Crystal structure analysis of ethyl 3-(4-chlorophenyl)-1,6-dimethyl-4-methylsulfanyl-1H-pyrazolo-[3,4-b]pyridine-5-carboxylate

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In the title compound, $C_{18}H_{18}ClN_3O_2S$, the dihedral angle between the fused pyrazole and pyridine rings is 3.81 (9)°. The benzene ring forms dihedral angles of 35.08 (10) and 36.26 (9)° with the pyrazole and pyridine rings, respectively. In the crystal, weak C—H···O hydrogen bonds connect molecules along [100].

1. Chemical context

The nitrogen-containing heterocyclic motif is a component in many medicinally important drugs. Molecules built around the pyrazolopyridine core structure exhibit diverse medicinal properties that include anti-microbial, anti-viral, anti-fungal, anti-hypertensive, analgesic, anti-cancer, anti-inflammatory, anti-Alzheimer's, anti-diabetic, anti-nociceptive, anti-tuberculosis, and anti-leishmanial activities (Hardy, 1984; Hawas et al. 2019; de Mello et al. 2004; Panchal et al. 2019; El-Gohary et al. 2019). In addition, some pyrazolopyridines have found uses for the treatment of hemorrhagic stress, infertility, and drug addiction (Parmar et al. 1974). Specifically, they act as inhibitors of enzymes such as glycogen synthase kinase-3 (Witherington et al. 2003) and as inhibitors for adenosine receptors (Timóteo et al. 2008). Furthermore, they have been identified as promising inhibitors of cycline dependent kinase, xanthine oxidase, interleukin-6 (IL-6), tumor necrosis factor alpha (TNF-α), phosphodiesterase-4, NAD(P)H oxidases and cholesterol formation (Gökhan-Kelekçi et al. 2007; Panchal et al. 2019; Fathy et al. 2015). Considering the aforementioned importance of derivatives of pyrazolopyridine, we have carried out a single-crystal X-ray diffraction study on the title compound and have analyzed the structure in terms of geometrical parameters, conformation, and intermolecular hydrogen-bonding interactions.
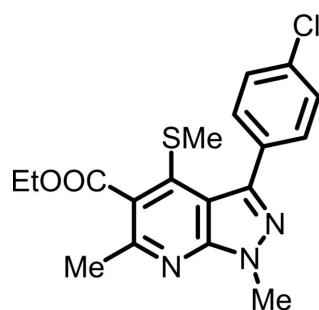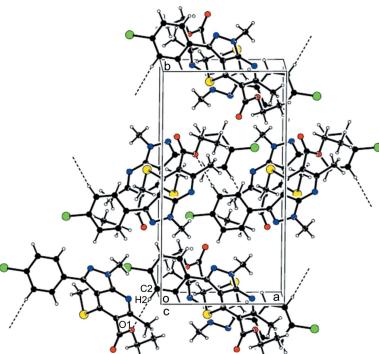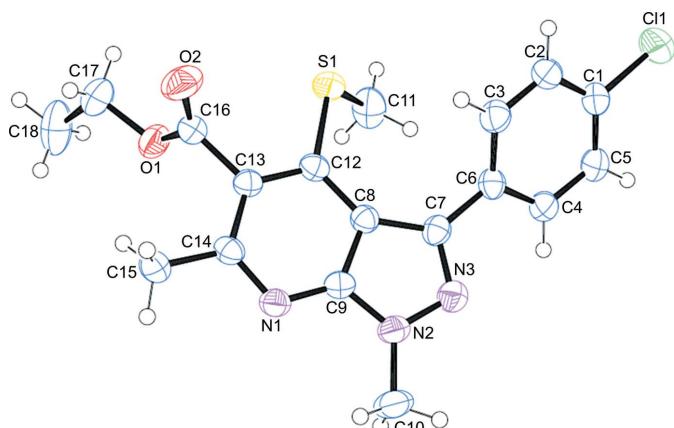
Figure 1
The molecular structure of the title compound with the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level

2. Structural commentary

The title compound has pyrazole[3,4-b]pyridine motif that is decorated by several substituents shown in Fig. 1. The chlorophenyl (C_6H_4Cl) group attached to the pyrazolopyridine moiety exhibits an (−)anticlinal conformation [N3—C7—C6—C3 = −141.96 (19)°], as does the methylthio (SCH_3) group attached to the pyrazolopyridine unit [C11—S1—C12—C13 = −128.93 (15) °] while the –$COOC_2H_5$ group attached to the pyrazolopyridine moiety has an (+)anti-periplanar conformation [N1—C14—C13—C16 = 177.00 (15)°, as do the methyl group attached to the pyridine sub-structure [C9—N1—C14—C15 = −176.20 (16)°] and the methyl group attached to the pyrazole ring (NCH_3) [C10—N2—C9—C8: −178.42 (19)°]. The fused pyrazole and pyridine rings are not exactly planar, subtending a dihedral angle of 3.81 (9)°. The dihedral angle between the planes of the benzene and pyrazole rings is 35.08 (10)° and that between the benzene and pyridine rings is 36.26 (9)°.

3. Supramolecular features

In the crystal, weak C—H⋯O hydrogen bonds link molecules into chains along [100] (Table 1 and Fig. 2).

4. Database survey

A search for the pyrazolopyridine scaffold in the Cambridge Structural Database (CSD, Version 5.40; Groom et al., 2016) gave 236 hits. Of these, the structures most closely related to the title compound are FIZLEI (ethyl 2,7-diamino-3,4-di-cyano-5-phenylpyrazolo[1,5-a]pyridine-6-carboxylate; Naik et al. 2019), ALAFID (Wu et al. 2016), DAWKAQ {[2-(4-chlorophenyl)pyrazolo[1,5-a]pyridin-3-yl(phenyl)methanone; Ravi et al. 2017}, NADPIU [3-(4-chlorophenyl)pyrazolo[1,5-a]pyridine; Wu et al. 2016] and ZOJWAW (Barrett et al. 1996). The geometrical parameters of the –$COOCH_2CH_3$ substituent in the title compound are comparable with those reported for

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C2—H2⋯O1[i]	0.93	2.59	3.513 (2)	170

Symmetry code: (i) $x - 1, y, z$.

FIZLEI. Similarly, the geometrical parameters of the –C_6H_4Cl unit in the title compound are comparable with those for in DAWKAQ and NADPIU. The bond lengths of the pyrazolo[3,4-b]pyridine scaffold of the title compound are closer to those in NADPIU. The pyrazolopyridine moiety (N1–N3/C7–C9/C12–C14) of the title compound is approximately plan, as is also observed for FIZLEI, ALAFID, DAWKAQ, NADPIU and ZOJWAW. Apart from the CSD database, two other important databases, namely Drug Bank (database for FDA-approved drugs, drugs under investigation or in clinical trials, etc; Law et al. 2013) and ZINC (database for commercially available compounds; Irwin et al. 2005) were also surveyed. The former database is used for drug repur-posing or drug re-profiling studies, and latter for high-throughput virtual screening against the binding site of drug target proteins to identify promising and putative inhibitors. In the Drug Bank database, there were 31 hits, based on a 0.5 similarity threshold, whereas the ZINC search gave only three hits (ZINCIDs: ZINC45166781, ZINC3852638 and ZINC39053824). Out of 31 molecules identified in the Drug Bank database, two molecules were in the approved drug category namely riciguat (accession No: DB08931, similarity score: 0.55) and teletristat ethyl (accession No: DB12095, similarity score: 0.511). The remaining 29 molecules belong to the experimental, investigational or other categories.
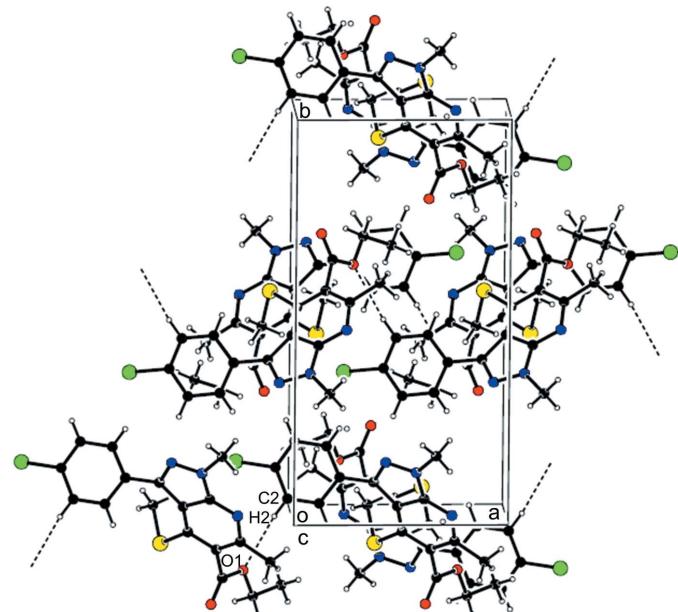

Figure 2
The crystal packing of title compound, viewed along the c axis, showing the weak intermolecular C—H⋯O hydrogen bonds as dotted lines

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{18}H_{18}ClN_3O_2S$
M_r	375.86
Crystal system, space group	Monoclinic, $P2_1/a$
Temperature (K)	298
a, b, c (Å)	8.9995 (5), 16.7778 (11), 12.3595 (8)
β (°)	98.892 (6)
V (Å^3)	1843.8 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.34
Crystal size (mm)	$0.65 \times 0.6 \times 0.24$
Data collection	
Diffractometer	Agilent Xcalibur Eos
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2014)
T_{min}, T_{max}	0.857, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13882, 4340, 3323
R_{int}	0.027
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.682
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.161, 1.10
No. of reflections	4340
No. of parameters	230
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, −0.41

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012), *PLATON* (Spek, 2020) and *Mercury* (Macrae *et al.*, 2020).

5. Synthesis and crystallization:

To a solution of 3-(4-chlorophenyl)-1-methyl-1*H*-pyrazol-5-amine (125 mg, 0.65 mmol) and ethyl 2-(bis(methylthio)-methylene)-3-oxobutanoate (145 mg, 0.65 mmol) in toluene (5 ml) under a blanket of dry N_2, a catalytic amount of tri-fluoroacetic acid (TFA; 30 mol%) was added. The resulting mixture was refluxed for 12 h, while monitoring progress by TLC (hexane:ethyl acetate, 99:1). After completion of the reaction, the resulting mixture was subjected to purification by column chromatography to furnish 182 mg of the title compound in 75% yield as a colourless solid, m.p. 415.85 K, R_f = 0.3 (hexane:ethyl acetate 99:01). A sample suitable for single-crystal X-ray analysis was obtained by recrystallization from dry methanol.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms were placed in calculated positions, with C—H = 0.93–0.97 Å and refined using a riding model with $U_{iso}(H) = 1.2\ U_{eq}(C)$ or $1.5\ U_{eq}(C$-methyl).

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supporting information

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Computing details

Data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO* (Agilent, 2014); data reduction: *CrysAlis PRO* (Agilent, 2014); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012), *PLATON* (Spek, 2020) and *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *ORTEP-3 for Windows* (Farrugia, 2012), *PLATON* (Spek, 2020) and *Mercury* (Macrae *et al.*, 2020).

Ethyl 3-(4-chlorophenyl)-1,6-dimethyl-4-methylsulfanyl-1*H*-pyrazolo[3,4-*b*]pyridine-5-carboxylate

Crystal data

$C_{18}H_{18}ClN_3O_2S$	$F(000) = 784$
$M_r = 375.86$	$D_x = 1.354$ Mg m^{-3}
Monoclinic, $P2_1/a$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.9995$ (5) Å	Cell parameters from 4472 reflections
$b = 16.7778$ (11) Å	$\theta = 3.9$–$29.0°$
$c = 12.3595$ (8) Å	$\mu = 0.34$ mm^{-1}
$\beta = 98.892$ (6)°	$T = 298$ K
$V = 1843.8$ (2) Å^3	Block, colourless
$Z = 4$	$0.65 \times 0.6 \times 0.24$ mm

Data collection

Agilent Xcalibur Eos diffractometer	13882 measured reflections
Radiation source: Enhance (Mo) X-ray Source	4340 independent reflections
Detector resolution: 15.9821 pixels mm^{-1}	3323 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.027$
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2014)	$\theta_{max} = 29.0°$, $\theta_{min} = 3.9°$
	$h = -11\rightarrow12$
	$k = -22\rightarrow22$
$T_{min} = 0.857$, $T_{max} = 1.000$	$l = -15\rightarrow16$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.049$	Secondary atom site location: difference Fourier map
$wR(F^2) = 0.161$	
$S = 1.10$	Hydrogen site location: inferred from neighbouring sites
4340 reflections	
230 parameters	H-atom parameters constrained
0 restraints	

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.006$

$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-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 (Å²)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
S1	0.38706 (5)	−0.06089 (3)	0.65888 (4)	0.04572 (19)
Cl1	−0.26383 (7)	0.13979 (4)	0.63284 (7)	0.0751 (3)
O1	0.77428 (16)	−0.12709 (8)	0.67467 (12)	0.0460 (4)
N1	0.73909 (16)	0.02099 (9)	0.95211 (12)	0.0363 (4)
N2	0.57052 (18)	0.12776 (9)	0.97183 (14)	0.0404 (4)
O2	0.62392 (19)	−0.20707 (9)	0.75585 (14)	0.0599 (4)
N3	0.42863 (18)	0.15124 (10)	0.92994 (14)	0.0409 (4)
C9	0.6093 (2)	0.06010 (10)	0.92252 (14)	0.0335 (4)
C7	0.37469 (19)	0.09887 (11)	0.85219 (15)	0.0347 (4)
C14	0.75435 (19)	−0.04529 (11)	0.89531 (15)	0.0340 (4)
C3	0.1239 (2)	0.04255 (12)	0.77078 (17)	0.0421 (5)
H3	0.161730	−0.008533	0.785668	0.051*
C8	0.48642 (19)	0.03902 (11)	0.84112 (14)	0.0323 (4)
C15	0.8936 (2)	−0.09402 (12)	0.93020 (17)	0.0430 (5)
H15A	0.968939	−0.061386	0.972304	0.064*
H15B	0.930807	−0.113697	0.866557	0.064*
H15C	0.869892	−0.138103	0.974026	0.064*
C6	0.21737 (19)	0.10825 (11)	0.79948 (15)	0.0345 (4)
C12	0.51150 (19)	−0.02733 (11)	0.77555 (14)	0.0329 (4)
C2	−0.0231 (2)	0.05183 (12)	0.72086 (17)	0.0435 (5)
H2	−0.083292	0.007504	0.701057	0.052*
C5	0.0072 (2)	0.19448 (12)	0.73163 (18)	0.0463 (5)
H5	−0.032853	0.245383	0.719599	0.056*
C13	0.64421 (19)	−0.06941 (10)	0.80566 (14)	0.0322 (4)
C4	0.1552 (2)	0.18420 (12)	0.78090 (17)	0.0410 (4)
H4	0.214097	0.228738	0.801982	0.049*
C10	0.6609 (3)	0.17282 (13)	1.05805 (19)	0.0525 (5)
H10A	0.723443	0.137017	1.105641	0.079*
H10B	0.596079	0.201357	1.099350	0.079*
H10C	0.722908	0.209945	1.026288	0.079*
C16	0.6758 (2)	−0.14269 (11)	0.74373 (15)	0.0372 (4)
C1	−0.0800 (2)	0.12802 (13)	0.70063 (17)	0.0439 (5)
C11	0.3529 (3)	0.02945 (16)	0.57990 (18)	0.0586 (6)
H11A	0.303494	0.067547	0.620089	0.088*
H11B	0.290191	0.017846	0.511611	0.088*
H11C	0.446915	0.051040	0.565940	0.088*

C17	0.8220 (3)	−0.19386 (15)	0.6139 (2)	0.0620 (7)
H17A	0.741429	−0.209688	0.556464	0.074*
H17B	0.847277	−0.238963	0.662333	0.074*
C18	0.9549 (3)	−0.16898 (19)	0.5657 (2)	0.0784 (9)
H18A	0.928634	−0.124659	0.517341	0.118*
H18B	0.988342	−0.212571	0.525243	0.118*
H18C	1.034070	−0.153518	0.623018	0.118*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0408 (3)	0.0500 (3)	0.0424 (3)	0.0014 (2)	−0.0061 (2)	−0.0113 (2)
Cl1	0.0410 (3)	0.0734 (5)	0.1034 (6)	0.0093 (3)	−0.0123 (3)	−0.0214 (4)
O1	0.0491 (8)	0.0400 (8)	0.0522 (8)	0.0015 (6)	0.0179 (7)	−0.0078 (6)
N1	0.0350 (8)	0.0336 (8)	0.0387 (8)	−0.0032 (6)	0.0005 (6)	−0.0019 (7)
N2	0.0426 (9)	0.0337 (9)	0.0426 (9)	−0.0007 (6)	−0.0009 (7)	−0.0074 (7)
O2	0.0696 (10)	0.0392 (9)	0.0749 (11)	−0.0140 (7)	0.0236 (8)	−0.0115 (8)
N3	0.0411 (9)	0.0371 (9)	0.0436 (9)	0.0035 (7)	0.0040 (7)	−0.0016 (7)
C9	0.0356 (9)	0.0319 (9)	0.0327 (9)	−0.0041 (7)	0.0042 (7)	−0.0007 (7)
C7	0.0375 (9)	0.0305 (9)	0.0368 (9)	0.0014 (7)	0.0084 (7)	0.0017 (7)
C14	0.0308 (8)	0.0332 (9)	0.0370 (9)	−0.0045 (7)	0.0027 (7)	0.0027 (8)
C3	0.0426 (10)	0.0332 (10)	0.0522 (12)	0.0002 (8)	0.0122 (9)	0.0019 (9)
C8	0.0312 (8)	0.0317 (9)	0.0339 (9)	−0.0015 (7)	0.0048 (7)	0.0008 (7)
C15	0.0360 (9)	0.0422 (11)	0.0476 (11)	0.0032 (8)	−0.0030 (8)	−0.0006 (9)
C6	0.0323 (8)	0.0373 (10)	0.0357 (9)	0.0010 (7)	0.0105 (7)	0.0015 (8)
C12	0.0306 (8)	0.0361 (9)	0.0319 (9)	−0.0044 (7)	0.0049 (7)	0.0006 (7)
C2	0.0375 (10)	0.0416 (11)	0.0531 (12)	−0.0053 (8)	0.0122 (8)	−0.0061 (9)
C5	0.0408 (10)	0.0391 (11)	0.0590 (13)	0.0088 (8)	0.0075 (9)	−0.0040 (10)
C13	0.0320 (8)	0.0312 (9)	0.0334 (9)	−0.0030 (7)	0.0050 (7)	−0.0004 (7)
C4	0.0376 (9)	0.0355 (10)	0.0511 (11)	−0.0009 (8)	0.0101 (8)	−0.0049 (9)
C10	0.0624 (13)	0.0420 (12)	0.0490 (12)	−0.0044 (10)	−0.0044 (10)	−0.0149 (10)
C16	0.0333 (9)	0.0364 (10)	0.0405 (10)	0.0003 (7)	0.0015 (7)	−0.0031 (8)
C1	0.0349 (10)	0.0494 (12)	0.0487 (11)	0.0037 (8)	0.0098 (8)	−0.0067 (9)
C11	0.0595 (13)	0.0778 (17)	0.0367 (10)	0.0189 (12)	0.0022 (9)	0.0032 (11)
C17	0.0615 (14)	0.0577 (15)	0.0692 (15)	0.0088 (11)	0.0179 (12)	−0.0218 (12)
C18	0.0790 (19)	0.092 (2)	0.0719 (17)	0.0399 (16)	0.0366 (15)	0.0135 (16)

Geometric parameters (Å, º)

S1—C12	1.7752 (18)	C15—H15C	0.9600
S1—C11	1.803 (3)	C6—C4	1.396 (3)
Cl1—C1	1.746 (2)	C12—C13	1.388 (2)
O1—C16	1.347 (2)	C2—C1	1.385 (3)
O1—C17	1.450 (2)	C2—H2	0.9300
N1—C14	1.333 (2)	C5—C1	1.383 (3)
N1—C9	1.340 (2)	C5—C4	1.387 (3)
N2—C9	1.359 (2)	C5—H5	0.9300
N2—N3	1.360 (2)	C13—C16	1.499 (2)

N2—C10	1.449 (2)	C4—H4	0.9300
O2—C16	1.195 (2)	C10—H10A	0.9600
N3—C7	1.337 (2)	C10—H10B	0.9600
C9—C8	1.420 (2)	C10—H10C	0.9600
C7—C8	1.442 (2)	C11—H11A	0.9600
C7—C6	1.473 (2)	C11—H11B	0.9600
C14—C13	1.426 (2)	C11—H11C	0.9600
C14—C15	1.502 (3)	C17—C18	1.476 (3)
C3—C2	1.380 (3)	C17—H17A	0.9700
C3—C6	1.399 (3)	C17—H17B	0.9700
C3—H3	0.9300	C18—H18A	0.9600
C8—C12	1.415 (2)	C18—H18B	0.9600
C15—H15A	0.9600	C18—H18C	0.9600
C15—H15B	0.9600		
C12—S1—C11	101.91 (10)	C1—C5—H5	120.4
C16—O1—C17	117.03 (16)	C4—C5—H5	120.4
C14—N1—C9	114.90 (15)	C12—C13—C14	122.00 (17)
C9—N2—N3	111.25 (15)	C12—C13—C16	120.27 (16)
C9—N2—C10	127.70 (17)	C14—C13—C16	117.74 (16)
N3—N2—C10	121.05 (16)	C5—C4—C6	121.27 (18)
C7—N3—N2	107.38 (15)	C5—C4—H4	119.4
N1—C9—N2	124.05 (17)	C6—C4—H4	119.4
N1—C9—C8	128.45 (16)	N2—C10—H10A	109.5
N2—C9—C8	107.43 (16)	N2—C10—H10B	109.5
N3—C7—C8	110.17 (16)	H10A—C10—H10B	109.5
N3—C7—C6	117.73 (15)	N2—C10—H10C	109.5
C8—C7—C6	131.99 (16)	H10A—C10—H10C	109.5
N1—C14—C13	121.99 (16)	H10B—C10—H10C	109.5
N1—C14—C15	116.87 (16)	O2—C16—O1	124.26 (18)
C13—C14—C15	121.14 (17)	O2—C16—C13	124.64 (17)
C2—C3—C6	121.48 (19)	O1—C16—C13	111.07 (15)
C2—C3—H3	119.3	C5—C1—C2	121.04 (19)
C6—C3—H3	119.3	C5—C1—Cl1	119.79 (16)
C12—C8—C9	115.20 (15)	C2—C1—Cl1	119.16 (16)
C12—C8—C7	140.99 (16)	S1—C11—H11A	109.5
C9—C8—C7	103.74 (15)	S1—C11—H11B	109.5
C14—C15—H15A	109.5	H11A—C11—H11B	109.5
C14—C15—H15B	109.5	S1—C11—H11C	109.5
H15A—C15—H15B	109.5	H11A—C11—H11C	109.5
C14—C15—H15C	109.5	H11B—C11—H11C	109.5
H15A—C15—H15C	109.5	O1—C17—C18	108.3 (2)
H15B—C15—H15C	109.5	O1—C17—H17A	110.0
C4—C6—C3	117.87 (17)	C18—C17—H17A	110.0
C4—C6—C7	120.25 (17)	O1—C17—H17B	110.0
C3—C6—C7	121.83 (17)	C18—C17—H17B	110.0
C13—C12—C8	116.96 (16)	H17A—C17—H17B	108.4
C13—C12—S1	117.71 (14)	C17—C18—H18A	109.5

C8—C12—S1	125.32 (13)	C17—C18—H18B	109.5
C3—C2—C1	119.14 (19)	H18A—C18—H18B	109.5
C3—C2—H2	120.4	C17—C18—H18C	109.5
C1—C2—H2	120.4	H18A—C18—H18C	109.5
C1—C5—C4	119.13 (19)	H18B—C18—H18C	109.5
C9—N2—N3—C7	−0.4 (2)	C9—C8—C12—S1	−173.01 (13)
C10—N2—N3—C7	179.58 (18)	C7—C8—C12—S1	3.2 (3)
C14—N1—C9—N2	178.40 (16)	C11—S1—C12—C13	−128.93 (15)
C14—N1—C9—C8	1.6 (3)	C11—S1—C12—C8	51.29 (17)
N3—N2—C9—N1	−175.78 (16)	C6—C3—C2—C1	−1.2 (3)
C10—N2—C9—N1	4.2 (3)	C8—C12—C13—C14	−2.9 (3)
N3—N2—C9—C8	1.6 (2)	S1—C12—C13—C14	177.35 (13)
C10—N2—C9—C8	−178.42 (19)	C8—C12—C13—C16	177.08 (15)
N2—N3—C7—C8	−0.9 (2)	S1—C12—C13—C16	−2.7 (2)
N2—N3—C7—C6	175.72 (15)	N1—C14—C13—C12	−3.1 (3)
C9—N1—C14—C13	3.7 (2)	C15—C14—C13—C12	176.81 (16)
C9—N1—C14—C15	−176.20 (16)	N1—C14—C13—C16	177.00 (15)
N1—C9—C8—C12	−7.2 (3)	C15—C14—C13—C16	−3.1 (3)
N2—C9—C8—C12	175.55 (15)	C1—C5—C4—C6	0.1 (3)
N1—C9—C8—C7	175.22 (17)	C3—C6—C4—C5	−2.5 (3)
N2—C9—C8—C7	−2.00 (19)	C7—C6—C4—C5	−179.85 (17)
N3—C7—C8—C12	−174.7 (2)	C17—O1—C16—O2	−1.7 (3)
C6—C7—C8—C12	9.4 (4)	C17—O1—C16—C13	176.52 (18)
N3—C7—C8—C9	1.81 (19)	C12—C13—C16—O2	−79.4 (3)
C6—C7—C8—C9	−174.18 (18)	C14—C13—C16—O2	100.5 (2)
C2—C3—C6—C4	3.1 (3)	C12—C13—C16—O1	102.39 (19)
C2—C3—C6—C7	−179.64 (17)	C14—C13—C16—O1	−77.7 (2)
N3—C7—C6—C4	35.3 (2)	C4—C5—C1—C2	1.8 (3)
C8—C7—C6—C4	−148.98 (19)	C4—C5—C1—Cl1	−177.07 (15)
N3—C7—C6—C3	−141.96 (19)	C3—C2—C1—C5	−1.3 (3)
C8—C7—C6—C3	33.8 (3)	C3—C2—C1—Cl1	177.61 (15)
C9—C8—C12—C13	7.2 (2)	C16—O1—C17—C18	−166.05 (19)
C7—C8—C12—C13	−176.6 (2)		

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O1[i]	0.93	2.59	3.513 (2)	170

Symmetry code: (i) x−1, y, z.