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The Crystal Structure of Perchloro-all-*cis*-tricyclo [5.2.1.0^{4,10}]deca-2,5,8-triene

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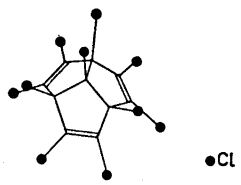
The crystal and molecular structure of the chlorocarbon perchloro-all-*cis*-tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene, $C_{10}Cl_{10}$, has been studied with the aid of three-dimensional X-ray diffractometer data. The symmetry is orthorhombic, space group *Pbca*. The unit cell contains eight molecules $C_{10}Cl_{10}$ and has the dimensions $a = 12.666$ Å, $b = 15.630$ Å, and $c = 15.509$ Å.

The structure has been refined to an R-value of 0.029 (1837 independent reflections). The molecules $C_{10}Cl_{10}$ deviate slightly from their ideal symmetry C_{3v}. Most of the *intra*- and *inter*-molecular distances are normal. A few short non-bonded Cl – Cl distances do, however, occur and are discussed in the text.

A chlorocarbon $C_{10}Cl_{10}$ has been synthesized by chlorination of all-*cis*-tricyclo[5.2.1.0^{4,10}]decane by Jacobson.[1] Considering chemical and spectroscopic properties of the compound, Jacobson arrived at the following possible structural formula:



The compound may thus be denoted perchloro-all-*cis*-tricyclo[5.2.1.0^{4,10}]-deca-2,5,8-triene. It seemed of interest to get a more direct proof of the molecular structure in question and therefore the present X-ray investigation of

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$C_{10}Cl_{10}$ was undertaken. It was hoped that the bonding distances found would further elucidate the proposed formula. In the present paper the chlorocarbon $C_{10}Cl_{10}$ will be denoted PCT.

UNIT CELL AND SPACE GROUP

A specimen of PCT,[2] where the crystals had been grown in chloroform, was kindly supplied by Dr. Jacobson. From this sample a small crystal, $V \approx 0.003$ mm^3, was selected. From Weissenberg and precession photographs the Laue symmetry was found to be *mmm*. The following restrictions limited possible reflections:

$$0kl,\ k = 2n;\ hk0,\ h = 2n;\ h0l,\ l = 2n.$$

This is characteristic of the orthorhombic space group *Pbca* (No. 61). The cell dimensions found from the Weissenberg and precession photographs were used to interpret powder photographs (*cf.* Table 1), taken in a Guinier-Hägg focussing camera. Strictly monochromatized Cu$K\alpha_1$ radiation was used and KCl ($a = 6.2909$ Å) added as an internal standard. The following lattice parameters were obtained with the aid of least-squares calculations:

$$a = 12.666(5)\ \text{Å},\ b = 15.630(5)\ \text{Å},\ c = 15.509(7)\ \text{Å}.$$

The density of the specimen as determined by the flotation method is 2.08 g cm^{-3}, in good agreement with the calculated value of 2.05 g cm^{-3} for eight molecules $C_{10}Cl_{10}$ per unit cell.

DATA COLLECTION AND DATA REDUCTION

The crystal structure was originally solved using photographic intensity data. Later, data were collected by means of a Pailred linear diffractometer for a refinement of the structure.

Photographic intensity data. Cu$K\alpha$ radiation was used when collecting the film data. A small crystal was mounted with [011] as rotation axis in an integrating Weissenberg camera. The multiple film technique was used and the intensities of the registered 3002 reflections were estimated visually. After correcting for Lorentz and polarization effects in the usual way, symmetry-related reflections belonging to different layers were put on a common scale by means of least-squares calculations and mean values of $|F_o|$ were calculated. In this way 2297 independent reflections resulted. The film data were regarded as preliminary and no absorption correction was made, though the linear absorption coefficient is 165 cm^{-1}.

Diffractometer intensity data. The intensity data were collected using Mo$K\alpha$ radiation monochromatized by reflection off the (002) planes of a graphite crystal, the monochromator angle being 6.08°. The single crystal used was a nearly pentagonal plate with the edges 0.15 mm and the thickness 0.075 mm. The plate was mounted along one of its edges which coincides with the direction of the crystallographic *b*-axis. The reflections of the layer lines $h0l - h15l$ were collected for the copper range, $\sin\theta/\lambda \leq 0.65$, using equi-inclination and ω-scan techniques with a scan rate of 1.0°/min. The scan range was 3.0° for all reflections except for those with $\sin\theta < 0.1$ in the layers $6 - 16$, where the scan range was 4.0°. The stationary background counts were measured for 40 sec at each end of the scan interval. The aperture size of the detector was 2.0°. As a check of the electronic stability during the period of data collection, the intensity of one standard reflection

Table 1. X-Ray powder data of perchloro-all-*cis*-tricyclo[5.2.1.$0^{4,10}$]deca-2,5,8-triene. Guinier focusing camera of 80 mm diameter with Cu$K\alpha_1$ radiation and KCl as an internal standard.

h k l	$10^5 \sin^2 \theta_{obs}$	$10^5 \sin^2 \theta_{calc}$	I_{obs}
1 1 1	858	859	vw
0 2 1	1214	1218	w
1 0 2	1354	1356	w
1 2 1	1592	1588	w
1 1 2	–	1599	–
0 2 2	1958	1958	w
2 1 1	–	1969	–
1 1 3	2823	2833	vvw
2 2 2	3435	3437	vw
2 3 0	3666	3665	vw
3 1 1	3823	3818	vw
2 1 3	3932	3942	m
0 0 4	–	3947	–
0 4 1	4121	4132	w
3 0 2	4318	4315	vw
1 0 4	–	4317	–
1 4 1	4503	4502	vw
3 2 1	–	4546	–
3 1 2	4560	4558	vvw
1 1 4	–	4559	–
2 2 3	4681	4671	vw
1 3 3	4784	4775	vvw
0 2 4	4919	4918	vvw
3 2 2	5282	5286	w
1 2 4	–	5288	–
2 4 0	5364	5365	w
2 1 4	5676	5669	vw
4 1 0	6166	6160	vw
2 2 4	–	6397	–
4 1 1	6412	6406	vw
3 3 2	–	6500	–
1 3 4	6504	6502	m
3 2 3	–	6520	–
1 5 1	6694	6687	vw
4 2 0	6886	6888	vw
4 0 2	–	6904	–
4 2 1	–	7135	–
0 2 5	–	7138	–
4 1 2	7145	7146	vw
1 2 5	–	7508	–
3 1 4	7504	7518	m
2 5 0	7560	7550	w
2 4 3	–	7585	–
2 5 1	7797	7797	vw
3 4 2	–	8200	–
1 4 4	8197	8202	m
3 2 4	8235	8246	vw
4 3 1	8342	8349	vw

was measured at regular intervals. The largest difference measured was 1.4 %. Reflections for which the two measured background values differed more than 3.09 times the e.s.d. of their difference were omitted. The integrated peak counts I were calculated from the total integrated peak counts, the background counts, and the counting times in the usual way. If $\sigma(I)/I \geq 0.5$, the reflection was considered unobserved. For each layer line both the reflections hkl and $\bar{h}kl$ were measured, giving a total of 7121 reflections. Of these, 3214 were omitted because of the above-mentioned restrictions. In the final step of refinement mean values of the reflections hkl and $\bar{h}kl$ were taken and only those pairs were considered for which both hkl and $\bar{h}kl$ occurred in the reduced intensity list. In this way 1837 independent reflections finally resulted from the diffractometer measurements. The corrections for Lorentz and polarization effects were performed using the standard procedure. With Mo$K\alpha$ radiation the linear absorption coefficient is only 18 cm^{-1}. Therefore no absorption correction was made.

Comparison between the two data sets. The final R-factor, using anisotropic temperature factors for all atoms, was 0.109 for 2297 independent reflections measured with the multiple film technique and 0.029 for 1837 independent reflections using diffractometer data.

The positional parameters obtained from the two data sets agree within 3 e.s.d.'s of the parameters obtained from the film data. The σ-values of the positional parameters were 1.5 – 2.0 times larger for film data than for diffractometer data.

STRUCTURE DETERMINATION

The unit cell contains 80 chlorine and 80 carbon atoms. As the space group is unique and has a centre of symmetry, the best way of attacking the problem seemed to be to use sign relationships.

To perform these calculations the program GAASA [3] was used which one of us (Malmros) had adapted to the computer Univac 1108. According to the method of Wilson, an approximate scale factor and an overall temperature factor was first calculated, followed by a calculation of normalized structure factors. Thereafter, sign relations for 306 reflections with $E > 1.7$ were deduced and sign symbols were introduced for the 10 largest E-values. From this basic set new symbols were calculated, using the restriction that those which had a lower probability than 0.975 were discarded. Equations between the remaining symbols were derived and solved if their probabilities were larger than 0.998. After four reiterations 268 phases were described by three symbols, which could, however, be chosen arbitrarily. Thus the phases for the 268 reflections were in fact determined. Starting with the now known 268 phases, all 306 phases but one could be determined.

Using E-values a three-dimensional Fourier function was then calculated, which revealed the positions of all chlorine atoms. Based on all observed reflections the parameters of the chlorine atoms were then refined by means of least-squares calculations, giving an R-factor of 0.29. The positions of all carbon atoms in the unit cell could be deduced from a three-dimensional difference Fourier function, where the contributions of the chlorine atoms were subtracted. (At this stage it was observed that the carbon atom positions could as well have been obtained from the E-map, though other peaks of the same heights occurred there).

Table 2. Weight analysis obtained in the final cycle of least-squares refinement. w = weighting factor. $\Delta = ||F_o| - |F_c||$.

Interval $\|F_o\|$	Number of reflections	$w\Delta^2$	Interval sin θ	Number of reflections	$w\Delta^2$
0.0 – 18.5	182	1.777	0.000 – 0.274	547	0.735
18.5 – 21.3	183	1.137	0.274 – 0.345	481	0.658
21.3 – 24.4	185	1.192	0.345 – 0.395	351	1.036
24.4 – 28.0	182	1.106	0.395 – 0.435	251	0.882
28.0 – 32.4	184	0.770	0.435 – 0.468	156	1.188
32.4 – 38.8	184	0.786	0.468 – 0.498	44	2.012
38.8 – 47.0	183	1.159	0.498 – 0.524	5	0.491
47.0 – 59.5	184	0.949			
59.5 – 85.8	184	0.510			
85.8 – 388.2	184	0.614			

Table 3. Positional and thermal parameters of the atoms of PCT. All numbers are multiplied by 10^5. Estimated standard deviations are given within brackets. The anisotropic thermal parameters are based on the expression exp $[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl(1)	1444(9)	25842(7)	32611(7)	570(7)	257(5)	331(4)	122(4)	– 60(5)	24(4)
Cl(2)	– 12212(9)	11033(9)	43928(8)	396(6)	515(6)	450(6)	4(5)	121(5)	– 35(5)
Cl(3)	– 7102(11)	– 6101(8)	32630(11)	625(9)	333(6)	816(9)	– 182(5)	1(7)	– 97(5)
Cl(4)	10993(11)	– 45(8)	18240(7)	819(10)	453(6)	283(5)	59(6)	– 75(5)	– 171(4)
Cl(5)	18552(11)	– 13986(8)	33085(10)	834(10)	198(5)	681(7)	39(5)	– 99(7)	– 78(5)
Cl(6)	35994(9)	– 3701(8)	44744(8)	521(7)	380(5)	484(6)	128(5)	– 97(6)	82(4)
Cl(7)	38033(8)	14764(7)	34079(8)	359(6)	357(5)	453(5)	51(4)	103(5)	19(4)
Cl(8)	30554(9)	16094(8)	54496(7)	555(7)	474(6)	324(4)	6(5)	– 176(5)	– 64(4)
Cl(9)	6778(9)	24344(7)	53232(7)	645(8)	432(6)	267(4)	115(5)	30(5)	– 139(4)
Cl(10)	19246(10)	17782(7)	22307(6)	693(8)	366(5)	221(4)	11(5)	82(5)	73(3)
C(1)	7116(29)	16365(23)	37163(23)	383(23)	207(16)	232(14)	31(14)	– 51(15)	– 6(11)
C(2)	– 1163(29)	9567(26)	37836(23)	349(22)	352(19)	219(14)	35(16)	17(15)	0(14)
C(3)	1038(31)	2576(26)	33419(27)	398(24)	246(19)	338(18)	– 14(15)	– 73(18)	– 21(13)
C(4)	11727(32)	2586(26)	29323(24)	466(25)	263(17)	231(15)	12(16)	– 11(17)	– 58(12)
C(5)	19532(32)	– 3193(26)	33928(27)	506(26)	193(17)	348(18)	23(16)	50(20)	– 52(13)
C(6)	26558(29)	1068(25)	38526(25)	340(24)	274(18)	280(16)	71(15)	2(16)	– 3(13)
C(7)	25668(28)	10548(25)	37835(24)	321(21)	275(17)	238(14)	– 49(14)	37(15)	5(13)
C(8)	22419(28)	15244(23)	45833(23)	403(23)	227(16)	226(14)	– 46(15)	– 63(15)	– 8(12)
C(9)	12721(30)	18461(23)	45396(24)	415(24)	217(16)	228(14)	– 21(14)	31(17)	– 48(12)
C(10)	15989(28)	11855(24)	31500(22)	341(21)	238(16)	199(14)	20(13)	21(14)	22(11)

A least-squares refinement of the parameters of all atoms in the unit cell, based on the final diffractometer intensity data set described above, resulted in an R-factor of 0.029 (1837 independent reflections), when anisotropic temperature factors were introduced for the atoms. Cruickshank's weighting scheme, with $a = 18.0$, $c = 0.0015$ and $d = 0$, was used in the calculations. The weighting scheme for the last cycle of the refinement is given in Table 2. The final param-

eters of the atoms are presented in Table 3. Lists of observed and calculated structure factors are available on request to the Division of Inorganic Chemistry 2, Chemical Center, Lund.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The labelling of the atoms and the ring planes in the crystal structure of PCT is indicated in a clinographic drawing given in Fig. 1. A stereographic picture of the molecule is presented in Fig. 2. It is immediately seen that the structure of the molecule as obtained from the present investigation confirms the model deduced by Jacobson (*cf.* p. 3172). This model implies a C_{3v} or pseudo-C_{3v} symmetry of the molecule.

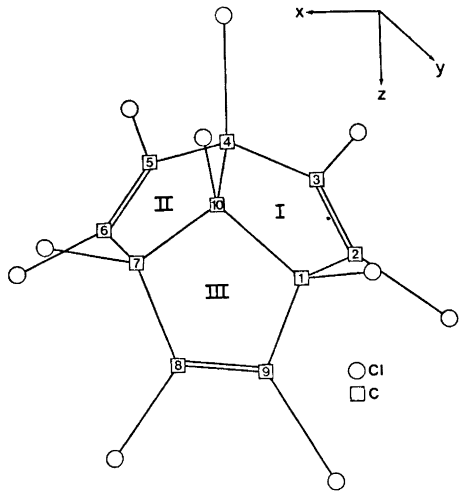

Fig. 1. A clinographic view of the molecule of PCT showing the labelling of the carbon atoms (*cf.* Table 3) and the ring planes. Each carbon atom is bonded to a chlorine atom of the same number, C(1) to Cl(1) *etc.* The positions of the three formal double bonds of the molecule are also given.

As seen from Fig. 1, the threefold or pseudo-threefold axis extends along the line C(10) – Cl(10). The present investigation shows a small but significant deviation from C_{3v} symmetry. Neither the threefold axis nor the mirror planes are exactly fulfilled in the molecule.

Intra- and *inter*-molecular distances in the structure are given in Table 4 together with the angles within a molecule. The various distances within a molecule are visualized in Fig. 3. As seen from this drawing the deviation from C_{3v} symmetry is quite small. A slight decrease of the distance C(4) – C(5) and a slight increase of the distance C(4) – Cl(4) would remove most of the asymmetry of the distances.

When discussing the bond distances within a molecule on the whole, one may, however, neglect the deviations from C_{3v} and use mean values. With this simplification the molecule may be described with the aid of asymmetric units of composition C_5Cl_5 (*cf.* Fig. 4 and Table 4).

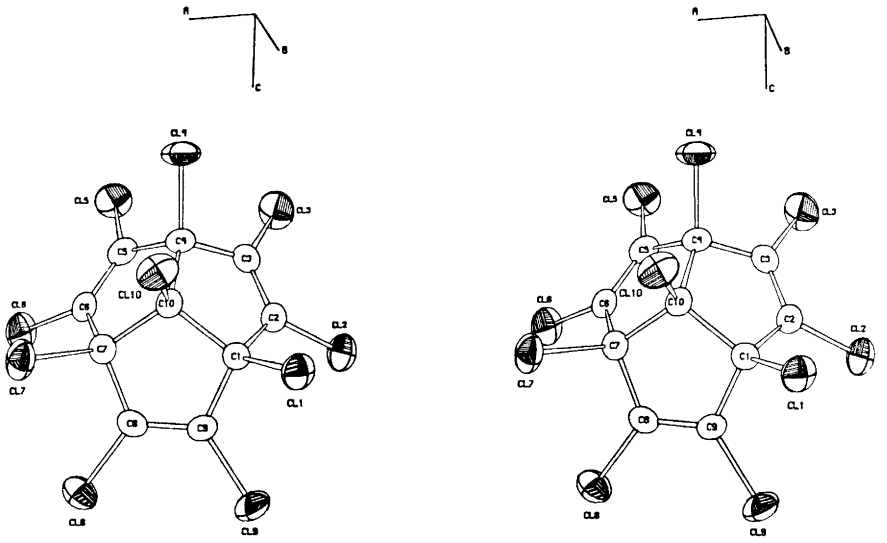

Fig. 2. A stereographic view of the molecule of PCT.

The five-membered rings. The distance $C(x)-C(x')$ (*cf.* Fig. 4) has a mean length of 1.323(6) Å, in fair agreement with the value 1.337(6) Å given in Ref. 4 for a double carbon-carbon bond. The formal double bond $C(x)-C(x')$ is the shortest one within the ring. The mean value, 1.499(18) Å, of the bonds $C(x)-C(y)$ and $C(x')-C(y')$, which may be considered identical in the simplified model, is not far from the value given for a shortened single bond in the presence

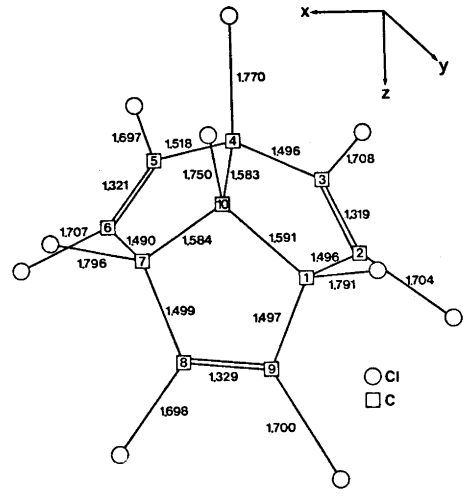

Fig. 3. A clinographic view of the molecule of PCT showing the various bonding distances. Notations of the atoms, *cf.* Table 3.

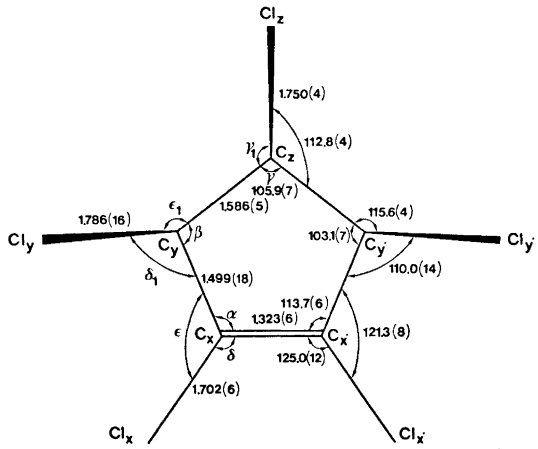

Fig. 4. A schematic view of the asymmetric unit C_5Cl_5 of PCT. The carbon and the chlorine atoms are marked x, x', y, y', and z. The angles in the five-membered ring are denoted α, β, γ; remaining angles in the planar part δ and ε.

of a double bond, 1.53(1) Å.[4] These bonds are the next shortest ones of the ring. The mean value of the bonds C(y) – C(z) and C(y') – C(z) is 1.586(5) Å, definitely longer than a single paraffinic bond, 1.541(3) Å.[4] Lengthened tetrahedral carbon-carbon bonds are not unusual for cage molecules. Thus distances C – C of 1.60 – 1.62 Å have been observed for photoaldrin.[5]

A structure with more specific bearing on the present one is that of hexacyclo [10.3.1.$0^{2,10}$.$0^{3,7}$.$0^{6,15}$.$0^{9,14}$]hexadecane.[6] In this structure the longest C – C bond is 1.55(2) Å. The reason for the lengthening is assumed to be the interaction of two pairs of eclipsed hydrogen atoms on the respective carbon atoms. Making the same assumption for PCT, the long C(y) – C(z) and C(y') – C(z) distances would be due to the interaction of the eclipsed chlorine atoms Cl(y) – Cl(z) and Cl(y') – Cl(z), which are at short mutual distances. Mean values of the angles are given in Fig. 4 (*cf.* Table 4).

Both the angles and the distances of the five-membered rings show good agreement with the predictions that could be made for the proposed structure.

The carbon-chlorine distances. The carbon-chlorine distances fall within three ranges:

(*i*) In the simplified model the distances C(x) – Cl(x) and C(x') – Cl(x') may be considered to be identical. The mean value of the bond length is *1.702(6) Å*, in good agreement with the values given for the non-equivalent C – Cl distances in 1,2,3,4-tetrachlorobutadiene,[7] 1.701(12) and 1.715(11) Å. The bond length C(x) – Cl(x) in PCT is also not far from the value, 1.70 Å, given for an aromatic carbon-chlorine bond.[4]

(*ii*) In the idealized model mean values may be taken for the C(y) – Cl(y) and the C(y') – Cl(y') distances. The mean value is *1.786(16) Å*, in fair agreement with 1.767(2) Å, given for a paraffinic carbon-chlorine bond.[4]

(*iii*) The C(z) and Cl(z) atoms are unique in the molecule of PCT. The bond

Table 4a. Selected distances (Å) in the crystal structure of PCT. Estimated standard deviations are given within brackets. Notations, *cf.* Figs. 1 and 4. Mean values of equivalent distances within the five-membered rings are given, in addition to the total mean values between the rings. It is also noted which least-squares plane the atoms belong to (*cf.* Tables 5 and 6).

Atoms	Bonding distance	Mean value in the rings	Mean value between the rings	Notations *cf.* Figs. 1, 4	Planes (Tables 5, 6)
C(2) – C(3)	1.319(6)				I
C(5) – C(6)	1.321(6)		1.323(6)	C(x) – C(x')	II
C(8) – C(9)	1.329(5)				III
C(1) – C(2)	1.496(5)	1.496			I
C(3) – C(4)	1.496(6)				I
C(4) – C(5)	1.518(6)	1.504	1.499(5)	C(x) – C(y)	II
C(6) – C(7)	1.490(6)			C(x') – C(y')	II
C(7) – C(8)	1.499(5)	1.498			III
C(1) – C(9)	1.497(5)				III
C(1) – C(10)	1.591(5)				I, III
C(4) – C(10)	1.583(6)		1.586(5)	C(y) – C(z)	I, II
C(7) – C(10)	1.584(5)			C(y') – C(z)	II, III
C(2) – Cl(2)	1.704(4)	1.705			I
C(3) – Cl(3)	1.706(4)				I
C(5) – Cl(5)	1.697(4)	1.702	1.702(5)	C(x) – Cl(x)	II
C(6) – Cl(6)	1.707(4)			C(x') – Cl(x')	II
C(8) – Cl(8)	1.698(4)	1.699			III
C(9) – Cl(9)	1.700(4)				III
C(1) – Cl(1)	1.791(4)				IV
C(4) – Cl(4)	1.770(4)		1.786(10)	C(y) – Cl(y)	V
C(7) – Cl(7)	1.796(4)			C(y') – Cl(y')	VI
C(10) – Cl(10)	1.750(4)			C(z) – Cl(z)	IV, V, VI
	Intra-molecular distances Cl – Cl < 3.6 Å				
Cl(1) – Cl(10)	3.037(1)				IV
Cl(4) – Cl(10)	3.042(2)		3.039(3)	Cl(y') – Cl(z)	V
Cl(7) – Cl(10)	3.036(2)				VI
Cl(2) – Cl(3)	3.265(2)				I
Cl(5) – Cl(6)	3.276(2)		3.274(8)	Cl(x) – Cl(x')	II
Cl(8) – Cl(9)	3.282(2)				III
Cl(1) – Cl(2)	3.381(2)	3.359			I
Cl(3) – Cl(4)	3.336(2)				I
Cl(4) – Cl(5)	3.311(2)	3.324	3.326(56)	Cl(x) – Cl(y)	II
Cl(6) – Cl(7)	3.336(2)				II
Cl(7) – Cl(8)	3.312(2)	3.295			III
Cl(9) – Cl(1)	3.277(2)				III
	Inter-molecular distances Cl – Cl < 3.6 Å				
Cl(4) – Cl(8)	3.461(2)				
Cl(5) – Cl(7)	3.428(2)				

Table 4b. Angles (°) in the approximately planar parts C_6Cl_5 of the crystal structure of PCT. Estimated standard deviations are given within brackets. Notations, *cf.* Figs. 1 and 4.

Plane I: Atoms C(1), C(2), C(3), C(4), C(10), Cl(2), Cl(3)
Plane II: Atoms C(4), C(5), C(6), C(7), C(10), Cl(5), Cl(6)
Plane III: Atoms C(1), C(7), C(8), C(9), C(10), Cl(8), Cl(9)

Atoms	Angle	Mean value in the rings	Mean value between the rings	Notations *cf.* Fig. 4	Planes (Tables 5, 6)
C(1) – C(2) – C(3)	113.8(3)	114.1			I
C(2) – C(3) – C(4)	114.3(4)				I
C(4) – C(5) – C(6)	113.1(4)	113.7	113.7(6)	α	II
C(5) – C(6) – C(7)	114.3(4)				II
C(7) – C(8) – C(9)	113.3(3)	113.4			III
C(8) – C(9) – C(1)	113.5(3)				III
C(3) – C(4) – C(10)	102.7(3)	102.7			I
C(10) – C(1) – C(2)	102.6(3)				I
C(6) – C(7) – C(10)	103.4(3)	103.1	103.1(7)	β	II
C(10) – C(4) – C(5)	102.8(3)				II
C(9) – C(1) – C(10)	103.5(3)	103.6			III
C(10) – C(7) – C(8)	103.8(3)				III
C(4) – C(10) – C(1)	106.4(3)				I
C(7) – C(10) – C(4)	106.2(3)		105.9(7)	γ	II
C(1) – C(10) – C(7)	105.2(3)				III
C(3) – C(2) – Cl(2)	124.9(3)	124.8			I
C(2) – C(3) – Cl(3)	124.6(3)				I
C(6) – C(5) – Cl(5)	126.3(3)	125.1	125.0(12)	δ	II
C(5) – C(6) – Cl(6)	123.8(3)				II
C(9) – C(8) – Cl(8)	124.9(3)	125.1			III
C(8) – C(9) – Cl(9)	125.3(3)				III
C(1) – C(2) – Cl(2)	121.3(3)	121.2			I
C(4) – C(3) – Cl(3)	121.1(3)				I
C(4) – C(5) – Cl(5)	120.5(3)	121.2	121.3(8)	ε	II
C(7) – C(6) – Cl(6)	121.9(3)				II
C(7) – C(8) – Cl(8)	121.8(3)	121.5			III
C(1) – C(9) – Cl(9)	121.2(3)				III

Angles (°) in the approximately planar parts C_2Cl_2 of the crystal structure of PCT. The atoms are situated at the bridge head positions.

Plane IV: Atoms C(1), C(10), Cl(1), Cl(10)
Plane V: Atoms C(4), C(10), Cl(4), Cl(10)
Plane VI: Atoms C(7), C(10), Cl(7), Cl(10)

Atoms	Angle	Mean value	Notations	Planes
Cl(10) – C(10) – C(1)	112.4(3)			IV
Cl(10) – C(10) – C(4)	113.0(2)	112.8(4)	γ_1	V
Cl(10) – C(10) – C(7)	113.0(2)			VI
Cl(1) – C(1) – C(10)	115.6(2)			IV
Cl(4) – C(1) – C(10)	116.0(3)	115.6(4)	ε_1	V
Cl(7) – C(7) – C(10)	115.2(2)			VI

Table 4. Continued.

Angles (°) in the non-planar parts of the molecule of PCT.

Atoms	Angle	Mean value
C(2) – C(1) – Cl(1)	109.5(3)	109.9(4)
C(9) – C(1) – Cl(1)	110.2(3)	
C(5) – C(4) – Cl(4)	110.7(3)	111.1(4)
C(3) – C(4) – Cl(4)	111.4(3)	
C(8) – C(7) – Cl(7)	109.2(3)	109.2(2)
C(6) – C(7) – Cl(7)	108.8(3)	

Total mean value 110.0 (14), notated δ_1 in Fig. 4.

length C(z) – Cl(z) of *1.750(4) Å* falls in between the values discussed above for paraffinic and olefinic carbon-chlorine bonds.

Mean values of the various C – C – Cl angles are given in Table 4 but will not be further discussed here.

The architecture of the molecule. Each five-membered ring in the molecule of PCT approximately forms a plane together with the chlorine atoms at each end of the double C – C bond. The least-squares planes (I, II, III) of the actual atoms are given in Table 5 together with the distances of the various atoms to the best plane. The planes each deviate significantly from planarity but no atom has a larger distance from the best plane than 0.08 Å (*cf.* Tables 5 and 3).

The carbon atoms at the bridge head positions and their attached chlorine atoms, *viz.* the atoms Cl(y), C(y), C(z), Cl(z) and Cl(z), C(z), C(y'), Cl(y') (Fig. 4) each form a plane. The least-squares planes, denoted IV, V, and VI, through these atoms are given in Table 6 together with the distances from the various atoms to the best plane. Considering the e.s.d.'s in the positional parameters (Table 3) of the constituting atoms, not all groups are strictly planar. The deviation from planarity is 0.03 Å or less. A simple interpretation of the structural formula proposed for PCT would predict planarity of the groups.

Non-bonded chlorine-chlorine contacts within the molecule. Within a molecule of PCT there are five different chlorine-chlorine distances shorter than 3.3 Å. The mean value of the Cl(x) – Cl(x') contact is 3.274(8) Å. This distance is, as expected, shorter than the sum of the van der Waals radii, and compares well to the value of 3.292(5) Å found for the corresponding distance in 1,2,3,4-tetrachlorobutadiene.[7]

The mean value of the Cl(y) – Cl(z) and Cl(y') – Cl(z) distances (Table 4) is 3.039(3) Å. These distances are considerably shorter than those usually found between chlorine atoms bound to adjacent carbon atoms, *e.g.* 3.08 Å, in octachlorocyclobutane.[8,9] The discussed distance is also shorter than contacts of the same type, given by Rudman [10] in his survey over chlorine-chlorine distances in aromatic compounds.

As indicated above the long C(y) – C(z) and C(y') – C(z) distances may be a consequence of these short Cl – Cl distances.

Inter-molecular distances. There are no short C – C or C – Cl intermolecular contacts (Table 4). The shortest Cl – Cl distances between different molecules

are 3.428(2) and 3.461(2) Å. The values are not abnormally low compared to those given by Rudman.[10]

Concluding remarks. The present X-ray investigation has in all main features confirmed the structure of PCT as proposed by Jacobson.[1] As to the details, the X-ray investigation has revealed that the molecule as it appears in the crystalline state shows a small but significant deviation from the expected C_{3v} symmetry, if the standard deviations resulting from the least-squares refinements are reliable and not underestimated. Further work is needed to conclude if the deviation from this symmetry persists also in solution or if it is due to crystal forces.

Table 5. Least-squares planes defined by the five-membered carbon ring and the Cl(x) atoms (*cf.* Fig. 4). The normalized equations are given in a Cartesian coordinate system (unit 1 Å) with the axes parallel to the crystallographic ones. All atoms are given unit weight. The distances (Å) of the atoms to the best plane are also presented.

Plane I[a]		Plane II[b]		Plane III[c]	
Atom	Distance	Atom	Distance	Atom	Distance
C(1)	−0.05	C(4)	0.05	C(1)	−0.08
C(2)	−0.01	C(5)	0.00	C(7)	−0.01
C(3)	−0.02	C(6)	0.00	C(8)	0.00
C(4)	0.06	C(7)	−0.01	C(9)	−0.01
C(10)	0.00	C(10)	−0.02	C(10)	0.07
Cl(2)	0.05	Cl(5)	−0.03	Cl(8)	−0.01
Cl(3)	−0.04	Cl(6)	0.02	Cl(9)	0.04

[a] Plane I: $0.4373\,x - 0.3909\,y + 0.8099\,z - 4.1147 = 0$
[b] Plane II: $-0.6200\,x - 0.0016\,y + 0.7846\,z - 2.5992 = 0$
[c] Plane III: $0.3714\,x + 0.8506\,y - 0.3723\,z - 0.4398 = 0$

Table 6. Least-squares planes defined by two carbon and two chlorine atoms at the bridge head positions. The normalized equations and the distances of the atoms are given as in Table 5.

Plane IV[a]		Plane V[b]		Plane VI[c]	
Atom	Distance	Atom	Distance	Atom	Distance
C(1)	−0.03	C(4)	0.00	C(7)	−0.02
C(10)	0.03	C(10)	0.00	C(10)	0.02
Cl(1)	0.02	Cl(4)	0.00	Cl(7)	0.01
Cl(10)	−0.02	Cl(10)	0.00	Cl(10)	−0.01

[a] Plane IV: $-0.6749\,x - 0.5353\,y - 0.5079\,z - 4.8722 = 0$
[b] Plane V: $-0.9331\,x + 0.3578\,y - 0.0362\,z - 1.4049 = 0$
[c] Plane VI: $0.2037\,x - 0.8563\,y - 0.4747\,z - 3.5144 = 0$

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