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(–)-(P)-N,N′-Bis[(5-bromo-2-hydroxy-phenyl)methylidene]-6,6′-dimethyl-1,1′-biphenyl-2,2′-dimethanamine

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Key indicators

Single-crystal X-ray study

T = 173 K

Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$

R factor = 0.048

wR factor = 0.105

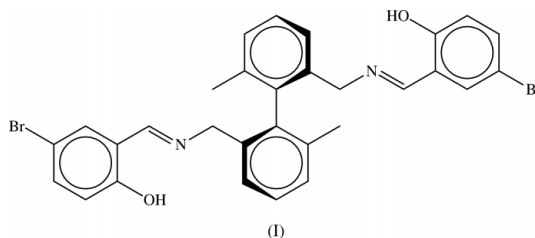
Data-to-parameter ratio = 18.0

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

The absolute configuration of the enantiopure, axially chiral title compound, $\text{C}_{30}\text{H}_{26}\text{Br}_2\text{N}_2\text{O}_2$, has been determined. The molecule has approximate C_2 symmetry and intramolecular $\text{O}-\text{H} \cdots \text{N}$ hydrogen bonds occur within each of the imine side chains of the molecule. The planes of the biphenyl aromatic rings are bent significantly from the axis of the central $\text{C}-\text{C}$ bond.

Comment

Axially chiral compounds containing a biphenyl moiety have been used extensively as chiral auxiliaries for asymmetric synthesis (Schmid *et al.*, 1988), and we have been using some new axially chiral diimine ligands in asymmetric catalysis (Keller & Rippert, 1999). The title compound, (I), was synthesized by a condensation reaction between enantiomerically pure (P)-6,6′-dimethyl-1,1′-biphenyl-2,2′-dimethylamine and 5-bromosalicylaldehyde. The structure of (I) was determined in order to confirm the absolute configuration of the chiral axis. With this structure in hand, the correlation between the Cotton effect displayed by the CD-spectrum of (I) and those of related biphenyl compounds that we have synthesized could then be used to deduce the absolute configurations of these latter compounds (Keller & Rippert, 1999).



The refined value of the absolute structure parameter [0.013 (9); Flack & Bernardinelli, 2000] unambiguously confirmed that the title compound is enantiopure and that the chiral axis has the P-configuration. The angle between the planes of the two phenyl rings of the 1,1′-biphenyl moiety is $79.88 (14)^\circ$, where the acute angle is subtended by the two imine substituents. The ring planes, particularly that defined by C7–C12, are bent slightly away from the C1–C7 axis, so that neither atom C4 nor C10 lies on the continuation of this axis. Atoms C7 and C10 lie $0.104 (7)$ and $0.294 (12) \text{ \AA}$, respectively, from the mean plane through the ring defined by atoms C1–C6, while atoms C1 and C4 lie $0.026 (8)$ and $0.036 (12) \text{ \AA}$, respectively, from the mean plane through the ring defined by atoms C7–C12. An analysis of the conformations adopted by the biphenyl moieties in 682 error-free ordered organic structures stored in the Cambridge Structural

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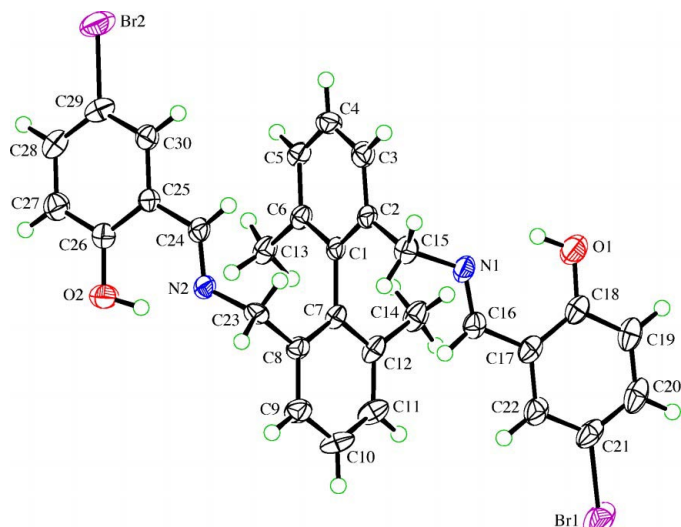


Figure 1

View of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

Database (Version 5.24 of November, 2002; Allen, 2002) indicated that the bending of the ring planes away from the C1–C7 axis follows a normal distribution pattern, with no or very little deviation being displayed by the largest proportion of the structures, but that deviations of the magnitude observed for (I) are also quite common.

The imine groups are almost coplanar with their adjacent 5-bromo-2-hydroxyphenyl groups. The r.m.s. deviation of atoms N1, O1, Br1 and C16–C22 from their mean plane is 0.022 Å, with the maximum deviation being 0.041 (3) Å for atom N1. This planar system makes an angle of 76.84 (12)° with the plane of the adjacent phenyl ring defined by atoms C1–C6. In the other corresponding phenylimine moiety, the r.m.s. deviation of the constituent atoms from their mean plane is 0.020 Å, with the maximum deviation being 0.044 (3) Å for atom N2, and the plane makes an angle of 78.45 (11)° with the plane of the adjacent phenyl ring defined by atoms C7–C12. The planes of the phenylimine moieties lie such that the O···Br axes are almost parallel to the biphenyl C4···C10 axis. When viewed along the C4···C10 axis, the molecule has a distinct 'W' conformation. The molecule has approximate C_2 symmetry about an axis passing perpendicularly through the mid-point of the C1–C7 bond. The r.m.s. deviation of the atoms of the molecule from perfect C_2 symmetry is 0.158 Å. Within each phenylimine moiety, the hydroxy group forms an intramolecular O–H···N hydrogen bond with the imine N atom (Table 1), thereby creating a six-membered loop which has a graph-set motif of $S(6)$ (Bernstein *et al.*, 1995).

Experimental

The synthesis of the title compound has been described by Keller & Rippert (1999); m.p. 360 K. Spectroscopic analysis: $[\alpha]_D^{25} -20^\circ$ (c 1.05, ethanol); CD spectrum (c 3.45×10^{-3} , ethanol, λ , nm): 217 (–26.5), 235 (26.9), 254 (9.8), 263 (7.9), 318 (0.8), 349 (–0.25). Suitable crystals were obtained by cooling a saturated solution in ethanol to 273 K.

Crystal data

$C_{30}H_{26}Br_2N_2O_2$
 $M_r = 606.35$
 Orthorhombic, $P2_12_12_1$
 $a = 17.496$ (5) Å
 $b = 18.590$ (2) Å
 $c = 8.074$ (7) Å
 $V = 2626$ (2) Å³
 $Z = 4$
 $D_x = 1.534$ Mg m^{–3}

Mo K α radiation
 Cell parameters from 24 reflections
 $\theta = 17.0$ – 19.5°
 $\mu = 3.12$ mm^{–1}
 $T = 173$ (1) K
 Prism, yellow
 $0.38 \times 0.28 \times 0.23$ mm

Data collection

Rigaku AFC-5R diffractometer
 ω – 2θ scans
 Absorption correction: analytical (de Meulenaer & Tompa, 1965)
 $T_{\min} = 0.384$, $T_{\max} = 0.632$
 8236 measured reflections
 6049 independent reflections
 3460 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.047$
 $\theta_{\text{max}} = 27.6^\circ$
 $h = -22 \rightarrow 22$
 $k = -24 \rightarrow 24$
 $l = -10 \rightarrow 10$
 3 standard reflections every 150 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.106$
 $S = 0.98$
 6049 reflections
 336 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.41$ e Å^{–3}
 $\Delta\rho_{\text{min}} = -0.59$ e Å^{–3}
 Absolute structure: Flack & Bernardinelli (2000); 2630 Friedel pairs
 Flack parameter = 0.013 (9)

Table 1

Hydrogen-bonding geometry (Å, °).

D–H···A	D–H	H···A	D···A	D–H···A
O1–H1···N1	0.91 (5)	1.88 (6)	2.627 (6)	138 (5)
O2–H2···N2	0.90 (5)	1.80 (5)	2.588 (5)	145 (4)

The hydroxy H atoms were located in a difference Fourier map and their positions were refined freely along with individual isotropic displacement parameters. The methyl H atoms were constrained to an ideal geometry (C–H = 0.98 Å), with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$, but were allowed to rotate freely about the C–C bonds. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C–H distances in the range 0.95–0.99 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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