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3-(3,5-Dichlorophenyl)benzene-1,2-diol

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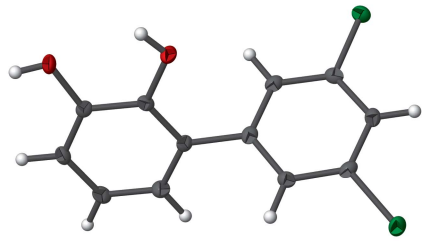
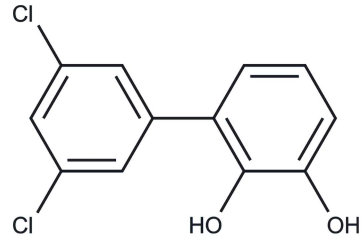
The title structure, $C_{12}H_8Cl_2O_2$, is a putative metabolite of 3,5-dichlorobiphenyl (PCB 14). The dihedral angle between the two benzene rings of the title compounds is 58.86 (4)°. In the crystal, it displays intra- and intermolecular O—H···O hydrogen bonding and intermolecular O—H···Cl hydrogen···chlorine interactions. The intermolecular interactions form a two-dimensional network parallel to (010).

3D view



Chemical scheme



Structure description

Humans are exposed to polychlorinated biphenyls (PCBs), a class of persistent organic pollutants, *via* their diet (Schecter *et al.*, 2010; Shin *et al.*, 2015) and by inhalation (Dhakal *et al.*, 2014; Hu *et al.*, 2010). In particular, lower chlorinated PCBs are oxidized by cytochrome P450 enzymes to the corresponding monohydroxylated and further to di-hydroxylated compounds (Grimm *et al.*, 2015; Kania-Korwel & Lehmler, 2016). Di-hydroxylated PCBs can be oxidized to reactive PCB quinones. Both dihydroxylated PCBs and the corresponding quinones are highly toxic, for example because they can promote oxidative stress or bind to nucleophilic sites on cellular macromolecules (Grimm *et al.*, 2015). To better understand the mechanism(s) of toxicity of these molecules in living organisms, it is important to characterize the three-dimensional structure of these PCB metabolites (Lehmler, Parkin *et al.*, 2002; Shaikh *et al.*, 2008).

3-(3,5-Dichlorophenyl)benzene-1,2-diol (Fig. 1) is a putative metabolite of PCB 14 (3,5-dichlorobiphenyl). The dihedral angle between the least-squares planes of the two benzene rings is 58.84 (4)°. For comparison, the dihedral angle of other PCB derivatives with one OH group *ortho* to the phenyl–phenyl bond ranges from 48 to 59.5° (Lehmler, Robertson *et al.*, 2002; Perrin *et al.*, 1987). Dihedral angles of PCB derivatives without any *ortho* chlorine substituents are in the range 4.9 to 43.9° (Dhakal *et al.*, 2019*a*), whereas PCB derivatives with one *ortho* chlorine substituent range from 47.34 to 59.92° (Dhakal

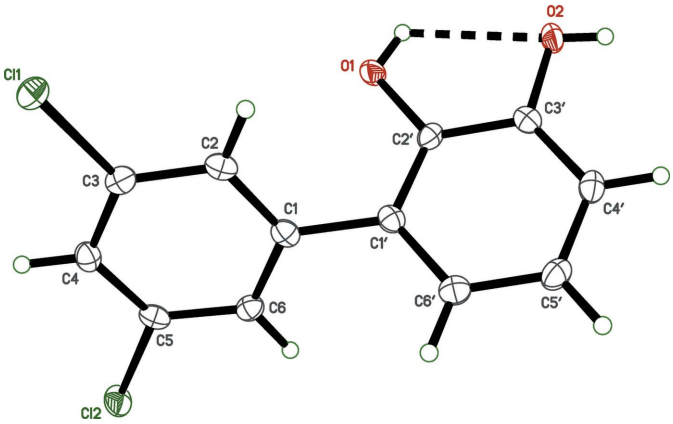


Figure 1
View of the title compound showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. The intramolecular hydrogen bond is shown as a dashed line. For information regarding the hydrogen-bond geometry, see Table 1.

et al., 2019*b*). The title compound crystallizes in the monoclinic space group $P2_1/c$ and displays intra- and intermolecular molecular O—H···O hydrogen bonding (Fig. 2, Table 1) and intermolecular O—H···Cl interactions (Fig. 3, Table 1). The intermolecular interactions lead to the formation of a two-dimensional network parallel to (010).

Synthesis and crystallization

The title compound was synthesized *via* a Suzuki cross-coupling reaction of 1-bromo-3,5-dichlorobenzene with 2,3-dimethoxyphenyl boronic acid in the presence of $Pd(PPh_3)_4$, and a 2 *M* aqueous solution of Na_2CO_3 followed by demethylation with BBr_3 (Bauer *et al.*, 1995). Crystals suitable for crystal-structure analysis were obtained by recrystallization from diethyl ether:hexanes (approximately 1:3, *v*/*v*) as described by Bauer *et al.* (1995).

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···Cl2^{i}	0.79	2.73	3.2538 (12)	126
O1—H1*O*···O2	0.79	2.20	2.6459 (16)	117
O2—H2*O*···O1^{ii}	0.77	2.02	2.7708 (16)	169

Symmetry codes: (i) $x+1, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_8Cl_2O_2$
M_r	255.08
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	90
a, *b*, *c* (Å)	6.2198 (3), 16.9271 (8), 10.4460 (5)
β (°)	101.013 (3)
V (Å^3)	1079.53 (9)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.58
Crystal size (mm)	0.28 × 0.25 × 0.25
Data collection	
Diffractometer	Nonius KappaCCD diffractometer
Absorption correction	Multi-scan (*SCALEPACK*; Otwinowski & Minor, 2006)
T_{min}, T_{max}	0.855, 0.869
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6641, 2470, 2029
R_{int}	0.037
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.033, 0.074, 1.04
No. of reflections	2470
No. of parameters	149
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.31, −0.28

Computer programs: *COLLECT* (Nonius, 1998), *SCALEPACK* and *DENZO-SMN* (Otwinowski & Minor, 2006), *XP* in *SHELXTL*, *SHELXS* and *SHELX* (Sheldrick, 2008), *SHELXL2018/3* (Sheldrick, 2015) and *CIFFIX* (Parkin, 2013).

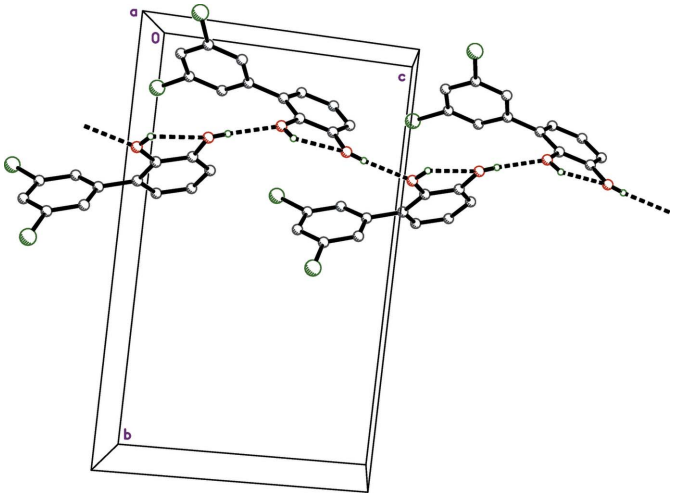


Figure 2
A packing plot viewed approximately along the *a* axis. Intra- and intermolecular hydrogen bonds are drawn as thick dashed lines. For information regarding the hydrogen-bond geometry, see Table 1.

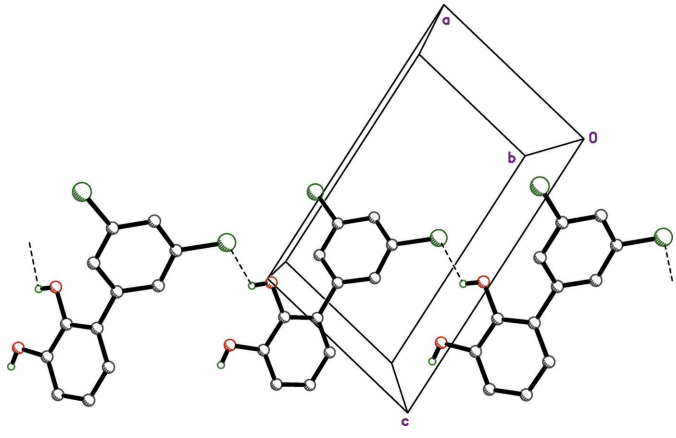


Figure 3
A packing plot viewed approximately along the *b* axis. Intermolecular hydrogen···chlorine interactions are drawn as thin dashed lines. For information regarding the hydrogen-bond geometry, see Table 1.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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Funding information

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full crystallographic data

IUCrData (2019). **4**, x191202 [https://doi.org/10.1107/S2414314619012021]

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Crystal data

$C_{12}H_8Cl_2O_2$
M_r = 255.08
Monoclinic, $P2_1/c$
a = 6.2198 (3) Å
b = 16.9271 (8) Å
c = 10.4460 (5) Å
β = 101.013 (3)°
V = 1079.53 (9) Å^3
Z = 4
$F(000)$ = 520
D_x = 1.569 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5954 reflections
θ = 1.0–27.5°
μ = 0.58 mm^{-1}
T = 90 K
Block, colourless
0.28 × 0.25 × 0.25 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed-tube
Detector resolution: 9.1 pixels mm^{-1}
φ and ω scans at fixed χ = 55°
Absorption correction: multi-scan (*Scalepack*; Otwinowski & Minor, 2006)
T_{min} = 0.855, T_{max} = 0.869
6641 measured reflections
2470 independent reflections
2029 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 27.5°, θ_{min} = 2.3°
h = −7→8
k = −21→21
l = −11→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.074
S = 1.04
2470 reflections
149 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0259P)^2 + 0.363P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Special details

Experimental. The crystal was mounted using polyisobutene oil on the tip of a fine glass fibre, which was fastened in a copper mounting pin with electrical solder. It was placed directly into the cold gas stream of a liquid-nitrogen based cryostat.
Diffraction data were collected with the crystal at 90K, which is standard practice in this laboratory for the majority of flash-cooled crystals.

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. H atoms were found in difference Fourier maps. Carbon-bound H atoms were subsequently included in the refinement using riding models, with constrained distances set to 0.95 Å ($C_{sp2}H$). Hydroxyl O—H distances were refined. U_{iso}(H) parameters were set to values of either $1.2U_{eq}$ or $1.5U_{eq}$ (OH only) of the attached atom.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	1.06252 (7)	0.51040 (2)	0.70416 (4)	0.02025 (12)
Cl2	0.30147 (7)	0.35884 (3)	0.52162 (4)	0.02112 (13)
O1	0.98156 (18)	0.29232 (7)	1.03073 (11)	0.0180 (3)
H1O	1.064 (3)	0.2671 (12)	1.0814 (15)	0.027*
O2	0.98599 (18)	0.25308 (7)	1.27641 (11)	0.0189 (3)
H2O	0.9675 (16)	0.2391 (11)	1.343 (2)	0.028*
C1	0.6550 (3)	0.38712 (9)	0.88020 (16)	0.0151 (4)
C2	0.8333 (3)	0.43045 (9)	0.85610 (16)	0.0156 (4)
H2	0.948128	0.444585	0.926113	0.019*
C3	0.8430 (3)	0.45292 (10)	0.72976 (16)	0.0157 (4)
C4	0.6808 (3)	0.43163 (9)	0.62473 (16)	0.0165 (4)
H4	0.689666	0.446218	0.538081	0.020*
C5	0.5060 (3)	0.38841 (10)	0.65118 (16)	0.0162 (4)
C6	0.4880 (3)	0.36663 (9)	0.77716 (16)	0.0154 (4)
H6	0.363533	0.338240	0.792445	0.018*
C1′	0.6450 (3)	0.36330 (9)	1.01653 (16)	0.0146 (3)
C2′	0.8112 (3)	0.31794 (9)	1.08832 (16)	0.0140 (3)
C3′	0.8095 (3)	0.29685 (9)	1.21704 (16)	0.0145 (4)
C4′	0.6384 (3)	0.32091 (10)	1.27509 (16)	0.0171 (4)
H4′	0.636353	0.307008	1.362959	0.020*
C5′	0.4694 (3)	0.36558 (10)	1.20385 (17)	0.0193 (4)
H5′	0.351157	0.382046	1.243162	0.023*
C6′	0.4723 (3)	0.38623 (10)	1.07594 (17)	0.0190 (4)
H6′	0.355134	0.416388	1.028058	0.023*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0179 (2)	0.0205 (2)	0.0225 (2)	−0.00488 (18)	0.00431 (17)	0.00181 (18)
Cl2	0.0210 (2)	0.0269 (2)	0.0137 (2)	−0.00667 (18)	−0.00082 (17)	−0.00019 (17)
O1	0.0150 (6)	0.0252 (7)	0.0139 (6)	0.0082 (5)	0.0030 (5)	0.0026 (5)
O2	0.0195 (6)	0.0251 (7)	0.0123 (6)	0.0048 (5)	0.0041 (5)	0.0055 (5)
C1	0.0169 (8)	0.0130 (8)	0.0150 (8)	0.0045 (7)	0.0022 (7)	−0.0008 (7)
C2	0.0149 (8)	0.0138 (8)	0.0170 (8)	0.0020 (7)	0.0000 (7)	−0.0026 (7)
C3	0.0151 (8)	0.0113 (8)	0.0211 (9)	0.0004 (7)	0.0045 (7)	−0.0002 (7)
C4	0.0193 (9)	0.0152 (8)	0.0152 (8)	0.0022 (7)	0.0039 (7)	0.0018 (7)
C5	0.0145 (8)	0.0158 (8)	0.0164 (8)	0.0014 (7)	−0.0018 (7)	−0.0021 (7)
C6	0.0143 (8)	0.0140 (8)	0.0183 (9)	0.0003 (7)	0.0041 (7)	−0.0001 (7)

C1′	0.0157 (8)	0.0138 (8)	0.0135 (8)	−0.0017 (7)	0.0008 (7)	−0.0011 (7)
C2′	0.0139 (8)	0.0154 (8)	0.0134 (8)	−0.0024 (7)	0.0045 (7)	−0.0047 (7)
C3′	0.0156 (8)	0.0116 (8)	0.0153 (8)	−0.0019 (7)	0.0006 (7)	−0.0002 (7)
C4′	0.0201 (9)	0.0176 (8)	0.0142 (8)	−0.0041 (7)	0.0052 (7)	−0.0006 (7)
C5′	0.0182 (9)	0.0215 (9)	0.0198 (9)	0.0010 (8)	0.0079 (7)	−0.0029 (7)
C6′	0.0171 (9)	0.0201 (9)	0.0199 (9)	0.0030 (7)	0.0040 (7)	0.0005 (7)

Geometric parameters (Å, º)

Cl1—C3	1.7386 (17)	C4—H4	0.9500
Cl2—C5	1.7445 (16)	C5—C6	1.392 (2)
O1—C2′	1.3842 (18)	C6—H6	0.9500
O1—H1O	0.79 (2)	C1′—C2′	1.387 (2)
O2—C3′	1.3704 (19)	C1′—C6′	1.395 (2)
O2—H2O	0.77 (2)	C2′—C3′	1.393 (2)
C1—C6	1.390 (2)	C3′—C4′	1.383 (2)
C1—C2	1.392 (2)	C4′—C5′	1.390 (2)
C1—C1′	1.493 (2)	C4′—H4′	0.9500
C2—C3	1.386 (2)	C5′—C6′	1.385 (2)
C2—H2	0.9500	C5′—H5′	0.9500
C3—C4	1.389 (2)	C6′—H6′	0.9500
C4—C5	1.381 (2)		
C2′—O1—H1O	109.5	C5—C6—H6	120.6
C3′—O2—H2O	109.5	C2′—C1′—C6′	118.12 (15)
C6—C1—C2	119.67 (15)	C2′—C1′—C1	120.19 (15)
C6—C1—C1′	120.70 (15)	C6′—C1′—C1	121.69 (15)
C2—C1—C1′	119.64 (15)	O1—C2′—C1′	119.45 (14)
C3—C2—C1	119.85 (15)	O1—C2′—C3′	119.12 (14)
C3—C2—H2	120.1	C1′—C2′—C3′	121.42 (15)
C1—C2—H2	120.1	O2—C3′—C4′	125.29 (15)
C2—C3—C4	121.61 (15)	O2—C3′—C2′	114.97 (14)
C2—C3—Cl1	118.58 (13)	C4′—C3′—C2′	119.73 (15)
C4—C3—Cl1	119.81 (13)	C3′—C4′—C5′	119.48 (15)
C5—C4—C3	117.39 (15)	C3′—C4′—H4′	120.3
C5—C4—H4	121.3	C5′—C4′—H4′	120.3
C3—C4—H4	121.3	C6′—C5′—C4′	120.41 (16)
C4—C5—C6	122.57 (15)	C6′—C5′—H5′	119.8
C4—C5—Cl2	118.82 (13)	C4′—C5′—H5′	119.8
C6—C5—Cl2	118.61 (13)	C5′—C6′—C1′	120.82 (16)
C1—C6—C5	118.87 (15)	C5′—C6′—H6′	119.6
C1—C6—H6	120.6	C1′—C6′—H6′	119.6
C6—C1—C2—C3	0.1 (2)	C2—C1—C1′—C6′	121.12 (18)
C1′—C1—C2—C3	−179.80 (15)	C6′—C1′—C2′—O1	178.10 (14)
C1—C2—C3—C4	−1.6 (2)	C1—C1′—C2′—O1	−2.6 (2)
C1—C2—C3—Cl1	177.41 (12)	C6′—C1′—C2′—C3′	−1.3 (2)
C2—C3—C4—C5	1.3 (2)	C1—C1′—C2′—C3′	178.05 (15)

Cl1—C3—C4—C5	−177.66 (12)	O1—C2′—C3′—O2	1.7 (2)
C3—C4—C5—C6	0.4 (2)	C1′—C2′—C3′—O2	−178.96 (14)
C3—C4—C5—Cl2	−178.77 (12)	O1—C2′—C3′—C4′	−178.90 (14)
C2—C1—C6—C5	1.6 (2)	C1′—C2′—C3′—C4′	0.5 (2)
C1′—C1—C6—C5	−178.52 (15)	O2—C3′—C4′—C5′	179.68 (15)
C4—C5—C6—C1	−1.9 (2)	C2′—C3′—C4′—C5′	0.3 (2)
Cl2—C5—C6—C1	177.29 (12)	C3′—C4′—C5′—C6′	−0.3 (3)
C6—C1—C1′—C2′	121.97 (18)	C4′—C5′—C6′—C1′	−0.5 (3)
C2—C1—C1′—C2′	−58.2 (2)	C2′—C1′—C6′—C5′	1.3 (3)
C6—C1—C1′—C6′	−58.8 (2)	C1—C1′—C6′—C5′	−178.00 (16)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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