**Discussion.** Our X-ray analysis has established the molecular structure and relative stereochemistry of (+)-jaborol. A stereoview of the molecule is given in Fig. 1 with our crystallographic numbering scheme. Fig. 2 is a stereoview of the crystal structure showing molecular packing. Bond distances, angles and important torsion angles are listed in Table 2. In the molecule of (+)-jaborol, the aromatic ring *A* is essentially planar to within 0·007 (2) Å. Ring *B*, a tetrahydrofuran ring, has a C(7)-envelope conformation with C(7) 0·654 (2) Å out of the plane of atoms O(2), C(8), C(9), C(10). This ring is *cis*-fused to ring *C*. Ring *C* itself has a twist-boat conformation with C(11) and C(14) 0·476 (2) and 0·637 (2) Å above the C(8), C(9), C(12), C(13) plane. Ring *D* is *trans*-fused with ring *C* and has a C(13)-envelope conformation with C(13) 0·626 (2) Å above the C(14)–C(17) plane. The six-membered ring *E* has a half-chair conformation with C(22) 0·611 (2) Å above the plane of atoms O(5), C(23), C(24), C(25) and C(26).

The molecular dimensions in (+)-jaborol are unexceptional, mean values being C($sp^3$)–C($sp^3$) 1·534 (3), C($sp^3$)–C($sp^2$) 1·498 (3), C($sp^2$)–C($sp^2$) 1·481 (3), aromatic C–C 1·388 (3), C=C 1·336 (2), C($sp^3$)–O 1·445 (3), C($sp^2$)–O 1·342 (3) and C=O 1·221 (2) Å.

One of the two hydroxy groups is involved in H bonding through its H atom with a ketonic O atom [O(6$^i$)···H(O1) 1·96 Å and O(1)–H(O1)···O(6$^i$) 159·6°].

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# 3,3′,5,5′-Tetrachloro-4,4′-dihydroxybiphenyl. A Coplanar Polychlorinated Biphenyl in the Solid State

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**Abstract.** $C_{12}H_6Cl_4O_2$, $M_r = 323·99$, monoclinic, $P2_1/c$, $a = 6·5696$ (7), $b = 4·7887$ (7), $c = 19·460$ (3) Å, $\beta = 95·10$ (1)°, $V = 609·8$ (2) Å$^3$, $Z = 2$, $D_x = 1·76$ g cm$^{-3}$, $\lambda$(Cu $K\bar{\alpha}$) = 1·54178 Å, $\mu = 87·5$ cm$^{-1}$, $F(000) = 324$, $T = 297$ K, $R = 0·050$ for 785 observed reflections. Non-*ortho*-substituted polychlorinated biphenyls (PCB's) have shown significantly higher binding affinities to certain receptor proteins when compared with their *ortho*-substituted counterparts. An important property of such PCB's is the accessibility of the more polarizable coplanar conformation that has been shown to be important in the crystalline form of certain biphenyl systems. 3,3′,5,5′-Tetrachloro-4,4′-dihydroxybiphenyl, which has shown strong receptor protein binding activity, crystallizes in the coplanar state. This compound is essentially isostructural with the related 'coplanar-toxic' PCB's. It is proposed that the dispersion-energy gain from a coplanar alignment of the phenyl rings stabilizes the interactions of these PCB compounds with important macromolecules some of which mediate their responses in biological systems, probably involving stacking interactions with aromatic (or conjugated) rings in amino acids or heme groups.

**Introduction.** The biological properties of PCB's vary considerably and are remarkably dependent on the number and positions of halogen atoms in the molecular structure (Goldstein, 1980). Non-*ortho*-sub-

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stituted PCB's have shown significantly higher binding affinities to certain receptor proteins when compared with their *ortho*-substituted counterparts (Bandiera, Safe & Okey, 1982; McKinney, Fannin, Jordan, Chae, Rickenbacher & Pedersen, 1987). Because *ortho* substitution plays a dominant role in determining the pivot bond or phenyl-ring twist angle, it would be desirable to be able to accurately assess conformational properties of PCB structures in correlations with biological activity. One modern approach to this problem which has met with some success (McKinney & Pedersen, 1986; Darden, McKinney, Gottschalk, Maynard & Pedersen, 1986) is the use of energy-minimization calculations such as molecular mechanics. X-ray crystallographic determinations can provide a highly accurate picture of molecular geometry in a specific solid-state environment. For most uncharged molecules like the PCB's, a structure observed in the solid state is at or very near a local minimum-energy conformation. However, an advantage of the experimental X-ray method is that it also provides information on the packing arrangement which may point to intermolecular forces of importance in binding interactions. A number of non-*ortho*-substituted biphenyl compounds have been shown (McKinney & Pedersen, 1986; McKinney & Singh, 1981) to crystallize at or near the coplanar state suggesting that the coplanar packing arrangements are favorable. However, a coplanar PCB structure has not yet been established crystallographically.

Approximate equilibrium dissociation constants involving the binding of non-*ortho*-substituted PCB's to the dioxin (Ah) receptor were reported (Bandiera *et al.*, 1982) to be 1 to 3 orders of magnitude smaller than those for the *ortho*-substituted PCB's. Recently, we have also described (McKinney *et al.*, 1987) a hydroxylated PCB compound, 3,3′,5,5′-tetrachloro-4,4′-dihydroxybiphenyl, that showed a remarkably high affinity ($K_a = 5{\cdot}86 \times 10^{10} M^{-1}$) for thyroxine-specific binding sites [which share some properties with the Ah receptor (McKinney *et al.*, 1987)] in rat-liver nuclear extracts while the isomeric, but di-*ortho*-substituted compound, 2,3,5,6-tetrachloro-4,4′-dihydroxybiphenyl, which cannot achieve coplanarity (McKinney, Gottschalk & Pedersen, 1983*a*), showed an affinity about 22 times weaker. In comparison, 3,3′,5,5′-tetrachlorodiphenoquinone, which has a rigid coplanar structure, showed an affinity about 3·2 times stronger. These results strongly suggested the involvement of a coplanar state in enhancing binding activity. In this work, we report that the molecular structure of 3,3′,5,5′-tetrachloro-4,4′-dihydroxybiphenyl in the crystalline state is coplanar.

**Experimental.** 3,3′,5,5′-Tetrachloro-4,4′-dihydroxybiphenyl was purchased from ULTRA Scientific, Hope, RI, USA. The commercial product contained crystals large enough for structure analysis. A plate-like crystal of dimensions 0·40 × 0·10 × 0·04 mm was mounted on a thin glass fiber attached to a eucentric goniometer head, which was then transferred to a Nicolet $R3m/\mu$ diffractometer equipped with a copper X-ray tube, a graphite monochromator and a pulse-height analyzer. Lattice parameters were determined at 297 K using 25 reflections in the range $40 \le 2\theta \le 70°$. Intensities were measured by the $\theta/2\theta$ scan technique in the range $4 \le 2\theta \le 115°$, $h$: −7 to 7, $k$: 0 to 5 and $l$: 0 to 21 at a scan rate of 2° min$^{-1}$ with stationary background counts for half the scan time on each side of the peak. Two standard reflections, $\bar{1}13$ and 108, were measured after every 48 measurements to check the stability of the crystal and the instrument. Of the 903 reflections measured 785 were found to have intensities greater than $2\sigma(I)$ and were used in the structure refinement. Data were processed by making the usual background and Lorentz and polarization corrections, plus an empirical absorption correction *via* $\psi$ scan. The minimum and maximum transmission factors were 0·07 and 0·31, respectively. The structure was solved by direct methods using the *SOLV* routine of the *SHELXTL** (Sheldrick, 1983) system of programs supplied by the Nicolet Corporation for the Data General Desktop Microeclipse computer. The non-H atoms were located from an $E$ map and the H atoms from a subsequent difference Fourier map. The structure was refined by the block-diagonal least-squares technique to $R = 0{\cdot}050$, $wR = 0{\cdot}069$, $S = 1{\cdot}5$, the function minimized being $\sum w(|\,|F_o| - |F_c|\,|)^2$, where $w = 1/[\sigma^2(F_o) + 0{\cdot}002F_o^2]$. The non-H atoms were refined with anisotropic, and the H atoms with isotropic thermal-vibration parameters. A secondary-extinction parameter was also refined. Its final value, $4 \times 10^{-5}$, however, is rather high. The largest shift/$\sigma$ in the last cycle of refinement was 0·04. The final difference Fourier map was featureless, the largest peak being 0·60 e Å$^{-3}$. The atomic scattering factors including the anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974).

**Discussion.** The fractional coordinates derived from the last cycle of refinement are presented in Tables 1 and 2.† The bond distances and bond angles are shown in Fig. 1. The two carbon–chlorine bonds, C(3)–Cl(1) and C(5)–Cl(2) with bond distances 1·738 (3) and 1·735 (3) Å, respectively, are similar to such bonds in other biphenyls (McKinney & Singh, 1981) and so is

* *SHELXTL* was used for all crystallographic calculations and drawings.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44537 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$) *for non-*H *atoms*

| | $x$ | $y$ | $z$ | $U_{eq}$* |
|---|---|---|---|---|
| Cl(1) | 881 (1) | 5167 (2) | 1982 (1) | 44 (1) |
| Cl(2) | 6124 (1) | −2443 (2) | 1157 (1) | 49 (1) |
| O | 4691 (4) | 1660 (6) | 2079 (1) | 44 (1) |
| C(1) | 711 (5) | 288 (6) | 310 (2) | 32 (1) |
| C(2) | 238 (5) | 2249 (7) | 799 (2) | 36 (1) |
| C(3) | 1556 (5) | 2739 (6) | 1378 (2) | 33 (1) |
| C(4) | 3387 (4) | 1318 (6) | 1505 (1) | 32 (1) |
| C(5) | 3856 (4) | −593 (7) | 1012 (2) | 34 (1) |
| C(6) | 2569 (5) | −1115 (7) | 431 (1) | 37 (1) |

* Equivalent isotropic $U$ defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

Table 2. *Atomic coordinates* ($\times 10^3$) *and isotropic thermal parameters* ($Å^2 \times 10^2$) *for* H *atoms*

| | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|
| HC(2)* | −91 (5) | 330 (6) | 76 (1) | 2 (1) |
| HC(6) | 300 (5) | −253 (7) | 9 (2) | 4 (1) |
| HO | 444 (6) | 267 (8) | 225 (2) | 3 (1) |

* HC(2) refers to the H atom attached to C(2), *etc.*

Table 3. *Short intermolecular distances* (Å)

| $A^{i}\cdots B$ | Distance | Sum of van der Waals radii[ii] | Symmetry of $B^{i}$ |
|---|---|---|---|
| Cl(1)···Cl(1) | 3·400 | 3·60 | $-x, \frac{1}{2}+y, \frac{1}{2}-z$ |
| Cl(1)···Cl(1) | 3·400 | 3·60 | $-x, -\frac{1}{2}+y, \frac{1}{2}-z$ |
| C(5)···Cl(1) | 3·487 | 3·40 | $x, -1+y, z$ |
| Cl(2)···Cl(1) | 3·572 | 3·60 | $1+x, -1+y, z$ |
| HC(2)···Cl(2) | 2·969 | 3·00 | $-1+x, 1+y, z$ |

(i) $A$ is defined as the original atom in the molecule from Table 1 and $B$ as the atom with the indicated coordinates.
(ii) Pauling (1960).

the pivot bond C(1)—C(1′) with a bond distance of 1·485 Å (McKinney & Singh, 1981). The C(4)—O bond distance, 1·355 (4) Å, is slightly shorter than those given for the C—O bond in the monoclinic form, 1·375 (1) Å, and the orthorhombic form, 1·385 (4) Å, of 4-hydroxybiphenyl (Brock & Haller, 1984). Short intermolecular contacts are given in Table 3. Unit-cell packing is shown in Fig. 2.

Since there are only two molecules in a unit cell of this crystal which belongs to the space group $P2_1/c$ the molecules necessarily possess an inversion center and are, therefore, planar. Such crystallographically imposed symmetry has been observed in other related molecules, *e.g.* biphenyl (Charbonneau & Delugeard, 1976) and 4,4′-dihydroxybiphenyl (Akhmad, Farag & Amin, 1971). The two crystalline forms of 4-hydroxybiphenyl cited above (Brock & Haller, 1984) also contain planar biphenyl molecules. In these crystals, however, no crystallographic symmetry is imposed on the molecules. Coplanarity of the two benzene rings in biphenyl and its derivatives is unfavorable energetically since it results in a close contact, approximately 2·0 Å, between the two *ortho* H atoms on the two rings, *viz* H(2)···H(2′) and H(6)···H(6′). It has been shown (Busing, 1983; Cailleau, Baudour, Meinnel, Dworkin, Moussa & Zeyen, 1980; Burkert & Allinger, 1982; Bowen & Allinger, unpublished calculations) that the coplanarity of the two rings in the crystalline form of biphenyl is due to favorable intermolecular interactions that can stabilize biphenyl conformations close to the intramolecular energy maximum at a twist angle $\psi = 0°$ in a well ordered structure without abnormally large thermal parameters. These stabilizing interactions would oppose the intramolecular interactions due to *ortho* H atoms that would favor a nonplanar conformation (McKinney, Gottschalk & Pedersen, 1983*a*). The importance of the coplanar state in characterizing these intermolecular interactions suggests that a stacking arrangement may underlie the effect. In fact, there is evidence of stacking contacts between two molecules involving groups [Cl(1) and C(4)—C(5), 3·54 and 3·49 Å respectively] in different phenyl rings for the non-*ortho*-substituted biphenyl crystalline form studied in this work that are close to the value of 3·54 Å

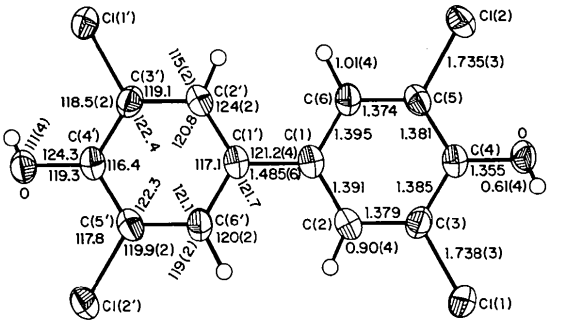


Fig. 1. A view of the molecule down the normal to the benzene rings showing the atom-numbering scheme, and bond distances (Å) and bond angles (°). The e.s.d.'s, if not shown, are 0·003 Å for bond distances and 0·3° for bond angles. Thermal ellipsoids are drawn to 50% probability. H atoms are shown as open circles of arbitrary size.

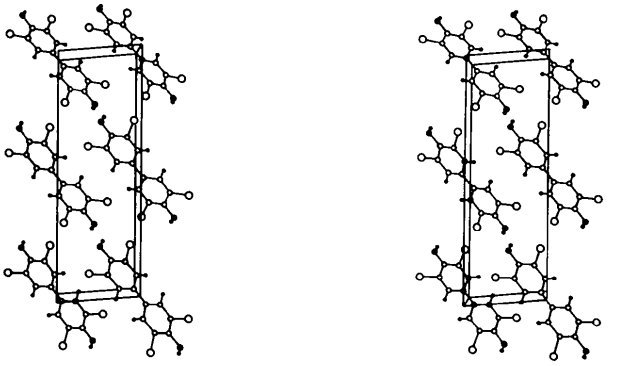

Fig. 2. Stereographic diagram of the unit cell looking down the *b* axis; the *a* axis is horizontal and the *c* axis vertical. Large circles are Cl atoms and filled circles OH groups.

reported (Czikkely, Forsterling & Kuhn, 1970) between the planes in layered aromatic hydrocarbons. In the absence of these intermolecular stabilizing interactions, calculations (Casalone, Mariani, Mugnoli & Simonetta, 1968; Burkert & Allinger, 1982; McKinney & Pedersen, 1986) and gas-phase determinations (Almenningen & Bastiansen, 1958) indicate that the minimum-energy structure for non-*ortho*-substituted biphenyls has a twist angle between 35 and 45°. In preliminary, molecular-mechanics calculations (Posner & McKinney, unpublished observations), we find an angle of about 36° for 3,3′,5,5′-tetrachloro-4,4′-dihydroxybiphenyl.

The OH groups form a hydrogen-bonded polymeric chain around the twofold screw axes parallel to **b** at $x = \frac{1}{2}$, $z = \frac{1}{4}$ and at $x = \frac{1}{2}$, $z = \frac{3}{4}$, the O···O distance being 2·909 Å. The H atom, HO, was located from a difference Fourier map and although the O–H bond distance, 0·61 Å, is somewhat short, it is pointing in the right direction for hydrogen bonding with an O–H···O angle of 151° and H···O distance of 2·36 Å. Short contacts of 3·400 Å occur between Cl(1) atoms around the remaining twofold screw axes. Previous workers (Brock, 1980) have reported similar behavior for *para*-halogenated biphenyls. For example, in 4-bromobiphenyl, weak attractions between the polarizable halogens seem to account for the presence of chains of edge-sharing, Br-atom tetrahedra that are analogous to the hydrogen-bonded chains in crystals of 4-hydroxybiphenyl. Polarizable halogens and a coplanar alignment of the phenyl rings would maximize the extent of polarizability necessary for a strong dispersion-stacking interaction between molecules (McKinney, Darden, Lyerly & Pedersen, 1985). The presence of less polarizable groups could explain in part why all non-*ortho*-substituted biphenyls are not coplanar in the crystalline state. For example, the crystal structure of 4,4′-dichloro-3,3′,5,5′-tetrafluorobiphenyl has a twist angle of 33·7° in agreement with the energy-minimized structure (34·5°) using molecular-mechanics calculations (Singh, Posner & McKinney, 1987). The carbon–fluorine bond would be about 7 times less polarized [see Korolkovas (1970) for group polarizabilities relative to hydrogen] relative to chlorine (about 1·2 times less relative to hydrogen) and the neighboring *ortho* F atoms considerably reduce the polarization of chlorine in the *para* position. Consistent with this hypothesis is the fact that 4,4′-dichloro-3,3′,5,5′-tetrafluorobiphenyl is relatively non-toxic compared to 3,3′,4,4′,5,5′-hexachlorobiphenyl (McKinney, Singh, Levy & Walker, 1980) suggesting that a coplanar alignment of the phenyl rings in this compound is also not expressed in its interactions with proteins. However, other factors (Brock, 1979) may affect the planarity of biphenyl in the crystal.

Using *ab initio* and molecular-mechanics methods to assign PCB's to stereochemical classes, we have developed a theoretical model for the interactions of PCB's with cytosol receptors (dioxin or Ah receptor) interpreted in terms of a linear free-energy relationship (McKinney *et al.*, 1985; McKinney, Gottschalk & Pedersen, 1983*b*). The essential molecular parameters in this model are the PCB polarizability and the receptor-to-PCB separation distance which depends on steric factors. The advantage of this model is that it incorporates the stereoelectronic effects of chlorine substitution on binding free energy. A graphic representation of this model that was based on molecular-mechanics minimization of the PCB–porphine interactions (McKinney *et al.*, 1985) was also presented. This work suggested that the *ortho* effect is important in determining the receptor-to-PCB separation distance (~3·50 Å). Although experimentally hydroxy-PCB's have relatively lower binding affinities to the Ah receptor than their halogen-substituted counterparts, this is believed (Long, McKinney & Pedersen, 1987) to be due to large differences in desolvation energy (because of the potential for hydrogen bonding) rather than to differences in intrinsic binding properties. The theoretical model based on molecular parameters complements the results of others (Safe, Bandiera, Sawyer, Zmudzka, Mason, Romkes, Denomme, Sparling, Okey & Fujita, 1985) which indicate that hydrophobic and electronic substituent constants and a variable for hydrogen-bond formation are significant parameters describing relative binding activities for the Ah receptor. The theoretical model, however, is more detailed with regard to molecular structure and the nature of the molecular interaction than the statistical correlation method and offers a physicochemical or mechanistic basis for understanding the occurrence of outliers.

The persistence of the same general structure across a fairly wide range of non-*ortho*-substituted biphenyls in the crystalline state (Brock, 1980; McKinney & Singh, 1981; Brock & Haller, 1984) is an indication that the intermolecular interactions (probably initially dispersion-stacking but ultimately electrostatic in nature) observed in the packing arrangement are very favorable. Such an interpretation coupled with the success of our theoretical modeling work provide a plausible explanation for the high binding activity of 3,3′,5,5′-tetrachloro-4,4′-dihydroxybiphenyl and the related 3,3′,5,5′-tetrachlorodiphenoquinone in nuclear extracts (McKinney *et al.*, 1987). The small binding-*K*-ratio enhancement (3·2) found experimentally for these two structurally related compounds is consistent with a dispersion-energy gain in the coplanar state which assists in overcoming the small rotational barrier to planarity in the dihydroxy compound. These compounds are essentially isostructural with the related toxic compounds 3,3′,4,4′,5,5′-hexachlorobiphenyl and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. We believe that the same or similar interactions are important in the

binding interactions of 'toxic-coplanar' PCB's in biological systems. Likely binding sites in proteins for stacking interactions are the rigid side chains of aromatic amino acids as well as the heme prosthetic group in hemoproteins as represented by the PCB–porphine interaction model (McKinney *et al.*, 1985).

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# Structure of 5,5′-Dibromo-2,2′-bithiophene

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**Abstract.** $C_8H_4Br_2S_2$, $M_r = 324{\cdot}06$, orthorhombic, *Pccn*, $a = 7{\cdot}525$ (1), $b = 22{\cdot}333$ (3), $c = 5{\cdot}828$ (1) Å, $V = 979{\cdot}4$ (2) Å$^3$, $Z = 4$, $D_m = 2{\cdot}21$ (1), $D_x = 2{\cdot}198$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) $= 0{\cdot}71073$ Å, $\mu = 8{\cdot}55$ mm$^{-1}$, $F(000) = 616$, $T = 296$ K, $R = 0{\cdot}048$ for 538 independent reflections. The bithiophene molecule is completely planar. The C—Br bond length is 1·869 (8) Å and the C—S bond length is 1·728 (9) Å. The C—S—C bond angle is 91·0 (4)°. The major deviations from 2*mm* ($C_{2v}$) symmetry involve the bond angles at C(3) and C(4) which are 114·1 (7) and 111·6 (8)° respectively.

**Introduction.** Substituted 2,2′-bithiophenes and polythienyls have nematocidal activity strongly dependent on the number and type of substituents present in the

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