

# Organotin compounds bearing mesogenic sidechains: synthesis, X-ray structures and polymerisation chemistry

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## Abstract

Organotin compounds  $R_3Sn(CH_2)_{n+2}OC_6H_4C_6H_4Y$  ( $R_3 = Ph_3, Ph_2Bu$ ;  $Y = H, CN$ ;  $n = 1-3$ ) and  $RX_2Sn(CH_2)_{n+2}OC_6H_4C_6H_4Y$  ( $R = Ph, Bu$ ;  $Y = H, CN$ ;  $X = Br, I$ ;  $n = 1-3$ ) have been synthesised and characterised by  $^1H$ -,  $^{13}C$ -,  $^{119}Sn$ -NMR and Mössbauer spectroscopies. X-ray crystallography reveals tetrahedral geometries for  $Ph_3Sn(CH_2)_4OC_6H_4C_6H_5$  and  $Ph_3Sn(CH_2)_3OC_6H_4C_6H_4CN$ , a six-coordinated, bromine-bridged dimeric structure for  $PhBr_2Sn(CH_2)_3OC_6H_4C_6H_5$  containing a *mer*- $Br_3C_2OSn$  coordination sphere about tin and a five-coordinated monomeric structure for  $PhBr_2Sn(CH_2)_3OC_6H_4C_6H_4CN$ . In all cases there is strong alignment of mesogenic groups in the solid-state but only  $PhBr_2Sn(CH_2)_3OC_6H_4C_6H_4CN$  shows any indication of liquid-crystal behaviour. Wurtz polymerisation of  $RBr_2Sn(CH_2)_5OC_6H_4C_6H_5$  ( $R = Ph, Bu$ ), both of which contain non-chelating ether functions, generated polystannanes  $(RR'Sn)_n$  with  $M_n 2.3 \times 10^5$ ;  $M_w 3.0 \times 10^5$ ;  $M_w/M_n 1.30$  and  $M_n 1.3 \times 10^5$ ;  $M_w 2.5 \times 10^5$ ;  $M_w/M_n 1.96$ , respectively, while no polymer was obtained from chelated  $PhBr_2Sn(CH_2)_3OC_6H_4C_6H_5$ .

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**Keywords:** Tin; Mesogen; X-ray; Mössbauer; Polymer

## 1. Introduction

The synthesis and materials properties of catenated Group 14 polymers  $(R_2M)_n$  ( $M = Si, Ge, Sn$ ) continues to be a fertile area of chemical investigation [1–5]. As the  $M-M$  bond energy decreases down the group so also does the ease of polymer formation, achievable chain length and polymer photostability tends to decrease, making the poly-(diorganostannanes) the Cinderellas of the triad. Synthetic methods for achieving relatively high molecular weight  $(R_2Sn)_n$  have evolved from conventional Wurtz reduction ( $R_2SnCl_2-Na$ ) [3] to milder dehydrogenative coupling of  $R_2SnH_2$  monomers promoted by a variety of transition metal catalysts [2,6–8]. Electrochemical methods [9] and reduction using  $SmI_2$  have also been reported in recent years [10].

Central to the interest in these Group 14 homopolymers are their optical and electronic properties, which show optical  $\sigma-\sigma^*$  bandgaps in the range 300–430 nm as a result of delocalisation of  $\sigma$ -electrons along the  $M_n$  backbone. The larger, more diffuse Sn atomic orbitals enhance  $\sigma$ -delocalisation and hence these polymers show bandgaps  $> 390$  nm [1,2,4], some 70 nm or more red-shifted from their better known poly-(diorganosilane) analogues [11]. There have been several attempts to reduce further the bandgap in poly-(diorganostannanes), focussing on one of two approaches. Firstly, the use of aromatic substituents on tin affords some  $\sigma-\pi$  delocalisation from the polymer backbone to the side-chain and the bandgap for  $H[(o-Et-p-^nBuOC_6H_3)_2Sn]_nH$  (2.3 eV; 550 nm), some 30–40 nm red-shifted with respect to the poly-dialkylstannanes  $(R_2Sn)_n$  ( $R = ^nHex, ^nOct$ ), is the lowest yet reported [12]. Secondly, the conformation of the polymer backbone can also influence the bandgap, which reduces as the contribution of planar, zigzag sections of the  $M_n$  chain increases [13–15]. This conformational ordering can be induced by appropriate alignment of the side-chain substituents, and was first noticed in the case of

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$[(^n\text{Hex})_2\text{Si}]_n$  [15] which shows a thermochromic shift in the  $\sigma\text{--}\sigma^*$  transition from 374 nm in an ordered film to 317 nm when the same film is heated to 100 °C [15]. Similar effects have been noted in the case of polystannanes [1,2,16].

Our interest in the synthesis of poly-(diorganostannanes) [3] has prompted us to explore the possibility of forming polymers in which mesogenic substituents on tin are used to influence the tertiary structure of the polymer. The deployment of liquid-crystal sidechains is not new in polymer chemistry and numerous examples exist which reflect the important applications of such materials in opto-electronic devices [17–19]. As an initial step in this direction, we now report the synthesis and structural chemistry of  $\text{R}_3\text{Sn}(\text{CH}_2)_{n+2}\text{OC}_6\text{H}_4\text{C}_6\text{H}_3\text{Y}$  ( $\text{R}_3 = \text{Ph}_3, \text{Ph}_2\text{Bu}$ ;  $\text{Y} = \text{H}, \text{CN}$ ;  $n = 1\text{--}3$ ) and  $\text{RX}_2\text{Sn}(\text{CH}_2)_n\text{OC}_6\text{H}_4\text{C}_6\text{H}_3\text{Y}$  ( $\text{R} = \text{Ph}, \text{Bu}$ ;  $\text{Y} = \text{H}, \text{CN}$ ;  $\text{X} = \text{Br}, \text{I}$ ;  $n = 1\text{--}3$ ), along with preliminary observations on the attempted polymerisation *via* Wurtz coupling of these latter monomers. The liquid-crystal properties of these compounds have been briefly explored.

## 2. Results and discussion

### 2.1. Synthesis

We have synthesised a series of tetraorganotin compounds **5–9** in which one of the organic groups [4- $\text{YC}_6\text{H}_4\text{C}_6\text{H}_4\text{O}(\text{CH}_2)_{n+2}$ :  $\text{Y} = \text{H}$ ,  $n = 1\text{--}3$ ;  $\text{Y} = \text{CN}$ ,  $n = 1$ ] has the potential to induce liquid-crystal (LC) ordering of molecules. The synthetic methodology is shown in Scheme 1 and involves the hydrostannation of a [4-biphenyloxy]-1-alkene **1–4** using a 2:1 ratio of alkene to triorganotin hydride. In 1:1 stoichiometry significant amounts of hexaorganoditin are produced, reducing the overall yield of the desired  $\text{R}_3\text{SnR}'$ . Separation of **5–9**

from the excess alkene is easily achieved by column chromatography ( $\text{SiO}_2$ , eluent gradient 60–80 petroleum ether– $\text{CH}_2\text{Cl}_2$ ).

Products **5–9** were produced in 53–90% yield as colourless crystalline solids melting in the range 65–117 °C, save for **9** which was a waxy solid; all compounds were soluble in common organic solvents.

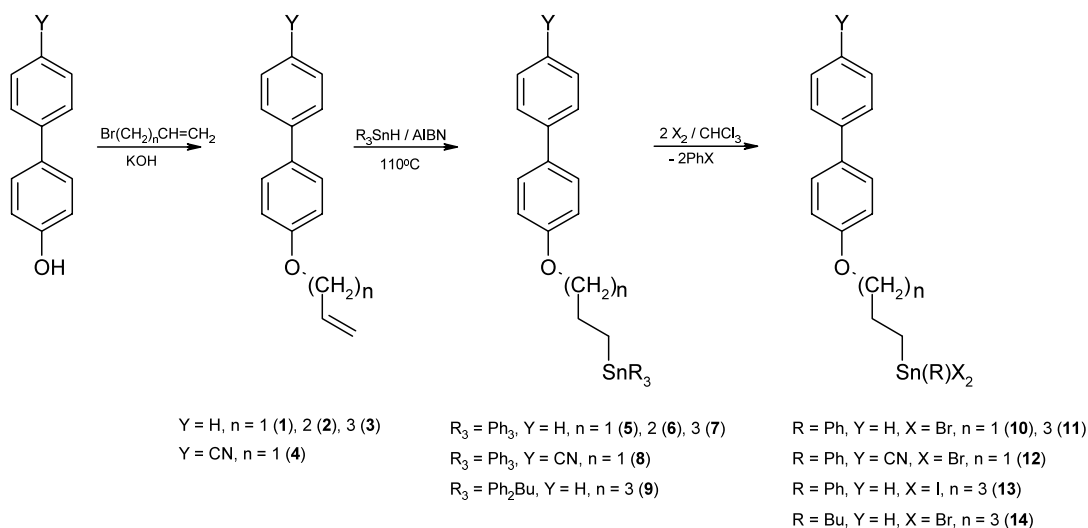
Cleavage of the Sn–Ph bonds with halogen ( $\text{Br}_2, \text{I}_2$ ) afforded the mixed diorganotin dihalides  $\text{RR}'\text{SnX}_2$  **10–14** in 43–88% yield. In the case of **14**, the Sn–Ph bonds were cleaved in preference to the Sn–Bu bonds, in line with established protocols [20,21].

All compounds **1–14** gave satisfactory microanalyses;  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR confirm the composition of the products but are otherwise unexceptional (see Section 3).

### 2.2. Structural studies

The structures of the two unsymmetrical tetraorganotin **6, 8** are unexceptional (Figs. 1 and 3). The geometry about each tin is tetrahedral, with bond angles at tin in the range 105–113°. This is consistent with their singlet Mössbauer spectra and  $^{119}\text{Sn}$ -NMR chemical shifts (–101.2, –100.4 ppm, respectively) [22,23]. In the lattice of **6**, there is a head-to-tail alignment of molecules such that the biphenyloxybutyl- ligands run parallel to each other (Fig. 2). The greater polarity of **8** resulting from the incorporation of the nitrile group at the extremity of the 4-cyanobiphenyloxypropyl-ligand has a marked effect on the lattice packing, and a more extensive alignment of mesogenic molecules is observed in a distinctive herringbone arrangement (Fig. 4).

$\text{PhBr}_2\text{Sn}(\text{CH}_2)_3\text{OC}_6\text{H}_4\text{C}_6\text{H}_4$  (**10**) adopts a dimeric structure (Fig. 5) in which the two halves of the dimer are linked by weak intermolecular  $\text{Br}(1)\cdots\text{Sn}(1')$  bridges [4.318(1) Å;  $\angle \text{Sn}(1)\text{--Br}(1)\text{--Sn}(1')$ : 93.13(2)°]. Chela-



Scheme 1.

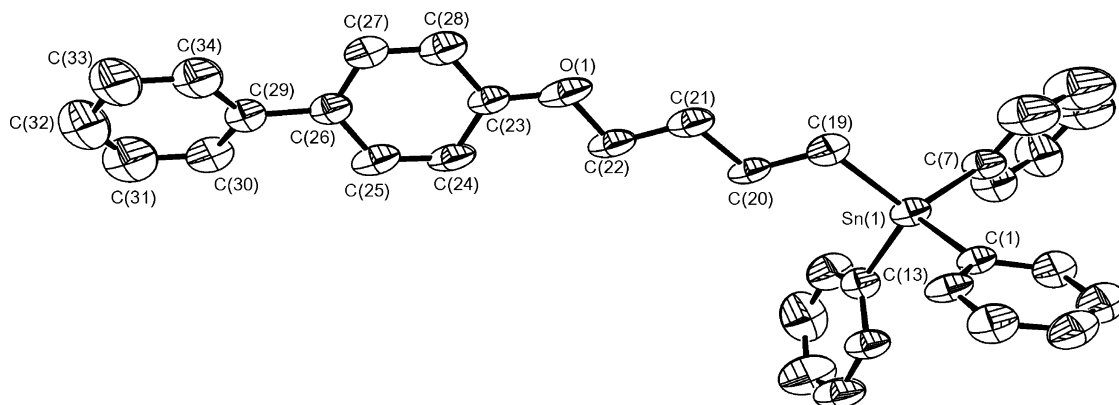


Fig. 1. The structure of **6** showing the labelling scheme; thermal ellipsoids are at the 30% level. Selected geometric data: Sn(1)–C(1) 2.140(12), Sn(1)–C(7) 2.142(11), Sn(1)–C(13) 2.143(13), Sn(1)–C(19) 2.147(13) Å; C(1)–Sn(1)–C(13) 105.8(5), C(1)–Sn(1)–C(7) 107.2(5), C(13)–Sn(1)–C(7) 108.1(5), C(1)–Sn(1)–C(19) 112.3(5), C(13)–Sn(1)–C(19) 110.9(5), C(7)–Sn(1)–C(19) 112.3(5)°.

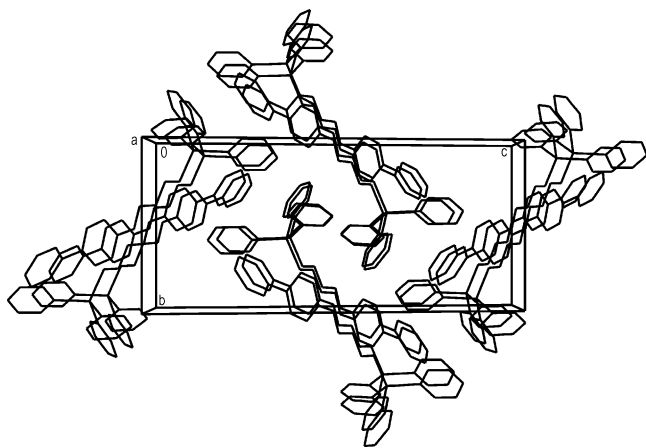


Fig. 2. The unit cell of **6** viewed along *b* showing the alignment of the biphenylether units.

tion by the ether oxygen [O(1)··Sn(1): 2.734(4) Å] completes an octahedral coordination sphere about the metal in which the three halogens are in a *mer*-arrangement while the two carbon atoms are mutually *trans*- to each other. To the best of our knowledge this is

the first crystallographically authenticated example of a Br<sub>3</sub>C<sub>2</sub>O coordination sphere about tin. The chelating O:→Sn interaction is relatively weak, though such bonds are easily influenced by both coordination number and the Lewis acidity of the tin. In general, for di-organotin species with CN = 6 the dative O:→Sn bond is longer (e.g. 2.540–2.667 Å) [24,25] than when CN = 5 (e.g. 2.382–2.448 Å) [26], though in cases where the acidity of tin is increased by the presence of additional electronegative atoms, chelation is enhanced e.g. Cl<sub>3</sub>(H<sub>2</sub>O)Sn(CH<sub>2</sub>)<sub>3</sub>O(CH<sub>2</sub>)<sub>3</sub>OMe, O:→Sn: 2.442 Å [24]. In the lattice, columns of dimers of **10** are separated from each other by columns of mesogenic biphenyloxypentyl-groups (Fig. 6).

Remarkably, when the substituent most remote from tin on the biphenyl group is changed from Y = H (**10**) to Y = CN (**12**) (Scheme 1), the dimeric nature of the complex changes to that of a monomer (Fig. 7). The decreased Lewis acidity at tin in **12** is also manifested in an extremely weak O:→Sn interaction [O(1)··Sn(1): 2.918(7) Å], though the approach of O(1) *trans* to Br(1) [∠ O(1)–Sn(1)–Br(1): 169.0(1)°] is such that the co-

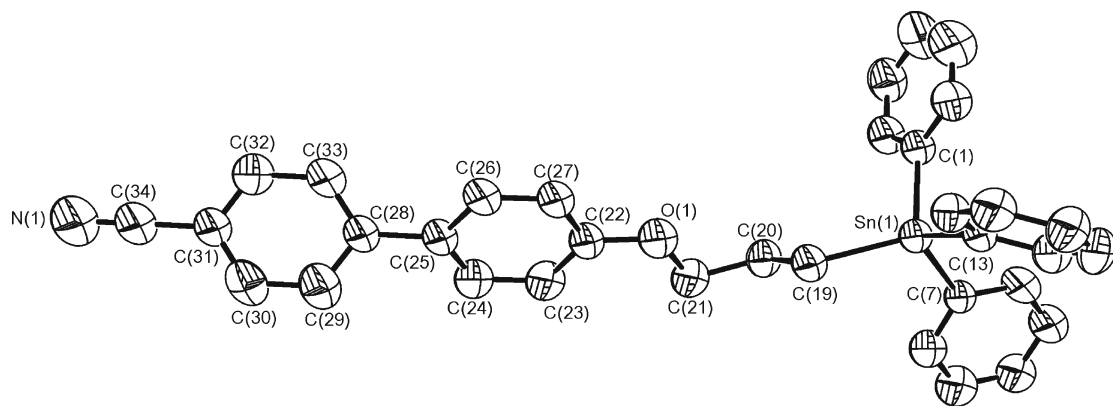


Fig. 3. The structure of **8** showing the labelling scheme; thermal ellipsoids are at the 30% level. Selected geometric data: Sn(1)–C(1) 2.144(3), Sn(1)–C(7) 2.146(3), Sn(1)–C(13) 2.133(3), Sn(1)–C(19) 2.146(3) Å; C(13)–Sn(1)–C(1) 106.19(12), C(13)–Sn(1)–C(7) 109.64(11), C(1)–Sn(1)–C(7) 110.29(11), C(13)–Sn(1)–C(19) 111.37(12), C(1)–Sn(1)–C(19) 110.49(13), C(7)–Sn(1)–C(19) 108.84(13)°.

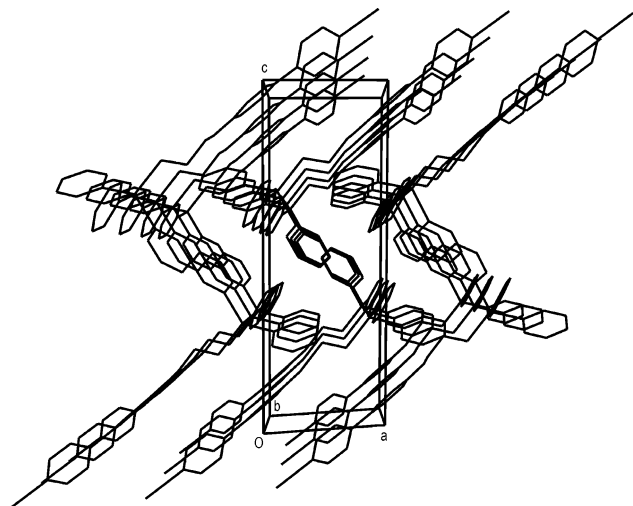


Fig. 4. The unit cell of **8** viewed along *b* showing the alignment of the biphenylether units and the herringbone packing.

ordination sphere about tin is best described as trigonal bipyramidal. In the lattice, despite the monomeric nature of **12** the molecules organise themselves into parallel head-to-tail stacks such that the pairs of Br<sub>2</sub>Sn moieties are to the interior, sheathed by columns of highly aligned mesogenic 4'-cyanobiphenyloxypropyl ligands (Fig. 8).

In the light of the above structures, the spectroscopic data for the remaining compounds synthesised can be analysed with some confidence. The remaining R<sub>3</sub>SnR' compounds **5**, **7**, **9** are tetrahedral at tin, as evidenced by singlet Mössbauer spectra (i.s. = 1.27–1.31 mm s<sup>-1</sup>) and <sup>119</sup>Sn chemical shifts corresponding to four-coordinate tin ( $\delta = -100.1, -100.4, -72.3$  ppm, respectively). The NMR data for **10** ( $-53.3$  ppm) and **12** ( $-47.6$  ppm) clearly represent a common structural motif in solution, and this will be the same as the

structure of **12** in the solid-state. There is no reason to believe that dissolution would disrupt the intramolecular chelation by the phenyloxypropyl group in either compound, while the weak Br...Sn bridges in **10** would be susceptible to rupture in solution. The weakness of the Br...Sn bridging interactions is also manifested in the Mössbauer q.s. data, which are virtually identical for the two species (3.14, 3.17 mms<sup>-1</sup>, respectively), despite the absence of such dimer formation in **12**. Both of **11** and **14** appear to be tetrahedral in solution from their downfield <sup>119</sup>Sn-NMR chemical shifts (3.5, 88.6 ppm), while **13** also fits into this category as it has  $\delta(^{119}\text{Sn})$  of  $-157.2$  ppm, which is comparable with that of Me<sub>2</sub>SnI<sub>2</sub> ( $-157$  ppm) [27]. In each case this rules out intramolecular chelation by the phenyloxypropyl moiety, which is not unreasonable as it would require formation of a seven-membered ring. This lack of intramolecular chelation is also reflected in the solid state, where both **11** and **13** show reduced Mössbauer q.s. values (2.73, 2.57 mms<sup>-1</sup>, respectively), typical of four-coordinate tin. The q.s. exhibited by **14** (3.35 mm s<sup>-1</sup>) could, however, indicate some ordering of molecules in the solid-state. Et<sub>2</sub>SnBr<sub>2</sub> has a q.s. of 3.54 mm s<sup>-1</sup> [28] and whose X-ray structure reveals a linear array of molecules linked by pairs of Br...Sn bridges [3.777(4) Å] [29].

Of the compounds investigated, only **12** showed the possibility of an intermediate phase transition, in addition to the melting point, in a DSC analysis. That the compounds lacking a terminal –CN did not form liquid crystals is not surprising given the additional polarity that is often needed to enhance intermolecular interactions. In comparing **12** with **8**, the lack of mesogenic behaviour in the latter may be due to the larger triphenyl headgroup preventing a sufficiently close approach of the cyanobiphenyl tails. Further work is needed to fully characterise potentially mesogenic behaviour in these compounds as well as the nature of any mesophase.

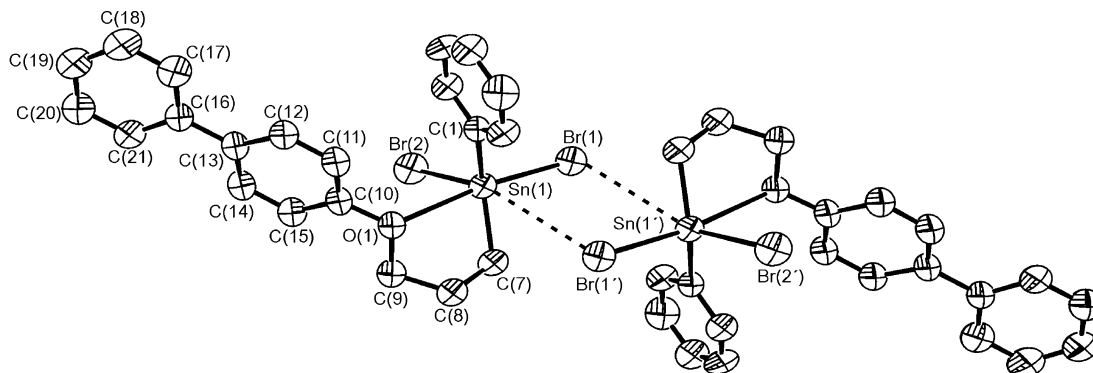
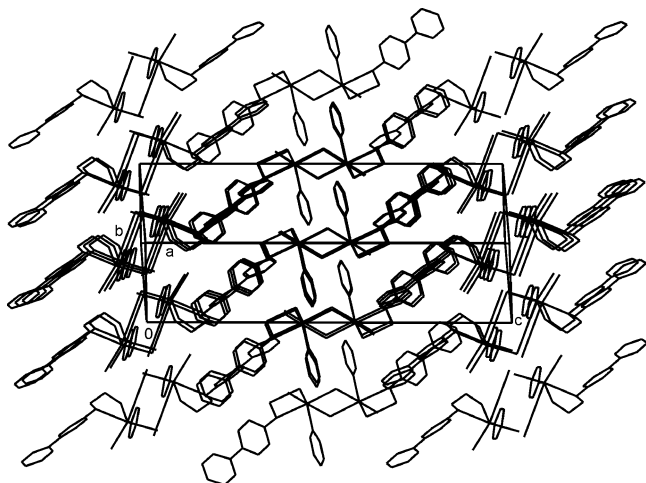


Fig. 5. The dimeric structure of **10** showing the labelling scheme; thermal ellipsoids are at the 30% level. Selected geometric data: Sn(1)–C(1) 2.105(6), Sn(1)–C(7) 2.120(6), Sn(1)–Br(1) 2.5449(9), Sn(1)–Br(2) 2.4906(9), Sn(1)–O(1) 2.734(4), Sn(1)–Br(1') 4.318(1) Å; C(1)–Sn(1)–C(7) 137.4(2), C(1)–Sn(1)–O(1) 83.4(2), C(1)–Sn(1)–Br(1) 100.7(2), C(1)–Sn(1)–Br(2) 106.7(2), C(1)–Sn(1)–Br(1') 83.6(2), C(7)–Sn(1)–O(1) 72.9(2), C(7)–Sn(1)–Br(1) 99.9(2), C(7)–Sn(1)–Br(2) 105.6(2), C(7)–Sn(1)–Br(1') 60.8(2), Br(1)–Sn(1)–O(1) 172.33(9), Br(2)–Sn(1)–O(1) 84.38(9), O(1)–Sn(1)–Br(1') 87.11(9), Br(2)–Sn(1)–Br(1) 100.56(3), Br(1)–Sn(1)–Br(1') 86.86(3), Br(2)–Sn(1)–Br(1') 165.75(3)°.

Fig. 6. Unit cell of **10**.

### 2.3. Polymerisation reactions

Solutions of diorganotin dihalides **10**, **11** and **14** in toluene were treated, in the dark, with Na/15-crown-5 to effect Wurtz coupling, using a protocol which we have found capable of generating poly(organostannanes) of very high molecular weight [3]. The key to controlling the Wurtz coupling is the reaction time, since degradation of the polymer takes place with time. Under these conditions, both **11** and **14** gave brown, polymeric (RR'Sn)<sub>n</sub>, while no high molecular weight material was generated by **10**. The failure of **10** to polymerise under Wurtz conditions is possibly due to its structure, which in solution is five-coordinate at tin as a result of the chelating propylether functionality. Since Wurtz-type polymerisation occurs at the surface of sodium [30],

this additional chelation will presumably add steric hindrance and hence may explain the lack of reaction.

In contrast, both **11** and **14** incorporate pentylether groups which do not participate in intramolecular chelation to the tin. It would appear that a coordination number for tin of four in solution is a requirement for the reaction to proceed. GPC of the extremely light-sensitive polystannanes in toluene yielded a higher average molecular weight material (polystyrene equivalent) from **11** ( $M_n$   $2.3 \times 10^5$ ;  $M_w$   $3.0 \times 10^5$ ) and lower polydispersity ( $M_w/M_n$  1.30) than polymer derived from **14** ( $M_n$   $1.3 \times 10^5$ ;  $M_w$   $2.5 \times 10^5$ ;  $M_w/M_n$  1.96). In addition, a higher proportion of low molecular weight material (cyclic oligomers Sn<sub>5,6</sub> of mass up to ca. 1000 amu) was noted from reaction of **14** (polymer: cyclics ca. 1:4) than in the case of **11** (ca. 1:1). By analogy with the reaction in silicon based chains, low molar mass material results from a back-biting reaction at the surface so that again the steric influence of Ph or Bu groups at tin may influence the relative efficiency of the chain propagation versus cyclisation. It was recently shown [31] that the molecular weight and bimodality of the polymer fraction is heavily influenced by the optimum chain length for a stable backbone conformation to form, so that again steric factors as well as the electronic influence of the metal substituent on the  $\sigma$  conjugation may play a part. However, it should be stressed that these are preliminary conclusions and further work on a range of systems is needed to fully elucidate these effects.

Disappointingly, the uv spectra of the polymers generated from **11** and **14** showed intense ( $\epsilon \sim 20,000$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>)  $\lambda_{\max}$  at 255 nm due to the mesogen,

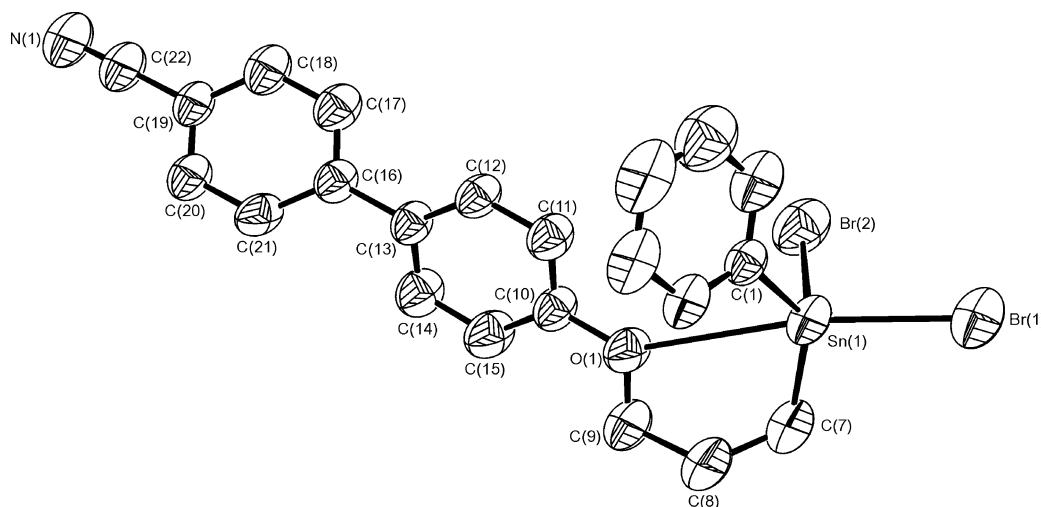


Fig. 7. The structure of **12** showing the labelling scheme; thermal ellipsoids are at the 30% level. Selected geometric data: Sn(1)–C(1) 2.126(10), Sn(1)–C(7) 2.136(11), Sn(1)–Br(1) 2.515(2), Sn(1)–Br(2) 2.509(2), Sn(1)–O(1) 2.918(7) Å; C(1)–Sn(1)–C(7) 132.7(5), C(1)–Sn(1)–Br(1) 107.8(3), C(1)–Sn(1)–Br(2) 103.6(3), C(1)–Sn(1)–O(1) 81.3(3), C(7)–Sn(1)–Br(1) 102.3(3), C(7)–Sn(1)–Br(2) 107.6(4), C(7)–Sn(1)–O(1) 66.7(3), Br(1)–Sn(1)–Br(2) 97.72(6), Br(1)–Sn(1)–O(1) 169.0(1), Br(2)–Sn(1)–O(1) 85.9(2)°.



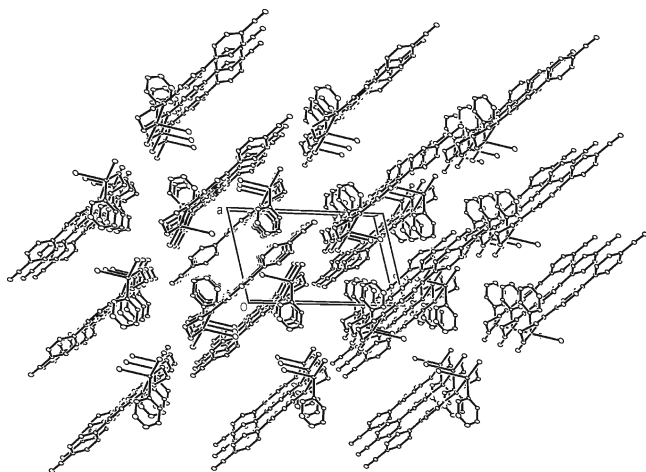


Fig. 8. The unit cell of **12** viewed along *b*.

tailing off at  $\lambda > 310$  nm. No absorbances due to polymeric material at  $\lambda > 380$  nm were observable.

### 3. Experimental

Infrared spectra ( $\text{cm}^{-1}$ ) were recorded between NaCl plates using a Nicolet 510P FT-IR spectrometer, while elemental analyses were performed using an Carlo-Erba Strumentazione E.A. model 1106 microanalyser operating at 500 °C.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded on a JEOL JNM-GX270 FT spectrometer and  $^{119}\text{Sn}$ -NMR spectra were recorded on a JEOL JNM-EX400 FT spectrometer, all using saturated  $\text{CDCl}_3$  solutions unless indicated otherwise; chemical shifts are in ppm with respect to either  $\text{Me}_4\text{Si}$  or  $\text{Me}_4\text{Sn}$ , coupling constants in Hz. Differential scanning calorimetry (DSC) was carried out on a TA instruments 2910 calorimeter using aluminium pans with an empty pan of equal mass used as the reference. Calibration was achieved by comparison with authentic liquid crystalline materials (M24 from Merck Ltd.). Details of our Mössbauer spectrometer and related procedures are given elsewhere [32]; data are in  $\text{mm s}^{-1}$ . Dry solvents were obtained by distillation under inert atmosphere from the following drying agents: sodium-benzophenone (toluene, ether, THF), calcium hydride ( $\text{CH}_2\text{Cl}_2$ ), sodium (hexane). Standard Schlenk techniques were used throughout. Starting materials were commercially obtained and used without further purification.  $\text{Ph}_3\text{SnBu}$  was prepared from  $\text{Ph}_3\text{SnCl}$  and  $\text{BuMgCl}$  following literature methodology [ $\delta(^{119}\text{Sn})$ :  $-100.1$  ppm] [33].

#### 3.1. Synthesis of 3-(4-biphenyloxy)-1-propene (**1**)

4-Hydroxybiphenyl (17.0 g, 100 mmol), potassium hydroxide (5.61 g, 100 mmol) and a few crystals of

potassium iodide were dissolved in a mixture of ethanol–water (4:1) (440 ml). 3-Bromopropene (9 ml, 100 mmol) was added to the resulting solution which was then refluxed for 5 h. Removal of solvent in vacuo resulted in a pure white solid. This was dissolved in  $\text{CH}_2\text{Cl}_2$  and filtered through a Celite column to remove KBr. Removal of solvent yielded (**1**) as a colourless crystalline solid (18.3 g, 87%) m.p. 68 °C. Anal. Found (Calc. for  $\text{C}_{15}\text{H}_{14}\text{O}$ ): C, 85.5 (85.7); H, 6.72 (6.67)%.  $^1\text{H}$ -NMR: 4.52 (d, 2H,  $\text{CH}_2$ ); 5.27 (d, 1H, *trans*-CH); 5.40 (d, 1H, *cis*-CH); 6.04 (m, 1H, =CH); 6.95 (d, 2H, *o*- $\text{C}_6\text{H}_4\text{O}$ ); 7.20–7.60 (m, 7H,  $\text{H}_{\text{aryl}}$ ).  $^{13}\text{C}$ -NMR: 68.8 ( $\text{CH}_2$ ); 115.0 (*o*- $\text{C}_6\text{H}_4\text{O}$ ); 115.6 (=CH); 117.6 (=CH $_2$ ); 126.6 (*p*- $\text{C}_6\text{H}_5$ ); 126.7 (*m*- $\text{C}_6\text{H}_4\text{O}$ ); 128.0 (*o*- $\text{C}_6\text{H}_5$ ); 128.7 (*m*- $\text{C}_6\text{H}_5$ ); 133.8 (*i*- $\text{C}_6\text{H}_5$ ); 140.7 (*i*- $\text{C}_6\text{H}_4$ ); 158.1 (*i*- $\text{C}_6\text{H}_4\text{O}$ ). IR (Nujol): 2955, 2855, 1606, 1522, 1379, 1290, 1271, 1254, 1120, 989, 925, 833, 763, 696.

#### 3.2. Synthesis of 4-(4-biphenyloxy)-1-butene (**2**)

This compound was synthesised *via* a similar method to **1**, employing 4-hydroxybiphenyl (12.61 g, 74 mmol), potassium hydroxide (4.16 g, 74 mmol) and 4-bromo-1-butene (10.0 g, 74 mmol) in ethanol–water (4:1) (400 ml). A similar work-up procedure yielded **2** as colourless crystals (13.5 g, 81%) m.p. 77 °C. Anal. Found (Calc. for  $\text{C}_{16}\text{H}_{16}\text{O}$ ): C, 85.4 (85.7); H, 7.15 (7.14)%.  $^1\text{H}$ -NMR: 2.54 (m, 2H,  $\text{CH}_2\text{CH}=\text{}$ ); 4.00 (t, 2H,  $\text{CH}_2\text{O}$ ); 5.13 (m, 2H, = $\text{CH}_2$ ); 5.90 (m, 1H, =CH); 6.95 (d, 2H, *o*- $\text{C}_6\text{H}_4\text{O}$ ); 7.26–7.55 (m, 7H,  $\text{H}_{\text{aryl}}$ ).  $^{13}\text{C}$ -NMR: 33.7 ( $\text{CH}_2\text{CH}=\text{}$ ); 67.3 ( $\text{CH}_2\text{O}$ ); 114.9 (*o*- $\text{C}_6\text{H}_4\text{O}$ ); 115.6 ( $\text{CH}=\text{CH}_2$ ); 117.0 (=CH $_2$ ); 126.6 (*m*- $\text{C}_6\text{H}_4\text{O}$ ); 126.7 (*p*- $\text{C}_6\text{H}_5\text{Ar}$ ); 128.1 (*o*- $\text{C}_6\text{H}_5\text{Ar}$ ); 128.7 (*m*- $\text{C}_6\text{H}_5\text{Ar}$ ); 133.8 (*i*- $\text{C}_6\text{H}_5\text{Ar}$ ); 140.8 (*i*- $\text{C}_6\text{H}_4\text{Ph}$ ); 158.5 (*i*- $\text{C}_6\text{H}_4\text{O}$ ). IR (Nujol): 2924, 2853, 1608, 1522, 1489, 1377, 1288, 1269, 1245, 1033, 833, 760, 688.

#### 3.3. Synthesis of 5-(4-biphenyloxy)-1-pentene (**3**)

This compound was synthesised *via* a similar method employing 4-hydroxybiphenyl (6.16 g, 36 mmol), potassium hydroxide (2.00 g, 36 mmol) and 5-bromopentene (5.36 g, 36 mmol) in ethanol–water (4:1) (200 ml). A similar work-up procedure yielded (**3**) as colourless crystals (6.3g, 74%) m.p. 60 °C. Anal. Found (Calc. for  $\text{C}_{17}\text{H}_{18}\text{O}$ ): C, 85.2 (85.7); H, 7.55 (7.56)%.  $^1\text{H}$ -NMR: 1.86 (m, 2H,  $\text{CH}_2$ ); 2.22 (m, 2H, = $\text{CHCH}_2$ ); 3.94 (t, 2H,  $\text{CH}_2\text{O}$ ); 5.00 (d, 1H, *trans*-=CH); 5.05 (d, 1H, *cis*-=CH); 5.83 (m, 1H, =CH); 6.92 (d, 2H, *o*- $\text{C}_6\text{H}_4\text{O}$ ); 7.20–7.60 (m, 7H,  $\text{H}_{\text{aryl}}$ ).  $^{13}\text{C}$ -NMR: 28.3 ( $\text{CH}_2$ ); 30.1 ( $\text{CH}_2$ ); 67.2 ( $\text{CH}_2\text{O}$ ); 114.8 (*o*- $\text{C}_6\text{H}_4\text{O}$ ); 114.9 (HC=); 117.5 (=CH $_2$ ); 126.5 (*m*- $\text{C}_6\text{H}_4\text{O}$ ); 126.6 (*p*- $\text{C}_6\text{H}_5$ ); 128.0 (*o*- $\text{C}_6\text{H}_4$ ); 128.6 (*m*- $\text{C}_6\text{H}_5$ ); 133.5 (*i*- $\text{C}_6\text{H}_5$ ); 140.8 (*i*- $\text{C}_6\text{H}_4$ ); 158.6 (*i*- $\text{C}_6\text{H}_4\text{O}$ ). IR (Nujol): 2924, 2855, 1643, 1608, 1522, 1489, 1377, 1286, 1271, 1201, 1074, 1039, 1022, 908, 827, 758, 711, 688.

### 3.4. Synthesis of 3-(4'-cyano-4-biphenylphenoxy)-1-propene (**4**)

This compound was prepared in an analogous fashion from 4'-hydroxy-4-biphenylcarbonitrile (4.00 g, 21 mmol), potassium hydroxide (1.10 g, 21 mmol) and allyl bromide (3.00 g, 2.4 mmol) in isopropyl alcohol (100 ml). Recrystallisation from ethanol yielded **4** as yellow cubic crystals (4.00 g, 80%) m.p. 71 °C. The identical procedure performed in ethanol gave no reaction. Anal. Found (Calc. for C<sub>16</sub>H<sub>13</sub>NO): C, 81.3 (81.7); H, 5.80 (5.53); N, 5.95 (5.95)%. <sup>1</sup>H-NMR: 4.58 (d, 2H, CH<sub>2</sub>O); 5.32 (dd, 1H, *trans*-=CH); 5.44 (dd, 1H, *cis*-CH); 6.08 (m, 1H, CH=CH<sub>2</sub>); 7.01 (d, 2H, *o*-C<sub>6</sub>N<sub>4</sub>O); 7.50–7.70 (m, 6H, H<sub>aryl</sub>). <sup>13</sup>C-NMR: 68.8 (CH<sub>2</sub>O); 110.0 (CN); 115.3 (HC=, *o*-C<sub>6</sub>N<sub>4</sub>O); 117.8 (=CH<sub>2</sub>); 119.0 (*i*-C<sub>6</sub>H<sub>4</sub>CN); 127.0 (*m*-C<sub>6</sub>N<sub>4</sub>O); 128.2 (*o*-C<sub>6</sub>H<sub>4</sub>CN); 131.5 (*i*-C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>N<sub>4</sub>O); 132.5 (*m*-C<sub>6</sub>H<sub>4</sub>CN); 145.1 (*i*-C<sub>6</sub>H<sub>4</sub>CN); 159.1 (*i*-C<sub>6</sub>N<sub>4</sub>O). IR (Nujol): 2924, 2222, 1604, 1518, 1466, 1377, 1290, 1248, 1178, 1116, 995, 841, 852, 823, 563, 534.

### 3.5. Synthesis of triphenyl[3-(4-biphenyloxy)propyl]tin (**5**)

Triphenyltin hydride (1.67 g, 4.8 mmol) and **1** (2.00 g, 9.5 mmol) were heated as a melt with ca. 50 mg AIBN to 140 °C under nitrogen for 1 h; the mixture solidified to a grey mass on cooling. Column chromatography on SiO<sub>2</sub> employing a gradient of 60–80 petroleum ether–CH<sub>2</sub>Cl<sub>2</sub> as elutant yielded **5** as a colourless crystalline solid (2.4 g, 90%) m.p. 74 °C. Anal. Found (Calc. for C<sub>33</sub>H<sub>30</sub>OSn): C, 70.1 (70.6); H, 5.35 (5.35)%. <sup>1</sup>H-NMR: 1.63 (t, 2H, CH<sub>2</sub>Sn); 2.20 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 3.96 (t, 2H, CH<sub>2</sub>O); 6.82 (d, 2H, *o*-C<sub>6</sub>H<sub>4</sub>O); 7.25–7.65 (m, 22H, H<sub>aryl</sub>). <sup>13</sup>C-NMR: 6.9 (CH<sub>2</sub>Sn); 26.3 (CH<sub>2</sub>CH<sub>2</sub>Sn); 70.6 (CH<sub>2</sub>O); 114.7 (*o*-C<sub>6</sub>H<sub>4</sub>O); 126.6 (*m*-C<sub>6</sub>H<sub>4</sub>O); 128.0 (*o*-C<sub>6</sub>H<sub>5</sub>); 128.5 (*m*-C<sub>6</sub>H<sub>5</sub>Sn); 128.7 (*m*-C<sub>6</sub>H<sub>5</sub>); 128.9 (*p*-C<sub>6</sub>H<sub>5</sub>Sn); 133.6 (*i*-C<sub>6</sub>H<sub>5</sub>); 137.0 (*o*-C<sub>6</sub>H<sub>5</sub>Sn); 137.4 (*p*-C<sub>6</sub>H<sub>5</sub>); 138.6 (*i*-C<sub>6</sub>H<sub>5</sub>Sn); 140.8 (*i*-C<sub>6</sub>H<sub>4</sub>); 158.5 (*i*-C<sub>6</sub>H<sub>4</sub>O); <sup>119</sup>Sn-NMR: –100.1. <sup>119</sup>mSn Mössbauer (mms<sup>-1</sup>): i.s. = 1.26; q.s. = 0.0; Γ = 0.98. IR (KBr): 3059, 2915, 2853, 1605, 1585, 1520, 1491, 1464, 1427, 1387, 1290, 1269, 1248, 1190, 1176, 1147, 1072, 1022, 1012, 997, 893, 835, 758, 729, 694, 501, 457, 447.

### 3.6. Synthesis of triphenyl[4-(4-biphenyloxy)butyl]tin (**6**)

Prepared as for **5** using triphenyltin hydride (3.15 g, 9.0 mmol) and **(2)** (4.10 g, 18.0 mmol). Column chromatography on SiO<sub>2</sub> employing a gradient of 60–80 petroleum ether–CH<sub>2</sub>Cl<sub>2</sub> as elutant yielded **6** as a colourless crystalline solid (3.00 g, 58%) m.p. 65 °C. Anal. Found (Calc. for C<sub>34</sub>H<sub>32</sub>OSn): C, 70.7 (71.0); H, 5.64 (5.57)%. <sup>1</sup>H-NMR: 1.56 (t, 2H, CH<sub>2</sub>Sn); 1.87 (m,

4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 3.95 (t, 2H, CH<sub>2</sub>O); 6.90 (d, 2H, *o*-C<sub>6</sub>H<sub>4</sub>O); 7.27–7.60 (m, 22H, H<sub>aryl</sub>). <sup>13</sup>C-NMR: 10.6 (CH<sub>2</sub>Sn); 23.2 (CH<sub>2</sub>CH<sub>2</sub>Sn); 33.6 (CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Sn); 67.2 (CH<sub>2</sub>O); 114.7 (*o*-C<sub>6</sub>H<sub>4</sub>O); 126.6 (*m*-C<sub>6</sub>H<sub>4</sub>O); 128.1 (*o*-C<sub>6</sub>H<sub>5</sub>); 128.5 (*m*-C<sub>6</sub>H<sub>5</sub>Sn); 128.7 (*o*-C<sub>6</sub>H<sub>5</sub>); 128.9 (*p*-C<sub>6</sub>H<sub>5</sub>Sn); 133.5 (*i*-C<sub>6</sub>H<sub>5</sub>); 137.0 (*o*-C<sub>6</sub>H<sub>5</sub>Sn); 137.2 (*p*-C<sub>6</sub>H<sub>5</sub>); 138.8 (*i*-C<sub>6</sub>H<sub>5</sub>Sn); 140.9 (*i*-C<sub>6</sub>H<sub>4</sub>); 158.6 (*i*-C<sub>6</sub>H<sub>4</sub>O). <sup>119</sup>Sn-NMR: –101.2. <sup>119</sup>mSn Mössbauer (mm s<sup>-1</sup>): i.s. = 1.26; q.s. = 0.0; Γ = 0.96. IR (Nujol): 2926, 2856, 1520, 1423, 1377, 1286, 1251, 1074, 997, 836, 753, 731, 700, 659.

### 3.7. Synthesis of triphenyl[5-(4-biphenyloxy)pentyl]tin (**7**)

Preparation and isolation as for **5** using triphenyltin hydride (2.91 g, 8.3 mmol) and **3** (4.18 g, 16.6 mmol) yielded **7** as a colourless crystalline solid (4.20 g, 84%) m.p. 86 °C. Anal. Found (Calc. for C<sub>35</sub>H<sub>34</sub>OSn): C, 70.5 (71.3); H, 5.88 (5.78)%. <sup>1</sup>H-NMR [δ (ppm), CDCl<sub>3</sub>]: 1.54 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>Sn); 1.78 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O); 3.78 (t, 2H, CH<sub>2</sub>O); 6.88 (d, 2H, *o*-C<sub>6</sub>H<sub>4</sub>O); 7.28–7.60 (m, 22H, H<sub>aryl</sub>). <sup>13</sup>C-NMR [δ (ppm), CDCl<sub>3</sub>]: 10.9 (CH<sub>2</sub>Sn, <sup>1</sup>J = 367, 395 Hz); 26.4 (CH<sub>2</sub>CH<sub>2</sub>Sn); 28.7 (CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Sn); 30.6 (CH<sub>2</sub>CH<sub>2</sub>O); 67.8 (CH<sub>2</sub>O); 114.7 (*o*-C<sub>6</sub>H<sub>4</sub>O); 126.6 (*m*-C<sub>6</sub>H<sub>4</sub>O); 126.7 (*p*-C<sub>6</sub>H<sub>5</sub>); 128.0 (*o*-C<sub>6</sub>H<sub>5</sub>); 128.5 (*m*-C<sub>6</sub>H<sub>5</sub>Sn); 128.7 (*m*-C<sub>6</sub>H<sub>5</sub>); 128.8 (*p*-C<sub>6</sub>H<sub>5</sub>Sn); 133.5 (*i*-C<sub>6</sub>H<sub>5</sub>); 137.0 (*o*-C<sub>6</sub>H<sub>5</sub>Sn); 138.9 (*i*-C<sub>6</sub>H<sub>5</sub>Sn); 140.8 (*i*-C<sub>6</sub>H<sub>4</sub>); 158.6 (*i*-C<sub>6</sub>H<sub>4</sub>O); <sup>119</sup>Sn-NMR [δ (ppm), CDCl<sub>3</sub>]: –100.4. <sup>119</sup>mSn Mössbauer (mms<sup>-1</sup>): I.S. = 1.27; Q.S. = 0.0; Γ = 0.99. IR (KBr): 3061, 2936, 2869, 1605, 1520, 1487, 1473, 1427, 1286, 1269, 1248, 1198, 1074, 1041, 761, 731, 698, 447.

### 3.8. Synthesis of triphenyl[4-(4'-cyano-4-biphenyloxy)propyl]tin (**8**)

Preparation and isolation as for **5** using triphenyltin hydride (0.75 g, 2.13 mmol) and **4** (1.00 g, 4.25 mmol) yielded **8** as a colourless crystalline solid (0.80 g, 66%) m.p. 117 °C. Anal. Found (Calc. for C<sub>34</sub>H<sub>29</sub>NOSn): C, 69.3 (69.7); H, 4.79 (4.95); N, 2.42 (2.39)%. <sup>1</sup>H-NMR: 1.70 (t, 2H, CH<sub>2</sub>Sn); 2.26 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>O); 3.97 (t, 2H, CH<sub>2</sub>O); 6.85 (d, 2H, *o*-C<sub>6</sub>H<sub>4</sub>O); 7.34–7.68 (m, 22H, H<sub>aryl</sub>). <sup>13</sup>C-NMR: 6.8 (CH<sub>2</sub>Sn); 26.2 (CH<sub>2</sub>CH<sub>2</sub>Sn); 70.6 (CH<sub>2</sub>O); 110.0 (CN); 115.1 (*o*-C<sub>6</sub>H<sub>4</sub>O); 119.1 (*i*-C<sub>6</sub>H<sub>4</sub>CN); 127.1 (*m*-C<sub>6</sub>H<sub>4</sub>O); 128.2 (*o*-C<sub>6</sub>H<sub>4</sub>CN); 128.5 (*m*-C<sub>6</sub>H<sub>5</sub>Sn); 128.9 (*p*-C<sub>6</sub>H<sub>5</sub>Sn); 131.3 (*i*-C<sub>6</sub>H<sub>4</sub>); 132.5 (*m*-C<sub>6</sub>H<sub>4</sub>CN); 137.0 (*o*-C<sub>6</sub>H<sub>5</sub>Sn); 138.5 (*i*-C<sub>6</sub>H<sub>5</sub>Sn); 145.3 (*i*-C<sub>6</sub>H<sub>4</sub>); 159.5 (*i*-C<sub>6</sub>H<sub>4</sub>O). <sup>119</sup>Sn-NMR: –100.4. <sup>119</sup>mSn Mössbauer (mm s<sup>-1</sup>): i.s. = 1.22; q.s. = 0.0; Γ = 0.98. IR (Nujol): 2924, 2222, 1576, 1240, 1155, 1076, 972, 823, 727, 700.

### 3.9. Synthesis of diphenylbutyltin iodide

Iodine (6.24 g, 48.0 mmol) in chloroform (600 ml) was added dropwise over 2.5 h to a stirred solution of  $\text{Ph}_3\text{BuSn}$  (10.0 g, 24.6 mmol) in chloroform (100 ml) at 0 °C. Stirring was continued for 24 h giving a very pale pink solution. This was evaporated to yield a brown oil which upon distillation on a Kugelrohr apparatus gave  $\text{Ph}_2\text{BuSnI}$  as a colourless oil (9.4 g, 84%) b.p. 165 °C/0.06 mmHg. Anal. Found (Calc. for  $\text{C}_{16}\text{H}_{19}\text{ISn}$ ): C, 41.8 (42.1); H, 4.09 (4.16)%.  $^1\text{H-NMR}$ : 0.98 (t, 3H,  $\text{CH}_3$ ); 1.48 (m, 2H,  $\text{CH}_2\text{CH}_2\text{Sn}$ ); 1.65–1.84 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Sn}$ ); 7.42–7.74 (m, 15H,  $\text{C}_6\text{H}_5$ ).  $^{13}\text{C-NMR}$ : 13.5 ( $\text{CH}_3$ ); 17.0 ( $\text{CH}_2\text{Sn}$ ); 26.5 ( $\text{CH}_2(\text{CH}_2)_2\text{Sn}$ ); 28.8 ( $\text{CH}_2\text{CH}_2\text{Sn}$ ); 128.8 (*m*- $\text{C}_6\text{H}_5$ ); 129.6 (*p*- $\text{C}_6\text{H}_5$ ); 136.0 (*o*- $\text{C}_6\text{H}_5$ ).  $^{119}\text{Sn-NMR}$ : -53.0.  $^{119}\text{mSn}$  Mössbauer (mm s<sup>-1</sup>): i.s. = 1.41; q.s. = 2.46;  $\Gamma$  = 1.05.

### 3.10. Synthesis of diphenylbutyltin hydride

A solution of diphenylbutyltin iodide (8.68 g, 19.0 mmol) in diethyl ether (40 ml) was added slowly to a suspension of  $\text{LiAlH}_4$  (0.72 g, 19.0 mmol) in diethyl ether (30 ml) under nitrogen. The resulting suspension was refluxed for 3 h and stirred at ambient temperature for a further 18 h. Careful hydrolysis with a hydroquinone solution in water (0.1 g in 3 ml) resulted in a grey suspension which was filtered and the filtrate subsequently dried over magnesium sulphate. Filtration and evaporation of the solvent yielded diphenylbutyltin hydride as a yellow oil (4.25 g, 68%). Anal. Found (Calc. for  $\text{C}_{16}\text{H}_{20}\text{Sn}$ ): C, 58.7 (58.1); H, 5.21 (6.05)%.  $^1\text{H-NMR}$ : 0.90 (t, 3H,  $\text{CH}_3$ ); 1.38–1.46 (m, 2H,  $\text{CH}_2\text{CH}_2\text{Sn}$ ); 1.68–1.81 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Sn}$ ); 7.38–7.46 (m, 6H, *m,p*- $\text{C}_6\text{H}_5\text{Sn}$ ); 7.59–7.61 (m, 4H, *o*- $\text{C}_6\text{H}_5\text{Sn}$ ).  $^{13}\text{C-NMR}$ : 13.5 ( $\text{CH}_3$ ); 17.4 ( $\text{CH}_2\text{Sn}$ ,  $^1J$  = 410, 428 Hz); 26.7 ( $\text{CH}_2(\text{CH}_2)_2\text{Sn}$ ); 28.8 ( $\text{CH}_2\text{CH}_2\text{Sn}$ ); 128.9 (*m*- $\text{C}_6\text{H}_5\text{Sn}$ ); 130.0 (*p*- $\text{C}_6\text{H}_5\text{Sn}$ ); 135.7 (*o*- $\text{C}_6\text{H}_5\text{Sn}$ ); 138.9 (*i*- $\text{C}_6\text{H}_5\text{Sn}$ );  $^{119}\text{Sn-NMR}$ : 15.9.  $^{119}\text{mSn}$  Mössbauer (mm s<sup>-1</sup>): i.s. = 1.30; q.s. = 0.00;  $\Gamma$  = 1.26. IR (liquid film): 1832 [ $\nu(\text{Sn-H})$ ].

### 3.11. Synthesis of diphenylbutyl[5-(4-biphenyloxy)pentyl]tin (9)

Preparation and isolation as for **5** using diphenylbutyltin hydride (4.24 g, 12.8 mmol) and **3** (6.10 g, 25.6 mmol) yielded **9** as an oil which solidified to a colourless waxy solid on standing (3.8 g, 53%). Anal. Found (Calc. for  $\text{C}_{33}\text{H}_{39}\text{OSn}$ ): C, 69.2 (69.6); H, 6.41 (6.68)%.  $^1\text{H-NMR}$ : 0.87 (t, 3H,  $\text{CH}_3$ ); 1.25–1.80 (m, 14H, 7  $\text{CH}_2$ ); 3.90 (t, 2H,  $\text{CH}_2\text{O}$ ); 6.90 (d, 2H, *o*- $\text{C}_6\text{H}_4\text{O}$ ); 7.24–7.54 (m, 17H,  $\text{H}_{\text{aryl}}$ ).  $^{13}\text{C-NMR}$ : 10.2 ( $\text{CH}_2\text{Sn}$ ); 10.5 ( $\text{CH}_2\text{Sn}$ ); 13.6 ( $\text{CH}_3$ ); 26.5 ( $\text{CH}_2\text{CH}_2\text{Sn}$ ); 27.3 ( $\text{CH}_2(\text{CH}_2)_2\text{Sn}$ ); 28.7 ( $\text{CH}_2\text{CH}_2\text{O}$ ); 28.9 ( $\text{CH}_2\text{CH}_2\text{Sn}$ ); 30.6 ( $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{Sn}$ ); 67.9 ( $\text{CH}_2\text{O}$ ); 114.7 (*o*- $\text{C}_6\text{H}_4\text{O}$ );

126.6 (*m*- $\text{C}_6\text{H}_4\text{O}$ ); 126.7 (*p*- $\text{C}_6\text{H}_5$ ); 128.1 (*o*- $\text{C}_6\text{H}_5$ ); 128.2 (*m*- $\text{C}_6\text{H}_5\text{Sn}$ ); 128.4 (*m*- $\text{C}_6\text{H}_5$ ); 128.7 (*p*- $\text{C}_6\text{H}_5\text{Sn}$ ); 133.5 (*i*- $\text{C}_6\text{H}_5$ ); 136.7 (*o*- $\text{C}_6\text{H}_5\text{Sn}$ ); 140.2 (*i*- $\text{C}_6\text{H}_5\text{Sn}$ ); 140.8 (*i*- $\text{C}_6\text{H}_4$ ); 158.6 (*i*- $\text{C}_6\text{H}_4\text{O}$ ).  $^{119}\text{Sn}$ : -72.3.  $^{119}\text{mSn}$  Mössbauer (mm s<sup>-1</sup>): i.s. = 1.31; q.s. = 0.0;  $\Gamma$  = 1.20.

### 3.12. Synthesis of phenyl[3-(4-biphenyloxy)propyl]tin dibromide (10)

A solution of bromine (0.74 g, 9.26 mmol) in chloroform (50 ml) was added dropwise at 0 °C to a solution of **5** (1.29 g, 2.3 mmol) in chloroform (50 ml). The resulting colourless solution was stirred for 24 h at which point the solvent was removed under vacuum to yield a yellow oil. Prolonged pumping to remove bromobenzene produced an oil which solidified on standing. Recrystallisation from petrol–chloroform yielded **10** as colourless crystals (1.10 g, 78%) m.p. 72 °C. Anal. Found (Calc. for  $\text{C}_{21}\text{H}_{20}\text{Br}_2\text{OSn}$ ): C, 45.4 (44.5); H, 3.53 (3.53)%.  $^1\text{H-NMR}$ : 2.20 (m, 2H,  $\text{CH}_2\text{Sn}$ ); 2.36 (m, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ); 4.05 (t, 2H,  $\text{CH}_2\text{O}$ ); 6.63 (d, 2H, *o*- $\text{C}_6\text{H}_4\text{O}$ ); 7.15–7.55 (m, 12H,  $\text{H}_{\text{aryl}}$ ).  $^{13}\text{C-NMR}$ : 23.1 ( $\text{CH}_2\text{Sn}$ ); 25.7 ( $\text{CH}_2\text{CH}_2\text{Sn}$ ); 69.6 ( $\text{CH}_2\text{O}$ ); 115.9 (*o*- $\text{C}_6\text{H}_4\text{O}$ ); 126.7 (*m*- $\text{C}_6\text{H}_4\text{O}$ ); 126.8 (*p*- $\text{C}_6\text{H}_5$ ); 127.8 (*o*- $\text{C}_6\text{H}_5$ ); 128.7 (*m*- $\text{C}_6\text{H}_5$ ); 129.1 (*p*- $\text{C}_6\text{H}_5\text{Sn}$ ); 130.8 (*m*- $\text{C}_6\text{H}_5\text{Sn}$ ); 134.7 (*o*- $\text{C}_6\text{H}_5\text{Sn}$ ); 135.0 (*i*- $\text{C}_6\text{H}_5$ ); 140.0 (*i*- $\text{C}_6\text{H}_5\text{Sn}$ ); 140.4 (*i*- $\text{C}_6\text{H}_4\text{Ph}$ ); 156.9 (*i*- $\text{C}_6\text{H}_4\text{O}$ ).  $^{119}\text{Sn-NMR}$ : -53.3.  $^{119}\text{mSn}$  Mössbauer (mm s<sup>-1</sup>): i.s. = 1.53; q.s. = 3.14;  $\Gamma$  = 0.82. IR (KBr): 3054, 2948, 2907, 1601, 1585, 1520, 1485, 1471, 1431, 1408, 1381, 1230, 1197, 1176, 1153, 1068, 999, 991, 908, 837, 765, 729, 729, 692, 446.

### 3.13. Synthesis of phenyl[5-(4-biphenyloxy)pentyl]tin dibromide (11)

This compound was prepared *via* a similar method as outlined above for **10** from bromine (3.32 g, 41.6 mmol) in chloroform (250 ml) and **7** (6.12 g, 10.4 mmol). Recrystallisation from 40–60 petrol yielded **11** as colourless crystals (5.40 g, 88%) m.p. 47 °C. Anal. Found (Calc. for  $\text{C}_{23}\text{H}_{24}\text{Br}_2\text{OSn}$ ): C, 46.0 (46.4); H, 4.00 (4.04)%.  $^1\text{H-NMR}$ : 1.61–2.09 (m, 8H,  $(\text{CH}_2)_4\text{Sn}$ ); 3.95 (t, 2H,  $\text{CH}_2\text{O}$ ); 6.91 (d, 2H, *o*- $\text{C}_6\text{H}_4\text{O}$ ); 7.24–7.66 (m, 12H,  $\text{H}_{\text{aryl}}$ );  $^{13}\text{C-NMR}$ : 25.3 ( $\text{CH}_2\text{Sn}$ ); 26.1 ( $\text{CH}_2\text{CH}_2\text{Sn}$ ); 28.6 ( $\text{CH}_2(\text{CH}_2)_2\text{Sn}$ ); 29.3 ( $\text{CH}_2(\text{CH}_2)_3\text{Sn}$ ); 67.4 ( $\text{CH}_2\text{O}$ ); 114.7 (*o*- $\text{C}_6\text{H}_4\text{O}$ ); 126.6 (*m*- $\text{C}_6\text{H}_4\text{O}$ ); 128.0 (*p*- $\text{C}_6\text{H}_5$ ); 128.7 (*o*- $\text{C}_6\text{H}_5$ ); 129.4 (*m*- $\text{C}_6\text{H}_5$ ); 131.3 (*m*- $\text{C}_6\text{H}_5\text{Sn}$ ); 133.6 (*i*- $\text{C}_6\text{H}_5\text{Ar}$ ); 134.5 (*o*- $\text{C}_6\text{H}_5\text{Sn}$ ); 134.8 (*p*- $\text{C}_6\text{H}_5\text{Sn}$ ); 139.0 (*i*- $\text{C}_6\text{H}_5\text{Sn}$ ); 140.7 (*i*- $\text{C}_6\text{H}_4$ ); 158.4 (*i*- $\text{C}_6\text{H}_4\text{O}$ ).  $^{119}\text{Sn-NMR}$ : 3.50.  $^{119}\text{mSn}$  Mössbauer (mm s<sup>-1</sup>): i.s. = 1.41; q.s. = 2.73;  $\Gamma$  = 0.93. IR (KBr): 2930, 2905, 2860, 1607, 1520, 1487, 1469, 1431, 1290, 1274, 1246, 1190, 1138, 1068, 995, 835, 765, 729, 692, 681.



### 3.14. Synthesis of phenyl[4-(4'-cyano-4-biphenyloxy)propyl]tin dibromide (**12**)

This compound was prepared in a manner analogous to that of **10**, using **8** (0.23 g, 0.4 mmol) and bromine (0.13 g, 0.8 mmol) in dichloromethane (100 ml). After removal of all volatiles *in vacuo*, the remaining solid was crystallised from 40–60 petrol–CH<sub>2</sub>Cl<sub>2</sub> (1:1) (0.15 g, 65%) m.p. 96 °C, clearing point 142 °C. Anal. Found (Calc. for C<sub>22</sub>H<sub>19</sub>Br<sub>2</sub>NOSn): C, 42.8 (44.6); H, 3.21 (3.21); N, 2.28 (2.37)%. <sup>13</sup>C-NMR: 23.6 (CH<sub>2</sub>Sn); 25.7 (CH<sub>2</sub>CH<sub>2</sub>Sn); 69.4 (CH<sub>2</sub>O); 110.4 (CN); 116.0 (*o*-C<sub>6</sub>H<sub>4</sub>O); 119.0 (*i*-C<sub>6</sub>H<sub>4</sub>CN); 127.1–145.0 (m, aryl); 158.1 (*i*-C<sub>6</sub>H<sub>4</sub>O). <sup>119</sup>Sn-NMR: –47.6. <sup>119m</sup>Sn Mössbauer (mm s<sup>–1</sup>): i.s. = 1.50; q.s. = 3.17;  $\Gamma$  = 0.98. IR (KBr):  $\nu$ (CN) 2228.

### 3.15. Synthesis of phenyl(5-(4-biphenyloxy)pentyl]tin diiodide (**13**)

This compound was prepared *via* a similar method as outlined above for **10** from iodine (2.16 g, 17.0 mmol) in chloroform (250 ml) and **7** (2.50 g, 4.25 mmol). Recrystallisation from 40–60 petrol yielded **13** as a pale brown solid (1.40 g, 48%) m.p. 58 °C. Anal. Found (Calc. for C<sub>23</sub>H<sub>24</sub>I<sub>2</sub>OSn): C, 40.0 (40.1); H, 3.49 (3.63)%. <sup>1</sup>H-NMR: 1.63 (m, 2H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>Sn); 1.85 (m, 4H, (CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>Sn); 2.14 (t, 2H, CH<sub>2</sub>Sn); 3.97 (t, 2H, CH<sub>2</sub>O); 6.94 (d, 2H, *o*-C<sub>6</sub>H<sub>4</sub>O); 7.21–7.64 (m, 12H, H<sub>aryl</sub>). <sup>13</sup>C-NMR: 25.6 (CH<sub>2</sub>Sn); 26.8 (CH<sub>2</sub>CH<sub>2</sub>Sn); 28.6 (CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Sn); 28.8 (CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>Sn); 67.5 (CH<sub>2</sub>O); 114.7 (*o*-C<sub>6</sub>H<sub>4</sub>O); 26.6 (*m*-C<sub>6</sub>H<sub>4</sub>O); 126.7 (*p*-C<sub>6</sub>H<sub>5</sub>); 128.1 (*o*-C<sub>6</sub>H<sub>5</sub>); 128.7 (*m*-C<sub>6</sub>H<sub>5</sub>); 129.1 (*p*-C<sub>6</sub>H<sub>5</sub>Sn); 130.9 (*m*-C<sub>6</sub>H<sub>5</sub>Sn); 133.6 (*i*-C<sub>6</sub>H<sub>5</sub>); 134.5 (*o*-C<sub>6</sub>H<sub>5</sub>Sn); 136.9 (*i*-C<sub>6</sub>H<sub>5</sub>Sn); 140.8 (*i*-C<sub>6</sub>H<sub>4</sub>); 158.6 (*i*-C<sub>6</sub>H<sub>4</sub>O). <sup>119</sup>Sn-NMR: –157.2. <sup>119m</sup>Sn Mössbauer (mms<sup>–1</sup>): i.s. = 1.52; q.s. = 2.57;  $\Gamma$  = 0.80. IR (KBr): 3063, 3026, 2944, 2867, 1605, 1518, 1487, 1471, 1429, 1290, 1267, 1244, 1190, 1176, 1142, 1055, 1038, 987, 839, 763, 723, 696, 688, 673, 439.

### 3.16. Synthesis of butyl[5-(4-biphenyloxy)pentyl]tin dibromide (**14**)

This compound was prepared *via* a similar method as outlined above for **10** from bromine (2.08 g, 26.0 mmol) in chloroform (250 ml) and **9** (3.70 g, 6.50 mmol). Recrystallisation from hexane yielded **14** as a colourless crystalline solid (1.60 g, 43%) m.p. 62 °C. Anal. Found (Calc. for C<sub>21</sub>H<sub>28</sub>Br<sub>2</sub>OSn): C, 44.2 (43.9); H, 4.87 (4.87)%. <sup>1</sup>H-NMR: 0.87 (t, 3H, CH<sub>3</sub>); 1.10–1.87 (m, 14H, 7 CH<sub>2</sub>); 3.93 (t, 2H, CH<sub>2</sub>O); 6.88 (d, 2H, *o*-C<sub>6</sub>H<sub>4</sub>O); 7.16–7.49 (m, 12H, H<sub>aryl</sub>). <sup>13</sup>C-NMR: 13.5 (CH<sub>3</sub>); 25.4 (CH<sub>2</sub>Sn); 26.0 (CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>Sn); 26.8 (CH<sub>2</sub>CH<sub>2</sub>Sn); 26.9 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Sn); 27.6 (CH<sub>3</sub>CH<sub>2</sub>); 28.6 (CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Sn); 29.4 (CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>Sn);

67.5 (CH<sub>2</sub>O); 114.7 (*o*-C<sub>6</sub>H<sub>4</sub>O); 126.6 (*m*-C<sub>6</sub>H<sub>4</sub>O); 126.7 (*p*-C<sub>6</sub>H<sub>5</sub>); 128.1 (*o*-C<sub>6</sub>H<sub>5</sub>); 128.7 (*m*-C<sub>6</sub>H<sub>5</sub>); 133.7 (*i*-C<sub>6</sub>H<sub>5</sub>); 140.8 (*i*-C<sub>6</sub>H<sub>4</sub>); 158.5 (*i*-C<sub>6</sub>H<sub>4</sub>O). <sup>119</sup>Sn-NMR: 88.6. <sup>119m</sup>Sn Mössbauer (mm s<sup>–1</sup>): i.s. = 1.66; q.s. = 3.35;  $\Gamma$  = 0.94; IR (KBr): 2926, 1520, 1487, 1470, 1289, 1251, 1176, 835, 763, 685, 601.

### 3.17. Polymerisations

The procedure used conditions optimised for the Wurtz coupling of Bu<sub>2</sub>SnCl<sub>2</sub> described elsewhere [3]. Typically, 0.5 g of either **10**, **11** or **14** was dissolved in toluene (10 ml) and treated with 15-crown-5 (0.1 ml) and 30% sodium dispersion in toluene (0.8 ml) in a nitrogen-filled Schlenk tube, wrapped in foil to exclude light. The resulting mixture was heated at 60 °C for 4 h, canula filtered and the solvent removed *in vacuo*, again with exclusion of ambient light. Any residual traces of sodium were quenched by the addition of dry methanol (5 ml). The polymer was then isolated as a sticky brown solid by solvent evaporation. Samples for GPC were taken by dissolving the material in toluene and keeping the solution in the dark and cooled until required for analysis.

### 3.18. X-ray crystallography

Experimental and crystallographic details are given in Table 1. In each case data were collected at 293 K on an Enraf Nonius CAD4 automatic diffractometer using Mo–K $\alpha$  radiation ( $\lambda$  = 0.71069 Å). Data were corrected for Lp effects and, in the case of **10** and **12**, absorption. Refinement was based on  $F^2$ ; hydrogen atoms were included at calculated positions.

The asymmetric unit of **12** was found to consist of one molecule of the tin complex, and a disordered fragment of solvent. The latter could not be fully modelled, but best convergence was achieved by assigning the two largest peaks in the electron density map to one full chlorine atom and one half of a carbon atom respectively. The disorder was compounded by the proximate location of the solvent fragment to an inversion centre implicit in the space group.

Data have also been collected on Ph<sub>3</sub>Sn(CH<sub>2</sub>)<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>5</sub> (**5**).<sup>2</sup> However, as a consequence of poor sample quality, less than desirable sample shape and a sharp fall-off in the crystal diffracting power at  $\theta$  values beyond 15°, relatively high esd values and refinement factors were associated with this structure determination. As a corollary of mediocre data, the intramolecular bond lengths in the C19–C20–

<sup>2</sup> C<sub>33</sub>H<sub>30</sub>OSn,  $M$  = 561.26, triclinic,  $a$  = 7.284(1),  $b$  = 18.423(4),  $c$  = 20.913(5) Å,  $\alpha$  = 99.23(2),  $\beta$  = 97.17(2),  $\gamma$  = 93.19(2)°,  $U$  = 2740.2(10) Å<sup>3</sup>, space group  $P\bar{1}$  (no. 2),  $Z$  = 4.

Table 1  
Crystallographic data for **6**, **8**, **10** and **12**

	<b>6</b>	<b>8</b>	<b>10</b>	<b>12</b>
Empirical formula	C <sub>34</sub> H <sub>32</sub> OSn	C <sub>34</sub> H <sub>29</sub> NOSn	C <sub>21</sub> H <sub>20</sub> Br <sub>2</sub> OSn	C <sub>22.5</sub> H <sub>20</sub> Br <sub>2</sub> CINOSn
Formula weight	1150.57	586.27	566.88	634.36
Colour	Colourless	Colourless	Colourless	Colourless
Crystal size (mm)	0.20 × 0.20 × 0.30	0.25 × 0.25 × 0.25	0.2 × 0.2 × 0.15	0.2 × 0.2 × 0.25
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$ (no. 2)
Unit cell dimensions				
<i>a</i> (Å)	11.141(2)	7.413(1)	9.854 (1)	9.234(2)
<i>b</i> (Å)	10.778(2)	10.178(2)	7.630 (1)	10.259(2)
<i>c</i> (Å)	24.291(3)	19.924(3)	27.932(3)	13.806(4)
$\alpha$ (°)		81.81(1)		108.79(2)
$\beta$ (°)	102.35(2)	89.46(1)	94.97(1)	100.78(2)
$\gamma$ (°)		71.55(2)		94.30(2)
<i>V</i> (Å <sup>3</sup> )	2849.3(8)	1410.4(4)	2092.2(4)	1203.4(5)
<i>Z</i>	4	2	4	2
$\mu$ (Mo–K $\alpha$ ) (mm <sup>-1</sup> )	0.920	0.932	5.047	4.506
Reflections collected	4055	4821	3491	3771
Independent reflections	3947 [ <i>R</i> <sub>int</sub> = 0.0621]	4433 [ <i>R</i> <sub>int</sub> = 0.0117]	3280 [ <i>R</i> <sub>int</sub> = 0.0317]	3771 [ <i>R</i> <sub>int</sub> = 0.0482]
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.068	0.946	1.098	1.083
<i>R</i> , <i>R</i> <sub>w</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0630, 0.1786	0.0267, 0.0631	0.0329, 0.0669	0.0554, 0.1090
<i>R</i> , <i>R</i> <sub>w</sub> (all data)	0.1508, 0.2889	0.0429, 0.0738	0.0873, 0.0862	0.1378, 0.1511

C21–O1 fragment of one of two molecules in the asymmetric unit had to be restrained to ideal values in the latter stages of refinement. While the geometry about each tin in the asymmetric unit was, as expected, tetrahedral, the distortions in the bond angles about Sn(2) (89.5–121.8°) make meaningful structural comparisons with compounds (**6**) and (**8**) impossible. No further comments are made on the structure of this compound.

Software used: SHELX-86 [34], SHELX-93 [35], DIFABS [36], ORTEX [37].

#### 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 213854–213857 for compounds **6**, **8**, **10** and **12**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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