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Crystal structure of 5,5′-dibromo-3,3′-di-*tert*-butyl-6,6′-dimethylbiphenyl-2,2′-diol

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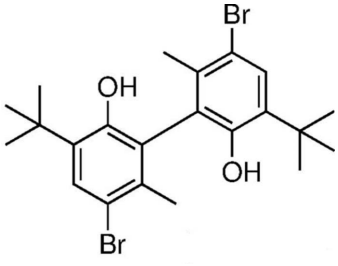
The whole molecule of the title compound, $C_{22}H_{28}Br_2O_2$, is generated by twofold rotation symmetry. The dihedral angle of the biphenyl moiety is 85.05 (11)°. The hydroxy groups show intramolecular O—H···π interactions without any other hydrogen-bond acceptors. In the crystal, there are no other significant intermolecular interactions present.

Keywords: crystal structure; biphenyl; axial chirality; O—H···π interactions.

CCDC reference: 1056738

1. Related literature

For the synthesis of the title compound using a transition-metal catalyst, see: Kubota *et al.* (2012). For the determination of the absolute configuration of the corresponding (+)-chloro derivative, *viz.* *S*, see: Gutierrez *et al.* (2010). For the crystal structure of a similar compound, *i.e.* 5,5′-dimethoxy-6,6′-dimethylbiphenyl-2,2′-diol dichloromethane solvate, see: Guo *et al.* (2011).



2. Experimental

2.1. Crystal data

$C_{22}H_{28}Br_2O_2$
M_r = 484.24
Orthorhombic, *Pba*2
a = 7.3680 (5) Å
b = 22.4243 (14) Å
c = 6.6148 (4) Å
V = 1092.91 (12) Å^3
Z = 2
Mo *K*α radiation
μ = 3.72 mm^{-1}
T = 299 K
0.16 × 0.15 × 0.10 mm

2.2. Data collection

Bruker D8 VENTURE diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2014)
T_{min} = 0.630, T_{max} = 0.773
9406 measured reflections
1966 independent reflections
1615 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.065
S = 1.06
1966 reflections
123 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Absolute structure: Flack *x* determined using 621 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.034 (9)

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

Cg is the centroid of benzene ring C3–C8.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···*Cg*^{i}	0.82	2.54	3.047 (5)	122

Symmetry code: (i) $-x+2, -y+2, z$.

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL2014* and *publCIF* (Westrip, 2010).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SU5104).

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supporting information

Acta Cryst. (2015). E**71**, o278–o279 [doi:10.1107/S2056989015006313]

Crystal structure of 5,5′-dibromo-3,3′-di-*tert*-butyl-6,6′-dimethylbiphenyl-2,2′-diol

Rika Obata, Shigeru Ohba, Yasuaki Einaga and Shigeru Nishiyama

S1. Synthesis and crystallization

The synthesis of the title compound, (I), is described in Fig. 2. It was prepared using iodine-mediated coupling method from 4-bromo-2-*tert*-butyl-5-methylphenol. To the solution of 4-bromo-2-*tert*-butyl-5-methylphenol (0.242 g, 1 mmol) in dichloromethane (1 mL) was added *N*-iodosuccinimide (abbreviated to NIS, 0.225 g, 1 mmol) and 3% H_2O_2 (1 mL). After shaking (200 rpm) the reaction mixture for 24 h at room temperature, it was poured into saturated $Na_2S_2O_3$ solution, and extracted with chloroform. The organic layer was washed with saturated NaCl and dried over anhydrous Na_2SO_4. The mixture was evaporated and purified by silica-gel column chromatography to give title compound (I) as white solid (yield: 0.138 g, 57%). ^{1}H-NMR (400 MHz, $CDCl_3$) 1.32 (18H, s), 1.92 (6H, s), 4.80 (2H, s), 7.47 (2H, s). Tof-MS ES(-) Anal. 481.0357, Calcd. 481.0378 for $C_{22}H_{27}O_2Br_2$. The crystals were grown by slow evaporation from a toluene/*n*-hexane (1/4) solution.

S2. Refinement

Crystal data, data collection and structure refinement details are summarized in the experimental table. The hydroxyl H atom was located from a difference Fourier map but was refined as riding (AFIX 147) with U_{iso}(H) = 1.5U_{eq}(O). C-Bound H atoms were included in calculated positions and refined as riding: C—H = 0.93–0.96 Å with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C) for other H atoms.

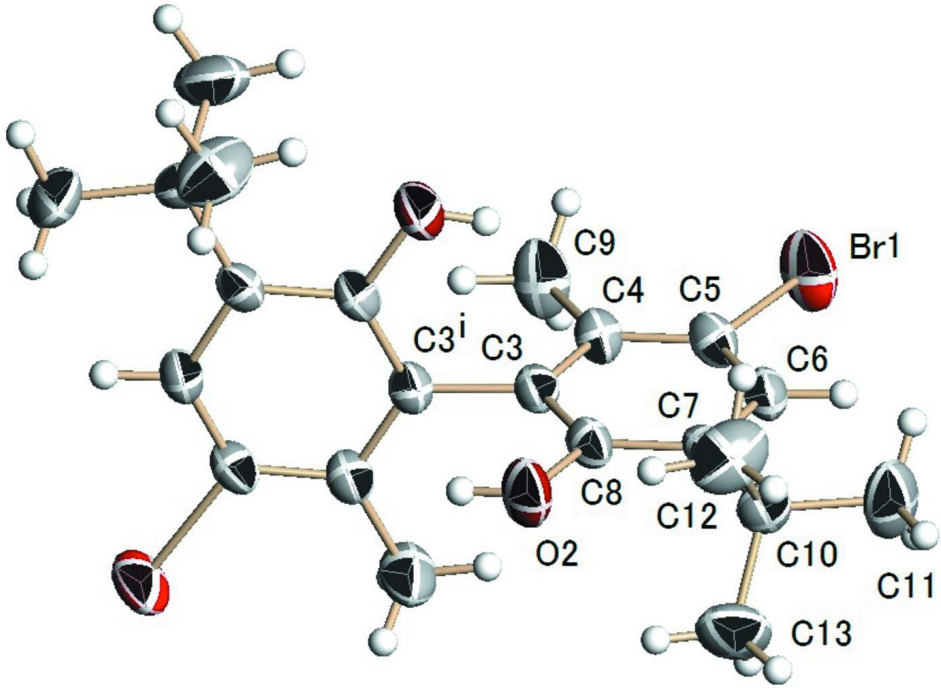

Figure 1

The molecular structure of the title compound, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

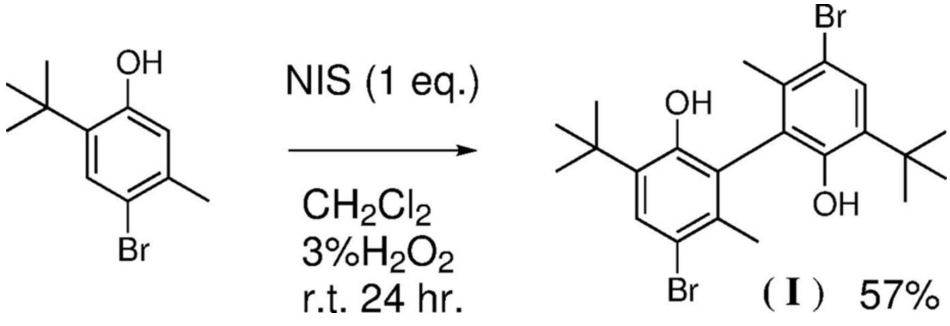

Figure 2

The synthesis of the title compound, (I).

5,5′-Dibromo-3,3′-di-*tert*-butyl-6,6′-dimethylbiphenyl-2,2′-diol

Crystal data

$C_{22}H_{28}Br_2O_2$
M_r = 484.24
Orthorhombic, *Pba*2
a = 7.3680 (5) Å
b = 22.4243 (14) Å
c = 6.6148 (4) Å
V = 1092.91 (12) Å^3
Z = 2
F(000) = 492

D_x = 1.472 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4121 reflections
θ = 2.9–23.6°
μ = 3.72 mm^{-1}
T = 299 K
Prism, colourless
0.16 × 0.15 × 0.10 mm

Data collection

Bruker D8 VENTURE diffractometer
Radiation source: fine-focus sealed tube
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2014)
T_{min} = 0.630, T_{max} = 0.773
9406 measured reflections
1966 independent reflections
1615 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 25.3°, θ_{min} = 2.9°
h = −8→8
k = −26→26
l = −7→7

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.065
S = 1.06
1966 reflections
123 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0176P)^2 + 0.3778P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Absolute structure: Flack x determined using 621 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.034 (9)

Special details

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

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

	x	y	z	U_{iso}*/U_{eq}
Br1	1.18668 (8)	0.81211 (2)	0.48288 (15)	0.0681 (2)
O2	0.7528 (4)	0.98204 (13)	0.9897 (9)	0.0576 (8)
H2	0.7777	1.0166	0.9607	0.086*
C3	0.9856 (6)	0.96676 (17)	0.7429 (7)	0.0352 (10)
C4	1.0903 (6)	0.9290 (2)	0.6223 (7)	0.0388 (11)
C5	1.0536 (6)	0.8689 (2)	0.6397 (7)	0.0399 (11)
C6	0.9212 (6)	0.84644 (19)	0.7649 (7)	0.0394 (11)
H6	0.9023	0.8054	0.7685	0.047*
C7	0.8150 (6)	0.88292 (19)	0.8859 (7)	0.0360 (10)
C8	0.8518 (6)	0.94415 (19)	0.8707 (7)	0.0370 (11)
C9	1.2322 (7)	0.9538 (2)	0.4852 (15)	0.0650 (14)
H9A	1.1993	0.9460	0.3473	0.098*
H9B	1.3467	0.9353	0.5143	0.098*
H9C	1.2417	0.9960	0.5058	0.098*
C10	0.6668 (5)	0.8582 (2)	1.0234 (8)	0.0428 (15)
C11	0.6564 (7)	0.7905 (2)	1.0111 (14)	0.074 (2)
H11A	0.6243	0.7789	0.8761	0.111*
H11B	0.5661	0.7762	1.1039	0.111*
H11C	0.7722	0.7737	1.0456	0.111*

C12	0.7053 (8)	0.8746 (3)	1.2449 (9)	0.0756 (18)
H12A	0.8260	0.8623	1.2802	0.113*
H12B	0.6195	0.8548	1.3311	0.113*
H12C	0.6944	0.9170	1.2619	0.113*
C13	0.4827 (6)	0.8829 (2)	0.9625 (15)	0.0760 (17)
H13A	0.4791	0.9249	0.9894	0.114*
H13B	0.3893	0.8632	1.0387	0.114*
H13C	0.4634	0.8760	0.8208	0.114*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0866 (4)	0.0458 (3)	0.0718 (4)	0.0118 (2)	0.0311 (4)	−0.0118 (4)
O2	0.0646 (19)	0.0366 (16)	0.072 (2)	0.0049 (14)	0.018 (3)	−0.009 (3)
C3	0.040 (3)	0.030 (2)	0.036 (3)	0.0016 (19)	−0.004 (2)	0.001 (2)
C4	0.048 (3)	0.033 (3)	0.035 (3)	0.003 (2)	0.002 (2)	0.000 (2)
C5	0.048 (3)	0.035 (3)	0.037 (3)	0.009 (2)	0.003 (2)	−0.003 (2)
C6	0.046 (3)	0.028 (2)	0.045 (3)	0.002 (2)	−0.002 (2)	−0.002 (2)
C7	0.036 (3)	0.034 (2)	0.038 (2)	0.008 (2)	−0.005 (2)	−0.002 (2)
C8	0.042 (3)	0.031 (3)	0.038 (2)	0.006 (2)	0.000 (2)	−0.005 (2)
C9	0.084 (3)	0.048 (3)	0.063 (3)	0.003 (2)	0.033 (5)	−0.003 (5)
C10	0.035 (3)	0.045 (3)	0.048 (4)	−0.0010 (19)	0.008 (3)	0.003 (2)
C11	0.070 (3)	0.048 (3)	0.104 (6)	−0.013 (2)	0.036 (5)	0.008 (4)
C12	0.078 (4)	0.099 (5)	0.049 (4)	−0.021 (4)	0.010 (3)	0.002 (3)
C13	0.039 (3)	0.086 (4)	0.103 (5)	0.005 (2)	0.012 (4)	0.020 (5)

Geometric parameters (Å, º)

Br1—C5	1.913 (4)	C9—H9B	0.9600
O2—C8	1.369 (6)	C9—H9C	0.9600
O2—H2	0.8200	C10—C13	1.520 (7)
C3—C8	1.394 (6)	C10—C11	1.521 (7)
C3—C4	1.396 (6)	C10—C12	1.537 (8)
C3—C3^{i}	1.506 (8)	C11—H11A	0.9600
C4—C5	1.379 (6)	C11—H11B	0.9600
C4—C9	1.491 (8)	C11—H11C	0.9600
C5—C6	1.375 (6)	C12—H12A	0.9600
C6—C7	1.386 (6)	C12—H12B	0.9600
C6—H6	0.9300	C12—H12C	0.9600
C7—C8	1.403 (6)	C13—H13A	0.9600
C7—C10	1.526 (6)	C13—H13B	0.9600
C9—H9A	0.9600	C13—H13C	0.9600
C8—O2—H2	109.5	C13—C10—C11	107.7 (4)
C8—C3—C4	121.1 (4)	C13—C10—C7	110.4 (5)
C8—C3—C3^{i}	117.3 (4)	C11—C10—C7	111.5 (4)
C4—C3—C3^{i}	121.6 (4)	C13—C10—C12	109.3 (5)
C5—C4—C3	115.9 (4)	C11—C10—C12	107.4 (5)

C5—C4—C9	123.5 (4)	C7—C10—C12	110.5 (4)
C3—C4—C9	120.5 (4)	C10—C11—H11A	109.5
C6—C5—C4	123.2 (4)	C10—C11—H11B	109.5
C6—C5—Br1	116.5 (3)	H11A—C11—H11B	109.5
C4—C5—Br1	120.3 (3)	C10—C11—H11C	109.5
C5—C6—C7	122.2 (4)	H11A—C11—H11C	109.5
C5—C6—H6	118.9	H11B—C11—H11C	109.5
C7—C6—H6	118.9	C10—C12—H12A	109.5
C6—C7—C8	115.3 (4)	C10—C12—H12B	109.5
C6—C7—C10	122.2 (4)	H12A—C12—H12B	109.5
C8—C7—C10	122.5 (4)	C10—C12—H12C	109.5
O2—C8—C3	120.0 (4)	H12A—C12—H12C	109.5
O2—C8—C7	117.6 (4)	H12B—C12—H12C	109.5
C3—C8—C7	122.4 (4)	C10—C13—H13A	109.5
C4—C9—H9A	109.5	C10—C13—H13B	109.5
C4—C9—H9B	109.5	H13A—C13—H13B	109.5
H9A—C9—H9B	109.5	C10—C13—H13C	109.5
C4—C9—H9C	109.5	H13A—C13—H13C	109.5
H9A—C9—H9C	109.5	H13B—C13—H13C	109.5
H9B—C9—H9C	109.5		

C8—C3—C4—C5	−0.5 (6)	C3^{i}—C3—C8—O2	0.0 (6)
C3^{i}—C3—C4—C5	178.5 (4)	C4—C3—C8—C7	0.1 (7)
C8—C3—C4—C9	179.6 (5)	C3^{i}—C3—C8—C7	−179.0 (4)
C3^{i}—C3—C4—C9	−1.4 (7)	C6—C7—C8—O2	−178.9 (4)
C3—C4—C5—C6	0.9 (7)	C10—C7—C8—O2	1.9 (6)
C9—C4—C5—C6	−179.3 (6)	C6—C7—C8—C3	0.1 (6)
C3—C4—C5—Br1	179.9 (3)	C10—C7—C8—C3	−179.1 (4)
C9—C4—C5—Br1	−0.2 (7)	C6—C7—C10—C13	−118.6 (5)
C4—C5—C6—C7	−0.8 (7)	C8—C7—C10—C13	60.5 (6)
Br1—C5—C6—C7	−179.8 (3)	C6—C7—C10—C11	1.0 (6)
C5—C6—C7—C8	0.3 (7)	C8—C7—C10—C11	−179.8 (5)
C5—C6—C7—C10	179.4 (4)	C6—C7—C10—C12	120.4 (5)
C4—C3—C8—O2	179.0 (4)	C8—C7—C10—C12	−60.5 (6)

Symmetry code: (i) −*x*+2, −*y*+2, *z*.

Hydrogen-bond geometry (Å, º)

Cg is the centroid of benzene ring C3–C8.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···*Cg*^{i}	0.82	2.54	3.047 (5)	122

Symmetry code: (i) −*x*+2, −*y*+2, *z*.