Table 5. χ^2 *tests for hydrazinium sulphate derived parameters*

(*a*) Neutron thermal parameters

$R^2_{\beta 11} = 68{\cdot}5$ $\quad R^2_{\beta 13} = 12{\cdot}5$
$R^2_{\beta 22} = 155{\cdot}5$ $\quad R^2_{\beta 23} = 19{\cdot}8$
$R^2_{\beta 33} = 136{\cdot}3$ $\quad \chi^2_{2.5,80} = 106{\cdot}6$
$R^2_{\beta 12} = 8{\cdot}65$ $\quad \chi^2_{97.5,80} = 57{\cdot}15$

(*b*) Neutron positional parameters

$R^2_x = 43{\cdot}7$ $\quad \chi^2_{2.5,40} = 59{\cdot}34$
$R^2_y = 16{\cdot}5$ $\quad \chi^2_{97.5,40} = 24{\cdot}43$
$R^2_z = 8{\cdot}8$

(*c*) Neutron (this investigation) X-ray positional parameters

$R^2_x = 15{\cdot}2$ $\quad \chi^2_{2.5,21} = 35{\cdot}48$
$R^2_y = 15{\cdot}0$ $\quad \chi^2_{97.5,21} = 10{\cdot}28$
$R^2_z = 19{\cdot}5$

(*d*) Neutron X-ray positional parameters (Jönsson & Hamilton)

$R^2_x = 19{\cdot}0$ $\quad \chi^2_{2.5,21} = 35{\cdot}48$
$R^2_y = 10{\cdot}6$ $\quad \chi^2_{97.5,21} = 10{\cdot}28$
$R^2_z = 8{\cdot}0$

rameters are well known and will not be commented on further here. The differences between the neutron thermal parameters are probably due to the dissimilar extinction behaviours exhibited by the two crystals, since the form of the extinction function correlates very strongly with the thermal parameters.

In conclusion it may be noted that the two neutron diffraction investigations have produced identical descriptions of the molecular geometries of hydrazinium sulphate, although carried out at different reactors using different samples. The less severe extinction effects in the present investigation have probably led to somewhat improved thermal parameters.

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The Crystal Structure of 1,2,3,4-Tetrachloro-9-t-butyltriptycene

By M. Mikami, K. Toriumi, M. Konno and Y. Saito

The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, *Japan*

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1,2,3,4-Tetrachloro-9-t-butyltriptycene forms monoclinic crystals with the space group $P2_1/c$, lattice constants $a = 10{\cdot}231$ (1), $b = 18{\cdot}865$ (2), $c = 10{\cdot}631$ (1) Å, $\beta = 99{\cdot}60$ (1)° and $Z = 4$. The structure was solved by conventional Patterson and Fourier techniques and refined by the block-diagonal least-squares method to an R value of 0·049 for the 3038 observed reflexions collected by diffractometry. On account of the bulky t-butyl and chlorine substituents in the *peri* position, the molecule is overcrowded and C(9)–C(17) and C(9)–C(21) are 1·603 and 1·576 Å long and, as expected, contribute to the relaxation. Also, the t-butyl and *peri* chlorine substituents are inclined in opposite directions. Some of the shortest intramolecular distances between chlorine and hydrogen atoms are 2·604, 2·685 and 2·590 Å.

Introduction

Triptycene is known to have a rigid molecular structure. In the case of its 9-substituted derivatives, the internal rotation around C(9)–C(21) is restricted by the steric effect, and some rotational isomers were confirmed by a proton magnetic resonance study (Suzuki, Ōki & Nakanishi, 1974). 1,2,3,4-Tetrachloro-9-t-butyltriptycene has an overcrowded molecular structure, and considerable distortion is expected owing to the bulky substituents. Crystals of this compound have been subjected to X-ray crystal analysis in order to elucidate the conformational details of the molecule. In other triptycene derivatives such as 1-bromotriptycene (Palmer & Templeton, 1968) and β-chloroethyltriptycene (Karle & Estlin, 1969) the effect of substituents on the molecular conformation has been discussed.

Experimental

Crystals of the compound grown from a cyclohexane solution were kindly supplied by Professor M. Ōki of this University. The rhomboidal crystals were colourless and transparent. The space group and the approximate cell dimensions were determined by oscillation and Weissenberg photographs with Cu $K\alpha$ radiation. The lattice constants were later refined by the least-squares method with higher-order reflexions measured on a diffractometer. An attempt to shape the crystal into a sphere failed and a bullet-formed crystal with dimensions $0{\cdot}31 \times 0{\cdot}27 \times 0{\cdot}26$ mm was used for intensity measurement. 4987 independent reflexions within the range $2\theta \leq 60°$ were measured using Mo $K\alpha$ radiation on an automated four-circle diffractometer; 3038 reflexions with $|F| > 3\sigma$ were regarded as 'observed' and used for refinement. The ω–2θ scan technique was employed at a scan rate of 4° min^{-1} in ω and the scan range was calculated by $1{\cdot}5° + 0{\cdot}5° \tan\theta$. Three standard reflexions were counted every fifty reflexions and background intensities were obtained at each end of the scan. The intensity fluctuations were less than 2 %, and some weak reflexions were counted repeatedly up to three times. The usual corrections were made for Lorentz and polarization effects, but no correction was applied for absorption or extinction.

Crystal data

$C_{24}H_{18}Cl_4$, M.W. 448·23, m.p. 284°C. Space group: monoclinic, $P2_1/c$ (from systematic absences); $a = 10{\cdot}231\ (1)$, $b = 18{\cdot}865\ (2)$, $c = 10{\cdot}631\ (1)$ Å, $\beta = 99{\cdot}60\ (1)°$; $U = 2004$ Å^3, $Z = 4$, $D_m = 1{\cdot}47$, $D_x = 1{\cdot}49$ g cm^{-3}, $\mu = 6{\cdot}04$ cm^{-1} (for Mo $K\alpha$, $\lambda = 0{\cdot}7107$).

Structure determination

Three-dimensional sharpened Patterson maps were synthesized. They were interpreted straightforwardly in terms of chlorine atoms only, which, from the known molecular structure, were thought to lie on a plane. Calculation of structure factors based on the chlorine atoms gave an R value of 0·66. The conventional Fourier syntheses and successive difference syntheses indicated all the lighter atoms including 18 hydrogens. The structure was refined by the block-diagonal least-squares program *HBLS* written by Dr Ashida, with anisotropic temperature factors assigned to the non-hydrogen atoms and isotropic ones to the hydrogen atoms. Anomalous dispersion corrections were introduced for the chlorine atoms. At the final stage of the refinement all the parameter shifts were less than one sixth of the corresponding standard de-

Table 2. *The final positional and thermal parameters with estimated standard deviations*

The anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

Non-hydrogen atoms ($\times 10^4$)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl(1)	6009 (1)	1730 (1)	2943 (1)	76 (1)	64 (1)	163 (1)	−32 (1)	11 (1)	11 (1)
Cl(2)	6865 (1)	1298 (1)	5624 (1)	85 (1)	56 (1)	153 (1)	11 (1)	−54 (1)	−30 (1)
Cl(3)	5012 (1)	581 (1)	7196 (1)	210 (2)	52 (0)	60 (1)	41 (1)	−25 (1)	−2 (1)
Cl(4)	2061 (1)	300 (1)	6021 (1)	166 (1)	44 (0)	82 (1)	1 (1)	56 (1)	16 (0)
C(1)	4818 (3)	1298 (7)	3635 (3)	62 (3)	24 (1)	84 (3)	1 (1)	7 (2)	−8 (1)
C(2)	5265 (3)	1109 (2)	4909 (3)	66 (3)	26 (1)	90 (3)	10 (1)	−23 (3)	−16 (2)
C(3)	4441 (4)	793 (2)	5630 (3)	119 (4)	25 (1)	53 (3)	23 (2)	−14 (3)	−7 (1)
C(4)	3135 (3)	664 (2)	5081 (3)	104 (4)	22 (1)	63 (3)	9 (2)	26 (3)	1 (1)
C(5)	−392 (3)	1694 (2)	2935 (4)	65 (3)	35 (1)	108 (4)	1 (2)	21 (3)	−8 (2)
C(6)	−802 (3)	2346 (2)	2404 (4)	73 (4)	36 (1)	145 (5)	14 (2)	21 (1)	−14 (2)
C(7)	−86 (4)	2672 (2)	1589 (4)	93 (4)	25 (1)	140 (5)	14 (2)	1 (3)	1 (2)
C(8)	1054 (3)	2363 (2)	1293 (3)	84 (3)	23 (1)	93 (3)	5 (2)	7 (3)	2 (2)
C(9)	2751 (3)	1264 (2)	1606 (3)	56 (3)	20 (1)	57 (2)	1 (1)	8 (2)	1 (1)
C(10)	1295 (3)	679 (2)	3163 (3)	60 (3)	26 (6)	75 (3)	−8 (1)	15 (2)	6 (1)
C(11)	1437 (3)	204 (2)	2056 (3)	63 (3)	20 (1)	88 (3)	−1 (1)	−12 (2)	1 (1)
C(12)	864 (3)	−469 (2)	1857 (4)	76 (4)	27 (1)	138 (5)	−6 (2)	−10 (3)	6 (2)
C(13)	1080 (4)	−867 (2)	819 (4)	112 (5)	23 (1)	170 (6)	−1 (2)	−43 (4)	−17 (2)
C(14)	1860 (4)	−606 (2)	14 (4)	117 (4)	31 (1)	121 (4)	14 (2)	−25 (4)	−25 (2)
C(15)	2435 (3)	69 (2)	213 (3)	97 (4)	29 (1)	80 (3)	11 (2)	−7 (3)	10 (2)
C(16)	2218 (3)	495 (2)	1235 (3)	63 (3)	19 (1)	67 (3)	5 (1)	−11 (2)	−1 (1)
C(17)	3521 (3)	1153 (2)	3034 (3)	56 (3)	18 (1)	61 (3)	0 (1)	6 (2)	−4 (1)
C(18)	2696 (3)	829 (2)	3819 (3)	62 (3)	20 (1)	62 (3)	0 (1)	8 (2)	−1 (1)
C(19)	1501 (3)	1706 (2)	1814 (3)	58 (3)	21 (1)	66 (3)	1 (1)	2 (2)	−6 (1)
C(20)	747 (3)	1384 (2)	2634 (3)	58 (3)	23 (1)	73 (3)	−1 (1)	2 (2)	−6 (1)
C(21)	3513 (3)	1610 (2)	586 (3)	98 (4)	28 (1)	75 (3)	3 (2)	25 (3)	9 (2)
C(22)	3939 (4)	2390 (2)	932 (4)	111 (4)	31 (1)	147 (5)	14 (2)	34 (4)	19 (2)
C(23)	4732 (4)	1143 (2)	396 (4)	100 (4)	44 (2)	104 (4)	6 (2)	46 (3)	3 (2)
C(24)	2584 (4)	1651 (2)	−740 (4)	145 (5)	43 (2)	74 (3)	12 (2)	23 (3)	17 (2)

Table 2 (*cont.*)

Positional parameters for hydrogen atoms ($\times 10^3$)

	x	y	z
H(5)	−85 (3)	144 (2)	356 (3)
H(6)	−163 (4)	257 (2)	260 (4)
H(7)	−34 (4)	313 (2)	119 (4)
H(8)	155 (3)	260 (2)	76 (3)
H(10)	75 (3)	46 (2)	374 (3)
H(12)	37 (3)	−58 (2)	246 (3)
H(13)	65 (4)	−135 (2)	64 (4)
H(14)	211 (4)	−92 (2)	−77 (4)
H(15)	297 (3)	26 (2)	−38 (3)
H(22*a*)	409 (4)	250 (2)	171 (3)
H(22*b*)	490 (4)	251 (2)	74 (3)
H(22*c*)	338 (4)	271 (2)	33 (3)
H(23*a*)	546 (4)	147 (2)	34 (4)
H(23*b*)	509 (4)	78 (2)	110 (3)
H(23*c*)	452 (4)	85 (2)	−33 (4)
H(24*a*)	226 (4)	120 (2)	−107 (4)
H(24*b*)	316 (4)	188 (2)	−135 (4)
H(24*c*)	180 (4)	199 (2)	−78 (4)

viations. The final R value became 0·049 for the 3038 observed reflexions. Unit weight was given to all the reflexions. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final difference electron-density maps showed only peaks which could be attributed to bonding electrons. The observed and calculated structure factors are compared in Table 1.* The atomic parameters and their standard deviations are listed in Table 2.

Table 3. *Rigid-body thermal parameters*

Principal axes of the molecule in the form $La+Mb+Nc$

Moment of inertia (atomic weight × Å)	L	M	N
1076·3	0·0417	0·0472	0·0098
1127·7	−0·0701	−0·0107	−0·0750
1697·7	0·0564	0·0217	−0·0581

Molecular vibrational tensors

	328 (16)	−1 (1)	1 (2)	
$\mathbf{T}(\times 10^4)$		323 (16)	5 (2)	Å^2
			318 (21)	
	119 (10)	50 (7)	−6 (7)	
$\omega(\times 10)$		136 (10)	0 (7)	deg^2
			26 (7)	

Principal axes of the **T** and ω tensors relative to the molecular axes.

R.m.s. amplitude	Direction cosines		
0·165 Å	−0·235	−0·660	0·713
0·182	−0·966	0·241	−0·095
0·191	0·110	0·711	0·694
1·59°	0·079	−0·037	0·996
2·78	−0·760	0·644	0·084
4·22	0·645	0·764	−0·023

Thermal motion

The motion of the molecule has been analysed in terms of the rigid-body tensors of translation (**T**) and libration (ω) (Cruickshank, 1956). Rigid-body parameters listed in Table 3 indicate that the translation of the molecule is quite isotropic whereas the libration is anisotropic. The r.m.s. discrepancy ΔU_{ij} between the observed and calculated thermal parameter is $5{\cdot}82\times 10^{-3}$ Å^2, which within one order of magnitude is larger than the case of a simpler rigid planar molecule. Thus the molecule is not expected to behave strictly as a rigid body. The thermal motion ellipsoids were plotted by *ORTEP* (Johnson, 1965). The peripheral atoms showed moderately large thermal motion, while the atoms in the cage are fairly rigid. Chlorine atoms and methyl carbon atoms undergo considerable libration.

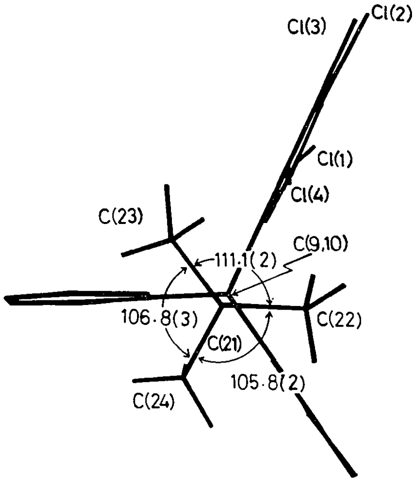

Fig. 1. A projection of the molecule viewed along the C(9)–C(10) axis.

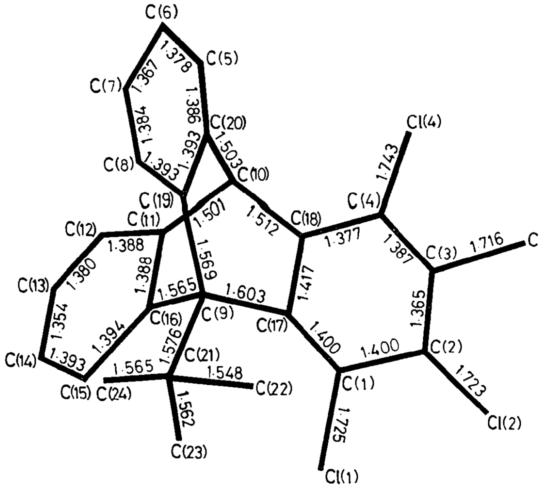

Fig. 2. Bond distances (Å).

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* Table 1 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31057 (23 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Description of the structure and discussion

Fig. 1 is a projection of the molecule viewed along the C(9)–C(10) axis. Although the 9-t-butyltriptycene skeleton is expected to be trigonal, this compound is somewhat distorted from trigonal symmetry on account of the four chlorine atoms on one of the benzene rings. The dihedral angles between the three benzene planes are almost equal; however, the angles between the three methyl carbons of the t-butyl group are significantly different. The largest angle, 111·1 (2)°, is that bisected by the benzene plane with the four chlorine atoms. This is clearly due to the steric effect of the t-butyl and chlorine substituents. C(21) is not collinear with the C(9)–C(10) axis, which indicates the inclination of the C(9)–C(21) bond from that expected for normal triptycene.

The molecular shape and the bond lengths are shown in Fig. 2. Bond angles are tabulated in Table 4. The standard deviations for the bond length as computed from the output of the least-squares program are 0·004 Å for C–Cl bonds and 0·005 Å for C–C bonds. Concerning the eight-membered cage of triptycene, an average bond length of 1·534 Å is reported for 2,5-dimethoxy-7-dimethylaminotriptycene hydrobromide (Sakabe, Sakabe, Minakata & Tanaka, 1972). In the present compound the three bonds adjacent to C(9) are longer and on the other side, bonds connected to C(10) are shorter than 1·534 Å. The average bond lengths are 1·579 and 1·505 Å respectively. The longest bond is 1·603 Å which is considerably longer than the usual C–C single bond. The bond angles around C(9) are smaller than the corresponding angles around C(10), whereas the bond lengths to C(9) are longer than those involving C(10). This means that the distortion of triptycene is distributed among angles and bonds of the rigid cage structure of the molecule. On the whole, the molecular structure of this triptycene skeleton does not have a propeller-like shape; the three benzene rings are almost parallel to the C(9)–C(10) axis. The largest inclination is only 3° between C(9)–C(10) and C(17)–C(18).

Table 4. *Bond angles* (°)

C(18)C(10)C(20)	106·0 (1)	C(17)C(9)C(19)	102·6 (2)
C(11)C(10)C(18)	105·2 (2)	C(16)C(9)C(17)	102·4 (1)
C(11)C(10)C(20)	107·7 (2)	C(16)C(9)C(19)	105·1 (2)
C(17)C(18)C(10)	114·8 (2)	C(18)C(17)C(9)	111·5 (2)
C(10)C(20)C(19)	113·7 (2)	C(9)C(19)C(20)	114·3 (2)
C(10)C(11)C(16)	113·7 (2)	C(9)C(16)C(11)	114·5 (2)
C(4)C(18)C(10)	112·5 (3)	C(1)C(17)C(9)	133·3 (2)
C(5)C(20)C(10)	123·8 (2)	C(8)C(19)C(9)	128·9 (2)
C(12)C(11)C(10)	124·1 (3)	C(15)C(16)C(9)	128·7 (2)
C(19)C(20)C(5)	122·6 (2)	C(16)C(11)C(12)	113·7 (2)
C(20)C(5)C(6)	119·0 (3)	C(11)C(12)C(13)	119·4 (3)
C(5)C(6)C(7)	119·6 (3)	C(12)C(13)C(14)	120·0 (3)
C(6)C(7)C(8)	121·3 (3)	C(13)C(14)C(15)	120·6 (3)
C(7)C(8)C(19)	120·7 (3)	C(14)C(15)C(16)	121·7 (3)
C(8)C(19)C(20)	116·8 (2)	C(15)C(16)C(11)	116·8 (2)
C(1)C(2)C(3)	121·4 (3)	C(17)C(1)Cl(1)	125·4 (2)
C(2)C(3)C(4)	118·7 (3)	C(1)C(2)Cl(2)	120·5 (2)
C(3)C(4)C(18)	120·4 (3)	C(2)C(3)Cl(3)	120·2 (3)
C(4)C(18)C(17)	122·7 (3)	C(3)C(4)Cl(4)	118·8 (2)
C(18)C(7)C(1)	115·2 (2)	C(2)C(1)Cl(1)	113·0 (2)
C(17)C(1)C(2)	121·6 (3)	C(3)C(2)Cl(2)	118·1 (2)
		C(4)C(3)Cl(3)	121·2 (2)
		C(18)C(4)Cl(4)	120·8 (2)
C(17)C(9)C(21)	118·9 (2)	C(9)C(21)C(22)	112·0 (2)
C(16)C(9)C(21)	113·2 (2)	C(9)C(21)C(23)	110·9 (2)
C(19)C(9)C(21)	113·0 (2)	C(9)C(21)C(24)	110·2 (3)
C(22)C(21)C(23)	111·1 (2)	C(23)C(21)C(24)	106·8 (3)
C(24)C(21)C(22)	105·8 (2)		

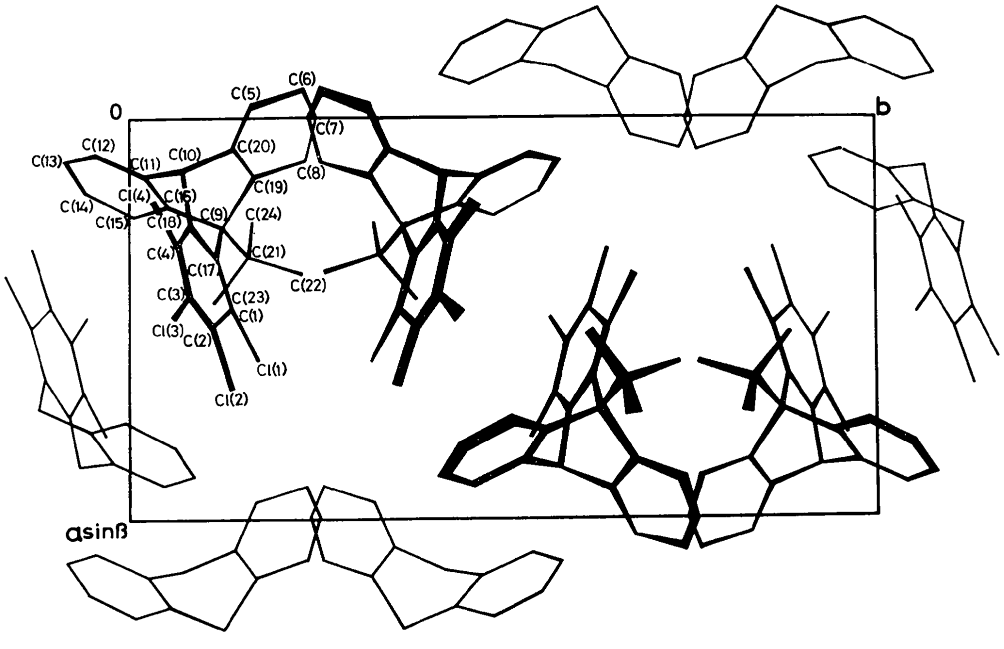

Fig. 3. The structure viewed along the *c* axis.

The average bond lengths of the benzene rings are 1·383, 1·384 Å and that for the benzene ring with the four chlorine atoms, 1·391 Å. The increasing trend of bond lengths C(6)–C(7) → C(6)–C(5) → C(20)–C(19) is the same as that reported for triptycene itself (Anzenhofer & de Boer, 1970). The equations of the three benzene rings and deviations of atoms from them are given in Table 5, where X, Y, Z are coordinates in Å referred to the crystal axes a, b and c. C(9)–C(21) which connects the t-butyl group to triptycene is 1·576 Å, which is also significantly longer than that in other compounds.

Table 5. *The equations of the least-squares planes of benzene and atomic shifts from them* (Å)

A $\quad 0{\cdot}3252X-0{\cdot}9029Y-0{\cdot}2811Z+1{\cdot}8528=0$
B $\quad -0{\cdot}7235X+0{\cdot}4069Y-0{\cdot}5576Z+1{\cdot}8405=0$
C $\quad -0{\cdot}4228X-0{\cdot}4696Y-0{\cdot}7751Z+3{\cdot}4818=0$

Plane *A*		Plane *B*		Plane *C*	
C(1)	−0·015	C(11)	−0·007	C(20)	0·002
C(2)	0·006	C(16)	0·011	C(19)	−0·002
C(3)	0·009	C(15)	−0·006	C(8)	−0·001
C(4)	−0·015	C(14)	−0·003	C(7)	0·003
C(18)	0·006	C(13)	0·008	C(6)	−0·003
C(17)	0·010	C(12)	−0·003	C(5)	0·000
C(10)	0·024	C(10)	−0·045	C(10)	−0·007
C(9)	0·069	C(9)	0·033	C(9)	−0·002
Cl(1)	−0·104	C(21)	0·197	C(21)	0·118
Cl(2)	−0·035				
Cl(3)	0·005				
Cl(4)	−0·088				
C(21)	0·099				

In this compound the t-butyl could be said to have retained most of its tetrahedral disposition of methyl groups. However, the mean bond length is 1·563 Å, which is significantly longer than the usual C–C bond length of 1·540 Å.

The mean C–Cl bond length is 1·726 Å, in good agreement with the C(sp^2)–Cl bond length of 1·721 Å in trichlorobenzene (Hazell, Lehmann & Pawley, 1972). The out-of-plane bending of the C–Cl bonds is shown in Table 5. The average C–Cl bond lengths in olefinic and aromatic compounds are 1·719 (5) and 1·70 (1) Å respectively. In this compound the bond length is closer to that of olefins than to that of aromatics. This may be due to the repulsion between the four substituted chlorine atoms, for in 1,2,3,4-tetrachloro-5,6-di-n-propylcalicene (Shimanouchi, Sasada, Ashida, Kakudo, Murata & Kitahara, 1969), where angles between the chlorines on a five-membered ring are larger and the repulsion is expected to be less, the mean bond length is 1·704 Å. The relatively large deviation of the C(4)–Cl(4) distance may partly be due to the packing and H(10).

As mentioned earlier, the molecular geometry of this compound exhibits eminent distortion. The steric effects of the *peri* chlorine and t-butyl groups appear in the extraordinary bond length of C(9)–C(17) and the inclinations of C(1)–Cl(1) and C(9)–C(21) in opposite directions (Table 5). These indicate the release of intramolecular steric repulsion in the overcrowded structure. The C–C bonds in the t-butyl group are lengthened and three methyl groups are disposed far from the triptycene nucleus. When considering the internal rotation, the energy barrier for it may be determined by transitional and ground-state energy levels. In the case of the t-butyl group the transitional state may be determined by the steric repulsion in the eclipsed form and ground state caused by the non-bonded interactions involving hydrogen atoms. Accordingly, the longer t-butyl bond length will contribute to a decrease in the energy barrier for rotation. Some of the shortest intramolecular distances between methyl hydrogens and the *peri* chlorine are 2·604 and 2·685 Å, being slightly shorter than the sum of the van der Waals radii. This evidence supports the idea drawn from the simulation calculation of the energy barrier based on the n.m.r. spectrum (Suzuki, Ōki & Nakanishi, 1973). Our X-ray evidence suggests no continuous internal rotation of the t-butyl and methyl groups judging from the peaks in Fourier and difference Fourier syntheses at room temperature.

Fig. 3 shows a projection of the structure viewed along the c axis. The benzene rings with four chlorine atoms form columns about centres of symmetry to build up the structure. Such a structure may be constructed by dipole–dipole interactions involving a chlorine–benzene moiety and close packing. The distance between the chlorine planes is 3·70 Å. No extraordinary short intermolecular distance was observed.

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