	Conformational energies <sup>b</sup> in kcal/mol			Deviations from staggered form Δφ(1-2) <sup>o</sup> Δφ(2-3) <sup>o</sup>		
	AA	XHX	30	13	30	17
HCCCX		13	8.4	13		
XHX		30	13	30		
AG	XHH	15	4.7	15	2.6	32
	HCCCX	11	4.0	11		
	XHX	30	13	31		
GG''	XHX	30	11	15	40	-40
	XCCCX	11	2.6	3.9		
	HHH	15	3.9	8		
GG	XHH	15	3.9	8	6.0	6.0
	XCCCX	11	0	3.9		
	HHX	31	11	15		

<sup>a</sup> For meaning of table, consult text. <sup>b</sup> All energies are relative to the energy (0) of the GG form.

forms, not corresponding to energy minima, are 0.2, 7.3, 7.1 and 9.1 kcal/mol, respectively. Each energy minimum (represented by the central number in each block of Table 1) is surrounded by torsional barriers (represented by the remaining eight numbers in each block) corresponding to forms with one or both terminal groups eclipsing the central CH<sub>2</sub> group as indicated. The horizontal variation in energy values corresponds to a change in the torsional angle φ(1-2), while the vertical variation corresponds to a change in φ(2-3). A small barrier is found for the transition GG''(2.6)→(3.9)→GG(0). A still smaller barrier (0.7) is found for the transition between enantiomeric forms of AG. The AA conformer exists also as enantiomeric forms since the minimum does not have C<sub>2v</sub> but merely C<sub>2</sub> symmetry because of the deviation from staggered form. The barrier between them is also 0.7 kcal/mol.

One of the lowest-energy paths for the transition between enantiomeric forms of the GG conformer is as follows:



The positions of terminal H atoms have been indicated. Transition forms with energy 3.9 have one

terminal group staggered and one eclipsed with respect to the central CH<sub>2</sub> group. The form with energy 2.6 is one of the enantiomeric forms of the GG'' conformer.

The calculated energies suggest that GG should be the only conformer present in detectable amounts at 62 °C.

*Calculations of vibrational quantities.* A normal-coordinate analysis was carried out for the GG conformer using the program developed by Gwinn.<sup>16</sup> The force constants used in this work are found in earlier work<sup>11</sup> in this series except for the diagonal torsional force constant *F* which was calculated from the formula reported.<sup>17</sup> The mean amplitudes of vibration<sup>18</sup> (*u*) were computed. An adjustment of *F*<sub>φ</sub> was carried out as explained previously.<sup>11</sup> The final value of *F*<sub>φ</sub> was 0.24 mdyne Å(rad)<sup>-2</sup> in agreement with the initial value<sup>17</sup> and the value 0.20 obtained from molecular mechanics calculations. The value of the non-diagonal torsional force constant obtained from molecular mechanics calculations was -0.07 mdyne Å(rad)<sup>-2</sup>. This force constant was ignored in the normal-coordinate analysis.

The calculated *u*-values for the important intermolecular distances are listed in Table 2 while the calculated fundamental frequencies are compared with the experimental values in Table 5.

Table 2. Calculated mean amplitudes of vibration,  $u$  for the GG conformer of 1,1,3,3-tetrachloropropane.

Type of distance( $r$ )	$r(\text{\AA})$	$u(\text{\AA})$
C-H	1.09	0.079
C-C	1.527	0.052
C-X	1.782	0.053
H <sub>1</sub> ...X <sub>1</sub>	2.36	0.108
C <sub>1</sub> ...C <sub>3</sub>	2.55	0.072
C <sub>2</sub> ...X	2.70	0.071
X <sub>1</sub> ...X <sub>3</sub>	2.90	0.072
C <sub>1</sub> ...X <sub>3</sub> (g)	3.17	0.146
C <sub>1</sub> ...X <sub>3</sub> (a)	4.10	0.073
X <sub>1</sub> ...X <sub>3</sub> (gg)	3.98	0.244
X <sub>1</sub> ...X <sub>3</sub> (ag)	4.73	0.165
X <sub>1</sub> ...X <sub>3</sub> (aa)	5.37	0.102

## RESULTS AND DISCUSSION

**Structure.** Clearly the predominant conformer is GG (reproduced in Fig. 1). In calculating intensities<sup>10</sup> for the least-squares refinements only GG was considered. It was assumed that the C-CHX<sub>2</sub> groups are equivalent and possess C<sub>s</sub> symmetry, the C-CH<sub>2</sub>-C group possesses C<sub>2v</sub> symmetry, and all C-H bonds have equal lengths. The symmetry of GG is thus C<sub>2</sub>.

Parameters from the final least-squares refinements and standard deviations ( $\sigma$ ) corrected for correlation<sup>19</sup> are given in Table 3. The  $u$ -values corresponding to important internuclear distances were refined with the geometry parameters at the end of the analysis. The differences between refined and calculated  $u$ -values were always less than  $2\sigma$ .

Except for the torsional deviation angles, all calculated geometry values agree with the experimental values within  $\pm 2\sigma$ . Agreement with observed vibrational frequencies is good, and calculated  $u$ -values fit the ED data well.

Table 3. Structural parameters for the GG conformer of 1,1,3,3-tetrachloropropane. Standard deviations ( $\sigma$ ) given in parentheses apply to the last digit given. The following correlation coefficients ( $\rho$ ) had absolute values greater than 0.5:  $\rho(\text{C-C}, \text{CCX}) = -0.72$ ,  $\rho(\text{C-C}, \text{XCX}) = -0.65$ ,  $\rho(\text{XCX}, \text{CCX}) = 0.93$ ,  $\rho(u(\text{X}_1\cdots\text{H}_1), u(\text{C}_1\cdots\text{C}_3)) = 0.57$ , and  $\rho(\text{scale}, u(\text{C-X})) = 0.54$ .

Bond lengths $r_g$ values in $\text{\AA}$		Bond angles $\angle_\alpha$ in deg.	
C-Cl	1.782(2) <sup>a</sup>	CCCl	109.8(5)
C-C	1.527(10) <sup>a</sup>	CCC	114.2(7)
C-H	1.090(16) <sup>a</sup>	C <sub>2</sub> C <sub>1</sub> H	109.9(27)
		C <sub>1</sub> C <sub>2</sub> H	108.9 <sup>b</sup>
		CiCCl	109.5(5)

Torsional deviation from exact staggered form:  
2.0°(6)

<sup>a</sup> The uncertainty in the  $s$ -scale (0.14 %) has been included in the standard deviations for bond lengths. <sup>b</sup> Value obtained from molecular mechanics calculations.

**Spectral interpretations.** Our IR and Raman spectra agree fairly well with those reported earlier.<sup>1,2</sup> Since the IR data below 500 cm<sup>-1</sup> have not been previously reported, the far IR spectra of TCP as a vapour, liquid and crystalline solid are given in Figs. 2-4, respectively. A Raman spectrum of the liquid is shown in Fig. 5, and the observed wavenumbers are listed in Table 4. Important low frequency Raman bands at 108 and 53 cm<sup>-1</sup> were not reported by Gerding and Haring,<sup>1</sup> and furthermore we believe our polarization measurements to be more reliable than theirs. A number of bands were observed in the far IR region most of which were interpreted as fundamentals. However, in spite of large efforts using the 6 m gas cell and 2 mm thick liquid cells no IR band around 50 cm<sup>-1</sup> was

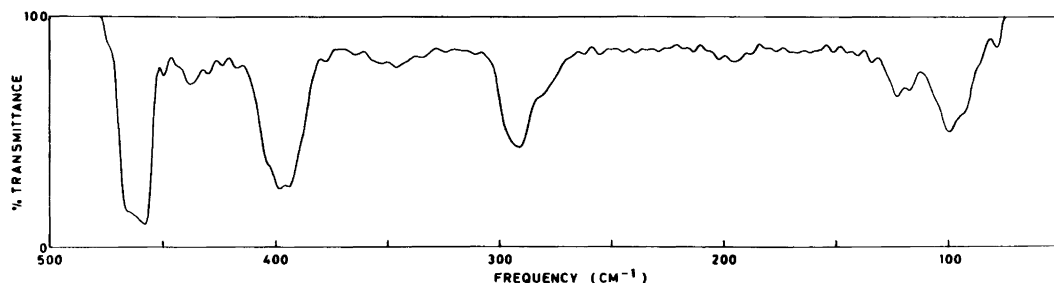


Fig. 2. Far IR vapour spectrum 6 m path, saturation pressure.

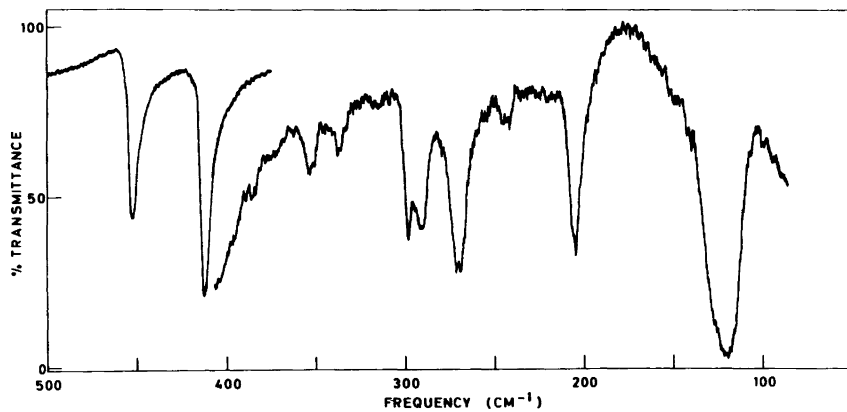


Fig. 3. Far IR liquid spectrum, *ca.* 0.5 mm path, polyethylene windows.

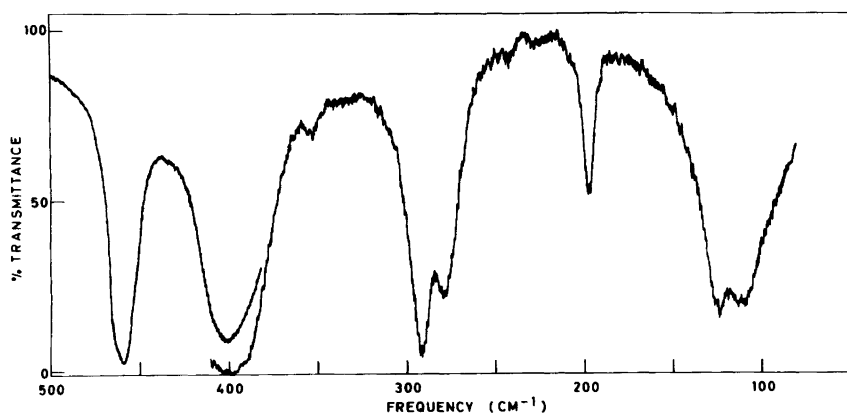


Fig. 4. Far IR crystal spectrum ( $-180^{\circ}\text{C}$ ) *ca.* 0.5 mm path, polyethylene windows.

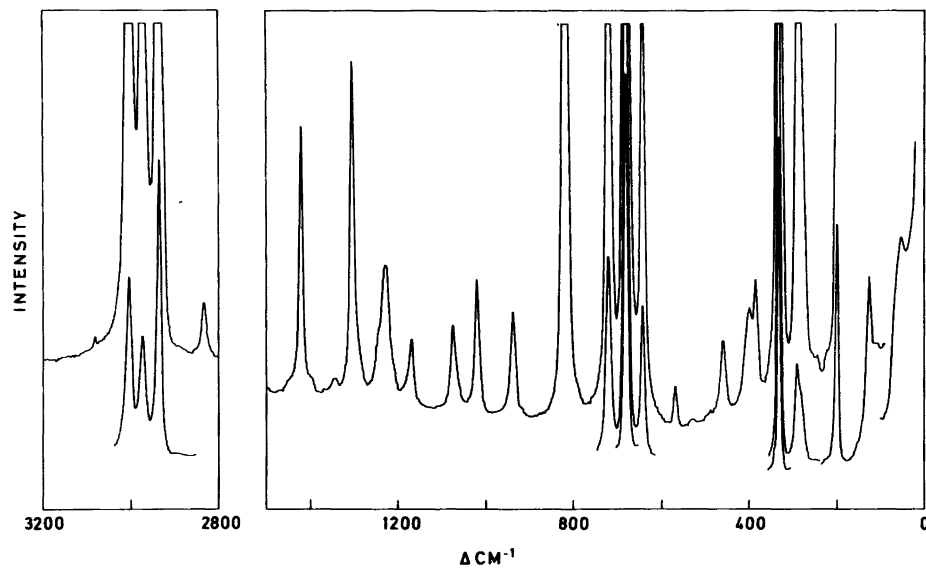


Fig. 5. Raman spectrum of liquid 1,1,3,3-tetrachloropropane.

Table 4. Infrared and Raman spectral data<sup>a</sup> for 1,1,3,3-tetrachloropropane.

Vapour	Liquid		Crystalline <sup>b</sup> (-180 °C)		Assignments
IR	IR	Raman	IR	Raman	
3020vw <sup>c</sup>	3010m 2976w,sd	3002s P 2973s D	3010m	3010s	$\nu_1$ a fund $\nu_{15}$ b fund $\nu_{16}$ b fund $\nu_2$ a fund
2938vw	2935w,sd 1450w	2936vs P	2956w 2921vw 1453vw	2957m 2922s	
1428m	1424s 1400w,sd	1425m P 1404vw	1443vw 1429vw,sd 1422m 1419w,sd 1404vw 1396w 1372w 1355vw,sd 1348w,sd 1341m	1423m	$\nu_3$ a fund $\nu_{17}$ b fund
1353m 1349m 1345m	1347s	1347vw	1305m 1296w 1248s 1235s 1221m 1172vw,sd 1135vw 1118vw 1096w 1074s 1067m 1031w 1029w 1020s 1011w 1006w 950w,sd 940s 934w,sd 884vw 844w 821s 814s 798w 726s 714s 708w,sd	1313m 1306w 1244w 1234vw 1170w 1077w	$\nu_{18}$ b fund $\nu_4$ a fund $\nu_5$ a fund $\nu_6$ a fund $\nu_{19}$ b fund $\nu_{20}$ b fund
1308w	1308m	1309m P	1067m 1031w 1029w 1020s 1011w 1006w	1022w	$\nu_7$ a fund
1254s 1235m	1248s 1228s 1170m	1248w,sd 1232w P 1172w D	950w,sd 940s 934w,sd 884vw 844w 821s 814s 798w 726s 714s 708w,sd	1170w	$\nu_{21}$ b fund
1083m 1079m 1075m	1076s	1079w D	821s 814s 798w 726s 714s 708w,sd	823s 812vw	$\nu_8$ a fund
1022m	1020s	1024w P	726s 714s 708w,sd	728s,sd 725s	$\nu_{22}$ b fund
944s	940s 880w	941w D	677s 668m,sd 648s 571w 532vw	679vs 647s	$\nu_9$ a fund $\nu_{23}$ b fund
832s	822s 791m,sd	822s P	532vw 516w		

Table 4. Continued.

460m	459m	460w D	452s	456w	$\nu_{24}$ b fund
394m	401m	400w P	412s	411m	$\nu_{10}$ a fund
	353vw	333vs P	353vw		
		291s D	338vw	338vs	$\nu_{11}$ a fund
292w	292m	291s D	301m } 291m }	300s } 292w }	$\nu_{25}$ b fund
	279m	283s, sd	271m	271w	$\nu_{26}$ b fund
		245vw			
		226vw	226vw		
	198w	197s P	206m	205s	$\nu_{12}$ a fund
120w	125m	125m D		129m	$\nu_{13}$ a fund
98w	110m	108vw D	120s	119m	$\nu_{27}$ b fund
		53w		49w	$\nu_{14}$ a fund

<sup>a</sup> Weak bands above  $3050\text{ cm}^{-1}$  and between  $2900$  and  $1500\text{ cm}^{-1}$  were omitted. <sup>b</sup> The vapour cooled to  $-180\text{ }^\circ\text{C}$  and the solid was then annealed. <sup>c</sup> The following abbreviations have been used: s, strong; m, medium; w, weak; v, very; sd, shoulder; P, polarized and D, depolarized.

detected as a counterpart to the lowest Raman band.

It is highly significant that unlike the halogenated 1,2-,<sup>20</sup> and 1,3-dihalopropanes<sup>4</sup> and the 1,2,3-trihalopropanes,<sup>21</sup> no significant IR or Raman bands in liquid TCP disappear in the crystalline spectra. Therefore, it can be concluded with confidence that the GG conformer identified by electron diffraction in the vapour state is present in the liquid and crystalline states as well. Moreover, any additional conformer which might be present in the

Table 5. Observed and calculated fundamentals of the GG conformer of 1,1,3,3-tetrachloropropane.

No.	Obs. <sup>a</sup>	Calc. <sup>b</sup>	Description
a			
$\nu_1$	3010	2993	CH stretch
$\nu_2$	2935	2860	CH <sub>2</sub> stretch
$\nu_3$	1424	1384	CH <sub>2</sub> scissor
$\nu_4$	1308	1299	CH def.
$\nu_5$	1248	1240	CH <sub>2</sub> twist
$\nu_6$	1228	1206	CH def.
$\nu_7$	1020	1036	CC stretch
$\nu_8$	822	833	CCl stretch, P <sub>C</sub>
$\nu_9$	682	709	CCl stretch, P <sub>H</sub>
$\nu_{10}$	401	385	CCC bend
$\nu_{11}$	333 <sup>c</sup>	336	skelet. bend
$\nu_{12}$	198	199	skelet. bend
$\nu_{13}$	125	110	skelet. bend
$\nu_{14}$	53 <sup>c</sup>	57	torsion

Table 5. Continued.

b			
$\nu_{15}$	2976	2993	CH stretch
$\nu_{16}$	2958 <sup>d</sup>	2915	CH <sub>2</sub> stretch
$\nu_{17}$	1400	1375	CH <sub>2</sub> wag
$\nu_{18}$	1347	1273	CH def.
$\nu_{19}$	1170	1227	CH def.
$\nu_{20}$	1076	1090	CC stretch
$\nu_{21}$	940	966	CH <sub>2</sub> rock
$\nu_{22}$	723	730	CCl stretch, P <sub>C</sub>
$\nu_{23}$	644	686	CCl stretch, P <sub>H</sub>
$\nu_{24}$	459	491	skelet. bend
$\nu_{25}$	292	331	skelet. bend
$\nu_{26}$	279	289	skelet. bend
$\nu_{27}$	110	87	torsion

<sup>a</sup> IR liquid values except when noted. <sup>b</sup> For force field, see Ref. 11, with the exception of  $F_\phi$  (torsion) =  $0.24\text{ m dyn/\AA rad.}^2$  <sup>c</sup> Raman liquid value. <sup>d</sup> Infrared solid value.

vapour or liquid states will probably be of less than 3% abundance, since no vanishing bands were detected upon crystallization.

The assigned fundamentals for the GG conformer of TCP are listed in Table 5 and compared with the results of the normal coordinate analysis. The GG conformer has  $C_2$  symmetry and the fundamental vibrations divide themselves between 14 of species a and 13 of b. The IR vapour contours were ill-

defined and not suitable for distinguishing between the *a* and *b* fundamentals. The fundamentals generally corresponded to intense IR and/or Raman bands and were assigned with considerable confidence based upon the polarization values. Exceptions are the fundamentals  $\nu_4$ ,  $\nu_5$ ,  $\nu_{14}$ ,  $\nu_{16}$ ,  $\nu_{17}$  and  $\nu_{26}$  which were generally intense in IR but weak in the Raman spectra and therefore without reliable polarization data. The  $125\text{ cm}^{-1}$  band appeared depolarized, but was tentatively assigned as the *a* mode  $\nu_{13}$ .

As mentioned previously, no IR band was detected around  $50\text{ cm}^{-1}$  and the Raman bands appeared as weak shoulders on the Rayleigh wing. Therefore, the lowest torsional mode ( $\nu_{14}$ ) should be considered very uncertain. Quite good agreement between the observed and calculated torsional frequencies has previously been obtained for halogenated propanes.<sup>22</sup>

Much better correspondence between the observed and the calculated frequencies could have been achieved by refining the force field. It was considered more meaningful to transfer<sup>11</sup> a simplified force field to TCP which has been successfully employed for other halogenated propanes. As discussed previously<sup>11,22</sup> torsional force constants can be estimated from electron diffraction data and also from molecular mechanics calculations.

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