

# Crystal structure of 4,4'-bis(4-bromophenyl)-1,1',3,3'-tetrathiafulvalene

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**Keywords:** crystal structure; tetrathiafulvalene; derivative; weak interactions; Hirshfeld surface analysis; DFT calculations.

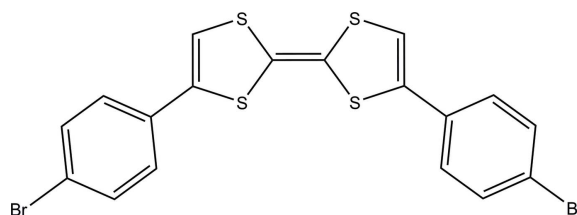
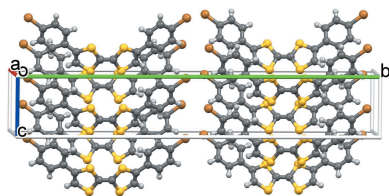
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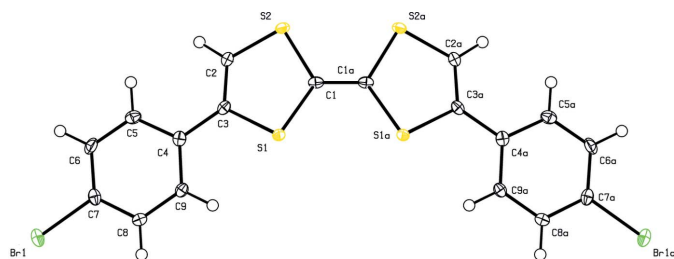
**Supporting information:** this article has supporting information at journals.iucr.org/e

The molecule of the title compound,  $C_{18}H_{10}Br_2S_4$ , has a C-shape, with  $C_s$  molecular symmetry. The dihedral angle between the planes of the dithiol and phenyl rings is  $8.35(9)^\circ$ . In the crystal, molecules form helical chains along [001], the shortest interactions being  $\pi \cdots S$  contacts within the helices. The intermolecular interactions were investigated by Hirshfeld surface analysis. Density functional theory (DFT) was used to calculate HOMO–LUMO energy levels of the title compound and its *trans* isomer.

## 1. Chemical context

So far significant progress has been achieved in improving the performance of organic field-effect transistors (OFETs) using such materials as oligoacenes, oligothiophenes and polythiophenes (Mas-Torrent & Rovira, 2011; Pfattner, *et al.*, 2016). Numerous derivatives of the sulfur heterocycle 2,2'-bis(1,3-dithiolylidene), known as tetrathiafulvalene (TTF), have been noted as components of OFETs (Fourmigué & Batail, 2004; Bendikov *et al.*, 2004). High charge mobilities have been reported for thiophene-fused TTF and dibenzo-TTF in single-crystal OFETs obtained from solutions, as well as in tetra(octadecylthio)-TTF films (Mas-Torrent *et al.*, 2004a,b). A comparatively high mobility was reported for biphenyl-substituted TTF (Noda *et al.*, 2005, 2007). Correlations between mobilities and herring-bone crystal structures have been investigated (Pfattner, *et al.*, 2016; Mas-Torrent & Rovira, 2011), including for phenyl-substituted oligothiophenes (Noda *et al.*, 2007). Among the numerous reported halogenated tetrathiafulvalenes (Fourmigué & Batail, 2004), only a few have been crystallographically characterized. The synthesis and characterization of two halogen TTF derivatives, 4,4'-bis(4-chlorophenyl)tetrathiafulvalene and 4,4'-bis(4-bromophenyl)tetrathiafulvalene have been reported, but only the crystal structure of the chloro-substituted compound has been documented (Madhu & Das, 2008), which shows short  $Cl \cdots Cl$  contacts. Herein, we report the crystal structure, the Hirshfeld surface analysis and the molecular orbital analysis of the title compound, 4,4'-bis(4-bromophenyl)-1,1',3,3'-tetrathiafulvalene (BBP-TTF).





**Figure 1**  
A view of the molecular structure of the title compound with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. Suffix *a* corresponds to the symmetry operation  $x, -y + \frac{3}{2}, z$ .

## 2. Structural commentary

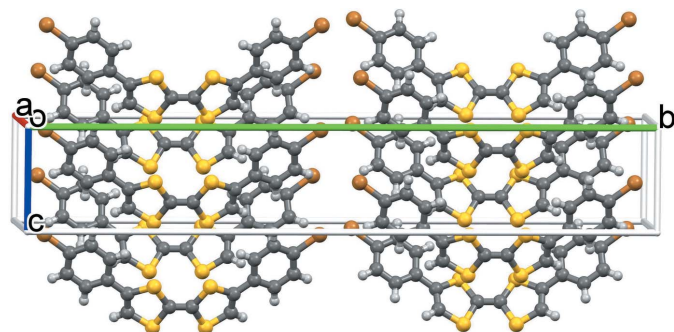
The molecular structure of the title compound is illustrated in Fig. 1. The molecule has a  $C_s$  molecular symmetry and resides on the mirror plane passing through the central  $C1=C1(x, -y + \frac{3}{2}, z)$  bond [1.343 (7) Å]. The C–S distances in the TTF moiety are in the range 1.729 (4)–1.778 (4) Å and correspond to reported values (CSD version 5.40, last update November 2018; Groom *et al.*, 2016). The dihedral angle between the dithiol and phenyl rings is 8.35 (9)°.

## 3. Supramolecular features

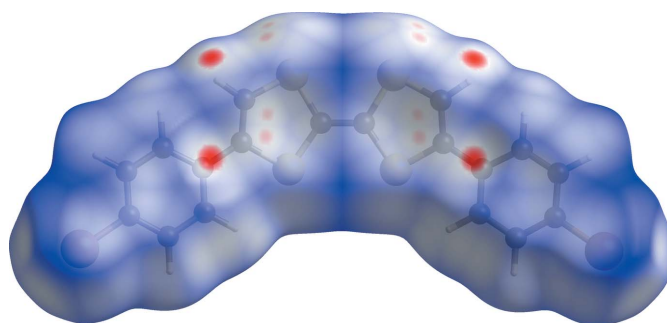
In the crystal (Fig. 2), no significant intermolecular interactions were found. Molecules related by the twofold screw axis form helices along the *c*-axis direction. The dihedral angle between the mean planes of the adjacent molecules in the helix is 36.59 (3)° and the helical pitch is 6.1991 (5) Å. The shortest interactions within the chain, as indicated by *Mercury* (Macrae *et al.*, 2006), are the  $S \cdots \pi$  contacts  $C3 \cdots S2(1 - x, y, z - \frac{1}{2}) = 3.458$  (4) and  $C2 \cdots S2(1 - x, y, z - \frac{1}{2}) = 3.465$  (4) Å, followed by the  $C2-H2 \cdots C4(1 - x, y, \frac{1}{2} + z)$  [2.72, 3.467 (5) Å] short contacts that are in agreement with the Hirshfeld (1977) surface analysis.

## 4. Hirshfeld surface analysis

*CrystalExplorer17.5* (Wolff *et al.*, 2012, Mackenzie *et al.*, 2017) was used to generate the molecular Hirshfeld surface. The



**Figure 2**  
The crystal packing of the title compound.

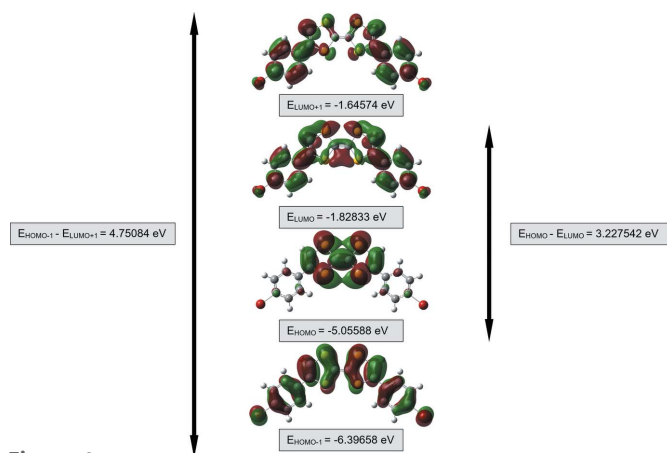


**Figure 3**  
Hirshfeld surface mapped over  $d_{norm}$  for the title compound in the range  $-0.1138$  to  $1.1257$  a.u.

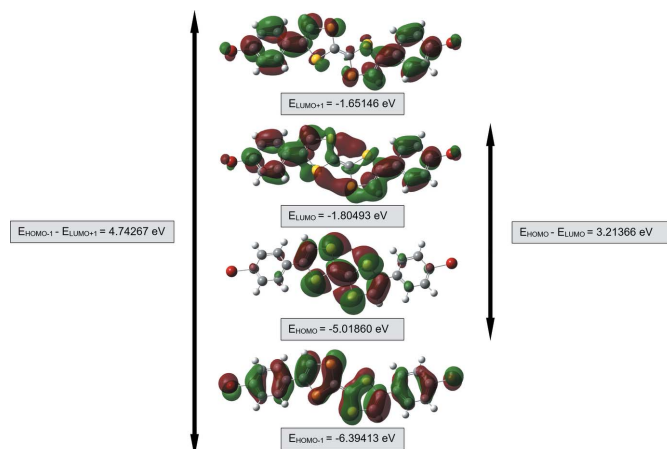
total  $d_{norm}$  surface of the title compound is shown in Fig. 3 where the red spots correspond to the most significant interactions in the crystal. In the studied molecule, they include only weak  $C-H \cdots \pi$  interactions at distances that are slightly higher than the sum of van der Waals radii.

## 5. Frontier molecular orbital calculations

The highest occupied molecular orbital (HOMO) acts as an electron donor and the lowest unoccupied molecular orbital



**Figure 4**  
Molecular orbital energy levels of the title compound (*cis* isomer).



**Figure 5**  
Molecular orbital energy levels of the *trans* isomer of the title compound.

**Table 1**

Calculated frontier molecular orbital energies (eV) for the title compound, its *trans* isomer and unsubstituted TTF and the conformational energy differences (kJ mol<sup>-1</sup>) between the *cis* and *trans* isomers.

	<i>cis</i> isomer	<i>trans</i> isomer	TTF
<i>E</i> (HOMO)	-5.0559	-5.0186	-4.8488
<i>E</i> (LUMO)	-1.8283	-1.8049	-1.1252
<i>E</i> (HOMO-1)	-6.3966	-6.3941	-6.6303
<i>E</i> (LUMO+1)	-1.6457	-1.6515	-0.7140
$\Delta E$ (HOMO-LUMO)	3.2275	3.2137	3.7236
$\Delta E$ (HOMO-1-LUMO+1)	4.7508	4.7427	5.9163
Chemical hardness ( $\eta$ )	1.6138	1.6068	1.8618
Chemical potential ( $\mu$ )	3.4421	3.4118	2.9870
Electronegativity ( $\chi$ )	-3.4421	-3.4118	-2.9870
Electrophilicity index ( $\omega$ )	3.6709	3.6221	2.3961
$\Delta E$ ( <i>cis-trans</i> )	1.6331		

(LUMO) acts as an electron acceptor. A small HOMO-LUMO energy gap indicates a highly polarizable molecule and high chemical reactivity. Molecular orbital energy levels for the title compound were calculated with *Gaussian 16W* software (Frisch *et al.*, 2016) using density functional theory (DFT) at the B3LYP/6-311+G(d,p) level of theory. The frontier orbitals of the title compound and its *trans*-isomer are shown in Figs. 4 and 5, respectively. The energy gap determines chemical hardness, chemical potential, electronegativity and the electrophilicity index. The orbital energy values for the title compound, its *trans*-isomer and unsubstituted TTF are summarized in Table 1. The conformation energy difference between the *cis*- and *trans* isomers is 1.6331 kJ mol<sup>-1</sup>. For both isomers the energy gap is large; hence both molecules are considered to be hard materials and would be difficult to polarize. As seen from Table 1, the bromophenyl substituents reduce the HOMO-LUMO energy gap and therefore the unsubstituted TTF molecule would be even more difficult to polarize.

## 6. Database survey

A search of the Cambridge Structural Database (CSD version 5.40, last update November 2018, Groom *et al.*, 2016) for substituted TTF-phenyl derivatives related to the title compound yielded six structures. They include: bis(4,4'-diphenyltetrathiafulvalenium)bis(pentafluorophenyl)gold(I) (CAKTAJ; Cerrada *et al.*, 1998), 4,5'-diphenyltetrathiafulvalene (DPTFUL; Escande & Lapasset, 1979, and DPTFUL01; Noda *et al.*, 2007), 4,4'-bis(4-chlorophenyl)-1,1',3,3'-tetrathiafulvalene (GOBVUP; Madhu & Das, 2008), 4,5'-bis(*p*-tolyl)tetrathiafulvalene (MOPJOR; Noda *et al.*, 2007), 4,5'-bis(4-ethylphenyl)tetrathiafulvalene (MOPJUX; Noda *et al.*, 2007), and 4,5'-bis(4-(trifluoromethyl)phenyl)tetrathiafulvalene (MOPKEI; Noda *et al.*, 2007). Contrary to the title compound, they all exhibit inversion or pseudo-inversion symmetry with a *trans*-arrangement of the phenyl substituents about the central C=C bond. The C=C bond lengths vary from 1.339 Å (MOPJUX) to 1.353 Å (DPTFUL);

**Table 2**

Experimental details.

Crystal data	
Chemical formula	C <sub>18</sub> H <sub>10</sub> Br <sub>2</sub> S <sub>4</sub>
<i>M<sub>r</sub></i>	514.32
Crystal system, space group	Orthorhombic, <i>Abm2</i>
Temperature (K)	90
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.5981 (6), 37.411 (3), 6.1991 (5)
<i>V</i> (Å <sup>3</sup> )	1762.1 (2)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
$\mu$ (mm <sup>-1</sup> )	5.07
Crystal size (mm)	0.17 × 0.11 × 0.05
Data collection	
Diffractionmeter	Bruker APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2016)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.625, 0.747
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	34235, 1580, 1530
<i>R<sub>int</sub></i>	0.066
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.594
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.017, 0.041, 1.09
No. of reflections	1580
No. of parameters	109
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.29, -0.29
Absolute structure	Flack <i>x</i> determined using 663 quotients [( <i>I</i> <sup>+</sup> ) - ( <i>I</i> <sup>-</sup> )] / [( <i>I</i> <sup>+</sup> ) + ( <i>I</i> <sup>-</sup> )] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.014 (5)

Computer programs: *APEX2* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

the value observed for the title compound falls within this limit. All of the above molecules are almost planar, with tilt angles between the dithiol and phenyl rings varying from 5.39 to 10.18° for the two independent molecules in DPTFUL01 to 28.28° in GOBVUP and 30.29° in MOPKEI; the greatest twisting was observed for halogen-substituted derivatives.

## 7. Crystallization

The single crystals of the title compound were obtained in attempt to co-crystallize it with tetracyanoquinodimethane (TCNQ) in a 1:1 molar ratio. A saturated solution of 4,4'-bis(4-bromophenyl)-1,1',3,3'-tetrathiafulvalene (2 mg, Aldrich) in chloroform was mixed with a saturated solution of TCNQ (1 mg, Aldrich) in acetonitrile and left at room temperature. Red prismatic crystals suitable for the X-ray diffraction analysis were obtained after a week of slow evaporation.

## 8. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The hydrogen atoms were positioned geometrically and refined using a riding model: C-H = 0.93 Å with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C).

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## supporting information

*Acta Cryst.* (2019). E75, 1195-1198 [https://doi.org/10.1107/S2056989019009952]

## Crystal structure of 4,4'-bis(4-bromophenyl)-1,1',3,3'-tetrathiafulvalene

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## Computing details

Data collection: *APEX2* (Bruker, 2016); cell refinement: *SAINT* (Bruker, 2016); data reduction: *SAINT* (Bruker, 2016); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

## 4,4'-Bis(4-bromophenyl)-1,1',3,3'-tetrathiafulvalene

## Crystal data

$C_{18}H_{10}Br_2S_4$

$M_r = 514.32$

Orthorhombic, *Abm2*

$a = 7.5981$  (6) Å

$b = 37.411$  (3) Å

$c = 6.1991$  (5) Å

$V = 1762.1$  (2) Å<sup>3</sup>

$Z = 4$

$F(000) = 1008$

$D_x = 1.939$  Mg m<sup>-3</sup>

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

Cell parameters from 9390 reflections

$\theta = 2.2$ – $28.4^\circ$

$\mu = 5.07$  mm<sup>-1</sup>

$T = 90$  K

Prism, red

$0.17 \times 0.11 \times 0.05$  mm

## Data collection

Bruker APEXII CCD  
diffractometer

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2016)

$T_{\min} = 0.625$ ,  $T_{\max} = 0.747$

34235 measured reflections

1580 independent reflections

1530 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.066$

$\theta_{\max} = 25.0^\circ$ ,  $\theta_{\min} = 1.1^\circ$

$h = -9 \rightarrow 9$

$k = -44 \rightarrow 44$

$l = -7 \rightarrow 7$

## Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.017$

$wR(F^2) = 0.041$

$S = 1.09$

1580 reflections

109 parameters

1 restraint

Primary atom site location: dual

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0126P)^2 + 2.1911P]$

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

$(\Delta/\sigma)_{\max} = 0.003$

$\Delta\rho_{\max} = 0.29$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.29$  e Å<sup>-3</sup>

Absolute structure: Flack  $x$  determined using

663 quotients  $[(I^-)-(I)]/[(I^+)+(I)]$  (Parsons *et al.*,  
2013)

Absolute structure parameter: 0.014 (5)

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.79020 (5)	0.53149 (2)	0.04905 (9)	0.02338 (12)
S1	0.84814 (9)	0.70527 (2)	0.54322 (17)	0.01212 (17)
S2	0.64506 (12)	0.70791 (2)	0.95068 (14)	0.01322 (19)
C1	0.7514 (4)	0.73205 (10)	0.7447 (6)	0.0120 (7)
C2	0.6459 (5)	0.66817 (10)	0.8081 (6)	0.0122 (8)
H2	0.583254	0.648059	0.861560	0.015*
C3	0.7350 (5)	0.66579 (9)	0.6225 (6)	0.0117 (8)
C4	0.7515 (4)	0.63362 (9)	0.4874 (6)	0.0125 (8)
C5	0.6886 (4)	0.60030 (9)	0.5600 (9)	0.0159 (7)
H5	0.637106	0.598599	0.699223	0.019*
C6	0.7004 (5)	0.56997 (10)	0.4326 (7)	0.0182 (8)
H6	0.658485	0.547656	0.484660	0.022*
C7	0.7737 (5)	0.57250 (10)	0.2289 (7)	0.0148 (8)
C8	0.8384 (4)	0.60494 (10)	0.1519 (6)	0.0133 (7)
H8	0.890749	0.606365	0.012995	0.016*
C9	0.8253 (4)	0.63529 (10)	0.2817 (6)	0.0129 (8)
H9	0.867405	0.657541	0.228922	0.015*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.0322 (2)	0.01276 (17)	0.02519 (19)	−0.00010 (14)	0.0039 (2)	−0.0046 (2)
S1	0.0126 (4)	0.0117 (4)	0.0120 (4)	−0.0005 (3)	0.0032 (5)	0.0006 (5)
S2	0.0148 (4)	0.0149 (4)	0.0100 (4)	0.0001 (4)	0.0030 (4)	0.0018 (4)
C1	0.0071 (15)	0.0181 (17)	0.0109 (16)	0.0014 (14)	0.0010 (12)	0.0008 (15)
C2	0.0111 (17)	0.0111 (19)	0.0145 (18)	−0.0007 (13)	−0.0011 (14)	0.0022 (14)
C3	0.0089 (17)	0.0126 (19)	0.0134 (18)	0.0024 (13)	−0.0025 (12)	0.0042 (13)
C4	0.0074 (15)	0.0130 (18)	0.017 (2)	0.0019 (12)	−0.0022 (12)	0.0010 (13)
C5	0.0136 (15)	0.0191 (17)	0.0149 (16)	0.0002 (12)	0.0022 (19)	0.002 (2)
C6	0.022 (2)	0.0124 (19)	0.020 (2)	0.0007 (15)	0.0009 (16)	0.0067 (17)
C7	0.0141 (18)	0.0119 (19)	0.0186 (19)	0.0014 (14)	−0.0036 (16)	−0.0017 (16)
C8	0.0121 (18)	0.0160 (19)	0.0117 (17)	−0.0007 (14)	0.0003 (15)	0.0017 (15)
C9	0.0115 (17)	0.0127 (19)	0.0144 (18)	0.0007 (14)	−0.0014 (14)	0.0029 (15)

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

Br1—C7	1.901 (4)	C4—C9	1.394 (5)
S1—C1	1.762 (4)	C5—H5	0.9500
S1—C3	1.778 (4)	C5—C6	1.385 (6)

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S2—C1	1.760 (4)	C6—H6	0.9500
S2—C2	1.729 (4)	C6—C7	1.384 (6)
C1—C1 <sup>i</sup>	1.343 (7)	C7—C8	1.394 (5)
C2—H2	0.9500	C8—H8	0.9500
C2—C3	1.338 (5)	C8—C9	1.396 (6)
C3—C4	1.472 (5)	C9—H9	0.9500
C4—C5	1.409 (5)		
C1—S1—C3	94.28 (17)	C6—C5—C4	121.4 (4)
C2—S2—C1	93.94 (18)	C6—C5—H5	119.3
S2—C1—S1	114.5 (2)	C5—C6—H6	120.3
C1 <sup>i</sup> —C1—S1	124.66 (13)	C7—C6—C5	119.4 (4)
C1 <sup>i</sup> —C1—S2	120.87 (12)	C7—C6—H6	120.3
S2—C2—H2	120.1	C6—C7—Br1	120.5 (3)
C3—C2—S2	119.9 (3)	C6—C7—C8	120.9 (4)
C3—C2—H2	120.1	C8—C7—Br1	118.6 (3)
C2—C3—S1	115.3 (3)	C7—C8—H8	120.5
C2—C3—C4	125.9 (3)	C7—C8—C9	119.1 (3)
C4—C3—S1	118.7 (2)	C9—C8—H8	120.5
C5—C4—C3	120.9 (3)	C4—C9—C8	121.3 (3)
C9—C4—C3	121.2 (3)	C4—C9—H9	119.3
C9—C4—C5	117.9 (4)	C8—C9—H9	119.3
C4—C5—H5	119.3		

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