

Crystal structures of (1*E*,4*E*)-1,5-bis(5-bromothiophen-2-yl)-2,4-dimethylpenta-1,4-dien-3-one and (*E*)-4-(5-bromothiophen-2-yl)-1,3-diphenylbut-3-en-2-one

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Keywords: crystal structure; Claisen–Schmidt; 5-bromothiophene-2-carbaldehyde; pentan-3-one; dibenzylacetone

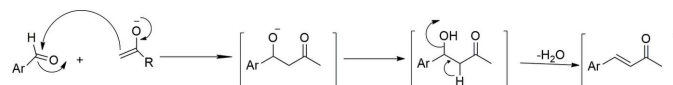
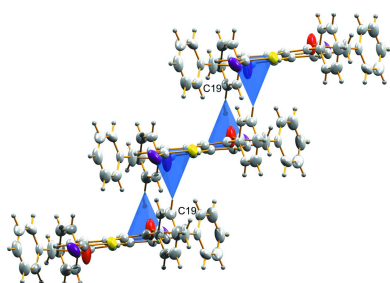
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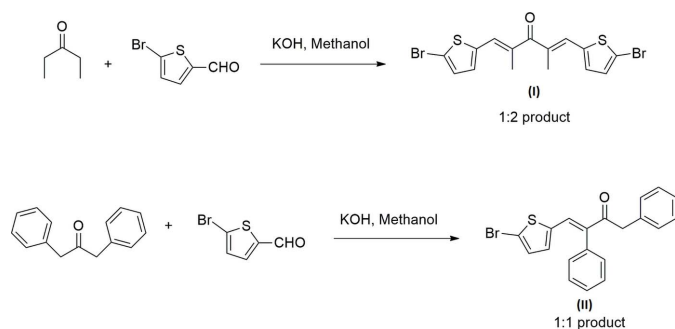
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The title compounds, C₁₅H₁₂Br₂OS₂, (I), and C₂₀H₁₅BrOS, (II), were synthesized by employing Claisen–Schmidt condensation of pentan-3-one and dibenzylacetone with 5-bromothiophene-2-carbaldehyde in the presence of methanolic KOH. Even though 1:2 products were expected in both of the reactions, 1:2 and 1:1 products were obtained as (I) and (II), respectively. In (I), the two methyl groups are *trans* to each other, 29.5 (7) and 28.7 (7)° away from the central carbonyl bond between them, whereas the two phenyl rings of dibenzylacetone subtend a dihedral angle of 53.09 (18)°. In the crystal of (I), C–H···O hydrogen bonds define molecular chains along *c*. A second type of molecular chain is formed along *b* by means of C–Br···π interactions. These two families of molecular chains are stacked by π–π interactions, forming a three-dimensional supramolecular architecture. In (II), similar C–H···O hydrogen bonds as in (I) define inversion dimers, whilst C–H···π interactions build a staircase structure along the *a* axis.

1. Chemical context

Claisen–Schmidt reaction (Claisen & Claparede, 1881; Schmidt, 1881) is the condensation of aromatic aldehydes (or between ketones and aldehydes lacking α-hydrogen with aliphatic or mixed alkyl aryl ketones in the presence of a relatively strong base to form α,β-unsaturated ketones. This reaction is of tremendous value in synthetic organic chemistry (Wayne & Adkins 1940; Marvel & King, 1944) and is frequently encountered as a key step in several elegant total synthesis protocols. Claisen–Schmidt condensation can also be catalysed by acid. The first step is a condensation of an aldol type; enols or enolates are involved as intermediates in this reaction. This reaction involves the nucleophilic addition of enol or an enolate ion derived from methyl ketone to the carbonyl carbon of the aromatic aldehyde. Dehydration of the hydroxylketone to form the conjugated unsaturated carbonyl compound occurs spontaneously (see Scheme 1) (Stiles *et al.*, 1959). Cycloalkanones like cyclohexanone, cycloheptanone readily undergo Claisen–Schmidt condensation (Nithya *et al.*, 2014). In addition to cycloalkanones we attempted open-chain alkanones.





The title compounds (I) and (II) were synthesized by employing Claisen–Schmidt condensation of pentan-3-one and dibenzylacetone with 5-bromothiophene-2-carbaldehyde in the presence of methanolic KOH (Schemes 1 and 2). Although we anticipated getting 1:2 products in both of the reactions, a 1:2 product was obtained for the former case, (I), and a 1:1 product for the latter, (II). In compound (II), the bulky phenyl ring hinders the possibility of a second bromothiophene ring being attached and hence only a 1:1 product was formed in this case. We present herein the structures of (*E,E*)-1,5-bis(5-bromothiophen-2-yl)-2,4-dimethylpentan-1,4-dien-3-one (I) and (*E*)-4-(5-bromothiophen-2-yl)-1,3-diphenylbut-3-en-2-one (II).

2. Structural commentary

The molecular structures of (I) and (II) are shown in Fig. 1. The asymmetric unit of (I) comprises one molecule of bis(bromothiophenyl)dimethylpentanone and two of

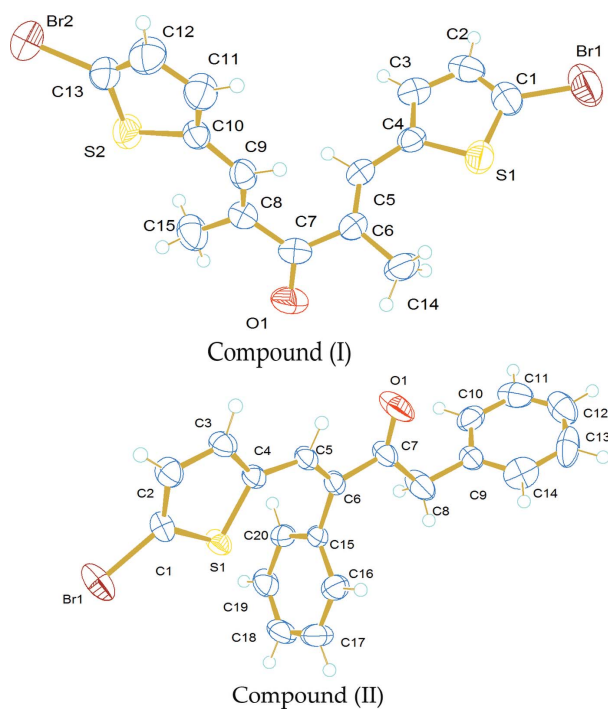


Figure 1
View of the title compounds (I) and (II) drawn with 50% probability displacement ellipsoids for the non-H atoms.

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

<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>
C3–H3···O1 ⁱ	0.93	2.57	3.233 (7)	129

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

Table 2
Hydrogen-bond geometry (Å, °) for (II).

C_g is the centroid of the C1–C4/S1 ring.

<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>
C3–H3···O1 ⁱ	0.93	2.54	3.320 (4)	141
C19–H19··· <i>C_g</i> ⁱⁱ	0.93	2.90	3.768 (3)	156

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

5-bromothiophenyldiphenylbutanone. The two methyl groups (C14 and C15) of (I) are twisted away from each other with C14–C6–C7–O1 and C15–C8–C7–O1 torsion angles of 29.5 (7) and 28.7 (7)°, respectively.

The asymmetric unit of (II) comprises one molecule of 5-bromothiophene-2-carbaldehyde with one molecule of dibenzylacetone. The two phenyl rings of the dibenzylacetone subtend a dihedral angle of 53.09 (18)°. One of the phenyl rings (C15–C20) of the dibenzylacetone and the thiophene ring are normal to one another, forming a dihedral angle of 89.96 (16)°.

3. Supramolecular features

In the crystal structure of (I), a non-classical C–H···O hydrogen bond (Table 1) links the molecules into a chain along the *c* axis (Fig. 2). Another molecular chain is formed along the *b* axis through a C13–Br2··· π (C1–C4/S1)ⁱⁱ interaction [symmetry code: (ii) $1 - x, 1 + y, \frac{1}{2} - z$], Br···*C_g* = 3.556 (2) Å (Fig. 3). The two molecular chains are in turn stacked by π – π interactions between the two thiophene rings, (C1–C4/S1) and (C10–C13/S2)ⁱⁱⁱ [symmetry code: (iii) $1 - x, y, \frac{1}{2} - z$], *C_g*···*C_g* = 3.718 (3) Å, forming a three-dimensional supramolecular architecture (Fig. 4).

In structure (II) a C–H···O hydrogen bond (Table 2) links pairs of molecules, forming inversion dimers (Fig. 5). The dimers are linked together by means of C19–H19··· π (C1–C4/

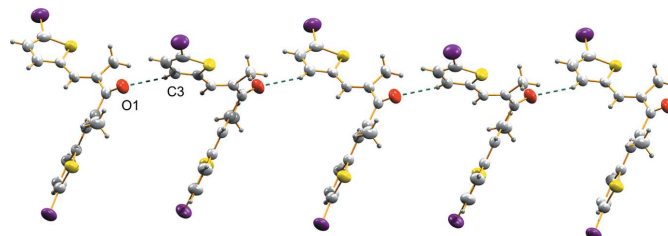


Figure 2
C–H···O hydrogen-bonding interaction in (I), forming a molecular chain along the *c* axis.

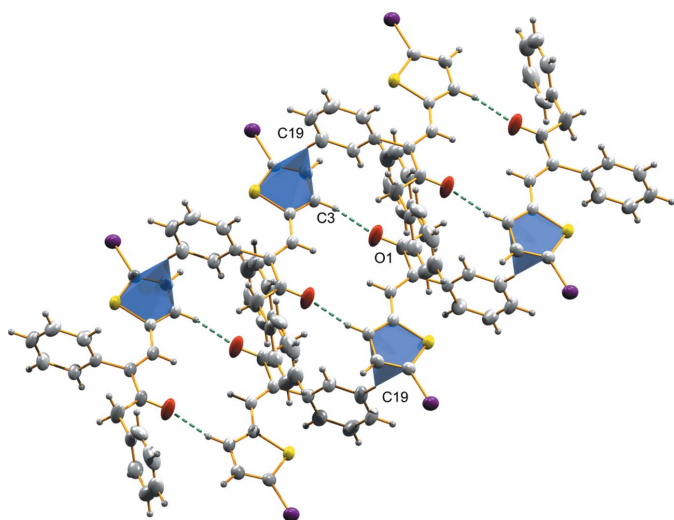


Figure 3
The molecular chain in (I), formed along the *b* axis through C—Br $\cdots\pi$ interactions.

S1) interaction, building a staircase structure along the *a* axis (Fig. 6).

4. Synthesis and crystallization

The title compounds were prepared by adapting a reported procedure (Alkskas *et al.*, 2013). Title compound (I) was prepared by adding a mixture of pentan-3-one (0.50 g, 1.2 mmol) and 5-bromothiophene-2-carbaldehyde (2.2 g, 2.4 mmol) in methanol (25 mL) and potassium hydroxide pellets (0.2 g, 2.4 mmol) was also added. The reaction mixture was stirred at room temperature overnight whilst a pale-yellow product separated out. The crude product was washed several times with cold ethanol (1 mL). Good quality single crystals suitable for X-ray analysis were obtained by recrystallization from chloroform, m.p. 401–403 K. Yield: 85%. IR (KBr): 1680 (C=O), 3061(=C—H). $^1\text{H NMR}$: (CDCl_3): δ 2.20 (3H, *s*), δ 6.97–6.96 (1H, *d*), δ 7.08–7.07 (1H, *d*), δ 7.18–7.17 (1H, *s*). MS: m/z 431 (M^+); analysis calculated for $\text{C}_{15}\text{H}_{12}\text{Br}_2\text{S}_2\text{O}$: C: 41.69, H: 2.80, Br: 36.98, S: 14.84; found: C: 41.59, H: 2.78, Br: 36.90, S: 14.74.

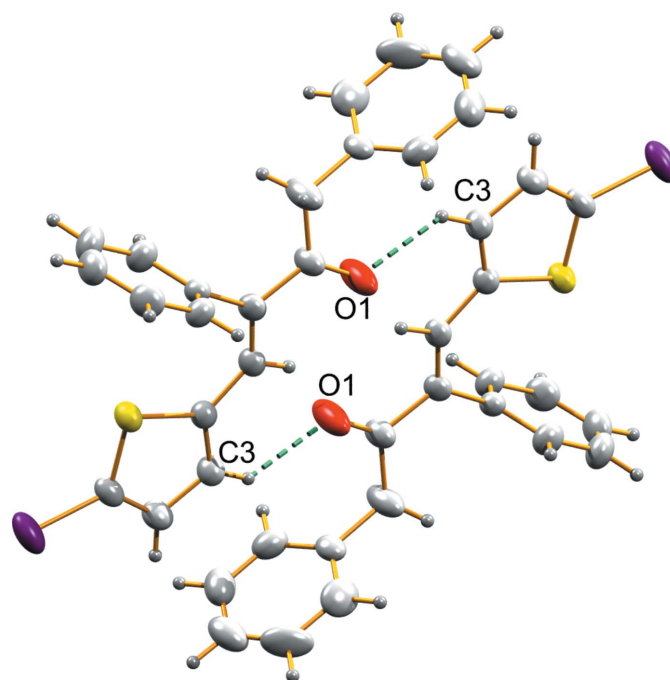


Figure 5
C—H \cdots O interactions in (II), forming an inversion dimer.

Title compound (II) was prepared by mixing dibenzylketone (1 g, 4.7 mmol) and 5-bromothiophene-2-carbaldehyde (1.8 g, 9.5 mmol) in methanol (25 mL) and potassium hydroxide pellets (0.6 g, 9.5 mmol) were also added. The reaction mixture was stirred at room temperature overnight whilst a yellow product separated out. The crude product was washed several times with cold ethanol (1 mL). Good quality

Title compound (II) was prepared by mixing dibenzylketone (1 g, 4.7 mmol) and 5-bromothiophene-2-carbaldehyde (1.8 g, 9.5 mmol) in methanol (25 mL) and potassium hydroxide pellets (0.6 g, 9.5 mmol) were also added. The reaction mixture was stirred at room temperature overnight whilst a yellow product separated out. The crude product was washed several times with cold ethanol (1 mL). Good quality

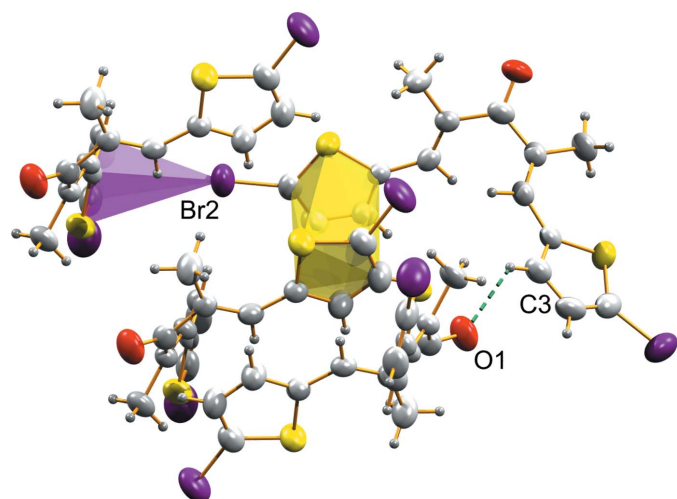


Figure 4
The two molecular chains in (I), stacked by π – π interactions to form a three-dimensional supramolecular architecture.

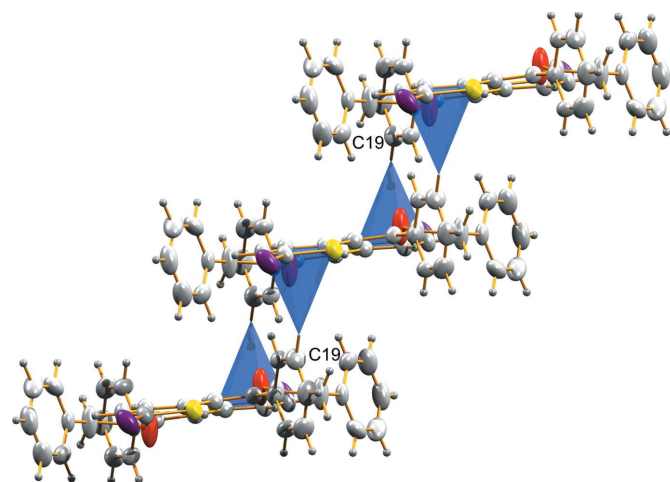


Figure 6
Dimers in (II) linked together by means of C—H $\cdots\pi$ interactions building a staircase structure along the *a* axis.

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	C ₁₅ H ₁₂ Br ₂ OS ₂	C ₂₀ H ₁₅ BrOS
<i>M_r</i>	432.19	383.29
Crystal system, space group	Monoclinic, <i>P</i> 2/ <i>c</i>	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	296	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	16.564 (2), 6.3581 (7), 15.962 (2)	7.5879 (4), 8.5361 (6), 14.0970 (8)
α , β , γ (°)	90, 105.239 (5), 90	99.510 (3), 97.673 (3), 101.956 (3)
<i>V</i> (Å ³)	1622.0 (4)	867.58 (9)
<i>Z</i>	4	2
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	5.25	2.49
Crystal size (mm)	0.60 × 0.50 × 0.40	0.60 × 0.50 × 0.35
Data collection		
Diffractometer	Bruker Kappa APEXII CCD	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2004)	Multi-scan (<i>SADABS</i> ; Bruker, 2004)
<i>T</i> _{min} , <i>T</i> _{max}	0.049, 0.115	0.307, 0.456
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	13847, 4051, 2012	6863, 4363, 3040
<i>R</i> _{int}	0.059	0.025
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.667	0.670
Refinement		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.059, 0.181, 0.98	0.043, 0.118, 1.05
No. of reflections	4042	4363
No. of parameters	183	208
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.88, -0.80	0.56, -0.86

Computer programs: *APEX2*, *SAINT* and *XPREP* (Bruker, 2004), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *DIAMOND* (Brandenburg, 2010) and *pubCIF* (Westrip, 2010).

single crystals suitable for X-ray analysis were obtained by recrystallization from chloroform, m.p. 383–385 K. Yield: 90%. IR (KBr): 1627 (C=O), 3080 (=C–H). ¹H NMR (CDCl₃): δ 3.78 (2H, s), δ 7.80 (1H, s), 7.51–7.48 (1H, m), 7.47 (1H, m), 7.23–7.20 (2H, m), 7.15–7.14 (2H, m), 7.13–7.12 (2H, m), 7.04–7.02 (2H, m), 6.97–6.96 (1H, d), 6.90–6.89 (1H, d). MS: *m/z* 383 (*M*⁺); analysis calculated for C₂₀H₁₅BrOS: C: 62.67, H: 3.94, Br: 20.85, S: 8.37; found: C: 62.57, H: 3.92, Br: 20.77, S: 8.27.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. In both compounds, all H atoms on C were placed in calculated positions, guided by difference Fourier maps, with C–H bond distances of 0.93–0.97 Å. H atoms were assigned as *U*_{iso}(H) = 1.2*U*_{eq}(carrier) or 1.5*U*_{eq} (methyl C). Four reflections were omitted owing to bad agreement for compound (I).

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supporting information

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Crystal structures of (1*E*,4*E*)-1,5-bis(5-bromothiophen-2-yl)-2,4-dimethylpenta-1,4-dien-3-one and (*E*)-4-(5-bromothiophen-2-yl)-1,3-diphenylbut-3-en-2-one

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Computing details

For both compounds, 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: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

(I) (1*E*,4*E*)-1,5-Bis(5-bromothiophen-2-yl)-2,4-dimethylpenta-1,4-dien-3-one

Crystal data

C₁₅H₁₂Br₂OS₂

M_r = 432.19

Monoclinic, *P2/c*

a = 16.564 (2) Å

b = 6.3581 (7) Å

c = 15.962 (2) Å

β = 105.239 (5)°

V = 1622.0 (4) Å³

Z = 4

F(000) = 848

D_x = 1.770 Mg m⁻³

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 3021 reflections

θ = 2.6–23.4°

μ = 5.25 mm⁻¹

T = 296 K

Block, yellow

0.60 × 0.50 × 0.40 mm

Data collection

Bruker Kappa APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω and φ scan

Absorption correction: multi-scan

(*SADABS*; Bruker, 2004)

T_{min} = 0.049, *T_{max}* = 0.115

13847 measured reflections

4051 independent reflections

2012 reflections with *I* > 2σ(*I*)

R_{int} = 0.059

θ_{max} = 28.3°, θ_{min} = 2.7°

h = -22→21

k = -5→8

l = -21→21

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.059

wR(*F*²) = 0.181

S = 0.98

4042 reflections

183 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0913P)^2 + 0.2774P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.88 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.80 \text{ e } \text{\AA}^{-3}$$

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.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.0832 (3)	0.4182 (8)	0.1493 (4)	0.0604 (15)
C2	0.1111 (4)	0.5540 (9)	0.0976 (4)	0.0642 (15)
H2	0.1009	0.5392	0.0377	0.077*
C3	0.1566 (3)	0.7172 (8)	0.1450 (4)	0.0578 (15)
H3	0.1809	0.8227	0.1195	0.069*
C4	0.1631 (3)	0.7115 (7)	0.2316 (3)	0.0455 (12)
C5	0.2056 (3)	0.8689 (7)	0.2940 (3)	0.0462 (12)
H5	0.2398	0.9604	0.2733	0.055*
C6	0.2036 (3)	0.9036 (7)	0.3762 (3)	0.0453 (12)
C7	0.2488 (3)	1.0879 (8)	0.4230 (3)	0.0505 (12)
C8	0.3296 (3)	1.1597 (7)	0.4070 (3)	0.0466 (12)
C9	0.3833 (3)	1.0165 (7)	0.3931 (3)	0.0456 (12)
H9	0.3643	0.8784	0.3904	0.055*
C10	0.4668 (3)	1.0418 (7)	0.3816 (3)	0.0435 (11)
C11	0.5166 (3)	0.8833 (8)	0.3700 (4)	0.0636 (16)
H11	0.5000	0.7433	0.3691	0.076*
C12	0.5950 (3)	0.9419 (10)	0.3595 (4)	0.0687 (17)
H12	0.6358	0.8485	0.3522	0.082*
C13	0.6027 (3)	1.1518 (9)	0.3616 (4)	0.0572 (14)
C14	0.1503 (4)	0.7812 (9)	0.4221 (4)	0.0624 (15)
H14A	0.1493	0.8519	0.4750	0.094*
H14B	0.1731	0.6426	0.4353	0.094*
H14C	0.0943	0.7709	0.3854	0.094*
C15	0.3465 (4)	1.3911 (8)	0.4187 (4)	0.0690 (17)
H15A	0.3019	1.4570	0.4371	0.104*
H15B	0.3500	1.4514	0.3646	0.104*
H15C	0.3984	1.4128	0.4619	0.104*
S1	0.11240 (8)	0.4921 (2)	0.25627 (10)	0.0591 (4)
S2	0.51728 (9)	1.2768 (2)	0.37862 (11)	0.0610 (4)
Br2	0.69420 (4)	1.31159 (11)	0.34996 (5)	0.0869 (3)
Br1	0.01821 (5)	0.17864 (10)	0.11612 (6)	0.0937 (3)
O1	0.2192 (3)	1.1834 (6)	0.4736 (3)	0.0749 (12)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.044 (3)	0.057 (3)	0.077 (4)	0.004 (3)	0.009 (3)	-0.013 (3)
C2	0.065 (4)	0.077 (4)	0.050 (4)	0.009 (3)	0.014 (3)	-0.016 (3)
C3	0.060 (3)	0.063 (3)	0.055 (4)	0.004 (3)	0.025 (3)	0.002 (3)
C4	0.039 (3)	0.054 (3)	0.047 (3)	0.001 (2)	0.017 (2)	-0.003 (2)
C5	0.045 (3)	0.052 (3)	0.046 (3)	-0.002 (2)	0.020 (2)	0.005 (2)
C6	0.044 (3)	0.047 (3)	0.048 (3)	0.000 (2)	0.018 (2)	0.004 (2)
C7	0.057 (3)	0.057 (3)	0.039 (3)	0.007 (2)	0.015 (3)	-0.002 (3)
C8	0.049 (3)	0.047 (3)	0.042 (3)	0.001 (2)	0.012 (2)	-0.004 (2)
C9	0.052 (3)	0.039 (2)	0.044 (3)	-0.006 (2)	0.009 (2)	0.002 (2)
C10	0.048 (3)	0.038 (2)	0.045 (3)	-0.004 (2)	0.012 (2)	-0.004 (2)
C11	0.058 (3)	0.046 (3)	0.088 (5)	0.003 (2)	0.023 (3)	-0.003 (3)
C12	0.054 (3)	0.067 (4)	0.087 (5)	0.009 (3)	0.022 (3)	-0.004 (3)
C13	0.050 (3)	0.068 (4)	0.053 (4)	-0.009 (3)	0.013 (3)	-0.006 (3)
C14	0.064 (4)	0.081 (4)	0.050 (4)	-0.005 (3)	0.029 (3)	0.005 (3)
C15	0.062 (4)	0.050 (3)	0.094 (5)	0.000 (3)	0.020 (3)	-0.019 (3)
S1	0.0566 (8)	0.0638 (8)	0.0565 (10)	-0.0148 (7)	0.0141 (7)	-0.0001 (7)
S2	0.0586 (8)	0.0455 (7)	0.0828 (12)	-0.0091 (6)	0.0255 (8)	-0.0096 (7)
Br2	0.0666 (4)	0.1003 (6)	0.1022 (6)	-0.0286 (4)	0.0372 (4)	-0.0157 (4)
Br1	0.0836 (5)	0.0756 (5)	0.1146 (7)	-0.0153 (3)	0.0128 (4)	-0.0333 (4)
O1	0.077 (3)	0.087 (3)	0.069 (3)	0.000 (2)	0.036 (2)	-0.028 (2)

Geometric parameters (\AA , $^\circ$)

C1—C2	1.357 (8)	C9—C10	1.450 (6)
C1—S1	1.714 (6)	C9—H9	0.9300
C1—Br1	1.860 (5)	C10—C11	1.346 (7)
C2—C3	1.385 (7)	C10—S2	1.720 (4)
C2—H2	0.9300	C11—C12	1.403 (8)
C3—C4	1.358 (7)	C11—H11	0.9300
C3—H3	0.9300	C12—C13	1.340 (8)
C4—C5	1.456 (7)	C12—H12	0.9300
C4—S1	1.727 (5)	C13—S2	1.705 (6)
C5—C6	1.340 (7)	C13—Br2	1.874 (5)
C5—H5	0.9300	C14—H14A	0.9600
C6—C7	1.483 (7)	C14—H14B	0.9600
C6—C14	1.505 (7)	C14—H14C	0.9600
C7—O1	1.213 (6)	C15—H15A	0.9600
C7—C8	1.497 (7)	C15—H15B	0.9600
C8—C9	1.332 (6)	C15—H15C	0.9600
C8—C15	1.500 (7)		
C2—C1—S1	112.3 (4)	C11—C10—C9	125.0 (4)
C2—C1—Br1	127.7 (5)	C11—C10—S2	109.1 (4)
S1—C1—Br1	119.9 (4)	C9—C10—S2	125.9 (3)
C1—C2—C3	111.6 (5)	C10—C11—C12	115.9 (5)

C1—C2—H2	124.2	C10—C11—H11	122.0
C3—C2—H2	124.2	C12—C11—H11	122.0
C4—C3—C2	115.0 (5)	C13—C12—C11	110.3 (5)
C4—C3—H3	122.5	C13—C12—H12	124.9
C2—C3—H3	122.5	C11—C12—H12	124.9
C3—C4—C5	124.9 (5)	C12—C13—S2	113.0 (4)
C3—C4—S1	109.9 (4)	C12—C13—Br2	127.7 (4)
C5—C4—S1	125.2 (4)	S2—C13—Br2	119.3 (3)
C6—C5—C4	130.6 (4)	C6—C14—H14A	109.5
C6—C5—H5	114.7	C6—C14—H14B	109.5
C4—C5—H5	114.7	H14A—C14—H14B	109.5
C5—C6—C7	119.0 (4)	C6—C14—H14C	109.5
C5—C6—C14	124.1 (5)	H14A—C14—H14C	109.5
C7—C6—C14	116.5 (4)	H14B—C14—H14C	109.5
O1—C7—C6	119.5 (5)	C8—C15—H15A	109.5
O1—C7—C8	119.8 (5)	C8—C15—H15B	109.5
C6—C7—C8	120.7 (4)	H15A—C15—H15B	109.5
C9—C8—C7	119.1 (4)	C8—C15—H15C	109.5
C9—C8—C15	125.4 (5)	H15A—C15—H15C	109.5
C7—C8—C15	115.0 (4)	H15B—C15—H15C	109.5
C8—C9—C10	130.3 (4)	C1—S1—C4	91.2 (3)
C8—C9—H9	114.9	C13—S2—C10	91.7 (2)
C10—C9—H9	114.9		
S1—C1—C2—C3	0.4 (6)	C7—C8—C9—C10	-175.6 (5)
Br1—C1—C2—C3	178.9 (4)	C15—C8—C9—C10	-3.3 (9)
C1—C2—C3—C4	-1.0 (7)	C8—C9—C10—C11	178.2 (6)
C2—C3—C4—C5	-178.1 (5)	C8—C9—C10—S2	-3.0 (8)
C2—C3—C4—S1	1.2 (6)	C9—C10—C11—C12	179.6 (5)
C3—C4—C5—C6	166.0 (5)	S2—C10—C11—C12	0.6 (7)
S1—C4—C5—C6	-13.1 (8)	C10—C11—C12—C13	-1.3 (8)
C4—C5—C6—C7	-175.4 (5)	C11—C12—C13—S2	1.4 (7)
C4—C5—C6—C14	-2.5 (8)	C11—C12—C13—Br2	-179.5 (4)
C5—C6—C7—O1	143.9 (5)	C2—C1—S1—C4	0.2 (4)
C14—C6—C7—O1	-29.5 (7)	Br1—C1—S1—C4	-178.4 (3)
C5—C6—C7—C8	-34.8 (7)	C3—C4—S1—C1	-0.8 (4)
C14—C6—C7—C8	151.8 (5)	C5—C4—S1—C1	178.5 (4)
O1—C7—C8—C9	144.4 (5)	C12—C13—S2—C10	-1.0 (5)
C6—C7—C8—C9	-36.9 (7)	Br2—C13—S2—C10	179.9 (3)
O1—C7—C8—C15	-28.7 (7)	C11—C10—S2—C13	0.2 (5)
C6—C7—C8—C15	150.0 (5)	C9—C10—S2—C13	-178.7 (5)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3 \cdots O1 ⁱ	0.93	2.57	3.233 (7)	129

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

(II) (E)-4-(5-Bromothiophen-2-yl)-1,3-diphenylbut-3-en-2-one

Crystal data

$C_{20}H_{15}BrOS$	$Z = 2$
$M_r = 383.29$	$F(000) = 388$
Triclinic, $P\bar{1}$	$D_x = 1.467 \text{ Mg m}^{-3}$
$a = 7.5879 (4) \text{ \AA}$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$b = 8.5361 (6) \text{ \AA}$	Cell parameters from 3038 reflections
$c = 14.0970 (8) \text{ \AA}$	$\theta = 2.5\text{--}28.2^\circ$
$\alpha = 99.510 (3)^\circ$	$\mu = 2.49 \text{ mm}^{-1}$
$\beta = 97.673 (3)^\circ$	$T = 296 \text{ K}$
$\gamma = 101.956 (3)^\circ$	Block, yellow
$V = 867.58 (9) \text{ \AA}^3$	$0.60 \times 0.50 \times 0.35 \text{ mm}$

Data collection

Bruker Kappa APEXII CCD diffractometer	6863 measured reflections
Radiation source: fine-focus sealed tube	4363 independent reflections
Graphite monochromator	3040 reflections with $I > 2\sigma(I)$
ω and ϕ scan	$R_{\text{int}} = 0.025$
Absorption correction: multi-scan (SADABS; Bruker, 2004)	$\theta_{\text{max}} = 28.4^\circ$, $\theta_{\text{min}} = 2.5^\circ$
$T_{\text{min}} = 0.307$, $T_{\text{max}} = 0.456$	$h = -10 \rightarrow 8$
	$k = -7 \rightarrow 11$
	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.043$	H-atom parameters constrained
$wR(F^2) = 0.118$	$w = 1/[\sigma^2(F_o^2) + (0.0571P)^2 + 0.3404P]$
$S = 1.05$	where $P = (F_o^2 + 2F_c^2)/3$
4363 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
208 parameters	$\Delta\rho_{\text{max}} = 0.56 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.86 \text{ e \AA}^{-3}$
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.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.2982 (4)	0.1132 (4)	0.6105 (2)	0.0364 (6)
C2	0.4114 (4)	0.0812 (4)	0.6841 (2)	0.0415 (7)
H2	0.4737	-0.0019	0.6772	0.050*
C3	0.4219 (4)	0.1897 (4)	0.7720 (2)	0.0382 (7)
H3	0.4943	0.1863	0.8299	0.046*
C4	0.3170 (4)	0.3012 (3)	0.76546 (19)	0.0316 (6)
C5	0.3029 (4)	0.4239 (4)	0.84553 (19)	0.0337 (6)
H5	0.3787	0.4288	0.9040	0.040*

C6	0.1973 (4)	0.5323 (3)	0.84900 (19)	0.0333 (6)
C7	0.2176 (4)	0.6463 (4)	0.9441 (2)	0.0438 (7)
C8	0.1294 (6)	0.7885 (5)	0.9442 (3)	0.0665 (12)
H8A	0.1660	0.8438	0.8927	0.080*
H8B	-0.0022	0.7469	0.9287	0.080*
C9	0.1747 (4)	0.9109 (4)	1.0380 (2)	0.0388 (7)
C10	0.0910 (5)	0.8834 (4)	1.1161 (3)	0.0503 (8)
H10	0.0046	0.7861	1.1105	0.060*
C11	0.1308 (6)	0.9941 (6)	1.2013 (3)	0.0640 (11)
H11	0.0704	0.9724	1.2526	0.077*
C12	0.2550 (6)	1.1327 (6)	1.2122 (3)	0.0657 (11)
H12	0.2831	1.2062	1.2717	0.079*
C13	0.3413 (5)	1.1690 (5)	1.1382 (4)	0.0695 (12)
H13	0.4260	1.2680	1.1461	0.083*
C14	0.3023 (5)	1.0560 (5)	1.0490 (3)	0.0585 (10)
H14	0.3624	1.0792	0.9978	0.070*
C15	0.0666 (4)	0.5442 (3)	0.76278 (18)	0.0319 (6)
C16	0.1236 (4)	0.6394 (4)	0.6970 (2)	0.0449 (7)
H16	0.2433	0.7016	0.7084	0.054*
C17	0.0051 (5)	0.6430 (5)	0.6150 (2)	0.0562 (9)
H17	0.0446	0.7085	0.5718	0.067*
C18	-0.1706 (5)	0.5505 (5)	0.5968 (2)	0.0541 (9)
H18	-0.2493	0.5506	0.5402	0.065*
C19	-0.2302 (4)	0.4582 (4)	0.6615 (2)	0.0487 (8)
H19	-0.3504	0.3971	0.6497	0.058*
C20	-0.1119 (4)	0.4551 (4)	0.7449 (2)	0.0392 (7)
H20	-0.1535	0.3925	0.7891	0.047*
O1	0.3037 (4)	0.6264 (4)	1.01810 (17)	0.0792 (10)
S1	0.20165 (10)	0.27183 (10)	0.64654 (5)	0.03775 (18)
Br1	0.24497 (5)	0.00369 (5)	0.48059 (2)	0.05710 (15)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0317 (14)	0.0387 (17)	0.0340 (14)	0.0078 (12)	0.0032 (11)	-0.0036 (12)
C2	0.0421 (17)	0.0437 (18)	0.0401 (15)	0.0192 (14)	0.0055 (13)	0.0022 (13)
C3	0.0386 (15)	0.0444 (18)	0.0317 (13)	0.0158 (13)	-0.0006 (11)	0.0060 (12)
C4	0.0297 (13)	0.0339 (15)	0.0284 (12)	0.0067 (11)	-0.0008 (10)	0.0043 (11)
C5	0.0323 (14)	0.0356 (16)	0.0283 (12)	0.0059 (12)	-0.0033 (10)	0.0020 (11)
C6	0.0334 (14)	0.0305 (15)	0.0306 (13)	0.0051 (12)	-0.0027 (11)	0.0006 (11)
C7	0.0514 (18)	0.0439 (18)	0.0333 (14)	0.0233 (15)	-0.0089 (13)	-0.0029 (13)
C8	0.090 (3)	0.063 (2)	0.0447 (18)	0.050 (2)	-0.0185 (18)	-0.0109 (17)
C9	0.0452 (17)	0.0361 (17)	0.0362 (14)	0.0227 (14)	-0.0028 (12)	0.0013 (12)
C10	0.053 (2)	0.0428 (19)	0.059 (2)	0.0140 (16)	0.0056 (16)	0.0203 (16)
C11	0.085 (3)	0.077 (3)	0.0439 (19)	0.045 (3)	0.0142 (19)	0.0162 (19)
C12	0.073 (3)	0.065 (3)	0.056 (2)	0.038 (2)	-0.007 (2)	-0.0122 (19)
C13	0.0398 (19)	0.039 (2)	0.113 (4)	0.0005 (16)	-0.009 (2)	-0.002 (2)
C14	0.046 (2)	0.070 (3)	0.071 (2)	0.0238 (19)	0.0259 (17)	0.022 (2)

C15	0.0385 (15)	0.0278 (14)	0.0277 (12)	0.0102 (12)	-0.0012 (11)	0.0034 (11)
C16	0.0454 (18)	0.0441 (19)	0.0448 (17)	0.0057 (15)	0.0059 (13)	0.0154 (14)
C17	0.074 (3)	0.061 (2)	0.0400 (17)	0.022 (2)	0.0095 (16)	0.0229 (16)
C18	0.068 (2)	0.062 (2)	0.0315 (15)	0.0255 (19)	-0.0081 (15)	0.0069 (15)
C19	0.0401 (17)	0.050 (2)	0.0470 (18)	0.0074 (15)	-0.0093 (14)	0.0025 (15)
C20	0.0413 (16)	0.0378 (17)	0.0378 (15)	0.0082 (13)	-0.0001 (12)	0.0124 (13)
O1	0.116 (2)	0.082 (2)	0.0394 (13)	0.0695 (18)	-0.0269 (14)	-0.0153 (12)
S1	0.0383 (4)	0.0438 (4)	0.0285 (3)	0.0154 (3)	-0.0040 (3)	0.0001 (3)
Br1	0.0493 (2)	0.0780 (3)	0.03575 (18)	0.01993 (18)	0.00201 (13)	-0.01404 (15)

Geometric parameters (Å, °)

C1—C2	1.357 (4)	C10—C11	1.355 (5)
C1—S1	1.706 (3)	C10—H10	0.9300
C1—Br1	1.863 (3)	C11—C12	1.323 (6)
C2—C3	1.401 (4)	C11—H11	0.9300
C2—H2	0.9300	C12—C13	1.347 (6)
C3—C4	1.368 (4)	C12—H12	0.9300
C3—H3	0.9300	C13—C14	1.408 (6)
C4—C5	1.439 (4)	C13—H13	0.9300
C4—S1	1.737 (3)	C14—H14	0.9300
C5—C6	1.343 (4)	C15—C20	1.376 (4)
C5—H5	0.9300	C15—C16	1.385 (4)
C6—C7	1.489 (4)	C16—C17	1.376 (5)
C6—C15	1.494 (4)	C16—H16	0.9300
C7—O1	1.211 (4)	C17—C18	1.369 (5)
C7—C8	1.503 (4)	C17—H17	0.9300
C8—C9	1.493 (4)	C18—C19	1.363 (5)
C8—H8A	0.9700	C18—H18	0.9300
C8—H8B	0.9700	C19—C20	1.389 (4)
C9—C10	1.372 (5)	C19—H19	0.9300
C9—C14	1.377 (5)	C20—H20	0.9300
C2—C1—S1	113.4 (2)	C9—C10—H10	119.1
C2—C1—Br1	126.5 (2)	C12—C11—C10	120.6 (4)
S1—C1—Br1	120.05 (16)	C12—C11—H11	119.7
C1—C2—C3	111.1 (3)	C10—C11—H11	119.7
C1—C2—H2	124.5	C11—C12—C13	120.9 (4)
C3—C2—H2	124.5	C11—C12—H12	119.5
C4—C3—C2	114.5 (2)	C13—C12—H12	119.5
C4—C3—H3	122.8	C12—C13—C14	119.6 (4)
C2—C3—H3	122.8	C12—C13—H13	120.2
C3—C4—C5	125.0 (2)	C14—C13—H13	120.2
C3—C4—S1	110.0 (2)	C9—C14—C13	119.5 (3)
C5—C4—S1	124.9 (2)	C9—C14—H14	120.2
C6—C5—C4	130.1 (2)	C13—C14—H14	120.2
C6—C5—H5	114.9	C20—C15—C16	118.5 (3)
C4—C5—H5	114.9	C20—C15—C6	120.5 (2)

C5—C6—C7	116.9 (2)	C16—C15—C6	120.9 (3)
C5—C6—C15	123.1 (2)	C17—C16—C15	120.7 (3)
C7—C6—C15	120.0 (2)	C17—C16—H16	119.7
O1—C7—C6	121.4 (3)	C15—C16—H16	119.7
O1—C7—C8	121.3 (3)	C18—C17—C16	120.2 (3)
C6—C7—C8	117.3 (2)	C18—C17—H17	119.9
C9—C8—C7	115.1 (3)	C16—C17—H17	119.9
C9—C8—H8A	108.5	C19—C18—C17	120.0 (3)
C7—C8—H8A	108.5	C19—C18—H18	120.0
C9—C8—H8B	108.5	C17—C18—H18	120.0
C7—C8—H8B	108.5	C18—C19—C20	120.1 (3)
H8A—C8—H8B	107.5	C18—C19—H19	119.9
C10—C9—C14	117.5 (3)	C20—C19—H19	119.9
C10—C9—C8	121.5 (3)	C15—C20—C19	120.4 (3)
C14—C9—C8	121.0 (3)	C15—C20—H20	119.8
C11—C10—C9	121.8 (4)	C19—C20—H20	119.8
C11—C10—H10	119.1	C1—S1—C4	90.98 (13)
S1—C1—C2—C3	-0.8 (4)	C11—C12—C13—C14	-1.7 (6)
Br1—C1—C2—C3	178.9 (2)	C10—C9—C14—C13	-0.2 (5)
C1—C2—C3—C4	0.7 (4)	C8—C9—C14—C13	179.7 (3)
C2—C3—C4—C5	179.2 (3)	C12—C13—C14—C9	0.9 (5)
C2—C3—C4—S1	-0.3 (3)	C5—C6—C15—C20	90.7 (4)
C3—C4—C5—C6	-175.7 (3)	C7—C6—C15—C20	-90.4 (4)
S1—C4—C5—C6	3.7 (5)	C5—C6—C15—C16	-86.7 (4)
C4—C5—C6—C7	-179.0 (3)	C7—C6—C15—C16	92.2 (4)
C4—C5—C6—C15	-0.1 (5)	C20—C15—C16—C17	-0.9 (5)
C5—C6—C7—O1	-10.8 (5)	C6—C15—C16—C17	176.5 (3)
C15—C6—C7—O1	170.2 (3)	C15—C16—C17—C18	-0.8 (5)
C5—C6—C7—C8	168.2 (3)	C16—C17—C18—C19	2.0 (6)
C15—C6—C7—C8	-10.7 (5)	C17—C18—C19—C20	-1.3 (5)
O1—C7—C8—C9	6.9 (6)	C16—C15—C20—C19	1.5 (5)
C6—C7—C8—C9	-172.1 (3)	C6—C15—C20—C19	-175.9 (3)
C7—C8—C9—C10	-78.8 (5)	C18—C19—C20—C15	-0.4 (5)
C7—C8—C9—C14	101.3 (4)	C2—C1—S1—C4	0.6 (3)
C14—C9—C10—C11	0.2 (5)	Br1—C1—S1—C4	-179.13 (18)
C8—C9—C10—C11	-179.7 (3)	C3—C4—S1—C1	-0.2 (2)
C9—C10—C11—C12	-0.9 (5)	C5—C4—S1—C1	-179.7 (3)
C10—C11—C12—C13	1.7 (6)		

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

Cg is the centroid of the C1—C4/S1 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>
C3—H3 \cdots O1 ⁱ	0.93	2.54	3.320 (4)	141
C19—H19 \cdots Cg ⁱⁱ	0.93	2.90	3.768 (3)	156

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