organic compounds

2,2'-[5-Bromo-o-phenylenebis(nitrilo-methylidyne)]diphenol

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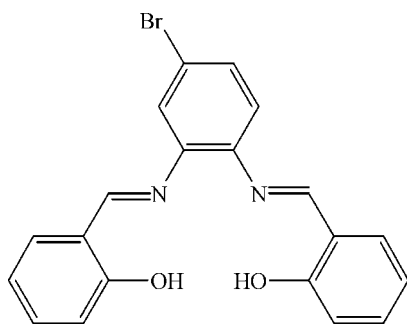Correspondence e-mail: gaojing_mmu@163.com

A new tetradentate unsymmetrical Schiff base, $C_{20}H_{15}BrN_2O_2$, has been synthesized from 4-bromo-o-phenylenediamine and salicylaldehyde in refluxing ethanol. The dihedral angles between the two hydroxyphenyl rings and the bromo-o-phenylenediiminatoin group are 68.6 (1) and 8.7 (1)°; the dihedral angle between the two hydroxyphenyl rings is 70.3 (1)°. There are two relatively strong intramolecular of O—H···N hydrogen bonds.

Related literature

For the biological activity of Schiff bases, see: Boskovic *et al.* (2003); Koizumi *et al.* (2005); Oshiob *et al.* (2005). For related structures, see: Kannappan *et al.* (2005); Zhang *et al.* (2003).

Experimental

Crystal data

$C_{20}H_{15}BrN_2O_2$	M_r = 395.25
Monoclinic, $P2_1/c$	Z = 4
a = 12.8744 (10) Å	Mo $K\alpha$ radiation
b = 5.9968 (10) Å	μ = 2.43 mm^{-1}
c = 22.106 (2) Å	T = 297 K
β = 91.221 (1)°	0.12 × 0.10 × 0.08 mm
V = 1706.3 (3) Å^3	

Data collection

Bruker APEXII CCD area-detector diffractometer	8088 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)	3009 independent reflections
T_{min} = 0.760, T_{max} = 0.830	2140 reflections with $I > 2\sigma(I)$
	R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045	2 restraints
$wR(F^2)$ = 0.141	H-atom parameters constrained
S = 1.00	$\Delta\rho_{max}$ = 0.78 e Å^{-3}
3009 reflections	$\Delta\rho_{min}$ = −0.62 e Å^{-3}
228 parameters	

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2A···N2	0.82	1.87	2.578 (4)	145
O1—H1···N3	0.82	1.90	2.614 (5)	145

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

References

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supporting information

2,2′-[5-Bromo-*o*-phenylenebis(nitrilomethylidyne)]diphenol

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S1. Comment

During the past decades, Schiff bases have been intensively studied due to their strong coordination capability as well as their diverse biological activities, such as antibacterial, antitumor, *etc*. (Koizumi *et al.*, 2005; Boskovic *et al.*, 2003; Oshiob *et al.*, 2005). The halide groups in schiff base ligands can effectively optimize the properties of the coordination complexes.

X-ray diffraction analysis indicates that (I) is a unsymmetrical Schiff (Fig. 1). The imide bond lengths of 1.276 (5) and 1.280 (5) Å for C(7)—N(3) and C(14)—N(2) are slightly longer than that found in 4-Bromo-2-(2-pyridylmethylimino-methyl)phenol (1.269 (4) Å) (Zhang *et al.*, 2003) .There are two relatively strong intramolecular hydrogen bonds (Table 1), which are similar to its derivative 4-Bromo-2-(2-pyridylmethyliminomethyl)phenol (Zhang *et al.*,2003).

S2. Experimental

(I) was prepared according to the method reported in the literature (Kannappan *et al.*, 2005). 4-bromo-*o*-phenylenedi-amine (2.16 g, 0.02 mol) was added to a stirred ethanol solution of salicylaldehyde (3.04 g, 0.02 mol (10 ml). The reaction mixture was stirred for about 3 h and then the mixture was allowed to stand at room temperature for about two days. Yellow cystals suitable for X-ray diffraction analysis were then collected with a yield of 25%.

S3. Refinement

H atoms bound to C and O atoms were visible in difference maps and were placed using the HFIX commands in *SHELXL97*. All H atoms were allowed for as riding atoms (C–H 0.97 Å, O–H 0.86 Å) with the constraint $U_{iso}(H)$ = $1.5U_{eq}$(methyl carrier), $1.5U_{eq}$(O) and $1.2U_{eq}$(carrier) for all other H atoms.
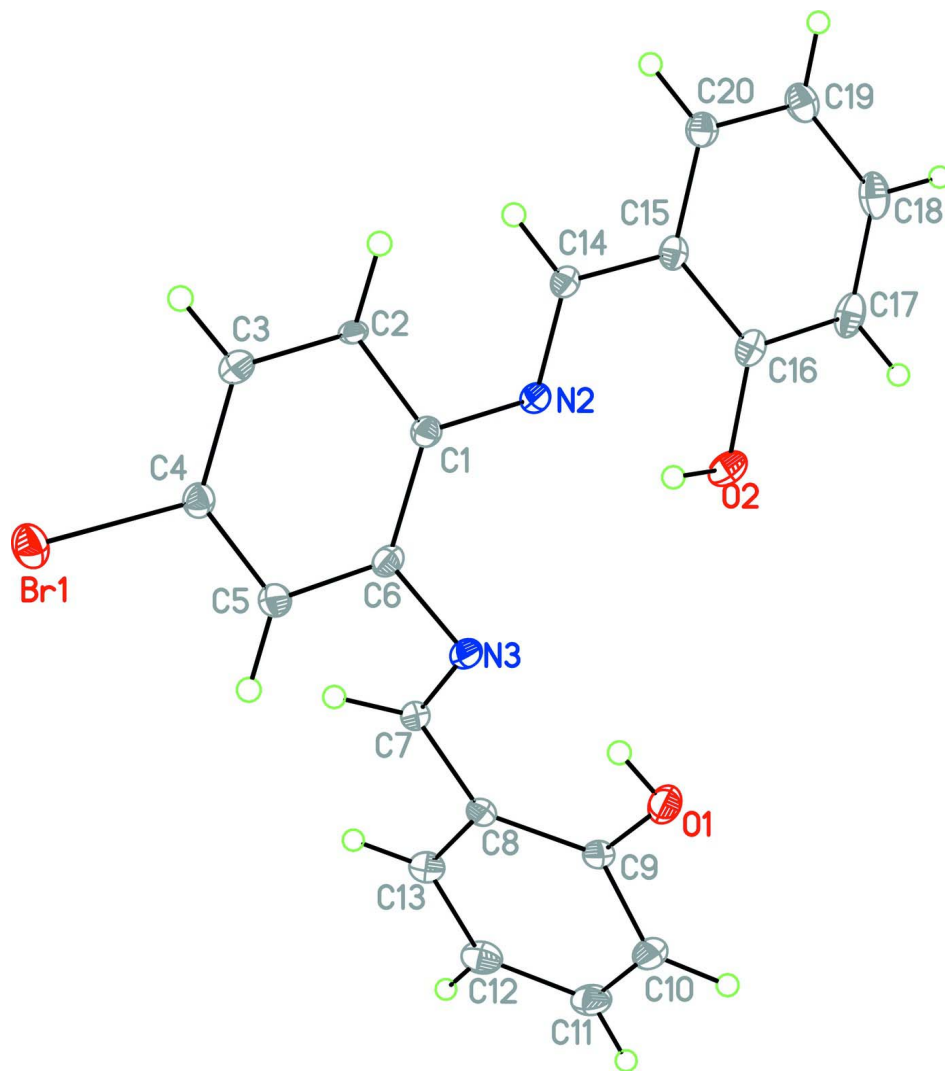
Figure 1

A view of the structure of (I), showing the atmoic numbering scheme and 30% probability displacement ellipsoids.

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Crystal data

$C_{20}H_{15}BrN_2O_2$

$M_r = 395.25$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 12.8744 (10)$ Å

$b = 5.9968 (10)$ Å

$c = 22.106 (2)$ Å

$\beta = 91.221 (1)°$

$V = 1706.3 (3)$ Å^3

$Z = 4$

$F(000) = 800$

$D_x = 1.539$ Mg m^{-3}

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

Cell parameters from 3171 reflections

$\theta = 1.6–25.5°$

$\mu = 2.43$ mm^{-1}

$T = 297$ K

Block, yellow

$0.12 \times 0.10 \times 0.08$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer	8088 measured reflections
Radiation source: fine-focus sealed tube	3009 independent reflections
Graphite monochromator	2140 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.027$
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)	$\theta_{max} = 25.1°$, $\theta_{min} = 1.6°$
	$h = -14 \rightarrow 15$
	$k = -6 \rightarrow 7$
$T_{min} = 0.760$, $T_{max} = 0.830$	$l = -24 \rightarrow 26$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.045$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.141$	
$S = 1.00$	H-atom parameters constrained
3009 reflections	$w = 1/[\sigma^2(F_o^2) + (0.085P)^2 + 0.9153P]$ where $P = (F_o^2 + 2F_c^2)/3$
228 parameters	
2 restraints	$(\Delta/\sigma)_{max} = 0.002$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.78$ e Å^{-3}
	$\Delta\rho_{min} = -0.62$ e Å^{-3}

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 $F^2 > \sigma(F^2)$ 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	0.27473 (4)	0.20430 (9)	1.05914 (2)	0.0635 (2)
C1	0.1838 (3)	0.8216 (6)	0.94539 (16)	0.0417 (9)
C2	0.1078 (2)	0.7023 (5)	0.97413 (14)	0.0317 (8)
H2	0.0386	0.7461	0.9718	0.038*
C3	0.1377 (3)	0.5168 (5)	1.00639 (16)	0.0481 (10)
H3	0.0878	0.4316	1.0255	0.058*
C4	0.2398 (3)	0.4554 (7)	1.01079 (17)	0.0447 (9)
C5	0.3167 (3)	0.5727 (7)	0.98216 (18)	0.0486 (10)
H5	0.3860	0.5298	0.9853	0.058*
C6	0.2863 (3)	0.7566 (7)	0.94862 (18)	0.0446 (10)
C7	0.4151 (3)	0.7950 (7)	0.87700 (19)	0.0464 (10)
H7	0.4002	0.6486	0.8660	0.056*
C8	0.4988 (3)	0.9113 (7)	0.84710 (18)	0.0449 (9)
C9	0.5316 (3)	1.1220 (8)	0.8668 (2)	0.0517 (10)
C10	0.6197 (4)	1.2177 (9)	0.8394 (2)	0.0662 (13)
H10	0.6438	1.3558	0.8528	0.079*

C11	0.6688 (4)	1.1140 (10)	0.7950 (2)	0.0676 (13)
H11	0.7260	1.1814	0.7776	0.081*
C12	0.6359 (4)	0.9088 (10)	0.7746 (2)	0.0663 (13)
H12	0.6706	0.8387	0.7434	0.080*
C13	0.5525 (3)	0.8076 (8)	0.79998 (19)	0.0547 (11)
H13	0.5309	0.6685	0.7860	0.066*
C14	0.0595 (3)	1.0603 (7)	0.90197 (16)	0.0425 (9)
H14	0.0075	0.9705	0.9174	0.051*
C15	0.0308 (3)	1.2554 (7)	0.86720 (17)	0.0436 (9)
C16	0.1076 (3)	1.3984 (7)	0.84457 (16)	0.0485 (10)
C17	0.0765 (4)	1.5884 (8)	0.81293 (19)	0.0637 (13)
H17	0.1263	1.6840	0.7975	0.076*
C18	−0.0274 (5)	1.6360 (8)	0.8042 (2)	0.0671 (14)
H18	−0.0468	1.7656	0.7839	0.081*
C19	−0.1025 (4)	1.4960 (8)	0.8251 (2)	0.0629 (12)
H19	−0.1724	1.5278	0.8180	0.076*
C20	−0.0733 (3)	1.3075 (7)	0.85666 (19)	0.0525 (10)
H20	−0.1243	1.2131	0.8713	0.063*
N2	0.1546 (2)	1.0078 (6)	0.91204 (14)	0.0425 (8)
N3	0.3615 (2)	0.8877 (6)	0.91782 (16)	0.0501 (8)
O1	0.4841 (3)	1.2338 (6)	0.91170 (19)	0.0761 (11)
H1	0.4403	1.1533	0.9269	0.114*
O2	0.2093 (2)	1.3554 (6)	0.85188 (15)	0.0654 (9)
H2A	0.2175	1.2538	0.8764	0.098*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0748 (4)	0.0534 (3)	0.0618 (3)	0.0087 (2)	−0.0108 (2)	0.0073 (2)
C1	0.040 (2)	0.041 (2)	0.044 (2)	−0.0021 (17)	−0.0003 (16)	−0.0050 (18)
C2	0.0219 (16)	0.037 (2)	0.0360 (18)	−0.0026 (15)	0.0033 (14)	0.0062 (16)
C3	0.045 (2)	0.051 (3)	0.049 (2)	−0.0092 (19)	−0.0011 (18)	0.002 (2)
C4	0.049 (2)	0.040 (2)	0.045 (2)	−0.0010 (18)	−0.0053 (18)	−0.0017 (18)
C5	0.045 (2)	0.045 (3)	0.056 (2)	0.0010 (19)	0.0008 (19)	−0.007 (2)
C6	0.043 (2)	0.043 (2)	0.048 (2)	−0.0090 (18)	0.0065 (18)	−0.0074 (18)
C7	0.039 (2)	0.040 (2)	0.060 (3)	−0.0005 (18)	−0.0018 (19)	0.003 (2)
C8	0.038 (2)	0.044 (2)	0.052 (2)	0.0042 (18)	−0.0049 (17)	0.0056 (19)
C9	0.037 (2)	0.049 (3)	0.069 (3)	−0.0003 (19)	0.002 (2)	0.005 (2)
C10	0.049 (3)	0.060 (3)	0.089 (4)	−0.011 (2)	0.000 (3)	0.012 (3)
C11	0.047 (3)	0.085 (4)	0.071 (3)	−0.005 (3)	0.008 (2)	0.015 (3)
C12	0.055 (3)	0.092 (4)	0.053 (3)	0.005 (3)	0.011 (2)	0.007 (3)
C13	0.050 (2)	0.066 (3)	0.049 (2)	0.002 (2)	0.001 (2)	0.001 (2)
C14	0.046 (2)	0.040 (2)	0.042 (2)	−0.0061 (18)	0.0042 (17)	0.0001 (17)
C15	0.056 (2)	0.039 (2)	0.036 (2)	−0.0036 (18)	0.0029 (18)	−0.0023 (16)
C16	0.065 (3)	0.046 (2)	0.035 (2)	−0.011 (2)	0.0036 (19)	−0.0024 (19)
C17	0.103 (4)	0.048 (3)	0.041 (2)	−0.018 (3)	0.010 (2)	0.004 (2)
C18	0.109 (4)	0.045 (3)	0.046 (3)	0.010 (3)	−0.013 (3)	0.005 (2)
C19	0.074 (3)	0.056 (3)	0.058 (3)	0.012 (3)	−0.006 (2)	0.003 (2)

C20	0.057 (3)	0.050 (3)	0.051 (2)	0.000 (2)	0.000 (2)	0.001 (2)
N2	0.0408 (18)	0.0416 (19)	0.0453 (18)	−0.0045 (14)	0.0014 (14)	0.0006 (15)
N3	0.0393 (18)	0.046 (2)	0.065 (2)	−0.0065 (16)	0.0084 (16)	−0.0063 (18)
O1	0.063 (2)	0.052 (2)	0.114 (3)	−0.0116 (16)	0.028 (2)	−0.021 (2)
O2	0.060 (2)	0.072 (2)	0.065 (2)	−0.0218 (17)	0.0083 (16)	0.0092 (17)

Geometric parameters (Å, º)

Br1—C4	1.895 (4)	C11—C12	1.375 (8)
C1—C6	1.377 (6)	C11—H11	0.9300
C1—C2	1.378 (5)	C12—C13	1.364 (6)
C1—N2	1.385 (5)	C12—H12	0.9300
C2—C3	1.372 (4)	C13—H13	0.9300
C2—H2	0.9300	C14—N2	1.279 (5)
C3—C4	1.367 (5)	C14—C15	1.443 (5)
C3—H3	0.9300	C14—H14	0.9300
C4—C5	1.379 (6)	C15—C20	1.391 (6)
C5—C6	1.381 (6)	C15—C16	1.409 (6)
C5—H5	0.9300	C16—O2	1.341 (5)
C6—N3	1.430 (5)	C16—C17	1.391 (6)
C7—N3	1.275 (5)	C17—C18	1.377 (7)
C7—C8	1.454 (6)	C17—H17	0.9300
C7—H7	0.9300	C18—C19	1.367 (7)
C8—C9	1.399 (6)	C18—H18	0.9300
C8—C13	1.408 (6)	C19—C20	1.377 (6)
C9—O1	1.354 (5)	C19—H19	0.9300
C9—C10	1.419 (6)	C20—H20	0.9300
C10—C11	1.333 (7)	O1—H1	0.8200
C10—H10	0.9300	O2—H2A	0.8200
C6—C1—C2	121.2 (3)	C12—C11—H11	119.6
C6—C1—N2	120.3 (3)	C13—C12—C11	120.2 (5)
C2—C1—N2	118.5 (3)	C13—C12—H12	119.9
C3—C2—C1	117.8 (3)	C11—C12—H12	119.9
C3—C2—H2	121.1	C12—C13—C8	120.7 (5)
C1—C2—H2	121.1	C12—C13—H13	119.6
C4—C3—C2	121.0 (3)	C8—C13—H13	119.6
C4—C3—H3	119.5	N2—C14—C15	121.7 (4)
C2—C3—H3	119.5	N2—C14—H14	119.2
C3—C4—C5	121.9 (4)	C15—C14—H14	119.2
C3—C4—Br1	118.1 (3)	C20—C15—C16	119.0 (4)
C5—C4—Br1	120.0 (3)	C20—C15—C14	120.4 (4)
C4—C5—C6	117.1 (4)	C16—C15—C14	120.6 (4)
C4—C5—H5	121.4	O2—C16—C17	119.2 (4)
C6—C5—H5	121.4	O2—C16—C15	122.1 (4)
C1—C6—C5	121.0 (3)	C17—C16—C15	118.7 (4)
C1—C6—N3	118.5 (4)	C18—C17—C16	120.6 (4)
C5—C6—N3	120.5 (4)	C18—C17—H17	119.7

N3—C7—C8	122.0 (4)	C16—C17—H17	119.7
N3—C7—H7	119.0	C19—C18—C17	121.1 (5)
C8—C7—H7	119.0	C19—C18—H18	119.4
C9—C8—C13	118.7 (4)	C17—C18—H18	119.4
C9—C8—C7	120.9 (4)	C18—C19—C20	119.2 (5)
C13—C8—C7	120.3 (4)	C18—C19—H19	120.4
O1—C9—C8	122.5 (4)	C20—C19—H19	120.4
O1—C9—C10	119.3 (4)	C19—C20—C15	121.4 (4)
C8—C9—C10	118.1 (4)	C19—C20—H20	119.3
C11—C10—C9	121.5 (5)	C15—C20—H20	119.3
C11—C10—H10	119.3	C14—N2—C1	122.6 (3)
C9—C10—H10	119.3	C7—N3—C6	118.6 (4)
C10—C11—C12	120.8 (5)	C9—O1—H1	109.5
C10—C11—H11	119.6	C16—O2—H2A	109.5

Hydrogen-bond geometry (Å, º)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O2—H2*A*⋯N2	0.82	1.87	2.578 (4)	145
O1—H1⋯N3	0.82	1.90	2.614 (5)	145