Table 9. *Comparison with related molecules*

	$PO(NH_2)_3$	$C_6H_5OPO(NH_2)_2$	$(C_6H_5O)_3PO$
	(Bullen *et al.*, 1969)	(This work)	(Corbridge, 1966)
P=O	1·510 Å	1·482 Å	1·43 Å
P–N$_{tet}$*	1·658, 1·661	1·628	–
P–N$_{trig}$	1·648	1·604	–
P–O	–	1·598	1·55–1·60
C–O	–	1·400	1·39–1·43
P–O–C	–	123·7°	123–125°

* The subscripts 'tet' and 'trig' signify atoms in tetrahedral and trigonal hydrogen-bond environments.

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The Crystal Structure of Pentamethylbenzotrichloride

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The crystal structure of pentamethylbenzotrichloride [$(CH_3)_5C_6CCl_3$] at 143°K was determined from densitometer measurements of photographic precession camera data (1035 independent reflections). The orthorhombic unit-cell dimensions are $a=19·133$ (3), $b=11·898$ (4), $c=10·666$ (1) Å, space group = *Pbca*, $Z=8$, $D_c=1·45$ g cm^{-3}, $D_m=1·32$ (2) (by flotation). The structure was solved by the symbolic-addition method and refined by the full-matrix least-squares method to $R=8·6\%$. The $C_6(CH_3)_5$-fragment of the molecule shows significant deviations from planarity with the methyl group *ortho* to the –CCl$_3$ group forced 0·3 Å out of the plane. The carbon atom of the –CCl$_3$ group is displaced 0·4 Å out of the plane in the opposite direction. The average C–Cl bond length of 1·796 (11) Å is longer than the typical C–Cl bond length of 1·76 Å.

Hart & Fish (1958, 1962) proposed the formation of dications (II) by the loss of two chlorine atoms from the trichloromethyl group of various polymethylbenzotrichlorides (I), and Hart & Fleming (1962) reported the preparation of such a salt of pentamethylbenzotrichloride. Gillespie & Robinson (1964, 1965) and others (Deno, Friedman & Mockus, 1964; Robinson & Ciruna, 1964) proposed that the monocation (III) was formed instead and contended that the experimental observations of Hart & Fish were consistent with this model. The formation of the dication has never been repeated by other workers, but, in any event, the formation of even the monocation species is undoubtedly aided by overcrowding in the trichloromethyl group. The crystal structure of pentamethyl benzotrichloride has been carried out to determine the extent of this distortion in the parent molecule due to the interaction of the bulky methyl and trichloromethyl groups.

(I)   (II)   (III)
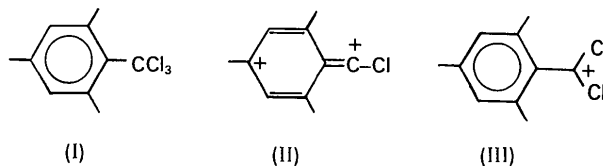
Experimental

Pentamethylbenzotrichloride, $(CH_3)_5C_6CCl_3$, (PMBTC), was prepared according to the method of Hart & Fish (1958). Colorless crystals of symmetry

mmm were obtained by allowing a solution of PMBTC in n-pentane to evaporate slowly.

Because PMBTC is subject to hydrolysis by the moisture in the air and reacts with or dissolves in the solvents used in most adhesives, the crystals were mounted in a sealed glass capillary. The data were collected at low temperature by allowing a cooled stream of nitrogen gas to flow onto the capillary containing the crystal. The cooling apparatus is described elsewhere (Richards, 1964). The temperature at the crystal has been estimated to be approximately 143 °K (Simpson, 1968).

Cell constants and their estimated standard deviations were calculated from measurements taken from low temperature equi-inclination Weissenberg single-crystal back-reflection films (Cu $K\alpha_1 = 1\cdot54051$, $K\alpha_2 = 1\cdot54433$ Å). The cell is orthorhombic with dimensions: $a = 19\cdot133 \pm 0\cdot003$, $b = 11\cdot898 \pm 0\cdot004$, $c = 10\cdot666 \pm 0\cdot01$ Å, $V = 2428\cdot06$ Å^3.

The systematic extinctions $0kl$, k odd; $h0l$, l odd; $hk0$, h odd, are consistent with the unique orthorhombic space group *Pbca*, and were observed from the equi-inclination Weissenberg films $0kl$ through $3kl$. The crystallographic density, $D_c = 1\cdot45$ g cm^{-3}, was calculated for $Z = 8$. A density of $1\cdot32$ (2) g cm^{-3} was measured by the flotation method using a FeCl$_3$ solution. The slightly lower observed density is thought to

be due to the slow formation of gas on the crystal, due to hydrolysis.

Non-integrated precession data (Mo $K\alpha = 0\cdot7107$ Å) were collected at low temperature using several crystals. A crystal ($0\cdot4 \times 0\cdot5 \times 0\cdot4$ mm: $a \times b \times c$), mounted with **c** along the axis of the capillary, was used to obtain $h0l$ to $h4l$ and $0kl$ to $2kl$. The data $hk0$ to $hk3$ were
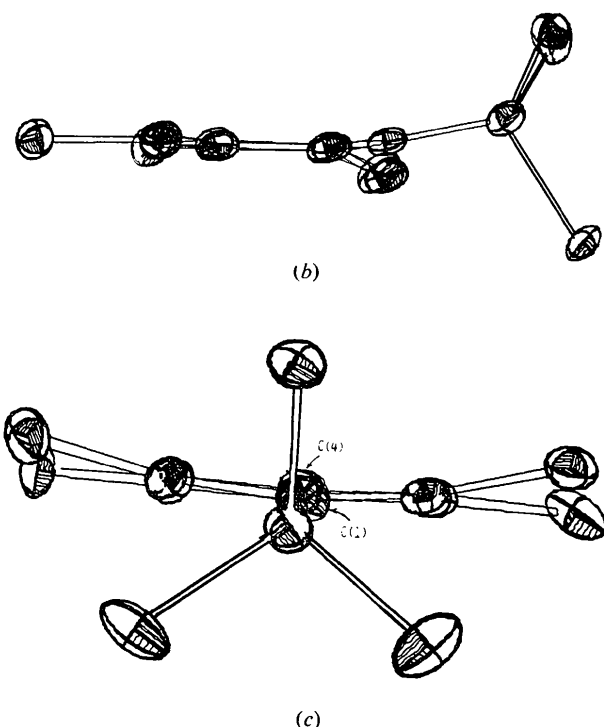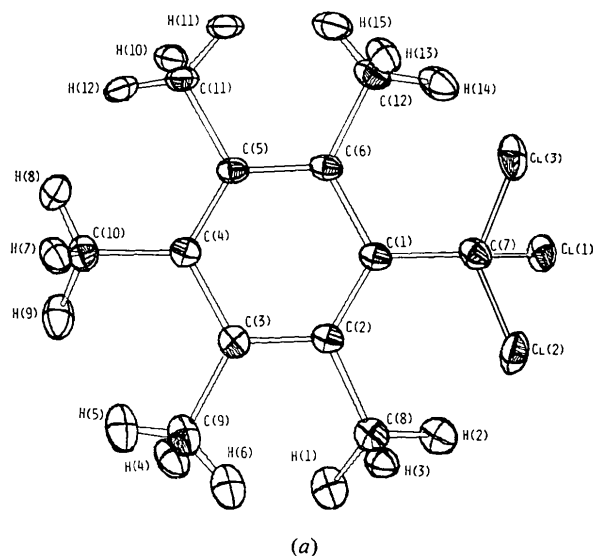

(a)

Table 1. *Calculated and observed structure factors for pentamethylbenzotrichloride*

The values of F_o and F_c are multiplied by a factor of 4.

(b)

(c)

Fig. 1. The structure of the pentamethylbenzotrichloride molecular unit. (a) Viewed normal to the plane of the molecule. (b) Viewed edge on, perpendicular to the C(1)–C(4) vector. (c) Viewed edge on, along the C(1)–C(4) vector.

collected from another crystal ($0.3 \times 0.5 \times 0.4$ mm: $a \times b \times c$) mounted along **a**. In order to be able to use a densitometer to obtain values for the intensities from the non-integrated films, a working curve, relative integrated intensity (intensity scale made by timed exposures of typical crystal reflections) *versus* observed intensity (densitometer), was constructed. A quadratic function was fitted to the curve by the method of least squares. The peak density of a spot was read by the densitometer, the observed intensity was calculated and converted to relative integrated intensity. Each reflection was estimated several times in order to obtain a value for the standard deviation in the mean of the intensity. These standard deviations were later used to calculate the weights used during refinement. A total of 1035 independent present reflections were observed.

The intensities were corrected for Lorentz and polarization factors. No correction for absorption was made ($\mu = 6.9$ cm^{-1}, $\mu R \simeq 0.14$). The neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Both real and imaginary dispersion corrections were applied to Cl during refinement. Full-matrix least-squares refinement was carried out using a locally written program for the IBM 360 computer. The discrepancy indices, ($\Delta F = |F_o| - |F_c|$),

$$R_1 = \Sigma \Delta F / \Sigma F_o$$

and

$$R_2 = \left[\frac{\Sigma w (\Delta F)^2}{\Sigma w F_o^2} \right]^{1/2}$$

were used to follow the progress of refinement. The function minimized was $\Sigma w (\Delta F)^2$. Refinement was carried out using present reflections. The 'smoothing' function $\%S = 0.00833(F - 85)^2 + 6.0$ was fitted to the curve of $\%S$ (percent standard deviation in the mean of the intensity of a reflection) *versus* I, the intensity of the reflection. The weights were then calculated $w = 1/S_F^2$ $[S_F = (\%S)F/100]$. The effect of the smoothing function was to give each reflection a weight of the same magnitude as other reflections of similar intensity.

Structure determination

The structure was solved by the symbolic addition method (Karle & Karle, 1963) from E maps prepared by using phases assigned by a phase determining Fortran computer programs, *FAME, MAGIC*, and *LINK* (Dewar & Stone, private communication). In the symbolic-addition step, 419 reflections were assigned phases based on five symbolic values and three

Table 2. *Atomic parameters for pentamethylbenzotrichloride*

Fractional coordinates with standard deviations in brackets ($\times 10^4$). The U_{ij}'s (Å^2) are given together with standard deviations in brackets ($\times 10^3$), and defined such that the atomic temperature factor is given by:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})].$$

All atoms other than Cl(1), Cl(2), Cl(3) entered refinement as part of a group which had the same translational and librational parameters. The mean-square vibration parameters given in the table for these atoms are calculated from the **T** and **ω** values given in Table 3.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(1)	4943 (1)	1886 (6)	3550 (3)	16 (2)	22 (2)	26 (2)	−4 (2)	−4 (2)	−4 (2)
Cl(2)	4486 (1)	1533 (7)	1007 (3)	18 (2)	50 (3)	20 (2)	−4 (2)	3 (2)	5 (3)
Cl(3)	4670 (1)	−332 (6)	2530 (4)	19 (2)	20 (2)	49 (3)	4 (2)	8 (2)	−12 (3)
C(1)	3614 (6)	1222 (23)	3044 (11)	20	17	13	0	−4	−2
C(2)	3172 (5)	2014 (23)	2569 (12)	21	16	14	−0	−3	−3
C(3)	2453 (6)	1996 (23)	2761 (11)	21	17	18	1	−1	−5
C(4)	2170 (6)	1091 (23)	3545 (11)	20	18	15	0	−1	−2
C(5)	2622 (6)	365 (22)	4115 (11)	21	17	13	−1	−2	1
C(6)	3340 (5)	396 (23)	3936 (11)	21	16	15	0	−4	0
C(7)	4352 (6)	1088 (23)	2601 (12)	19	20	23	1	−5	−2
C(8)	3427 (6)	3116 (23)	1950 (12)	24	18	22	−2	−3	−5
C(9)	1968 (6)	2826 (25)	2094 (13)	23	18	36	3	−1	−10
C(10)	1385 (6)	1060 (24)	3793 (13)	20	23	26	−0	1	−3
C(11)	2333 (6)	−523 (22)	4995 (12)	24	18	21	−3	−3	6
C(12)	3806 (6)	−314 (23)	4787 (13)	26	18	31	1	−9	1
H(1)	2990	3700	1690	28	18	33	−1	−2	−9
H(2)	3690	2840	1160	24	17	24	−2	−3	1
H(3)	3810	3750	2460	29	25	24	−5	−4	−9
H(4)	1430	2690	2360	23	21	46	4	−0	−13
H(5)	2020	2740	1060	26	16	42	3	−6	−5
H(6)	2140	3650	2370	28	22	41	2	2	−16
H(7)	1240	420	4480	21	25	27	−3	1	1
H(8)	1090	990	2970	19	23	34	2	−4	−5
H(9)	1210	1900	4270	23	30	34	−1	7	−7
H(10)	2780	1029	5340	28	17	30	−2	−5	7
H(11)	1980	1009	4500	23	18	22	−3	−3	3
H(12)	2100	−99	5800	29	25	22	−7	−0	12
H(13)	4360	−119	4520	25	20	39	3	−11	−2
H(14)	3650	1089	4520	25	15	36	2	−6	−2
H(15)	3770	−169	5820	34	24	36	−2	−13	9

phases chosen to assign an origin. Approximately 700 of the largest E's were used in the phase assignment step. The E maps were prepared from the eight sign combinations showing the fewest inconsistencies. The structure was solved from the map prepared from the set showing the third lowest number of inconsistencies (204).

The atom positions determined from the E map gave $R_2 = 0.40$. Refinement with individual isotropic temperature factors for all atoms (60 parameters plus scale parameters) brought R_2 to 0.096. Proton positions were not clearly evident in difference electron-density maps, although some peaks were found in reasonable positions about the methyl carbon atoms.

Refinement using anisotropic temperature factors for all atoms except hydrogen was carried out but was discontinued when several diagonal elements of the thermal-parameter matrix for carbon atoms became negative. In an effort to use a model for calculation

which would approximate the actual situation in the crystal, the whole molecule including methyl protons was assumed to have the same thermal translational and librational parameters. The refinement was carried out on the individual atom positional parameters (excluding H atoms which were fixed) and the values of a single T (translational) and ω (librational) tensor for the whole molecule (57 parameters and scale) giving $R_2 = 0.106$. As a modification to this model, the three chlorine atoms were allowed to vibrate anisotropically independent of the remainder of the molecule (75 parameters plus scale) giving $R_2 = 0.100$. Refinement with only atoms C(1) to C(6) as the thermal group did not lead to a decrease in R_2.

Using the 75-parameter model, additional refinement was carried out on four models which differed only in the orientation of the methyl protons about the $C_{ring}-C_{methyl}$ axis. The resulting R_2 values ranged from 0.096 to 0.101. Since the change in R was relatively insensitive to the proton orientation, no significant conclusion can be drawn concerning the actual orientation. The model which yielded the lowest R_2 value is depicted in the figures and the hydrogen-atom positions are given in Table 2. The conventional R_1 for this model is 0.086; $R_2 = 0.096$. The average change in parameters in the last cycle of the full-matrix least-squares refinement was 15 % of the estimated standard deviation.

The final values of the observed and calculated structure factors are listed in Table 1. Table 2 lists the final positional and vibrational parameters of PMBTC. The tensors describing the thermal motion of the pentamethylphenyl fragment of the molecule are given in Table 3. The relatively small translational and librational motion observed is reasonable for a molecule at 140°K.

Table 3. Translational and librational tensors for the rigid-group analysis of pentamethylbenzotrichloride

T(Å^2) is referred to molecular axes. The molecular axes chosen are $u_1 = C(1) \rightarrow C(4)$, $u_2 = C(2) \rightarrow C(6)$; $u_3 = u_1 \wedge u_2$ is perpendicular to the plane of the molecule. The rigid group included all carbon and hydrogen atoms. ω is in (degrees)^2. Estimated standard deviations are in parentheses.

T_{ij}	$j = 1$	2	3
$i = 1$	0.0182 (21)		
2	0.0010 (13)	0.0144 (22)	
3	−0.0040 (19)	−0.0012 (21)	0.0098 (31)

ω_{ij}	$j = 1$	2	3
$i = 1$	7 (2)		
2	3 (1)	6 (2)	
3	1 (1)	0.3 (1.0)	1 (1)

Table 4. Interatomic distances and angles for pentamethylbenzotrichloride

The estimated standard deviation in the last digit is given in parentheses.

Cl(1)–Cl(2)	2.881 (5) Å	C(7)–Cl(1)	1.791 (18) Å	C(4)–C(5)–C(6)	123.3 (1.2)°
Cl(1)–Cl(3)	2.902 (10)	C(7)–Cl(2)	1.799 (13)	C(4)–C(5)–C(11)	119.0 (1.0)
Cl(2)–Cl(3)	2.772 (9)	C(7)–Cl(3)	1.797 (29)	C(6)–C(5)–C(11)	117.7 (1.2)
		average	1.796		
C(1)–C(2)	1.36 (3)	C(2)–C(8)	1.55 (3)	C(5)–C(6)–C(7)	117.5 (1.5)
C(2)–C(2)	1.39 (1)	C(3)–C(9)	1.53 (3)	C(5)–C(6)–C(12)	123.2 (1.1)
C(3)–C(4)	1.47 (3)	C(4)–C(10)	1.53 (2)	C(7)–C(6)–C(12)	118.8 (0.9)
C(4)–C(5)	1.37 (3)	C(5)–C(11)	1.52 (2)		
C(5)–C(6)	1.39 (2)	C(6)–C(12)	1.53 (2)	Cl(1)–C(7)–Cl(2)	106.7 (0.3)
C(6)–C(1)	1.46 (2)	average	1.532	Cl(1)–C(7)–Cl(3)	107.9 (0.9)
average	1.407	C(1)–C(7)	1.50 (2)	Cl(1)–C(7)–C(1)	111.1 (0.9)
C(2)–C(1)–C(6)	118.8 (1.2)°			Cl(2)–C(7)–Cl(3)	100.9 (0.4)
C(2)–C(1)–C(7)	122.8 (1.2)			Cl(2)–C(7)–C(1)	113.7 (1.2)
C(6)–C(1)–C(7)	118.1 (1.6)			Cl(3)–C(7)–C(1)	115.7 (1.3)
C(1)–C(2)–C(3)	123.3 (1.2)				
C(1)–C(2)–C(8)	123.2 (1.0)				
C(3)–C(2)–C(8)	112.9 (1.2)				
C(2)–C(3)–C(4)	117.4 (1.4)				
C(2)–C(3)–C(9)	121.5 (0.9)				
C(4)–C(3)–C(9)	120.9 (1.2)				
C(3)–C(4)–C(5)	119.0 (1.2)				
C(3)–C(4)–C(10)	118.7 (1.5)				
C(5)–C(4)–C(10)	122.1 (1.0)				

Discussion of the structure

The structure of a molecular unit is shown in Fig. 1. Interatomic distances and angles are given in Table 4. The displacement of atoms from a least-squares plane fitted to the atoms C(2), C(3), C(4), C(5), C(6), C(9), C(10), and C(11) (hereafter described as the phenyl plane), Table 5, shows that significant departures from planarity occur for atoms C(1, 7, 8, 12) in the vicinity of the trichloromethyl group. The remaining 8 carbon atoms are planar within 3 standard deviations in the uncertainty in the positions of the atoms. The carbon atom, C(7), of the trichloromethyl group is displaced positively from the plane by 0·43 Å. The adjacent methyl groups, C(8, 12), are displaced 0·35 and 0·26 Å, respectively, to the opposite side of the plane. The undisturbed PMBTC molecule might be expected to assume C_s symmetry with atoms Cl(1), C(1, 4, 7, 10) contained in the mirror plane perpendicular to the benzene ring. The idealized model of the molecule would find the methyl groups, C(8, 12), equally displaced to the same side of the plane of the ring. That the methyl groups differ significantly from each other in their displacements is thought to be caused by the packing of the molecules in the cell. Two effects may be considered: the rotation of the trichloromethyl group about the C(1, 7) axis to place Cl(2) slightly closer to the phenyl plane than Cl(3), and the placement of the methyl group, C(12), closer to the phenyl plane than C(8).

Table 5. Out-of-plane displacements for pentamethylbenzotrichloride

The values in parentheses are the averaged estimated standard deviations in the positional parameters (Table 9) of that atom. Atoms included in the calculation of the plane are denoted by an asterisk.

Cl(1)	− 1·051 (14) Å	C(6)*	0·008 (17)
Cl(2)	1·410 (4)	C(7)	0·432 (17)
Cl(3)	1·475 (5)	C(8)	− 0·347 (17)
C(1)	0·097 (17)	C(9)*	0·008 (18)
C(2)*	− 0·009 (17)	C(10)*	− 0·008 (18)
C(3)*	− 0·027 (17)	C(11)*	− 0·019 (17)
C(4)*	0·035 (17)	C(12)	− 0·264 (18)
C(5)*	0·012 (16)		

The equation of the least-squares plane, calculated by the method of Blow (1960), is

$$-0.09398X - 0.61669Y - 0.78158Z + 4.18100 = 0.$$

The normal to the plane makes angles of 95·4, 128·1, and 141·4° with the x, y and z axes respectively.

A total of 79 non-bonded interactions at distances less than 4·00 Å between symmetry related molecular units in the cell were computed. Several of these are close enough to the distance of van der Waals contact to be considered significant (Table 6). The interactions are shown in Fig. 2. Interactions to rotate the trichloromethyl group appear to cancel, while the Cl(1^i)–Cl(2^v) interaction, which is the most intense interac

tion of the trichloromethyl group, apparently exerts only a small torque, if any, on Cl(1^i). (The superscript on the atom designation refers to the symmetry equivalent molecule as specified in Table 6.) The apparent rotation of the trichloromethyl group may be in response to crowding by the adjacent methyl groups.

Table 6. Non-bonded interactions of pentamethylbenzotrichloride

The tabulated interactions occur at distances (Å) less than the sum of van der Waals radii.

Cl(1^i)–Cl(2^v)	3·34	C(8^i)—C(5^v)	3·84
Cl(1^i)–Cl(3^{vi})	3·58	C(8^i)—C(6^v)	3·67
Cl(1^i)–C(12^{ii})	3·52	C(8^i)—C(12^v)	3·56
Cl(2^i)–Cl(1^v)	3·34	C(9^i)—C(6^{iii})	3·68
Cl(2^i)–C(10^{vii})	3·68	C(9^i)—C(5^{iii})	3·79
Cl(3)–Cl(1^{vi})	3·58	C(9^i)—C(11^{viii})	3·78
C(1^i)–C(11^{viii})	3·82	C(10^i)–Cl(2^{vii})	3·68
C(2^i)–C(11^{viii})	3·41	C(11^i)–C(1^{viii})	3·82
C(3^i)–C(11^{iii})	3·82	C(11^i)–C(2^{viii})	3·41
C(3^i)–C(11^{viii})	3·46	C(11^i)–C(3^{iii})	3·82
C(5^i)–C(8^v)	3·84	C(11^i)–C(3^{viii})	3·46
C(5^i)–C(9^{iii})	3·79	C(11^i)–C(9^{viii})	3·78
C(6^i)–C(8^v)	3·67	C(12^i)–Cl(1^{ii})	3·52
C(6^i)–C(9^{iii})	3·68	C(12^i)–C(8^v)	3·56

	x	y	z;		x	$\frac{1}{2}-y$	$\frac{1}{2}+z$
i	x	y	z;	v	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$
ii	$-x$	$-y$	$-z$;	vi	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
iii	$\frac{1}{2}-x$	$\frac{1}{2}+y$	z;	vii	$\frac{1}{2}+x$	y	$\frac{1}{2}-z$
iv	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$-z$;	viii	$\frac{1}{2}-x$	$-y$	$\frac{1}{2}+z$

The atom C(12) appears 0·08 Å closer to the phenyl plane than C(8). In Fig. 2 it can be seen that the interaction of C(8^v) with C(12^i) would be effective in moving C(12^i) towards the plane since the interatomic distance is less than the sum of van der Waals radii, and the interaction geometry allows a very large torque to be exerted on C(12^i). Other interactions to C(12) and C(8) either are not effective in causing torque, or in the case of C(8), tend to move C(8) away from the phenyl plane. It is felt that this mechanism operates to cause the observed displacements, and is probably more important in causing the rotation of the trichloromethyl group than interactions directly to that group.

The C(1) carbon atom of the benzene ring is displaced 0·10 Å from the phenyl plane. Considering the uncertainty in the positions of C(1) to be 0·02 Å, as is calculated by averaging the uncertainties in the position of C(1) in the directions of the cell axes (Table 2), the atom appears about 5 standard deviations from the plane of the ring. Since differences of 3 or more standard deviations are usually accepted as significant, it may be concluded that the results of this study show that the C(1) position of the benzene ring is significantly displaced from the phenyl plane.

The dihedral angle between the plane containing C(1, 2, 6) and the phenyl plane is 8·0°. The C(1)–C(7) bond makes an angle of 16·7° with the phenyl plane. The C(2)–C(8) and the C(5)–C(12) bonds make angles of 12·9 and 9·9° respectively, with the phenyl plane.

The expected tetrahedral bonding geometry at C(7)

is distorted by the crowding effect of the adjacent methyl groups. The trichloromethyl groups in tri-chloronitromethane, chloroform, and hexachloroethane all give Cl–C–Cl bond angles of 111° as determined by Barss (1957), Wolfe (1956) and Morino & Hirota (1958) respectively. In contrast, all Cl–C–Cl bond angles for PMBTC (Table 4), are less than the tetrahedral angle (109·5°). Particularly noticeable is the effect on Cl(2) and Cl(3) to reduce the angle to 100·9°. The remaining angles are 106·7 and 107·9°.
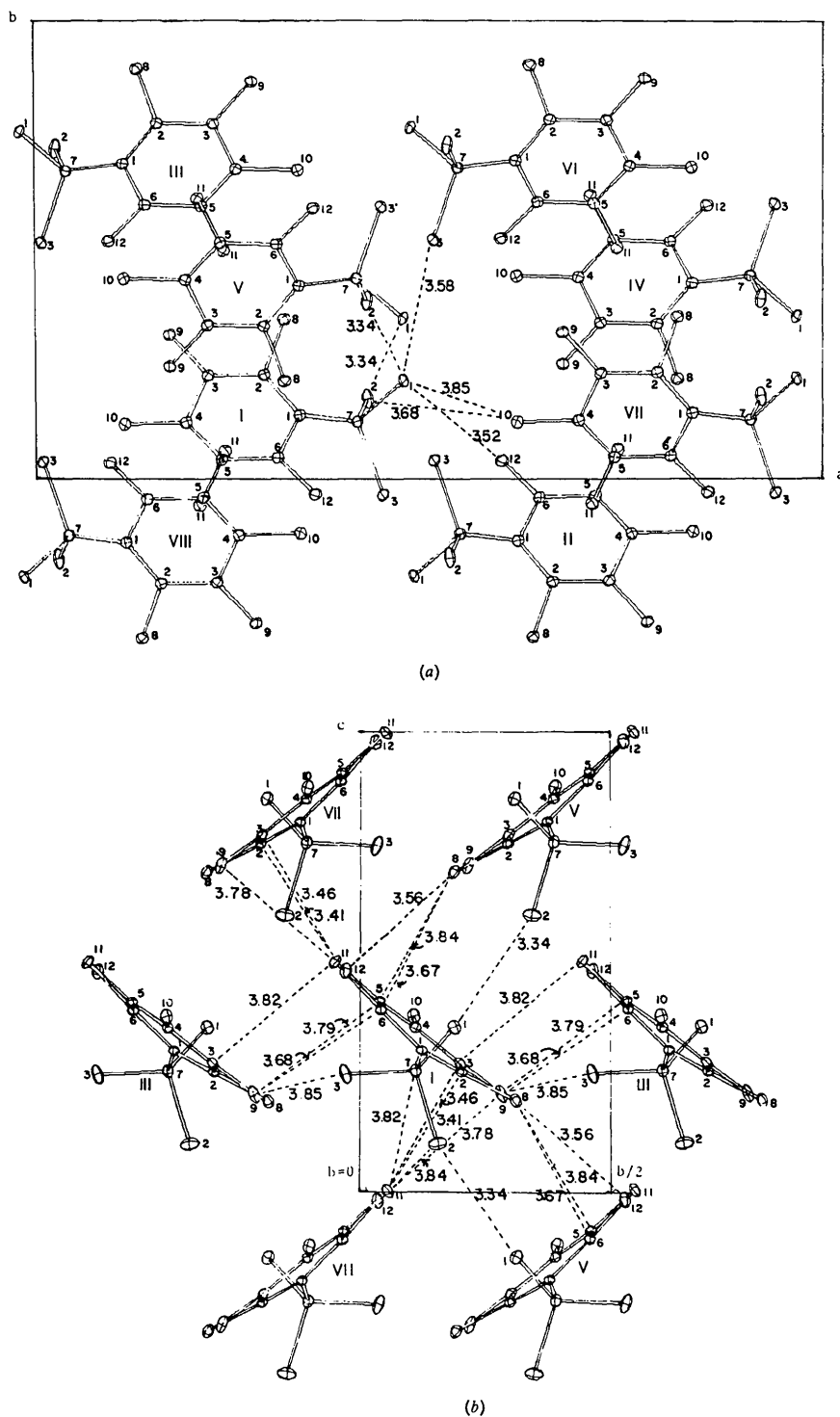

(a)

(b)

Fig. 2. The packing of pentamethylbenzotrichloride molecules. (a) Projected along [001]. (b) Projected along [100].

Table 7. *Some C–Cl distances* (Å)

Standard deviations in parentheses when reported.

C–Cl	Compound	Reference
1·75 (1)	CCl_3NO_2	Barss (1957)
1·77 (3)	CCl_3SiCl_3	Morino & Hirota (1958)
1·762	$CHCl_3$	Wolfe (1956)
1·76 (1) 1·767	CCl_3CCl_3	Morino & Hirota (1958) Sutton (1958)
1·766 (3) 1·77 (1)	CCl_4	Bartell, Brockway & Schwendeman (1955) Karle & Karle (1949)
1·77 (1)		Morino & Kuchitsu (1958)
1·77 (2)	CCl_3CH_3	Coutts & Livingston (1953)
1·7724 (5)	CH_2Cl_2	Meyers & Guinn (1952)
1·76	α-Trichloromethyl-N-methylolethenimine	Shibaeva & Atovmyan (1965)
1·77 (2)	$CH_3CH_2CH_2Cl$	Morino & Kuchitsu (1958)
1·810 (2)	9,10-Bis(chloromethyl)-anthracene	Gabe & Glusker (1971)
1·839 (13) 1·830 (8)	α-Chlorotropane monohydrate	Vooren, Schenk & MacGillavry (1970)

Table 8. *Some recent* $C_{Ar}–C_{Me}$ *distances* (Å)

$C_{Ar}–C_{Me}$	Compound	Reference
1·51 (1) 1·52	Nitromesitylene	Trotter (1959) Sutton (1958)
1·538 (7) 1·547 (7) 1·533 (9)	2,4,6-Trimethylbenzoic acid	Florencio & Smith (1970)
1·523 (6) 1·516 (7) 1·526 (6)	3,4,5-Trimethylbenzoic acid	Cano, Martínez-Carrera & García-Blanco (1970)
1·500 (6) 1·529 (6)	2,3-Dimethylbenzoic acid	Smith, Florencio & García-Blanca (1971)
1·53 (1) 1·52 (1)	2,6-Dimethylbenzoic acid	Anca, Martínez-Carrera & García-Blanco (1967)
1·515 (24)	2-Hydroxy-3-methylbenzoic acid	Gupta & Prasad (1971)
1·528 (9)*	p-Nitrotoluene	Barve & Pant (1971)
1·514 (11)*	p-Toluic acid	Takwale & Pant (1971)
1·514† 1·520†	p-Cresol	Bois (1971)
1·507 (4)	p-Toluoyl-acetophenon-enol	Kato (1971)
1·519 (2)	p-Methyl-m-mitro-N-methylaniline	Chiaroni (1971)
1·533 (av.)	Dimesityl sulfone	Chawdhury & Hargreaves (1971)
1·48 (1)-o 1·50 (1)-o 1·50 (1)-p 1·53 (1)-m 1·53 (1)-m	Heptamethylbenzene-tetrachloroaluminate	Baenziger & Nelson (1968)
1·532 (av.)	Pentamethylbenzotrichloride	This paper

* Corrected for thermal motion.
† At −150°C.

The average C–Cl bond length of 1·796 (11) Å is larger than the bond lengths listed in Table 7 although the values agree within 3 standard deviations. The average C–C bond length in the benzene ring is 1·407 which is in agreement with the value of 1·398 (Sutton, 1958, 1965). The average C_{ring}–C_{methyl} bond distance of 1·53 Å is in reasonable agreement with bond distances reported for various compounds (Table 8). The C(1)–C(7) bond distance of 1·50 (2) Å is not significantly different from the ring–methyl distances.

The bond distances have not been corrected for thermal motion. If one assumes that the rigid-molecule thermal-motion treatment is valid, the librational parameters indicate that the maximum bond-length corrections would be less than 0·002 Å. The small correction is most likely due to the fact that the crystal was studied at low temperatures.

In conclusion, pentamethylbenzotrichloride is found to be non-planar in the region of the trichloromethyl group. The trichloromethyl group and the C(1) carbon atom of the benzene ring are displaced 0·43 and 0·10 Å to one side of the least-squares plane through the remainder of the benzene ring while the adjacent methyl groups, C(8) and C(12), are moved 0·35 and 0·26 Å to the other side of the phenyl plane. The C(1)–C(7), C(2)–C(8), and C(6)–C(12) bonds make angles of 16·7, 12·9 and 9·9° with the plane of the ring. The Cl–C–Cl bond angles, found to be 111° for some other compounds (Barss, 1957; Wolfe, 1956; Morino & Hirota, 1958) are decreased to 100·9 (4), 106·7 (3) and 107·9 (9)°. Average bond lengths C_{ar}–C_{ar}, 1·41 (5) Å and C_{ar}–C_{Me}, 1·53 (1) Å were found; C_{ar}–C_{CCl_3} is 1·50 (2) Å. Non-bonding interactions between different molecular units in the cell, particularly to C(12), cause distortion of the molecule from C_s symmetry.

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