

Synthesis, structural characterization of some germanium substituted chiral diethyltin derivatives

Imtiaz-ud-Din ^{a,*}, M. Mazhar ^a, K.C. Molloy ^b, Khalid M. Khan ^c

^a Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan

^b Department of Chemistry, University of Bath, Bath BA2 7AY, UK

^c HEJ Research Institute of Chemistry, University of Karachi, Karachi 75270, Pakistan

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Abstract

Some new bimetallic carboxylates of tin and germanium with general formula $[C_2H_5]_2Sn[O_2CCH_2CH(R^2)GeR_3]_2$ where $R^1 = m-CH_3C_6H_4$, $p-CH_3C_6H_4$, C_6H_5 , $R^2 = o-CH_3C_6H_4$, $p-CH_3C_6H_4$, $o-CH_3OC_6H_4$, C_6H_5 , CH_3 , have been prepared by the condensation reaction of diethyltin oxide and triarylgermyl(substituted)propanoic acid in 1:2 mole ratio, respectively, and characterized by multinuclear (1H , ^{13}C , ^{119}Sn) NMR, ^{119m}Sn Mössbauer and IR spectroscopy. The X-ray crystal structure of the ligand **I**₄ $[(C_6H_5)_3GeCH(o-CH_3OC_6H_4)CH_2COOH]$ delineate four coordinated germanium atom with a peculiarity of having a molecule of solvent ($CHCl_3$). The chiral center in the synthesized compounds was identified on the basis of 1H NMR data and measurements of angle of rotations. © 2005 Elsevier B.V. All rights reserved.

Keywords: Diethyltin; Germanium; Spectroscopy; Specific rotations; X-ray structure

1. Introduction

Organotin compounds have been employed as stabilizers, glass coatings or as biocides for agricultural applications, preservatives for timber, paper and leathers [1,2]. Alkyltin compounds are generally more toxic than aryl ones, in general, the toxicity decreases from tri- to monoalkyltins [3]. There has been an established link between the bioactive properties of organotin and organogermanium compounds [4]. Gielen and others have described some active compounds that exhibited high in vitro antitumour activities and within the $R_2Sn(IV)^{2+}$ class, the highest activity is exerted by dibutyltin and diphenyltin compounds [5,6]. Our previous reports [7,8] demonstrated that the toxicity of the organotin compounds has been decreased by the incorporation of germanium without affecting their biological significance. Now we have synthesized some new chiral diethyltin carboxylates containing germanium as a part of carboxylate ligand with the general formula:



where

$$R^1 = m-CH_3C_6H_4, \quad R^2 = C_6H_5 \quad (1)$$

$$R^1 = p-CH_3C_6H_4, \quad R^2 = o-CH_3C_6H_4 \quad (2)$$

$$R^1 = p-CH_3C_6H_4, \quad R^2 = p-CH_3C_6H_4 \quad (3)$$

$$R^1 = C_6H_5, \quad R^2 = o-CH_3OC_6H_4 \quad (4)$$

$$R^1 = C_6H_5, \quad R^2 = CH_3 \quad (5)$$

The measurements of rotation angle and then specific rotation testified the presence of chiral center in these compounds. They can be exploited for their possible biological and industrial applications particularly in the field of CVD.

2. Experimental

Diethyltin oxide was prepared by alkaline hydrolysis of diethyltin dichloride by the reported procedure [9]. All the chemicals used were of reagent grade and all organic

* Corresponding author.

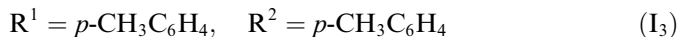
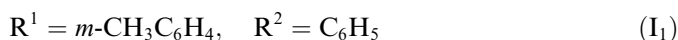
E-mail address: drimtiazuddin@yahoo.com (Imtiaz-ud-Din).

solvents were dried prior to their use by the standard methods [10]. Details of apparatus and instruments used are given elsewhere [7,11]. The rotation angle, α , measured with digital polarimeter, Polax-DIATAGO, Tokyo, Japan for chiral compounds in solution (CHCl_3). The X-ray crystal data set was collected at 150 K on a Nonius Kappa CCD diffractometer using Mo $K\alpha$ radiation; Lp and absorption corrections (semi-empirical from equivalents) were applied. Refinement was full-matrix least squares on F^2 . The molecular structure of **I**₄ along with selected geometric data are given in Fig. 1. Software used: SHELXS-86 [12], SHELXL-97 [13], ORTEP [14].

3. Synthesis

3.1. Synthesis of triarylgermyl(substituted)propanoic acids (**I**)

The ligands **I**₁–**I**₅ with general formula $\text{R}_3\text{GeCH}(\text{R}^2)\text{-CH}_2\text{COOH}$ were synthesized by a methodology as reported earlier [15] where



3.2. Synthesis of compounds **1**–**5**

The compounds were prepared by the following general procedure: In a two necked flask, appropriate triarylgermyl(substituted)propanoic acid (**I**) and diethyltin

oxide was added in 2:1 molar ratio in toluene (25 cm^3). The contents were refluxed for 8–9 h by azeotropic removal of water, using Dean and Stark trap, then allowed to cool at room temperature and toluene was removed under reduced pressure. The resulting mass was recrystallized in chloroform/*n*-hexane mixture to yield the product as white crystalline solid.

3.2.1. Synthesis of bis[3-(tri-*m*-tolylgermyl)-3-phenylpropionato]diethyltin(IV) (**1**)

Quantities used were 1.00 g (2 mmol) **I**₁, 0.19 g (1 mmol) of diethyltin oxide in toluene. Yield = 72%; m.p. = 176–178 °C. Anal. Calc. for $\text{C}_{64}\text{H}_{68}\text{Ge}_2\text{O}_4\text{Sn}$ ($M_w = 1131$): C, 67.78; H, 6.00. Found: C, 67.87, H, 6.15%. ^1H NMR (400 MHz, CDCl_3 , ppm, $^nJ(^1\text{H}\text{-}^1\text{H})$ in Hz); 0.71 (t, 6H, 7.68), 0.92 (m, 4H) ($\text{CH}_3\text{CH}_2\text{Sn}$), 7.03–7.19 (m, 24H, Ph-R¹), 2.34 (s, 18H, $\text{H}_3\text{C-R}^1$), 6.89–6.91 (m, 10H, Ph-R²), 2.98–3.10 (m, 4H, CH_AH_B , $J_{\text{gem}} = 15.5 \text{ Hz}$, $J_{\text{vic}} = 4.0$, 12.9 Hz), 3.58 (dd, 2H, CH_xGe). ^{13}C NMR (100 MHz, CDCl_3 , ppm, $^nJ(^{19}\text{Sn}\text{-}^{13}\text{C})$ in Hz); 8.7 [45], 17.1 [610] ($\text{CH}_3\text{CH}_2\text{-Sn}$), 141.7, 135.8, 139.1, 128.3, 129.3, 131.9 (Ph-R¹), 21.9 ($\text{H}_3\text{C-R}^1$), 33.1 (CH), 36.8 (CH_2), 183.3 (COO). ^{119}Sn NMR (CDCl_3 , ppm); -146.9. $^{119\text{m}}\text{Sn}$ Mössbauer data (mms^{-1}); QS (3.26), IS (1.41), ρ (2.31). IR (KBr disc, cm^{-1}); 487 $\nu(\text{Sn-O})$, 591 $\nu(\text{Sn-C})$, 652 $\nu(\text{Ge-C})$, 1592 $\nu_{\text{asym}}(\text{COO})$, 1396 $\nu_{\text{sym}}(\text{COO})$, $\Delta\nu$ 206. $[\alpha]_{\text{D}}^{25} -129.4$.

3.2.2. Synthesis of bis[3-(tri-*p*-tolylgermyl)-3-*o*-tolylpropionato]diethyltin(IV) (**2**)

Quantities used were 1.02 g (2 mmol) **I**₂, 0.19 g (1 mmol) of diethyltin oxide in toluene. Yield = 76%; m.p. = 224–225 °C. Anal. Calc. for $\text{C}_{66}\text{H}_{72}\text{Ge}_2\text{O}_4\text{Sn}$ ($M_w = 1193$): C, 66.38; H, 6.04. Found: C, 66.82; H, 6.25%. ^1H NMR (400 MHz, CDCl_3 , ppm, $^nJ(^1\text{H}\text{-}^1\text{H})$ in Hz); 0.62 (t, 6H, 7.74), 0.94 (m, 4H) ($\text{CH}_3\text{CH}_2\text{Sn}$), 7.12–7.23 (m, 24H,

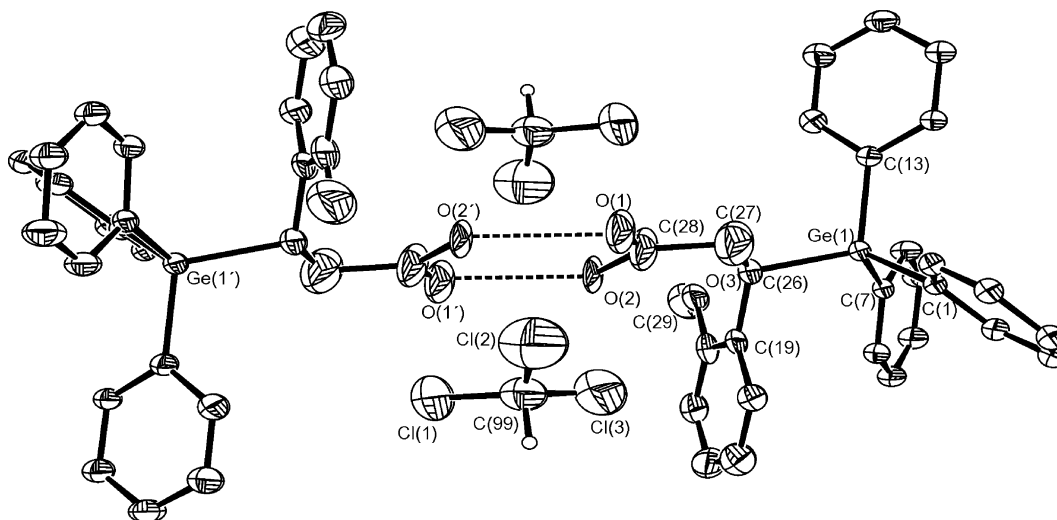


Fig. 1. The structure of compound $[(\text{C}_6\text{H}_5)_3\text{GeCH}(o\text{-CH}_3\text{OC}_6\text{H}_4)\text{CH}_2\text{COOH}]$ with thermal ellipsoids are at the 30% probability level. Only one component of the disordered methoxy phenyl group and the disordered solvent (CHCl_3) are shown for clarity. Selected geometric data: $\text{Ge}(1)\text{-C}(7)$ 1.947 (4), $\text{Ge}(1)\text{-C}(13)$ 1.948 (4), $\text{Ge}(1)\text{-C}(1)$ 1.952 (4), $\text{Ge}(1)\text{-C}(26)$ 1.993 (4), $\text{O}(1)\text{-C}(28)$ 1.28 (2), $\text{O}(2)\text{-C}(28)$ 1.26 (3), $\text{O}(3)\text{-C}(24)$ 1.328 (11) Å and $\text{C}(7)\text{-Ge}(1)\text{-C}(13)$ 109.17 (16), $\text{C}(7)\text{-Ge}(1)\text{-C}(1)$ 109.14 (15), $\text{C}(13)\text{-Ge}(1)\text{-C}(1)$ 109.52 (16), $\text{C}(7)\text{-Ge}(1)\text{-C}(26)$ 110.32 (16), $\text{C}(13)\text{-Ge}(1)\text{-C}(26)$ 107.83 (17), $\text{C}(1)\text{-Ge}(1)\text{-C}(26)$ 110.82 (17), $\text{C}(6)\text{-C}(1)\text{-Ge}(1)$ 121.20 (3), $\text{C}(8)\text{-C}(7)\text{-Ge}(1)$ 120.50 (3), $\text{O}(2)\text{-C}(28)\text{-O}(1)$ 117.60 (15), $\text{Cl}(2)\text{-C}(99)\text{-Cl}(3)$ 113.90 (12)°.

Ph-R¹), 2.36 (s, 18H, H₃C-R¹), 6.86–6.97 (m, 8H, Ph-R²), 2.18 (s, 6H, H₃C-R²), 2.67–2.79 (m, 4H, CH_AH_B, $J_{\text{gem}} = 15.0$ Hz, $J_{\text{vic}} = 5.7, 13.5$ Hz), 4.24 (dd, 2H, CH_XGe). ¹³C NMR (100 MHz, CDCl₃, ppm, $^nJ[^{119}\text{Sn}-^{13}\text{C}]$ in Hz); 8.4 [42]; 17.8 [618] (CH₃CH₂-Sn), 138.8, 135.5, 129.0, 136.3, (Ph-R¹), 21.1 (H₃C-R¹), 140.2, 131.7, 128.9, 126.0, 125.0, 131.8 (Ph-R²), 20.8 (H₃C-R²), 31.8, (CH), 36.8 (CH₂), 182.2 (COO). ¹¹⁹Sn NMR (CDCl₃, ppm); -147.8. ^{119m}Sn Mössbauer data (mms⁻¹); QS (4.05), IS (1.58), ρ (2.56). IR (KBr disc, cm⁻¹); 482 ν (Sn-O), 589 ν (Sn-C), 644 ν (Ge-C), 1584 ν_{asym} (COO), 1376 ν_{sym} (COO), $\Delta\nu$ 208. $[\alpha]_{\text{D}}^{25} -127.5$.

3.2.3. Synthesis of bis[3-(tri-*p*-tolylgermyl)-3-*p*-tolylpropionato]diethyltin(IV) (3)

Quantities used were 1.02 g (2 mmol) I₃, 0.19 g (1 mmol) of diethyltin oxide in toluene. Yield = 81%; m.p. = 155–156 °C. Anal. Calc. for C₆₆H₇₂Ge₂O₄Sn ($M_{\text{W}} = 1193$): C, 66.38; H, 6.04. Found: C, 66.28; H, 6.25%. ¹H NMR (400 MHz, CDCl₃, ppm, $^nJ(^1\text{H}-^1\text{H})$ in Hz); 0.64 (t, 6H, 7.93), 0.93 (m, 4H) (CH₃CH₂Sn), 7.09–7.19 (m, 24H, Ph-R¹), 2.32 (s, 18H, H₃C-R¹), 6.75–6.87 (m, 8H, Ph-R²), 2.3 (s, 6H, H₃C-R²), 2.85–2.95 (m, 4H, CH_AH_B, $J_{\text{gem}} = 15.3$ Hz, $J_{\text{vic}} = 4.5, 12.8$ Hz), 3.55 (dd, 2H, CH_XGe). ¹³C NMR (100 MHz, CDCl₃, ppm, $^nJ[^{119}\text{Sn}-^{13}\text{C}]$ in Hz); 8.2 [41], 17.1 [612] (CH₃CH₂-Sn), 138.7, 135.5, 128.3, 134.6, (Ph-R¹), 21.4 (H₃C-R¹), 138.2, 128.6, 128.9, 131.9 (Ph-R²), 20.9 (H₃C-R²), 32.3, (CH), 36.7 (CH₂), 183.0 (COO). ¹¹⁹Sn NMR (CDCl₃, ppm); -147.1. ^{119m}Sn Mössbauer data (mms⁻¹); QS (3.26), IS (1.32), ρ (2.47). IR (KBr disc, cm⁻¹); 487 ν (Sn-O), 590 ν (Sn-C), 661 ν (Ge-C), 1588 ν_{asym} (COO), 1374 ν_{sym} (COO), $\Delta\nu$ 214. $[\alpha]_{\text{D}}^{25} -131.8$.

3.2.4. Synthesis of bis[3-(triphenylgermyl)-3-*o*-methoxyphenylpropionato]diethyltin(IV) (4)

Quantities used were 0.97 g (2 mmol) I₄, 0.19 g (1 mmol) of diethyltin oxide in toluene. Yield = 66%; m.p. = 190–191 °C. Anal. Calc. for C₆₀H₆₀Ge₂O₆Sn ($M_{\text{W}} = 1142$): C, 62.04; H, 5.25. Found: C, 62.82; H, 5.45%. ¹H NMR (400 MHz, CDCl₃, ppm, $^nJ(^1\text{H}-^1\text{H})$ in Hz); 0.77 (t, 6H, 7.85), 0.98 (m, 4H) (CH₃CH₂Sn), 7.27–7.33 (m, 24H, Ph-R¹), 2.33 (s, 18H, H₃C-R¹), 6.89–6.92 (m, 8H, Ph-R²), 3.18 (s, 6H, H₃CO-R²), 2.89–2.96 (m, 4H, CH_AH_B, $J_{\text{gem}} = 16.4$ Hz, $J_{\text{vic}} = 5.0, 11.5$ Hz), 3.99 (dd, 2H, CH_XGe). ¹³C NMR (100 MHz, CDCl₃, ppm, $^nJ[^{119}\text{Sn}-^{13}\text{C}]$ in Hz); 8.3 [45], 17.1 [614] (CH₃CH₂-Sn), 136.2, 135.7, 128.2, 130.2, (Ph-R¹), 128.3, 156.9, 110.7, 126.8, 120.7, 128.0 (Ph-R²), 54.8 (H₃CO-R²), 31.7, (CH), 35.9 (CH₂), 180.6 (COO). ¹¹⁹Sn NMR (CDCl₃, ppm); -147.9. IR (KBr disc, cm⁻¹); 488 ν (Sn-O), 587 ν (Sn-C), 658 ν (Ge-C), 1596 ν_{asym} (COO), 1393 ν_{sym} (COO), $\Delta\nu$ 203. $[\alpha]_{\text{D}}^{25} -129.4$.

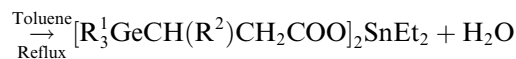
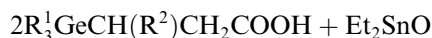
3.2.5. Synthesis of bis[3-(triphenylgermyl)-3-methylphenylpropionato]diethyl tin(IV) (5)

Quantities used were 0.78 g (2 mmol) I₅, 0.19 g (1 mmol) of diethyltin oxide in toluene. Yield = 82%; m.p. = 144–

145 °C. Anal. Calc. for C₄₈H₅₂Ge₂O₄Sn ($M_{\text{W}} = 957$): C, 60.18; H, 5.43. Found: C, 59.63; H, 5.85%. ¹H NMR (400 MHz, CDCl₃, ppm, $^nJ(^1\text{H}-^1\text{H})$ in Hz); 0.74 (t, 6H, 7.84), 0.96 (m, 4H) (CH₃CH₂Sn), 7.33–7.52 (m, 30H, Ph-R¹), 1.26 (d, 6H, 6.6, H₃C-R²), 2.24–2.87 (m, 4H), 2.98 (m, 2H, CHGe). ¹³C NMR (100 MHz, CDCl₃, ppm, $^nJ[^{119}\text{Sn}-^{13}\text{C}]$ in Hz); 9.5 [45]; 17.8 [612] (CH₃CH₂-Sn), 136.0, 135.5, 128.5, 129.2, (Ph-R¹), 16.9 (CH₃-R²), 30.1, (CH), 40.3 (CH₂), 179.7 (COO). ¹¹⁹Sn NMR (CDCl₃, ppm); -147.6. ^{119m}Sn Mössbauer data (mms⁻¹); QS (3.28), IS (1.36), ρ (2.41). IR (KBr disc, cm⁻¹); 493 ν (Sn-O), 590 ν (Sn-C), 663 ν (Ge-C), 1578 ν_{asym} (COO), 1369 ν_{sym} (COO), $\Delta\nu$ 209. $[\alpha]_{\text{D}}^{25} -128.0$.

4. Results and discussion

Triarylgermyl substituted diethyltin dicarboxylates were prepared by the condensation of diethyltin oxide and triarylgermyl(substituted)propanoic acids in 1:2 mole ratio by use of a Dean and Stark apparatus.



The compounds are soluble in chloroform, toluene, DMSO and are quite stable in air and moisture. The multinuclear (¹H, ¹³C, ¹¹⁹Sn) NMR, ^{119m}Sn Mössbauer, IR spectroscopic and other physico-analytical data are presented in experimental section. IR absorption bands have been assigned on the basis of earlier publications [16,17]. The bands in the region 482–488 cm⁻¹ are assigned to Sn-O whereas those appearing around 590 cm⁻¹ indicate the presence of the Sn-C bond. The existence of Ge-C bond was established on the basis of absorption around 650 cm⁻¹. The conclusive evidence of tin-carboxylate bond formation comes from the parameter $\Delta\nu[\Delta\nu = \nu(\text{COO})_{\text{asym}} - \nu(\text{COO})_{\text{sym}}]$ as the coordination number of tin affects the absorption vibration frequency of carbonyl group [17]. The $\Delta\nu$ value is also used to infer the nature of bonding of the carboxylate to tin(IV) and the values (203–214 cm⁻¹) demonstrated the bidentate nature of the carboxylate ligand.

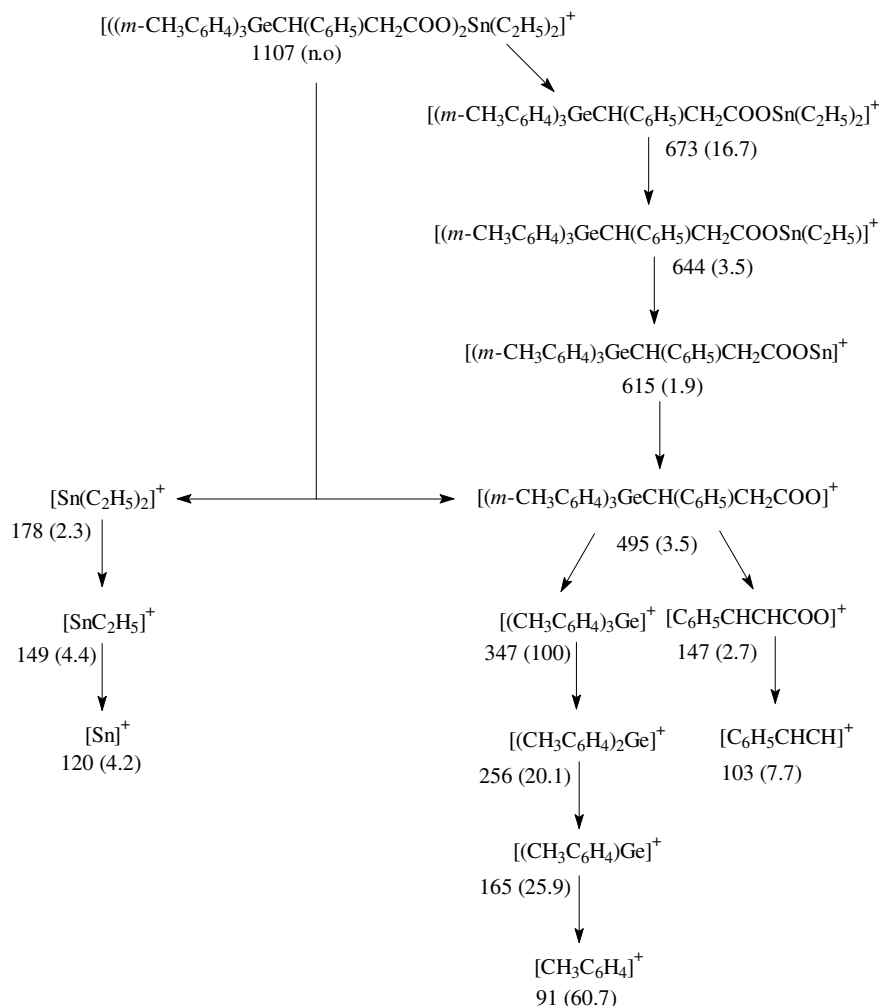
The ¹H NMR spectral data (in CDCl₃) identified all the protons in the compounds 1–5 by their intensity and multiplicity pattern and the total number of protons calculated from the integration curve are in agreement with the expected molecular structures. The unit CH₂CHGe comprises ABX system and for the figure see elsewhere [8]. The sub-spectral analysis of two multiplets, in region of ca. 2.90 and 4.24 ppm, revealed three chemical shifts for H_A, H_B and H_X nuclei respectively in the compounds along with geminal coupling constant (J_{AB}), and two different vicinal coupling constants (J_{AX} , J_{BX}). Methylene protons (A, B) of the carboxylate portion resonate at 2.67–2.99 ppm demonstrating the H_A-atom located slightly downfield shows a pseudoquartet in range 2.79–2.99 ppm ($J_{\text{gem}} 15.3 \pm 1$ Hz, $J_{\text{vic}} 4.8 \pm 1$ Hz) and the H_B-atom

resonated slightly upfield gives a pseudoquartet in range 2.67–2.90 ppm ($J_{\text{gem}} 15.30 \pm 1$ Hz, $J_{\text{vic}} 12.58 \pm 1$ Hz) [18]. The HX of the chiral center resonates further downfield shows a quartet at 3.50 ± 0.6 ppm. Signals for aromatic protons appear in two distinct multiplets (6.8 and 7.1 ppm) due to the presence of two environmentally different aromatic groups (R^1 and R^2). The compounds exhibited a multiplet in region of 0.92–1.02 ppm for the existence of CH_2 group attached to tin atom while a prominent triplet in region of 0.62–0.82 ppm clearly shows terminal methyl protons of the diethyltin moiety with $^nJ(^1\text{H}-^1\text{H})$ value 7.54–7.97 Hz [19]. Their chirality was also established on the basis of specific rotation, the magnitude and direction manifested the Laevo rotatory nature of the compounds.

The ^{13}C NMR spectral data clearly resolved all the resonances due to the presence of all unique carbon atoms in compounds (1–5). The carbon directly attached to tin resonates at ca. 17 ppm in diethyltin compounds. The aromatic carbon resonances were assigned by comparison of experimental chemical shift with those calculated from incremental method [20]. The magnitude of $^1J(^{119}\text{Sn}-^{13}\text{C})$

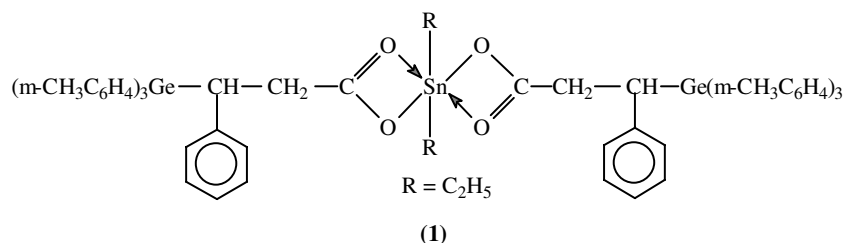
for diethyltin derivatives has been measured in range 617 ± 5 Hz which is in agreement with the literature data [21]. The ^{119}Sn NMR chemical shifts for these compounds were observed as a single resonance at ca. -147 ppm indicating five coordinate tin center [21]. It appears that a weakly hexacoordinated tin generates a deformed octahedron or a skew trapezoidal bipyramid with four strong and two somewhat weaker bonds as indicated by the upfield ^{119}Sn chemical shift [22]. Thus, NMR parameters support coordination number of more than four at tin(IV) in solution (CDCl_3).

^{119}mSn Mössbauer parameters, quadrupole splitting (QS) and isomer shift (IS) are diagnostic for structure elucidation and the observed QS values ($3.26\text{--}4.05$ mm s^{-1}) correspond to monomeric hexa-coordinated *trans*- C_2SnO_4 geometry around tin atom in the solid phase for these organotins. From QS values, using the Sham and Bancroft model [23], C–Sn–C angles for the compounds are found to be in range $144\text{--}168^\circ$ and are in good agreement with already reported X-ray crystal structure of $[\eta\text{-C}_4\text{H}_9]_2\text{Sn}[\text{O-COCH}_2\text{CH}(o\text{-CH}_3\text{C}_6\text{H}_4)\text{Ge}(p\text{-CH}_3\text{C}_6\text{H}_4)_3]_2$ [22b]. The IS values for these complexes are in range $1.32\text{--}1.58$ mms^{-1} .



Scheme 1. Mass spectrum showing fragmentation pattern for $[(m\text{-CH}_3\text{C}_6\text{H}_4)_3\text{GeCH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COO})_2\text{Sn}(\text{C}_2\text{H}_5)_2]^+$.

The ρ -values (QS/IS) for the compounds fall in range 2.31–2.61 which demonstrated coordination number greater than four around the tin atom [24]. The proposed structure in the light of multinuclear (^1H , ^{13}C , ^{119}Sn) NMR and Mössbauer data can be delineated as follows (compound **1**):



Mass fragmentation pattern of a representative compound **1** is shown in Scheme 1. Here primary decomposition occurred by the loss of one ligand, followed by the loss of R-groups directly attached to tin and/or to germanium moiety. In these compounds the base peak is due to the presence of the species $[\text{R}_3\text{Ge}]^+$, where $\text{R}^1 = \text{CH}_3\text{C}_6\text{H}_4$, C_6H_5 , other ions containing germanium and tin are also quite intense but devoid of any molecular ion peak. Thus, the fragment ions found are in agreement with the expected molecular structure of the compound.

The X-ray crystal structure of the ligand is shown in Fig. 1. Crystallographic data are presented in Table 1.

Table 1
Crystal data and structure refinement for (**I**₄)

	I ₄
Empirical formula	$\text{C}_{28.25}\text{H}_{26.25}\text{Cl}_{0.75}\text{GeO}_3$
Formula weight	512.92
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
<i>a</i> (Å)	8.2530(2)
<i>b</i> (Å)	9.6740(3)
<i>c</i> (Å)	16.9230(5)
α (°)	86.7550(10)
β (°)	89.5880(10)
γ (°)	68.7010(10)
Volume (Å ³)	1256.69(6)
Z	2
$\mu(\text{Mo K}\alpha)$ (mm ⁻¹)	1.325
Crystal size	0.50 × 0.40 × 0.20
θ_{max} (°)	27.55
Reflections collected	19423
Independent reflections (R_{int})	5758 (0.039)
Reflections observed $I > 2\sigma(I)$	5248
Maximum and minimum transmission	0.47, 0.67
Data/restraints/parameters	5758/39/398
Goodness-of-fit on F^2	1.350
Final R_1 , wR_2 [$I > 2\sigma(I)$]	0.0549, 0.1427
Final R_1 , wR_2 (all data)	0.0609, 0.1451
ρ_{max} , ρ_{min} (e Å ⁻³)	0.859, -1.150

CCDC No. 236410.

The germanium atom adopts a tetrahedral geometry [C–Ge–C: 107.83(17)–110.82(17)°] in the compound. The Ge–C_{sp³} distance is significantly longer [1.993(4) Å] than the Ge–C_{sp²} distances between the germanium and three phenyl groups which are identical within experimental error with the mean value of 1.949(4) Å [25]. The molecule

form dimeric pairs about inversion centers through hydrogen bonds between carboxylic acid groups in a conventional manner. The hydrogen bond is relatively strong [O(1)··O(2): 2.661(2) Å; H(2A)–O(1′): 1.80(4) Å; $\angle\text{O}(2)\text{--H}(2\text{A})\text{--O}(1′)$: 162(4)°] and delocalization of the double-bond character renders two C–O bond lengths indistinguishable [C(28)–O(2): 1.26(2) Å and C(28)–O(1): 1.28(2) Å]. The Fig. 1 depicts one molecule of solvent (CHCl₃) in each asymmetric unit and the loose association of it with the carboxylic acid but the orientation of the two fragments rules out any meaningful hydrogen bond.

Acknowledgements

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