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4-Chloro-3′,4′-dihydroxybiphenyl

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Key indicators

Single-crystal X-ray study
T = 144 K
Mean σ(C–C) = 0.003 Å
R factor = 0.036
wR factor = 0.075
Data-to-parameter ratio = 15.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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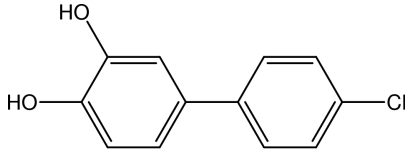
The crystal structure of a metabolite of 4-chlorobiphenyl (PCB 3), 4-chloro-3′,4′-dihydroxybiphenyl ($C_{12}H_9ClO_2$), is described. The dihedral angle of the title compound is 43.1 (3)°, which is in reasonable agreement with the calculated value of 37.2°.

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 retardency (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



(I)

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 49–58, 58–67 and 86–87°, 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-

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 *MACROMODEL*5.0 (Still *et al.*, 1990).

Crystal data

$C_{12}H_9ClO_2$
M_r = 220.64
Orthorhombic, $Pna2_1$
a = 18.358 (1) Å
b = 6.621 (2) Å
c = 8.356 (3) Å
V = 1015.7 (5) Å^3
Z = 4
D_x = 1.443 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4573 reflections
θ = 1.0–27.5°
μ = 0.35 mm^{-1}
T = 144 (1) K
Irregular fragment from large slab, pale yellow
0.32 × 0.18 × 0.18 mm

Data collection

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

Refinement

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

Initial space group assignment as $Pna2_1$ 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 $Pna2_1$. 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 refined using a riding model with U values set to $1.5U_{iso}$ of their corresponding O atoms.

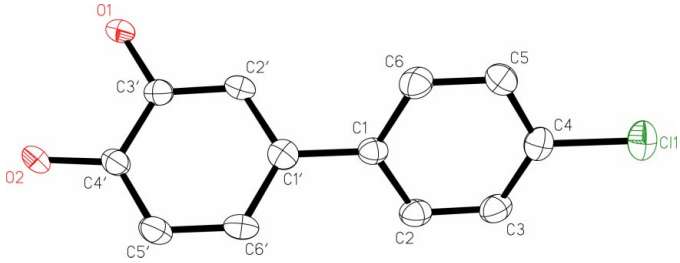


Figure 1
A view of 4-chloro-3′,4′-dihydroxybiphenyl. Displacement ellipsoids are drawn at the 50% probability level.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in Siemens *SHELXTL* (Sheldrick, 1994); software used to prepare material for publication: *SHELX*97 and local programs.

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