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# *cis,trans,cis*-1,2,3,4-Tetrakis[2-(ethylsulfanyl)phenyl]cyclobutane

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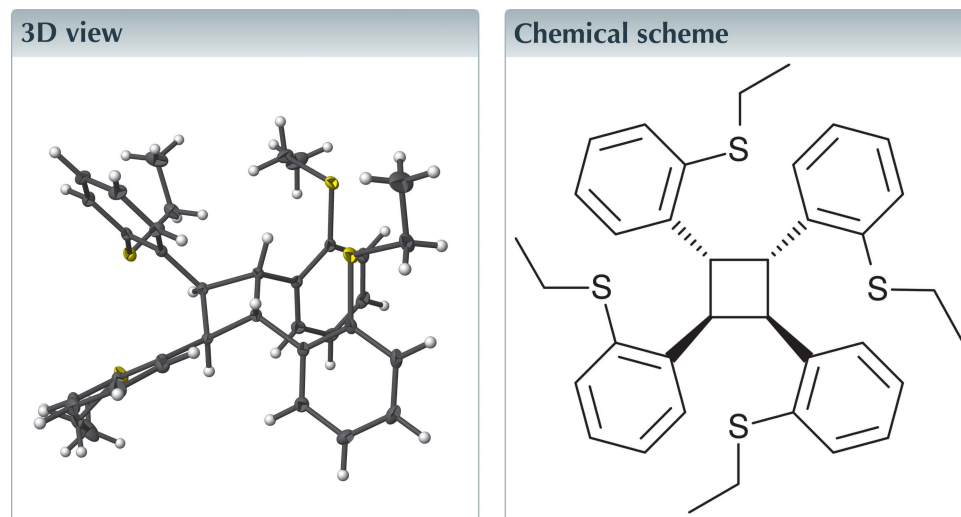
Keywords: crystal structure; cyclobutane; sulfide; conformation; [2 + 2] cycloaddition.

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Structural data: full structural data are available from [iucrdata.iucr.org](http://iucrdata.iucr.org)

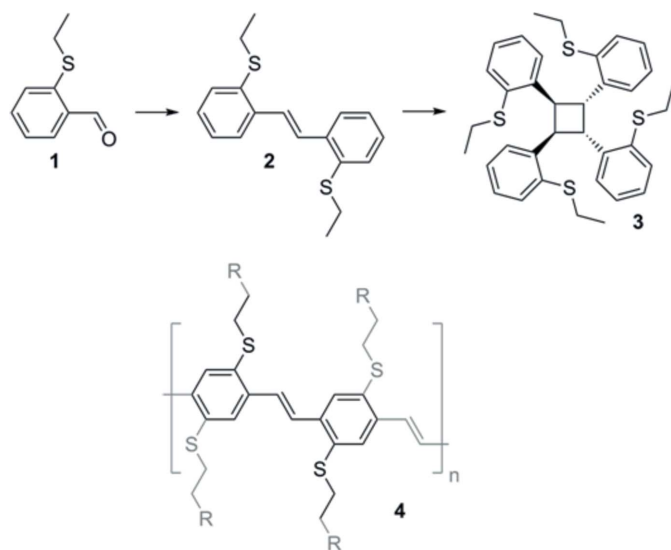
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The title cyclobutane derivative, C<sub>36</sub>H<sub>40</sub>S<sub>4</sub>, formed serendipitously through a photochemically initiated [2 + 2] cycloaddition. The asymmetric unit contains half a molecule with the 2-(ethylsulfanyl)phenyl substituents in a *cis* configuration, the other half of the molecule being generated by the application of a twofold rotation operation. The substituents in both halves of the molecules are in a *trans* arrangement relative to each other. The cyclobutane ring shows angular and torsional strains, with C–C–C bond angles of 89.80 (8) and 88.40 (8)°, and an average absolute torsion angle of 14.28 (10)°. The angle of pucker in the ring is 20.27 (12)°. The C<sub>cb</sub>–C<sub>cb</sub>–C<sub>b</sub> angles between the cyclobutane (cb) ring atoms and the attached benzene (b) ring atoms are widened and range from 115.19 (10) to 121.66 (10)°. A weak intramolecular C–H···S hydrogen-bonding interaction between one of the cyclobutane ring H atoms and the S atom may help to establish the molecular conformation. No specific intermolecular interactions are found.



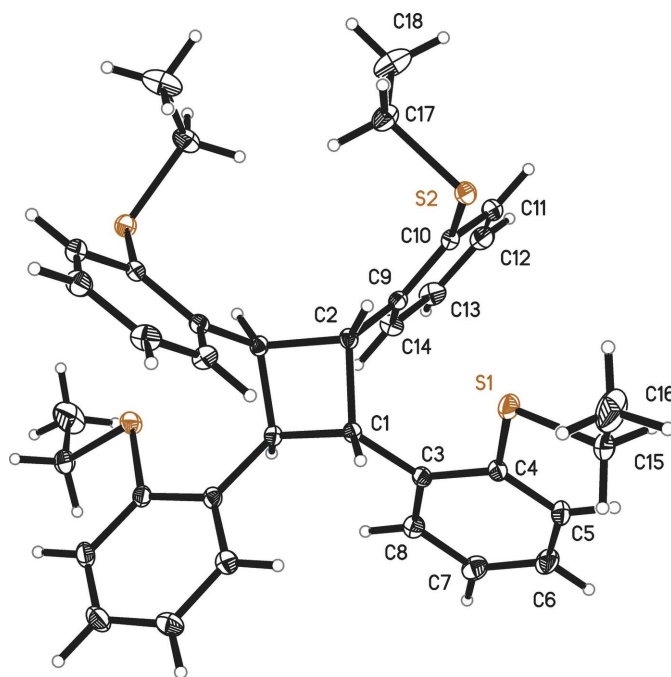
## Structure description

The title compound was obtained from a bis-thioethyl-substituted stilbene by an unintentional [2 + 2] cycloaddition (Figs. 1 and 2). A weak intramolecular C–H···S hydrogen-bonding interaction between one of the cyclobutane ring H atoms and the S atom may help to establish the molecular conformation (Fig. 3 and Table 1). The stilbene was synthesized as a model compound for thioalkyl-substituted poly(*p*-phenylene vinylene) (PPV). PPVs were among the first materials applied in organic solar cells as well as organic LEDs and have become one of the materials of choice for studies on the



**Figure 1**  
Reaction scheme to obtain the title compound (top) and the originally intended product (bottom).

basic photophysics of conjugated polymers (Blayney *et al.*, 2014). For synthetic details, see: Diéguez *et al.* (2010); Tzur *et al.* (2010). For a review on conformations and configurations of cyclobutanes, see: Berg (2005).



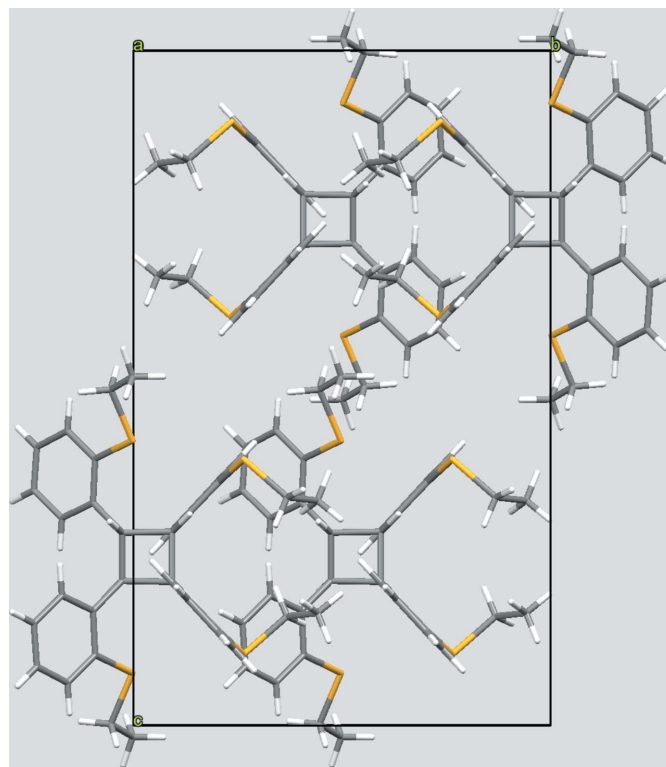
**Figure 2**  
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level; H atoms are given as spheres of arbitrary radius. Non-labelled atoms are generated by symmetry code  $-x + 2, y, -z + \frac{1}{2}$ .

**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>
C2–H1c2···S2	0.96	2.47	3.1939 (12)	132

### Synthesis and crystallization

The reaction pathway involving compounds 1–3 and the originally intended reaction product 4 are schematically shown (Fig. 1). The synthesis of stilbene 2 was carried out following a McMurry reaction protocol of Diéguez *et al.* (2010). Zinc (2.94 g, 45 mmol) and titanocene dichloride (5.60 g, 22.5 mmol) were dissolved in 40 ml dry, degassed tetrahydrofuran under argon atmosphere. The solution was stirred for 5 min and aldehyde 1 (2.49 g, 15 mmol), which was prepared by a modified procedure of Tzur *et al.* (2010), was added to the reaction mixture as a solution in 30 ml dry, degassed tetrahydrofuran. The reaction was heated to reflux for 3 h, cooled to room temperature and quenched with 30 ml diisopropyl ether. The solvent was evaporated *in vacuo*, the residue was dissolved in dichloromethane and washed with 1M HCl and brine. The organic layer was then dried over anhydrous sodium sulfate and the solvent was again evaporated *in vacuo*. The resulting dark-orange oil was purified by column chromatography using silica gel as stationary phase and a



**Figure 3**  
The packing of the molecules in the crystal structure of the title compound in a view along [100].

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	C <sub>36</sub> H <sub>40</sub> S <sub>4</sub>
<i>M<sub>r</sub></i>	600.92
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.2972 (8), 13.0708 (10), 21.3833 (17)
$\beta$ (°)	98.400 (2)
<i>V</i> (Å <sup>3</sup> )	3123.7 (4)
<i>Z</i>	4
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.33
Crystal size (mm)	0.65 × 0.62 × 0.48
Data collection	
Diffractometer	Bruker APEXII CCD diffractometer
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2014)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.80, 0.88
No. of measured, independent and observed [ <i>I</i> > 3 $\sigma$ ( <i>I</i> )] reflections	31669, 5518, 4606
<i>R<sub>int</sub></i>	0.023
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.758
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.041, 0.058, 3.21
No. of reflections	5518
No. of parameters	181
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.57, -0.51

Computer programs: *APEX2* (Bruker, 2014), *SAINT* (Bruker, 2014), *SUPERFLIP* (Palatinus & Chapuis, 2007), *JANA2006* (Petříček *et al.*, 2014), *XP* in *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2006), *pubCIF* (Westrip, 2010).

petroleum ether:dichloromethane mixture (5:1 to 3:1 *v/v*) as eluent. A second column using aluminum oxide yielded **2** as a colorless oil (0.88 g, 2.9 mmol, 39%). Storage of **2** at room temperature and without light protection resulted in the quantitative formation of crystals of the title compound **3** in the form of translucent blocks within two weeks. <sup>1</sup>H NMR

(CDCl<sub>3</sub>, 200 MHz):  $\delta$  = 7.41–7.32 (*m*, 4H), 7.21–7.13 (*m*, 4H), 7.09–6.98 (*m*, 8H), 5.01 (*s*, 4H), 2.87–2.59 (*m*, 8H), 1.16 (*t*, 12H), *J* = 7.5 Hz) p.p.m. <sup>13</sup>C NMR (APT) (CDCl<sub>3</sub>, 50 MHz):  $\delta$  = 140.1 (*s*), 136.9 (*s*), 128.9 (*d*), 127.6 (*d*), 126.4 (*d*), 125.3 (*d*), 44.8 (*d*), 28.3 (*t*), 14.2 (*q*) p.p.m.

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

## Acknowledgements

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## full crystallographic data

*IUCrData* (2016). **1**, x152426 [doi:10.1107/S2414314615024268]

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*cis,trans,cis-1,2,3,4-Tetrakis[2-(ethylsulfanyl)phenyl]cyclobutane*

*Crystal data*

$C_{36}H_{40}S_4$	$F(000) = 1280$
$M_r = 600.92$	$D_x = 1.278 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: $-C 2yc$	Cell parameters from 9001 reflections
$a = 11.2972 (8) \text{ \AA}$	$\theta = 2.9\text{--}32.6^\circ$
$b = 13.0708 (10) \text{ \AA}$	$\mu = 0.33 \text{ mm}^{-1}$
$c = 21.3833 (17) \text{ \AA}$	$T = 100 \text{ K}$
$\beta = 98.400 (2)^\circ$	Block, translucent colourless
$V = 3123.7 (4) \text{ \AA}^3$	$0.65 \times 0.62 \times 0.48 \text{ mm}$
$Z = 4$	

*Data collection*

Bruker APEXII CCD diffractometer	31669 measured reflections
Radiation source: X-ray tube	5518 independent reflections
Graphite monochromator	4606 reflections with $I > 3\sigma(I)$
$\omega$ and $\varphi$ -scans	$R_{\text{int}} = 0.023$
Absorption correction: multi-scan ( <i>SADABS</i> ; Bruker, 2014)	$\theta_{\text{max}} = 32.6^\circ$ , $\theta_{\text{min}} = 1.9^\circ$
$T_{\text{min}} = 0.80$ , $T_{\text{max}} = 0.88$	$h = -17 \rightarrow 17$
	$k = -19 \rightarrow 19$
	$l = -32 \rightarrow 32$

*Refinement*

Refinement on $F$	80 constraints
$R[F^2 > 2\sigma(F^2)] = 0.041$	H-atom parameters constrained
$wR(F^2) = 0.058$	Weighting scheme based on measured s.u.'s $w =$ $1/(\sigma^2(F) + 0.0001F^2)$
$S = 3.21$	$(\Delta/\sigma)_{\text{max}} = 0.019$
5518 reflections	$\Delta\rho_{\text{max}} = 0.57 \text{ e \AA}^{-3}$
181 parameters	$\Delta\rho_{\text{min}} = -0.51 \text{ e \AA}^{-3}$
0 restraints	

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.87910 (3)	0.00251 (3)	0.077753 (15)	0.01809 (10)
S2	0.95635 (3)	-0.26468 (3)	0.105586 (15)	0.01571 (9)
C1	0.97736 (10)	0.02697 (9)	0.21431 (5)	0.0109 (3)
C2	0.99420 (11)	-0.09281 (9)	0.21282 (5)	0.0111 (3)
C3	1.03225 (11)	0.09664 (9)	0.17023 (6)	0.0122 (3)
C4	0.99249 (11)	0.09175 (9)	0.10458 (6)	0.0135 (3)

C5	1.04055 (12)	0.15814 (10)	0.06346 (6)	0.0183 (4)
C6	1.12381 (12)	0.23133 (11)	0.08726 (7)	0.0204 (4)
C7	1.16082 (12)	0.23866 (10)	0.15155 (7)	0.0196 (4)
C8	1.11571 (11)	0.17117 (10)	0.19249 (6)	0.0155 (3)
C9	1.10217 (10)	-0.13204 (9)	0.18639 (6)	0.0118 (3)
C10	1.09395 (11)	-0.20633 (10)	0.13841 (6)	0.0133 (3)
C11	1.19725 (13)	-0.23932 (10)	0.11493 (6)	0.0176 (4)
C12	1.30895 (12)	-0.20113 (10)	0.13908 (7)	0.0193 (4)
C13	1.31825 (12)	-0.12954 (10)	0.18711 (7)	0.0187 (4)
C14	1.21622 (11)	-0.09526 (10)	0.20995 (6)	0.0158 (4)
C15	0.81195 (12)	0.05410 (11)	0.00215 (6)	0.0201 (4)
C16	0.69192 (16)	0.00156 (14)	-0.01675 (8)	0.0362 (5)
C17	0.95165 (12)	-0.36869 (10)	0.16180 (6)	0.0197 (4)
C18	1.05717 (13)	-0.44112 (11)	0.16675 (9)	0.0311 (5)
H1c1	0.901213	0.056516	0.198149	0.013*
H1c2	0.936693	-0.134784	0.187075	0.0133*
H1c5	1.015758	0.15293	0.018686	0.0219*
H1c6	1.155904	0.277157	0.058921	0.0244*
H1c7	1.217541	0.290186	0.167956	0.0235*
H1c8	1.142779	0.176151	0.237076	0.0186*
H1c11	1.19035	-0.289135	0.0816	0.0212*
H1c12	1.379047	-0.224093	0.122669	0.0231*
H1c13	1.395355	-0.10342	0.204747	0.0224*
H1c14	1.224302	-0.04479	0.242917	0.0189*
H1c15	0.799702	0.12634	0.006158	0.0241*
H2c15	0.863011	0.040274	-0.029004	0.0241*
H1c16	0.657192	0.024312	-0.058067	0.0435*
H2c16	0.703434	-0.071188	-0.01731	0.0435*
H3c16	0.63938	0.018387	0.013187	0.0435*
H1c17	0.945536	-0.340933	0.202767	0.0237*
H2c17	0.878734	-0.406582	0.151001	0.0237*
H1c18	1.045087	-0.496526	0.194607	0.0374*
H2c18	1.0643	-0.467761	0.125628	0.0374*
H3c18	1.129027	-0.40502	0.183155	0.0374*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.02583 (19)	0.01681 (17)	0.01032 (15)	-0.00304 (13)	-0.00175 (12)	0.00162 (11)
S2	0.01991 (17)	0.01504 (16)	0.01128 (14)	-0.00217 (12)	-0.00074 (12)	-0.00097 (11)
C1	0.0103 (5)	0.0125 (5)	0.0098 (5)	0.0012 (5)	0.0014 (4)	0.0000 (4)
C2	0.0115 (5)	0.0123 (6)	0.0092 (5)	-0.0010 (4)	0.0004 (4)	-0.0008 (4)
C3	0.0122 (5)	0.0129 (6)	0.0120 (5)	0.0029 (5)	0.0038 (4)	0.0003 (4)
C4	0.0166 (6)	0.0134 (6)	0.0110 (5)	0.0024 (5)	0.0035 (4)	-0.0001 (4)
C5	0.0250 (7)	0.0187 (6)	0.0125 (6)	0.0033 (5)	0.0074 (5)	0.0022 (5)
C6	0.0224 (7)	0.0193 (7)	0.0214 (6)	0.0003 (6)	0.0101 (5)	0.0056 (5)
C7	0.0187 (6)	0.0175 (7)	0.0231 (7)	-0.0042 (5)	0.0049 (5)	0.0023 (5)
C8	0.0156 (6)	0.0162 (6)	0.0146 (6)	0.0003 (5)	0.0022 (5)	0.0008 (5)

C9	0.0130 (6)	0.0111 (6)	0.0117 (5)	0.0005 (5)	0.0027 (4)	0.0015 (4)
C10	0.0175 (6)	0.0122 (6)	0.0106 (5)	-0.0006 (5)	0.0030 (4)	0.0013 (4)
C11	0.0235 (7)	0.0146 (6)	0.0163 (6)	0.0021 (5)	0.0082 (5)	0.0002 (5)
C12	0.0178 (6)	0.0177 (6)	0.0245 (7)	0.0048 (5)	0.0105 (5)	0.0043 (5)
C13	0.0120 (6)	0.0175 (6)	0.0271 (7)	0.0003 (5)	0.0050 (5)	0.0022 (5)
C14	0.0145 (6)	0.0147 (6)	0.0180 (6)	-0.0001 (5)	0.0024 (5)	-0.0022 (5)
C15	0.0290 (7)	0.0199 (7)	0.0106 (5)	0.0004 (6)	0.0001 (5)	0.0012 (5)
C16	0.0430 (10)	0.0410 (10)	0.0196 (7)	-0.0122 (8)	-0.0125 (7)	0.0072 (7)
C17	0.0197 (7)	0.0189 (7)	0.0198 (6)	-0.0047 (5)	0.0004 (5)	0.0044 (5)
C18	0.0253 (8)	0.0228 (8)	0.0443 (10)	-0.0013 (7)	0.0018 (7)	0.0133 (7)

*Geometric parameters (Å, °)*

S1—C4	1.7652 (13)	C11—C12	1.3849 (19)
S2—C10	1.7810 (13)	C11—H1c11	0.96
C1—C1 <sup>i</sup>	1.5373 (16)	C12—C13	1.382 (2)
C1—C3	1.5076 (18)	C12—H1c12	0.96
C1—H1c1	0.96	C13—C14	1.3901 (19)
C2—C9	1.5072 (18)	C13—H1c13	0.96
C2—H1c2	0.96	C14—H1c14	0.96
C3—C4	1.4115 (17)	C15—C16	1.521 (2)
C3—C8	1.3905 (17)	C15—H1c15	0.96
C4—C5	1.4000 (19)	C15—H2c15	0.96
C5—C6	1.3852 (19)	C16—H1c16	0.96
C5—H1c5	0.96	C16—H2c16	0.96
C6—C7	1.381 (2)	C16—H3c16	0.96
C6—H1c6	0.96	C17—C18	1.514 (2)
C7—C8	1.391 (2)	C17—H1c17	0.96
C7—H1c7	0.96	C17—H2c17	0.96
C8—H1c8	0.96	C18—H1c18	0.96
C9—C10	1.4057 (17)	C18—H2c18	0.96
C9—C14	1.3983 (17)	C18—H3c18	0.96
C10—C11	1.404 (2)		
C1 <sup>i</sup> —C1—C3	120.87 (10)	C10—C11—H1c11	119.48
C1 <sup>i</sup> —C1—H1c1	120.54	C12—C11—H1c11	119.48
C3—C1—H1c1	87.75	C11—C12—C13	119.17 (13)
C9—C2—H1c2	96.17	C11—C12—H1c12	120.41
C1—C3—C4	119.63 (10)	C13—C12—H1c12	120.41
C1—C3—C8	121.97 (11)	C12—C13—C14	120.16 (12)
C4—C3—C8	118.26 (11)	C12—C13—H1c13	119.92
S1—C4—C3	117.61 (9)	C14—C13—H1c13	119.92
S1—C4—C5	122.35 (9)	C9—C14—C13	122.02 (12)
C3—C4—C5	120.01 (11)	C9—C14—H1c14	118.99
C4—C5—C6	120.15 (12)	C13—C14—H1c14	118.99
C4—C5—H1c5	119.93	C16—C15—H1c15	109.47
C6—C5—H1c5	119.93	C16—C15—H2c15	109.47
C5—C6—C7	120.28 (13)	H1c15—C15—H2c15	110.86

C5—C6—H1c6	119.86	C15—C16—H1c16	109.47
C7—C6—H1c6	119.86	C15—C16—H2c16	109.47
C6—C7—C8	119.82 (12)	C15—C16—H3c16	109.47
C6—C7—H1c7	120.09	H1c16—C16—H2c16	109.47
C8—C7—H1c7	120.09	H1c16—C16—H3c16	109.47
C3—C8—C7	121.43 (12)	H2c16—C16—H3c16	109.47
C3—C8—H1c8	119.29	C18—C17—H1c17	109.47
C7—C8—H1c8	119.29	C18—C17—H2c17	109.47
C2—C9—C10	122.54 (10)	H1c17—C17—H2c17	103.93
C2—C9—C14	120.10 (11)	C17—C18—H1c18	109.47
C10—C9—C14	117.37 (11)	C17—C18—H2c18	109.47
S2—C10—C9	122.98 (10)	C17—C18—H3c18	109.47
S2—C10—C11	116.79 (9)	H1c18—C18—H2c18	109.47
C9—C10—C11	120.22 (11)	H1c18—C18—H3c18	109.47
C10—C11—C12	121.03 (12)	H2c18—C18—H3c18	109.47

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

*Hydrogen-bond geometry* ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H1c2 $\cdots$ S2	0.96	2.47	3.1939 (12)	132