

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

6-Bromo-4-hydrazinylidene-1-methyl-3*H*-2λ⁶,1-benzothiazine-2,2-dioneMuhammad Shafiq,^a Islam Ullah Khan,^a Muhammad Zia-ur-Rehman,^b Muhammad Nadeem Arshad^{c,a*} and Abdullah M. Asiri^d

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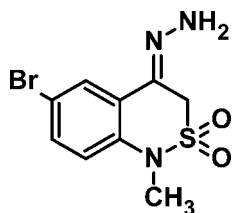
Received 24 June 2011; accepted 12 July 2011

Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.032; wR factor = 0.079; data-to-parameter ratio = 17.9.

In the title molecule, $\text{C}_9\text{H}_{10}\text{BrN}_3\text{O}_2\text{S}$, the thiazine ring has an envelope conformation with the S atom at the flap. The geometry around the S atom is distorted tetrahedral. In the crystal, inversion dimers linked by pairs of $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds occur, generating $R_2^2(6)$ ring motifs. $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds and $\text{C}-\text{H}\cdots\text{O}$ interactions connect the dimers, forming a three-dimensional network structure.

Related literature

For the related structures of 6-bromo-1-methyl-1*H*-2,1-benzothiazin-4(3*H*)-one 2,2-dioxide and 6-bromo-1-ethyl-1*H*-2,1-benzothiazin-4(3*H*)-one 2,2-dioxide, see: Shafiq *et al.* (2009*a,b*), respectively. For the structures of other benzothiazine derivatives, see: Shafiq *et al.* (2011); Arshad *et al.* (2011). For graph-set notation, see: Bernstein *et al.* (1995). For puckering parameters, see: Cremer & Pople (1975).



Experimental

Crystal data

$\text{C}_9\text{H}_{10}\text{BrN}_3\text{O}_2\text{S}$
 $M_r = 304.17$

Monoclinic, $P2_1/n$
 $a = 10.1483$ (5) Å

$b = 9.6375$ (4) Å
 $c = 11.2118$ (5) Å
 $\beta = 92.278$ (2)°
 $V = 1095.69$ (9) Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 3.93$ mm⁻¹
 $T = 296$ K
 $0.21 \times 0.09 \times 0.07$ mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2001)
 $T_{\min} = 0.492$, $T_{\max} = 0.771$

12176 measured reflections
2719 independent reflections
1972 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.079$
 $S = 1.01$
2719 reflections
152 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.40$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.35$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N3}-\text{H32}\cdots\text{N2}^{\text{i}}$	0.85 (4)	2.47 (4)	3.198 (4)	144 (3)
$\text{N3}-\text{H31}\cdots\text{O1}^{\text{ii}}$	0.90 (4)	2.38 (4)	3.252 (4)	162 (3)
$\text{C3}-\text{H3}\cdots\text{O1}^{\text{iii}}$	0.93	2.45	3.323 (3)	156

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

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997) and PLATON (Spek, 2009); software used to prepare material for publication: WinGX (Farrugia, 1999) and PLATON.

The authors acknowledge the Higher Education Commission of Pakistan for providing a grant for the project to strengthen the Materials Chemistry Laboratory at GC University, Lahore, Pakistan.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2288).

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supporting information

Acta Cryst. (2011). E67, o2078 [doi:10.1107/S1600536811027930]

6-Bromo-4-hydrazinylidene-1-methyl-3H-2λ⁶,1-benzothiazine-2,2-dione

Muhammad Shafiq, Islam Ullah Khan, Muhammad Zia-ur-Rehman, Muhammad Nadeem Arshad and Abdullah M. Asiri

S1. Comment

Continuing our research on the synthesis (Shafiq *et al.*, 2011; Arshad *et al.*, 2011) and crystal structure studies of benzothiazine derivatives (Shafiq *et al.*, 2009a), we present herein the crystal structure of the title compound, (I).

The molecular structure of the title molecule, (I), is illustrated in Fig. 1. The structure differs to a similar published compound, 6-Bromo-1-methyl-1*H*-2,1-benzothiazin-4(3*H*)-one 2,2-dioxide (II) [Shafiq *et al.*, 2009a], in that the carbonyl group in (II) has been replaced with a hydrazide moiety in (I). The bond lengths and angles in the title compound are similar to those of (II) and in 6-Bromo-1-ethyl-1*H*-2,1-benzothiazin-4(3*H*)-one 2,2-dioxide (III) (Shafiq *et al.*, 2009b). In (I) atom Br1, attached to the planar aromatic ring (C1—C6), lies out of the plane by 0.0547 (3) Å, while in (II) and (III) the deviations are slightly greater, i.e. 0.064 (4) and 0.073 (4) Å, respectively. The thiazine ring, (C1/C6/C7/C8/S1/N1), has an envelope conformation with atom S1 as the flap [puckering parameters: Q (puckering amplitude) = 0.5873 (18) Å, $\theta = 124.31$ (19) °, and $\varphi = 185.9$ (3) ° (Cromer & Pople, 1975)].

In the crystal structure of compound (I) the functional hydrazide group is involved in the formation of inversion dimers, through N3—H32⋯N2 hydrogen bonding, and generates a six-membered $R_2^2(6)$ ring motif (Bernstein *et al.*, 1995). These dimers are further connected through N—H⋯O hydrogen bonds and weak C—H⋯O interactions to form a three dimensional network structure (Table 1, Fig. 2).

S2. Experimental

A mixture of 1-methyl-2,2-dioxo-2,3-dihydro-1*H*-2λ⁶-benzo [*c*][1,2]thiazin-4-one (10.60 g; 50.0 mmoles), hydrazine hydrate (85%) (5.0 ml) and ethanol (200 ml) was reacted at 318 K using an ultrasound reaction bath for about 35 mins. After completion of the reaction, excess hydrazine and solvent were removed under vacuum. The crude product obtained was washed with water and dried; Yield: 74%. Suitable crystals were produced through recrystallization in methanol under slow evaporation.

S3. Refinement

The NH H-atom was located in a difference Fourier map and refined with $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{N})$. The C-bound H-atoms were included in calculated positions and treated as riding atoms: C-H = 0.93, 0.96, and 0.97 Å for CH(aromatic), CH₃ and CH₂ H-atoms, respectively, with $U_{\text{iso}}(\text{H}) = k \times U_{\text{eq}}(\text{parent C-atom})$, where $k = 1.5$ for CH₃ H-atoms and $k = 1.2$ for all other H-atoms.

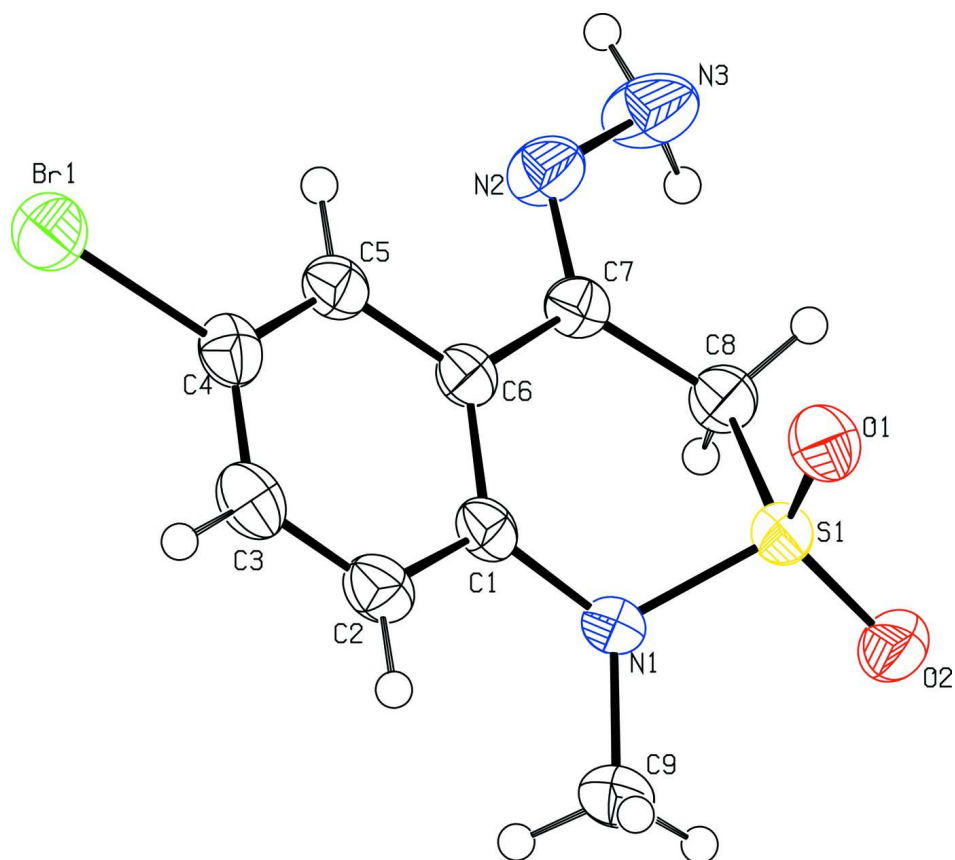


Figure 1

A view of the molecular structure of the title molecule, (I), showing the labelling scheme and 50% displacement ellipsoids.

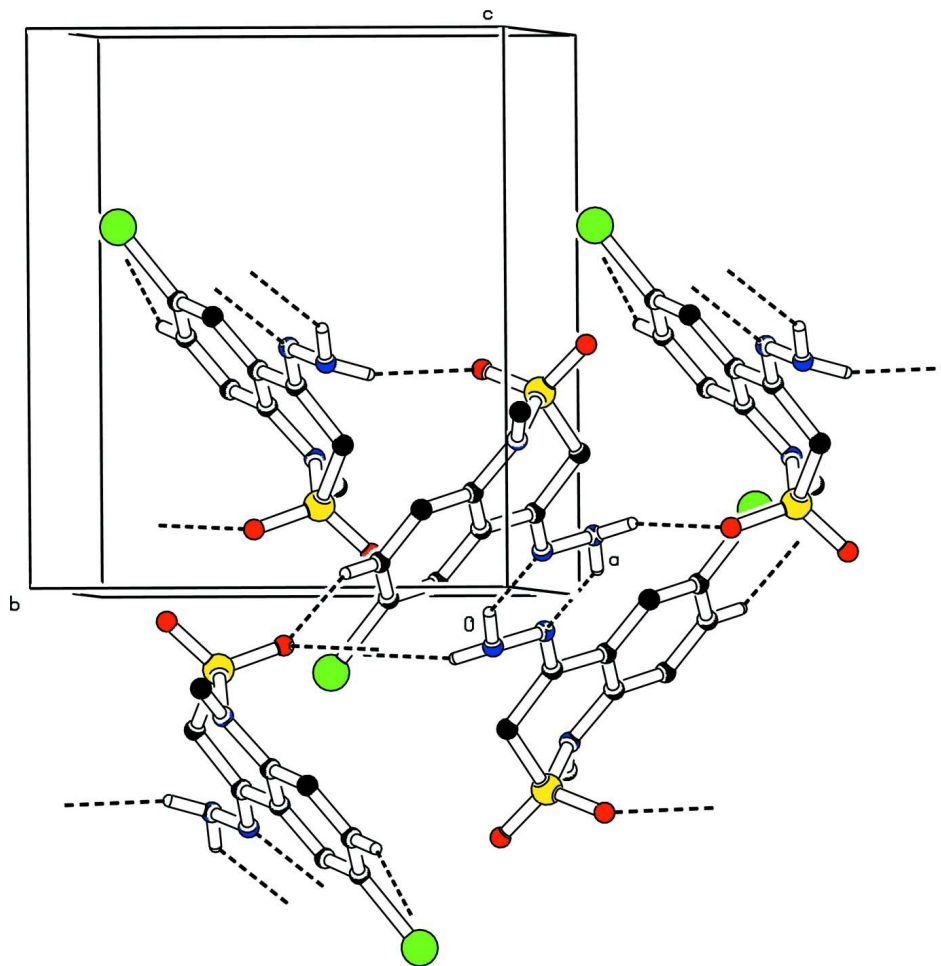


Figure 2

A perspective view of the crystal packing of compound (I), showing the inversion dimers formed through N—H...N hydrogen bonds (dashed lines; see Table 1 for details).

6-Bromo-4-hydrazinylidene-1-methyl-3*H*-2*l*⁶,1-benzothiazine-2,2-dione

Crystal data

$C_9H_{10}BrN_3O_2S$

$M_r = 304.17$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2_1n$

$a = 10.1483\ (5)\ \text{\AA}$

$b = 9.6375\ (4)\ \text{\AA}$

$c = 11.2118\ (5)\ \text{\AA}$

$\beta = 92.278\ (2)^\circ$

$V = 1095.69\ (9)\ \text{\AA}^3$

$Z = 4$

$F(000) = 608$

$D_x = 1.844\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3531 reflections

$\theta = 2.7\text{--}24.7^\circ$

$\mu = 3.93\ \text{mm}^{-1}$

$T = 296\ \text{K}$

Needle, yellow

$0.21 \times 0.09 \times 0.07\ \text{mm}$

Data collection

Bruker Kappa APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator
 φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2001)
 $T_{\min} = 0.492$, $T_{\max} = 0.771$
12176 measured reflections
2719 independent reflections
1972 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$
 $\theta_{\max} = 28.3^\circ$, $\theta_{\min} = 2.7^\circ$
 $h = -13 \rightarrow 13$
 $k = -12 \rightarrow 7$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.079$
 $S = 1.01$
2719 reflections
152 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 atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0403P)^2 + 0.1092P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.40 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.35 \text{ e } \text{Å}^{-3}$

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.94817 (3)	0.62148 (3)	1.15166 (3)	0.04753 (12)
S1	0.86913 (6)	1.05109 (6)	0.65175 (5)	0.03060 (16)
O1	0.81377 (18)	0.92236 (19)	0.60884 (16)	0.0413 (4)
O2	0.90132 (19)	1.15392 (19)	0.56664 (16)	0.0433 (5)
N1	1.00013 (19)	1.0224 (2)	0.73776 (18)	0.0321 (5)
N2	0.6567 (2)	1.0222 (2)	0.9307 (2)	0.0400 (5)
N3	0.5556 (3)	1.1148 (3)	0.9019 (3)	0.0551 (7)
H32	0.507 (4)	1.115 (3)	0.962 (3)	0.066*
H31	0.586 (3)	1.199 (4)	0.881 (3)	0.066*
C1	0.9838 (2)	0.9263 (2)	0.8314 (2)	0.0290 (5)
C2	1.0852 (3)	0.8338 (3)	0.8633 (2)	0.0363 (6)
H2	1.1616	0.8335	0.8202	0.044*
C3	1.0743 (3)	0.7436 (3)	0.9567 (2)	0.0377 (6)
H3	1.1427	0.6829	0.9774	0.045*
C4	0.9602 (3)	0.7443 (2)	1.0195 (2)	0.0341 (6)
C5	0.8576 (2)	0.8322 (2)	0.9895 (2)	0.0319 (6)
H5	0.7813	0.8299	1.0328	0.038*
C6	0.8669 (2)	0.9253 (2)	0.8943 (2)	0.0274 (5)

C7	0.7567 (2)	1.0212 (2)	0.8646 (2)	0.0290 (5)
C8	0.7637 (3)	1.1175 (2)	0.7582 (2)	0.0343 (6)
H8A	0.7954	1.2077	0.7848	0.041*
H8B	0.6761	1.1295	0.7219	0.041*
C9	1.1299 (3)	1.0488 (3)	0.6900 (3)	0.0457 (7)
H9A	1.1927	1.0658	0.7546	0.069*
H9B	1.1250	1.1284	0.6385	0.069*
H9C	1.1571	0.9694	0.6454	0.069*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.04682 (19)	0.04001 (17)	0.0552 (2)	-0.00435 (13)	-0.00552 (14)	0.01513 (13)
S1	0.0277 (3)	0.0349 (3)	0.0292 (3)	0.0003 (3)	0.0004 (3)	0.0005 (2)
O1	0.0432 (11)	0.0436 (10)	0.0366 (10)	-0.0068 (9)	-0.0041 (8)	-0.0078 (8)
O2	0.0411 (11)	0.0484 (11)	0.0406 (11)	0.0029 (9)	0.0046 (9)	0.0129 (8)
N1	0.0234 (11)	0.0400 (11)	0.0330 (12)	-0.0015 (9)	0.0008 (9)	0.0032 (9)
N2	0.0375 (13)	0.0384 (12)	0.0447 (14)	0.0089 (10)	0.0113 (11)	0.0073 (10)
N3	0.0439 (16)	0.0518 (16)	0.071 (2)	0.0180 (13)	0.0243 (14)	0.0177 (14)
C1	0.0265 (13)	0.0311 (12)	0.0290 (13)	-0.0005 (10)	-0.0034 (10)	-0.0058 (10)
C2	0.0283 (14)	0.0411 (14)	0.0394 (16)	0.0041 (11)	0.0000 (12)	-0.0047 (11)
C3	0.0337 (15)	0.0352 (13)	0.0436 (16)	0.0073 (11)	-0.0062 (12)	-0.0033 (11)
C4	0.0395 (15)	0.0257 (11)	0.0362 (14)	-0.0052 (10)	-0.0086 (12)	-0.0002 (10)
C5	0.0300 (14)	0.0319 (12)	0.0335 (14)	-0.0037 (10)	-0.0015 (11)	-0.0033 (10)
C6	0.0283 (13)	0.0259 (11)	0.0279 (13)	-0.0023 (10)	-0.0021 (10)	-0.0050 (9)
C7	0.0276 (13)	0.0293 (12)	0.0302 (13)	-0.0001 (10)	0.0022 (10)	-0.0035 (10)
C8	0.0322 (14)	0.0348 (13)	0.0360 (14)	0.0045 (11)	0.0028 (11)	0.0017 (11)
C9	0.0265 (14)	0.0676 (19)	0.0432 (16)	-0.0013 (13)	0.0049 (12)	0.0035 (14)

Geometric parameters (Å, °)

Br1—C4	1.904 (2)	C2—H2	0.9300
S1—O2	1.4228 (19)	C3—C4	1.380 (4)
S1—O1	1.4369 (19)	C3—H3	0.9300
S1—N1	1.635 (2)	C4—C5	1.374 (3)
S1—C8	1.755 (3)	C5—C6	1.400 (3)
N1—C1	1.415 (3)	C5—H5	0.9300
N1—C9	1.464 (3)	C6—C7	1.479 (3)
N2—C7	1.280 (3)	C7—C8	1.515 (3)
N2—N3	1.388 (3)	C8—H8A	0.9700
N3—H32	0.85 (4)	C8—H8B	0.9700
N3—H31	0.90 (4)	C9—H9A	0.9600
C1—C2	1.397 (4)	C9—H9B	0.9600
C1—C6	1.404 (3)	C9—H9C	0.9600
C2—C3	1.369 (4)		
O2—S1—O1	118.29 (11)	C5—C4—Br1	120.2 (2)
O2—S1—N1	108.09 (11)	C3—C4—Br1	118.40 (19)

O1—S1—N1	110.45 (11)	C4—C5—C6	120.6 (2)
O2—S1—C8	111.38 (11)	C4—C5—H5	119.7
O1—S1—C8	107.55 (12)	C6—C5—H5	119.7
N1—S1—C8	99.44 (11)	C5—C6—C1	118.1 (2)
C1—N1—C9	121.3 (2)	C5—C6—C7	120.0 (2)
C1—N1—S1	115.59 (16)	C1—C6—C7	121.9 (2)
C9—N1—S1	118.49 (17)	N2—C7—C6	118.9 (2)
C7—N2—N3	117.8 (2)	N2—C7—C8	120.9 (2)
N2—N3—H32	105 (2)	C6—C7—C8	120.1 (2)
N2—N3—H31	112 (2)	C7—C8—S1	111.17 (16)
H32—N3—H31	115 (3)	C7—C8—H8A	109.4
C2—C1—C6	119.7 (2)	S1—C8—H8A	109.4
C2—C1—N1	120.0 (2)	C7—C8—H8B	109.4
C6—C1—N1	120.2 (2)	S1—C8—H8B	109.4
C3—C2—C1	121.4 (2)	H8A—C8—H8B	108.0
C3—C2—H2	119.3	N1—C9—H9A	109.5
C1—C2—H2	119.3	N1—C9—H9B	109.5
C2—C3—C4	118.8 (2)	H9A—C9—H9B	109.5
C2—C3—H3	120.6	N1—C9—H9C	109.5
C4—C3—H3	120.6	H9A—C9—H9C	109.5
C5—C4—C3	121.4 (2)	H9B—C9—H9C	109.5
O2—S1—N1—C1	177.43 (17)	C4—C5—C6—C1	-0.3 (3)
O1—S1—N1—C1	-51.7 (2)	C4—C5—C6—C7	-178.8 (2)
C8—S1—N1—C1	61.13 (19)	C2—C1—C6—C5	1.4 (3)
O2—S1—N1—C9	-26.3 (2)	N1—C1—C6—C5	-177.3 (2)
O1—S1—N1—C9	104.5 (2)	C2—C1—C6—C7	179.8 (2)
C8—S1—N1—C9	-142.6 (2)	N1—C1—C6—C7	1.1 (3)
C9—N1—C1—C2	-13.4 (3)	N3—N2—C7—C6	179.0 (2)
S1—N1—C1—C2	142.1 (2)	N3—N2—C7—C8	-0.3 (4)
C9—N1—C1—C6	165.3 (2)	C5—C6—C7—N2	3.4 (3)
S1—N1—C1—C6	-39.2 (3)	C1—C6—C7—N2	-174.9 (2)
C6—C1—C2—C3	-1.4 (4)	C5—C6—C7—C8	-177.2 (2)
N1—C1—C2—C3	177.3 (2)	C1—C6—C7—C8	4.4 (3)
C1—C2—C3—C4	0.4 (4)	N2—C7—C8—S1	-155.8 (2)
C2—C3—C4—C5	0.6 (4)	C6—C7—C8—S1	24.9 (3)
C2—C3—C4—Br1	-178.47 (19)	O2—S1—C8—C7	-165.88 (17)
C3—C4—C5—C6	-0.7 (4)	O1—S1—C8—C7	63.0 (2)
Br1—C4—C5—C6	178.42 (17)	N1—S1—C8—C7	-52.11 (19)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H32 \cdots N2 ⁱ	0.85 (4)	2.47 (4)	3.198 (4)	144 (3)
N3—H31 \cdots O1 ⁱⁱ	0.90 (4)	2.38 (4)	3.252 (4)	162 (3)
C3—H3 \cdots O1 ⁱⁱⁱ	0.93	2.45	3.323 (3)	156

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