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N'-[(3-Methyl-2-thienyl)carbonyl]-isonicotinohydrazide

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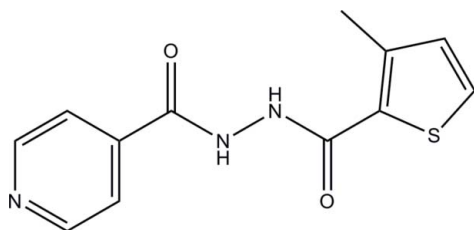
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 Key indicators: single-crystal X-ray study; *T* = 100 K; mean $\sigma(\text{C}-\text{C})$ = 0.002 Å; *R* factor = 0.036; *wR* factor = 0.097; data-to-parameter ratio = 26.4.

In the title compound, C₁₂H₁₁N₃O₂S, the pyridine ring is inclined to the thiophene ring, forming a dihedral angle of 34.96 (7)°. The mean plane through the hydrazide unit forms dihedral angles of 21.57 (8) and 53.08 (8)°, respectively, with the pyridine and thiophene rings. The two O atoms are twisted away from each other, as indicated by the C–N–N–C torsion angle of –81.27 (15)°. In the crystal structure, molecules are linked into an extended three-dimensional network by intermolecular N–H···N, N–H···O and C–H···O hydrogen bonds. The crystal structure also features a short S···O [3.2686 (10) Å] interaction and a weak intermolecular C–H··· π interaction.

Related literature

For general background to and application of isoniazid derivatives, see: Janin (2007); Maccari *et al.* (2005); Slayden *et al.* (2000). For the preparation of the title compound, see: Besra *et al.* (1993). For bond-length data, see: Allen *et al.* (1987). For a closely related structure, see: Naveenkumar *et al.* (2009). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).


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Experimental

Crystal data

C₁₂H₁₁N₃O₂S
M_r = 261.30
 Orthorhombic, *P*2₁2₁2₁
a = 8.9206 (1) Å
b = 10.7552 (2) Å
c = 12.4934 (2) Å
V = 1198.65 (3) Å³
Z = 4
 Mo *K*α radiation
 μ = 0.27 mm⁻¹
T = 100 K
 0.58 × 0.20 × 0.15 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.861, *T_{max}* = 0.961
 17333 measured reflections
 4355 independent reflections
 4078 reflections with *I* > 2σ(*I*)
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
 $wR(F^2)$ = 0.097
S = 1.05
 4355 reflections
 165 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}}$ = 0.79 e Å⁻³
 $\Delta\rho_{\text{min}}$ = –0.43 e Å⁻³
 Absolute structure: Flack (1983),
 1856 Friedel pairs
 Flack parameter: –0.04 (6)

Table 1

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>
N2–H1N2···N1 ⁱ	0.86	2.14	2.9068 (17)	149
N3–H1N3···O2 ⁱⁱ	0.86	1.99	2.8034 (15)	158
C4–H4A···O1 ⁱⁱⁱ	0.93	2.58	3.2047 (17)	125
C10–H10A···O2 ^{iv}	0.93	2.51	3.3928 (19)	159
C11–H11A···Cg1 ^v	0.93	2.80	3.3760 (17)	121

Symmetry codes: (i) $-x, y + \frac{1}{2}, -z - \frac{1}{2}$; (ii) $x + \frac{1}{2}, -y + \frac{3}{2}, -z$; (iii) $-x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$; (iv) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (v) $-x, y + \frac{3}{2}, -z + \frac{1}{2}$. Cg1 is centroid of the C1/C2/N1/C3–C5 ring.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINTE* (Bruker, 2005); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; 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: IS2451).

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supporting information

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N'*-(3-Methyl-2-thienyl)carbonylisonicotinohydrazide*H. S. Naveenkumar, Amirin Sadikun, Pazilah Ibrahim, Jia Hao Goh and Hoong-Kun Fun****S1. Comment**

In the search of new compounds, isoniazid derivatives have been found to possess potential tuberculostatic activity (Janin, 2007; Maccari *et al.*, 2005; Slayden *et al.*, 2000). As a part of a current work on synthesis of such derivatives, in this paper we present the crystal structure of the title compound, (I) which was synthesized in our lab.

In (I), the pyridine ring (C1/C2/N1/C3–C5) is inclined to the thiophene ring (C8–C11/S1), forming a dihedral angle of 34.96 (7)° (Fig. 1). The mean plane through the hydrazide unit (C7/N2/N3/O2) forms dihedral angles of 21.57 (8) and 53.08 (8)°, respectively, with the pyridine and thiophene rings. The O1 and O2 atoms are twisted away from each other as indicated by torsion angle C6–N2–N3–C7 [–81.27 (15)°]. The bond lengths (Allen *et al.*, 1987) and angles are comparable to a closely related structure (Naveenkumar *et al.*, 2009).

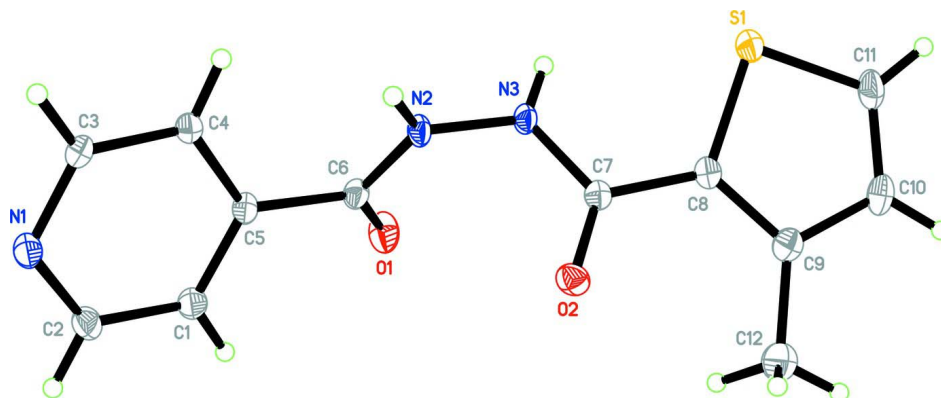
In the crystal structure (Fig. 2), the molecules are linked into an extended three-dimensional network by intermolecular C4—H4A···O1, C10—H10A···O2, N2—H1N2···N1 and N3—H1N3···O2 hydrogen bonds (Table 1). The crystal structure is further stabilized by short S1···O2 interactions of 3.2686 (10) Å [symmetry code: 1/2+x, 3/2-y, -z] and by weak intermolecular C11—H11A···Cg1 interactions (Table 1; Cg1 is the centroid of the pyridine ring).

S2. Experimental

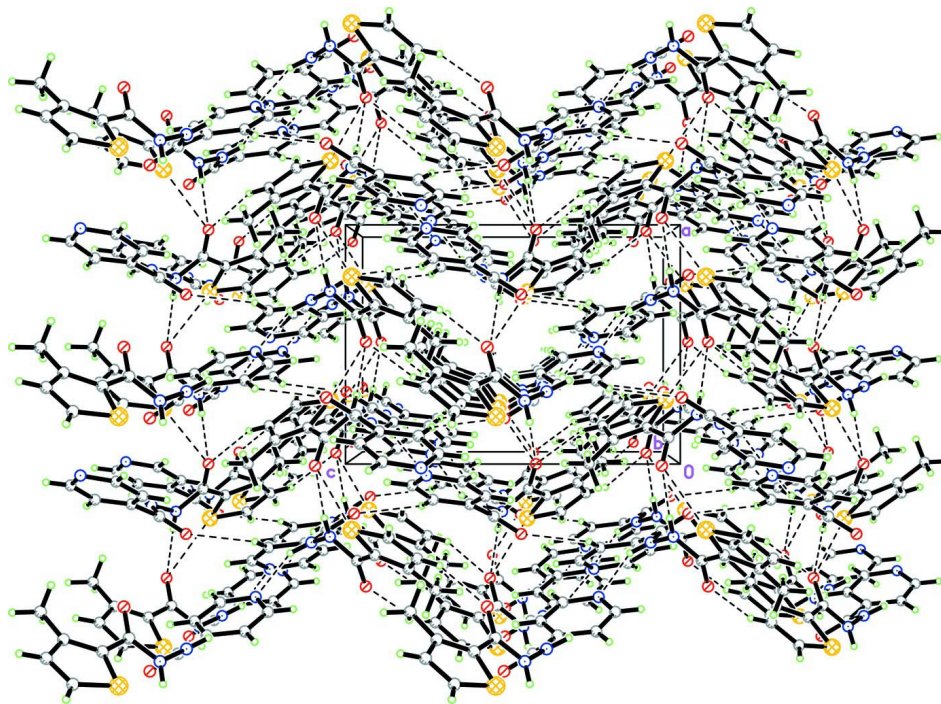
Compound (I) was prepared following the procedure by literature (Besra *et al.*, 1993). Dry dichloromethane (30 ml) and 4-dimethylaminopyridine (4-DMAP) (1.2 eq) was added to 3-methylthiophene-2-carbonyl chloride followed by isoniazid (1.1 eq). The reaction mixture was kept in an ice bath for 1 h and then left stirring under nitrogen atmosphere overnight at room temperature. Dichloromethane (20 ml) was added to the reaction mixture, which was then washed with water, and the organic layer dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure to afford the crude product which was purified by column chromatography and recrystallized from ethanol to afford colorless single crystals.

S3. Refinement

All the H atoms were placed in calculated positions, with N—H = 0.86 Å, $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{N})$, C—H = 0.93 Å, $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ for aromatic, and C—H = 0.96 Å, $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$ for methyl group. These H atoms were refined as riding on their parent atoms. A rotating group model was used for the methyl group.

**Figure 1**

The molecular structure of the (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. Hydrogen atoms are shown as spheres of arbitrary radius.

**Figure 2**

Three dimensional extended network, viewed along the *b* axis. Intermolecular interactions are shown as dashed lines.

N'-[(3-Methyl-2-thienyl)carbonyl]isonicotinohydrazide

Crystal data

$C_{12}H_{11}N_3O_2S$

$M_r = 261.30$

Orthorhombic, $P2_12_12_1$

Hall symbol: $P\ 2ac\ 2ab$

$a = 8.9206\ (1)\ \text{\AA}$

$b = 10.7552\ (2)\ \text{\AA}$

$c = 12.4934\ (2)\ \text{\AA}$

$V = 1198.65\ (3)\ \text{\AA}^3$

$Z = 4$

$F(000) = 544$

$D_x = 1.448\ \text{Mg m}^{-3}$

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

Cell parameters from 9634 reflections

$\theta = 2.5\text{--}32.7^\circ$

$\mu = 0.27 \text{ mm}^{-1}$
 $T = 100 \text{ K}$

Block, colourless
 $0.58 \times 0.20 \times 0.15 \text{ mm}$

Data collection

Bruker SMART APEXII CCD area-detector
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2005)
 $T_{\min} = 0.861, T_{\max} = 0.961$

17333 measured reflections
 4355 independent reflections
 4078 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$
 $\theta_{\max} = 32.7^\circ, \theta_{\min} = 2.5^\circ$
 $h = -13 \rightarrow 13$
 $k = -14 \rightarrow 16$
 $l = -17 \rightarrow 18$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.097$
 $S = 1.05$
 4355 reflections
 165 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-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0542P)^2 + 0.3319P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.79 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack (1983), 1856 Friedel
 pairs
 Absolute structure parameter: $-0.04 (6)$

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cyrosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1)K.

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.

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.26735 (4)	0.98879 (3)	0.04525 (3)	0.01858 (8)
O1	0.29108 (13)	0.48575 (10)	0.02488 (8)	0.0221 (2)
O2	0.01066 (11)	0.69442 (9)	0.07046 (8)	0.01664 (19)
N1	0.03034 (14)	0.21406 (11)	-0.25010 (10)	0.0159 (2)
N2	0.18343 (13)	0.62066 (10)	-0.09379 (9)	0.0137 (2)
H1N2	0.1404	0.6288	-0.1550	0.016*
N3	0.21647 (13)	0.72506 (10)	-0.03274 (9)	0.01367 (19)
H1N3	0.2954	0.7684	-0.0458	0.016*
C1	0.11893 (17)	0.29049 (12)	-0.08076 (11)	0.0165 (2)
H1A	0.1343	0.2764	-0.0081	0.020*

C2	0.05396 (17)	0.19936 (13)	-0.14457 (11)	0.0174 (2)
H2A	0.0255	0.1248	-0.1128	0.021*
C3	0.07732 (15)	0.32069 (12)	-0.29452 (11)	0.0153 (2)
H3A	0.0653	0.3306	-0.3680	0.018*
C4	0.14288 (15)	0.41719 (12)	-0.23723 (11)	0.0143 (2)
H4A	0.1741	0.4894	-0.2716	0.017*
C5	0.16079 (15)	0.40323 (12)	-0.12698 (10)	0.0136 (2)
C6	0.21924 (14)	0.50531 (11)	-0.05670 (10)	0.0138 (2)
C7	0.12212 (14)	0.75769 (11)	0.04814 (11)	0.0125 (2)
C8	0.15680 (15)	0.87488 (12)	0.10399 (11)	0.0142 (2)
C9	0.10620 (16)	0.91137 (14)	0.20356 (11)	0.0177 (2)
C10	0.15852 (18)	1.03210 (14)	0.23047 (13)	0.0209 (3)
H10A	0.1356	1.0716	0.2947	0.025*
C11	0.24567 (18)	1.08445 (13)	0.15288 (12)	0.0214 (3)
H11A	0.2883	1.1631	0.1581	0.026*
C12	0.0117 (2)	0.83596 (16)	0.27738 (13)	0.0259 (3)
H12A	0.0530	0.7538	0.2835	0.039*
H12B	-0.0884	0.8309	0.2496	0.039*
H12C	0.0097	0.8745	0.3466	0.039*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.02092 (15)	0.01399 (13)	0.02083 (16)	-0.00198 (11)	0.00366 (12)	-0.00283 (12)
O1	0.0302 (5)	0.0186 (4)	0.0176 (5)	0.0033 (4)	-0.0104 (4)	-0.0021 (4)
O2	0.0134 (4)	0.0166 (4)	0.0200 (5)	-0.0026 (3)	0.0000 (3)	0.0000 (4)
N1	0.0187 (5)	0.0131 (5)	0.0160 (5)	-0.0004 (4)	-0.0017 (4)	-0.0018 (4)
N2	0.0177 (5)	0.0113 (4)	0.0120 (5)	-0.0003 (4)	-0.0028 (4)	-0.0031 (4)
N3	0.0150 (5)	0.0122 (4)	0.0138 (5)	-0.0024 (4)	0.0005 (4)	-0.0046 (4)
C1	0.0229 (6)	0.0140 (6)	0.0125 (5)	0.0003 (5)	-0.0015 (5)	0.0011 (4)
C2	0.0226 (6)	0.0123 (5)	0.0173 (6)	-0.0006 (5)	-0.0006 (5)	0.0004 (5)
C3	0.0182 (6)	0.0163 (6)	0.0114 (5)	-0.0001 (4)	0.0005 (4)	-0.0028 (4)
C4	0.0172 (6)	0.0127 (5)	0.0131 (5)	-0.0014 (4)	-0.0001 (4)	-0.0011 (4)
C5	0.0158 (5)	0.0123 (5)	0.0128 (5)	0.0014 (4)	-0.0015 (4)	-0.0018 (4)
C6	0.0159 (5)	0.0133 (5)	0.0122 (5)	0.0008 (4)	-0.0012 (4)	-0.0018 (4)
C7	0.0129 (5)	0.0123 (5)	0.0124 (5)	0.0012 (4)	-0.0020 (4)	0.0002 (4)
C8	0.0139 (5)	0.0128 (5)	0.0160 (6)	0.0008 (4)	-0.0015 (4)	-0.0016 (4)
C9	0.0180 (6)	0.0188 (6)	0.0165 (6)	0.0005 (5)	-0.0001 (5)	-0.0021 (5)
C10	0.0230 (6)	0.0194 (6)	0.0205 (6)	0.0026 (5)	-0.0022 (5)	-0.0084 (5)
C11	0.0246 (7)	0.0152 (5)	0.0245 (7)	-0.0008 (5)	-0.0006 (5)	-0.0079 (5)
C12	0.0299 (8)	0.0246 (7)	0.0234 (7)	-0.0028 (6)	0.0019 (6)	-0.0040 (6)

Geometric parameters (Å, °)

S1—C11	1.7041 (14)	C3—C4	1.3898 (18)
S1—C8	1.7355 (14)	C3—H3A	0.9300
O1—C6	1.2222 (15)	C4—C5	1.3948 (19)
O2—C7	1.2367 (15)	C4—H4A	0.9300

N1—C3	1.3412 (18)	C5—C6	1.4994 (18)
N1—C2	1.3445 (18)	C7—C8	1.4736 (17)
N2—C6	1.3623 (16)	C8—C9	1.3803 (19)
N2—N3	1.3890 (14)	C9—C10	1.420 (2)
N2—H1N2	0.8600	C9—C12	1.489 (2)
N3—C7	1.3611 (17)	C10—C11	1.364 (2)
N3—H1N3	0.8600	C10—H10A	0.9300
C1—C2	1.3899 (19)	C11—H11A	0.9300
C1—C5	1.3940 (18)	C12—H12A	0.9600
C1—H1A	0.9300	C12—H12B	0.9600
C2—H2A	0.9300	C12—H12C	0.9600
C11—S1—C8	91.61 (7)	O1—C6—C5	123.00 (12)
C3—N1—C2	117.21 (12)	N2—C6—C5	112.71 (11)
C6—N2—N3	119.98 (11)	O2—C7—N3	121.52 (11)
C6—N2—H1N2	120.0	O2—C7—C8	122.19 (12)
N3—N2—H1N2	120.0	N3—C7—C8	116.25 (11)
C7—N3—N2	119.00 (11)	C9—C8—C7	126.96 (13)
C7—N3—H1N3	120.5	C9—C8—S1	111.48 (10)
N2—N3—H1N3	120.5	C7—C8—S1	121.53 (10)
C2—C1—C5	119.18 (12)	C8—C9—C10	111.46 (13)
C2—C1—H1A	120.4	C8—C9—C12	126.03 (14)
C5—C1—H1A	120.4	C10—C9—C12	122.50 (13)
N1—C2—C1	123.01 (13)	C11—C10—C9	113.35 (13)
N1—C2—H2A	118.5	C11—C10—H10A	123.3
C1—C2—H2A	118.5	C9—C10—H10A	123.3
N1—C3—C4	123.85 (12)	C10—C11—S1	112.10 (11)
N1—C3—H3A	118.1	C10—C11—H11A	124.0
C4—C3—H3A	118.1	S1—C11—H11A	124.0
C3—C4—C5	118.45 (12)	C9—C12—H12A	109.5
C3—C4—H4A	120.8	C9—C12—H12B	109.5
C5—C4—H4A	120.8	H12A—C12—H12B	109.5
C1—C5—C4	118.16 (12)	C9—C12—H12C	109.5
C1—C5—C6	119.18 (11)	H12A—C12—H12C	109.5
C4—C5—C6	122.64 (12)	H12B—C12—H12C	109.5
O1—C6—N2	124.29 (12)		
C6—N2—N3—C7	-81.27 (15)	N2—N3—C7—C8	-175.15 (11)
C3—N1—C2—C1	2.3 (2)	O2—C7—C8—C9	21.3 (2)
C5—C1—C2—N1	0.6 (2)	N3—C7—C8—C9	-161.26 (13)
C2—N1—C3—C4	-2.5 (2)	O2—C7—C8—S1	-156.60 (11)
N1—C3—C4—C5	-0.2 (2)	N3—C7—C8—S1	20.83 (16)
C2—C1—C5—C4	-3.4 (2)	C11—S1—C8—C9	-0.12 (11)
C2—C1—C5—C6	175.06 (12)	C11—S1—C8—C7	178.09 (12)
C3—C4—C5—C1	3.2 (2)	C7—C8—C9—C10	-178.07 (13)
C3—C4—C5—C6	-175.20 (12)	S1—C8—C9—C10	0.02 (15)
N3—N2—C6—O1	-6.2 (2)	C7—C8—C9—C12	3.3 (2)
N3—N2—C6—C5	173.77 (11)	S1—C8—C9—C12	-178.58 (13)

C1—C5—C6—O1	32.1 (2)	C8—C9—C10—C11	0.12 (19)
C4—C5—C6—O1	-149.49 (14)	C12—C9—C10—C11	178.78 (14)
C1—C5—C6—N2	-147.86 (13)	C9—C10—C11—S1	-0.21 (17)
C4—C5—C6—N2	30.54 (18)	C8—S1—C11—C10	0.19 (12)
N2—N3—C7—O2	2.30 (18)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H1N2 \cdots N1 ⁱ	0.86	2.14	2.9068 (17)	149
N3—H1N3 \cdots O2 ⁱⁱ	0.86	1.99	2.8034 (15)	158
C4—H4A \cdots O1 ⁱⁱⁱ	0.93	2.58	3.2047 (17)	125
C10—H10A \cdots O2 ^{iv}	0.93	2.51	3.3928 (19)	159
C11—H11A \cdots Cg1 ^v	0.93	2.80	3.3760 (17)	121

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