

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

## 4-Methoxy-2-[(E)-[(thiophen-2-yl)methyl-imino]methyl]phenol

 Esen Nur Kantar,<sup>a\*</sup> Yavuz Köysal,<sup>b</sup> Mustafa Macit,<sup>c</sup> Ebru Er<sup>c</sup> and Mustafa Serkan Soylu<sup>d</sup>

<sup>a</sup>Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, TR-55139 Samsun, Turkey, <sup>b</sup>Yesilyurt Demir Celik Vocational School, Ondokuz Mayıs University, TR-55139 Samsun, Turkey, <sup>c</sup>Department of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayıs University, Kurupelit, 55139 Samsun, Turkey, and <sup>d</sup>Department of Physics, Faculty of Arts and Sciences, Giresun University, Giresun, Turkey

Correspondence e-mail: esen.nur@oposta.omu.edu.tr

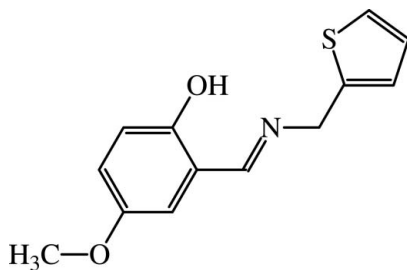
Received 19 July 2012; accepted 22 August 2012

 Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å;  $R$  factor = 0.047;  $wR$  factor = 0.109; data-to-parameter ratio = 11.4.

The title Schiff base,  $\text{C}_{13}\text{H}_{13}\text{NO}_2\text{S}$ , adopts the phenol–imine tautomeric form and reveals an intramolecular  $\text{O}-\text{H}\cdots\text{N}$  hydrogen bond involving the hydroxy group and the imino N atom, forming an  $S(6)$  ring. The molecule is highly twisted with respect to the central imine group, which is reflected in the dihedral angle of  $67.83$  ( $10$ )° formed by the thienyl and phenol rings. The crystal packing is characterized by weak  $\text{C}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\pi$  interactions.

### Related literature

Schiff bases of salicylaldehyde may exhibit thermochromism or photochromism, depending on the planarity or non-planarity, respectively, of the molecule, see: Amimoto & Kawato (2005); Schmidt & Cohen (1964). For a related structure, see: Kantar *et al.* (2012). For hydrogen-bond motifs, see: Bernstein *et al.* (1995)



### Experimental

#### Crystal data

 $\text{C}_{13}\text{H}_{13}\text{NO}_2\text{S}$ 
 $M_r = 247.30$ 

Monoclinic,  $P2_1$   
 $a = 5.6325$  (3) Å  
 $b = 8.1666$  (3) Å  
 $c = 13.4836$  (6) Å  
 $\beta = 96.798$  (4)°  
 $V = 615.86$  (5) Å<sup>3</sup>

$Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.25$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.20 \times 0.15 \times 0.10$  mm

#### Data collection

Oxford Diffraction SuperNova  
 (single source at offset) Eos  
 diffractometer  
 Absorption correction: multi-scan  
 (*CrysAlis PRO*; Oxford)

Diffraction, 2007)  
 $T_{\min} = 0.951$ ,  $T_{\max} = 0.975$   
 2221 measured reflections  
 1809 independent reflections  
 1472 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.015$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$   
 $wR(F^2) = 0.109$   
 $S = 1.06$   
 1809 reflections  
 159 parameters  
 2 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 0.16$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.21$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983),  
 640 Friedel pairs  
 Flack parameter: 0.04 (13)

**Table 1**

Hydrogen-bond geometry (Å, °).

 $Cg1$  is the centroid of the C1–C6 ring.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1}-\text{H1}\cdots\text{N1}$	1.10 (6)	1.63 (7)	2.616 (4)	147 (5)
$\text{C8}-\text{H8A}\cdots\text{O2}^i$	0.97	2.77	3.592 (4)	143
$\text{C2}-\text{H2}\cdots\text{Cg1}^{ii}$	0.93	3.00	3.631 (4)	127

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2007); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; 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: *WinGX* (Farrugia, 1999).

The authors acknowledge the Faculty of Arts and Sciences, Giresun University, Turkey, for the use of the diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZQ2177).

### References

- Amimoto, K. & Kawato, T. (2005). *J. Photochem. Photobiol. C*, **6**, 207–226.  
 Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.  
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.  
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.  
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
 Kantar, E. N., Köysal, Y., Gümüş, S., Ağar, E. & Soylu, M. S. (2012). *Acta Cryst.* **E68**, o1587.  
 Oxford Diffraction (2007). *CrysAlis PRO*. Oxford Diffraction Ltd, Abingdon, England.  
 Schmidt, G. M. J. & Cohen, M. D. (1964). *J. Chem. Soc.* pp. 1996–2000.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

## supporting information

*Acta Cryst.* (2012). E68, o2801 [doi:10.1107/S1600536812036586]

## 4-Methoxy-2-*{(E)-[(thiophen-2-yl)methylimino]methyl}*phenol

Esen Nur Kantar, Yavuz Köysal, Mustafa Macit, Ebru Er and Mustafa Serkan Soylu

### S1. Comment

The title Schiff base, C<sub>13</sub>H<sub>13</sub>NO<sub>2</sub>S, adopts in the crystal structure the phenol-imine tautomeric form and reveals an intramolecular O—H···N hydrogen bond between the hydroxy O atom and the imino N atom (Kantar *et al.*, 2012) generating a nearly planar six-membered ring, a S(6) ring motif according to Bernstein *et al.* (1995).

It is known that Schiff bases of salicylaldehyde may exhibit thermochromism or photochromism, depending on planarity or non-planarity of the molecule (Schmidt & Cohen, 1964; Amimoto & Kawato, 2005). The X-ray diffraction study of the title compound shows that the molecule is highly twisted with respect to the central imine group, which is reflected in the dihedral angle of 67.83 (10)<sup>o</sup> formed by the thienyl and phenol rings.

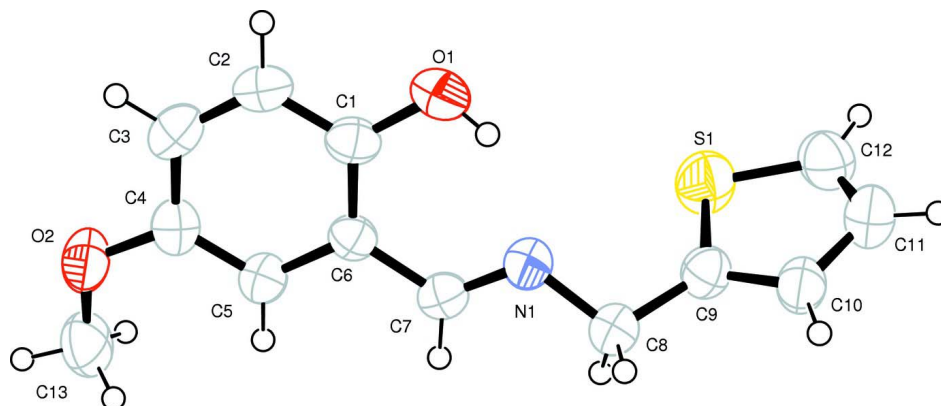
The crystal packing is characterized by weak C—H···O (see Table 1) and C—H··· $\pi$  interactions: the distance between C2—H2 and Cg1<sup>ii</sup> (C1-C6 ring) is 3.00 Å [symmetry code: *ii* = 1-*x*, 0.5+*y*, 1-*z*].

### S2. Experimental

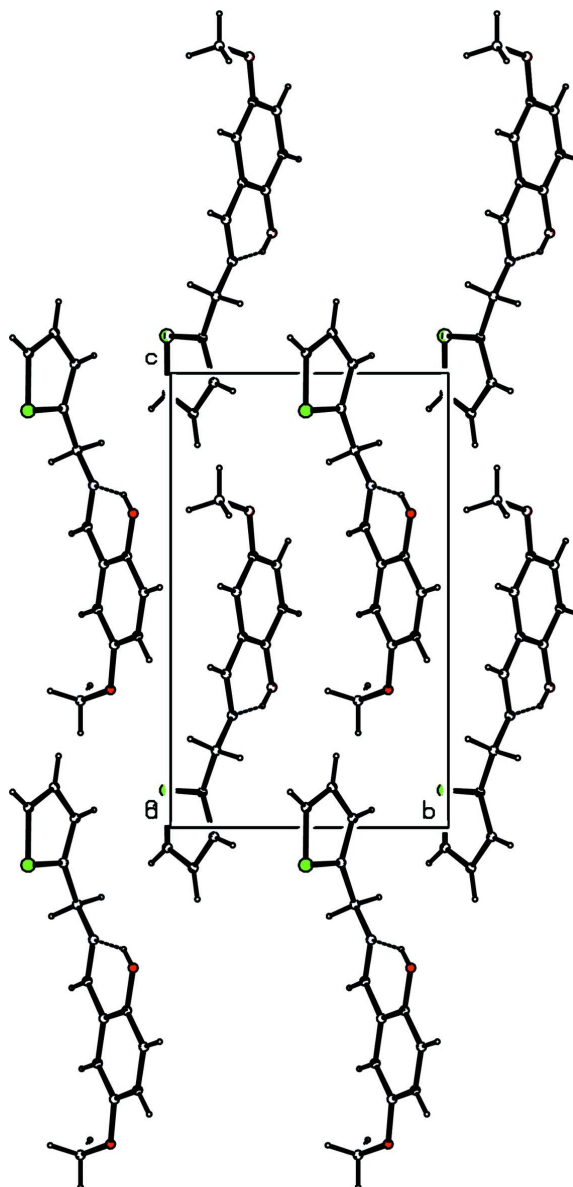
The title compound was prepared by refluxing a mixture of a solution containing 2-hydroxy-5-methoxybenzaldehyde (15.22 mg, 0.1 mmol) in ethanol (20 ml) and a solution containing 2-thiophenemethylamine (11.32 mg, 0.1 mmol) in ethanol (20 ml). The reaction mixture was stirred for 5 h under reflux. Single crystals of the title compound suitable for X-ray analysis were obtained by slow evaporation of the ethanol solution (yield 64%; m.p. 353–355 K).

### S3. Refinement

The structure was solved by direct methods and refined by full-matrix least-square techniques. All hydrogen positions, except H1 which was located in a difference Fourier map and freely refined), were calculated after each cycle of refinement using a riding model, with C—H = 0.93 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for aromatic H atoms, with C—H = 0.97 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for methine H atoms, and with C—H = 0.96 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl H atoms. The Flack *x* parameter was refined to 0.04 (13) based on 640 Friedel pairs.

**Figure 1**

A view of the title compound with the atom-numbering scheme and 50% probability displacement ellipsoids.

**Figure 2**

Packing diagram of the title compound along the *a* axis.

#### 4-Methoxy-2-[(*E*)-[(thiophen-2-yl)methylimino]methyl]phenol

##### *Crystal data*

$C_{13}H_{13}NO_2S$

$M_r = 247.30$

Monoclinic,  $P2_1$

Hall symbol:  $P\ 2_1y$

$a = 5.6325\ (3)\ \text{\AA}$

$b = 8.1666\ (3)\ \text{\AA}$

$c = 13.4836\ (6)\ \text{\AA}$

$\beta = 96.798\ (4)^\circ$

$V = 615.86\ (5)\ \text{\AA}^3$

$Z = 2$

$F(000) = 260$

$D_x = 1.334\ \text{Mg m}^{-3}$

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

Cell parameters from 958 reflections

$\theta = 3.6\text{--}28.7^\circ$

$\mu = 0.25\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, yellow

$0.20 \times 0.15 \times 0.10\ \text{mm}$

*Data collection*

Oxford Diffraction SuperNova (single source at offset) Eos diffractometer  
 Radiation source: fine-focus sealed tube  
 Graphite monochromator  
 Detector resolution: 16.0454 pixels mm<sup>-1</sup>  
 $\omega$  scans  
 Absorption correction: multi-scan (CrysAlis PRO; Oxford Diffraction, 2007)

$T_{\min} = 0.951$ ,  $T_{\max} = 0.975$   
 2221 measured reflections  
 1809 independent reflections  
 1472 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.015$   
 $\theta_{\max} = 25.0^\circ$ ,  $\theta_{\min} = 3.6^\circ$   
 $h = -3 \rightarrow 6$   
 $k = -9 \rightarrow 9$   
 $l = -15 \rightarrow 16$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.047$   
 $wR(F^2) = 0.109$   
 $S = 1.06$   
 1809 reflections  
 159 parameters  
 2 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  
 $w = 1/[\sigma^2(F_o^2) + (0.0439P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.009$   
 $\Delta\rho_{\max} = 0.16 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$   
 Absolute structure: Flack (1983), 640 Friedel pairs  
 Absolute structure parameter: 0.04 (13)

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.3932 (6)	0.8415 (4)	0.5974 (3)	0.0481 (9)
C2	0.4982 (7)	0.9033 (4)	0.5174 (3)	0.0551 (10)
H2	0.6417	0.9604	0.5289	0.066*
C3	0.3927 (7)	0.8808 (4)	0.4220 (3)	0.0562 (10)
H3	0.4663	0.9221	0.3691	0.067*
C4	0.1768 (7)	0.7970 (4)	0.4023 (3)	0.0500 (9)
C5	0.0698 (7)	0.7362 (4)	0.4812 (2)	0.0449 (9)
H5	-0.0738	0.6795	0.4689	0.054*
C6	0.1748 (6)	0.7589 (4)	0.5800 (2)	0.0415 (8)
C7	0.0515 (7)	0.6993 (4)	0.6618 (3)	0.0440 (9)
H7	-0.0921	0.6433	0.6472	0.053*
C8	-0.0063 (7)	0.6629 (5)	0.8305 (3)	0.0586 (11)
H8A	-0.1025	0.5702	0.8050	0.070*
H8B	-0.1139	0.7489	0.8468	0.070*

C9	0.1489 (7)	0.6132 (4)	0.9223 (3)	0.0506 (9)
C10	0.1217 (7)	0.6557 (5)	1.0203 (3)	0.0562 (10)
H10	0.0014	0.7232	1.0389	0.067*
C11	0.3051 (8)	0.5809 (6)	1.0888 (3)	0.0726 (13)
H11	0.3178	0.5960	1.1576	0.087*
C12	0.4554 (8)	0.4878 (7)	1.0440 (3)	0.0725 (12)
H12	0.5821	0.4302	1.0781	0.087*
C13	-0.1056 (9)	0.6748 (6)	0.2794 (3)	0.0737 (13)
H13A	-0.1514	0.6756	0.2085	0.111*
H13B	-0.2383	0.7091	0.3128	0.111*
H13C	-0.0587	0.5661	0.3004	0.111*
N1	0.1345 (6)	0.7215 (4)	0.7533 (2)	0.0528 (8)
O1	0.5060 (5)	0.8643 (3)	0.6917 (2)	0.0659 (8)
O2	0.0879 (6)	0.7829 (3)	0.30331 (18)	0.0652 (8)
S1	0.3895 (2)	0.48631 (16)	0.91768 (8)	0.0757 (4)
H1	0.386 (11)	0.814 (9)	0.743 (4)	0.17 (2)*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.040 (2)	0.046 (2)	0.058 (2)	0.0053 (19)	0.0061 (18)	-0.0043 (18)
C2	0.041 (2)	0.056 (2)	0.069 (3)	-0.006 (2)	0.009 (2)	0.0000 (19)
C3	0.060 (3)	0.049 (2)	0.063 (3)	0.001 (2)	0.022 (2)	0.0059 (19)
C4	0.061 (3)	0.044 (2)	0.045 (2)	0.004 (2)	0.0071 (19)	-0.0015 (16)
C5	0.050 (2)	0.0383 (18)	0.047 (2)	-0.0017 (18)	0.0080 (17)	0.0000 (16)
C6	0.0394 (19)	0.0395 (18)	0.045 (2)	0.0054 (18)	0.0042 (16)	-0.0009 (15)
C7	0.042 (2)	0.0389 (19)	0.051 (2)	0.0017 (18)	0.0079 (18)	0.0005 (16)
C8	0.052 (2)	0.078 (3)	0.047 (2)	0.002 (2)	0.0097 (19)	0.003 (2)
C9	0.054 (2)	0.049 (2)	0.050 (2)	0.001 (2)	0.0098 (19)	0.0036 (16)
C10	0.060 (2)	0.064 (2)	0.045 (2)	0.004 (2)	0.0089 (19)	0.0020 (18)
C11	0.078 (3)	0.091 (3)	0.050 (3)	-0.005 (3)	0.011 (2)	0.003 (2)
C12	0.069 (3)	0.080 (3)	0.066 (3)	-0.001 (3)	-0.001 (2)	0.017 (3)
C13	0.087 (3)	0.086 (3)	0.045 (2)	-0.006 (3)	0.000 (2)	-0.008 (2)
N1	0.0490 (19)	0.063 (2)	0.0468 (18)	0.0014 (17)	0.0085 (15)	0.0032 (15)
O1	0.0475 (16)	0.085 (2)	0.0622 (19)	-0.0050 (16)	-0.0050 (14)	-0.0040 (15)
O2	0.085 (2)	0.0653 (17)	0.0457 (16)	-0.0113 (17)	0.0085 (15)	0.0064 (13)
S1	0.0763 (8)	0.0815 (8)	0.0709 (7)	0.0178 (7)	0.0153 (6)	-0.0011 (6)

*Geometric parameters (Å, °)*

C1—O1	1.365 (4)	C8—H8A	0.9700
C1—C2	1.385 (5)	C8—H8B	0.9700
C1—C6	1.398 (5)	C9—C10	1.392 (5)
C2—C3	1.364 (5)	C9—S1	1.713 (4)
C2—H2	0.9300	C10—C11	1.438 (5)
C3—C4	1.393 (5)	C10—H10	0.9300
C3—H3	0.9300	C11—C12	1.334 (6)
C4—O2	1.374 (4)	C11—H11	0.9300

C4—C5	1.375 (5)	C12—S1	1.699 (4)
C5—C6	1.404 (4)	C12—H12	0.9300
C5—H5	0.9300	C13—O2	1.410 (5)
C6—C7	1.456 (4)	C13—H13A	0.9600
C7—N1	1.279 (4)	C13—H13B	0.9600
C7—H7	0.9300	C13—H13C	0.9600
C8—N1	1.462 (4)	O1—H1	1.10 (6)
C8—C9	1.486 (5)		
O1—C1—C2	118.7 (3)	C9—C8—H8B	109.3
O1—C1—C6	121.7 (3)	H8A—C8—H8B	108.0
C2—C1—C6	119.6 (3)	C10—C9—C8	127.1 (4)
C3—C2—C1	120.4 (4)	C10—C9—S1	111.2 (3)
C3—C2—H2	119.8	C8—C9—S1	121.7 (3)
C1—C2—H2	119.8	C9—C10—C11	110.6 (4)
C2—C3—C4	121.2 (4)	C9—C10—H10	124.7
C2—C3—H3	119.4	C11—C10—H10	124.7
C4—C3—H3	119.4	C12—C11—C10	113.4 (4)
O2—C4—C5	125.3 (4)	C12—C11—H11	123.3
O2—C4—C3	115.8 (3)	C10—C11—H11	123.3
C5—C4—C3	118.8 (3)	C11—C12—S1	112.5 (3)
C4—C5—C6	120.8 (3)	C11—C12—H12	123.7
C4—C5—H5	119.6	S1—C12—H12	123.7
C6—C5—H5	119.6	O2—C13—H13A	109.5
C5—C6—C1	119.1 (3)	O2—C13—H13B	109.5
C5—C6—C7	119.4 (3)	H13A—C13—H13B	109.5
C1—C6—C7	121.5 (3)	O2—C13—H13C	109.5
N1—C7—C6	122.1 (3)	H13A—C13—H13C	109.5
N1—C7—H7	119.0	H13B—C13—H13C	109.5
C6—C7—H7	119.0	C7—N1—C8	118.2 (3)
N1—C8—C9	111.6 (3)	C1—O1—H1	106 (3)
N1—C8—H8A	109.3	C4—O2—C13	117.3 (3)
C9—C8—H8A	109.3	C12—S1—C9	92.2 (2)
N1—C8—H8B	109.3		
O1—C1—C2—C3	179.0 (3)	C1—C6—C7—N1	1.1 (5)
C6—C1—C2—C3	-1.5 (5)	N1—C8—C9—C10	132.6 (4)
C1—C2—C3—C4	0.6 (5)	N1—C8—C9—S1	-49.0 (5)
C2—C3—C4—O2	179.7 (3)	C8—C9—C10—C11	178.8 (3)
C2—C3—C4—C5	-0.1 (5)	S1—C9—C10—C11	0.3 (4)
O2—C4—C5—C6	-179.3 (3)	C9—C10—C11—C12	-0.8 (6)
C3—C4—C5—C6	0.4 (5)	C10—C11—C12—S1	0.9 (5)
C4—C5—C6—C1	-1.3 (5)	C6—C7—N1—C8	177.7 (3)
C4—C5—C6—C7	177.3 (3)	C9—C8—N1—C7	149.1 (3)
O1—C1—C6—C5	-178.7 (3)	C5—C4—O2—C13	-11.4 (5)
C2—C1—C6—C5	1.8 (5)	C3—C4—O2—C13	168.9 (3)
O1—C1—C6—C7	2.7 (5)	C11—C12—S1—C9	-0.6 (4)
C2—C1—C6—C7	-176.8 (3)	C10—C9—S1—C12	0.1 (3)

C5—C6—C7—N1                      -177.5 (3)                      C8—C9—S1—C12                      -178.5 (3)

*Hydrogen-bond geometry (Å, °)*

Cg1 is the centroid of the C1—C6 ring.

<i>D—H···A</i>	<i>D—H</i>	<i>H···A</i>	<i>D···A</i>	<i>D—H···A</i>
O1—H1···N1	1.10 (6)	1.63 (7)	2.616 (4)	147 (5)
C8—H8A···O2 <sup>i</sup>	0.97	2.77	3.592 (4)	143
C2—H2···Cg1 <sup>ii</sup>	0.93	3.00	3.631 (4)	127

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