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3,3′,5,5′-Tetrabromo-4,4′-dihydroxybiphenyl

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Key indicators

Single-crystal X-ray study
T = 90 K
Mean σ(C–C) = 0.005 Å
R factor = 0.022
wR factor = 0.048
Data-to-parameter ratio = 16.7

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

The dihedral angle between the benzene rings in the title compound, $C_{13}H_6Cl_6O$, is 49.06 (8)°. The molecule has crystallographic twofold rotation symmetry.

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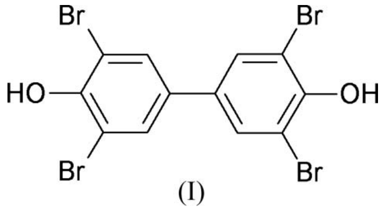
Comment

Brominated flame retardants (BFRs), which are used in a wide range of electrical and electronic equipment, are regarded as some of the most highly effective flame retardants used in the plastics industry today (Tange & Drohmann, 2005). Environmental studies have detected BFRs, such as polybrominated diphenylethers (PBDEs) or hexabromocyclododecane (HBCD), in a wide range of environmental matrixes and in human blood and tissue samples, thus raising human health concerns (Birnbaum & Staskal, 2004; de Boer, 2004; Domingo, 2004). To reduce the environmental risk associated with conventional BFRs, there is an interest in reactive BFRs, which are incorporated into the polymer, thus reducing their potential to leach out of the plastic and enter the environment (Borms & Georlette, 2004). The title compound, (I), is one example of such a reactive BFR.



(I)

The toxicity of (I) has been poorly investigated. Similar to other biphenyls of environmental relevance, such as polybrominated and polychlorinated biphenyls, the three-dimensional structure of the title compound will be one important determinant of its mechanisms of toxicity (Kania-Korwel *et al.*, 2004; Lehmler, Parkin & Robertson, 2002; Lehmler, Parkin & Robertson, 2001; Lehmler, Robertson & Parkin, 2001; Lehmler, Robertson *et al.*, 2002; McKinney & Singh, 1988). In particular, binding to molecular target sites will be determined by the dihedral angle between the two benzene rings. The crystal structure of (I) presented here provides an accurate depiction of its three-dimensional structure, thus adding to our understanding of its interactions with potential target sites in biological systems.

The molecule of (I) has crystallographic twofold rotation symmetry in the solid state. The dihedral angle between the benzene rings is 49.06 (8)°, which is surprisingly large compared with the calculated value of 38° in an aqueous solution [calculated with *MM2* using GB/SA water solvent

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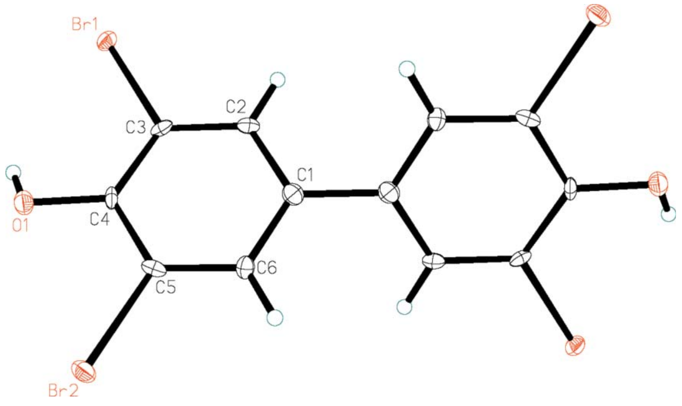

Figure 1
View of the title compound, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Unlabeled atoms are at the symmetry position $(2 - x, -y, -z)$.

continuum as implemented by *MACROMODEL* 5.0 (Still *et al.*, 1990)]. This is in contrast with other non-*ortho*-substituted brominated biphenyls, which typically display dihedral angles near or below the calculated angle in solution. For example, the two independent molecules in 4-bromobiphenyl have dihedral angles of 20.4 and 17.8° (Brock, 1980), whereas the two independent molecules in 4,4′-dibromobiphenyl have dihedral angles of 38 and 42° (Kronebusch *et al.*, 1976). The chloro analog of (I), 3,3′,5,5′-tetrachloro-4,4′-dihydroxybiphenyl, is even planar in the crystalline form (McKinney & Singh, 1988). This tendency of non-*ortho*-substituted biphenyl derivatives to adopt a more planar conformation in the crystal structure is due to stabilizing intermolecular interactions resulting from a stacking arrangement of the benzene rings (McKinney & Singh, 1988).

Molecules of the title compound form stacks along the *b* axis (Fig. 2). Within these stacks, the distance between the planes (defined by the C atoms in the benzene rings) is 3.526 (3) Å. This value is close to the distance of 3.49–3.54 Å between 3,3′,5,5′-tetrachloro-4,4′-dihydroxybiphenyl molecules (McKinney & Singh, 1988) and of 3.54 Å between the planes in layered aromatic hydrocarbons (Czikkely *et al.*, 1970), thus suggesting the presence of π interactions between 3,3′,5,5′-tetrabromo-4,4′-dihydroxybiphenyl molecules. Despite these intermolecular interactions, (I) does not adopt a planar conformation in the crystalline form. This observation suggests that, in comparison with related compounds such as 3,3′,5,5′-tetrachloro-4,4′-dihydroxybiphenyl, (I) may interact differently with molecular targets sites and, thus, may have different mechanism(s) of toxicity.

Experimental

The title compound was synthesized by bromination of 4,4′-dihydroxybiphenyl (5 g) with a slight excess of bromine in warm glacial acetic acid (150 ml). The reaction mixture was allowed to cool to ambient temperature and the crude product was filtered off. Colorless crystals were obtained upon crystallization from ethanol at 277 K.

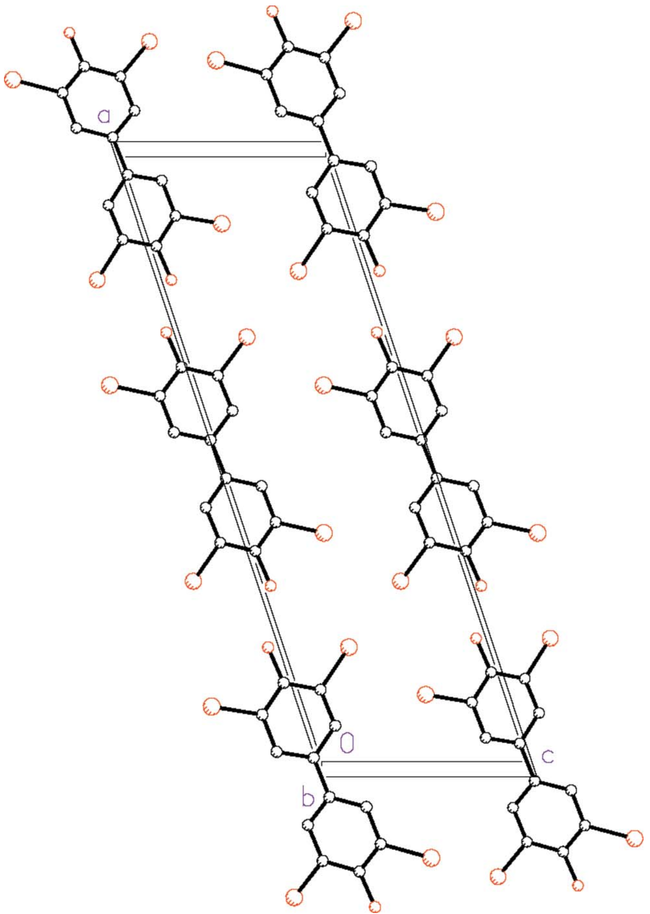

Figure 2
The crystal packing of (I), viewed approximately down the *b* axis, illustrating the stacking of the molecules along the *b* axis. H atoms have been omitted.

Crystal data

$C_{12}H_6Br_4O_2$
$M_r = 501.77$
Monoclinic, $C2$
$a = 23.4583$ (9) Å
$b = 3.8928$ (2) Å
$c = 7.5495$ (3) Å
$\beta = 108.376$ (2)°
$V = 654.26$ (5) Å^3
$Z = 2$
$D_x = 2.547$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3354 reflections
$\theta = 1.0$–27.5°
$\mu = 12.29$ mm^{-1}
$T = 90.0$ (2) K
Flattened rod, colorless
0.38 × 0.15 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
ω scans at fixed $\chi = 90°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{\min} = 0.183$, $T_{\max} = 0.541$
3668 measured reflections
1403 independent reflections
1341 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.037$
$\theta_{\max} = 27.4°$
$h = -27 \rightarrow 30$
$k = -5 \rightarrow 4$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.048$
$S = 1.07$
1403 reflections
84 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0142P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.005$
$\Delta\rho_{\max} = 0.55$ e Å^{-3}
$\Delta\rho_{\min} = -0.56$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0014 (4)
Absolute structure: Flack (1983), with 554 Friedel pairs
Flack parameter: 0.055 (17)

H atoms were found in difference Fourier maps and subsequently refined using a riding model, in which the H-atom coordinates were either determined geometrically ($C_{ar}-H$) or placed in the maximum electron density calculated in a toroid beyond the parent atom (O—H). Bond distances for H were fixed at $C_{ar}-H = 0.95$ Å and $O-H = 0.84$ Å, while $U_{iso}(H)$ values were defined as either $1.2U_{eq}$ or $1.5U_{eq}$ of the atom to which they were connected, respectively.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1994); software used to prepare material for publication: *SHELX97-2* (Sheldrick, 1997) and local procedures.

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