A chiral photochromic Schiff base: (*R*)-4-bromo-2-[(1-phenylethyl)iminomethyl]phenol

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The title chiral photochromic Schiff base compound, $C_{15}H_{14}BrNO$, was synthesized from (*R*)-1-phenylethylamine and 5-bromosalicylaldehyde. The molecule is the phenol–imine tautomer, the C=N and N—C bond distances being 1.261 (7) and 1.482 (7) Å, respectively. There is an intramolecular O—H···N hydrogen bond with an O···N distance of 2.593 (7) Å.

Comment

Schiff base compounds are one of the most extensively used class of ligands in the field of coordination chemistry (Yamada, 1999). Because of structural flexibility and their application for switching materials, we have investigated Schiff base Cu^{II} or Ni^{II} complexes from the point of view of thermally induced structural phase transitions in the solid state (Akitsu & Einaga, 2004), structural change by occlusion of solvents (Akitsu & Einaga, 2005*a*), and chiral conformational change in solution induced by a photochromic solute (Akitsu & Einaga, 2005*b*, 2006). On the other hand, free Schiff base ligands (Akitsu *et al.*, 2004) have been also studied with respect to photochromic (and thermochromic) fluorescence materials (Hadjoudis *et al.*, 2004) and photochromic non-linear optical materials (Sliwa *et al.*, 2005). In order to clarify the relationship between structure and function such as tautomerism and photochromism (Hadjoudis *et al.*, 1987), the crystal structure of the title compound, (I), has been determined.

(I)
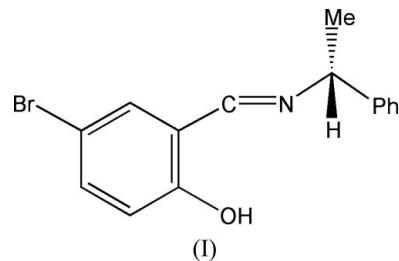
The crystal structure of (I) is isomorphous with that of the Cl derivative (Santoni & Rehder, 2004), although the reported structure is of the *S* enantiomer. The molecule of (I) (Fig. 1) adopts an *E* configuration with respect to the imine C=N double bond, with a C6—C7—N1—C8 torsion angle of 179.6 (5)°. Thus, the π-conjugation system around the imine group is essentially planar. The maximum deviation from the O1/C1/C6/C7/N1 least-squares plane is only 0.0035 (5) Å for atom C7. The C1—O1 bond distance of 1.335 (7) Å suggests that the compound is the phenol–imine tautomer. The contraction of the C7=N1 bond is also in agreement with the
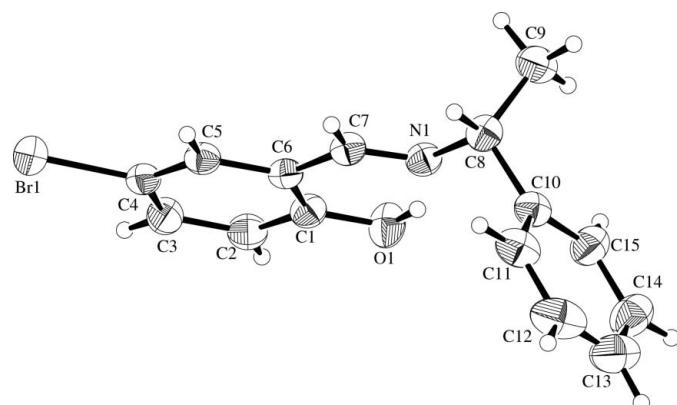
Figure 1
The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level.

phenol–imine tautomer. The dihedral angle between benzene rings C1–C6 and C9–C14 is 79.2 (2)°. Furthermore, geometric parameters reported here (Table 1) agree with the corresponding values for analogous Schiff base compounds containing the 1-phenylethylamine group (Antonov *et al.*, 1995; Liu *et al.*, 1997). The planarity of (I) is stabilized by an intramolecular O—H···N hydrogen bond (Table 2).

Experimental

Treatment of equimolar (*R*)-1-phenylethylamine and 5-bromo-salicylaldehyde in methanol (30 ml) at 298 K overnight gave rise to the green compound (I). Prismatic crystals of (I) were grown from the resulting solution over a period of several days (yield 31.6%). Analysis found: C 59.10, H 4.33, N 4.84%; calculated for $C_{15}H_{14}BrNO$: C 59.23, H 4.64, N 4.60%; m.p. 410 K; IR (KBr, ν, cm^{-1}): 1633 (imine band). UV–Vis (diffuse reflectance, cm^{-1}): 16800.

Crystal data

$C_{15}H_{14}BrNO$	$Z = 4$
$M_r = 304.18$	$D_x = 1.467$ Mg m^{-3}
Monoclinic, $C2$	Mo $K\alpha$ radiation
$a = 20.955$ (8) Å	$\mu = 2.97$ mm^{-1}
$b = 5.795$ (3) Å	$T = 297$ (2) K
$c = 14.611$ (7) Å	Prism, green
$\beta = 129.07$ (3)°	$0.30 \times 0.30 \times 0.20$ mm
$V = 1377.5$ (13) Å^3	

Data collection

Rigaku AFC-7R diffractometer	1425 reflections with $I > 2\sigma(I)$
ω–2θ scans	$R_{int} = 0.113$
Absorption correction: ψ scan	$\theta_{max} = 27.6°$
(North *et al.*, 1968)	3 standard reflections
$T_{min} = 0.396$, $T_{max} = 0.552$	every 150 reflections
1907 measured reflections	intensity decay: 1.4%
1743 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0737P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.046$	$+ 0.6987P]$
$wR(F^2) = 0.128$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} < 0.001$
1743 reflections	$\Delta\rho_{max} = 0.73$ e Å^{-3}
164 parameters	$\Delta\rho_{min} = -0.49$ e Å^{-3}
H-atom parameters constrained	Absolute structure: Flack (1983), no Friedel pairs
	Flack parameter: −0.01 (2)

Table 1
Selected geometric parameters (Å, °).

Br1—C4	1.921 (6)	N1—C7	1.261 (7)
O1—C1	1.335 (7)	N1—C8	1.482 (7)
C7—N1—C8	118.8 (5)	N1—C7—C6	121.3 (5)
C8—N1—C7—C6	−179.6 (5)	C7—N1—C8—C9	−115.9 (6)
C1—C6—C7—N1	0.3 (7)	C7—N1—C8—C10	120.4 (5)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···N1	0.81	1.88	2.593 (7)	146

All H atoms were placed in calculated positions, with C—H = 0.93–0.98 Å and O—H = 0.82 Å, and included in the final cycles of refinement using a riding model, with $U_{iso}(H) = 1.2U_{eq}$(parent atom).

Data collection: *WinAFC Diffractometer Control Software* (Rigaku, 1999); cell refinement: *WinAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); 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: *TEXSAN*.

References

Akitsu, T. & Einaga, Y. (2004). *Acta Cryst.* C**60**, m640–m642.
Akitsu, T. & Einaga, Y. (2005*a*). *Polyhedron*, **24**, 1869–1877.
Akitsu, T. & Einaga, Y. (2005*b*). *Polyhedron*, **24**, 2933–2943.
Akitsu, T. & Einaga, Y. (2006). *Polyhedron*, **25**, 1089–1095.
Akitsu, T., Takeuchi, Y. & Einaga, Y. (2004). *Acta Cryst.* C**60**, o801–o802.
Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Antonov, D. Y., Belokon, Y. N., Ikonnikov, N. S., Orlova, S. A., Pisarevsky, A. P., Raevski, N. I., Rozenberg, V. I., Sergeeva, E. V., Struchkov, Y. T., Tararov, V. I. & Vorontsov, E. V. (1995). *J. Chem. Soc. Perkin Trans. 1*, pp. 1873–1879.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Hadjoudis, E., Rontoyianni, A., Ambroziak, K., Dziembowska, T. & Mavridis, I. M. (2004). *J. Photochem. Photobiol. A*, **162**, 521–530.
Hadjoudis, E., Vitterakis, M. & Mavridis, I. M. (1987). *Tetrahedron*, **43**, 1345–1360.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Liu, Q., Ding, M., Lin, Y. & Xing, Y. (1997). *J. Organomet. Chem.* **548**, 139–142.
Molecular Structure Corporation. (2001). *TEXSAN*. Version 1.11. MSC, The Woodlands, Texas, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Rigaku (1999). *WinAFC Diffractometer Control Software*. Rigaku Corporation, Tokyo, Japan.

Santoni, G. & Rehder, D. (2004). *J. Inorg. Biochem.* **98**, 758–764.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Sliwa, M., Letrard, S., Malfant, I., Nierlich, M., Lacroix, P. G., Asahi, T., Masuhara, H., Yu, P. & Nakatani, K. (2005). *Chem. Mater.* **17**, 4727–4735.

Yamada, S. (1999). *Coord. Chem. Rev.* **190–192**, 537–555.