



Crystal structure of 2-[[5-nitrothiophen-2-yl)methylidene]amino}phenol

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Received 9 May 2015; accepted 14 May 2015

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

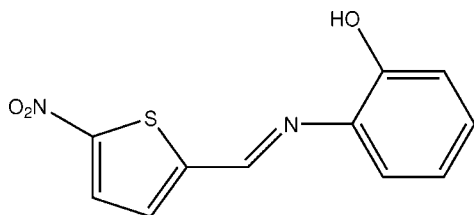
The title compound, C₁₁H₈N₂O₃S, is roughly planar; the dihedral angle between the planes of the thiophene and benzene rings is 8.38 (10)°. An intramolecular O—H···N hydrogen bond generates an S(5) ring motif. In the crystal, molecules are linked into centrosymmetric dimers by pairs of O—H···O hydrogen bonds with an R₂²(22) graph-set motif. Aromatic π–π stacking interactions [centroid–centroid separations = 3.653 (3) and 3.852 (3) Å] link the dimers into a three-dimensional network.

Keywords: crystal structure; Schiff bases; phenol; hydrogen bonding; π–π stacking.

CCDC reference: 1400935

1. Related literature

For Schiff bases as ligands, see: Aydoğan *et al.* (2001); Tanak *et al.* (2009). For related structures, see: Tanak *et al.* (2013, 2014).



2. Experimental

2.1. Crystal data

C ₁₁ H ₈ N ₂ O ₃ S	V = 1087.3 (10) Å ³
M _r = 248.25	Z = 4
Monoclinic, P2 ₁ /c	Mo Kα radiation
a = 10.642 (5) Å	μ = 0.29 mm ⁻¹
b = 7.043 (5) Å	T = 293 K
c = 14.535 (5) Å	0.68 × 0.37 × 0.15 mm
β = 93.566 (5)°	

2.2. Data collection

Stoe IPDS diffractometer	7883 measured reflections
Absorption correction: integration (X-RED32; Stoe & Cie, 2002)	2254 independent reflections
T _{min} = 0.877, T _{max} = 0.965	1696 reflections with I > 2σ(I)
	R _{int} = 0.114

2.3. Refinement

R[F ² > 2σ(F ²)] = 0.064	H atoms treated by a mixture of independent and constrained refinement
wR(F ²) = 0.100	Δρ _{max} = 0.89 e Å ⁻³
S = 0.98	Δρ _{min} = -0.45 e Å ⁻³
2254 reflections	
186 parameters	

Table 1

Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H1···O2 ⁱ	0.78 (3)	2.54 (3)	3.192 (3)	141 (3)
O3—H1···N2	0.78 (3)	2.23 (3)	2.711 (2)	121 (3)

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

Data collection: X-Area (Stoe & Cie, 2002); cell refinement: X-Area; data reduction: X-RED32 (Stoe & Cie, 2002); 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); software used to prepare material for publication: WinGX (Farrugia, 2012).

Acknowledgements

This study was supported financially by the Research Center of Amasya University (Project No. FMB-BAP 15-091).

Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7421).

References

- Aydoğan, F., Öcal, N., Turgut, Z. & Yolaçan, C. (2001). *Bull. Korean Chem. Soc.* **22**, 476–480.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Stoe & Cie (2002). X-Area and X-RED32. Stoe & Cie, Darmstadt, Germany.
- Tanak, H., Agar, A. A. & Büyükgüngör, O. (2013). *J. Mol. Struct.* **1048**, 41–50.
- Tanak, H., Agar, A. A. & Büyükgüngör, O. (2014). *Spectrochim. Acta Part A*, **118**, 672–682.
- Tanak, H., Erşahin, F., Ağar, E., Yavuz, M. & Büyükgüngör, O. (2009). *Acta Cryst.* **E65**, o2291.

supporting information

Acta Cryst. (2015). E71, o418 [doi:10.1107/S2056989015009202]

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S1. Comment

Schiff bases have long been employed as ligands for the complexation of metal ions (Aydoğan *et al.*, 2001; Tanak *et al.*, 2009).

In the title compound (Fig. 1), the molecular structure is almost planar. The dihedral angle between the C1—C4/S1 thiophene and the C6—C11 phenyl rings is 8.38 (10)°. The imino group is coplanar with the nitrothiophene ring as it can be shown by the C3—C4—C5—N2 torsion angle is 178.60 (19)°. The length of the C5=N2 double bond is 1.264 (2) Å, it is slightly shorter than standart 1.28 Å value of C=N double bond and consistent with the related sturctures (Tanak *et al.*, 2013; Tanak *et al.*, 2014). The C1—S1 and C4—S1 bond lengths of the thiophene ring are slightly different than the accepted value for an *Csp*²—S single bond (1.76 Å), resulting from the conjugation of the electrons of atom S1 with atoms C1 and C4 (Tanak *et al.*, 2014).

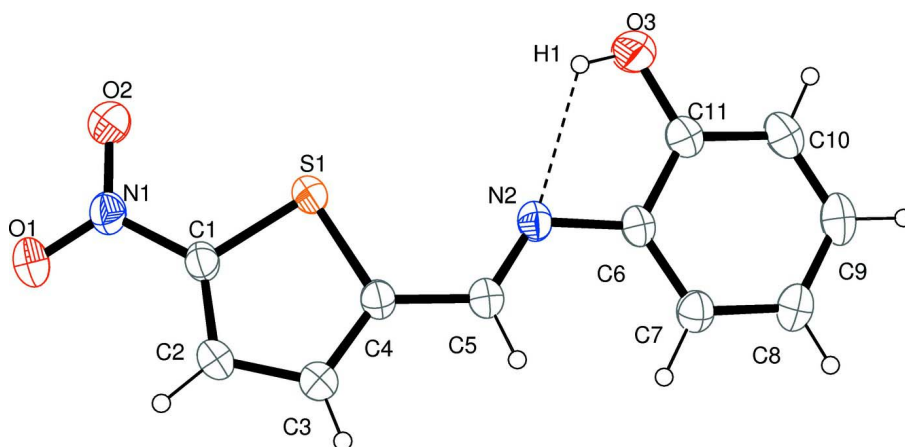
The crystal structure is stabilized by O—H...N and O—H...O type intra and intermolecular hydrogen bonds. An intramolecular O3—H1...N2 interaction (Table 1 and Fig. 1) generates an S(5) ring motif, (1995). In the crystal structure, pairs of O3—H1...O2 hydrogen bond link the molecules to form inversion dimer (Fig. 2) with an R₂²(22) ring motif. The crystal structure also feaures π — π stacking interactions with distances of Cg1...Cg2 = 3.653 (3) Å [symmetry code = 1 - x, -1/2 + y, 1/2 - z] and Cg1...Cg2 = 3.852 (3) Å [symmetry code = 1 - x, 1/2 + y, 1/2 - z], where Cg1 and Cg2 are the centroids of C1—C4/S1 and C6—C11 rings, respectively. The details of the hydrogen bonds are summarized in Table 1. A packing diagram of the title compound is shown in Fig. 3.

S2. Experimental

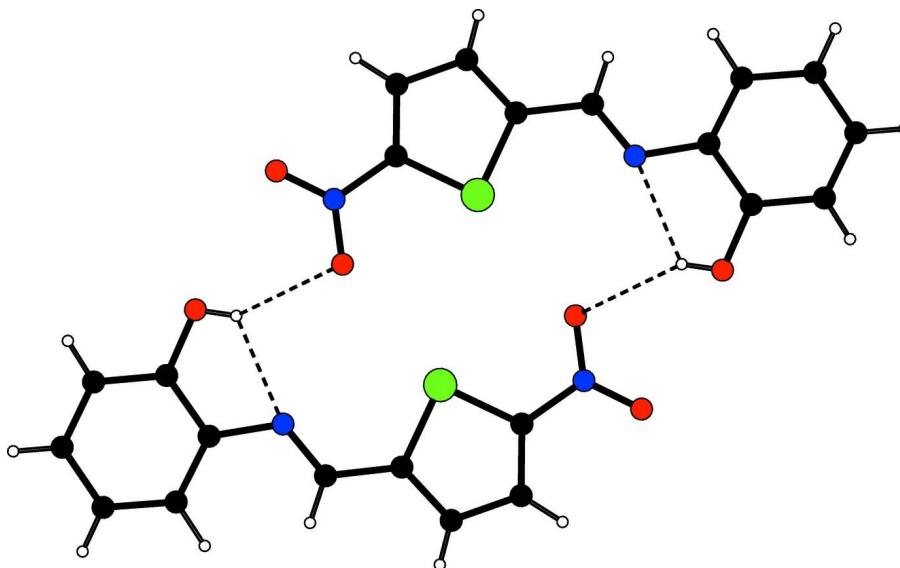
The title compound was prepared by refluxing a mixture of a solution containing 5-nitrothiophene-2-carbaldehyde (18.4 mg, 0.117 mmol) in ethanol (20 ml) and a solution containing 2-aminophenol (12.8 mg, 0.117 mmol) in ethanol (20 ml). The reaction mixture was stirred for 5 h under reflux. Single crystals of the title compound for X-ray analysis were obtained by slow evaporation of an ethanol solution (yield 60%; m.p. 430–432 K).

S3. Refinement

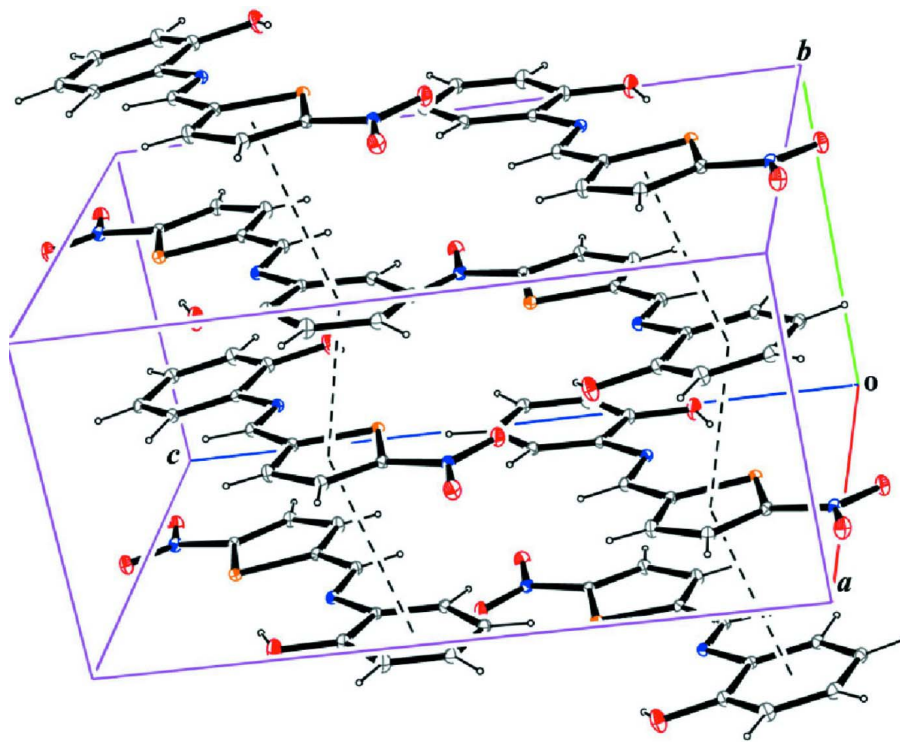
C-bound H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The position of the H1 atom was obtained from a difference map of the electron density in the unit-cell and was refined freely.

**Figure 1**

The molecular structure of the title compound, showing 30% probability displacement ellipsoids.

**Figure 2**

Centrosymmetric dimer with a central $R_2^2(22)$ ring motif. Dashed lines indicate hydrogen bonds.

**Figure 3**

Packing diagram of the title compound.

2-[[5-Nitrothiophen-2-yl)methylidene]amino}phenol

Crystal data

$C_{11}H_8N_2O_3S$

$M_r = 248.25$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 10.642\ (5)\ \text{\AA}$

$b = 7.043\ (5)\ \text{\AA}$

$c = 14.535\ (5)\ \text{\AA}$

$\beta = 93.566\ (5)^\circ$

$V = 1087.3\ (10)\ \text{\AA}^3$

$Z = 4$

$F(000) = 512$

$D_x = 1.516\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71069\ \text{\AA}$

Cell parameters from 9881 reflections

$\theta = 1.9\text{--}29.0^\circ$

$\mu = 0.29\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Prism, dark brown

$0.68 \times 0.37 \times 0.15\ \text{mm}$

Data collection

Stoe IPDS

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: $6.67\ \text{pixels mm}^{-1}$

rotation method scans

Absorption correction: integration

(*X-RED32*; Stoe & Cie, 2002)

$T_{\min} = 0.877$, $T_{\max} = 0.965$

7883 measured reflections

2254 independent reflections

1696 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.114$

$\theta_{\max} = 26.5^\circ$, $\theta_{\min} = 1.9^\circ$

$h = -13 \rightarrow 13$

$k = -8 \rightarrow 8$

$l = -18 \rightarrow 18$

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.064$ $wR(F^2) = 0.100$ $S = 0.98$

2254 reflections

186 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sitesH atoms treated by a mixture of independent
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0675P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.89 \text{ e } \text{Å}^{-3}$ $\Delta\rho_{\min} = -0.45 \text{ e } \text{Å}^{-3}$ *Special details***Experimental.** 360 frames, detector distance = 80 mm**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	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.58190 (4)	0.11508 (6)	0.11107 (3)	0.04605 (16)
N2	0.41409 (13)	0.10939 (19)	0.27382 (9)	0.0449 (3)
N1	0.77113 (14)	0.1231 (2)	-0.00532 (10)	0.0532 (4)
C1	0.73710 (15)	0.1181 (2)	0.08813 (11)	0.0453 (4)
C4	0.62428 (15)	0.1069 (2)	0.22648 (11)	0.0460 (4)
C6	0.32806 (15)	0.1149 (2)	0.34380 (11)	0.0438 (4)
O2	0.68543 (14)	0.1159 (2)	-0.06611 (9)	0.0733 (4)
C5	0.53109 (16)	0.1040 (3)	0.29481 (12)	0.0496 (4)
C7	0.35846 (18)	0.1360 (3)	0.43745 (12)	0.0512 (4)
C3	0.75216 (17)	0.1053 (3)	0.24363 (13)	0.0625 (5)
O1	0.88152 (13)	0.1329 (3)	-0.02073 (10)	0.0807 (5)
C2	0.81816 (17)	0.1119 (3)	0.16344 (13)	0.0581 (5)
O3	0.16507 (15)	0.0835 (3)	0.22346 (11)	0.0904 (6)
C8	0.26579 (19)	0.1470 (3)	0.49960 (13)	0.0574 (5)
C11	0.20103 (17)	0.1045 (3)	0.31379 (13)	0.0584 (5)
C9	0.1415 (2)	0.1387 (3)	0.46888 (15)	0.0665 (5)
C10	0.1095 (2)	0.1179 (4)	0.37699 (17)	0.0748 (6)
H2	0.904 (2)	0.113 (3)	0.1586 (14)	0.068 (6)*
H3	0.787 (2)	0.107 (3)	0.2986 (17)	0.073 (7)*
H5	0.564 (2)	0.096 (3)	0.3560 (17)	0.079 (7)*
H7	0.447 (2)	0.150 (3)	0.4606 (13)	0.063 (6)*
H10	0.028 (3)	0.112 (4)	0.3543 (19)	0.100 (9)*
H9	0.080 (2)	0.151 (3)	0.5109 (16)	0.078 (7)*

H8	0.288 (2)	0.167 (3)	0.5609 (16)	0.069 (6)*
H1	0.227 (3)	0.069 (4)	0.198 (2)	0.097 (10)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0373 (2)	0.0531 (3)	0.0481 (2)	−0.00158 (18)	0.00516 (15)	0.00117 (19)
N2	0.0434 (7)	0.0456 (8)	0.0468 (7)	−0.0009 (6)	0.0106 (5)	−0.0022 (6)
N1	0.0513 (8)	0.0589 (9)	0.0506 (8)	−0.0077 (7)	0.0128 (6)	0.0009 (7)
C1	0.0413 (8)	0.0481 (9)	0.0475 (8)	−0.0043 (7)	0.0102 (6)	−0.0017 (7)
C4	0.0415 (8)	0.0509 (10)	0.0463 (8)	−0.0008 (7)	0.0083 (6)	−0.0016 (7)
C6	0.0416 (8)	0.0412 (8)	0.0496 (8)	0.0020 (7)	0.0113 (6)	0.0011 (7)
O2	0.0625 (8)	0.1093 (12)	0.0482 (7)	−0.0094 (8)	0.0035 (6)	0.0076 (7)
C5	0.0433 (9)	0.0598 (11)	0.0463 (9)	0.0000 (8)	0.0086 (7)	−0.0012 (8)
C7	0.0498 (9)	0.0535 (11)	0.0510 (9)	0.0034 (8)	0.0087 (7)	0.0005 (8)
C3	0.0435 (9)	0.0957 (16)	0.0482 (10)	−0.0015 (9)	0.0028 (7)	−0.0021 (10)
O1	0.0533 (8)	0.1232 (14)	0.0681 (9)	−0.0151 (8)	0.0234 (7)	−0.0032 (9)
C2	0.0368 (8)	0.0814 (13)	0.0567 (10)	−0.0030 (9)	0.0072 (7)	−0.0037 (9)
O3	0.0490 (8)	0.160 (2)	0.0621 (9)	0.0045 (10)	0.0003 (7)	−0.0177 (10)
C8	0.0652 (11)	0.0581 (12)	0.0506 (10)	0.0055 (9)	0.0174 (9)	0.0026 (8)
C11	0.0448 (9)	0.0739 (13)	0.0572 (10)	−0.0007 (9)	0.0077 (7)	−0.0046 (9)
C9	0.0600 (11)	0.0721 (14)	0.0707 (13)	0.0035 (10)	0.0295 (10)	0.0010 (10)
C10	0.0410 (10)	0.1066 (19)	0.0783 (14)	−0.0021 (11)	0.0147 (9)	−0.0058 (13)

Geometric parameters (Å, °)

S1—C1	1.7054 (18)	C7—C8	1.380 (3)
S1—C4	1.7107 (18)	C7—H7	0.99 (2)
N2—C5	1.264 (2)	C3—C2	1.399 (3)
N2—C6	1.411 (2)	C3—H3	0.86 (2)
N1—O1	1.212 (2)	C2—H2	0.92 (2)
N1—O2	1.231 (2)	O3—C11	1.353 (2)
N1—C1	1.428 (2)	O3—H1	0.78 (3)
C1—C2	1.352 (3)	C8—C9	1.370 (3)
C4—C3	1.368 (3)	C8—H8	0.92 (2)
C4—C5	1.447 (2)	C11—C10	1.383 (3)
C6—C7	1.387 (3)	C9—C10	1.366 (3)
C6—C11	1.396 (2)	C9—H9	0.93 (2)
C5—H5	0.94 (2)	C10—H10	0.91 (3)
C1—S1—C4	89.58 (8)	C4—C3—C2	113.16 (17)
C5—N2—C6	120.03 (15)	C4—C3—H3	122.7 (16)
O1—N1—O2	123.60 (15)	C2—C3—H3	124.1 (16)
O1—N1—C1	118.92 (15)	C1—C2—C3	110.35 (16)
O2—N1—C1	117.48 (15)	C1—C2—H2	121.6 (13)
C2—C1—N1	125.76 (16)	C3—C2—H2	128.0 (13)
C2—C1—S1	114.73 (13)	C11—O3—H1	106 (2)
N1—C1—S1	119.50 (13)	C9—C8—C7	119.92 (19)

C3—C4—C5	126.26 (16)	C9—C8—H8	120.7 (14)
C3—C4—S1	112.18 (13)	C7—C8—H8	119.3 (14)
C5—C4—S1	121.56 (13)	O3—C11—C10	118.94 (18)
C7—C6—C11	118.31 (16)	O3—C11—C6	121.26 (17)
C7—C6—N2	126.03 (16)	C10—C11—C6	119.80 (18)
C11—C6—N2	115.62 (15)	C10—C9—C8	120.01 (18)
N2—C5—C4	122.75 (16)	C10—C9—H9	120.7 (14)
N2—C5—H5	122.4 (15)	C8—C9—H9	119.3 (14)
C4—C5—H5	114.9 (15)	C9—C10—C11	120.9 (2)
C8—C7—C6	121.03 (18)	C9—C10—H10	122.2 (18)
C8—C7—H7	118.6 (12)	C11—C10—H10	116.8 (18)
C6—C7—H7	120.3 (12)		
O1—N1—C1—C2	-4.2 (3)	C5—C4—C3—C2	-179.07 (19)
O2—N1—C1—C2	175.3 (2)	S1—C4—C3—C2	0.4 (2)
O1—N1—C1—S1	177.06 (14)	N1—C1—C2—C3	-179.06 (17)
O2—N1—C1—S1	-3.4 (2)	S1—C1—C2—C3	-0.3 (2)
C4—S1—C1—C2	0.44 (16)	C4—C3—C2—C1	0.0 (3)
C4—S1—C1—N1	179.27 (14)	C6—C7—C8—C9	-0.6 (3)
C1—S1—C4—C3	-0.44 (16)	C7—C6—C11—O3	-179.9 (2)
C1—S1—C4—C5	179.02 (15)	N2—C6—C11—O3	2.3 (3)
C5—N2—C6—C7	7.5 (3)	C7—C6—C11—C10	0.9 (3)
C5—N2—C6—C11	-174.84 (17)	N2—C6—C11—C10	-176.96 (19)
C6—N2—C5—C4	-177.11 (16)	C7—C8—C9—C10	0.6 (3)
C3—C4—C5—N2	178.60 (19)	C8—C9—C10—C11	0.1 (4)
S1—C4—C5—N2	-0.8 (3)	O3—C11—C10—C9	179.8 (2)
C11—C6—C7—C8	-0.1 (3)	C6—C11—C10—C9	-0.9 (4)
N2—C6—C7—C8	177.44 (17)		

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>
O3—H1...O2 ⁱ	0.78 (3)	2.54 (3)	3.192 (3)	141 (3)
O3—H1...N2	0.78 (3)	2.23 (3)	2.711 (2)	121 (3)

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