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Ethyl 5-chloromethyl-2-methylsulfanyl-7-phenyl-4,7-dihydro-1,2,4-triazolo[1,5-*a*]-pyrimidine-6-carboxylate

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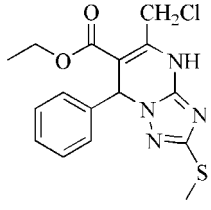
Key indicators: single-crystal X-ray study; T = 292 K; mean σ(C–C) = 0.005 Å; R factor = 0.055; wR factor = 0.155; data-to-parameter ratio = 14.8.

In the title compound, $C_{16}H_{17}ClN_4O_2S$, the bicyclic triazolopyrimidine ring system is nearly planar and oriented with respect to the benzene ring at a dihedral angle of 87.24 (3)°. In the crystal structure, intermolecular N—H···N hydrogen bonds link the molecules into centrosymmetric dimers; an intramolecular C—H···O hydrogen bond is also present.

Related literature

For related literature, see: Fedorova *et al.* (2003). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{16}H_{17}ClN_4O_2S$
M_r = 364.85
Triclinic, $P\overline{1}$
a = 8.9280 (8) Å
b = 9.8217 (9) Å
c = 11.3775 (10) Å
α = 106.022 (2)°
β = 102.631 (2)°
γ = 109.919 (2)°
V = 845.85 (13) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.37 mm^{-1}
T = 292 (2) K
0.20 × 0.10 × 0.02 mm

Data collection

Bruker SMART 4K CCD area-detector diffractometer
Absorption correction: none
6662 measured reflections
3281 independent reflections
2295 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.156
S = 1.02
3281 reflections
222 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4···N2^{i}	0.85 (3)	2.11 (3)	2.939 (3)	164 (3)
C7—H7B···O2	0.97	2.15	2.888 (4)	132

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL* (Bruker, 2001).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2399).

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supporting information

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Ethyl 5-chloromethyl-2-methylsulfanyl-7-phenyl-4,7-dihydro-1,2,4-triazolo[1,5-*a*]pyrimidine-6-carboxylate

Dan-Dan Song and Qiong Chen

S1. Comment

In recent years, growing attention has been paid to analogues of purines and nucleosides, including azolopyrimidines containing the bridge head nitrogen atom and their dihydro derivatives, among which promising biologically active compounds were found (Fedorova *et al.*, 2003). We synthesized a novel class of ethyl 7-alkylthio-4,7-dihydro-1,2,4-triazolo[1,5-*a*]pyrimidine-6-carboxylate derivatives by three component condensation of 3-amino-5-alkylthio-1,2,4 -triazoles with aromatic aldehydes and *β*-keto ester. We report herein the crystal structure of one such analogue, a triazolopyrimidine derivative, the title compound, (I).

In the molecule of (I), (Fig. 1) the bond lengths and angles are within normal ranges (Allen *et al.*, 1987). Rings A (N1—N3/C2/C3), B (N3/N4/C3—C6) and C (C11—C16) are, of course, planar. The bicyclic triazolopyrimidine ring system (N1—N4/C2—C6) is nearly planar with a maximum deviation of 0.152 (3) Å (for atom C6), and it is oriented with respect to ring C at a dihedral angle of 87.24 (3)°.

In the crystal structure, intermolecular N—H···N hydrogen bonds (Table 1, Fig 2) link the molecules into centrosymmetric dimers; an intramolecular C—H···O hydrogen bond (Table 1) is also present.

S2. Experimental

For the preparation of the title compound, a mixture of 4-chloro acetylacetic ester (1 mmol), benzaldehyde (1 mmol), and 3-amino-5-methylthio-1,2,4-triazole (1 mmol) in EtOH (3 ml) was added into a microwave tube. The sealed tube was placed in a Smith synthesizer and irradiated at 333 K for 30 min. The reaction mixture was cooled to room temperature, and the precipitate was filtered and recrystallized from ethanol to give the title compound, (I). Single crystals of (I) suitable for X-ray analysis were grown from an acetone solution at 293 K. ^{1}H NMR (CDCl3, 400 MHz): σ 10.56(s, 1 H), 7.28–7.33(m, 5 H), 6.40(s, 1H), 5.14(d, 1H), 4.95(d, 1H), 4.11(q,2 H), 2.51(s, 3H),1.15(t, 3H).

S3. Refinement

H atom (for NH) was located in a difference sythesis and refined [N—H = 0.85 (3) Å and U_{iso}(H) = 1.2U_{eq}(N)]. The remaining H atoms were positioned geometrically, with C—H = 0.93, 0.98, 0.97 and 0.96 Å for aromatic, methine, methylene and methyl H, respectively, and constrained to ride on their parent atoms, with U_{iso}(H) = xU_{eq}(C), where x = 1.5 for methyl H, and x = 1.2 for all other H atoms.

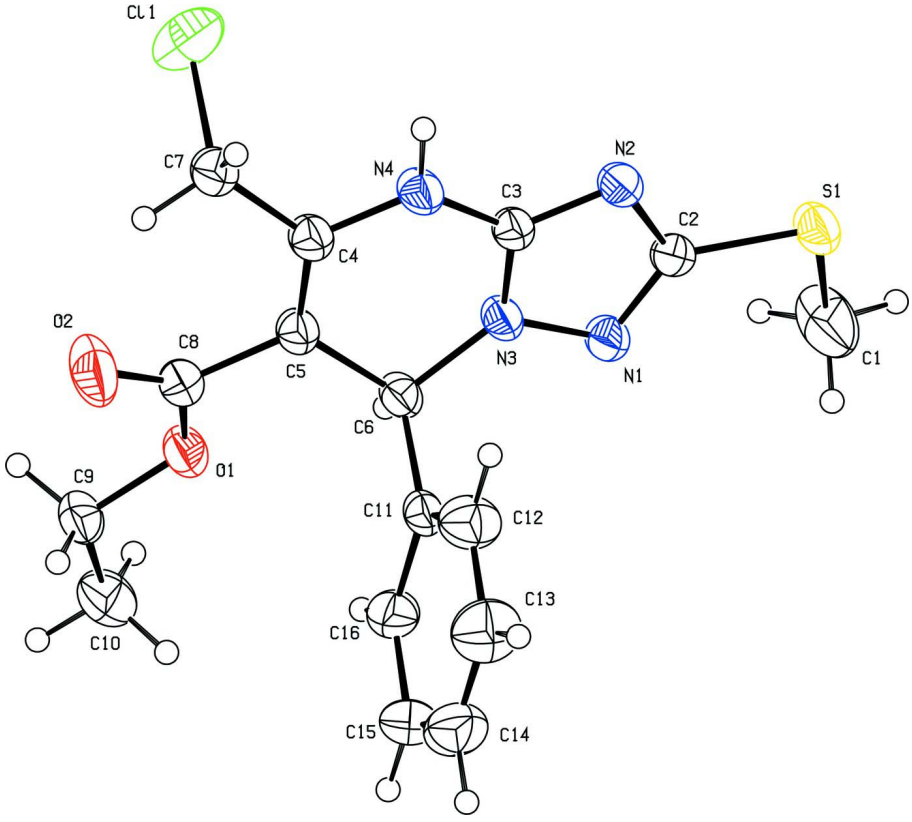

Figure 1

The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

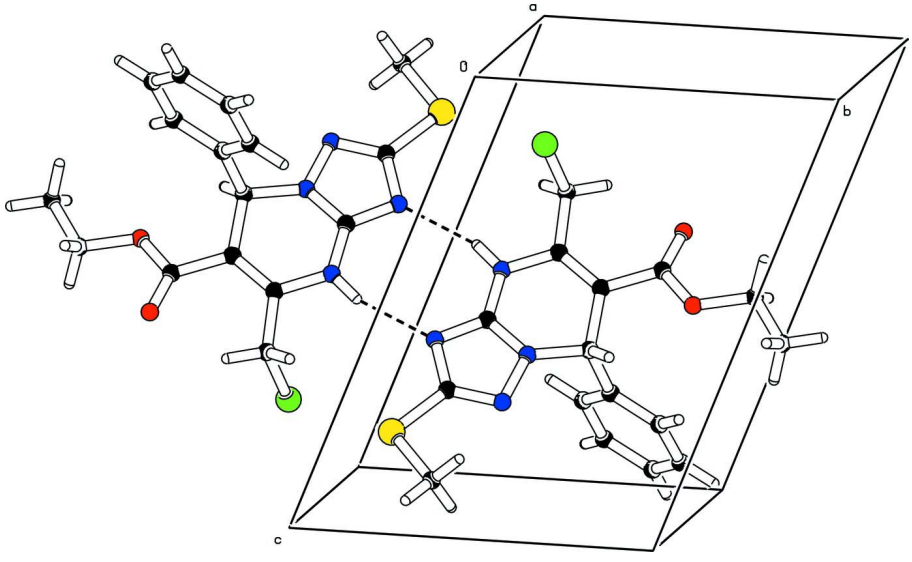

Figure 2

A packing diagram of (I). Hydrogen bonds are shown as dashed lines.

Ethyl 5-chloromethyl-2-methylsulfanyl-7-phenyl-4,7-dihydro- 1,2,4-triazolo[1,5-*a*]pyrimidine-6-carboxylate

Crystal data

$C_{16}H_{17}ClN_4O_2S$
$M_r = 364.85$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 8.9280\ (8)$ Å
$b = 9.8217\ (9)$ Å
$c = 11.3775\ (10)$ Å
$\alpha = 106.022\ (2)°$
$\beta = 102.631\ (2)°$
$\gamma = 109.919\ (2)°$
$V = 845.85\ (13)$ Å^3
$Z = 2$
$F(000) = 380$
$D_x = 1.433$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1660 reflections
$\theta = 2.4–22.5°$
$\mu = 0.37$ mm^{-1}
$T = 292$ K
Block, colorless
0.20 × 0.10 × 0.02 mm

Data collection

Bruker SMART 4K CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
6662 measured reflections
3281 independent reflections
2295 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 26.0°$, $\theta_{min} = 2.4°$
$h = -10\rightarrow11$
$k = -12\rightarrow12$
$l = -14\rightarrow13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.156$
$S = 1.02$
3281 reflections
222 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0839P)^2P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.52275 (12)	0.20019 (13)	0.21023 (8)	0.0802 (4)
S1	0.33719 (10)	0.12878 (9)	0.82617 (8)	0.0506 (3)
O1	0.7924 (2)	0.7426 (2)	0.57614 (18)	0.0458 (5)

O2	0.8859 (3)	0.6249 (3)	0.4314 (2)	0.0745 (8)
N1	0.5299 (3)	0.3688 (3)	0.7737 (2)	0.0399 (6)
N2	0.4832 (3)	0.1259 (2)	0.6417 (2)	0.0394 (6)
N3	0.6027 (3)	0.3760 (2)	0.6786 (2)	0.0378 (5)
N4	0.6300 (3)	0.2107 (3)	0.5023 (2)	0.0423 (6)
H4	0.603 (4)	0.119 (4)	0.448 (3)	0.051*
C1	0.3128 (5)	0.2917 (4)	0.9220 (4)	0.0875 (14)
H1A	0.4175	0.3619	0.9926	0.131*
H1B	0.2245	0.2552	0.9564	0.131*
H1C	0.2831	0.3456	0.8687	0.131*
C2	0.4589 (3)	0.2173 (3)	0.7451 (3)	0.0372 (6)
C3	0.5739 (3)	0.2331 (3)	0.6044 (2)	0.0355 (6)
C4	0.6994 (3)	0.3357 (3)	0.4670 (3)	0.0396 (7)
C5	0.7350 (3)	0.4840 (3)	0.5433 (3)	0.0373 (6)
C6	0.7104 (3)	0.5239 (3)	0.6746 (3)	0.0371 (6)
H6	0.6505	0.5913	0.6795	0.045*
C7	0.7226 (4)	0.2871 (3)	0.3381 (3)	0.0480 (8)
H7A	0.7719	0.2125	0.3329	0.058*
H7B	0.7995	0.3778	0.3290	0.058*
C8	0.8112 (4)	0.6191 (3)	0.5077 (3)	0.0434 (7)
C9	0.8778 (4)	0.8879 (3)	0.5616 (3)	0.0488 (8)
H9A	0.8284	0.8785	0.4733	0.059*
H9B	0.9972	0.9124	0.5791	0.059*
C10	0.8580 (4)	1.0149 (4)	0.6559 (3)	0.0606 (9)
H10A	0.7394	0.9875	0.6405	0.091*
H10B	0.9090	1.1114	0.6446	0.091*
H10C	0.9127	1.0274	0.7433	0.091*
C11	0.8775 (3)	0.6081 (3)	0.7886 (3)	0.0361 (6)
C12	0.9729 (4)	0.5313 (4)	0.8217 (3)	0.0583 (9)
H12	0.9337	0.4245	0.7752	0.070*
C13	1.1272 (5)	0.6119 (5)	0.9238 (4)	0.0715 (11)
H13	1.1902	0.5587	0.9461	0.086*
C14	1.1866 (4)	0.7682 (5)	0.9914 (3)	0.0668 (10)
H14	1.2904	0.8218	1.0595	0.080*
C15	1.0946 (4)	0.8466 (4)	0.9596 (3)	0.0609 (9)
H15	1.1353	0.9536	1.0058	0.073*
C16	0.9403 (4)	0.7662 (3)	0.8584 (3)	0.0489 (8)
H16	0.8778	0.8202	0.8371	0.059*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0749 (7)	0.1054 (8)	0.0463 (5)	0.0385 (6)	0.0133 (5)	0.0154 (5)
S1	0.0548 (5)	0.0413 (4)	0.0518 (5)	0.0097 (3)	0.0306 (4)	0.0165 (4)
O1	0.0558 (13)	0.0343 (11)	0.0494 (12)	0.0146 (9)	0.0248 (10)	0.0193 (9)
O2	0.110 (2)	0.0528 (14)	0.0817 (18)	0.0305 (14)	0.0683 (17)	0.0341 (13)
N1	0.0438 (13)	0.0347 (12)	0.0378 (13)	0.0112 (10)	0.0208 (11)	0.0105 (10)
N2	0.0406 (13)	0.0330 (12)	0.0386 (13)	0.0095 (10)	0.0172 (10)	0.0107 (10)

N3	0.0428 (13)	0.0293 (11)	0.0386 (13)	0.0089 (10)	0.0217 (11)	0.0112 (10)
N4	0.0532 (15)	0.0280 (12)	0.0428 (14)	0.0125 (11)	0.0260 (12)	0.0084 (10)
C1	0.112 (3)	0.058 (2)	0.099 (3)	0.025 (2)	0.081 (3)	0.019 (2)
C2	0.0364 (15)	0.0345 (14)	0.0341 (14)	0.0096 (11)	0.0135 (12)	0.0096 (11)
C3	0.0370 (15)	0.0319 (14)	0.0339 (14)	0.0100 (11)	0.0155 (12)	0.0109 (11)
C4	0.0403 (16)	0.0363 (15)	0.0401 (15)	0.0121 (12)	0.0184 (13)	0.0133 (12)
C5	0.0394 (16)	0.0350 (14)	0.0375 (15)	0.0129 (12)	0.0182 (13)	0.0140 (12)
C6	0.0421 (16)	0.0276 (13)	0.0412 (15)	0.0113 (11)	0.0198 (13)	0.0127 (11)
C7	0.0542 (18)	0.0405 (16)	0.0429 (17)	0.0122 (14)	0.0226 (14)	0.0126 (13)
C8	0.0467 (17)	0.0381 (16)	0.0400 (16)	0.0109 (13)	0.0170 (14)	0.0147 (13)
C9	0.0513 (18)	0.0415 (16)	0.0533 (19)	0.0133 (14)	0.0162 (15)	0.0274 (15)
C10	0.064 (2)	0.0424 (17)	0.072 (2)	0.0197 (16)	0.0217 (18)	0.0227 (16)
C11	0.0405 (15)	0.0315 (14)	0.0370 (15)	0.0113 (12)	0.0202 (12)	0.0140 (11)
C12	0.062 (2)	0.0453 (18)	0.061 (2)	0.0243 (16)	0.0141 (17)	0.0144 (16)
C13	0.062 (2)	0.079 (3)	0.074 (3)	0.038 (2)	0.012 (2)	0.028 (2)
C14	0.050 (2)	0.075 (3)	0.053 (2)	0.0146 (19)	0.0068 (16)	0.0160 (19)
C15	0.067 (2)	0.0408 (17)	0.0473 (19)	0.0064 (16)	0.0113 (17)	0.0051 (15)
C16	0.0585 (19)	0.0382 (16)	0.0425 (17)	0.0175 (14)	0.0136 (15)	0.0118 (13)

Geometric parameters (Å, º)

N1—N3	1.385 (3)	C7—H7B	0.9700
N4—H4	0.85 (3)	C8—O2	1.207 (3)
C1—S1	1.782 (4)	C8—O1	1.334 (3)
C1—H1A	0.9600	C9—O1	1.446 (3)
C1—H1B	0.9600	C9—C10	1.494 (4)
C1—H1C	0.9600	C9—H9A	0.9700
C2—N1	1.312 (3)	C9—H9B	0.9700
C2—N2	1.378 (3)	C10—H10A	0.9600
C2—S1	1.740 (3)	C10—H10B	0.9600
C3—N3	1.324 (3)	C10—H10C	0.9600
C3—N2	1.326 (3)	C11—C16	1.374 (4)
C3—N4	1.356 (3)	C11—C12	1.376 (4)
C4—C5	1.357 (4)	C12—C13	1.387 (4)
C4—N4	1.384 (3)	C12—H12	0.9300
C4—C7	1.495 (4)	C13—C14	1.358 (5)
C5—C8	1.480 (4)	C13—H13	0.9300
C5—C6	1.521 (4)	C14—C15	1.361 (5)
C6—N3	1.463 (3)	C14—H14	0.9300
C6—C11	1.521 (4)	C15—C16	1.382 (4)
C6—H6	0.9800	C15—H15	0.9300
C7—Cl1	1.780 (3)	C16—H16	0.9300
C7—H7A	0.9700		
C2—S1—C1	99.99 (15)	C4—C7—H7B	109.7
C8—O1—C9	116.3 (2)	Cl1—C7—H7B	109.7
C2—N1—N3	101.5 (2)	H7A—C7—H7B	108.2
C3—N2—C2	101.5 (2)	O2—C8—O1	122.2 (3)

C3—N3—N1	109.8 (2)	O2—C8—C5	127.1 (3)
C3—N3—C6	127.0 (2)	O1—C8—C5	110.6 (2)
N1—N3—C6	122.9 (2)	O1—C9—C10	108.3 (2)
C3—N4—C4	119.2 (2)	O1—C9—H9A	110.0
C3—N4—H4	121 (2)	C10—C9—H9A	110.0
C4—N4—H4	118 (2)	O1—C9—H9B	110.0
S1—C1—H1A	109.5	C10—C9—H9B	110.0
S1—C1—H1B	109.5	H9A—C9—H9B	108.4
H1A—C1—H1B	109.5	C9—C10—H10A	109.5
S1—C1—H1C	109.5	C9—C10—H10B	109.5
H1A—C1—H1C	109.5	H10A—C10—H10B	109.5
H1B—C1—H1C	109.5	C9—C10—H10C	109.5
N1—C2—N2	115.8 (2)	H10A—C10—H10C	109.5
N1—C2—S1	124.5 (2)	H10B—C10—H10C	109.5
N2—C2—S1	119.64 (19)	C16—C11—C12	118.2 (3)
N3—C3—N2	111.5 (2)	C16—C11—C6	120.1 (3)
N3—C3—N4	120.3 (2)	C12—C11—C6	121.7 (2)
N2—C3—N4	128.2 (2)	C11—C12—C13	120.5 (3)
C5—C4—N4	121.2 (2)	C11—C12—H12	119.8
C5—C4—C7	125.8 (3)	C13—C12—H12	119.8
N4—C4—C7	113.0 (2)	C14—C13—C12	120.3 (3)
C4—C5—C8	121.9 (2)	C14—C13—H13	119.9
C4—C5—C6	122.5 (2)	C12—C13—H13	119.9
C8—C5—C6	115.5 (2)	C13—C14—C15	120.2 (3)
N3—C6—C11	111.1 (2)	C13—C14—H14	119.9
N3—C6—C5	106.7 (2)	C15—C14—H14	119.9
C11—C6—C5	112.6 (2)	C14—C15—C16	119.7 (3)
N3—C6—H6	108.8	C14—C15—H15	120.2
C11—C6—H6	108.8	C16—C15—H15	120.2
C5—C6—H6	108.8	C11—C16—C15	121.3 (3)
C4—C7—Cl1	109.7 (2)	C11—C16—H16	119.4
C4—C7—H7A	109.7	C15—C16—H16	119.4
Cl1—C7—H7A	109.7		

N4—C4—C5—C8	179.2 (3)	N2—C2—N1—N3	1.7 (3)
C7—C4—C5—C8	−3.1 (4)	S1—C2—N1—N3	−177.30 (19)
N4—C4—C5—C6	3.4 (4)	N3—C3—N2—C2	0.4 (3)
C7—C4—C5—C6	−179.0 (3)	N4—C3—N2—C2	−177.2 (3)
C4—C5—C6—N3	−15.7 (4)	N1—C2—N2—C3	−1.3 (3)
C8—C5—C6—N3	168.2 (2)	S1—C2—N2—C3	177.67 (19)
C4—C5—C6—C11	106.4 (3)	N2—C3—N3—N1	0.6 (3)
C8—C5—C6—C11	−69.7 (3)	N4—C3—N3—N1	178.4 (2)
C5—C4—C7—Cl1	−102.2 (3)	N2—C3—N3—C6	174.0 (2)
N4—C4—C7—Cl1	75.7 (3)	N4—C3—N3—C6	−8.2 (4)
C4—C5—C8—O2	−18.9 (5)	C2—N1—N3—C3	−1.3 (3)
C6—C5—C8—O2	157.3 (3)	C2—N1—N3—C6	−175.0 (2)
C4—C5—C8—O1	163.3 (3)	C11—C6—N3—C3	−104.4 (3)
C6—C5—C8—O1	−20.5 (3)	C5—C6—N3—C3	18.7 (4)

N3—C6—C11—C16	−135.1 (3)	C11—C6—N3—N1	68.2 (3)
C5—C6—C11—C16	105.3 (3)	C5—C6—N3—N1	−168.8 (2)
N3—C6—C11—C12	47.4 (4)	N3—C3—N4—C4	−7.7 (4)
C5—C6—C11—C12	−72.2 (3)	N2—C3—N4—C4	169.7 (3)
C16—C11—C12—C13	0.7 (5)	C5—C4—N4—C3	9.7 (4)
C6—C11—C12—C13	178.2 (3)	C7—C4—N4—C3	−168.2 (2)
C11—C12—C13—C14	−0.7 (6)	O2—C8—O1—C9	−4.6 (4)
C12—C13—C14—C15	0.4 (6)	C5—C8—O1—C9	173.3 (2)
C13—C14—C15—C16	0.0 (6)	C10—C9—O1—C8	−173.8 (2)
C12—C11—C16—C15	−0.3 (5)	N1—C2—S1—C1	10.4 (3)
C6—C11—C16—C15	−177.8 (3)	N2—C2—S1—C1	−168.5 (3)
C14—C15—C16—C11	−0.1 (5)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···N2^{i}	0.85 (3)	2.11 (3)	2.939 (3)	164 (3)
C7—H7*B*···O2	0.97	2.15	2.888 (4)	132

Symmetry code: (i) −*x*+1, −*y*, −*z*+1.