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2-Bromo-4-chloro-6-[(*E*)-(2-chlorophenyl)iminomethyl]phenol

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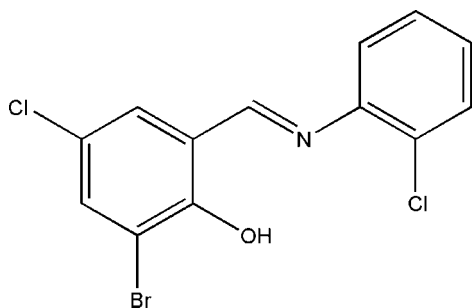
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.032; wR factor = 0.077; data-to-parameter ratio = 14.0.

The title compound, $\text{C}_{13}\text{H}_8\text{BrCl}_2\text{NO}$, was obtained by reaction of 3-bromo-5-chlorosalicylaldehyde and 2-chlorobenzeneamine in methanol. The molecule displays an *E* configuration with respect to the imine $\text{C}=\text{N}$ double bond. The dihedral angle between the two benzene rings is 4.57 (11)°. The molecular conformation is stabilized by an intramolecular $\text{O}-\text{H}\cdots\text{N}$ hydrogen bond. In the crystal structure, molecules are linked by intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions into zigzag chains running parallel to the *b* axis. Intermolecular $\text{Br}\cdots\text{Cl}$ [3.5289 (11) Å] and $\text{Cl}\cdots\text{Cl}$ [3.5042 (12) Å] interactions are present.

Related literature

For the biological activities of Schiff base complexes, see: Cukurovali *et al.* (2002); Tarafder *et al.* (2002); Ali *et al.* (2002). For halogen-halogen interactions, see: Saruma *et al.* (1986); Moorthy *et al.* (2002).



Experimental

Crystal data

 $\text{C}_{13}\text{H}_8\text{BrCl}_2\text{NO}$ $M_r = 345.01$

Monoclinic, $P2_1/c$
 $a = 8.4299$ (10) Å
 $b = 14.0115$ (16) Å
 $c = 11.4194$ (14) Å
 $\beta = 104.5120$ (10)°
 $V = 1305.8$ (3) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 3.54$ mm⁻¹
 $T = 298$ K
 $0.45 \times 0.38 \times 0.36$ mm

Data collection

Siemens SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Siemens, 1996)
 $T_{\min} = 0.230$, $T_{\max} = 0.279$

6450 measured reflections
 2295 independent reflections
 1726 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.077$
 $S = 1.03$
 2295 reflections

164 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.39$ e Å⁻³
 $\Delta\rho_{\min} = -0.58$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{O1}-\text{H1}\cdots\text{N1}$ | 0.82 | 1.86 | 2.586 (3) | 147 |
| $\text{C11}-\text{H11}\cdots\text{O1}^i$ | 0.93 | 2.56 | 3.324 (5) | 139 |

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

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; 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.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2298).

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supplementary materials

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2-Bromo-4-chloro-6-[(*E*)-(2-chlorophenyl)iminomethyl]phenol

X. Zhang

Comment

Schiff base complexes are of great interests for inorganic and bioinorganic chemistry. To the best of our knowledge, in the past two decades Schiff base ligands have demonstrated significant biological activities and new examples have been tested for their antitumor, antimicrobial and antiviral activities (Tarafder *et al.*, 2002; Cukurovali *et al.*, 2002; Ali *et al.*, 2002). As an extension of the work on the structural characterization of Schiff base compounds, the crystal structure of the title compound is reported here.

The molecular structure and crystal packing of the title compound are illustrated in Fig. 1 and 2, respectively. The C1=N1 bond distance (1.279 (4) Å) is shorter than expected. The molecule is not strictly planar, the maximum deviations from the planarity are 0.199 (5) and 0.162 (5) for atoms C11 and C12. The dihedral angle formed by the benzene rings is 4.57 (11)°. The molecular conformation is stabilized by an intramolecular O—H...N hydrogen bond (Table 1). In the crystal packing, the molecules are linked via intermolecular C—H...O hydrogen bonds into zig-zag chains running parallel to the *b* axis. In addition, intermolecular Br...Cl and Cl...Cl interactions are observed (Fig. 2) falling in the typical range of halogen-halogen interactions (Saruma & Desiraju, 1986, Moorthy *et al.*, 2002): Br1...Cl1ⁱ = 3.5289 (11) Å; Cl1...Cl2ⁱⁱ = 3.5042 (12) Å; symmetry codes: (i) *x*, 3/2-*y*, -1/2+*z*; (ii) 1+*x*, *y*, 1+*z*.

Experimental

3-Bromo-5-chlorosalicylaldehyde (0.1 mmol, 23.6 mg) and 2-chlorobenzeneamine (0.1 mmol, 12.8 mg) were dissolved in methanol (10 ml). The mixture was stirred at room temperature for 1 h and then filtered. After allowing the filtrate to stand in air for 7 d, yellow block-shaped crystals of the title compound were formed by slow evaporation of the solvent. The crystals were collected, washed with methanol and dried in a vacuum desiccator using anhydrous CaCl₂ (yield 52%).

Refinement

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.93 Å, O—H = 0.82 Å and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C}, \text{O})$.

Figures

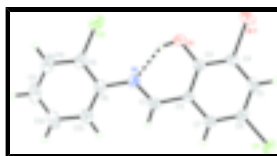


Fig. 1. The structure of the title compound with 30% probability ellipsoids. H atoms are shown as spheres of arbitrary radii. The dashed line represents a hydrogen bond.

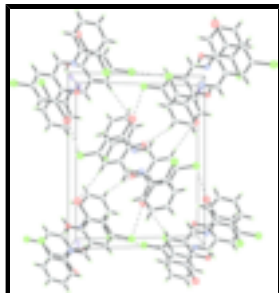


Fig. 2. The crystal packing of the title compound viewed along the *a* axis. Halogen-halogen interactions are shown as dashed lines.

2-Bromo-4-chloro-6-[(*E*)-(2-chlorophenyl)iminomethyl]phenol

Crystal data

$C_{13}H_8BrCl_2NO$

$M_r = 345.01$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 8.4299$ (10) Å

$b = 14.0115$ (16) Å

$c = 11.4194$ (14) Å

$\beta = 104.5120$ (10)°

$V = 1305.8$ (3) Å³

$Z = 4$

$F_{000} = 680$

$D_x = 1.755$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 2353 reflections

$\theta = 2.4$ – 25.2 °

$\mu = 3.54$ mm⁻¹

$T = 298$ K

Block, yellow

$0.45 \times 0.38 \times 0.36$ mm

Data collection

Siemens SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 298$ K

φ and ω scans

Absorption correction: multi-scan (SADABS; Siemens, 1996)

$T_{\min} = 0.230$, $T_{\max} = 0.279$

6450 measured reflections

2295 independent reflections

1726 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\text{max}} = 25.0$ °

$\theta_{\text{min}} = 2.4$ °

$h = -10 \rightarrow 9$

$k = -14 \rightarrow 16$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

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

$wR(F^2) = 0.077$

$S = 1.03$

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0256P)^2 + 0.9771P]$$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\text{max}} = 0.39$ e Å⁻³

2295 reflections

$$\Delta\rho_{\min} = -0.57 \text{ e } \text{\AA}^{-3}$$

164 parameters

Extinction correction: SHELXL97 (Sheldrick, 2008),

$$F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$$

Primary atom site location: structure-invariant direct methods

Extinction coefficient: 0.0127 (8)

Secondary atom site location: difference Fourier map

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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|---------------|--------------|--------------|----------------------------------|
| Br1 | 0.54350 (5) | 0.75675 (2) | 0.54203 (4) | 0.06096 (18) |
| Cl1 | 0.70198 (11) | 0.53128 (7) | 0.95100 (8) | 0.0596 (3) |
| Cl2 | -0.01427 (12) | 0.49417 (8) | 0.22925 (8) | 0.0767 (3) |
| N1 | 0.1581 (3) | 0.43674 (18) | 0.4723 (2) | 0.0434 (7) |
| O1 | 0.3040 (3) | 0.59685 (15) | 0.45663 (19) | 0.0500 (6) |
| H1 | 0.2386 | 0.5532 | 0.4344 | 0.075* |
| C1 | 0.2481 (4) | 0.4266 (2) | 0.5798 (3) | 0.0436 (8) |
| H1A | 0.2359 | 0.3725 | 0.6238 | 0.052* |
| C2 | 0.3687 (4) | 0.4978 (2) | 0.6346 (3) | 0.0381 (7) |
| C3 | 0.3916 (4) | 0.5800 (2) | 0.5697 (3) | 0.0387 (7) |
| C4 | 0.5108 (4) | 0.6456 (2) | 0.6259 (3) | 0.0420 (8) |
| C5 | 0.6058 (4) | 0.6305 (2) | 0.7418 (3) | 0.0461 (8) |
| H5 | 0.6860 | 0.6744 | 0.7777 | 0.055* |
| C6 | 0.5809 (4) | 0.5499 (2) | 0.8042 (3) | 0.0453 (8) |
| C7 | 0.4644 (4) | 0.4838 (2) | 0.7520 (3) | 0.0436 (8) |
| H7 | 0.4492 | 0.4296 | 0.7950 | 0.052* |
| C8 | 0.0439 (4) | 0.3675 (2) | 0.4143 (3) | 0.0457 (8) |
| C9 | -0.0435 (4) | 0.3866 (3) | 0.2963 (3) | 0.0528 (9) |
| C10 | -0.1548 (5) | 0.3222 (4) | 0.2313 (4) | 0.0741 (13) |
| H10 | -0.2122 | 0.3362 | 0.1524 | 0.089* |
| C11 | -0.1804 (5) | 0.2369 (3) | 0.2839 (5) | 0.0814 (14) |
| H11 | -0.2550 | 0.1931 | 0.2403 | 0.098* |
| C12 | -0.0967 (5) | 0.2165 (3) | 0.3997 (5) | 0.0751 (12) |
| H12 | -0.1145 | 0.1589 | 0.4349 | 0.090* |
| C13 | 0.0149 (5) | 0.2818 (3) | 0.4650 (4) | 0.0622 (10) |
| H13 | 0.0711 | 0.2677 | 0.5440 | 0.075* |

supplementary materials

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|---------------|-------------|--------------|
| Br1 | 0.0721 (3) | 0.0385 (2) | 0.0755 (3) | -0.00233 (18) | 0.0246 (2) | 0.00929 (18) |
| Cl1 | 0.0696 (6) | 0.0611 (6) | 0.0377 (5) | 0.0104 (5) | -0.0059 (4) | -0.0064 (4) |
| Cl2 | 0.0649 (6) | 0.1111 (9) | 0.0489 (6) | -0.0086 (6) | 0.0043 (5) | 0.0204 (6) |
| N1 | 0.0443 (15) | 0.0433 (15) | 0.0400 (16) | -0.0012 (12) | 0.0058 (13) | -0.0021 (13) |
| O1 | 0.0568 (14) | 0.0463 (13) | 0.0419 (14) | -0.0019 (11) | 0.0033 (11) | 0.0102 (11) |
| C1 | 0.053 (2) | 0.0336 (17) | 0.045 (2) | 0.0022 (15) | 0.0139 (17) | 0.0005 (15) |
| C2 | 0.0456 (18) | 0.0347 (16) | 0.0339 (16) | 0.0025 (14) | 0.0100 (14) | -0.0008 (14) |
| C3 | 0.0413 (18) | 0.0372 (17) | 0.0376 (18) | 0.0075 (14) | 0.0100 (15) | 0.0012 (14) |
| C4 | 0.0472 (19) | 0.0302 (16) | 0.051 (2) | 0.0046 (14) | 0.0159 (16) | 0.0037 (14) |
| C5 | 0.0457 (19) | 0.0396 (18) | 0.051 (2) | 0.0001 (15) | 0.0078 (17) | -0.0093 (16) |
| C6 | 0.052 (2) | 0.0444 (19) | 0.0365 (18) | 0.0114 (16) | 0.0050 (15) | -0.0022 (15) |
| C7 | 0.056 (2) | 0.0365 (17) | 0.0375 (18) | 0.0046 (16) | 0.0096 (16) | 0.0017 (15) |
| C8 | 0.0420 (18) | 0.048 (2) | 0.047 (2) | 0.0008 (15) | 0.0108 (16) | -0.0116 (16) |
| C9 | 0.042 (2) | 0.073 (2) | 0.043 (2) | 0.0002 (18) | 0.0108 (16) | -0.0120 (18) |
| C10 | 0.057 (2) | 0.111 (4) | 0.052 (2) | -0.013 (2) | 0.011 (2) | -0.029 (3) |
| C11 | 0.066 (3) | 0.088 (3) | 0.091 (4) | -0.021 (2) | 0.020 (3) | -0.052 (3) |
| C12 | 0.073 (3) | 0.055 (2) | 0.099 (4) | -0.018 (2) | 0.023 (3) | -0.022 (3) |
| C13 | 0.065 (2) | 0.051 (2) | 0.065 (3) | -0.0089 (19) | 0.006 (2) | -0.0048 (19) |

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

| | | | |
|-----------|-----------|------------|-----------|
| Br1—C4 | 1.885 (3) | C5—H5 | 0.9300 |
| Cl1—C6 | 1.750 (3) | C6—C7 | 1.373 (5) |
| Cl2—C9 | 1.736 (4) | C7—H7 | 0.9300 |
| N1—C1 | 1.279 (4) | C8—C13 | 1.381 (5) |
| N1—C8 | 1.409 (4) | C8—C9 | 1.390 (5) |
| O1—C3 | 1.338 (3) | C9—C10 | 1.377 (5) |
| O1—H1 | 0.8200 | C10—C11 | 1.379 (6) |
| C1—C2 | 1.449 (4) | C10—H10 | 0.9300 |
| C1—H1A | 0.9300 | C11—C12 | 1.364 (7) |
| C2—C7 | 1.394 (4) | C11—H11 | 0.9300 |
| C2—C3 | 1.409 (4) | C12—C13 | 1.388 (5) |
| C3—C4 | 1.394 (4) | C12—H12 | 0.9300 |
| C4—C5 | 1.381 (4) | C13—H13 | 0.9300 |
| C5—C6 | 1.378 (4) | | |
| C1—N1—C8 | 123.1 (3) | C6—C7—H7 | 120.0 |
| C3—O1—H1 | 109.5 | C2—C7—H7 | 120.0 |
| N1—C1—C2 | 121.4 (3) | C13—C8—C9 | 117.8 (3) |
| N1—C1—H1A | 119.3 | C13—C8—N1 | 125.0 (3) |
| C2—C1—H1A | 119.3 | C9—C8—N1 | 117.2 (3) |
| C7—C2—C3 | 119.9 (3) | C10—C9—C8 | 121.4 (4) |
| C7—C2—C1 | 119.5 (3) | C10—C9—C12 | 118.9 (3) |
| C3—C2—C1 | 120.6 (3) | C8—C9—C12 | 119.7 (3) |
| O1—C3—C4 | 119.2 (3) | C9—C10—C11 | 119.5 (4) |

| | | | |
|--------------|------------|-----------------|------------|
| O1—C3—C2 | 122.4 (3) | C9—C10—H10 | 120.3 |
| C4—C3—C2 | 118.3 (3) | C11—C10—H10 | 120.3 |
| C5—C4—C3 | 121.2 (3) | C12—C11—C10 | 120.3 (4) |
| C5—C4—Br1 | 119.4 (2) | C12—C11—H11 | 119.8 |
| C3—C4—Br1 | 119.4 (2) | C10—C11—H11 | 119.8 |
| C6—C5—C4 | 119.6 (3) | C11—C12—C13 | 119.9 (4) |
| C6—C5—H5 | 120.2 | C11—C12—H12 | 120.1 |
| C4—C5—H5 | 120.2 | C13—C12—H12 | 120.1 |
| C7—C6—C5 | 120.9 (3) | C8—C13—C12 | 121.1 (4) |
| C7—C6—C11 | 119.8 (3) | C8—C13—H13 | 119.5 |
| C5—C6—C11 | 119.3 (3) | C12—C13—H13 | 119.5 |
| C6—C7—C2 | 120.1 (3) | | |
| C8—N1—C1—C2 | 177.5 (3) | C11—C6—C7—C2 | -179.4 (2) |
| N1—C1—C2—C7 | -179.9 (3) | C3—C2—C7—C6 | -0.2 (5) |
| N1—C1—C2—C3 | -0.8 (5) | C1—C2—C7—C6 | 178.9 (3) |
| C7—C2—C3—O1 | 179.6 (3) | C1—N1—C8—C13 | 0.1 (5) |
| C1—C2—C3—O1 | 0.6 (4) | C1—N1—C8—C9 | -178.6 (3) |
| C7—C2—C3—C4 | 0.0 (4) | C13—C8—C9—C10 | -0.4 (5) |
| C1—C2—C3—C4 | -179.1 (3) | N1—C8—C9—C10 | 178.4 (3) |
| O1—C3—C4—C5 | -179.1 (3) | C13—C8—C9—C12 | 178.9 (3) |
| C2—C3—C4—C5 | 0.6 (4) | N1—C8—C9—C12 | -2.3 (4) |
| O1—C3—C4—Br1 | 0.8 (4) | C8—C9—C10—C11 | 0.0 (6) |
| C2—C3—C4—Br1 | -179.6 (2) | C12—C9—C10—C11 | -179.3 (3) |
| C3—C4—C5—C6 | -1.0 (5) | C9—C10—C11—C12 | 0.3 (6) |
| Br1—C4—C5—C6 | 179.2 (2) | C10—C11—C12—C13 | -0.1 (7) |
| C4—C5—C6—C7 | 0.8 (5) | C9—C8—C13—C12 | 0.6 (6) |
| C4—C5—C6—C11 | 180.0 (2) | N1—C8—C13—C12 | -178.1 (3) |
| C5—C6—C7—C2 | -0.2 (5) | C11—C12—C13—C8 | -0.4 (6) |

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|----------------------------------|-------|-------------|-------------|---------------|
| O1—H1 \cdots N1 | 0.82 | 1.86 | 2.586 (3) | 147 |
| C11—H11 \cdots O1 ⁱ | 0.93 | 2.56 | 3.324 (5) | 139 |

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

Fig. 1

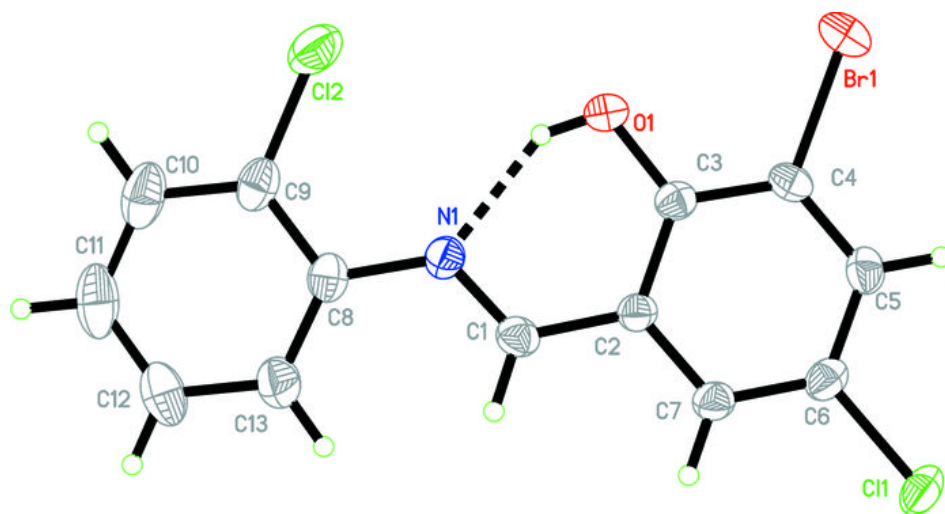


Fig. 2

