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(2*E*,7*E*)-2,7-Bis[(thiophen-2-yl)methylidene]cycloheptanoneC. Nithya,^a M. Sithambaresan,^{b*} S. Prathapan^a and M. R. Prathapachandra Kurup^a^aDepartment of Applied Chemistry, Cochin University of Science and Technology, Kochi 682 022, India, and ^bDepartment of Chemistry, Faculty of Science, Eastern University, Sri Lanka, Chenkalady, Sri Lanka

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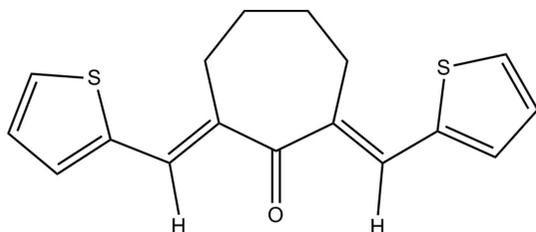
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Key indicators: single-crystal X-ray study; *T* = 296 K; mean $\sigma(\text{C}-\text{C})$ = 0.004 Å; *R* factor = 0.049; *wR* factor = 0.162; data-to-parameter ratio = 14.1.

The whole molecule of the title compound, C₁₇H₁₆OS₂, is generated by two-fold rotational symmetry. The carbonyl C and O atoms of the cycloheptanone ring lie on the twofold rotation axis which bisects the opposite –CH₂–CH₂– bond of the ring. The molecule exists in an *E,E* conformation with respect to the C=C double bond. The cycloheptanone ring exhibits a twisted chair conformation and its mean plane makes a dihedral angle of 50.12 (19)° with the planes of the thiophene rings. The two S atoms are in an *anti* arrangement with respect the carbonyl O atom and the dihedral angle between the two thiophene ring planes is 69.38 (7)°. In the molecule, there are two intramolecular C–H···S hydrogen bond, forming *S*(6) ring motifs. In the crystal, inversion dimers are generated *via* pairs of C–H···O hydrogen bonds. These dimers are interconnected by another interaction of the same kind with a neighbouring molecule, forming a molecular chain along the *c*-axis direction.

Related literature

For applications of thiophene derivatives in conducting polymers and biology, see: Kolodziejczyk *et al.* (2013); Mishra *et al.* (2011). For the synthesis of related compounds, see: Alkskas *et al.* (2013). For related structures, see: Liang *et al.* (2007); Layana *et al.* (2014).



Experimental

Crystal data

C₁₇H₁₆OS₂
M_r = 300.44
 Orthorhombic, *Pbcn*
a = 16.383 (2) Å
b = 11.6119 (14) Å
c = 7.8213 (7) Å
V = 1487.9 (3) Å³
Z = 4
 Mo *K*α radiation
 μ = 0.35 mm⁻¹
T = 296 K
 0.40 × 0.25 × 0.20 mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.873, *T_{max}* = 0.933
 4249 measured reflections
 1296 independent reflections
 970 reflections with *I* > 2σ(*I*)
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
 $wR(F^2)$ = 0.162
S = 1.03
 1296 reflections
 92 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}}$ = 0.20 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.33 e Å⁻³

Table 1

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>
C7–H7A···S1	0.97	2.53	3.205 (3)	126
C7–H7B···O1 ⁱ	0.97	2.53	3.282 (3)	135

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT* (Bruker, 2004); data reduction: *SAINT* and *XPREP* (Bruker, 2004); 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) and *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *SHELXL97* and *publCIF* (Westrip, 2010).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: ZL2588).

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supporting information

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(2*E*,7*E*)-2,7-Bis[(thiophen-2-yl)methylidene]cycloheptanone

C. Nithya, M. Sithambaresan, S. Prathapan and M. R. Prathapachandra Kurup

S1. Comment

Thiophenes are often a subject of considerable interest due to their numerous and interesting conducting properties as polymers and for their biological properties. The incorporation of rigid spacers into the thiophene backbone is anticipated to offer several distinct advantages. A polymer can be extended to afford a more planar conformation through diminished steric effects so that a maximum degree of delocalization of the π electrons is achieved (Kolodziejczyk *et al.*, 2013). Some thiophene derivatives were also evaluated for anti-cancer activity against PC-3 cell lines, for *in vitro* antioxidant potential and for β -glucuronidase and α -glucosidase inhibitory activities. Some also showed a potent DPPH radical scavenging antioxidant activity (Mishra *et al.*, 2011).

The title compound (Scheme 1, Fig. 1) crystallizes in the orthorhombic space group *Pbcn*. It has an *E* configuration with respect to the C6=C7 bond on both sides of the cycloheptanone ring. The central moiety (cycloheptanone) exists in a twisted chair form making a dihedral angle of 50.12 (19)° with the thiophene ring. The C9–O1 (1.227 (5) Å) bond distance is very close to the reported bond lengths (1.222 (3) Å) of a keto group of a similar structure (Liang *et al.*, 2007). The two sulfur atoms are in an *anti* arrangement with respect to the carbonyl O atom and the dihedral angle between the two five-membered thiophene ring planes is 69.38 (7)°. There are no classical hydrogen bond interactions present in the structure. However, an intramolecular H bond interaction between one of the H atoms at C7 atom and the S1 atom forms a five membered ring with a D···A distance of 3.205 (3) Å (Fig. 2) within the molecule whereas two C—H···O intermolecular hydrogen bond interactions with a D···A distance of 3.282 (3) Å (Table 1) between H7A and O1 generate a centrosymmetric dimer (Layana *et al.*, 2014) and also chain these centrosymmetric dimers into a 1-D chain along the *c* axis in the lattice (Fig. 3). In addition to this, there are two very weak π ··· π interactions found in the crystal between the thiophene rings with centroid-centroid distances of greater than 4 Å. Fig. 4 shows the packing of the title compound along *c* axis.

S2. Experimental

The title compound was prepared by adapting a reported procedure (Alkskas *et al.*, 2013). To a mixture of cycloheptanone (0.50 g, 4.4 mmol) and thiophene-2-carboxaldehyde (1.01 g, 8.7 mmol) in methanol (25 ml) taken up in a 100 ml flask, potassium hydroxide pellets (0.5 g, 8.7 mmol) were added and the reaction mixture was stirred at room temperature for 15 minutes whilst a yellow product separated out. The mixture was heated in a hot water bath at 60 °C for 6 h. until an appreciable amount of solid formed. The flask was then cooled in ice and the precipitate that separated out was collected by vacuum filtration. The crude product was washed several times with ice cold 1 ml portions of ethanol. Recrystallization from methanol gave diffraction quality crystals (yield 98%). m.p: 144–146 °C.

IR (KBr, ν in cm^{-1}): 2906, 1598, 1401, 1297. ^1H NMR (400 MHz, CDCl_3 , δ , p.p.m): 7.58 (d, 1H), 7.46(d, 1H), 7.31(t, 1H), 7.10 (s, 1H), 2.80 (t, 2H), 1.95 (m, 2H).

S3. Refinement

All H atoms on C were placed in calculated positions, guided by difference maps, with C—H bond distances of 0.93–0.97 Å. H atoms were assigned $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{carrier})$.

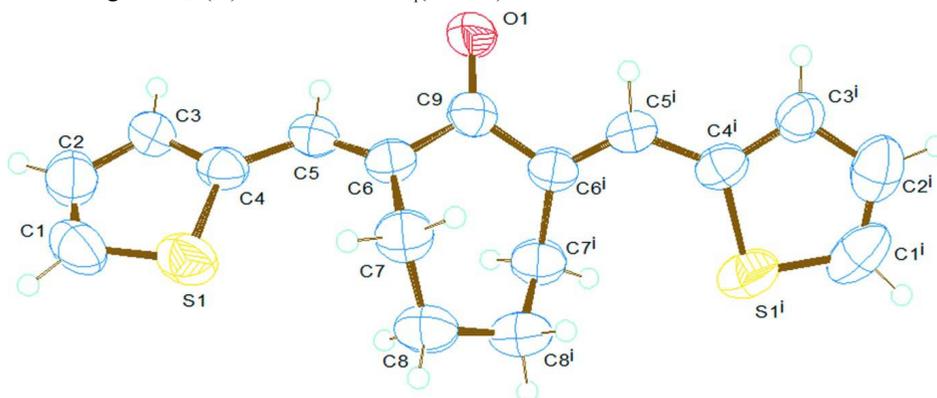


Figure 1

ORTEP view of the compound, drawn with 50% probability displacement ellipsoids for the non-H atoms. Symmetry operator (i): (i) $-x+2, y, -z+1/2$.

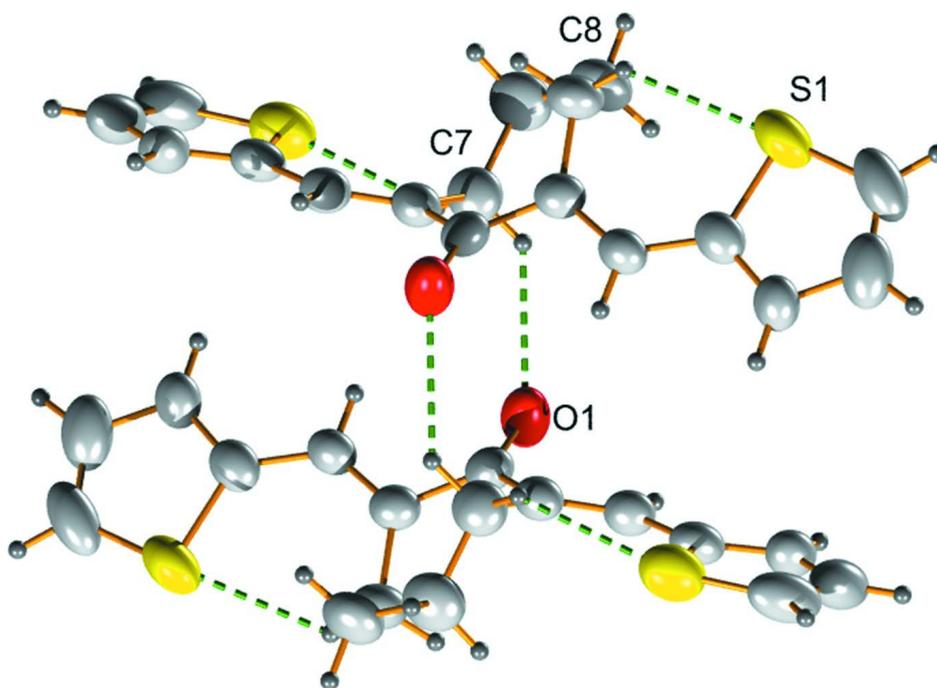


Figure 2

Centrosymmetric dimer formed by means of C—H...O interaction found in the title compound $\text{C}_{17}\text{H}_{16}\text{OS}_2$.

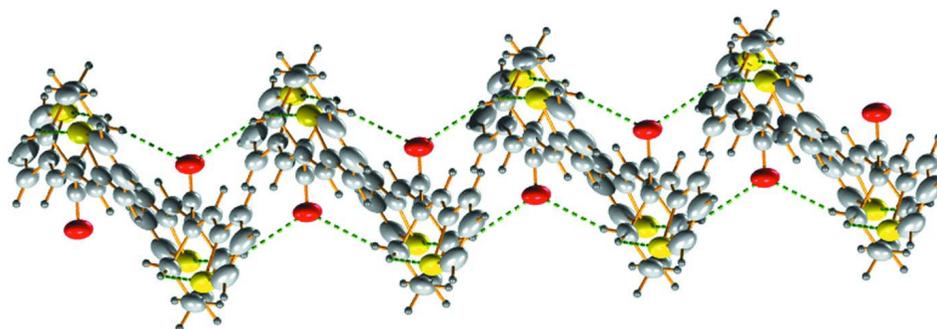


Figure 3

C—H...O interactions forming a 1-D molecular chain along the *c* axis.

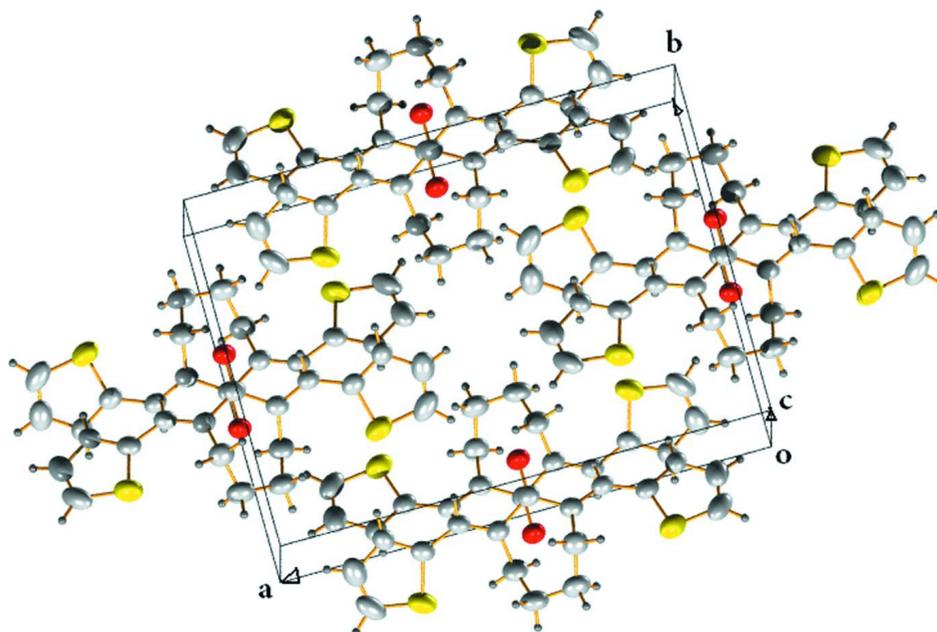


Figure 4

A view of the unit cell along the *c* axis.

(2*E*,7*E*)-2,7-Bis[(thiophen-2-yl)methylidene]cycloheptanone

Crystal data

$C_{17}H_{16}OS_2$

$M_r = 300.44$

Orthorhombic, *Pbcn*

Hall symbol: -P 2n 2ab

$a = 16.383$ (2) Å

$b = 11.6119$ (14) Å

$c = 7.8213$ (7) Å

$V = 1487.9$ (3) Å³

$Z = 4$

$F(000) = 632$

$D_x = 1.341$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1331 reflections

$\theta = 2.5$ – 28.4°

$\mu = 0.35$ mm⁻¹

$T = 296$ K

Block, colorless

$0.40 \times 0.25 \times 0.20$ mm

Data collection

Bruker APEXII CCD diffractometer	4249 measured reflections
Radiation source: fine-focus sealed tube	1296 independent reflections
Graphite monochromator	970 reflections with $I > 2\sigma(I)$
Detector resolution: 8.33 pixels mm^{-1}	$R_{\text{int}} = 0.025$
ω and φ scan	$\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 2.5^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 2004)	$h = -19 \rightarrow 9$
$T_{\text{min}} = 0.873$, $T_{\text{max}} = 0.933$	$k = -12 \rightarrow 13$
	$l = -9 \rightarrow 5$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.049$	H-atom parameters constrained
$wR(F^2) = 0.162$	$w = 1/[\sigma^2(F_o^2) + (0.0941P)^2 + 0.5613P]$
$S = 1.03$	where $P = (F_o^2 + 2F_c^2)/3$
1296 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
92 parameters	$\Delta\rho_{\text{max}} = 0.20 \text{ e } \text{\AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.33 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

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	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.6448 (2)	0.2975 (4)	0.3099 (5)	0.0826 (12)
H1	0.6039	0.2459	0.3403	0.099*
C2	0.6311 (2)	0.3968 (4)	0.2293 (5)	0.0817 (11)
H2	0.5793	0.4217	0.1976	0.098*
C3	0.70218 (17)	0.4600 (3)	0.1968 (4)	0.0570 (8)
H3	0.7028	0.5309	0.1413	0.068*
C4	0.77149 (18)	0.4051 (2)	0.2567 (3)	0.0541 (7)
C5	0.85397 (16)	0.4491 (2)	0.2406 (3)	0.0503 (7)
H5	0.8575	0.5190	0.1831	0.060*
C6	0.92557 (17)	0.4079 (2)	0.2929 (3)	0.0502 (7)
C7	0.9388 (2)	0.2988 (3)	0.3929 (4)	0.0635 (8)
H7A	0.8902	0.2839	0.4604	0.076*
H7B	0.9836	0.3112	0.4719	0.076*
C8	0.9573 (2)	0.1929 (3)	0.2876 (5)	0.0744 (9)
H8A	0.9180	0.1876	0.1952	0.089*
H8B	0.9508	0.1252	0.3589	0.089*

C9	1.0000	0.4747 (3)	0.2500	0.0527 (10)
O1	1.0000	0.5804 (2)	0.2500	0.0718 (9)
S1	0.74489 (6)	0.27612 (8)	0.35060 (12)	0.0737 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.087 (3)	0.077 (3)	0.083 (2)	-0.033 (2)	0.035 (2)	-0.0259 (19)
C2	0.064 (2)	0.088 (3)	0.093 (3)	-0.0080 (18)	0.0067 (18)	-0.036 (2)
C3	0.0537 (18)	0.0508 (16)	0.0664 (18)	-0.0055 (12)	-0.0001 (14)	-0.0088 (13)
C4	0.0653 (19)	0.0458 (15)	0.0511 (15)	-0.0061 (13)	0.0077 (13)	-0.0088 (13)
C5	0.0605 (18)	0.0406 (14)	0.0497 (15)	-0.0045 (12)	0.0015 (12)	0.0009 (12)
C6	0.0611 (18)	0.0449 (15)	0.0447 (14)	0.0029 (12)	-0.0001 (12)	-0.0012 (11)
C7	0.076 (2)	0.0562 (18)	0.0583 (17)	0.0009 (15)	-0.0001 (15)	0.0126 (14)
C8	0.095 (3)	0.0469 (16)	0.081 (2)	-0.0040 (16)	0.0034 (19)	0.0095 (15)
C9	0.060 (2)	0.047 (2)	0.051 (2)	0.000	-0.0125 (18)	0.000
O1	0.0603 (18)	0.0437 (16)	0.111 (3)	0.000	-0.0167 (16)	0.000
S1	0.0880 (7)	0.0573 (6)	0.0757 (6)	-0.0154 (4)	0.0209 (4)	0.0017 (4)

Geometric parameters (Å, °)

C1—C2	1.333 (5)	C6—C9	1.484 (3)
C1—S1	1.689 (4)	C6—C7	1.504 (4)
C1—H1	0.9300	C7—C8	1.511 (4)
C2—C3	1.400 (5)	C7—H7A	0.9700
C2—H2	0.9300	C7—H7B	0.9700
C3—C4	1.384 (4)	C8—C8 ⁱ	1.517 (7)
C3—H3	0.9300	C8—H8A	0.9700
C4—C5	1.450 (4)	C8—H8B	0.9700
C4—S1	1.724 (3)	C9—O1	1.227 (5)
C5—C6	1.332 (4)	C9—C6 ⁱ	1.484 (3)
C5—H5	0.9300		
C2—C1—S1	112.4 (3)	C9—C6—C7	116.1 (2)
C2—C1—H1	123.8	C6—C7—C8	115.5 (3)
S1—C1—H1	123.8	C6—C7—H7A	108.4
C1—C2—C3	113.5 (3)	C8—C7—H7A	108.4
C1—C2—H2	123.3	C6—C7—H7B	108.4
C3—C2—H2	123.3	C8—C7—H7B	108.4
C4—C3—C2	112.3 (3)	H7A—C7—H7B	107.5
C4—C3—H3	123.9	C7—C8—C8 ⁱ	113.4 (2)
C2—C3—H3	123.9	C7—C8—H8A	108.9
C3—C4—C5	124.9 (3)	C8 ⁱ —C8—H8A	108.9
C3—C4—S1	109.7 (2)	C7—C8—H8B	108.9
C5—C4—S1	125.4 (2)	C8 ⁱ —C8—H8B	108.9
C6—C5—C4	131.8 (3)	H8A—C8—H8B	107.7
C6—C5—H5	114.1	O1—C9—C6	121.53 (16)
C4—C5—H5	114.1	O1—C9—C6 ⁱ	121.53 (16)

C5—C6—C9	117.8 (2)	C6—C9—C6 ⁱ	116.9 (3)
C5—C6—C7	126.1 (3)	C1—S1—C4	92.15 (18)
S1—C1—C2—C3	0.1 (4)	C9—C6—C7—C8	-86.3 (3)
C1—C2—C3—C4	-0.2 (4)	C6—C7—C8—C8 ⁱ	73.2 (4)
C2—C3—C4—C5	179.5 (3)	C5—C6—C9—O1	36.8 (3)
C2—C3—C4—S1	0.2 (3)	C7—C6—C9—O1	-143.08 (18)
C3—C4—C5—C6	178.9 (3)	C5—C6—C9—C6 ⁱ	-143.2 (3)
S1—C4—C5—C6	-2.0 (4)	C7—C6—C9—C6 ⁱ	36.92 (18)
C4—C5—C6—C9	178.3 (2)	C2—C1—S1—C4	0.0 (3)
C4—C5—C6—C7	-1.8 (5)	C3—C4—S1—C1	-0.1 (2)
C5—C6—C7—C8	93.8 (4)	C5—C4—S1—C1	-179.4 (2)

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

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
C7—H7A...S1	0.97	2.53	3.205 (3)	126
C7—H7B...O1 ⁱⁱ	0.97	2.53	3.282 (3)	135

Symmetry code: (ii) $-x+2, -y+1, -z+1$.