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5-Bromo-2-hydroxybenzaldehyde 4-ethylthiosemicarbazone

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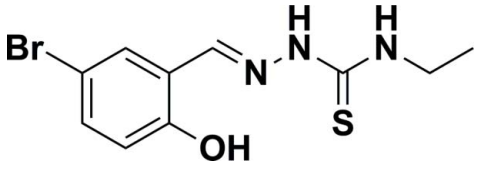
Key indicators: single-crystal X-ray study; T = 123 K; mean σ(C–C) = 0.005 Å; R factor = 0.042; wR factor = 0.114; data-to-parameter ratio = 15.0.

In the title Schiff base compound, $C_{10}H_{12}BrN_3OS$, the C—N—N—C torsion angle is 172.07 (11)°. An intramolecular hydrogen bond exists between the hydroxy H atom and the azomethine N atom. In the crystal, pairs of hydrogen bonds involving the imino H atom and the S atom give rise to supramolecular dimers.

Related literature

For the isostructural compound 5-chloro-2-hydroxybenzaldehyde 4-ethylthiosemicarbazone, see: Lo *et al.* (2011)



Experimental

Crystal data

$C_{10}H_{12}BrN_3OS$
M_r = 302.20
Monoclinic, $C2/c$
a = 22.040 (4) Å
b = 11.844 (2) Å
c = 9.5102 (19) Å
β = 101.69 (3)°
V = 2431.1 (8) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 3.54 mm^{-1}
T = 123 K
0.20 × 0.10 × 0.05 mm

Data collection

Rigaku Saturn70 diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2008)
T_{min} = 0.661, T_{max} = 0.838
4201 measured reflections
2331 independent reflections
1760 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.114
S = 0.95
2331 reflections
155 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.70 e Å^{-3}
$\Delta\rho_{min}$ = −1.01 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···N1	0.84 (3)	2.00 (2)	2.674 (3)	137 (3)
N2—H2A···S1^{i}	0.88 (3)	2.47 (3)	3.316 (3)	161 (2)
N3—H3A···S1^{ii}	0.87 (3)	2.75 (3)	3.510 (3)	146 (3)

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

Data collection: *CrystalClear* (Rigaku, 2008); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; 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: *publCIF* (Westrip, 2010).

The authors would like to thank the China Scholarship Council (CSC).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG5322).

References

Lo, K. M. & Ng, S. W. (2011). *Acta Cryst.* E**67**, o1453.
Rigaku (2008). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2013). E**69**, o762 [https://doi.org/10.1107/S1600536813008787]

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S1. Comment

A Schiff ligand was synthesized through one-pot reaction with high yield using 5-bromo-2-hydroxybenzaldehyde and 4-ethyl-3-thiosemicarbazide (Fig. 1). The title compound can be used as tridentate chelating ligand to construct spin-crossover complexes. Isostructural 5-chloro-2-hydroxybenzaldehyde-4-ethylthiosemicarbazone was reported previously (Lo *et al.*, 2011).

In the title compound, a strong intramolecular hydrogen bond O—H···N is observed. An intermolecular N—H···S hydrogen bond connects two molecules into a supramolecular dimer as shown in Figure 2.

S2. Experimental

5-Bromo-2-hydroxybenzaldehyde (4.02 g, 20 mmol) in 50 ml ethanol and 4-ethyl-3-thiosemicarbazide (2.38 g, 20 mmol) were reacted for 6 h at 350 K. Slow evaporation of the yellow solution gave large colorless crystals.

S3. Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H 0.95, 0.98 and 0.99 Å) and were included in the refinement in the riding model approximation, with U_{iso}(H) =1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C) for the others. The hydroxy and amino H atoms were located in a difference Fourier map, and were refined with distance restraints of O—H 0.85±0.01 and N—H 0.88±0.01 Å; with U_{iso}(H) =1.2U_{eq}(N and O).

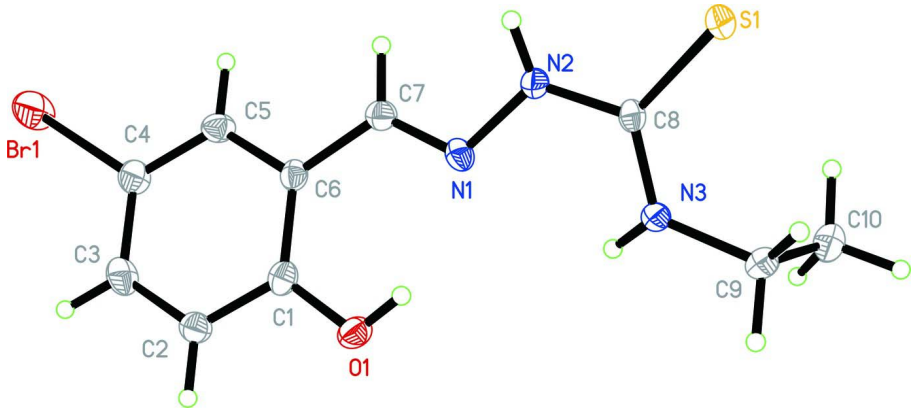

Figure 1

Displacement ellipsoid plot (50% probability level) of the title compound, with atom numbering of structurally unique non-H atoms and the H atoms.

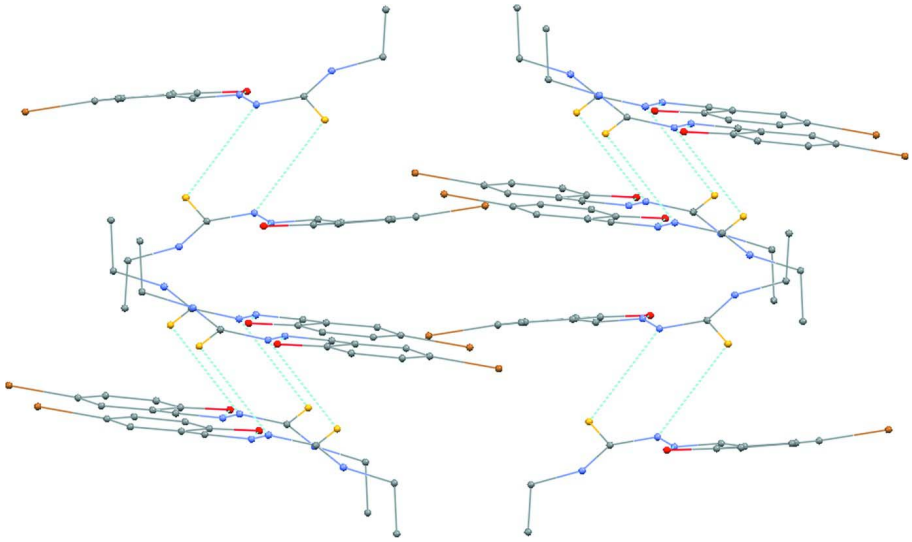

Figure 2

The packing diagram of the title compound, with H atoms omitted for clarity. Hydrogen bonds are shown as dashed lines.

5-Bromo-2-hydroxybenzaldehyde 4-ethylthiosemicarbazone

Crystal data

$C_{10}H_{12}BrN_3OS$
$M_r = 302.20$
Monoclinic, $C2/c$
Hall symbol: -C 2yc
$a = 22.040$ (4) Å
$b = 11.844$ (2) Å
$c = 9.5102$ (19) Å
$\beta = 101.69$ (3)°
$V = 2431.1$ (8) Å^3
$Z = 8$
$F(000) = 1216$
$D_x = 1.651$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.710747$ Å
Cell parameters from 3650 reflections
$\theta = 3.1$–$27.5°$
$\mu = 3.54$ mm^{-1}
$T = 123$ K
Block, colourless
0.20 × 0.10 × 0.05 mm

Data collection

Rigaku Saturn70 diffractometer
Radiation source: Rotating Anode
Confocal monochromator
Detector resolution: 28.5714 pixels mm^{-1}
dtprofit.ref scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2008)
$T_{min} = 0.661$, $T_{max} = 0.838$
4201 measured reflections
2331 independent reflections
1760 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 26.0°$, $\theta_{min} = 3.1°$
$h = -27\rightarrow20$
$k = -9\rightarrow14$
$l = -11\rightarrow10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.114$
$S = 0.95$
2331 reflections
155 parameters
3 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0752P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.70$ e Å^{-3}
$\Delta\rho_{min} = -1.01$ 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	0.484097 (17)	0.67444 (4)	1.01744 (4)	0.04059 (19)
C1	0.69767 (15)	0.6276 (2)	1.0597 (3)	0.0180 (7)
C2	0.67216 (16)	0.6364 (3)	1.1818 (3)	0.0197 (7)
H2	0.6985	0.6352	1.2742	0.024*
C3	0.60893 (17)	0.6470 (3)	1.1699 (4)	0.0227 (7)
H3	0.5919	0.6537	1.2536	0.027*
C4	0.57021 (16)	0.6476 (3)	1.0343 (4)	0.0222 (7)
C5	0.59471 (16)	0.6361 (3)	0.9125 (3)	0.0198 (7)
H5	0.5678	0.6343	0.8208	0.024*
C6	0.65841 (15)	0.6271 (3)	0.9228 (3)	0.0164 (7)
C7	0.68243 (15)	0.6269 (3)	0.7906 (3)	0.0179 (7)
H7	0.6542	0.6340	0.7012	0.021*
C8	0.81461 (14)	0.6124 (2)	0.6421 (3)	0.0150 (6)
C9	0.91521 (15)	0.5238 (3)	0.7381 (3)	0.0216 (7)
H9A	0.9408	0.5182	0.8363	0.026*
H9B	0.9339	0.5821	0.6855	0.026*
C10	0.91576 (17)	0.4111 (3)	0.6625 (4)	0.0270 (8)
H10A	0.9008	0.3519	0.7190	0.040*
H10B	0.9581	0.3935	0.6524	0.040*
H10C	0.8887	0.4152	0.5672	0.040*
H1A	0.7730 (17)	0.634 (3)	1.002 (2)	0.032*
H2A	0.7325 (16)	0.680 (2)	0.600 (3)	0.032*
H3A	0.8346 (17)	0.525 (3)	0.810 (3)	0.032*
N1	0.74029 (12)	0.6174 (2)	0.7914 (3)	0.0169 (6)
N2	0.75628 (13)	0.6333 (2)	0.6594 (3)	0.0177 (6)
N3	0.85244 (13)	0.5580 (2)	0.7468 (3)	0.0172 (6)
O1	0.75977 (11)	0.62315 (19)	1.0781 (2)	0.0207 (5)
S1	0.83506 (4)	0.65794 (7)	0.48834 (9)	0.0201 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0165 (2)	0.0815 (4)	0.0261 (2)	0.00156 (19)	0.00976 (16)	0.00158 (19)
C1	0.0186 (18)	0.0130 (14)	0.0228 (17)	0.0006 (13)	0.0052 (14)	−0.0009 (13)
C2	0.0227 (19)	0.0187 (15)	0.0172 (16)	0.0008 (13)	0.0031 (14)	0.0002 (13)
C3	0.026 (2)	0.0234 (16)	0.0223 (16)	−0.0019 (14)	0.0134 (15)	0.0023 (14)
C4	0.0145 (18)	0.0314 (18)	0.0221 (17)	−0.0023 (14)	0.0066 (14)	−0.0001 (14)
C5	0.0163 (17)	0.0239 (16)	0.0180 (16)	−0.0019 (13)	0.0010 (13)	0.0013 (13)
C6	0.0173 (17)	0.0151 (14)	0.0180 (16)	0.0018 (13)	0.0065 (13)	0.0018 (13)
C7	0.0176 (17)	0.0187 (15)	0.0172 (15)	0.0003 (13)	0.0032 (13)	0.0011 (13)
C8	0.0166 (17)	0.0131 (14)	0.0162 (15)	0.0007 (12)	0.0056 (13)	−0.0023 (13)
C9	0.0152 (17)	0.0291 (17)	0.0198 (16)	0.0029 (14)	0.0017 (13)	0.0026 (14)
C10	0.021 (2)	0.033 (2)	0.0274 (18)	0.0060 (15)	0.0064 (15)	−0.0024 (15)
N1	0.0195 (15)	0.0169 (12)	0.0158 (13)	−0.0005 (11)	0.0073 (11)	0.0006 (11)
N2	0.0166 (15)	0.0213 (13)	0.0164 (13)	0.0046 (11)	0.0060 (11)	0.0034 (11)
N3	0.0145 (14)	0.0227 (14)	0.0145 (13)	0.0024 (11)	0.0036 (11)	0.0030 (11)
O1	0.0153 (13)	0.0259 (12)	0.0205 (12)	0.0017 (10)	0.0031 (10)	0.0040 (10)
S1	0.0192 (5)	0.0253 (4)	0.0175 (4)	0.0038 (3)	0.0079 (3)	0.0032 (3)

Geometric parameters (Å, º)

Br1—C4	1.899 (4)	C8—N3	1.329 (4)
C1—O1	1.345 (4)	C8—N2	1.351 (4)
C1—C2	1.393 (5)	C8—S1	1.703 (3)
C1—C6	1.410 (5)	C9—N3	1.460 (4)
C2—C3	1.381 (5)	C9—C10	1.517 (5)
C2—H2	0.9500	C9—H9A	0.9900
C3—C4	1.395 (5)	C9—H9B	0.9900
C3—H3	0.9500	C10—H10A	0.9800
C4—C5	1.380 (5)	C10—H10B	0.9800
C5—C6	1.391 (4)	C10—H10C	0.9800
C5—H5	0.9500	N1—N2	1.384 (3)
C6—C7	1.460 (4)	N2—H2A	0.879 (10)
C7—N1	1.278 (4)	N3—H3A	0.876 (10)
C7—H7	0.9500	O1—H1A	0.846 (10)
O1—C1—C2	117.8 (3)	N3—C8—S1	124.2 (2)
O1—C1—C6	122.5 (3)	N2—C8—S1	118.0 (2)
C2—C1—C6	119.6 (3)	N3—C9—C10	111.7 (3)
C3—C2—C1	120.6 (3)	N3—C9—H9A	109.3
C3—C2—H2	119.7	C10—C9—H9A	109.3
C1—C2—H2	119.7	N3—C9—H9B	109.3
C2—C3—C4	119.7 (3)	C10—C9—H9B	109.3
C2—C3—H3	120.2	H9A—C9—H9B	107.9
C4—C3—H3	120.2	C9—C10—H10A	109.5
C5—C4—C3	120.4 (3)	C9—C10—H10B	109.5
C5—C4—Br1	120.0 (3)	H10A—C10—H10B	109.5

C3—C4—Br1	119.5 (3)	C9—C10—H10C	109.5
C4—C5—C6	120.6 (3)	H10A—C10—H10C	109.5
C4—C5—H5	119.7	H10B—C10—H10C	109.5
C6—C5—H5	119.7	C7—N1—N2	114.8 (3)
C5—C6—C1	119.1 (3)	C8—N2—N1	120.6 (3)
C5—C6—C7	118.4 (3)	C8—N2—H2A	120 (3)
C1—C6—C7	122.2 (3)	N1—N2—H2A	116 (3)
N1—C7—C6	122.0 (3)	C8—N3—C9	123.4 (3)
N1—C7—H7	119.0	C8—N3—H3A	115 (3)
C6—C7—H7	119.0	C9—N3—H3A	119 (3)
N3—C8—N2	117.8 (3)	C1—O1—H1A	114 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···N1	0.84 (3)	2.00 (2)	2.674 (3)	137 (3)
N2—H2*A*···S1^{i}	0.88 (3)	2.47 (3)	3.316 (3)	161 (2)
N3—H3*A*···S1^{ii}	0.87 (3)	2.75 (3)	3.510 (3)	146 (3)

Symmetry codes: (i) −*x*+3/2, −*y*+3/2, −*z*+1; (ii) *x*, −*y*+1, *z*+1/2.