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# Investigating intermolecular bonding in diphenylbismuth(III) chalcogenolates: X-ray crystal structures of (Ph<sub>2</sub>BiSR') (R' = Ph; 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)

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# ABSTRACT

The reaction of Ph<sub>2</sub>BiCl with (PhS)Li or (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>S)Li yielded [Ph<sub>2</sub>BiSPh]<sub>∞</sub> (**7**) or Ph<sub>2</sub>BiS(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)] (**8**), respectively. Both compounds have been characterized by elemental analysis, melting point, FT-IR, FT-Raman, solution <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR, and X-ray crystallography. The solid-state structure of **7** is polymeric via long intermolecular Bi···S interactions and  $\mu$ -SPh groups, yielding a distorted  $\psi$ -trigonal bipyramidal C<sub>2</sub>S<sub>2</sub> bonding environment for bismuth. Increasing steric bulk at the phenyl thiolate ligand in **8** results in the isolation of a monomeric species, which exhibits a distorted  $\psi$ -tetrahedral C<sub>2</sub>S bonding environment for bismuth. Comparison to previously reported structures of diorganobismuth chalcogenolates shows the effect of altering the chalcogen on intermolecular Bi···E (E = O, S, Se) bond formation. DFT calculations are employed to rationalize the bonding environments at bismuth and the observed polymeric structures. This work represents the first examples of structurally characterized R<sub>2</sub>BiSR' species and advances our understanding of intermolecular bonding in bismuth chalcogenolates.

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# 1. Introduction

There has been increasing interest in heavier main group element compounds as synthons for supramolecular systems, due to their tendency to form strong, reversible and directional secondary bonding interactions [1]. For example, bismuth chalcogenolates  $[(RE)_3Bi]_n$  exhibit extensive intermolecular Bi...E bonding (E = O, S, Se) in the solid-state, which typically results in high coordination numbers for bismuth and complex polymeric structures [2–5]. Diorganobismuth chalcogenolates ( $[R_2BiER']_n$ ) (E = O, S, Se) are excellent candidates for investigating Bi ... E bonding interactions, as they provide individual molecular Bi-E units and limited intermolecular bonding as compared to tris-chalcogenolate species. Structural characterization of diorganobismuth alkoxides  $(R_2BiOR')$  [Et<sub>2</sub>BiOPh]<sub> $\infty$ </sub> (1), [Et<sub>2</sub>BiO(C<sub>6</sub>F<sub>5</sub>)]<sub> $\infty$ </sub> (2) [6], [Ph<sub>2</sub>BiOEt]<sub> $\infty$ </sub> (3) [7],  $[Me_2BiOMe]_{\infty}$  (4) [8] and  $[(o-tolyl)_2BiOMe]_{\infty}$  (5) [9] has revealed strong intermolecular Bi...O interactions and polymeric structures. With respect to heavier chalcogen analogs (i.e.  $[R_2BiER']_n$  where E = S or Se), the only structurally characterized example is Ph<sub>2</sub>BiSePh (**6**) [10], which is essentially monomeric in the solid-state and exhibits no Bi...Se intermolecular interactions. Although lower melting points for thiolate versus alkoxide derivatives [11] suggest weak intermolecular bonding interactions in the solid-state, no simple R<sub>2</sub>BiSR' species have been structurally characterized. In this context, we now report the preparation and structural characterization of  $[Ph_2BiSPh]_{\infty}$  (7) and  $Ph_2BiS(2,6-Me_2C_6H_3)$  (8) for comparison of intermolecular Bi $\cdots$ E bonding properties to those of  $[R_2BiER']_n$  (E = O, Se) species 1–6. Further, we have performed DFT calculations of  $Ph_2BiEPh$  (E = O, S, Se) and  $Ph_2BiS(2,6-Me_2C_6H_3)$  to investigate intramolecular Bi–E and intermolecular Bi $\cdots$ E bonding in bismuth chalcogenolate compounds.





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# 2. Results and discussion

# 2.1. Syntheses

The reaction of Ph<sub>2</sub>BiCl with (PhS)Li or  $(2,6-Me_2C_6H_3S)Li$  resulted in an immediate yellow colored reaction mixture, indicative of the formation of a bismuth thiolate. Both reactions were complete within three hours as determined via <sup>1</sup>H NMR spectra of reaction mixture. Crystalline products were isolated from reaction mixture (**8**) or after removal of the reaction solvent and extraction into methanol (**7**). Reported yields are for isolated crystalline materials. Attempts to prepare Ph<sub>2</sub>BiTePh via the reaction of Ph<sub>2</sub>BiCl and PhTeLi at low temperature resulted in the precipitation of elemental tellurium upon warming of the reaction mixture to room temperature [5].

#### 2.2. X-ray crystal structures

Crystals suitable for X-ray crystallography were isolated from methanol at 4 °C (**7**), or by the slow evaporation of the thf reaction mixture at 23 °C (**8**). Selected bond distances and angles are given in Table 1.

The crystal structure of  $[Ph_2BiSPh]_{\infty}$  (7) (Fig. 1) shows the compound to be a zig–zag polymer in the solid-state via bridging  $\mu$ -SPh groups, giving a four coordinate  $C_2S_2$  bonding environment and a distorted disphenoidal geometry at bismuth. If the stereochemically active lone pair is considered, the metal bonding environment is  $\psi$ -trigonal bipyramidal, with the two thiolate sulfur atoms in

 Table 1

 Selected bond distances (Å) and angles (deg) for 6–7.

	6	7
Bi1-C1	2.248(5)	2.262(4)
Bi1-C7	2.248(5)	2.245(4)
Bi1-S1	2.588(1)	2.545(1)
Bi1-S1*	3.309(1)	
C1-Bi1-C7	94.0(2)	92.6(2)
C1-Bi1-S1	82.8(1)	92.2(1)
C7-Bi1-S1	95.4(2)	96.1(1)
C13-S1-Bi1	107.8(2)	98.3(1)
S1-Bi1-S1*	154.98(4)	
Bi1-S1-Bi1*	116.42(5)	
C1-Bi-S-C13	170.1(2)	-142.9(2)
C7-Bi-S-C13	-96.5(2)	124.3(2)



**Fig. 1.** X-ray structure of **7** (30% probability ellipsoids). Hydrogen atoms are not shown for clarity. Symmetry transformations used to generate equivalent atoms: (\*) x - 0.5, -y + 1.5, -z; (\*\*) x + 0.5, -y + 1.5, -z.

axial positions  $[S1-Bi-S1^* = 154.98(4)^\circ]$ , and the two phenyl carbon atoms  $[C1-Bi-C7 = 93.99(20)^\circ]$  and the lone pair in equatorial positions. The Bi–C bond distances [Bi-C1 = 2.249(5) Å], Bi-C7 = 2.248(5) Å] are similar to those in other  $-BiPh_2$  compounds [2.24(5)-2.27 (2) Å] [12]. The Bi–S1 bond distance [2.588(1) Å] is within the range reported for other bismuth arylthiolates [2.55(2)-2.634(5)] [13,14], while the Bi–S1\* bond distance is significantly longer [3.309(1) Å]. The latter is, however, within the sum of the van der Waals radii of Bi and S (~3.8 Å) [15], and similar to intermolecular Bi···S contacts found in  $[(RS)_3Bi]_n$  compounds [3.323(2)-3.583(1) Å] [3,16]. The two phenyl rings on bismuth are near perpendicular to one another, and are rotated such that one [C1-C6] is nearly coplanar with the phenyl ring [C13-C18] of the more closely bonded thiolate group.

Unlike **7**, the structure of Ph<sub>2</sub>BiS(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (**8**) (Fig. 2) shows the compound to be monomeric in the solid-state. The nearest Bi···S1\* intermolecular contact in **8** is 3.940(2) Å, which is outside of the sum of the van der Waals radii of Bi and S, and there is a different packing arrangement of the molecules as compared to **7**. This results in a three-coordinate C<sub>2</sub>S bonding environment and a distorted  $\psi$ -tetrahedral geometry at bismuth [sum of angles ~281°]. The Bi-C bond distances [Bi-C1 = 2.262(4) Å; Bi-C7 = 2.245(5) Å] are similar to those in **7**. The Bi-S1 distance [2.544(2) Å] is significantly shorter, and at the low. This is presumably due to the lower coordination number of bismuth and the absence of the *trans* influence of S1\*, as observed in **7** (*vide infra*). Comparison of the Bi-S-C bond angles in **7** and **8** shows the former to be much larger [**7**: Bi1-S1-C13 = 107.8(2)°; **8**: Bi1-S1-C13 = 98.3(1)°].

# 2.3. Comparison to previously reported $[R_2BiER']_n$ (E = O, Se) structures

The R<sub>2</sub>BiOR' compounds 1-4 all show polymeric structures via intermolecular Bi $\cdots$ O interactions, with distorted  $\psi$ -trigonal bipyramidal C<sub>2</sub>E<sub>2</sub> bonding environments at bismuth, and oxygen atoms in axial positions (Table 2) [6-8]. The Bi-O bonds are equal within esd values in 1, 2 and 4, and differ by only  $\sim$ 0.02 Å ( $\sim$ 1%) in 3. Compound **5** features a relatively acute O–Bi–O\* bond angle [123.7(3)°], and a  $\sim$ 0.1 Å ( $\sim$ 4%) difference in Bi–O bond distances [9]. In all cases, Bi-O bond distances are short and intermolecular contacts may be considered strong [17,18]. The Bi–S bond distances in 7 differ by  $\sim$ 0.75 Å ( $\sim$ 28%), and the polymeric structure may be considered weakly associated. Interestingly, the selenolate analog 6 crystallizes in the same space group as 7 [P2(1)2(1)2(1)], and the molecules are packed in a similar (polymeric) arrangement [10]. However, the Bi–Se and Bi $\cdots$ Se\* distances in **6** differ by ~1.19 Å ( $\sim$ 44%). Further, the intermolecular Bi $\cdots$ Se\* distance [3.897(3) Å; sum of van der Waals radii of ~3.9 Å)] [16] is greater than those observed in polymeric  $[(RSe)_3Bi]_{\infty}$  species [3.466(1)-3.572(2) Å][16]. This suggests there are no intermolecular Bi...Se contacts and that 6 is monomeric in the solid-state.



Fig. 2. X-ray structure of  ${\bf 8}$  (30% probability ellipsoids). Hydrogen atoms are not shown for clarity.

# Table 2 Selected bond distances (Å) and angles (deg) for polymeric structures 1–7.

	1	2	3	4	5	6	7
Bi-E	2.382(7)	2.4105(7)	2.327(2)	2.344(6)	2.295(5)	2.704(3)	2.588(1)
Bi · · · E*	2.382(7)	2.4105(7)	2.400(2)	2.359(6)	2.399(5)	3.897(3)	3.309(1)
C-Bi-C	81.2(9)	80.0(2)	94.6(1)	96.3(4)	96.2(2)	90.8(4)	94.00(2)
E-Bi-E*	179.0(3)	179.54(4)	176.27(3)	170.2(1)	123.7(3)	176.75(7)	154.98(4)
Bi-E-Bi*	115.38(3)	113.57(2)	125.04(9)	123.4(3)	123.7(3)	84.76(7)	116.42(5)

1-5: E = O; Refs [6-9].

6: E = Se; Ref [10].

7: E = S; this work.

# 2.4. DFT studies

To probe bonding at bismuth and further examine intermolecular Bi $\cdots$ E bonding interactions, we have performed DFT calculations of the monomeric structures Ph<sub>2</sub>BiEPh [E = O, S, Se] and Ph<sub>2</sub>BiS(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). Representations of the geometry-optimized structures and selected molecular orbitals of Ph<sub>2</sub>BiSPh and Ph<sub>2</sub>BiS(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) are shown in Fig. 3 (others are found in the Supplementary data). Calculated energies of the frontier molecular orbitals (eV) and Mulliken atomic charges ( $e^-$ ) of Bi and E for all compounds are given in Table 3. A comparison of bond distances and angles show that the geometry optimized structures resemble those of corresponding compounds in the solid-state (see Supplementary data). Important structural differences are highlighted in the discussion below.



Fig. 3. DFT geometry-optimized structures and selected molecular orbitals of  $Ph_2BiSPh$  and  $Ph_2BiS(2,6-Me_2C_6H_3)$ .

Table 3		
DFT calculated orbital e	energies (eV) and Mull	iken atomic charges ( $e^{-}$ ).

	Ph <sub>2</sub> BiOPh	Ph <sub>2</sub> BiSPh	$Ph_2BiS(2,6\text{-}Me_2C_6H_3)$	Ph <sub>2</sub> BiSePh
LUMO	-1.35	-1.42	-1.42	-1.39
HOMO	-5.53	-5.90	-6.03	-5.76
HOMO-1	-6.67	-6.48	-6.06	-6.35
q(Bi)	0.90	0.63	0.63	0.66
q(E)	-0.72	-0.20	-0.20	-0.31

The calculated Bi–S bond distance (2.58 Å) in Ph<sub>2</sub>BiSPh is very similar to the solid-state structure of **7** [2.588(1) Å], which is unexpected given the absence of a *trans* influence of a Bi $\cdots$ S intermolecular contact in the geometry optimized monomer (*vide infra*). A similar Bi–S bond distance is calculated for Ph<sub>2</sub>BiS(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) [2.58 Å], though the value in the solid-state structure is slightly smaller [**8**: 2.545(1) Å]. The most significant difference in the polymeric solid-state and monomeric calculated structures of Ph<sub>2</sub>BiSPh is the Bi-S-C bond angle [**7**: Bi1–S1–C13 = 107.8(2)°; calculate = 100.5°]. Again, a similar value (101.1°) is calculated for Ph<sub>2</sub>BiS(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), which is much closer to the experimental value for **8** [Bi1–S1–C13 = 98.3(1)°].

Analysis of the frontier molecular orbitals and MO coefficients of Ph<sub>2</sub>BiSPh shows that the LUMO is a Bi(6p)–S(3p)  $\sigma$ -antibonding orbital, the HOMO is a Bi(6p)–S(3p)  $\sigma$ -bonding orbital, the HOMO–1 represents a S(3p) lone pair, and the HOMO–2 represents the Bi lone pair (Fig. 3). It is clear from the orientation of the LUMO and HOMO–1 that these are the electron acceptor and donor orbitals, respectively, that are involved in intermolecular Bi $\cdots$ S bonding observed in the solid-state structure of **7** (Figs. 1 and 4). Analysis of the frontier molecular orbitals of Ph<sub>2</sub>BiS(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) shows similar LUMO, HOMO and HOMO–1 orbitals to Ph<sub>2</sub>BiSPh, with the HOMO–3 representing the Bi lone pair. The S(3p) lone pair (HOMO–1) is coplanar with the benzenethiolate ring and is oriented toward the 2,6-methyl groups. This suggests that the nominal sterics provided by the benzenethiolate methyl groups preclude intermolecular Bi $\cdots$ S bonding in **8**.

Geometry optimized structures of  $Ph_2BiOPh$  and  $Ph_2BiSePh$  show similar structural arrangements and frontier molecular orbitals to that of  $Ph_2BiSPh$ . In the case of  $Ph_2BiOPh$ , however, the O(2p) lone pair is the HOMO versus the HOMO-1. In the absence of a *trans* intermolecular Bi $\cdots$ O contact, the calculated Bi–O bond



Fig. 4. Schematic representation of orbital overlap responsible for intermolecular  $Bi \cdots E$  bonding in  $R_2BiER'$  yielding a zig-zag polymeric arrangement.

distance in Ph<sub>2</sub>BiOPh of 2.14 Å is significantly shorter that that observed in structures **1–5** [2.295(5)–2.4105(7) Å; Table 2] [6–9]. This supports the identification of the LUMO Bi(6p)–E(np)  $\sigma$ -antibonding orbital as the electron acceptor in Ph<sub>2</sub>BiEPh intermolecular Bi $\cdots$ E interactions. The Bi-Se bond distance in Ph<sub>2</sub>BiSePh is similar in the calculated and solid-state (**6**) structures [2.69 Å and 2.704(3), respectively], while the calculated Bi–Se–C bond angle (97.5°) is only slightly more acute than in the solid-state structure [100.0(4)°]. The lack of an increase in Bi–Se bond distance and Bi–Se–C angle in the solid-state structure of **6** versus the calculated structures further suggests the absence of significant intermolecular Bi $\cdots$ Se contacts.

Although the LUMO energy of Ph<sub>2</sub>BiOPh is similar to Ph<sub>2</sub>BiSPh, the energy of the O(2p) lone pair (HOMO) is significantly higher than that of the S(3p) lone pair (HOMO–1) (Table 3). Further, the difference in the Mulliken atomic charges of Bi and E is much larger for Ph<sub>2</sub>BiOPh (1.62  $e^-$ ) as compared to Ph<sub>2</sub>BiSPh (0.82  $e^-$ ) or Ph<sub>2</sub>Bi-SePh (0.96  $e^-$ ). This suggests that strong intermolecular Bi···O bonding observed in [R<sub>2</sub>BiOR']<sub>n</sub> (**1–5**) is influenced by more effective orbital overlap and larger electrostatic interactions. Given the relative similarity of LUMO/HOMO–1 frontier orbital energies and Bi/S and Bi/Se Mulliken atoms charges in Ph<sub>2</sub>BiEPh (E = S, Se), the absence of intermolecular interactions in Ph<sub>2</sub>BiSePh is presumably due to poor Bi(6p)–Se(4p) orbital overlap.

#### 3. Conclusions

The formation of a polymeric structure for 7 and a monomeric structure for 8 in the solid-state demonstrates that a modest amount of steric bulk at sulfur is sufficient to preclude intermolecular Bi...S bonding in bismuth-thiolate species. DFT studies of Ph<sub>2</sub>BiEPh (E = O, S, Se) rationalize the observed  $\psi$ -trigonal bipyramidal metal bonding environments and zig-zag arrangement of solid-state polymeric structures, as well as the observed E...Bi-E trans influence. Analysis of atomic charges shows the significance of electrostatic interactions in forming strong intermolecular Bi ··· E bonds in  $[R_2BiOR']_{\infty}$  species, as compared to thiolate and selenolate analogs. Computational studies of Ph<sub>2</sub>BiS(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) confirm that the absence of intermolecular bonding in 8 is a result of the orientation of the HOMO-1 lone pair of the thiolate sulfur atom toward the 2,6-dimethyl substituents. This work represents the first examples of structurally characterized R<sub>2</sub>BiSR' species, and advances our understanding of covalent and intermolecular Bi-E (E = O, S, Se) bonding in bismuth chalcogenolates.

#### 4. Experimental

#### 4.1. General considerations

Bismuth(III) chloride (99.999%), benzenethiol ( $\geq$ 98%), 2,6-dimethylbenzenthiol (95%), and *n*-butyllithium (1.6 M in hexanes) were used as received from Aldrich. Triphenylbismuth (99.999%) was used as received from Strem. Methanol, tetrahydrofuran and diethyl ether were dried using an MBraun SPS column solvent purification system. Ph<sub>2</sub>BiCl was prepared by literature procedures from the 2:1 reaction of Ph<sub>3</sub>Bi and BiCl<sub>3</sub> in thf [19]. Lithium benzenethiolates were prepared via the reaction of the appropriate benzenethiol with a stoichiometric amount of *n*-BuLi (1.6 M in hexanes) in diethyl ether at 23 °C, followed by solvent removal *in vacuo*. Products were used without further purification. All reactions were carried out under dinitrogen atmosphere using standard Schlenk techniques.

Solution <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded at 23 °C on a JEOL GMX 270 MHz spectrometer (270.2 and 67.9 MHz, respectively) or a Varian MERCURYplus 200 MHz spectrometer (200.0

and 50.3 MHz, respectively), and chemical shifts are calibrated to the residual solvent signal. FT-IR spectra were recorded as Nujol mulls with NaCl plates on a Mattson Genesis II FT-IR spectrometer in the range of 4000–400 cm<sup>-1</sup>. FT-Raman spectra were recorded on a Thermo Nicolet NXR 9600 Series FT-Raman spectrometer in the range 3900–70 cm<sup>-1</sup>. Melting points were recorded on an Electrothermal MEL-TEMP melting point apparatus and are uncorrected. Elemental analyses were performed by Chemisar Laboratories Inc., Guelph, Ontario.

# 4.2. Preparation of Ph<sub>2</sub>BiSPh (6)

 $LiSC_6H_5$  (0.100 g, 0.530 mmol) was added to a suspension of Ph<sub>2</sub>BiCl (0.211 g, 0.530 mmol) in tetrahydrofuran (10 mL). The reaction mixture turned from cloudy white to cloudy yellow within seconds. The reaction was allowed to stir for 3 h. after which the solvent was removed in vacuo and the remaining solid extracted with methanol (5 mL). The mixture was then filtered and allowed to sit at 4 °C for 1 d, after which yellow crystals of 6 were collected by filtration (0.034 g, 0.072 mmol, 14%). M.p. 102 °C. Anal. Calc. for C<sub>18</sub>H<sub>15</sub>BiS: C, 45.77; H, 3.20; N, 0.00. Found: C, 46.44; H, 3.28; N, 0.00%. FT-Raman (cm<sup>-1</sup>): 114 m, 168 vs, 194 w, 212 w, 244 s, 339 vs, 419 m, 480 vw, 615 vw, 645 m, 696 w, 998 vs, 1017 w, 1081 m, 1117 w, 1155 w, 1187 w, 1264 vw, 1328 vw, 1433 vw, 1473 w, 1572 m, 3042 s, 3135 w. FT-IR (cm<sup>-1</sup>): 688 m, 721 m, 735 m, 955 w, 1020 w, 1055 w, 1078 w, 1119 vw, 1157 w, 1263 vw, 1296 w, 1431 m, 1568 m, 1622 w, 1651 w, 1718 w. NMR data (thf- $d_8$ ): <sup>1</sup>H NMR,  $\delta$  = 7.00 (m, 1H, Ph<sub>2</sub>BiSPh), 7.09 (m, 2H, Ph<sub>2</sub>BiSPh), 7.27–7.32 (m, 4H, Ph<sub>2</sub>BiSPh), 7.49 (t,  ${}^{3}J_{H-H}$  = 5.7 Hz, 4H, *Ph*<sub>2</sub>BiSPh), 8.15 (d,  ${}^{3}J_{H-H}$  = 5.3 Hz, 4H, *Ph*<sub>2</sub>BiSPh).  ${}^{13}C$  {<sup>1</sup>H} NMR,  $\delta = 125.4$  (s, Ph<sub>2</sub>BiSPh), 127.7 (s, Ph<sub>2</sub>BiSPh), 128.1 (s, Ph<sub>2</sub>BiSPh), 130.9 (s, Ph<sub>2</sub>BiSPh), 134.4 (s, Ph<sub>2</sub>BiSPh), 137.3 (s, Ph<sub>2</sub>BiSPh).

## 4.3. Preparation of $Ph_2BiS(2,6-Me_2C_6H_3)$ (7)

 $LiS(2,6-Me_2C_6H_3)$  (0.090 g, 0.627 mmol) was added to a suspension of Ph<sub>2</sub>BiCl (0.250 g, 0.627 mmol) in methanol (10 mL) to give a clear vellow solution. The reaction mixture was allowed to stir for 3 h, filtered, and the filtrate was allowed to sit at 23 °C. After 1 d yellow crystals of **7** were collected by filtration (0.030 g, 0.060 mmol, 10%). M.p. 104 °C. Anal. Calc. for C<sub>20</sub>H<sub>19</sub>BiS: C, 48.00; H, 3.83; N, 0.00. Found: C, 48.61; H, 3.93; N, 0.00%. FT-IR (cm<sup>-1</sup>): 692 w, 723 m, 766 vw, 800 vw, 845 w, 997 vw, 1016 vw, 1049 vw, 1109 vw, 1155 vw, 1589 w. FT-Raman (cm<sup>-1</sup>): 110 vs, 140 m, 155 m, 188 s, 209 s, 223 m, 244 s, 331 s, 418 m, 534 w, 589 m, 615 w, 645 s, 726 vw, 766 m, 853 vw, 910 w, 997 vs, 1016 m, 1051 m, 1156 w, 1171 w, 1186 w, 1250 m, 1327 vw, 1375 vw, 1427 w, 1455 vw, 1474 w, 1568 m, 1583 m, 2908 m, 2941 w, 2975 w, 3035 s, 3133 w. NMR data (thf- $d_8$ ): <sup>1</sup>H NMR,  $\delta = 2.37$  (s, 6H, Ph<sub>2</sub>BiS-2,6- $Me_2C_6H_3$ ), 6.86 (m, 1H, Ph<sub>2</sub>BiS-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 7.00 (m, 2H, Ph<sub>2</sub>BiS-2,6- $Me_2C_6H_3$ ), 7.28 (m, 2H,  $Ph_2BiS-2,6-Me_2C_6H_3$ ), 7.48 (t,  ${}^{3}J_{H-H} =$ 5.3 Hz, 4H, Ph<sub>2</sub>BiS-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 8.12 (m, 4H, Ph<sub>2</sub>BiS-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR,  $\delta$  = 23.0 (s, Ph<sub>2</sub>BiS-2,6-*Me*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 125.9 (s, Ph<sub>2</sub>BiS-2, 6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 128.0 (s, Ph<sub>2</sub>BiS-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 130.2 (s, Ph<sub>2</sub>BiS-2, 6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 130.7 (s, Ph<sub>2</sub>BiS-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 137.4 (s, Ph<sub>2</sub>BiS-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 143.1 (s, Ph<sub>2</sub>BiS-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>).

#### 4.4. X-ray crystallography

Crystals of **7** and **8** suitable for X-ray crystallography were prepared as indicated above. Single crystals were coated with Paratone-N oil, mounted using a polyimide MicroMount and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using  $\omega$  and  $\theta$  scans with a scan width of 0.3° and 10 s exposure times. The detector distance was 5 cm. The data were reduced 800

Crystallographic data for 7 and 8.

	7	8
Formula	C <sub>18</sub> H <sub>15</sub> BiS	C <sub>20</sub> H <sub>19</sub> BiS
Formula weight	472.34	500.39
Crystal system	orthorhombic	triclinic
Space group	P2(1)2(1)2(1)	ΡĪ
a (Å)	9.6228(16)	5.4890(6)
b (Å)	9.9948(17)	12.129(1)
c (Å)	16.399(3)	14.050(2)
α (deg)	90	70.754(1)
$\beta$ (deg)	90	86.530(1)
γ (deg)	90	88.857(1)
V (Å <sup>3</sup> )	1577.3(5)	881.5(2)
Ζ	4	2
F(000)	888	476
$ ho_{ m calc.}( m gcm^{-3})$	1.989	1.885
$\mu$ (mm <sup>-1</sup> )	11.298	10.113
T (K)	198(1)	198(1)
λ (Å)	0.71073	0.71073
$R_1^a$	0.0246	0.0270
$wR_2^b$	0.0613	0.0705

<sup>a</sup>  $R_1 = [\Sigma ||F_o| - |F_c||] / [\Sigma |F_o|]$  for  $[F_o^2 > 2\sigma (F_o^2)]$ .

<sup>b</sup>  $wR_2 = \{ [\Sigma w (F_0^2 - F_c^2)^2] / [\Sigma w (F_0^4)] \}^{\frac{1}{2}}.$ 

(SAINT) [20] and corrected for absorption (SADABS) [21]. The structures were solved by direct methods and refined by full-matrix least squares on  $F^2$  (SHELXTL) [22] on all data. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and refined using a riding model. Crystallographic data are given in Table 4.

#### 4.5. Computational methods

DFT calculations were performed using GAUSSIAN 09 at the B3LYP 6-31G\* level of theory for all atoms except Bi, for which Stuttgart electron core pseudo-potentials (sdd) were employed [23]. All structures were geometry optimized and structural parameters for input files were derived from crystal structure data where possible. Structural parameters for proposed monomeric structures were derived from the crystal structure data of **6**. Frequency calculations were performed on all structures and gave no imaginary frequencies. Molecular orbital representations and structural parameters are given in the Supplementary data.

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#### Appendix A. Supplementary data

CCDC 836302 and 836303, contains the supplementary crystallographic data for **7** and **8**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly. 2011.11.011.

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