



# Crystal structure and Hirshfeld surface analysis of (Z)-3-methyl-4-(thiophen-2-ylmethylidene)isoxazol-5(4H)-one

Rima Laroum,<sup>a</sup> Assia Benouatas,<sup>b</sup> Noudjoud Hamdouni,<sup>b\*</sup> Wissame Zemamouche,<sup>b</sup> Ali Boudjada<sup>b</sup> and Abdelmadjid Debache<sup>a</sup>

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<sup>a</sup>Laboratoire de Synthèse de Molécules d'Intérêts Biologiques, Département de Chimie, Université Mentouri Constantine, 25000, Algeria, and <sup>b</sup>Laboratoire de Cristallographie, Département de Physique, Université Mentouri Constantine, 25000, Algeria. \*Correspondence e-mail: n\_hamdouni@yahoo.fr

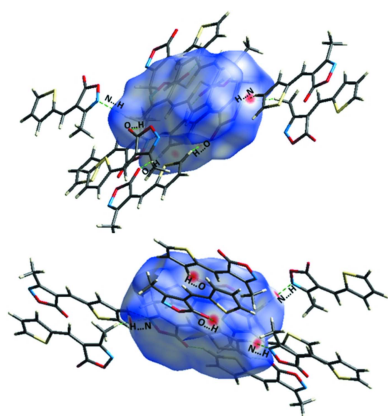
The title compound, C<sub>9</sub>H<sub>7</sub>NO<sub>2</sub>S crystallizes with two independent molecules (*A* and *B*) in the asymmetric unit with *Z* = 8. Both molecules are almost planar with a dihedral angle between the isoxazole and thiophen rings of 3.67 (2)° in molecule *A* and 10.00 (1)° in molecule *B*. The packing of molecules *A* and *B* is of an *ABAB*... type along the *b*-axis direction, the configuration about the C=C bond is *Z*. In the crystal, the presence of C—H...O, C—H...N and  $\pi$ - $\pi$  interactions [centroid-centroid distances of 3.701 (2) and 3.766 (2) Å] link the molecules into a three-dimensional architecture. An analysis of Hirshfeld surfaces shows the importance of C—H...O and C—H...N hydrogen bonds in the packing mechanism of the crystalline structure.

## 1. Chemical context

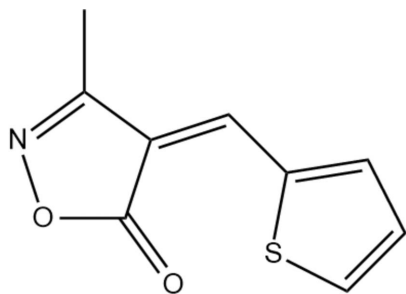
Isoxazolones show some interesting biological properties. They are inhibitors of the factorization of tumor necrosis alpha (TNF- $\alpha$ ) (Laughlin *et al.*, 2005) and antimicrobial (Mazimba *et al.*, 2014). They are used for the treatment of cerebrovascular disorders and as muscle relaxants. They are also herbicides (Tomita *et al.*, 1977) and fungicides (Miyake *et al.*, 2012). On other hand, isoxazolone derivatives constitute excellent intermediates for the synthesis of various heterocycles such as pyridopyrimidines (Tu *et al.*, 2006), quinolines (Abbiati *et al.*, 2003) and undergo various chemical transformations (Batra & Bhaduri, 1994). Some cycloaddition reactions are also described and provide access to several types of polycycles (Badrey & Gomha, 2014). For these reasons, these compounds have been the subject of several investigations. The present method for their synthesis is a three-component polycondensation between an aromatic aldehyde, ethyl acetoacetate and hydroxylamine hydrochloride under different conditions and for our part we propose here the use of K<sub>2</sub>CO<sub>3</sub>, a food additive, tolerated in organic agriculture, very inexpensive, highly available and a safe catalyst, in an aqueous medium. In the present study, we report on the synthesis, molecular and crystal structure together with a Hirshfeld surface analysis of the title isoxazole derivative.

## 2. Structural commentary

The molecular structure of the title compound is shown in (Fig. 1). It crystallizes with two independent molecules (*A* and *B*) in the asymmetric unit. The molecular structure adopts a



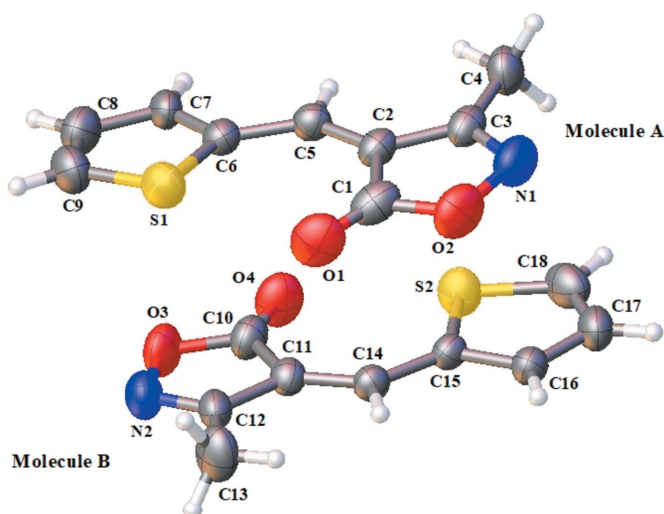
*Z*-configuration about the C=C [1.354 (3) Å in molecule *A* and 1.357 (3) Å in molecule *B*] double bonds.



The bond lengths in the two molecules are practically equal, while there are slight differences in bond angles; with for example C2–C3–C4 (molecule *A*) and C11–C12–C13 (molecule *B*) differing by 0.8 (2)°. Also, a slight difference of 0.3 (2)° is observed between the angles C2–C5–C6 and C11–C14–C15. In molecule *A*, the angle between the normal of the molecular plane (O2*A*/N1*A*/C1*A*–C3*A*) and the normal of the (S1*A*/C6*A*–C9*A*) plane is 3.67 (2)°. An important difference is observed in molecule *B*, where the angle between the normal of the molecular plane (O3*B*/N2*B*/C10*B*–C12*B*) and the normal of the (S2*B*/C15*B*–C18*B*) plane is 10.00 (1)°. In the molecular skeleton, the angle between the mean planes of the molecules *A* and *B* is 4.09 (1)°. Each of the two methyl groups, C4 and C13, has a C–H bond lying in the mean plane of the molecular skeleton, and they are oriented toward the thiophene group.

### 3. Supramolecular features

In the crystal, the structure consists of wavy layers containing molecules of the same type, forming an alternated packing described by an *ABAB*... sequence (Fig. 2). The molecules form infinite chains along the *b*-axis direction. They are linked by offset  $\pi$ - $\pi$  interactions: [*Cg*1...*Cg*2<sup>i</sup> = 3.701 (2) Å and *Cg*3...*Cg*4<sup>ii</sup> = 3.766 (2) Å where *Cg*1, *Cg*2, *Cg*3 and *Cg*4 are



**Figure 1**  
The molecular structure of the title compound, with atom labelling and displacement ellipsoids drawn at the 50% probability level.

**Table 1**  
Hydrogen-bond geometry (Å, °).

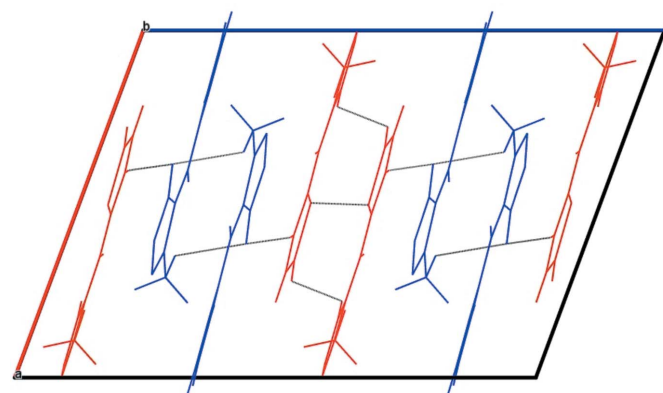
<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C7–H7...O4 <sup>i</sup>	0.93	2.51	3.387 (3)	156
C8–H8...N1 <sup>ii</sup>	0.93	2.58	3.491 (5)	166
C13–H13c...N1 <sup>iii</sup>	0.96	2.57	3.487 (4)	160

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

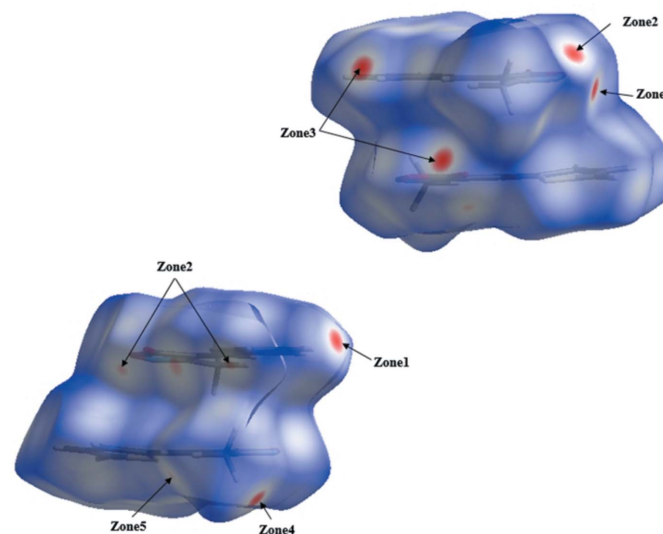
the centroids of the O2*A*/N1*A*/C1*A*–C3*A*, S2*B*/C15*B*–C18*B*, S1*A*/C6*A*–C9*A* and O3*B*/N2*B*/C10*B*–C12*B* rings, respectively; symmetry codes: (i)  $-x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (ii)  $-x, \frac{1}{2} - y, \frac{1}{2} + z$ ]. The two molecules *A* and *B* are involved in intermolecular C–H...O and C–H...N hydrogen bonds (Table 1).

### 4. Analysis of the Hirshfeld surfaces

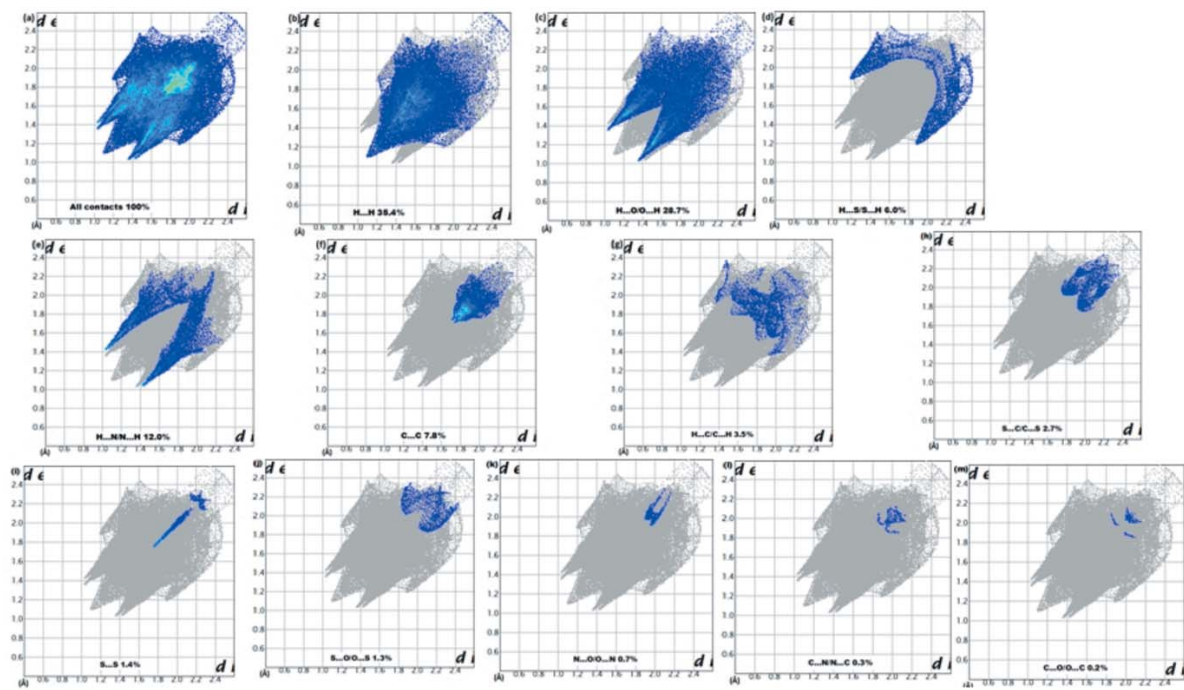
The Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) and the associated two-dimensional fingerprint plots



**Figure 2**  
A view along the *b* axis of the crystal packing of the title compound (molecule *A* in blue and molecule *B* in red).



**Figure 3**  
Two views of the Hirshfeld surface mapped over  $d_{\text{norm}}$ .

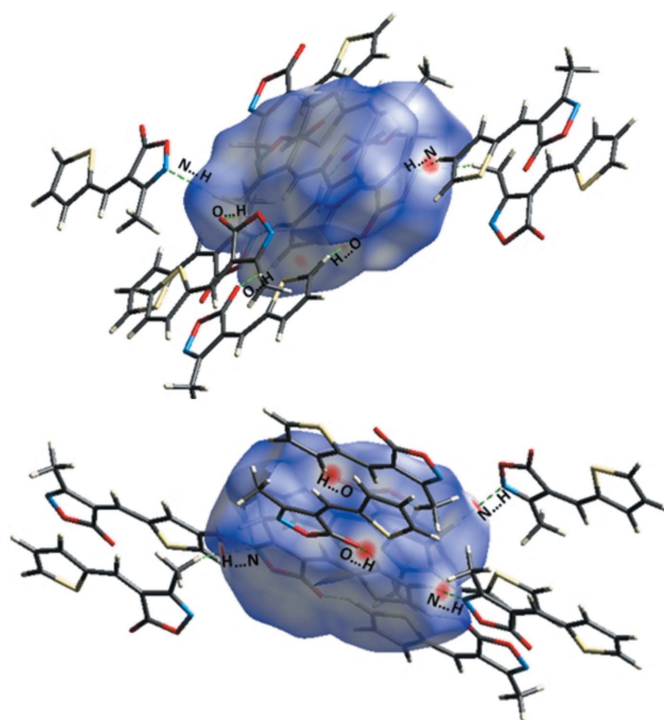


**Figure 4** Two-dimensional fingerprint plots: (a) overall, and delineated into contributions from different contacts: (b) H ··· H, (c) H ··· O/O ··· H, (d) H ··· S/S ··· H, (e) H ··· N/N ··· H and (f) C ··· C.

(McKinnon *et al.*, 2007) were generated with *CrystalExplorer* (Turner *et al.*, 2017). The analysis of Hirshfeld surface mapped over  $d_{\text{norm}}$  is shown in (Fig. 3). The interactions between the corresponding donor and acceptor atoms are visualized as bright-red spots on both sides (zones 1, 2, 3 and 4) of the Hirshfeld surfaces (Fig. 3), corresponding to C17–H17 ··· N2, C4–H4C ··· N2, C16–H16 ··· O2 and C18–H18 ··· O4 hydrogen bonds, respectively. Two other red spots exist, corresponding to C4–H4A ··· O interactions (Fig. 3, zone 5), are considered to be very weak interactions, comparing them to the van der Waals radii. The overall two-dimensional fingerprint plot of the structure and H ··· S/S ··· H, H ··· H, H ··· O/O ··· H, H ··· N/N ··· H and C ··· C contacts are illustrated in Fig. 4a–m). The H ··· H contacts, accounting for about 35.4% of the Hirshfeld surface (Fig. 4b) represent the largest contribution and are seen in the fingerprint plot as a pair of shorts pikes at  $d_e + d_i = 2.2 \text{ \AA}$ ; comparing this to van der Waals radius, we find the difference between them is about  $1 \text{ \AA}$ , which means it is a very powerful interaction. H ··· O/O ··· H contacts (Fig. 4c) make a contribution of 28.7%, with a distinctive peak in the fingerprint plot at  $d_e + d_i = 2.4 \text{ \AA}$ ; the van der Waals radius sum for this interaction is about  $2.7 \text{ \AA}$ .

The pair of short peaks at  $d_e + d_i = 3.1$ , *i.e.* almost equal to the sum of the van der Waals radius, in the fingerprint plot delineated into H ··· S/S ··· H contacts are indicative of short interatomic contacts in the crystal (6% contribution, Fig. 4d). Although the H ··· N /N ··· H interactions have a notable contribution of 12% to the Hirshfeld surface (Fig. 4e), their interatomic distances ( $d_e + d_i = 2.4 \text{ \AA}$ ) are less than their van der Waals radius ( $2.7 \text{ \AA}$ ), which means that it is a very strong interaction in this structure. The presence of  $\pi$ – $\pi$  stacking

reflects the presence of C ··· C contacts (Fig. 4f), which account for 7.9% of the Hirshfeld surface with  $d_e + d_i = 3.4 \text{ \AA}$ ; the van der Waals radius is  $3.4 \text{ \AA}$ , so we can confirm the presence of  $\pi$ – $\pi$  stacking. Two further views of the Hirshfeld surface are shown in Fig. 5.



**Figure 5** Two views of the Hirshfeld surface mapped over  $d_{\text{norm}}$ , with interactions to neighbouring molecules shown as green dashed lines.

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	C <sub>9</sub> H <sub>7</sub> NO <sub>2</sub> S
<i>M<sub>r</sub></i>	193.22
Crystal system, space group	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>c</i>
Temperature (K)	301
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.4660 (4), 12.1614 (5), 14.7636 (6)
$\beta$ (°)	110.362 (1)
<i>V</i> (Å <sup>3</sup> )	1761.71 (12)
<i>Z</i>	8
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.33
Crystal size (mm)	0.31 × 0.20 × 0.10
Data collection	
Diffraction	Agilent Technologies Xcalibur, Eos
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Agilent, 2013))
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.758, 0.968
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	72470, 6743, 4110
<i>R<sub>int</sub></i>	0.084
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.770
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.079, 0.239, 1.07
No. of reflections	6743
No. of parameters	235
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.60, -0.54

Computer programs: *CrysAlis PRO* (Agilent, 2013), *SHELXT* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *ORTEP-3 for Windows* and *WinGX* publication routines (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2020).

## 5. Database survey

A search of the Cambridge Structural Database (CSD, v5.40, last update May 2019; Groom *et al.*, 2016) for the (Z)-4-(thiophen-2-ylmethylidene)isoxazol-5(4*H*)-one unit gave five hits: 4-(2-hydroxybenzylidene)-3-methylisoxazol-5(4*H*)-one (AJESAK; Cheng *et al.*, 2009), 2-(naphthalen-1-yl)-4-(thiophen-2-ylmethylidene)-1,3-oxazol-5(4*H*)-one (ERIXIN; Gündoğdu *et al.*, 2011), (Z)-4-benzylidene-3-methylisoxazol-5(4*H*)-one (MBYIOZ01; Chandra *et al.*, 2012), 2-methyl-4-(thiophen-2-ylmethylidene)-1,3-oxazol-5(4*H*)-one (WOYPIL; Sharma *et al.*, 2015) and (Z)-4-(4-hydroxybenzylidene)-3-methylisoxazol-5(4*H*)-one (VIDSAF; Zemamouche *et al.*, 2018).

The asymmetric unit of the title compound contains two crystallographically independent molecules, as found for ERIXIN and WOYPIL while in AJESAK, MBYIOZ01 and VIDSAF, there is only one molecule per asymmetric unit. The configuration about the C=C bond is *Z* in all five compounds and in each molecule, the oxazol and thiophene rings are inclined to one another by 3.67 (2), 10.00 (1), 0.86 (9), 7.02 (8), 2.65 (16), 4.55 (15), 6.50 (1), 7.98 (8) and 3.18 (8)°, respectively.

In the crystal of WOYPIL, the individual molecules are linked *via* C—H···O hydrogen bonds, forming *ABAB* chains along the [10 $\bar{1}$ ] direction, similarly in the crystal of the title compound, the packing of molecules *A* and *B* is of an

*ABAB*··· type along the [100] direction. In our compound, the cohesion of the crystal is ensured by interactions of the type C—H···O, C—H··· $\pi$  and  $\pi$ — $\pi$  [intercentroid distances of 3.701 (2) and 3.766 (2) Å compared with 3.811 (2) and 3.889 (2) Å in ERIXIN and 3.767 (2) and 3.867 (2) Å in WOYPIL].

## 6. Synthesis and crystallization

Thiophene-2-carbaldehyde (C<sub>5</sub>H<sub>4</sub>OS, 1 mmol), hydroxylamine hydrochloride (ClH<sub>4</sub>NO, 1 mmol), ethyl acetoacetate (C<sub>6</sub>H<sub>10</sub>O<sub>3</sub>, 1 mmol) and K<sub>2</sub>CO<sub>3</sub> (5 mol%) were mixed in a 25 mL flask equipped with a magnetic stirrer. The mixture was refluxed in 5 mL of water for 3h (followed by TLC). When the reaction was judged to be finished, the mixture was gradually poured into ice-cold water. Stirring was maintained for a few minutes and the obtained solid was filtered and purified by crystallization from ethanol (yield 72%).

## 7. Refinement details

Crystal data, data collection and structure refinement details for the title compound are summarized in Table 2. H atoms were placed in calculated positions (C—H = 0.93–0.96 Å) and refined as riding with *U*<sub>iso</sub>(H) = 1.2–1.5*U*<sub>eq</sub>(C).

## Acknowledgements

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## supporting information

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## Crystal structure and Hirshfeld surface analysis of (Z)-3-methyl-4-(thiophen-2-ylmethylidene)isoxazol-5(4H)-one

Rima Laroum, Assia Benouatas, Noudjoud Hamdouni, Wissame Zemamouche, Ali Boudjada and Abdelmadjid Debache

### Computing details

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO* (Agilent, 2013); data reduction: *CrysAlis PRO* (Agilent, 2013); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 2012).

### (Z)-3-Methyl-4-(thiophen-2-ylmethylidene)isoxazol-5(4H)-one

#### Crystal data

C<sub>9</sub>H<sub>7</sub>NO<sub>2</sub>S

$M_r = 193.22$

Monoclinic, *P2<sub>1</sub>/c*

Hall symbol: -P 2ybc

$a = 10.4660$  (4) Å

$b = 12.1614$  (5) Å

$c = 14.7636$  (6) Å

$\beta = 110.362$  (1)°

$V = 1761.71$  (12) Å<sup>3</sup>

$Z = 8$

$F(000) = 800$

$D_x = 1.457$  Mg m<sup>-3</sup>

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

Cell parameters from 6745 reflections

$\theta = 2.2$ – $33.2$ °

$\mu = 0.33$  mm<sup>-1</sup>

$T = 301$  K

Needle, white

$0.31 \times 0.20 \times 0.10$  mm

#### Data collection

Agilent Technologies Xcalibur, Eos diffractometer

Radiation source: Enhance (Mo) X-ray Source

Detector resolution: 8.02 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2013)

$T_{\min} = 0.758$ ,  $T_{\max} = 0.968$

72470 measured reflections

6743 independent reflections

4110 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.084$

$\theta_{\max} = 33.2$ °,  $\theta_{\min} = 2.2$ °

$h = -16 \rightarrow 16$

$k = -18 \rightarrow 18$

$l = -22 \rightarrow 22$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.079$

$wR(F^2) = 0.239$

$S = 1.07$

6743 reflections

235 parameters

0 restraints

0 constraints

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

$$w = 1/[\sigma^2(F_o^2) + (0.1035P)^2 + 1.1548P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.60 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.54 \text{ e } \text{\AA}^{-3}$$

*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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.50289 (8)	0.12735 (6)	0.55602 (6)	0.0497 (2)
S2	0.83062 (8)	0.29525 (7)	0.33090 (6)	0.0532 (2)
O4	0.6147 (3)	0.42483 (17)	0.34895 (19)	0.0640 (6)
O3	0.3944 (3)	0.40232 (18)	0.32977 (18)	0.0637 (6)
O2	0.9633 (2)	0.1945 (2)	0.58548 (19)	0.0614 (6)
O1	0.7799 (3)	0.09198 (18)	0.57358 (19)	0.0621 (6)
N1	0.9970 (3)	0.3094 (2)	0.5893 (2)	0.0568 (7)
C5	0.6521 (2)	0.32586 (19)	0.57740 (17)	0.0341 (5)
H5	0.644338	0.401627	0.582265	0.041*
C11	0.5024 (3)	0.2451 (2)	0.31621 (16)	0.0363 (5)
N2	0.2960 (3)	0.3124 (2)	0.3099 (2)	0.0592 (7)
C14	0.5970 (3)	0.1692 (2)	0.31523 (17)	0.0361 (5)
H14	0.563541	0.097687	0.305693	0.043*
C3	0.8908 (3)	0.3632 (2)	0.58677 (19)	0.0418 (6)
C16	0.8203 (3)	0.0795 (3)	0.3326 (2)	0.0465 (6)
H16	0.79039	0.007312	0.331323	0.056*
C15	0.7368 (3)	0.1771 (2)	0.32585 (17)	0.0364 (5)
C6	0.5301 (2)	0.2673 (2)	0.56833 (16)	0.0324 (4)
C9	0.3378 (3)	0.1419 (3)	0.5469 (2)	0.0550 (8)
H9	0.277609	0.083236	0.537456	0.066*
C10	0.5189 (3)	0.3637 (2)	0.3330 (2)	0.0465 (6)
C12	0.3616 (3)	0.2241 (2)	0.30278 (18)	0.0416 (6)
C7	0.4104 (3)	0.3206 (2)	0.56579 (19)	0.0418 (6)
H7	0.403306	0.39636	0.570886	0.05*
C2	0.7769 (2)	0.2927 (2)	0.58031 (17)	0.0355 (5)
C8	0.3026 (3)	0.2476 (3)	0.5548 (2)	0.0519 (7)
H8	0.216544	0.269318	0.553016	0.062*
C1	0.8307 (3)	0.1822 (2)	0.5786 (2)	0.0443 (6)
C13	0.2887 (3)	0.1175 (3)	0.2820 (2)	0.0532 (7)
H13A	0.350705	0.060565	0.279027	0.08*
H13B	0.253353	0.100902	0.332377	0.08*
H13C	0.214967	0.121852	0.221289	0.08*
C18	0.9717 (3)	0.2218 (3)	0.3399 (3)	0.0583 (8)
H18	1.053929	0.253953	0.343547	0.07*
C4	0.8928 (4)	0.4854 (3)	0.5881 (3)	0.0646 (9)
H4A	0.805554	0.512482	0.585866	0.097*

H4B	0.961917	0.510612	0.646195	0.097*
H4C	0.912103	0.512135	0.533023	0.097*
C17	0.9534 (3)	0.1117 (3)	0.3413 (3)	0.0566 (8)
H17	1.022934	0.061462	0.347417	0.068*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0513 (4)	0.0345 (3)	0.0660 (5)	−0.0054 (3)	0.0238 (3)	−0.0015 (3)
S2	0.0498 (4)	0.0494 (4)	0.0636 (5)	−0.0118 (3)	0.0237 (3)	−0.0100 (3)
O4	0.0809 (17)	0.0329 (10)	0.0859 (16)	−0.0047 (11)	0.0387 (14)	−0.0056 (10)
O3	0.0730 (16)	0.0448 (12)	0.0793 (15)	0.0232 (11)	0.0341 (13)	0.0034 (11)
O2	0.0423 (11)	0.0631 (14)	0.0834 (16)	0.0140 (10)	0.0278 (11)	−0.0066 (12)
O1	0.0627 (14)	0.0389 (11)	0.0916 (17)	0.0077 (10)	0.0354 (13)	−0.0033 (11)
N1	0.0374 (12)	0.0693 (18)	0.0679 (16)	−0.0039 (12)	0.0237 (11)	−0.0109 (13)
C5	0.0345 (11)	0.0299 (10)	0.0394 (11)	0.0009 (9)	0.0147 (9)	−0.0022 (8)
C11	0.0417 (12)	0.0362 (12)	0.0331 (11)	0.0051 (10)	0.0157 (9)	0.0013 (9)
N2	0.0530 (15)	0.0618 (17)	0.0671 (16)	0.0191 (13)	0.0263 (13)	0.0006 (13)
C14	0.0374 (12)	0.0318 (11)	0.0422 (12)	−0.0015 (9)	0.0176 (10)	−0.0020 (9)
C3	0.0337 (12)	0.0526 (15)	0.0426 (12)	−0.0043 (11)	0.0176 (10)	−0.0049 (11)
C16	0.0339 (12)	0.0606 (17)	0.0494 (14)	−0.0057 (12)	0.0203 (11)	−0.0100 (12)
C15	0.0354 (12)	0.0373 (12)	0.0385 (11)	−0.0018 (9)	0.0152 (9)	−0.0033 (9)
C6	0.0322 (11)	0.0333 (11)	0.0336 (10)	−0.0009 (8)	0.0139 (8)	−0.0031 (8)
C9	0.0515 (17)	0.0628 (19)	0.0546 (16)	−0.0228 (15)	0.0234 (14)	−0.0033 (14)
C10	0.0633 (18)	0.0370 (13)	0.0442 (13)	0.0105 (12)	0.0250 (13)	0.0043 (10)
C12	0.0399 (13)	0.0478 (14)	0.0395 (12)	0.0097 (11)	0.0168 (10)	0.0036 (10)
C7	0.0351 (12)	0.0447 (14)	0.0470 (13)	0.0004 (10)	0.0159 (10)	−0.0069 (11)
C2	0.0322 (11)	0.0377 (12)	0.0384 (11)	−0.0002 (9)	0.0147 (9)	−0.0011 (9)
C8	0.0327 (12)	0.072 (2)	0.0532 (15)	−0.0035 (13)	0.0182 (11)	−0.0082 (14)
C1	0.0399 (14)	0.0447 (14)	0.0525 (14)	0.0071 (11)	0.0212 (11)	−0.0010 (11)
C13	0.0348 (13)	0.0605 (18)	0.0669 (18)	0.0018 (12)	0.0209 (13)	−0.0016 (14)
C18	0.0392 (15)	0.068 (2)	0.070 (2)	−0.0122 (14)	0.0218 (14)	−0.0102 (16)
C4	0.0546 (19)	0.0530 (18)	0.093 (2)	−0.0161 (15)	0.0339 (18)	−0.0061 (17)
C17	0.0416 (15)	0.064 (2)	0.0678 (19)	0.0066 (14)	0.0238 (14)	−0.0052 (15)

*Geometric parameters (Å, °)*

S1—C9	1.695 (3)	C3—C4	1.487 (4)
S1—C6	1.725 (2)	C16—C17	1.410 (4)
S2—C18	1.691 (4)	C16—C15	1.457 (4)
S2—C15	1.727 (3)	C16—H16	0.93
O4—C10	1.204 (4)	C6—C7	1.399 (3)
O3—C10	1.370 (4)	C9—C8	1.354 (5)
O3—N2	1.460 (4)	C9—H9	0.93
O2—C1	1.365 (4)	C12—C13	1.481 (4)
O2—N1	1.437 (4)	C7—C8	1.400 (4)
O1—C1	1.210 (4)	C7—H7	0.93
N1—C3	1.280 (4)	C2—C1	1.460 (4)



C5—C2	1.354 (3)	C8—H8	0.93
C5—C6	1.427 (3)	C13—H13A	0.96
C5—H5	0.93	C13—H13B	0.96
C11—C14	1.357 (3)	C13—H13C	0.96
C11—C12	1.440 (4)	C18—C17	1.354 (5)
C11—C10	1.463 (4)	C18—H18	0.93
N2—C12	1.299 (4)	C4—H4A	0.96
C14—C15	1.420 (3)	C4—H4B	0.96
C14—H14	0.93	C4—H4C	0.96
C3—C2	1.444 (4)	C17—H17	0.93
C9—S1—C6	91.80 (14)	N2—C12—C11	112.7 (3)
C18—S2—C15	91.80 (15)	N2—C12—C13	119.5 (3)
C10—O3—N2	110.2 (2)	C11—C12—C13	127.8 (2)
C1—O2—N1	109.8 (2)	C6—C7—C8	112.8 (3)
C3—N1—O2	107.3 (2)	C6—C7—H7	123.6
C2—C5—C6	132.6 (2)	C8—C7—H7	123.6
C2—C5—H5	113.7	C5—C2—C3	126.2 (2)
C6—C5—H5	113.7	C5—C2—C1	130.3 (2)
C14—C11—C12	126.4 (2)	C3—C2—C1	103.5 (2)
C14—C11—C10	129.0 (3)	C9—C8—C7	112.3 (3)
C12—C11—C10	104.6 (2)	C9—C8—H8	123.9
C12—N2—O3	106.3 (3)	C7—C8—H8	123.9
C11—C14—C15	132.9 (2)	O1—C1—O2	121.1 (3)
C11—C14—H14	113.6	O1—C1—C2	132.2 (3)
C15—C14—H14	113.6	O2—C1—C2	106.6 (2)
N1—C3—C2	112.8 (3)	C12—C13—H13A	109.5
N1—C3—C4	120.2 (3)	C12—C13—H13B	109.5
C2—C3—C4	127.0 (3)	H13A—C13—H13B	109.5
C17—C16—C15	109.3 (3)	C12—C13—H13C	109.5
C17—C16—H16	125.4	H13A—C13—H13C	109.5
C15—C16—H16	125.4	H13B—C13—H13C	109.5
C14—C15—C16	121.5 (2)	C17—C18—S2	113.6 (2)
C14—C15—S2	127.6 (2)	C17—C18—H18	123.2
C16—C15—S2	110.91 (19)	S2—C18—H18	123.2
C7—C6—C5	122.3 (2)	C3—C4—H4A	109.5
C7—C6—S1	109.93 (19)	C3—C4—H4B	109.5
C5—C6—S1	127.71 (18)	H4A—C4—H4B	109.5
C8—C9—S1	113.2 (2)	C3—C4—H4C	109.5
C8—C9—H9	123.4	H4A—C4—H4C	109.5
S1—C9—H9	123.4	H4B—C4—H4C	109.5
O4—C10—O3	120.8 (3)	C18—C17—C16	114.4 (3)
O4—C10—C11	133.0 (3)	C18—C17—H17	122.8
O3—C10—C11	106.1 (3)	C16—C17—H17	122.8
C1—O2—N1—C3	1.2 (3)	O3—N2—C12—C13	-179.7 (2)
C10—O3—N2—C12	0.6 (3)	C14—C11—C12—N2	178.3 (3)
C12—C11—C14—C15	179.0 (3)	C10—C11—C12—N2	-0.4 (3)

C10—C11—C14—C15	-2.7 (5)	C14—C11—C12—C13	-2.2 (4)
O2—N1—C3—C2	-0.5 (3)	C10—C11—C12—C13	179.2 (3)
O2—N1—C3—C4	-179.0 (3)	C5—C6—C7—C8	178.9 (2)
C11—C14—C15—C16	173.0 (3)	S1—C6—C7—C8	0.4 (3)
C11—C14—C15—S2	-8.0 (4)	C6—C5—C2—C3	177.9 (2)
C17—C16—C15—C14	179.2 (2)	C6—C5—C2—C1	-2.6 (5)
C17—C16—C15—S2	0.0 (3)	N1—C3—C2—C5	179.3 (3)
C18—S2—C15—C14	-178.4 (2)	C4—C3—C2—C5	-2.3 (5)
C18—S2—C15—C16	0.7 (2)	N1—C3—C2—C1	-0.3 (3)
C2—C5—C6—C7	-179.2 (3)	C4—C3—C2—C1	178.1 (3)
C2—C5—C6—S1	-0.9 (4)	S1—C9—C8—C7	1.8 (4)
C9—S1—C6—C7	0.5 (2)	C6—C7—C8—C9	-1.4 (4)
C9—S1—C6—C5	-177.9 (2)	N1—O2—C1—O1	179.3 (3)
C6—S1—C9—C8	-1.3 (3)	N1—O2—C1—C2	-1.4 (3)
N2—O3—C10—O4	-179.7 (3)	C5—C2—C1—O1	0.6 (6)
N2—O3—C10—C11	-0.8 (3)	C3—C2—C1—O1	-179.8 (3)
C14—C11—C10—O4	0.8 (5)	C5—C2—C1—O2	-178.6 (3)
C12—C11—C10—O4	179.4 (3)	C3—C2—C1—O2	1.0 (3)
C14—C11—C10—O3	-177.9 (2)	C15—S2—C18—C17	-1.2 (3)
C12—C11—C10—O3	0.7 (3)	S2—C18—C17—C16	1.5 (4)
O3—N2—C12—C11	-0.1 (3)	C15—C16—C17—C18	-0.9 (4)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C7—H7 $\cdots$ O4 <sup>i</sup>	0.93	2.51	3.387 (3)	156
C8—H8 $\cdots$ N1 <sup>ii</sup>	0.93	2.58	3.491 (5)	166
C13—H13c $\cdots$ N1 <sup>iii</sup>	0.96	2.57	3.487 (4)	160

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