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(Z)-N-Methyl-2-(5-nitro-2-oxoindolin-3-ylidene)hydrazinecarbothioamide

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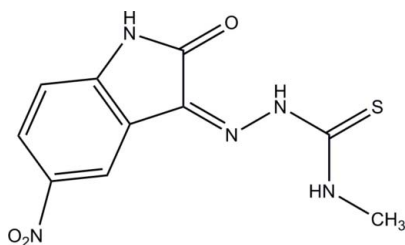
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 Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.048; wR factor = 0.102; data-to-parameter ratio = 14.6.

In the title compound, $\text{C}_{10}\text{H}_9\text{N}_5\text{O}_3\text{S}$, an intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond generates an $S(6)$ ring motif. In the crystal, molecules are linked *via* $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds into a zigzag chain along the b axis. $\text{C}-\text{H}\cdots\text{O}$ interactions are observed between the chains.

Related literature

For related structures, see: Qasem Ali *et al.* (2011a,b); Ferrari *et al.* (2002); Pervez *et al.* (2010); Ramzan *et al.* (2010). For various biological activities of Schiff bases, see: Bhandari *et al.* (2008); Bhardwaj *et al.* (2010); Pandeya *et al.* (1999); Sridhar *et al.* (2002); Suryavanshi & Pai (2006). For the cytotoxic and anticancer activity of isatin and its derivatives, see: Vine *et al.* (2009). For graph-set analysis, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$\text{C}_{10}\text{H}_9\text{N}_5\text{O}_3\text{S}$
 $M_r = 279.28$
 Monoclinic, $P2_1/c$
 $a = 4.6316$ (4) Å
 $b = 9.3157$ (8) Å

$c = 26.458$ (2) Å
 $\beta = 94.485$ (2)°
 $V = 1138.09$ (17) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

$\mu = 0.30$ mm⁻¹
 $T = 100$ K

$0.36 \times 0.12 \times 0.07$ mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2005)
 $T_{\min} = 0.900$, $T_{\max} = 0.979$

10734 measured reflections
 2710 independent reflections
 2177 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.102$
 $S = 1.10$
 2710 reflections
 185 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.40$ e Å⁻³
 $\Delta\rho_{\min} = -0.29$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N3}-\text{H1N3}\cdots\text{O1}$	0.84 (3)	2.02 (3)	2.697 (2)	137 (3)
$\text{N1}-\text{H1N1}\cdots\text{S1}^{\text{i}}$	0.81 (3)	2.52 (3)	3.320 (2)	171 (3)
$\text{C2}-\text{H2A}\cdots\text{O1}^{\text{ii}}$	0.95	2.39	3.317 (3)	165
$\text{C10}-\text{H10A}\cdots\text{O2}^{\text{iii}}$	0.98	2.56	3.079 (3)	113

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

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS5048).

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(Z)-N-Methyl-2-(5-nitro-2-oxindolin-3-ylidene)hydrazinecarbothioamide

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S1. Comment

Isatin (2,3-dioxindole) is an endogenous compound identified in humans, and its effect has been studied in a variety of systems. Biological properties of isatin and its derivatives include a range of actions in the brain, offer protection against bacterial (Suryavanshi & Pai, 2006) and antifungal infections and possess anticonvulsant, anti-HIV (Pandeya *et al.*, 1999), anti-depressant and anti-inflammatory activities (Bhandari *et al.*, 2008). Recently, we reported the crystal structure of (Z)-2-(5-chloro-2-oxindolin-3-ylidene)-N-phenylhydrazinecarbothioamide (Qasem Ali *et al.*, 2011a). In the present paper we describe the single-crystal X-ray diffraction study of title compound, Fig. 1.

In this compound (Fig. 1), the chain N2/N3//C9/S1/N4/C10 connected to the nine-membered 5-nitroindolin-2-one ring system in C7. In this chain, C7—N2—N3—C9 and C10—N4—C9—S1 have torsion angles 177.82 (19) and -0.9 (3)°, respectively. The essentially planar conformation of the molecule is maintained by an intramolecular N3—H1N3···O1 hydrogen bond (Table 1) with a graph-set *S*(6) (Bernstein *et al.*, 1995) In the crystal, molecules are linked *via* an intermolecular N1—H1N1···S1ⁱ hydrogen bond into an infinite one-dimensional chain along the *b* axis (Table 1 and Fig. 2). C2—H2A···O1ⁱⁱ and C10—H10A···O2ⁱⁱⁱ hydrogen bonds (Table 1) are also observed between the chains.

S2. Experimental

The Schiff base have been synthesized by refluxing the reaction mixture of hot ethanolic solution (30 ml) of 5-methyl-3-thiosemicarbazide (0.01 mol) and hot ethanolic solution (30 ml) of 5-nitroisatin (0.01 mol) for 2 hrs. The precipitate formed during reflux was filtered, washed with cold EtOH and recrystallized from hot EtOH (yield 80%, m.p. 579.8–580.3 K). The orange crystals were grown in an acetone-DMF (3:1) solution by slow evaporation at room temperature.

S3. Refinement

N-bound H atoms were located in a difference Fourier map and were refined freely. The remaining H atoms were positioned geometrically and refined using a riding model, with C—H = 0.95 Å for aromatic ring and C—H = 0.98 Å for methyl group, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for aromatic ring and methyl group, respectively. The highest residual electron density peak is located at 0.81 Å from C6 and the deepest hole is located at 0.36 Å from S1.

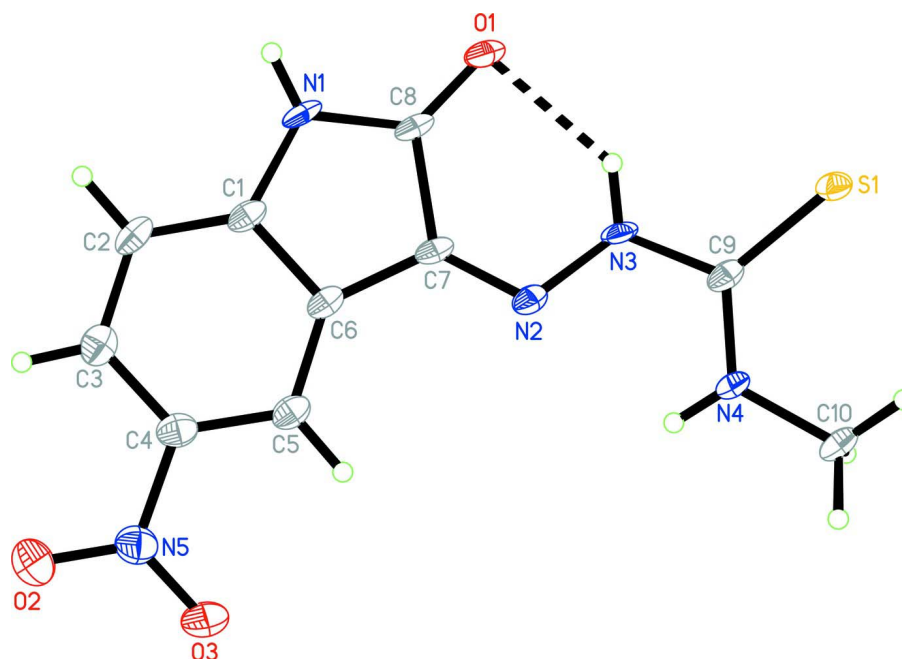


Figure 1

The molecular structure of the title compound, with 50% probability displacement ellipsoids and the atom-numbering scheme.

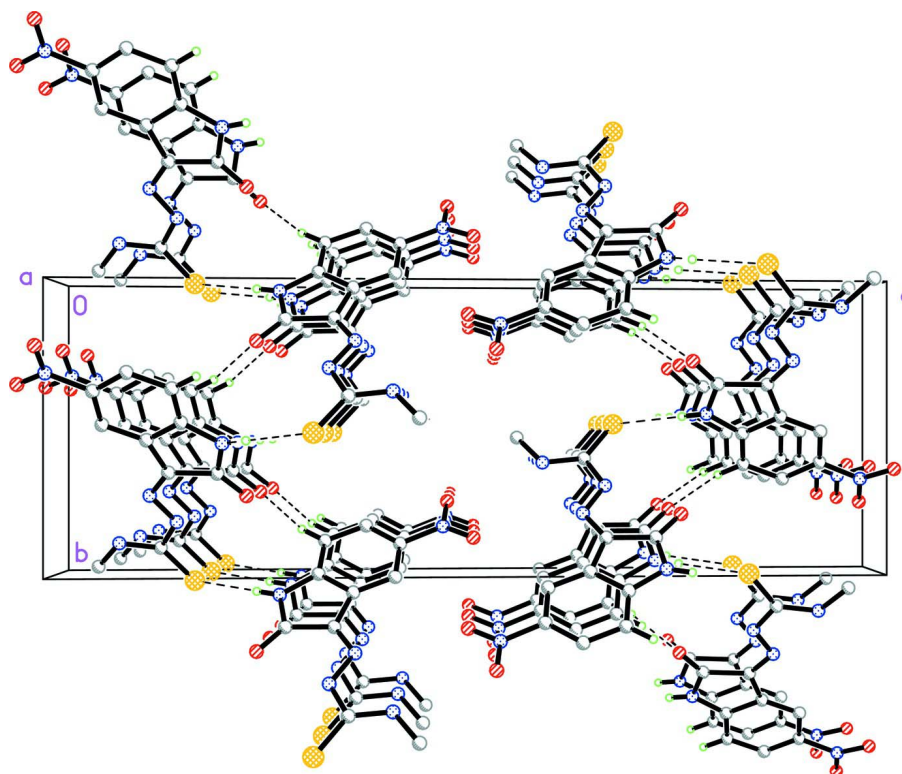


Figure 2

The crystal packing of the title compound viewed down the *a* axis. Hydrogen bonds are shown as dashed lines.

(Z)-N-Methyl-2-(5-nitro-2-oxindolin-3-ylidene)hydrazinecarbothioamide*Crystal data*C₁₀H₉N₅O₃S $M_r = 279.28$ Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

 $a = 4.6316$ (4) Å $b = 9.3157$ (8) Å $c = 26.458$ (2) Å $\beta = 94.485$ (2)° $V = 1138.09$ (17) Å³ $Z = 4$ $F(000) = 576$ $D_x = 1.630$ Mg m⁻³

Melting point = 579.8–580.3 K

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

Cell parameters from 3870 reflections

 $\theta = 2.7$ – 30.1 ° $\mu = 0.30$ mm⁻¹ $T = 100$ K

Needle, orange

 $0.36 \times 0.12 \times 0.07$ mm*Data collection*Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 φ and ω scansAbsorption correction: multi-scan
(*SADABS*; Bruker, 2005) $T_{\min} = 0.900$, $T_{\max} = 0.979$

10734 measured reflections

2710 independent reflections

2177 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.045$ $\theta_{\max} = 28.0$ °, $\theta_{\min} = 2.3$ ° $h = -6 \rightarrow 6$ $k = -11 \rightarrow 12$ $l = -34 \rightarrow 34$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.048$ $wR(F^2) = 0.102$ $S = 1.10$

2710 reflections

185 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sitesH atoms treated by a mixture of independent
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0189P)^2 + 1.8143P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.40$ e Å⁻³ $\Delta\rho_{\min} = -0.29$ e Å⁻³*Special details*

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 $F^2 > \sigma(F^2)$ 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 (Å²)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	1.21633 (12)	0.51362 (6)	0.32848 (2)	0.01849 (15)
O1	0.5410 (3)	0.21885 (18)	0.25632 (6)	0.0199 (4)
O2	-0.1914 (4)	-0.2525 (2)	0.47157 (8)	0.0409 (5)

O3	0.1838 (4)	-0.1372 (2)	0.50290 (7)	0.0304 (4)
N1	0.2084 (4)	0.0484 (2)	0.27784 (8)	0.0187 (4)
N2	0.6885 (4)	0.2193 (2)	0.36918 (7)	0.0159 (4)
N3	0.8430 (4)	0.3086 (2)	0.34179 (7)	0.0166 (4)
N4	1.0960 (4)	0.3840 (2)	0.41442 (7)	0.0189 (4)
N5	0.0142 (5)	-0.1717 (2)	0.46698 (8)	0.0242 (5)
C1	0.1322 (5)	-0.0181 (2)	0.32196 (8)	0.0167 (5)
C2	-0.0740 (5)	-0.1225 (3)	0.32723 (9)	0.0198 (5)
H2A	-0.1871	-0.1592	0.2986	0.024*
C3	-0.1108 (5)	-0.1721 (3)	0.37559 (9)	0.0212 (5)
H3A	-0.2502	-0.2444	0.3807	0.025*
C4	0.0580 (5)	-0.1154 (3)	0.41667 (9)	0.0198 (5)
C5	0.2677 (5)	-0.0110 (3)	0.41212 (9)	0.0185 (5)
H5A	0.3813	0.0249	0.4408	0.022*
C6	0.3033 (5)	0.0383 (2)	0.36375 (8)	0.0166 (5)
C7	0.4952 (5)	0.1430 (2)	0.34383 (8)	0.0155 (4)
C8	0.4257 (5)	0.1451 (2)	0.28722 (8)	0.0166 (5)
C9	1.0477 (5)	0.3984 (2)	0.36484 (8)	0.0164 (5)
C10	1.3117 (5)	0.4679 (3)	0.44437 (9)	0.0257 (6)
H10A	1.2463	0.4842	0.4782	0.039*
H10B	1.3383	0.5604	0.4277	0.039*
H10C	1.4959	0.4157	0.4473	0.039*
H1N3	0.803 (6)	0.317 (3)	0.3104 (11)	0.020 (7)*
H1N4	1.013 (6)	0.318 (3)	0.4291 (10)	0.021 (7)*
H1N1	0.123 (6)	0.039 (3)	0.2501 (11)	0.024 (7)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0212 (3)	0.0194 (3)	0.0137 (3)	0.0002 (2)	-0.0055 (2)	0.0021 (2)
O1	0.0248 (8)	0.0222 (9)	0.0117 (8)	0.0021 (7)	-0.0052 (7)	-0.0004 (7)
O2	0.0460 (12)	0.0433 (12)	0.0332 (11)	-0.0198 (10)	0.0027 (9)	0.0087 (10)
O3	0.0335 (10)	0.0384 (11)	0.0183 (9)	-0.0006 (8)	-0.0046 (8)	0.0046 (8)
N1	0.0225 (10)	0.0215 (10)	0.0107 (10)	0.0014 (8)	-0.0081 (8)	-0.0037 (8)
N2	0.0173 (9)	0.0160 (9)	0.0135 (9)	0.0022 (7)	-0.0039 (7)	-0.0008 (8)
N3	0.0211 (10)	0.0193 (10)	0.0082 (9)	0.0007 (8)	-0.0062 (7)	0.0012 (8)
N4	0.0221 (10)	0.0222 (11)	0.0111 (10)	-0.0047 (8)	-0.0055 (8)	-0.0006 (8)
N5	0.0274 (11)	0.0227 (11)	0.0224 (11)	0.0017 (9)	0.0013 (9)	0.0036 (9)
C1	0.0173 (10)	0.0165 (11)	0.0153 (11)	0.0060 (9)	-0.0047 (8)	-0.0041 (9)
C2	0.0190 (11)	0.0189 (12)	0.0203 (12)	0.0019 (9)	-0.0066 (9)	-0.0068 (10)
C3	0.0216 (11)	0.0155 (11)	0.0258 (13)	0.0013 (9)	-0.0015 (10)	-0.0016 (10)
C4	0.0226 (11)	0.0186 (12)	0.0177 (12)	0.0045 (9)	-0.0012 (9)	0.0010 (9)
C5	0.0183 (10)	0.0188 (12)	0.0176 (11)	0.0039 (9)	-0.0037 (9)	-0.0020 (9)
C6	0.0165 (10)	0.0170 (11)	0.0155 (11)	0.0037 (8)	-0.0041 (9)	-0.0034 (9)
C7	0.0175 (10)	0.0170 (11)	0.0111 (11)	0.0053 (8)	-0.0043 (8)	-0.0016 (9)
C8	0.0190 (11)	0.0182 (11)	0.0113 (11)	0.0049 (9)	-0.0063 (8)	-0.0032 (9)
C9	0.0174 (10)	0.0156 (11)	0.0152 (11)	0.0047 (9)	-0.0048 (9)	-0.0036 (9)
C10	0.0283 (13)	0.0315 (14)	0.0157 (12)	-0.0081 (11)	-0.0086 (10)	-0.0036 (11)

Geometric parameters (Å, °)

S1—C9	1.675 (2)	C1—C2	1.378 (3)
O1—C8	1.222 (3)	C1—C6	1.410 (3)
O2—N5	1.227 (3)	C2—C3	1.383 (3)
O3—N5	1.227 (3)	C2—H2A	0.9500
N1—C8	1.359 (3)	C3—C4	1.392 (3)
N1—C1	1.391 (3)	C3—H3A	0.9500
N1—H1N1	0.81 (3)	C4—C5	1.387 (3)
N2—C7	1.289 (3)	C5—C6	1.382 (3)
N2—N3	1.346 (3)	C5—H5A	0.9500
N3—C9	1.371 (3)	C6—C7	1.446 (3)
N3—H1N3	0.84 (3)	C7—C8	1.507 (3)
N4—C9	1.320 (3)	C10—H10A	0.9800
N4—C10	1.454 (3)	C10—H10B	0.9800
N4—H1N4	0.84 (3)	C10—H10C	0.9800
N5—C4	1.460 (3)		
C8—N1—C1	112.00 (19)	C5—C4—N5	118.6 (2)
C8—N1—H1N1	123 (2)	C3—C4—N5	117.8 (2)
C1—N1—H1N1	125 (2)	C6—C5—C4	116.7 (2)
C7—N2—N3	115.95 (19)	C6—C5—H5A	121.7
N2—N3—C9	121.06 (19)	C4—C5—H5A	121.7
N2—N3—H1N3	120.3 (18)	C5—C6—C1	120.1 (2)
C9—N3—H1N3	118.3 (18)	C5—C6—C7	133.1 (2)
C9—N4—C10	122.9 (2)	C1—C6—C7	106.81 (19)
C9—N4—H1N4	119.1 (19)	N2—C7—C6	127.1 (2)
C10—N4—H1N4	117.7 (19)	N2—C7—C8	126.5 (2)
O2—N5—O3	122.6 (2)	C6—C7—C8	106.34 (19)
O2—N5—C4	118.3 (2)	O1—C8—N1	127.4 (2)
O3—N5—C4	119.1 (2)	O1—C8—C7	127.0 (2)
C2—C1—N1	128.5 (2)	N1—C8—C7	105.67 (19)
C2—C1—C6	122.4 (2)	N4—C9—N3	116.0 (2)
N1—C1—C6	109.2 (2)	N4—C9—S1	125.82 (18)
C1—C2—C3	117.8 (2)	N3—C9—S1	118.22 (17)
C1—C2—H2A	121.1	N4—C10—H10A	109.5
C3—C2—H2A	121.1	N4—C10—H10B	109.5
C2—C3—C4	119.5 (2)	H10A—C10—H10B	109.5
C2—C3—H3A	120.2	N4—C10—H10C	109.5
C4—C3—H3A	120.2	H10A—C10—H10C	109.5
C5—C4—C3	123.6 (2)	H10B—C10—H10C	109.5
C7—N2—N3—C9	177.82 (19)	C2—C1—C6—C7	179.3 (2)
C8—N1—C1—C2	-178.9 (2)	N1—C1—C6—C7	-0.7 (2)
C8—N1—C1—C6	1.1 (3)	N3—N2—C7—C6	179.3 (2)
N1—C1—C2—C3	-179.9 (2)	N3—N2—C7—C8	-0.4 (3)
C6—C1—C2—C3	0.0 (3)	C5—C6—C7—N2	-0.5 (4)
C1—C2—C3—C4	0.3 (3)	C1—C6—C7—N2	-179.7 (2)

C2—C3—C4—C5	-0.7 (4)	C5—C6—C7—C8	179.3 (2)
C2—C3—C4—N5	-179.4 (2)	C1—C6—C7—C8	0.1 (2)
O2—N5—C4—C5	172.4 (2)	C1—N1—C8—O1	179.1 (2)
O3—N5—C4—C5	-7.9 (3)	C1—N1—C8—C7	-1.0 (2)
O2—N5—C4—C3	-8.9 (3)	N2—C7—C8—O1	0.2 (4)
O3—N5—C4—C3	170.8 (2)	C6—C7—C8—O1	-179.6 (2)
C3—C4—C5—C6	0.8 (3)	N2—C7—C8—N1	-179.7 (2)
N5—C4—C5—C6	179.5 (2)	C6—C7—C8—N1	0.5 (2)
C4—C5—C6—C1	-0.5 (3)	C10—N4—C9—N3	178.2 (2)
C4—C5—C6—C7	-179.5 (2)	C10—N4—C9—S1	-0.9 (3)
C2—C1—C6—C5	0.1 (3)	N2—N3—C9—N4	4.5 (3)
N1—C1—C6—C5	180.0 (2)	N2—N3—C9—S1	-176.25 (16)

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>
N3—H1N3...O1	0.84 (3)	2.02 (3)	2.697 (2)	137 (3)
N1—H1N1...S1 ⁱ	0.81 (3)	2.52 (3)	3.320 (2)	171 (3)
C2—H2A...O1 ⁱⁱ	0.95	2.39	3.317 (3)	165
C10—H10A...O2 ⁱⁱⁱ	0.98	2.56	3.079 (3)	113

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