

Ethyl 2-[(3-methylquinoxalin-2-yl)sulfanyl]acetate

Mohcine Missioui,^{a*} Joel T Mague,^b Mohammed El Fal,^c Jamal Taoufik,^a El Mokhtar Essassi^c and Youssef Ramli^a

^aLaboratory of Medicinal Chemistry, Faculty of Medicine and Pharmacy, Mohammed V University, Rabat, Morocco,

^bDepartment of Chemistry, Tulane University, New Orleans, LA 70118, USA, and ^cLaboratoire de Chimie Organique Heterocyclique URAC 21, Av. Ibn Battouta, BP, 1014, Faculte des Sciences, Universite Mohammed V, Rabat, Morocco.

*Correspondence e-mail: mohcinemissioui@yahoo.com

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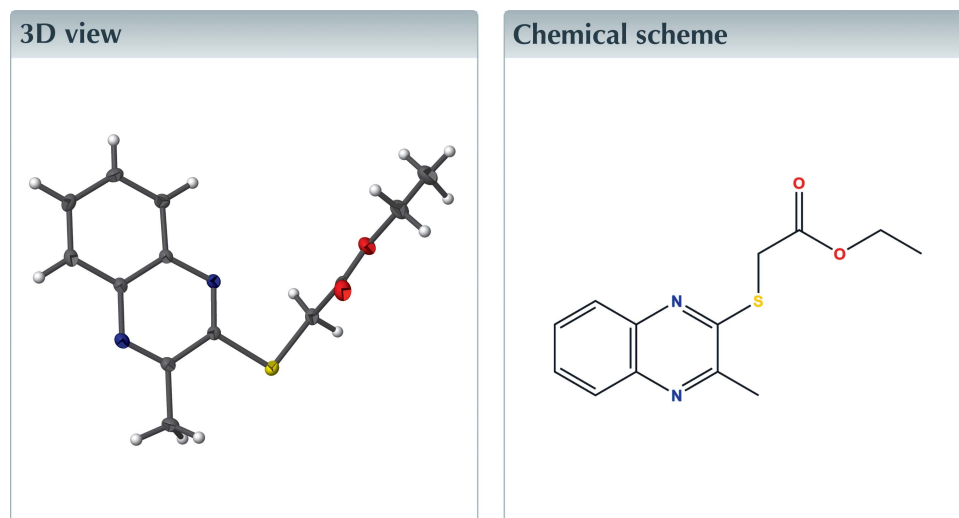
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Keywords: crystal structure; quinoxaline; thioacetate; hydrogen bonds; π - π stacking.

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Structural data: full structural data are available from iucrdata.iucr.org

In the title molecule, C₁₃H₁₄N₂O₂S, the dihedral angle between the pyrazine and benzene ring planes is 2.21 (5)°. The mean plane of the quinoxaline ring system is inclined to the sulfanylacetate substituent by 81.74 (2)°. In the crystal, inversion-related C—H···N hydrogen bonds form dimers, which are linked into oblique stacks along the *a*-axis direction by C—H···O hydrogen bonds and π - π stacking interactions.



Structure description

Among the various classes of nitrogen heterocyclic compounds, quinoxaline derivatives display a broad spectrum of biological activity (Ramli *et al.*, 2014). The chemistry of quinoxaline and its derivatives has attracted increasing attention because of their diverse pharmacological properties. These include use as cytotoxic, anti-inflammatory, antimicrobial, antioxidant, antifungal and antiviral agents (Ramli & Essassi, 2015). In light of these facts and as a continuation of our work on the synthesis of quinoxaline-2-thione derivatives in order to evaluate their pharmacological activity (Ramli *et al.*, 2011, 2013*a,b*, 2017; Caleb *et al.*, 2016), the title compound (Fig. 1) was synthesized and its structure is reported here.

The dihedral angle between the mean planes (r.m.s. deviation = 0.001 Å for each) of the N1/C1/C8/N2/C7/C2 and C2—C7 rings is 2.21 (5)°. The plane through all atoms of the methylquinoxaline ring system is inclined to the plane through the S1/O1/O2/C10—C13 atoms of the sulfanylacetate substituent by 81.74 (2)°.

In the crystal, centrosymmetric dimers form through inversion-related C6—H6···N2 hydrogen bonds with the mean plane of the dimer inclined at 69.15 (6)° to [001] (Table 1 and Fig. 2). The dimers are formed into oblique stacks extending along the *a*-axis

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C6-H6\cdots N2^i$	0.956 (14)	2.584 (14)	3.5398 (15)	179.1 (12)
$C10-H10B\cdots O1^{ii}$	0.959 (14)	2.320 (15)	3.2770 (14)	175.2 (12)

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

direction by a combination of $C10-H10B\cdots O1$ hydrogen bonds and π -stacking interactions between the $C2-C7$ ring of one molecule and an adjacent $C1/N1/C2/C7/N2/C8$ ring (Table 1 and Figs. 2 and 3). The dihedral angle between these planes is $2.12(5)^\circ$, and the centroid-centroid distance is $3.7756(6)$ Å.

Synthesis and crystallization

To a solution of 3-methylquinoxaline-2(1*H*)-thione (5.67 mmol, 1 g) in 20 ml of DMF was added ethyl bromo acetate (5.67 mmol), K_2CO_3 (5.67 mmol) and a catalytic amount of tetrabutylammonium bromide. The mixture was stirred at room temperature for 4 h. Progress was monitored by TLC and, when complete, the solid material was removed by filtration and the solvent evaporated under vacuum. The solid product was purified by recrystallization from ethanol solution to afford colourless block-like crystals of the title compound (yield 70%).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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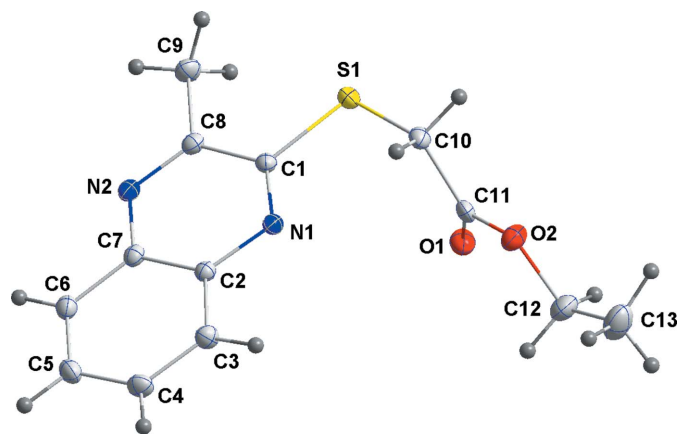


Figure 1
The title molecule with the atom-labeling scheme and 50% probability ellipsoids.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{13}H_{14}N_2O_2S$
M_r	262.32
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	100
a, b, c (Å)	4.8078 (3), 7.7314 (4), 17.8011 (10)
α, β, γ (°)	93.412 (1), 94.564 (1), 103.050 (1)
V (Å ³)	640.50 (6)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.25
Crystal size (mm)	0.24 × 0.19 × 0.14
Data collection	
Diffractometer	Bruker SMART APEX CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2016)
T_{min}, T_{max}	0.90, 0.97
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12471, 3429, 2989
R_{int}	0.022
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.687
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.036, 0.106, 1.13
No. of reflections	3429
No. of parameters	219
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.51, -0.24

Computer programs: *APEX3* (Bruker, 2016), *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL2016/6* (Sheldrick, 2015b), *DIAMOND* (Brandenburg & Putz, 2012), *SHELXTL* (Sheldrick, 2008).

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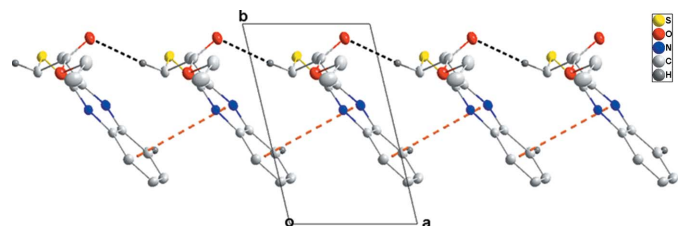


Figure 2
One of the oblique stacks viewed along the c -axis direction. $C-H\cdots O$ hydrogen bonds and π -stacking interactions are shown, respectively, by black and orange dashed lines.

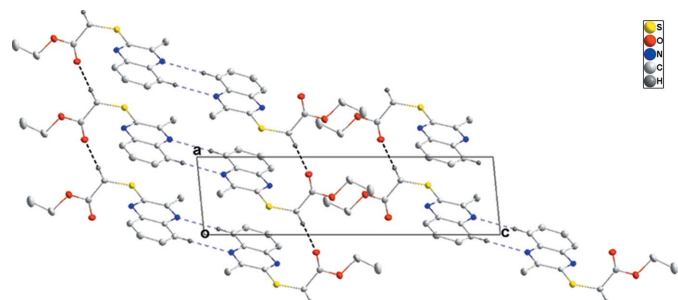


Figure 3
Packing viewed along the b -axis direction showing the $C-H\cdots O$ and inversion-related $C-H\cdots N$ hydrogen bonds.

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full crystallographic data

IUCrData (2017). 2, x171763 [https://doi.org/10.1107/S2414314617017631]

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Crystal data

$C_{13}H_{14}N_2O_2S$

$M_r = 262.32$

Triclinic, $P\bar{1}$

$a = 4.8078$ (3) Å

$b = 7.7314$ (4) Å

$c = 17.8011$ (10) Å

$\alpha = 93.412$ (1)°

$\beta = 94.564$ (1)°

$\gamma = 103.050$ (1)°

$V = 640.50$ (6) Å³

$Z = 2$

$F(000) = 276$

$D_x = 1.360$ Mg m⁻³

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

Cell parameters from 7128 reflections

$\theta = 2.3$ – 29.2 °

$\mu = 0.25$ mm⁻¹

$T = 100$ K

Block, colourless

$0.24 \times 0.19 \times 0.14$ mm

Data collection

Bruker SMART APEX CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.3333 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2016)

$T_{\min} = 0.90$, $T_{\max} = 0.97$

12471 measured reflections

3429 independent reflections

2989 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$

$\theta_{\max} = 29.2$ °, $\theta_{\min} = 2.3$ °

$h = -6 \rightarrow 6$

$k = -10 \rightarrow 10$

$l = -24 \rightarrow 24$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.106$

$S = 1.13$

3429 reflections

219 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0715P)^2 + 0.0147P]$

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

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

$\Delta\rho_{\max} = 0.51$ e Å⁻³

$\Delta\rho_{\min} = -0.23$ e Å⁻³

Special details

Experimental. The diffraction data were obtained from 3 sets of 400 frames, each of width 0.5° in ω , collected at $\varphi = 0.00$, 90.00 and 180.00° and 2 sets of 800 frames, each of width 0.45° in φ , collected at $\omega = -30.00$ and 210.00°. The scan time was 15 sec/frame.

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 $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.36572 (5)	0.83809 (3)	0.22771 (2)	0.01635 (10)
O1	0.77627 (17)	0.92958 (11)	0.37270 (5)	0.02107 (19)
O2	0.48291 (17)	0.75362 (11)	0.44375 (4)	0.02113 (19)
N1	0.62989 (18)	0.57047 (11)	0.23657 (5)	0.01322 (19)
N2	0.77521 (19)	0.59410 (12)	0.08561 (5)	0.01459 (19)
C1	0.5584 (2)	0.68682 (14)	0.19277 (6)	0.0128 (2)
C2	0.7772 (2)	0.45609 (14)	0.20461 (6)	0.0126 (2)
C3	0.8533 (2)	0.32286 (14)	0.24738 (6)	0.0166 (2)
H3	0.787 (3)	0.3094 (18)	0.2980 (8)	0.022 (3)*
C4	1.0070 (2)	0.21126 (15)	0.21664 (7)	0.0183 (2)
H4	1.050 (3)	0.128 (2)	0.2451 (10)	0.038 (4)*
C5	1.0920 (2)	0.22905 (15)	0.14311 (6)	0.0184 (2)
H5	1.194 (4)	0.148 (3)	0.1226 (11)	0.049 (5)*
C6	1.0180 (2)	0.35609 (15)	0.09980 (6)	0.0168 (2)
H6	1.076 (3)	0.3690 (19)	0.0499 (8)	0.023 (3)*
C7	0.8555 (2)	0.47049 (14)	0.12995 (6)	0.0135 (2)
C8	0.6262 (2)	0.69891 (14)	0.11535 (6)	0.0141 (2)
C9	0.5263 (3)	0.82984 (16)	0.06723 (6)	0.0194 (2)
H9A	0.314 (4)	0.817 (2)	0.0642 (10)	0.040 (4)*
H9B	0.594 (3)	0.949 (2)	0.0911 (9)	0.031 (4)*
H9C	0.588 (3)	0.820 (2)	0.0185 (9)	0.034 (4)*
C10	0.3034 (2)	0.76191 (15)	0.31903 (6)	0.0160 (2)
H10A	0.251 (3)	0.637 (2)	0.3185 (8)	0.025 (4)*
H10B	0.145 (3)	0.8045 (19)	0.3360 (8)	0.025 (4)*
C11	0.5520 (2)	0.82636 (14)	0.37907 (6)	0.0158 (2)
C12	0.6999 (3)	0.80583 (19)	0.50825 (7)	0.0264 (3)
H12A	0.860 (3)	0.764 (2)	0.4947 (9)	0.033 (4)*
H12B	0.751 (3)	0.938 (2)	0.5145 (8)	0.026 (4)*
C13	0.5698 (4)	0.7234 (2)	0.57545 (8)	0.0343 (3)
H13A	0.699 (4)	0.756 (2)	0.6176 (10)	0.041 (5)*
H13B	0.539 (4)	0.601 (3)	0.5704 (12)	0.063 (6)*
H13C	0.389 (4)	0.768 (2)	0.5829 (10)	0.050 (5)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01682 (16)	0.01777 (16)	0.01610 (15)	0.00755 (11)	0.00186 (10)	0.00039 (10)

O1	0.0150 (4)	0.0250 (4)	0.0216 (4)	0.0024 (3)	0.0022 (3)	-0.0026 (3)
O2	0.0207 (4)	0.0253 (4)	0.0158 (4)	0.0030 (3)	-0.0007 (3)	0.0010 (3)
N1	0.0118 (4)	0.0152 (4)	0.0127 (4)	0.0029 (3)	0.0018 (3)	0.0013 (3)
N2	0.0131 (4)	0.0170 (4)	0.0129 (4)	0.0019 (3)	0.0011 (3)	0.0015 (3)
C1	0.0106 (5)	0.0140 (5)	0.0132 (5)	0.0023 (4)	0.0005 (4)	0.0001 (4)
C2	0.0113 (4)	0.0139 (5)	0.0122 (5)	0.0019 (4)	0.0010 (4)	0.0010 (3)
C3	0.0172 (5)	0.0173 (5)	0.0160 (5)	0.0045 (4)	0.0029 (4)	0.0035 (4)
C4	0.0202 (5)	0.0150 (5)	0.0207 (5)	0.0064 (4)	0.0000 (4)	0.0030 (4)
C5	0.0172 (5)	0.0177 (5)	0.0208 (5)	0.0064 (4)	0.0020 (4)	-0.0029 (4)
C6	0.0155 (5)	0.0193 (5)	0.0147 (5)	0.0031 (4)	0.0016 (4)	-0.0020 (4)
C7	0.0122 (5)	0.0152 (5)	0.0122 (5)	0.0011 (4)	0.0010 (4)	0.0004 (4)
C8	0.0127 (5)	0.0156 (5)	0.0130 (5)	0.0017 (4)	-0.0001 (4)	0.0015 (4)
C9	0.0217 (6)	0.0221 (6)	0.0162 (5)	0.0078 (5)	0.0013 (4)	0.0053 (4)
C10	0.0119 (5)	0.0204 (6)	0.0158 (5)	0.0039 (4)	0.0026 (4)	-0.0012 (4)
C11	0.0161 (5)	0.0173 (5)	0.0159 (5)	0.0086 (4)	0.0027 (4)	-0.0027 (4)
C12	0.0250 (6)	0.0356 (7)	0.0178 (6)	0.0087 (5)	-0.0046 (5)	-0.0014 (5)
C13	0.0503 (9)	0.0335 (8)	0.0195 (6)	0.0115 (7)	-0.0006 (6)	0.0034 (5)

Geometric parameters (Å, °)

S1—C1	1.7626 (10)	C5—H5	0.954 (19)
S1—C10	1.7863 (11)	C6—C7	1.4153 (14)
O1—C11	1.2057 (13)	C6—H6	0.956 (14)
O2—C11	1.3438 (13)	C8—C9	1.4986 (14)
O2—C12	1.4607 (14)	C9—H9A	1.001 (17)
N1—C1	1.3100 (13)	C9—H9B	0.966 (16)
N1—C2	1.3762 (13)	C9—H9C	0.944 (16)
N2—C8	1.3121 (13)	C10—C11	1.5111 (15)
N2—C7	1.3760 (13)	C10—H10A	0.938 (15)
C1—C8	1.4448 (14)	C10—H10B	0.959 (14)
C2—C3	1.4121 (14)	C12—C13	1.5029 (19)
C2—C7	1.4138 (14)	C12—H12A	0.945 (16)
C3—C4	1.3734 (15)	C12—H12B	0.997 (16)
C3—H3	0.983 (14)	C13—H13A	0.921 (18)
C4—C5	1.4071 (16)	C13—H13B	0.92 (2)
C4—H4	0.892 (18)	C13—H13C	1.02 (2)
C5—C6	1.3748 (16)		
C1—S1—C10	100.96 (5)	C8—C9—H9A	113.1 (10)
C11—O2—C12	115.87 (9)	C8—C9—H9B	110.2 (9)
C1—N1—C2	115.99 (9)	H9A—C9—H9B	101.0 (13)
C8—N2—C7	117.64 (9)	C8—C9—H9C	109.9 (10)
N1—C1—C8	123.63 (9)	H9A—C9—H9C	110.8 (13)
N1—C1—S1	119.73 (8)	H9B—C9—H9C	111.5 (13)
C8—C1—S1	116.64 (8)	C11—C10—S1	114.95 (8)
N1—C2—C3	119.39 (9)	C11—C10—H10A	107.2 (9)
N1—C2—C7	121.19 (9)	S1—C10—H10A	113.0 (9)
C3—C2—C7	119.42 (9)	C11—C10—H10B	106.9 (9)

C4—C3—C2	119.76 (10)	S1—C10—H10B	108.0 (9)
C4—C3—H3	121.7 (8)	H10A—C10—H10B	106.2 (12)
C2—C3—H3	118.5 (8)	O1—C11—O2	123.78 (10)
C3—C4—C5	120.75 (10)	O1—C11—C10	127.14 (10)
C3—C4—H4	117.3 (11)	O2—C11—C10	109.05 (9)
C5—C4—H4	121.9 (11)	O2—C12—C13	107.04 (11)
C6—C5—C4	120.79 (10)	O2—C12—H12A	106.0 (10)
C6—C5—H5	120.1 (12)	C13—C12—H12A	113.7 (10)
C4—C5—H5	119.0 (12)	O2—C12—H12B	107.2 (9)
C5—C6—C7	119.34 (10)	C13—C12—H12B	112.8 (9)
C5—C6—H6	121.1 (9)	H12A—C12—H12B	109.7 (13)
C7—C6—H6	119.6 (9)	C12—C13—H13A	109.5 (11)
N2—C7—C2	121.00 (9)	C12—C13—H13B	111.4 (13)
N2—C7—C6	119.11 (9)	H13A—C13—H13B	103.8 (16)
C2—C7—C6	119.89 (10)	C12—C13—H13C	108.0 (10)
N2—C8—C1	120.45 (9)	H13A—C13—H13C	110.2 (15)
N2—C8—C9	118.66 (9)	H13B—C13—H13C	113.9 (17)
C1—C8—C9	120.88 (9)		
C2—N1—C1—C8	-0.08 (15)	C3—C2—C7—C6	-2.32 (15)
C2—N1—C1—S1	179.30 (7)	C5—C6—C7—N2	-178.20 (10)
C10—S1—C1—N1	-4.60 (10)	C5—C6—C7—C2	1.54 (16)
C10—S1—C1—C8	174.83 (8)	C7—N2—C8—C1	1.87 (15)
C1—N1—C2—C3	-177.86 (9)	C7—N2—C8—C9	-177.65 (9)
C1—N1—C2—C7	2.65 (15)	N1—C1—C8—N2	-2.29 (16)
N1—C2—C3—C4	-178.24 (10)	S1—C1—C8—N2	178.31 (8)
C7—C2—C3—C4	1.26 (16)	N1—C1—C8—C9	177.21 (9)
C2—C3—C4—C5	0.57 (17)	S1—C1—C8—C9	-2.19 (14)
C3—C4—C5—C6	-1.36 (17)	C1—S1—C10—C11	81.32 (9)
C4—C5—C6—C7	0.29 (17)	C12—O2—C11—O1	-0.45 (16)
C8—N2—C7—C2	0.66 (15)	C12—O2—C11—C10	-178.80 (9)
C8—N2—C7—C6	-179.60 (9)	S1—C10—C11—O1	4.50 (15)
N1—C2—C7—N2	-3.08 (16)	S1—C10—C11—O2	-177.22 (7)
C3—C2—C7—N2	177.42 (9)	C11—O2—C12—C13	175.03 (10)
N1—C2—C7—C6	177.18 (9)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C6—H6 \cdots N2 ⁱ	0.956 (14)	2.584 (14)	3.5398 (15)	179.1 (12)
C10—H10B \cdots O1 ⁱⁱ	0.959 (14)	2.320 (15)	3.2770 (14)	175.2 (12)

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