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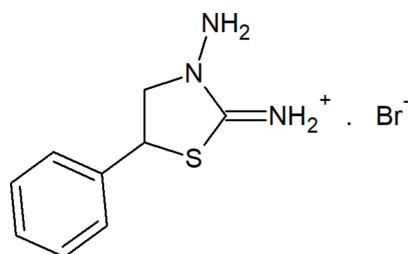
Crystal structure and Hirshfeld surface analysis of 3-amino-5-phenylthiazolidin-2-iminium bromide

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In the cation of the title salt, C₉H₁₂N₃S⁺·Br⁻, the thiazolidine ring adopts an envelope conformation with the C atom adjacent to the phenyl ring as the flap. In the crystal, N—H···Br hydrogen bonds link the components into a three-dimensional network. Weak π–π stacking interactions between the phenyl rings of adjacent cations also contribute to the molecular packing. A Hirshfeld surface analysis was conducted to quantify the contributions of the different intermolecular interactions and contacts.

1. Chemical context

As well as their synthetic utility, thiazolidine derivatives possess a broad spectrum of biological activities such as antimalarial, antibacterial, antimicrobial, anti-inflammatory, anticancer, *etc.* The biological activities of compounds containing a thiazolidine core, such as 1,3-thiazolidines, 2,4-dione-, 4-oxo-thiazolidine, *etc.* were summarized in a recent review (Makwana & Malani, 2017). On the other hand, as hydrazones these N-containing ligands have been widely used in the synthesis of coordination compounds (Gurbanov *et al.*, 2018*a,b*). The non-covalent donor or acceptor properties of N-containing ligands can also contribute to their catalytic activity, among other properties (Mahmudov *et al.*, 2019; Zubkov *et al.*, 2018). As part of our ongoing work in this area, we now describe the synthesis and structure of the title molecular salt, C₉H₁₂N₃S⁺·Br⁻, (I).



2. Structural commentary

In the cation of (I) (Fig. 1), the thiazolidine ring (S1/N1/C1–C3) adopts an envelope conformation with puckering parameters of $Q(2) = 0.317(2)$ Å and $\varphi(2) = 225.2(4)^\circ$: the flap atom is C1. In the arbitrarily chosen asymmetric unit, C1 has an *R* configuration, but symmetry generates a racemic mixture

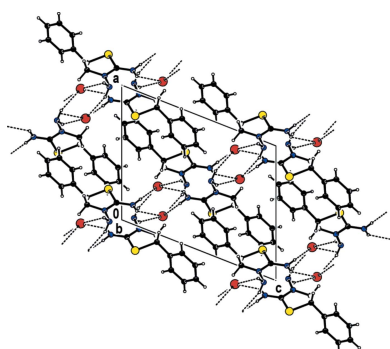


Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2A\cdots Br1^i$	0.90	2.68	3.530 (2)	158
$N2-H2B\cdots Br1^{ii}$	0.90	2.73	3.524 (2)	148
$N3-H3A\cdots Br1$	0.90	2.38	3.271 (2)	169
$N3-H3B\cdots Br1^{iii}$	0.90	2.56	3.337 (2)	145

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

in the crystal. The dihedral angle between the mean plane of the thiazolidine ring (all atoms) and the phenyl ring (C4–C9) is 89.27 (13)°.

3. Supramolecular features and Hirshfeld surface analysis

In the crystal, each cation forms $N-H\cdots Br$ hydrogen bonds (Table 1) as well as aromatic $\pi-\pi$ stacking interactions between the phenyl rings of adjacent cations [$Cg2\cdots Cg2^{iv} = 3.7758$ (16) Å; symmetry code: (iv) $1-x, 1-y, 2-z$; where $Cg2$ is the centroid of the phenyl ring of the cation]: chains of cations form along the [101] direction (Fig. 2). Taking into account the hydrogen bonding and $\pi-\pi$ stacking, the overall connectivity is three-dimensional.

Hirshfeld surface analysis (Spackman & Jayatilaka, 2009; Spackman & McKinnon, 2002) was carried out with *Crystal-Explorer3.1* (Wolff *et al.*, 2012) to further investigate the presence of hydrogen bonds and intermolecular interactions in the crystal structure (see supporting information). Fig. 3(a) shows the two-dimensional fingerprint of the sum of the contacts contributing to the Hirshfeld surface represented in normal mode while those delineated into $H\cdots H$ (41.5%), $Br\cdots N/N\cdots Br$ (24.1%), $C\cdots H/H\cdots C$ (13.8%) and $S\cdots H/H\cdots S$ (11.7%) contacts, respectively, are shown in Fig. 3b–e. All contacts are listed in Table 2.

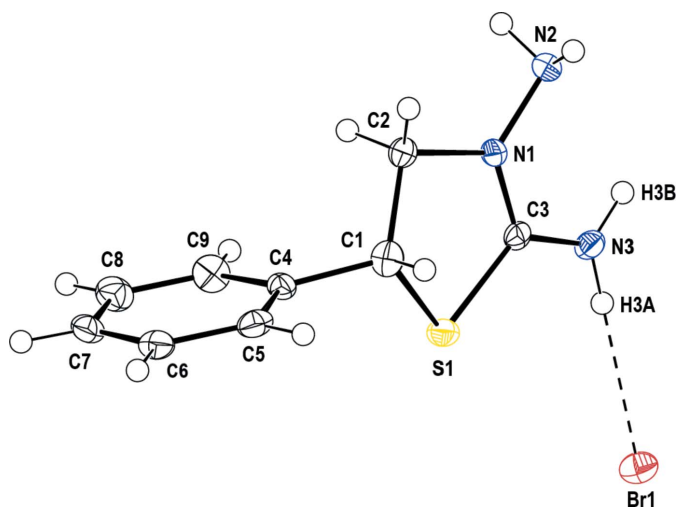


Figure 1
The molecular structure of the title salt. Displacement ellipsoids are drawn at the 50% probability level and the $H\cdots Br$ hydrogen bond is indicated by a dashed line.

Table 2
Percentage contributions of interatomic contacts to the Hirshfeld surface for the title salt.

Contact	Percentage contribution
$H\cdots H$	41.5
$Br\cdots N/N\cdots Br$	24.1
$C\cdots H/H\cdots C$	13.8
$S\cdots H/H\cdots S$	11.7
$N\cdots H/H\cdots N$	3.6
$C\cdots C$	3.3
$N\cdots C/C\cdots N$	1.5
$N\cdots N$	0.3
$S\cdots C/C\cdots S$	0.3

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.40, February 2019; Groom *et al.*, 2016) for 2-thiazolidinium compounds gave eight hits, *viz.* BOBWIB (Khalilov *et al.*, 2019), UDELUN (Akkurt *et al.*, 2018), WILBIC (Marthi *et al.*, 1994), WILBOI (Marthi *et al.*, 1994), WILBOI01 (Marthi *et al.*, 1994), YITCEJ (Martem'yanova *et al.*, 1993a), YITCAF (Martem'yanova *et al.*, 1993b) and YOPLUK (Marthi *et al.*, 1995).

In the crystal of BOBWIB (Khalilov *et al.*, 2019), the thiazolidine ring adopts an envelope conformation. In the crystal, centrosymmetrically related cations and anions are linked into dimeric units *via* $N-H\cdots Br$ hydrogen bonds, which are further connected by weak $C-H\cdots Br$ hydrogen bonds into chains parallel to [110]. In the crystal of UDELUN (Akkurt *et al.*, 2018), $C-H\cdots Br$ and $N-H\cdots Br$ hydrogen bonds link the components into a three-dimensional network with the cations and anions stacked along the b -axis direction. Weak $C-H\cdots \pi$ interactions, which only involve the minor disorder component of the ring, also contribute to the molecular packing. In

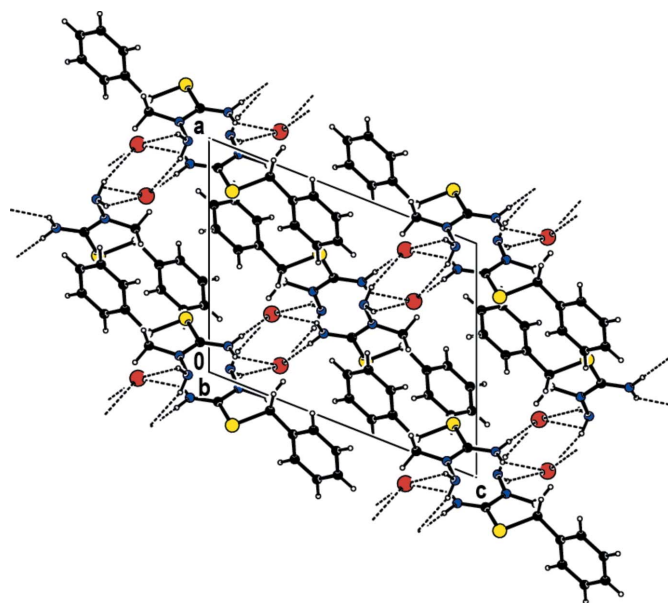


Figure 2
Part of the crystal structure of the title compound, showing the formation of $N-H\cdots Br$ hydrogen bonds in the ac plane.

addition, there are also inversion-related Cl...Cl halogen bonds and C—Cl... π (ring) contacts. In the other structures, the 3-N atom carries a C substituent: the first three crystal structures were determined for racemic (WILBIC; Marthi *et al.*, 1994) and two optically active samples (WILBOI and WILBOI01; Marthi *et al.*, 1994) of 3-(2'-chloro-2'-phenylethyl)-2-thiazolidiniminium *p*-toluenesulfonate. In all three structures, the most disordered fragment of these molecules is the asymmetric C atom and the Cl atom attached to it. The disorder of the cation in the racemate corresponds to the presence of both enantiomers at each site in the ratio 0.821 (3): 0.179 (3). The system of hydrogen bonds connecting two cations and two anions into 12-membered rings is identical in the racemic and in the optically active crystals. YITCEJ (Martem'yanova *et al.*, 1993a) is a product of the interaction of 2-amino-5-methylthiazoline with methyl iodide, with alkylation at the endocyclic nitrogen atom, while YITCAF

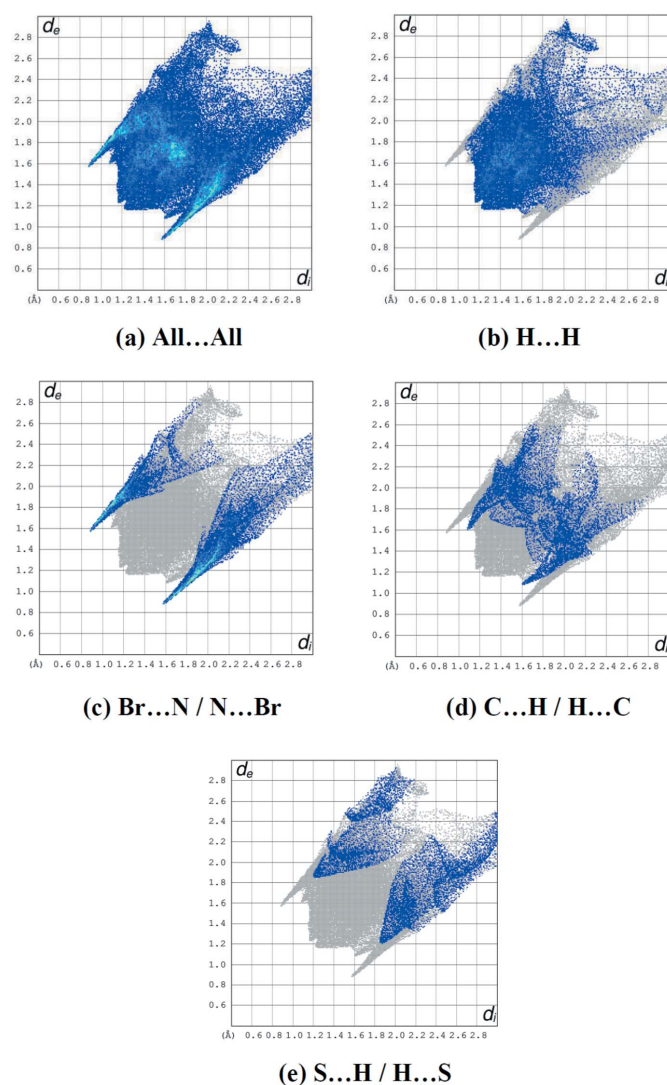


Figure 3
The two-dimensional fingerprint plots of the title salt, showing (a) all interactions, and delineated into (b) H...H, (c) Br...N/N...Br, (d) C...H/H...C and (e) S...H/H...S interactions [d_e and d_i represent the distances from a point on the Hirshfeld surface to the nearest atoms outside (external) and inside (internal) the surface, respectively].

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_9H_{12}N_3S^+ \cdot Br^-$
M_r	274.19
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	150
a, b, c (Å)	10.5986 (5), 8.7168 (3), 13.0308 (5)
β (°)	111.513 (2)
V (Å ³)	1119.99 (8)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	3.82
Crystal size (mm)	0.18 × 0.14 × 0.11
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (SADABS; Bruker, 2003)
T_{min}, T_{max}	0.534, 0.661
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8461, 2303, 1998
R_{int}	0.029
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.626
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.027, 0.070, 1.02
No. of reflections	2303
No. of parameters	127
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.61, -0.33

Computer programs: APEX2 and SAINT (Bruker, 2003), SHELXT2014 (Sheldrick, 2015a), SHELXL2016 (Sheldrick, 2015b), ORTEP-3 for Windows (Farrugia, 2012) and PLATON (Spek, 2003).

(Martem'yanova *et al.*, 1993b) is a product of the reaction of 3-nitro-5-methoxy-, 3-nitro-5-chloro-, and 3-bromo-5-nitrosalicylaldehyde with the heterocyclic base to form the salt-like complexes.

5. Synthesis and crystallization

To a solution of 2.2 mmol (0.6 g) (1,2-dibromoethyl)benzene in 20 ml of ethanol were added 2.3 mmol (0.3 g) of thiosemicarbazide hydrochloride; 3-4 drops of piperidine were added and the mixture was refluxed for 7 h. The reaction mixture was cooled to room temperature and the solid product was precipitated from solution, collected by filtration and recrystallized from ethanol solution to give colourless crystals of (I) with a yield of 88%, m.p. = 468 K. Analysis calculated for $C_9H_{12}BrN_3S$: C 39.43; H 4.41; N 15.33. Found: C 39.40; H 4.39; N 15.30%. ¹H NMR (300 MHz, DMSO- d_6): 4.16 (*q*, 1H, CH₂, ³ $J_{H-H} = 5.4$); 4.45 (*t*, 1H, CH₂, ³ $J_{H-H} = 8.4$); 5.25 (*t*, 1H, CH-Ar, ³ $J_{H-H} = 5.4$); 7.32–7.50 (*m*, 5H, 5Ar-H); 9.12 (*s*, 2H, NH₂); 9.78 (*s*, 1H, NH=). ¹³C NMR (75 MHz, DMSO- d_6): 44.42, 62.06, 127.59, 128.76, 129.17, 138.85, 168.53. MS (ESI), *m/z*: 194.28 [$C_9H_{12}N_3S$]⁺ and 79.88 Br⁻.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms on C atoms were placed at calculated positions (C—H = 0.95–1.00 Å) and

refined using a riding model. The N-bound hydrogen atoms were located from difference-Fourier maps and relocated to idealized locations ($N-H = 0.90 \text{ \AA}$) and refined as riding atoms. The constraint $U_{iso}(H) = 1.2U_{eq}(\text{carrier})$ was applied in all cases. One outlier ($\bar{1}01$) was omitted in the final cycles of refinement.

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Crystal structure and Hirshfeld surface analysis of 3-amino-5-phenylthiazolidin-2-iminium bromide

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Computing details

Data collection: *APEX2* (Bruker, 2003); cell refinement: *SAINTE* (Bruker, 2003); data reduction: *SAINTE* (Bruker, 2003); program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2003).

3-Amino-5-phenylthiazolidin-2-iminium bromide

Crystal data

$C_9H_{12}N_3S^+Br^-$

$M_r = 274.19$

Monoclinic, $P2_1/n$

$a = 10.5986$ (5) Å

$b = 8.7168$ (3) Å

$c = 13.0308$ (5) Å

$\beta = 111.513$ (2)°

$V = 1119.99$ (8) Å³

$Z = 4$

$F(000) = 552$

$D_x = 1.626$ Mg m⁻³

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

Cell parameters from 3357 reflections

$\theta = 2.9$ – 26.3 °

$\mu = 3.82$ mm⁻¹

$T = 150$ K

Block, colorless

$0.18 \times 0.14 \times 0.11$ mm

Data collection

Bruker APEXII CCD
diffractometer

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2003)

$T_{\min} = 0.534$, $T_{\max} = 0.661$

8461 measured reflections

2303 independent reflections

1998 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

$\theta_{\max} = 26.4$ °, $\theta_{\min} = 2.9$ °

$h = -13 \rightarrow 13$

$k = -10 \rightarrow 10$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.070$

$S = 1.02$

2303 reflections

127 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0381P)^2 + 0.5896P]$

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

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

$$\Delta\rho_{\max} = 0.61 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.33 \text{ e } \text{\AA}^{-3}$$

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.

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	0.14662 (3)	0.38142 (3)	0.26547 (2)	0.02369 (10)
S1	0.31116 (7)	0.46985 (7)	0.58677 (5)	0.02034 (15)
N1	0.4802 (2)	0.6893 (2)	0.61070 (15)	0.0159 (4)
N2	0.5487 (2)	0.8083 (2)	0.57955 (15)	0.0183 (4)
H2A	0.635551	0.776693	0.607350	0.022*
H2B	0.535901	0.891753	0.615230	0.022*
N3	0.3577 (2)	0.6293 (2)	0.42850 (16)	0.0179 (4)
H3A	0.292719	0.572157	0.379225	0.021*
H3B	0.390509	0.709317	0.402415	0.021*
C1	0.4372 (3)	0.5007 (3)	0.72776 (19)	0.0214 (5)
H1A	0.513995	0.427032	0.741377	0.026*
C2	0.4890 (3)	0.6645 (3)	0.72463 (19)	0.0189 (5)
H2C	0.432008	0.739798	0.744749	0.023*
H2D	0.583832	0.675080	0.776759	0.023*
C3	0.3879 (2)	0.6085 (3)	0.53385 (19)	0.0154 (5)
C4	0.3746 (2)	0.4760 (3)	0.81375 (18)	0.0168 (5)
C5	0.4280 (3)	0.3584 (3)	0.8912 (2)	0.0212 (5)
H5A	0.497585	0.293462	0.886358	0.025*
C6	0.3773 (3)	0.3379 (3)	0.97571 (19)	0.0208 (5)
H6A	0.412191	0.258553	1.028582	0.025*
C7	0.2769 (3)	0.4330 (3)	0.9816 (2)	0.0225 (5)
H7A	0.244208	0.420521	1.039905	0.027*
C8	0.2230 (3)	0.5463 (3)	0.9041 (2)	0.0265 (6)
H8A	0.152610	0.610477	0.908407	0.032*
C9	0.2715 (3)	0.5662 (3)	0.8203 (2)	0.0249 (6)
H9A	0.233208	0.643424	0.766388	0.030*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02460 (15)	0.02084 (15)	0.02181 (15)	−0.00181 (11)	0.00401 (11)	−0.00181 (10)
S1	0.0263 (3)	0.0175 (3)	0.0173 (3)	−0.0062 (3)	0.0081 (2)	−0.0012 (2)
N1	0.0197 (10)	0.0165 (10)	0.0132 (9)	−0.0036 (8)	0.0078 (8)	−0.0004 (8)
N2	0.0208 (11)	0.0162 (10)	0.0198 (10)	−0.0030 (9)	0.0099 (9)	−0.0004 (8)
N3	0.0239 (11)	0.0151 (10)	0.0144 (10)	−0.0011 (9)	0.0066 (8)	−0.0014 (8)
C1	0.0215 (13)	0.0233 (13)	0.0184 (12)	0.0033 (11)	0.0061 (10)	0.0023 (10)
C2	0.0225 (13)	0.0215 (12)	0.0126 (11)	−0.0041 (10)	0.0064 (10)	−0.0018 (10)

C3	0.0176 (12)	0.0121 (11)	0.0178 (12)	0.0027 (9)	0.0082 (10)	-0.0009 (9)
C4	0.0171 (12)	0.0193 (12)	0.0131 (11)	-0.0054 (10)	0.0046 (9)	-0.0010 (9)
C5	0.0175 (12)	0.0183 (12)	0.0255 (13)	-0.0020 (10)	0.0051 (10)	-0.0066 (10)
C6	0.0244 (13)	0.0193 (12)	0.0147 (12)	-0.0050 (10)	0.0027 (10)	0.0016 (10)
C7	0.0215 (13)	0.0253 (13)	0.0214 (13)	-0.0100 (11)	0.0085 (11)	-0.0029 (11)
C8	0.0208 (13)	0.0258 (14)	0.0335 (15)	-0.0012 (11)	0.0108 (12)	-0.0007 (12)
C9	0.0219 (13)	0.0246 (13)	0.0266 (14)	0.0041 (11)	0.0070 (11)	0.0036 (11)

Geometric parameters (Å, °)

S1—C3	1.735 (2)	C2—H2C	0.9900
S1—C1	1.853 (2)	C2—H2D	0.9900
N1—C3	1.318 (3)	C4—C9	1.374 (4)
N1—N2	1.408 (3)	C4—C5	1.404 (3)
N1—C2	1.469 (3)	C5—C6	1.403 (4)
N2—H2A	0.9000	C5—H5A	0.9500
N2—H2B	0.9000	C6—C7	1.373 (4)
N3—C3	1.303 (3)	C6—H6A	0.9500
N3—H3A	0.9000	C7—C8	1.378 (4)
N3—H3B	0.9000	C7—H7A	0.9500
C1—C4	1.513 (3)	C8—C9	1.378 (4)
C1—C2	1.535 (4)	C8—H8A	0.9500
C1—H1A	1.0000	C9—H9A	0.9500
C3—S1—C1	91.16 (11)	N3—C3—N1	123.6 (2)
C3—N1—N2	119.48 (18)	N3—C3—S1	123.08 (18)
C3—N1—C2	116.3 (2)	N1—C3—S1	113.33 (17)
N2—N1—C2	123.48 (18)	C9—C4—C5	119.6 (2)
N1—N2—H2A	102.6	C9—C4—C1	122.7 (2)
N1—N2—H2B	104.8	C5—C4—C1	117.7 (2)
H2A—N2—H2B	111.4	C6—C5—C4	119.2 (2)
C3—N3—H3A	120.2	C6—C5—H5A	120.4
C3—N3—H3B	121.7	C4—C5—H5A	120.4
H3A—N3—H3B	117.4	C7—C6—C5	119.6 (2)
C4—C1—C2	114.2 (2)	C7—C6—H6A	120.2
C4—C1—S1	111.16 (17)	C5—C6—H6A	120.2
C2—C1—S1	104.09 (16)	C6—C7—C8	120.9 (2)
C4—C1—H1A	109.1	C6—C7—H7A	119.5
C2—C1—H1A	109.1	C8—C7—H7A	119.5
S1—C1—H1A	109.1	C9—C8—C7	119.7 (3)
N1—C2—C1	105.85 (19)	C9—C8—H8A	120.1
N1—C2—H2C	110.6	C7—C8—H8A	120.1
C1—C2—H2C	110.6	C4—C9—C8	120.9 (2)
N1—C2—H2D	110.6	C4—C9—H9A	119.5
C1—C2—H2D	110.6	C8—C9—H9A	119.5
H2C—C2—H2D	108.7		
C3—S1—C1—C4	147.17 (19)	C2—C1—C4—C9	53.9 (3)

C3—S1—C1—C2	23.78 (17)	S1—C1—C4—C9	-63.5 (3)
C3—N1—C2—C1	26.7 (3)	C2—C1—C4—C5	-124.2 (2)
N2—N1—C2—C1	-163.3 (2)	S1—C1—C4—C5	118.4 (2)
C4—C1—C2—N1	-152.1 (2)	C9—C4—C5—C6	-1.7 (4)
S1—C1—C2—N1	-30.7 (2)	C1—C4—C5—C6	176.5 (2)
N2—N1—C3—N3	1.9 (3)	C4—C5—C6—C7	-0.2 (4)
C2—N1—C3—N3	172.3 (2)	C5—C6—C7—C8	1.5 (4)
N2—N1—C3—S1	-178.62 (16)	C6—C7—C8—C9	-0.9 (4)
C2—N1—C3—S1	-8.2 (3)	C5—C4—C9—C8	2.2 (4)
C1—S1—C3—N3	169.2 (2)	C1—C4—C9—C8	-175.8 (2)
C1—S1—C3—N1	-10.29 (19)	C7—C8—C9—C4	-1.0 (4)

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N2—H2A...Br1 ⁱ	0.90	2.68	3.530 (2)	158
N2—H2B...Br1 ⁱⁱ	0.90	2.73	3.524 (2)	148
N3—H3A...Br1	0.90	2.38	3.271 (2)	169
N3—H3B...Br1 ⁱⁱⁱ	0.90	2.56	3.337 (2)	145

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x+1/2, -y+3/2, z+1/2$; (iii) $-x+1/2, y+1/2, -z+1/2$.