

(E)-4-Bromo-2-[(2-hydroxy-5-methylphenyl)iminomethyl]phenol

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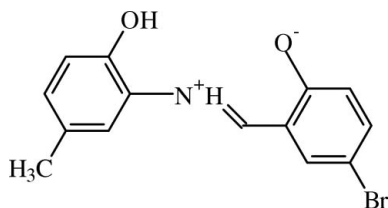
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 Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.008$ Å; R factor = 0.043; wR factor = 0.084; data-to-parameter ratio = 15.3.

The molecule of the title compound, $\text{C}_{14}\text{H}_{12}\text{BrNO}_2$, crystallizes in a zwitterionic form, with a strong intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond. The dihedral angle between the aromatic rings is $9.3(3)^\circ$. Intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds generate $C(8)$ chains running parallel to the $[100]$ direction.

Related literature

Schiff base compounds can be classified by their photochromic and thermochromic characteristics (Cohen *et al.*, 1964; Hadjoudis *et al.*, 1987). For hydrogen-bonding motif details, see: Bernstein *et al.* (1995). For related literature, see: Calligaris *et al.* (1972); Dey *et al.* (2001); Hökelek *et al.* (2000); Petek *et al.* (2006).



Experimental

Crystal data

 $\text{C}_{14}\text{H}_{12}\text{BrNO}_2$
 $M_r = 306.16$

 Orthorhombic, $P2_12_12_1$
 $a = 8.2763(8)$ Å

 $b = 8.4451(9)$ Å

 $c = 18.795(2)$ Å

 $V = 1313.7(2)$ Å³
 $Z = 4$

 Mo $K\alpha$ radiation

 $\mu = 3.12$ mm⁻¹
 $T = 296$ K

 $0.80 \times 0.37 \times 0.13$ mm

Data collection

Stoe IPDS II diffractometer

Absorption correction: integration

 (*X-RED32*; Stoe & Cie, 2002)

 $T_{\min} = 0.289$, $T_{\max} = 0.680$

6028 measured reflections

2549 independent reflections

 1541 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.073$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.084$
 $S = 0.91$

2549 reflections

167 parameters

H atoms treated by a mixture of

independent and constrained

refinement

 $\Delta\rho_{\text{max}} = 0.31$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.30$ e Å⁻³

Absolute structure: Flack (1983);

1052 Friedel pairs

 Flack parameter: $-0.010(15)$
Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O2}-\text{H2}\cdots\text{O1}^{\dagger}$	0.82	1.75	2.566 (5)	171
$\text{N1}-\text{H1}\cdots\text{O1}$	0.82 (5)	1.84 (5)	2.547 (6)	144 (5)

 Symmetry code: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2507).

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supplementary materials

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(E)-4-Bromo-2-[(2-hydroxy-5-methylphenyl)iminomethyl]phenol

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Comment

Schiff bases have been extensively used as ligands in the field of coordination chemistry (Calligaris *et al.*, 1972). There are two characteristic properties of Schiff bases, *viz.* photochromism and thermochromism (Cohen *et al.*, 1964). These properties result from proton transfer from the hydroxyl O atom to the imine N atom (Hadjoudis *et al.*, 1987). Schiff bases display two possible tautomeric forms, namely the phenol-imine and keto-amine forms. In the solid state, the keto-amine tautomer has been found in naphthaldimine (Hökelek *et al.*, 2000). Nevertheless, in the solid state, it has been established that there is keto-amine tautomerism in naphthaldimine, while the phenol-imine form exists in salicylaldimine Schiff bases (Dey *et al.*, 2001). Our investigations show that compound (I) exists in a zwitterionic form.

An ORTEP-3 (Farrugia, 1997) plot of the molecule of (I) is shown in Fig.1. The C1—C7, C7=N1 and N1—C8 bond lengths are 1.406 (6), 1.289 (6) and 1.409 (6) Å, respectively (Table 1), and agree with the corresponding distances in (Z)-6-[(2-fluorophenyliminio)methylene]-2,3-dihydroxyphenolate [1.419 (3), 1.295 (2) and 1.412 (2) Å; Petek *et al.*, 2006]. In the zwitterionic form, the molecule of the title compound is nearly planar, with a dihedral angle between the aromatic rings of 9.3 (3)°.

Fig.1 also shows a strong intramolecular hydrogen bond (N1—H1...O1) can be described as an S(6) motif (Bernstein *et al.*, 1995). Atom O2 in the reference molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor, *via* H2, to O1 in the molecule at (1/2 + *x*, 3/2 - *y*, 1 - *z*), so forming a C(8) chain running parallel to the [100] direction (Fig.2).

Experimental

A solution of 5-bromosalicylaldehyde (0.05 g, 0.25 mmol) in ethanol (20 ml) was added to a solution of 2-hydroxy-5-nitroaniline (0.038 g 0.25 mmol) in ethanol (20 ml). The reaction mixture was stirred for 1 h under reflux. Single crystals of the title compound suitable for X-ray analysis were obtained from ethanol by slow evaporation (yield 71%; m.p. 456–459 K).

Refinement

Atom H1 was located in a difference map and refined freely. The remaining H atoms were placed in calculated positions and constrained to ride on their parents atoms, with C—H = 0.93–0.96 Å and $U_{\text{iso}}(\text{H}) = kU_{\text{eq}}(\text{parent atom})$, where *k* = 1.5 for methyl and hydroxyl H atoms, and 1.2 for other H atoms.

Figures

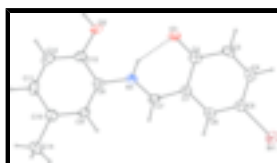


Fig. 1. The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

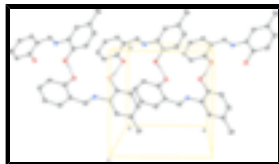


Fig. 2. View of the crystal packing of (I). Hydrogen bonds are drawn as dashed lines. H atoms not involved in the interactions have been omitted for clarity.

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Crystal data

$C_{14}H_{12}BrNO_2$	$F_{000} = 616$
$M_r = 306.16$	$D_x = 1.548 \text{ Mg m}^{-3}$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
Hall symbol: P2ac 2ab	$\lambda = 0.71073 \text{ \AA}$
$a = 8.2763 (8) \text{ \AA}$	Cell parameters from 5730 reflections
$b = 8.4451 (9) \text{ \AA}$	$\theta = 2.2\text{--}29.5^\circ$
$c = 18.795 (2) \text{ \AA}$	$\mu = 3.12 \text{ mm}^{-1}$
$V = 1313.7 (2) \text{ \AA}^3$	$T = 296 \text{ K}$
$Z = 4$	Prism, brown
	$0.80 \times 0.37 \times 0.13 \text{ mm}$

Data collection

Stoe IPDS II diffractometer	2549 independent reflections
Radiation source: fine-focus sealed tube	1541 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.073$
Detector resolution: $6.67 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 26.0^\circ$
$T = 296 \text{ K}$	$\theta_{\text{min}} = 2.2^\circ$
rotation method scans	$h = -10 \rightarrow 10$
Absorption correction: integration (X-RED32; Stoe & Cie, 2002)	$k = -10 \rightarrow 6$
$T_{\text{min}} = 0.289$, $T_{\text{max}} = 0.680$	$l = -23 \rightarrow 23$
6028 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.043$	$w = 1/[\sigma^2(F_o^2) + (0.0287P)^2]$
$wR(F^2) = 0.084$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.91$	$(\Delta/\sigma)_{\text{max}} = 0.001$
2549 reflections	$\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$
167 parameters	$\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$
	Extinction correction: none

Primary atom site location: structure-invariant direct methods Absolute structure: Flack (1983); 1052 Friedel pairs
 Secondary atom site location: difference Fourier map Flack parameter: -0.010 (15)

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.5123 (5)	0.4814 (6)	0.6768 (3)	0.0472 (11)
C2	0.4416 (5)	0.6051 (8)	0.6358 (2)	0.0529 (15)
C3	0.2843 (5)	0.6545 (7)	0.6554 (3)	0.0558 (15)
H3	0.2355	0.7366	0.6304	0.067*
C4	0.2033 (6)	0.5854 (7)	0.7097 (3)	0.0551 (16)
H4	0.0991	0.6185	0.7207	0.066*
C5	0.2749 (6)	0.4652 (7)	0.7491 (2)	0.0509 (14)
C6	0.4245 (6)	0.4155 (7)	0.7336 (2)	0.0558 (16)
H6	0.4712	0.3359	0.7609	0.067*
C7	0.6666 (6)	0.4226 (6)	0.6601 (2)	0.0526 (13)
H7	0.7082	0.3397	0.6870	0.063*
C8	0.9084 (5)	0.4353 (7)	0.5857 (2)	0.0450 (13)
C9	0.9898 (6)	0.3034 (7)	0.6103 (2)	0.0498 (13)
H9	0.9424	0.2399	0.6449	0.060*
C10	1.1407 (7)	0.2646 (7)	0.5841 (3)	0.0591 (14)
C11	1.2065 (6)	0.3619 (10)	0.5315 (3)	0.0684 (17)
H11	1.3066	0.3364	0.5121	0.082*
C12	1.1267 (6)	0.4950 (8)	0.5073 (2)	0.0607 (15)
H12	1.1738	0.5589	0.4727	0.073*
C13	0.9777 (6)	0.5331 (7)	0.5346 (2)	0.0497 (13)
C14	1.2316 (7)	0.1219 (9)	0.6121 (3)	0.086 (2)
H14A	1.2118	0.1107	0.6622	0.129*
H14B	1.3453	0.1361	0.6041	0.129*
H14C	1.1954	0.0285	0.5878	0.129*
N1	0.7527 (5)	0.4790 (6)	0.6088 (2)	0.0493 (12)
H1	0.703 (6)	0.544 (7)	0.585 (2)	0.059*
O1	0.5191 (4)	0.6667 (5)	0.58287 (17)	0.0631 (12)
O2	0.8903 (4)	0.6614 (5)	0.51439 (17)	0.0657 (11)
H2	0.9404	0.7111	0.4841	0.098*
Br1	0.15523 (6)	0.36922 (9)	0.82415 (3)	0.0725 (2)

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.045 (2)	0.043 (3)	0.053 (2)	0.004 (2)	0.001 (3)	0.009 (3)
C2	0.058 (3)	0.049 (5)	0.052 (3)	-0.008 (3)	-0.014 (2)	0.001 (3)
C3	0.059 (3)	0.036 (4)	0.072 (3)	0.009 (3)	-0.016 (2)	0.003 (3)
C4	0.047 (3)	0.057 (5)	0.061 (3)	0.005 (3)	-0.004 (2)	-0.008 (3)
C5	0.054 (3)	0.048 (4)	0.051 (3)	0.002 (3)	-0.001 (2)	0.001 (3)
C6	0.054 (3)	0.053 (5)	0.060 (3)	0.005 (3)	0.000 (2)	0.014 (3)
C7	0.059 (3)	0.051 (3)	0.047 (3)	0.000 (3)	-0.001 (2)	0.020 (2)
C8	0.050 (3)	0.042 (4)	0.043 (2)	-0.004 (2)	-0.002 (2)	0.006 (2)
C9	0.058 (3)	0.044 (4)	0.048 (3)	-0.003 (3)	0.009 (2)	0.008 (2)
C10	0.068 (3)	0.040 (4)	0.069 (3)	-0.003 (3)	0.009 (3)	-0.006 (3)
C11	0.071 (3)	0.067 (5)	0.067 (3)	0.000 (4)	0.028 (3)	-0.019 (4)
C12	0.075 (4)	0.055 (4)	0.052 (3)	-0.014 (3)	0.010 (3)	0.004 (3)
C13	0.059 (3)	0.039 (4)	0.051 (3)	-0.006 (3)	-0.001 (2)	0.004 (3)
C14	0.085 (4)	0.056 (5)	0.117 (5)	0.022 (4)	0.025 (3)	0.016 (5)
N1	0.047 (2)	0.046 (3)	0.054 (3)	0.004 (2)	-0.0036 (19)	0.013 (2)
O1	0.064 (2)	0.056 (3)	0.069 (2)	0.003 (2)	-0.0036 (17)	0.031 (2)
O2	0.073 (2)	0.058 (3)	0.0655 (19)	0.003 (2)	0.0138 (17)	0.030 (2)
Br1	0.0639 (3)	0.0783 (5)	0.0753 (3)	-0.0022 (4)	0.0147 (3)	0.0103 (4)

Geometric parameters (\AA , $^\circ$)

C1—C6	1.406 (6)	C8—N1	1.409 (6)
C1—C7	1.406 (6)	C9—C10	1.382 (7)
C1—C2	1.424 (7)	C9—H9	0.93
C2—O1	1.293 (6)	C10—C11	1.397 (8)
C2—C3	1.415 (7)	C10—C14	1.515 (8)
C3—C4	1.354 (7)	C11—C12	1.380 (9)
C3—H3	0.93	C11—H11	0.93
C4—C5	1.389 (7)	C12—C13	1.373 (7)
C4—H4	0.93	C12—H12	0.93
C5—C6	1.340 (6)	C13—O2	1.357 (6)
C5—Br1	1.905 (5)	C14—H14A	0.96
C6—H6	0.93	C14—H14B	0.96
C7—N1	1.289 (6)	C14—H14C	0.96
C7—H7	0.93	N1—H1	0.82 (5)
C8—C9	1.381 (7)	O2—H2	0.82
C8—C13	1.390 (7)		
C6—C1—C7	119.9 (5)	C8—C9—H9	119.6
C6—C1—C2	119.3 (4)	C10—C9—H9	119.6
C7—C1—C2	120.8 (4)	C9—C10—C11	117.7 (5)
O1—C2—C3	122.5 (5)	C9—C10—C14	121.0 (5)
O1—C2—C1	120.5 (4)	C11—C10—C14	121.4 (5)
C3—C2—C1	117.0 (5)	C12—C11—C10	121.7 (5)
C4—C3—C2	121.6 (5)	C12—C11—H11	119.1

C4—C3—H3	119.2	C10—C11—H11	119.1
C2—C3—H3	119.2	C13—C12—C11	119.8 (5)
C3—C4—C5	120.4 (5)	C13—C12—H12	120.1
C3—C4—H4	119.8	C11—C12—H12	120.1
C5—C4—H4	119.8	O2—C13—C12	124.1 (5)
C6—C5—C4	120.5 (5)	O2—C13—C8	116.6 (4)
C6—C5—Br1	120.5 (4)	C12—C13—C8	119.3 (5)
C4—C5—Br1	118.9 (4)	C10—C14—H14A	109.5
C5—C6—C1	121.2 (5)	C10—C14—H14B	109.5
C5—C6—H6	119.4	H14A—C14—H14B	109.5
C1—C6—H6	119.4	C10—C14—H14C	109.5
N1—C7—C1	122.6 (5)	H14A—C14—H14C	109.5
N1—C7—H7	118.7	H14B—C14—H14C	109.5
C1—C7—H7	118.7	C7—N1—C8	129.7 (5)
C9—C8—C13	120.6 (5)	C7—N1—H1	112 (3)
C9—C8—N1	123.6 (5)	C8—N1—H1	118 (3)
C13—C8—N1	115.8 (5)	C13—O2—H2	109.5
C8—C9—C10	120.9 (5)		
C6—C1—C2—O1	-179.4 (5)	N1—C8—C9—C10	178.3 (5)
C7—C1—C2—O1	-0.7 (8)	C8—C9—C10—C11	-0.9 (8)
C6—C1—C2—C3	0.0 (8)	C8—C9—C10—C14	178.7 (5)
C7—C1—C2—C3	178.6 (5)	C9—C10—C11—C12	1.8 (9)
O1—C2—C3—C4	178.0 (5)	C14—C10—C11—C12	-177.8 (6)
C1—C2—C3—C4	-1.3 (8)	C10—C11—C12—C13	-1.0 (9)
C2—C3—C4—C5	1.5 (8)	C11—C12—C13—O2	179.8 (5)
C3—C4—C5—C6	-0.4 (8)	C11—C12—C13—C8	-0.7 (8)
C3—C4—C5—Br1	-179.2 (4)	C9—C8—C13—O2	-178.9 (4)
C4—C5—C6—C1	-0.9 (8)	N1—C8—C13—O2	1.9 (6)
Br1—C5—C6—C1	177.8 (4)	C9—C8—C13—C12	1.6 (7)
C7—C1—C6—C5	-177.5 (5)	N1—C8—C13—C12	-177.6 (5)
C2—C1—C6—C5	1.1 (8)	C1—C7—N1—C8	179.4 (5)
C6—C1—C7—N1	-179.6 (5)	C9—C8—N1—C7	9.0 (8)
C2—C1—C7—N1	1.7 (8)	C13—C8—N1—C7	-171.8 (5)
C13—C8—C9—C10	-0.8 (7)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2 \cdots O1 ⁱ	0.82	1.75	2.566 (5)	171
N1—H1 \cdots O1	0.82 (5)	1.84 (5)	2.547 (6)	144 (5)

Symmetry codes: (i) $x+1/2, -y+3/2, -z+1$.

Fig. 1

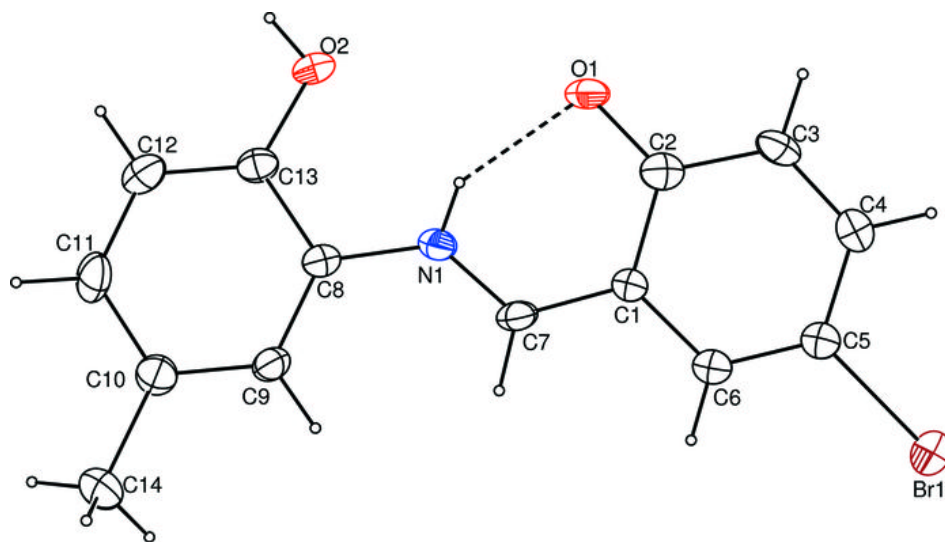


Fig. 2

