

Structure of 2,4'-Dichlorobiphenyl (PCB 8)

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Abstract. $C_{12}H_8Cl_2$, $M_r = 223.1$, monoclinic, $P2_1$, $a = 3.976(2)$, $b = 11.558(7)$, $c = 11.166(8)$ Å, $\beta = 91.73(12)^\circ$, $V = 512.9(5)$ Å³, $Z = 2$, $D_x = 1.445$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54184$ Å, $\mu = 54.1$ cm⁻¹, $F(000) = 228$, $T = 290$ K, $R = 0.057$ for 1709 unique observed diffractometer data [$F \geq 6\sigma(F)$]. The structure determination confirms the Cl-atom substitution pattern of the biphenyl moiety inferred from spectroscopic methods. The dihedral angle between the two phenyl groups is $49.6(1)^\circ$.

Introduction. Polychlorinated biphenyls (PCB's) are compounds marked by their persistence in terrestrial and aquatic systems and by their bioaccumulation in certain animal tissue (Wolff, Thornton, Fischbein, Lillis & Selikoff, 1982). The evidence continues to mount that PCB's represent a potential threat to animal physiology. There are a total of 209 possible PCB isomers. Bioaccumulation and activity is isomer dependent. *Ortho* substitution appears to decrease this activity (McKinney, Gottschalk & Pedersen, 1983). The unequivocal characterization of the title compound forms part of the reference-materials program initiated by the European Community Bureau of Reference (Directorate General for Science, Research and Development, Commission of the European Communities, 200 Rue de la Loi, B-1049 Brussels, Belgium†). The overall aim of this program is the production of a series of ten environmentally

important PCB isomers as analytical reference materials of certified purity and identity.

Experimental. The title compound was kindly provided by Professor J. Jacobs, Biochemisches Institut für Umweltcarcinogenen, Ahrensburg/Holstein, Federal Republic of Germany. Earlier work with PCB 35 (3,3',4-trichlorobiphenyl; van der Sluis, Moes, Behm, Smykalla, Beurskens & Lenstra, 1990) and PCB 20 (2,3,3'-trichlorobiphenyl; Moes & Lenstra, 1986) provided the necessary experience for finding a suitable crystallization method. PCB 8 (9.0 mg) was dissolved in 200 μ l DMSO in a small test tube and 40 μ l water was added, resulting in a precipitate. The tube was sealed and the precipitate was dissolved by heating the tube gradually to 313–318 K in an oil bath. A few tiny crystals were obtained by careful heating and cooling. These crystals were allowed to grow for 2 weeks by cooling the solution at a rate of 2 K per day for the first week and relaxation of the solution for the second week. Data were collected on a CAD-4F diffractometer for a transparent crystal (1.4 \times 0.25 \times 0.23 mm) mounted in a glass capillary. Data collection was hampered by streaks near the strongest low-order reflections, possibly as a result of the poor quality of the crystal. The cell parameters were calculated by least squares from the setting angles of 25 reflections with $20 \leq \theta \leq 39^\circ$. 3500 reflections were scanned ($h - 4$ to 4 , $k - 13$ to 13 , $l - 13$ to 13 ; $\theta \leq 65^\circ$; $\omega/2\theta$ -scan mode; $\Delta\omega = 1.5^\circ$; graphite-monochromatized Cu $K\alpha$ radiation). Three reference reflections measured every 30 min showed a small decay of less than 2% during the X-ray exposure time. Profile analysis was performed on all

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† PCB 8 is available from this source as certified reference material.

Table 1. Final fractional coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
Cl(2)	0.4616 (2)	0.2723 (1)	0.00442 (7)	0.0617 (3)
Cl(4)'	0.3529 (3)	0.7400 (1)	0.3523 (1)	0.0836 (4)
C(1)	0.1968 (7)	0.2367 (3)	0.2310 (3)	0.0502 (9)
C(1)Y	0.2333 (7)	0.3613 (3)	0.2601 (3)	0.0468 (9)
C(2)	0.2872 (8)	0.1880 (3)	0.1207 (3)	0.051 (1)
C(2)Y	0.3851 (8)	0.3957 (4)	0.3667 (3)	0.056 (1)
C(3)	0.2571 (9)	0.0709 (4)	0.0978 (4)	0.060 (1)
C(3)Y	0.4184 (9)	0.5106 (4)	0.3949 (3)	0.058 (1)
C(4)	0.122 (1)	-0.0010 (3)	0.1853 (4)	0.068 (1)
C(4)Y	0.3021 (9)	0.5938 (3)	0.3186 (3)	0.057 (1)
C(5)	0.029 (1)	0.0442 (4)	0.2968 (4)	0.067 (1)
C(5)Y	0.1444 (9)	0.5633 (4)	0.2139 (3)	0.056 (1)
C(6)	0.0696 (8)	0.1612 (4)	0.3189 (3)	0.059 (1)
C(6)Y	0.1125 (8)	0.4486 (3)	0.1864 (3)	0.050 (1)

Table 2. Bond distances (Å), bond angles (°) and selected torsion angles (°)

Cl(2)—C(2)	1.781 (4)	C(2)Y—C(3)Y	1.370 (7)	C(3)—H(3)	1.00 (4)
Cl(4)Y—C(4)Y	1.741 (4)	C(3)—C(4)	1.401 (6)	C(3)Y—H(3)Y	0.95 (5)
C(1)—C(1)Y	1.482 (5)	C(3)Y—C(4)Y	1.357 (5)	C(4)—H(4)	1.00 (5)
C(1)—C(2)	1.411 (5)	C(4)—C(5)	1.410 (6)	C(5)—H(5)Y	0.92 (5)
C(1)Y—C(2)Y	1.377 (5)	C(4)Y—C(5)Y	1.356 (5)	C(5)—H(5)	0.96 (5)
C(1)—C(6)	1.418 (5)	C(5)—C(6)	1.383 (7)	C(6)—H(6)	1.08 (4)
C(1)Y—C(6)Y	1.379 (5)	C(5)Y—C(6)Y	1.366 (6)	C(6)Y—H(6)Y	0.89 (6)
C(2)—C(3)	1.382 (6)	C(2)Y—H(2)Y	0.94 (5)		
C(1)—C(1)Y—C(2)Y	120.5 (3)	C(1)—C(6)—C(5)	121.3 (4)		
C(1)Y—C(1)—C(2)	123.6 (3)	C(1)Y—C(6)Y—C(5)Y	123.2 (3)		
C(1)Y—C(1)—C(6)	118.7 (3)	C(1)—C(2)Y—H(2)Y	115 (3)		
C(1)—C(2)—C(6)	123.4 (3)	C(3)Y—C(2)Y—H(2)Y	124 (3)		
C(2)—C(1)—C(6)	117.7 (3)	C(2)—C(3)—H(3)	117 (3)		
C(2)Y—C(1)Y—C(6)Y	116.1 (4)	C(2)Y—C(3)Y—H(3)Y	124 (4)		
Cl(2)—C(2)—C(1)	122.2 (3)	C(4)Y—C(3)Y—H(3)Y	115 (4)		
Cl(2)—C(2)—C(3)	115.8 (3)	C(4)—C(3)—H(3)	124 (3)		
C(1)Y—C(2)Y—C(3)Y	121.0 (4)	C(3)—C(4)—H(4)	119 (2)		
C(1)—C(2)—C(3)	122.0 (4)	C(5)—C(4)—H(4)	120 (2)		
C(2)Y—C(3)Y—C(4)Y	120.9 (3)	C(4)Y—C(5)Y—H(5)Y	115 (3)		
C(2)—C(3)—C(4)	119.0 (4)	C(4)—C(5)—H(5)	118 (3)		
Cl(4)Y—C(4)Y—C(3)Y	121.1 (3)	C(6)Y—C(5)Y—H(5)Y	126 (3)		
Cl(4)Y—C(4)Y—C(5)Y	119.1 (3)	C(6)—C(5)—H(5)	123 (3)		
C(3)—C(4)—C(5)	120.8 (4)	C(1)Y—C(6)Y—H(6)Y	120 (2)		
C(3)Y—C(4)Y—C(5)Y	119.8 (4)	C(1)Y—C(6)Y—H(6)Y	121 (4)		
C(4)—C(5)—C(6)	119.2 (4)	C(5)Y—C(6)Y—H(6)Y	118 (2)		
C(4)Y—C(5)Y—C(6)Y	118.9 (4)	C(5)Y—C(6)Y—H(6)Y	115 (4)		
C(2)—C(1)—C(1)Y—C(6)Y	50.8 (5)	C(6)—C(1)—C(1)Y—C(2)Y	47.7 (4)		

reflections (Lehmann & Larsen, 1974; Grant & Gabe, 1978). The data were corrected for Lp and for absorption [empirical correction using ψ scans (North, Phillips & Mathews, 1968); correction factors in the range 0.59–1.00], resulting in a unique set of 1750 reflections ($R_{int} = \sum F - \langle F \rangle / \sum F = 0.024$) of which 1709 were considered observed [$F > 6\sigma(F)$]. The structure was solved in *P1* using *DIRDIF* (Beurskens, Bosman, Doesburg, van den Hark, Prick, Noordik, Beurskens, Gould & Parthasarathi, 1983) employing automated vector-search rotation functions (Beurskens, Beurskens, Strumpel & Nordman, 1986). The idealized molecule, with a dihedral angle of 45° , gave all the non-H atoms of

the two molecules in the unit cell, thereby locating the position of the screw axis. Isotropic refinement converged to $R = 0.12$. An additional empirical absorption correction was applied (Walker & Stuart, 1983), resulting in a further decrease of R to 0.10 (correction factors in the range 0.79–1.44). The structure was refined by full-matrix least squares on F using *SHELX76* (Sheldrick, 1976). At this stage the Bijvoet coefficient was calculated (Beurskens, Noordik & Beurskens, 1980) resulting in a value of 0.9923 (2) based on 477 Friedel pairs, showing that the absolute structure is correct. The H atoms were found from a $\Delta\rho$ map and were included in the refinement. Anisotropic temperature factors were used for all non-H atoms. Final convergence was reached at $R = 0.057$, $wR = 0.055$; $w = 1.0/[\sigma^2(F) + 0.0003F^2]$; $S = 4.69$; $(\Delta/\sigma)_{max} = 0.01$; number of refined parameters = 159. No residual density outside the range $\pm 0.63 \text{ e \AA}^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). The final atomic coordinates and equivalent isotropic temperature factors are listed in Table 1.* The program package *EUCLID* (Spek, 1982) was used for geometrical calculations and illustrations.

Discussion. Bond lengths, bond angles and selected torsion angles are collected in Table 2. A perspective view of the molecule with atomic labeling is depicted in Fig. 1. The bond distances for the C(1)—C(6) phenyl ring range from 1.382 to 1.418 Å and for the C(1)Y—C(6)Y phenyl ring from 1.356 to 1.379 Å. The mean C—C distance of the phenyl rings is 1.384 Å, which is in good agreement with those of 2,2'-dichlorobiphenyl (1.382 Å; Rømming, Seip & Øymo, 1974) and 4,4'-dichlorobiphenyl (1.381 Å; Brock, Kuo & Levy, 1978). The two internal ring bond angles, at C(1) and C(1)Y [117.7 (3) and 116.1 (4)°

* Lists of anisotropic thermal parameters, H-atom positions, torsion angles, least-squares planes and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53063 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

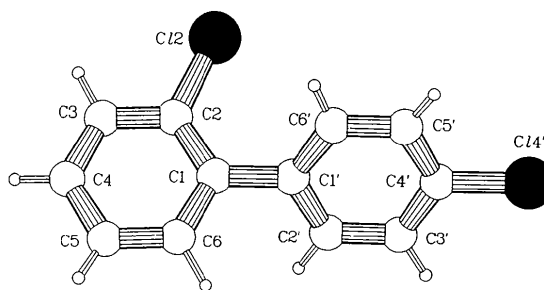


Fig. 1. *PLUTON* (Spek, 1982) drawing of the molecular structure of PCB 8 with adopted labeling.

respectively], are significantly less than the ideal value of 120° . Similar values of this angle have been reported for 2,2'-dichlorobiphenyl [116.2 (2) $^\circ$; Rømming, Seip & Øymo, 1974], 4,4'-dichlorobiphenyl [116.9 (4) and 118.2 (5) $^\circ$; Brock, Kuo & Levy, 1978] and biphenyl (118.9 $^\circ$; Trotter, 1961). The phenyl rings are planar to within 0.013 Å.

The C(4)—Cl(4') bond distance, 1.741 (4) Å, is nearly the same as those found in 2,2'-dichlorobiphenyl [1.741 (3) Å] and 4,4'-dichlorobiphenyl [1.733 (5) and 1.754 (5) Å], but the C(2)—Cl(2) bond distance, 1.781 (4) Å, is greater.

The dihedral angle between the two phenyl rings is 49.6 (1) $^\circ$. In 2,2'-dichlorobiphenyl (Rømming, Seip & Øymo, 1974) this angle is larger due to double *ortho* substitution (66.8 $^\circ$) and in 4,4'-dichlorobiphenyl (Brock, Kuo & Levy, 1978) these angles are smaller 38.7 and 42.1 $^\circ$ due to the absence of *ortho* substitution.

The crystallization method developed for PCB 35 (van der Sluis, Moes, Behm, Smykalla, Beurskens & Lenstra, 1990) has proven its usefulness for obtaining single crystals of PCB 8 as well. It is anticipated that the method will be generally applicable to other PCB's, thereby offering possibilities for determining their molecular structures by X-ray diffraction. The molecular geometry data provided by these analyses might prove useful in determining structure-activity relationships for toxicological studies of PCB's (cf. McKinney, Gottschalk & Pedersen, 1983).

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Conformation of the Xyl- β -(1 \rightarrow 2)-Man Glycosidic Linkage. Structure of 3,4,6-Tri-O-acetyl-1-O-methyl-2-O-(2,3,4-tri-O-acetyl- β -D-xylopyranosyl)- β -D-mannopyranose

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Abstract. C₂₄H₃₄O₁₆, *M_r* = 578.52, monoclinic, *P*2₁, *a* = 5.580 (2), *b* = 18.959 (4), *c* = 13.415 (3) Å, β = 92.71 (1) $^\circ$, *V* = 1417.6 (7) Å³, *Z* = 2, *D_x* = 1.355 g cm⁻³, λ (Mo *K* α) = 0.71073 Å, μ = 1.1 cm⁻¹, *F*(000) = 612, *T* = 295 K, *R* = 0.070 for 507 unique observed diffractometer data [*I* \geq 3 σ (*I*)]. Only very

small crystals could be obtained, but the resulting moderate quality of the diffraction data did not prevent the determination of the important conformational features of the title compound. Both glycopyranosyl moieties have the normal ⁴C₁ conformation. For the title compound, values of the β -(1 \rightarrow 2) glycosidic linkage angles ψ and φ are found to agree well with those observed in four related compounds as determined by NMR experiments.

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