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Crystal structure of ethyl 5-acetyl-2-{[(dimethylamino)methylidene]amino}-4-methylthiophene-3-carboxylate

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In the title thiophene derivative, $C_{13}H_{18}N_2O_3S$, the dihedral angles between the thiophene ring and the [(dimethylamino)-methylidene]amino side chain (r.m.s. deviation = 0.009 Å) and the $-CO_2$ ester group are 3.01 (16) and 59.9 (3)°, respectively. In the crystal, inversion dimers linked by pairs of C—H···O hydrogen bonds generate $R_2^2(16)$ loops. The dimers are linked by another weak C—H···O interaction, forming chains along [001]. In addition, weak C—H···π interactions are observed, which link the chains into (001) layers.

Keywords: crystal structure; thiophene derivative; hydrogen bonding; C—H···π interactions.

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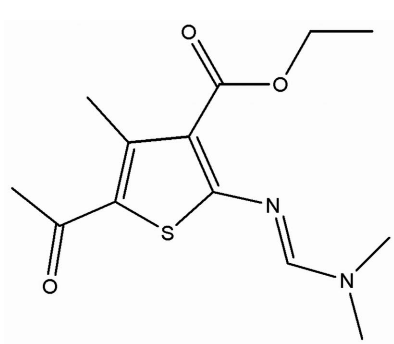
1. Related literature

For background to the applications of thiophene derivatives, see: Sabnis *et al.* (1999). For a related structure, see: Mukhtar *et al.* (2010). For further synthetic details, see: Gewald *et al.* (1966).



2. Experimental

2.1. Crystal data

$C_{13}H_{18}N_2O_3S$
M_r = 282.35
Orthorhombic, *Pbca*
a = 12.218 (3) Å
b = 7.332 (2) Å
c = 30.923 (8) Å
V = 2769.9 (13) Å^3
Z = 8
Mo *Kα* radiation
μ = 0.24 mm^{-1}
T = 100 K
0.29 × 0.26 × 0.10 mm

2.2. Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.958, T_{max} = 0.963
15478 measured reflections
3012 independent reflections
2140 reflections with $I > 2\sigma(I)$
R_{int} = 0.076

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.173
S = 1.19
3012 reflections
177 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}

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

Cg is the centroid of the C2/C3/C4/C5/S1 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9*A*···O2^{i}	0.99	2.45	3.270 (3)	139
C11—H11···O1^{ii}	0.95	2.47	3.312 (4)	147
C7—H7*C*···*Cg*^{iii}	0.98	2.86	3.693 (2)	143

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+1, -y, -z+1$; (iii) $x+\frac{1}{2}, -y+\frac{3}{2}, -z$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7483).

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supporting information

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Crystal structure of ethyl 5-acetyl-2-{[(dimethylamino)methylidene]amino}-4-methylthiophene-3-carboxylate

N. L. Prasad, M. S. Krishnamurthy, H. Nagarajaiah and Noor Shahina Begum

S1. Comment

Thiophene belongs to a class of heterocyclic compounds containing a five membered ring made up of one sulfur as heteroatom, that are widely used as building blocks in many agrochemicals and pharmaceuticals. 2-Aminothiophenes attract special attention because of their applications in pharmaceuticals, agriculture, pesticides and dyes (Sabnis *et al.*, 1999). The most convergent and well established classical approach for the preparation of 2-aminothiophenes is Gewald's method (Gewald *et al.*, 1966), which involves the multicomponent condensation of a ketone with an activated nitrile and elemental sulfur in the presence of diethylamine as a catalyst. Herein, we report the structure of the title compound, (I).

The molecular structure of the compound is shown in Fig. 1. In the title compound, $C_{13}H_{18}N_2O_3S$, a thiophene derivative with dimethylamino- methyleneamino, acetyl, methyl and ethyl carboxylate substituents attached to a central thiophene ring. The thiophene ring and all the substituents are almost planar except the carboxyl group (C10/C9/O3/C8), it is slightly deviating from the plane at -83.474 (3)°. The carbonyl group of the exocyclic ester at C3 and acetyl at C5 adopts a *trans* orientation with C3=C2 and C5=C4 double bond respectively. The crystal structure features C—H···O interactions. The C11—H11···O1 hydrogen bonds resulting in a centrosymmetric head to head dimer with graph set $R^2_2(16)$ notation, which are in turn linked by another weak C9—H9A···O2 interactions to form chains of rings along [001] (Table.1; Fig. 2). In addition, weak C—H···*π* interactions of the type C7—H7C···*Cg* [*Cg* being the centroid of the thiophene ring (C2/C3/C4/C5/S1)] link the chains into layers parallel to (001) with a distance 2.864 Å is also observed (Fig. 3).

S2. Experimental

Step-1: 3.3 g of cyano ethyl acetate was weighed and transferred to RB flask and 5 g of acetyl acetone and 10 to 15 ml of ethanol were added to it. The whole mixture was stirred for 10 min. After stirring 1.6 g of elemental sulfur was added to the mixture and cold condition was maintained by using crushed ice. Later 5 ml of diethyl amine was added drop by drop the solution changes its color to red. After the completion of addition the solution was again kept for stirring (10 min). Ice pack was removed and stirring was continued for about an hour. The precipitated product (**1**) was filtered, dried and recrystallized from ethanol (yield: 68%, m.p. 430 K)

Step-2: A mixture of compound **1** (10 mmol) and DMF—DMA (5 ml) was stirred at room temperature for 30 minutes. To this was added ethanol and kept in room temperature to give a solid product (title compound) that was collected by filtration. The compound was recrystallized by slow evaporation from ethanol, yielding single crystals suitable for X-ray diffraction studies.

S3. Refinement

The H atoms were placed at calculated positions in the riding-model approximation with C—H = 0.96° A, 0.97 ° A and 0.93 ° A for methyl, methylene and methyne H-atoms respectively, with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and U_{iso}(H) = 1.2Ueq(C) for other hydrogen atoms.

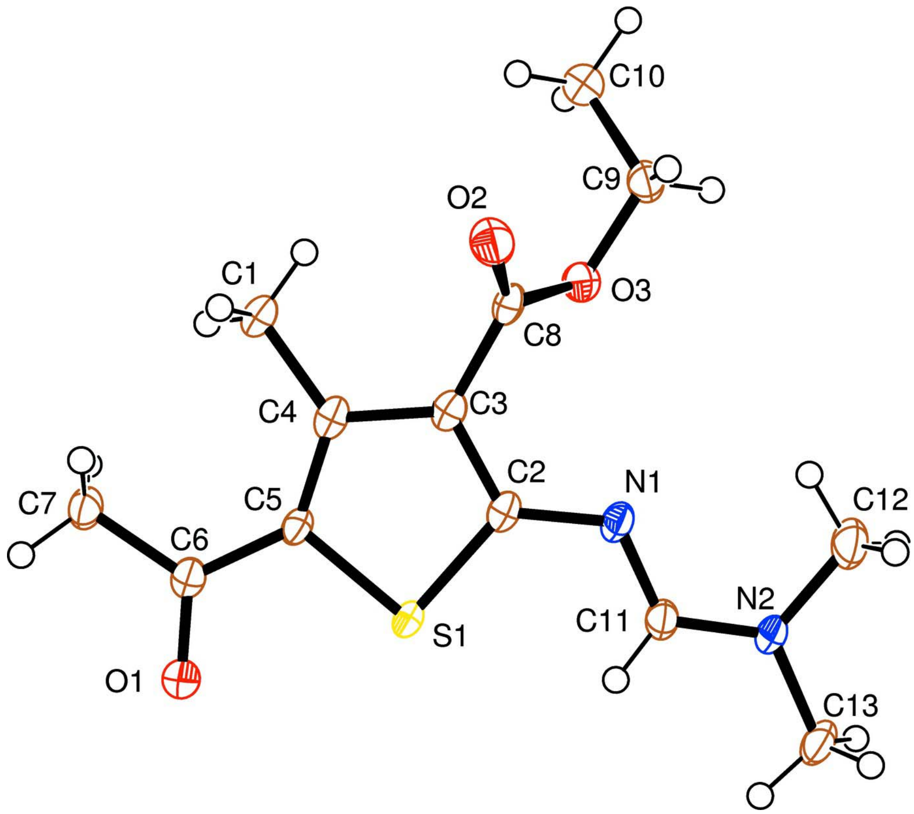

Figure 1

The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are presented as small spheres of arbitrary radius.

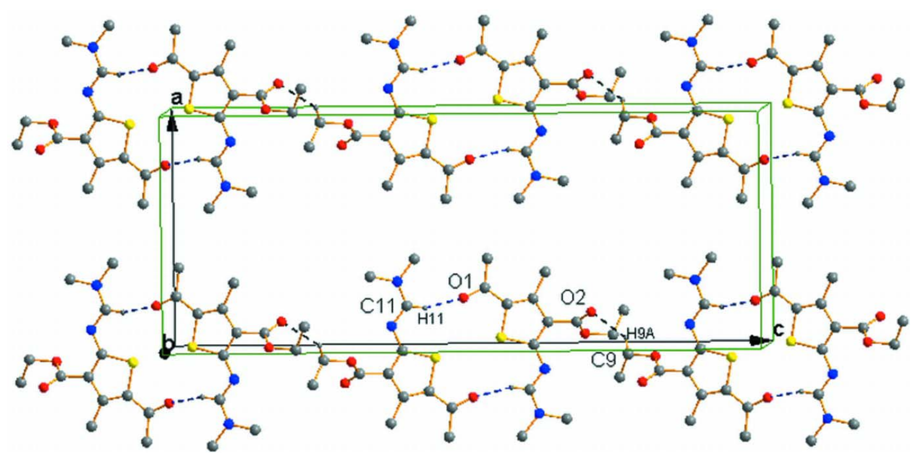

Figure 2

Unit cell packing of the title compound showing intermolecular C—H···O interactions with dotted lines. H-atoms not involved in hydrogen bonding have been excluded.

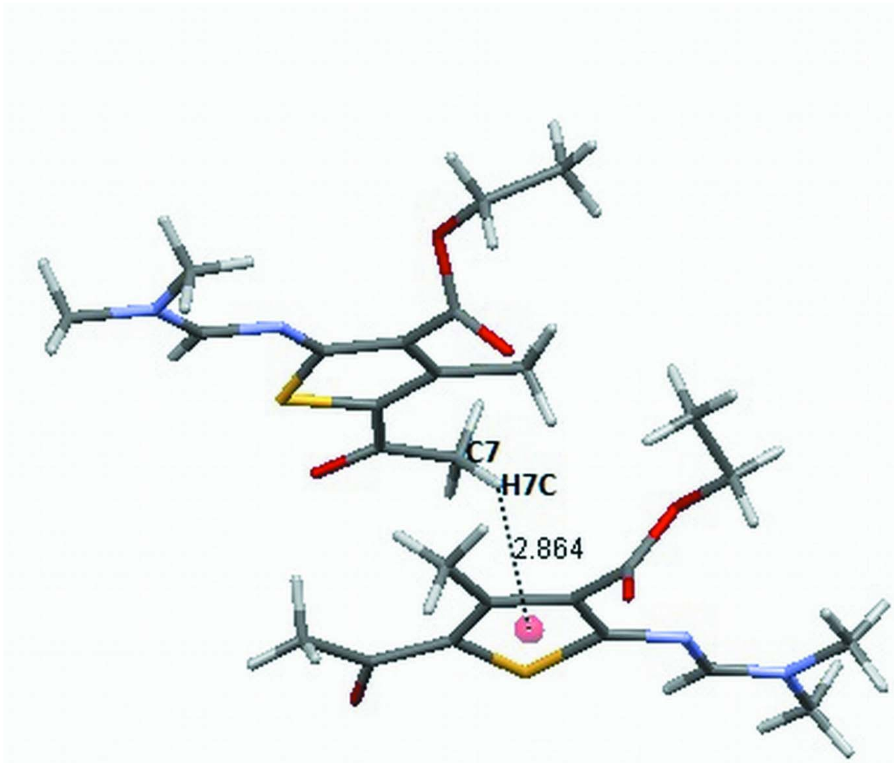

Figure 3

Unit cell packing depicting C—H···π interactions with dotted lines.

Ethyl 5-acetyl-2-{[(dimethylamino)methylidene]amino}-4-methylthiophene-3-carboxylate

Crystal data

$C_{13}H_{18}N_2O_3S$
M_r = 282.35
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
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c = 30.923 (8) Å
V = 2769.9 (13) Å^3
Z = 8
$F(000)$ = 1200
D_x = 1.354 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3012 reflections
θ = 2.1–27.0°
μ = 0.24 mm^{-1}
T = 100 K
Block, colorless
0.29 × 0.26 × 0.10 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.958, T_{max} = 0.963
15478 measured reflections
3012 independent reflections
2140 reflections with $I > 2\sigma(I)$
R_{int} = 0.076
θ_{max} = 27.0°, θ_{min} = 2.1°
$h = -14 \rightarrow 15$
$k = -9 \rightarrow 9$
$l = -39 \rightarrow 35$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.173$
$S = 1.19$
3012 reflections
177 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0811P)^2 + 0.3374P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.52$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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}
C1	0.8067 (2)	0.2414 (4)	0.37436 (9)	0.0219 (6)
H1A	0.8527	0.3124	0.3942	0.033*
H1B	0.7973	0.3089	0.3473	0.033*
H1C	0.8419	0.1240	0.3684	0.033*
C2	0.5031 (2)	0.1973 (4)	0.39447 (9)	0.0194 (6)
C3	0.5979 (2)	0.2312 (4)	0.37104 (9)	0.0193 (6)
C4	0.6967 (2)	0.2091 (4)	0.39477 (9)	0.0196 (6)
C5	0.6764 (2)	0.1574 (4)	0.43709 (9)	0.0190 (6)
C6	0.7476 (2)	0.1108 (4)	0.47350 (9)	0.0211 (6)
C7	0.8697 (2)	0.1198 (4)	0.46853 (9)	0.0252 (7)
H7A	0.9048	0.0694	0.4944	0.038*
H7B	0.8923	0.2471	0.4648	0.038*
H7C	0.8919	0.0488	0.4431	0.038*
C8	0.5956 (2)	0.2660 (4)	0.32370 (9)	0.0203 (6)
C9	0.5315 (2)	0.4612 (4)	0.26762 (9)	0.0251 (7)
H9A	0.4661	0.5384	0.2628	0.030*
H9B	0.5215	0.3467	0.2511	0.030*
C10	0.6313 (2)	0.5590 (5)	0.25110 (10)	0.0321 (7)
H10A	0.6411	0.6730	0.2672	0.048*
H10B	0.6219	0.5864	0.2203	0.048*
H10C	0.6958	0.4814	0.2550	0.048*
C11	0.3149 (2)	0.1822 (4)	0.40202 (9)	0.0216 (6)
H11	0.3262	0.1544	0.4317	0.026*
C13	0.1194 (2)	0.1650 (4)	0.41533 (10)	0.0287 (7)
H13A	0.1452	0.1305	0.4442	0.043*

H13B	0.0736	0.0673	0.4035	0.043*
H13C	0.0765	0.2776	0.4173	0.043*
C12	0.1888 (2)	0.2409 (5)	0.34251 (10)	0.0323 (8)
H12A	0.2567	0.2747	0.3277	0.048*
H12B	0.1377	0.3439	0.3418	0.048*
H12C	0.1558	0.1356	0.3280	0.048*
N1	0.40009 (18)	0.2074 (3)	0.37699 (7)	0.0216 (5)
N2	0.21291 (18)	0.1943 (3)	0.38709 (7)	0.0218 (5)
O1	0.70690 (16)	0.0608 (3)	0.50809 (6)	0.0285 (5)
O2	0.63937 (18)	0.1686 (3)	0.29724 (6)	0.0308 (5)
O3	0.54047 (16)	0.4187 (3)	0.31356 (6)	0.0244 (5)
S1	0.53616 (5)	0.13387 (10)	0.44751 (2)	0.0202 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0151 (15)	0.0206 (15)	0.0301 (16)	−0.0008 (11)	0.0015 (11)	−0.0017 (12)
C2	0.0147 (14)	0.0169 (14)	0.0267 (15)	0.0005 (11)	−0.0003 (11)	−0.0026 (11)
C3	0.0166 (15)	0.0142 (14)	0.0270 (15)	0.0008 (10)	0.0002 (11)	−0.0016 (11)
C4	0.0154 (15)	0.0127 (14)	0.0308 (15)	−0.0002 (10)	−0.0009 (11)	−0.0039 (11)
C5	0.0125 (14)	0.0223 (15)	0.0220 (14)	0.0018 (11)	0.0012 (11)	−0.0017 (11)
C6	0.0176 (15)	0.0189 (15)	0.0268 (15)	0.0001 (11)	−0.0015 (12)	−0.0001 (11)
C7	0.0170 (15)	0.0281 (16)	0.0304 (16)	−0.0015 (12)	−0.0037 (12)	0.0031 (12)
C8	0.0133 (14)	0.0197 (15)	0.0278 (16)	−0.0041 (11)	−0.0025 (12)	−0.0015 (12)
C9	0.0231 (16)	0.0261 (16)	0.0262 (15)	−0.0016 (12)	−0.0041 (12)	0.0043 (12)
C10	0.0262 (17)	0.0424 (19)	0.0276 (16)	−0.0008 (14)	−0.0002 (14)	0.0053 (14)
C11	0.0165 (15)	0.0236 (15)	0.0248 (15)	0.0010 (11)	−0.0026 (12)	0.0007 (12)
C13	0.0131 (15)	0.0363 (18)	0.0368 (18)	−0.0005 (12)	0.0015 (13)	0.0009 (14)
C12	0.0196 (16)	0.043 (2)	0.0341 (18)	0.0057 (13)	−0.0040 (13)	−0.0024 (15)
N1	0.0140 (13)	0.0235 (13)	0.0275 (13)	0.0013 (10)	−0.0003 (10)	0.0009 (10)
N2	0.0130 (12)	0.0285 (14)	0.0240 (12)	0.0006 (10)	0.0000 (10)	0.0005 (10)
O1	0.0216 (11)	0.0385 (13)	0.0254 (11)	−0.0008 (9)	−0.0010 (9)	0.0059 (9)
O2	0.0307 (12)	0.0372 (13)	0.0245 (11)	0.0088 (10)	−0.0012 (9)	−0.0060 (9)
O3	0.0225 (11)	0.0257 (11)	0.0251 (11)	0.0029 (8)	0.0001 (8)	0.0028 (9)
S1	0.0121 (4)	0.0250 (4)	0.0237 (4)	−0.0003 (3)	0.0004 (3)	0.0017 (3)

Geometric parameters (Å, º)

C1—C4	1.504 (4)	C9—O3	1.458 (3)
C1—H1A	0.9800	C9—C10	1.504 (4)
C1—H1B	0.9800	C9—H9A	0.9900
C1—H1C	0.9800	C9—H9B	0.9900
C2—N1	1.372 (3)	C10—H10A	0.9800
C2—C3	1.388 (4)	C10—H10B	0.9800
C2—S1	1.752 (3)	C10—H10C	0.9800
C3—C4	1.422 (4)	C11—N1	1.310 (3)
C3—C8	1.486 (4)	C11—N2	1.332 (3)
C4—C5	1.385 (4)	C11—H11	0.9500

C5—C6	1.464 (4)	C13—N2	1.454 (4)
C5—S1	1.752 (3)	C13—H13A	0.9800
C6—O1	1.235 (3)	C13—H13B	0.9800
C6—C7	1.501 (4)	C13—H13C	0.9800
C7—H7A	0.9800	C12—N2	1.450 (4)
C7—H7B	0.9800	C12—H12A	0.9800
C7—H7C	0.9800	C12—H12B	0.9800
C8—O2	1.210 (3)	C12—H12C	0.9800
C8—O3	1.343 (3)		

C4—C1—H1A	109.5	C10—C9—H9A	109.2
C4—C1—H1B	109.5	O3—C9—H9B	109.2
H1A—C1—H1B	109.5	C10—C9—H9B	109.2
C4—C1—H1C	109.5	H9A—C9—H9B	107.9
H1A—C1—H1C	109.5	C9—C10—H10A	109.5
H1B—C1—H1C	109.5	C9—C10—H10B	109.5
N1—C2—C3	123.4 (3)	H10A—C10—H10B	109.5
N1—C2—S1	126.5 (2)	C9—C10—H10C	109.5
C3—C2—S1	110.1 (2)	H10A—C10—H10C	109.5
C2—C3—C4	114.7 (3)	H10B—C10—H10C	109.5
C2—C3—C8	122.0 (2)	N1—C11—N2	121.9 (3)
C4—C3—C8	122.9 (2)	N1—C11—H11	119.0
C5—C4—C3	111.5 (2)	N2—C11—H11	119.0
C5—C4—C1	126.8 (2)	N2—C13—H13A	109.5
C3—C4—C1	121.6 (3)	N2—C13—H13B	109.5
C4—C5—C6	133.2 (3)	H13A—C13—H13B	109.5
C4—C5—S1	112.1 (2)	N2—C13—H13C	109.5
C6—C5—S1	114.7 (2)	H13A—C13—H13C	109.5
O1—C6—C5	119.7 (3)	H13B—C13—H13C	109.5
O1—C6—C7	120.2 (2)	N2—C12—H12A	109.5
C5—C6—C7	120.1 (2)	N2—C12—H12B	109.5
C6—C7—H7A	109.5	H12A—C12—H12B	109.5
C6—C7—H7B	109.5	N2—C12—H12C	109.5
H7A—C7—H7B	109.5	H12A—C12—H12C	109.5
C6—C7—H7C	109.5	H12B—C12—H12C	109.5
H7A—C7—H7C	109.5	C11—N1—C2	119.2 (2)
H7B—C7—H7C	109.5	C11—N2—C12	122.3 (2)
O2—C8—O3	123.7 (3)	C11—N2—C13	121.1 (2)
O2—C8—C3	123.8 (3)	C12—N2—C13	116.5 (2)
O3—C8—C3	112.5 (2)	C8—O3—C9	116.3 (2)
O3—C9—C10	111.8 (2)	C2—S1—C5	91.56 (13)
O3—C9—H9A	109.2		

N1—C2—C3—C4	−178.5 (2)	C2—C3—C8—O2	−117.1 (3)
S1—C2—C3—C4	−0.6 (3)	C4—C3—C8—O2	55.5 (4)
N1—C2—C3—C8	−5.4 (4)	C2—C3—C8—O3	63.5 (3)
S1—C2—C3—C8	172.5 (2)	C4—C3—C8—O3	−124.0 (3)
C2—C3—C4—C5	0.0 (3)	N2—C11—N1—C2	178.5 (2)

C8—C3—C4—C5	−173.0 (2)	C3—C2—N1—C11	−176.6 (3)
C2—C3—C4—C1	−179.7 (2)	S1—C2—N1—C11	5.8 (4)
C8—C3—C4—C1	7.3 (4)	N1—C11—N2—C12	−1.7 (4)
C3—C4—C5—C6	177.1 (3)	N1—C11—N2—C13	179.7 (3)
C1—C4—C5—C6	−3.2 (5)	O2—C8—O3—C9	2.1 (4)
C3—C4—C5—S1	0.6 (3)	C3—C8—O3—C9	−178.4 (2)
C1—C4—C5—S1	−179.8 (2)	C10—C9—O3—C8	−83.4 (3)
C4—C5—C6—O1	−176.9 (3)	N1—C2—S1—C5	178.6 (2)
S1—C5—C6—O1	−0.4 (3)	C3—C2—S1—C5	0.7 (2)
C4—C5—C6—C7	1.8 (5)	C4—C5—S1—C2	−0.8 (2)
S1—C5—C6—C7	178.2 (2)	C6—C5—S1—C2	−178.0 (2)

Hydrogen-bond geometry (Å, º)

Cg is the centroid of the C2/C3/C4/C5/S1 ring .

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9*A*···O2^{i}	0.99	2.45	3.270 (3)	139
C11—H11···O1^{ii}	0.95	2.47	3.312 (4)	147
C7—H7*C*···*Cg*^{iii}	0.98	2.86	3.693 (2)	143

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+1/2; (ii) −*x*+1, −*y*, −*z*+1; (iii) *x*+1/2, −*y*+3/2, −*z*.