Crystal and Molecular Structures of Overcrowded Halogenated Compounds. VIII.* Two Overcrowded Naphthalenes — Octachloronaphthalene and Tetrabenznaphthalene (Dibenzo[g,p]chrysene)

By F. H. Herbstein

Department of Chemistry, Technion–Israel Institute of Technology, Haifa, Israel

Abstract

The crystal structures of octachloronaphthalene [monoclinic, $a = 19.579$ (8), $b = 7.289$ (4), $c = 9.797$ (5) Å, $\beta = 111.76$ (9)°, $P2_1/a$, $Z = 4$] and tetrabenznaphthalene (dibenzo[g,p]chrysene) [monoclinic, $a = 17.731$ (7), $b = 7.693$ (4), $c = 12.191$ (5) Å, $\beta = 97.15$ (8)°, $P2_1/n$, $Z = 4$] have been refined from intensities measured by a four-circle diffractometer (Mo $K\alpha$). For octachloronaphthalene 2447 independent reflections were used, and the final R was 7.04%; for tetrabenznaphthalene the corresponding values were 1973 and 7.94%. The two crystal structures are similar, both being based on quasi-hexagonal close packing of stacks of molecules, each stack containing only one enantiomorph. The molecular shapes and symmetries are also similar; there are appreciable out-of-plane displacements in both molecules. Tetrabenznaphthalene approximates to symmetry 222 while octachloronaphthalene approximates to symmetry 2; in octachloronaphthalene the two pairs of *peri* Cl atoms have different out-of-plane displacements, and this is ascribed to the influence of packing. The bond lengths in the C atom skeleton of octachloronaphthalene are similar to those of naphthalene, and those of tetrabenznaphthalene are similar to the results of quantum-mechanical calculations, thus leading to the conclusion that neither out-of-plane distortions nor substitution of H by Cl has an appreciable effect on the bond lengths in aromatic molecules (however, the overcrowding does cause changes in bond angles and torsion angles). The values of C—Cl lengths reported for a number of perchlorinated aromatic hydrocarbons have been analysed statistically, leading to the conclusion that the C—Cl lengths are approximately normally distributed, with mean 1.717 Å and e.s.d. 0.008 Å (values not corrected for thermal motion).

* Part VII: Herbstein, Kapon & Merksamer (1976).

1. Introduction

Naphthalenes substituted by bulky groups in the *peri* positions are distorted from planarity: both octa-chloronaphthalene $C_{10}Cl_8$ and tetrabenznaphthalene $C_{26}H_{16}$ are molecules of this type. The available information [$C_{10}Cl_8$, isotropic refinement of visual intensities, $R = 21\%$ (Gafner & Herbstein, 1963); $C_{26}H_{16}$, x,z coordinates only (Herbstein & Schmidt, 1954)] is inadequate and the structures have therefore been redetermined with intensities measured on a four-circle diffractometer. The new coordinates are in remarkably good agreement with those determined by photographic methods.

Peri interactions in substituted naphthalenes have been reviewed by Balasubramaniyan (1966) and intra-molecular overcrowding by Ferguson & Robertson (1963) and Avoyan, Struchkov & Dashevskii (1966).

Table 1. *Crystal data — cell dimensions measured on four-circle diffractometer*

	$C_{26}H_{16}$*	$C_{10}Cl_8$‡
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$†	$P2_1/a$
a (Å)	17.731 (7)	19.579 (8)
b (Å)	7.693 (4)	7.289 (4)
c (Å)	12.191 (5)	9.797 (5)
β (°)	97.15 (8)	111.76 (9)
V (Å³)	1649.9 (15)	1298.5 (12)
Z	4	4
$F(000)$	688	784
μ(Mo $K\alpha$) (mm⁻¹)	0.038	1.586
FW	328.41	403.74
m.p. (K)	488	471
λ(Mo $K\bar{a}$) (Å)		0.7107

* Sample from Aldrich Chemical Co.

† Space group was $P2_1/a$ according to Herbstein & Schmidt (1954). Reorientation matrix is (new axes, indices) = |101/0$\bar{1}$0/00$\bar{1}$| × (old axes, indices).

‡ Sample from Dr B. J. Wakefield (Clark, Maynard & Wakefield, 1976).

2. Experimental

All measurements were made on a Philips PW 1100 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Crystal data are given in Table 1, other experimental details in Table 2. The structure of $C_{26}H_{16}$ was solved with MULTAN

Table 2. Experimental details

	$C_{26}H_{16}$	$C_{10}Cl_8$
Crystal size and shape	Needle, 0.46×0.30 $\times 0.17$ mm	Needle, 0.25×0.07 $\times 0.03$ mm
Scan method	ω–2θ, $0.05°$ s^{-1} in ω, $1.4°$ (ω) width; scan and total background count durations equal	ω–2θ, $0.032°$ s^{-1} in ω, $1.6°$ (ω) width; scan and total background count durations equal
Maximum sin θ/λ	0.538 Å^{-1}	0.617 Å^{-1}
Standard reflections	$201, \bar{1}0\bar{1}, 220$	$402, 021, 220$
	Remeasured after every 120 min, no significant variations	
Absorption correction	Not applied	
Atomic scattering factors	International Tables for X-ray Crystallography (1974)	
Number of reflections included	1973	2447
Number of parameters refined	300	163
Refinement scheme	Refine on F, separate blocks for C, H parameters	Full matrix on F
Weighting scheme (SHELX 76)	$0.2974/[\sigma^2(F^2) + 0.04F^2]$	$1.00/[\sigma^2(F) + 0.02F^2]$
Final R factors: R_F	0.0794	0.0704
weighted R_F	0.1068	0.0910
Ratio |parameter shift|/ e.s.d. in last refinement cycle		
Mean	0.085	0.089
Max.	0.428	0.341
Number of elements in final correlation matrix > 0.6	0	0

Table 3. Octachloronaphthalene – fractional atomic coordinates ($\times 10^4$)

E.s.d.'s in parentheses are in units of least significant digit.

	x	y	z
C(1)	1850 (3)	3640 (7)	−1080 (6)
C(2)	1539 (3)	3881 (7)	−2587 (6)
C(3)	1972 (3)	4279 (7)	−3400 (6)
C(4)	2730 (3)	4179 (7)	−2748 (6)
C(5)	3839 (3)	3242 (7)	−545 (6)
C(6)	4173 (3)	3181 (7)	954 (6)
C(7)	3773 (3)	3571 (7)	1841 (6)
C(8)	3022 (3)	3753 (7)	1223 (6)
C(9)	2638 (3)	3702 (7)	−341 (5)
C(10)	3071 (3)	3693 (7)	−1235 (5)
Cl(1)	1262 (1)	3146 (2)	−194 (2)
Cl(2)	596 (1)	3755 (3)	−3477 (3)
Cl(3)	1558 (1)	4857 (3)	−5228 (2)
Cl(4)	3228 (1)	4926 (3)	−3758 (2)
Cl(5)	4332 (1)	2444 (3)	−1566 (2)
Cl(6)	5090 (1)	2631 (3)	1767 (2)
Cl(7)	4228 (1)	3782 (3)	3704 (2)
Cl(8)	2578 (1)	4257 (2)	2410 (2)

(Germain, Main & Woolfson, 1971); coordinates obtained from MULTAN gave a false minimum at $R = 42\%$ but comparison with the 1954 results showed that the molecule had been shifted along [001] by ~ 0.6 Å. Correction of this error led to straightforward refinement. The structure of $C_{10}Cl_8$ was refined with the parameters of Gafner & Herbstein (1963) as a starting point; with the new intensities and parameters of 1963 the initial value of R was 21%. Refinement was straightforward. Atomic parameters are given in Tables 3 and 4.*

Table 4. Tetrabenznaphthalene – fractional atomic coordinates (for C $\times 10^4$, for H $\times 10^3$)

E.s.d.'s in parentheses are in units of least significant digit.

	x	y	z
C(1)	985 (2)	2369 (5)	2776 (3)
C(2)	282 (2)	1933 (6)	3026 (4)
C(3)	85 (2)	2339 (7)	4066 (4)
C(4)	604 (2)	3113 (6)	4854 (4)
C(5)	1710 (3)	5035 (6)	6438 (3)
C(6)	2261 (4)	5807 (6)	7189 (3)
C(7)	3006 (3)	5919 (6)	6974 (3)
C(8)	3208 (2)	5228 (5)	6020 (3)
C(9)	4211 (2)	2803 (5)	4913 (3)
C(10)	4910 (2)	2185 (6)	4734 (4)
C(11)	5080 (2)	1918 (6)	3671 (4)
C(12)	4549 (2)	2297 (6)	2789 (3)
C(13)	3452 (2)	3538 (5)	930 (3)
C(14)	2930 (2)	3977 (5)	56 (3)
C(15)	2184 (2)	4293 (5)	244 (3)
C(16)	1973 (2)	4100 (4)	1288 (3)
C(17)	1537 (2)	3225 (4)	3546 (3)
C(18)	1340 (2)	3557 (5)	4610 (3)
C(19)	1910 (2)	4323 (5)	5457 (3)
C(20)	2677 (2)	4367 (4)	5234 (3)
C(21)	3658 (2)	3261 (4)	4020 (3)
C(22)	3829 (2)	2974 (4)	2937 (3)
C(23)	3262 (2)	3342 (4)	2004 (3)
C(24)	2498 (2)	3594 (4)	2191 (3)
C(25)	2304 (2)	3534 (4)	3313 (3)
C(26)	2879 (2)	3731 (6)	4190 (4)
HC(1)	113 (2)	212 (4)	206 (2)
HC(2)	−9 (2)	113 (6)	237 (3)
HC(3)	−43 (2)	215 (5)	427 (3)
HC(4)	49 (2)	331 (6)	563 (3)
HC(5)	117 (2)	486 (5)	661 (3)
HC(6)	206 (2)	610 (6)	776 (3)
HC(7)	345 (2)	641 (6)	762 (3)
HC(8)	383 (2)	539 (4)	585 (2)
HC(9)	405 (2)	287 (7)	572 (4)
HC(10)	529 (2)	186 (6)	540 (3)
HC(11)	562 (2)	150 (6)	352 (3)
HC(12)	468 (2)	212 (6)	199 (3)
HC(13)	397 (2)	332 (4)	74 (2)
HC(14)	310 (2)	415 (5)	−73 (3)
HC(15)	181 (2)	464 (5)	−38 (3)
HC(16)	142 (2)	440 (5)	134 (3)

Table 5. Equations of planes

The planes were calculated with *CRYM* (Duchamp, Trus & Westphal, 1969; Schomaker, Waser, Marsh & Bergman, 1959; Waser, Marsh & Cordes, 1973). All planes are given as: $lx + my + nz - d = 0$, where l,m,n are direction cosines of plane normal with respect to the *crystal* axes, d is the origin to plane distance and x,y,z are coordinates in Å in the crystal axial system. Deviations of atoms from these planes are given in Figs. 1 and 2.

(i) $C_{10}Cl_8$

   (a) Mean molecular plane

$$0.0625x + 0.9941y + 0.0592z - 2.998 = 0$$

(ii) $C_{26}H_{16}$

   (a) Mean molecular plane

$$0.0237x + 0.9869y - 0.1612z - 2.081 = 0$$

   (b) Mean plane of naphthalene portion of molecule

$$0.0225x + 0.9865z - 0.1639y - 2.079 = 0$$

   (c) Ring A

$$-0.3062x + 0.8953y - 0.2830z - 0.145 = 0$$

   (d) Ring B

$$0.1321x - 0.8751y + 0.4454z - 0.511 = 0$$

   (e) Ring C

$$0.3671x + 0.9301y - 0.0587z - 4.413 = 0$$

   (f) Ring D

$$0.1858x + 0.9644y + 0.1636z - 3.943 = 0$$

Refinement was carried out with *SHELX* 76 (Sheldrick, 1976) and calculations of molecule geometry with *SHELX* 76 and *CRYM* (Duchamp, Trus & Westphal, 1969). Results of planarity calculations are summarized in Table 5 and Figs. 1 and 2.

3. Results

3.1. Molecular structures

$C_{10}Cl_8$: the results summarized in Figs. 1 and 3 show that the molecular symmetry is approximately 222 (D_2) with adjacent α and β Cl atoms displaced in the same direction with respect to the mean molecular plane (but note that opposite displacement senses for α and β Cl atoms could also give symmetry 222). The C atom skeleton conforms more closely to 222 than does the molecule as a whole. The angles at C(9) and C(10) deviate appreciably from 120° and the torsion angles also show that the distortions are largest in this region of the molecule.

The Cl atoms are disposed with symmetry almost 2 (C_2), with the twofold axis approximately along the C(9)—C(10) direction. The non-bonded Cl···Cl distances match this symmetry particularly well. There is a striking difference of ~0·2 Å between the out-of-plane displacements of Cl(1) and Cl(8), on the one hand, and Cl(4) and Cl(5) on the other.
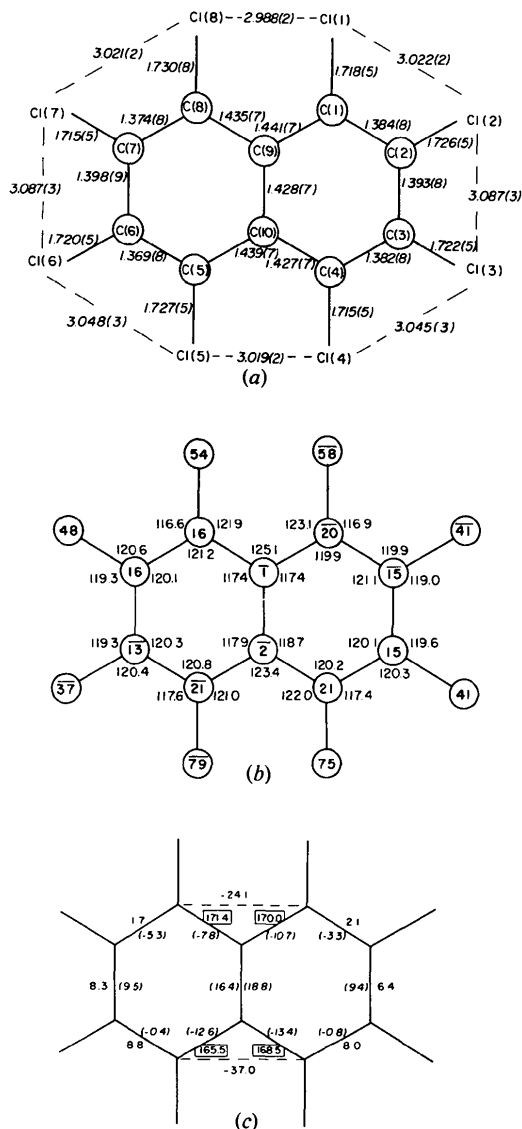

Fig. 1. Geometry of the octachloronaphthalene molecule (outline of molecule is projected on to the mean molecular plane). (a) Numbering of atoms, bond lengths (Å) (e.s.d.'s are in parentheses). (b) Bond angles (e.s.d.'s of C—C—C angles are ~0·5° and of C—C—Cl angles ~0·4°), with deviations from best molecular plane (units of 10^{-2} Å; e.s.d.'s Cl 0·002 Å, C 0·006 Å). (c) Torsion angles (°) – a torsion angle $i-j-k-l$ is defined as positive if, when looking along $j-k$, a clockwise rotation makes $i-j$ superimpose $k-l$. The torsion angles in parentheses refer to the atoms of the skeleton which are *cis* to one another, e.g. $\tau[C(8)-C(9)-C(10)-C(5)] = 16.4°$; the boxed values also refer to the C atom skeleton but concern atoms which are *trans* to one another, e.g. $\tau[C(7)-C(8)-C(9)-C(1)] = 171.4°$. The following two values are not conveniently inserted in the diagram: $\tau[C(5)-C(10)-C(9)-C(1)] = 163.0$, $\tau[C(4)-C(10)-C(9)-C(8)] = 161.9°$. The unbracketed values are for torsion angles involving C—Cl bonds. The values alongside the broken lines refer to torsion of the C—Cl bonds about these lines. E.s.d.'s of torsion angles are $\sigma[\tau(C-C-C)] \sim 0.6°$, $\sigma[\tau(Cl-C-C-Cl)] \sim 0.6°$ for Cl atoms *ortho* to one another, $\sigma[\tau(Cl-C-C-Cl)] \sim 0.3°$ for Cl atoms *peri* to one another.
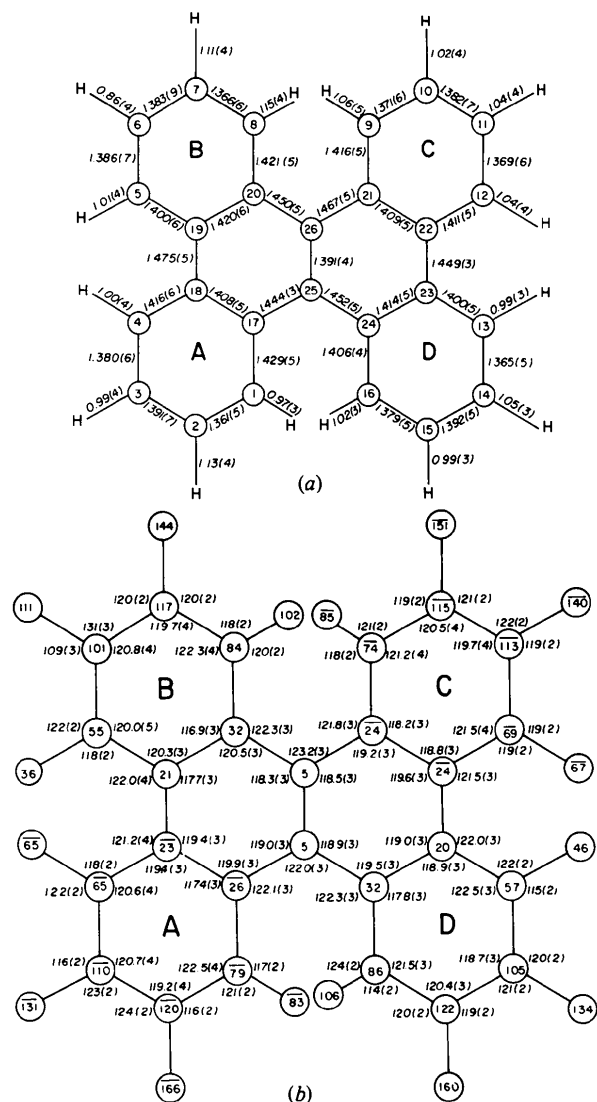
Fig. 2. Geometry of the tetrabenznaphthalene molecule (outline of the molecule is projected on to the mean molecular plane). (a) Numbering of C atoms (H atoms are numbered according to the C atoms to which they are attached); bond lengths (Å) (e.s.d.'s are in parentheses). The following distances (Å) in the overcrowded regions are of interest: C(8)–C(9) 3·011 (5), C(1)–C(16) 2·988 (16), HC(8)–HC(9) 1·98 (6), HC(1)–HC(16) 2·05 (4), HC(4)–HC(5) 1·99 (6), HC(12)–HC(13) 2·07 (5). (b) Bond angles (°) and deviations from best molecular plane in units of 10^{-2} Å (e.s.d.'s C ~ 0·004, H ~ 0·04 Å).

$C_{26}H_{16}$: this molecule also has approximate 222 (D_2) symmetry (as was deduced in 1954 from the x and z coordinates), with adjacent rings displaced in opposite directions from the naphthalene skeleton (Figs. 2 and 4). The torsion angles show that the main distortions are concentrated in the naphthalene region of the molecule while the four peripheral six-membered rings are essentially planar but inclined to the mean plane at angles of ~21°.

Fig. 2 (cont.). (c) Torsion angles (°) (see caption of Fig. 1 for definition); note that only cis torsion angles are included, e.g. $\tau[C(1)-C(17)-C(25)-C(24)] = 22 \cdot 7°$; e.s.d.'s of torsion angles are ~0·6°; deviations (units of 10^{-2} Å) from planarity in naphthalene ring system and deviations (units of 10^{-2} Å) from planarity (circled values) for each of the rings A, B, C, D.
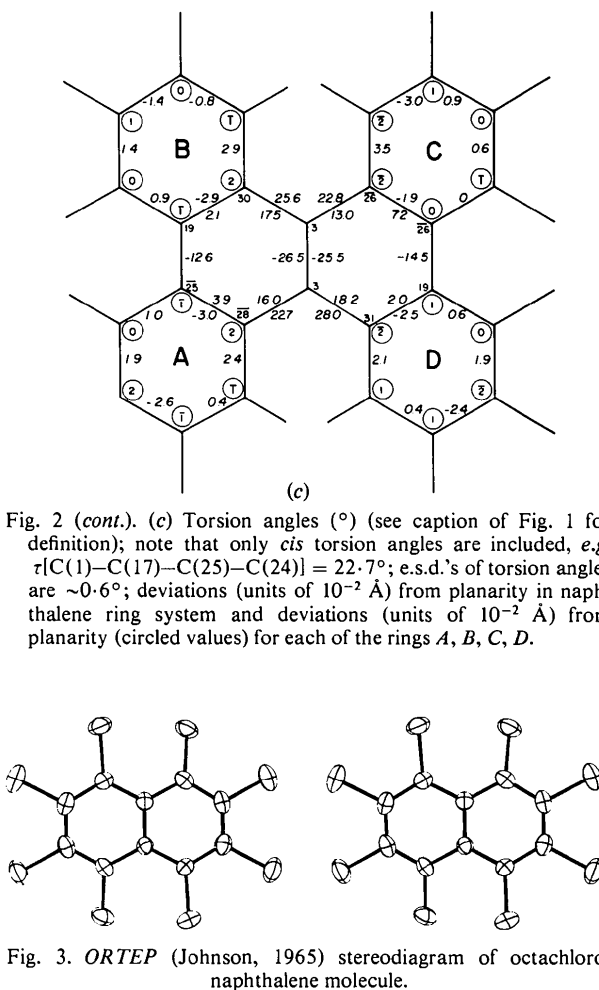

Fig. 3. ORTEP (Johnson, 1965) stereodiagram of octachloronaphthalene molecule.

3.2. Molecular arrangement

The two crystals are racemic and also isostructural, with both structures based on a quasi-hexagonal close packing of stacks of ellipsoidal cross-section (Figs. 5 and 6). A particular stack will contain molecules of one handedness only, successive molecules being related by the crystallographic twofold screw axes which are the stack axes. Stacks of the same handedness are segregated in infinite slices of the crystal parallel to (100), successive slices having alternating handedness.

4. Discussion

4.1. Molecular geometry

The bond lengths in the C atom skeletons of $C_{10}Cl_8$ and perchloro-1,2,3-triphenylnaphthalene (Gali, Solans, Miravitlles, Font-Altaba & Armet, 1978) agree well with those in naphthalene (Table 6). Brown &
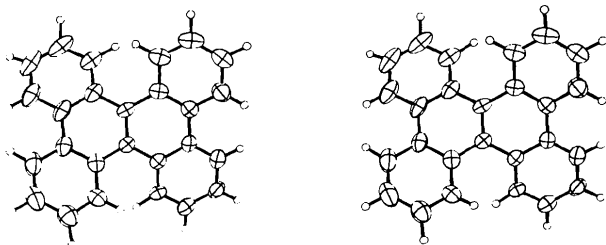
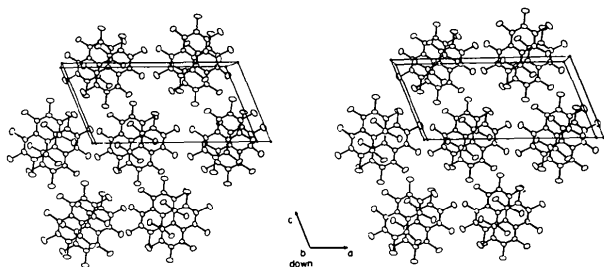Fig. 4. *ORTEP* stereodiagram of tetrabenznaphthalene molecule.

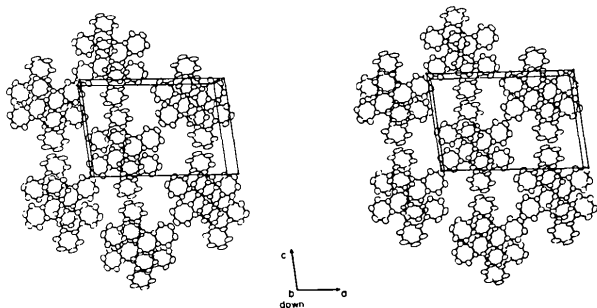Fig. 5. *ORTEP* stereodiagram of octachloronaphthalene crystal structure.

Fig. 6. *ORTEP* stereodiagram of tetrabenznaphthalene crystal structure.

Strydom (1974) have noted that the benzene rings in C_6H_6 and C_6Cl_6 have similar bond lengths, as do those in pyrene and decachloropyrene (Hazell & Jagner, 1976) and phenanthrene and decachlorophenanthrene (Herbstein, Kapon & Merksamer, 1976). Furthermore the measured bond lengths in $C_{26}H_{16}$ agree well with those obtained by molecular orbital calculations (Table 7; Vasudevan & Laidlaw, 1969; Dewar & Trinajstic, 1970), although the bond lengths in the naphthalene portion of $C_{26}H_{16}$ differ significantly from those of naphthalene itself. Thus we infer that neither distortions from planarity nor substitution of H by Cl has much effect on the bond lengths in aromatic ring systems, but that the bond lengths are affected when the overall size of the aromatic region is changed.
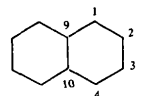
The average displacements of the atoms from the mean molecular planes are rather similar in $C_{10}Cl_8$ and octamethylnaphthalene (Hart, 1978) (Table 8).

However, $C_{10}(CH_3)_8$ has exact 222 (D_2) symmetry (Donaldson & Robertson, 1953) while $C_{10}Cl_8$ has significantly different displacements for the two pairs of α Cl atoms. This feature was ascribed to an unsymmetrical packing of the molecules (Gafner & Herbstein, 1963). This contention has been appreciably strengthened by Hazell's two sets of results for decachloropyrene – in the neat crystals which have an unsymmetrical molecular arrangement similar to that in octachloronaphthalene, the decachloropyrene molecule is unsymmetrically distorted from planarity [$\sum |\Delta_i| = 3.865$ for Cl(2)—Cl(7) and 2.927 Å for Cl(9)—Cl(14) (Hazell & Jagner, 1976)] while in decachloropyrene:benzene, where the packing is more symmetrical, the corresponding values of $\sum |\Delta_i|$ are 3.462 and 3.801 Å respectively (Hazell, 1978). These results show that some overcrowded molecules are flexible enough for their configurations to be sensibly perturbed by the environment and this must be taken into account in calculations of strain and lattice energies of such systems (Gafner, Herbstein & Lee, 1972).

The deviations from planarity in perchloro-1,2,3-triphenylnaphthalene (Gali, Solans, Miravitlles, Font-Altaba & Armet, 1978) and in the hexachloro-naphthalene-1,8-dithiolate ligands of $Ni_3(PPh_3)_3$-

Table 6. *Bond lengths* (Å) *in naphthalene portions of various molecules*

Bonds are designated as in the diagram:

	1–9	1–2	2–3	9–10
Naphthalene	1.421 ($\frac{3}{2}$)	1.369 ($\frac{4}{1}$)	1.409 ($\frac{6}{4}$)	1.416 ($\frac{5}{3}$)
$C_{10}Cl_8$	1.436 ($\frac{3}{4}$)	1.377 ($\frac{6}{2}$)	1.395 ($\frac{3}{6}$)	1.428 ($\frac{1}{7}$)
Perchloro-1,2,3-triphenylnaphthalene	1.428 ($\frac{14}{4}$)	1.381 ($\frac{9}{4}$)	1.418 ($\frac{15}{4}$)	1.416 ($\frac{3}{8}$)
$C_{26}H_{16}$	1.450 ($\frac{9}{2}$)	1.412 ($\frac{3}{3}$)	1.456 ($\frac{15}{4}$)	1.391 ($\frac{9}{8}$)

Notes

(1) The bond lengths in the table are weighted means of chemically equivalent bond lengths, *i.e.*

$$\bar{l} = \sum_{i=1}^{n} l_i/\sigma_i^2$$

where σ_i is the experimental e.s.d. of the ith bond.

(2) For naphthalene we have taken weighted means of values cited by Wilkerson, Chodak & Strouse (1975) for crystalline and gas-phase naphthalene, naphthalene in naphthalene–tetrachlorophthalic anhydride (120 K), and the neutron diffraction values (constrained refinement) of Pawley & Yeats (1969) for crystalline $C_{10}D_8$.

(3) The upper values in parentheses are the e.s.d.'s of the means of the lengths of chemically equivalent bonds:

$$\sigma(\bar{l}) = |s^2/n|^{1/2} \text{ where } s^2 = \left[\sum_{i=1}^{n} (l_i - \bar{l})^2 \right] / (n - 1).$$

The lower values are the e.s.d.'s of the means as calculated from the experimental e.s.d.'s, $\sigma_x(\bar{l}) = 1/\sum(1/\sigma_i^2)$.

Table 7. $C_{26}H_{16}$: *comparison of measured bond lengths (Å) [averaged according to molecular symmetry 222 (D_2)] with those calculated by the method of molecular orbitals [assumed molecular symmetry mmm (D_{2h})]*

C—C bond	Measured*	Calculated (a)	(b)
1–2	1·369 (3_8)	1·389	1·383
2–3	1·387 (2_6)	1·407	1·410
3–4	1·375 (4_8)	1·389	1·384
4–18	1·407 (4_0)	1·410	1·413
18–17	1·413 (2_8)	1·412	1·401
17–1	1·418 (4_8)	1·411	1·413
18–19	1·462 (13_0)	1·443	1·451
17–25	1·453 (4_9)	1·441	1·448
25–26	1·391 (–)	1·394	1·378
R.m.s. deviation†		0·013	0·012

References: (a) Vasudevan & Laidlaw (1969). (b) Dewar & Trinajstic (1970).

* Not corrected for thermal vibration effects. The values in parentheses are the e.s.d.'s of the means of the lengths of chemically equivalent bonds (see note 2 to Table 6). The experimental e.s.d.'s of individual bond lengths are given in Fig. 2(a).

† R.m.s. deviation = $\{[\sum(l_{meas} - l_{calc})^2]/9\}^{1/2}$.

Table 8. *Displacements (Å) of atoms from mean molecular planes in octachloronaphthalene and octamethylnaphthalene (Hart, 1978)*

	Cl/CH$_3$		Ring C atom	
	α	β	α	β
$C_{10}Cl_8$ Measured*	0·66	0·41	0·20	0·15
Calculated†	0·76	0·41	0·22	0·13
$C_{10}(CH_3)_8$‡	0·75	0·40	0·24	0·17

* Mean absolute displacement.
† 222 symmetry assumed (Kitaigorodsky, 1973).
‡ Molecular symmetry is 222.

Fig. 7. Non-bonded distances (Å) and deviations from planarity (units of 10^{-2} Å) in hexachloronaphthalene-1,8-dithiolate ligand [calculated from the atomic coordinates of Bosman & van der Linden (1977)]. The values for the three crystallographically independent ligands in the molecule have been averaged in order to give an overall picture of the shape of the ligand; however, there may well be small but significant differences in the shapes of the three ligands. Internal evidence suggests that the results suffer from systematic errors as the range of C—Cl lengths (1·683–1·869 Å) is much larger than that found for $C_{10}Cl_8$ and other perchlorinated aromatic hydrocarbons. [Note that the S atoms in the figure of Bosman & van der Linden's paper have been wrongly numbered – the three ligands have atoms S(6), S(3), Cl 11–16; S(5), S(2), Cl 21–26; S(1), S(4), Cl 31–36 respectively.]

Table 9. *Values of r.m.s. torsion angles (°) in the central naphthalene ring systems of four overcrowded molecules*

	$\left(\dfrac{\sum \gamma_i^2}{12}\right)^{1/2}$	Remarks
Benzo[c]phenanthrene	8·0	Calculated by Roberts & Ferguson (1977), from results of Hirshfeld et al. (1963).
$C_{10}Cl_8$	10·6	Present paper.
β-Tribenzopyrene (rings B, D)	12·6	Roberts & Ferguson (1977).
$C_{26}H_{16}$	15·4	Present paper.

$(S_2C_{10}Cl_6)_3$ (Bosman & van der Linden, 1977) (Fig. 7) are similar to those in $C_{10}Cl_8$ and $C_{10}(CH_3)_8$. In all these moieties the individual six-membered rings of the naphthalene ring system have chair conformations. An exception is provided by 1,4,5,8-tetraphenylnaphthalene (Evrard, Piret & Van Meerssche, 1972) where the individual rings have boat conformations.

The conformation and strain energy of $C_{10}Cl_8$ have been calculated by Kitaigorodsky (1973); the out-of-plane displacements (Table 8) are in excellent agreement with experiment. The strain energy of the hypothetical planar molecule is 752 kJ mol^{-1} and that of the equilibrium structure 568 kJ mol^{-1}.

The r.m.s. torsion angles in the naphthalene portions of the four overcrowded molecules of Table 9 show that $C_{26}H_{16}$ is the most severely distorted.
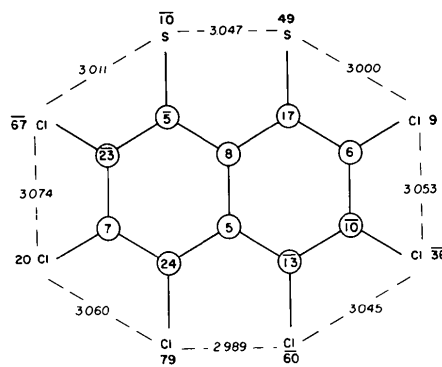
The Cl^{35} NQR spectrum of $C_{10}Cl_8$ has been measured over the range 77–313 K, with eight lines found at 77 K (frequency range 38·742–38·202 MHz) (Grechishkin & Soifer, 1963). This is close to the mean frequency found for C_6Cl_6 at 77 K [38·43 MHz; see Bray, Barnes & Bersohn (1956) for summary of NQR results for polychlorobenzenes]. According to Scrocco (1963) [see also Lucken (1969)] the increase in NQR frequency in a polychloroaromatic compared to the corresponding monochloroaromatic compound is mainly due to the inductive effect of the other C—Cl bonds on a particular C—Cl bond in the molecule. Using Scrocco's values for the ortho, meta and para influences and the measured NQR spectrum of 1,4,5,8-

tetrachloronaphthalene (Grechishkin & Soifer, 1964) to estimate the *peri* effect, we calculate frequencies of 38·2 MHz for both α and β Cl atoms, in reasonable agreement with experiment. The crystal-field and non-planarity effects are evidently much more subtle and assignment of frequencies to individual Cl atoms would be necessary before they could be usefully discussed.

In 4,5-dichloro-1,3,6,8-tetrafluoro-2,7-naphthyridine (van den Ham & van Hummel, 1977) the F atoms are all essentially coplanar with the undistorted part of the naphthyridine skeleton, while the *peri* Cl atoms are displaced up and down (by 0·16 and −0·13 Å respectively), together with their associated C atoms, very much as in 1,4,5,8-tetrachloronaphthalene (Gafner & Herbstein, 1962; Davydova & Struchkov, 1962). Octa-fluoronaphthalene is not significantly non-planar in its molecular complex with naphthalene (Potenza & Mastropaolo, 1975); $C_{10}F_8$ itself is disordered (Mandel & Donohue, 1972; Ahmed, 1973). The planarity of $C_{10}F_8$ was assumed in structural studies by powder neutron diffraction at pressures up to 7×10^5 Pa [see Mackenzie, Buras & Pawley (1978) for summary].

4.2. Symmetry of overcrowded molecules

The overcrowding in most substituted naphthalenes leads to chiral non-planar molecules with at least 2 symmetry; $C_{10}Cl_8$, $C_{26}H_{16}$, $C_{10}(CH_3)_8$, decachloro-phenanthrene (Herbstein *et al.*, 1976), benzo[c]phen-anthrene and 1,12-dimethylbenzo[c]phenanthrene (Hirshfeld, Sandler & Schmidt, 1963) are all examples. Diphenanthro[5,4,3-abcd:5',4',3'-jklm]perylene (Robertson & Trotter, 1959; Oonishi, Fujisawa, Aoki & Danno, 1978), tetrabenzo[a,cd,j,lm]perylene (Kohno, Konno, Saito & Inokuchi, 1975) and tetra-benzo[de,hi,op,st]pentacene (Rossmann, 1959) also have twofold symmetry rather than centres of symmetry. However, achiral distortions are also possible as shown by the $mm2$ (C_{2v}) symmetry of decachloro-pyrene, the m (C_s) symmetry of β-tribenzopyrene and the $2/m$ (C_{2h}) symmetry of 1,4,5,8-tetraphenyl-naphthalene (Evrard *et al.*, 1972). The balance is some-times delicate – the second polymorph of 1,4,5,8-tetra-phenylnaphthalene crystallizing in space group $P2_12_12_1$ (Harnik, Herbstein & Schmidt, 1951) presumably does not have $2/m$ symmetry but it is not known whether this is due to a change in the disposition of the phenyl rings or of the naphthalene ring system.

4.3. Symmetry of molecular arrangement

Both $C_{10}Cl_8$ and $C_{26}H_{16}$ crystallize in racemic crystals but with segregation of molecules of alternate handedness on to alternate planes in the crystal [see Herbstein *et al.* (1976) for discussion]. In decachloro-pyrene and β-tribenzopyrene a somewhat similar arrangement of layers of alternating chirality is found but the segregation is with respect to the sense of the saddle-shaped molecules, alternate (200) planes con-taining 'saddles' pointing towards and away from the observer looking down [010] [see Fig. 3 of Hazell & Jagner (1976) and Fig. 5 of Roberts & Ferguson (1977)]. Segregation of enantiomers into separate stacks or planes is also found in diphenanthro-[5,4,3-abcd:5',4',3'-jklm]perylene and tetrabenzo-[de,hi,op,st]pentacene (space group $P2_1$, so spon-taneous resolution has occurred) but not in tetrabenzo-[a,cd,j,lm]perylene (space group $Pcab$) where the enantiomers alternate up the stacks.

4.4. The C–Cl bond distance

Values of the C–Cl length are now available for seven perchlorinated aromatic hydrocarbons (Table 10). As only half the values have been corrected for thermal vibrations, we chose to use uncorrected values throughout although this may cause systematic errors because of the uncertainty in the absolute values. We test the null hypothesis that all these data sets belong to the same population by using the F test. The only pair with significantly different variances (at the 5% level) are decachlorophenanthrene and hexachlorobenzene [calculated variance ratio 26·32, critical value (5% level) for four and two degrees of freedom 19·25]; this is not surprising as these represent the least and most precise sets of measurements respectively. Further-more application of student's t test to the various pairs of mean values of the C–Cl lengths shows that none of these differences are significant at the 5% level. Thus we consider that all the samples come from the same population. The appropriateness of the experimental e.s.d.'s can be checked for decachloropyrene by comparing C–Cl lengths in the neat crystal and the benzene complex by an Abrahams & Keve (1971) analysis. This shows that the pooled e.s.d.'s have been underestimated by ~25%: one possibility would be to replace the e.s.d.'s of 0·004 Å in Table 10 by values of 0·005 Å. The experimental e.s.d.'s (from the structure analyses) and the sample e.s.d.'s (σ_n) (calculated from the distributions of measured C–Cl lengths) do not differ appreciably. The individual values of C–Cl lengths give a histogram (Fig. 8) to which can be fitted a normal distribution with mean C–Cl $= 1\cdot717$ Å and $\sigma = 0\cdot008$ Å; the value of χ^2 for nine intervals, *i.e.* ignoring the highest value, is 5·13, with $v = 6$. The value of $\chi^2_{0\cdot95}$ for $v = 6$ is 12·59 and thus the hypothesis that the available measured C–Cl lengths belong to a normally distributed population $(\bar{x} = 1\cdot717$ Å) cannot be rejected at the 5% significance level. The correction for thermal motion in hexachlorobenzene, decachloro-biphenyl and decachloropyrene is 0·003–0·005 Å and thus the mean corrected C–Cl length is 1·721 (8) Å. The essential point in this argument is that most of the

Table 10. *Statistical parameters for* C—Cl *distances in perchlorinated aromatic hydrocarbons*

	Number of independent bonds	Weighted mean C—Cl (Å)	Experimental e.s.d. of mean (Å)	Population e.s.d. (Å)	Mean e.s.d. of individual bond length (Å)	Range (Å)	Reference
Hexachlorobenzene	3	1·715	0·001₂	0·002	0·002	0·004	Brown & Strydom (1974).
Octachloronaphthalene	8	1·722	0·001₈	0·006	0·006	0·015	Present paper.
Decachlorobiphenyl	5	1·718	0·001₃	0·007	0·003	0·020	Pedersen (1975).
Decachlorophenanthrene	5	1·722	0·005₄	0·009	0·012	0·023	Herbstein *et al.* (1976).
Decachloropyrene	10	1·715	0·001₃	0·007	0·004	0·029	Hazell & Jagner (1976).
Decachloropyrene in molecular complex with benzene	10	1·717	0·001₃	0·005	0·004	0·015	Hazell (1978).
Perchloro-1,2,3-triphenylnaphthalene	20	1·717	0·001₅	0·010	0·006	0·043	Gali *et al.* (1978).
Weighted mean	61	1·7167	0·0005₅	0·007₈	–	0·043	

Notes
(1) Uncorrected values have been used for C—Cl lengths except for decachlorobiphenyl where only corrected values (corrections $\simeq$ 0·003 Å) have been reported.
(2) For definition of weighted mean see note (1) to Table 6.
(3) Population e.s.d. is defined as $\{[\sum(l_i - \bar{l})^2]/(n - 1)\}^{1/2}$ where n is the number of independent bond lengths.
(4) Experimental e.s.d. of the mean is defined in note (3) to Table 6.

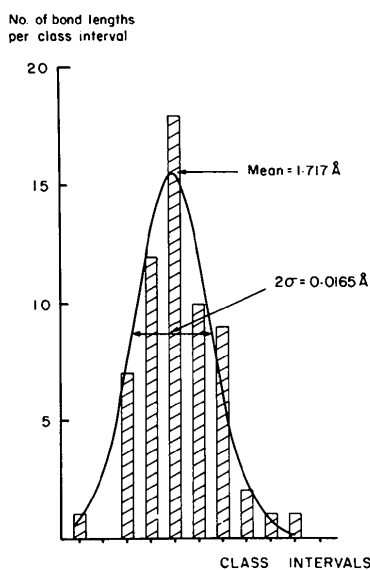No. of bond lengths per class interval

Fig. 8. Histogram of C—Cl lengths (uncorrected for thermal motion) for the perchlorinated aromatic hydrocarbons of Table 10. The class intervals are 1·695–1·699; ...; 1·740–1·744 Å. The total number of entries is 61.

experimentally found scatter of C—Cl lengths in perchlorinated aromatic hydrocarbons can be accounted for in terms of experimental error; we have, of course, neglected the contribution from differing corrections for thermal motion.

Similar arguments cannot be applied to the C—C distances where the sample e.s.d.'s are 0·027 for $C_{10}Cl_8$ and 0·030 Å for $C_{26}H_{16}$ [using the measured bond distances given in Figs. 1(*a*) and 2(*a*)]. These values are

respectively 3–4 and 5–6 times the experimental e.s.d.'s of the bond lengths and thus the scatter cannot be ascribed to experimental error.

A widely quoted view on the lengths of C—Cl bonds (where the C atom is part of an aromatic system) is due to Rudman (1971) who inferred from a survey of the available results that the mean C—Cl length was 1·709 when the compound contained two or more *ortho* C—Cl bonds, and 1·737 Å when the compound contained isolated C—Cl bonds. The analysis given above suggests that the first of these values is too low and should be replaced by 1·717 Å (uncorrected) or 1·721 Å (with a rough correction for thermal motion). We note that the more recent value C—Cl = 1·712 (2) Å in tetrachlorophthalic anhydride [in naphthalene: TCPA at 120 K (Wilkerson, Chodak & Strouse, 1975)] is appreciably larger than that given by Rudman (1971) [1·682 (8) Å, uncorrected] for TCPA itself; this is in accordance with our proposed value as are the values of 1·716 (σ_{n-1} = 0·002, σ_{exp} = 0·002 Å) for octachloro-*p*-dioxin (Neuman, North & Boer, 1972) and of 1·720 (3) Å for α-*N*-(*p*-tolyl)tetrachlorophthalimide (Kaftory, 1978). It is more difficult to give a definitive value for the C—Cl length in isolated C—Cl bonds. We have surveyed the fifteen issues of *Acta Cryst.* B from January 1977 to March 1978 and found 18 separate values from 12 different crystal structures (Table 11). The values (all uncorrected for thermal motion) range from 1·726 (4) to 1·754 (5) Å, with a mean of 1·739 Å, in excellent agreement with Rudman's proposal. However, the value of σ_n is 0·009 Å, about twice the mean value of the experimental e.s.d. (0·004 Å), suggesting that the scatter is not due to experimental error alone. It appears that the thermal-

Table 11. *Some isolated* C—Cl *lengths* (Å) *in aromatic moieties*

Structures have been included when (1) no disorder or other structural problems are present; (2) authors quote σ(C—Cl) < 0·006 Å; (3) Cl is heaviest atom in molecule. The values listed are not corrected for thermal motion.

	C—Cl	Reference
5-Chloro-7-nitro-2,3-dihydroxyquinoxaline	1·726 (4)	Grabowski, Stępień, Cygler & Wajsman (1977).
	1·727 (4)	
5-Chloro-7-amino-2,3-dihydroxyquinoxaline	1·727 (3)	Stępień (1977).
Chlorimipramine . HCl	1·742 (3)	Post & Horn (1977).
1,4-Dichloro-p-chlorophenyl-1'-dimethylamino-	1·744 (3)	Chentli-Benchicka, Declercq, Germain, Van
4'-diaza-2,3-butadiene	1·732 (4)	Meerssche, Duchene & Viehe (1977).
α- and β-1,3-Diphenyl-5(p-chlorophenyl)-2-pyrazoline	1·745 (3)	Kimura, Kai, Yasuoka & Kasai (1977).
	1·747 (6)	
1-{4-[4-(p-Chlorophenyl)-4-hydroxypiperidino]-2,2-	1·727 (5)	Germain, Declercq, Van Meerssche & Koch (1977).
diphenylbutyryl}pyrrolidine		
(1R,2S)-2-[(S)-(p-Chlorophenyl)sulfinyl]-	1·753 (3)	Chidester & Duchamp (1977).
N,N,3,3-tetramethylcyclopropylamine		
2,2-Bis(p-chlorophenyl)acetic acid	1·744 (4)	Hovmöller, Norrestam & Palm (1977).
	1·747 (4)	
1-{4-[4-(p-Chlorophenyl)-4-hydroxypiperidino]-	1·733 (4)	Declercq, Germain, Van Meerssche & Koch (1977).
2,2-diphenylvaleryl}pyrrolidine		
2,4-Hexadiynylene bis(p-chlorobenzenesulfonate)	1·734 (3)	Mayerle & Clarke (1978).
4,4'-Dichlorobiphenyl	1·733 (5)	Brock, Kuo & Levy (1978).
	1·746 (5)	
	1·737 (5)	
	1·754 (5)	

motion corrections are much larger for Cl atoms in *p*-chlorophenyl groups than in perchlorinated aromatics [*e.g.* for 4,4'-dichlorodiphenyl the proposed thermal-motion correction is ~0·018 Å (Brock, Kuo & Levy, 1978)]. Thus low-temperature studies seem to be essential for obtaining accurate values of C—Cl lengths for isolated C—Cl bonds.

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Polymorphism of the Crystalline Methylchloromethane Compounds. VI.* The Crystal and Molecular Structure of Ordered Carbon Tetrachloride

BY SHMUEL COHEN, ROSLYN POWERS AND REUBEN RUDMAN

Department of Chemistry, Adelphi University, Garden City, New York 11530, USA

Abstract

The structure of phase II of CCl_4 has been determined from single-crystal diffractometer data at 195 K. In this phase, crystals of CCl_4 are monoclinic with $a = 20\cdot181$ (8), $b = 11\cdot350$ (4), $c = 19\cdot761$ (6) Å, $\beta = 111\cdot46$ (3)°, $Z = 32$, and space group $C2/c$. There are four molecules per asymmetric unit with four C—Cl bonds per molecule for a total of sixteen crystallographically unique C—Cl distances. Within the limits of experimental error, the molecules are regular tetrahedra, with average C—Cl and intramolecular Cl$\cdots$Cl distances, uncorrected for thermal motion, of 1·751 (13) and 2·859 (6) Å, respectively. These same distances, corrected for thermal motion using a rigid-body treatment, are 1·773 and 2·889 Å. The average of the four shortest intermolecular Cl$\cdots$Cl distances is 3·582 (7) Å, thus indicating a van der Waals radius for Cl of $1\cdot79_1$ Å.

* Part V: Rudman (1977).