

Crystal structure and synthesis of 3-(1*H*-pyrrol-2-yl)-1-(thiophen-2-yl)propanone

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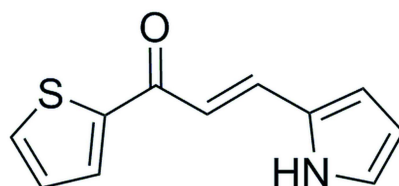
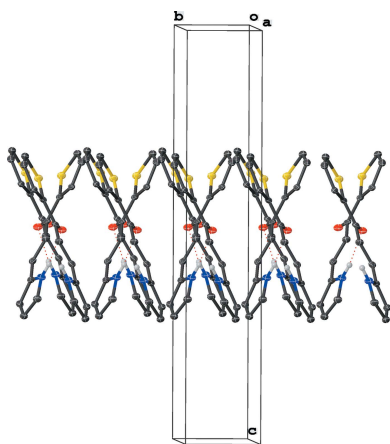
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The title compound, C₁₁H₉NOS, was obtained in an improved yield compared to previous literature methods. The molecule is essentially planar with a maximum deviation of 0.085 Å from the mean plane through all non-H atoms. There is directive intermolecular hydrogen bonding in the form of N–H···O hydrogen bonds with a distance of 2.889 (3) Å between the pyrrole amine and the ketone carbonyl O atom. The resulting hydrogen-bonding network defines a ribbon parallel to the *a* axis. These ribbons form offset stacks along the *b* axis.

1. Chemical context

In nature, pyrroles are often present in tetrapyrrolic ring systems such as heme and chlorophyll. These macrocyclic compounds carry out a multitude of biochemical reactions and are responsible for oxygen transport in the body and harvesting light for food production in plants, respectively. Pyrroles are also widely incorporated in drugs, catalysts and advanced materials (Michlik & Kempe, 2013; Estévez *et al.*, 2014). The incorporation of pyrroles and thiophenes into boron-dipyrromethene (BODIPY) dyes creates the possibility of long-wavelength absorptions and emissions (Schmidt *et al.*, 2009; Zrig *et al.*, 2008; Collado *et al.*, 2011; Rihn *et al.*, 2009; Gresser *et al.*, 2011; Ulrich *et al.*, 2007; Benniston *et al.*, 2008; Goeb & Ziessel, 2008). BODIPYs continue to be studied for their potential in fluorescence sensors, photodynamic therapy (PDT) and dye-sensitized solar cells (DSSCs) (Callaghan & Senge, 2018; Filatov *et al.*, 2018; Boens *et al.*, 2011, 2012; Antina *et al.*, 2017; Kamkaew *et al.*, 2013; Singh & Gayathri, 2014; Loudet & Burgess, 2007; Er *et al.*, 2015; Kand *et al.*, 2015; Cheng *et al.*, 2016). Changing the *meso*-carbon of the BODIPY to a nitrogen atom creates an aza-BODIPY compound. The absorption and emission in an aza-BODIPY is shifted more towards the near infra-red region compared to BODIPY (Lu *et al.*, 2014; Balsukuri, *et al.*, 2018). Herein, we report the improved synthesis and crystal structure of a previously synthesized ketone (Stark *et al.*, 2016) that can be further functionalized to create a sophisticated aza-BODIPY.



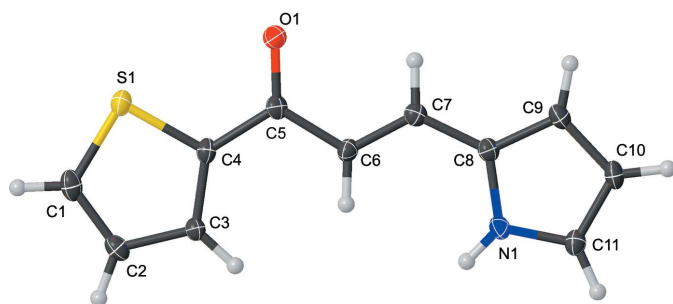


Figure 1
The molecular structure of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

2. Structural commentary

The title compound **1** crystallizes in a polar non-centrosymmetric space group ($Pna2_1$) and is almost planar in its crystalline form (Fig. 1; Table 1) with deviations ranging from -0.059 (3) (C11) to 0.085 Å (C7) from the mean plane of all non-hydrogen atoms. The pyrrole ring (N1/C8–C11) is rotated out of the plane through the ketone and thiophenyl groups (S1/O1/C1–C7) by 4.32 (10)°. The aliphatic chain linking the two ring systems has a *trans* conformation and the nitrogen atom (N1) of the pyrrole ring is protonated. Atom N1 is oriented opposite to the sulfur atom S1 of the thiophene ring to enable intermolecular hydrogen bonding (Fig. 2). Atom S1 lies on the same side of the molecular backbone as the oxygen of the ketone (O1).

3. Supramolecular features

Hydrogen bonding dominates the crystal packing of **1** and occurs between the amine group and the carbonyl oxygen (Fig. 2, Table 1), linking the molecules into a head-to-head ribbon-type assembly that extends down the *a* axis in an

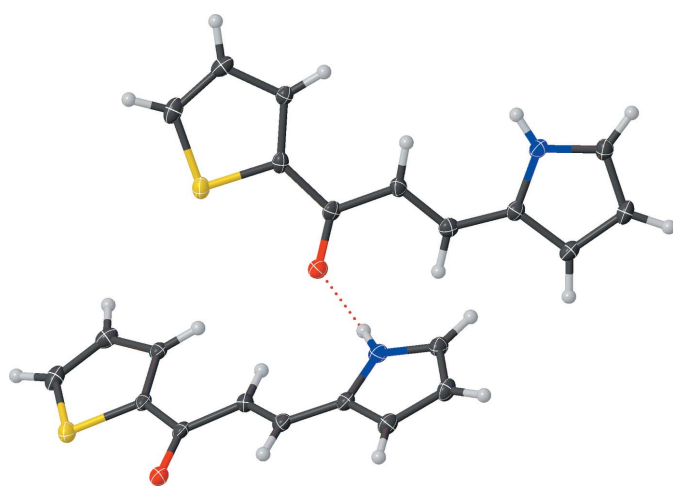


Figure 2
The hydrogen bonding (dashed line) between the amine group and the carbonyl oxygen atom (Table 1). Displacement ellipsoids are drawn at the 50% probability level.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1A\cdots O1^i$	0.84 (4)	2.06 (4)	2.889 (3)	171 (3)
$C6-H6\cdots O1^i$	0.95	2.50	3.396 (3)	158

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

alternating X-pattern (Fig. 3). The angle between the alternating molecules in this X-pattern is 88.804 (8)°. The ribbons form offset stacks along the *b* axis with centroid–centroid distances of 3.9257 (15) Å between the centroids of adjacent pyrrole or thiophene rings and a plane shift distance of 1.89 (3) Å between any two molecules in the three-dimensional crystal structure. C–H...O interactions also occur.

4. Database survey

A search of the Cambridge Structural Database (CSD, version 5.39; Groom *et al.*, 2016) gave two structures of aza-BODIPY precursor derivatives of **1** (Table 2). In (*E*)-1,3-di(thiophen-2-yl)prop-2-en-1-one (LINFET; Li & Su, 1995), a thiophene ring replaces the pyrrole ring, yielding a di-thiophene-linked α,β -unsaturated ketone aliphatic chain. LINFET contains two independent molecules in the asymmetric unit. One dithiophene-linked chain is less planar than in **1** (LINFET A) while the other is more planar (LINFET B; Table 2). The deviations from the plane of LINFET A range from -0.127 Å (C5) to

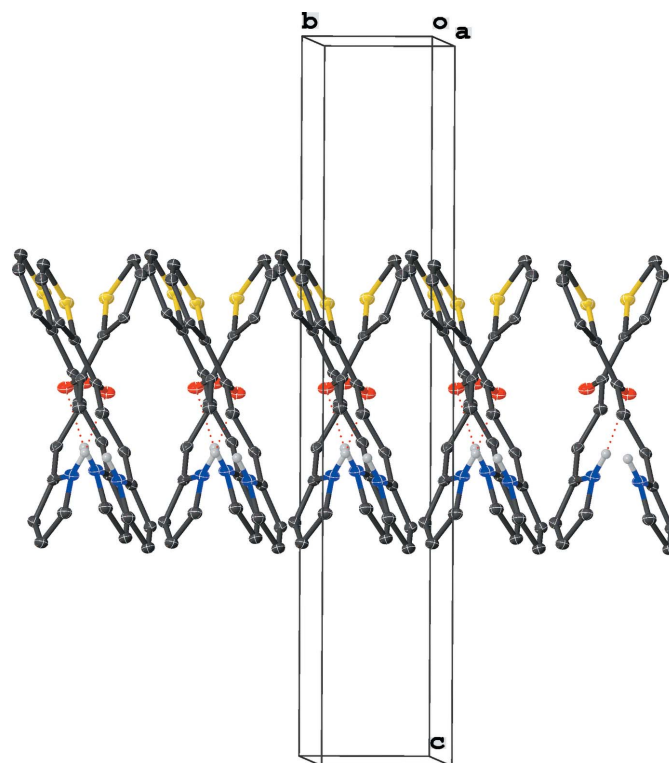


Figure 3
View of the X-pattern in the packing, viewed approximately along the *a* axis. Displacement ellipsoids are drawn at the 50% probability level.

Table 2

r. m. s. deviations and twist (\AA , $^\circ$) angles.

The twist angle is the dihedral angle between the five-membered heterocycle and the keto-aromatic plane.

Compound	r.m.s. deviation	Twist angle
1	0.04 (8)	4.32 (10)
LINFET A ^a	0.111 (2)	10.21 (12)
LINFET B ^a	0.023 (2)	1.19 (15)
SANRIJ A ^b	0.104 (15)	8.98 (4)
SANRIJ B ^b	0.122 (20)	9.67 (6)

Notes: (a) Li & Su (1995); (b) Ocak İskeleli *et al.* (2005).

0.233 \AA (S1); the deviations in LINFET B are smaller ranging from -0.032\AA for C22 to 0.055\AA for O2. They both exhibit the same *trans* conformation seen in the title molecule. Non-classical hydrogen bonding exists between a C–H group and the carbonyl oxygen, O1 with a C–H...O distance of $3.326 (6) \text{\AA}$. This bonding network results in three separate sheets, parallel to the *a*-axis. A second non-classical hydrogen-bonding network [C–H...O = $2.381 (4) \text{\AA}$] is observed extending along the *c*-axis direction, generating a staggered ribbon. The combination of these two networks gives rise to a three-dimensional structure.

(*E*)-1,3-Di(furan-2-yl)prop-2-en-1-one (SANRIJ; Ocak İskeleli *et al.*, 2005) comprises two furan heterocycles linked by an α,β -unsaturated ketone aliphatic chain. There are also two independent molecules in the asymmetric unit (SANRIJ A and SANRIJ B), both of which are less planar than **1**, LINFET A and LINFET B. The largest deviation from the molecular plane is for C17 (0.157\AA) in SANRIJ A and C18 (-0.152\AA) in SANRIJ B. Again, a non-classical hydrogen bonding network exists [C–H...O = $2.473 (18) \text{\AA}$] between aryl C–H atoms and the carbonyl oxygen. Each molecule participates in two hydrogen bonds and the network extends in a linear fashion along the *b*-axis direction, forming a network structure.

5. Synthesis and crystallization

The title compound was synthesized *via* an elimination unimolecular conjugate base (E1cB) reaction between 2-pyrrole-carbaldehyde (376.87 mg, 3.96 mmol, 1.0 eq.) and 2-acetylthiophene (500 mg, 3.96 mmol, 1.0 eq.) in 1:1 MeOH:H₂O (10 ml) using NaOH (15.85 mg, 396.28 μmol , 0.1 eq.) as a base. The resulting precipitate was filtered and then crystallized using a solution of CHCl₃, layered with hexane to give a single crystal suitable for X-ray diffraction. [C₁₁H₉NOS]: yield 85% m.p 420–430 K.

¹H NMR (CDCl₃, ppm, 400MHz): δ 6.34 (*dd*, *J* = 5.9, 2.6 Hz, 1H, =C–H), 6.74 (*s*, 1H, Ar-H), 7.01 (*s*, 1H, Ar-H), 7.06–7.10 (*d*, 1H, Ar-H), 7.15 (*t*, *J* = 8.7 Hz, 1H, Ar-H), 7.63 (*d*, *J* = 4.9 Hz, 1H, Ar-H), 7.81 (*t*, 1H, Ar-H), 7.83 (*d*, *J* = 10.3 Hz, 1H, =C–H), 9.17 (*s*, 1H, NH). ¹³C NMR (CDCl₃, ppm, 400 MHz): δ 111.54, 115.16, 123.30, 128.15, 129.16, 131.11, 133.17, 133.98, 145.89, 182.05. HRMS (ESI): *m/z* calculated for C₁₁H₉NOS: 204.047690 (*M* + H)⁺. Found: 204.04776.

Table 3

Experimental details.

Crystal data	
Chemical formula	C ₁₁ H ₉ NOS
<i>M_r</i>	203.25
Crystal system, space group	Orthorhombic, <i>Pna</i> 2 ₁
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (\AA)	11.1559 (3), 3.9258 (1), 21.6293 (6)
<i>V</i> (\AA^3)	947.27 (4)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm^{-1})	0.30
Crystal size (mm)	0.2 × 0.09 × 0.07
Data collection	
Diffractometer	Bruker SMART APEXII area detector
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.658, 0.746
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	25996, 2159, 2070
<i>R_{int}</i>	0.049
(<i>sin</i> θ / λ) _{max} (\AA^{-1})	0.650
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.032, 0.082, 1.06
No. of reflections	2159
No. of parameters	131
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (<i>e</i> \AA^{-3})	0.28, -0.17
Absolute structure	Flack <i>x</i> determined using 956 quotients [(<i>I</i> ⁺) – (<i>I</i> [−])] / [(<i>I</i> ⁺) + (<i>I</i> [−])] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.00 (4)

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms were placed in their expected calculated positions and refined as riding: C–H = 0.95–0.98 \AA with *U*_{iso}(H) = 1.2 *U*_{eq}(C).

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Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *S SAINT* (Bruker, 2016); data reduction: *S SAINT* (Bruker, 2016); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

3-(1*H*-Pyrrol-2-yl)-1-(thiophen-2-yl)propanone

Crystal data

C₁₁H₉NOS

M_r = 203.25

Orthorhombic, *Pna*2₁

a = 11.1559 (3) Å

b = 3.9258 (1) Å

c = 21.6293 (6) Å

V = 947.27 (4) Å³

Z = 4

F(000) = 424

D_x = 1.425 Mg m⁻³

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 9918 reflections

θ = 3.7–27.5°

μ = 0.30 mm⁻¹

T = 100 K

Triangular, yellow

0.2 × 0.09 × 0.07 mm

Data collection

Bruker SMART APEXII area detector
diffractometer

Radiation source: standard sealed X-ray tube,
Siemens, KFF Mo 2K -90 C

Graphite monochromator

Detector resolution: 7.9 pixels mm⁻¹

ω and φ scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

T_{min} = 0.658, *T_{max}* = 0.746

25996 measured reflections

2159 independent reflections

2070 reflections with *I* > 2σ(*I*)

R_{int} = 0.049

θ_{max} = 27.5°, θ_{min} = 1.9°

h = -14→14

k = -5→5

l = -27→28

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.032

wR(*F*²) = 0.082

S = 1.06

2159 reflections

131 parameters

1 restraint

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0533*P*)² + 0.3056*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.28 e Å⁻³

Δρ_{min} = -0.17 e Å⁻³

Absolute structure: Flack x determined using
 956 quotients $[(F^+)-(F^-)]/[(F^+)+(F^-)]$ (Parsons *et al.*,
 2013)
 Absolute structure parameter: 0.00 (4)

Special details

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.4383 (3)	0.3593 (7)	0.30581 (13)	0.0220 (6)
H1	0.4090	0.2839	0.2669	0.026*
C2	0.5545 (3)	0.3241 (7)	0.32434 (13)	0.0199 (5)
H2	0.6149	0.2208	0.2997	0.024*
C3	0.5754 (2)	0.4580 (6)	0.38425 (12)	0.0146 (5)
H3	0.6510	0.4546	0.4045	0.018*
C4	0.4712 (2)	0.5956 (7)	0.40983 (12)	0.0154 (5)
C5	0.4521 (2)	0.7623 (7)	0.46958 (11)	0.0158 (5)
C6	0.5566 (2)	0.7940 (7)	0.51008 (13)	0.0167 (5)
H6	0.6303	0.6917	0.4983	0.020*
C7	0.5498 (2)	0.9663 (7)	0.56396 (12)	0.0166 (5)
H7	0.4753	1.0719	0.5733	0.020*
C8	0.6436 (2)	1.0055 (7)	0.60829 (13)	0.0160 (5)
C9	0.6393 (2)	1.1517 (7)	0.66686 (12)	0.0183 (5)
H9	0.5713	1.2570	0.6852	0.022*
C10	0.7529 (3)	1.1168 (7)	0.69428 (12)	0.0195 (5)
H10	0.7758	1.1928	0.7343	0.023*
C11	0.8247 (2)	0.9509 (7)	0.65194 (13)	0.0182 (6)
H11	0.9065	0.8924	0.6579	0.022*
N1	0.7588 (2)	0.8850 (6)	0.60020 (11)	0.0179 (5)
H1A	0.787 (3)	0.791 (9)	0.5687 (16)	0.019 (8)*
O1	0.35144 (16)	0.8661 (6)	0.48409 (9)	0.0199 (4)
S1	0.35151 (5)	0.55340 (15)	0.36015 (3)	0.01928 (17)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0338 (15)	0.0180 (12)	0.0144 (12)	-0.0026 (11)	-0.0025 (10)	0.0009 (10)
C2	0.0266 (13)	0.0172 (13)	0.0160 (12)	-0.0001 (10)	0.0048 (10)	-0.0005 (11)
C3	0.0173 (11)	0.0139 (11)	0.0126 (11)	-0.0020 (9)	0.0005 (9)	0.0009 (9)
C4	0.0187 (12)	0.0154 (12)	0.0120 (11)	-0.0046 (9)	-0.0014 (9)	0.0023 (9)
C5	0.0200 (12)	0.0166 (10)	0.0108 (11)	-0.0016 (10)	0.0010 (10)	0.0036 (10)
C6	0.0158 (11)	0.0201 (12)	0.0140 (11)	-0.0006 (10)	-0.0014 (10)	0.0010 (11)
C7	0.0188 (12)	0.0165 (12)	0.0146 (12)	-0.0002 (10)	0.0013 (10)	0.0030 (10)
C8	0.0195 (12)	0.0155 (12)	0.0130 (12)	-0.0010 (10)	0.0007 (9)	0.0016 (9)

C9	0.0244 (13)	0.0168 (12)	0.0138 (12)	0.0011 (10)	0.0017 (10)	-0.0013 (10)
C10	0.0274 (13)	0.0182 (12)	0.0129 (12)	-0.0024 (10)	-0.0025 (10)	-0.0010 (10)
C11	0.0194 (13)	0.0205 (13)	0.0149 (12)	-0.0040 (10)	-0.0010 (10)	0.0006 (10)
N1	0.0191 (11)	0.0218 (11)	0.0129 (11)	-0.0012 (9)	0.0016 (9)	-0.0015 (9)
O1	0.0183 (9)	0.0272 (9)	0.0143 (9)	0.0008 (8)	0.0013 (7)	0.0014 (8)
S1	0.0198 (3)	0.0223 (3)	0.0157 (3)	-0.0019 (2)	-0.0033 (3)	0.0002 (3)

Geometric parameters (Å, °)

C1—H1	0.9500	C6—C7	1.350 (4)
C1—C2	1.364 (4)	C7—H7	0.9500
C1—S1	1.702 (3)	C7—C8	1.428 (4)
C2—H2	0.9500	C8—C9	1.392 (4)
C2—C3	1.418 (4)	C8—N1	1.381 (3)
C3—H3	0.9500	C9—H9	0.9500
C3—C4	1.397 (4)	C9—C10	1.406 (4)
C4—C5	1.464 (3)	C10—H10	0.9500
C4—S1	1.722 (3)	C10—C11	1.380 (4)
C5—C6	1.463 (3)	C11—H11	0.9500
C5—O1	1.236 (3)	C11—N1	1.364 (4)
C6—H6	0.9500	N1—H1A	0.84 (4)
C2—C1—H1	123.7	C6—C7—C8	126.4 (3)
C2—C1—S1	112.5 (2)	C8—C7—H7	116.8
S1—C1—H1	123.7	C9—C8—C7	129.1 (2)
C1—C2—H2	123.6	N1—C8—C7	124.1 (2)
C1—C2—C3	112.8 (3)	N1—C8—C9	106.8 (2)
C3—C2—H2	123.6	C8—C9—H9	125.9
C2—C3—H3	124.2	C8—C9—C10	108.2 (2)
C4—C3—C2	111.6 (2)	C10—C9—H9	125.9
C4—C3—H3	124.2	C9—C10—H10	126.6
C3—C4—C5	130.0 (2)	C11—C10—C9	106.8 (2)
C3—C4—S1	111.2 (2)	C11—C10—H10	126.6
C5—C4—S1	118.77 (19)	C10—C11—H11	125.6
C6—C5—C4	116.8 (2)	N1—C11—C10	108.7 (2)
O1—C5—C4	120.2 (2)	N1—C11—H11	125.6
O1—C5—C6	122.9 (2)	C8—N1—H1A	127 (2)
C5—C6—H6	119.5	C11—N1—C8	109.4 (2)
C7—C6—C5	121.0 (2)	C11—N1—H1A	124 (2)
C7—C6—H6	119.5	C1—S1—C4	91.90 (14)
C6—C7—H7	116.8		
C1—C2—C3—C4	-0.2 (3)	C7—C8—C9—C10	177.3 (3)
C2—C1—S1—C4	0.4 (2)	C7—C8—N1—C11	-177.4 (3)
C2—C3—C4—C5	-179.2 (2)	C8—C9—C10—C11	0.2 (3)
C2—C3—C4—S1	0.5 (3)	C9—C8—N1—C11	0.3 (3)
C3—C4—C5—C6	0.0 (4)	C9—C10—C11—N1	0.0 (3)
C3—C4—C5—O1	-179.5 (3)	C10—C11—N1—C8	-0.2 (3)

C3—C4—S1—C1	-0.5 (2)	N1—C8—C9—C10	-0.3 (3)
C4—C5—C6—C7	175.0 (2)	O1—C5—C6—C7	-5.6 (4)
C5—C4—S1—C1	179.2 (2)	S1—C1—C2—C3	-0.2 (3)
C5—C6—C7—C8	177.7 (2)	S1—C4—C5—C6	-179.67 (19)
C6—C7—C8—C9	-173.4 (3)	S1—C4—C5—O1	0.9 (3)
C6—C7—C8—N1	3.8 (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 ⁱ	0.84 (4)	2.06 (4)	2.889 (3)	171 (3)
C6—H6...O1 ⁱ	0.95	2.50	3.396 (3)	158

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

Root mean square (r. m. s.) deviations and twist angles of the two five-membered heterocycles in 1 and the two derivatives known in literature (Li & Su, 1995; Ocak İskeleli et al., 2005)

Compound	R. M. S. deviation (Å)	Twist angle (°)
1	0.056	2.87 (11)
2 (First independent molecule)	0.093 (2)	7.15 (6)
Second independent molecule	0.02 (2)	0.20 (15)
3 (First independent molecule)	0.104	8.41 (6)
Second independent molecule	0.122	11.11 (7)