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Decachlorobiphenyl, $C_{12}Cl_{10}$: the Crystal and Molecular Structure

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Abstract. $C_{12}Cl_{10}$, orthorhombic, *Pbcn*, $a=13·372$ (2), $b=10·497$ (3), $c=11·992$ (2) Å, $Z=4$, $D_x=1·968$ g cm^{-3}, m.p. 304°, $F(000)=968$, F.W. 498·66, μ(Mo $K\alpha$) $=1·63$ mm^{-1}, $R=0·048$ for 2107 measured reflexions (457 unobserved). The molecule has a twofold axis normal to the biphenyl bridge. The carbon skeleton of each ring is planar, but all Cl atoms deviate by 0·02 to 0·05 Å from these planes. The rings are twisted 86·7 (5)° relative to each other, and the normals to the ring planes are bent 2° from a position normal to the bridge. All intramolecular distances and angles have normal values. The bridge bond is 1·522 (5) Å.

Introduction. Preliminary diffraction data showed an orthorhombic primitive lattice with the following systematic absences: $hk0$, $h+k=2n+1$; $0kl$, $k=2n+1$; $h0l$, $l=2n+1$. The space group is *Pbcn* (No. 60) with eight general positions. As $Z=4$, the space group requires the decachlorobiphenyl (DCB) molecules to lie on special positions of 2 or $\bar{1}$ symmetry.

A well-formed, transparent, prismatic *c* crystal was used for data collection on a Picker FACS I automatic diffractometer. Intensities of 2107 reflexions ($2\theta_{max}=55·0°$) were measured by the $\theta/2\theta$ scan technique with Nb-filtered (0·04 mm) Mo $K\alpha$ radiation. The intensities of two reflexions were monitored periodically to ensure a common scale. Reflexions with $I<2\sigma$ were considered unobserved, giving a total of 1650 observed reflexions. All calculations were performed on a CDC 3300 computer using standard programs (Dahl, Gram, Groth, Klewe & Rømming, 1970). The scattering factors were taken from Hanson, Herman, Lea & Skillman (1964).

The structure was determined from a sharpened Patterson function, combined with known intramolecular distances and possible intermolecular contacts. The structure was refined by full-matrix least-squares analyses, minimizing the function $\sum w(F_o-F_c)^2$ where w is the inverse of the variance of $F(1/\sigma^2)$. The refinement converged to a final conventional R of 0·048. Final positional and thermal parameters are in Table 1.† Results from a **TLS** analysis for one phenyl ring $[(\Delta U_{ij}^2)^{1/2}=23\times10^{-4}$ Å$^2]$ show a reasonably isotropic librational motion with amplitudes of 4·8°, 4·4° and 3·5°. The translational motion has an r.m.s. amplitude of 0·21 Å approximately normal to the phenyl ring,

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† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31286 (23 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final positional and thermal parameters* ($\times10^5$) *and their estimated standard deviations*

(See Fig. 1 for the identities of the atoms.) Temperature factor: $\exp\{-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)\}$.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	44439 (20)	37755 (28)	23826 (28)	368 (20)	729 (34)	525 (28)	63 (44)	−57 (43)	92 (59)
C(2)	40402 (22)	29464 (29)	16103 (27)	385 (20)	736 (36)	560 (29)	90 (46)	−60 (41)	51 (59)
C(3)	30117 (23)	28937 (31)	14118 (29)	389 (21)	863 (41)	729 (34)	−170 (51)	−250 (45)	225 (64)
C(4)	34012 (23)	36966 (35)	19996 (31)	292 (20)	1153 (48)	858 (37)	99 (53)	−120 (48)	506 (75)
C(5)	27788 (23)	45532 (33)	27572 (29)	429 (23)	1059 (46)	710 (34)	509 (55)	125 (47)	316 (70)
C(6)	38109 (24)	45902 (29)	29482 (28)	551 (23)	805 (41)	562 (31)	191 (52)	−113 (47)	−59 (59)
Cl(2)	48272 (7)	19642 (9)	8665 (8)	543 (6)	1097 (11)	928 (9)	323 (15)	−174 (13)	−634 (19)
Cl(3)	25336 (7)	18189 (10)	4880 (9)	671 (6)	1242 (12)	1192 (11)	−475 (16)	−761 (16)	−129 (23)
Cl(4)	11316 (6)	36350 (10)	17909 (11)	312 (5)	2056 (17)	1587 (15)	84 (17)	−196 (15)	648 (28)
Cl(5)	20158 (7)	55751 (10)	34748 (9)	751 (7)	1637 (14)	1075 (11)	1244 (18)	431 (15)	252 (23)
Cl(6)	43069 (7)	56586 (10)	38769 (8)	860 (7)	1283 (13)	916 (10)	485 (18)	−388 (15)	−848 (20)

Positional parameters ($\times10^5$) corrected for thermal motion

	x	y	z		x	y	z
C(1)	44408 (20)	37761 (28)	23821 (28)	Cl(2)	48260 (6)	19575 (9)	8605 (8)
C(2)	40355 (21)	29423 (29)	16067 (27)	Cl(3)	25270 (7)	18136 (10)	4836 (9)
C(3)	30046 (22)	28900 (31)	14086 (29)	Cl(4)	11231 (6)	36335 (10)	17898 (11)
C(4)	23931 (23)	36953 (35)	19985 (31)	Cl(5)	20081 (7)	55783 (10)	34774 (9)
C(5)	27711 (23)	45545 (33)	27583 (29)	Cl(6)	43045 (7)	56652 (9)	38821 (8)
C(6)	38055 (23)	45929 (29)	29502 (28)				

0·16 Å along the major axis of DCB and 0·19 Å in the ring plane and normal to the two other translational components.

Discussion. Fig. 1 shows the molecule viewed down the *b* axis and the bond lengths and angles calculated from the coordinates of Table 1 corrected for thermal motion. E.s.d.'s for C–Cl bonds are 0·003 Å and for C–C bonds, 0·004 Å; for angles 0·2–0·3°. C–C bonds range from 1·373 (4) to 1·403 (4) Å. The mean value, 1·388 Å, is not significantly different from the value in benzene, 1·397 (1) Å (Stoicheff, 1954). Small, but significant differences in the C–C bond lengths in DCB are, however, observed. The largest difference, 0·030 Å corresponds to 5σ. A similar deviation from regularity of the aromatic ring is described for biphenyl (Robertson, 1961) where the difference between corresponding C–C bonds was found to be 0·0252 Å or 8σ. C–Cl distances range from 1·708 (3) to 1·728 (3) Å; the mean value of 1·718 Å is in agreement with previously determined C–Cl distances in fully chlorinated aromatic compounds: 1·715 (2) Å in hexachlorobenzene (Brown & Strydom, 1974) and 1·716 (4) Å in octachlorodibenzo-*p*-dioxin (Neuman, North & Boer 1972).

The angles in the phenyl ring range from 118·4 (3)° to 121·7 (3)° and differ significantly from the mean value, 120·0°. The equations to the best planes through the C atoms in phenyl rings I [C(1)–C(6)] and I′ [C(1)′–C(6)′] are:

$$\text{(I)}\quad (0{\cdot}0074a+0{\cdot}0654b-0{\cdot}0601c)R-1{\cdot}262=0$$

$$\text{(I}')\quad (-0{\cdot}0074a+0{\cdot}0654b+0{\cdot}0601c)R-4{\cdot}251=0\,.$$

Deviations of atoms from these planes are given in Table 2. The C atoms are coplanar, but all Cl atoms deviate from the planes by 0·019 to 0·047 Å. Furthermore, the long axis of the molecule is not linear. The deviations from plane I to C(1)′, C(4)′ and Cl(4)′ are respectively 0·064, 0·180, and 0·236 Å. This means that the molecular axis is bent at C(1) and C(1)′.

Table 2. *Deviations* ($\times 10^3$ Å) *of atoms from plane* I

C(1)	−9	Cl(3)	−37
C(2)	6	Cl(4)	−41
C(3)	2	Cl(5)	19
C(4)	−8	Cl(6)	38
C(5)	4	C(1)′	−64
C(6)	4	C(4)′	−180
Cl(2)	46	Cl(4)′	−236

The two rings are not quite mutually normal to each other, the angle between the ring planes being 86·6 (5)°. Because of the bending of the longest molecular axis, which derives from rotations of 2·1° of the rings about axes in the respective ring planes through C(1) or C(1′), the dihedral angles C(2)–C(1)–C(1)′–C(2)′ and C(6)–C(1)–C(1)′–C(6)′ will be slightly different from 86·7 (5)°, 85·8 (5)° and 87·9 (5)°. Similar deformations of biphenyl derivatives have been reported for 4,4′-diamino-3,3′-dimethylbiphenyl (Chawdhury, Hargreaves & Sullivan, 1968), and 2,2′-dichlorobiphenyl (Rømming, Seip & Aanesen Øymo, 1974) where angles of bend of 3° and 2·4° have been found. In biphenyl (Robertson, 1961) a 0·20 Å perpendicular separation between the planes of the two rings has been observed.

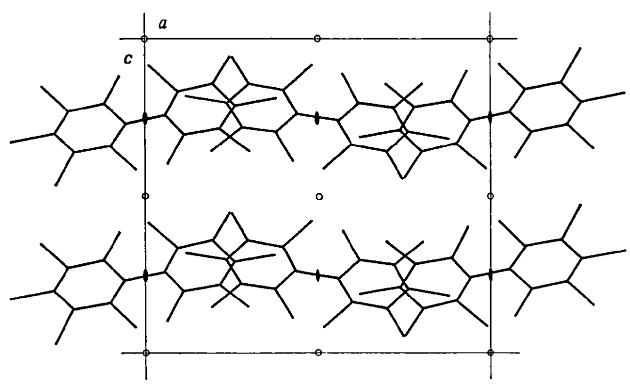

Fig. 2. The packing in the crystal of DCB viewed along **b**.

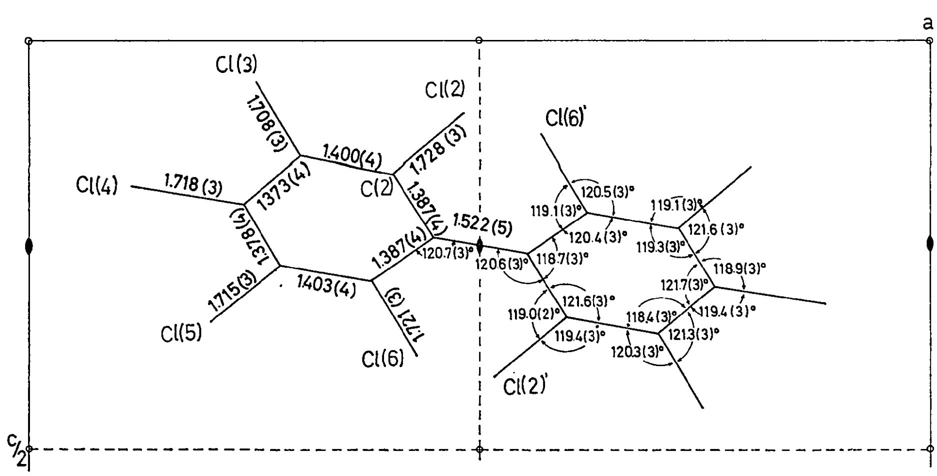

Fig. 1. Bond distances and angles in decachlorobiphenyl (DCB) corrected for thermal motion.

Fig. 2 shows the packing in the crystal viewed along **b**. The DCB molecules are packed in layers normal to **c** at $z=\frac{1}{4}$ and $\frac{3}{4}$. There are extensive van der Waals contacts between the molecules both within each layer and between the layers.

Biphenyl and several substituted biphenyls have previously been studied both in the gas phase and/or as solids. Only for one compound, unsubstituted biphenyl, does the conformation change drastically upon crystallization. The rings are coplanar in the solid, but twisted 42° in the gas phase (Almenningen & Bastiansen, 1958). Calculations have been performed to try to explain this difference semiquantitatively, and reasonable agreement is obtained with electron diffraction, X-ray, and thermal data (Fischer-Hjalmars, 1963; Casalone, Mariani, Mugnoli & Simonetta, 1968). The geometry of the isolated molecule is found to be mainly determined by a balance of π-electron and non-bonded energies, while in the crystal the most important forces seem to be the intermolecular C···H attractions.

In all substituted biphenyl compounds studied, the two rings are twisted about the central C–C bond. The angle of twist is dependent on the nature, site and size of the substituents, and values range from 33 to 86°. The C–C bridge bond in biphenyls ranges from 1·48 to 1·52 Å, but based on the quoted e.s.d.'s of all but two of the published values, there are no significant differences. There is, however, a significant difference between the C–C bonds in 2,2′-dichlorobiphenyl and DCB, the lengths being respectively 1·493 (5) and 1·522 (5) Å, with twist angles 69·2 (5)° and 86·7 (3)°. The corresponding bond is 1·4966 (25) Å in planar biphenyl. In these chlorinated compounds the lengths of the C–Cl bonds are also different: 1·748 (3) and 1·718 Å (mean value for DCB). This may indicate that a larger proportion of the π-electrons are engaged in C–Cl interaction in DCB, which consequently leads to a lowering of the electron density in the C–C bridge, with a corresponding lengthening of the bond.

The average C–Cl bond length in DCB, 1·718 Å, is consistant with Rudman's (1971) inference from available data, that C–Cl bonds on aromatic and quinoid rings are significantly shorter when the bonds are *ortho* to each other, than when they are more widely separated or isolated.

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Sodium Thiocyanate

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Abstract. NaSCN, orthorhombic, *Pnma*, $a=13{\cdot}38$ (1), $b=4{\cdot}09$ (1), $c=5{\cdot}66$ (1) Å, $Z=4$. The thiocyanate group is linear and the Na^+ ion is octahedrally surrounded by three S and three N atoms in *fac* arrangement.

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Introduction. To assist with the interpretation of the high-pressure phase diagram of NaSCN, an approximate structure based on space-group data and packing considerations was proposed by Pistorius & Boeyens (1968). The structure was confirmed by infrared work (Iqbal, 1971) and has been discussed in at least one review (Iqbal, 1972). To prevent perpetuation