

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

N'-[(*E*)-[5-(Hydroxymethyl)furan-2-yl]-methylidene]pyridine-4-carbohydrazide dihydrate

M. K. Prasanna,^a M. Sithambaresan,^{b*} K. Pradeepkumar^a and M. R. Prathapachandra Kurup^c

^aDepartment of Chemistry and Research Centre, PRNSS College, Mattanur 670 702, Kannur, Kerala, India, ^bDepartment of Chemistry, Faculty of Science, Eastern University, Sri Lanka, Chenkalady, Sri Lanka, and ^cDepartment of Applied Chemistry, Cochin University of Science and Technology, Kochi 682 022, India
Correspondence e-mail: eesans@yahoo.com

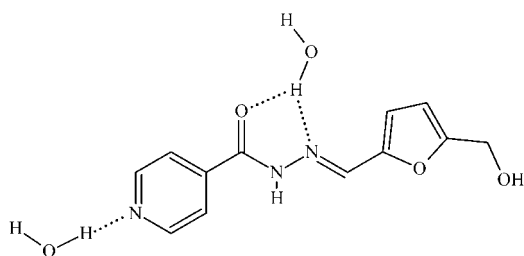
Received 30 June 2013; accepted 20 July 2013

Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.038; wR factor = 0.114; data-to-parameter ratio = 15.2.

In the title compound, $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_3 \cdot 2\text{H}_2\text{O}$, the dihedral angle formed by the planes of the pyridine and the furan rings of the organic carbohydrazide molecule is 4.66 (7)°. In the crystal, these molecules form stacks along the b -axis direction, neighbouring molecules within each stack being related by inversion and the shortest distance between the centroids of the pyridine and furan rings being 3.714 (1) Å. Molecules from neighboring stacks are linked by pairs of $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds. The water molecules fill the channels between the stacks being linked by $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds into helices along [010]. Besides this, water molecules are involved in $\text{O}-\text{H} \cdots \text{N}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds with the carbohydrazide molecules, thus forming a three-dimensional network, augmented by weak $\text{C}-\text{H} \cdots \text{O}$ interactions.

Related literature

For biological properties of carbohydrazide and its derivatives, see: Rollas & Kucukguzel (2007); Bakir & Brown (2002). For the synthesis of related compounds, see: Sreeja & Kurup (2005). For related structures, see: Nair *et al.* (2012); Reshma *et al.* (2012); Prasanna *et al.* (2013).



Experimental

Crystal data

$\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_3 \cdot 2\text{H}_2\text{O}$
 $M_r = 281.27$
Monoclinic, $P2_1/c$
 $a = 10.7020$ (14) Å
 $b = 7.0263$ (8) Å
 $c = 18.024$ (3) Å
 $\beta = 106.252$ (7)°

$V = 1301.2$ (3) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.11$ mm⁻¹
 $T = 296$ K
 $0.50 \times 0.25 \times 0.25$ mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2007)
 $T_{\min} = 0.946$, $T_{\max} = 0.972$

9681 measured reflections
3139 independent reflections
2308 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.114$
 $S = 1.03$
3139 reflections
206 parameters
6 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.23$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.19$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{O2S}-\text{H2A} \cdots \text{N3}$	0.85 (2)	2.49 (2)	3.2272 (17)	146 (2)
$\text{O2S}-\text{H2A} \cdots \text{O1}$	0.85 (2)	2.22 (2)	2.9648 (15)	146 (2)
$\text{O3}-\text{H3} \cdots \text{O1S}^i$	0.89 (2)	1.90 (2)	2.7937 (16)	174.9 (18)
$\text{O2S}-\text{H2B} \cdots \text{O1S}^{ii}$	0.86 (2)	2.06 (2)	2.9145 (18)	171 (2)
$\text{O1S}-\text{H1B} \cdots \text{O2S}^{iii}$	0.87 (2)	1.94 (2)	2.7924 (17)	167 (2)
$\text{N2}-\text{H2} \cdots \text{O3}^{iv}$	0.876 (18)	2.024 (18)	2.8485 (16)	156.3 (16)
$\text{O1S}-\text{H1A} \cdots \text{N1}$	0.87 (2)	2.03 (2)	2.8501 (16)	157 (2)
$\text{C4}-\text{H4} \cdots \text{O3}^{iv}$	0.93	2.50	3.3897 (18)	160
$\text{C12}-\text{H12B} \cdots \text{O1}^v$	0.97	2.43	3.3621 (19)	162

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

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, 2012) and DIAMOND (Brandenburg, 2010); software used to prepare material for publication: SHELXL97 and publCIF (Westrip, 2010).

MKP is thankful to the University Grants Commission, Bangalore, India, for the award of a Teacher Fellowship. MRPK is thankful to the UGC, New Delhi, for a UGC-BSR one-time grant to Faculty. The authors are grateful to the Sophisticated Analytical Instruments Facility, Cochin University of Science and Technology, Kochi-22, India, for the single-crystal X-ray diffraction measurements.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: YK2097).

References

- Bakir, M. & Brown, O. (2002). *J. Mol. Struct.* **609**, 129–136.
- Brandenburg, K. (2010). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Bruker (2007). *SADABS*, *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Nair, Y., Sithambaresan, M. & Kurup, M. R. P. (2012). *Acta Cryst.* **E68**, o2709.
- Prasanna, M. K., Sithambaresan, M., Pradeepkumar, K. & Kurup, M. R. P. (2013). *Acta Cryst.* **E69**, o881.
- Reshma, P. R., Sithambaresan, M. & Kurup, M. R. P. (2012). *Acta Cryst.* **E68**, o2785.
- Rollas, S. & Kucukguzel, S. G. (2007). *Molecules*, **12**, 1910–1939.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sreeja, P. B. & Kurup, M. R. P. (2005). *Spectrochim. Acta Part A*, **61**, 331–336.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2013). E69, o1342–o1343 [doi:10.1107/S1600536813020114]

***N'*-{(E)-[5-(Hydroxymethyl)furan-2-yl]methylidene}pyridine-4-carbohydrazide dihydrate**

M. K. Prasanna, M. Sithambaresan, K. Pradeepkumar and M. R. Prathapachandra Kurup

S1. Comment

Heterocyclic carbohydrazides are compounds with a wide spectrum of biological and analytical applications. They form stable metal chelates which find applications in molecular sensing (Bakir & Brown, 2002). The title compound is a derivative of isoniazid which is one of the first line drug used in the treatment of tuberculosis. A number of hydrazones derived from isoniazid were reported to be active antitubercular agents and were found to be less toxic than isoniazid (Rollas & Kucukguzel, 2007).

The compound crystallizes in monoclinic $P2_1/c$ space group. The molecule exists in a *E* configuration with respect to the $C7=N3$ bond, typical of such kind of compounds (Reshma *et al.*, 2012), with the $C8-C7-N3-N2$ torsion angle of $178.04(11)^\circ$ (Fig 1). The $N3-N2-C6-O1$ torsion angle of $-2.72(18)^\circ$ indicates the *cis* configuration of the O1 atom with respect to the hydrazine nitrogen atom N3 (Nair *et al.*, 2012). $C7=N3$ [1.267(3) Å] and $C6=O1$ [1.217(8) Å] bond distances are very close to the formal double $C=N$ and $C=O$ bond lengths (Prasanna, *et al.*, 2013) confirming that the carbohydrazide exists in solid state as an amido tautomer.

Seven classical hydrogen bonds are present in the crystal (Fig. 2). One of the nitrogen atoms of pyridine-4-carbohydrazide molecule is involved in classical intermolecular hydrogen bond of the $N-H\cdots O$ type with oxygen atom of the hydroxymethyl group of the neighboring molecule with a $D\cdots A$ distance of 2.8483(16) Å. There are two hydrogen bonds of the $O-H\cdots O$ type between the two water molecules: $O2S-H2B\cdots O1S$ and $O1S-H1B\cdots O2S$ with $D\cdots A$ distances of 2.9146(18) Å and 2.7923(17) Å, respectively. Each water molecule is involved in other $O-H\cdots O$ and $O-H\cdots N$ hydrogen bonds: $O2S-H2A\cdots O1$ and $O3-H3'\cdots O1S$ with $D\cdots A$ distances of 2.9647(15) Å and 2.7937(16) Å and $O2S-H2A\cdots N3$ and $O1S-H1A\cdots N1$ with $D\cdots A$ distances of 3.2272(17) Å and 2.8501(16) Å, respectively. Additionally, there are non-classical intermolecular $C-H\cdots O$ hydrogen bonds between the hydrogen atoms attached to C4 and C12 carbon atoms and the O3 and O1 atoms of the neighboring molecule with $D\cdots A$ distances of 3.390(2) Å and 3.362(2) Å, respectively. These interactions are augmented by weak $\pi\cdots\pi$ interactions which connect the molecules with a centroid-centroid distances of 3.714(1) Å and 3.760(1) Å (Fig. 3). The packing diagram showing the molecular assembly of the title compound along the *b* axis is shown in Fig. 4.

S2. Experimental

The title compound was prepared by adapting a reported procedure (Sreeja & Kurup, 2005). To a warm methanolic solution of 5-(hydroxymethyl)furan-2-carbaldehyde (0.126 g, 1 mmol), a methanolic solution of pyridine-4-carbohydrazide (0.137 g, 1 mmol) was added and the resulting solution was stirred well with slight heating for 75 minutes. A colorless compound formed was filtered off, washed with water, ethanol and finally with ether and dried. Single crystals suitable for X-ray diffraction studies were obtained by recrystallization from a mixture of methanol, ethanol and DMF.

S3. Refinement

All H atoms on C were placed in calculated positions, guided by difference maps, with C–H bond distances 0.93–0.97 Å. H atoms were assigned as $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{carrier})$ or $1.5U_{\text{eq}}$ (methyl C). The H atoms of the water molecule were located from difference maps and restrained using DFIX and DANG instructions. Omitted owing to disagreement was the reflection (1 1 0).

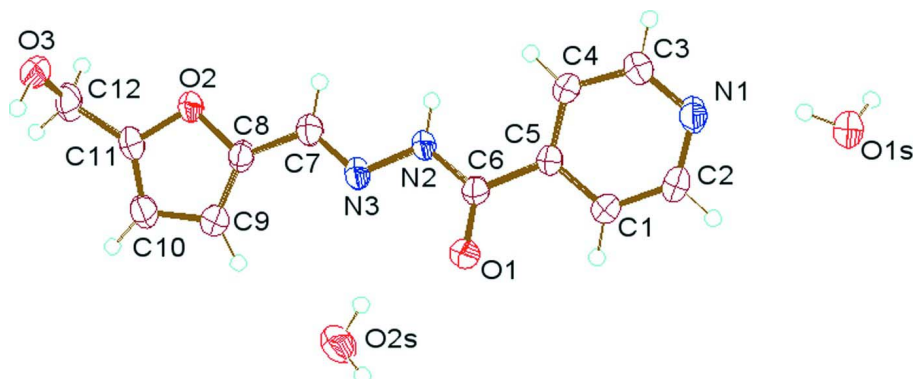


Figure 1

View of the structure of the title compound, showing the atom-labelling scheme and displacement ellipsoids for the non-H atoms drawn at the 50% probability level.

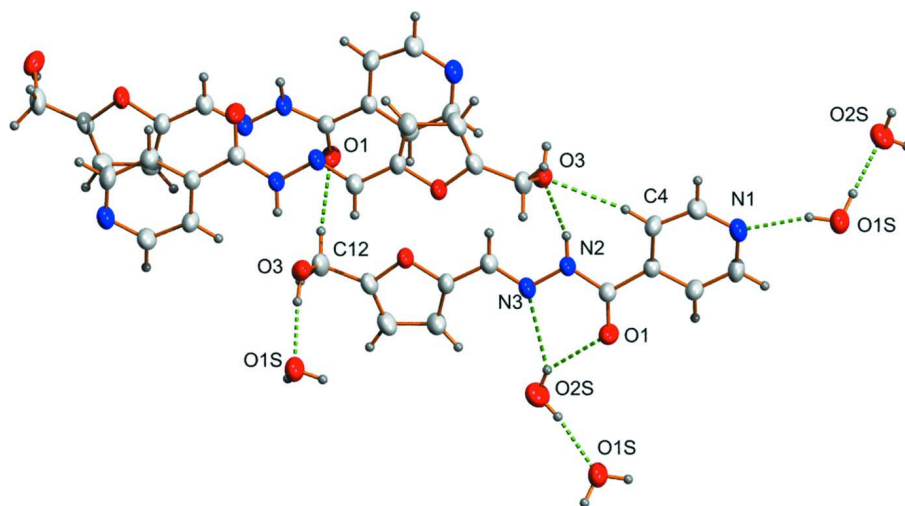
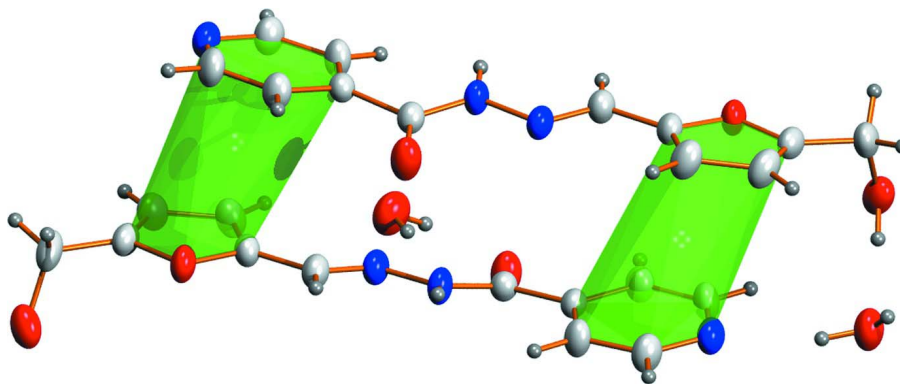
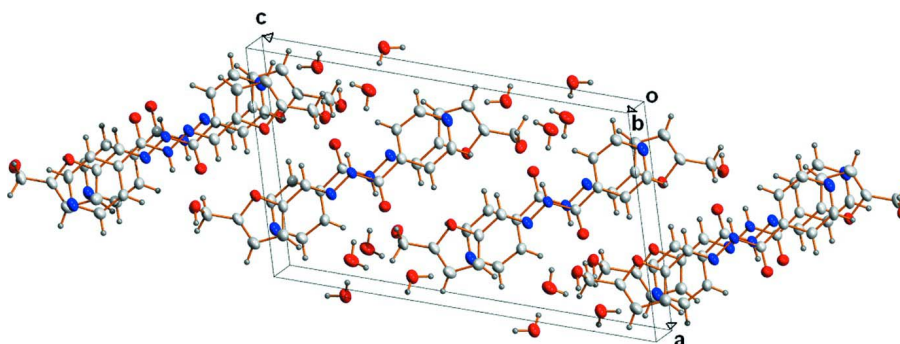


Figure 2

Hydrogen bonding in the crystal of the title compound.

**Figure 3**

The $\pi \cdots \pi$ stacking interactions in the title compound.

**Figure 4**

A view of the unit cell along the *b* axis.

N'-{(*E*)-[5-(Hydroxymethyl)furan-2-yl]methylidene}pyridine-4-carbohydrazide dihydrate

Crystal data

$C_{12}H_{11}N_3O_3 \cdot 2H_2O$

$M_r = 281.27$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 10.7020$ (14) Å

$b = 7.0263$ (8) Å

$c = 18.024$ (3) Å

$\beta = 106.252$ (7)°

$V = 1301.2$ (3) Å³

$Z = 4$

$F(000) = 592$

$D_x = 1.436$ Mg m⁻³

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

Cell parameters from 3182 reflections

$\theta = 2.4$ – 28.2 °

$\mu = 0.11$ mm⁻¹

$T = 296$ K

Block, colorless

$0.50 \times 0.25 \times 0.25$ mm

Data collection

Bruker Kappa APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.33 pixels mm⁻¹

ω and φ scan

Absorption correction: multi-scan

(*SADABS*; Bruker, 2007)

$T_{\min} = 0.946$, $T_{\max} = 0.972$

9681 measured reflections

3139 independent reflections

2308 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 28.0$ °, $\theta_{\min} = 3.1$ °

$h = -14 \rightarrow 14$

$k = -9 \rightarrow 9$

$l = -23 \rightarrow 16$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.114$
 $S = 1.03$
 3139 reflections
 206 parameters
 6 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
 $w = 1/[\sigma^2(F_o^2) + (0.0564P)^2 + 0.1806P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.23 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.19 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick,
 2008), $F_c^* = kFc[1 + 0.001x \text{Fc}^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0056 (14)

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 $F^2 > \sigma(F^2)$ 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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O2	0.65878 (8)	0.90209 (13)	1.02711 (5)	0.0361 (2)
N3	0.59249 (10)	0.91380 (15)	0.82424 (6)	0.0352 (3)
N1	0.17508 (11)	0.89401 (16)	0.49077 (6)	0.0405 (3)
N2	0.48334 (11)	0.90481 (16)	0.76219 (6)	0.0340 (3)
O3	0.74289 (10)	1.09936 (16)	1.18406 (6)	0.0456 (3)
O1	0.60410 (9)	0.97315 (16)	0.68198 (6)	0.0459 (3)
O1S	0.05219 (11)	0.82845 (18)	0.33090 (6)	0.0484 (3)
O2S	0.87042 (11)	0.96561 (18)	0.78948 (7)	0.0553 (3)
C1	0.40194 (13)	0.8935 (2)	0.55313 (8)	0.0379 (3)
H1	0.4862	0.8853	0.5486	0.046*
C5	0.38137 (12)	0.91494 (16)	0.62455 (7)	0.0291 (3)
C4	0.25460 (13)	0.9228 (2)	0.62766 (8)	0.0382 (3)
H4	0.2358	0.9350	0.6748	0.046*
C2	0.29770 (15)	0.8844 (2)	0.48870 (8)	0.0427 (3)
H2	0.3138	0.8708	0.4409	0.051*
C3	0.15595 (13)	0.9122 (2)	0.55978 (8)	0.0421 (3)
H3	0.0706	0.9181	0.5626	0.051*
C7	0.57428 (13)	0.89688 (18)	0.89043 (8)	0.0353 (3)
H7	0.4906	0.8833	0.8955	0.042*
C8	0.68443 (13)	0.89898 (17)	0.95717 (7)	0.0328 (3)
C11	0.77674 (13)	0.90344 (18)	1.08159 (7)	0.0348 (3)
C10	0.87211 (14)	0.8998 (2)	1.04728 (9)	0.0439 (4)
H10	0.9610	0.8996	1.0719	0.053*

C12	0.77600 (15)	0.9152 (2)	1.16286 (8)	0.0441 (4)
H12B	0.7141	0.8236	1.1719	0.053*
H12A	0.8615	0.8810	1.1956	0.053*
C9	0.81354 (14)	0.8965 (2)	0.96715 (9)	0.0437 (3)
H9	0.8559	0.8931	0.9286	0.052*
C6	0.49926 (12)	0.93343 (17)	0.69202 (7)	0.0304 (3)
H1A	0.067 (2)	0.853 (3)	0.3797 (9)	0.089 (7)*
H2'	0.4086 (18)	0.875 (2)	0.7700 (10)	0.058 (5)*
H1B	-0.0138 (16)	0.751 (3)	0.3174 (11)	0.077 (6)*
H2B	0.888 (2)	1.017 (3)	0.7503 (11)	0.094 (8)*
H3'	0.808 (2)	1.176 (3)	1.1820 (11)	0.075 (6)*
H2A	0.7875 (15)	0.961 (3)	0.7772 (12)	0.083 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0314 (5)	0.0508 (5)	0.0229 (5)	-0.0029 (4)	0.0023 (4)	0.0017 (4)
N3	0.0323 (6)	0.0432 (6)	0.0257 (6)	-0.0023 (4)	0.0009 (5)	-0.0009 (4)
N1	0.0406 (7)	0.0478 (7)	0.0282 (6)	-0.0018 (5)	0.0016 (5)	-0.0017 (5)
N2	0.0276 (6)	0.0488 (6)	0.0224 (6)	-0.0037 (5)	0.0019 (5)	0.0008 (4)
O3	0.0446 (6)	0.0623 (7)	0.0327 (6)	-0.0122 (5)	0.0156 (5)	-0.0072 (4)
O1	0.0300 (5)	0.0750 (7)	0.0327 (5)	-0.0025 (5)	0.0089 (4)	0.0011 (5)
O1S	0.0448 (6)	0.0656 (7)	0.0315 (6)	-0.0005 (5)	0.0052 (5)	-0.0008 (5)
O2S	0.0374 (6)	0.0725 (8)	0.0497 (7)	0.0006 (5)	0.0019 (5)	0.0059 (6)
C1	0.0339 (7)	0.0518 (8)	0.0293 (7)	0.0009 (6)	0.0107 (6)	-0.0013 (5)
C5	0.0307 (6)	0.0311 (6)	0.0241 (6)	0.0005 (5)	0.0053 (5)	0.0013 (4)
C4	0.0344 (7)	0.0559 (8)	0.0247 (7)	0.0008 (6)	0.0088 (5)	0.0010 (5)
C2	0.0474 (8)	0.0551 (8)	0.0246 (7)	-0.0006 (6)	0.0086 (6)	-0.0048 (6)
C3	0.0317 (7)	0.0582 (9)	0.0334 (8)	-0.0005 (6)	0.0042 (6)	0.0006 (6)
C7	0.0333 (7)	0.0427 (7)	0.0271 (7)	-0.0013 (5)	0.0040 (5)	0.0007 (5)
C8	0.0363 (7)	0.0372 (6)	0.0233 (6)	-0.0017 (5)	0.0058 (5)	-0.0013 (5)
C11	0.0326 (7)	0.0378 (7)	0.0279 (7)	-0.0010 (5)	-0.0018 (5)	0.0012 (5)
C10	0.0327 (7)	0.0562 (9)	0.0377 (8)	0.0011 (6)	0.0010 (6)	-0.0092 (6)
C12	0.0474 (8)	0.0527 (8)	0.0255 (7)	-0.0084 (6)	-0.0006 (6)	0.0065 (6)
C9	0.0369 (7)	0.0594 (9)	0.0347 (8)	-0.0013 (6)	0.0100 (6)	-0.0095 (6)
C6	0.0289 (6)	0.0350 (6)	0.0264 (6)	0.0022 (5)	0.0065 (5)	-0.0005 (5)

Geometric parameters (Å, °)

O2—C8	1.3634 (15)	C1—H1	0.9300
O2—C11	1.3654 (15)	C5—C4	1.3745 (18)
N3—C7	1.2671 (17)	C5—C6	1.4928 (17)
N3—N2	1.3741 (15)	C4—C3	1.3763 (18)
N1—C3	1.3221 (17)	C4—H4	0.9300
N1—C2	1.3248 (19)	C2—H2	0.9300
N2—C6	1.3379 (16)	C3—H3	0.9300
N2—H2'	0.876 (18)	C7—C8	1.4294 (18)
O3—C12	1.4218 (18)	C7—H7	0.9300

O3—H3'	0.89 (2)	C8—C9	1.3427 (19)
O1—C6	1.2178 (15)	C11—C10	1.333 (2)
O1S—H1A	0.865 (16)	C11—C12	1.4694 (19)
O1S—H1B	0.872 (15)	C10—C9	1.405 (2)
O2S—H2B	0.860 (16)	C10—H10	0.9300
O2S—H2A	0.853 (15)	C12—H12B	0.9700
C1—C2	1.3683 (19)	C12—H12A	0.9700
C1—C5	1.3737 (18)	C9—H9	0.9300
C8—O2—C11	106.27 (10)	N3—C7—C8	118.91 (12)
C7—N3—N2	116.25 (11)	N3—C7—H7	120.5
C3—N1—C2	116.53 (12)	C8—C7—H7	120.5
C6—N2—N3	117.28 (11)	C9—C8—O2	110.02 (11)
C6—N2—H2'	123.5 (12)	C9—C8—C7	133.47 (13)
N3—N2—H2'	119.1 (12)	O2—C8—C7	116.50 (11)
C12—O3—H3'	106.2 (12)	C10—C11—O2	109.88 (12)
H1A—O1S—H1B	108.4 (18)	C10—C11—C12	132.98 (13)
H2B—O2S—H2A	104.8 (19)	O2—C11—C12	117.09 (12)
C2—C1—C5	119.61 (12)	C11—C10—C9	107.34 (13)
C2—C1—H1	120.2	C11—C10—H10	126.3
C5—C1—H1	120.2	C9—C10—H10	126.3
C1—C5—C4	117.48 (12)	O3—C12—C11	112.99 (11)
C1—C5—C6	116.89 (11)	O3—C12—H12B	109.0
C4—C5—C6	125.60 (11)	C11—C12—H12B	109.0
C5—C4—C3	118.81 (12)	O3—C12—H12A	109.0
C5—C4—H4	120.6	C11—C12—H12A	109.0
C3—C4—H4	120.6	H12B—C12—H12A	107.8
N1—C2—C1	123.54 (13)	C8—C9—C10	106.49 (13)
N1—C2—H2	118.2	C8—C9—H9	126.8
C1—C2—H2	118.2	C10—C9—H9	126.8
N1—C3—C4	124.02 (13)	O1—C6—N2	122.77 (12)
N1—C3—H3	118.0	O1—C6—C5	120.18 (11)
C4—C3—H3	118.0	N2—C6—C5	117.05 (11)
C7—N3—N2—C6	176.19 (11)	C8—O2—C11—C12	177.41 (11)
C2—C1—C5—C4	1.17 (19)	O2—C11—C10—C9	0.14 (16)
C2—C1—C5—C6	-177.08 (12)	C12—C11—C10—C9	-177.28 (15)
C1—C5—C4—C3	-1.08 (19)	C10—C11—C12—O3	103.43 (18)
C6—C5—C4—C3	177.01 (12)	O2—C11—C12—O3	-73.84 (15)
C3—N1—C2—C1	-0.4 (2)	O2—C8—C9—C10	-0.54 (16)
C5—C1—C2—N1	-0.4 (2)	C7—C8—C9—C10	-179.70 (14)
C2—N1—C3—C4	0.5 (2)	C11—C10—C9—C8	0.25 (17)
C5—C4—C3—N1	0.2 (2)	N3—N2—C6—O1	-2.72 (18)
N2—N3—C7—C8	178.04 (11)	N3—N2—C6—C5	177.35 (10)
C11—O2—C8—C9	0.62 (14)	C1—C5—C6—O1	16.96 (17)
C11—O2—C8—C7	179.94 (11)	C4—C5—C6—O1	-161.14 (13)
N3—C7—C8—C9	-8.1 (2)	C1—C5—C6—N2	-163.11 (12)
N3—C7—C8—O2	172.79 (11)	C4—C5—C6—N2	18.79 (18)

C8—O2—C11—C10 -0.46 (14)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O2 <i>S</i> —H2 <i>A</i> \cdots N3	0.85 (2)	2.49 (2)	3.2272 (17)	146 (2)
O2 <i>S</i> —H2 <i>A</i> \cdots O1	0.85 (2)	2.22 (2)	2.9648 (15)	146 (2)
O3—H3' \cdots O1 <i>S</i> ⁱ	0.89 (2)	1.90 (2)	2.7937 (16)	174.9 (18)
O2 <i>S</i> —H2 <i>B</i> \cdots O1 <i>S</i> ⁱⁱ	0.86 (2)	2.06 (2)	2.9145 (18)	171 (2)
O1 <i>S</i> —H1 <i>B</i> \cdots O2 <i>S</i> ⁱⁱⁱ	0.87 (2)	1.94 (2)	2.7924 (17)	167 (2)
N2—H2' \cdots O3 ^{iv}	0.876 (18)	2.024 (18)	2.8485 (16)	156.3 (16)
O1 <i>S</i> —H1 <i>A</i> \cdots N1	0.87 (2)	2.03 (2)	2.8501 (16)	157 (2)
C4—H4 \cdots O3 ^{iv}	0.93	2.50	3.3897 (18)	160
C12—H12 <i>B</i> \cdots O1 ^v	0.97	2.43	3.3621 (19)	162

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