Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structure and Hirshfeld surface analysis of ethyl 2-({5-acetyl-3-cyano-6-methyl-4-[(*E*)-2-phenylethenyl]pyridin-2-yl}sulfanyl)acetate

Safiyyah A. H. Al-Waleedy,[a]* Shaaban K. Mohamed,[b,c]* Joel T. Mague,[d] Mehmet Akkurt,[e] Mohamed S. Abbady[f] and Etify A. Bakhite[f]

[a]Department of Chemistry, Faculty of Science, Taiz University, Taiz, Yemen, [b]Chemistry and Environmental Division, Manchester Metropolitan University, Manchester, M1 5GD, England, [c]Chemistry Department, Faculty of Science, Minia University, 61519 El-Minia, Egypt, [d]Department of Chemistry, Tulane University, New Orleans, LA 70118, USA, [e]Department of Physics, Faculty of Sciences, Erciyes University, 38039 Kayseri, Turkey, and [f]Chemistry Department, Faculty of Science, Assiut University, Assiut 71516, Egypt. *Correspondence e-mail: safiyyahalwaleedy@gmail.com, shaabankamel@yahoo.com

Received 13 May 2021
Accepted 1 June 2021

Edited by M. Weil, Vienna University of Technology, Austria

Keywords: crystal structure; pyridine; styryl; ester; hydrogen bond; Hirshfeld surface analysis.

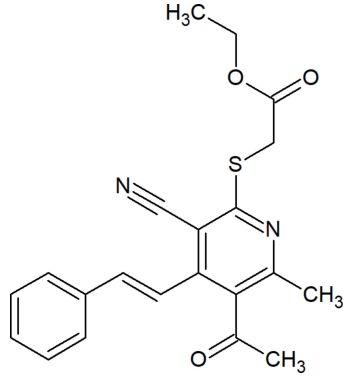
CCDC reference: 2087180

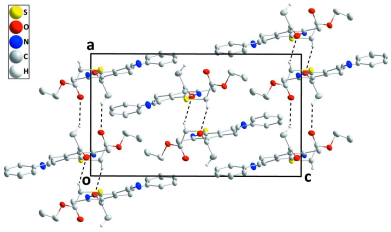
Supporting information: this article has supporting information at journals.iucr.org/e

In the title molecule, $C_{21}H_{20}N_2O_3S$, the styryl and ester substituents are displaced to opposite sides of the plane of the pyridine ring. In the crystal, C—H···O hydrogen bonds form chains extending parallel to the *a*-axis direction, which pack with partial intercalation of the styryl and ester substituents. A Hirshfeld surface analysis indicates that the most significant contributions to the crystal packing are from H···H (43.6%), C···H/H···C (15.6%), O···H/H···O (14.9%) and N···H/H···N (11.2%) contacts.

1. Chemical context

Numerous pyridine-containing natural products and synthetic organic compounds with various biophysio- and pharmacological activities have been reported (Gibson *et al.*, 2007; Vidaillac *et al.*, 2007). These scaffolds are also of widespread interest in supramolecular and coordination chemistry, as well as for materials science (Balasubramanian & Keay, 1996). The above findings promoted us to study the crystal structure of the title compound, $C_{21}H_{20}N_2O_3S$.





2. Structural commentary

The styryl substituent and the ester group are displaced to opposite sides of the plane of the pyridine ring (Fig. 1). The dihedral angle between the mean planes of the phenyl (C8–C13) and pyridine (N1/C1–C5) rings is 27.86 (3)°. The C1—C2—C14—C15 torsion angle of 68.1 (2)° indicates that the

OPEN ACCESS

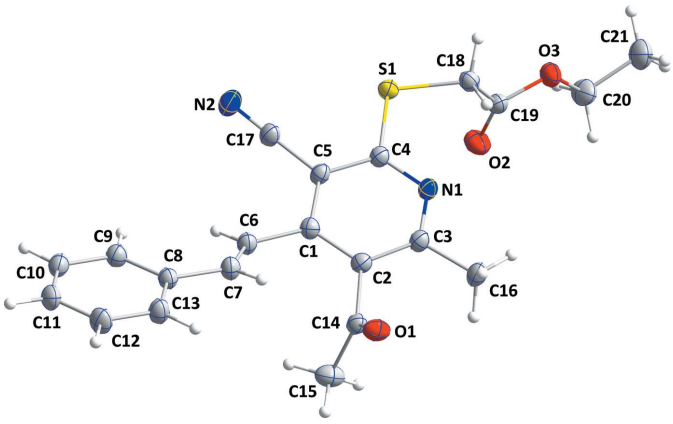


Figure 1
The title molecule with labelling scheme and displacement ellipsoids at the 50% probability level.

acetyl group is rotated well out of the plane of the pyridine ring, while the N1—C4—S1—C18 torsion angle of −5.66 (12)° shows that the link to the ester group is nearly coplanar with the pyridine ring.

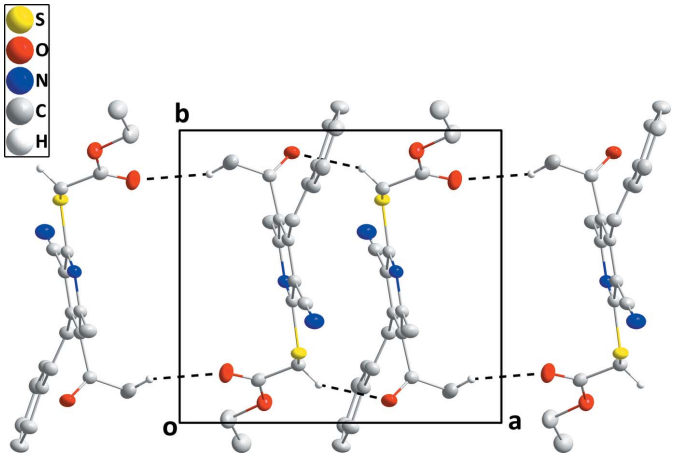


Figure 2
A portion of one hydrogen–bonded chain in a view along the *c*-axis direction. C—H···O hydrogen bonds are depicted by dashed lines.

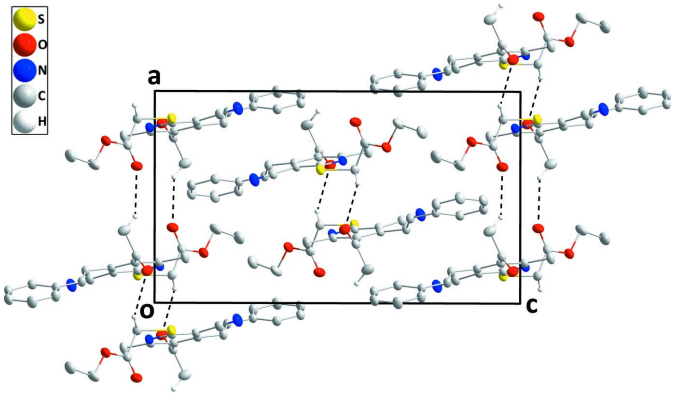


Figure 3
Packing of the molecules in the title compound in a view along the *b*-axis direction. C—H···O hydrogen bonds are depicted by dashed lines.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15*A*···O2^{i}	0.98 (2)	2.56 (2)	3.375 (2)	139.9 (17)
C18—H18*B*···O1^{ii}	0.965 (17)	2.493 (17)	3.2989 (17)	140.9 (13)

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

Table 2
Summary of short interatomic contacts (Å) in the title compound.

Contact	Distance	Symmetry operation
H20*B*···H16*B*	2.53	$x, 1+y, z$
H18*B*···H7	2.42	$1-x, 1-y, 1-z$
O2···H10	2.613	$\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
H15*A*···O2	2.56	$2-x, 1-y, 1-z$
N2···H20*A*	2.63	$-\frac{1}{2}+x, \frac{3}{2}-y, -\frac{1}{2}+z$
H11···H11	2.31	$1-x, -y, -z$
H12···H20*A*	2.47	$-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$
H16*A*···H21*B*	2.49	$\frac{3}{2}-x, -\frac{1}{2}+y, \frac{3}{2}-z$

3. Supramolecular features

In the crystal, inversion dimers are formed by intermolecular C15—H15*A*···O2 hydrogen bonds between a methyl H atom of the acetyl group and the carbonyl O atom of the ester function. These dimers are further linked by inversion-related C18—H18*B*···O1 hydrogen bonds between a methylene H atom and the carbonyl O atom of the acetyl group (Table 1) to form ribbons of molecules extending parallel to the *a*-axis direction (Fig. 2). The chains pack with a partial intercalation of the styryl and ester substituents (Fig. 3).

4. Hirshfeld surface analysis

To quantify the intermolecular interactions in the title compound, a Hirshfeld surface analysis was performed and two-dimensional fingerprint plots were generated using *Crystal Explorer* (Turner *et al.*, 2017). The Hirshfeld surface mapped over d_{norm} in the range −0.1607 to +1.3888 arbitrary

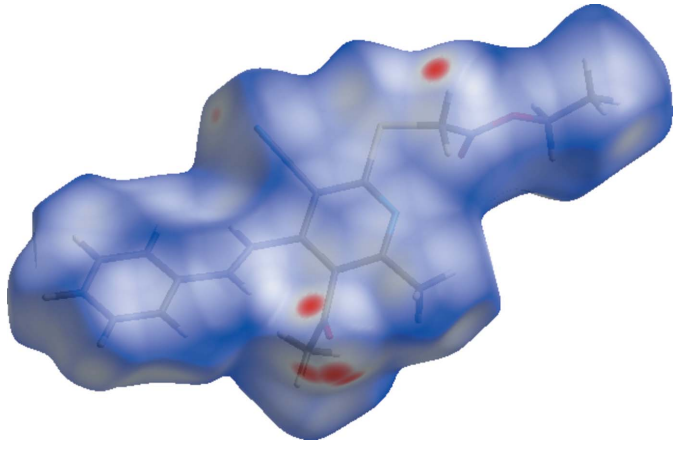


Figure 4
A view of the three-dimensional Hirshfeld surface for the title compound, plotted over d_{norm} in the range −0.1607 to +1.3888 a.u.

units is depicted in Fig. 4, where the red regions indicate apparent hydrogen bonds in this structure. The intensities of the red areas are greater for C15—H15*A*···O2 and C18—H18*B*···O1, indicating the strongest interactions as compared to other red spots on the Hirshfeld surface; Table 2 lists corresponding close intermolecular contacts. The two-dimensional fingerprint plots (Fig. 5) reveal that the largest contributions are from H···H (43.6%; Fig. 5*b*), C···H/H···C (15.6%; Fig. 5*c*), O···H/H···O (14.9%; Fig. 5*d*) and N···H/H···N (11.2%; Fig. 5*e*) interactions. Other interactions contributing less to the crystal packing are S···H/H···S (5.9%), C···C (4.4%), N···C/C···N (1.5%), S···O/O···S (1.1%), O···C/C···O (1.0%), O···O (0.3%), N···N (0.2%) and S···C/C···S (0.2%).

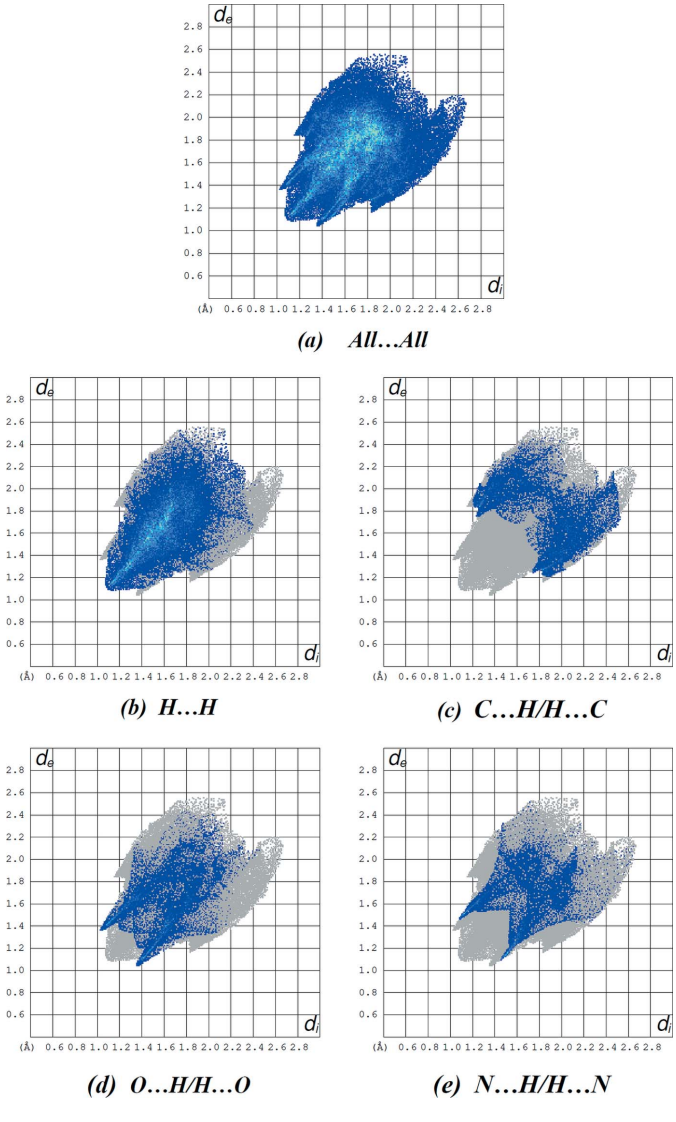


Figure 5
A view of the two-dimensional fingerprint plots for the title compound, showing (*a*) all interactions, and delineated into (*b*) H···H, (*c*) C···H/H···C, (*d*) O···H/H···O and (*e*) N···H/H···N interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface.

5. Database survey

A search of the Cambridge Structural Database (version 5.42, update 1, Feb 2021; Groom *et al.*, 2016) for related structures with the 2-sulfanylpyridine-3-carbonitrile moiety of the title compound gave the following matches: ethyl 4-methyl-2-phenyl-6-thioxo-1,6-dihydro-5-pyrimidinecarboxylate monohydrate (DEWCIS; Cunha *et al.*, 2007), ethyl 4-(5-ethoxycarbonyl-6-methyl-2-phenyl-4-pyrimidinyldisulfanyl)-6-methyl-2-phenyl-5-pyrimidinecarboxylate (DEWCAK; Cunha *et al.*, 2007), ethyl 4-{[(4-chlorophenyl)methyl]sulfanyl}-6-methyl-2-phenylpyrimidine-5-carboxylate (NILKOL; Stolarczyk *et al.*, 2018), (4-{[(4-chlorophenyl)methyl]sulfanyl}-6-methyl-2-phenylpyrimidin-5-yl)methanol (NILKUR; Stolarczyk *et al.*, 2018) and 4-{[(4-chlorophenyl)methyl]sulfanyl}-5,6-dimethyl-2-phenylpyrimidine (NILLAY; Stolarczyk *et al.*, 2018).

Compound DEWCIS crystallizes in the space group $P2_1/c$ with one molecule in the asymmetric unit. N—H···O, O—H···N and O—H···S interactions involving the water molecules, as well as π–π stacking interactions between the molecules along the *b* axis contribute to the formation of layers parallel to the *bc* plane. The stability of the molecular packing is achieved by van der Waals interactions between these layers. Compound DEWCAK crystallizes in the space group $P\overline{1}$ with one molecule in the asymmetric unit. In the crystal structure of DEWCAK, there are no classical hydrogen bonds. The molecular packing is stabilized by C—H···π interactions and π–π stacking interactions. Compound NILKOL crystallizes in the space group $P\overline{1}$ with one molecule in the asymmetric unit, whereas compounds NILKUR and NILLAY crystallize in the space group $P2_1/c$ with two and one molecules, respectively, in their asymmetric units. The conformation of each molecule is best defined by the dihedral angles formed between the pyrimidine ring and the planes of the two aryl substituents attached at the 2- and 4-positions. The only structural difference between the three compounds is the substituent at the 5-position of the pyrimidine ring, but they present significantly different features in their hydrogen-bonding interactions. NILKOL displays a chain structure whereby the chains are further extended into a two-dimensional network. In NILKUR and NILLAY, the hydrogen-bonded chains have no further aggregation.

6. Synthesis and crystallization

A mixture of 5-acetyl-3-cyano-6-methyl-4-styrylpyridine-2(1*H*)-thione (3.24 g, 10 mmol), ethyl chloroacetate (1.1 ml, 10 mmol) and sodium acetate trihydrate (1.5 g, 11 mmol) in ethanol (40 ml) was heated under reflux for 30 min. The solid that formed after dilution with water (20 ml) was filtered off and recrystallized from methanol in the form of fine colourless crystals of the title compound, yield 85%; m.p. 343–344 K. Its IR spectrum showed characteristic absorption bands at 2219 cm^{-1} for (C≡N), at 1748 cm^{-1} for (C=O, non conjugated ester) and at 1724 cm^{-1} for (C=O, conjugated ester). The ^{1}H NMR spectrum (400 MHz, DMSO-d_6) displayed a multiplet at δ = 6.60–7.63 ppm (7H: CH=CH and Ar-Hs), a

multiplet at δ = 4.16–4.37 ppm (6H: two OCH_2 and SCH_2), a singlet at δ = 2.52 ppm (3H, CH_3 at C-6, overlapped with solvent signal) and a multiplet at δ = 1.21–1.27 ppm (6H: two CH_3 of ester groups).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The C-bound H atoms were refined freely, while the H atoms of the C16 methyl group were placed geometrically (C—H = 0.98 Å) and refined as riding atoms with U_{iso}(H) = 1.5U_{eq}(C).

Acknowledgements

Author contributions are as follows: Conceptualization, EAB, MSA and SKM; methodology, JTM, EAB and MA; investigation, JTM, SKM, and EAB; writing (original draft), JTM, AM, SKM and EAB; writing (review and editing of the manuscript), MA and SKM; visualization, MA, SKM and JTM; funding acquisition, SAHA and SKM; resources, MA, JTM, EAB and SKM. AAA, VNK and FNN; supervision, SKM and MA.

Funding information

The support of NSF-MRI grant No. 1228232 for the purchase of the diffractometer and Tulane University for support of the Tulane Crystallography Laboratory are gratefully acknowledged.

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_{21}H_{20}N_2O_3S$
M_r	380.45
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	150
a, b, c (Å)	10.7365 (4), 9.7590 (3), 18.5600 (7)
β (°)	90.066 (1)
V (Å^3)	1944.67 (12)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	1.67
Crystal size (mm)	0.27 × 0.12 × 0.05
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.80, 0.92
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14722, 3912, 3520
R_{int}	0.034
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.033, 0.088, 1.04
No. of reflections	3912
No. of parameters	314
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.22, −0.29

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012) and *publCIF* (Westrip, 2010).

References

Balasubramanian, M. & Keay, J. G. (1996). In *Comprehensive Heterocyclic Chemistry II*, edited by A. R Katritzky, C. W. Rees & E. F. V. Scriven, pp. 245–300. Oxford: Pergamon.

Brandenburg, K. & Putz, H. (2012). *DIAMOND*, Crystal Impact GbR, Bonn, Germany.

Bruker (2016). *APEX3* and *SAINT*. Bruker AXS, Inc., Madison, Wisconsin, USA.

Cunha, S., Bastos, R. M., Silva, P. O., Nobre Costa, G. A., Vencato, I., Lariucci, C., Napolitano, H. B., de Oliveira, C. M. A., Kato, L., da Silva, C. C., Menezes, D. & Vannier-Santos, M. A. (2007). *Monatsh. Chem.* **138**, 111–119.

Gibson, V. C., Redshaw, C. & Solan, G. A. (2007). *Chem. Rev.* **107**, 1745–1776.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

Stolarczyk, M., Bryndal, I., Matera-Witkiewicz, A., Lis, T., Królewska-Golińska, K., Cieślak, M., Kaźmierczak-Barańska, J. & Cieplik, J. (2018). *Acta Cryst.* C**74**, 1138–1145.

Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *Crystal Explorer 17*. University of Western Australia. http://hirshfeldsurface.net

Vidaillac, C., Guillon, J., Arpin, C., Forfar-Bares, I., Ba, B. B., Grellet, J., Moreau, S., Caignard, D. H., Jarry, C. & Quentin, C. (2007). *Antimicrob. Agents Chemother.* **51**, 831–838.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2021). E**77**, 730-733 [https://doi.org/10.1107/S2056989021005600]

Crystal structure and Hirshfeld surface analysis of ethyl 2-({5-acetyl-3-cyano-6-methyl-4-[(*E*)-2-phenylethenyl]pyridin-2-yl}sulfanyl)acetate

Safiyyah A. H. Al-Waleedy, Shaaban K. Mohamed, Joel T. Mague, Mehmet Akkurt, Mohamed S. Abbady and Etify A. Bakhite

Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINT* (Bruker, 2016); data reduction: *SAINT* (Bruker, 2016); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015*b*); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Ethyl 2-({5-acetyl-3-cyano-6-methyl-4-[(*E*)-2-phenylethenyl]pyridin-2-yl}sulfanyl)acetate

Crystal data

$C_{21}H_{20}N_2O_3S$
M_r = 380.45
Monoclinic, $P2_1/n$
a = 10.7365 (4) Å
b = 9.7590 (3) Å
c = 18.5600 (7) Å
β = 90.066 (1)°
V = 1944.67 (12) Å^3
Z = 4
$F(000)$ = 800
D_x = 1.299 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 9951 reflections
θ = 4.8–74.6°
μ = 1.67 mm^{-1}
T = 150 K
Column, colourless
0.27 × 0.12 × 0.05 mm

Data collection

Bruker D8 VENTURE PHOTON 100 CMOS diffractometer
Radiation source: INCOATEC IμS micro–focus source
Mirror monochromator
Detector resolution: 10.4167 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min} = 0.80, T_{max} = 0.92
14722 measured reflections
3912 independent reflections
3520 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 74.6°, θ_{min} = 4.8°
h = −13→12
k = −11→12
l = −21→22

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.088
S = 1.04
3912 reflections
314 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
$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2 + 0.7692P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Extinction correction: *SHELXL 2018/3* (Sheldrick, 2015*b*), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0041 (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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ 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. Independent refinement of the hydrogen atoms attached to C16 led to an unreasonable geometry so these were included as riding contributions (C—H = 0.98 Å) with an AFIX 137 instruction.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.62964 (3)	0.76240 (3)	0.45327 (2)	0.02319 (11)
O1	0.65133 (9)	0.07606 (9)	0.47995 (6)	0.0295 (2)
O2	0.85513 (10)	0.82982 (12)	0.54910 (6)	0.0367 (3)
O3	0.73641 (9)	0.93032 (11)	0.63373 (5)	0.0304 (2)
N1	0.67271 (10)	0.51703 (11)	0.51422 (6)	0.0222 (2)
N2	0.58138 (13)	0.65298 (13)	0.27261 (7)	0.0351 (3)
C1	0.66330 (11)	0.37425 (13)	0.38230 (7)	0.0203 (3)
C2	0.69019 (12)	0.30604 (13)	0.44698 (7)	0.0202 (3)
C3	0.69103 (12)	0.38044 (13)	0.51167 (7)	0.0215 (3)
C4	0.65042 (12)	0.58371 (13)	0.45305 (7)	0.0201 (3)
C5	0.64281 (12)	0.51610 (13)	0.38647 (7)	0.0208 (3)
C6	0.64972 (13)	0.30725 (14)	0.31165 (7)	0.0233 (3)
H6	0.6751 (17)	0.363 (2)	0.2711 (10)	0.038 (5)*
C7	0.59846 (13)	0.18469 (14)	0.30086 (7)	0.0239 (3)
H7	0.5717 (16)	0.1327 (18)	0.3420 (10)	0.033 (4)*
C8	0.57238 (12)	0.12114 (13)	0.23083 (7)	0.0222 (3)
C9	0.58480 (13)	0.19075 (14)	0.16518 (7)	0.0245 (3)
H9	0.6136 (17)	0.284 (2)	0.1648 (9)	0.034 (5)*
C10	0.55575 (13)	0.12655 (16)	0.10077 (8)	0.0276 (3)
H10	0.5629 (17)	0.178 (2)	0.0567 (10)	0.041 (5)*
C11	0.51380 (14)	−0.00811 (16)	0.10078 (8)	0.0295 (3)
H11	0.4913 (18)	−0.0529 (19)	0.0555 (10)	0.040 (5)*
C12	0.50215 (15)	−0.07840 (15)	0.16501 (8)	0.0312 (3)
H12	0.4716 (17)	−0.170 (2)	0.1652 (10)	0.037 (5)*
C13	0.53114 (14)	−0.01448 (15)	0.22967 (8)	0.0279 (3)
H13	0.5240 (17)	−0.0659 (18)	0.2763 (10)	0.036 (5)*
C14	0.72087 (12)	0.15479 (13)	0.44955 (7)	0.0220 (3)
C15	0.84103 (15)	0.10914 (17)	0.41681 (10)	0.0351 (3)
H15A	0.907 (2)	0.149 (2)	0.4470 (12)	0.056 (6)*

H15B	0.846 (2)	0.008 (2)	0.4173 (12)	0.058 (6)*
H14C	0.8516 (19)	0.147 (2)	0.3658 (12)	0.051 (6)*
C16	0.71490 (14)	0.31393 (14)	0.58331 (7)	0.0282 (3)
H16A	0.723453	0.384753	0.620421	0.042*
H16B	0.791792	0.260036	0.580824	0.042*
H16C	0.645041	0.253596	0.595442	0.042*
C17	0.60967 (13)	0.59215 (14)	0.32293 (7)	0.0245 (3)
C18	0.63109 (13)	0.80140 (14)	0.54760 (7)	0.0231 (3)
H18A	0.6100 (17)	0.717 (2)	0.5740 (10)	0.037 (5)*
H18B	0.5672 (16)	0.8694 (18)	0.5554 (9)	0.027 (4)*
C19	0.75457 (13)	0.85366 (14)	0.57467 (7)	0.0244 (3)
C20	0.84825 (15)	0.98717 (19)	0.66682 (9)	0.0380 (4)
H20A	0.904 (2)	0.910 (2)	0.6807 (12)	0.053 (6)*
H20B	0.896 (2)	1.047 (2)	0.6298 (12)	0.056 (6)*
C21	0.80775 (18)	1.0701 (2)	0.73071 (10)	0.0410 (4)
H21A	0.883 (2)	1.109 (2)	0.7550 (13)	0.065 (7)*
H21B	0.762 (2)	1.014 (2)	0.7639 (12)	0.051 (6)*
H21C	0.751 (2)	1.144 (2)	0.7167 (11)	0.049 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.03027 (19)	0.01732 (17)	0.02199 (18)	0.00121 (12)	−0.00303 (12)	−0.00091 (11)
O1	0.0316 (5)	0.0202 (5)	0.0367 (6)	0.0000 (4)	0.0043 (4)	0.0046 (4)
O2	0.0248 (5)	0.0464 (7)	0.0389 (6)	0.0060 (4)	−0.0025 (4)	−0.0121 (5)
O3	0.0289 (5)	0.0356 (6)	0.0266 (5)	0.0020 (4)	−0.0059 (4)	−0.0092 (4)
N1	0.0257 (6)	0.0202 (5)	0.0208 (6)	−0.0021 (4)	−0.0033 (4)	−0.0004 (4)
N2	0.0473 (8)	0.0295 (6)	0.0285 (7)	−0.0007 (6)	−0.0097 (6)	0.0023 (5)
C1	0.0199 (6)	0.0200 (6)	0.0209 (6)	−0.0030 (5)	−0.0009 (5)	−0.0009 (5)
C2	0.0203 (6)	0.0180 (6)	0.0224 (6)	−0.0021 (5)	−0.0018 (5)	0.0007 (5)
C3	0.0224 (6)	0.0201 (6)	0.0220 (7)	−0.0025 (5)	−0.0032 (5)	0.0008 (5)
C4	0.0199 (6)	0.0192 (6)	0.0211 (6)	−0.0021 (5)	−0.0023 (5)	−0.0002 (5)
C5	0.0223 (6)	0.0203 (6)	0.0199 (6)	−0.0022 (5)	−0.0033 (5)	0.0012 (5)
C6	0.0283 (7)	0.0222 (6)	0.0195 (6)	−0.0010 (5)	−0.0012 (5)	−0.0010 (5)
C7	0.0281 (7)	0.0245 (7)	0.0193 (6)	−0.0024 (5)	0.0000 (5)	−0.0010 (5)
C8	0.0233 (6)	0.0230 (6)	0.0201 (6)	−0.0001 (5)	−0.0010 (5)	−0.0028 (5)
C9	0.0271 (7)	0.0233 (7)	0.0232 (7)	−0.0021 (5)	−0.0012 (5)	0.0003 (5)
C10	0.0290 (7)	0.0329 (7)	0.0209 (7)	0.0010 (6)	−0.0022 (5)	0.0007 (6)
C11	0.0337 (7)	0.0323 (7)	0.0226 (7)	0.0009 (6)	−0.0057 (6)	−0.0064 (6)
C12	0.0418 (8)	0.0230 (7)	0.0287 (8)	−0.0048 (6)	−0.0045 (6)	−0.0046 (6)
C13	0.0368 (8)	0.0240 (7)	0.0228 (7)	−0.0035 (6)	−0.0018 (6)	−0.0006 (5)
C14	0.0244 (6)	0.0202 (6)	0.0214 (6)	−0.0002 (5)	−0.0042 (5)	−0.0005 (5)
C15	0.0311 (8)	0.0294 (8)	0.0448 (10)	0.0052 (6)	0.0068 (7)	0.0029 (7)
C16	0.0393 (8)	0.0239 (7)	0.0214 (7)	−0.0016 (6)	−0.0065 (6)	0.0022 (5)
C17	0.0293 (7)	0.0211 (6)	0.0231 (7)	−0.0022 (5)	−0.0044 (5)	−0.0016 (5)
C18	0.0257 (7)	0.0207 (6)	0.0230 (7)	0.0004 (5)	0.0007 (5)	−0.0027 (5)
C19	0.0277 (7)	0.0223 (6)	0.0231 (6)	0.0038 (5)	−0.0038 (5)	−0.0008 (5)
C20	0.0329 (8)	0.0429 (9)	0.0383 (9)	0.0026 (7)	−0.0140 (7)	−0.0119 (7)

C21	0.0458 (10)	0.0446 (10)	0.0324 (9)	−0.0011 (8)	−0.0100 (7)	−0.0095 (7)

Geometric parameters (Å, º)

S1—C4	1.7581 (13)	C9—H9	0.960 (19)
S1—C18	1.7918 (14)	C10—C11	1.389 (2)
O1—C14	1.2112 (16)	C10—H10	0.96 (2)
O2—C19	1.2026 (17)	C11—C12	1.381 (2)
O3—C19	1.3417 (17)	C11—H11	0.98 (2)
O3—C20	1.4578 (18)	C12—C13	1.388 (2)
N1—C4	1.3301 (17)	C12—H12	0.956 (19)
N1—C3	1.3482 (17)	C13—H13	1.003 (19)
N2—C17	1.1473 (19)	C14—C15	1.4946 (19)
C1—C2	1.4025 (18)	C15—H15A	0.98 (2)
C1—C5	1.4038 (18)	C15—H15B	0.99 (2)
C1—C6	1.4723 (18)	C15—H14C	1.02 (2)
C2—C3	1.4032 (18)	C16—H16A	0.9800
C2—C14	1.5130 (17)	C16—H16B	0.9800
C3—C16	1.5013 (18)	C16—H16C	0.9800
C4—C5	1.4032 (18)	C18—C19	1.5061 (19)
C5—C17	1.4378 (18)	C18—H18A	0.988 (19)
C6—C7	1.332 (2)	C18—H18B	0.965 (17)
C6—H6	0.968 (19)	C20—C21	1.500 (2)
C7—C8	1.4669 (18)	C20—H20A	1.00 (2)
C7—H7	0.961 (18)	C20—H20B	1.04 (2)
C8—C13	1.3958 (19)	C21—H21A	1.00 (2)
C8—C9	1.4016 (19)	C21—H21B	0.96 (2)
C9—C10	1.385 (2)	C21—H21C	0.97 (2)
C4—S1—C18	102.24 (6)	C12—C13—H13	120.2 (10)
C19—O3—C20	115.85 (11)	C8—C13—H13	119.0 (10)
C4—N1—C3	118.68 (11)	O1—C14—C15	122.21 (12)
C2—C1—C5	116.93 (11)	O1—C14—C2	119.95 (12)
C2—C1—C6	124.86 (12)	C15—C14—C2	117.77 (12)
C5—C1—C6	118.14 (11)	C14—C15—H15A	105.7 (13)
C1—C2—C3	119.21 (12)	C14—C15—H15B	109.9 (13)
C1—C2—C14	122.32 (11)	H15A—C15—H15B	110.5 (18)
C3—C2—C14	118.47 (11)	C14—C15—H14C	111.5 (12)
N1—C3—C2	122.74 (12)	H15A—C15—H14C	107.7 (17)
N1—C3—C16	114.90 (11)	H15B—C15—H14C	111.2 (17)
C2—C3—C16	122.34 (12)	C3—C16—H16A	109.5
N1—C4—C5	122.14 (12)	C3—C16—H16B	109.5
N1—C4—S1	120.40 (10)	H16A—C16—H16B	109.5
C5—C4—S1	117.46 (10)	C3—C16—H16C	109.5
C4—C5—C1	120.22 (12)	H16A—C16—H16C	109.5
C4—C5—C17	119.59 (12)	H16B—C16—H16C	109.5
C1—C5—C17	120.16 (12)	N2—C17—C5	178.94 (16)
C7—C6—C1	124.98 (12)	C19—C18—S1	113.86 (10)

C7—C6—H6	120.3 (11)	C19—C18—H18A	108.7 (11)
C1—C6—H6	114.6 (11)	S1—C18—H18A	107.8 (11)
C6—C7—C8	126.26 (13)	C19—C18—H18B	110.0 (10)
C6—C7—H7	118.6 (11)	S1—C18—H18B	106.7 (10)
C8—C7—H7	115.1 (11)	H18A—C18—H18B	109.7 (14)
C13—C8—C9	118.47 (12)	O2—C19—O3	124.17 (13)
C13—C8—C7	118.34 (12)	O2—C19—C18	126.38 (13)
C9—C8—C7	123.18 (12)	O3—C19—C18	109.43 (11)
C10—C9—C8	120.64 (13)	O3—C20—C21	107.39 (14)
C10—C9—H9	119.7 (11)	O3—C20—H20A	108.7 (13)
C8—C9—H9	119.7 (11)	C21—C20—H20A	112.2 (13)
C9—C10—C11	120.03 (13)	O3—C20—H20B	110.0 (12)
C9—C10—H10	118.6 (12)	C21—C20—H20B	111.1 (12)
C11—C10—H10	121.4 (12)	H20A—C20—H20B	107.4 (17)
C12—C11—C10	119.98 (13)	C20—C21—H21A	109.1 (13)
C12—C11—H11	119.8 (11)	C20—C21—H21B	110.5 (13)
C10—C11—H11	120.2 (11)	H21A—C21—H21B	109.7 (18)
C11—C12—C13	120.18 (13)	C20—C21—H21C	111.6 (12)
C11—C12—H12	120.1 (11)	H21A—C21—H21C	110.1 (18)
C13—C12—H12	119.7 (11)	H21B—C21—H21C	105.8 (18)
C12—C13—C8	120.69 (13)		

C5—C1—C2—C3	2.15 (18)	C5—C1—C6—C7	−140.67 (14)
C6—C1—C2—C3	−175.01 (12)	C1—C6—C7—C8	173.53 (13)
C5—C1—C2—C14	−176.70 (11)	C6—C7—C8—C13	172.91 (14)
C6—C1—C2—C14	6.15 (19)	C6—C7—C8—C9	−8.2 (2)
C4—N1—C3—C2	1.39 (19)	C13—C8—C9—C10	0.5 (2)
C4—N1—C3—C16	−179.73 (12)	C7—C8—C9—C10	−178.32 (13)
C1—C2—C3—N1	−3.20 (19)	C8—C9—C10—C11	0.0 (2)
C14—C2—C3—N1	175.69 (12)	C9—C10—C11—C12	−0.6 (2)
C1—C2—C3—C16	177.99 (12)	C10—C11—C12—C13	0.6 (2)
C14—C2—C3—C16	−3.12 (19)	C11—C12—C13—C8	0.0 (2)
C3—N1—C4—C5	1.39 (19)	C9—C8—C13—C12	−0.5 (2)
C3—N1—C4—S1	−178.47 (10)	C7—C8—C13—C12	178.38 (14)
C18—S1—C4—N1	−5.66 (12)	C1—C2—C14—O1	−114.75 (15)
C18—S1—C4—C5	174.48 (10)	C3—C2—C14—O1	66.40 (17)
N1—C4—C5—C1	−2.31 (19)	C1—C2—C14—C15	68.12 (17)
S1—C4—C5—C1	177.55 (10)	C3—C2—C14—C15	−110.73 (15)
N1—C4—C5—C17	175.55 (12)	C4—S1—C18—C19	98.96 (10)
S1—C4—C5—C17	−4.59 (17)	C20—O3—C19—O2	0.6 (2)
C2—C1—C5—C4	0.44 (18)	C20—O3—C19—C18	179.32 (12)
C6—C1—C5—C4	177.79 (12)	S1—C18—C19—O2	−26.34 (19)
C2—C1—C5—C17	−177.42 (12)	S1—C18—C19—O3	154.93 (10)
C6—C1—C5—C17	−0.06 (18)	C19—O3—C20—C21	179.23 (14)
C2—C1—C6—C7	36.5 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15*A*···O2^{i}	0.98 (2)	2.56 (2)	3.375 (2)	139.9 (17)
C18—H18*B*···O1^{ii}	0.965 (17)	2.493 (17)	3.2989 (17)	140.9 (13)

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