

Crystal structure of ethyl 2-(3-amino-5-oxo-2-tosyl-2,5-dihydro-1*H*-pyrazol-1-yl)acetateNadia H. Metwally,<sup>a</sup> Galal H. Elgemeie<sup>b</sup> and Peter G. Jones<sup>c\*</sup><sup>a</sup>Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt, <sup>b</sup>Chemistry Department, Faculty of Science, Helwan University, Cairo, Egypt, and <sup>c</sup>Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30, D-38106 Braunschweig, Germany. \*Correspondence e-mail: p.jones@tu-bs.de

Received 3 May 2021

Accepted 6 May 2021

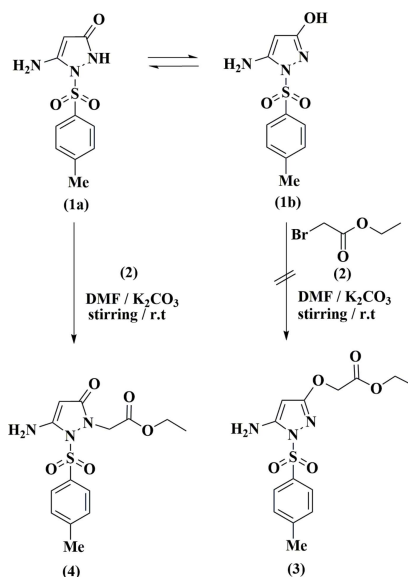
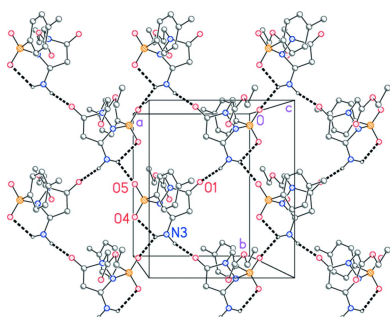
Edited by M. Zeller, Purdue University, USA

**Keywords:** pyrazole; tosyl; hydrogen bond; crystal structure.**CCDC reference:** 2082046**Supporting information:** this article has supporting information at journals.iucr.org/e

In the title compound, C<sub>14</sub>H<sub>17</sub>N<sub>3</sub>O<sub>5</sub>S, the five-membered ring is essentially planar. The substituents at the nitrogen atoms subtend a C–N–S torsion angle of  $-95.52(6)^\circ$ . The amino group forms an intramolecular hydrogen bond to a sulfonyl oxygen atom; two intermolecular hydrogen bonds from the amino group, to the other S=O group and to the oxo substituent, form a layer structure parallel to the *ab* plane. The structure determination confirms that the title compound is *N*- rather than *O*-alkylated.

## 1. Chemical context

Recently we have been attempting to develop synthetic strategies for heterocyclic ring systems containing *N*-sulfonylamino- and *N*-sulfonyl moieties. The products may be biologically active, displaying for instance anti-viral activity (Azzam *et al.*, 2017, 2019, 2020; Zhu *et al.*, 2013; Elgemeie *et al.*, 2017, 2019). Also, some of our reported *N*-arylsulfonylpyrazole derivatives (Elgemeie *et al.*, 1998, 2013; Elgemeie & Hanfy, 1999) proved to be inhibitors of the NS2B-NS3 virus and the enzyme cathepsin B16 (Myers *et al.*, 2007; Sidique *et al.*, 2009). In a continuation of our research investigating new approaches to other new derivatives of *N*-sulfonylpyrazoles, seeking various scaffolds for use as encouraging chemotherapeutics (Zhang *et al.*, 2020; Elgemeie & Jones, 2002), we have now synthesized the N1-substituted derivative of *N*-sulfonylpyrazole **1** (the structure of which we have reported; Elgemeie *et al.*, 2013).



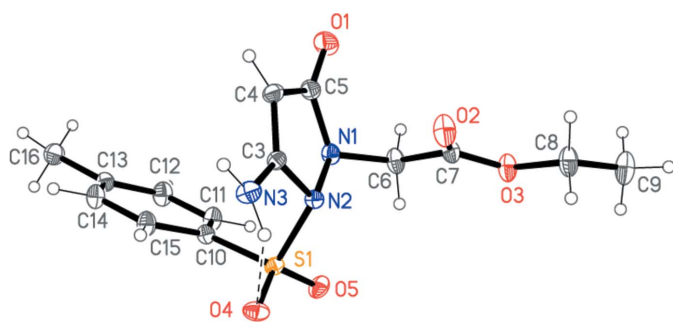
**Table 1**  
Selected geometric parameters (Å, °).

N1—C5	1.4157 (9)	N2—S1	1.7154 (6)
N1—N2	1.4296 (8)	C3—C4	1.3661 (9)
N1—C6	1.4549 (9)	C4—C5	1.4203 (10)
N2—C3	1.4273 (8)		
C5—N1—N2	107.67 (5)	C4—C3—N2	110.21 (6)
C5—N1—C6	117.34 (6)	C3—C4—C5	107.94 (6)
N2—N1—C6	115.11 (5)	O1—C5—N1	120.24 (7)
C3—N2—N1	105.89 (5)	O1—C5—C4	131.82 (7)
C3—N2—S1	116.65 (4)	N1—C5—C4	107.90 (6)
N1—N2—S1	109.25 (4)		
C6—N1—N2—S1	−95.52 (6)	C6—C7—O3—C8	−179.18 (6)
N1—C6—C7—O3	170.80 (6)	C9—C8—O3—C7	−168.27 (7)

The reaction of **1** with ethyl bromoacetate **2** in dry *N,N*-dimethylformamide containing anhydrous potassium carbonate at room temperature afforded a product for which two possible isomeric structures, the *N*-alkylated or *O*-alkylated *N*-sulfonylpyrazoles **3** or **4**, were feasible. The <sup>1</sup>H NMR spectrum of the product showed four singlet signals at  $\delta = 2.41, 4.31, 4.40$  and  $7.15$  ppm assigned to CH<sub>3</sub>, pyrazole-CH, CH<sub>2</sub> and NH<sub>2</sub> protons, along with triplet and quartet signals at  $\delta = 1.17$  and  $4.09$  ppm, assigned to ethyl groups. The spectroscopic data cannot differentiate between structures **3** and **4**. We therefore determined the X-ray structure of this product, which proved to be the *N*-alkylated-*N*-sulfonylpyrazole **4**.

## 2. Structural commentary

The molecule of compound **4** is shown in Fig. 1. Molecular dimensions, a selection of which are presented in Table 1, may be considered normal (e.g. the N1—N2 bond length corresponds to a single bond and these atoms display a pyramidal geometry). The substituents S1 and C6 of the five-membered ring, which is effectively planar (r.m.s. deviation 0.026 Å) lie significantly outside the ring plane [by 1.2344 (8) and 0.8468 (19) Å, respectively] in opposite directions; the corresponding torsion angle C6—N1—N2—S1 is  $-95.52$  (6)°. The side chain at N1 exhibits an extended conformation. An intramolecular hydrogen bond is formed from the amino



**Figure 1**  
The structure of compound **4** in the crystal. Ellipsoids represent 50% probability levels. The dashed line indicates an intramolecular hydrogen bond.

**Table 2**  
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—H01···O1 <sup>i</sup>	0.913 (13)	1.897 (13)	2.7884 (8)	164.7 (12)
N3—H02···O4	0.861 (13)	2.394 (13)	2.8291 (8)	111.8 (10)
N3—H02···O5 <sup>ii</sup>	0.861 (13)	2.294 (13)	3.0139 (8)	141.3 (12)
C6—H6B···O4 <sup>iii</sup>	0.99	2.50	3.2642 (9)	133
C8—H8B···O1 <sup>iv</sup>	0.99	2.43	3.2663 (11)	142

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

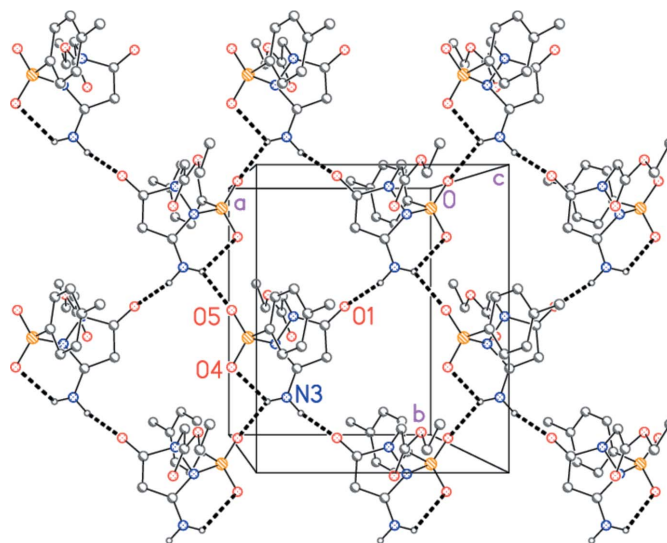
group to the sulfonyl oxygen atom O4 (Table 2). The ring planes subtend an interplanar angle of  $57.01$  (3)°.

## 3. Supramolecular features

The molecules of **4** are linked by two classical hydrogen bonds, from the NH<sub>2</sub> hydrogen atoms H01 and H02 to the acceptors O5=S1 and O1=C5, to form layers parallel to the *ab* plane (Fig. 2, Table 2). The hydrogen atom H02 is thus involved in a three-centre hydrogen bond, taking the above-mentioned intramolecular interaction into account. The additional ‘weak’ interactions H6B···O4 (within the layers; operator  $-x + 2, y - \frac{1}{2}, -z + \frac{1}{2}$ ) and H8B···O1 (between layers; operator  $-x + 1, -y + 1, -z$ ) are not shown in the Figure. The shortest distance between ring centroids is  $3.97$  Å for the ring C10—C15 (operator  $2 - x, 1 - y, 1 - z$ ).

## 4. Database survey

A database search (CSD Version 5.41) for the same ring system as in **4**, and bearing the same substituents at C5 (oxo) and C3 (amino), gave eight hits involving uncharged species. However, none of these was substituted at both ring nitrogen



**Figure 2**  
Packing diagram of compound **4** viewed perpendicular to the *ab* plane in the region  $z \approx 0.25$ . Dashed lines indicate hydrogen bonds. Hydrogen atoms not involved in hydrogen bonding are omitted for clarity.

**Table 3**  
Experimental details.

Crystal data	
Chemical formula	C <sub>14</sub> H <sub>17</sub> N <sub>3</sub> O <sub>5</sub> S
<i>M<sub>r</sub></i>	339.36
Crystal system, space group	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>c</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.1398 (2), 11.1525 (2), 16.3795 (3)
$\beta$ (°)	97.081 (2)
<i>V</i> (Å <sup>3</sup> )	1656.85 (6)
<i>Z</i>	4
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.22
Crystal size (mm)	0.24 × 0.20 × 0.08
Data collection	
Diffractometer	XtaLAB Synergy, Single source at offset/far, HyPix
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Rigaku OD, 2021)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.805, 1.000
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	128543, 7466, 6502
<i>R<sub>int</sub></i>	0.040
( $\sin \theta/\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.825
Refinement	
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , <i>S</i>	0.031, 0.094, 1.05
No. of reflections	7466
No. of parameters	218
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.58, -0.30

Computer programs: *CrysAlis PRO* (Rigaku OD, 2021), *SHELXT* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b) and *XP* (Siemens, 1994).

atoms. Two (our previous structures: Elgemeie *et al.*, 1998, 2013) have a hydrogen atom at N1, while the other six have a hydrogen at N2; the other *N*-substituents are 9-thioxanthanyl (DOJKIW; Kimura, 1986), C(=S)NH<sub>2</sub>Et (LUPDUW; Pitucha *et al.*, 2010), C(=O)NHCH<sub>2</sub>COOEt (MAVJUK) and C(=O)NH<sup>*n*</sup>Bu (MAVKAX; Pitucha *et al.*, 2011), C(=O)NHCH(Ph)CH<sub>3</sub> (TIRVAT; Kaczor *et al.*, 2013) and C(O)NH-1-naphthyl (VOQGOZ; Kaczor *et al.*, 2014). It is notable that the *X*-N-N-*X* (*X* = H or substituent atom) torsion angles are very variable; in four cases the absolute value lies between 0 and 11°, whereas for the bulky substituents in DOJKIW and VOQGOZ the values are 63.7 and 32.1°, respectively.

## 5. Synthesis and crystallization

A mixture of 5-amino-1-tosyl-1,2-dihydro-3*H*-pyrazol-3-one **1** (0.01 mol), ethyl bromoacetate **2** (0.01 mol) and anhydrous potassium carbonate (0.01 mol) in *N,N*-dimethylformamide (5 mL) was stirred at room temperature for 3 h. The mixture was poured onto ice-water; the solid thus formed was filtered off and recrystallized from ethanol to give pale yellow crystals in 64% yield, m.p. = 415–416 K. IR (KBr, cm<sup>-1</sup>):  $\nu$  3460, 3297 (NH<sub>2</sub>), 1752 (ester C=O), 1700 (ring C=O); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  = 1.17 (*t*, 3H, *J* = 7.2 Hz, CH<sub>3</sub>), 2.41 (*s*, 3H, CH<sub>3</sub>),

4.09 (*q*, 2H, *J* = 7.2 Hz, CH<sub>2</sub>), 4.31 (*s*, 1H, CH pyrazole), 4.40 (*s*, 2H, CH<sub>2</sub>), 7.15 (*s*, 2H, NH<sub>2</sub>), 7.45 (*d*, 2H, *J* = 8.4 Hz, Ar), 7.73 (*d*, 2H, *J* = 8.4 Hz, Ar). Analysis: calculated C<sub>14</sub>H<sub>17</sub>N<sub>3</sub>O<sub>5</sub>S (339.36); C, 49.55; H, 5.05; N, 12.38; S, 9.45. Found: C, 49.38; H, 5.23; N, 12.59; S, 9.27%.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The hydrogen atoms of the NH<sub>2</sub> group were refined freely. The methyl groups were refined as idealized rigid groups allowed to rotate but not tip (AFIX 137; C–H = 0.98 Å, H–C–H = 109.5°). Other hydrogens were included using a riding model starting from calculated positions (C–H<sub>aromatic</sub> = 0.95, C–H<sub>methylene</sub> = 0.99 Å). The *U*<sub>iso</sub>(H) values were fixed at 1.5 (for the methyl H) or 1.2 times the equivalent *U*<sub>eq</sub> value of the parent carbon atoms.

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## supporting information

*Acta Cryst.* (2021). E77, 615-617 [https://doi.org/10.1107/S2056989021004795]

## Crystal structure of ethyl 2-(3-amino-5-oxo-2-tosyl-2,5-dihydro-1H-pyrazol-1-yl)acetate

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### Computing details

Cell refinement: *CrysAlis PRO* (Rigaku OD, 2021); data reduction: *CrysAlis PRO* (Rigaku OD, 2021); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL2018/3* (Sheldrick, 2015b).

### Ethyl 2-[3-amino-2-(4-methylbenzenesulfonyl)-5-oxo-2,5-dihydro-1H-pyrazol-1-yl]acetate

#### Crystal data

$C_{14}H_{17}N_3O_5S$

$M_r = 339.36$

Monoclinic,  $P2_1/c$

$a = 9.1398$  (2) Å

$b = 11.1525$  (2) Å

$c = 16.3795$  (3) Å

$\beta = 97.081$  (2)°

$V = 1656.85$  (6) Å<sup>3</sup>

$Z = 4$

$F(000) = 712$

$D_x = 1.360$  Mg m<sup>-3</sup>

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

Cell parameters from 78897 reflections

$\theta = 2.2$ – $36.1$ °

$\mu = 0.22$  mm<sup>-1</sup>

$T = 100$  K

Tablet, colourless

$0.24 \times 0.20 \times 0.08$  mm

#### Data collection

XtaLAB Synergy, Single source at offset/far,

HyPix

diffractometer

Radiation source: micro-focus sealed X-ray tube

Detector resolution: 10.0000 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan

(*CrysAlisPro*; Rigaku OD, 2021)

$T_{\min} = 0.805$ ,  $T_{\max} = 1.000$

128543 measured reflections

7466 independent reflections

6502 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.040$

$\theta_{\max} = 35.9$ °,  $\theta_{\min} = 2.2$ °

$h = -14$ → $15$

$k = -17$ → $18$

$l = -26$ → $26$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.094$

$S = 1.05$

7466 reflections

218 parameters

0 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0543P)^2 + 0.3217P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.58 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.30 \text{ e } \text{\AA}^{-3}$$

### Special details

**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.

Least-squares planes (x,y,z in crystal coordinates) and deviations from them (\* indicates atom used to define plane)

- 0.4791 (0.0031) x - 2.3604 (0.0036) y + 15.9693 (0.0013) z = 2.0024 (0.0032)

\* 0.0342 (0.0004) N1 \* -0.0209 (0.0004) N2 \* -0.0003 (0.0004) C3 \* 0.0215 (0.0004) C4 \* -0.0345 (0.0004) C5 -0.8468 (0.0010) C6 0.0094 (0.0011) N3 -0.1626 (0.0011) O1 1.2344 (0.0008) S1

Rms deviation of fitted atoms = 0.0255

7.3350 (0.0016) x - 0.2526 (0.0037) y + 8.0701 (0.0042) z = 9.4209 (0.0022)

Angle to previous plane (with approximate esd) = 57.006 ( 0.025 )

\* -0.0031 (0.0005) C10 \* -0.0009 (0.0005) C11 \* 0.0057 (0.0006) C12 \* -0.0065 (0.0005) C13 \* 0.0025 (0.0005) C14 \* 0.0022 (0.0005) C15 -0.0668 (0.0010) S1 -0.0236 (0.0012) C16

Rms deviation of fitted atoms = 0.0040

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.71924 (7)	0.51318 (5)	0.22496 (4)	0.01525 (10)
N2	0.80727 (6)	0.61874 (5)	0.23976 (3)	0.01313 (9)
C3	0.70693 (7)	0.71323 (6)	0.25200 (4)	0.01349 (10)
C4	0.56556 (7)	0.67098 (6)	0.24288 (4)	0.01709 (11)
H4	0.479736	0.716052	0.249768	0.021*
C5	0.56954 (8)	0.54779 (6)	0.22128 (4)	0.01753 (12)
O1	0.47057 (7)	0.47513 (6)	0.19955 (4)	0.02624 (12)
N3	0.75894 (7)	0.82301 (5)	0.27039 (4)	0.01797 (11)
H01	0.6933 (15)	0.8832 (12)	0.2762 (8)	0.029 (3)*
H02	0.8476 (15)	0.8402 (12)	0.2619 (8)	0.029 (3)*
C6	0.75926 (9)	0.43604 (6)	0.15959 (4)	0.01874 (12)
H6A	0.692061	0.366114	0.153801	0.022*
H6B	0.860733	0.405756	0.174982	0.022*
C7	0.75148 (8)	0.50043 (6)	0.07754 (4)	0.01746 (12)
C8	0.81058 (10)	0.48513 (7)	-0.05858 (5)	0.02349 (14)
H8A	0.884230	0.550504	-0.056465	0.028*
H8B	0.712342	0.518726	-0.078401	0.028*
O2	0.70022 (8)	0.59873 (5)	0.06371 (4)	0.02588 (12)
O3	0.80980 (7)	0.43200 (5)	0.02284 (3)	0.02152 (11)
C9	0.84936 (12)	0.38700 (8)	-0.11506 (5)	0.02858 (17)
H9A	0.856512	0.420399	-0.169766	0.043*
H9B	0.772657	0.325136	-0.119119	0.043*
H9C	0.944187	0.351494	-0.093111	0.043*
S1	0.94519 (2)	0.59188 (2)	0.31853 (2)	0.01400 (4)
O4	1.02319 (6)	0.70299 (5)	0.33031 (4)	0.02030 (10)
O5	1.01852 (6)	0.48758 (5)	0.29250 (3)	0.01987 (10)
C10	0.85810 (7)	0.55582 (6)	0.40445 (4)	0.01440 (10)
C11	0.83563 (9)	0.43557 (6)	0.42138 (4)	0.01902 (12)

H11	0.869968	0.374683	0.387917	0.023*
C12	0.76214 (9)	0.40563 (7)	0.48806 (5)	0.02152 (13)
H12	0.747436	0.323625	0.500452	0.026*
C13	0.70971 (8)	0.49456 (7)	0.53699 (4)	0.01845 (12)
C14	0.73476 (9)	0.61451 (7)	0.51909 (5)	0.02110 (13)
H14	0.700833	0.675486	0.552637	0.025*
C15	0.80858 (9)	0.64644 (6)	0.45295 (4)	0.01932 (12)
H15	0.824955	0.728372	0.441058	0.023*
C16	0.62816 (9)	0.46037 (9)	0.60792 (5)	0.02581 (15)
H16A	0.699167	0.440717	0.655867	0.039*
H16B	0.565744	0.390460	0.592686	0.039*
H16C	0.566462	0.527646	0.621388	0.039*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.0188 (2)	0.0120 (2)	0.0151 (2)	-0.00278 (17)	0.00269 (18)	-0.00152 (17)
N2	0.0136 (2)	0.0110 (2)	0.0147 (2)	-0.00006 (16)	0.00156 (16)	-0.00001 (16)
C3	0.0135 (2)	0.0126 (2)	0.0146 (2)	0.00057 (18)	0.00261 (18)	0.00023 (18)
C4	0.0130 (2)	0.0188 (3)	0.0197 (3)	-0.0009 (2)	0.0032 (2)	-0.0015 (2)
C5	0.0173 (3)	0.0193 (3)	0.0161 (3)	-0.0050 (2)	0.0029 (2)	-0.0004 (2)
O1	0.0242 (3)	0.0283 (3)	0.0262 (3)	-0.0140 (2)	0.0030 (2)	-0.0038 (2)
N3	0.0167 (2)	0.0115 (2)	0.0261 (3)	-0.00030 (18)	0.0040 (2)	-0.00131 (19)
C6	0.0296 (3)	0.0122 (2)	0.0145 (3)	0.0014 (2)	0.0028 (2)	-0.0007 (2)
C7	0.0228 (3)	0.0151 (3)	0.0142 (3)	0.0014 (2)	0.0011 (2)	-0.0009 (2)
C8	0.0373 (4)	0.0182 (3)	0.0157 (3)	0.0052 (3)	0.0060 (3)	0.0023 (2)
O2	0.0418 (3)	0.0172 (2)	0.0188 (2)	0.0097 (2)	0.0042 (2)	0.00153 (18)
O3	0.0327 (3)	0.0179 (2)	0.0144 (2)	0.0073 (2)	0.00453 (19)	0.00122 (17)
C9	0.0462 (5)	0.0220 (3)	0.0196 (3)	0.0069 (3)	0.0121 (3)	0.0011 (3)
S1	0.01253 (7)	0.01380 (7)	0.01577 (7)	0.00071 (4)	0.00218 (5)	0.00157 (5)
O4	0.0162 (2)	0.0189 (2)	0.0251 (2)	-0.00522 (17)	-0.00029 (18)	0.00314 (18)
O5	0.0189 (2)	0.0205 (2)	0.0210 (2)	0.00769 (18)	0.00564 (18)	0.00221 (18)
C10	0.0165 (3)	0.0128 (2)	0.0139 (2)	0.00007 (19)	0.00173 (19)	-0.00002 (19)
C11	0.0266 (3)	0.0136 (3)	0.0178 (3)	0.0004 (2)	0.0068 (2)	0.0007 (2)
C12	0.0293 (4)	0.0174 (3)	0.0188 (3)	-0.0025 (2)	0.0070 (3)	0.0021 (2)
C13	0.0172 (3)	0.0239 (3)	0.0141 (3)	-0.0017 (2)	0.0014 (2)	-0.0004 (2)
C14	0.0251 (3)	0.0207 (3)	0.0182 (3)	0.0013 (2)	0.0052 (2)	-0.0039 (2)
C15	0.0255 (3)	0.0142 (3)	0.0187 (3)	0.0004 (2)	0.0045 (2)	-0.0026 (2)
C16	0.0223 (3)	0.0393 (4)	0.0165 (3)	-0.0045 (3)	0.0053 (2)	0.0009 (3)

*Geometric parameters (Å, °)*

N1—C5	1.4157 (9)	C13—C14	1.3944 (11)
N1—N2	1.4296 (8)	C13—C16	1.5046 (10)
N1—C6	1.4549 (9)	C14—C15	1.3913 (11)
N2—C3	1.4273 (8)	C4—H4	0.9500
N2—S1	1.7154 (6)	N3—H01	0.913 (13)
C3—N3	1.3343 (8)	N3—H02	0.861 (13)

C3—C4	1.3661 (9)	C6—H6A	0.9900
C4—C5	1.4203 (10)	C6—H6B	0.9900
C5—O1	1.2337 (8)	C8—H8A	0.9900
C6—C7	1.5177 (10)	C8—H8B	0.9900
C7—O2	1.2027 (8)	C9—H9A	0.9800
C7—O3	1.3367 (9)	C9—H9B	0.9800
C8—O3	1.4601 (9)	C9—H9C	0.9800
C8—C9	1.5033 (11)	C11—H11	0.9500
S1—O4	1.4308 (6)	C12—H12	0.9500
S1—O5	1.4334 (5)	C14—H14	0.9500
S1—C10	1.7470 (7)	C15—H15	0.9500
C10—C11	1.3899 (9)	C16—H16A	0.9800
C10—C15	1.3950 (9)	C16—H16B	0.9800
C11—C12	1.3914 (10)	C16—H16C	0.9800
C12—C13	1.3966 (11)		
C5—N1—N2	107.67 (5)	C3—C4—H4	126.0
C5—N1—C6	117.34 (6)	C5—C4—H4	126.0
N2—N1—C6	115.11 (5)	C3—N3—H01	118.5 (8)
C3—N2—N1	105.89 (5)	C3—N3—H02	119.0 (9)
C3—N2—S1	116.65 (4)	H01—N3—H02	119.8 (12)
N1—N2—S1	109.25 (4)	N1—C6—H6A	109.1
N3—C3—C4	130.31 (6)	C7—C6—H6A	109.1
N3—C3—N2	119.47 (6)	N1—C6—H6B	109.1
C4—C3—N2	110.21 (6)	C7—C6—H6B	109.1
C3—C4—C5	107.94 (6)	H6A—C6—H6B	107.8
O1—C5—N1	120.24 (7)	O3—C8—H8A	110.3
O1—C5—C4	131.82 (7)	C9—C8—H8A	110.3
N1—C5—C4	107.90 (6)	O3—C8—H8B	110.3
N1—C6—C7	112.54 (6)	C9—C8—H8B	110.3
O2—C7—O3	124.92 (7)	H8A—C8—H8B	108.5
O2—C7—C6	124.94 (7)	C8—C9—H9A	109.5
O3—C7—C6	110.15 (6)	C8—C9—H9B	109.5
O3—C8—C9	107.14 (6)	H9A—C9—H9B	109.5
C7—O3—C8	115.33 (6)	C8—C9—H9C	109.5
O4—S1—O5	119.96 (4)	H9A—C9—H9C	109.5
O4—S1—N2	104.95 (3)	H9B—C9—H9C	109.5
O5—S1—N2	104.19 (3)	C10—C11—H11	120.5
O4—S1—C10	111.08 (3)	C12—C11—H11	120.5
O5—S1—C10	109.21 (3)	C11—C12—H12	119.6
N2—S1—C10	106.30 (3)	C13—C12—H12	119.6
C11—C10—C15	121.27 (6)	C15—C14—H14	119.4
C11—C10—S1	118.43 (5)	C13—C14—H14	119.4
C15—C10—S1	120.27 (5)	C14—C15—H15	120.6
C10—C11—C12	119.05 (6)	C10—C15—H15	120.6
C11—C12—C13	120.87 (7)	C13—C16—H16A	109.5
C14—C13—C12	118.93 (6)	C13—C16—H16B	109.5
C14—C13—C16	121.02 (7)	H16A—C16—H16B	109.5

C12—C13—C16	120.05 (7)	C13—C16—H16C	109.5
C15—C14—C13	121.14 (7)	H16A—C16—H16C	109.5
C14—C15—C10	118.72 (7)	H16B—C16—H16C	109.5
C5—N1—N2—C3	5.12 (7)	C3—N2—S1—O4	-58.13 (5)
C6—N1—N2—C3	138.08 (6)	N1—N2—S1—O4	-178.12 (4)
C5—N1—N2—S1	131.52 (5)	C3—N2—S1—O5	174.95 (5)
C6—N1—N2—S1	-95.52 (6)	N1—N2—S1—O5	54.96 (5)
N1—N2—C3—N3	177.46 (6)	C3—N2—S1—C10	59.64 (5)
S1—N2—C3—N3	55.69 (7)	N1—N2—S1—C10	-60.35 (5)
N1—N2—C3—C4	-1.86 (7)	O4—S1—C10—C11	-151.48 (6)
S1—N2—C3—C4	-123.63 (5)	O5—S1—C10—C11	-16.96 (7)
N3—C3—C4—C5	178.65 (7)	N2—S1—C10—C11	94.90 (6)
N2—C3—C4—C5	-2.13 (8)	O4—S1—C10—C15	30.51 (7)
N2—N1—C5—O1	171.51 (6)	O5—S1—C10—C15	165.03 (6)
C6—N1—C5—O1	39.75 (9)	N2—S1—C10—C15	-83.11 (6)
N2—N1—C5—C4	-6.48 (7)	C15—C10—C11—C12	0.06 (11)
C6—N1—C5—C4	-138.24 (6)	S1—C10—C11—C12	-177.93 (6)
C3—C4—C5—O1	-172.33 (8)	C10—C11—C12—C13	0.78 (12)
C3—C4—C5—N1	5.35 (8)	C11—C12—C13—C14	-1.31 (12)
C5—N1—C6—C7	69.88 (8)	C11—C12—C13—C16	178.92 (7)
N2—N1—C6—C7	-58.40 (8)	C12—C13—C14—C15	1.01 (12)
N1—C6—C7—O2	-9.23 (11)	C16—C13—C14—C15	-179.22 (7)
N1—C6—C7—O3	170.80 (6)	C13—C14—C15—C10	-0.20 (11)
O2—C7—O3—C8	0.85 (12)	C11—C10—C15—C14	-0.35 (11)
C6—C7—O3—C8	-179.18 (6)	S1—C10—C15—C14	177.60 (6)
C9—C8—O3—C7	-168.27 (7)		

## 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—H01...O1 <sup>i</sup>	0.913 (13)	1.897 (13)	2.7884 (8)	164.7 (12)
N3—H02...O4	0.861 (13)	2.394 (13)	2.8291 (8)	111.8 (10)
N3—H02...O5 <sup>ii</sup>	0.861 (13)	2.294 (13)	3.0139 (8)	141.3 (12)
C6—H6B...O4 <sup>iii</sup>	0.99	2.50	3.2642 (9)	133
C8—H8B...O1 <sup>iv</sup>	0.99	2.43	3.2663 (11)	142

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