

Indole-3-thiuronium iodide

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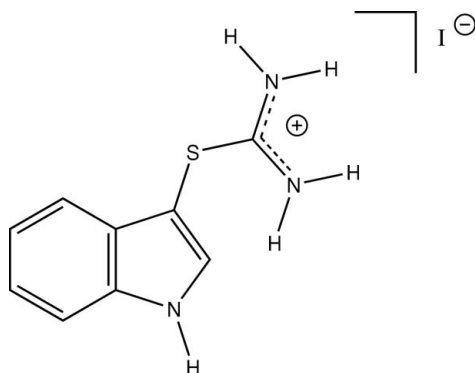
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Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.018; wR factor = 0.045; data-to-parameter ratio = 16.0.

In the title compound, $\text{C}_9\text{H}_{10}\text{N}_3\text{S}^+\text{I}^-$, the indole ring system and the thiuronium group are essentially perpendicular, with a dihedral angle of 89.87 (8)°. By intermolecular hydrogen bonding, a three-dimensional network is formed, which is additionally supported by intermolecular $\text{C}-\text{H}\cdots\pi$ interactions.

Related literature

For the synthesis of the title compound, see: Harris (1969); van der Geer *et al.* (2007). For the crystal structures of similar compounds, see: Lutz *et al.* (2008); Ng (1995). For the characterization of $\text{C}-\text{H}\cdots\pi$ interactions, see: Malone *et al.* (1997). For thermal-motion analysis, see: Schomaker & Trueblood (1998). For the Cambridge Structural Database (update of August 2007), see: Allen (2002).



Experimental

Crystal data

$\text{C}_9\text{H}_{10}\text{N}_3\text{S}^+\text{I}^-$
 $M_r = 319.16$

Monoclinic, $P2_1/c$
 $a = 10.5098$ (2) Å

$b = 10.6264$ (3) Å
 $c = 10.6951$ (4) Å
 $\beta = 102.648$ (2)°
 $V = 1165.46$ (6) Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 2.89$ mm⁻¹
 $T = 150$ (2) K
 $0.30 \times 0.30 \times 0.30$ mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan
(*SADABS*; Sheldrick, 2002)
 $T_{\min} = 0.24$, $T_{\max} = 0.42$

15531 measured reflections
2668 independent reflections
2470 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.018$
 $wR(F^2) = 0.045$
 $S = 1.09$
2668 reflections

167 parameters
All H-atom parameters refined
 $\Delta\rho_{\text{max}} = 0.50$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.53$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1N}\cdots\text{I1}^i$	0.76 (2)	2.91 (2)	3.6295 (17)	158 (2)
$\text{N2}-\text{H2N}\cdots\text{I1}$	0.86 (3)	2.76 (3)	3.5736 (18)	158 (2)
$\text{N2}-\text{H3N}\cdots\text{I1}^{ii}$	0.80 (2)	2.97 (2)	3.6269 (17)	141 (2)
$\text{N3}-\text{H4N}\cdots\text{I1}^{iii}$	0.75 (3)	2.86 (3)	3.5990 (19)	165 (2)
$\text{N3}-\text{H5N}\cdots\text{I1}$	0.88 (3)	2.95 (3)	3.7258 (19)	149 (2)
$\text{C1}-\text{H1}\cdots\text{Cg1}^{iv}$	0.91 (2)	2.91 (2)	3.794 (2)	162.8 (18)

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, -y+1, -z$; (iii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (iv) $x, -y+\frac{1}{2}, z-\frac{1}{2}$. Cg1 is the centroid of the six-membered ring.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *PEAKREF* (Schreurs, 2005); data reduction: *EVALI4* (Duisenberg *et al.*, 2003) and *SADABS* (Sheldrick, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2659).

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.
Geer, E. P. L. van der, Li, Q., van Koten, G., Klein Gebbink, R. J. M. & Hessen, B. (2007). *Inorg. Chim. Acta*, doi:10.1016/j.ica.2007.09.021.
Harris, R. L. N. (1969). *Tetrahedron Lett.* 4465–4466.
Lutz, M., Spek, A. L., van der Geer, E. P. L., van Koten, G. & Klein Gebbink, R. J. M. (2008). *Acta Cryst.* **E64**, o194.
Malone, J. F., Murray, C. M., Charlton, M. H., Docherty, R. & Lavery, A. J. (1997). *J. Chem. Soc. Faraday Trans.* **93**, 3429–3436.
Ng, S. W. (1995). *Acta Cryst.* **C51**, 1143–1144.
Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
Schomaker, V. & Trueblood, K. N. (1998). *Acta Cryst.* **B54**, 507–514.
Schreurs, A. M. M. (2005). *PEAKREF*. Utrecht University, The Netherlands.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2002). *SADABS*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supporting information

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S1. Comment

Uronium and thiuronium ions are positively charged with the charge delocalized over the N—C—N group. In crystal engineering this group is therefore complementary to the negatively charged carboxylate group, not only in charge distribution but also in hydrogen-bonding ability.

The molecular geometry of the cation of title compound indole-3-thiuronium iodide (I) (Fig. 1) is very similar to the corresponding nitrate salt (Lutz *et al.*, 2007). The C—N bond lengths of 1.306 (2) and 1.317 (2) Å show significant double bond character while the C—S bond of 1.7533 (19) Å is in the expected range for a single bond. Similar distances and angles have also been found in the benzylthiuronium cation (Ng, 1995).

As in the nitrate salt, the cation consists of two planar subunits, *i.e.* the indole and the thiuronium moieties, which are perpendicular to each other with an angle of 89.87 (8)° between the corresponding least squares planes. The weighted *R* value of a thermal motion analysis using the program THMA11 (Schomaker & Trueblood, 1998) results in a low weighted *R* value of 0.106, which is slightly higher than in the nitrate salt (0.084).

The iodide anion is surrounded by five N—H groups which act as hydrogen bond donors (Fig. 2). This results in a three dimensional hydrogen bonded network. The H···I distances of 2.76 (3) to 2.97 (2) Å are in the same range as found for other N—H···I hydrogen bonds in the Cambridge Structural Database (update August 2007; Allen, 2002), where we calculate an average H···I distance of 2.80 Å. In general, N—H···I hydrogen bonds are relatively weak; the average hydrogen bonded intermolecular N···I distance is 3.65 Å in the Cambridge Structural Database, which is not shorter than the sum of van der Waals radii of 1.55 (nitrogen) plus 1.98 Å (iodine).

In addition to the N—H···I hydrogen bonds there are weak intermolecular C—H··· π interactions between H1 and the six-membered ring of the indole moiety (Fig. 3). The distance of H1 to the least squares plane of the six-membered ring is 2.83 (2) Å and the distance to the center of gravity of this ring is 2.91 (2) Å (Table 2). According to the classification of Malone *et al.* (1997) this is a "Type I" C—H··· π interaction.

S2. Experimental

Indole-3-thiuronium iodide was prepared as described in literature (Harris, 1969; van der Geer *et al.*, 2007) and crystallized by diethyl ether vapor diffusion into an acetone solution.

S3. Refinement

All H atoms were freely refined.

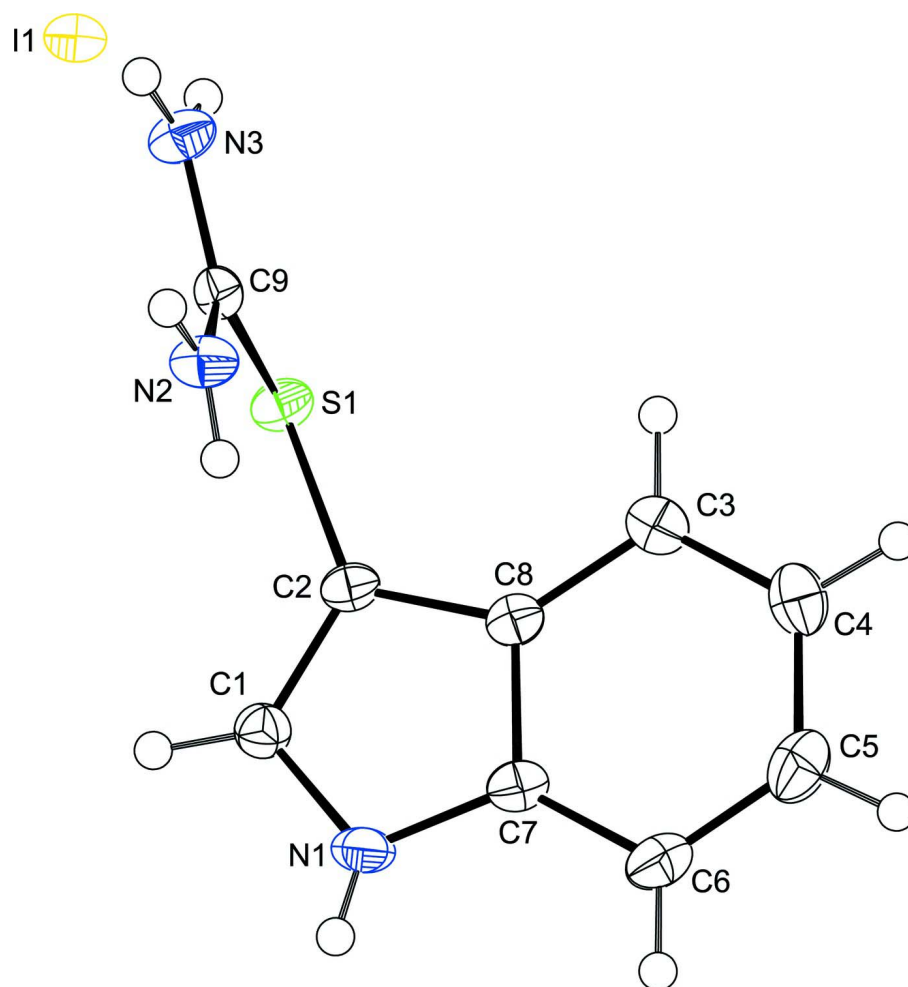


Figure 1

The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

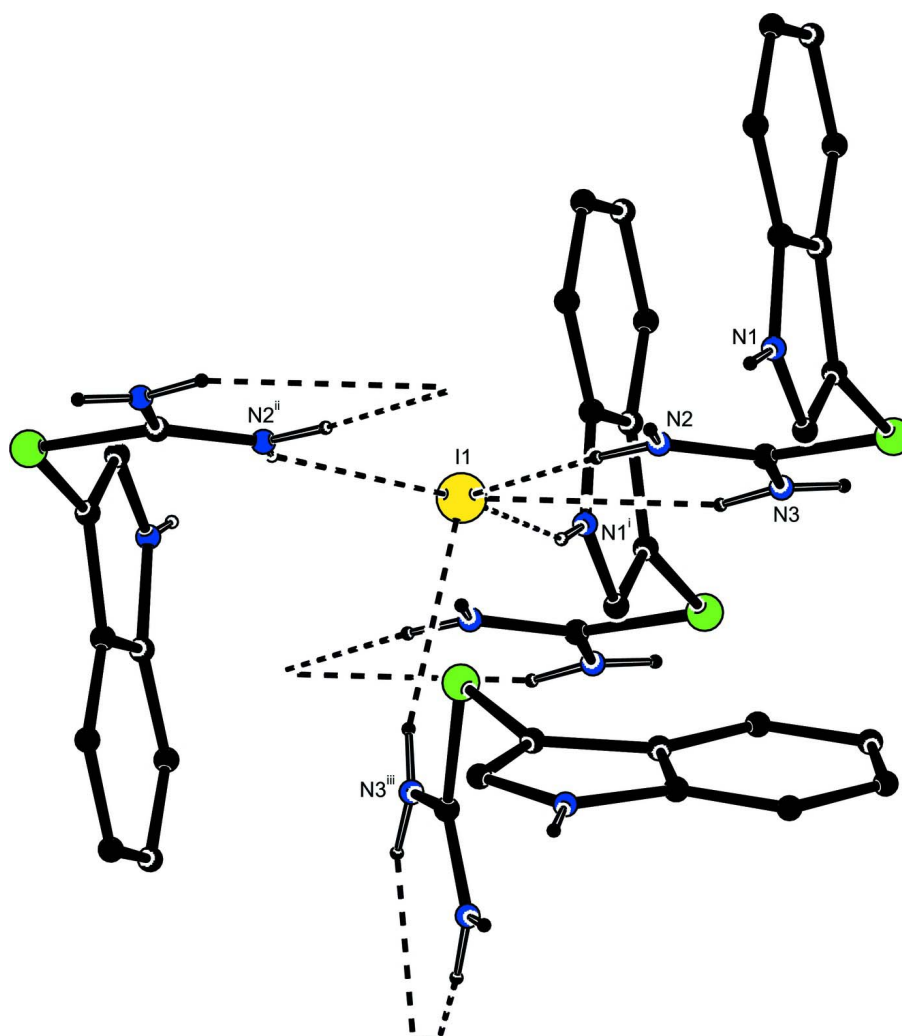


Figure 2

Hydrogen bonded environment of the iodide in (I). C—H hydrogen atoms are omitted for clarity. Symmetry operations i: $1 + x, y, z$; ii: $1 - x, 1 - y, -z$; iii: $x, 0.5 - y, z - 1/2$.

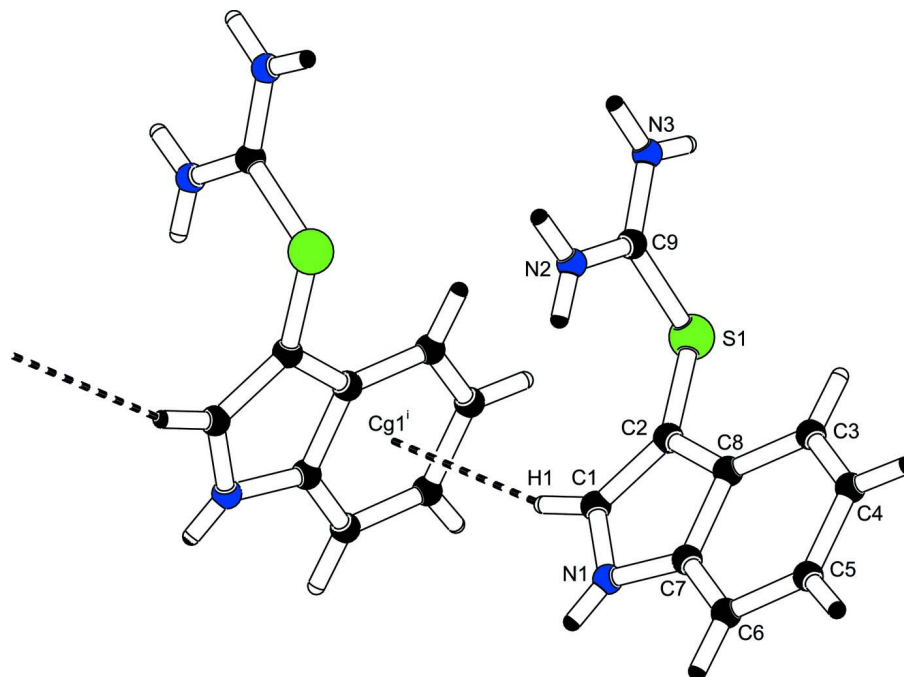


Figure 3

C—H... π interaction in (I). View along the crystallographic b axis. Symmetry operation i : $x, 0.5 - y, z - 1/2$.

Indole-3-thiuronium iodide

Crystal data

$C_9H_{10}N_3S^+I^-$

$M_r = 319.16$

Monoclinic, $P2_1/c$

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

$a = 10.5098\ (2)\ \text{\AA}$

$b = 10.6264\ (3)\ \text{\AA}$

$c = 10.6951\ (4)\ \text{\AA}$

$\beta = 102.648\ (2)^\circ$

$V = 1165.46\ (6)\ \text{\AA}^3$

$Z = 4$

$F(000) = 616$

$D_x = 1.819\ \text{Mg m}^{-3}$

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

Cell parameters from 11915 reflections

$\theta = 2.0\text{--}27.5^\circ$

$\mu = 2.89\ \text{mm}^{-1}$

$T = 150\ \text{K}$

Block, colourless

$0.30 \times 0.30 \times 0.30\ \text{mm}$

Data collection

Nonius KappaCCD

diffractometer

Radiation source: rotating anode

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 2002)

$T_{\min} = 0.24, T_{\max} = 0.42$

15531 measured reflections

2668 independent reflections

2470 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\max} = 27.5^\circ, \theta_{\min} = 2.0^\circ$

$h = -13 \rightarrow 13$

$k = -13 \rightarrow 13$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.018$
 $wR(F^2) = 0.045$
 $S = 1.09$
 2668 reflections
 167 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: difference Fourier map
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0216P)^2 + 0.5241P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.003$
 $\Delta\rho_{\max} = 0.50 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.53 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.43028 (5)	0.17217 (4)	0.29661 (4)	0.02089 (10)
N1	0.08974 (16)	0.33441 (15)	0.18625 (17)	0.0243 (3)
H1N	0.024 (2)	0.343 (2)	0.140 (2)	0.017 (5)*
N2	0.49115 (18)	0.34694 (16)	0.13906 (16)	0.0237 (3)
H2N	0.541 (3)	0.384 (3)	0.097 (2)	0.039 (7)*
H3N	0.415 (2)	0.365 (2)	0.123 (2)	0.025 (6)*
N3	0.65635 (17)	0.21727 (17)	0.23827 (18)	0.0247 (3)
H4N	0.680 (2)	0.170 (2)	0.291 (2)	0.025 (6)*
H5N	0.711 (2)	0.251 (2)	0.196 (3)	0.040 (7)*
C1	0.18173 (18)	0.24948 (18)	0.17078 (18)	0.0220 (4)
H1	0.168 (2)	0.198 (2)	0.101 (2)	0.032 (6)*
C2	0.29152 (17)	0.26651 (17)	0.26602 (17)	0.0193 (3)
C3	0.3378 (2)	0.42952 (18)	0.45307 (19)	0.0238 (4)
H3	0.422 (2)	0.402 (2)	0.491 (2)	0.022 (5)*
C4	0.2801 (2)	0.52789 (19)	0.5048 (2)	0.0287 (4)
H4	0.325 (3)	0.574 (3)	0.577 (3)	0.047 (8)*
C5	0.1524 (2)	0.5675 (2)	0.4494 (2)	0.0312 (5)
H5	0.117 (2)	0.635 (2)	0.487 (2)	0.027 (6)*
C6	0.0801 (2)	0.5097 (2)	0.3418 (2)	0.0277 (4)
H6	-0.004 (3)	0.536 (2)	0.304 (3)	0.034 (7)*
C7	0.13841 (18)	0.40987 (18)	0.29061 (18)	0.0218 (4)
C8	0.26581 (17)	0.36941 (16)	0.34426 (17)	0.0189 (3)
C9	0.53403 (17)	0.25457 (16)	0.21755 (16)	0.0183 (3)
I1	0.770943 (11)	0.454617 (11)	0.031246 (11)	0.02163 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0194 (2)	0.0196 (2)	0.0242 (2)	0.00360 (16)	0.00591 (17)	0.00584 (17)
N1	0.0146 (8)	0.0273 (8)	0.0288 (9)	0.0010 (6)	-0.0001 (7)	-0.0015 (7)
N2	0.0188 (8)	0.0262 (8)	0.0259 (8)	0.0001 (7)	0.0045 (7)	0.0077 (6)
N3	0.0202 (8)	0.0272 (9)	0.0278 (9)	0.0059 (7)	0.0076 (7)	0.0069 (7)
C1	0.0210 (9)	0.0227 (9)	0.0222 (9)	-0.0008 (7)	0.0047 (7)	-0.0001 (7)
C2	0.0160 (8)	0.0200 (8)	0.0227 (9)	0.0001 (7)	0.0058 (7)	0.0032 (7)
C3	0.0238 (10)	0.0234 (9)	0.0232 (9)	-0.0020 (7)	0.0032 (8)	0.0034 (7)
C4	0.0367 (13)	0.0238 (10)	0.0251 (10)	-0.0043 (8)	0.0059 (9)	-0.0023 (8)
C5	0.0365 (13)	0.0231 (10)	0.0378 (12)	0.0020 (8)	0.0165 (10)	-0.0032 (8)
C6	0.0219 (10)	0.0273 (10)	0.0354 (11)	0.0049 (8)	0.0094 (9)	0.0003 (8)
C7	0.0180 (9)	0.0211 (8)	0.0266 (9)	0.0004 (7)	0.0058 (7)	0.0023 (7)
C8	0.0185 (9)	0.0184 (8)	0.0210 (8)	-0.0006 (7)	0.0067 (7)	0.0042 (7)
C9	0.0198 (9)	0.0175 (8)	0.0173 (8)	-0.0007 (7)	0.0031 (6)	-0.0014 (6)
H1	0.01614 (8)	0.02314 (8)	0.02444 (8)	0.00029 (4)	0.00192 (5)	0.00236 (4)

Geometric parameters (\AA , $^\circ$)

S1—C2	1.7406 (18)	C1—H1	0.91 (2)
S1—C9	1.7533 (19)	C2—C8	1.438 (2)
N1—C1	1.359 (2)	C3—C4	1.383 (3)
N1—C7	1.379 (3)	C3—C8	1.396 (3)
N1—H1N	0.76 (2)	C3—H3	0.94 (2)
N2—C9	1.306 (2)	C4—C5	1.407 (4)
N2—H2N	0.86 (3)	C4—H4	0.95 (3)
N2—H3N	0.80 (2)	C5—C6	1.377 (3)
N3—C9	1.317 (2)	C5—H5	0.94 (2)
N3—H4N	0.75 (3)	C6—C7	1.396 (3)
N3—H5N	0.88 (3)	C6—H6	0.93 (3)
C1—C2	1.374 (3)	C7—C8	1.404 (3)
C2—S1—C9	101.87 (9)	C3—C4—C5	121.3 (2)
C1—N1—C7	109.70 (16)	C3—C4—H4	122.2 (18)
C1—N1—H1N	124.2 (16)	C5—C4—H4	116.5 (18)
C7—N1—H1N	125.7 (16)	C6—C5—C4	121.3 (2)
C9—N2—H2N	121.1 (18)	C6—C5—H5	119.9 (14)
C9—N2—H3N	120.1 (17)	C4—C5—H5	118.8 (14)
H2N—N2—H3N	118 (2)	C5—C6—C7	117.18 (19)
C9—N3—H4N	118.3 (18)	C5—C6—H6	121.6 (15)
C9—N3—H5N	120.9 (17)	C7—C6—H6	121.2 (15)
H4N—N3—H5N	121 (2)	N1—C7—C6	129.98 (18)
N1—C1—C2	109.07 (17)	N1—C7—C8	107.73 (16)
N1—C1—H1	120.7 (15)	C6—C7—C8	122.29 (18)
C2—C1—H1	130.0 (15)	C3—C8—C7	119.67 (17)
C1—C2—C8	107.29 (17)	C3—C8—C2	134.13 (18)
C1—C2—S1	126.63 (15)	C7—C8—C2	106.20 (16)

C8—C2—S1	125.81 (14)	N2—C9—N3	121.41 (18)
C4—C3—C8	118.29 (19)	N2—C9—S1	121.45 (15)
C4—C3—H3	121.6 (14)	N3—C9—S1	117.12 (14)
C8—C3—H3	120.1 (14)		
C7—N1—C1—C2	1.0 (2)	C4—C3—C8—C7	0.1 (3)
N1—C1—C2—C8	-0.6 (2)	C4—C3—C8—C2	-179.7 (2)
N1—C1—C2—S1	173.64 (14)	N1—C7—C8—C3	-179.32 (17)
C9—S1—C2—C1	96.99 (19)	C6—C7—C8—C3	0.4 (3)
C9—S1—C2—C8	-89.75 (17)	N1—C7—C8—C2	0.5 (2)
C8—C3—C4—C5	-0.3 (3)	C6—C7—C8—C2	-179.74 (18)
C3—C4—C5—C6	0.1 (3)	C1—C2—C8—C3	179.9 (2)
C4—C5—C6—C7	0.4 (3)	S1—C2—C8—C3	5.5 (3)
C1—N1—C7—C6	179.4 (2)	C1—C2—C8—C7	0.1 (2)
C1—N1—C7—C8	-0.9 (2)	S1—C2—C8—C7	-174.27 (14)
C5—C6—C7—N1	179.0 (2)	C2—S1—C9—N2	-11.53 (17)
C5—C6—C7—C8	-0.7 (3)	C2—S1—C9—N3	170.10 (14)

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 <i>N</i> ...I1 ⁱ	0.76 (2)	2.91 (2)	3.6295 (17)	158 (2)
N2—H2 <i>N</i> ...I1	0.86 (3)	2.76 (3)	3.5736 (18)	158 (2)
N2—H3 <i>N</i> ...I1 ⁱⁱ	0.80 (2)	2.97 (2)	3.6269 (17)	141 (2)
N3—H4 <i>N</i> ...I1 ⁱⁱⁱ	0.75 (3)	2.86 (3)	3.5990 (19)	165 (2)
N3—H5 <i>N</i> ...I1	0.88 (3)	2.95 (3)	3.7258 (19)	149 (2)
C1—H1...C <i>g</i> 1 ^{iv}	0.91 (2)	2.91 (2)	3.794 (2)	162.8 (18)

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