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1-(5-Bromo-2-oxindolin-3-ylidene)thiosemicarbazone

 Katlen C. T. Bandeira,^a Leandro Bresolin,^a Christian Näther,^b Inke Jess^b and Adriano B. Oliveira^{c*}

^aEscola de Química e Alimentos, Universidade Federal do Rio Grande, Av. Itália km 08, Campus Carreiros, 96203-903 Rio Grande-RS, Brazil, ^bInstitut für Anorganische Chemie, Christian-Albrechts-Universität zu Kiel, Max-Eyth Strasse 2, D-24118 Kiel, Germany, and ^cDepartamento de Química, Universidade Federal de Sergipe, Av. Marechal Rondon s/n, Campus, 49100-000 São Cristóvão-SE, Brazil
Correspondence e-mail: adriano@daad-alumni.de

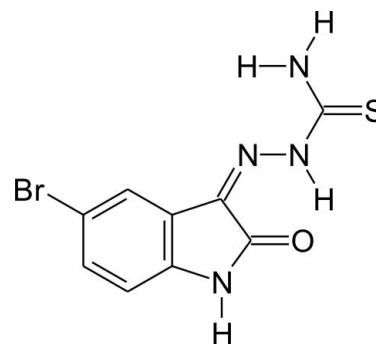
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.039; wR factor = 0.091; data-to-parameter ratio = 16.2.

The title molecule, $\text{C}_9\text{H}_7\text{BrN}_4\text{OS}$, is essentially planar [r.m.s. deviation = 0.066 (2) Å], the maximum deviation from the mean plane through the non-H atoms being 0.190 (3) Å for the terminal amine N atom. In the crystal, molecules are linked through $\text{N}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{S}$ interactions, generating infinite chains along the b -axis direction. In turn, the chains are stacked along the a axis via $\pi-\pi$ interactions [centroid-centroid distance = 3.470 (2) Å] and further connected by $\text{N}-\text{H}\cdots\text{Br}$ interactions into a three-dimensional network. An intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond is also observed.

Related literature

For the pharmacological properties of isatin-thiosemicarbazone derivatives against cruzain, falcipain-2 and rhodesain, see: Chiyanzu *et al.* (2003). For the synthesis of 5-bromoisatin-3-thiosemicarbazone, see: Campaigne & Archer (1952). For the crystal structure of 1-(5-bromo-2-oxindolin-3-ylidene)thiosemicarbazide acetonitrile monosolvate, see: Pederzoli *et al.* (2011).



Experimental

Crystal data

$\text{C}_9\text{H}_7\text{BrN}_4\text{OS}$
 $M_r = 299.16$
 Orthorhombic, $P2_12_12_1$
 $a = 4.0185$ (2) Å
 $b = 14.6418$ (8) Å
 $c = 18.8276$ (11) Å

$V = 1107.78$ (10) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 3.88$ mm⁻¹
 $T = 293$ K
 $0.10 \times 0.06 \times 0.04$ mm

Data collection

Stoe IPDS-1 diffractometer
 7791 measured reflections
 2405 independent reflections

2106 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.051$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.091$
 $S = 1.02$
 2405 reflections
 148 parameters
 H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.73$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.55$ e Å⁻³
 Absolute structure: Flack (1983),
 951 Friedel pairs
 Absolute structure parameter:
 -0.015 (13)

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1}\cdots\text{S1}^i$	0.86	2.82	3.507 (3)	139
$\text{N3}-\text{H3}\cdots\text{O1}$	0.86	2.04	2.726 (4)	135
$\text{N4}-\text{H2N4}\cdots\text{Br1}^{ii}$	0.83	2.91	3.665 (4)	152
$\text{N4}-\text{H1N4}\cdots\text{O1}^{iii}$	0.87	1.99	2.851 (4)	167

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

Data collection: *X-Area* (Stoe & Cie, 2008); cell refinement: *X-Area*; data reduction: *X-Red32* (Stoe & Cie, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

We gratefully acknowledge financial support by the State of Schleswig-Holstein, Germany. We thank Professor Dr Wolfgang Bensch for access to his experimental facilities. We gratefully acknowledge financial support through the DECIT/SCTIE-MS-CNPq-FAPERGS-Pronem-# 11/2029-1 and PRONEX-CNPq-FAPERGS projects. KCTB thanks FAPESP for the award of a scholarship and ABO acknowledges financial support through the FAPITEC/SE/FUNTEC/CNPq PPP 04/2011 program.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LR2109).

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supporting information

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1-(5-Bromo-2-oxoindolin-3-ylidene)thiosemicarbazone

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S1. Comment

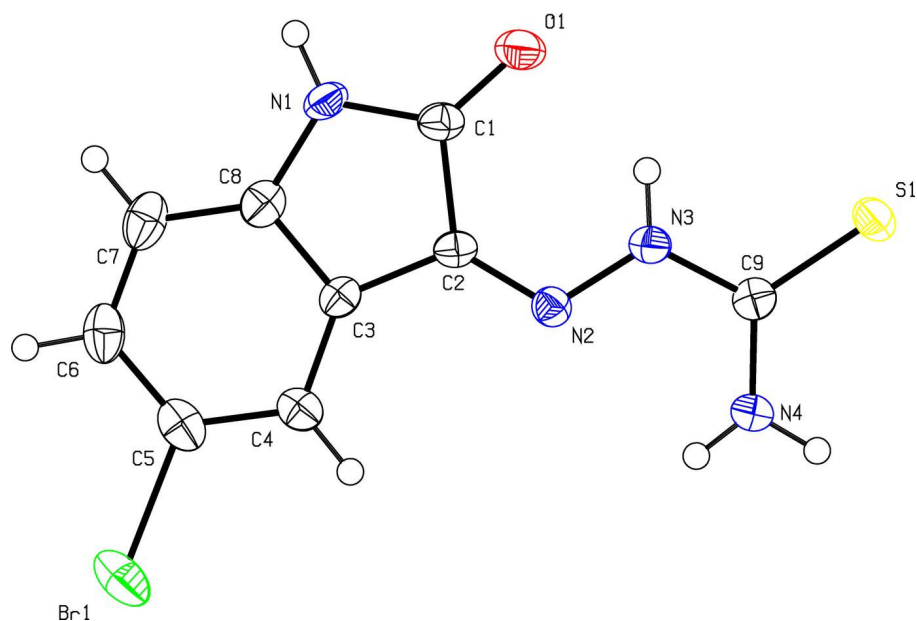
Thiosemicarbazone derivatives have a wide range of biological properties. For example, isatin-based synthetic thiosemicarbazones show pharmacological activity against cruzain, falcipain-2 and rhodesain (Chiyanzu *et al.*, 2003). As part of our study of thiosemicarbazone derivatives, we report herein the crystal structure of 5-bromoisatin-3-thiosemicarbazone (Campaigne & Archer, 1952). In the title compound, in which the molecular structure matches the asymmetric unit, the maximal deviation from the least squares plane through all non-hydrogen atoms amount to 0.1896 (32) Å for N4. The molecule shows an *E* conformation for the atoms about the N2—N3 bond (Fig. 1). The *E* conformation for the thiosemicarbazone fragment is also observed in the crystal structure of the 5-bromoisatin-3-thiosemicarbazone acetonitrile monosolvate (Pederzoli *et al.*, 2011) and is related with the intramolecular N—H···O H-interaction (Table 1). The mean deviations from the least squares planes for the C1—C8/Br1/N1 and C9/N2—N4/S1 fragments amount to 0.0568 (26) Å for O1 and 0.0394 (27) Å for N3, respectively, and the dihedral angle between the two planes is 9.01 (12)°. The molecules are connected *via* centrosymmetric pairs of N—H···S and N—H···O interactions and additionally by N—H···Br interactions (Fig. 2 and Table 1) forming a three-dimensional hydrogen-bonded network, which stabilizes the crystal packing. Additionally, π - π -interactions are observed, with C···C distances = 3.396 (6) Å. The molecules are arranged in layers and are stacked into the crystallographic *a*-axis direction (Fig. 3).

S2. Experimental

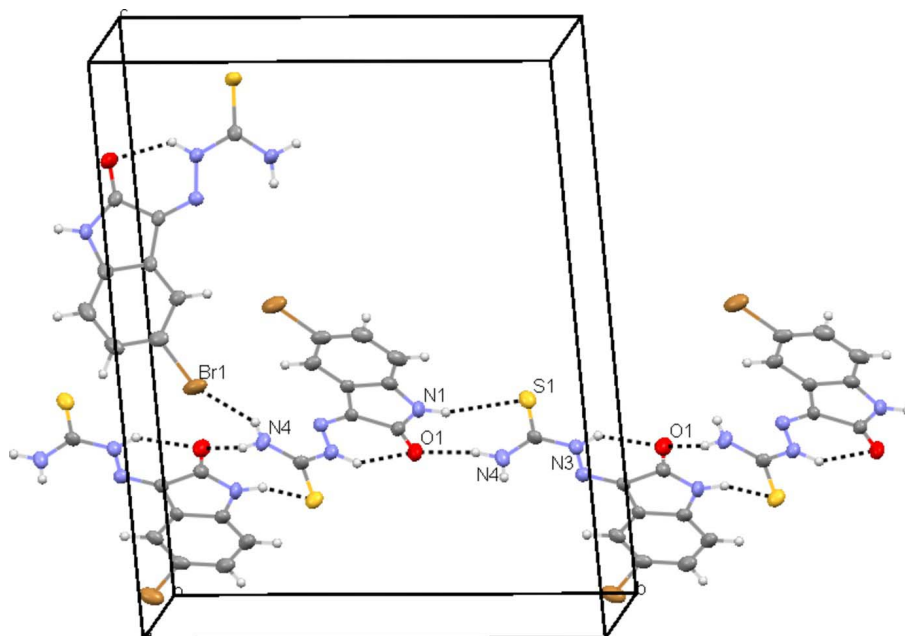
Starting materials were commercially available and were used without further purification. The 5-bromoisatine-3-thiosemicarbazone synthesis was adapted from a procedure reported previously (Campaigne & Archer, 1952). A mixture of 5-bromoisatin (8,83 mmol) and thiosemicarbazide (8,83 mmol) in ethanol (50 ml) in the presence of a catalytic amount of hydrochloric acid was refluxed for 6 h. After cooling and filtering, the title compound was obtained. Crystals suitable for X-ray diffraction of 5-bromoisatine-3-thiosemicarbazone were obtained unexpectedly from an unsuccessful reaction of SnCl₂ dihydrate with the title compound in methanol and dichloromethane by the slow evaporation of the solvents. Elemental analysis(%): Calc. 36.01 C, 2.69 H, 18.67 N, 10.68 S; found 35.95 C, 2.25 H, 18.67 N, 10.60 S.

S3. Refinement

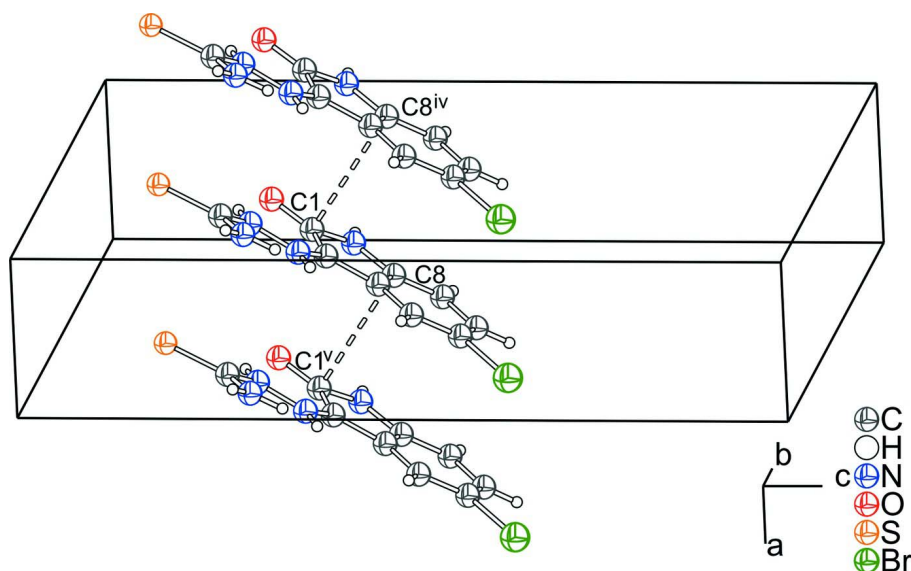
All non-hydrogen atoms were refined anisotropically. All C—H and N—H atoms were located in difference map but were positioned with idealized geometry and refined isotropically with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ using a riding model with C—H = 0.93 Å for aromatic and N—H = 0.86 Å for methyl H atoms. The terminal N—H atoms were located in difference map, their bond lengths were set to 0.86 Å and afterwards they were refined isotropically with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{N})$ using a riding model.

**Figure 1**

The molecular structure of the title compound with displacement ellipsoids drawn at the 40% probability level.

**Figure 2**

Molecules of the title compound connected *via* N—H...S, N—H...O and N—H...Br interactions. H-interactions are indicated as dashed lines and the Figure is simplified for clarity.

**Figure 3**

A view of the stacking along the crystallographic *a*-axis. The π - π -interactions are drawn as dashed lines. Symmetry codes are: (iv) $x - 1, y, z$; (v) $x + 1, y, z$.

1-(5-Bromo-2-oxoindolin-3-ylidene)thiosemicarbazone

Crystal data

$C_9H_7BrN_4OS$

$M_r = 299.16$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 4.0185$ (2) Å

$b = 14.6418$ (8) Å

$c = 18.8276$ (11) Å

$V = 1107.78$ (10) Å³

$Z = 4$

$F(000) = 592$

$D_x = 1.794$ Mg m⁻³

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

$\mu = 3.88$ mm⁻¹

$T = 293$ K

Prism, yellow

$0.10 \times 0.06 \times 0.04$ mm

Data collection

Stoe IPDS-1

diffractometer

Radiation source: fine-focus sealed tube, Stoe

IPDS-1

Graphite monochromator

φ scans

7791 measured reflections

2405 independent reflections

2106 reflections with $I > 2\sigma(I)$

$R_{int} = 0.051$

$\theta_{max} = 27.0^\circ$, $\theta_{min} = 2.6^\circ$

$h = -4 \rightarrow 5$

$k = -18 \rightarrow 17$

$l = -24 \rightarrow 24$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.091$

$S = 1.02$

2405 reflections

148 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

$w = 1/[\sigma^2(F_o^2) + (0.0516P)^2 + 0.9296P]$

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

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

$\Delta\rho_{max} = 0.73$ e Å⁻³

$\Delta\rho_{min} = -0.55$ e Å⁻³

Extinction correction: *SHELXL97* (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001x\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0123 (16)

Absolute structure: Flack (1983), 951 Friedel pairs
 Absolute structure parameter: -0.015 (13)

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 $F^2 > \sigma(F^2)$ 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	1.14379 (13)	0.36317 (4)	0.59001 (2)	0.04209 (17)
S1	-0.1204 (3)	0.31338 (7)	0.15460 (5)	0.0298 (2)
O1	0.2574 (8)	0.5699 (2)	0.26587 (16)	0.0352 (8)
N1	0.5769 (10)	0.6107 (2)	0.36442 (17)	0.0271 (8)
H1	0.5788	0.6690	0.3590	0.033*
N2	0.3785 (9)	0.3806 (2)	0.32307 (15)	0.0223 (6)
N3	0.2026 (9)	0.3844 (2)	0.26195 (17)	0.0248 (7)
H3	0.1764	0.4359	0.2406	0.030*
N4	0.0979 (10)	0.2311 (2)	0.27236 (17)	0.0285 (7)
H1N4	0.0154	0.1799	0.2562	0.029 (13)*
H2N4	0.1793	0.2242	0.3124	0.038 (15)*
C1	0.4265 (11)	0.5512 (3)	0.31935 (19)	0.0254 (9)
C2	0.4870 (10)	0.4577 (2)	0.3483 (2)	0.0209 (7)
C3	0.6801 (9)	0.4700 (2)	0.4126 (2)	0.0213 (7)
C4	0.8021 (10)	0.4087 (3)	0.4623 (2)	0.0253 (8)
H4	0.7701	0.3461	0.4574	0.030*
C5	0.9739 (11)	0.4448 (3)	0.5197 (2)	0.0299 (9)
C6	1.0274 (11)	0.5383 (3)	0.5283 (2)	0.0335 (10)
H6	1.1455	0.5597	0.5674	0.040*
C7	0.9031 (13)	0.5993 (3)	0.4782 (2)	0.0344 (10)
H7	0.9363	0.6618	0.4832	0.041*
C8	0.7292 (10)	0.5647 (3)	0.4210 (2)	0.0269 (9)
C9	0.0663 (9)	0.3069 (3)	0.2340 (2)	0.0227 (8)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0320 (2)	0.0652 (3)	0.0290 (2)	-0.0030 (3)	-0.0044 (2)	0.0148 (2)
S1	0.0302 (5)	0.0322 (5)	0.0270 (4)	-0.0033 (5)	-0.0081 (5)	0.0052 (4)
O1	0.052 (2)	0.0260 (14)	0.0281 (14)	0.0089 (13)	-0.0046 (13)	0.0020 (12)
N1	0.038 (2)	0.0155 (15)	0.0274 (16)	0.0004 (13)	0.0009 (15)	-0.0012 (11)
N2	0.0221 (15)	0.0232 (15)	0.0218 (13)	0.0011 (14)	-0.0005 (14)	-0.0003 (11)

N3	0.030 (2)	0.0213 (16)	0.0228 (14)	0.0008 (13)	-0.0016 (13)	0.0024 (12)
N4	0.035 (2)	0.0228 (16)	0.0272 (16)	-0.0010 (15)	-0.0076 (16)	0.0050 (12)
C1	0.030 (2)	0.0227 (18)	0.0233 (18)	0.0025 (16)	0.0038 (16)	0.0031 (14)
C2	0.0209 (18)	0.0195 (17)	0.0223 (17)	0.0033 (14)	0.0046 (14)	0.0013 (14)
C3	0.0202 (19)	0.0214 (16)	0.0224 (16)	-0.0034 (14)	0.0063 (17)	-0.0001 (14)
C4	0.020 (2)	0.0313 (19)	0.0241 (17)	-0.0021 (15)	0.0031 (15)	0.0055 (15)
C5	0.021 (2)	0.046 (2)	0.0223 (18)	-0.0016 (17)	0.0043 (15)	0.0033 (17)
C6	0.029 (2)	0.045 (3)	0.027 (2)	-0.0087 (19)	0.0034 (17)	-0.0087 (18)
C7	0.036 (3)	0.036 (2)	0.0306 (19)	-0.010 (2)	0.010 (2)	-0.0104 (16)
C8	0.030 (2)	0.0275 (19)	0.0236 (19)	-0.0019 (15)	0.0086 (15)	-0.0031 (15)
C9	0.018 (2)	0.0256 (18)	0.0248 (17)	-0.0018 (14)	0.0051 (14)	0.0014 (15)

Geometric parameters (Å, °)

Br1—C5	1.910 (4)	N4—H2N4	0.8285
S1—C9	1.675 (4)	C1—C2	1.494 (5)
O1—C1	1.245 (5)	C2—C3	1.449 (6)
N1—C1	1.358 (5)	C3—C4	1.387 (5)
N1—C8	1.400 (5)	C3—C8	1.409 (5)
N1—H1	0.8598	C4—C5	1.386 (6)
N2—C2	1.299 (5)	C4—H4	0.9300
N2—N3	1.352 (4)	C5—C6	1.396 (6)
N3—C9	1.367 (5)	C6—C7	1.392 (7)
N3—H3	0.8600	C6—H6	0.9300
N4—C9	1.330 (5)	C7—C8	1.381 (6)
N4—H1N4	0.8746	C7—H7	0.9300
C1—N1—C8	111.2 (3)	C5—C4—C3	117.1 (4)
C1—N1—H1	124.5	C5—C4—H4	121.4
C8—N1—H1	124.3	C3—C4—H4	121.4
C2—N2—N3	116.8 (3)	C4—C5—C6	122.8 (4)
N2—N3—C9	120.2 (3)	C4—C5—Br1	118.7 (3)
N2—N3—H3	119.9	C6—C5—Br1	118.5 (3)
C9—N3—H3	119.9	C7—C6—C5	119.7 (4)
C9—N4—H1N4	119.3	C7—C6—H6	120.2
C9—N4—H2N4	129.3	C5—C6—H6	120.2
H1N4—N4—H2N4	111.2	C8—C7—C6	118.4 (4)
O1—C1—N1	127.3 (4)	C8—C7—H7	120.8
O1—C1—C2	125.9 (4)	C6—C7—H7	120.8
N1—C1—C2	106.7 (3)	C7—C8—N1	129.6 (4)
N2—C2—C3	126.4 (3)	C7—C8—C3	121.3 (4)
N2—C2—C1	127.4 (4)	N1—C8—C3	109.1 (3)
C3—C2—C1	106.1 (3)	N4—C9—N3	116.4 (3)
C4—C3—C8	120.7 (4)	N4—C9—S1	125.1 (3)
C4—C3—C2	132.3 (3)	N3—C9—S1	118.4 (3)
C8—C3—C2	106.9 (3)		
C2—N2—N3—C9	-176.8 (4)	C3—C4—C5—C6	-0.3 (6)

C8—N1—C1—O1	176.5 (4)	C3—C4—C5—Br1	179.5 (3)
C8—N1—C1—C2	-0.5 (5)	C4—C5—C6—C7	0.5 (7)
N3—N2—C2—C3	-179.9 (4)	Br1—C5—C6—C7	-179.3 (3)
N3—N2—C2—C1	3.1 (6)	C5—C6—C7—C8	0.0 (7)
O1—C1—C2—N2	0.6 (7)	C6—C7—C8—N1	179.1 (4)
N1—C1—C2—N2	177.7 (4)	C6—C7—C8—C3	-0.6 (6)
O1—C1—C2—C3	-176.9 (4)	C1—N1—C8—C7	-179.1 (4)
N1—C1—C2—C3	0.2 (4)	C1—N1—C8—C3	0.6 (5)
N2—C2—C3—C4	0.9 (7)	C4—C3—C8—C7	0.8 (6)
C1—C2—C3—C4	178.4 (4)	C2—C3—C8—C7	179.3 (4)
N2—C2—C3—C8	-177.4 (4)	C4—C3—C8—N1	-178.9 (3)
C1—C2—C3—C8	0.1 (4)	C2—C3—C8—N1	-0.4 (4)
C8—C3—C4—C5	-0.3 (6)	N2—N3—C9—N4	4.4 (6)
C2—C3—C4—C5	-178.4 (4)	N2—N3—C9—S1	-174.7 (3)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...S1 ⁱ	0.86	2.82	3.507 (3)	139
N3—H3...O1	0.86	2.04	2.726 (4)	135
N4—H2N4...Br1 ⁱⁱ	0.83	2.91	3.665 (4)	152
N4—H1N4...O1 ⁱⁱⁱ	0.87	1.99	2.851 (4)	167

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