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(*E*)-4-Bromo-2-(2-methoxyphenyliminomethyl)phenol

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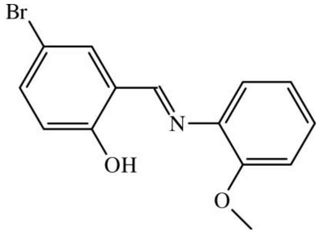
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.004 Å; R factor = 0.032; wR factor = 0.078; data-to-parameter ratio = 15.2.

The molecule of the title compound, $C_{14}H_{12}BrNO_2$, is almost planar and the dihedral angle between the planes of the two aromatic rings is 3.8 (2)°. The molecule exists in the crystal structure in the phenol–imine tautomeric form, with the H atom located on O rather than on N. This H atom is involved in a strong intramolecular hydrogen bond.

Related literature

Schiff base compounds can be classified by their photochromic and thermochromic characteristics (Cohen *et al.*, 1964; Hadjoudis *et al.*, 1987). For other relevant literature, see: Bernstein *et al.* (1995); Calligaris *et al.* (1972); Dey *et al.* (2001); Farrugia (1999); Gül *et al.* (2007); Hökelek *et al.* (2000); Işık *et al.* (1998); Karadayı *et al.* (2003); Şahin *et al.* (2005).



Experimental

Crystal data

$C_{14}H_{12}BrNO_2$
M_r = 306.16
Monoclinic, $C2/c$
a = 32.926 (3) Å
b = 4.5564 (2) Å
c = 17.7214 (16) Å
β = 108.465 (7)°
V = 2521.8 (4) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 3.25 mm^{-1}
T = 296 K
0.80 × 0.38 × 0.08 mm

Data collection

Stoe IPDS II diffractometer
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002) T_{min} = 0.221, T_{max} = 0.712
12218 measured reflections
2480 independent reflections
1712 reflections with $I > 2\sigma(I)$
R_{int} = 0.052

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.078
S = 0.98
2480 reflections
163 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···N1	0.82	1.85	2.575 (3)	147

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); 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: LW2037).

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supplementary materials

Acta Cryst. (2007). E**63**, o4241 [**doi:10.1107/S1600536807047824**]

(*E*)-4-Bromo-2-(2-methoxyphenyliminomethyl)phenol

Z. S. Gül, F. Ersahin, E. Agar and S. Isik

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) adopts the phenol–imine tautomeric form. An *ORTEP-3* (Farrugia, 1997) plot of the molecule of (I) is shown in Fig. 1. The C8—N1 and C1—C7 bond lengths are 1.413 (3) and 1.453 (3) Å, respectively (Table 1), and agree with the corresponding distances in (*E*)-2-Methoxy-6-[(2-trifluoromethylphenylimino)methyl]phenol [1.418 (5) and 1.454 (5) Å; Şahin *et al.*, 2005]. The N1═C7 bond length of 1.274 (3) Å is typical of a double bond, similar to the corresponding bond length in *N*-[3,5-Bis(trifluoromethyl)phenyl]salicylaldimine [1.276 (4) Å; Karadayı *et al.*, 2003]. The O2—C4 distance of 1.338 (3) Å is close to the value of 1.349 (6) Å in 3-*tert*-butyl-2-hydroxy-5-methoxyazobenzene (Işık *et al.*, 1998).

Fig. 1 also shows a strong intramolecular hydrogen bond (O2—H2···N1) can be described as an S(6) motif (Bernstein *et al.*, 1995). The O1—N1 distance of 2.575 (3) Å is comparable to those observed for analogous hydrogen bonds in (*E*)-2-[4-(Dimethylamino)phenyliminomethyl]-6-methylphenol [2.574 (3) Å; Gül *et al.*, 2007].

Experimental

The compound (*E*)-2-[(2-Methoxyphenylimino)methyl]-4-bromophenol was prepared by reflux a mixture of a solution containing 5-bromosalicylaldehyde (0.05 g 0.25 mmol) in 20 ml e thanol and a solution containing *o*-Anisidine (0.03 g 0.37 mmol) in 20 ml e thanol. The reaction mixture was stirred for 1 h under reflux. The crystals of (*E*)-2-[(2-Methoxyphenylimino)methyl]-4-bromophenol suitable for X-ray analysis were obtained from ethylalcohol by slow evaporation (yield % 70; m.p. 385–387 K).

Refinement

The H2 atom was located in a difference map and refined freely (distances given in Table 2). All other H atoms were placed in calculated positions and constrained to ride on their parents atoms, with C—H = 0.93–0.96 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) or 1.5$U_{\rm eq}$(C).

Figures

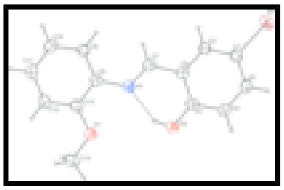

Fig. 1. The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability.

(*E*)-4-Bromo-2-(2-methoxyphenyliminomethyl)phenol

Crystal data

$C_{14}H_{12}BrNO_2$

$M_r = 306.16$

Monoclinic, $C2/c$

Hall symbol: -C 2yc

$a = 32.926$ (3) Å

$b = 4.5564$ (2) Å

$c = 17.7214$ (16) Å

$\beta = 108.465$ (7)°

$V = 2521.8$ (4) Å^3

$Z = 8$

$F_{000} = 1232$

$D_x = 1.613$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Cell parameters from 12164 reflections

$\theta = 2.4$–29.5°

$\mu = 3.25$ mm^{-1}

$T = 296$ K

Prism, brown

0.80 × 0.38 × 0.08 mm

Data collection

Stoe IPDS II
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 6.67 pixels mm^{-1}

$T = 296$ K

ω scans

Absorption correction: integration
(X-RED32; Stoe & Cie, 2002)

$T_{min} = 0.221$, $T_{max} = 0.712$

12218 measured reflections

2480 independent reflections

1712 reflections with $I > 2\sigma(I)$

$R_{int} = 0.052$

$\theta_{max} = 26.0$°

$\theta_{min} = 2.4$°

$h = -40 \rightarrow 40$

$k = -5 \rightarrow 5$

$l = -21 \rightarrow 21$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.078$

$S = 0.98$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0418P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

2480 reflections	$\Delta\rho_{max} = 0.26$ e Å^{-3}
163 parameters	$\Delta\rho_{min} = -0.45$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.234247 (8)	−0.00729 (8)	0.138938 (19)	0.06755 (13)
O2	0.41248 (5)	0.4833 (4)	0.22498 (11)	0.0609 (5)
H2	0.4147	0.5989	0.1910	0.091*
N1	0.38806 (6)	0.7855 (4)	0.09558 (12)	0.0442 (5)
C1	0.29059 (8)	0.1497 (6)	0.16474 (16)	0.0456 (6)
C8	0.39867 (7)	0.9886 (6)	0.04460 (14)	0.0421 (5)
C9	0.37013 (8)	1.1040 (6)	−0.02393 (16)	0.0492 (6)
H9	0.3415	1.0472	−0.0391	0.059*
O1	0.46804 (6)	0.9510 (5)	0.13433 (11)	0.0636 (6)
C3	0.34117 (7)	0.4621 (5)	0.13301 (14)	0.0401 (5)
C4	0.37255 (7)	0.3770 (6)	0.20377 (15)	0.0440 (6)
C10	0.38344 (9)	1.3026 (6)	−0.07027 (16)	0.0533 (7)
H10	0.3640	1.3775	−0.1165	0.064*
C2	0.30006 (7)	0.3460 (6)	0.11415 (15)	0.0453 (6)
H22	0.2791	0.4014	0.0674	0.054*
C7	0.35084 (8)	0.6732 (6)	0.07962 (15)	0.0453 (6)
H7	0.3296	0.7271	0.0331	0.054*
C5	0.36185 (8)	0.1758 (6)	0.25349 (16)	0.0519 (7)
H5	0.3825	0.1166	0.3003	0.062*
C13	0.44153 (8)	1.0756 (6)	0.06709 (16)	0.0492 (7)
C6	0.32113 (9)	0.0640 (6)	0.23411 (16)	0.0506 (7)
H6	0.3142	−0.0694	0.2678	0.061*
C12	0.45450 (9)	1.2780 (7)	0.02073 (18)	0.0646 (8)
H12	0.4829	1.3394	0.0359	0.078*
C11	0.42538 (10)	1.3882 (7)	−0.04772 (18)	0.0621 (8)
H11	0.4344	1.5219	−0.0788	0.075*
C14	0.51133 (9)	1.0510 (9)	0.1620 (2)	0.0876 (12)
H14A	0.5266	0.9471	0.2097	0.131*

H14B	0.5118	1.2574	0.1731	0.131*
H14C	0.5247	1.0156	0.1220	0.131*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.04646 (16)	0.0750 (2)	0.0816 (2)	−0.01226 (15)	0.02084 (14)	0.0042 (2)
O2	0.0431 (9)	0.0699 (12)	0.0585 (11)	−0.0084 (10)	−0.0001 (8)	0.0139 (11)
N1	0.0433 (11)	0.0431 (12)	0.0450 (12)	−0.0022 (9)	0.0125 (9)	0.0001 (10)
C1	0.0409 (12)	0.0454 (14)	0.0517 (15)	−0.0011 (11)	0.0161 (12)	−0.0004 (13)
C8	0.0450 (12)	0.0389 (12)	0.0427 (12)	−0.0022 (12)	0.0145 (10)	−0.0045 (14)
C9	0.0462 (14)	0.0480 (14)	0.0496 (15)	−0.0037 (11)	0.0098 (12)	−0.0006 (12)
O1	0.0456 (10)	0.0797 (15)	0.0555 (11)	−0.0110 (10)	0.0019 (8)	0.0151 (11)
C3	0.0400 (11)	0.0388 (14)	0.0403 (12)	0.0008 (10)	0.0113 (10)	−0.0036 (12)
C4	0.0378 (13)	0.0453 (13)	0.0456 (14)	0.0021 (10)	0.0083 (11)	−0.0022 (12)
C10	0.0612 (16)	0.0525 (17)	0.0435 (15)	0.0005 (13)	0.0126 (13)	0.0031 (13)
C2	0.0401 (13)	0.0468 (14)	0.0452 (14)	0.0002 (11)	0.0082 (11)	0.0006 (12)
C7	0.0456 (14)	0.0432 (15)	0.0436 (14)	0.0018 (11)	0.0093 (11)	−0.0006 (12)
C5	0.0508 (15)	0.0559 (17)	0.0444 (15)	0.0025 (12)	0.0084 (12)	0.0086 (14)
C13	0.0453 (14)	0.0537 (17)	0.0458 (15)	−0.0038 (11)	0.0105 (12)	−0.0015 (12)
C6	0.0556 (15)	0.0505 (18)	0.0490 (15)	−0.0009 (12)	0.0211 (12)	0.0056 (12)
C12	0.0513 (16)	0.078 (2)	0.0624 (19)	−0.0161 (15)	0.0152 (14)	0.0107 (17)
C11	0.0629 (18)	0.0669 (18)	0.0599 (18)	−0.0091 (15)	0.0241 (15)	0.0138 (15)
C14	0.0432 (15)	0.137 (4)	0.072 (2)	−0.0155 (19)	0.0029 (14)	0.022 (2)

Geometric parameters (Å, °)

Br1—C1	1.904 (2)	C4—C5	1.392 (4)
O2—C4	1.338 (3)	C10—C11	1.367 (4)
O2—H2	0.8200	C10—H10	0.9300
N1—C7	1.274 (3)	C2—H22	0.9300
N1—C8	1.413 (3)	C7—H7	0.9300
C1—C2	1.370 (4)	C5—C6	1.372 (4)
C1—C6	1.376 (4)	C5—H5	0.9300
C8—C9	1.382 (4)	C13—C12	1.389 (4)
C8—C13	1.397 (3)	C6—H6	0.9300
C9—C10	1.383 (4)	C12—C11	1.381 (4)
C9—H9	0.9300	C12—H12	0.9300
O1—C13	1.358 (3)	C11—H11	0.9300
O1—C14	1.427 (3)	C14—H14A	0.9600
C3—C2	1.392 (3)	C14—H14B	0.9600
C3—C4	1.404 (3)	C14—H14C	0.9600
C3—C7	1.453 (3)		
C4—O2—H2	109.5	N1—C7—C3	121.0 (2)
C7—N1—C8	122.4 (2)	N1—C7—H7	119.5
C2—C1—C6	121.1 (2)	C3—C7—H7	119.5
C2—C1—Br1	119.63 (19)	C6—C5—C4	120.6 (2)
C6—C1—Br1	119.26 (19)	C6—C5—H5	119.7

C9—C8—C13	119.1 (2)	C4—C5—H5	119.7
C9—C8—N1	125.0 (2)	O1—C13—C12	124.3 (2)
C13—C8—N1	115.8 (2)	O1—C13—C8	116.2 (2)
C8—C9—C10	121.0 (2)	C12—C13—C8	119.4 (3)
C8—C9—H9	119.5	C5—C6—C1	119.9 (2)
C10—C9—H9	119.5	C5—C6—H6	120.1
C13—O1—C14	117.6 (2)	C1—C6—H6	120.1
C2—C3—C4	119.6 (2)	C11—C12—C13	120.2 (3)
C2—C3—C7	119.5 (2)	C11—C12—H12	119.9
C4—C3—C7	120.9 (2)	C13—C12—H12	119.9
O2—C4—C5	118.9 (2)	C10—C11—C12	120.6 (3)
O2—C4—C3	122.1 (2)	C10—C11—H11	119.7
C5—C4—C3	119.0 (2)	C12—C11—H11	119.7
C11—C10—C9	119.6 (3)	O1—C14—H14A	109.5
C11—C10—H10	120.2	O1—C14—H14B	109.5
C9—C10—H10	120.2	H14A—C14—H14B	109.5
C1—C2—C3	119.8 (2)	O1—C14—H14C	109.5
C1—C2—H22	120.1	H14A—C14—H14C	109.5
C3—C2—H22	120.1	H14B—C14—H14C	109.5

C7—N1—C8—C9	4.9 (4)	O2—C4—C5—C6	179.4 (3)
C7—N1—C8—C13	−175.3 (2)	C3—C4—C5—C6	−0.6 (4)
C13—C8—C9—C10	0.1 (4)	C14—O1—C13—C12	4.7 (4)
N1—C8—C9—C10	179.9 (2)	C14—O1—C13—C8	−175.6 (3)
C2—C3—C4—O2	−179.6 (2)	C9—C8—C13—O1	−179.1 (2)
C7—C3—C4—O2	−0.4 (4)	N1—C8—C13—O1	1.1 (3)
C2—C3—C4—C5	0.4 (4)	C9—C8—C13—C12	0.7 (4)
C7—C3—C4—C5	179.6 (2)	N1—C8—C13—C12	−179.1 (2)
C8—C9—C10—C11	−0.5 (4)	C4—C5—C6—C1	0.4 (4)
C6—C1—C2—C3	−0.2 (4)	C2—C1—C6—C5	0.0 (4)
Br1—C1—C2—C3	179.73 (19)	Br1—C1—C6—C5	−179.9 (2)
C4—C3—C2—C1	0.0 (4)	O1—C13—C12—C11	178.6 (3)
C7—C3—C2—C1	−179.2 (2)	C8—C13—C12—C11	−1.1 (4)
C8—N1—C7—C3	179.3 (2)	C9—C10—C11—C12	0.1 (5)
C2—C3—C7—N1	179.3 (2)	C13—C12—C11—C10	0.7 (5)
C4—C3—C7—N1	0.2 (4)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···N1	0.82	1.85	2.575 (3)	147

Fig. 1