

1'-Acetyl-3-phenyl-6-oxa-4-thia-2-aza-spiro[bicyclo[3.2.0]hept-2-ene-7,3'-indolin]-2'-one

Hoong-Kun Fun,^{a,*} Jia Hao Goh,^{a,§} Yang Liu^b and Yan Zhang^b

^aX-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and ^bSchool of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, People's Republic of China
Correspondence e-mail: hkfun@usm.my

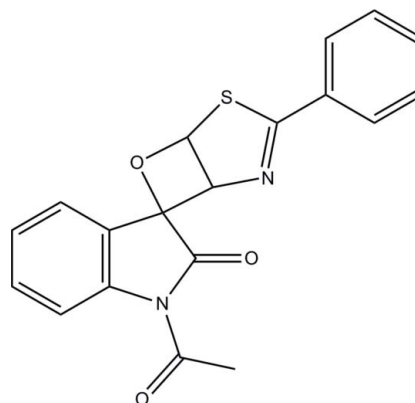
Received 2 August 2010; accepted 3 August 2010

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.058; wR factor = 0.128; data-to-parameter ratio = 16.0.

In the title indoline compound, $\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_3\text{S}$, the pyrrolidine ring adopts an envelope conformation with the four-connected (spiro) C atom as the flap [displacement = 0.148 (3) Å]. The mean plane formed through the indoline unit is inclined at dihedral angles of 89.92 (16) and 59.54 (12)° with the thiazole and phenyl rings, respectively; the dihedral angle between the latter rings is 9.55 (14)°. In the crystal, pairs of intermolecular C—H...O hydrogen bonds link neighbouring molecules into inversion dimers, producing $R_2^2(6)$ hydrogen-bond ring motifs. Weak intermolecular C—H... π as well as π – π interactions [centroid–centroid distance = 3.4041 (15) Å] further consolidate the crystal structure.

Related literature

For general background to and applications of compounds related to the title indoline compound, see: Aanandhi *et al.* (2008); Crews *et al.* (1988); Cutignano *et al.* (2001); DeRoy & Charette (2003); Gao *et al.* (2010); Kaleta *et al.* (2006); Lawrence *et al.* (2008); Muthukumar *et al.* (2008); Shi *et al.* (2010); Tsuruni *et al.* (1995); Wang *et al.* (2005); Williams *et al.* (2001); Xue *et al.* (2000); Yoshimura *et al.* (1995); Zhang *et al.* (2004). For ring conformations, see: Cremer & Pople (1975). For graph-set theory of hydrogen-bond ring motifs, see: Bernstein *et al.* (1995). For closely related structures, see: Fun *et al.* (2010); Usman *et al.* (2001, 2002). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_3\text{S}$
 $M_r = 350.38$
 Triclinic, $P\bar{1}$
 $a = 7.5054$ (3) Å
 $b = 9.4936$ (3) Å
 $c = 11.6359$ (4) Å
 $\alpha = 103.502$ (3)°
 $\beta = 91.163$ (3)°
 $\gamma = 100.200$ (3)°
 $V = 791.79$ (5) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.23$ mm⁻¹
 $T = 100$ K
 $0.24 \times 0.10 \times 0.05$ mm

Data collection

Bruker SMART APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2009)
 $T_{\min} = 0.948$, $T_{\max} = 0.989$
 10748 measured reflections
 3627 independent reflections
 2548 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.062$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.058$
 $wR(F^2) = 0.128$
 $S = 1.05$
 3627 reflections
 227 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.35$ e Å⁻³
 $\Delta\rho_{\min} = -0.42$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of C1–C6 phenyl ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C10—H10A...O1 ⁱ	0.98	2.56	3.261 (3)	129
C14—H14A...Cg1 ⁱⁱ	0.93	2.67	3.423 (3)	139

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

HKF and JHG thank Universiti Sains Malaysia (USM) for a Research University Golden Goose grant (No. 1001/PFIZIK/811012). Financial support from the Ministry of Science and Technology of China of the Austria–China Cooperation project (2007DFA41590) is acknowledged. JHG also thanks USM for the award of a USM fellowship.

* Thomson Reuters ResearcherID: A-3561-2009.

§ Thomson Reuters ResearcherID: C-7576-2009.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5595).

References

- Aanandhi, M. V., Vaidhyalingam, V. & George, S. (2008). *Asian J. Chem.* **20**, 4588–4594.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bruker (2009). *APEX2, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Crews, P., Kakou, Y. & Quinoa, E. (1988). *J. Am. Chem. Soc.* **110**, 4365–4368.
- Cutignano, A., Bruno, I., Bifulco, G., Casapullo, A., Debitus, C., Gomez-Paloma, L. & Riccio, R. (2001). *Eur. J. Org. Chem.* pp. 775–778.
- DeRoy, P. L. & Charette, A. B. (2003). *Org. Lett.* **5**, 4163–4165.
- Fun, H.-K., Goh, J. H., Liu, Y. & Zhang, Y. (2010). *Acta Cryst. E* **66**, o737–o738.
- Gao, X., Pan, Y.-M., Lin, M., Chen, L. & Zhan, Z.-P. (2010). *Org. Biomol. Chem.* **8**, 3259–3266.
- Kaleta, Z., Makowshi, B. T., So'os, T. & Dembinski, R. (2006). *Org. Lett.* **8**, 1625–1628.
- Lawrence, H. R., Pireddu, R., Chen, L., Luo, Y., Sung, S.-S., Szymanski, A. M., Yip, M. L. R., Guida, W. C., Sebti, S. M., Wu, J. & Lawrence, N. J. (2008). *J. Med. Chem.* **51**, 4948–4956.
- Muthukumar, V. A., George, S. & Vaidhyalingam, V. (2008). *Biol. Pharm. Bull.* **31**, 1461–1464.
- Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.
- Shi, B., Blake, A. J., Lewis, W., Campbell, I. B., Judkins, B. D. & Moody, C. J. (2010). *J. Org. Chem.* **75**, 152–161.
- Spek, A. L. (2009). *Acta Cryst. D* **65**, 148–155.
- Tsuruni, Y., Ueda, H., Hayashi, K., Takase, S., Nishikawa, M., Kiyoto, S. & Okuhara, M. (1995). *J. Antibiot.* **48**, 1066–1072.
- Usman, A., Razak, I. A., Fun, H.-K., Chantrapromma, S., Zhang, Y. & Xu, J.-H. (2001). *Acta Cryst. E* **57**, o1070–o1072.
- Usman, A., Razak, I. A., Fun, H.-K., Chantrapromma, S., Zhang, Y. & Xu, J.-H. (2002). *Acta Cryst. E* **58**, o37–o39.
- Wang, L., Zhang, Y., Hu, H.-Y., Fun, H. K. & Xu, J.-X. (2005). *J. Org. Chem.* **70**, 3850–3858.
- Williams, D. R., Patnaik, S. & Clark, M. P. (2001). *J. Org. Chem.* **66**, 8463–8469.
- Xue, J., Zhang, Y., Wang, X.-L., Fun, H. K. & Xu, J.-X. (2000). *Org. Lett.* **2**, 2583–2586.
- Yoshimura, S., Tsuruni, Y., Takase, S. & Okuhara, M. (1995). *J. Antibiot.* **48**, 1073–1075.
- Zhang, Y., Wang, L., Zhang, M., Fun, H.-K. & Xu, J.-X. (2004). *Org. Lett.* **6**, 4893–4895.

supplementary materials

Acta Cryst. (2010). E66, o2257-o2258 [doi:10.1107/S1600536810031016]

1'-Acetyl-3-phenyl-6-oxa-4-thia-2-azaspiro[bicyclo[3.2.0]hept-2-ene-7,3'-indolin]-2'-one

H.-K. Fun, J. H. Goh, Y. Liu and Y. Zhang

Comment

Oxindole and spiroindole are important heterocyclic compounds with diverse bioactivities (Aanandhi *et al.*, 2008; Muthukumar *et al.*, 2008; Lawrence *et al.*, 2008). Photoreactions of *N*-acetylisisatin with alkenes or oxazoles are convenient ways to construct spiroindole frameworks (Wang *et al.*, 2005; Zhang *et al.*, 2004; Xue *et al.*, 2000). Thiazole-containing compounds, such as the mycothiazole (Crews *et al.*, 1988; Cutignano *et al.*, 2001), cystothiazole A (Williams *et al.*, 2001; DeRoy & Charette, 2003) and WS75624 B (Yoshimura *et al.*, 1995; Tsuruni *et al.*, 1995) have attracted considerable interest due to their potential application as bio-active species. Synthesis of organic molecules containing thiazole moieties therefore has been of current research interest (Gao *et al.*, 2010; Shi *et al.*, 2010; Kaleta *et al.*, 2006). The title compound, (I), which contains spiroindole and thiazole rings is now described.

In the title indoline compound (Fig. 1), the pyrrolidine ring (C1/C6/N1/C7/C8) of the indoline moiety adopts an envelope conformation with the C8 atom as the flap atom; the puckering parameters are $Q = 0.090$ (3) Å and $\phi = 106.4^\circ$ (Cremer & Pople, 1975). The essentially planar thiazole ring (C9/C10/S1/C11/N2) and C12-C17 phenyl ring are inclined at dihedral angles of 89.92 (16) and 59.54 (12)°, respectively, with respect to the mean plane formed through the indoline moiety (C1-C8/N1). The geometric parameters agree well with those observed in the closely related structures (Fun *et al.*, 2010; Usman *et al.*, 2001, 2002).

In the crystal structure (Fig. 2), pairs of intermolecular C10—H10A...O1 hydrogen bonds (Table 1) link neighbouring molecules into dimers incorporating $R^2_2(6)$ hydrogen bond ring motifs (Bernstein *et al.*, 1995). The crystal structure is further stabilized by weak intermolecular C14—H14A...Cg1 (Table 1) as well as $Cg2...Cg3$ [$Cg2...Cg3 = 3.4041$ (15); symmetry code: x, y, z] interactions where $Cg1$, $Cg2$ and $Cg3$ are the centroids of C1-C6 phenyl, thiazole and pyrrolidine rings, respectively.

Experimental

The title compound was one of the products from the photoreaction between *N*-acetylisisatin and 2-phenylthiazole. The compound was purified by flash column chromatography with ethyl acetate/petroleum ether (1:4) as eluents. Colourless blocks of (I) were obtained from slow evaporation of an acetone and petroleum ether (1:6) solution. *M.p.* 442–444 K.

Refinement

All hydrogen atoms were placed in their calculated positions, with C—H = 0.93–0.98 Å, and refined using a riding model, with $U_{iso}(H) = 1.2$ or $1.5U_{eq}(C)$. The rotating group model was applied to the methyl group.

Figures

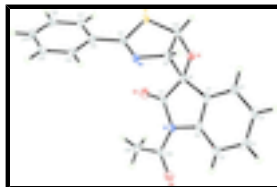


Fig. 1. The asymmetric unit of (I) with displacement ellipsoids for non-hydrogen atoms are drawn at the 50 % probability level.

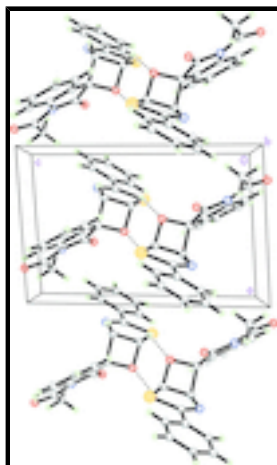


Fig. 2. The crystal structure of (I), viewed along the *b* axis, showing adjacent molecules being linked into dimers. Intermolecular hydrogen bonds are shown as dashed lines.

1'-Acetyl-3-phenyl-6-oxa-4-thia-2-azaspiro[bicyclo[3.2.0]hept-2-ene- 7,3'-indolin]-2'-one

Crystal data

$C_{19}H_{14}N_2O_3S$

$M_r = 350.38$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 7.5054 (3) \text{ \AA}$

$b = 9.4936 (3) \text{ \AA}$

$c = 11.6359 (4) \text{ \AA}$

$\alpha = 103.502 (3)^\circ$

$\beta = 91.163 (3)^\circ$

$\gamma = 100.200 (3)^\circ$

$V = 791.79 (5) \text{ \AA}^3$

$Z = 2$

$F(000) = 364$

$D_x = 1.470 \text{ Mg m}^{-3}$

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

Cell parameters from 2361 reflections

$\theta = 2.5\text{--}29.9^\circ$

$\mu = 0.23 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Block, colourless

$0.24 \times 0.10 \times 0.05 \text{ mm}$

Data collection

Bruker SMART APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube
graphite

ϕ and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2009)

3627 independent reflections

2548 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.062$

$\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 1.8^\circ$

$h = -9 \rightarrow 9$

$T_{\min} = 0.948$, $T_{\max} = 0.989$
10748 measured reflections

$k = -12 \rightarrow 10$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Primary atom site location: structure-invariant direct methods

Least-squares matrix: full

Secondary atom site location: difference Fourier map

$R[F^2 > 2\sigma(F^2)] = 0.058$

Hydrogen site location: inferred from neighbouring sites

$wR(F^2) = 0.128$

H-atom parameters constrained

$S = 1.05$

$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2 + 0.6382P]$

where $P = (F_o^2 + 2F_c^2)/3$

3627 reflections

$(\Delta/\sigma)_{\max} < 0.001$

227 parameters

$\Delta\rho_{\max} = 0.35 \text{ e } \text{Å}^{-3}$

0 restraints

$\Delta\rho_{\min} = -0.42 \text{ e } \text{Å}^{-3}$

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1)K.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.31424 (10)	0.63788 (7)	0.48799 (6)	0.01816 (18)
O1	0.5459 (3)	0.90182 (19)	0.58975 (16)	0.0190 (4)
O2	0.6257 (3)	0.7176 (2)	0.74453 (17)	0.0244 (5)
O3	0.8183 (3)	0.9955 (2)	1.07309 (17)	0.0229 (5)
N1	0.6758 (3)	0.9398 (2)	0.89013 (19)	0.0156 (5)
N2	0.2265 (3)	0.7250 (2)	0.70929 (19)	0.0158 (5)
C1	0.5502 (4)	1.0821 (3)	0.7864 (2)	0.0161 (6)
C2	0.5067 (4)	1.2098 (3)	0.7631 (2)	0.0186 (6)
H2A	0.4462	1.2074	0.6919	0.022*
C3	0.5566 (4)	1.3413 (3)	0.8498 (3)	0.0204 (6)
H3A	0.5333	1.4291	0.8358	0.025*
C4	0.6407 (4)	1.3411 (3)	0.9567 (3)	0.0212 (6)
H4A	0.6693	1.4293	1.0143	0.025*
C5	0.6845 (4)	1.2135 (3)	0.9816 (2)	0.0180 (6)

supplementary materials

H5A	0.7404	1.2149	1.0540	0.022*
C6	0.6399 (4)	1.0849 (3)	0.8924 (2)	0.0159 (6)
C7	0.6062 (4)	0.8429 (3)	0.7805 (2)	0.0173 (6)
C8	0.5034 (4)	0.9279 (3)	0.7127 (2)	0.0161 (6)
C9	0.2983 (4)	0.8603 (3)	0.6760 (2)	0.0156 (6)
H9A	0.2192	0.9334	0.6934	0.019*
C10	0.3596 (4)	0.8344 (3)	0.5480 (2)	0.0168 (6)
H10A	0.3038	0.8885	0.4995	0.020*
C11	0.2314 (4)	0.6112 (3)	0.6260 (2)	0.0156 (6)
C12	0.1634 (4)	0.4594 (3)	0.6374 (2)	0.0157 (6)
C13	0.0699 (4)	0.4403 (3)	0.7366 (2)	0.0180 (6)
H13A	0.0553	0.5223	0.7949	0.022*
C14	-0.0011 (4)	0.3003 (3)	0.7486 (2)	0.0198 (6)
H14A	-0.0637	0.2881	0.8148	0.024*
C15	0.0213 (4)	0.1773 (3)	0.6613 (3)	0.0213 (6)
H15A	-0.0262	0.0829	0.6691	0.026*
C16	0.1142 (4)	0.1963 (3)	0.5632 (3)	0.0217 (6)
H16A	0.1287	0.1142	0.5050	0.026*
C17	0.1866 (4)	0.3371 (3)	0.5504 (2)	0.0181 (6)
H17A	0.2497	0.3491	0.4844	0.022*
C18	0.7757 (4)	0.9051 (3)	0.9798 (2)	0.0170 (6)
C19	0.8273 (4)	0.7560 (3)	0.9534 (3)	0.0240 (7)
H19D	0.8923	0.7446	1.0216	0.036*
H19A	0.9029	0.7467	0.8875	0.036*
H19B	0.7197	0.6812	0.9343	0.036*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0253 (4)	0.0130 (3)	0.0158 (3)	0.0014 (3)	0.0011 (3)	0.0044 (3)
O1	0.0228 (11)	0.0163 (9)	0.0174 (10)	0.0026 (8)	0.0010 (8)	0.0037 (8)
O2	0.0338 (13)	0.0134 (10)	0.0266 (11)	0.0091 (9)	-0.0044 (9)	0.0030 (8)
O3	0.0289 (12)	0.0223 (10)	0.0180 (10)	0.0053 (9)	0.0006 (9)	0.0060 (9)
N1	0.0201 (13)	0.0111 (10)	0.0167 (11)	0.0030 (9)	0.0020 (9)	0.0054 (9)
N2	0.0177 (12)	0.0115 (11)	0.0184 (12)	0.0027 (9)	0.0012 (9)	0.0042 (9)
C1	0.0174 (15)	0.0109 (12)	0.0202 (14)	0.0008 (11)	0.0042 (11)	0.0052 (11)
C2	0.0188 (15)	0.0152 (13)	0.0237 (14)	0.0041 (11)	-0.0008 (12)	0.0081 (11)
C3	0.0198 (15)	0.0101 (13)	0.0332 (16)	0.0044 (11)	0.0041 (12)	0.0074 (12)
C4	0.0237 (17)	0.0133 (13)	0.0241 (15)	0.0022 (12)	0.0052 (12)	0.0002 (11)
C5	0.0167 (15)	0.0166 (13)	0.0196 (14)	0.0016 (11)	0.0023 (11)	0.0034 (11)
C6	0.0167 (15)	0.0125 (12)	0.0204 (14)	0.0027 (11)	0.0025 (11)	0.0075 (11)
C7	0.0210 (16)	0.0120 (13)	0.0192 (14)	0.0026 (11)	0.0010 (11)	0.0050 (11)
C8	0.0226 (16)	0.0111 (12)	0.0151 (13)	0.0020 (11)	0.0023 (11)	0.0049 (11)
C9	0.0196 (15)	0.0118 (12)	0.0162 (13)	0.0018 (11)	0.0015 (11)	0.0055 (11)
C10	0.0193 (15)	0.0116 (12)	0.0202 (14)	0.0018 (11)	-0.0006 (11)	0.0062 (11)
C11	0.0160 (14)	0.0149 (13)	0.0180 (13)	0.0045 (11)	0.0003 (11)	0.0066 (11)
C12	0.0145 (14)	0.0134 (12)	0.0191 (14)	0.0012 (11)	-0.0019 (11)	0.0049 (11)
C13	0.0235 (16)	0.0155 (13)	0.0149 (13)	0.0045 (12)	0.0013 (11)	0.0027 (11)

C14	0.0211 (16)	0.0212 (14)	0.0193 (14)	0.0032 (12)	0.0025 (12)	0.0100 (12)
C15	0.0213 (16)	0.0119 (13)	0.0314 (16)	0.0016 (11)	0.0001 (13)	0.0079 (12)
C16	0.0244 (17)	0.0136 (13)	0.0256 (15)	0.0046 (12)	0.0013 (13)	0.0011 (12)
C17	0.0175 (15)	0.0171 (14)	0.0197 (14)	0.0044 (11)	0.0029 (11)	0.0033 (11)
C18	0.0166 (15)	0.0184 (13)	0.0178 (14)	0.0017 (11)	0.0025 (11)	0.0086 (11)
C19	0.0275 (17)	0.0188 (14)	0.0282 (16)	0.0086 (12)	-0.0068 (13)	0.0083 (12)

Geometric parameters (Å, °)

S1—C11	1.790 (3)	C7—C8	1.538 (4)
S1—C10	1.801 (3)	C8—C9	1.568 (4)
O1—C8	1.446 (3)	C9—C10	1.544 (4)
O1—C10	1.452 (3)	C9—H9A	0.9800
O2—C7	1.201 (3)	C10—H10A	0.9800
O3—C18	1.212 (3)	C11—C12	1.479 (4)
N1—C18	1.406 (3)	C12—C17	1.390 (4)
N1—C7	1.415 (3)	C12—C13	1.393 (4)
N1—C6	1.444 (3)	C13—C14	1.382 (4)
N2—C11	1.278 (3)	C13—H13A	0.9300
N2—C9	1.444 (3)	C14—C15	1.396 (4)
C1—C6	1.385 (4)	C14—H14A	0.9300
C1—C2	1.393 (3)	C15—C16	1.380 (4)
C1—C8	1.490 (4)	C15—H15A	0.9300
C2—C3	1.396 (4)	C16—C17	1.394 (4)
C2—H2A	0.9300	C16—H16A	0.9300
C3—C4	1.383 (4)	C17—H17A	0.9300
C3—H3A	0.9300	C18—C19	1.498 (4)
C4—C5	1.400 (4)	C19—H19D	0.9600
C4—H4A	0.9300	C19—H19A	0.9600
C5—C6	1.389 (4)	C19—H19B	0.9600
C5—H5A	0.9300		
C11—S1—C10	90.03 (12)	C8—C9—H9A	113.1
C8—O1—C10	92.80 (19)	O1—C10—C9	91.54 (19)
C18—N1—C7	126.1 (2)	O1—C10—S1	116.58 (17)
C18—N1—C6	124.7 (2)	C9—C10—S1	106.43 (17)
C7—N1—C6	109.1 (2)	O1—C10—H10A	113.4
C11—N2—C9	112.1 (2)	C9—C10—H10A	113.4
C6—C1—C2	121.3 (2)	S1—C10—H10A	113.4
C6—C1—C8	110.1 (2)	N2—C11—C12	122.6 (2)
C2—C1—C8	128.5 (2)	N2—C11—S1	118.4 (2)
C1—C2—C3	117.9 (3)	C12—C11—S1	118.90 (19)
C1—C2—H2A	121.0	C17—C12—C13	120.0 (2)
C3—C2—H2A	121.0	C17—C12—C11	121.5 (2)
C4—C3—C2	120.0 (2)	C13—C12—C11	118.5 (2)
C4—C3—H3A	120.0	C14—C13—C12	120.3 (2)
C2—C3—H3A	120.0	C14—C13—H13A	119.8
C3—C4—C5	122.7 (3)	C12—C13—H13A	119.8
C3—C4—H4A	118.7	C13—C14—C15	119.9 (3)
C5—C4—H4A	118.7	C13—C14—H14A	120.0

supplementary materials

C6—C5—C4	116.4 (3)	C15—C14—H14A	120.0
C6—C5—H5A	121.8	C16—C15—C14	119.7 (2)
C4—C5—H5A	121.8	C16—C15—H15A	120.2
C1—C6—C5	121.6 (2)	C14—C15—H15A	120.2
C1—C6—N1	109.4 (2)	C15—C16—C17	120.8 (3)
C5—C6—N1	128.9 (2)	C15—C16—H16A	119.6
O2—C7—N1	126.9 (2)	C17—C16—H16A	119.6
O2—C7—C8	125.5 (2)	C12—C17—C16	119.3 (3)
N1—C7—C8	107.6 (2)	C12—C17—H17A	120.3
O1—C8—C1	117.7 (2)	C16—C17—H17A	120.3
O1—C8—C7	111.3 (2)	O3—C18—N1	119.7 (2)
C1—C8—C7	102.8 (2)	O3—C18—C19	123.0 (2)
O1—C8—C9	90.84 (19)	N1—C18—C19	117.2 (2)
C1—C8—C9	118.2 (2)	C18—C19—H19D	109.5
C7—C8—C9	116.3 (2)	C18—C19—H19A	109.5
N2—C9—C10	113.0 (2)	H19D—C19—H19A	109.5
N2—C9—C8	116.6 (2)	C18—C19—H19B	109.5
C10—C9—C8	84.8 (2)	H19D—C19—H19B	109.5
N2—C9—H9A	113.1	H19A—C19—H19B	109.5
C10—C9—H9A	113.1		
C6—C1—C2—C3	0.1 (4)	C11—N2—C9—C8	-94.8 (3)
C8—C1—C2—C3	176.1 (3)	O1—C8—C9—N2	114.4 (2)
C1—C2—C3—C4	-2.3 (4)	C1—C8—C9—N2	-123.2 (2)
C2—C3—C4—C5	2.1 (4)	C7—C8—C9—N2	0.0 (3)
C3—C4—C5—C6	0.4 (4)	O1—C8—C9—C10	1.18 (17)
C2—C1—C6—C5	2.4 (4)	C1—C8—C9—C10	123.6 (2)
C8—C1—C6—C5	-174.2 (3)	C7—C8—C9—C10	-113.2 (2)
C2—C1—C6—N1	-177.0 (3)	C8—O1—C10—C9	1.27 (18)
C8—C1—C6—N1	6.4 (3)	C8—O1—C10—S1	-107.98 (19)
C4—C5—C6—C1	-2.6 (4)	N2—C9—C10—O1	-117.9 (2)
C4—C5—C6—N1	176.7 (3)	C8—C9—C10—O1	-1.18 (17)
C18—N1—C6—C1	175.4 (3)	N2—C9—C10—S1	0.4 (3)
C7—N1—C6—C1	-0.3 (3)	C8—C9—C10—S1	117.15 (17)
C18—N1—C6—C5	-3.9 (4)	C11—S1—C10—O1	99.1 (2)
C7—N1—C6—C5	-179.7 (3)	C11—S1—C10—C9	-1.19 (19)
C18—N1—C7—O2	-2.6 (5)	C9—N2—C11—C12	-179.1 (2)
C6—N1—C7—O2	173.1 (3)	C9—N2—C11—S1	-2.2 (3)
C18—N1—C7—C8	178.8 (2)	C10—S1—C11—N2	2.1 (2)
C6—N1—C7—C8	-5.6 (3)	C10—S1—C11—C12	179.2 (2)
C10—O1—C8—C1	-124.1 (2)	N2—C11—C12—C17	-173.5 (3)
C10—O1—C8—C7	117.6 (2)	S1—C11—C12—C17	9.6 (3)
C10—O1—C8—C9	-1.26 (18)	N2—C11—C12—C13	8.2 (4)
C6—C1—C8—O1	-132.0 (2)	S1—C11—C12—C13	-168.7 (2)
C2—C1—C8—O1	51.7 (4)	C17—C12—C13—C14	-0.5 (4)
C6—C1—C8—C7	-9.3 (3)	C11—C12—C13—C14	177.8 (3)
C2—C1—C8—C7	174.4 (3)	C12—C13—C14—C15	0.2 (4)
C6—C1—C8—C9	120.4 (3)	C13—C14—C15—C16	-0.1 (4)
C2—C1—C8—C9	-55.9 (4)	C14—C15—C16—C17	0.2 (4)
O2—C7—C8—O1	-42.9 (4)	C13—C12—C17—C16	0.6 (4)

N1—C7—C8—O1	135.8 (2)	C11—C12—C17—C16	-177.7 (3)
O2—C7—C8—C1	-169.8 (3)	C15—C16—C17—C12	-0.4 (4)
N1—C7—C8—C1	8.9 (3)	C7—N1—C18—O3	-175.5 (3)
O2—C7—C8—C9	59.3 (4)	C6—N1—C18—O3	9.5 (4)
N1—C7—C8—C9	-122.0 (2)	C7—N1—C18—C19	5.5 (4)
C11—N2—C9—C10	1.1 (3)	C6—N1—C18—C19	-169.5 (2)

Hydrogen-bond geometry (\AA , $^\circ$)

Cg1 is the centroid of C1–C6 phenyl ring.

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C10—H10A \cdots O1 ⁱ	0.98	2.56	3.261 (3)	129
C14—H14A \cdots Cg1 ⁱⁱ	0.93	2.67	3.423 (3)	139

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

Fig. 1

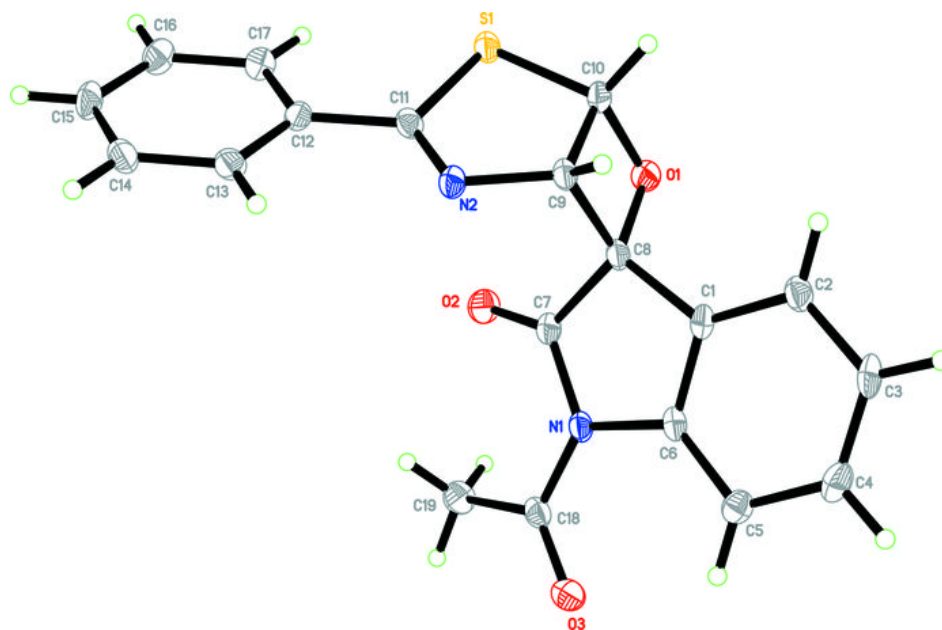


Fig. 2

