

Inorg Chem. Author manuscript; available in PMC 2011 February 1.

Published in final edited form as:

Inorg Chem. 2010 February 1; 49(3): 960–968. doi:10.1021/ic901800c.

Intramolecular chalcogen-tin interactions in [(o-MeE-C₆H₄) CH₂]₂SnPh_{2-n}CI_n; E = S, O, CH₂, n = 0, 1, 2 and intermolecular chlorine-tin interactions in the *meta* and *para*-methoxy isomers

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Abstract

Organotin(IV) compounds of the type [(o-MeE- C_6H_4)CH₂]₂SnPh_{2-n}Cl_n were synthesized, E = O, n = 0 (1), n = 1 (2), n = 2 (3), E = S, n = 0 (4), n = 1 (5), n = 2 (6) and E = CH₂, n = 0 (7), n = 1 (8), n = 2 (9). The dichloro compounds 3 and 6 have been investigated by single crystal X-ray diffraction and exhibit bi-capped 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 non-equivalent Sn···O interactions. Upon 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, 72.9; and 76.3% of the Σ vdW 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.

Keywords

¹⁹Sn NMR; tin-oxygen coordination; tin-sulfur coordination; chloride-tin coordination; intramolecular contacts; intermolecular contacts

Introduction

We recently demonstrated the capacity of the o-methoxy-benzyl 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-MeEC $_6$ H $_4$ CH $_2$) Ph $_3$ -nSnCl $_n$, n = 0, 1, 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 intra-molecular interactions. 2

Inter(intra)molecular secondary bonding of the type $Sn \cdot \cdot \cdot E$, E = S, O, N has been suggested to be important with respect to the biological activity of organotins (OTs).³ Our current interest

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Supplementary material. 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.

is related to the specific capacity of OTs to reduce the capacity of human natural killer (HNK) cells to function. ^{4a} Since these cells are an essential part of our immune system, and OTs are found in our blood stream 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,4c,4d} we have initiated a study of simple OTs in which O, S and N atoms are placed within the coordination sphere, but without direct sigma 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 formation of penta- and/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

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, 1M tin tetrachloride in methylene chloride, 1-bromo-3-chloropropane, methanethiol and 1M HCl in diethyl ether were purchased from Aldrich; 2-thiomethylbenzyl chloride was synthesized by published methods. 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 CDCl₃ or C_6D_6 as 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**, 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 MoK $_{\alpha}$ 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. 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. 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 SOCl₂ (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 benzene) was added dropwise and the mixture was stirred for 30 min. The mixture was then refluxed for 2 h, 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 NaHCO₃. 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, b.p. 60-62 °C. Yield 2.72 g (48%). 1 H NMR (CDCl₃) δ 2.07 (3H, t, -CH₃, J = 7.5 Hz), 3.54 (2, q, -CH₂CH₃, J = 7.5 Hz), 5.41 (2H, s, -CH₂Cl), 8.26-7.75 (4H, m, Ph). 13 C NMR (CDCl₃) δ 15.3 (-CH₃), 25.3 (-CH₂CH₃), 44.4 (-CH₂Cl), 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 $_2$ SnCl $_2$ (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: 1.48g (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.

¹H NMR (CDCl₃) δ 3.29 (4H, s, Ar-C<u>H</u>₂Sn, ²J(^{117/119}Sn, ¹H) = 20.12/33.26 Hz), 4.15 (6H, s, <u>Me</u>-O-Ar), 8.00-7.31 (18H, m, Ph, Ar). ¹³C NMR (CDCl₃) δ 15.49 (2C, Ar-<u>C</u>H₂Sn, ¹J(¹³C, ¹¹⁷/¹¹⁹Sn) = 312.74/327.23 Hz), 54.60 (2C, <u>Me</u>-O-Ar), 109.51 (2C, C3-Ar, ⁴J(¹³C, ¹¹⁹Sn) = 12.9 Hz), 120.50 (2C, C5-Ar, ⁴J(¹³C, ¹¹⁹Sn) = 11.7 Hz), 125.12 (2C, C4-Ar, ⁵J(¹³C, ¹¹⁹Sn) = 15.67 Hz), 127.97 (4C, C2-Ph), 128.36, (2C, C4-Ph), 128.67 (2C, C6-Ar, ³J(¹³C, ¹¹⁹Sn) = 29.7 Hz), 130.34 (2C, C1-Ar, ²J(¹³C, ¹¹⁹Sn) = 21.0 Hz), 136.37 (4C, C3-Ph, ³J(¹³C, ¹¹⁹Sn) = 33.37 Hz), 141.36 (2C, C1-Ph, ¹J(¹³C, ¹¹⁷/¹¹⁹Sn) = 434.17/454.57 Hz), 155.90 (2C, C2-Ph, ³J(¹³C, ¹¹⁹Sn) = 10.80 Hz). ¹¹⁹Sn NMR (CDCl₃) δ -96.6.

Using the same synthetic approach we obtained the following compounds:

 $[(o-MeSC_6H_4)CH_2]_2SnPh_2$ (4), 1.6 g (50%); mp 72-74 °C.

¹H NMR (CDCl₃) δ 2.87 (6H, s, <u>Me</u>-S-Ar), 3.45 (4H, s, Ar-C<u>H</u>₂-Sn, ²J(^{117/119}Sn, ¹H) = 19.88/31.51 Hz), 7.95-7.74 (18H, m, Ph, Ar). ¹³C NMR (CDCl₃) δ 15.57 (2C, <u>Me</u>-S-Ar), 22.84 (2C, Ar-<u>C</u>H₂Sn, ¹J(¹³C, ¹¹⁷/¹¹⁹Sn) = 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(¹³C, ¹¹⁹Sn = 25.27 Hz), 136.55 (4C, C3-Ph, ³J(¹³C, ¹¹⁹Sn) = 33.9 Hz), 139.69 (2C, C1-Ar, ²J(¹³C, ¹¹⁹Sn) = 42.3 Hz), 141.07 (2C, C1-Ph, ¹J(¹³C, ¹¹⁹Sn) = 436.42/470.1 Hz). ¹¹⁹Sn NMR (CDCl₃) δ -98.8: Anal. Calcd for C₂₈H₂₈S₂Sn: C, 61.44; H, 5.16. Found: C, 61.50; H, 5.13.

$[(o-EtC_6H_4)CH_2]_2SnPh_2$ (7), 2.15 g (65%).

¹H NMR (CDCl₃) δ 1.79 (6H, t, Ar-CH₂Me, ³*J*(H,H) = 7.5 Hz), 3.07 (4H, q, -CH₂CH₃, ³*J* (H,H) = 7.5 Hz), 3.41 (4H, s, Ar-CH₂-Sn, ²*J*(^{117/119}Sn, ¹H) = 31.72/32.74 Hz), 8.04-7.67 (18H, m, Ph, Ar). ¹³C NMR (CDCl₃) δ 14.01 (2C, Ar-CH₂Me), 17.53 (2C, Ar-CH₂Sn, ¹*J* (¹³C, ^{119/117}Sn) = 290.82/304.25 Hz), 26.36 (2C, Ar-CH₂Me), 124.55 (2C, C3-Ar, ⁴*J* (¹³C, ¹¹⁹Sn) = 16.87 Hz), 126.15 (2C, C-Ar, *J*(¹³C, ¹¹⁹Sn) = 13.8 Hz), 128.01 (2C, C-Ar, *J* (¹³C, ¹¹⁹Sn) = 14.55 Hz), 128.49 (2C, C4-Ph), 128.5 (4C, C2-Ph), 128.90 (2C, C-Ar, *J* (¹³C, ¹¹⁹Sn) = 10.65 Hz), 136.63 (4C, C3-Ph, ³*J*(¹³C, ¹¹⁹Sn) = 33.37 Hz), 138.89 (2C, C1-Ph), 139.69 (2C, C2-Ar). ¹¹⁹Sn NMR (CDCl₃) δ -103.7: Anal. Calcd for C₃₀H₃₂Sn: C, 70.47; H, 6.31. Found: C, 70.51; H, 6.39.

Synthesis of [(o-MeOC₆H₄)CH₂]₂SnPhCl (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 $^{\circ}$ C, 0.32 g (35%).

 1 H NMR (CDCl₃) δ 3.35 (4H, s, Ar-C<u>H</u>₂-Sn, 2 $J(^{117/119}$ Sn, 1 H) = 20.98/34.12 Hz), 4.07 (6H, s, Ar-O<u>Me</u>), 8.03-7.20 (13H, m, Ar, Ph): 13 C NMR (CDCl₃) δ 21.76 (2C, Ar-<u>C</u>H₂-Sn), 54.57 (2C, Ar-O<u>Me</u>), 109.38 (2C, C3-Ar), 121.01 (2C, C5-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 (CDCl₃) δ -11.9: Anal. Calcd for C₂₂H₂₃ClO₂Sn: C, 55.80; H, 4.90. Found: C, 56.01; H, 5.04.

 $[(o-MeSC_6H_4)CH_2]_2SnPhCl$ (5) as a liquid product, 0.35g (38%).

 1 H NMR (CDCl₃) δ 2.16 (6H, s, Ar-S<u>Me</u>), 3.07 (4H, s, Ar-C<u>H</u>₂-Sn, 2 $J(^{117/119}$ Sn, 1 H) = 20.43/33.18 Hz), 7.74-6.99 (13H, m, Ar, Ph): 13 C NMR (CDCl₃) δ 16.37 (2C, Ar-S<u>Me</u>), 29.52 (Ar-C<u>H</u>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 (CDCl₃) δ -20.2. Anal. Calcd for C₂₂H₂₃ClS₂Sn: C, 52.25; H, 4.58. Found: C, 52.32; H, 4.69.

[(o-EtC₆H₄)CH₂]₂SnPhCl (8), 2.47 g (90%).

¹H NMR (CDCl₃) δ 1.85 (6H, t, Ar-CH₂Me, ³J(¹H, ¹H) = 7.4 Hz), 3.14 (4H, q, Ar-C<u>H</u>₂Me, ³J(¹H, ¹H) = 7.4Hz), 3.64 (4H, s, Ar-CH₂-Sn, ²J(^{117/119}Sn, ¹H) = 33.27/35.30 Hz), 8.12-7.67 (13H, m, Ar, Ph): ¹³C NMR (CDCl₃) δ 14.32 (2C, Ar-CH₂Me), 24.08 (2C, Ar-CH₂Sn, ¹J(¹³C, ^{119/117}Sn) = 287.44/318.72 Hz), 26.45 (2C, Ar-<u>C</u>H₂Me), 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): ¹¹⁹Sn NMR (CDCl₃) δ -11.9: Anal. Calcd for C₂₄H₂₇ClSn: C, 61.38; H, 5.79. Found: C, 61.42; H, 5.82.

Synthesis of [(o-MeOC₆H₄)CH₂]₂SnCl₂ (3)—To tin powder (1.52 g, 11.6 mmol) was added 3 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 hrs of reflux, the solution was cooled, 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%), m.p. 92-94 °C.

¹H NMR (CDCl₃) δ 3.66 (4H, s, Ar-C<u>H</u>₂-Sn, ²*J*(^{117/119}Sn, ¹H) = 20.58/48.84 Hz), 3.95 (6H, s, Ar-O-<u>Me</u>), 7.90-7.17 (8H, m, Ar): ¹³C NMR (CDCl₃) δ 55.15 (2C, Ar-O-<u>Me</u>), 31.09 (2C, Ar-<u>CH</u>₂Sn, ¹*J*(¹³C, ¹¹⁹Sn) = 539.25/564.3 Hz), 109.41 (2C, C3-Ar, ⁴*J*(¹³C, ¹¹⁹Sn) = 19.87 Hz), 121.40 (2C, C5-Ar), 125.15 (2C, C1-Ar, ²*J*(¹³C, ¹¹⁹Sn) = 53.55 Hz), 127.76 (2C, C4-Ar, ⁵*J*(¹³C, ¹¹⁹Sn) = 18.75 Hz), 129.46 (2C, C6-Ar, ³*J*(¹³C, ¹¹⁹Sn) = 43.05 Hz), 155.05 (2C, C2-Ar, ³*J*(¹³C, ¹¹⁹Sn) = 35.85 Hz). ¹¹⁹Sn NMR (CDCl₃) δ -35.39: Anal. Calcd. for C₁₆H₁₈Cl₂O₂Sn: 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-MeSC₆H₄)CH₂]₂SnCl₂ (6), yield 1.75g (65%). mp 154-156 °C.

 $^{1}\text{H NMR (CDCl}_{3}) \ \delta \ 2.95 \ (6\text{H, s, Ar-S-C}\underline{H}_{3}), \ 3.96 \ (4\text{H, s, Ar-C}\underline{H}_{2}\text{-Sn, }^{2}J(^{117/119}\text{Sn,}^{1}\text{H}) = 12.95/33.01 \ \text{Hz}), \ 8.01\text{-}7.89 \ (8\text{H, m, Ar}). \ ^{13}\text{C NMR (CDCl}_{3}) \ \delta \ 15.48 \ (2\text{C, Ar-S-C}\underline{H}_{3}), \ 41.78 \ (2\text{C, Ar-C}\underline{H}_{2}\text{Sn,}^{1}J(^{13}\text{C,}^{117/119}\text{Sn}) = 541.05/566.25 \ \text{Hz}), \ 127.18 \ (2\text{C)}, \ 127.48 \ (2\text{C}), \ 127.66 \ (2\text{C}), \ 130.00 \ (2\text{C, C6-Ar,}^{3}J(^{13}\text{C,}^{119}\text{Sn}) = 76.125 \ \text{Hz}), \ 134.50 \ (2\text{C, C2-Ar,}^{3}J(^{13}\text{C,}^{119}\text{Sn}) = 26.10 \ \text{Hz}), \ 137.58 \ (2\text{C, C1-Ar,}^{2}J(^{13}\text{C,}^{119}\text{Sn}) = 51.45 \ \text{Hz}). \ ^{119}\text{Sn NMR (CDCl}_{3}) \ \delta \ -54.7: \ \text{Anal.} \ \text{Calcd for C}_{16}\underline{H}_{18}\text{Cl}_{2}\text{S}_{2}\text{Sn: C, } 41.41; \ \text{H, } 3.91. \ \text{Found: C, } 41.79; \ \text{H, } 3.74.$

[(o-EtC₆H₄)CH₂]₂SnCl₂ (9), 2.39 g (70%); mp 110-112 °C.

¹H NMR (CDCl₃) δ 1.89 (6H, t, Ar-CH₂-Me, ${}^3J({}^1H, {}^1H) = 7.4$ Hz, 3.15 (4H, q, Ar-CH₂-Me, ${}^3J({}^1H, {}^1H) = 7.4$ Hz, 3.15 (4H, q, Ar-CH₂-Me, ${}^3J({}^1H, {}^1H) = 7.4$ Hz), 3.90 (4H, s, Ar-CH₂Sn, ${}^2J({}^{117/119}Sn, {}^1H) = 38.16/39.69$ Hz), 7.88-7.67 (8H, m, Ar): ¹³C NMR (CDCl₃) δ 14.42 (Ar-CH₂-Me), 26.43 (Ar-CH₂-Me), 31.24 (Ar-CH₂-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). ¹¹⁹Sn NMR (CDCl₃) δ 40.3. Anal. Calcd for C₁₈H₂₂Cl₂Sn: C, 50.51; H, 5.18. Found: C, 50.42; H, 5.03.

[(m-MeOC₆H₄)CH₂]₂SnCl₂ (10), 0.52 g (57%); mp. 142-145°C.

¹H NMR (CDCl₃) δ 3.08 (4H, s, Ar-C<u>H</u>₂-Sn, ²*J*(^{117/119}Sn, ¹H) = 41.16/48.84 Hz), 3.70 (6H, s, Ar-O-<u>Me</u>), 6.54-6.70 (8H, m, Ar). ¹³C NMR (CDCl₃) δ 55.1 (2C, Ar-O-<u>Me</u>), 32.4 (2C, Ar-<u>CH</u>₂-Sn), 112.1 (2C, C2-Ar), 113.6 (2C, C4-Ar), 120.5 (2C, C5-Ar), 130.1 (2C, C6-Ar), 136.2 (2C, C1-Ar), 150.2 (2C, C3-Ar). ¹¹⁹Sn NMR (CDCl₃) δ 31.8. Anal. Calcd. for C₁₆H₁₈Cl₂O₂Sn: C, 44.49; H, 4.20. Found: C, 45.74; H, 4.17.

 $[(p-MeOC_6H_4)CH_2]_2SnCl_2(11)$, 0.62 g (70%); mp. 138-141 °C.

¹H NMR (CDCl₃) δ 3.08 (4H, s, CH₂-Sn, $^2J(^{117/119}Sn,^1H) = 41.16/48.84$ Hz), 3.74 (6H, s, Ar-O-<u>Me</u>), 6.70-6.6.80 (8H, m, Ar). ¹³C NMR (CDCl₃) δ 55.2 (2C, Ar-O-<u>C</u>H₃), 31.6 (2C, Ar-<u>C</u>H₂-Sn), 114.8 (2C, C3-Ar), 126.3 (2C, C1-Ar), 129.3 (2C, C2-Ar), 158.2 (2C, C4-Ar). ¹¹⁹Sn NMR (CDCl₃) δ 30.7

Results and Discussion

We prepared the $[(o-MeE-C_6H_4)CH_2]_2Ph_{2-n}Cl_nSn$ 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.

$$\begin{split} Ph_2SnCl_2 + 2[\,(o - MeEC_6H_4)CH_2]MgCl & \rightarrow [\,(o - MeEC_6H_4)CH_2]_2Ph_2Sn + 2MgCl_2 \\ & E = O(1), E = S(4), E = CH_2(7) \end{split} \tag{1}$$

$$2(o - MeEC_6H_4)CH_2Cl + Sn^0 \rightarrow [(o - MeEC_6H_4)CH_2]_2SnCl_2$$

E=O(3), E=S(6), E=CH₂(9) (3)

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: $\mathbf{1} \to \mathbf{2}$ (-96.6 \to -11.9 ppm), $\mathbf{4} \to \mathbf{5}$ (-98.8 \to -20.2 ppm) and $\mathbf{7} \to \mathbf{8}$ (-103.7 \to -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 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. We have prepared [(o-CH₃CH₂-C₆H₄)CH₂]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 non-coordinating methylene group. We also synthesized the unsubstituted dibenzyl compound (C₆H₄CH₂)₂SnCl₂ (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, i.e. 12 and 9. The 119 Sn chemical shifts for the latter are 35.4 ppm 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 $\bf 6$ than for $\bf 3$ as judged by the greater upfield shift observed in the 119 Sn NMR spectrum o $\bf 6$.

In the case of the *meta* and *para* isomers $[(m(p)-MeO-C_6H_4)CH_2]_2SnCl_2$, **10** and **11**, the ¹¹⁹Sn NMR chemical shifts at 31.9 ppm 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.

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. Selected geometrical parameters are summarized in Tables 2 and 3 and illustrate that the various Sn-C bond distances for this series of compounds 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 $[r(Sn\cdots O) = 2.630(4) \text{ for } 3', 2.692(4) \text{ and } 2.711(4) \text{ Å for } 3''].$ These interactions are 71.3, 72.9, and 73.5% of the Σ vdW 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-tbutyl-5methylphenyl)methaneSnPhCl₂.^{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 analysis 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 is 1620. For the structures 3' and 3" the observed values are 1552 and 1562 showing that they have 95.5 and 81.5% of 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 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, e.g. dichloro-bis(2,6-bis(tbutoxymethyl)phenyl)-tin (IV), 10 dibromo-bis(1,2-diethoxycarbonyl-ethyl)-tin(IV), 13 bis(2-carboethoxyethyl)diiodotin(IV).14

As noted in Figure 1, the major difference between the conformers $\bf 3'$ and $\bf 3''$ is the orientation of the aromatic rings, in the case of $\bf 3'$ they have a tilt angle of only $7.65(20)^{\circ}$ because there is a π - π interaction between them, while in $\bf 3''$ the tilt angle is $111.82(11)^{\circ}$ an unusual distinction within a single molecular species.

In the polymorph 3 the conformer 3' generates a 2-D network (Fig. 5) in the plane [001] via hydrogen bonds (HB's) with the chlorine atoms acting as acceptors [HB1, r(H5···Cl1) = 2.90 Å]^a and the THF molecule occupies the cavities left in the 2-D framework of 3' and it is fixed in them by two HB's. The first one is a bifurcated HB symmetrically equivalent from O1S (S = solvent) toward the methyl group of two 3' molecules [HB2, r(H8C···O1S) = 2.81 Å], the

second one is as HB donor to the methoxy oxygen [HB3, $r(H1SB\cdots O1) = 2.76 \text{ Å}$] and in total these interactions generate a chain motif in the *a* direction that reinforces the 2D network (Fig. 5).

There is second motif which is responsible for the 3D nature of the crystal structure, this new motif is a chain $\cdot (\cdot THF\cdots 3''\cdots 3''\cdots 3'')_n \cdot formed$ 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 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 c direction through $H\cdots\pi$ bonds side on side type involving the methylene and the methyl groups [HB9, r(H1B···R_{C2}) = 2.77 Å; HB10, r (R_{C10}···H16C) = 2.81 Å], Fig. 6. These chains are interlinked by Cl···H interactions which are longer than in 3 [HB11, r(H6···C11) = 3.04 Å; HB12, r(H14···C12) = 3.03 Å; HB13, r (H8···CC12) = 2.99 Å; HB14, r(H12···C12) = 2.85 Å].

For the sulfur analog **6** (Fig. 2) the distance Sn···S, 3.029(1), is 76.5% of the Σ vdW 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 to both conformers of **3** (Fig. 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 (Fig. 7) formed by H··· π [HB15, r(H1A···R_{C2}) = 2.87 Å] interlinked by means of Cl···H bonds [HB16, r(C11···H4) = 2.89 Å; HB17, r(C11···H6) = 2.83 Å]. The differences observed in the conformation and the crystal structure of **6** with repect to **3** is 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*-[(MeO-C₆H₄)CH₂]₂SnCl₂ compounds (**10** and **11**), exhibit neither intra-, nor inter-molecular Sn···O secondary bonding. Indeed the *meta*-compound **10** is isostructural with the **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 Σ vdW 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 in the coordination geometry at Sn which is tetrahedral for **10** and for the following structures which bear the same structural arrangement: (ClCH₂)₂SnCl₂·¹⁷ dichloro-bis(2-fluorobenzyl)-tin, ¹⁸ and bis(p-chlorobenzyl)-dichloro-tin. 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 2 HBs, [HB18, r(O1···H8A) = 2.60 Å; HB19 r(Ol···H6) = 2.78 Å], with an angle of 92° between them. The HB18 links identical enantiomers thereby generating zig-zag layers along the *ab* plane [001] and the 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 CSD²⁰ 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 3-methoxyphenylsalicyladimine (3.05 Å)²³ which is overridden by the cooperative effect of the non-covalent interactions.

^aThe complementary geometrical parameters for each HB are listed together with the symmetry operations used to generate the equivalent atoms in the table S1 in the supplementary material.

The structure of $\bf 11$ has a conformation similar to that of $\bf 10$; however, the methyl groups are orientated to the same side resulting in a slight difference between the angles Cl1-Sn1-Cl [110.25(08)°] and Cl2-Sn1-Cl [104.86(15)°]. The coordination geometry at Sn is monocapped tetrahedral against the tetrahedral geometry described above for $\bf 10$. The crystal structure is also different from $\bf 10$ since the contacts Cl···Sn are inequivalent with one larger than the Σ vdW radii (3.943 Å) and the other 89.3% of the Σ vdW radii (3.502 Å) suggesting that only the second one is important, forming the major chain motif (Fig. 10). Besides this interaction two HB's 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 HB's as in $\bf 10$.

In summary we have synthesized bis-benzyltindichloride compounds with MeO-, MeS-, MeCH₂- and H- ortho substituents that clearly illustrate 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 $^{119}{\rm Sn~NMR}$ spectroscopy. The related isomeric meta- and para- MeO-substituted compounds exhibit neither inter- nor intramolecular O..Sn interactions and form polymeric structures involving bridging chlorine..Sn linkages.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This research was supported by grants from the Welch Foundation, Houston, Texas (Grant # AH-0546) and the NIH-SCORE program (Grant # GM-08012). The authors also wish to thank the Kresge Foundation for funds that helped purchase, and help upkeep, our NMR facility.

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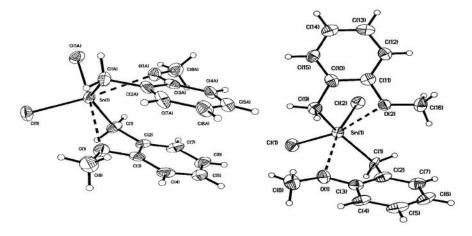


Figure 1. ORTEP diagrams of conformers 3' and 3'' found in the polymorphs of 3. Each conformer is independent oriented and the THF molecule is excluded for clarity. The Figure corresponds from left to right to 3' and 3'' respectively.

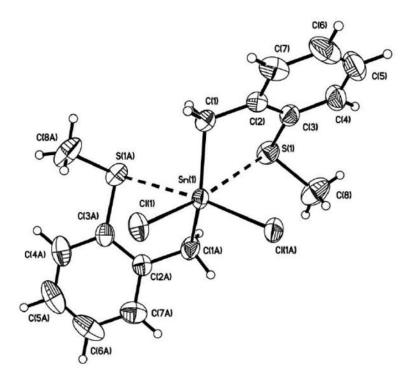


Figure 2. ORTEP diagram of compound **6**.

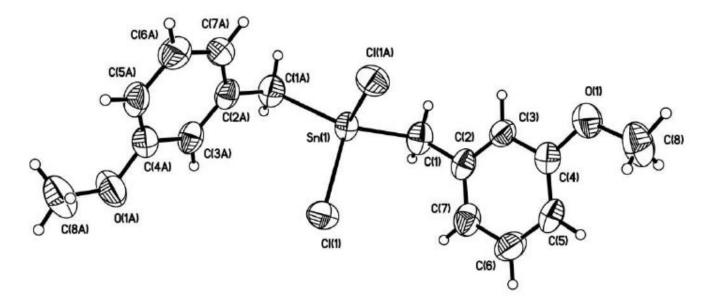


Figure 3. ORTEP diagram of compound **10**.

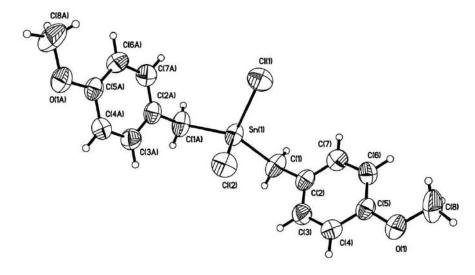


Figure 4. ORTEP diagram of compound **11**.

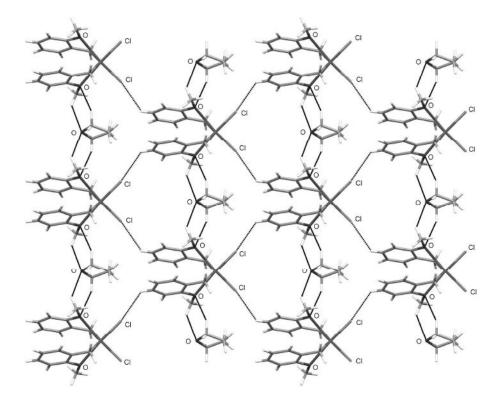


Figure 5. The 2-D architecture generated by conformer **3'** via Cl···H HBs in the polymorph **3**. The encapsulation of THF molecules via further HBs is shown.



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

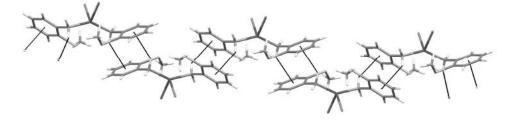


Figure 7. The chain motif parallel to c direction found in the crystal structure of c formed by c bonds. The chain is interlinked to other via c bonds not shown for clarity.

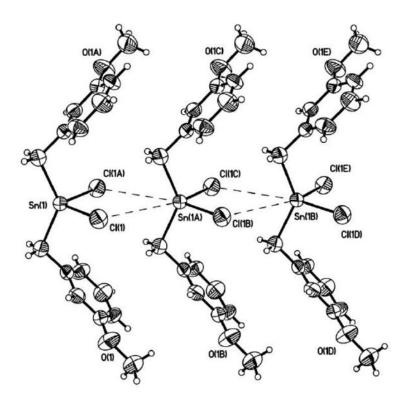


Figure 8. Segment of the chain of 10 with the two equivalent contacts Cl···Sn. The H··· π interaction is not shown here for simplicity.

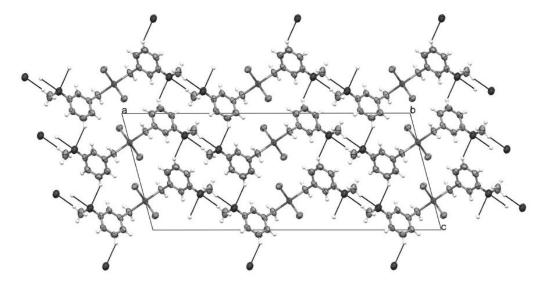


Figure 9. Crystal packing of 10 along b axis with the HBs formed by the oxygen displaying zig-zag layers linked by HB with the aromatic hydrogens.

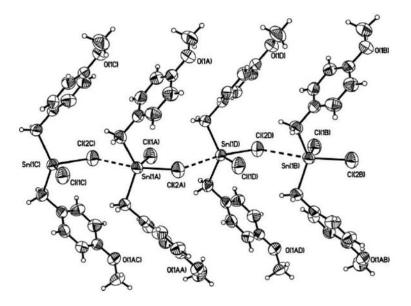


Figure 10.

The chain generated by Cl···Sn interactions in the crystal structure of 11 is shown, only the heavy atoms are labeled, the rest of the atoms are omitted for clarity.

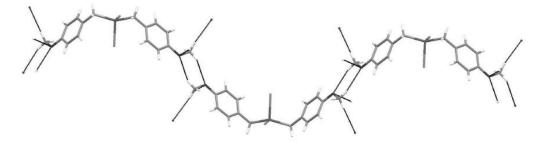


Figure 11. The secondary chain motif generated in the crystal structure of 11besides the Sn···Cl chain (omitted for clarity) through HB20 which are coplanar with the aromatic rings is shown, the hanging contacts are the second HB who binds the chains.

Table 1

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Crystal data and refinement parameters

Crystal Structure	3A (3' and 3")	3B (3')	9	10	11
Formula	3(C16 H18 C12 O2 Sn1) • THF	C16 H18 C12 O2 Sn	C16 H18 Cl2 S2 Sn	C16 H18 C12 O2 Sn	C16 H18 C12 O2 Sn
Formula weight	1367.79	431.89	464.01	431.89	431.89
Crystal System	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Space Group	$C222_{1}$	P-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)
a (°)	06	89.699(2)	06	06	06
β (°)	06	81.920(2)	125.650(2)	104.941(2)	06
γ (°)	06	81.005(2)	06	06	06
$V\left(\mathring{\mathbf{A}}^{3} ight)$	5529.9(9)	880.0(2)	1870.1(5)	1683.4(3)	1708.3(3)
Z	4	2	4	4	4
$ ho_{ m calc}~({ m gcm}^{-3})$	1.643	1.630	1.648	1.704	1.679
$\mu(Mo~K\alpha)~(mm^{-1})$	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)
$2\theta_{ m max}$ for data collection (°), % 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 reflections	23064	8299	8708	8752	17629
Independent reflections $[R_{ m int}]$	3968[0.0453]	3058[0.0369]	1654[0.0186]	1791[0.0524]	1901[0.0851]
Refinement methods		Full-mat	Full-matrix least-squares on F2		
Data/restraints/parameters	3968/0/314	3058/0/190	1654/57/97	1791/0/96	1901/0/100
${f Goodness-of-fit}$ on ${f F}^2$	1.154	0.880	1.023	1.054	1.140
R_I [I>2 σ (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

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Table 2

Selected Bond lengths [Å], angles $[^{\circ}]^{\neq}$

	3A 3′, X=O ^{&}	3A 3", X=0	3B 3", X=0	6, , X=S#	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

*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.

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 $^{\mathcal{R}}$ The X denoted in each column correspond to the atom which is making the intra- or intermolecular contact.

 $^{\#}$ For compound 6, Cl(1) and Cl(2) in the table corresponds to Cl(1A) and Cl(1) respectively in the figures and CIF file.

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Table 3

Selected angles $[^{\circ}]^{
eq}$

11, X=Cl [⇔]	57.63(5)	149.99(7)	80.49(18)	80.49(18)	144.39(4)	157.98(4)	65.61(6)	84.06(17)	84.06(17)	x, 1.5-y, z
10, X=Cl⇔	102.49(4)	158.52(3)	69.64(12)	69.99(12)	56.03(3)	158.52(3)	102.49(4)	69.99(12)	69.64(12)	-x+2, y, -z+1/2
6, , X=S#	85.01(3)	171.63(2) ⁿ	68.81(9)	85.88(10)	94.53(4)	171.63(2)	85.01(3)	85.88(10)	68.81(9)	-x+2, y, -z+1/2
3B 3", X=0	80.78(09)	168.10(11)	66.80(16)	85.39(21)	101.45(13)	169.82(10)	83.41(10)	84.23(18)	66.53(20)	
3A 3", X=0	85.93(09)	167.72(10)	66.23(18)	84.94(19)	101.26(12)	165.13(09)	79.12(09)	85.64(19)	65.84(18)	
3A 3', X=O ^{&}	82.38(10)	172.88(10)	67.61(18)	82.06(21)	101.23(18)	172.88(10)	82.38(10)	82.06(21)	67.61(18)	2-x, y, 1.5-z
	X(1)···Sn(1)-Cl(1)	X(1)···Sn(1)–Cl(2)	X(1)···Sn(1)-C(1)	X(1)···Sn(1)-C(2)	$X(1)\cdots Sn(1)\cdots X(2)$	X(2)···Sn(1)-Cl(1)	X(2)···Sn(1)-Cl(2)	X(2)···Sn(1)-C(1)	X(2)···Sn(1)-C(2)	

The atoms X1, C1, C1, C3, C8, C3 and C2 are equivalents to X2, C2, C12, C11, and C10 respectively for compounds 3', 6, 10, and 11 by the appropriate symop listed at the end of each column

^RThe X denoted in each column correspond to the atom which is making the intra- or intermolecular contact.

 $^{\#}$ For compound 6, Cl(1) and Cl(2) in the table corresponds to Cl(1A) and Cl(1) respectively in the figures and CIF file.

 $\stackrel{\textstyle \leftrightarrow}{\sim}$ For compounds 10 and 11 C2 and C3 corresponds to C3 and C4, C4 and C5 respectively

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