Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

4-(5-Bromo-2-hydroxybenzoyl)thiosemicarbazide

Long-Fei Jin

College of Chemistry and Materials Science, South-Central University for Nationalities, Wuhan 430074, People's Republic of China
Correspondence e-mail: jlfing@yahoo.com.cn

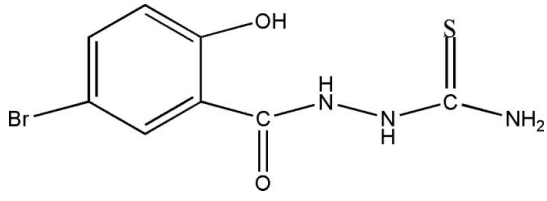
Received 29 June 2007; accepted 6 July 2007

Key indicators: single-crystal X-ray study; T = 292 K; mean σ(C–C) = 0.009 Å; R factor = 0.058; wR factor = 0.168; data-to-parameter ratio = 12.6.

In the title molecule, $C_8H_8BrN_3O_2S$, there are two intramolecular hydrogen bonds, one involving the hydrazo group and the O atom of the hydroxyl group, and the other involving the amino group and the N atom of the hydrazo group. In the crystal structure, intermolecular O—H···S, N—H···S and N—H···O hydrogen bonds connect molecules into a two-dimensional network perpendicular to the c axis.

Related literature

For related crystal structures, see: Jin & Xiao (2005); Xiao *et al.* (2005). For bond length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_8H_8BrN_3O_2S$
M_r = 290.14
Triclinic, $P\overline{1}$
a = 4.4937 (5) Å
b = 8.6731 (10) Å
c = 14.4036 (17) Å
α = 101.341 (2)°
β = 91.787 (2)°
γ = 103.660 (2)°
V = 533.06 (11) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 4.03 mm^{-1}
T = 292 (2) K
0.25 × 0.18 × 0.15 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.422, T_{max} = 0.547
3551 measured reflections
1896 independent reflections
1492 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.168
S = 1.11
1896 reflections
151 parameters
5 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.83 e Å^{-3}
$\Delta\rho_{min}$ = −0.62 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···S1^{i}	0.81 (4)	2.34 (4)	3.144 (5)	169 (8)
N1—H1A···S1^{ii}	0.91 (3)	2.81 (5)	3.481 (6)	132 (5)
N2—H2A···S1^{iii}	0.89 (3)	2.49 (4)	3.331 (5)	158 (6)
N3—H3A···O2^{iv}	0.88 (3)	2.08 (4)	2.938 (7)	164 (7)
N1—H1A···O1	0.91 (3)	1.95 (6)	2.618 (7)	129 (6)
N3—H3A···N1	0.88 (3)	2.36 (7)	2.686 (7)	102 (5)

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+1, -y+1, -z$; (iii) $-x+2, -y+1, -z$; (iv) $x-1, y, z$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

This work was supported by the Natural Science Foundation of South-Central University for Nationalities (grant No. YZZ07005).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2450).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Bruker (2001). *SMART* (Version 5.628), *SAINT* (Version 6.45) and *SHELXTL* (Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA.
Jin, L.-F. & Xiao, F.-P. (2005). *Acta Cryst.* E**61**, o1105–o1106.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Xiao, F.-P., Li, F.-F., Jin, L.-F. & Wu, Y.-F. (2005). *Acta Cryst.* E**61**, o4171–o4172.

 doi:10.1107/S1600536807033211

supplementary materials

Acta Cryst. (2007). E**63**, o3465 [**doi:10.1107/S1600536807033211**]

4-(5-Bromo-2-hydroxybenzoyl)thiosemicarbazide

L.-F. Jin

Comment

We have already reported the crystal structures of active esters and other related ligands containing salicyl groups *i.e.* ethyl 5-bromosalicylate (Jin & Xiao, 2005) and methyl 5-bromosalicylate (Xiao *et al.*, 2005). Part of our studies is to find new methods to synthesize derivatives of 5-bromo sylicylic acid *e.g.* di-4-(5-bromo salicyloyl) hydrazino-bithiazole. In this paper we report the crystal structure of the title compound.

The title molecule (Fig. 1) contains two intramolecular hydrogen bonds. These are between the hydrazo group and the O atom of the hydroxyl group, and the amino group and the N atom of the hydrazo group. Bond lengths and angles show normal values (Allen *et al.*, 1987). The atoms C1—C6 lie in a plane with an r.m.s deviation of 0.0099 Å. In the crystal structure, molecules are linked by intermolecular O—H···S, N—H···S and N—H···O hydrogen bonds to form a two-dimensional network perpendicular to the *c* axis (Fig. 2).

Experimental

5-Bromo salicylhydrazide (24.8 g, 0.10 mol) and KSCN (14.4 g, 0.20 mol) were added to 100 ml of water at 273 K and stirred for 10 minutes. Then 20 ml of concentrated hydrochloric acid were added, and stirred for 1 h. The reaction mixture was slowly warmed to 366 K and stirred for a further 8 h. After staying for 1 h in a refrigerator, the resulting light-yellow precipitate was filtered and rinsed with water to pH6. A light-yellow solid formed was recrystallized from warm water to give 23.2 g (80% yield) of 4-(5-bromo salicyloyl) thiosemicarbazide. A plate-like crystal suitable for X-ray analysis was grown from a solution of the title compound in methanol at room temperature by slow evaporation.

Refinement

The hydroxyl, hydrazo and amino H atoms were located in a difference Fourier map and their positions were refined. All other H atoms were included in the riding-model approximation, with C—H distances of 0.93 Å. The isotropic displacement parameters were set equal to $1.2U_{eq}$ of the carrier atom for the aromatic and hydrazo and amino H atoms, and to $1.5U_{eq}$ of the carrier for hydroxyl H atoms.

Figures

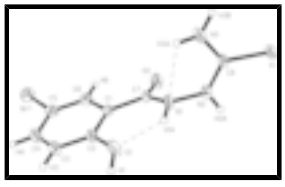


Fig. 1. The molecular structure showing ellipsoids at 30% probability level.

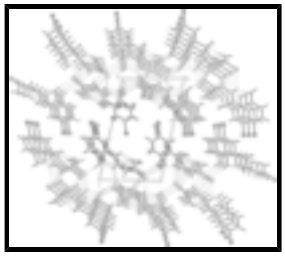


Fig. 2. The packing of the title compound showing hydrogen bonds as dashed lines.

4-(5-Bromo-2-hydroxybenzoyl)thiosemicarbazide

Crystal data

$C_8H_8BrN_3O_2S$	$Z = 2$
$M_r = 290.14$	$F_{000} = 288$
Triclinic, $P\overline{1}$	$D_x = 1.808$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 4.4937$ (5) Å	Cell parameters from 1175 reflections
$b = 8.6731$ (10) Å	$\theta = 2.5$–26.7º
$c = 14.4036$ (17) Å	$\mu = 4.03$ mm^{-1}
$\alpha = 101.341$ (2)º	$T = 292$ (2) K
$\beta = 91.787$ (2)º	Plate, colorless
$\gamma = 103.660$ (2)º	0.25 × 0.18 × 0.15 mm
$V = 533.06$ (11) Å^3	

Data collection

Bruker SMART CCD diffractometer	1896 independent reflections
Radiation source: fine-focus sealed tube	1492 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.028$
$T = 292$(2) K	$\theta_{max} = 25.3$º
φ and ω scans	$\theta_{min} = 2.5$º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -5 \rightarrow 5$
$T_{min} = 0.422$, $T_{max} = 0.547$	$k = -10 \rightarrow 10$
3551 measured reflections	$l = -17 \rightarrow 16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.058$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.168$	$w = 1/[\sigma^2(F_o^2) + (0.0918P)^2 + 0.5449P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} < 0.001$

1896 reflections	$\Delta\rho_{max}$ = 0.83 e Å^{-3}
151 parameters	$\Delta\rho_{min}$ = −0.61 e Å^{-3}
5 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

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	1.40000 (18)	1.27910 (9)	0.54471 (5)	0.0549 (3)
C1	0.9979 (13)	0.9875 (7)	0.2863 (4)	0.0301 (13)
C2	0.8402 (14)	1.0883 (7)	0.2499 (4)	0.0320 (14)
C3	0.8572 (15)	1.2431 (7)	0.2997 (5)	0.0390 (15)
H3	0.7525	1.3085	0.2750	0.047*
C4	1.0256 (16)	1.3012 (8)	0.3847 (6)	0.0474 (18)
H4	1.0401	1.4072	0.4168	0.057*
C5	1.1756 (15)	1.2044 (8)	0.4241 (5)	0.0400 (16)
C6	1.1646 (15)	1.0498 (8)	0.3748 (5)	0.0386 (15)
H6	1.2697	0.9858	0.4008	0.046*
C7	1.0080 (14)	0.8197 (7)	0.2383 (4)	0.0291 (13)
C8	0.6261 (14)	0.4642 (7)	0.1119 (4)	0.0292 (13)
N1	0.8087 (12)	0.7505 (6)	0.1619 (4)	0.0332 (12)
H1A	0.713 (13)	0.807 (7)	0.129 (4)	0.040*
N2	0.8288 (13)	0.6018 (6)	0.1093 (4)	0.0365 (12)
H2A	0.977 (12)	0.605 (8)	0.070 (4)	0.044*
N3	0.4082 (13)	0.4717 (6)	0.1724 (5)	0.0435 (14)
H3A	0.371 (16)	0.567 (5)	0.197 (5)	0.052*
H3B	0.300 (15)	0.376 (5)	0.176 (5)	0.052*
O1	0.6661 (12)	1.0276 (5)	0.1664 (4)	0.0481 (12)
H1	0.64 (2)	1.087 (9)	0.132 (5)	0.072*
O2	1.1829 (11)	0.7491 (6)	0.2675 (3)	0.0460 (12)
S1	0.6597 (4)	0.28795 (18)	0.04272 (12)	0.0371 (4)

Atomic displacement parameters (Å^2)

U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}

Br1	0.0649 (6)	0.0472 (5)	0.0377 (5)	−0.0050 (4)	−0.0034 (3)	−0.0023 (3)
C1	0.034 (3)	0.025 (3)	0.029 (3)	0.005 (2)	0.008 (3)	0.000 (2)
C2	0.036 (3)	0.023 (3)	0.033 (3)	0.004 (3)	0.002 (3)	0.000 (3)
C3	0.044 (4)	0.027 (3)	0.044 (4)	0.008 (3)	0.000 (3)	0.004 (3)
C4	0.051 (4)	0.026 (3)	0.064 (5)	0.008 (3)	0.024 (4)	0.005 (3)
C5	0.041 (4)	0.036 (4)	0.041 (4)	0.003 (3)	0.007 (3)	0.010 (3)
C6	0.037 (4)	0.037 (4)	0.045 (4)	0.010 (3)	0.009 (3)	0.016 (3)
C7	0.035 (3)	0.023 (3)	0.027 (3)	0.005 (3)	0.003 (3)	0.002 (2)
C8	0.037 (3)	0.023 (3)	0.026 (3)	0.010 (2)	−0.008 (2)	0.001 (2)
N1	0.043 (3)	0.022 (3)	0.034 (3)	0.015 (2)	−0.002 (2)	−0.002 (2)
N2	0.046 (3)	0.023 (3)	0.039 (3)	0.011 (2)	0.006 (2)	−0.001 (2)
N3	0.045 (3)	0.022 (3)	0.063 (4)	0.011 (2)	0.011 (3)	0.004 (3)
O1	0.070 (3)	0.026 (2)	0.046 (3)	0.014 (2)	−0.015 (2)	0.004 (2)
O2	0.059 (3)	0.040 (3)	0.041 (3)	0.025 (2)	−0.005 (2)	0.000 (2)
S1	0.0479 (10)	0.0216 (8)	0.0394 (9)	0.0088 (7)	0.0003 (7)	0.0009 (6)

Geometric parameters (Å, °)

Br1—C5	1.896 (7)	C7—O2	1.215 (7)
C1—C6	1.399 (9)	C7—N1	1.342 (8)
C1—C2	1.412 (9)	C8—N2	1.327 (8)
C1—C7	1.495 (8)	C8—N3	1.337 (8)
C2—O1	1.354 (8)	C8—S1	1.694 (6)
C2—C3	1.376 (9)	N1—N2	1.386 (7)
C3—C4	1.359 (10)	N1—H1A	0.91 (3)
C3—H3	0.9300	N2—H2A	0.89 (3)
C4—C5	1.383 (10)	N3—H3A	0.88 (3)
C4—H4	0.9300	N3—H3B	0.87 (3)
C5—C6	1.377 (9)	O1—H1	0.81 (4)
C6—H6	0.9300		
C6—C1—C2	117.6 (5)	C1—C6—H6	119.5
C6—C1—C7	116.4 (5)	O2—C7—N1	121.9 (6)
C2—C1—C7	126.0 (6)	O2—C7—C1	122.1 (6)
O1—C2—C3	121.1 (6)	N1—C7—C1	115.9 (5)
O1—C2—C1	118.5 (5)	N2—C8—N3	117.3 (5)
C3—C2—C1	120.5 (6)	N2—C8—S1	119.7 (5)
C4—C3—C2	120.5 (6)	N3—C8—S1	123.0 (4)
C4—C3—H3	119.7	C7—N1—N2	118.2 (5)
C2—C3—H3	119.7	C7—N1—H1A	124 (4)
C3—C4—C5	120.7 (7)	N2—N1—H1A	114 (4)
C3—C4—H4	119.7	C8—N2—N1	122.5 (5)
C5—C4—H4	119.7	C8—N2—H2A	121 (5)
C6—C5—C4	119.6 (7)	N1—N2—H2A	116 (5)
C6—C5—Br1	118.7 (5)	C8—N3—H3A	120 (5)
C4—C5—Br1	121.7 (6)	C8—N3—H3B	112 (5)
C5—C6—C1	121.0 (6)	H3A—N3—H3B	128 (7)
C5—C6—H6	119.5	C2—O1—H1	120 (7)
C6—C1—C2—O1	−177.0 (5)	C2—C1—C6—C5	−0.4 (8)
C7—C1—C2—O1	4.0 (8)	C7—C1—C6—C5	178.7 (5)

C6—C1—C2—C3	1.2 (8)	C6—C1—C7—O2	−9.7 (8)
C7—C1—C2—C3	−177.8 (5)	C2—C1—C7—O2	169.3 (6)
O1—C2—C3—C4	178.1 (6)	C6—C1—C7—N1	169.2 (5)
C1—C2—C3—C4	−0.1 (9)	C2—C1—C7—N1	−11.8 (8)
C2—C3—C4—C5	−1.9 (10)	O2—C7—N1—N2	−7.3 (8)
C3—C4—C5—C6	2.7 (9)	C1—C7—N1—N2	173.8 (5)
C3—C4—C5—Br1	−177.7 (5)	N3—C8—N2—N1	−4.3 (9)
C4—C5—C6—C1	−1.5 (9)	S1—C8—N2—N1	177.9 (4)
Br1—C5—C6—C1	178.9 (4)	C7—N1—N2—C8	106.4 (7)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···S1^{i}	0.81 (4)	2.34 (4)	3.144 (5)	169 (8)
N1—H1A···S1^{ii}	0.91 (3)	2.81 (5)	3.481 (6)	132 (5)
N2—H2A···S1^{iii}	0.89 (3)	2.49 (4)	3.331 (5)	158 (6)
N3—H3A···O2^{iv}	0.88 (3)	2.08 (4)	2.938 (7)	164 (7)
N1—H1A···O1	0.91 (3)	1.95 (6)	2.618 (7)	129 (6)
N3—H3A···N1	0.88 (3)	2.36 (7)	2.686 (7)	102 (5)

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

Fig. 1

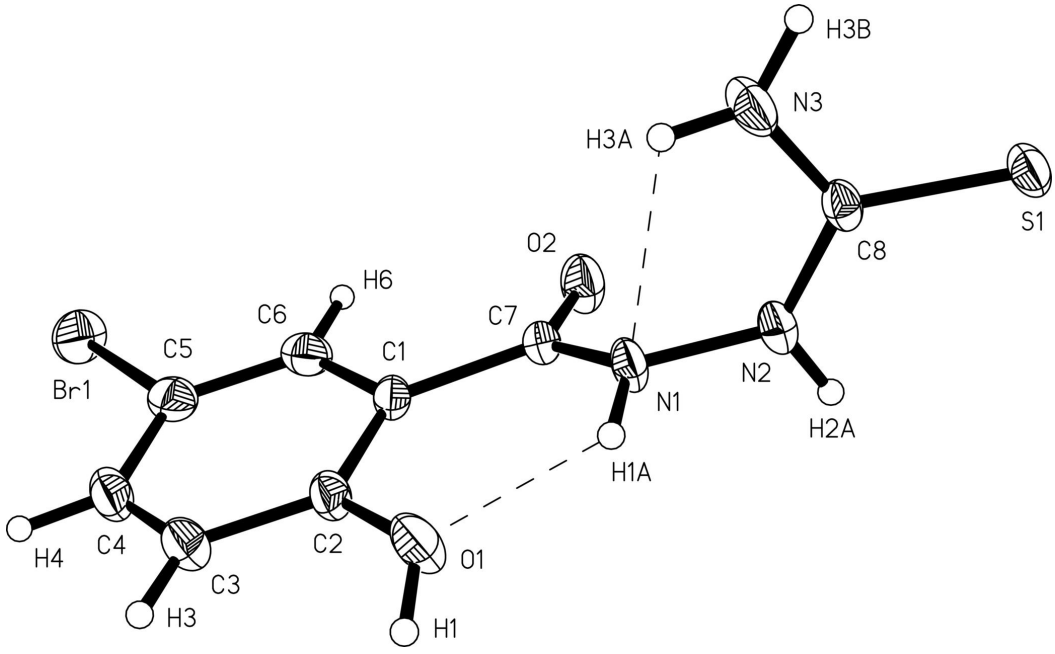

H3B
N3
H3A
S1
C8
O2
H6
C6
C7
C5
C1
N2
Br1
N1
H2A
H1A
H4
C4
C2
O1
C3
H3
H1

Fig. 2