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## Structure Reports

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4-Hydrazinylidene-1-methyl-3*H*-2λ<sup>6</sup>,1-benzothiazine-2,2-dioneMuhammad Shafiq,<sup>a</sup> Islam Ullah Khan,<sup>a</sup> Muhammad Zia-ur-Rehman,<sup>b</sup> Muhammad Nadeem Arshad<sup>c\*‡</sup> and Abdullah M. Asiri<sup>d</sup>

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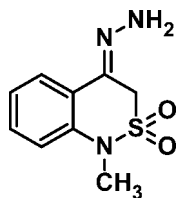
Received 26 June 2011; accepted 9 July 2011

Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.036;  $wR$  factor = 0.111; data-to-parameter ratio = 17.0.

In the title compound,  $\text{C}_9\text{H}_{11}\text{N}_3\text{O}_2\text{S}$ , the thiazine ring adopts a half-chair conformation. In the crystal structure  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bonds connect two molecules into a centrosymmetric dimer, forming an  $R_2^2(6)$  ring motif. These dimers are further connected into chains by  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds.

## Related literature

For the synthesis of the title compound, see: Shafiq *et al.* (2011*b*). For information on 1,2 and 2,1-benzothiazine, see: Shafiq *et al.* (2011*a*); Arshad *et al.* (2011). For related structures, see: Tahir *et al.* (2008); Khan *et al.* (2010); Shafiq *et al.* (2009); Arshad *et al.* (2009). For graph-set notation of hydrogen bonds, see: Bernstein *et al.* (1995).



## Experimental

## Crystal data

 $\text{C}_9\text{H}_{11}\text{N}_3\text{O}_2\text{S}$  $M_r = 225.27$ Monoclinic,  $P2_1/n$  $a = 6.6643$  (2) Å $b = 9.6834$  (3) Å $c = 15.5890$  (5) Å $\beta = 97.699$  (1)° $V = 996.94$  (5) Å<sup>3</sup>

<sup>‡</sup> Materials Chemistry Laboratory, Department of Chemistry, GC University, Lahore 54000, Pakistan.

$Z = 4$   
Mo  $K\alpha$  radiation  
 $\mu = 0.31$  mm<sup>-1</sup>

$T = 296$  K  
 $0.41 \times 0.22 \times 0.18$  mm

## Data collection

Bruker Kappa APEXII CCD diffractometer  
Absorption correction: multi-scan (SADABS; Bruker, 2007)  
 $T_{\min} = 0.884$ ,  $T_{\max} = 0.947$

8966 measured reflections  
2426 independent reflections  
2114 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.020$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.111$   
 $S = 0.93$   
2426 reflections  
143 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.30$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.29$  e Å<sup>-3</sup>

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

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N3}-\text{H1N}\cdots\text{O1}^i$	0.86 (2)	2.46 (2)	3.221 (2)	147.7 (17)
$\text{N3}-\text{H2N}\cdots\text{N2}^{ii}$	0.790 (19)	2.376 (19)	3.094 (2)	151.8 (19)
$\text{C8}-\text{H8A}\cdots\text{O1}^i$	0.97	2.59	3.4178 (19)	144

Symmetry codes: (i)  $-x + \frac{5}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (ii)  $-x + 3, -y, -z$ .

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.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5565).

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## supporting information

*Acta Cryst.* (2011). E67, o2038 [doi:10.1107/S1600536811027577]

**4-Hydrazinylidene-1-methyl-3*H*-2λ<sup>6</sup>,1-benzothiazine-2,2-dione**

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

**S1. Comment**

We are already engaged in the synthesis (Shafiq *et al.*, 2011*a*), (Arshad *et al.*, 2011) and crystallographic studies of 1,2- & 2,1-benzothiazine molecules (Arshad *et al.*, 2009), (Shafiq *et al.*, 2009). Here in, we report the crystal structure of hydrazide (I), synthesized from 1-methyl-1*H*-2,1-benzothiazin-4(3*H*)-one 2,2-dioxide (II) (Tahir *et al.*, 2008).

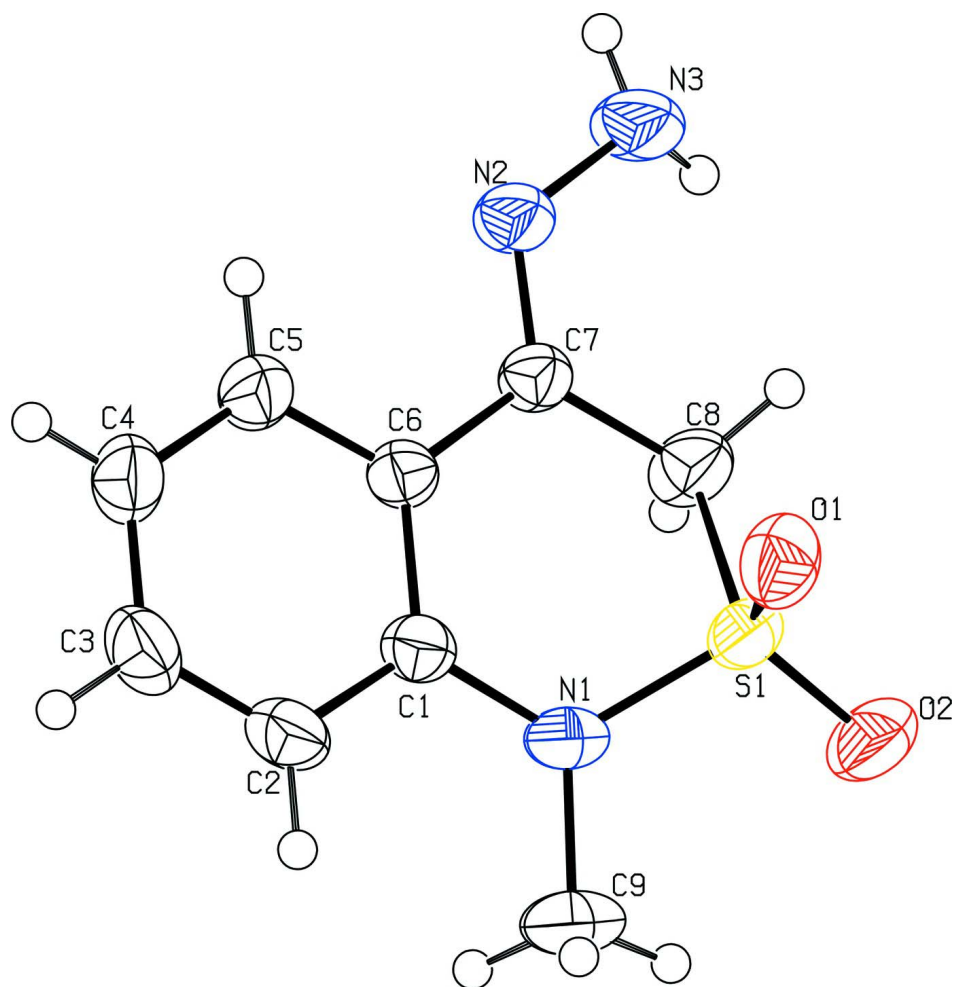
In the crystal structure of title compound, the bond lengths and angles are almost similar to structurally similar molecules (II) and 1-propyl-1*H*-2,1-benzothiazin-4(3*H*)-one 2,2-dioxide (III) (Khan *et al.*, 2010). The fused aromatic and thiazine rings are twisted at dihedral angle of 11.13 (8)°. The thiazine ring (C1/C6/C7/C8/S1/N1) adopted the sofa shape with the r. m. s. deviation of fitted atoms of 0.2380 Å showing the maximum deviation for the S1 (0.3969 (8) Å) & C8 (0.2687 (7) Å). The molecules in the crystal structure dimerized through N—H···N hydrogen bonding forming six-membered  $R_2^2(6)$  ring motif (Bernstein *et al.*, 1995). There are C—H···O and N—H···N type interactions which connect the dimers in zig-zag mode along *c* axis and *a* axis and generate another seven membered ring motif  $R_2^1(7)$ .

**S2. Experimental**

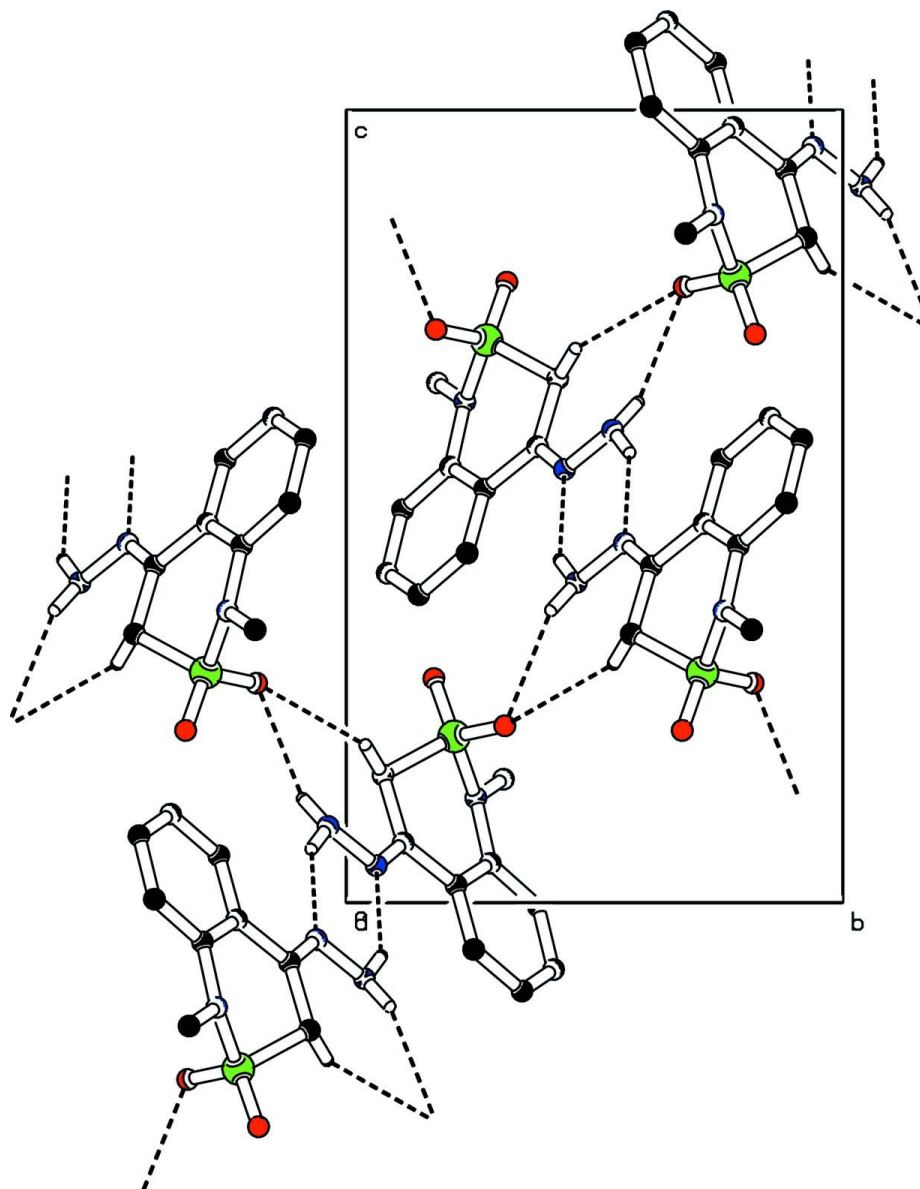
The synthesis of title compound have already been reported (Shafiq *et al.*, 2011*b*). Suitable crystals were grown in dry ethanol under slow evaporation.

**S3. Refinement**

H-atoms bonded to C were positioned with idealized geometry with C—H = 0.93 Å for aromatic, C—H = 0.96 Å for methyl group and C—H = 0.97 Å for methylene group and were refined using a riding model with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$  for aromatic and methylene and with  $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$  for methyl carbon atoms. The coordinates of the H atoms bonded to N were refined with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{N})$ . Four reflections (-1 0 1, 0 1 1, 0 0 2 and -1 0 9) have been omitted in final refinement.

**Figure 1**

The molecular structure of the title compound with displacement ellipsoids drawn at 50% probability level.



**Figure 2**

Perspective view showing the dimers and hydrogen bonding via dashed lines, hydrogen atoms not involved in hydrogen bonding have been omitted for clarity.

#### 4-Hydrazinylidene-1-methyl-3H-2λ<sup>6</sup>,1-benzothiazine-2,2-dione

##### Crystal data

$C_9H_{11}N_3O_2S$

$M_r = 225.27$

Monoclinic,  $P2_1/n$

Hall symbol:  $-P\ 2_1/n$

$a = 6.6643\ (2)\ \text{\AA}$

$b = 9.6834\ (3)\ \text{\AA}$

$c = 15.5890\ (5)\ \text{\AA}$

$\beta = 97.699\ (1)^\circ$

$V = 996.94\ (5)\ \text{\AA}^3$

$Z = 4$

$F(000) = 472$

$D_x = 1.501\ \text{Mg m}^{-3}$

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

Cell parameters from 5698 reflections

$\theta = 3.7\text{--}28.3^\circ$

$\mu = 0.31\ \text{mm}^{-1}$

$T = 296$  K  $0.41 \times 0.22 \times 0.18$  mm  
 Needle, yellow

*Data collection*

Bruker Kappa APEXII CCD diffractometer Radiation source: fine-focus sealed tube Graphite monochromator $\varphi$ and $\omega$ scans Absorption correction: multi-scan (SADABS; Bruker, 2007) $T_{\min} = 0.884$ , $T_{\max} = 0.947$	8966 measured reflections 2426 independent reflections 2114 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.020$ $\theta_{\text{max}} = 28.3^\circ$ , $\theta_{\text{min}} = 3.7^\circ$ $h = -6 \rightarrow 8$ $k = -11 \rightarrow 12$ $l = -19 \rightarrow 20$
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*Refinement*

Refinement on $F^2$ Least-squares matrix: full $R[F^2 > 2\sigma(F^2)] = 0.036$ $wR(F^2) = 0.111$ $S = 0.93$ 2426 reflections 143 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 $w = 1/[\sigma^2(F_o^2) + (0.0763P)^2 + 0.3098P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} < 0.001$ $\Delta\rho_{\text{max}} = 0.30 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.29 \text{ e } \text{\AA}^{-3}$
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*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.8692 (2)	0.28978 (14)	0.04960 (9)	0.0354 (3)
C2	0.7617 (2)	0.38627 (17)	-0.00433 (10)	0.0460 (4)
H2	0.6510	0.4306	0.0138	0.055*
C3	0.8167 (3)	0.41727 (17)	-0.08437 (11)	0.0491 (4)
H3	0.7420	0.4811	-0.1200	0.059*
C4	0.9815 (3)	0.35393 (17)	-0.11144 (10)	0.0468 (4)
H4	1.0209	0.3765	-0.1647	0.056*
C5	1.0884 (2)	0.25656 (16)	-0.05909 (10)	0.0409 (3)
H5	1.1990	0.2134	-0.0781	0.049*
C6	1.0349 (2)	0.22102 (13)	0.02180 (9)	0.0328 (3)
C7	1.1508 (2)	0.11464 (13)	0.07523 (8)	0.0341 (3)
C8	1.0878 (3)	0.07413 (16)	0.16103 (10)	0.0454 (4)
H8A	1.2040	0.0386	0.1987	0.054*

H8B	0.9866	0.0017	0.1524	0.054*
C9	0.6206 (3)	0.3164 (2)	0.15568 (14)	0.0609 (5)
H9A	0.6343	0.4141	0.1652	0.091*
H9B	0.5906	0.2723	0.2076	0.091*
H9C	0.5128	0.2991	0.1096	0.091*
N1	0.80990 (19)	0.26108 (15)	0.13215 (9)	0.0446 (3)
N2	1.30403 (19)	0.06040 (13)	0.04671 (8)	0.0427 (3)
N3	1.4169 (2)	-0.03646 (17)	0.09606 (11)	0.0565 (4)
O1	1.14407 (18)	0.31926 (13)	0.22310 (7)	0.0515 (3)
O2	0.8941 (2)	0.17659 (15)	0.28274 (8)	0.0587 (3)
S1	0.98824 (5)	0.21730 (4)	0.20972 (2)	0.03865 (15)
H1N	1.357 (3)	-0.087 (2)	0.1305 (13)	0.046*
H2N	1.494 (3)	-0.070 (2)	0.0678 (12)	0.046*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0314 (6)	0.0370 (7)	0.0375 (7)	0.0038 (5)	0.0035 (5)	-0.0031 (5)
C2	0.0376 (7)	0.0488 (8)	0.0501 (8)	0.0144 (6)	0.0008 (6)	-0.0016 (7)
C3	0.0513 (8)	0.0484 (8)	0.0442 (8)	0.0120 (7)	-0.0065 (6)	0.0047 (6)
C4	0.0572 (9)	0.0476 (8)	0.0345 (7)	0.0076 (7)	0.0028 (6)	0.0034 (6)
C5	0.0457 (8)	0.0419 (7)	0.0356 (7)	0.0095 (6)	0.0075 (6)	-0.0007 (6)
C6	0.0338 (6)	0.0312 (6)	0.0334 (6)	0.0043 (5)	0.0040 (5)	-0.0026 (5)
C7	0.0363 (6)	0.0317 (6)	0.0350 (6)	0.0052 (5)	0.0076 (5)	-0.0005 (5)
C8	0.0563 (9)	0.0386 (7)	0.0445 (8)	0.0131 (6)	0.0188 (7)	0.0076 (6)
C9	0.0404 (8)	0.0763 (12)	0.0702 (12)	0.0155 (8)	0.0231 (8)	0.0002 (10)
N1	0.0331 (6)	0.0560 (7)	0.0470 (7)	0.0112 (5)	0.0137 (5)	0.0033 (6)
N2	0.0440 (6)	0.0422 (6)	0.0437 (6)	0.0151 (5)	0.0122 (5)	0.0063 (5)
N3	0.0554 (8)	0.0581 (9)	0.0595 (9)	0.0307 (7)	0.0210 (7)	0.0176 (7)
O1	0.0558 (7)	0.0577 (7)	0.0402 (6)	-0.0082 (5)	0.0041 (5)	-0.0058 (5)
O2	0.0627 (7)	0.0715 (8)	0.0479 (7)	0.0109 (6)	0.0288 (6)	0.0109 (6)
S1	0.0408 (2)	0.0428 (2)	0.0345 (2)	0.00504 (13)	0.01310 (14)	0.00140 (12)

*Geometric parameters (Å, °)*

C1—C2	1.390 (2)	C8—S1	1.7532 (15)
C1—C6	1.4068 (19)	C8—H8A	0.9700
C1—N1	1.4234 (19)	C8—H8B	0.9700
C2—C3	1.380 (2)	C9—N1	1.4616 (19)
C2—H2	0.9300	C9—H9A	0.9600
C3—C4	1.373 (2)	C9—H9B	0.9600
C3—H3	0.9300	C9—H9C	0.9600
C4—C5	1.381 (2)	N1—S1	1.6338 (14)
C4—H4	0.9300	N2—N3	1.3721 (18)
C5—C6	1.398 (2)	N3—H1N	0.86 (2)
C5—H5	0.9300	N3—H2N	0.790 (19)
C6—C7	1.4761 (18)	O1—S1	1.4278 (12)
C7—N2	1.2801 (17)	O2—S1	1.4270 (12)

C7—C8	1.5063 (19)		
C2—C1—C6	119.61 (14)	S1—C8—H8A	109.6
C2—C1—N1	119.68 (13)	C7—C8—H8B	109.6
C6—C1—N1	120.71 (13)	S1—C8—H8B	109.6
C3—C2—C1	121.03 (14)	H8A—C8—H8B	108.1
C3—C2—H2	119.5	N1—C9—H9A	109.5
C1—C2—H2	119.5	N1—C9—H9B	109.5
C4—C3—C2	120.07 (14)	H9A—C9—H9B	109.5
C4—C3—H3	120.0	N1—C9—H9C	109.5
C2—C3—H3	120.0	H9A—C9—H9C	109.5
C3—C4—C5	119.60 (15)	H9B—C9—H9C	109.5
C3—C4—H4	120.2	C1—N1—C9	120.59 (14)
C5—C4—H4	120.2	C1—N1—S1	117.21 (10)
C4—C5—C6	121.84 (14)	C9—N1—S1	118.42 (13)
C4—C5—H5	119.1	C7—N2—N3	119.27 (13)
C6—C5—H5	119.1	N2—N3—H1N	118.0 (13)
C5—C6—C1	117.81 (13)	N2—N3—H2N	108.4 (14)
C5—C6—C7	120.23 (12)	H1N—N3—H2N	121 (2)
C1—C6—C7	121.95 (13)	O2—S1—O1	117.61 (8)
N2—C7—C6	118.14 (12)	O2—S1—N1	107.94 (8)
N2—C7—C8	122.12 (12)	O1—S1—N1	111.81 (8)
C6—C7—C8	119.74 (11)	O2—S1—C8	111.06 (8)
C7—C8—S1	110.19 (10)	O1—S1—C8	107.46 (8)
C7—C8—H8A	109.6	N1—S1—C8	99.48 (8)
C6—C1—C2—C3	-0.9 (2)	C6—C7—C8—S1	-33.65 (17)
N1—C1—C2—C3	179.38 (15)	C2—C1—N1—C9	9.0 (2)
C1—C2—C3—C4	-0.9 (3)	C6—C1—N1—C9	-170.69 (15)
C2—C3—C4—C5	1.7 (3)	C2—C1—N1—S1	-148.76 (13)
C3—C4—C5—C6	-0.7 (3)	C6—C1—N1—S1	31.55 (18)
C4—C5—C6—C1	-1.1 (2)	C6—C7—N2—N3	178.54 (14)
C4—C5—C6—C7	178.92 (14)	C8—C7—N2—N3	-0.9 (2)
C2—C1—C6—C5	1.9 (2)	C1—N1—S1—O2	-172.78 (11)
N1—C1—C6—C5	-178.42 (13)	C9—N1—S1—O2	28.97 (17)
C2—C1—C6—C7	-178.15 (13)	C1—N1—S1—O1	56.36 (14)
N1—C1—C6—C7	1.5 (2)	C9—N1—S1—O1	-101.89 (15)
C5—C6—C7—N2	2.4 (2)	C1—N1—S1—C8	-56.87 (13)
C1—C6—C7—N2	-177.54 (13)	C9—N1—S1—C8	144.88 (15)
C5—C6—C7—C8	-178.13 (13)	C7—C8—S1—O2	169.33 (11)
C1—C6—C7—C8	1.9 (2)	C7—C8—S1—O1	-60.75 (13)
N2—C7—C8—S1	145.78 (13)	C7—C8—S1—N1	55.82 (12)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H1N $\cdots$ O1 <sup>i</sup>	0.86 (2)	2.46 (2)	3.221 (2)	147.7 (17)

N3—H2N $\cdots$ N2 <sup>ii</sup>	0.790 (19)	2.376 (19)	3.094 (2)	151.8 (19)
C8—H8A $\cdots$ O1 <sup>i</sup>	0.97	2.59	3.4178 (19)	144

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Symmetry codes: (i)  $-x+5/2, y-1/2, -z+1/2$ ; (ii)  $-x+3, -y, -z$ .