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Intramolecular Chalcogen−Tin Interactions in $[(o\text{-MeEC}_6H_4)CH_2]_2SnPh_{2-n}Cl_n$ (E = S, O, CH_2; n = 0, 1, 2) and Intermolecular Chlorine−Tin Interactions in the *meta*- and *para*-Methoxy Isomers

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Organotin(IV) compounds of the type $[(o\text{-MeEC}_6H_4)CH_2]_2SnPh_{2-n}Cl_n$ were synthesized, E = O, n = 0 (**1**), n = 1 (**2**), and n = 2 (**3**); E = S, n = 0 (**4**), n = 1 (**5**), and n = 2 (**6**); and E = CH_2, n = 0 (**7**), n = 1 (**8**), and n = 2 (**9**). The dichloro compounds **3** and **6** have been investigated by single-crystal X-ray diffraction and exhibit bicapped tetrahedral geometry at the tin atom as a consequence of significant intramolecular Sn···O (**3**) and Sn···S (**6**) secondary bonding, in monomolecular units. Compound **3**, when crystallized from a hexane/THF solvent mixture, shows two different conformers, **3′** and **3″**, in the crystal structure; **3′** has two equivalent Sn···O interactions, while **3″** has two nonequivalent Sn···O interactions. Upon the recrystallization of **3** from hexane, only a single structural form is observed, **3′**. The Sn···E distances in **3′**, **3″**, and **6** are 71.3, 73.5 and 72.9, and 76.3% of the ΣvdW radii, respectively. The meta- and para-substituted isomers of **3** (**10**, **11**) exhibit a distortion at the tin atom due to self-association via intermolecular Sn···Cl interactions, resulting in polymeric structures. ^{119}Sn NMR spectroscopy suggests that the intramolecular Sn···E interactions persist in solution for the dichloride compounds **3** and **6**.

Introduction

We recently demonstrated the capacity of the *o*-methoxybenzyl ligand, and its thio analog, to significantly modify the tetrahedral geometry at a central tetravalent tin atom via strong intramolecular Sn···E (E = O, S) secondary bonding in the compounds $(o\text{-MeEC}_6H_4CH_2)Ph_{3-n}SnCl_n$, n = 0, 1, and 2.[1] These examples were an illustration of the general ability of tetravalent tin to be coordinated by Lewis bases such as N, S, and O, via both inter- and intramolecular interactions.[2]

Inter(intra)molecular secondary bonding of the type Sn···E (E = S, O, N) has been suggested to be important with respect to the biological activity of organotins (OTs).[3] Our current interest is related to the specific capacity of OTs to reduce the capacity of human natural killer (HNK) cells to function.[4a]

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Table 1. Crystal Data and Refinement Parameters

cryst structure	**3A** (**3′** and **3″**)	**3B** (**3′**)	**6**	**10**	**11**
formula	$3(C_{16}H_{18}Cl_2O_2Sn)\cdot THF$	$C_{16}H_{18}Cl_2O_2Sn$	$C_{16}H_{18}Cl_2S_2Sn$	$C_{16}H_{18}Cl_2O_2Sn$	$C_{16}H_{18}Cl_2O_2Sn$
fw	1367.79	431.89	464.01	431.89	431.89
cryst syst	orthorhombic	triclinic	monoclinic	monoclinic	orthorhombic
space group	$C222_1$	$P\bar{1}$	$C2/c$	$C2/c$	$Pnma$
a (Å)	11.2125(13)	7.4570(12)	18.641(3)	29.155(3)	9.5239(11)
b (Å)	18.4339(13)	8.5940(14)	8.2600(12)	4.9005(5)	29.418(3)
c (Å)	26.755(2)	14.043(2)	14.947(2)	12.1948(12)	6.0974(7)
α (deg)	90	89.699(2)	90	90	90
β (deg)	90	81.920(2)	125.650(2)	104.941(2)	90
γ (deg)	90	81.005(2)	90	90	90
V (Å^3)	5529.9(9)	880.0(2)	1870.1(5)	1683.4(3)	1708.3(3)
Z	4	2	4	4	4
ρ_{calcd} (g cm^{-3})	1.643	1.630	1.648	1.704	1.679
μ(Mo Kα) (mm^{-1})	1.683	1.756	1.866	1.836	1.809
F(000)	2728	428	920	856	856
T (K)	100(2)	298(2)	293(2)	298(2)	298(2)
$2\theta_{max}$ for data collection (deg), % completed	46.50, 100	50.00, 98.8	50.00, 100	53.50, 100	53.90, 100
index ranges: $-h+h$, $-k+k$, $-l+l$	−12 12, −20 20, −29 29	−8 8, −10 10, −16 16	−22, 22, −9, 9, −17, 17	−36 36, −6 6, −15 15	−12 12, −37 37, −7 7
total number reflns	23064	8299	8708	8752	17629
independent reflns [R_{int}]	3968[0.0453]	3058[0.0369]	1654[0.0186]	1791[0.0524]	1901[0.0851]
refinement methods	full-matrix least-squares on F2				
data/restraints/params	3968/0/314	3058/0/190	1654/57/97	1791/0/96	1901/0/100
goodness-of-fit on F^2	1.154	0.880	1.023	1.054	1.140
R_1 [$I > 2\sigma(I)$]	0.0333	0.0404	0.0241	0.0408	0.0543
largest difference in peak and hole (e Å^{-3})	0.969 and −0.322	0.618 and −0.312	0.669 and −0.265	0.815 and −0.378	2.251 and −0.703

Since these cells are an essential part of our immune system, and OTs are found in our bloodstream from societal uses,[4b] there is a driving force to reduce this exposure. Since clear structure−activity relationships have been discovered in the interactions of OTs with HNK cells,[4a,c,d] we have initiated a study of simple OTs in which O, S, and N atoms are placed within the coordination sphere, but without direct σ bonding to the central tin atom, in the expectation of modifying this biological activity via potential intramolecular interactions. We now report OTs with two functionalized benzyl groups with MeO- and MeS- substituents which can permit the formation of penta- or hexa-coordinated tin atoms.[4e] We have also investigated the meta and para isomers of the O-containing ligand to determine if intermolecular E···Sn interactions can be observed, since the geometry precludes intramolecular interactions.

Experimental Section

Synthesis. All manipulations were carried out under nitrogen atmospheres using standard Schlenk techniques. Reagent-grade tetrahydrofuran (THF) was dried and distilled under nitrogen from a sodium benzophenone ketyl solution. Toluene, benzene, and hexane were dried and distilled from Na ribbon; pyridine was dried and distilled from NaOH. Diphenyltindichloride was purchased from Gelest. 2-Methoxybenzyl chloride, 2-ethylbenzyl alcohol, thionyl chloride, metallic tin, 1 M tin tetrachloride in methylene chloride, 1-bromo-3-chloropropane, methanethiol, and 1 M HCl in diethyl ether were purchased from Aldrich. 2-Thiomethylbenzyl chloride was synthesized using published methods.[5] NMR spectra, ^{1}H, ^{13}C, and ^{119}Sn, were recorded on a Bruker 300 MHz operating spectrometer at 300.00, 75.422, and 111.853 MHz, respectively, using $CDCl_3$ or C_6D_6 as the solvent. Elemental analyses were performed by Galbraith Laboratories.

X-Ray Diffraction. Crystals suitable for X-ray diffraction were obtained for compounds **3**, **6**, **10**, and **11**, and each was mounted on a cryoloop in a random orientation using paratone oil. The X-ray intensity data were collected with SMART[6a] on a Bruker APEX CCD diffractometer with monochromatized Mo Kα radiation (λ = 0.71073 Å). Cell refinement and data reduction were carried out with SAINT; incident beam and decay corrections were done with SADABS in the SAINT-Plus suite, v.6.23c.[6b] The structures were solved by direct methods with SHELXS and refined by full-matrix least-squares techniques with SHELXL in the SHELXTL suite, v.6.10.[6c] The corresponding experimental parameters for each compound are summarized in Table 1.

Synthesis of 2-Ethylbenzyl Chloride. 2-Ethylbenzyl alcohol (5 mL, 36.7 mmol) dissolved in benzene (10 mL) was added dropwise into a three-neck flask containing $SOCl_2$ (5.25 mL, 73.4 mmol) and benzene (40 mL) at 0 °C. After this addition, pyridine (6 mL, 73.4 mmol dissolved in 5 mL of benzene) was added dropwise, and the mixture was stirred for 30 min. The mixture was then refluxed for 2 h and transferred immediately to an ice bath for 20 min. Ice (40 g) was added and the pH increased to 6 with a saturated solution of $NaHCO_3$. The product was then extracted with diethylether three times; the ethereal fractions were collected and the solvent evaporated. The final product was distilled at 6 mmHg, bp 60−62 °C. Yield: 2.72 g (48%). ^{1}H NMR ($CDCl_3$): δ 2.07 (3H, t, $-CH_3$, J = 7.5 Hz), 3.54 (2, q, $-\underline{CH_2}CH_3$, J = 7.5 Hz), 5.41 (2H, s, $-CH_2Cl$), 8.26−7.75 (4H, m, Ph). ^{13}C NMR ($CDCl_3$): δ 15.3 ($-CH_3$), 25.3 ($-\underline{CH_2}CH_3$), 44.4 ($-CH_2Cl$), 126.4, 129.0, 129.2, 130.3, 135.1, 143.1 (−CH, Ph).

Synthesis of [(*o*-MeOC$_6$H$_4$)CH$_2$]$_2$SnPh$_2$ (1). Ph_2SnCl_2 (1.99 g, 5.81 mmol) was added to a mixture of 2-methoxybenzyl chloride (2 g, 12.8 mmol) and Mg turnings (0.31 g, 12.8 mmol) in THF (50 mL) at 0 °C. The reaction mixture was kept at 0 °C and allowed to stir overnight. The solvent was removed under reduced pressure, and the product was extracted with hexane and filtered. The crude material was recrystallized from hexane at −20 °C to yield **1** as a white solid. Yield: 1.48 g (45%); mp 68−70 °C. Anal. Calcd for $C_{28}H_{28}O_2Sn$: C, 65.27; H, 5.48. Found: C, 65.01; H, 5.47.

^{1}H NMR ($CDCl_3$): δ 3.29 (4H, s, Ar−$\underline{CH_2}$Sn, $^2J(^{117/119}Sn,^1H)$ = 20.12/33.26 Hz), 4.15 (6H, s, $\underline{Me}$−O−Ar), 8.00−7.31 (18H, m,

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Ph, Ar). ^{13}C NMR ($CDCl_3$): δ 15.49 (2C, Ar−$\underline{C}H_2$Sn, $^1J(^{13}C,^{117/119}Sn)$ = 312.74/327.23 Hz), 54.60 (2C, $\underline{Me}$−$\overline{O}$−Ar), 109.51 (2C, C3−Ar, $^4J(^{13}C,^{119}Sn)$ = 12.9 Hz), 120.50 (2C, C5−Ar, $^4J(^{13}C,^{119}Sn)$ = 11.7 Hz), 125.12 (2C, C4−Ar, $^5J(^{13}C,^{119}Sn)$ = 15.67 Hz), 127.97 (4C, C2−Ph), 128.36, (2C, C4−Ph), 128.67 (2C, C6−Ar, $^3J(^{13}C,^{119}Sn)$ = 29.7 Hz), 130.34 (2C, C1−Ar, $^2J(^{13}C,^{119}Sn)$ = 21.0 Hz), 136.37 (4C, C3−Ph, $^3J(^{13}C,^{119}Sn)$ = 33.37 Hz), 141.36 (2C, C1−Ph, $^1J(^{13}C,^{117/119}Sn)$ = 434.17/454.57 Hz), 155.90 (2C, C2−Ph, $^3J(^{13}C,^{119}Sn)$ = 10.80 Hz). ^{119}Sn NMR ($CDCl_3$): δ −96.6.

Using the same synthetic approach we obtained the following compounds:

[(*o*-MeSC$_6$H$_4$)CH$_2$]$_2$SnPh$_2$ (4). Yield: 1.6 g (50%); mp 72−74 °C. ^{1}H NMR ($CDCl_3$): δ 2.87 (6H, s, $\underline{Me}$−S−Ar), 3.45 (4H, s, Ar−$\underline{C}H_2$−Sn, $^2J(^{117/119}Sn,^1H)$ = 19.88/31.51 Hz), 7.95−7.74 (18H, m, Ph, Ar). ^{13}C NMR ($CDCl_3$): δ 15.57 (2C, $\underline{Me}$−S−Ar), 22.84 (2C, Ar−$\underline{C}H_2$Sn, $^1J(^{13}C,^{117/119}Sn)$ = 294.75/308.25 Hz), 124.86 (2C, Ar), 124.88 (2C, Ar), 124.96, (2C, Ar), 128.00 (4C, C2−Ph), 128.07 (2C, C4−Ph), 128.40 (2C, C6−Ar), 135.40 (2C, C2−Ar, $^3J(^{13}C,^{119}Sn$ = 25.27 Hz), 136.55 (4C, C3−Ph, $^3J(^{13}C,^{119}Sn)$ = 33.9 Hz), 139.69 (2C, C1−Ar, $^2J(^{13}C,^{119}Sn)$ = 42.3 Hz), 141.07 (2C, C1−Ph, $^1J(^{13}C,^{119}Sn)$ = 436.42/470.1 Hz). ^{119}Sn NMR ($CDCl_3$): δ −98.8. Anal. Calcd for $C_{28}H_{28}S_2Sn$: C, 61.44; H, 5.16. Found: C, 61.50; H, 5.13.

[(*o*-EtC$_6$H$_4$)CH$_2$]$_2$SnPh$_2$ (7). Yield: 2.15 g (65%). ^{1}H NMR ($CDCl_3$): δ 1.79 (6H, t, Ar−$CH_2\underline{Me}$, ^3J(H,H) = 7.5 Hz), 3.07 (4H, q, −$\underline{C}H_2CH_3$, ^3J(H,H) = 7.5 Hz), 3.41 (4H, s, Ar−$\underline{C}H_2$−Sn, $^2J(^{117/119}Sn,^1H)$ = 31.72/32.74 Hz), 8.04−7.67 (18H, m, Ph, Ar). ^{13}C NMR ($CDCl_3$): δ 14.01 (2C, Ar−$CH_2\underline{Me}$), 17.53 (2C, Ar−$\underline{C}H_2$Sn, $^1J(^{13}C,^{119/117}Sn)$ = 290.82/304.25 Hz), 26.36 (2C, Ar−$\overline{C}H_2$Me), 124.55 (2C, C3−Ar, $^4J(^{13}C,^{119}Sn)$ = 16.87 Hz), 126.15 (2C, C−Ar, $J(^{13}C,^{119}Sn)$ = 13.8 Hz), 128.01 (2C, C−Ar, $J(^{13}C,^{119}Sn)$ = 14.55 Hz), 128.49 (2C, C4−Ph), 128.5 (4C, C2-Ph), 128.90 (2C, C−Ar, $J(^{13}C,^{119}Sn)$ = 10.65 Hz), 136.63 (4C, C3−Ph, $^3J(^{13}C,^{119}Sn)$ = 33.37 Hz), 138.89 (2C, C1−Ph), 139.69 (2C, C2−Ar). ^{119}Sn NMR ($CDCl_3$): δ −103.7. Anal. Calcd for $C_{30}H_{32}Sn$: C, 70.47; H, 6.31. Found: C, 70.51; H, 6.39.

Synthesis of [(*o*-MeOC$_6$H$_4$)CH$_2$]$_2$SnPhCl (2). A solution of hydrogen chloride (1.0 M in diethyl ether, 1.94 mL, 1.94 mmol) was added dropwise to a solution of **1** (1 g, 1.94 mmol) in 10 mL of dried benzene. After 30 min, the reaction was complete, and the solvent was removed under reduced pressure. It was isolated as oil from a hexane solution of the crude left at −20 °C, 0.32 g (35%).

^{1}H NMR ($CDCl_3$): δ 3.35 (4H, s, Ar−$\underline{C}H_2$−Sn, $^2J(^{117/119}Sn,^1H)$ = 20.98/34.12 Hz), 4.07 (6H, s, Ar−O$\underline{Me}$), 8.03−7.20 (13H, m, Ar, Ph). ^{13}C NMR ($CDCl_3$): δ 21.76 (2C, Ar−$\underline{C}H_2$−Sn), 54.57 (2C, Ar−O$\underline{Me}$), 109.38 (2C, C3−Ar), 121.01 (2C, $\overline{C}$5−Ar), 126.53 (2C, C4−Ar), 128.52 (2C, C6−Ar), 128.90 (1C, C4−Ph), 129.46 (2C, C1−Ar), 127.97 (2C, C2−Ph), 135.38 (2C, C3-Ph), 142.25 (1C, C1−Ph), 155.68 (2C, C2−Ar). ^{119}Sn NMR ($CDCl_3$): δ −11.9. Anal. Calcd for $C_{22}H_{23}ClO_2Sn$: C, 55.80; H, 4.90. Found: C, 56.01; H, 5.04.

[(*o*-MeSC$_6$H$_4$)CH$_2$]$_2$SnPhCl (5). Yield as a liquid product: 0.35g (38%). ^{1}H NMR ($CDCl_3$): δ 2.16 (6H, s, Ar−S$\underline{Me}$), 3.07 (4H, s, Ar−$\underline{C}H_2$−Sn, $^2J(^{117/119}Sn,^1H)$ = 20.43/33.18 Hz), 7.74−6.99 (13H, m, Ar, Ph). ^{13}C NMR ($CDCl_3$): δ 16.37 (2C, Ar−S$\underline{Me}$), 29.52 (Ar−$\underline{C}H_2$−Sn), 125.84 (2C, C5−Ar), 126.10 (2C, C4−Ar), 128.39 (2C), 128.51 (2C), 128.76 (1C, C4−Ph), 129.03 (2C, C6−Ar), 134.94 (2C, C2−Ar), 135.39 (2C, C3-Ph), 138.41 (1C, C1−Ph), 141.75 (2C, C1−Ar). ^{119}Sn NMR ($CDCl_3$): δ −20.2. Anal. Calcd for $C_{22}H_{23}ClS_2Sn$: C, 52.25; H, 4.58. Found: C, 52.32; H, 4.69.

[(*o*-EtC$_6$H$_4$)CH$_2$]$_2$SnPhCl (8). Yield: 2.47 g (90%). ^{1}H NMR ($CDCl_3$): δ 1.85 (6H, t, Ar−$CH_2\underline{Me}$, $^3J(^1H,^1H)$ = 7.4 Hz), 3.14 (4H, q, Ar−$\underline{C}H_2Me$, $^3J(^1H,^1H)$ = 7.4 Hz), 3.64 (4H, s, Ar−$\underline{C}H_2$−Sn, $^2J(^{117/119}Sn,^1H)$ = 33.27/35.30 Hz), 8.12−7.67 (13H, m, Ar, Ph). ^{13}C NMR ($CDCl_3$): δ 14.32 (2C, Ar−$CH_2\underline{Me}$), 24.08 (2C, Ar−$\underline{C}H_2$Sn, $^1J(^{13}C,^{119/117}Sn)$ = 287.44/318.72 Hz), 26.45 (2C, Ar−$\overline{C}H_2$Me), 125.72 (2C, C5−Ar), 126.44 (2C, C4−Ar), 128.36 (2C), 128.40 (2C), 128.74 (1C, C4−Ph), 128.82 (2C), 130.05 (1C, C1−Ph), 135.46 (2C, C3−Ph), 135.93 (2C, C2−Ar), 140.44 (2C, C1−Ar). ^{119}Sn NMR ($CDCl_3$): δ −11.9. Anal. Calcd for $C_{24}H_{27}ClSn$: C, 61.38; H, 5.79. Found: C, 61.42; H, 5.82.

Synthesis of [(*o*-MeOC$_6$H$_4$)CH$_2$]$_2$SnCl$_2$ (3). To tin powder (1.52 g, 11.6 mmol) was added three drops of water, and the mixture was kneaded together. The resulting material was suspended in 50 mL of toluene under efficient stirring and heated by an external boiling water bath. To this suspension was added dropwise 2-methoxybenzyl chloride (2 g, 12.8 mmol) over 3 min. After 4 h of reflux, the solution was cooled and filtered, and the solvent was removed under reduced pressure. The crude material was recrystallized from hexane at −20 °C to yield **3** as a white solid, 1.93 g (70%), mp 92−94 °C.

^{1}H NMR ($CDCl_3$): δ 3.66 (4H, s, Ar−$\underline{C}H_2$−Sn, $^2J(^{117/119}Sn,^1H)$ = 20.58/48.84 Hz), 3.95 (6H, s, Ar−O−$\underline{Me}$), 7.90−7.17 (8H, m, Ar). ^{13}C NMR ($CDCl_3$): δ 55.15 (2C, Ar−O−$\underline{Me}$), 31.09 (2C, Ar−$\underline{C}H_2$Sn, $^1J(^{13}C,^{119}Sn)$ = 539.25/564.3 Hz), 109.41 (2C, C3−Ar, $^4J(^{13}C,^{119}Sn)$ = 19.87 Hz), 121.40 (2C, C5−Ar), 125.15 (2C, C1−Ar, $^2J(^{13}C,^{119}Sn)$ = 53.55 Hz), 127.76 (2C, C4−Ar, $^5J(^{13}C-^{119}Sn)$ = 18.75 Hz), 129.46 (2C, C6−Ar, $^3J(^{13}C,^{119}Sn)$ = 43.05 Hz), 155.05 (2C, C2−Ar, $^3J(^{13}C,^{119}Sn)$ = 35.85 Hz). ^{119}Sn NMR ($CDCl_3$): δ −35.39. Anal. Calcd for $C_{16}H_{18}Cl_2O_2Sn$: C, 44.49; H, 4.20. Found: C, 45.74; H, 4.17.

Also, the following compounds were synthesized using the same general approach:

[(*o*-MeSC$_6$H$_4$)CH$_2$]$_2$SnCl$_2$ (6). Yield: 1.75g (65%); mp 154−156 °C. ^{1}H NMR ($CDCl_3$): δ 2.95 (6H, s, Ar−S−$\underline{C}H_3$), 3.96 (4H, s, Ar−$\underline{C}H_2$−Sn, $^2J(^{117/119}Sn,^1H)$ = 12.95/33.01 Hz), 8.01−7.89 (8H, m, Ar). ^{13}C NMR ($CDCl_3$): δ 15.48 (2C, Ar−S−$\underline{C}H_3$), 41.78 (2C, Ar−$\underline{C}H_2$Sn, $^1J(^{13}C,^{117/119}Sn)$ = 541.05/566.25 Hz), 127.18 (2C), 127.48 (2C), 127.66 (2C), 130.00 (2C, C6−Ar, $^3J(^{13}C,^{119}Sn)$ = 76.125 Hz), 134.50 (2C, C2−Ar, $^3J(^{13}C,^{119}Sn)$ = 26.10 Hz), 137.58 (2C, C1−Ar, $^2J(^{13}C,^{119}Sn)$ = 51.45 Hz). ^{119}Sn NMR ($CDCl_3$): δ −54.7. Anal. Calcd for $C_{16}H_{18}Cl_2S_2Sn$: C, 41.41; H, 3.91. Found: C, 41.79; H, 3.74.

[(*o*-EtC$_6$H$_4$)CH$_2$]$_2$SnCl$_2$ (9). Yield: 2.39 g (70%); mp 110−112 °C. ^{1}H NMR ($CDCl_3$): δ 1.89 (6H, t, Ar−CH_2−$\underline{Me}$, $^3J(^1H,^1H)$ = 7.4 Hz, 3.15 (4H, q, Ar−CH_2−Me, $^3J(^1H,^1H)$ = 7.4 Hz), 3.90 (4H, s, Ar−$\underline{C}H_2$Sn, $^2J(^{117/119}Sn,^1H)$ = 38.16/39.69 Hz), 7.88−7.67 (8H, m, Ar). ^{13}C NMR ($CDCl_3$): δ 14.42 (Ar−CH_2−Me), 26.43 (Ar−CH_2−$\underline{Me}$), 31.24 (Ar−$\underline{C}H_2$−Sn, $^1J(^{13}C,^{119/117}Sn)$ = 344.25/361.95 Hz), 126.68 (2C, $J(^{13}C,^{119}Sn)$ = 26.1 Hz), 127.04 (2C, $J(^{13}C,^{119}Sn)$ = 31.12 Hz), 128.61 (2C, $J(^{13}C,^{119}Sn)$ = 26.62 Hz), 129.27 (2C, C6−Ar, $^3J(^{13}C,^{119}Sn)$ = 43.27 Hz), 132.55 (2C, C2−Ar, $^3J(^{13}C-^{119}Sn)$ = 58.5 Hz), 141.02 (2C, C1−Ar, $^2J(^{13}C,^{119}Sn)$ = 42.3 Hz). ^{119}Sn NMR ($CDCl_3$): δ 40.3. Anal. Calcd for $C_{18}H_{22}Cl_2Sn$: C, 50.51; H, 5.18. Found: C, 50.42; H, 5.03.

[(*m*-MeOC$_6$H$_4$)CH$_2$]$_2$SnCl$_2$ (10). Yield: 0.52 g (57%); mp 142−145 °C. ^{1}H NMR ($CDCl_3$): δ 3.08 (4H, s, Ar−$\underline{C}H_2$−Sn, $^2J(^{117/119}Sn,^1H)$ = 41.16/48.84 Hz), 3.70 (6H, s, Ar−$\overline{O}$−$\underline{Me}$), 6.54−6.70 (8H, m, Ar). ^{13}C NMR ($CDCl_3$): δ 55.1 (2C, Ar−$\overline{O}$−$\underline{Me}$), 32.4 (2C, Ar−$\underline{C}H_2$−Sn), 112.1 (2C, C2−Ar), 113.6 (2C, $\overline{C}$4−Ar), 120.5 (2C, $\overline{C}$5−Ar), 130.1 (2C, C6−Ar), 136.2 (2C, C1−Ar), 150.2 (2C, C3−Ar). ^{119}Sn NMR ($CDCl_3$): δ 31.8. Anal. Calcd for $C_{16}H_{18}Cl_2O_2Sn$: C, 44.49; H, 4.20. Found: C, 45.74; H, 4.17.

[(*p*-MeOC$_6$H$_4$)CH$_2$]$_2$SnCl$_2$ (11). Yield: 0.62 g (70%); mp 138−141 °C. ^{1}H NMR ($CDCl_3$): δ 3.08 (4H, s, CH_2−Sn, $^2J(^{117/119}Sn,^1H)$ = 41.16/48.84 Hz), 3.74 (6H, s, Ar−O−$\underline{Me}$), 6.70−6.6.80 (8H, m, Ar). ^{13}C NMR ($CDCl_3$): δ 55.2 (2C, Ar−O−$\underline{C}H_3$), 31.6 (2C, Ar−$\underline{C}H_2$−Sn), 114.8 (2C, C3−Ar), 126.3 (2C, C1−Ar), 129.3 (2C, C2−Ar), 158.2 (2C, C4−Ar). ^{119}Sn NMR ($CDCl_3$): δ 30.7

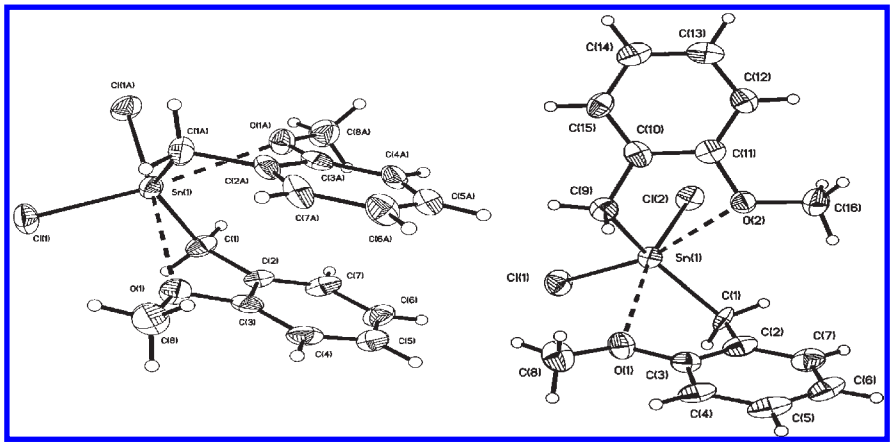

Figure 1. ORTEP diagrams of conformers **3′** (left) and **3″** (right) found in the polymorphs of **3**. Each conformer is independently oriented, and the THF molecule is excluded for clarity.

Results and Discussion

We prepared the $[(o\text{-MeEC}_6H_4)CH_2]_2Ph_{2-n}Cl_nSn$ compounds using the reactions outlined in eqs 1−3. The syntheses of the *m*- and *p*-$[(MeOC_6H_4)CH_2]_2SnCl_2$ isomers, **10** and **11**, followed the reaction noted in eq 3.

$$Ph_2SnCl_2 + 2[(o\text{-MeEC}_6H_4)CH_2]MgCl \rightarrow [(o\text{-MeEC}_6H_4)CH_2]_2Ph_2Sn + 2MgCl_2 \quad (1)$$

$$E = O\ (\mathbf{1}), E = S\ (\mathbf{4}), E = CH_2\ (\mathbf{7})$$

$$[(o\text{-MeEC}_6H_4)CH_2]_2Ph_2Sn + HCl/Et_2O \rightarrow [(o\text{-MeEC}_6H_4)CH_2]_2PhSnCl + PhH \quad (2)$$

$$E = O\ (\mathbf{2}), E = S\ (\mathbf{5}), E = CH_2\ (\mathbf{8})$$

$$2(o\text{-MeEC}_6H_4)CH_2Cl + Sn^0 \rightarrow [(o\text{-MeEC}_6H_4)CH_2]_2SnCl_2 \quad (3)$$

$$E = O\ (\mathbf{3}), E = S\ (\mathbf{6}), E = CH_2\ (\mathbf{9})$$

The progress of the chlorination reaction, eq 2, was conveniently monitored by ^{119}Sn NMR spectroscopy (without locking) because of the significant difference in chemical shift of the reactants and products: **1** → **2** (−96.6 → −11.9 ppm), **4** → **5** (−98.8 → −20.2 ppm), and **7** → **8** (−103.7 → −11.9 ppm). The "direct process" reaction between metallic tin and the benzyl chlorides used to obtain the bis-benzyltin dichlorides, eq 3, results in good to high yields for all of the examples studied.

Previous studies have indicated that ^{119}Sn NMR spectra exhibit an upfield shift of more than 40 ppm upon increasing the coordination number at the tin atom.[7] We have prepared $[(o\text{-}CH_3CH_2C_6H_4)CH_2]_2Ph_{2-n}Cl_nSn$ to permit us to note the variation upon introducing the O and S Lewis base atoms as replacements for the noncoordinating

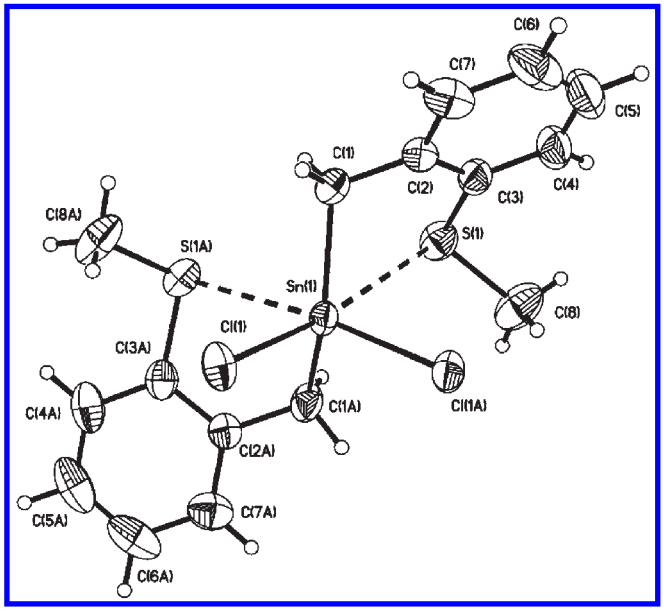

Figure 2. ORTEP diagram of compound **6**.

methylene group. We also synthesized the unsubstituted dibenzyl compound $(C_6H_4CH_2)_2SnCl_2$ (**12**). Within this family of organotins, the O- and S-substituted compounds, **3** and **6**, exhibit a clear change of chemical shift compared to those where no intramolecular secondary bonding can be expected, that is, **12** and **9**. The ^{119}Sn chemical shifts for the latter are 35.4 and 40.3 ppm, respectively, whereas the ortho-substituted MeE−benzyl compounds exhibit significantly shifted resonances at −54.7 ppm (E = S, **6**) and −35.4 ppm (E = O, **3**). This is a >70 ppm upfield shift with respect to **9** and **12**, reflecting significant Sn···E intramolecular interactions, even in solution. It can be also observed that the intramolecular coordination is stronger for **6** than for **3**, as judged by the greater upfield shift observed in the ^{119}Sn NMR spectrum of **6**.

In the case of the meta and para isomers $[(m(p)\text{-MeO-}C_6H_4)CH_2]_2SnCl_2$, **10** and **11**, the ^{119}Sn NMR chemical shifts at 31.9 and 30.7 ppm, respectively. These values are similar to the benzyl compounds (**9** and **12**) without any form of intramolecular bonding, suggesting that, at least in solution, there are no significant intermolecular interactions.

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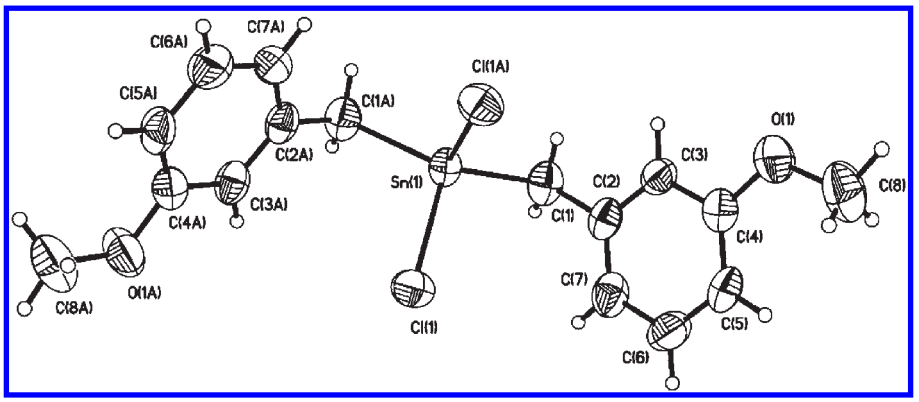

Figure 3. ORTEP diagram of compound **10**.

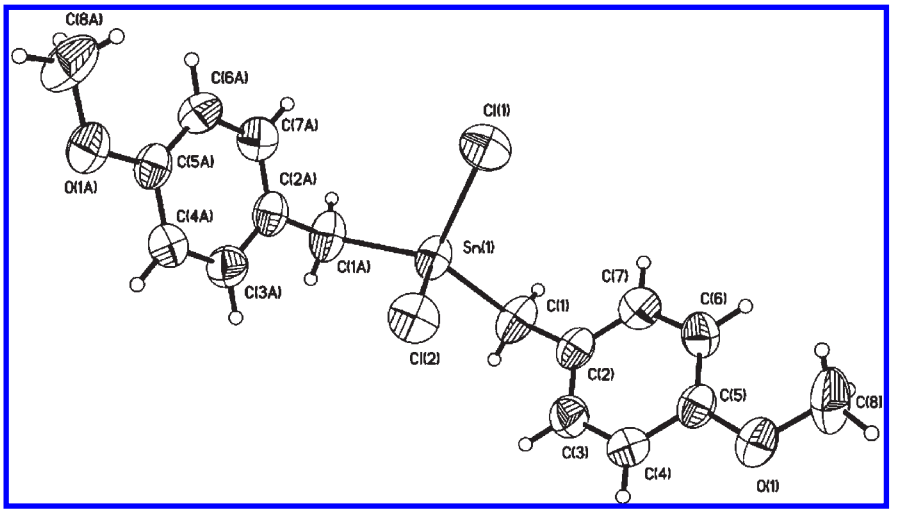

Figure 4. ORTEP diagram of compound **11**.

Crystal Structure Analysis. X-ray-quality crystals of compounds **3**, **6**, **10**, and **11** were obtained and used to determine the molecular structures which are presented in Figures 1, 2, 3, and 4, respectively. Selected geometrical parameters are summarized in Tables 2 and 3 and illustrate that compounds the various Sn−C bond distances for this series of exhibit no significant variation within the experimental error from the expected values and fall within the sum of the covalent radii [2.15(4) Å] for tin and carbon (Table 2).[8]

For compound **3**, we found two different conformers in the crystal structure obtained from hexane/THF, **3′** (symmetry related) and **3″** (asymmetric), both illustrated in Figure 1. Since this crystal structure included a THF molecule, we surmised that a different polymorph could be obtained by recrystallization from hexane, and indeed a new polymorph **3a** was obtained composed of only **3″**. In **3′** and **3″**, no short intermolecular contact is observed between Sn and Cl atoms, but intramolecular interactions of both oxygen atoms with the tin atom are observed [r(Sn···O) = 2.630(4) for **3′**, 2.692(4) and 2.711(4) Å for **3″**]. These interactions are 71.3, 72.9, and 73.5% of the ΣvdW radii (3.69 Å),[9] respectively. These distances are longer than those reported for dichloro-bis(2,6-bis(methoxymethyl)-phenyl)-(IV),[10] 2.508(2) and 2.343(2) Å, that correspond to 68.0 and 63.5% of the sum of VdW radii and longer than the related Sn···O distance of 2.559(4) Å in bis(2-methoxy-3-^{t}butyl-5-methylphenyl)methaneSnPhCl$_2$.[2g] The Sn atoms in these crystal structures have four covalent bonds and two short contacts [4 + 2] with the oxygen atoms. Thus, the coordination geometry at the tin atom can be described as a distorted bicapped tetrahedral or as a distorted octahedral geometry; however, the analyses of the angles around the tin atom show that it is best described as a distorted bicapped tetrahedron. The sum of all angles around the central atom in an ideal tetrahedral geometry is 1549, while for an ideal octahedral geometry, it is 1620. For the structures **3′** and **3″**, the observed values are 1552 and 1562, showing that they have 95.5 and 81.5% bicapped tetrahedral geometry character. The choice of the bicapped tetrahedral structure over octahedral shows that the donor strength of the O atoms in these structures is apparently insufficient to hybridize the tin atom, a situation similar to that well-recognized in related hexa-substituted silicon compounds[11]

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Table 2. Selected Bond Lengths [Å] and Angles [deg][a]

	3A, **3′**, X = O[b]	**3A**, **3″**, X = O	**3B**, **3″**, X = O	**6**, X = S[c]	**10**, X = Cl	**11**, X = Cl
Sn(1)−C(1)	2.136(6)	2.142(5)	2.138(5)	2.143(3)	2.135(4)	2.136(5)
Sn(1)−C(9)		2.150(6)	2.151(7)			
Sn(1)−Cl(1)	2.374(2)	2.381(1)	2.379(2)	2.399(1)	2.358(1)	2.356(2)
Sn(1)−Cl(9)		2.381(1)	2.372(2)			2.372(2)
Sn(1)···X(1)	2.630(4)	2.692(4)	2.666(4)	3.029(1)	3.816	3.943
Sn(1)···X(2)		2.711(4)	2.715(4)			3.502
C(1)−Sn(1)−C(9)	131.7(3)	134.7(2)	134.79(26)	142.8(2)	133.99(23)	127.73(27)
C(1)−Sn(1)−Cl(1)	105.03(19)	101.68(16)	105.66(17)	102.83(9)	104.98(13)	110.32(17)
C(1)−Sn(1)−Cl(2)	107.15(16)	109.21(17)	103.27(14)	101.7(1)	104.44(13)	104.86(14)
C(9)−Sn(1)−Cl(1)	107.15(16)	106.12(17)	103.99(20)	101.7(1)	104.44(13)	110.32(18)
C(9)−Sn(1)−Cl(2)	105.03(19)	102.30(17)	106.49(19)	102.83(9)	104.98(13)	104.86 (14)
Cl(1)−Sn(1)−Cl(2)	94.71(8)	96.63(6)	96.37(06)	96.66(4)	98.99(6)	92.37(7)
sym. operation	$2-x, y, 1.5-z$			$-x+2, y, -z+1/2$	$-x+2, y, -z+1/2$	$x, 1.5-y, z$

[a] The atoms C9, X2, and Cl2 for compounds **3′**, **6**, **10**, and **11** were generated with the appropriate symmetry operation listed at the end of each column, from the positions of C1, X1, and Cl1, respectively. [b] The X denoted in each column corresponds to the atom which is making the intra- or intermolecular contact. [c] For compound **6**, Cl(1) and Cl(2) in the table correspond to Cl(1A) and Cl(1), respectively, in the figures and CIF file.

Table 3. Selected Angles [deg][a]

	3A, **3′**, X = O[b]	**3A**, **3″**, X = O	**3B**, **3″**, X = O	**6**, X = S[c]	**10**, X = Cl[d]	**11**, X = Cl[d]
X(1)···Sn(1)−Cl(1)	82.38(10)	85.93(09)	80.78(09)	85.01(3)	102.49(4)	57.63(5)
X(1)···Sn(1)−Cl(2)	172.88(10)	167.72(10)	168.10(11)	171.63(2)[n]	158.52(3)	149.99(7)
X(1) ···Sn(1)−C(1)	67.61(18)	66.23(18)	66.80(16)	68.81(9)	69.64(12)	80.49(18)
X(1)··· Sn(1)−C(2)	82.06(21)	84.94(19)	85.39(21)	85.88(10)	69.99(12)	80.49(18)
X(1)···Sn(1)···X(2)	101.23(18)	101.26(12)	101.45(13)	94.53(4)	56.03(3)	144.39(4)
X(2)···Sn(1)−Cl(1)	172.88(10)	165.13(09)	169.82(10)	171.63(2)	158.52(3)	157.98(4)
X(2)···Sn(1)−Cl(2)	82.38(10)	79.12(09)	83.41(10)	85.01(3)	102.49(4)	65.61(6)
X(2) ···Sn(1)−C(1)	82.06(21)	85.64(19)	84.23(18)	85.88(10)	69.99(12)	84.06(17)
X(2)··· Sn(1)−C(2)	67.61(18)	65.84(18)	66.53(20)	68.81(9)	69.64(12)	84.06(17)
	$2-x, y, 1.5-z$			$-x+2, y, -z+1/2$	$-x+2, y, -z+1/2$	$x, 1.5-y, z$

[a] The atoms X1, C1, Cl1, C3, C8, C3, and C2 are equivalents to X2, C2, Cl2, C11, and C10, respectively, for compounds **3′**, **6**, **10**, and **11** by the appropriate symop listed at the end of each column. [b] The X denoted in each column corresponds to the atom which is making the intra- or intermolecular contact. [c] For compound **6**, Cl(1) and Cl(2) in the table correspond to Cl(1A) and Cl(1), respectively, in the figures and CIF file. [d] For compounds **10** and **11**, C2 and C3 correspond to C3 and C4 and to C4 and C5, respectively.

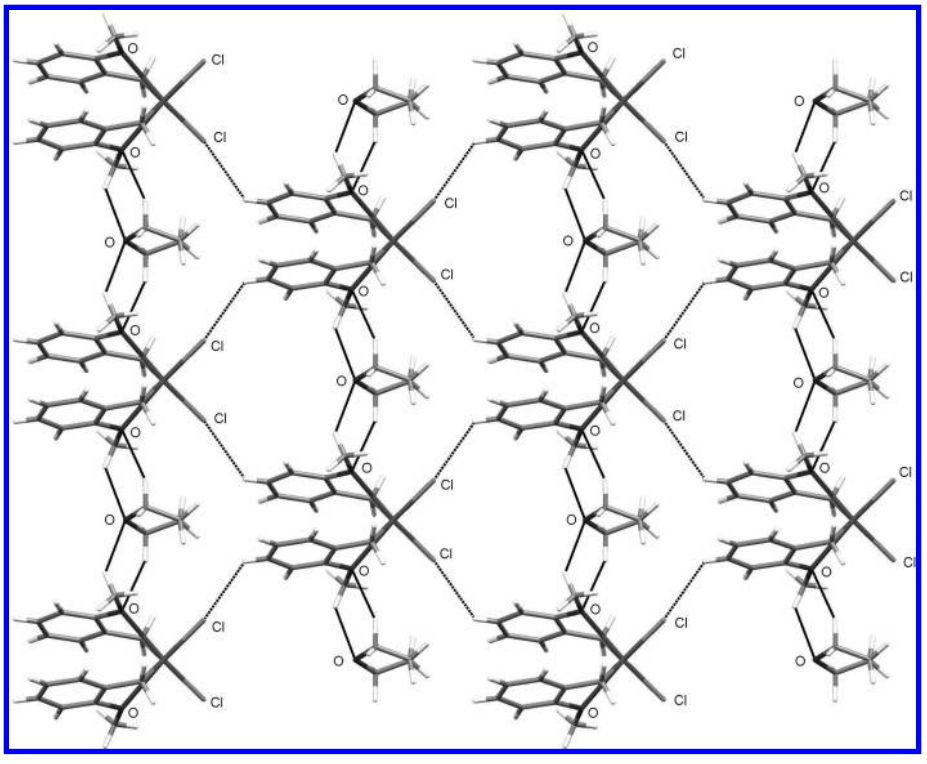

Figure 5. The 2-D architecture generated by conformer **3′** via Cl···H HBs in the polymorph **3**. The encapsulation of THF molecules via further HBs is shown.

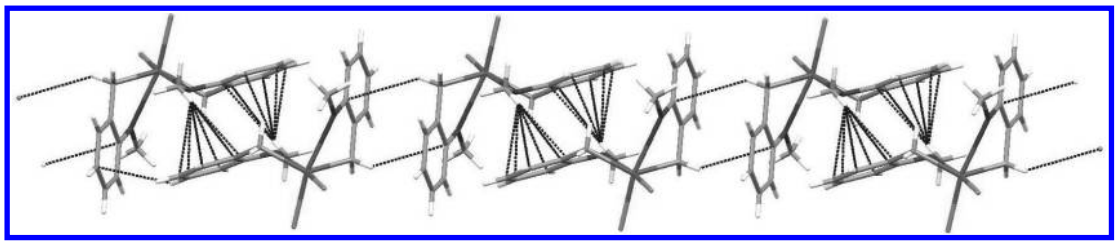

Figure 6. The chain motif formed in the polymorph **3B** along the *c* direction via H···π interactions with the methyl and methylene group.

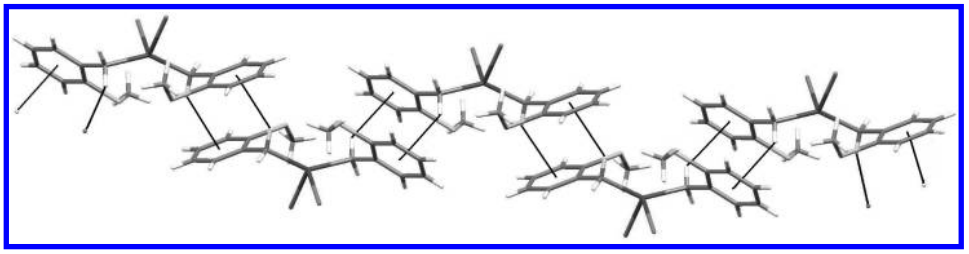

Figure 7. The chain motif parallel to the *c* direction found in the crystal structure of **6** formed by H···π bonds. The chain is interlinked to others via H···Cl bonds not shown for clarity.

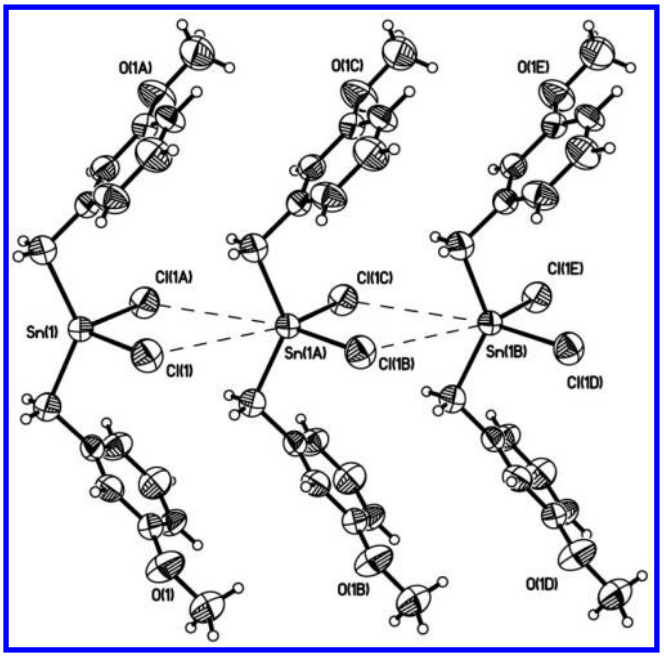

Figure 8. Segment of the chain of **10** with the two equivalent contacts Cl···Sn. The H···π interaction is not shown here for simplicity.

and other systems,[12] where it has been argued that ionic contributions to the higher coordination numbers predominate over any covalent contributions.[11d] Similar behavior is common to related tin compounds with intramolecular contacts, for example, dichloro-bis(2,6-bis('butoxymethyl)phenyl)-tin(IV),[10] dibromo-bis(1,2-diethoxycarbonyl-ethyl)-tin(IV),[13] and bis(2-carboethoxy-ethyl)-diiodo-tin(IV).[14]

As noted in Figure 1, the major difference between the conformers **3′** and **3″** is the orientation of the aromatic rings: in the case of **3′** they have a tilt angle of only 7.65(20)° because there is a $\pi-\pi$ interaction between them, while in **3″** the tilt angle is 111.82(11)°, an unusual distinction within a single molecular species.

In the polymorph **3**, the conformer **3′** generates a 2-D network (Figure 5) in the plane [001] via hydrogen bonds (HBs), with the chlorine atoms acting as acceptors [HB1, r(H5···Cl1) = 2.90 Å]. The THF molecule occupies the cavities left in the 2-D framework of **3′**, and it is fixed in them by two HBs. [The complementary geometrical parameters for each HB are listed together with the symmetry operations used to generate the equivalent atoms in Table S1 in the Supporting Information.] The first one is a bifurcated HB symmetrically equivalent to O1S (S = solvent) toward the methyl group of two **3′** molecules [HB2, r(H8C···O1S) = 2.81 Å]; the second one is a HB donor to the methoxy oxygen [HB3, r(H1SB···O1) = 2.76 Å], and in total these interactions generate a chain motif in the *a* direction that reinforces the 2D network (Figure 5).

There is a second motif which is responsible for the 3D nature of the crystal structure; this new motif is a chain, ·(·THF···**3″**···**3′**···**3″**·)$_n$·, formed by Cl···H interactions with conformer **3″** above and below the 2-D network [HB4, r(H13···Cl1) = 2.89 Å; HB5, r(H7···Cl2) = 2.69 Å] and to THF molecules from **3″** [HB6, r(H1SA···Cl1) = 2.84 Å]. Additionally, two intermolecular H···π interactions are noted,[15] which add force to the crystal structure just described, forming an helicoidal chain motif in the *c* direction [HB7, r(H8A···R_{C2}) = 2.66; HB8, r(R_{C2}···H16B) = 2.74 Å].

In the crystal structure of the polymorph **3a**, the architecture described for **3** is lost, because only **3″** is present. Now, **3″** forms chains along the *c* direction through H···π bonds of the side-on-side type involving the methylene and the methyl groups [HB9, r(H1B···R_{C2}) = 2.77 Å; HB10,

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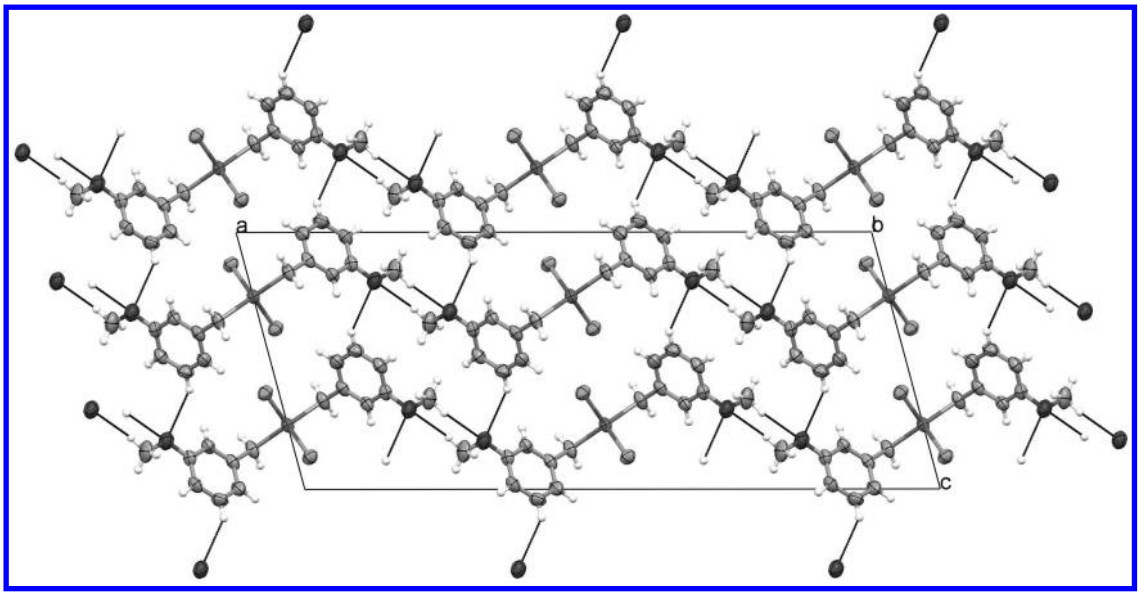

Figure 9. Crystal packing of **10** along the *b* axis with the HBs formed by the oxygen displaying zigzag layers linked by HB with the aromatic hydrogens.

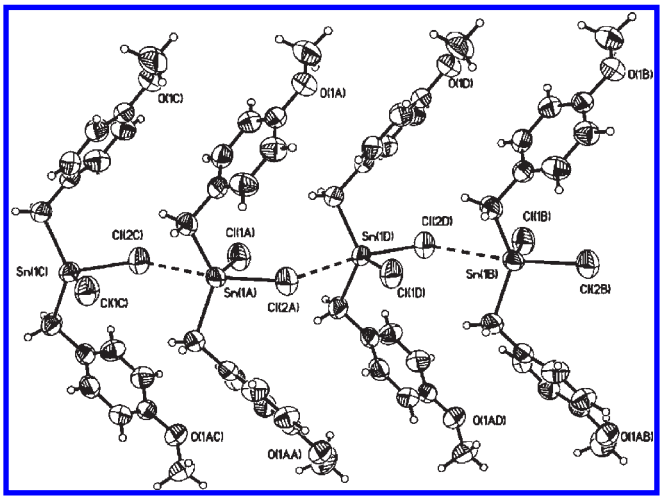

Figure 10. The chain generated by Cl···Sn interactions in the crystal structure of **11**. Only the heavy atoms are labeled; the rest of the atoms are omitted for clarity.

$r(R_{C10}\cdots H16C)$ = 2.81 Å], Figure 6. These chains are interlinked by Cl···H interactions which are longer than in **3** [HB11, r(H6···Cl1) = 3.04 Å; HB12, r(H14···Cl2) = 3.03 Å; HB13, r(H8···CCl2) = 2.99 Å; HB14, r(H12···Cl2) = 2.85 Å].

For the sulfur analog **6** (Figure 2), the distance Sn···S, 3.029(1), is 76.5% of the ΣvdW radii, and the coordination geometry around the tin atom in **6** is again a bicapped tetrahedral, 76% character, similar to **3″**. The structure is different from that of both conformers of **3** (Figure 1): the dihedral angle C2−C1−C1A−C2A is 179.86°, while in **3″** it is −103°, and the crystal structure consists of a chain along the *c* direction (Figure 7) formed by H···π [HB15, $r(H1A\cdots R_{C2})$ = 2.87 Å] interlinked by means of Cl···H bonds [HB16, r(Cl1···H4) = 2.89 Å; HB17, r(Cl1···H6) = 2.83 Å]. The differences observed in the conformation and the crystal structure of **6** with repect to **3** is a consequence of having the methyl group out of the aromatic plane.

In contrast to the crystal structures of **6** and **3**, the *meta*- and *para*-$(MeOC_6H_4)CH_2]_2SnCl_2$ compounds (**10** and **11**) exhibit neither intra- nor intermolecular Sn···O secondary bonding. Indeed the meta compound **10** is isostructural with **12**[16] and exhibits two equivalent Sn−Cl bonds (2.364 Å) and two equivalent Cl···Sn intermolecular contacts of 3.816 Å (97.3% of the ΣvdW radii of Sn and Cl), generating a typical chlorine-bridged polymeric structural arrangement (Figure 8). These intermolecular interactions are long and seem to have no effect on the coordination geometry at Sn, which is tetrahedral for **10** and for the following structures which bear the same structural arrangement: $(ClCH_2)_2SnCl_2$,[17] dichloro-bis-(2-fluorobenzyl)-tin,[18] and bis(*p*-chlorobenzyl)-dichlorotin.[19] Whether this structural arrangement is due to packing features or to dipolar interactions is presently an open question. Although no O···Sn interaction is present in the structure, the O atom contributes to the crystal structure via two HBs, [HB18, r(O1···H8A) = 2.60 Å; HB19 r(Ol···H6) = 2.78 Å], with an angle of 92° between them. HB18 links identical enantiomers, thereby generating zigzag layers along the *ab* plane [001], and HB19 interconnects these chains (Figure 9).

In the crystal structure of **10**, the aromatic rings are arranged head-to-head on the same plane, generating unfavorable interactions between the methyl hydrogens and the *p*-hydrogen [r(H···C8) = 2.97 Å). A search in the CSD[20] revealed three other crystal structures of phenols that bear this kind of unfavorable interaction: 2-((3-methoxyphenyl)-ethynyl)-6-methylpyridine (3.36 Å),[21] 1,1′-bis(3-methoxybenzyl)-3,3′-methylene-di-imidazolium dibromide (2.97 Å),[22] and 3-methoxyphenylsalicyladimine (3.05 Å),[23] which is

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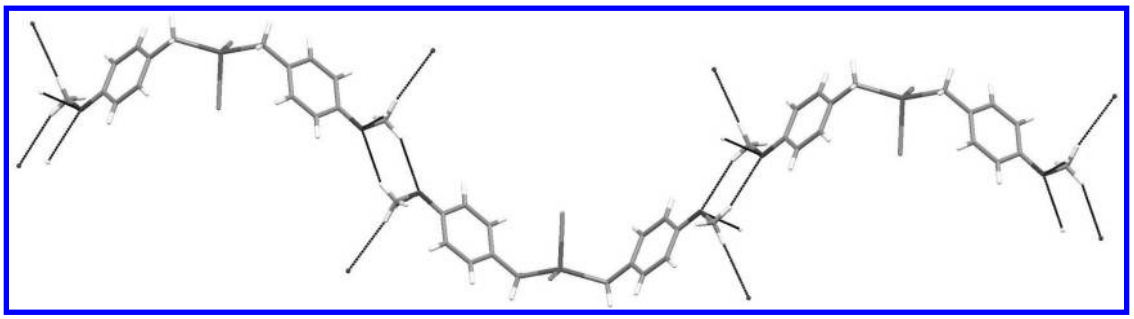

Figure 11. The secondary chain motif generated in the crystal structure of **11**, beside the Sn···Cl chain (omitted for clarity) through HB20, which is coplanar with the aromatic rings. The hanging contacts are the second HB that binds the chains.

overridden by the cooperative effect of the noncovalent interactions.

The structure of **11** has a conformation similar to that of **10**; however, the methyl groups are orientated toward the same side, resulting in a slight difference between the angles Cl1−Sn1−C1 [110.25(08)°] and Cl2−Sn1−C1 [104.86(15)°]. The coordination geometry at Sn is monocapped tetrahedral against the tetrahedral geometry described above for **10**. The crystal structure is also different from **10** since the contacts Cl···Sn are inequivalent, with one larger than the ΣvdW radii (3.943 Å) and the other 89.3% of the ΣvdW radii (3.502 Å), suggesting that only the second one is important, forming the major chain motif (Figure 10). Besides this interaction, two HBs with the methyl groups are formed; the first one is coplanar with the aromatic ring [HB20, r(O1···H8A) = 2.68 Å] generating a secondary chain motif (Figure 11), which is interconnected, through HB21 [r(O1···H8C) = 2.72 Å]. Then, the expansion of the crystal structure is done by oxygen-methyl group HBs as in **10**.

In summary, we have synthesized bis-benzyltindichloride compounds with MeO−, MeS−, $MeCH_2$−, and H− ortho substituents that clearly illustrate that a significant structural change occurs in the presence of the two Lewis base groups MeO− and MeS. The change results in intramolecular O(S)···Sn interactions, resulting in the formation of monomeric bicapped tetrahedral structures at tin with no intermolecular bridging chlorine interactions. Although weak, as determined by internuclear O(S)···Sn distances and geometric parameters at tin, the interactions are sufficiently strong to persist in solution as determined by ^{119}Sn NMR spectroscopy. The related isomeric meta- and para-MeO-substituted compounds exhibit neither inter- nor intramolecular O···Sn interactions and form polymeric structures involving bridging Cl···Sn linkages.

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Supporting Information Available: CIF files giving crystallographic data for **3**, **6**, **10**, and **11** together with a table containing the complementary geometrical parameters for each HB together with the symmetry operations used to generate the equivalent atoms. These data can be obtained free of charge via the Internet at http://pubs.acs.org.