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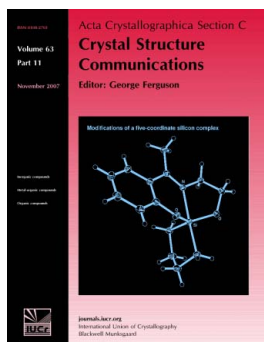
Hien Nguyen, Ngan Nguyen Bich, Tung T. Dang and Luc Van Meervelt

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# Stacking patterns of thieno[3,2-*b*]-thiophenes functionalized by sequential palladium-catalyzed Suzuki and Heck cross-coupling reactions

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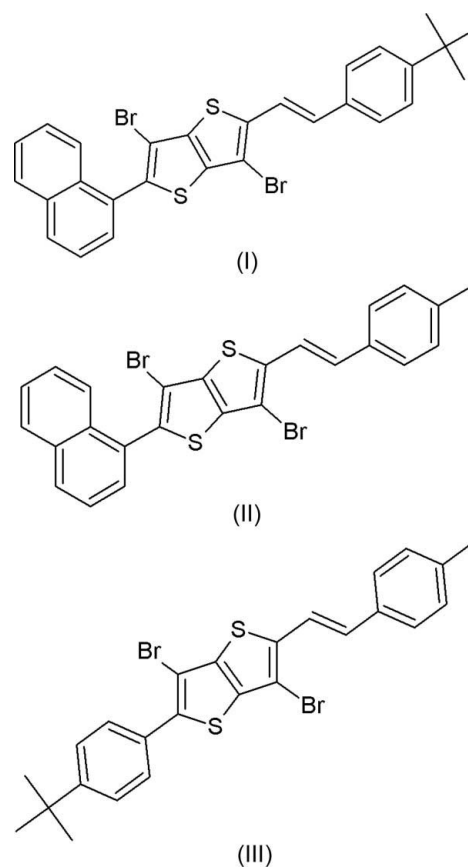
The crystal structures of three 5-alkenyl-2-arylthieno[3,2-*b*]-thiophenes, namely 3,6-dibromo-5-(4-*tert*-butylstyryl)-2-(naphthalen-1-yl)thieno[3,2-*b*]thiophene, C<sub>28</sub>H<sub>22</sub>Br<sub>2</sub>S<sub>2</sub>, (I), 3,6-dibromo-5-(4-methylstyryl)-2-(naphthalen-1-yl)thieno[3,2-*b*]thiophene, C<sub>25</sub>H<sub>16</sub>Br<sub>2</sub>S<sub>2</sub>, (II), and 3,6-dibromo-2-(4-*tert*-butylphenyl)-5-(4-methylstyryl)thieno[3,2-*b*]thiophene, C<sub>25</sub>H<sub>22</sub>Br<sub>2</sub>S<sub>2</sub>, (III), have been determined in order to evaluate the geometry of the molecules. The  $\pi$ -conjugated system containing the thieno[3,2-*b*]thiophene skeleton, the ethylene bridge and the phenyl rings is almost planar. The aromatic ring directly attached to the thieno[3,2-*b*]thiophene moiety is not coplanar with the thieno[3,2-*b*]thiophene moiety itself due to steric hindrance of the bromo substituent. The crystal packings are characterized by  $\pi$ - $\pi$  stacking [only for (II)] and C–Br $\cdots$  $\pi$  interactions. The long axes of the molecules in (I) are oriented in two directions; for the two other structures the long axis is oriented in one direction only.

**Keywords:** crystal structure; thieno[3,2-*b*]thiophene; Suzuki reactions;  $\pi$ -conjugated systems; Heck cross-coupling reactions; D- $\pi$ -A organic dyes; dye-sensitized solar cells; NMR analysis.

## 1. Introduction

In the last decade, scientists have been focusing on the development of organic  $\pi$ -conjugated molecules for application in electronic and photonic devices due to their ability to afford high operating speeds, large device densities, low manufacture cost and large-area flexible circuits. Fused thiophenes are the core structures in many p-type organic semiconductors, low band-gap conjugated oligomers and polymers, photovoltaic devices, dye-sensitizer solar cells and optical

materials (Deng *et al.*, 2011; Ito *et al.*, 2013; Kim *et al.*, 2014; Li *et al.*, 2013; Meager *et al.*, 2013). In 2007, Tokiyoshi and co-workers reported highly crystalline thin films of liquid-crystalline poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene] with charge mobilities of up to 0.44 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> (Tokiyoshi *et al.*, 2007). Very recently, new D- $\pi$ -A organic dyes developed by incorporating a thieno[3,2-*b*]thiophene moiety as a  $\pi$ -bridge for application in dye-sensitized solar cells (DSSCs) exhibited a remarkable long-term stability and a high energy conversion efficiency ( $\eta = 7.00\%$ ) comparable to that of the conventional Ru-based dye N719 ( $\eta = 7.24\%$ ) under the same conditions (Lee *et al.*, 2014). Materials containing thieno[3,2-*b*]thiophene may increase the electronic transport



between neighbouring molecules due to intermolecular S $\cdots$ S interactions. In addition, the introduction of substituents into the core structures of the materials may change their electronic properties, solubility and molecular packing. The potential application of thieno[3,2-*b*]thiophene in electronic materials prompted us to develop an efficient process for the functionalization of thieno[3,2-*b*]thiophene *via* a site-selective palladium(0)-catalyzed Suzuki reaction (Miyaura & Suzuki, 1995; Nicolaou *et al.*, 2005) of tetrabromothieno[3,2-*b*]thiophene (Nguyen *et al.*, 2014). In the present study, three 5-alkenyl-2-arylthieno[3,2-*b*]thiophenes, namely 3,6-dibromo-5-(4-*tert*-butylstyryl)-2-(naphthalen-1-yl)thieno[3,2-*b*]thiophene, (I), 3,6-dibromo-5-(4-methylstyryl)-2-(naphthalen-1-yl)thieno[3,2-*b*]thiophene, (II), and 3,6-dibromo-2-(4-*tert*-

butylphenyl)-5-(4-methylstyryl)thieno[3,2-*b*]thiophene, (III), were synthesized by sequential Suzuki and Heck cross-coupling reactions (Baletskaya & Cheprakov, 2000; Nicolaou *et al.*, 2005) and were structurally investigated by NMR and single-crystal X-ray diffraction.

## 2. Experimental

### 2.1. Synthesis and crystallization

A general procedure for the synthesis of 2-aryl-3,5,6-tribromothieno[3,2-*b*]thiophenes as given by Nguyen *et al.* (2014) was used to synthesize 2,3,6-tribromo-5-(naphthalen-1-yl)thieno[3,2-*b*]thiophene, (1*a*), and 2,3,6-tribromo-5-(4-*tert*-butylphenyl)thieno[3,2-*b*]thiophene, (1*b*).

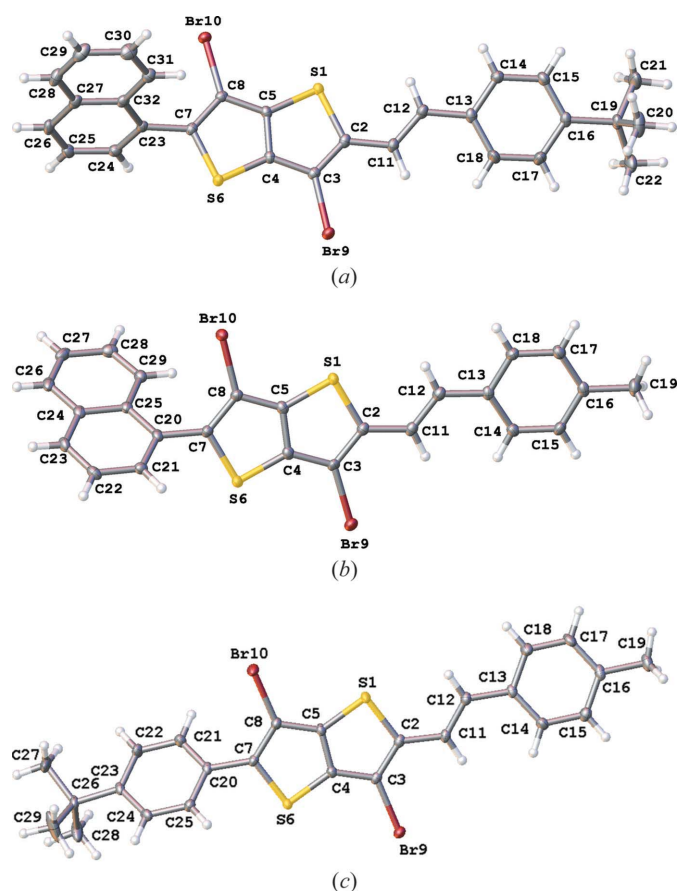
**2.1.1. General procedure for the synthesis of 5-alkenyl-2-aryl-3,6-dibromothieno[3,2-*b*]thiophenes (I)–(III).** Dimethylformamide (DMF, 4 ml) was deaerated and saturated with argon by exchanging between vacuum and a stream of argon ( $\times 3$ ). Pd(OAc)<sub>2</sub> (OAc is acetate; 0.1 equivalents) and P(Cy)<sub>3</sub> (Cy is cyclohexyl; 0.2 equivalents) were dissolved in this argon saturated solvent. The resulting brown–yellow solution was stirred at room temperature for a further 30 min to produce

the catalyst. 2-Aryl-3,5,6-tribromothieno[3,2-*b*]thiophene, (1*a*)/(1*b*) (1.0 equivalent), Na<sub>2</sub>CO<sub>3</sub> (6.0 equivalents) and the alkene (6.0–9.0 equivalents) were added to the solution of the catalyst under a stream of argon. The resulting solution was heated at 363 K with stirring under an argon atmosphere. The progress of the reaction was monitored by thin-layer chromatography (TLC; 100% hexane). When the starting material was completely consumed, as indicated by TLC (about 20–24 h), the brownish mixture was allowed to cool to room temperature and filtered to remove the brown precipitate. The filtrate was diluted with ethyl acetate, washed with water ( $\times 3$ ) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure by rotary evaporation and the residue was purified by SiO<sub>2</sub> column chromatography (100% hexane) to give the 5-alkenyl-2-aryl-3,6-dibromothieno[3,2-*b*]thiophene.

**2.1.2. Data for 3,6-dibromo-5-(4-*tert*-butylstyryl)-2-(naphthalen-1-yl)thieno[3,2-*b*]thiophene, (I).** Starting from (1*a*) (63 mg, 0.125 mmol) and 4-*tert*-butylstyrene (120 mg, 0.75 mmol), (I) was isolated (yield: 20 mg, 27%; m.p. 490–491 K) as an orange solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.97 (*d*, *J* = 8.0 Hz, 1H, Ar), 7.93 (*d*, *J* = 8.0 Hz, 1H, Ar), 7.84 (*d*, *J* = 7.5 Hz, 1H, Ar), 7.54 (*m*, 6H, Ar), 7.41 (*d*, *J* = 7.5 Hz, 2H, Ar), 7.32 (*d*, *J* = 16.0 Hz, 1H, *trans*-alkene), 7.07 (*d*, *J* = 16.0 Hz, 1H, *trans*-alkene), 1.35 (*s*, 9H, *tert*-butyl). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  31.2 (CH<sub>3</sub>), 34.8, 103.0, 103.9, 119.6, 125.1, 125.8, 125.9, 126.3, 126.5, 126.8, 128.4, 129.7, 130.0, 130.8, 131.9, 133.5, 133.6, 136.6, 138.4, 139.1, 139.4, 151.8. IR (KBr) ( $\nu$ , cm<sup>-1</sup>): 3064 (*w*), 2923 (*s*), 2866 (*m*), 1635 (*m*), 1591 (*w*), 1500 (*w*), 617 (*m*), 548 (*s*).

**2.1.3. Data for 3,6-dibromo-5-(4-methylstyryl)-2-(naphthalen-1-yl)thieno[3,2-*b*]thiophene, (II).** Starting from (1*a*) (63 mg, 0.125 mmol) and 4-methylstyrene (133 mg, 1.125 mmol), (II) was obtained (yield: 15 mg, 22%; m.p. 495–496 K) as a yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.96 (*d*, *J* = 7.5 Hz, 1H, Ar), 7.93 (*d*, *J* = 9.0 Hz, 1H, Ar), 7.85 (*d*, *J* = 9.0 Hz, 1H, Ar), 7.53 (*m*, 4H, Ar), 7.45 (*d*, *J* = 8.0 Hz, 2H, Ar), 7.32 (*d*, *J* = 16.0 Hz, 1H, *trans*-alkene), 7.19 (*d*, *J* = 7.5 Hz, 2H, Ar), 7.05 (*d*, *J* = 16.0 Hz, 1H, *trans*-alkene), 2.37 (*s*, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  21.3 (CH<sub>3</sub>), 102.9, 103.9, 119.3, 125.0, 125.9, 126.3, 126.7, 126.8, 128.4, 129.6, 129.7, 130.0, 130.9, 131.9, 133.5, 133.6, 136.6, 138.4, 138.6, 139.1, 139.3. IR (KBr) ( $\nu$ , cm<sup>-1</sup>): 3050 (*w*), 2929 (*m*), 1626 (*s*), 1546 (*m*), 1499 (*s*), 773 (*s*), 647 (*s*), 531 (*s*).

**2.1.4. Data for 3,6-dibromo-2-(4-*tert*-butylphenyl)-5-(4-methylstyryl)thieno[3,2-*b*]thiophene, (III).** Starting from (1*b*) (64 mg, 0.125 mmol) and 4-methylstyrene (133 mg, 1.125 mmol), (III) was obtained as a yellow solid (yield: 13 mg, 18%; m.p. 493–494 K). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.63 (*d*, *J* = 8.5 Hz, 2H, Ar), 7.46 (*d*, *J* = 8.5 Hz, 2H, Ar), 7.40 (*d*, *J* = 8.0 Hz, 2H, Ar), 7.24 (*d*, *J* = 16.0 Hz, 1H, *trans*-alkene), 7.16 (*d*, *J* = 7.5 Hz, 2H, Ar), 6.97 (*d*, *J* = 16.0 Hz, 1H, *trans*-alkene), 2.36 (*s*, 3H, CH<sub>3</sub>), 1.35 (*s*, 9H, *tert*-butyl). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  21.3, 31.2, 34.7, 99.9, 103.0, 119.4, 125.7, 126.6, 128.5, 129.5, 129.9, 130.6, 133.6, 137.7, 137.8, 138.4, 138.8, 140.1, 151.9. IR (KBr) ( $\nu$ , cm<sup>-1</sup>): 3060 (*w*), 2924 (*s*), 1619 (*w*), 1520 (*w*), 1462 (*w*), 543 (*s*).



**Figure 1**

Views of the asymmetric units in (a) (I), (b) (II) and (c) (III), showing the atom-labelling schemes. Displacement ellipsoids are drawn at the 50% probability level.

**Table 1**  
Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	C <sub>28</sub> H <sub>22</sub> Br <sub>2</sub> S <sub>2</sub>	C <sub>25</sub> H <sub>16</sub> Br <sub>2</sub> S <sub>2</sub>	C <sub>25</sub> H <sub>22</sub> Br <sub>2</sub> S <sub>2</sub>
<i>M<sub>r</sub></i>	582.40	540.32	546.37
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	100	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.3316 (3), 16.1749 (6), 18.1333 (6)	4.1522 (3), 13.2861 (14), 19.6117 (18)	9.5401 (12), 10.1575 (17), 12.1711 (16)
$\alpha$ , $\beta$ , $\gamma$ (°)	90, 96.677 (3), 90	106.464 (9), 94.945 (7), 93.016 (7)	106.933 (13), 98.599 (11), 92.192 (13)
<i>V</i> (Å <sup>3</sup> )	2427.13 (15)	1030.32 (16)	1111.4 (3)
<i>Z</i>	4	2	2
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	3.53	4.15	3.85
Crystal size (mm)	0.3 × 0.15 × 0.15	0.4 × 0.15 × 0.05	0.35 × 0.3 × 0.15
Data collection			
Diffractometer	Agilent SuperNova diffractometer (Single source at offset, Eos detector)	Agilent SuperNova diffractometer (Single source at offset, Eos detector)	Agilent SuperNova diffractometer (Single source at offset, Eos detector)
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Agilent, 2012)	Multi-scan ( <i>CrysAlis PRO</i> ; Agilent, 2012)	Multi-scan ( <i>CrysAlis PRO</i> ; Agilent, 2012)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.681, 1.000	0.455, 1.000	0.621, 1.000
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	25300, 4962, 4491	20862, 4207, 3705	22740, 4543, 4106
<i>R</i> <sub>int</sub>	0.030	0.043	0.029
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.625	0.625	0.625
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>	0.022, 0.051, 1.04	0.028, 0.074, 1.06	0.024, 0.063, 1.05
No. of reflections	4962	4207	4543
No. of parameters	292	263	266
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.43, -0.27	0.65, -0.49	0.86, -0.34

Computer programs: *CrysAlis PRO* (Agilent, 2012), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008) and *OLEX2* (Dolomanov *et al.*, 2009).

## 2.2. Refinement

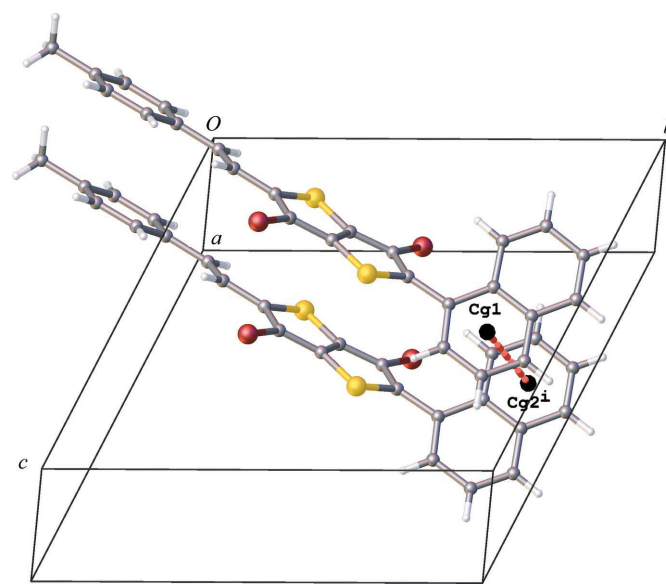
Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were placed in idealized positions and refined in riding mode, with *U*<sub>iso</sub>(H) values assigned as 1.2 times *U*<sub>eq</sub> of the parent atoms (1.5 times for methyl groups) and with C–H distances of 0.95 (aromatic and alkene) or 0.98 Å (methyl).

## 3. Results and discussion

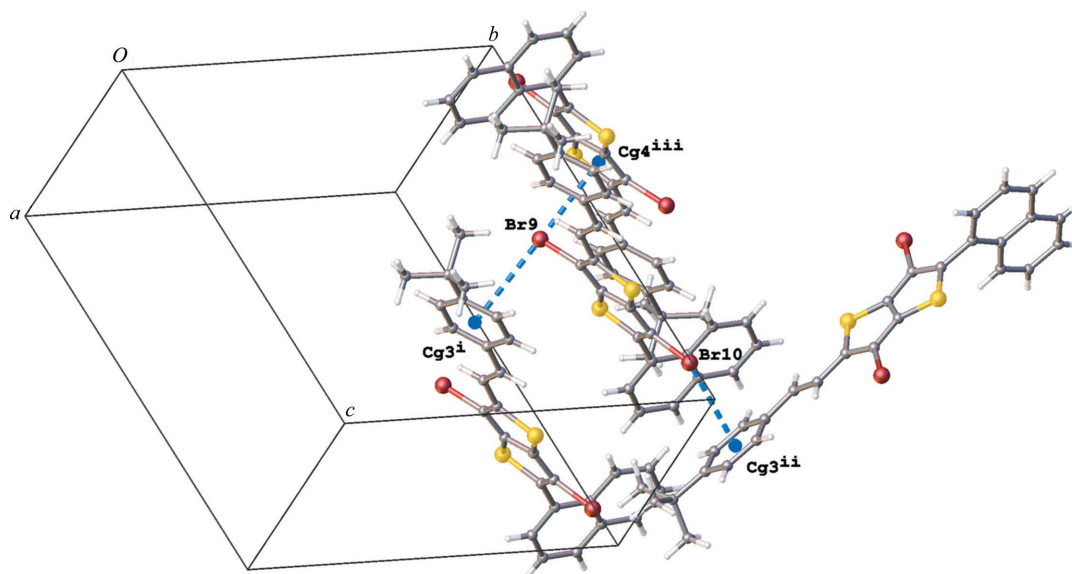
All three title compounds, (I)–(III), were characterized by spectroscopic methods (see *Experimental*, §2.1). In the <sup>1</sup>H NMR spectra of (I), (II) and (III), it is easy to recognize the signals of the two vicinal olefinic H atoms of the ethylene bridge at about 6.97–7.07 and 7.24–7.32 p.p.m. The splitting of the signals and the typically high coupling constants (16.0 Hz) of these two protons revealed that the cross-coupling happened selectively on the terminal end of the vinyl group, resulting in the formation of *trans*-alkenes. The regioselectivity of the Suzuki and Heck reactions of 2-aryl-3,5,6-tribromothieno[3,2-*b*]thiophene, (1), however, can only be clarified through single-crystal X-ray diffraction analysis.

The molecular structures of (I)–(III) are shown in Fig. 1. The bond lengths and angles are in good agreement with the average values in the Cambridge Structural Database (CSD, Version 5.35, February 2014; Allen, 2002). The thieno[3,2-*b*]thiophene rings are planar, as illustrated by the dihedral

angles between the planes of the thiophene rings, *viz.* 0.58 (9), 1.29 (12) and 1.74 (10)° for (I), (II) and (III), respectively. In the CSD, the value of this angle ranges between 0.0 and 7.2° and is not related to the substitution pattern [in 3,6-dibromo-2,5-bis(thiophen-2-yl)thieno[3,2-*b*]thiophene (refcode WEX-



**Figure 2**  
 $\pi$ - $\pi$  stacking (red dotted line) in (II) [Cg1 and Cg2 are the centroids of the C20–C25 and C25–C29 rings, respectively; symmetry code: (i)  $x + 1, y, z$ ].


**Figure 3**

C—Br $\cdots\pi$  interactions in (I) [Cg3 and Cg4 are the centroids of the C13–C18 and S1/C2–C5 rings, respectively; symmetry codes: (i)  $x + 1, y, z$ ; (ii)  $-x, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (iii)  $-x, -y + 2, -z + 1$ ].

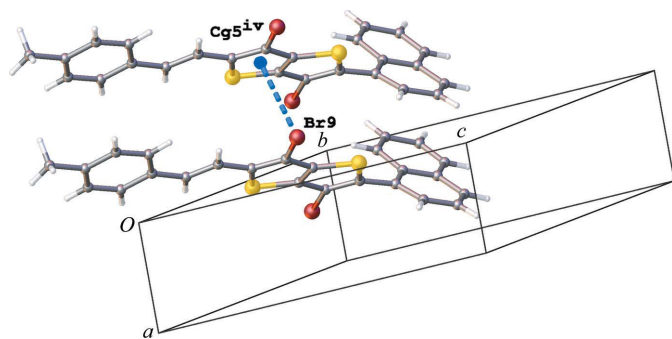
BEI; Liu *et al.*, 2013), the central thieno[3,2-*b*]thiophene system is planar due to the presence of an inversion centre].

In order to enlarge the  $\pi$ -conjugated system of thiophene, aromatic rings were introduced onto the thieno[3,2-*b*]thiophene core structure by sequential Suzuki and Heck cross-coupling reactions. In the resulting compounds, the regioselectivity occurred at the C-2 and C-5 atoms on opposite sides of the thieno[3,2-*b*]thiophene ring due to the electron deficiency at these positions.

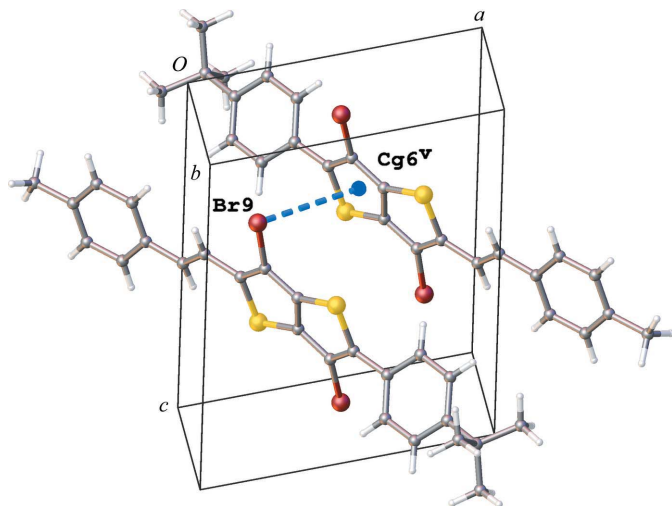
In all three title compounds, the plane of the phenyl fragment attached to the thieno[3,2-*b*]thiophene skeleton *via* an ethylene bridge and that of the thieno[3,2-*b*]thiophene ring itself make a dihedral angle of about 10°. The dihedral angle between these mean planes is 14.05 (7)° in (I), 10.04 (10)° in (II) and 10.09 (8)° in (III), illustrating that  $\pi$ -conjugation is still favourable due to the ethylene bridges. However, in the case of the *tert*-butyl group in (I), the dihedral angle is slightly larger. The CSD only lists three entries containing a thieno[3,2-*b*]thiophene skeleton and a phenyl ring linked to each other *via* an ethylene bridge [2,2'-(biphenyl-4,4'-diyl-

diethene-2,1-diyl)bis(thieno[3,2-*b*]thiophene) (CSD refcode ARIFEN; Li *et al.*, 2011), 2,6-bis(2-phenylvinyl)bisthieno[3,2-*b*:2',3'-*d*]thiophene (refcode GURQAM; Liu *et al.*, 2010) and 2,6-bis(2-phenylvinyl)thieno[3,2-*b*]thieno[2',3':4,5]thieno[2,3-*d*]thiophene (refcode GURQEQ; Liu *et al.*, 2010)]. In each case, the angle between the mean planes is less than 10°. In GURQAM and GURQEQ, the thieno[3,2-*b*]thiophene skeleton is further extended to bisthieno[3,2-*b*:2',3'-*d*]thiophene and thieno[3,2-*b*]thieno[2',3':4,5]thieno[2,3-*d*]thiophene, respectively. Also in ARIFEN, no substituents are present on the conjugated system. As expected, the stereochemistry around the ethylene bridge is always *E*. The aromatic rings directly connected to the thieno[3,2-*b*]thiophene moiety by the Suzuki reaction show no coplanarity with the rest of the molecule. In (I) and (II), the planes of the naphthalene rings are rotated out of the plane of the thieno[3,2-*b*]thiophene ring by dihedral angles of 65.77 (5) and 52.68 (7)°, respectively. This rotation reduces the repulsion between atoms Br10 $\cdots$ H31 and S6 $\cdots$ H24 in (I) and between atoms Br10 $\cdots$ H29 and S6 $\cdots$ H21 in (II). The dihedral angle between the plane of the thieno[3,2-*b*]thiophene system and that of the smaller phenyl ring in (III) is reduced to 41.49 (8)°, which correlates well with the related compounds (Liu *et al.*, 2013). However, the *tert*-butyl substituent makes the *tert*-butylphenyl group slightly bent. Thus, the angles between the C20–C7 and C26–C23 bonds and the benzene ring are 6.30 (14) and 6.48 (13)°, respectively.

The packing of (I) and (III) shows no  $\pi$ - $\pi$  stacking, although a number of aromatic fragments are present in each case. However, compound (II) displays  $\pi$ - $\pi$  stacking interactions between naphthalene rings [Cg1 $\cdots$ Cg2<sup>i</sup> = 3.6951 (16) Å; Cg1 and Cg2 are the centroids of the C20–C25 and C24–C29 rings, respectively; symmetry code: (i)  $x + 1, y, z$ ; Fig. 2]. This could be due to the absence of the *tert*-butyl group, allowing closer molecular contacts.


**Figure 4**

C—Br $\cdots\pi$  interactions in (II) [Cg5 is the centroid of the S1/C2–C5 ring; symmetry code: (iv)  $x - 1, y, z$ ].



**Figure 5**

C—Br $\cdots\pi$  interactions in (III) [ $Cg6$  is the centroid of the C4—C5/S6/C7—C8 ring; symmetry code: (v)  $-x + 1, -y + 1, -z + 1$ ].

All three title structures show to a certain extent C—Br $\cdots\pi$  interactions. This interaction is most favourable in (I) [ $C8—Br10\cdots Cg3^{ii} = 3.5695$  (10) Å,  $C3—Br9\cdots Cg4^{iii} = 3.5412$  (10) Å and  $C3—Br9\cdots Cg3^i = 3.8651$  (11) Å;  $Cg3$  and  $Cg4$  are the centroids of the C13—C18 and S1/C2—C5 rings, respectively; symmetry codes: (ii)  $-x, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (iii)  $-x, -y + 2, -z + 1$ ; Fig. 3]. The C—Br $\cdots\pi$  interactions are less prominent in the other two structures [ $C3—Br9\cdots Cg5^{iv} = 3.9496$  (11) Å for (II) and  $C3—Br9\cdots Cg6^v = 3.8542$  (10) Å for (III);  $Cg5$  and  $Cg6$  are the centroids of the S1/C2—C5 and C4—C5/S6/C7—C8 rings, respectively; symmetry codes: (iv)  $x - 1, y, z$ ; (v)  $-x + 1, -y + 1, -z + 1$ ; Figs. 4 and 5]. In the case of (I), the long axis of the molecules is oriented in two directions, *i.e.* [210] and  $\bar{2}10$ . For the two other structures, the long axis is oriented in only one direction, *i.e.* [031] for (II) and [110] for (III). Possible intermolecular S $\cdots$ S interactions, which may influence the

electronic transport between neighbouring molecules, are only observed for (I). However, this interaction is weak [ $S6\cdots S6^{vi} = 3.8278$  (6) Å; symmetry code: (vi)  $-x + 1, -y + 2, -z + 1$ ].

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## supporting information

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## Stacking patterns of thieno[3,2-*b*]thiophenes functionalized by sequential palladium-catalyzed Suzuki and Heck cross-coupling reactions

Hien Nguyen, Ngan Nguyen Bich, Tung T. Dang and Luc Van Meervelt

### Computing details

Data collection: *CrysAlis PRO*, Version 1.171.36.28 (Agilent, 2012) for (I); (*CrysAlis PRO*; Agilent, 2012) for (II), (III).  
 Cell refinement: *CrysAlis PRO*, Version 1.171.36.28 (Agilent, 2012) for (I); (*CrysAlis PRO*; Agilent, 2012) for (II), (III).  
 Data reduction: *CrysAlis PRO*, Version 1.171.36.28 (Agilent, 2012) for (I); (*CrysAlis PRO*; Agilent, 2012) for (II), (III).  
 Program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008) for (I); *XS* (Sheldrick, 2008) for (II), (III). For all compounds, program(s) used to refine structure: *XL* (Sheldrick, 2008); molecular graphics: *Olex2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *Olex2* (Dolomanov *et al.*, 2009).

### (I) 3,6-Dibromo-5-(4-*tert*-butylstyryl)2-(naphthalen-1-yl)thieno[3,2-*b*]thiophene

#### Crystal data

$C_{28}H_{22}Br_2S_2$

$M_r = 582.40$

Monoclinic,  $P2_1/c$

$a = 8.3316$  (3) Å

$b = 16.1749$  (6) Å

$c = 18.1333$  (6) Å

$\beta = 96.677$  (3)°

$V = 2427.13$  (15) Å<sup>3</sup>

$Z = 4$

$F(000) = 1168$

$D_x = 1.594$  Mg m<sup>-3</sup>

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

Cell parameters from 12479 reflections

$\theta = 3.1\text{--}29.0^\circ$

$\mu = 3.53$  mm<sup>-1</sup>

$T = 100$  K

Prism, orange

$0.3 \times 0.15 \times 0.15$  mm

#### Data collection

Agilent SuperNova  
 diffractometer (Single source at offset, Eos  
 detector)

Radiation source: SuperNova (Mo) X-ray  
 Source

Mirror monochromator

Detector resolution: 15.9631 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan  
 (*CrysAlis PRO*; Agilent, 2012)

$T_{\min} = 0.681$ ,  $T_{\max} = 1.000$

25300 measured reflections

4962 independent reflections

4491 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$

$\theta_{\max} = 26.4^\circ$ ,  $\theta_{\min} = 2.8^\circ$

$h = -10 \rightarrow 10$

$k = -20 \rightarrow 20$

$l = -22 \rightarrow 22$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.022$

$wR(F^2) = 0.051$

$S = 1.04$

4962 reflections

292 parameters

0 restraints

Primary atom site location: structure-invariant  
 direct methods

Secondary atom site location: difference Fourier map  
 Hydrogen site location: inferred from neighbouring sites  
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.019P)^2 + 1.8507P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.002$   
 $\Delta\rho_{\max} = 0.43 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$

*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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.00853 (5)	0.96982 (3)	0.68447 (2)	0.01444 (10)
C2	0.0013 (2)	0.91490 (12)	0.60029 (10)	0.0155 (4)
C3	0.1292 (2)	0.93567 (11)	0.56283 (10)	0.0147 (4)
C4	0.2305 (2)	0.99653 (11)	0.59933 (10)	0.0137 (4)
C5	0.1812 (2)	1.02135 (11)	0.66578 (10)	0.0136 (4)
S6	0.40170 (5)	1.04792 (3)	0.58019 (2)	0.01574 (10)
C7	0.4082 (2)	1.10340 (11)	0.66312 (10)	0.0147 (4)
C8	0.2845 (2)	1.08156 (11)	0.70254 (10)	0.0140 (4)
Br9	0.16772 (2)	0.890916 (11)	0.470787 (10)	0.01708 (5)
Br10	0.26100 (2)	1.123191 (12)	0.797833 (10)	0.01786 (6)
C11	-0.1291 (2)	0.85885 (12)	0.57696 (10)	0.0170 (4)
H11	-0.1181	0.8254	0.5348	0.020*
C12	-0.2641 (2)	0.84965 (12)	0.60935 (10)	0.0171 (4)
H12	-0.2750	0.8836	0.6512	0.021*
C13	-0.3968 (2)	0.79259 (12)	0.58677 (10)	0.0167 (4)
C14	-0.5332 (2)	0.79350 (12)	0.62447 (10)	0.0174 (4)
H14	-0.5410	0.8334	0.6623	0.021*
C15	-0.6577 (2)	0.73751 (12)	0.60799 (10)	0.0186 (4)
H15	-0.7488	0.7397	0.6350	0.022*
C16	-0.6528 (2)	0.67819 (12)	0.55286 (10)	0.0169 (4)
C17	-0.5183 (2)	0.67923 (14)	0.51340 (11)	0.0247 (5)
H17	-0.5128	0.6407	0.4742	0.030*
C18	-0.3934 (2)	0.73456 (13)	0.52972 (11)	0.0239 (4)
H18	-0.3038	0.7333	0.5018	0.029*
C19	-0.7904 (2)	0.61567 (12)	0.53462 (10)	0.0188 (4)
C20	-0.9133 (3)	0.65201 (15)	0.47382 (13)	0.0353 (6)
H20A	-0.9998	0.6118	0.4605	0.053*
H20B	-0.8593	0.6647	0.4299	0.053*
H20C	-0.9594	0.7028	0.4921	0.053*
C21	-0.8750 (3)	0.59631 (16)	0.60343 (12)	0.0348 (6)



H21A	-0.9546	0.5523	0.5916	0.052*
H21B	-0.9297	0.6461	0.6186	0.052*
H21C	-0.7946	0.5783	0.6440	0.052*
C22	-0.7260 (3)	0.53419 (13)	0.50670 (13)	0.0306 (5)
H22A	-0.6376	0.5140	0.5425	0.046*
H22B	-0.6861	0.5433	0.4586	0.046*
H22C	-0.8131	0.4932	0.5011	0.046*
C23	0.5400 (2)	1.16410 (12)	0.68043 (10)	0.0150 (4)
C24	0.6970 (2)	1.13650 (12)	0.69203 (10)	0.0178 (4)
H24	0.7178	1.0788	0.6905	0.021*
C25	0.8273 (2)	1.19146 (13)	0.70602 (10)	0.0208 (4)
H25	0.9347	1.1709	0.7142	0.025*
C26	0.7993 (2)	1.27443 (13)	0.70781 (10)	0.0210 (4)
H26	0.8879	1.3114	0.7173	0.025*
C27	0.6397 (2)	1.30641 (12)	0.69573 (10)	0.0189 (4)
C28	0.6092 (3)	1.39219 (13)	0.69696 (11)	0.0238 (4)
H28	0.6974	1.4296	0.7051	0.029*
C29	0.4560 (3)	1.42220 (13)	0.68672 (11)	0.0273 (5)
H29	0.4378	1.4801	0.6887	0.033*
C30	0.3238 (3)	1.36753 (13)	0.67316 (11)	0.0248 (4)
H30	0.2169	1.3889	0.6658	0.030*
C31	0.3483 (2)	1.28412 (12)	0.67051 (10)	0.0194 (4)
H31	0.2583	1.2481	0.6607	0.023*
C32	0.5070 (2)	1.25076 (12)	0.68225 (10)	0.0160 (4)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0126 (2)	0.0167 (2)	0.0141 (2)	-0.00241 (17)	0.00161 (17)	-0.00025 (17)
C2	0.0162 (9)	0.0146 (9)	0.0147 (9)	-0.0008 (7)	-0.0022 (7)	0.0011 (7)
C3	0.0160 (9)	0.0143 (9)	0.0135 (9)	0.0010 (7)	-0.0002 (7)	-0.0002 (7)
C4	0.0129 (9)	0.0130 (9)	0.0151 (9)	-0.0007 (7)	0.0006 (7)	0.0010 (7)
C5	0.0121 (9)	0.0142 (9)	0.0144 (9)	-0.0004 (7)	0.0007 (7)	0.0023 (7)
S6	0.0153 (2)	0.0176 (2)	0.0148 (2)	-0.00484 (18)	0.00368 (17)	-0.00338 (17)
C7	0.0150 (9)	0.0137 (9)	0.0148 (9)	0.0001 (7)	-0.0007 (7)	-0.0010 (7)
C8	0.0142 (9)	0.0147 (9)	0.0127 (8)	0.0023 (7)	0.0004 (7)	-0.0012 (7)
Br9	0.01942 (10)	0.01777 (10)	0.01416 (9)	-0.00291 (7)	0.00246 (7)	-0.00312 (7)
Br10	0.01814 (10)	0.02115 (10)	0.01455 (10)	-0.00166 (7)	0.00306 (7)	-0.00452 (7)
C11	0.0170 (9)	0.0174 (10)	0.0157 (9)	-0.0030 (8)	-0.0012 (7)	-0.0006 (7)
C12	0.0196 (10)	0.0175 (10)	0.0136 (9)	-0.0037 (8)	-0.0011 (7)	-0.0004 (7)
C13	0.0153 (9)	0.0189 (10)	0.0153 (9)	-0.0028 (8)	-0.0014 (7)	0.0032 (7)
C14	0.0186 (10)	0.0182 (10)	0.0154 (9)	-0.0008 (8)	0.0025 (7)	-0.0009 (7)
C15	0.0158 (9)	0.0215 (10)	0.0190 (10)	-0.0024 (8)	0.0043 (7)	0.0019 (8)
C16	0.0155 (9)	0.0190 (10)	0.0155 (9)	-0.0044 (8)	-0.0014 (7)	0.0031 (7)
C17	0.0256 (11)	0.0303 (12)	0.0191 (10)	-0.0100 (9)	0.0060 (8)	-0.0090 (9)
C18	0.0197 (10)	0.0328 (12)	0.0209 (10)	-0.0098 (9)	0.0092 (8)	-0.0049 (9)
C19	0.0175 (9)	0.0211 (10)	0.0176 (9)	-0.0082 (8)	0.0017 (8)	0.0011 (8)
C20	0.0265 (12)	0.0323 (13)	0.0430 (14)	-0.0126 (10)	-0.0130 (10)	0.0108 (10)

C21	0.0349 (13)	0.0426 (14)	0.0286 (12)	-0.0226 (11)	0.0116 (10)	-0.0054 (10)
C22	0.0262 (12)	0.0225 (12)	0.0441 (13)	-0.0104 (9)	0.0078 (10)	-0.0037 (10)
C23	0.0169 (9)	0.0177 (10)	0.0106 (8)	-0.0034 (7)	0.0022 (7)	-0.0020 (7)
C24	0.0183 (10)	0.0203 (10)	0.0149 (9)	0.0003 (8)	0.0025 (7)	-0.0021 (7)
C25	0.0143 (9)	0.0287 (11)	0.0191 (9)	-0.0010 (8)	0.0009 (8)	-0.0030 (8)
C26	0.0197 (10)	0.0270 (11)	0.0160 (9)	-0.0100 (8)	-0.0001 (8)	-0.0023 (8)
C27	0.0244 (10)	0.0201 (10)	0.0119 (9)	-0.0047 (8)	0.0005 (8)	-0.0017 (7)
C28	0.0314 (12)	0.0198 (10)	0.0186 (10)	-0.0078 (9)	-0.0037 (8)	0.0005 (8)
C29	0.0415 (13)	0.0159 (10)	0.0225 (11)	-0.0004 (9)	-0.0048 (9)	0.0004 (8)
C30	0.0261 (11)	0.0237 (11)	0.0231 (10)	0.0059 (9)	-0.0028 (8)	0.0012 (8)
C31	0.0214 (10)	0.0196 (10)	0.0165 (9)	-0.0004 (8)	-0.0003 (8)	0.0000 (7)
C32	0.0200 (9)	0.0172 (10)	0.0105 (8)	-0.0019 (8)	0.0006 (7)	-0.0005 (7)

*Geometric parameters (Å, °)*

S1—C2	1.7612 (18)	C19—C21	1.535 (3)
S1—C5	1.7297 (18)	C19—C22	1.531 (3)
C2—C3	1.370 (3)	C20—H20A	0.9800
C2—C11	1.440 (3)	C20—H20B	0.9800
C3—C4	1.411 (2)	C20—H20C	0.9800
C3—Br9	1.8809 (18)	C21—H21A	0.9800
C4—C5	1.378 (3)	C21—H21B	0.9800
C4—S6	1.7205 (18)	C21—H21C	0.9800
C5—C8	1.414 (3)	C22—H22A	0.9800
S6—C7	1.7467 (18)	C22—H22B	0.9800
C7—C8	1.367 (3)	C22—H22C	0.9800
C7—C23	1.479 (3)	C23—C24	1.375 (3)
C8—Br10	1.8858 (17)	C23—C32	1.429 (3)
C11—H11	0.9500	C24—H24	0.9500
C11—C12	1.337 (3)	C24—C25	1.403 (3)
C12—H12	0.9500	C25—H25	0.9500
C12—C13	1.462 (3)	C25—C26	1.363 (3)
C13—C14	1.393 (3)	C26—H26	0.9500
C13—C18	1.400 (3)	C26—C27	1.420 (3)
C14—H14	0.9500	C27—C28	1.411 (3)
C14—C15	1.383 (3)	C27—C32	1.424 (3)
C15—H15	0.9500	C28—H28	0.9500
C15—C16	1.390 (3)	C28—C29	1.358 (3)
C16—C17	1.398 (3)	C29—H29	0.9500
C16—C19	1.536 (3)	C29—C30	1.412 (3)
C17—H17	0.9500	C30—H30	0.9500
C17—C18	1.378 (3)	C30—C31	1.366 (3)
C18—H18	0.9500	C31—H31	0.9500
C19—C20	1.532 (3)	C31—C32	1.422 (3)
C5—S1—C2	91.06 (9)	C22—C19—C21	107.75 (17)
C3—C2—S1	110.85 (14)	C19—C20—H20A	109.5
C3—C2—C11	127.75 (17)	C19—C20—H20B	109.5

C11—C2—S1	121.37 (14)	C19—C20—H20C	109.5
C2—C3—C4	113.34 (16)	H20A—C20—H20B	109.5
C2—C3—Br9	124.64 (14)	H20A—C20—H20C	109.5
C4—C3—Br9	122.01 (13)	H20B—C20—H20C	109.5
C3—C4—S6	135.04 (14)	C19—C21—H21A	109.5
C5—C4—C3	112.97 (16)	C19—C21—H21B	109.5
C5—C4—S6	111.99 (14)	C19—C21—H21C	109.5
C4—C5—S1	111.76 (14)	H21A—C21—H21B	109.5
C4—C5—C8	112.68 (16)	H21A—C21—H21C	109.5
C8—C5—S1	135.55 (14)	H21B—C21—H21C	109.5
C4—S6—C7	91.04 (9)	C19—C22—H22A	109.5
C8—C7—S6	111.56 (14)	C19—C22—H22B	109.5
C8—C7—C23	130.29 (17)	C19—C22—H22C	109.5
C23—C7—S6	118.15 (13)	H22A—C22—H22B	109.5
C5—C8—Br10	123.73 (13)	H22A—C22—H22C	109.5
C7—C8—C5	112.71 (16)	H22B—C22—H22C	109.5
C7—C8—Br10	123.48 (14)	C24—C23—C7	119.10 (17)
C2—C11—H11	117.1	C24—C23—C32	119.78 (17)
C12—C11—C2	125.86 (18)	C32—C23—C7	121.08 (17)
C12—C11—H11	117.1	C23—C24—H24	119.2
C11—C12—H12	116.7	C23—C24—C25	121.61 (19)
C11—C12—C13	126.51 (18)	C25—C24—H24	119.2
C13—C12—H12	116.7	C24—C25—H25	120.1
C14—C13—C12	119.31 (17)	C26—C25—C24	119.80 (19)
C14—C13—C18	117.22 (17)	C26—C25—H25	120.1
C18—C13—C12	123.45 (17)	C25—C26—H26	119.5
C13—C14—H14	119.3	C25—C26—C27	120.99 (18)
C15—C14—C13	121.42 (18)	C27—C26—H26	119.5
C15—C14—H14	119.3	C26—C27—C32	119.37 (18)
C14—C15—H15	119.2	C28—C27—C26	121.53 (18)
C14—C15—C16	121.54 (17)	C28—C27—C32	119.10 (19)
C16—C15—H15	119.2	C27—C28—H28	119.4
C15—C16—C17	116.90 (17)	C29—C28—C27	121.17 (19)
C15—C16—C19	121.71 (17)	C29—C28—H28	119.4
C17—C16—C19	121.37 (17)	C28—C29—H29	119.9
C16—C17—H17	119.1	C28—C29—C30	120.1 (2)
C18—C17—C16	121.86 (18)	C30—C29—H29	119.9
C18—C17—H17	119.1	C29—C30—H30	119.7
C13—C18—H18	119.5	C31—C30—C29	120.5 (2)
C17—C18—C13	120.99 (18)	C31—C30—H30	119.7
C17—C18—H18	119.5	C30—C31—H31	119.7
C20—C19—C16	108.79 (16)	C30—C31—C32	120.65 (19)
C20—C19—C21	109.38 (18)	C32—C31—H31	119.7
C21—C19—C16	111.17 (16)	C27—C32—C23	118.45 (17)
C22—C19—C16	110.88 (16)	C31—C32—C23	123.13 (17)
C22—C19—C20	108.83 (18)	C31—C32—C27	118.42 (18)
S1—C2—C3—C4	-1.6 (2)	C11—C12—C13—C18	4.8 (3)

S1—C2—C3—Br9	179.68 (10)	C12—C13—C14—C15	-176.21 (18)
S1—C2—C11—C12	8.7 (3)	C12—C13—C18—C17	176.4 (2)
S1—C5—C8—C7	-179.54 (16)	C13—C14—C15—C16	-0.4 (3)
S1—C5—C8—Br10	3.5 (3)	C14—C13—C18—C17	-1.9 (3)
C2—S1—C5—C4	-0.83 (14)	C14—C15—C16—C17	-1.8 (3)
C2—S1—C5—C8	-179.7 (2)	C14—C15—C16—C19	179.73 (18)
C2—C3—C4—C5	1.0 (2)	C15—C16—C17—C18	2.1 (3)
C2—C3—C4—S6	-178.48 (16)	C15—C16—C19—C20	90.7 (2)
C2—C11—C12—C13	-179.42 (18)	C15—C16—C19—C21	-29.8 (3)
C3—C2—C11—C12	-169.04 (19)	C15—C16—C19—C22	-149.62 (19)
C3—C4—C5—S1	0.1 (2)	C16—C17—C18—C13	-0.2 (3)
C3—C4—C5—C8	179.22 (16)	C17—C16—C19—C20	-87.7 (2)
C3—C4—S6—C7	179.9 (2)	C17—C16—C19—C21	151.8 (2)
C4—C5—C8—C7	1.6 (2)	C17—C16—C19—C22	31.9 (3)
C4—C5—C8—Br10	-175.38 (13)	C18—C13—C14—C15	2.2 (3)
C4—S6—C7—C8	0.55 (15)	C19—C16—C17—C18	-179.42 (19)
C4—S6—C7—C23	-179.67 (15)	C23—C7—C8—C5	178.96 (18)
C5—S1—C2—C3	1.41 (15)	C23—C7—C8—Br10	-4.1 (3)
C5—S1—C2—C11	-176.66 (16)	C23—C24—C25—C26	-0.4 (3)
C5—C4—S6—C7	0.35 (15)	C24—C23—C32—C27	0.4 (3)
S6—C4—C5—S1	179.71 (9)	C24—C23—C32—C31	179.74 (17)
S6—C4—C5—C8	-1.1 (2)	C24—C25—C26—C27	0.0 (3)
S6—C7—C8—C5	-1.3 (2)	C25—C26—C27—C28	-179.58 (18)
S6—C7—C8—Br10	175.67 (10)	C25—C26—C27—C32	0.6 (3)
S6—C7—C23—C24	-64.6 (2)	C26—C27—C28—C29	-178.76 (18)
S6—C7—C23—C32	112.86 (17)	C26—C27—C32—C23	-0.8 (3)
C7—C23—C24—C25	177.69 (17)	C26—C27—C32—C31	179.82 (17)
C7—C23—C32—C27	-177.02 (16)	C27—C28—C29—C30	-1.2 (3)
C7—C23—C32—C31	2.3 (3)	C28—C27—C32—C23	179.38 (17)
C8—C7—C23—C24	115.1 (2)	C28—C27—C32—C31	0.0 (3)
C8—C7—C23—C32	-67.4 (3)	C28—C29—C30—C31	0.3 (3)
Br9—C3—C4—C5	179.76 (13)	C29—C30—C31—C32	0.8 (3)
Br9—C3—C4—S6	0.2 (3)	C30—C31—C32—C23	179.75 (18)
C11—C2—C3—C4	176.27 (18)	C30—C31—C32—C27	-0.9 (3)
C11—C2—C3—Br9	-2.4 (3)	C32—C23—C24—C25	0.2 (3)
C11—C12—C13—C14	-176.89 (19)	C32—C27—C28—C29	1.0 (3)

(II) 3,6-Dibromo-5-(4-methylstyryl)-2-(naphthalen-1-yl)thieno[3,2-*b*]thiophene

Crystal data

C<sub>25</sub>H<sub>16</sub>Br<sub>2</sub>S<sub>2</sub>

*M<sub>r</sub>* = 540.32

Triclinic, *P*1̄

*a* = 4.1522 (3) Å

*b* = 13.2861 (14) Å

*c* = 19.6117 (18) Å

α = 106.464 (9)°

β = 94.945 (7)°

γ = 93.016 (7)°

*V* = 1030.32 (16) Å<sup>3</sup>

*Z* = 2

*F*(000) = 536

*D<sub>x</sub>* = 1.742 Mg m<sup>-3</sup>

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 11208 reflections

θ = 3.2–29.0°

μ = 4.15 mm<sup>-1</sup>

*T* = 100 K

Prism, yellow

0.4 × 0.15 × 0.05 mm

Data collection

Agilent SuperNova diffractometer (Single source at offset, Eos detector)	$T_{\min} = 0.455$ , $T_{\max} = 1.000$ 20862 measured reflections 4207 independent reflections
Radiation source: SuperNova (Mo) X-ray Source	3705 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.043$
Mirror monochromator	$\theta_{\max} = 26.4^\circ$ , $\theta_{\min} = 3.1^\circ$
Detector resolution: 15.9631 pixels $\text{mm}^{-1}$	$h = -5 \rightarrow 5$
$\omega$ scans	$k = -16 \rightarrow 16$
Absorption correction: multi-scan ( <i>CrysAlis PRO</i> ; Agilent, 2012)	$l = -24 \rightarrow 24$

Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.028$	H-atom parameters constrained
$wR(F^2) = 0.074$	$w = 1/[\sigma^2(F_o^2) + (0.0365P)^2 + 0.857P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
4207 reflections	$(\Delta/\sigma)_{\max} = 0.001$
263 parameters	$\Delta\rho_{\max} = 0.65 \text{ e } \text{\AA}^{-3}$
0 restraints	$\Delta\rho_{\min} = -0.49 \text{ e } \text{\AA}^{-3}$
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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Br9	-0.35388 (6)	0.232660 (19)	0.371943 (13)	0.01906 (9)
Br10	0.39181 (6)	0.545455 (19)	0.192448 (12)	0.01776 (8)
C2	-0.1827 (6)	0.2195 (2)	0.23021 (13)	0.0158 (5)
C3	-0.1770 (6)	0.27901 (19)	0.30016 (13)	0.0154 (5)
C4	-0.0242 (6)	0.38101 (19)	0.31388 (13)	0.0158 (5)
C5	0.0795 (6)	0.4009 (2)	0.25420 (13)	0.0156 (5)
C7	0.2307 (6)	0.56396 (19)	0.33719 (13)	0.0153 (5)
C8	0.2226 (6)	0.5042 (2)	0.26721 (13)	0.0156 (5)
C11	-0.3148 (6)	0.1121 (2)	0.19773 (14)	0.0168 (5)
H11	-0.4334	0.0798	0.2263	0.020*
C12	-0.2850 (6)	0.0541 (2)	0.13097 (14)	0.0186 (5)
H12	-0.1671	0.0870	0.1026	0.022*
C13	-0.4148 (6)	-0.05453 (19)	0.09730 (13)	0.0156 (5)
C14	-0.5996 (6)	-0.1120 (2)	0.13151 (13)	0.0178 (5)
H14	-0.6502	-0.0792	0.1786	0.021*

C15	-0.7111 (7)	-0.2157 (2)	0.09825 (14)	0.0195 (6)
H15	-0.8339	-0.2533	0.1232	0.023*
C16	-0.6465 (6)	-0.26626 (19)	0.02888 (13)	0.0175 (5)
C17	-0.4658 (7)	-0.2095 (2)	-0.00600 (14)	0.0194 (6)
H17	-0.4201	-0.2421	-0.0535	0.023*
C18	-0.3510 (6)	-0.1059 (2)	0.02740 (13)	0.0184 (5)
H18	-0.2264	-0.0688	0.0025	0.022*
C19	-0.7751 (7)	-0.3789 (2)	-0.00734 (15)	0.0244 (6)
H19A	-0.7312	-0.4216	0.0253	0.037*
H19B	-0.6680	-0.4065	-0.0507	0.037*
H19C	-1.0095	-0.3819	-0.0201	0.037*
C20	0.3603 (6)	0.67262 (19)	0.37607 (13)	0.0153 (5)
C21	0.5603 (6)	0.6898 (2)	0.43878 (13)	0.0166 (5)
H21	0.6050	0.6320	0.4566	0.020*
C22	0.6998 (7)	0.7911 (2)	0.47697 (13)	0.0197 (6)
H22	0.8368	0.8010	0.5201	0.024*
C23	0.6391 (7)	0.8751 (2)	0.45228 (13)	0.0191 (6)
H23	0.7442	0.9425	0.4768	0.023*
C24	0.4210 (6)	0.8628 (2)	0.39039 (13)	0.0167 (5)
C25	0.2769 (6)	0.76085 (19)	0.35194 (13)	0.0146 (5)
C26	0.3404 (7)	0.9507 (2)	0.36704 (14)	0.0206 (6)
H26	0.4426	1.0184	0.3919	0.025*
C27	0.1192 (7)	0.9397 (2)	0.30972 (14)	0.0226 (6)
H27	0.0665	0.9995	0.2948	0.027*
C28	-0.0321 (7)	0.8394 (2)	0.27242 (14)	0.0213 (6)
H28	-0.1888	0.8319	0.2327	0.026*
C29	0.0448 (6)	0.7527 (2)	0.29288 (13)	0.0168 (5)
H29	-0.0594	0.6857	0.2670	0.020*
S1	-0.00132 (16)	0.29277 (5)	0.17990 (3)	0.01613 (14)
S6	0.05858 (16)	0.48915 (5)	0.38773 (3)	0.01611 (14)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br9	0.02471 (17)	0.01620 (14)	0.01796 (14)	0.00009 (11)	0.00276 (11)	0.00779 (10)
Br10	0.02196 (16)	0.01626 (14)	0.01408 (13)	-0.00284 (10)	0.00263 (10)	0.00339 (10)
C2	0.0156 (14)	0.0148 (12)	0.0180 (12)	0.0015 (10)	0.0012 (10)	0.0063 (10)
C3	0.0191 (14)	0.0136 (12)	0.0153 (12)	0.0022 (10)	0.0004 (10)	0.0072 (10)
C4	0.0173 (14)	0.0137 (12)	0.0160 (12)	0.0034 (10)	0.0007 (10)	0.0036 (10)
C5	0.0153 (13)	0.0151 (12)	0.0149 (12)	0.0024 (10)	-0.0002 (10)	0.0024 (10)
C7	0.0179 (14)	0.0131 (12)	0.0157 (12)	0.0014 (10)	0.0024 (10)	0.0055 (10)
C8	0.0173 (14)	0.0155 (12)	0.0145 (12)	0.0008 (10)	0.0000 (10)	0.0057 (10)
C11	0.0152 (13)	0.0156 (13)	0.0207 (13)	0.0004 (10)	-0.0012 (10)	0.0080 (10)
C12	0.0181 (14)	0.0175 (13)	0.0207 (13)	-0.0003 (11)	0.0004 (11)	0.0074 (11)
C13	0.0149 (13)	0.0137 (12)	0.0172 (12)	0.0019 (10)	-0.0019 (10)	0.0038 (10)
C14	0.0219 (15)	0.0158 (13)	0.0151 (12)	0.0024 (11)	0.0008 (10)	0.0035 (10)
C15	0.0233 (15)	0.0157 (13)	0.0207 (13)	-0.0015 (11)	0.0004 (11)	0.0085 (10)
C16	0.0179 (14)	0.0136 (12)	0.0188 (13)	0.0026 (10)	-0.0038 (10)	0.0026 (10)

C17	0.0231 (15)	0.0168 (13)	0.0169 (12)	0.0031 (11)	0.0014 (11)	0.0027 (10)
C18	0.0212 (15)	0.0178 (13)	0.0167 (12)	-0.0009 (11)	0.0026 (10)	0.0060 (10)
C19	0.0283 (16)	0.0137 (13)	0.0272 (14)	-0.0012 (12)	-0.0017 (12)	0.0016 (11)
C20	0.0171 (14)	0.0135 (12)	0.0138 (12)	0.0009 (10)	0.0054 (10)	0.0006 (10)
C21	0.0196 (14)	0.0164 (13)	0.0146 (12)	0.0046 (11)	0.0036 (10)	0.0049 (10)
C22	0.0197 (15)	0.0226 (14)	0.0133 (12)	0.0017 (11)	0.0008 (10)	-0.0001 (10)
C23	0.0191 (14)	0.0167 (13)	0.0174 (12)	-0.0044 (11)	0.0027 (10)	-0.0007 (10)
C24	0.0176 (14)	0.0154 (13)	0.0165 (12)	0.0015 (10)	0.0073 (10)	0.0018 (10)
C25	0.0163 (13)	0.0139 (12)	0.0137 (11)	0.0011 (10)	0.0045 (10)	0.0032 (10)
C26	0.0264 (16)	0.0147 (13)	0.0200 (13)	-0.0010 (11)	0.0113 (11)	0.0017 (10)
C27	0.0306 (17)	0.0181 (14)	0.0247 (14)	0.0087 (12)	0.0123 (12)	0.0114 (11)
C28	0.0217 (15)	0.0247 (14)	0.0199 (13)	0.0058 (12)	0.0058 (11)	0.0087 (11)
C29	0.0172 (14)	0.0170 (13)	0.0152 (12)	0.0002 (10)	0.0027 (10)	0.0032 (10)
S1	0.0215 (4)	0.0124 (3)	0.0129 (3)	-0.0017 (2)	0.0003 (2)	0.0019 (2)
S6	0.0227 (4)	0.0121 (3)	0.0129 (3)	0.0009 (3)	0.0025 (2)	0.0026 (2)

*Geometric parameters (Å, °)*

Br9—C3	1.877 (2)	C17—H17	0.9500
Br10—C8	1.880 (2)	C17—C18	1.385 (4)
C2—C3	1.373 (3)	C18—H18	0.9500
C2—C11	1.445 (4)	C19—H19A	0.9800
C2—S1	1.756 (3)	C19—H19B	0.9800
C3—C4	1.409 (4)	C19—H19C	0.9800
C4—C5	1.369 (4)	C20—C21	1.378 (4)
C4—S6	1.721 (2)	C20—C25	1.431 (3)
C5—C8	1.412 (4)	C21—H21	0.9500
C5—S1	1.726 (2)	C21—C22	1.407 (4)
C7—C8	1.373 (3)	C22—H22	0.9500
C7—C20	1.476 (3)	C22—C23	1.363 (4)
C7—S6	1.757 (3)	C23—H23	0.9500
C11—H11	0.9500	C23—C24	1.415 (4)
C11—C12	1.338 (4)	C24—C25	1.421 (3)
C12—H12	0.9500	C24—C26	1.415 (4)
C12—C13	1.458 (4)	C25—C29	1.417 (4)
C13—C14	1.393 (4)	C26—H26	0.9500
C13—C18	1.402 (3)	C26—C27	1.358 (4)
C14—H14	0.9500	C27—H27	0.9500
C14—C15	1.382 (4)	C27—C28	1.409 (4)
C15—H15	0.9500	C28—H28	0.9500
C15—C16	1.392 (4)	C28—C29	1.367 (4)
C16—C17	1.386 (4)	C29—H29	0.9500
C16—C19	1.510 (3)		
C3—C2—C11	128.2 (2)	C17—C18—C13	121.3 (2)
C3—C2—S1	110.50 (19)	C17—C18—H18	119.3
C11—C2—S1	121.31 (19)	C16—C19—H19A	109.5
C2—C3—Br9	124.7 (2)	C16—C19—H19B	109.5

C2—C3—C4	113.3 (2)	C16—C19—H19C	109.5
C4—C3—Br9	122.04 (18)	H19A—C19—H19B	109.5
C3—C4—S6	135.5 (2)	H19A—C19—H19C	109.5
C5—C4—C3	113.2 (2)	H19B—C19—H19C	109.5
C5—C4—S6	111.3 (2)	C21—C20—C7	118.8 (2)
C4—C5—C8	113.4 (2)	C21—C20—C25	119.0 (2)
C4—C5—S1	111.6 (2)	C25—C20—C7	122.1 (2)
C8—C5—S1	135.0 (2)	C20—C21—H21	119.3
C8—C7—C20	133.1 (2)	C20—C21—C22	121.4 (2)
C8—C7—S6	109.98 (19)	C22—C21—H21	119.3
C20—C7—S6	116.85 (18)	C21—C22—H22	119.9
C5—C8—Br10	119.77 (18)	C23—C22—C21	120.2 (2)
C7—C8—Br10	126.8 (2)	C23—C22—H22	119.9
C7—C8—C5	113.4 (2)	C22—C23—H23	119.7
C2—C11—H11	117.1	C22—C23—C24	120.6 (2)
C12—C11—C2	125.8 (2)	C24—C23—H23	119.7
C12—C11—H11	117.1	C23—C24—C25	119.4 (2)
C11—C12—H12	116.7	C23—C24—C26	120.9 (2)
C11—C12—C13	126.6 (2)	C26—C24—C25	119.6 (2)
C13—C12—H12	116.7	C24—C25—C20	119.1 (2)
C14—C13—C12	123.2 (2)	C29—C25—C20	123.1 (2)
C14—C13—C18	117.2 (2)	C29—C25—C24	117.7 (2)
C18—C13—C12	119.6 (2)	C24—C26—H26	119.5
C13—C14—H14	119.4	C27—C26—C24	121.0 (3)
C15—C14—C13	121.3 (2)	C27—C26—H26	119.5
C15—C14—H14	119.4	C26—C27—H27	120.1
C14—C15—H15	119.4	C26—C27—C28	119.8 (3)
C14—C15—C16	121.2 (2)	C28—C27—H27	120.1
C16—C15—H15	119.4	C27—C28—H28	119.7
C15—C16—C19	120.7 (2)	C29—C28—C27	120.6 (3)
C17—C16—C15	118.0 (2)	C29—C28—H28	119.7
C17—C16—C19	121.3 (2)	C25—C29—H29	119.4
C16—C17—H17	119.5	C28—C29—C25	121.2 (2)
C18—C17—C16	121.0 (2)	C28—C29—H29	119.4
C18—C17—H17	119.5	C5—S1—C2	91.37 (12)
C13—C18—H18	119.3	C4—S6—C7	91.93 (12)
Br9—C3—C4—C5	-178.01 (19)	C18—C13—C14—C15	0.9 (4)
Br9—C3—C4—S6	0.4 (4)	C19—C16—C17—C18	179.5 (3)
C2—C3—C4—C5	1.7 (3)	C20—C7—C8—Br10	0.5 (5)
C2—C3—C4—S6	-179.9 (2)	C20—C7—C8—C5	178.2 (3)
C2—C11—C12—C13	179.7 (2)	C20—C7—S6—C4	-178.9 (2)
C3—C2—C11—C12	-172.7 (3)	C20—C21—C22—C23	-0.1 (4)
C3—C2—S1—C5	0.4 (2)	C20—C25—C29—C28	178.8 (2)
C3—C4—C5—C8	177.9 (2)	C21—C20—C25—C24	4.6 (4)
C3—C4—C5—S1	-1.4 (3)	C21—C20—C25—C29	-172.6 (2)
C3—C4—S6—C7	-177.5 (3)	C21—C22—C23—C24	3.7 (4)
C4—C5—C8—Br10	178.14 (19)	C22—C23—C24—C25	-3.0 (4)



C4—C5—C8—C7	0.3 (3)	C22—C23—C24—C26	175.9 (2)
C4—C5—S1—C2	0.6 (2)	C23—C24—C25—C20	-1.1 (4)
C5—C4—S6—C7	0.9 (2)	C23—C24—C25—C29	176.2 (2)
C7—C20—C21—C22	177.9 (2)	C23—C24—C26—C27	-176.8 (2)
C7—C20—C25—C24	-177.4 (2)	C24—C25—C29—C28	1.6 (4)
C7—C20—C25—C29	5.4 (4)	C24—C26—C27—C28	-0.4 (4)
C8—C5—S1—C2	-178.5 (3)	C25—C20—C21—C22	-4.1 (4)
C8—C7—C20—C21	-129.6 (3)	C25—C24—C26—C27	2.1 (4)
C8—C7—C20—C25	52.4 (4)	C26—C24—C25—C20	180.0 (2)
C8—C7—S6—C4	-0.8 (2)	C26—C24—C25—C29	-2.7 (4)
C11—C2—C3—Br9	-1.2 (4)	C26—C27—C28—C29	-0.8 (4)
C11—C2—C3—C4	179.2 (2)	C27—C28—C29—C25	0.1 (4)
C11—C2—S1—C5	-180.0 (2)	S1—C2—C3—Br9	178.49 (14)
C11—C12—C13—C14	1.7 (4)	S1—C2—C3—C4	-1.2 (3)
C11—C12—C13—C18	-177.5 (3)	S1—C2—C11—C12	7.7 (4)
C12—C13—C14—C15	-178.3 (3)	S1—C5—C8—Br10	-2.8 (4)
C12—C13—C18—C17	179.0 (2)	S1—C5—C8—C7	179.4 (2)
C13—C14—C15—C16	-0.9 (4)	S6—C4—C5—C8	-0.9 (3)
C14—C13—C18—C17	-0.3 (4)	S6—C4—C5—S1	179.81 (13)
C14—C15—C16—C17	0.2 (4)	S6—C7—C8—Br10	-177.24 (15)
C14—C15—C16—C19	-178.8 (2)	S6—C7—C8—C5	0.4 (3)
C15—C16—C17—C18	0.5 (4)	S6—C7—C20—C21	48.1 (3)
C16—C17—C18—C13	-0.4 (4)	S6—C7—C20—C25	-129.9 (2)

**(III) 3,6-Dibromo-2-(4-*tert*-butylphenyl)-5-(4-methylstyryl)thieno[3,2-*b*]thiophene***Crystal data*C<sub>25</sub>H<sub>22</sub>Br<sub>2</sub>S<sub>2</sub> $M_r = 546.37$ Triclinic,  $P\bar{1}$  $a = 9.5401$  (12) Å $b = 10.1575$  (17) Å $c = 12.1711$  (16) Å $\alpha = 106.933$  (13)° $\beta = 98.599$  (11)° $\gamma = 92.192$  (13)° $V = 1111.4$  (3) Å<sup>3</sup> $Z = 2$  $F(000) = 548$  $D_x = 1.633$  Mg m<sup>-3</sup>Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 12025 reflections

 $\theta = 3.1$ – $29.1$ ° $\mu = 3.85$  mm<sup>-1</sup> $T = 100$  K

Block, yellow

 $0.35 \times 0.3 \times 0.15$  mm*Data collection*

Agilent SuperNova

diffractometer (Single source at offset, Eos detector)

Radiation source: SuperNova (Mo) X-ray

Source

Mirror monochromator

Detector resolution: 15.9631 pixels mm<sup>-1</sup> $\omega$  scans

Absorption correction: multi-scan

(CrysAlis PRO; Agilent, 2012)

 $T_{\min} = 0.621$ ,  $T_{\max} = 1.000$ 

22740 measured reflections

4543 independent reflections

4106 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.029$  $\theta_{\text{max}} = 26.4$ °,  $\theta_{\text{min}} = 2.9$ ° $h = -11$ → $11$  $k = -12$ → $12$  $l = -15$ → $15$

Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.024$   
 $wR(F^2) = 0.063$   
 $S = 1.05$   
 4543 reflections  
 266 parameters  
 0 restraints  
 Primary atom site location: structure-invariant  
 direct methods

Secondary atom site location: difference Fourier  
 map  
 Hydrogen site location: inferred from  
 neighbouring sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0284P)^2 + 1.021P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.86 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.34 \text{ e } \text{\AA}^{-3}$

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.

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

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
C2	0.1667 (2)	0.4087 (2)	0.52334 (18)	0.0149 (4)
C3	0.2415 (2)	0.5007 (2)	0.48676 (17)	0.0140 (4)
C4	0.3487 (2)	0.5848 (2)	0.57443 (18)	0.0135 (4)
C5	0.3561 (2)	0.5556 (2)	0.67867 (18)	0.0149 (4)
C7	0.5323 (2)	0.7369 (2)	0.73035 (17)	0.0134 (4)
C8	0.4616 (2)	0.6421 (2)	0.76726 (18)	0.0156 (4)
C11	0.0485 (2)	0.3098 (2)	0.45728 (18)	0.0154 (4)
H11	0.0143	0.3096	0.3798	0.018*
C12	-0.0158 (2)	0.2188 (2)	0.49791 (19)	0.0163 (4)
H12	0.0209	0.2196	0.5751	0.020*
C13	-0.1367 (2)	0.1182 (2)	0.43625 (18)	0.0147 (4)
C14	-0.1847 (2)	0.0836 (2)	0.31652 (19)	0.0184 (4)
H14	-0.1379	0.1268	0.2708	0.022*
C15	-0.2997 (2)	-0.0127 (2)	0.2636 (2)	0.0195 (4)
H15	-0.3298	-0.0352	0.1818	0.023*
C16	-0.3721 (2)	-0.0775 (2)	0.3276 (2)	0.0188 (4)
C17	-0.3245 (2)	-0.0435 (2)	0.4464 (2)	0.0222 (5)
H17	-0.3719	-0.0862	0.4921	0.027*
C18	-0.2088 (2)	0.0521 (2)	0.4994 (2)	0.0212 (5)
H18	-0.1778	0.0731	0.5810	0.025*
C19	-0.4989 (2)	-0.1807 (2)	0.2693 (2)	0.0257 (5)
H19A	-0.4753	-0.2481	0.2001	0.039*
H19B	-0.5798	-0.1324	0.2460	0.039*
H19C	-0.5240	-0.2286	0.3238	0.039*
C20	0.6407 (2)	0.8514 (2)	0.79371 (18)	0.0144 (4)

C21	0.6309 (2)	0.9344 (2)	0.90533 (19)	0.0204 (5)
H21	0.5599	0.9103	0.9448	0.024*
C22	0.7237 (2)	1.0518 (2)	0.95947 (19)	0.0222 (5)
H22	0.7145	1.1068	1.0355	0.027*
C23	0.8300 (2)	1.0912 (2)	0.90537 (18)	0.0156 (4)
C24	0.8424 (2)	1.0043 (2)	0.79612 (19)	0.0174 (4)
H24	0.9167	1.0255	0.7584	0.021*
C25	0.7490 (2)	0.8872 (2)	0.74042 (18)	0.0159 (4)
H25	0.7595	0.8311	0.6651	0.019*
C26	0.9213 (2)	1.2294 (2)	0.95810 (19)	0.0181 (4)
C27	0.9335 (4)	1.2808 (3)	1.0898 (2)	0.0466 (8)
H27A	0.9785	1.2132	1.1237	0.070*
H27B	0.8384	1.2928	1.1104	0.070*
H27C	0.9915	1.3694	1.1202	0.070*
C28	0.8494 (3)	1.3340 (3)	0.9067 (3)	0.0412 (7)
H28A	0.7556	1.3468	0.9300	0.062*
H28B	0.8382	1.3003	0.8216	0.062*
H28C	0.9080	1.4224	0.9354	0.062*
C29	1.0711 (3)	1.2170 (3)	0.9299 (4)	0.0579 (10)
H29A	1.0672	1.1951	0.8455	0.087*
H29B	1.1139	1.1432	0.9567	0.087*
H29C	1.1288	1.3046	0.9692	0.087*
S1	0.23075 (6)	0.42387 (5)	0.66948 (5)	0.01670 (11)
S6	0.47053 (5)	0.71827 (5)	0.58407 (4)	0.01402 (11)
Br9	0.21007 (2)	0.51931 (2)	0.336305 (17)	0.01818 (7)
Br10	0.50454 (2)	0.61519 (2)	0.914456 (19)	0.02445 (7)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C2	0.0146 (10)	0.0139 (10)	0.0142 (10)	0.0029 (8)	0.0000 (8)	0.0020 (8)
C3	0.0143 (10)	0.0134 (10)	0.0127 (10)	0.0033 (8)	0.0010 (8)	0.0017 (8)
C4	0.0133 (10)	0.0115 (10)	0.0152 (10)	0.0006 (8)	0.0021 (8)	0.0035 (8)
C5	0.0145 (10)	0.0117 (10)	0.0172 (10)	-0.0016 (8)	-0.0002 (8)	0.0041 (8)
C7	0.0139 (10)	0.0134 (10)	0.0116 (10)	0.0015 (8)	0.0000 (8)	0.0028 (8)
C8	0.0163 (10)	0.0151 (10)	0.0139 (10)	-0.0002 (8)	-0.0004 (8)	0.0037 (8)
C11	0.0136 (10)	0.0144 (10)	0.0153 (10)	0.0008 (8)	-0.0001 (8)	0.0014 (8)
C12	0.0142 (10)	0.0162 (10)	0.0169 (10)	0.0008 (8)	-0.0007 (8)	0.0040 (8)
C13	0.0114 (9)	0.0123 (10)	0.0196 (11)	0.0010 (8)	0.0006 (8)	0.0047 (8)
C14	0.0169 (10)	0.0193 (11)	0.0194 (11)	-0.0012 (8)	0.0052 (9)	0.0056 (9)
C15	0.0165 (10)	0.0220 (11)	0.0180 (11)	0.0020 (9)	0.0011 (9)	0.0038 (9)
C16	0.0136 (10)	0.0130 (10)	0.0277 (12)	0.0001 (8)	-0.0021 (9)	0.0056 (9)
C17	0.0197 (11)	0.0218 (12)	0.0281 (12)	-0.0051 (9)	0.0007 (9)	0.0148 (10)
C18	0.0213 (11)	0.0228 (12)	0.0200 (11)	-0.0029 (9)	-0.0024 (9)	0.0106 (9)
C19	0.0183 (11)	0.0216 (12)	0.0340 (14)	-0.0050 (9)	-0.0050 (10)	0.0089 (10)
C20	0.0142 (10)	0.0108 (10)	0.0165 (10)	0.0000 (8)	-0.0026 (8)	0.0044 (8)
C21	0.0197 (11)	0.0212 (11)	0.0189 (11)	-0.0052 (9)	0.0042 (9)	0.0044 (9)
C22	0.0263 (12)	0.0196 (11)	0.0159 (11)	-0.0062 (9)	0.0024 (9)	-0.0006 (9)

C23	0.0140 (10)	0.0130 (10)	0.0188 (11)	-0.0020 (8)	-0.0041 (8)	0.0067 (8)
C24	0.0121 (10)	0.0211 (11)	0.0203 (11)	-0.0015 (8)	0.0004 (8)	0.0097 (9)
C25	0.0158 (10)	0.0168 (10)	0.0135 (10)	0.0011 (8)	0.0009 (8)	0.0030 (8)
C26	0.0176 (10)	0.0147 (10)	0.0189 (11)	-0.0047 (8)	-0.0043 (8)	0.0046 (9)
C27	0.067 (2)	0.0429 (17)	0.0190 (13)	-0.0359 (15)	-0.0120 (13)	0.0069 (12)
C28	0.0457 (16)	0.0207 (13)	0.0498 (18)	-0.0154 (11)	-0.0257 (14)	0.0181 (12)
C29	0.0241 (14)	0.0310 (16)	0.100 (3)	-0.0138 (12)	0.0164 (16)	-0.0096 (17)
S1	0.0181 (3)	0.0153 (3)	0.0159 (3)	-0.0056 (2)	-0.0012 (2)	0.0062 (2)
S6	0.0145 (2)	0.0134 (2)	0.0135 (2)	-0.00256 (19)	0.00064 (19)	0.00445 (19)
Br9	0.02011 (12)	0.02063 (12)	0.01261 (11)	-0.00192 (8)	-0.00041 (8)	0.00521 (8)
Br10	0.03123 (14)	0.02441 (13)	0.01642 (12)	-0.01005 (9)	-0.00648 (9)	0.01090 (9)

*Geometric parameters (Å, °)*

C2—C3	1.367 (3)	C18—H18	0.9500
C2—C11	1.449 (3)	C19—H19A	0.9800
C2—S1	1.752 (2)	C19—H19B	0.9800
C3—C4	1.410 (3)	C19—H19C	0.9800
C3—Br9	1.876 (2)	C20—C21	1.393 (3)
C4—C5	1.377 (3)	C20—C25	1.389 (3)
C4—S6	1.717 (2)	C21—H21	0.9500
C5—C8	1.415 (3)	C21—C22	1.389 (3)
C5—S1	1.727 (2)	C22—H22	0.9500
C7—C8	1.371 (3)	C22—C23	1.394 (3)
C7—C20	1.471 (3)	C23—C24	1.390 (3)
C7—S6	1.742 (2)	C23—C26	1.535 (3)
C8—Br10	1.878 (2)	C24—H24	0.9500
C11—H11	0.9500	C24—C25	1.392 (3)
C11—C12	1.337 (3)	C25—H25	0.9500
C12—H12	0.9500	C26—C27	1.519 (3)
C12—C13	1.463 (3)	C26—C28	1.518 (3)
C13—C14	1.395 (3)	C26—C29	1.521 (3)
C13—C18	1.393 (3)	C27—H27A	0.9800
C14—H14	0.9500	C27—H27B	0.9800
C14—C15	1.384 (3)	C27—H27C	0.9800
C15—H15	0.9500	C28—H28A	0.9800
C15—C16	1.394 (3)	C28—H28B	0.9800
C16—C17	1.385 (3)	C28—H28C	0.9800
C16—C19	1.509 (3)	C29—H29A	0.9800
C17—H17	0.9500	C29—H29B	0.9800
C17—C18	1.385 (3)	C29—H29C	0.9800
C3—C2—C11	127.97 (19)	H19A—C19—H19C	109.5
C3—C2—S1	110.83 (15)	H19B—C19—H19C	109.5
C11—C2—S1	121.19 (16)	C21—C20—C7	120.91 (19)
C2—C3—C4	113.44 (19)	C25—C20—C7	120.93 (19)
C2—C3—Br9	125.30 (16)	C25—C20—C21	117.95 (19)
C4—C3—Br9	121.26 (15)	C20—C21—H21	119.6

C3—C4—S6	135.45 (16)	C22—C21—C20	120.7 (2)
C5—C4—C3	112.85 (18)	C22—C21—H21	119.6
C5—C4—S6	111.68 (16)	C21—C22—H22	119.1
C4—C5—C8	112.77 (18)	C21—C22—C23	121.8 (2)
C4—C5—S1	111.53 (16)	C23—C22—H22	119.1
C8—C5—S1	135.68 (17)	C22—C23—C26	122.09 (19)
C8—C7—C20	131.33 (19)	C24—C23—C22	116.81 (19)
C8—C7—S6	111.14 (15)	C24—C23—C26	120.91 (19)
C20—C7—S6	117.42 (15)	C23—C24—H24	119.1
C5—C8—Br10	121.61 (15)	C23—C24—C25	121.86 (19)
C7—C8—C5	112.82 (19)	C25—C24—H24	119.1
C7—C8—Br10	125.41 (16)	C20—C25—C24	120.8 (2)
C2—C11—H11	117.8	C20—C25—H25	119.6
C12—C11—C2	124.5 (2)	C24—C25—H25	119.6
C12—C11—H11	117.8	C27—C26—C23	111.81 (18)
C11—C12—H12	116.5	C27—C26—C29	107.7 (2)
C11—C12—C13	127.0 (2)	C28—C26—C23	107.46 (18)
C13—C12—H12	116.5	C28—C26—C27	108.8 (2)
C14—C13—C12	123.75 (19)	C28—C26—C29	109.7 (2)
C18—C13—C12	118.85 (19)	C29—C26—C23	111.25 (19)
C18—C13—C14	117.39 (19)	C26—C27—H27A	109.5
C13—C14—H14	119.6	C26—C27—H27B	109.5
C15—C14—C13	120.8 (2)	C26—C27—H27C	109.5
C15—C14—H14	119.6	H27A—C27—H27B	109.5
C14—C15—H15	119.3	H27A—C27—H27C	109.5
C14—C15—C16	121.5 (2)	H27B—C27—H27C	109.5
C16—C15—H15	119.3	C26—C28—H28A	109.5
C15—C16—C19	121.0 (2)	C26—C28—H28B	109.5
C17—C16—C15	117.8 (2)	C26—C28—H28C	109.5
C17—C16—C19	121.1 (2)	H28A—C28—H28B	109.5
C16—C17—H17	119.6	H28A—C28—H28C	109.5
C18—C17—C16	120.8 (2)	H28B—C28—H28C	109.5
C18—C17—H17	119.6	C26—C29—H29A	109.5
C13—C18—H18	119.2	C26—C29—H29B	109.5
C17—C18—C13	121.7 (2)	C26—C29—H29C	109.5
C17—C18—H18	119.2	H29A—C29—H29B	109.5
C16—C19—H19A	109.5	H29A—C29—H29C	109.5
C16—C19—H19B	109.5	H29B—C29—H29C	109.5
C16—C19—H19C	109.5	C5—S1—C2	91.35 (10)
H19A—C19—H19B	109.5	C4—S6—C7	91.58 (10)
C2—C3—C4—C5	0.4 (3)	C19—C16—C17—C18	-179.5 (2)
C2—C3—C4—S6	-177.73 (17)	C20—C7—C8—C5	175.1 (2)
C2—C11—C12—C13	179.0 (2)	C20—C7—C8—Br10	-9.6 (3)
C3—C2—C11—C12	177.1 (2)	C20—C7—S6—C4	-175.85 (16)
C3—C2—S1—C5	0.59 (16)	C20—C21—C22—C23	-0.3 (4)
C3—C4—C5—C8	-178.68 (17)	C21—C20—C25—C24	-1.5 (3)
C3—C4—C5—S1	0.1 (2)	C21—C22—C23—C24	-2.4 (3)

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C3—C4—S6—C7	177.8 (2)	C21—C22—C23—C26	172.5 (2)
C4—C5—C8—C7	0.7 (3)	C22—C23—C24—C25	3.1 (3)
C4—C5—C8—Br10	-174.92 (15)	C22—C23—C26—C27	26.8 (3)
C4—C5—S1—C2	-0.36 (17)	C22—C23—C26—C28	-92.6 (3)
C5—C4—S6—C7	-0.38 (17)	C22—C23—C26—C29	147.3 (3)
C7—C20—C21—C22	-172.5 (2)	C23—C24—C25—C20	-1.2 (3)
C7—C20—C25—C24	173.19 (19)	C24—C23—C26—C27	-158.5 (2)
C8—C5—S1—C2	178.0 (2)	C24—C23—C26—C28	82.1 (3)
C8—C7—C20—C21	-40.0 (3)	C24—C23—C26—C29	-38.0 (3)
C8—C7—C20—C25	145.4 (2)	C25—C20—C21—C22	2.2 (3)
C8—C7—S6—C4	0.75 (16)	C26—C23—C24—C25	-171.87 (19)
C11—C2—C3—C4	178.58 (19)	S1—C2—C3—C4	-0.7 (2)
C11—C2—C3—Br9	-1.3 (3)	S1—C2—C3—Br9	179.46 (11)
C11—C2—S1—C5	-178.72 (17)	S1—C2—C11—C12	-3.7 (3)
C11—C12—C13—C14	13.6 (3)	S1—C5—C8—C7	-177.65 (18)
C11—C12—C13—C18	-166.6 (2)	S1—C5—C8—Br10	6.8 (3)
C12—C13—C14—C15	179.9 (2)	S6—C4—C5—C8	-0.1 (2)
C12—C13—C18—C17	179.6 (2)	S6—C4—C5—S1	178.65 (10)
C13—C14—C15—C16	0.6 (3)	S6—C7—C8—C5	-0.9 (2)
C14—C13—C18—C17	-0.6 (3)	S6—C7—C8—Br10	174.46 (12)
C14—C15—C16—C17	-0.7 (3)	S6—C7—C20—C21	135.75 (18)
C14—C15—C16—C19	179.0 (2)	S6—C7—C20—C25	-38.8 (3)
C15—C16—C17—C18	0.1 (3)	Br9—C3—C4—C5	-179.72 (15)
C16—C17—C18—C13	0.5 (4)	Br9—C3—C4—S6	2.1 (3)
C18—C13—C14—C15	0.0 (3)		

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