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2-Amino-N-(2-methoxyphenyl)-4,5-dimethylthiophene-3-carboxamide

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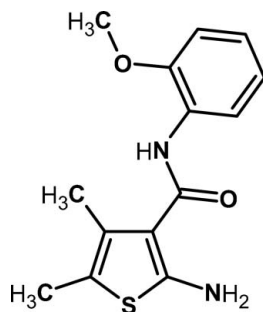
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Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.054; wR factor = 0.143; data-to-parameter ratio = 14.4.

In the title compound, $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$, the two aromatic rings make a dihedral angle of 13.9 (1)°. The crystal structure is stabilized by both inter- and intramolecular $\text{N}-\text{H}\cdots\text{O}$, $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{N}$ hydrogen bonds.

Related literature

For related literature, see: Gewald *et al.* (1966); Cohen *et al.* (1977); Csaszar & Morvay (1983); Lakshmi *et al.* (1985); Mohan & Saravanan (2003); Bruns *et al.* (1990).



Experimental

Crystal data

$\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$
 $M_r = 276.35$
 Monoclinic, $P2_1/n$
 $a = 8.606$ (2) Å
 $b = 7.5193$ (19) Å
 $c = 21.297$ (5) Å
 $\beta = 100.599$ (5)°

$V = 1354.7$ (6) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.24$ mm⁻¹
 $T = 291$ (2) K
 $0.45 \times 0.35 \times 0.28$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.908$, $T_{\max} = 0.937$
 9834 measured reflections
 2514 independent reflections
 1503 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.051$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.142$
 $S = 0.99$
 2514 reflections
 175 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.25$ e Å⁻³
 $\Delta\rho_{\min} = -0.18$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1A}\cdots\text{O1}$	0.86	2.15	2.724 (3)	124
$\text{N1}-\text{H1B}\cdots\text{O1}^i$	0.86	2.23	3.009 (4)	151
$\text{N2}-\text{H2}\cdots\text{O2}$	0.86	2.15	2.565 (3)	109
$\text{C8}-\text{H8}\cdots\text{O1}$	0.93	2.30	2.874 (4)	119

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

Data collection: SMART (Bruker, 1998); cell refinement: SMART; data reduction: SAINT (Bruker, 1998); 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, 1997); software used to prepare material for publication: PARST (Nardelli, 1995) and PLATON (Spek, 2003).

The authors are grateful to Professor T. N. Guru Row, Indian Institute of Science, and the Department of Science and Technology, India, for the data collection using the CCD facility, and Bangalore University. CK thanks the Management, Administrator and Principal of HKBK College of Engineering for encouragement and support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2721).

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supporting information

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2-Amino-N-(2-methoxyphenyl)-4,5-dimethylthiophene-3-carboxamide

K. Chandra Kumar, M. K. Kokila, Puttaraja, J. Saravanan and Manohar V. Kulkarni

S1. Comment

Thiophene derivatives containing amino and carboxyl functions have been found to exhibit anti-viral, anti-inflammatory and antimicrobial activities (Mohan & Saravanan, 2003). Specifically the 2-amino-carboxylic acid esters were recognized as allosteric enhancers for A1 adenosine receptors (Bruns *et al.*, 1990).

Interaction of 3-(2-thienyl alanine) with human phenyl alanine has been studied with a view to understand the mechanism of catalysis and substrate activation. Diffraction studies on bis 5-bromo-2-substituted thiophene derivatives have revealed the existence of S—S stacking interactions. Our earlier investigations on the structures of the biologically active thiophene carboxamide, has shown that the chloro substitution in the aryl amide group had a significant effect. The *ortho*-chloro group reversed the orientation of the amide linkage and favoured the formation of more intra molecular hydrogen bonds. The *para*-chloro substitution induces stabilizing effects *via* inter molecular hydrogen bonds. The compound in the present study bears a close structural relationship with the reported allosteric enhancers for adenosine and hence the structure has been investigated.

The molecular structure and the packing diagram are shown in Fig. 1 and 2, respectively. The molecular structure is stabilized by intra molecular C—H \cdots O, N—H \cdots O hydrogen bonds and intermolecular N—H \cdots O interactions. (Table 2) The intra molecular C8 - H8 \cdots O1 and N1 - H1 \cdots O1 hydrogen bonds form pseudo- six membered rings and N2 - H2 \cdots O2 forms a pseudo five membered ring thus locking the molecular conformation and eliminating conformational flexibility.

S2. Experimental

The title compound was synthesized by mixing of ethyl methyl ketone (0.72 g, 0.01 mol) and *o*-methoxycyanoacetanilide (1.94 g, 0.01 mol) and refluxing the mixture for 1 h (Gewald *et al.*, 1966) in the presence of 4.0 ml of diethylamine. Sulfur powder (1.28 g, 0.04 mol) and 40 ml ethanol were then added and the resulting solution was heated for 2 h at 323 K. Crystals were grown by slow evaporation in a solution of isopropyl alcohol (yield 50%).

S3. Refinement

H atoms were positioned geometrically [N—H = 0.86 Å, and C—H = 0.93 (CH), 0.97 (CH₂) and 0.96 Å (CH₃)] and constrained to ride on their parent atoms with $U_{iso}(H)$ values of 1.2 (1.5 for methyl) times $U_{eq}(C, N)$. A rotating group model was used for the methyl groups.

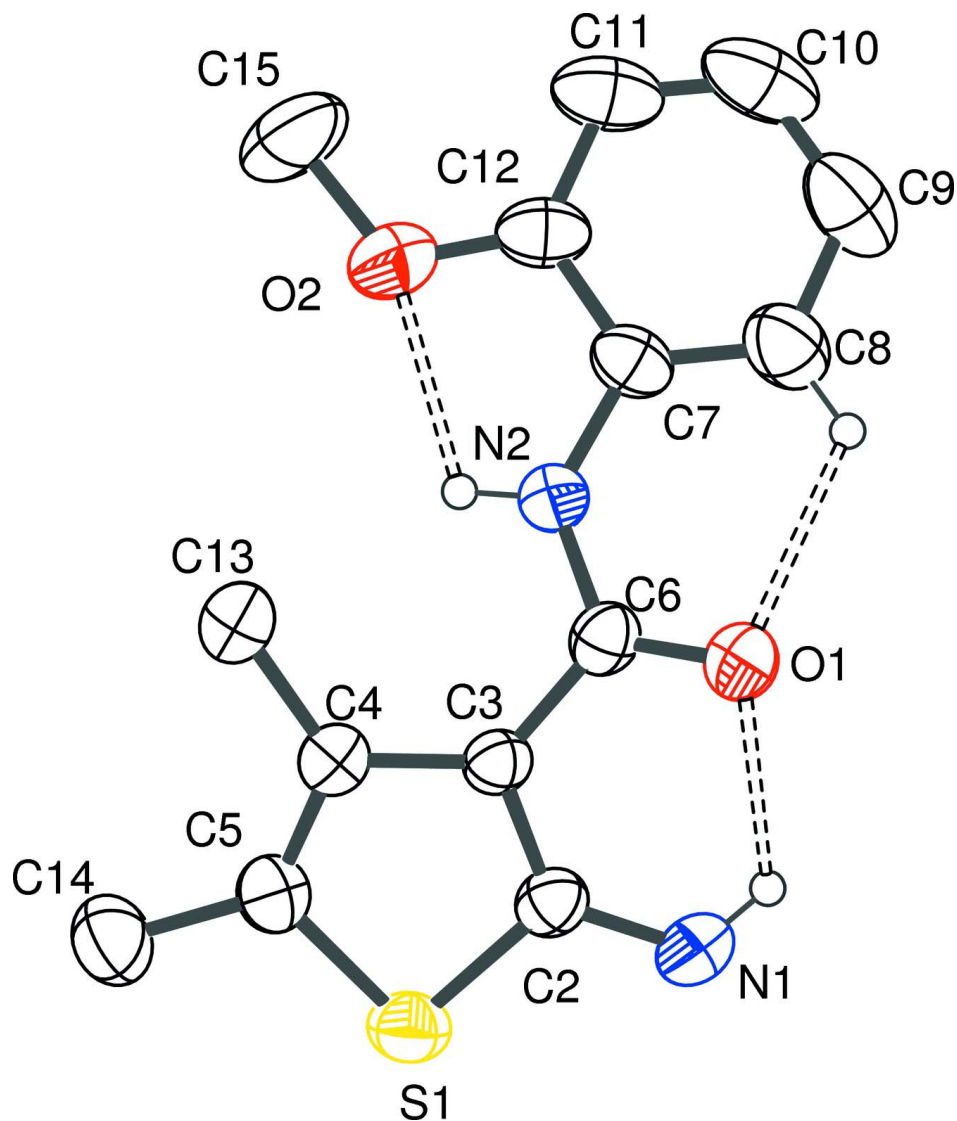


Figure 1

The molecular structure of (I), with atom labels and 50% probability displacement ellipsoids for non-H atoms. Dashed lines indicate intramolecular hydrogen bonds; H atoms not involved in hydrogen bonding have been omitted.

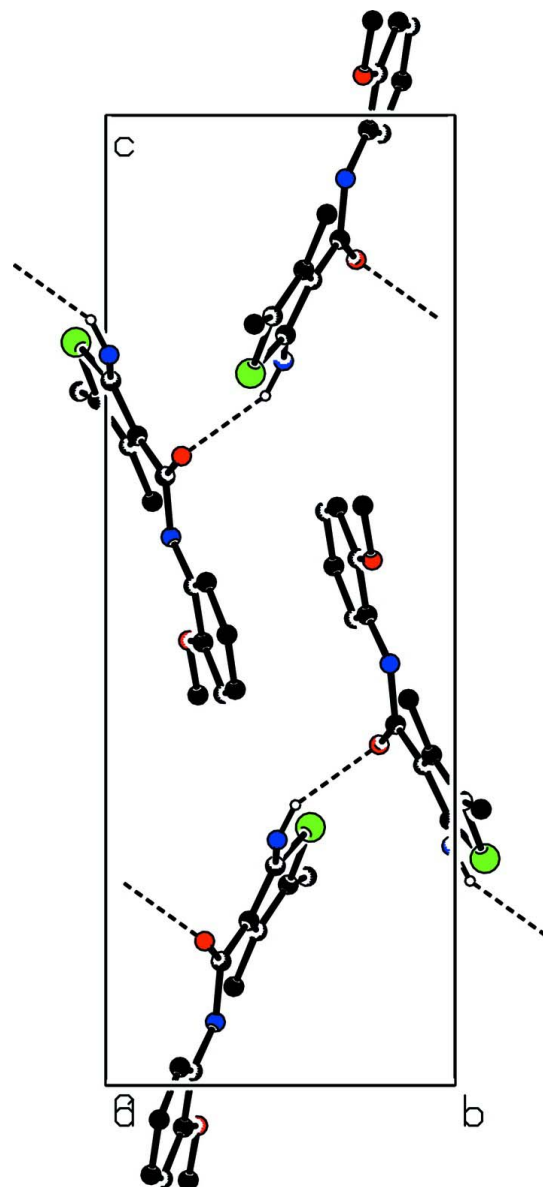


Figure 2

The packing of (I), viewed down the *a* axis shows molecules connected by N—H···O hydrogen bonds (dashedlines). H atoms not involved in hydrogen bonding have been omitted.

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Crystal data

$C_{14}H_{16}N_2O_2S$

$M_r = 276.35$

Monoclinic, $P2_1/n$

Hall symbol: $-P2_1/n$

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$c = 21.297(5) \text{ \AA}$

$\beta = 100.599(5)^\circ$

$V = 1354.7(6) \text{ \AA}^3$

$Z = 4$

$F(000) = 584$

$D_x = 1.355 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 670 reflections

$\theta = 2.0\text{--}28.5^\circ$

$\mu = 0.24 \text{ mm}^{-1}$

$T = 291$ K $0.45 \times 0.35 \times 0.28$ mm
 Block, yellow

Data collection

Bruker SMART CCD area-detector diffractometer Radiation source: fine-focus sealed tube Graphite monochromator ψ and ω scans Absorption correction: multi-scan (SADABS; Sheldrick, 1996) $T_{\min} = 0.908$, $T_{\max} = 0.937$	9834 measured reflections 2514 independent reflections 1503 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.051$ $\theta_{\text{max}} = 25.5^\circ$, $\theta_{\text{min}} = 2.0^\circ$ $h = -10 \rightarrow 10$ $k = -9 \rightarrow 9$ $l = -25 \rightarrow 23$
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Refinement

Refinement on F^2 Least-squares matrix: full $R[F^2 > 2\sigma(F^2)] = 0.053$ $wR(F^2) = 0.142$ $S = 0.99$ 2514 reflections 175 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 $w = 1/[\sigma^2(F_o^2) + (0.0749P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} = 0.001$ $\Delta\rho_{\text{max}} = 0.25 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.18 \text{ e } \text{\AA}^{-3}$
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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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.2740 (3)	0.5092 (4)	0.74695 (12)	0.0593 (8)
H1A	0.2056	0.5582	0.7662	0.071*
H1B	0.2436	0.4570	0.7109	0.071*
N2	0.4683 (3)	0.6863 (3)	0.93475 (11)	0.0480 (7)
H2	0.5646	0.6512	0.9455	0.058*
O1	0.2675 (3)	0.7169 (3)	0.85124 (9)	0.0630 (7)
O2	0.6570 (3)	0.7367 (3)	1.04138 (10)	0.0676 (7)
S1	0.56490 (10)	0.41424 (12)	0.73395 (4)	0.0535 (3)
C2	0.4302 (3)	0.5144 (4)	0.77352 (13)	0.0420 (7)
C3	0.5040 (3)	0.5902 (4)	0.83034 (12)	0.0377 (7)
C4	0.6745 (3)	0.5669 (4)	0.84070 (13)	0.0398 (7)
C5	0.7229 (3)	0.4775 (4)	0.79298 (15)	0.0467 (7)
C6	0.4057 (3)	0.6700 (4)	0.87196 (14)	0.0420 (7)
C7	0.3992 (4)	0.7521 (4)	0.98507 (14)	0.0473 (8)

C8	0.2397 (4)	0.7879 (4)	0.98133 (16)	0.0627 (9)
H8	0.1694	0.7726	0.9430	0.075*
C9	0.1854 (5)	0.8470 (5)	1.0354 (2)	0.0760 (11)
H9	0.0784	0.8705	1.0332	0.091*
C10	0.2894 (6)	0.8706 (5)	1.09189 (19)	0.0783 (12)
H10	0.2519	0.9096	1.1278	0.094*
C11	0.4478 (5)	0.8375 (4)	1.09617 (16)	0.0681 (11)
H11	0.5174	0.8549	1.1346	0.082*
C12	0.5028 (4)	0.7782 (4)	1.04318 (14)	0.0528 (8)
C13	0.7904 (4)	0.6333 (4)	0.89802 (14)	0.0574 (9)
H13A	0.7849	0.5590	0.9342	0.086*
H13B	0.7642	0.7534	0.9074	0.086*
H13C	0.8955	0.6298	0.8889	0.086*
C14	0.8866 (4)	0.4251 (5)	0.78467 (17)	0.0650 (9)
H14A	0.9630	0.4970	0.8119	0.097*
H14B	0.8970	0.4428	0.7410	0.097*
H14C	0.9043	0.3021	0.7958	0.097*
C15	0.7716 (5)	0.7639 (6)	1.09758 (16)	0.0876 (13)
H15A	0.7754	0.8879	1.1086	0.131*
H15B	0.8733	0.7265	1.0902	0.131*
H15C	0.7435	0.6959	1.1320	0.131*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0488 (17)	0.082 (2)	0.0435 (15)	−0.0024 (14)	−0.0015 (13)	−0.0087 (14)
N2	0.0424 (14)	0.0643 (17)	0.0367 (14)	0.0069 (12)	0.0056 (12)	−0.0021 (12)
O1	0.0517 (14)	0.0900 (18)	0.0449 (13)	0.0223 (12)	0.0019 (11)	0.0006 (12)
O2	0.0649 (16)	0.0908 (18)	0.0437 (13)	−0.0020 (14)	0.0012 (12)	−0.0051 (12)
S1	0.0587 (6)	0.0575 (5)	0.0451 (5)	−0.0032 (4)	0.0117 (4)	−0.0088 (4)
C2	0.0434 (17)	0.0445 (16)	0.0374 (16)	−0.0041 (14)	0.0055 (14)	0.0028 (13)
C3	0.0402 (17)	0.0392 (15)	0.0327 (15)	0.0016 (13)	0.0043 (13)	0.0021 (13)
C4	0.0418 (17)	0.0356 (15)	0.0410 (17)	−0.0004 (13)	0.0051 (13)	0.0033 (13)
C5	0.0457 (18)	0.0442 (17)	0.0508 (18)	0.0008 (14)	0.0106 (15)	0.0013 (14)
C6	0.0418 (18)	0.0429 (17)	0.0395 (17)	0.0021 (14)	0.0031 (14)	0.0067 (13)
C7	0.058 (2)	0.0443 (18)	0.0433 (18)	0.0022 (15)	0.0187 (16)	0.0033 (14)
C8	0.067 (2)	0.070 (2)	0.055 (2)	0.0124 (18)	0.0222 (18)	0.0090 (18)
C9	0.083 (3)	0.075 (3)	0.081 (3)	0.024 (2)	0.044 (2)	0.020 (2)
C10	0.126 (4)	0.061 (2)	0.060 (3)	0.019 (2)	0.046 (3)	0.0082 (19)
C11	0.109 (3)	0.055 (2)	0.044 (2)	0.002 (2)	0.023 (2)	0.0019 (16)
C12	0.075 (2)	0.0466 (18)	0.0370 (18)	−0.0016 (17)	0.0123 (17)	0.0028 (14)
C13	0.0458 (19)	0.068 (2)	0.055 (2)	0.0007 (16)	0.0024 (16)	−0.0063 (17)
C14	0.056 (2)	0.066 (2)	0.075 (2)	0.0058 (18)	0.0185 (19)	−0.0091 (19)
C15	0.088 (3)	0.123 (3)	0.044 (2)	−0.026 (3)	−0.010 (2)	0.007 (2)

Geometric parameters (Å, °)

N1—C2	1.360 (3)	C7—C8	1.387 (5)
N1—H1A	0.8600	C8—C9	1.392 (5)
N1—H1B	0.8600	C8—H8	0.9300
N2—C6	1.352 (3)	C9—C10	1.373 (5)
N2—C7	1.407 (4)	C9—H9	0.9300
N2—H2	0.8600	C10—C11	1.373 (5)
O1—C6	1.241 (3)	C10—H10	0.9300
O2—C12	1.370 (4)	C11—C12	1.376 (4)
O2—C15	1.419 (4)	C11—H11	0.9300
S1—C2	1.727 (3)	C13—H13A	0.9600
S1—C5	1.740 (3)	C13—H13B	0.9600
C2—C3	1.382 (4)	C13—H13C	0.9600
C3—C4	1.454 (4)	C14—H14A	0.9600
C3—C6	1.462 (4)	C14—H14B	0.9600
C4—C5	1.347 (4)	C14—H14C	0.9600
C4—C13	1.512 (4)	C15—H15A	0.9600
C5—C14	1.504 (4)	C15—H15B	0.9600
C7—C12	1.399 (4)	C15—H15C	0.9600
C2—N1—H1A	120.0	C8—C9—H9	119.9
C2—N1—H1B	120.0	C10—C9—H9	119.9
H1A—N1—H1B	120.0	C11—C10—C9	120.9 (4)
C6—N2—C7	129.6 (3)	C11—C10—H10	119.5
C6—N2—H2	115.2	C9—C10—H10	119.5
C7—N2—H2	115.2	C10—C11—C12	119.5 (4)
C12—O2—C15	118.0 (3)	C10—C11—H11	120.3
C2—S1—C5	91.95 (14)	C12—C11—H11	120.3
N1—C2—C3	129.5 (3)	O2—C12—C11	125.3 (3)
N1—C2—S1	119.1 (2)	O2—C12—C7	114.0 (3)
C3—C2—S1	111.4 (2)	C11—C12—C7	120.8 (3)
C2—C3—C4	111.8 (3)	C4—C13—H13A	109.5
C2—C3—C6	118.4 (2)	C4—C13—H13B	109.5
C4—C3—C6	129.6 (2)	H13A—C13—H13B	109.5
C5—C4—C3	112.9 (3)	C4—C13—H13C	109.5
C5—C4—C13	121.6 (3)	H13A—C13—H13C	109.5
C3—C4—C13	125.4 (3)	H13B—C13—H13C	109.5
C4—C5—C14	130.2 (3)	C5—C14—H14A	109.5
C4—C5—S1	111.9 (2)	C5—C14—H14B	109.5
C14—C5—S1	117.9 (2)	H14A—C14—H14B	109.5
O1—C6—N2	120.5 (3)	C5—C14—H14C	109.5
O1—C6—C3	121.6 (3)	H14A—C14—H14C	109.5
N2—C6—C3	117.9 (2)	H14B—C14—H14C	109.5
C12—C7—N2	115.7 (3)	O2—C15—H15A	109.5
C12—C7—C8	119.1 (3)	O2—C15—H15B	109.5
N2—C7—C8	125.2 (3)	H15A—C15—H15B	109.5
C9—C8—C7	119.6 (4)	O2—C15—H15C	109.5

C9—C8—H8	120.2	H15A—C15—H15C	109.5
C7—C8—H8	120.2	H15B—C15—H15C	109.5
C8—C9—C10	120.2 (4)		
C5—S1—C2—N1	179.1 (2)	C4—C3—C6—O1	163.3 (3)
C5—S1—C2—C3	-1.1 (2)	C2—C3—C6—N2	157.1 (3)
N1—C2—C3—C4	-179.5 (3)	C4—C3—C6—N2	-18.8 (4)
S1—C2—C3—C4	0.8 (3)	C6—N2—C7—C12	-170.1 (3)
N1—C2—C3—C6	3.9 (5)	C6—N2—C7—C8	11.3 (5)
S1—C2—C3—C6	-175.8 (2)	C12—C7—C8—C9	-0.7 (5)
C2—C3—C4—C5	0.1 (3)	N2—C7—C8—C9	177.8 (3)
C6—C3—C4—C5	176.3 (3)	C7—C8—C9—C10	0.4 (5)
C2—C3—C4—C13	-179.9 (3)	C8—C9—C10—C11	0.3 (6)
C6—C3—C4—C13	-3.8 (5)	C9—C10—C11—C12	-0.6 (5)
C3—C4—C5—C14	-179.9 (3)	C15—O2—C12—C11	-3.0 (5)
C13—C4—C5—C14	0.1 (5)	C15—O2—C12—C7	178.2 (3)
C3—C4—C5—S1	-1.0 (3)	C10—C11—C12—O2	-178.6 (3)
C13—C4—C5—S1	179.1 (2)	C10—C11—C12—C7	0.3 (5)
C2—S1—C5—C4	1.2 (2)	N2—C7—C12—O2	0.7 (4)
C2—S1—C5—C14	-179.7 (3)	C8—C7—C12—O2	179.4 (3)
C7—N2—C6—O1	0.1 (5)	N2—C7—C12—C11	-178.3 (3)
C7—N2—C6—C3	-177.8 (3)	C8—C7—C12—C11	0.4 (5)
C2—C3—C6—O1	-20.8 (4)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1A...O1	0.86	2.15	2.724 (3)	124
N1—H1B...O1 ⁱ	0.86	2.23	3.009 (4)	151
N2—H2...O2	0.86	2.15	2.565 (3)	109
C8—H8...O1	0.93	2.30	2.874 (4)	119

Symmetry code: (i) $-x+1/2, y-1/2, -z+3/2$.