

# Studies of distannylated-1,2-dithiolato compounds: Synthesis of 4,5-bis[(triorganostannylmethyl)thiolato]-1,3-dithiole-2-thiones, $(R_3SnCH_2)_2(dmit)$ , and 4,5-bis[(triorganostannylmethyl)thiolato]-1,3-dithiole-2-ones, $(R_3SnCH_2)_2(dmio)$ – Crystal structures of $(Ph_3SnCH_2)_2(dmit)$ and $(Ph_3SnCH_2)_2(dmio)$

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## Abstract

The syntheses of 4,5-bis[(triorganostannylmethyl)thiolato]-1,3-dithiole-2-thione,  $(R_3SnCH_2)_2(dmit)$  (**5**: R = Ph; **7**:  $R_3 = MePh_2$ ; **8**: R = Bu) and 4,5-bis[(triorganostannylmethyl)thiolato]-1,3-dithiole-2-one (**6**:  $Ph_3SnCH_2)_2(dmio)$ ], from the appropriate  $R_3SnCH_2I$  and  $[NEt_4]_2[Zn(dmit)_2]$  or  $[NEt_4]_2[Zn(dmio)_2]$  are reported. Characterisation of **5–8** were generally achieved by NMR and IR spectra and additionally for **5** and **6** by X-ray crystallography and mass spectrometry. Solution NMR data indicated four coordinate tin species, while the single crystal structure determinations for **5** and **6** indicated distorted tetrahedral geometries around the tin atoms with only very weak intermolecular interactions present, but none involve the tin atoms.

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## 1. Introduction

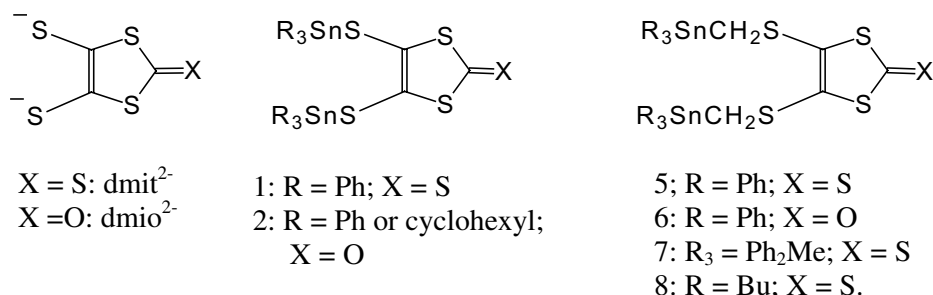
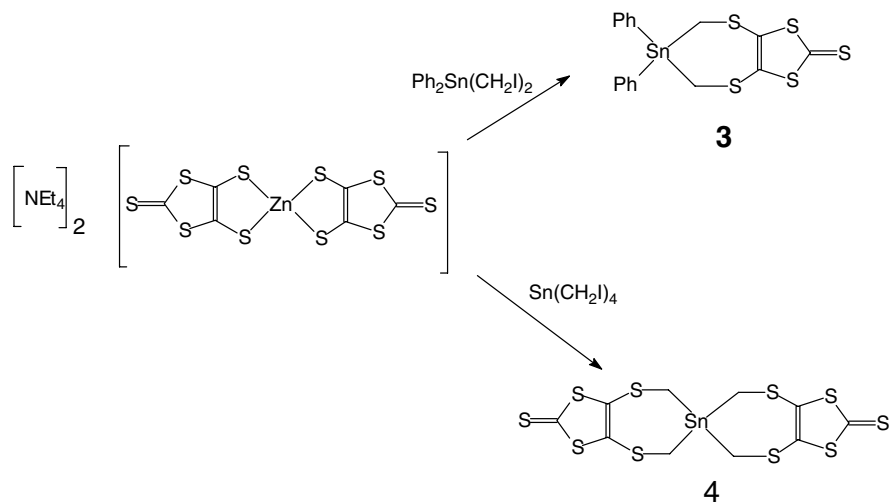
We have been investigating main group complexes of the poly-sulfur containing 1,2-dithiolates, 4,5-dimercapto-1,3-dithiole-2-thione, dmit, and 4,5-dimercapto-1,3-dithiole-2-one, dmio, or as alternatively abbreviated, dmio, for some time, see Fig. 1.

Tin dmit and dmio complexes have been of particular interest [1–5]. Among the compounds obtained have been the bis(triorganotin) species  $(Ph_3Sn)_2(dmit)$ , **1**  $(R_3Sn)_2-$

$(dmio)$  (**2**: R = cyclohexyl or phenyl) [1] and the stannacyclic compounds, **3** (6,6-diphenyl-6,7-dihydro-5H-1,3,4,8-tetrathia-6-stannazulene-2-thione) and **4** (6,6'-spirobi[6,7-dihydro-5H-1,3,4,8-tetrathia-6-stannazulene]-2, 2'-dithione) [5]. The latter two compounds, as shown in Scheme 1, were obtained from reactions of  $[NEt_4]_2[Zn(dmit)_2]$  with  $Ph_2Sn(CH_2I)_2$  and  $Sn(CH_2I)_4$ , respectively. We have continued this work with reactions of  $R_3SnCH_2I$  with the dmit and dmio precursors,  $[NEt_4]_2[Zn(dmit)_2]$  and  $[NEt_4]_2[Zn(dmio)_2]$ , respectively, and have obtained the bis(triorganostannylmethyl) derivatives, **5–8** and now we wish to report our findings. Of particular interest were the spatial arrangements of the two triorganostannyl moieties in the solid state and any intramolecular interactions involving the tin centres. Suitable crystals of **5** and **6** were obtained, but not, unfortunately, of **7**.

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Fig. 1. Formation of compounds **3** and **4**.

Scheme 1.

## 2. Experimental

### 2.1. General

All the synthetic procedures were carried out under argon atmospheres using standard Schlenk techniques with solvents dried prior to use. Compounds [NEt<sub>4</sub>]<sub>2</sub>[Zn(dmit)<sub>2</sub>] [6], [NEt<sub>4</sub>]<sub>2</sub>[Zn(dmio)<sub>2</sub>] [7], Ph<sub>3</sub>SnCH<sub>2</sub>I, MePh<sub>2</sub>CH<sub>2</sub>I and Bu<sub>3</sub>SnCH<sub>2</sub>I [8] were obtained by published procedures. Infrared spectra were obtained in CsI pellets on a Nicolet Magna 760 FT-IR instrument. <sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn NMR spectra were run on Variant 300 MHz or Bruker 400 MHz Instruments. Melting points were measured on a Melt-TempII. Elemental analyses were obtained using a Perkin–Elmer 2400 apparatus. MS data were obtained on a Waters Quattro Premier Triple quadruple instrument was used, in ES<sup>+</sup> and ES<sup>-</sup> modes, for the MS data on MeOH solutions, with source *T* = 100 °C and desolvation *T* = 150 °C: mass of tin containing peaks are based on Sn = 120. Daughter peaks were obtained with a collision voltage of 15 V.

### 2.2. Preparation of (Ph<sub>3</sub>SnCH<sub>2</sub>)<sub>2</sub>dmit (**5**)

(Iodomethyl)triphenylstannane (1.96 g, 4.0 mmol) was added to a solution of [NEt<sub>4</sub>]<sub>2</sub>[Zn(dmit)<sub>2</sub>] (0.73 g, 1.0 mmol) in acetone. The reaction mixture was refluxed

for 2 h, concentrated under vacuo and filtered. The crude solid product was recrystallized from chloroform/methanol. The red-brown crystals were found to be suitable for X-ray crystallography. Yield 54.5%, m.p. 127–128 °C.

Anal. Calc. for C<sub>41</sub>H<sub>34</sub>S<sub>5</sub>Sn<sub>2</sub>: C, 53.21; H, 3.81. Found: C, 52.99; H, 3.73%.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>); δ: 2.85 (s, 4H, *J*<sup>119,117</sup>Sn–<sup>1</sup>H = 45.1, 43.4 Hz), 7.45–7.52 (m, 18H, *p*- + *m*-Ph), 7.65–7.70 (m, 12H, *o*-Ph).

<sup>13</sup>C (75 MHz, CDCl<sub>3</sub>); δ: 15.2 (CH<sub>2</sub>, *J*<sup>119,117</sup>Sn–<sup>13</sup>C = 282, 270 Hz), 128.8 (<sup>119,117</sup>Sn–<sup>13</sup>C = 52 Hz, *m*-Ph), 129.5 (<sup>119,117</sup>Sn–<sup>13</sup>C = 12 Hz, *p*-Ph), 136.4 (*J*<sup>119,117</sup>Sn–<sup>13</sup>C = 542, 519 Hz, *i*-Ph), 136.9 (<sup>119,117</sup>Sn–<sup>13</sup>C = 39 Hz, *o*-Ph), 138.3 (C=C), 211.0 (C=S).

<sup>119</sup>Sn (113 MHz, CDCl<sub>3</sub>); δ: –119.9.

IR: (CsI): 3064, 3045, 3017, 2989, 2951, 2901, 1481, 1458, 1429, 1458, 1059, 728, 697, 516, 465, 446, 265, 243, 238 cm<sup>-1</sup>.

MS (ES<sup>+</sup>): 949 [(M + Na)<sup>+</sup> < 1%], 926 [M<sup>+</sup>, 0.2%], 383 [Ph<sub>3</sub>SnS<sup>+</sup>, <1%], 351 [Ph<sub>3</sub>Sn<sup>+</sup>, 12%], 197 [PhSn<sup>+</sup>, 4%], 130 [100%].

MS (ES<sup>-</sup>): 970, 958, 820, 561.

### 2.3. Preparation of (Ph<sub>3</sub>SnCH<sub>2</sub>)<sub>2</sub>dmio (**6**)

This was prepared analogously to **5** from Ph<sub>3</sub>SnCH<sub>2</sub>I (1.96 g, 4.0 mmol) and [NEt<sub>4</sub>]<sub>2</sub>[Zn(dmio)<sub>2</sub>] (0.68 g

1.0 mmol). The crude product was recrystallized from chloroform/methanol on cooling to give orange crystals. Yield 55%, m.p. 115–116 °C.

Anal. Calc. for  $C_{41}H_{34}S_4OSn_2$ : C, 54.15; H, 3.88. Found: C, 53.80; H, 3.80%.

$^1H$  NMR (400 MHz,  $CDCl_3$ );  $\delta$ : 2.84 (s, 4H,  $J^{119,117}Sn-^1H = 45.7, 44.8$  Hz), 7.32–7.41 (m, 18H, *p*- + *m*-Ph), 7.55–7.60 (m, 12H, *o*-Ph).

$^{13}C$  (100 MHz,  $CDCl_3$ );  $\delta$ : 15.1 ( $CH_2$ ,  $J^{119,117}Sn-^{13}C = 286, 273$  Hz), 128.7 ( $J^{119,117}Sn-^{13}C = 53.3$  Hz, C-*m*), 129.0 (C=C), 129.8 ( $J^{119,117}Sn-^{13}C = 12$  Hz C-*p*), 136.4 ( $J^{119,117}Sn-^{13}C = 541, 517$  Hz, C-*i*), 136.8 ( $J^{119,117}Sn-^{13}C = 38.6$  Hz, C-*o*), 190.0 (C=O).

$^{119}Sn$  (113 MHz,  $CDCl_3$ );  $\delta$ : -119.8.

IR (CsI): 3063, 3048, 3011, 2987, 2948, 1664, 1610, 1480, 1430, 1074, 998, 730, 698, 455, 444, 378, 268, 229  $cm^{-1}$ .

MS ( $ES^+$ , 60 eV): 409 [ $(Ph_3SnC_2H_2S)^+$ , 12%], 351 ( $Ph_3Sn^+$ , 100%), 197 ( $PhSn^+$ , 22%), 130 (20%).

MS ( $ES^-$ , 60 eV): 439 ( $Ph_3SnC_2H_2S_2^+$ , 78%), 407, ( $Ph_3SnC_2S^+$ , 8%), 383 ( $Ph_3SnS^+$ , 100%), 351 ( $Ph_3Sn^+$ , 42%).

MS ( $ES^-$ , 40 eV): 806 [(M-104) $^+$ , 5%], 545 [ $Ph_3SnCH_2(dmio)^+$ , 12%], 439 ( $Ph_3SnC_2H_2S_2^+$ , 100%), 383 ( $Ph_3SnS^+$ , 46%), 351 ( $Ph_3Sn^+$ , 20%).

MS ( $ES^-$ , 30 eV): 625 (75%), 545 [ $Ph_3SnCH_2(dmio)^+$ , 48%], 439 ( $Ph_3SnC_2S_2H_2^+$ , 59%), 383 ( $Ph_3SnS^+$ , 65%), 381 (100%).

#### 2.4. Preparation of $(MePh_2SnCH_2)_2dmit$ (7)

This was prepared analogously to **5** from  $MePh_2SnCH_2I$  (1.72 g, 4.0 mmol) and  $[NEt_4]_2[Zn(dmit)_2]$  (0.73 g 1.0 mmol). The crude product was recrystallized from chloroform/methanol on cooling to give orange crystals. Yield 62%.

$^1H$  NMR (400 MHz,  $CDCl_3$ );  $\delta$ : 0.67 (s, 6H,  $J^{119,117}Sn-^1H = 56$  Hz, Me), 2.66 (s, 4H,  $J^{119,117}Sn-^1H = 43.0$  Hz,  $CH_2$ ), 7.22–7.37 (m, 12H, *p*- + *m*-Ph), 7.43–7.55 (m, 8H, *o*-Ph).

$^{13}C$  (100 MHz,  $CDCl_3$ );  $\delta$ : -9.1 (Me,  $J^{119,117}Sn-^{13}C = 375, 356$  Hz), 13.3 ( $CH_2$ ,  $J^{119, 117}Sn-^{13}C = 258, 247$  Hz), 128.4 ( $^{119,117}Sn-^{13}C = 50$  Hz, *m*-Ph), 128.91 ( $^{119,117}Sn-^{13}C = 11$  Hz, *p*-Ph), 135.9 ( $^{119,117}Sn-^{13}C = 37$  Hz, *o*-Ph), 138.3 (C=C), 140.3 (*i*-Ph), 210.9 (C=S).

$^{119}Sn$  (113 MHz,  $CDCl_3$ );  $\delta$ : -74.1.

#### 2.5. Preparation of $(Bu_3SnCH_2)_2dmit$ (8)

This was prepared analogously to **5** from  $Bu_3SnCH_2I$  (1.71 g, 4.0 mmol) and  $[NEt_4]_2[Zn(dmit)_2]$  (0.68 g 1.0 mmol). A high boiling oil was obtained after work-up and was purified by column chromatography on silica gel using  $CHCl_3$ /hexane as eluent. Yield 47%.

Table 1

Crystal data and structure refinement for **5** and **6** at 120 K

	<b>5</b>	<b>6</b>
Empirical formula	$C_{41}H_{34}S_5Sn_2$	$C_{41}H_{34}OS_4Sn_2$
Formula weight	924.36	908.30
Temperature (K)	120(2)	120(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$
Unit cell dimensions		
<i>a</i> (Å)	19.3725(4)	13.2254(2)
<i>b</i> (Å)	9.4163(2)	30.8810(7)
<i>c</i> (Å)	21.3612 (4)	9.70930(10)
$\beta$ (°)	93.3864(8)	105.5886(7)
Volume (Å <sup>3</sup> )	3889.85(14)	3819.55(11)
Z, calculated density (Mg/m <sup>3</sup> )	4, 1.578	4, 1.580
Absorption coefficient (mm <sup>-1</sup> )	1.581	1.558
<i>F</i> (000)	1840	1808
Crystal size (mm)	0.36 × 0.26 × 0.13	0.40 × 0.20 × 0.20
Theta range for data collection (°)	2.99–27.51	3.29–27.49
Index ranges	-24 ≤ <i>h</i> ≤ 25, -12 ≤ <i>k</i> ≤ 11, -27 ≤ <i>l</i> ≤ 27	-17 ≤ <i>h</i> ≤ 17, -40 ≤ <i>k</i> ≤ 40, -12 ≤ <i>l</i> ≤ 12
Reflections collected/unique [ <i>R</i> (int)]	43 354/8902 [0.0430]	52 822/8774 [0.0385]
Completeness to $\theta_{max}$	0.996	0.995
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Maximum and minimum transmission	1.0000 and 0.7859	1.0000 and 0.8078
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data/restraints/parameters	8902/0/433	8774/0/433
Goodness-of-fit on $F^2$	1.033	1.036
Final <i>R</i> indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0277$ , $wR_2 = 0.0554$	$R_1 = 0.0241$ , $wR_2 = 0.0526$
<i>R</i> indices (all data)	$R_1 = 0.0433$ , $wR_2 = 0.0600$	$R_1 = 0.0326$ , $wR_2 = 0.0557$
Largest difference peak and hole (e/Å <sup>3</sup> )	0.446 and -0.584	0.457 and -0.673

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ );  $\delta$ : 0.72–1.02 (m), 1.22–1.38 (m), 1.40–1.57 (m), 2.29 (s, 4H,  $J^{119,117}\text{Sn}-^1\text{H} = 37$  Hz,  $\text{CH}_2\text{S}$ ).

$^{13}\text{C}$  (100 MHz,  $\text{CDCl}_3$ );  $\delta$ : 9.9, 13.7, 27.3, 28.9 (all Bu), 13.1 ( $\text{CH}_2$ ), 138.7 ( $\text{C}=\text{C}$ ), 211.6 ( $\text{C}=\text{S}$ ).

$^{119}\text{Sn}$  (113 MHz,  $\text{CDCl}_3$ );  $\delta$ :  $-7.9$ .

IR (CsI): 1460, 1074, 1057,  $\text{cm}^{-1}$ .

## 2.6. X-ray crystallography

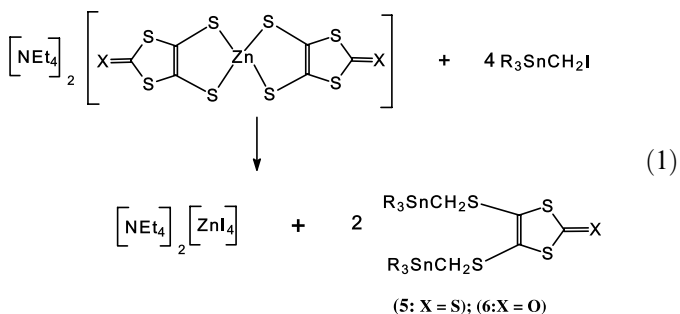
Intensity data were obtained at 120(2) K with Mo  $K\alpha$  radiation by means of the Enraf-Nonius Kappa CCD area detector diffractometer of the EPSRC National crystallographic service at the University of Southampton, UK. Data collection were carried out under the control of the program COLLECT [9] and data reduction and unit cell refinement was achieved with the COLLECT and DENZO [10] software combination. Correction for absorption, by comparison of the intensities of equivalent reflections, was applied by means of the program SADABS [11]. The program ORTEP-3 for Windows [12] has been used in the preparation of the figures and SHELXL-97 [13] and PLATON [14] in the calculation of molecular geometry.

Both structures were solved by direct methods using SHELXS-97 [15] and in each case the initial solution was expanded and fully refined by means of the program SHELXL-97 [13]. In the final stages of the refinements hydrogen atoms, as appropriate, were introduced in calculated positions with  $\text{C}-\text{H} = 0.95$ , and  $0.99$  Å for aryl and methylene, respectively, and refined with a riding model with isotropic displacement parameters set to 1.2 times the equivalent isotropic displacement parameter of the carbon atom to which they are attached. Crystal data and structure refinement details are in Table 1.

## 3. Results and discussion

### 3.1. Synthesis and spectra

Compounds **5–8** were synthesized from reactions of  $\text{R}_3\text{SnCH}_2\text{I}$  with either  $[\text{NEt}_4]_2[\text{Zn}(\text{dmit})_2]$  or  $[\text{NEt}_4]_2[\text{Zn}(\text{dmio})_2]$ , Eq. (1). Alkylation of the dmit and dmio moieties proceeded readily with all the (iodomethyl)triorganostannanes used. The targeted products were purified by recrystallisation of the reaction products, if solid, from chloroform/methanol mixtures or in the case of **8**, by chromatography.



The  $\delta^{119}\text{Sn}$  NMR values for **5** and **6** in  $\text{CDCl}_3$  solution are essentially the same,  $-119.9$  and  $-119.8$  ppm, and are in the range,  $-118$  to  $-121$  ppm, reported for  $\text{Ph}_3\text{Sn}-\text{CH}_2\text{SC}_6\text{H}_4\text{X}-p$  compounds in the same solvent [16]. Thus the different electronic effects of the mercaptide groups in these sulfidomethylstannanes are insulated from the tin centre by the intervening methylene group. The  $\delta^{119}\text{Sn}$  NMR values for **5** and **6** and those for **7** ( $-74.1$  ppm) and **8** ( $-7.9$  ppm) are all close to the values for the corresponding (iodomethyl)triorganostannanes [ $^{119}\text{Sn} = -120.0$ ,  $-70.1$  and  $-2.9$  for  $\text{Ph}_3\text{SnCH}_2\text{I}$ ,  $\text{MePh}_2\text{SnCH}_2\text{I}$  and  $\text{Bu}_3\text{SnCH}_2\text{I}$ , respectively]. Unambiguous proof of the formation of **5–8** came however from  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and IR spectra. Significant IR frequencies observed for **5** are 1458 ( $\nu\text{C}=\text{C}$ ) and  $1059$   $\text{cm}^{-1}$  ( $\nu\text{C}=\text{S}$ ), and for **6** at 1480 ( $\nu\text{C}=\text{C}$ ) and  $1664$   $\text{cm}^{-1}$  ( $\nu\text{C}=\text{O}$ ), close to values found for other tin-dmit and tin-dmio compounds [1–5].

Ready fragmentations of **5** and **6** were observed in the mass spectral experiments. For compound **5**, at a cone voltage of 60 eV and in the  $\text{ES}^+$  mode, a very low intensity  $m/e$  cluster,  $[\text{M}+\text{Na}]$ ,  $<1\%$ , was observed, along with cluster of ions,  $\text{Ph}_3\text{Sn}$  (12%) and  $\text{PhSn}$  [5%]. At the reduced cone voltage of 30 eV and in the  $\text{ES}^-$  mode, higher value  $m/e$  peaks, based on  $\text{Sn} = 120$ , were observed at 972  $[\text{M}+2\text{Na}]$  (5%), 822  $[\text{M}-104]$  (16%), 561  $[\text{Ph}_3\text{SnCH}_2(\text{dmit})]$  (100%).

Table 2  
Selected geometric parameters (Å, °), for **5** and **6**

	<b>5</b>	<b>6</b>
Sn1–C11	2.132(2)	2.139(2)
Sn1–C21	2.132(2)	2.133(2)
Sn1–C31	2.136(2)	2.141(2)
Sn1–C4	2.151(2)	2.164(2)
S1–C1	1.755(2)	1.757(2)
S1–C4	1.805(3)	1.799(2)
S2–C2	1.750(2)	1.755(2)
S2–C5	1.799(2)	1.799(2)
S3–C3	1.729(2)	1.773(2)
C1–S1–C4	101.06(11)	103.81(10)
C2–S2–C5	102.03(11)	103.27(10)
C3–S3–C1	97.93(12)	97.15(10)
C3–S4–C2	98.07(12)	97.04(10)
C2–C1–S3	115.92(19)	116.95(15)
C2–C1–S1	124.82(19)	123.87(16)
X5–C3–S4 <sup>a</sup>	122.16(15)	124.36(17)
Sn2–C51	2.126(2)	2.137(2)
Sn2–C61	2.133(2)	2.133(2)
Sn2–C41	2.141(2)	2.131(2)
Sn2–C5	2.170(2)	2.174(2)
S3–C1	1.749(3)	1.753(2)
S4–C3	1.738(3)	1.775(2)
S4–C2	1.742(2)	1.754(2)
X5–C3 <sup>a</sup>	1.647(3)	1.213(2)
C1–C2	1.357(3)	1.345(3)
S3–C1–S1	119.25(14)	118.76(11)
C1–C2–S4	115.79(19)	117.03(15)
C1–C2–S2	123.78(19)	125.86(16)
S4–C2–S2	120.43(14)	117.09(11)
S3–C3–S4	112.29(14)	111.76(12)
X5–C3–S3 <sup>a</sup>	125.54(15)	123.88(17)

<sup>a</sup> X for **5** = S; X for **6** is O.

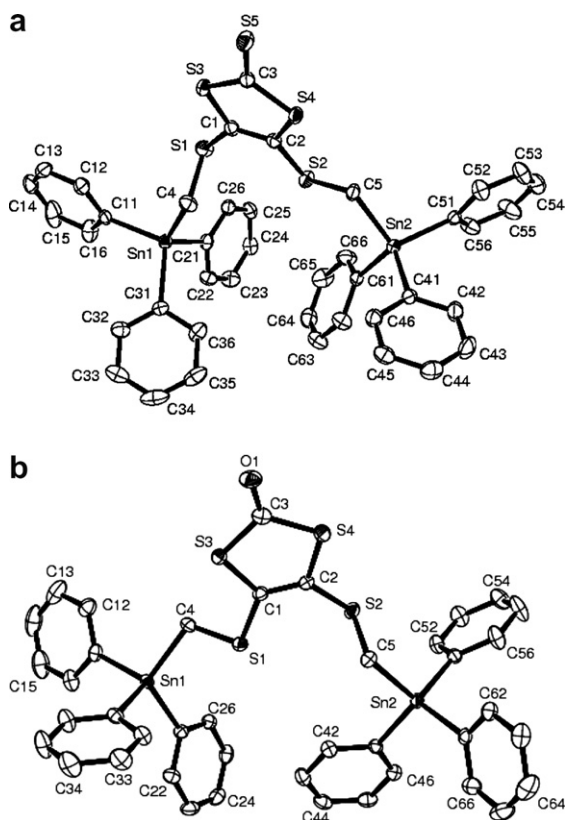


Fig. 2. (a) Atom arrangements and numbering scheme for **5**. (b) Atom arrangements and numbering scheme for **6**. Hydrogen atoms have been omitted for clarity and displacement ellipsoids are drawn at the 50% probability level in both cases.

The largest  $m/e$  values observed in the  $ES^+/MS$  for **6** at 60 eV were for clusters of ions  $[Ph_3SnC_2H_2S]$ ,  $[Ph_3Sn]$  and  $[PhSn]$ . At 60 eV in the  $ES^-/MS$  the largest  $m/e$  values were for clusters of ions,  $[Ph_3SnC_2S_2]$ ,  $[Ph_3SnS]$  and  $[Ph_3Sn]$ . The use of reduced cone voltages results in the detection of higher  $m/e$  fragments, thus at 40 eV clusters of ions, containing two tin atoms, around 806  $[M-106]$ , are seen.

The ion with  $m/e$  of 625 in the  $ES^-/MS$  of **6** at 30 eV remains unidentified. The envelope pattern of the ion clearly indicates the presence of only a single tin atom. The  $m/e$  value corresponds to  $M-285$ . Daughter ions derived from this ion (using cone and collision voltages of 30 and 15 eV) had  $m/e$  values of 545  $[Ph_3SnCH_2(dmio)]$ , 485  $[Ph_3SnC_3H_2S_3]$  (weak) and 439  $[Ph_3SnC_2S_2]$ , i.e., continuing fragmentation of the original dmio moiety is occurring.

The electronic effects on tin on changing the  $(CH_2)_2dmit$  moieties for phenyltin groups are clearly seen in the  $\delta^{119}Sn$  values for **3**  $\{Sn[(CH_2)_2dmit]_2\}$ , **4**,  $\{Ph_2Sn[(CH_2)_2dmit]\}$ , and **5**  $\{(Ph_3Sn)_2[(CH_2)_2dmit]\}$  of  $-30.0$ ,  $-94.8$  and  $-119.9$  ppm, respectively [5].

### 3.2. Solid state structures of **5** and **6**

Both compounds, **5** and **6**, contain 4-coordinate tin-centres, with the C–Sn–C bond angles ranging around the

ideal tetrahedral angle of  $109.5^\circ$ , being between  $107.80(9)$  and  $115.07(10)$  in **5**, and  $105.55(8)$  and  $115.69(8)^\circ$  in **6**. Selected bond lengths and angles are shown in Table 2. The atom arrangements and numbering systems are shown in Fig. 2. The Sn–C bond lengths and the geometric parameters of the dmit and dmio moieties are in the ranges found for other tin derivatives of these dithiolato ligands [1–5]. The dmit and dmio rings are essentially planar.

There are neither intramolecular Sn–Sn nor Sn–S interactions in either **5** or **6**. The compounds are essentially molecular with only weak intermolecular interactions present, none of which involve the tin centres, for example in **5**, there are a number of C–H– $\pi$  contacts and a C–H–S<sub>thione</sub> hydrogen-bond. Each triphenylstannyl moiety in **5** and **6** has a propeller arrangement and the orientations of the phenyl groups in neither compound allow for any intramolecular  $\pi$ – $\pi$  contacts.

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### Appendix A. Supplementary material

CCDC 654235 and 654236 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.09.008](https://doi.org/10.1016/j.jorganchem.2007.09.008).

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