Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

5-[(*E*)-(5-Bromo-2-hydroxybenzylidene)amino]-1,3,4-thiadiazole-2(3*H*)-thione

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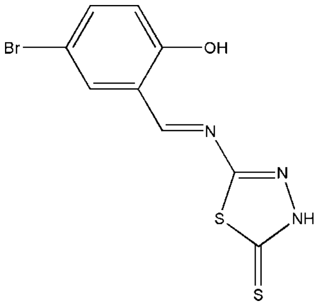
Received 13 November 2011; accepted 21 November 2011

Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.009 Å; R factor = 0.060; wR factor = 0.140; data-to-parameter ratio = 18.6.

In the title molecule, $C_9H_6BrN_3OS_2$, the dihedral angle between the benzene ring and the five-membered ring is 5.5 (3)°. An intramolecular O—H$\cdots$N hydrogen bond forms an $S(6)$ ring motif. In the crystal, N—H$\cdots$S hydrogen bonds link molecules into centrosymmetric dimers creating $R_2^2(8)$ ring motifs. In addition, there are intermolecular S$\cdots$S [3.430 (2) Å] contacts. The crystal used was a non-merohedral twin with a ratio of 0.113 (3):0.887 (3) for the components.

Related literature

For the biological versatility of thione ligands, see, for example: Kumar *et al.* (1988); Yadav *et al.* (1989). For related structures, see: Zhang (2003); Kargar *et al.* (2011). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For van der Waals radii, see: Bondi (1964). For standard bond lengths, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_9H_6BrN_3OS_2$
M_r = 316.20
Monoclinic, $P2_1/c$
a = 18.3690 (13) Å
b = 4.0016 (3) Å
c = 16.2877 (13) Å
β = 112.660 (4)°
V = 1104.82 (14) $Å^3$
Z = 4
Mo $K\alpha$ radiation
μ = 4.08 mm^{-1}
T = 291 K
0.11 × 0.05 × 0.02 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.663, T_{max} = 0.923
10313 measured reflections
2734 independent reflections
1760 reflections with $I > 2\sigma(I)$
R_{int} = 0.071

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.140
S = 1.08
2734 reflections
147 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.25 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.71 e $Å^{-3}$

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$N1	0.82	1.94	2.664 (7)	147
N3—H3$\cdots$S2^{i}	0.97	2.36	3.327 (5)	173

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

HK thanks PNU for financial support. RK thanks the Islamic Azad University. MNT thanks the GC University of Sargodha, Pakistan for research facilities.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5379).

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supporting information

Acta Cryst. (2011). E**67**, o3436 [https://doi.org/10.1107/S1600536811049920]

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S1. Comment

The biological versatility of compounds incorporating a thiadiazole ring is well known (Kumar *et al.*, 1988; Yadav *et al.*, 1989). In continuation of our work on the crystal structure of thione-Schiff base ligands (Kargar *et al.,* 2011), we have determined the crystal structure of the title compound.

The asymmetric unit of the title compound is shown in Fig. 1. The bond lengths (Allen *et al.,* 1987) and angles are within the normal ranges and are comparable to related structures (Kargar *et al.,* 2011; Zhang, 2003).

The dihedral angle between the benzene ring and the five-membered ring is 5.5 (3)°. An intramolecular O—H···N hydrogen bond forms an S(6) ring motif. Intermolecular N—H···S interactions link molecules into centrosymmetric dimers with $R_2^2(8)$ ring motifs (Bernstein *et al.*,1995). An interesting feature of the crystal structure is the short S1···S1^i [3.430 (2)Å; (i) 2 - x, -1/2 + y, 1/2 - z] contact which is shorter than the sum of the Van der Waals radius of S [3.60Å] atoms (Bondi, 1964). The crystal was a non-merohedral twin with a refined BASF ratio of 0.113 (3)/0.887 (3).

S2. Experimental

The title compound was synthesized by adding 5-bromo-salicylaldehyde (1 mmol) to a solution of 5-aminothiophene-2-thiol (1 mmol) in ethanol (30 ml). The mixture was refluxed with stirring for half an hour. The resultant solution was filtered. Yellow single crystals of the title compound suitable for *X*-ray structure determination were recrystallized from ethanol by slow evaporation of the solvent at room temperature over several days.

S3. Refinement

All hydrogen atoms were positioned geometrically with C—H = 0.93 Å, N—H = 0.97 Å, O—H = 0.82 Å and included in a riding-model approximation with $U_{iso}(H) = 1.2U_{eq}(C,N)$ and 1.5 $U_{eq}(O)$. The crystal was a non-merohedral twin {Twin Law (1 0 0)[5 0 2]} which was treated TwinRotMat routine in PLATON (Spek, 2009) with a refined BASF ratio of 0.113 (3)/0.887 (3).

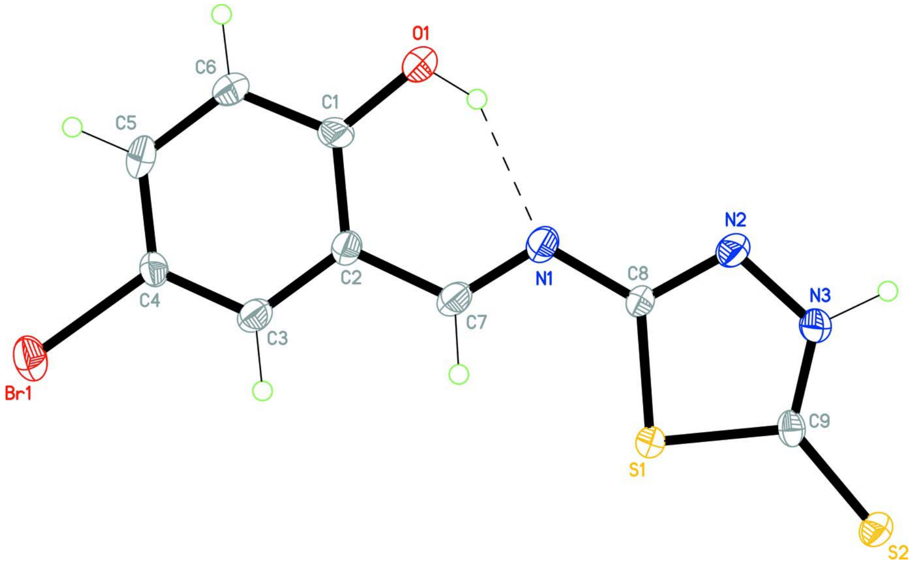

Figure 1

The molecular structure of the title compound, showing 40% probability displacement ellipsoids. The dashed line shows an intramolecular hydrogen bond.

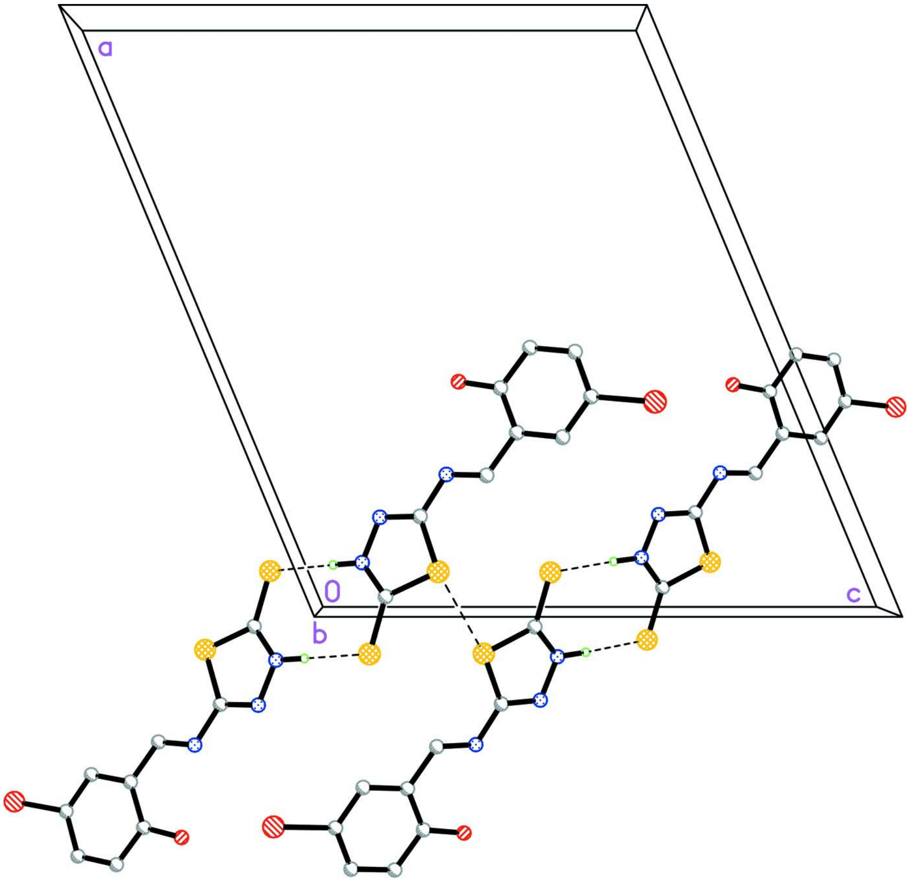

Figure 2

A packing diagram of the title compound viewed along the *b*-axis showing short intermolecular S···S contacts and centrosymmetric dimers formed by intermolecular N—H···S hydrogen bonds. The dashed lines indicate the intermolecular interactions.

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Crystal data

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c = 16.2877 (13) Å
β = 112.660 (4)°
V = 1104.82 (14) Å^3
Z = 4

F(000) = 624
D_x = 1.901 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2573 reflections
θ = 2.5–29.3°
μ = 4.08 mm^{-1}
T = 291 K
Block, yellow
0.11 × 0.05 × 0.02 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans

Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.663, T_{max} = 0.923
2734 measured reflections
10313 independent reflections

1760 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.071$
$\theta_{\max} = 28.3°$, $\theta_{\min} = 1.2°$
$h = -24 \rightarrow 24$
$k = -5 \rightarrow 5$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.140$
$S = 1.08$
2734 reflections
147 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 3.7473P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.71$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 > 2sigma(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	0.65016 (4)	0.82937 (19)	−0.22477 (5)	0.0438 (2)
S1	0.92727 (8)	0.4125 (4)	0.25824 (11)	0.0306 (4)
S2	1.06396 (9)	0.3421 (4)	0.43539 (10)	0.0329 (4)
O1	0.6140 (2)	0.1515 (13)	0.0870 (3)	0.0439 (12)
H1	0.6563	0.1408	0.1296	0.066*
N1	0.7683 (3)	0.2398 (13)	0.1762 (3)	0.0314 (12)
N2	0.8404 (3)	0.0884 (14)	0.3226 (4)	0.0355 (13)
N3	0.9159 (3)	0.1150 (13)	0.3865 (3)	0.0347 (13)
H3	0.9211	−0.0002	0.4408	0.042*
C1	0.6244 (3)	0.3022 (18)	0.0192 (4)	0.0340 (15)
C2	0.6990 (3)	0.4180 (15)	0.0246 (4)	0.0286 (13)
C3	0.7065 (3)	0.5752 (15)	−0.0484 (4)	0.0315 (14)
H3A	0.7556	0.6477	−0.0453	0.038*
C4	0.6402 (3)	0.6216 (15)	−0.1255 (4)	0.0313 (14)
C5	0.5670 (4)	0.5144 (17)	−0.1308 (4)	0.0365 (15)
H5A	0.5229	0.5488	−0.1829	0.044*
C6	0.5587 (3)	0.3570 (17)	−0.0598 (4)	0.0367 (15)
H6A	0.5091	0.2864	−0.0642	0.044*
C7	0.7688 (3)	0.3839 (16)	0.1055 (4)	0.0339 (15)
H7A	0.8162	0.4697	0.1066	0.041*
C8	0.8377 (3)	0.2352 (15)	0.2507 (4)	0.0260 (13)
C9	0.9707 (3)	0.2737 (14)	0.3678 (4)	0.0261 (13)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0511 (4)	0.0493 (4)	0.0304 (4)	0.0088 (3)	0.0152 (3)	0.0084 (3)
S1	0.0242 (7)	0.0387 (9)	0.0263 (8)	−0.0014 (6)	0.0067 (6)	0.0065 (7)
S2	0.0252 (7)	0.0429 (9)	0.0264 (9)	−0.0014 (7)	0.0055 (6)	−0.0007 (7)
O1	0.030 (2)	0.065 (3)	0.033 (3)	−0.009 (2)	0.008 (2)	0.008 (3)
N1	0.026 (3)	0.039 (3)	0.026 (3)	0.002 (2)	0.006 (2)	0.001 (2)
N2	0.024 (2)	0.051 (3)	0.029 (3)	−0.006 (2)	0.006 (2)	0.003 (3)
N3	0.033 (3)	0.047 (3)	0.024 (3)	−0.005 (2)	0.010 (2)	0.006 (3)
C1	0.029 (3)	0.053 (4)	0.024 (3)	−0.008 (3)	0.014 (3)	−0.004 (3)
C2	0.027 (3)	0.031 (3)	0.026 (3)	0.001 (2)	0.008 (3)	0.001 (3)
C3	0.024 (3)	0.041 (4)	0.028 (3)	0.002 (3)	0.008 (3)	0.000 (3)
C4	0.033 (3)	0.032 (3)	0.026 (3)	0.001 (3)	0.007 (3)	0.003 (3)
C5	0.033 (3)	0.044 (4)	0.025 (3)	0.003 (3)	0.003 (3)	−0.002 (3)
C6	0.024 (3)	0.045 (4)	0.037 (4)	−0.003 (3)	0.008 (3)	0.001 (3)
C7	0.023 (3)	0.042 (4)	0.034 (4)	0.002 (3)	0.007 (3)	−0.001 (3)
C8	0.021 (3)	0.033 (3)	0.023 (3)	0.003 (2)	0.007 (2)	0.003 (2)
C9	0.032 (3)	0.026 (3)	0.021 (3)	0.002 (2)	0.010 (3)	−0.003 (2)

Geometric parameters (Å, º)

Br1—C4	1.889 (6)	C1—C6	1.402 (8)
S1—C9	1.741 (6)	C1—C2	1.417 (8)
S1—C8	1.752 (6)	C2—C3	1.399 (8)
S2—C9	1.663 (6)	C2—C7	1.448 (8)
O1—C1	1.334 (7)	C3—C4	1.384 (8)
O1—H1	0.8200	C3—H3A	0.9300
N1—C7	1.292 (8)	C4—C5	1.382 (9)
N1—C8	1.381 (7)	C5—C6	1.377 (9)
N2—C8	1.293 (8)	C5—H5A	0.9300
N2—N3	1.381 (7)	C6—H6A	0.9300
N3—C9	1.322 (8)	C7—H7A	0.9300
N3—H3	0.9690		
C9—S1—C8	89.4 (3)	C5—C4—Br1	119.7 (5)
C1—O1—H1	109.5	C3—C4—Br1	119.6 (5)
C7—N1—C8	117.9 (5)	C6—C5—C4	120.6 (6)
C8—N2—N3	108.9 (5)	C6—C5—H5A	119.7
C9—N3—N2	119.8 (5)	C4—C5—H5A	119.7
C9—N3—H3	128.5	C5—C6—C1	120.6 (6)
N2—N3—H3	111.7	C5—C6—H6A	119.7
O1—C1—C6	118.9 (5)	C1—C6—H6A	119.7
O1—C1—C2	122.7 (6)	N1—C7—C2	123.0 (6)
C6—C1—C2	118.4 (6)	N1—C7—H7A	118.5
C3—C2—C1	120.3 (6)	C2—C7—H7A	118.5
C3—C2—C7	118.2 (5)	N2—C8—N1	120.1 (5)
C1—C2—C7	121.5 (6)	N2—C8—S1	114.4 (4)

C4—C3—C2	119.4 (5)	N1—C8—S1	125.5 (5)
C4—C3—H3A	120.3	N3—C9—S2	127.4 (5)
C2—C3—H3A	120.3	N3—C9—S1	107.5 (4)
C5—C4—C3	120.8 (6)	S2—C9—S1	125.1 (4)

C8—N2—N3—C9	0.2 (8)	C8—N1—C7—C2	−177.1 (5)
O1—C1—C2—C3	−179.9 (6)	C3—C2—C7—N1	−179.2 (6)
C6—C1—C2—C3	−1.7 (10)	C1—C2—C7—N1	1.9 (10)
O1—C1—C2—C7	−1.1 (10)	N3—N2—C8—N1	179.3 (5)
C6—C1—C2—C7	177.1 (6)	N3—N2—C8—S1	−0.1 (7)
C1—C2—C3—C4	1.1 (9)	C7—N1—C8—N2	−178.7 (6)
C7—C2—C3—C4	−177.7 (6)	C7—N1—C8—S1	0.6 (8)
C2—C3—C4—C5	−0.1 (9)	C9—S1—C8—N2	0.0 (5)
C2—C3—C4—Br1	−179.3 (5)	C9—S1—C8—N1	−179.3 (5)
C3—C4—C5—C6	−0.4 (10)	N2—N3—C9—S2	178.3 (5)
Br1—C4—C5—C6	178.8 (5)	N2—N3—C9—S1	−0.2 (7)
C4—C5—C6—C1	−0.1 (10)	C8—S1—C9—N3	0.1 (5)
O1—C1—C6—C5	179.4 (6)	C8—S1—C9—S2	−178.4 (4)
C2—C1—C6—C5	1.2 (10)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N1	0.82	1.94	2.664 (7)	147
N3—H3···S2^{i}	0.97	2.36	3.327 (5)	173

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