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2:1 Adduct of Perchloro-5,10-diphenyldibenzo[a,e]pentalene and Carbon Tetrachloride

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Abstract. $C_{28}Cl_{18}$. $\frac{1}{2}CCl_4$, $M_r = 1051.4$, monoclinic, C2/c, a = 25.794 (14), b = 8.676 (4), c = 17.258 (9) Å, $\beta = 94.47$ (4)°, V = 3849 (3) Å³, Z = 4, λ (Mo K α) = 0.71069 Å, $D_c = 1.81$ Mg m⁻³. The structure was solved with *MULTAN* and refined by block-diagonal least-squares methods. The final *R* value is 0.057 for 1610 observed reflections. The perchloro-5,10diphenyldibenzo[*a,e*]pentalene (PDP) and carbon tetrachloride molecules are located at special positions (inversion centres and twofold axes, respectively), with an occupancy factor of 0.5 for the carbon tetrachloride. The PDP molecule is slightly distorted due principally to repulsions between adjacent non-bonded Cl atoms.

Introduction. Ballester and co-workers have studied in detail the thermal reaction of perchlorodiphenylacetylene (Ballester, Castañer & Armet, 1979). Besides the initial compound, the reaction yields three products which are difficult to separate. The crystal structure of one of them, perchloro-1,2,3-triphenylnaphthalene, has

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been already established by X-ray diffraction (Gali, Solans, Miravitlles, Font-Altaba & Armet, 1978). The second unknown chlorocarbon compound, which is deep red in colour, was separated from the rest by fractional crystallization, advantage being taken of its solubility in carbon tetrachloride. The structure resolution of this product by spectral and chemical techniques (IR, UV, mass) posed insurmountable difficulties. For this reason, as in the case of perchloro-1,2,3-triphenylnaphthalene, it was considered that only X-ray analysis could provide the decisive data necessary to elucidate its structure.

Red prismatic crystals of the title compound were kindly supplied by Professor M. Ballester. They were grown by slow evaporation of a chloroform solution at room temperature. A crystal $0.2 \times 0.3 \times 0.4$ mm was used for the crystal-data and intensity measurements on a Syntex $P2_1$ four-circle diffractometer. The unit cell was measured by automatically centring 15 independent reflections and refining the orientation matrix and unit-cell parameters by least squares. Intensities were collected with Mo K_{α} graphite-monochromated radiation using the ω - 2θ scan technique. 2858 independent reflections were collected in the range $3^{\circ} \leq 2\theta \leq$ 47° . 1248 of these were considered as unobserved according to the criterion $I < 3\sigma(I)$. Only Lorentz and polarization corrections were made.

The observed systematic absences indicated that the possible space groups are C2/c (centrosymmetric) and Cc (non-centrosymmetric). The statistical results of $\langle |E|^2 - 1 \rangle$, $\langle |E| \rangle$, and the N(z) distribution (Howells, Phillips & Rogers, 1950) indicated that the most probable space group was C2/c, yet the structure was considered to be non-centrosymmetric during the resolution process. The phase problem was solved by direct methods (MULTAN; Main, Woolfson, Lessinger, Germain & Declercq, 1977), using 300 reflections with $|E| \ge 1.62$ and 3000 \sum_2 relationships that generated 32 sets of starting phases. An E map computed with the phases from the set with the highest combined figure of merit revealed peaks for 18 Cl and 28 C atoms in chemically sensible positions and showed that the compound is a diphenyldibenzopentalene derivative with a symmetry centre in the C(1)-C(1') bond. Block-diagonal least-squares refinement (modified version of SFLS; Ahmed, Hall, Pippy & Huber, 1966) initially with isotropic thermal parameters gave an R = 0.122, with all observed reflections. A subsequent electron density synthesis showed the existence of two new maxima. The electron density of each of these two maxima is approximately half that of a Cl atom. A new maximum on a binary axis was found in a difference electron density map at the same refinement stage. These three maxima were assigned to the Cl(25), Cl(26) and C(24) atoms respectively, which together with the atoms related by symmetry built up the carbon tetrachloride molecule.

Table 1. Final atomic parameters $(\times 10^5)$ with standard deviations in parentheses

	x	У	z
C(1)	26454 (17)	19048 (53)	48136 (28)
C(2)	23484 (18)	15511 (54)	40602 (27)
C(3)	24196 (17)	5361 (55)	34568 (30)
C(4)	20469 (19)	4739 (60)	28212 (29)
C(5)	16223 (19)	14373 (61)	27794 (30)
C(6)	15456 (19)	24562 (58)	33980 (31)
C(7)	19090 (18)	25256 (56)	40259 (26)
C(8)	19241 (18)	34601 (55)	47440 (30)
C(9)	15243 (17)	46704 (57)	49013 (30)
C(10)	15791 (20)	61663 (58)	46332 (34)
C(11)	12161 (21)	72998 (57)	47969 (33)
C(12)	7963 (19)	69442 (58)	52037 (30)
C(13)	7433 (18)	54543 (63)	54834 (32)
C(14)	11043 (18)	43271 (58)	53216 (32)
Cl(15)	29600 (5)	-6276 (18)	34609 (8)
Cl(16)	21257 (6)	-8248 (20)	20827 (9)
Cl(17)	11842 (5)	13798 (21)	19828 (9)
Cl(18)	10011 (6)	36048 (21)	33193 (10)
Cl(19)	20940 (6)	66019 (18)	40999 (11)
Cl(20)	13058 (7)	91632 (16)	44797 (11)
Cl(21)	3442 (5)	83167 (18)	53688 (9)
Cl(22)	2367 (5)	50163 (20)	60360 (10)
Cl(23)	10445 (6)	24798 (17)	56678 (10)
C(24)	50000	35472 (197)	25000
Cl(25)	44497 (15)	23314 (46)	22035 (18)
Cl(26)	48320 (21)	47401 (82)	33038 (40)

Taking into account the electron density as well as the results obtained from the elemental analysis and mass spectrometry, we concluded that the occupation factor for the carbon tetrachloride atoms should be about 0.5.

Cycles of isotropic refinement, where the atoms Cl(25), Cl(26) and C(24) were introduced with an occupation factor of 0.5, were made; the refinement was continued with anisotropic thermal parameters for all the atoms until an R = 0.057 with all observed reflections was reached.*

The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = \sigma(F)^{-2}$ and the *R* index was defined as $\sum ||F_o| - |F_c|| / \sum |F_o|$.

A final difference map showed no significant features. The final atomic positions are given in Table 1. Fig. 1 shows a view of the molecule and the numbering of the atoms, drawn by the ORTEP program (Johnson, 1965).

Discussion. Fig. 2 and Table 2 give the bond distances and angles of the PDP and carbon tetrachloride molecules respectively.

^{*} Lists of structure factors, anisotropic thermal parameters and least-squares mean planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34647 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



Fig. 1. View of the molecule (*ORTEP*; Johnson, 1965) showing thermal ellipsoids and the numbering of atoms.

Table	2.	Bond	distances	(Á)	and	bond	angles	(°)	in
			(CCl₄					

C(24)-Cl(25)	1.81 (1)	Cl(25)-C(24)-Cl(25')	108.7 (4)
C(24)Cl(26)	1.81 (1)	Cl(25)-C(24)-Cl(26')	110.2 (4)
Cl(25)C(24)Cl(26)	108.7 (4)	CI(26)-C(24)-Cl(26')	110.3 (4)

The bond lengths and angles in the pentachlorophenyl group [mean values: C-C = 1.39 (4), C-Cl =1.72(2) Å and C-C-C = $120(1)^{\circ}$ and in the benzene of the dibenzo[a,e]pentalene group [mean values: C-C = 1.39 (4), C-Cl = 1.72 (3) Å, and $C-C-C = 120(1)^{\circ}$ do not differ significantly from those found in other structures containing chlorinated benzene systems, e.g. hexachlorobenzene (Brown & Strydom, 1974), decachlorobiphenyl (Pedersen, 1975; Galí, 1975), perchlorodiphenylnitroxide (Solans, Galí, Miravitlles & Font-Altaba, 1978), perchlorobenzylidene-2,5-cyclohexadiene (Gali, Solans, Miravitlles & Plana, 1978) or in perchloro-1,2,3-triphenylnaphthalene (Galí, Solans, Miravitlles, Font-Altaba & Armet, 1978).

The geometries of the five-membered rings are similar to those of cyclopentadiene (Liebling & Marsh, 1965) and 9,10-dihydroindeno[1,2-a] indene (Matsuzaki, 1974). The distance C(1')-C(8) = 1.335 Å corresponds to a double bond.

The largest deviations from mean values, C(5)-C(6)-Cl(18) [117.7 (2) Å] and C(7)-C(6)-Cl(18) [122.6 (3) Å], are due to steric interactions between Cl(18) and C(9) (3.09 Å).

The PDP molecule is slightly distorted as are the majority of perchlorinated compounds in which there is



Fig. 2. Bond lengths (Å) (standard deviations are less than 0.008 Å for C-C and 0.006 Å for C-Cl distances), and bond angles (°) (standard deviations are less than 0.3°) in the PDP molecule.

Table 3. Selected Cl····Cl non-bonded distances (Å)

$Cl(15)\cdots Cl(16)$	3.085 (2)	$Cl(20)\cdots Cl(21)$	3.104 (3)
$Cl(16) \cdots Cl(17)$	3.085 (2)	$Cl(21)\cdots Cl(22)$	3.106 (2)
$Cl(17)\cdots Cl(18)$	3.072 (3)	$Cl(22)\cdots Cl(23)$	3.129 (2)
$Cl(19)\cdots Cl(20)$	3.116 (2)	$Cl(25)\cdots Cl(26)$	2.941 (8)

severe internal overcrowding as a consequence of steric interactions between Cl atoms (Table 3). The sizes of these distortions can be seen both from the torsion angles and from the deviations from planarity (Fig. 3).

The dihedral angle between mean planes defined by the pentachlorophenyl group and the dibenzo[a,e]-pentalene group is 92.3°.

The molecule of carbon tetrachloride exhibits high thermal motion and shows little deviation from the theoretical symmetry; the C–Cl and Cl–Cl distances are significantly longer than the accepted values of 1.766 and 2.887 Å, respectively (Sutton, 1964). These differences could be principally attributed to errors arising from the difficulty in refining the carbon tetrachloride molecule, and this is also why it is not worth discussing its thermal ellipsoids (Fig. 4). The same



Fig. 3. Distances of atoms from the mean planes $(\times 10^3 \text{ Å})$ (standard deviations are 0.005 Å for C atoms and 0.002 Å for Cl atoms), and torsion angles (°) less than 90° (standard deviations are less than 0.9°).



Fig. 4. View of the carbon tetrachloride molecule drawn by *ORTEP* (Johnson, 1965) showing thermal ellipsoids and the numbering of the atoms.

explanation could be used in the discussion of the thermal ellipsoids of some of the atoms of the PDP moelcule, namely C(4), Cl(5), Cl(18) and Cl(21).

As shown in Fig. 5, the crystal consists of stacks of alternating PDP and carbon tetrachloride molecules, parallel to $(2\bar{1}4)$. This, together with the fact that the crystals are not highly coloured and the method of preparation followed to obtain the adduct, suggests that little charge transfer could occur between the PDP and the carbon tetrachloride molecules.

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Fig. 5. A projection of the unit-cell contents down b.

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