Pentachlorotoluene: Rotational and Compositional Disorder

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Abstract

The structure of pentachlorotoluene, which is isostructural with most other $C_6Cl_n(CH_3)_{6-n}$ derivatives, has been redetermined at 294 (1) K. The methyl group is distributed almost randomly among six sites; there is little discrimination between the Cl and CH_3 substituents. The TL thermal-motion description suggests that the in-plane libration is moderate ($<\varphi^2> = 13$ deg^2); the barrier to in-plane rotation is estimated as 35 (3) kJ mol^{-1}. Compositional disorder is a possibility.

1. Introduction

The substituents —Cl and —CH_3 are very similar in size; the sum of the C—X bond length and the van der Waals radius of X is 1.70 + 1.80 = 3.50 Å for $X =$ Cl and 1.50 + 2.00 = 3.50 Å for $X = CH_3$ (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987; Pauling, 1960). Hexasubstituted benzene derivatives $C_6Cl_n(CH_3)_{6-n}$ are therefore usually disordered at *ca* 300 K over sites related by rotations of $2m\pi/6$.

Most Cl/CH_3 hexasubstituted benzene derivatives are isostructural; crystallographic studies are summarized in Table 1. At room temperature most of the structures belong to the group $P2_1/c$ (sometimes described as $P2_1/a$ or $P2_1/n$) with $Z = 2$ (imposed $\bar{1}$ symmetry) and have similar cell constants (8.2–8.3, 3.8–4.0 and 16.6–17.3 Å, and 116–120° for the $P2_1/c$ setting). The cells are pseudohexagonal.

The thermal motion and disorder in these compounds have been of special interest ever since measurements of the dielectric constant (White, Biggs & Morgan, 1940) for several of the derivatives suggested an abrupt increase in motion at a well defined T_{tr}. This behavior has been interpreted in terms of an in-plane molecular reorientation. For a review see Tazi, Meinnel, Sanquer, Nusimovici, Tonnard & Carrie (1995).

We decided to look at the structure of pentachlorotoluene (hereafter, PCT) because the published structure is very imprecise (Khotsyanova, Babushkina, Kuznetsov & Semin, 1972; $R = 0.147$ for $h0l$ data; complete rotational disorder). Furthermore, while the molecular volumes (V_{cell}/Z) of the $C_6Cl_n(CH_3)_{6-n}$ derivatives vary almost linearly with n (see Fig. 1), the published value for PCT (224 Å^3) is anomalous.

2. Experimental

PCT was purchased from K & K Laboratories. Its purity was checked by NMR and mass spectroscopy. Colorless needle-shaped crystals of PCT were grown by evaporation of heptane solutions. Pertinent crystal, data collection and refinement parameters are summarized in Table 2. Empirical absorption corrections were applied with the program *CAMEL* (Flack, 1977). The structure was refined with the program *SHELXL93* (Sheldrick, 1993), and the figures were made with the program *SHELXTL/PC* (Sheldrick, 1990). Refinement started from the coordinates for the isostructural tetrachloro-*p*-xylene (Khotsyanova, Babushkina, Kuznetsov & Semin, 1972).

The CH_3 group and Cl atom cannot be refined independently because the length difference between the CH_3—C and Cl—C bonds is only *ca* 0.2 Å. Authors of previous studies refined coordinates and displacement parameters for a single pseudo-atom X and estimated the fractional occupancy of the disordered site from the length of the C—X bond. We refined a pseudo-atom model to convergence and then displaced the Cln and methyl C(n + 3) atoms along the X—(Cl/CH_3) vectors to give standard C—Cl and C—CH_3 distances (Allen, Kennard, Watson, Brammer, Orpen & Taylor,
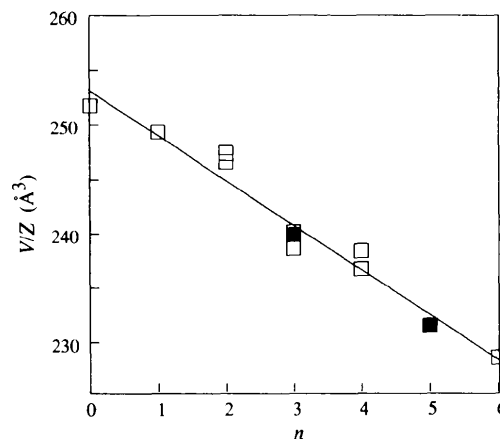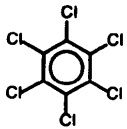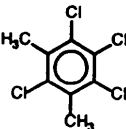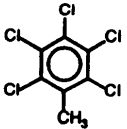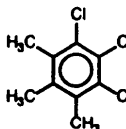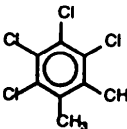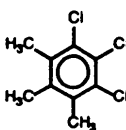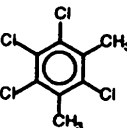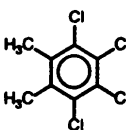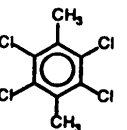

Fig. 1. Molecular volumes (V/Z) of hexasubstituted benzene derivatives $C_6Cl_n(CH_3)_{6-n}$. The equation of the straight line is (V/Z) = 253.0 (10) – n[4.1 (3)] Å^3. The marker for the volume determined in this study is darkened.

Table 1. Published $C_6Cl_n(CH_3)_{6-n}$ structures

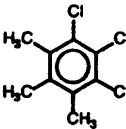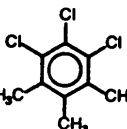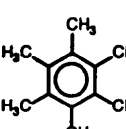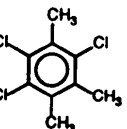| Compound	Temperature of structure determination (K)	Space group	Volume per molecule (Å³)	Compound	Temperature of structure determination (K)	Space group	Volume per molecule (Å³)
[structure: C6Cl6]	ca 300[a]	$P2_1/n$; $Z = 2$*	228.8	[structure]	150[g] / 297[g]	$P\bar{1}, Z = 2$ / $P\bar{1}, Z = 2$	232.6 / 239.0
[structure]	ca 300[b]	$P2_1/n$; $Z = 2$*	232.9 (1) [223.6[c]]				
[structure]				[structure]	ca 300[h]	$P2_1/c$; $Z = 2$*	246.6
[structure]	ca 300[c]	$P2_1/c$; $Z = 2$*	236.6	[structure]			
[structure]	ca 300[c]	$P2_1/c$; $Z = 2$*	235.0	[structure]	ca 300[j] / 70[j]	$P2_1/a$; $Z = 2$* / $P2_1/a$; $Z = 2$*	247.4 / 228.8
[structure]	ca 300[d] / 173[e]	$P2_1/c$; $Z = 2$* / $P\bar{1}$; $Z = 8$	238.6 / 230.9	[structure]	ca 300[k]	$P2_1/m$; $Z = 2$	249.3
[structure]	ca 300[f]	$P2_1/a$; $Z = 2$*	240.2	[structure]	ca 300[l]	$P\bar{1}$; $Z = 1$	251.8

* These crystals are isostructural; authors have chosen different settings of the same space group. (a) Brown & Strydom (1974); (b) this study; (c) Khotsyanova, Babushkina, Kuznetsov & Semin (1972); (d) Balcou & Meinnel (1966); (e) Fourme & Renaud (1972); (f) Charbonneau & Trotter (1967); (g) Tazi, Meinnel, Sanquer, Nusimovici, Tonnard & Carrie (1995); (h) Tulinsky & White (1958); (i) Messager & Blot (1971); (j) Messager, Cailleau & Yelon (1978); (k) Charbonneau & Trotter (1968); (l) Brockway & Robertson (1939).

1987). The C(n + 3) atom was then required to 'ride' on the Cln atom and to have the same displacement parameters, but the occupancy factors were varied within chemical restraints. Models with any additional degrees of freedom were unstable. Coordinates for Cl and C atoms are given in Table 3; H atoms were not included in the refinement.

The agreement factors [R = 0.052 (on F; $I > 2\sigma I$); wR = 0.161 (on F^2; all data)] are not especially high considering the disorder. The ellipsoids (see Fig. 2) are reasonable and the lengths of the three X—C bonds agree as well as can be expected given their e.s.d.'s (see Table 4). The final difference-Fourier map (Fig. 3), however, has unexpected features. The presence of C_6HCl_5 or

Table 2. *Experimental details*

	(1)	(2)
Crystal data		
Chemical formula	$C_7H_3Cl_5$	$C_7H_3Cl_5$
Chemical formula weight	264.4	264.4
Cell setting	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	8.0900 (8)	8.102 (2)
b (Å)	3.8472 (4)	3.8570 (10)
c (Å)	14.883 (2)	14.913 (3)
β (°)	91.730 (10)	91.78 (3)
V (Å^3)	463.02 (9)	465.8 (2)
Z	2	2
D_x (Mg m^{-3})	1.90	1.89
Radiation type	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073
No. of reflections for cell parameters	22	22
θ range (°)	11.8–13.0	11.4–13.2
μ (mm^{-1})	1.50	1.50
Temperature (K)	294 (1)	294 (1)
Crystal form	Needle	Needles.
Crystal size (mm)	0.50 × 0.50 × 0.20	0.45 × 0.20 × 0.15
Crystal color	Colorless	Colorless
Data collection		
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Data collection method	$\omega/2\theta$ scans	$\omega/2\theta$ scans
Absorption correction	Based on 10 ψ scans (*CAMEL*; Flack, 1977)	Based on 10 ψ scans (*CAMEL*; Flack, 1977)
T_{min}	0.45	0.46
T_{max}	0.74	0.80
No. of measured reflections	1055	1059
No. of independent reflections	1055	1059
No. of observed reflections	626	785
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
θ_{max} (°)	27.47	27.47
Range of h, k, l	$0 \rightarrow h \rightarrow 10$	$0 \rightarrow h \rightarrow 10$
	$0 \rightarrow k \rightarrow 4$	$0 \rightarrow k \rightarrow 5$
	$-19 \rightarrow l \rightarrow 19$	$-19 \rightarrow l \rightarrow 19$
No. of standard reflections	3	3
Frequency of standard reflections (min)	90	90
Intensity decay (%)	0.7	<0.5
Refinement		
Refinement on	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$	0.052	0.039
$wR(F^2)$	0.161	0.127
S	0.118	1.13
No. of reflections used in refinement	1055	1059
No. of parameters used	58	58
H-atom treatment	H atoms omitted	H atoms omitted
Weighting scheme	$w = 1[\sigma^2(F_o^2) + (0.0820P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0810P)^2 + 0.0120P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	<0.001	0.002
$\Delta\rho_{max}$ (e Å^{-3})	0.48	0.40
$\Delta\rho_{min}$ (e Å^{-3})	−0.42	−0.35
Extinction method	None	None
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C)	*International Tables for Crystallography* (1992, Vol. C)
Computer programs		
Data collection	*CAD*-4 (Enraf–Nonius, 1988)	*CAD*-4 (Enraf–Nonius, 1988)
Cell refinement	*CAD*-4 (Enraf–Nonius, 1988)	*CAD*-4 (Enraf–Nonius, 1988)
Structure solution	*SHELXTL/PC* (Sheldrick, 1990)	*SHELXTL/PC* (Sheldrick, 1990)
Structure refinement	*SHELXL93* (Sheldrick, 1993)	*SHELXL93* (Sheldrick, 1993)

$C_6HCl_4(CH_3)$ impurities disordered across the inversion center would explain these features (see Fig. 4), but neither the NMR nor the mass spectral data supported such an interpretation.

A second crystal of PCT, also grown from heptane, was studied. Although it was less attractive than the first and had several small cracks, it gave data that refined more satisfactorily than did the first crystal. The final difference-Fourier map (bottom half of Fig. 3) is clean.

Years later the remainder of the K & K PCT sample (originally 1 g) was dissolved in toluene. The components of the solution were separated and identified with a Hewlett Packard G1802A GC-MS system having a 25 m capillary column packed with

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$)*

$$U_{eq} = (1/3)\Sigma_i \Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	Occ.*	x	y	z	U_{eq}
In crystal (1)					
C1		−0.1511 (5)	−0.1104 (11)	0.0307 (3)	0.0376 (9)
C2		−0.0309 (5)	0.0185 (10)	0.0913 (3)	0.0386 (9)
C3		0.1215 (5)	0.1271 (10)	0.0591 (3)	0.0387 (9)
Cl1	0.849 (5)	−0.3370 (2)	−0.2509 (4)	0.06995 (10)	0.0607 (6)
C4	0.813 (7)	−0.3117 (2)	−0.2317 (4)	0.06461 (10)	0.0607 (6)
Cl2	0.838 (5)	−0.0701 (2)	0.0431 (5)	0.20348 (10)	0.0663 (7)
C5	0.151 (5)	−0.0648 (2)	0.0398 (5)	0.18819 (10)	0.0663 (7)
Cl3	0.187 (7)	0.2691 (2)	0.2848 (4)	0.13359 (10)	0.0576 (6)
C6	0.162 (5)	0.2489 (2)	0.2632 (4)	0.12342 (10)	0.0576 (6)
In structure (2)					
C1		−0.1512 (3)	−0.1095 (7)	0.0313 (2)	0.0412 (5)
C2		−0.0307 (3)	0.0171 (6)	0.0915 (2)	0.0428 (5)
C3		0.1209 (3)	0.1279 (6)	0.0594 (2)	0.0414 (5)
Cl1	0.843 (4)	−0.33724 (9)	−0.2508 (3)	0.07000 (6)	0.0629 (4)
C4	0.801 (4)	−0.31187 (9)	−0.2315 (3)	0.06472 (6)	0.0629 (4)
Cl2	0.856 (4)	−0.06952 (10)	0.0432 (3)	0.20358 (5)	0.0679 (4)
C5	0.157 (4)	−0.06423 (10)	0.0396 (3)	0.18831 (5)	0.0679 (4)
Cl3	0.199 (4)	0.26904 (10)	0.2849 (2)	0.13366 (6)	0.0618 (4)
C6	0.144 (4)	0.24882 (10)	0.2635 (2)	0.12353 (6)	0.0618 (4)

* The occupancy factors for Cln and C(n + 3) are x_n and $1 - x_n$, respectively; the sum of the three x_n was restrained to be 5/2. The distances between pairs of atoms Cln and C(n + 3) were fixed at 0.234 Å, but the two-atom group was allowed to translate and rotate freely. Displacement parameters for atoms Cln and C(n + 3) were constrained to be equal. † The assignment of the same e.s.d.'s to the corresponding coordinates of the Cl and C atoms of a two-atom group (Sheldrick, 1993) may overestimate the certainty of the C-atom position.

Table 4. *Selected geometric parameters ($\mathring{A}$, °)*

	(1)	(2)
C1—C2	1.398 (5)	1.394 (3)
C2—C3	1.400 (5)	1.384 (3)
C3—C1^i	1.367 (6)	1.399 (3)
Cl1—C1	1.717 (4)	1.719 (2)
Cl2—C2	1.711 (4)	1.714 (2)
Cl3—C3	1.715 (4)	1.718 (2)
C4—C1	1.483 (4)	1.485 (2)
C5—C2	1.478 (4)	1.480 (2)
C6—C3	1.481 (4)	1.484 (2)

Symmetry code: (i) $-x, -y, -z$.

5% methylphenylsilicone in dimethylsilicone. The solutions contained three components, which were identified easily and unambiguously by their masses and $^{35}Cl/^{37}Cl$ isotopic patterns.* The constituents included the expected $C_6Cl_5(CH_3)$ (97.5%) and two of the three possible isomers of $C_6HCl_4(CH_3)$ (2.0 and 0.5%). The fragmentation patterns showed that the presence of the $C_6HCl_4(CH_3)$ in the original mass spectrum would have been missed because its parent peak is overwhelmed by the peak arising from the loss of a Cl atom from PCT. The impurity fraction is low enough that its detection by NMR is unlikely. In any event the differences

between the two single crystals studied suggest that the impurity was not evenly distributed in the commercial sample. A small amount removed from the bottle for recrystallization or analysis might have had an impurity level either substantially higher or somewhat lower than 2.5%. Unfortunately, the two crystals used for data collection had already been discarded; otherwise we might have been able to measure the GC-MS patterns (which require a *ca* 1 mg sample) for each of them.

A refinement for the first crystal of a disorder model incorporating a CHX_5 molecule (X = 0.80Cl and 0.20CH$_3$) slightly offset from the inversion center (see Fig. 4) lowered R (wR) from 0.052 (0.161) to 0.049 (0.156) and lowered $\Delta\rho_{max}$ from 0.48 to 0.40 e Å^{-3}. The final occupancy fraction of the impurity was 0.029 (4).

3. Analysis of anisotropic displacement parameters

The U^{ij} values were analyzed using Trueblood's program *THMA*14 (Trueblood, 1978; Dunitz, Schomaker & Trueblood, 1988), assuming a pseudo-C_6Cl_6 molecule. Calculation of the r.m.s. [Δ_{A,B^2}] values (Hirshfeld, 1976; Rosenfield, Trueblood & Dunitz, 1978; see Table 5) showed that the quality of the displacement parameters (hereafter, ADP's) was substantially better for the second crystal than for the first. The Δ_{A,B^2} values show that internal motion between the C6 and Cl6 rings is important, but a fit of the 12 independent T^{ij} and L^{ij} values (S vanishes because of the imposed $\bar{1}$ symmetry) to the 18 independent U^{ij} values for the C$_6$ ring was unsuccessful because of the low ratio of observations to
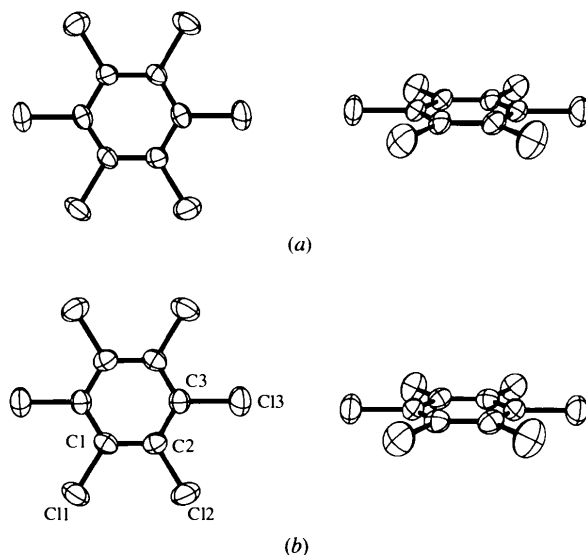

(a)

(b)

Fig. 2. Ellipsoid plot of the PCT molecule in (a) the first crystal and (b) the second crystal. The atom-numbering scheme is also shown. The ellipsoids are drawn at the 50% probability level. Only the Cl substituents are shown. The drawings on the right are related to those on the left by a 90° rotation around the horizontal axis.

variables and the conic-section singularity (Schomaker & Trueblood, 1968). The fits therefore used all $6 \times 6 = 36$ ADP's. No correction was made for internal motion.
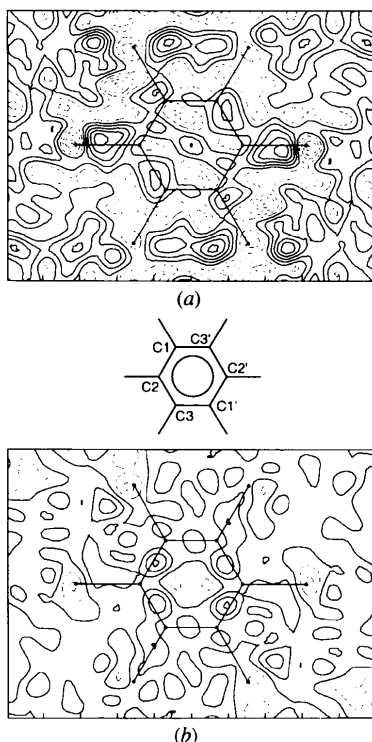

Fig. 3. Final difference-Fourier map calculated for (a) the first crystal and (b) the second crystal of PCT. Contours are at intervals of 0.10 e Å^{-3}. Dashed lines indicate negative contours.
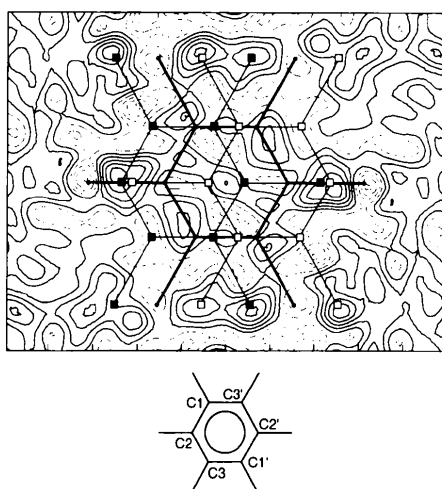

Fig. 4. Final difference-Fourier map calculated for the first crystal of PCT, showing the placement of the impurity molecules (3% CHX$_5$; see text). Contours are at intervals of 0.10 e Å^{-3}. Dashed lines indicate negative contours.

Table 5. *A model for the thermal motion of pentachloro-toluene*

	First crystal	Second crystal
$\langle\sigma^2(U^{ij})\rangle^{1/2}$ (Å^2)	0.0014	0.0008
$\langle\Delta^2(A, B)\rangle^{1/2}$ (Å^2)†		
C—C, C—Cl bonds (6)	0.0039	0.0007
C—C, C$\cdots$C in C$_6$ ring (6)	0.0038	0.0008
Cl$\cdots$Cl (6)	0.0018	0.0010
C—Cl, C$\cdots$Cl (18)	0.0035	0.0045
wR‡	0.030	0.030
$\langle\Delta U^2\rangle^{1/2}$ (Å^2)	0.0010	0.0010
GOF§	1.2	2.2

T (Å$^2 \times 10^3$)

In the Cartesian-crystal coordinate system ($\mathbf{x}\|\mathbf{a}, \mathbf{y}\|\mathbf{b}, \mathbf{z}\|\mathbf{c}^*$)

22 (1)	5 (1)	−4 (1)
	31 (2)	2 (1)
		40 (1)

32 (1)	5 (1)	−1 (1)
	32 (2)	2 (1)
		38 (1)

In the inertial coordinate system [$\mathbf{z} \perp$ molecular plane; $\mathbf{y}$ ∡ C2—Cl2 is $3°$ for crystal (1) and $19°$ for crystal (2)]

27	−2	7
	40	0
		26

36	−2	3
	37	1
		28

Eigenvalues: 40, 33, 19   38, 36, 26

L (deg^2):

In the Cartesian-crystal coordinate system ($\mathbf{x}\|\mathbf{a}, \mathbf{y}\|\mathbf{b}, \mathbf{z}\|\mathbf{c}^*$):

22 (1)	1 (1)	4 (1)
	12 (1)	−1 (1)
		16 (1)

22 (1)	0 (1)	4 (1)
	12 (1)	−1 (1)
		15 (1)

In the inertial coordinates system [$\mathbf{z} \perp$ molecular plane; $\mathbf{y}$ ∡ C2—Cl2 is $3°$ for crystal (1) and $19°$ for crystal (2)]

22	−1	−4
	14	2
		13

22	2	−4
	14	0
		13

Eigenvalues: 12, 14, 11   24, 14, 11

† Contributions from atoms C4, C5 and C6 are not included (see footnote to Table 3). ‡ $wR = [\Sigma w(U_o^{ij} - U_c^{ij})^2/\Sigma w U_o^{ij2}]^{1/2}$, where $w = \langle\sigma(U^{ij})\rangle^{-2}$. § GOF $= \{\Sigma[(U_o^{ij} - U_c^{ij})/\sigma(U_o^{ij})]\}^{1/2}/(N_o - N_v)^{1/2}$, where $N_o - N_v = (6)(6) - 12 = 24$.

The thermal motion descriptions for the two crystals (see Table 5) are very similar; only the T^{11} values differ significantly. It is interesting that the value of L^{33} in the inertial system (z is the axis perpendicular to the molecular plane) is not the largest of the three L^{ii} values.

The $(L^{33})_{\text{inertial}}$ value in PCT of 13 (1) deg^2 is similar to those found at *ca* 300 K for hexachlorobenzene (*ca* 8–19 deg^2 depending on the model; Brown & Strydom, 1974), hexamethylbenzene (*ca* 18 deg^2; Hamilton,

Edmonds, Tippe & Rush, 1969), 1,2,3-trichloro-4,5,6-trimethylbenzene (19 deg^2; Fourme, Renaud & André, 1972) and trichloromesitylene [10.5 (5) deg^2; Brock & Fu, 1990]. The r.m.s. value of L^{33} is *ca* 12% of the angular displacement necessary for molecular reorientation. The barrier to in-plane rotation estimated according to the procedure of Maverick & Dunitz (1987) is 35 (3) kJ mol^{-1}, which is within the range found by NMR studies for other hexasubstituted chloromethyl benzene derivatives (Chezeau, Strange & Brot, 1972).

4. Discussion

This study confirms the conclusion of Khotsyanova, Babushkina, Kuznetsov & Semin (1972) that PCT is isostructural at 300 K with most of the other $C_6Cl_n(CH_3)_{6-n}$ isomers (see Table 1). Like previous authors, we found almost complete rotational disorder, although there is a very weak tendency (see Table 3) for the methyl substituent to be located at position 2.

We were surprised to discover that PCT might form mixed crystals with at least one of the isomers of tetrachlorotoluene. The formation of mixed crystals with other $C_6Cl_n(CH_3)_{6-n}$ isomers would be no surprise. There is ample evidence (see, *e.g.* Tazi, Meinnel, Sanquer, Nusimovici, Tonnard & Carrie, 1995) that in-plane molecular rotation takes place on the NMR time scale. The effective volume difference between the CH_3 group and the Cl atom is only 4.1 (3) Å^3 (see Fig. 1). If there is rotational disorder, then compositional disorder of isomers is likely. The volume difference between $C_6Cl_5(CH_3)$ and $C_6HCl_4(CH_3)$, however, is more like 20 Å^3 (Stalick, 1983, 1986) or *ca* 9% of the molecular volume. The formation of a mixed crystal between molecules of such different sizes seems much less probable. On the other hand, the diffraction patterns at 293 and 103 K of 1-chloro-2,3,5,6-tetramethylbenzene
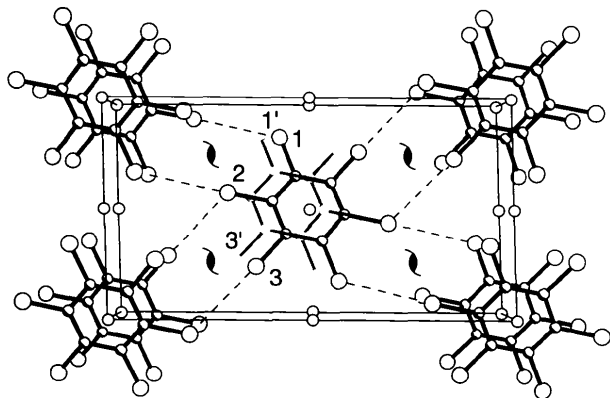

Fig. 5. Diagram showing the molecular packing in PCT. The *c* axis is horizontal, the *a* axis is approximately vertical and the *b* axis points out of the plane of the paper. The locations of the 2_1 axes and of some of the inversion centers are shown. Some of the shortest contacts are shown, as is one of the impurity molecules.

have been explained (Charbonneau & Meinnel, 1968) by a two-site disorder model involving the scrambling of the H and Cl substituents.

The evidence for the incorporation of the impurity is the final difference-Fourier map for crystal (1), the improved agreement factors for crystal (1) when the impurity is introduced and the GC-MS data. Inspection of the crystal packing (see Fig. 5), however, suggests that several impossibly short intermolecular contacts would result. The Cl1···Cl2 distance of 3.57 (1) Å across the 2_1 axis is reduced to 2.65 (1) Å for the Cl1'···Cl2 contact and the Cl3···Cl2 distance of 3.528 (1) Å across the other 2_1 axis is reduced to 3.11 Å for the Cl3'···Cl2 contact. The Cl3'···Cl3 distance across the 2_1 axis is 3.11 (1) Å. If the impurity really is present then either there must be correlation between impurity sites or the impurities must be located at defects or grain boundaries. There must in any case be correlations between the orientations of the molecules in the disordered crystals. If there were not, the molecular volumes of the C_6X_6, $X = $ Cl or CH_3, derivatives in the disordered isostructural crystals would all be the same (but see Fig. 1).

An alternate explanation for the difference-Fourier map for crystal (1) might be some type of twinning. Diffraction patterns for 'composite crystals' of isostructural hexabromobenzene have been described (Boonstra & Herbstein, 1963). We saw no evidence, however, of any extra peaks in the diffraction patterns.

There is little discussion of isomeric purity in the extensive literature on the compounds $C_6Cl_n(CH_3)_{6-n}$ [and of the related compounds $C_6Br_nCl_{6-n}$ (*e.g.* Khotsyanova, 1966)]. The question is important because the synthetic routes to these compounds usually produce a mixture of isomers as well as by-products in which one or more Cl or CH_3 substituent is missing, *i.e.* is replaced by an H atom. Both kinds of impurities are difficult to detect. If $C_6H_nX_{6-n}$ molecules are present and if the centers of the aromatic rings of the isomers coincide, then the only crystallographic consequences are C—X bond lengths that are slightly shorter and displacement parameters that are slightly larger than they would be otherwise – changes that could also be ascribed to increased thermal motion.

While the details of crystal structures may not be especially sensitive to the presence of impurities and the defects they cause, the tunneling rates measured by NMR spectroscopy and the transition temperatures measured by DSC may well be. If kinetic behavior is of interest then the use of GC-MS measurements to monitor crystal purity should be considered, especially if the synthetic route suggests the possibility of compositional disorder.

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