



# Synthesis, crystal structure and Hirshfeld surface of ethyl 2-[2-(methylsulfonyl)-5-oxo-4,4-diphenyl-4,5-dihydro-1*H*-imidazol-1-yl]acetate (thiophenytoin derivative)

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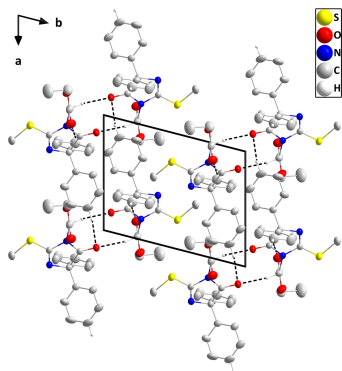
**Supporting information:** this article has supporting information at journals.iucr.org/e

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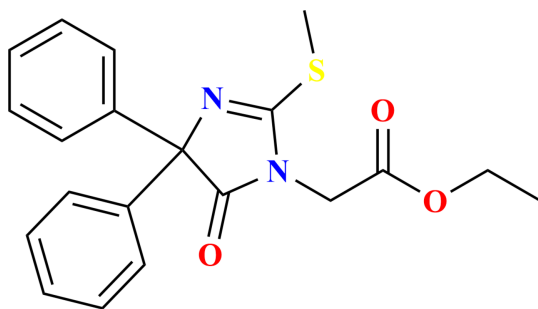
The dihydroimidazole ring in the title molecule, C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>S, is slightly distorted and the lone pair on the tri-coordinate nitrogen atom is involved in intra-ring  $\pi$  bonding. The methylsulfonyl substituent lies nearly in the plane of the five-membered ring while the ester substituent is rotated well out of that plane. In the crystal, C—H $\cdots$ O hydrogen bonds form inversion dimers, which are connected along the *a*- and *c*-axis directions by additional C—H $\cdots$ O hydrogen bonds, forming layers parallel to the *ac* plane. The major contributors to the Hirshfeld surface are C $\cdots$ H/H $\cdots$ C, O $\cdots$ H/H $\cdots$ O and S $\cdots$ H/H $\cdots$ S contacts at 20.5%, 14.7% and 4.9%, respectively.

## 1. Chemical context

The family of hydantoin drugs is important in medicinal chemistry because of the wide range of pharmacological activities exhibited, including antibacterial, antidiabetic, anti-inflammatory, anticonvulsant, anti-HIV and anticancer properties. Thiohydantoin, sulfur analogues of hydantoin, undergo replacement of one or both carbonyl groups with thiocarbonyl groups. This substitution enables versatile structural modifications, facilitating the customization of thiohydantoin to preferentially adopt specific structural types. Such modifications, achieved by introducing steric bulk, altering hydrophilic or hydrophobic interactions, or promoting stacking, afford control over the molecule's ability to form hydrogen-bonded arrays in the solid state. In particular, phenytoin and thiophenytoin derivatives and diphenyl-substituted hydantoin exhibit significant activity against tonic-clonic (grand mal) seizures (Cameron & Cameron, 1971). These chemicals are recognized for their anticonvulsant properties and have diverse pharmacological applications, including antifungal, herbicidal, anti-inflammatory, anti-HIV, antimicrobial, anticancer, and antibacterial activities, which vary based on the specific substitutions on the hydantoin ring (Cho *et al.*, 2019; Allah *et al.*, 2024; El Moutaouakil Ala Allah *et al.*, 2024a). The significance of this scaffold in drug discovery is underscored by several clinically used medications, including phenytoin, nitrofurantoin, and enzalutamide (Patocka *et al.*, 2020). Given the wide range of therapeutic

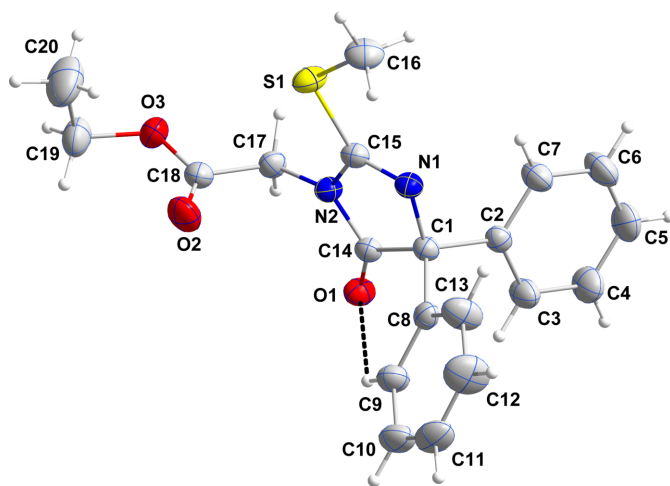


applications for such compounds, we have previously reported a route for the preparation of thiophenytaine derivatives using N-alkylation reactions carried out with ethyl bromoacetate (Guerrab *et al.*, 2020, 2022; Missioui *et al.* 2022). A similar approach yielded the title compound, C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>S (Fig. 1). In addition to the synthesis, we also report the molecular and crystal structure along with a Hirshfeld surface analysis.



## 2. Structural commentary

The dihydroimidazole ring is slightly distorted with C1 located 0.0166 (10) Å to one side of the mean plane and C14 positioned 0.0199 (10) Å on the other side (r.m.s. deviation of the fitted atoms = 0.0143 Å). The ethoxy group is disordered over two resolved sites in a 0.741 (7)/0.259 (6) ratio. The sum of the angles about N2 is 359.89 (15)°, indicating participation of its lone pair in N→C π bonding. This occurs to a slightly greater extent with C14 as the N2—C14 bond length is 1.371 (2) Å while the N2—C15 bond length is 1.406 (2) Å. By contrast, the N2—C17 bond length is 1.445 (2) Å. The C16 methyl group lies nearly in the plane of the dihydroimidazole ring as the C16—S1—C15—N2 torsion angle is −176.94 (14)° but the ester substituent is directed well out of this plane since the C15—N2—C17—C18 torsion angle is −76.6 (2)° (Fig. 2). The rotational orientation of the C8···C13 phenyl ring is partially



**Figure 1**  
The title molecule with the labeling scheme and 30% probability ellipsoids. The intramolecular C—H···O hydrogen bond is depicted by a dashed line and only the major component of the disorder is shown.

**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>
C5—H5···O2 <sup>i</sup>	0.93	2.63	3.502 (3)	156
C9—H9···O1	0.93	2.40	3.063 (3)	128
C11—H11···O1 <sup>ii</sup>	0.93	2.63	3.464 (3)	150
C17—H17A···O1 <sup>iii</sup>	0.97	2.45	3.185 (2)	132

Symmetry codes: (i) *x*, *y*, *z* + 1; (ii) *x* − 1, *y*, *z*; (iii) −*x* + 2, −*y*, −*z* + 1.

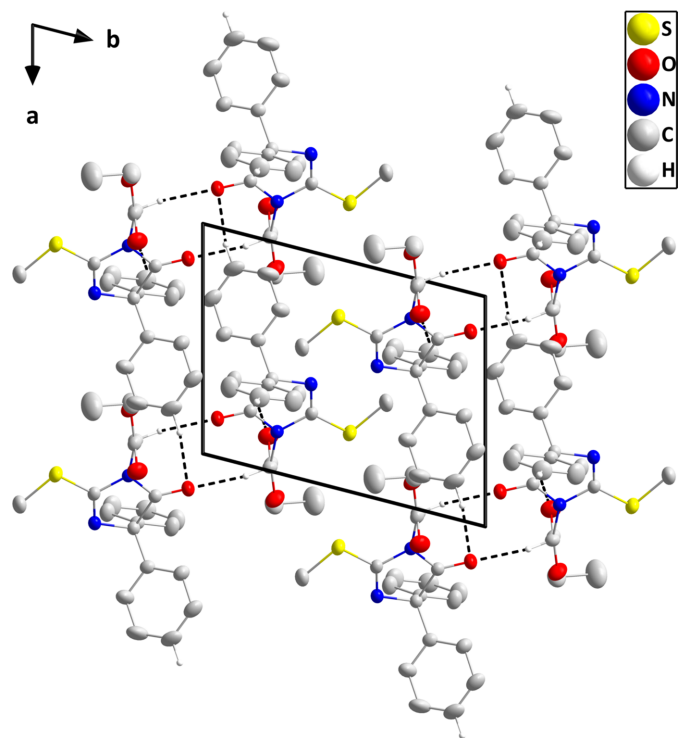
determined by the intramolecular C9—H9···O1 hydrogen bond (Fig. 2).

## 3. Supramolecular features

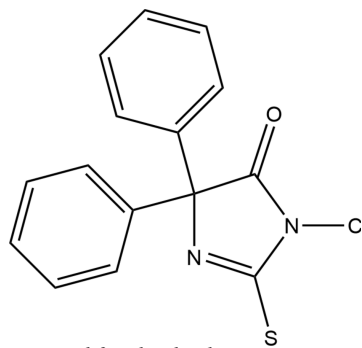
In the crystal, inversion dimers are formed by paired C17—H17A···O1 hydrogen bonds. The dimers are formed into chains extending along the *c*-axis direction by weak C5—H5···O2 hydrogen bonds and the chains are linked by weak C11—H11···O1 hydrogen bonds (Table 1) along the *a*-axis direction into layers parallel to the *ac* plane. The layers pack with normal van der Waals contacts (Fig. 2).

## 4. Database survey

A search of the Cambridge Structural Database (CSD; updated to May 31, 2024; Groom *et al.*, 2016) with the fragment shown in Fig. 3 yielded ten hits including those with methyl (YEYYA; El Moutaouakil Ala Allah *et al.*, 2023), ethyl (HOPQAI; Allah *et al.*, 2024a), *n*-propyl (RIJZIW; Akrad *et*



**Figure 2**  
Packing viewed along the *c*-axis direction giving end views of two adjacent layers. The C—H···O hydrogen bonds are depicted by dashed lines and non-interacting hydrogen atoms are omitted for clarity.



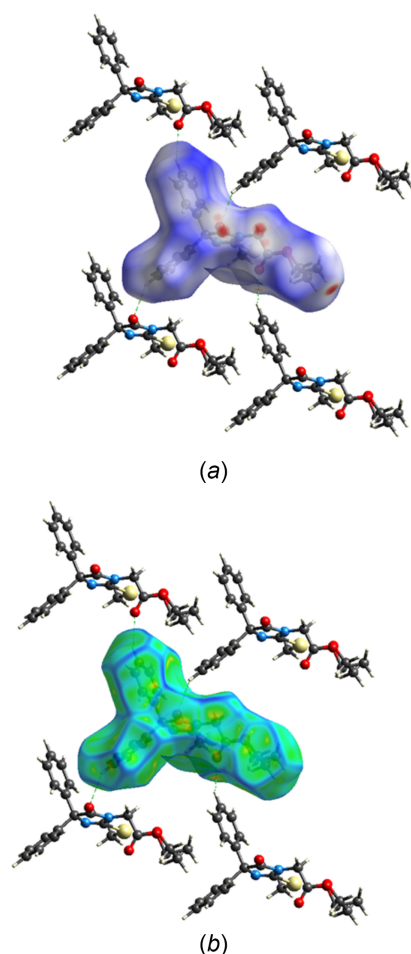
**Figure 3**  
The search fragment used for the database survey.

*al.*, 2018), benzyl (RAHGUF; Akrad *et al.*, 2017) and allyl (ROLJAH; El Moutaouakil Ala Allah *et al.*, 2024*b*) substituents on both nitrogen and sulfur. The remainder have the nitrogen and sulfur connected by a  $-\text{CH}_2\text{CH}_2-$  chain (DIYRAE; El Moutaouakil Ala Allah *et al.*, 2023), a  $-\text{CH}_2\text{CH}(\text{COOEt})-$  chain (FURFED; Karolak-Wojciechowska & Kiec-Kononowicz, 1987), a  $-\text{CH}_2\text{CH}_2\text{CH}_2-$  chain (IMTHZN; Kiec-Kononowicz *et al.*, 1981 and IMTHZN01; Guerrab *et al.*, 2019) and a  $-\text{CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_2\text{OCH}_2\text{CH}_2-$  chain (LIGWOR;

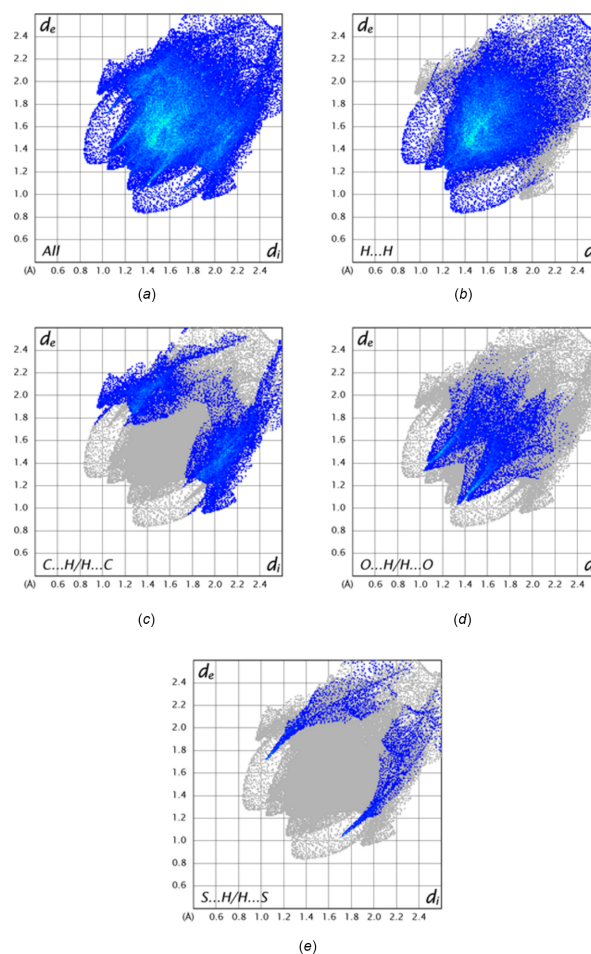
Guerrab *et al.*, 2023). In all cases, the dihydroimidazole ring is planar with the maximum deviation of a fitted atom from the mean plane ranging from 0.006 (1) Å (HOPQAI, r.m.s. deviation of the fitted atoms = 0.001 Å) to 0.023 (2) Å (RAHGUF, r.m.s. deviation of the fitted atoms = 0.002 Å) for those not have a ring fused to it and up to 0.029 (2) Å (IMTHZN01, r.m.s. deviation of the fitted atoms = 0.002 Å) where a fused ring is present. Particularly where the second ring size is relatively small (DIYRAE, FURFED, IMTHZN and IMTHZN01), it is likely that strain from the ring fusion contributes to the greater deviation from planarity. With the exception of the four just mentioned where geometrical constraints require it, all structures have the carbon attached to sulfur in the side chain very close to the mean plane of the dihydroimidazole ring as in the title molecule. The same group of structures has the  $\beta$ -carbon of the substituent on nitrogen oriented well out of that plane.

## 5. Hirshfeld surface analysis

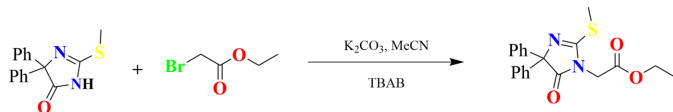
A Hirshfeld surface analysis of the intermolecular interactions of the title molecule was carried out with *Crystal Explorer 21.5*



**Figure 4**  
The Hirshfeld surface plotted over (a)  $d_{\text{norm}}$  and (b) curvature with four neighboring molecules.  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds are depicted by green dashed lines.



**Figure 5**  
Fingerprint plots showing (a) all intermolecular contacts and delineated into (b)  $\text{H}\cdots\text{H}$ , (c)  $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$ , (d)  $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$  contacts and (e)  $\text{S}\cdots\text{H}/\text{H}\cdots\text{O}$  contacts.



**Figure 6**  
Synthesis of the title compound.

(Spackman *et al.*, 2021) and descriptions of the graphical output and its interpretation have been published (Tan *et al.*, 2019). The  $d_{\text{norm}}$  surface calculated over the range  $-0.2373$  to  $1.3807$  in arbitrary units is shown in Fig. 4*a* together with four neighboring molecules illustrating the weak  $\text{C5}-\text{H5}\cdots\text{O2}$  and  $\text{C11}-\text{H11}\cdots\text{O1}$  hydrogen bonds while Fig. 4*b* shows the surface calculated over the curvature function. The latter shows that there are no extensive flat regions about the molecule, consistent with the absence of  $\pi$ -stacking interactions. Fig. 5 shows the 2-D fingerprint plot of all intermolecular interactions and those delineated into contributions from  $\text{H}\cdots\text{H}$ ,  $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$ ,  $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$  and  $\text{S}\cdots\text{H}/\text{H}\cdots\text{S}$  interactions. Here, the  $\text{H}\cdots\text{H}$  interactions comprise 56.4% of the total, consistent with the high hydrogen content of the molecule and the shape, which has many of the hydrogen atoms pointing outwards from the center of gravity. The other significant contributions are from  $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$ ,  $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$  and  $\text{S}\cdots\text{H}/\text{H}\cdots\text{S}$  contacts at 20.5%, 14.7% and 4.9%, respectively.

## 6. Synthesis and crystallization

To a solution of 2-(methylsulfanyl)-5,5-diphenyl-3,5-dihydro-4*H*-imidazol-4-one (0.5 g, 1.78 mmol) in acetonitrile (15 mL) were added  $\text{K}_2\text{CO}_3$  (0.3 g, 2 mmol) and ethyl bromoacetate (0.19 mL, 1.80 mmol) and a catalytic quantity of tetra-*n*-butylammonium bromide. The reaction scheme is shown in Fig. 6. The mixture was stirred for 8 h at room temperature. The solution was filtered and the solvent removed under reduced pressure. The solid obtained upon solvent removal was recrystallized from ethanol to afford thick, colorless, plate-like crystals of the title compound. Yield = 92%, m.p. = 515–517 K. **FT-IR** (ATR,  $\nu$ ,  $\text{cm}^{-1}$ ): 3082 (N–H), 3060 (H–C=C), 1731 (C=O), 1587, 1570, 1491, 1412 (Ar–C=C);  **$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  ppm 1.24 (*t*, 3H,  $-\text{O}-\text{CH}_2-\text{CH}_3$ ), 2.69 (*s*, 3H,  $\text{S}-\text{CH}_3$ ), 4.22 (*q*, 2H,  $-\text{O}-\text{CH}_2-\text{CH}_3$ ), 4.27 (*s*, 2H, N– $\text{CH}_2$ ), 7.25–7.54 (*m*, 10H, Ar–H);  **$^{13}\text{C}$  NMR**: 12.93 ( $-\text{O}-\text{CH}_2-\text{CH}_3$ ), 14.16 ( $-\text{S}-\text{CH}_3$ ), 41.75 ( $-\text{N}-\text{CH}_3$ ), 62.17 ( $-\text{O}-\text{CH}_2-\text{CH}_3$ ), 78.98 (C–2Ph), 127.22, 128.31, 128.76, 140.14 (C–Ar); 160.71 (C=N); 167.00 (C=O), 180.73 (C=O<sub>imidazole</sub>). **HRMS** (ESI): calculated for  $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$  [ $M - \text{H}$ ]<sup>+</sup> 369,1195; found 369,12579.

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms were included as riding contributions in idealized positions with isotropic displacement parameters tied to those of the attached atoms.

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	$\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$
$M_r$	368.44
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	293
$a, b, c$ (Å)	8.5473 (7), 10.4653 (10), 11.5360 (9)
$\alpha, \beta, \gamma$ (°)	88.258 (7), 74.622 (7), 75.593 (7)
$V$ (Å <sup>3</sup> )	962.96 (15)
$Z$	2
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>−1</sup> )	0.19
Crystal size (mm)	0.57 × 0.32 × 0.17
Data collection	
Diffractometer	SuperNova, Dual, Cu at home/ near, Atlas
Absorption correction	Gaussian ( <i>CrysAlis PRO</i> ; Rigaku OD, 2023)
$T_{\text{min}}, T_{\text{max}}$	0.592, 1.000
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	7781, 4523, 3377
$R_{\text{int}}$ ( $\sin \theta/\lambda$ ) <sub>max</sub> (Å <sup>−1</sup> )	0.019 0.699
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.050, 0.137, 1.09
No. of reflections	4523
No. of parameters	257
No. of restraints	106
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>−3</sup> )	0.24, −0.33

Computer programs: *CrysAlis PRO* (Rigaku OD, 2023), *SHELXT* (Sheldrick, 2015), *SHELXL2019/1* (Lübben *et al.*, 2019) and *DIAMOND* (Brandenburg & Putz, 2012).

The ethoxy group is disordered over two sites in a 0.741 (7)/0.259 (6) ratio. The two components were refined with restraints to make their geometries be comparable.

## Acknowledgements

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## supporting information

*Acta Cryst.* (2024). E80, 926-930 [https://doi.org/10.1107/S2056989024007345]

## Synthesis, crystal structure and Hirshfeld surface of ethyl 2-[2-(methylsulfanyl)-5-oxo-4,4-diphenyl-4,5-dihydro-1*H*-imidazol-1-yl]acetate (thiophenytin derivative)

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### Computing details

#### Ethyl 2-[2-(methylsulfanyl)-5-oxo-4,4-diphenyl-4,5-dihydro-1*H*-imidazol-1-yl]acetate

##### Crystal data

$C_{20}H_{20}N_2O_3S$

$M_r = 368.44$

Triclinic,  $P\bar{1}$

$a = 8.5473$  (7) Å

$b = 10.4653$  (10) Å

$c = 11.5360$  (9) Å

$\alpha = 88.258$  (7)°

$\beta = 74.622$  (7)°

$\gamma = 75.593$  (7)°

$V = 962.96$  (15) Å<sup>3</sup>

$Z = 2$

$F(000) = 388$

$D_x = 1.271$  Mg m<sup>-3</sup>

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

Cell parameters from 3430 reflections

$\theta = 3.9$ – $27.4$ °

$\mu = 0.19$  mm<sup>-1</sup>

$T = 293$  K

Block, colourless

$0.57 \times 0.32 \times 0.17$  mm

##### Data collection

SuperNova, Dual, Cu at home/near, Atlas diffractometer

$\omega$  scans

Absorption correction: gaussian (CrysAlisPro; Rigaku OD, 2023)

$T_{\min} = 0.592$ ,  $T_{\max} = 1.000$

7781 measured reflections

4523 independent reflections

3377 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.019$

$\theta_{\max} = 29.8$ °,  $\theta_{\min} = 3.5$ °

$h = -11 \rightarrow 11$

$k = -12 \rightarrow 13$

$l = -15 \rightarrow 14$

##### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.050$

$wR(F^2) = 0.137$

$S = 1.09$

4523 reflections

257 parameters

106 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.052P)^2 + 0.2326P]$

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

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

$\Delta\rho_{\max} = 0.24$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.32$  e Å<sup>-3</sup>

*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>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.5979 (2)	0.24490 (16)	0.72577 (15)	0.0416 (4)	
C2	0.6264 (2)	0.23182 (18)	0.85255 (15)	0.0442 (4)	
C3	0.6478 (3)	0.1096 (2)	0.90440 (19)	0.0633 (6)	
H3	0.639895	0.036969	0.863850	0.076*	
C4	0.6808 (4)	0.0945 (3)	1.0157 (2)	0.0769 (7)	
H4	0.695641	0.011916	1.049348	0.092*	
C5	0.6917 (3)	0.2012 (3)	1.0767 (2)	0.0768 (7)	
H5	0.714370	0.191190	1.151414	0.092*	
C6	0.6691 (4)	0.3215 (3)	1.0269 (2)	0.0821 (8)	
H6	0.674981	0.394015	1.068756	0.099*	
C7	0.6372 (3)	0.3383 (2)	0.91425 (19)	0.0639 (6)	
H7	0.623416	0.421097	0.880978	0.077*	
C8	0.4451 (2)	0.19605 (18)	0.72080 (15)	0.0449 (4)	
C9	0.4566 (3)	0.0756 (2)	0.67024 (19)	0.0609 (5)	
H9	0.561486	0.021073	0.634043	0.073*	
C10	0.3136 (3)	0.0344 (3)	0.6726 (2)	0.0747 (7)	
H10	0.323486	-0.046878	0.637062	0.090*	
C11	0.1604 (3)	0.1110 (3)	0.7260 (2)	0.0785 (7)	
H11	0.065117	0.081614	0.729605	0.094*	
C12	0.1461 (3)	0.2321 (3)	0.7747 (3)	0.0995 (10)	
H12	0.040598	0.285935	0.810314	0.119*	
C13	0.2884 (3)	0.2752 (3)	0.7712 (2)	0.0787 (7)	
H13	0.277336	0.358453	0.803302	0.094*	
C14	0.7617 (2)	0.16849 (17)	0.63784 (15)	0.0426 (4)	
C15	0.7038 (2)	0.38504 (17)	0.60131 (16)	0.0437 (4)	
C16	0.5733 (3)	0.6489 (2)	0.5983 (2)	0.0719 (6)	
H16A	0.470718	0.622454	0.608740	0.108*	
H16B	0.568596	0.727851	0.553355	0.108*	
H16C	0.588071	0.665361	0.675577	0.108*	
C17	0.9826 (2)	0.23788 (19)	0.47982 (16)	0.0484 (4)	
H17A	1.049766	0.152095	0.493094	0.058*	
H17B	1.039754	0.303695	0.491716	0.058*	
C18	0.9700 (3)	0.24075 (19)	0.35239 (17)	0.0532 (5)	
C19	1.1395 (8)	0.2528 (5)	0.1481 (3)	0.0862 (14)	0.741 (7)
H19A	1.075894	0.198513	0.123746	0.103*	0.741 (7)
H19B	1.257026	0.219412	0.106622	0.103*	0.741 (7)
C20	1.0784 (9)	0.3934 (5)	0.1203 (4)	0.127 (2)	0.741 (7)
H20A	0.962396	0.425004	0.162843	0.190*	0.741 (7)
H20B	1.090623	0.400299	0.035378	0.190*	0.741 (7)

H20C	1.142746	0.445500	0.144878	0.190*	0.741 (7)
O3	1.1147 (2)	0.25222 (17)	0.27909 (13)	0.0738 (5)	0.741 (7)
C19A	1.0825 (18)	0.2742 (19)	0.1595 (7)	0.084 (3)	0.259 (7)
H19C	0.975229	0.336314	0.165521	0.101*	0.259 (7)
H19D	1.083765	0.192018	0.122213	0.101*	0.259 (7)
C20A	1.223 (2)	0.3291 (17)	0.0899 (9)	0.117 (4)	0.259 (7)
H20D	1.202603	0.419795	0.114703	0.176*	0.259 (7)
H20E	1.230224	0.323440	0.005607	0.176*	0.259 (7)
H20F	1.326004	0.279434	0.104436	0.176*	0.259 (7)
O3A	1.1147 (2)	0.25222 (17)	0.27909 (13)	0.0738 (5)	0.259 (7)
N1	0.57653 (19)	0.38291 (14)	0.68826 (13)	0.0450 (3)	
N2	0.82123 (18)	0.26296 (14)	0.56738 (13)	0.0453 (3)	
O1	0.83139 (17)	0.05214 (12)	0.63157 (12)	0.0551 (3)	
O2	0.8505 (2)	0.23180 (18)	0.32206 (14)	0.0776 (5)	
S1	0.74520 (7)	0.52037 (5)	0.51841 (5)	0.06199 (18)	

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0425 (9)	0.0385 (9)	0.0441 (9)	-0.0092 (7)	-0.0129 (7)	0.0006 (7)
C2	0.0400 (9)	0.0484 (10)	0.0452 (9)	-0.0112 (7)	-0.0127 (7)	-0.0016 (7)
C3	0.0890 (16)	0.0551 (12)	0.0570 (12)	-0.0222 (11)	-0.0349 (11)	0.0072 (9)
C4	0.105 (2)	0.0726 (15)	0.0621 (14)	-0.0208 (14)	-0.0408 (14)	0.0151 (11)
C5	0.0902 (18)	0.0946 (19)	0.0543 (13)	-0.0213 (15)	-0.0359 (12)	0.0037 (12)
C6	0.110 (2)	0.0796 (17)	0.0719 (15)	-0.0264 (15)	-0.0445 (15)	-0.0138 (13)
C7	0.0821 (15)	0.0544 (12)	0.0632 (13)	-0.0175 (11)	-0.0319 (11)	-0.0033 (9)
C8	0.0445 (9)	0.0531 (10)	0.0407 (9)	-0.0151 (8)	-0.0154 (7)	0.0068 (7)
C9	0.0598 (12)	0.0613 (13)	0.0682 (13)	-0.0255 (10)	-0.0180 (10)	-0.0009 (10)
C10	0.0823 (18)	0.0812 (16)	0.0827 (16)	-0.0451 (14)	-0.0372 (14)	0.0096 (13)
C11	0.0690 (16)	0.103 (2)	0.0905 (17)	-0.0454 (15)	-0.0465 (14)	0.0271 (15)
C12	0.0446 (13)	0.113 (2)	0.139 (3)	-0.0153 (14)	-0.0239 (15)	-0.011 (2)
C13	0.0483 (12)	0.0789 (16)	0.109 (2)	-0.0124 (11)	-0.0215 (12)	-0.0191 (14)
C14	0.0427 (9)	0.0418 (9)	0.0459 (9)	-0.0120 (7)	-0.0145 (7)	0.0002 (7)
C15	0.0458 (10)	0.0384 (9)	0.0513 (10)	-0.0121 (7)	-0.0189 (8)	0.0023 (7)
C16	0.0719 (15)	0.0458 (11)	0.0958 (17)	-0.0059 (10)	-0.0274 (13)	0.0069 (11)
C17	0.0427 (9)	0.0521 (10)	0.0502 (10)	-0.0147 (8)	-0.0089 (8)	-0.0004 (8)
C18	0.0612 (12)	0.0475 (10)	0.0531 (11)	-0.0201 (9)	-0.0123 (9)	-0.0012 (8)
C19	0.100 (3)	0.087 (3)	0.055 (2)	-0.020 (2)	0.0046 (19)	0.0016 (18)
C20	0.160 (5)	0.106 (4)	0.087 (3)	-0.009 (3)	-0.013 (3)	0.030 (3)
O3	0.0843 (11)	0.0866 (11)	0.0528 (8)	-0.0398 (9)	-0.0054 (8)	0.0096 (7)
C19A	0.096 (5)	0.094 (5)	0.053 (4)	-0.028 (4)	0.001 (4)	0.002 (4)
C20A	0.119 (8)	0.145 (8)	0.075 (6)	-0.042 (7)	0.003 (6)	0.023 (6)
O3A	0.0843 (11)	0.0866 (11)	0.0528 (8)	-0.0398 (9)	-0.0054 (8)	0.0096 (7)
N1	0.0456 (8)	0.0386 (8)	0.0510 (8)	-0.0081 (6)	-0.0158 (7)	0.0022 (6)
N2	0.0427 (8)	0.0409 (8)	0.0508 (8)	-0.0112 (6)	-0.0090 (7)	0.0014 (6)
O1	0.0547 (8)	0.0396 (7)	0.0646 (8)	-0.0063 (6)	-0.0097 (6)	0.0000 (6)
O2	0.0765 (11)	0.0972 (13)	0.0711 (10)	-0.0292 (9)	-0.0318 (9)	-0.0105 (9)
S1	0.0646 (3)	0.0443 (3)	0.0763 (4)	-0.0191 (2)	-0.0135 (3)	0.0125 (2)



*Geometric parameters (Å, °)*

C1—N1	1.476 (2)	C15—N1	1.274 (2)
C1—C8	1.531 (2)	C15—N2	1.406 (2)
C1—C14	1.539 (2)	C15—S1	1.7415 (18)
C1—C2	1.542 (2)	C16—S1	1.786 (2)
C2—C7	1.376 (3)	C16—H16A	0.9600
C2—C3	1.387 (3)	C16—H16B	0.9600
C3—C4	1.382 (3)	C16—H16C	0.9600
C3—H3	0.9300	C17—N2	1.445 (2)
C4—C5	1.373 (4)	C17—C18	1.501 (3)
C4—H4	0.9300	C17—H17A	0.9700
C5—C6	1.359 (4)	C17—H17B	0.9700
C5—H5	0.9300	C18—O2	1.189 (2)
C6—C7	1.394 (3)	C18—O3A	1.331 (2)
C6—H6	0.9300	C18—O3	1.331 (2)
C7—H7	0.9300	C19—O3	1.470 (3)
C8—C13	1.372 (3)	C19—C20	1.489 (5)
C8—C9	1.376 (3)	C19—H19A	0.9700
C9—C10	1.388 (3)	C19—H19B	0.9700
C9—H9	0.9300	C20—H20A	0.9600
C10—C11	1.347 (4)	C20—H20B	0.9600
C10—H10	0.9300	C20—H20C	0.9600
C11—C12	1.366 (4)	C19A—O3A	1.477 (5)
C11—H11	0.9300	C19A—C20A	1.489 (6)
C12—C13	1.390 (3)	C19A—H19C	0.9700
C12—H12	0.9300	C19A—H19D	0.9700
C13—H13	0.9300	C20A—H20D	0.9600
C14—O1	1.210 (2)	C20A—H20E	0.9600
C14—N2	1.371 (2)	C20A—H20F	0.9600
N1—C1—C8	109.77 (14)	S1—C16—H16A	109.5
N1—C1—C14	104.73 (13)	S1—C16—H16B	109.5
C8—C1—C14	113.33 (14)	H16A—C16—H16B	109.5
N1—C1—C2	110.96 (13)	S1—C16—H16C	109.5
C8—C1—C2	111.13 (14)	H16A—C16—H16C	109.5
C14—C1—C2	106.73 (14)	H16B—C16—H16C	109.5
C7—C2—C3	118.83 (18)	N2—C17—C18	113.00 (16)
C7—C2—C1	121.37 (17)	N2—C17—H17A	109.0
C3—C2—C1	119.76 (16)	C18—C17—H17A	109.0
C4—C3—C2	120.7 (2)	N2—C17—H17B	109.0
C4—C3—H3	119.6	C18—C17—H17B	109.0
C2—C3—H3	119.6	H17A—C17—H17B	107.8
C5—C4—C3	120.1 (2)	O2—C18—O3A	125.7 (2)
C5—C4—H4	119.9	O2—C18—O3	125.7 (2)
C3—C4—H4	119.9	O2—C18—C17	125.19 (19)
C6—C5—C4	119.5 (2)	O3A—C18—C17	109.14 (18)
C6—C5—H5	120.3	O3—C18—C17	109.14 (18)

C4—C5—H5	120.3	O3—C19—C20	105.4 (3)
C5—C6—C7	121.2 (2)	O3—C19—H19A	110.7
C5—C6—H6	119.4	C20—C19—H19A	110.7
C7—C6—H6	119.4	O3—C19—H19B	110.7
C2—C7—C6	119.7 (2)	C20—C19—H19B	110.7
C2—C7—H7	120.2	H19A—C19—H19B	108.8
C6—C7—H7	120.2	C19—C20—H20A	109.5
C13—C8—C9	118.12 (19)	C19—C20—H20B	109.5
C13—C8—C1	118.49 (17)	H20A—C20—H20B	109.5
C9—C8—C1	123.38 (17)	C19—C20—H20C	109.5
C8—C9—C10	120.8 (2)	H20A—C20—H20C	109.5
C8—C9—H9	119.6	H20B—C20—H20C	109.5
C10—C9—H9	119.6	C18—O3—C19	120.7 (3)
C11—C10—C9	120.6 (2)	O3A—C19A—C20A	104.0 (6)
C11—C10—H10	119.7	O3A—C19A—H19C	111.0
C9—C10—H10	119.7	C20A—C19A—H19C	111.0
C10—C11—C12	119.5 (2)	O3A—C19A—H19D	111.0
C10—C11—H11	120.2	C20A—C19A—H19D	111.0
C12—C11—H11	120.2	H19C—C19A—H19D	109.0
C11—C12—C13	120.4 (3)	C19A—C20A—H20D	109.5
C11—C12—H12	119.8	C19A—C20A—H20E	109.5
C13—C12—H12	119.8	H20D—C20A—H20E	109.5
C8—C13—C12	120.5 (2)	C19A—C20A—H20F	109.5
C8—C13—H13	119.7	H20D—C20A—H20F	109.5
C12—C13—H13	119.7	H20E—C20A—H20F	109.5
O1—C14—N2	125.35 (16)	C18—O3A—C19A	105.2 (5)
O1—C14—C1	129.75 (16)	C15—N1—C1	106.59 (14)
N2—C14—C1	104.84 (14)	C14—N2—C15	108.10 (14)
N1—C15—N2	115.62 (15)	C14—N2—C17	124.14 (15)
N1—C15—S1	127.39 (14)	C15—N2—C17	127.65 (15)
N2—C15—S1	116.97 (13)	C15—S1—C16	100.45 (10)
N1—C1—C2—C7	-3.0 (2)	C2—C1—C14—O1	62.8 (2)
C8—C1—C2—C7	-125.40 (19)	N1—C1—C14—N2	3.28 (17)
C14—C1—C2—C7	110.6 (2)	C8—C1—C14—N2	122.90 (15)
N1—C1—C2—C3	179.46 (17)	C2—C1—C14—N2	-114.45 (15)
C8—C1—C2—C3	57.0 (2)	N2—C17—C18—O2	-17.6 (3)
C14—C1—C2—C3	-67.0 (2)	N2—C17—C18—O3A	163.59 (16)
C7—C2—C3—C4	-0.5 (3)	N2—C17—C18—O3	163.59 (16)
C1—C2—C3—C4	177.1 (2)	O2—C18—O3—C19	-0.9 (4)
C2—C3—C4—C5	0.4 (4)	C17—C18—O3—C19	177.8 (2)
C3—C4—C5—C6	0.3 (4)	C20—C19—O3—C18	88.0 (5)
C4—C5—C6—C7	-0.9 (4)	O2—C18—O3A—C19A	9.4 (8)
C3—C2—C7—C6	-0.1 (3)	C17—C18—O3A—C19A	-171.8 (8)
C1—C2—C7—C6	-177.7 (2)	C20A—C19A—O3A—C18	162.3 (12)
C5—C6—C7—C2	0.8 (4)	N2—C15—N1—C1	0.2 (2)
N1—C1—C8—C13	-47.2 (2)	S1—C15—N1—C1	178.45 (13)
C14—C1—C8—C13	-163.92 (19)	C8—C1—N1—C15	-124.10 (15)

C2—C1—C8—C13	75.9 (2)	C14—C1—N1—C15	-2.12 (18)
N1—C1—C8—C9	133.98 (19)	C2—C1—N1—C15	112.68 (16)
C14—C1—C8—C9	17.3 (2)	O1—C14—N2—C15	179.40 (17)
C2—C1—C8—C9	-102.9 (2)	C1—C14—N2—C15	-3.19 (18)
C13—C8—C9—C10	-1.4 (3)	O1—C14—N2—C17	-4.2 (3)
C1—C8—C9—C10	177.42 (19)	C1—C14—N2—C17	173.26 (15)
C8—C9—C10—C11	-0.9 (4)	N1—C15—N2—C14	2.1 (2)
C9—C10—C11—C12	2.1 (4)	S1—C15—N2—C14	-176.36 (12)
C10—C11—C12—C13	-1.1 (5)	N1—C15—N2—C17	-174.20 (16)
C9—C8—C13—C12	2.3 (4)	S1—C15—N2—C17	7.4 (2)
C1—C8—C13—C12	-176.5 (2)	C18—C17—N2—C14	107.66 (19)
C11—C12—C13—C8	-1.1 (5)	C18—C17—N2—C15	-76.6 (2)
N1—C1—C14—O1	-179.47 (18)	N1—C15—S1—C16	4.8 (2)
C8—C1—C14—O1	-59.8 (2)	N2—C15—S1—C16	-176.94 (14)

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

<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>
C5—H5 $\cdots$ O2 <sup>i</sup>	0.93	2.63	3.502 (3)	156
C9—H9 $\cdots$ O1	0.93	2.40	3.063 (3)	128
C11—H11 $\cdots$ O1 <sup>ii</sup>	0.93	2.63	3.464 (3)	150
C17—H17 <i>A</i> $\cdots$ O1 <sup>iii</sup>	0.97	2.45	3.185 (2)	132

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