

Hans-Joachim Lehmler,^a
Larry W. Robertson^{a*} and Sean
Parkin^b^aGraduate Center for Toxicology, University of
Kentucky, Lexington, KY 40536-0305, USA,
and ^bDepartment of Chemistry, University of
Kentucky, Lexington, KY 40506-0055, USACorrespondence e-mail:
lwrobe01@pop.uky.edu

Key indicators

Single-crystal X-ray study
 $T = 144\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.036
 wR factor = 0.075
Data-to-parameter ratio = 15.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

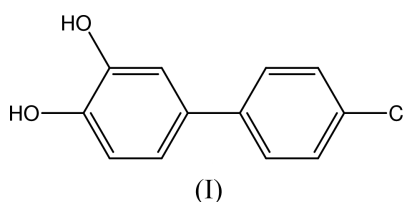
4-Chloro-3',4'-dihydroxybiphenyl

The crystal structure of a metabolite of 4-chlorobiphenyl (PCB 3), 4-chloro-3',4'-dihydroxybiphenyl ($\text{C}_{12}\text{H}_9\text{ClO}_2$), is described. The dihedral angle of the title compound is $43.1(3)^\circ$, which is in reasonable agreement with the calculated value of 37.2° .

Comment

Polychlorinated biphenyls (PCBs) were commercially manufactured and available as complex mixtures for use in transformers, capacitors and hydraulic fluids where they impart chemical stability and fire retardancy (Robertson & Hansen, 2001; Hansen, 1999). Their stability, lipophilic character and resistance to physical and biological decomposition contribute to the tendency of PCBs to accumulate in the food chain, where they persist and have become an environmental and human health hazard (Hansen, 1999). The varied mechanisms of PCB toxicity are still poorly understood, in part because the technical PCB products consist of many of the 209 possible PCB congeners.

PCBs are metabolized *in vivo* to hydroxy- and sulfur-containing metabolites. Hydroxylation proceeds primarily at the *meta* and *para* position either *via* an arene oxide or by direct insertion of a hydroxyl group (Letcher *et al.*, 2000). One of the many unanswered questions is how the three dimensional structure of these important PCB metabolites determines their biological and toxic effects. Few crystal structures



of PCB metabolites have been published, and improved knowledge about the three dimensional structure of PCB metabolites is urgently needed. 4-Chloro-3',4'-dihydroxybiphenyl, (I), is a major metabolite of 4-chlorobiphenyl (PCB 3) both *in vivo* and *in vitro* (McLean *et al.*, 1996). We report here the crystal structure of this important metabolite.

The solid-state dihedral angle between the two phenyl rings of PCBs and their metabolites appears to depend on the degree of chlorination in the *ortho* position. According to published data, mono-*ortho*, di-*ortho* and tetra-*ortho* substituted PCBs show a dihedral-angle range of $49\text{--}58$, $58\text{--}67$ and $86\text{--}87^\circ$, respectively (summarized by Miao *et al.*, 1997; see also Lehmler *et al.*, 2001; Mannila & Rissanen, 1994; Singh *et al.*, 1986). To the best of our knowledge, no crystal structures of metabolites of lower chlorinated PCBs such as 4-chlorobi-

Received 14 May 2001

Accepted 30 May 2001

Online 15 June 2001

phenyl have been published. The title compound shows a solid-state dihedral angle of 43.1 (3), which, as expected, is smaller than the dihedral angle of any *ortho* substituted PCB derivatives. The dihedral angle in aqueous solution was calculated to be 37.2°, which is close to the value observed in the solid state. The differences in the solid-state dihedral angle and the calculated angle are probably due to crystal packing effects.

Experimental

4-Chloro-3',4'-dihydroxybiphenyl was synthesized in as described by McLean *et al.* (1996). Pale-yellow irregular crystals were obtained from *n*-hexanes/chloroform; m.p. = 415–416 K. The dihedral angle of the title compound was calculated with *MM2** using GB/SA water solvent continuum as implemented by *MACROMODEL5.0* (Still *et al.*, 1990).

Crystal data

C ₁₂ H ₉ ClO ₂	Mo K α radiation
$M_r = 220.64$	Cell parameters from 4573 reflections
Orthorhombic, <i>Pna</i> 2 ₁	$\theta = 1.0\text{--}27.5^\circ$
$a = 18.358 (1) \text{ \AA}$	$\mu = 0.35 \text{ mm}^{-1}$
$b = 6.621 (2) \text{ \AA}$	$T = 144 (1) \text{ K}$
$c = 8.356 (3) \text{ \AA}$	Irregular fragment from large slab,
$V = 1015.7 (5) \text{ \AA}^3$	pale yellow
$Z = 4$	0.32 × 0.18 × 0.18 mm
$D_x = 1.443 \text{ Mg m}^{-3}$	

Data collection

Nonius KappaCCD diffractometer	$R_{\text{int}} = 0.038$
ω scans at fixed $\chi = 55^\circ$	$\theta_{\text{max}} = 27.4^\circ$
8374 measured reflections	$h = -23 \rightarrow 23$
2175 independent reflections	$k = -8 \rightarrow 8$
1886 reflections with $I > 2\sigma(I)$	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0296P)^2 + 0.0647P]$
$R[F^2 > 2\sigma(F^2)] = 0.036$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.075$	$(\Delta/\sigma)_{\text{max}} = 0.006$
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.23 \text{ e \AA}^{-3}$
2175 reflections	$\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$
137 parameters	Absolute structure: Flack (1983)
H-atom parameters constrained	Flack parameter = 0.51 (6)

Initial space group assignment as *Pna*2₁ was based upon systematic absences and intensity statistics. Space group *Pnma* was rejected because of the lack of a suitable solution and later by analysis of the structure. The assignment was confirmed by satisfactory solution and refinement in *Pna*2₁. There were no correlation coefficient matrix elements greater than 0.5. Nevertheless, the crystals are racemic twins, and this was accounted for using the *SHELXL TWIN* instruction. The hydroxyl H atoms were found in difference maps and

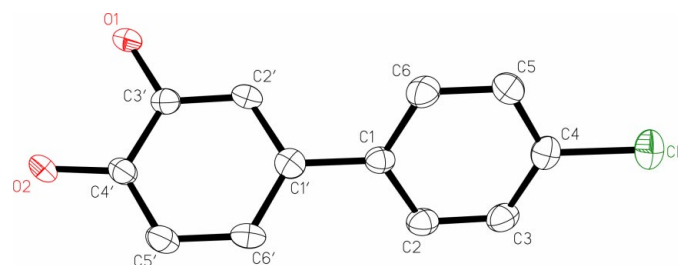


Figure 1

A view of 4-chloro-3',4'-dihydroxybiphenyl. Displacement ellipsoids are drawn at the 50% probability level.

refined using a riding model with U values set to $1.5U_{\text{iso}}$ of their corresponding O atoms.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in Siemens *SHELXTL* (Sheldrick, 1994); software used to prepare material for publication: *SHELX97* and local programs.

The authors would like to thank P. Willis for help with the calculation of the dihedral angles. This publication was made possible by grant number P42 ES 07380 from NIEHS.

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