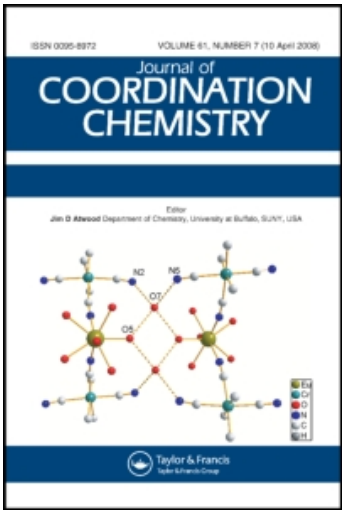


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# Di- and triorganotin(IV) complexes of 2-aminobenzoic acid with and without triphenylphosphine: synthesis, spectroscopy, semi-empirical study, and antimicrobial activities

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Eight organotin carboxylates have been synthesized in quantitative yield by reaction of NaL (L = 2-aminobenzoate) with the di- and triorganotin chlorides and triphenylphosphine. All the complexes have been characterized by elemental analysis, IR, multinuclear NMR ($^{1}$H, $^{13}$C, and $^{119}$Sn), and mass spectrometry. The spectroscopic data indicate 1 : 2/1 : 1 M : L stoichiometry in **1**, **3**, **5**, and **7** and 1 : 2 : 1/1 : 1 : 1 M : L : $PPh_3$ stoichiometry in **2**, **4**, **6**, and **8**. FT-IR spectra clearly demonstrate metal attachment with both oxygens of the ligand and bidentate coordination in **1**, **3**, **5**, and **7** while monodentate ligand for **2**, **4**, **6**, and **8**. In solid state, **1**, **2**, **5**, and **6** exhibit six coordination whereas **3**, **4**, **7**, and **8** show five coordination. The structural behavior is confirmed by semi-empirical study. NMR data reveal four-coordinate geometry in solution. These complexes were screened for antimicrobial activity *in vitro*. The screening tests show that tributyltin carboxylates are more potent antibacterial and fungicidal agents than corresponding methyl derivatives, and triphenylphosphine enhances the antibacterial and fungicidal activities of these complexes.

*Keywords*: Organotin complexes; Triphenylphosphine; IR; NMR; Mass; Semi-empirical study; Biological activity

## 1. Introduction

Organotin derivatives are potentially active biological agents with well-documented applications in agriculture and industries [1–4]. Interest in the chemistry of organotin(IV) compounds has led to extended studies on their reactions with different biomolecules, e.g., carbohydrates [5], nucleic acid derivatives [6], amino acids [7], and peptides [8].

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In general, triorganotin(IV) compounds display better biological activity than their diorganotin and mono-organotin analogs. This has been attributed to their ability to bind proteins [9]. Organotin(IV) carboxylates possess anticancer activity in a variety of tumor cells and the structure of these organotin(IV) compounds have been characterized in solid and solution [10].

Organotin(IV) carboxylates have been of interest for some time because of their biochemical and commercial applications [11]. In general, the biochemical activity of organotin(IV) carboxylates is greatly influenced by the structure and the coordination number of tin [12]. Recognition of the importance between biological properties and the structure of organotin(IV) carboxylates [13] has spurred the study of carboxylates of tin. Organotin(IV) compounds are also used for pharmacological applications as bactericides [14], as antitumor [15], antiinflammatory [16], and antituberculosis agents [17].

We have synthesized some new organotin(IV) derivatives with 2-aminobenzoic acid, with and without triphenylphosphine, in continuation of our previous work [18–21], to study possible structure activity correlations.



## 2. Experimental

### 2.1. *Chemicals and instrumentation*

2-Aminobenzoic acid, triphenylphosphine, tributyltin chloride, dibutyltin dichloride, trimethyltin chloride, dimethyltin dichloride, and sodium hydroxide were purchased from Aldrich. All these chemicals were of analytical grade and used without purification. Solvents were dried by standard procedures [22].

Melting points were determined by using an electromelting point apparatus model MP-D Mitamura Riken Kogyo (Japan) and are uncorrected. Elemental analyses (for carbon, hydrogen, and nitrogen) were done by CHN-932 elemental analyzer Lesco Corporation, USA. The $^{1}$H- and $^{13}$C-NMR spectra were recorded on a Bruker ARC 300 MHz FT-NMR spectrometer using $CDCl_3$ as an internal reference (for which $\delta(^{1}H) = 7.25$ ppm and $\delta(^{13}C) = 77.0$ ppm). IR spectra were recorded as KBr pellets on a Varian 2000 Schimtar series spectrophotometer from 4000 to 400 $cm^{-1}$. The molecules were modeled by MOPAC 2007 [23] program in gas phase using the PM3 method [24, 25]. Selected parts of the complexes not containing the metal ion were preoptimized using molecular mechanics methods. Several cycles of energy minimization had to be carried for each molecule. The root mean square gradient for molecules was all less than 1. Self consistent field was achieved in each case.

### 2.2. *Synthesis of 2-aminobenzoate (NaL)*

2-Aminobenzoic acid (1 mmol) and sodium hydroxide (1 mmol) were stirred together in distilled water in a round bottom flask at room temperature for 4 h. Then water was evaporated using a rotary evaporator to separate sodium salt of ligand.

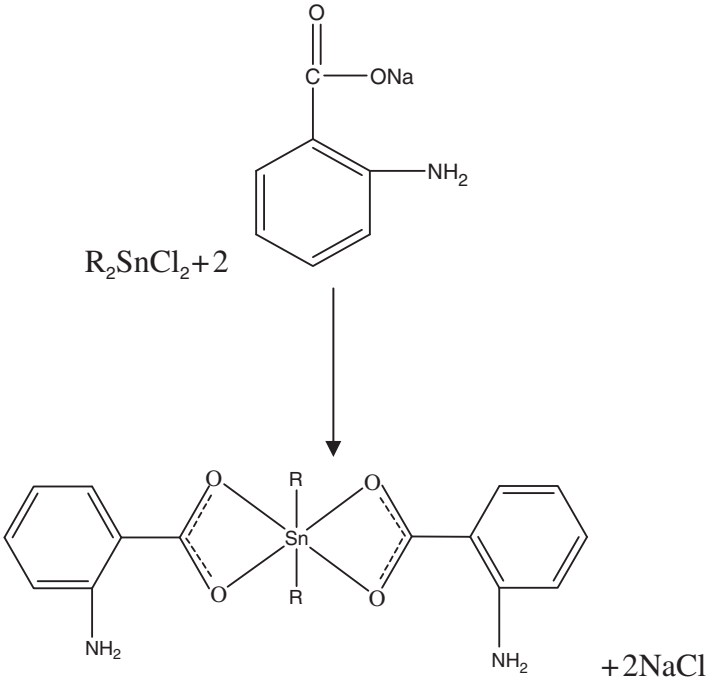
### 2.3. *General procedure for the synthesis of $R_2SnL_2/R_3SnL$ (1, 3, 5, and 7)*

Sodium salt of ligand (2/1 mmol) was suspended in dry toluene (100 mL) in a 250 mL two-necked round bottom flask equipped with water condenser and magnetic stirring bar. $R_2SnCl_2/R_3SnCl$ (1 mmol) in dry toluene (50 mL) was added dropwise with constant stirring. The reaction mixture was refluxed for 6–8 h. Sodium chloride was filtered off and the solvent was evaporated by rotary evaporator under reduced pressure. Purity of the product was checked by TLC. Solid obtained was recrystallized in chloroform : *n*-hexane (1 : 1).

### 2.4. *General procedure for the synthesis of $R_2SnL_2(PPh_3)_2/R_2SnLPPh_3$ (2, 4, 6, and 8)*

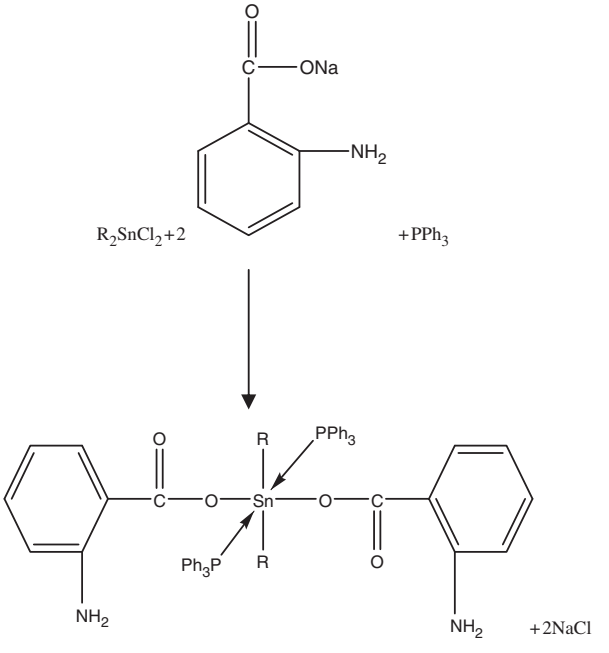
Sodium salt of ligand (2/1 mmol), $R_2SnCl_2/R_3SnCl$ (1 mmol), and $Ph_3P$ in (2/1 mmol) were stirred together in 40 mL dry chloroform in a round bottom flask at room temperature for 3 h. Sodium chloride was removed by filtration and the solvent was evaporated slowly at room temperature to get a solid product. Purity of the product was checked by TLC. The product was recrystallized in acetone : *n*-hexane (1 : 2).





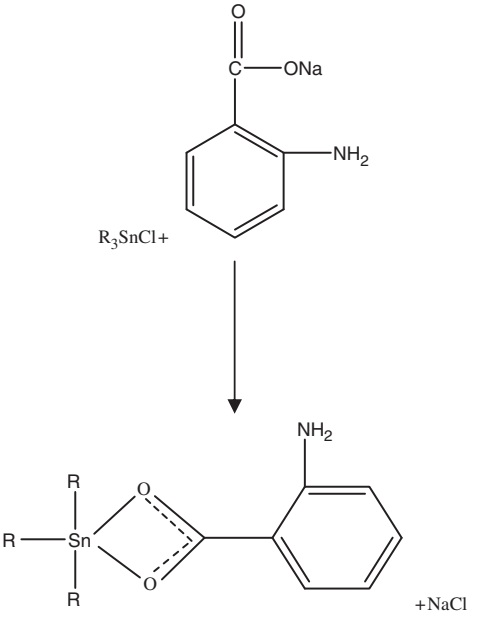

(R = *n*–$CH_3$, *n*–$C_4H_9$)

For **1** and **5**.



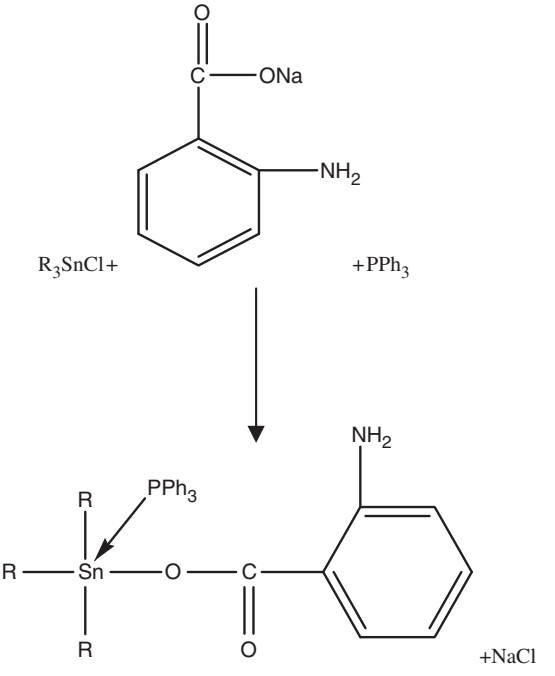

(R=*n*–$CH_3$, *n*–$C_4H_9$)

For **2** and **6**.




(R=*n*-$CH_3$, *n*-$C_4H_9$)

For **3** and **7**




(R=*n*–$CH_3$, *n*–$C_4H_9$)

For **4** and **8**.



## 3. Results and discussion

All the compounds have sharp melting points and are soluble in common organic solvents. Elemental analyses are in good agreement with the calculated values. Physical and elemental data for **1**–**8** are given in table 1.

### 3.1. *Infrared spectroscopy*

Infrared spectra of NaL and **1**–**8** were recorded from 4000 to 400 $cm^{-1}$ as KBr discs with characteristic vibrational frequencies identified by comparing spectra of the complexes with that of L. The IR absorptions of interest are $\nu(COO)_{sym}$, $\nu(COO)_{asym}$, $\nu$(Sn–C), and $\nu$(Sn–O).

The absence of broad band of $\nu$(OH) and the presence of $\nu$(Sn–O) at 465–450 $cm^{-1}$ indicate deprotonation of carboxylic acid and bond formation with tin. The $\nu$(Sn–C) were observed at 583–560 $cm^{-1}$. The vacant 5d orbital of tin tends toward high coordination with ligands containing lone pairs of electrons. Based on the difference between $\nu(COO)_{sym}$ and $\nu(COO)_{asym}$ (below 200 $cm^{-1}$ for bidentate carboxylate,

Table 1. Physical data of the synthesized organotin carboxylates.

| Compound No. | Molecular formula MW | % Yield | M.p. (°C) | CHN analysis %C Calcd Found | %H Calcd Found | %N Calcd Found |
|---|---|---|---|---|---|---|
| NaL | $C_7H_6NO_2Na$ | 93 | <250 | 52.84 | 3.80 | 8.80 |
| | 159.12 | | | 52.80 | 3.76 | 8.84 |
| **1** | $C_{16}H_{18}N_2O_4Sn$ | 76 | 122–124 | 45.60 | 4.31 | 6.65 |
| | 421.04 | | | 45.64 | 4.35 | 6.61 |
| **2** | $C_{52}H_{48}P_2N_2O_4Sn$ | 70 | 64–65 | 66.05 | 5.12 | 2.96 |
| | 945.61 | | | 66.09 | 5.16 | 3.00 |
| **3** | $C_{10}H_{15}NO_2Sn$ | 71 | 123–125 | 40.04 | 5.04 | 4.67 |
| | 299.94 | | | 40.00 | 5.08 | 4.63 |
| **4** | $C_{28}H_{30}PNO_2Sn$ | 75 | 68–70 | 59.82 | 5.38 | 2.49 |
| | 562.23 | | | 59.86 | 5.34 | 2.53 |
| **5** | $C_{22}H_{32}N_2O_4Sn$ | 60 | 108–110 | 52.10 | 6.36 | 5.52 |
| | 507.21 | | | 52.14 | 6.40 | 5.56 |
| **6** | $C_{58}H_{62}P_2N_2O_4Sn$ | 72 | 68–70 | 67.52 | 6.06 | 2.72 |
| | 1031.78 | | | 69.56 | 6.02 | 2.76 |
| **7** | $C_{19}H_{33}NO_2Sn$ | 60 | 111–113 | 53.55 | 7.80 | 3.29 |
| | 426.18 | | | 53.51 | 7.76 | 3.25 |
| **8** | $C_{37}H_{48}PNO_2Sn$ | 65 | 74–76 | 64.55 | 7.03 | 2.03 |
| | 688.47 | | | 64.60 | 7.07 | 2.07 |



Table 2. IR data ($cm^{-1}$) of synthesized organotin carboxylates.

| Compound No. | $\nu$(–NH) | $\nu$(COO) $\nu(COO)_{asym}$ | $\nu(COO)_{sym}$ | $\Delta\nu$ | $\nu$(Sn–C) | $\nu$(Sn–O) |
|---|---|---|---|---|---|---|
| NaL | 3220 | 1585 | 1365 | 220 | – | – |
| **1** | 3222 | 1585 | 1457 | 128 | 560 | 450 |
| **2** | 3221 | 1581 | 1362 | 219 | 562 | 462 |
| **3** | 3220 | 1590 | 1453 | 137 | 570 | 452 |
| **4** | 3222 | 1595 | 1386 | 209 | 574 | 451 |
| **5** | 3222 | 1588 | 1458 | 130 | 575 | 450 |
| **6** | 3221 | 1565 | 1341 | 224 | 583 | 455 |
| **7** | 3221 | 1592 | 1480 | 112 | 571 | 458 |
| **8** | 3220 | 1590 | 1368 | 222 | 580 | 465 |

but greater than 200 $cm^{-1}$ for monodentate carboxylate) $\Delta\nu$ for **1**, **3**, **5**, and **7** lie in the range 137–112 $cm^{-1}$, indicating bidentate carboxylate [26], while for **2**, **4**, **6**, and **8**, 224–209 $cm^{-1}$ indicates monodentate ligand. The $\nu(NH_2)$ is at 3222–3220 $cm^{-1}$. Important bands of complexes along with NaL are given in table 2.

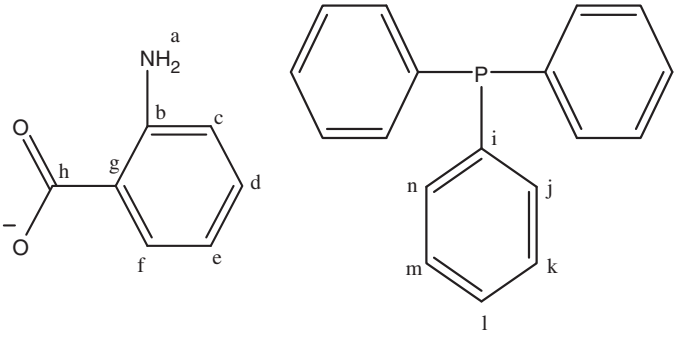
### 3.2. *NMR spectroscopy*

**3.2.1. $^1$H-NMR spectroscopy.** Characteristic resonances in the $^1$H-NMR spectra of the complexes, recorded in $CDCl_3$, are given in table 3. A broad resonance at $\delta$ 11.0 ppm

Table 3. $^{1}$H-NMR data of synthesized organotin carboxylates.

| Proton No. | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** |
|---|---|---|---|---|---|---|---|---|
| a | 5.71 s | 5.82 s | 5.74 s | 5.81 s | 5.75 s | 5.82 s | 5.74 s | 5.83 s |
| c | 6.67 d | 6.72 d | 6.66 d | 6.71 d | 6.67 d | 6.73 d | 6.67 d | 6.74 d |
| d | (7.6) | (7.6) | (7.6) | (7.6) | (7.6) | (7.6) | (7.6) | (7.6) |
| e | 7.34 m | 7.39 m | 7.35 m | 7.39 m | 7.33 m | 7.38 m | 7.34 m | 7.38 m |
| f | 7.22 m | 7.29 m | 7.22 m | 7.28 m | 7.23 m | 7.29 m | 7.22 m | 7.28 m |
| i, j, k, l, m, n | – | 7.31 s | – | 7.32 s | – | 7.31 s | – | 7.30 s |

**1** Sn–$CH_3$, 1.26 s [74].
**2** Sn–$CH_3$, 1.35 s [75].
**3** Sn–$CH_3$, 0.99 s [57].
**4** Sn–$CH_3$, 1.20 s [58].
**5** Sn–$CH_2$–$CH_2$–$CH_2$–$CH_3$, 0.90 t [60], 1.36–1.81 m.
**6** Sn–$CH_2$–$CH_2$–$CH_2$–$CH_3$, 0.98 t [60], 1.39–1.83 m.
**7** Sn–$CH_2$–$CH_2$–$CH_2$–$CH_3$, 0.92 t, 1.33–1.74 m.
**8** Sn–$CH_2$–$CH_2$–$CH_2$–$CH_3$, 0.98 t, 1.31–1.78 m.




due to carboxylic acid proton is absent in the complexes, indicating deprotonation of the carboxylic oxygen. The $CH_3$ protons of dimethyl- and trimethyltin(IV) derivatives (**1** and **3**) are sharp singlets at 1.26 and 0.99 ppm, both with well-defined satellites, $^{2}J[^{119}\text{Sn}, {}^{1}\text{H}] = 74$ and 57 Hz, respectively, which demonstrate diorganotin derivatives with coordination number greater than four, probably five or six; triorganotin derivatives show distorted tetrahedral geometry in solution. Protons of *n*-butyltin derivatives show a complex pattern and were assigned as reported earlier [27–29]. However, $\delta$-$CH_3$ protons of both di-*n*-butyl- and tri-*n*-butyltin(IV) moieties, **5** and **7**, appear as a triplet at 0.90 and 0.92 ppm, while the $\alpha$-$CH_2$, $\beta$-$CH_2$, and $\gamma$-$CH_2$ protons are multiplets [29].

**3.2.2. $^{13}$C-NMR spectroscopy.** $^{13}$C resonances associated with the carboxylate ligand are assigned by comparison with results obtained from the incremental method [30] and earlier reports [18, 31] (table 4). The carboxylic carbon shifts downfield in the complexes, suggesting coordination, through carboxylic oxygen, to organotin(IV).

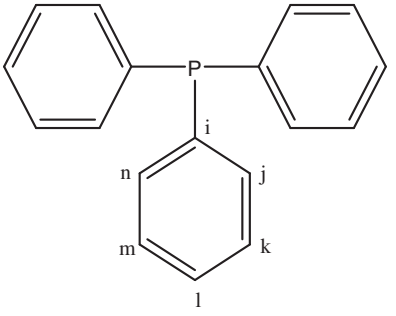
The value $^{1}J(^{119}\text{Sn}–^{13}\text{C})$ is different in di- and tri-organotin compounds for four- and five-coordinate tin. In diorganotin dicarboxylates, the geometry around tin could not be determined with certainty due to the fluxional behavior of the carboxylate oxygen; however, earlier reports suggest five or six coordination [18, 31].

$^{119}$Sn chemical shifts of organotin compound cover a range of $\pm$600 ppm. The $^{119}$Sn chemical shift in $CDCl_3$ is given in table 4. These values lie inside the range for

Table 4. $^{13}C$- and $^{119}Sn$-NMR data of synthesized organotin carboxylates.

| Carbon No. | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** |
|---|---|---|---|---|---|---|---|---|
| b | 150.64 | 151.01 | 150.25 | 151.25 | 150.61 | 151.84 | 150.18 | 151.80 |
| c | 116.46 | 118.52 | 116.23 | 118.23 | 116.40 | 118.51 | 116.16 | 118.16 |
| d | 134.76 | 138.88 | 133.59 | 134.88 | 134.63 | 134.19 | 133.40 | 134.62 |
| e | 119.57 | 120.54 | 119.47 | 120.47 | 119.54 | 120.53 | 119.54 | 120.43 |
| f | 132.97 | 134.62 | 132.65 | 134.65 | 133.06 | 134.64 | 132.76 | 134.74 |
| g | 128.63 | 129.65 | 128.61 | 129.65 | 128.65 | 129.68 | 128.63 | 129.63 |
| h | 177.34 | 179.76 | 179.30 | 178.28 | 178.29 | 179.21 | 178.16 | 179.29 |
| i | – | 128.73 | – | 128.77 | – | 128.75 | – | 128.74 |
| j, n | – | 132.521 | – | 137.101 | – | 132.161 | – | 132.061 |
| k, m | – | 28.46 | – | 28.47 | – | 28.49 | – | 28.56 |
| l | – | 128.37 | – | 128.36 | – | 128.35 | – | 128.37 |

**1** Sn–$CH_3$, −1.40 [536]; $^{119}Sn = -179.3$.
**2** Sn–$CH_3$, −1.52 [538]; $^{119}Sn = -180.3$.
**3** Sn–$CH_3$, −1.18 [397]; $^{119}Sn = +169.6$.
**4** Sn–$CH_3$, −2.17 [394]; $^{119}Sn = +169.6$.
**5** Sn–$CH_2$–$CH_2$–$CH_2$–$CH_3$, (C-$\alpha$) 29.36 [350], (C-$\beta$) 25.65 [21], (C-$\gamma$) 26.70 [65], (C-$\delta$) 13.58; $^{119}Sn = -138.6$.
**6** Sn–$CH_2$–$CH_2$–$CH_2$–$CH_3$, (C-$\alpha$) 26.98 [350], (C-$\beta$) 26.79 [21], (C-$\gamma$) 27.76 [69], (C-$\delta$) 14.59; $^{119}Sn = -138.0$.
**7** Sn–$CH_2$–$CH_2$–$CH_2$–$CH_3$, (C-$\alpha$) 27.91 [358], (C-$\beta$) 26.62 [22], (C-$\gamma$) 25.53 [66], (C-$\delta$) 13.70; $^{119}Sn = +155.2$.
**8** Sn–$CH_2$–$CH_2$–$CH_2$–$CH_3$, (C-$\alpha$) 27.99 [358], (C-$\beta$) 12.83 [22], (C-$\gamma$) 25.83 [67], (C-$\delta$) 14.72; $^{119}Sn = +156.4$.






four-coordinate di- and tri-organotin(IV) compounds with corresponding organic substituents. Four-coordinate structures show that no donor–acceptor connection between tin (electron–pair acceptor) and other donors of the ligands (electron–pair donor) occurs.

The coupling constants, $^{n}J[^{119}Sn, ^{13}C]$, are important parameters for the determination of C–Sn–C bond angles (data are given in table 5). For **7** and **8**, with $^{1}J[^{119}Sn–^{13}C]$ being 358 Hz and using the literature methods [32–34], a C–Sn–C bond angle was calculated as 112°, which corresponds to a quasi-tetrahedral geometry. The geometric data are consistent with tetrahedral geometries for the triorganotin(IV) species, i.e., monomers in solution. For the diorganotin(IV) species, for which earlier results indicate five coordination, the calculated C–Sn–C angles are consistent with skew-trapezoidal geometries, with the lower apparent coordination number arising from asymmetric coordination of the carboxylate.

### 3.3. *Mass spectrometry*

As tin has 10 naturally occurring isotopes, each ion appears in the mass spectrum as a series of peaks close to each other due to isotopic effects. Large organotin molecules

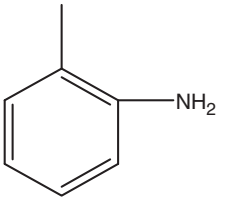
Table 5. (C–Sn–C) angles (°) based on NMR parameters.

| Compound No. | $^1J[^{119}Sn, ^{13}C]$ (Hz) | $^2J[^{119}Sn, ^1H]$ (Hz) | Angle (°) | |
|---|---|---|---|---|
| | | | $^1J$ | $^2J$ |
| **1** | 536 | 74 | 123 | 124 |
| **2** | 538 | 75 | 125 | 125 |
| **3** | 397 | 57 | 111 | 110 |
| **4** | 394 | 58 | 111 | 111 |
| **5** | 350 | 60 | 111 | 112 |
| **6** | 350 | 60 | 111 | 112 |
| **7** | 358 | – | 112 | – |
| **8** | 358 | – | 112 | – |

Table 6. Mass spectral data[a] of synthesized organotin carboxylates.

| Fragment ion | **1** $m/z$ (%) | **3** $m/z$ (%) |
|---|---|---|
| $[R_2SnOOR^{a\prime}]^+$ | 286 (65) | 154 (19) |
| $[RSnOOCR\prime]^+$ | 271 (13) | 109 (12) |
| $[R_2Sn]^+/[R_2SnH]^+$ | 150 (4)/151 (16) | 150 (6)/151 (18) |
| $[RSn]^+/[RSnH]^+$ | 135 (100)/136 (4) | 135 (100)/136 (4) |
| $[Sn]^+/[SnH]^+$ | 120 (16)/121 (8) | 120 (14)/121 (2) |

[a]R′=




suffer considerable fragmentation in the mass spectrometer, while small organotin molecules often show the molecular ion peaks [35]. In **1** and **3**, the base peak is due to $[RSn]^+$ with $m/z$ value of 135 which is obtained by the loss of R from the $[R_2Sn]^+$ followed by the removal of $CH_3$ radicals to give $[Sn]^+/[SnH]^+$ fragment at $m/z$ 120/121 (table 6). The fragmentation patterns of both di- and triorganotin(IV) carboxylates obey the established routes described in earlier reports [36].

### 3.4. *Semi-empirical study*

The two aminobenzoate ligands bind bidentate to Sn(IV) in **1**. The two methyl groups and the two benzoate ligands are octahedral. The Sn–O bond lengths are 2.03 and 2.60 Å and both Sn–C bond lengths are 2.08 Å. The C–O bond distances are 1.25 and 1.33 Å. The Sn–O–C bond angles are 86.7° and 112.6° and O–C–O angle is 108.7°.

Table 7. Selected bond lengths (Å) and angles (°) for **1**, **3**, **5**, and **7**.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Compound **1** | | | | | | | |
| Sn1 | O2 | 2.03 | | | Sn1 | C18 | 2.08 |
| Sn1 | C22 | 2.08 | | | C28 | C29 | 1.40 |
| O2 | Sn1 | C18 | 108.7 | O2 | Sn1 | C22 | 99.5 |
| C18 | Sn1 | O41 | 149.0 | O26 | Sn1 | O41 | 52.0 |
| O17 | Sn1 | O41 | 76.7 | C22 | Sn1 | O17 | 149.1 |
| Compound **3** | | | | | | | |
| C13 | C14 | 1.40 | | | O11 | C12 | 1.33 |
| Sn2 | C7 | 2.10 | | | O26 | Sn2 | 2.67 |
| O11 | Sn2 | C1 | 95.4 | O11 | Sn2 | C3 | 112.9 |
| C1 | Sn2 | O26 | 146.2 | C3 | Sn2 | C7 | 114.5 |
| C12 | O11 | Sn2 | 114.3 | C12 | O26 | Sn2 | 85.4 |
| Compound **5** | | | | | | | |
| Sn1 | C18 | 2.11 | | | Sn1 | C31 | 2.11 |
| Sn1 | O44 | 2.03 | | | C36 | C35 | 1.51 |
| O2 | Sn1 | C18 | 112.5 | O2 | Sn1 | C31 | 100.3 |
| C18 | Sn1 | O44 | 99.2 | C18 | Sn1 | O59 | 150.4 |
| C31 | Sn1 | O59 | 90.8 | C31 | Sn1 | O17 | 149.9 |
| Compound **7** | | | | | | | |
| Sn2 | O3 | 2.04 | | | C1 | Sn2 | 2.14 |
| Sn2 | C19 | 2.14 | | | Sn2 | C32 | 2.13 |
| Sn2 | C1 | C46 | 111.8 | O3 | Sn2 | C1 | 94.6 |
| C19 | Sn2 | C32 | 114.6 | C19 | Sn2 | O18 | 85.5 |
| C32 | Sn2 | O18 | 89.2 | Sn2 | C19 | C21 | 113.9 |



Both O–Sn–O angles are 52.0°. In **3**, the three methyl groups and benzoate are distorted trigonal bipyramidal. The Sn–O bond lengths are 2.04 and 2.67 Å and Sn–C 2.10, 2.10, and 2.11 Å. The Sn–O–C bond angles are 114.3° and 85.4° and the O–C–O angle is 109.5°. The O–Sn–O angle is 50.8°. The butyl groups and the two benzoates are distorted octahedral in **5**. The Sn–O bond lengths are 2.03 and 2.60 Å and both Sn–C bond lengths are 2.11 Å. The C–O bond distances are 1.33 and 1.25 Å. The Sn–O–C bond angles are 86.9°, 86.7°, 112.5°, and 112.7° and O–C–O angles are 108.7° and 108.6°. The O–Sn–O angles are 52.0° and 51.9°. The three butyls and the benzoate are distorted trigonal bipyramidal in **7**. The Sn–O bond lengths are 2.04 and 2.67 Å and the Sn–C bond lengths are 2.14, 2.14, and 2.13 Å. The C–O bond distances are 1.33 and 1.24 Å. The Sn–O–C bond angles are 114.2° and 85.5° and O–C–O angle is 109.5°. The O–Sn–O angle is 50.8°. All bond lengths and angles are comparable to literature values [37]. Selected bond lengths and angles of the optimized structure are tabulated in table 7. The optimized structure is shown in figures 1–4.

### 3.5. *Biological activity*

Biological activity tests of synthesized organotin carboxylates were carried out against two strains each of Gram-positive and Gram-negative bacteria by the agar-well diffusion method [38], and antifungal activity was determined by the tube diffusion method [38]. Data are given in table 8. The recommended concentration (1 mg mL$^{-1}$ in DMSO) was used for each respective test sample. The screening test shows that tributyltin carboxylates were potent antibacterial and antifungal agents, while

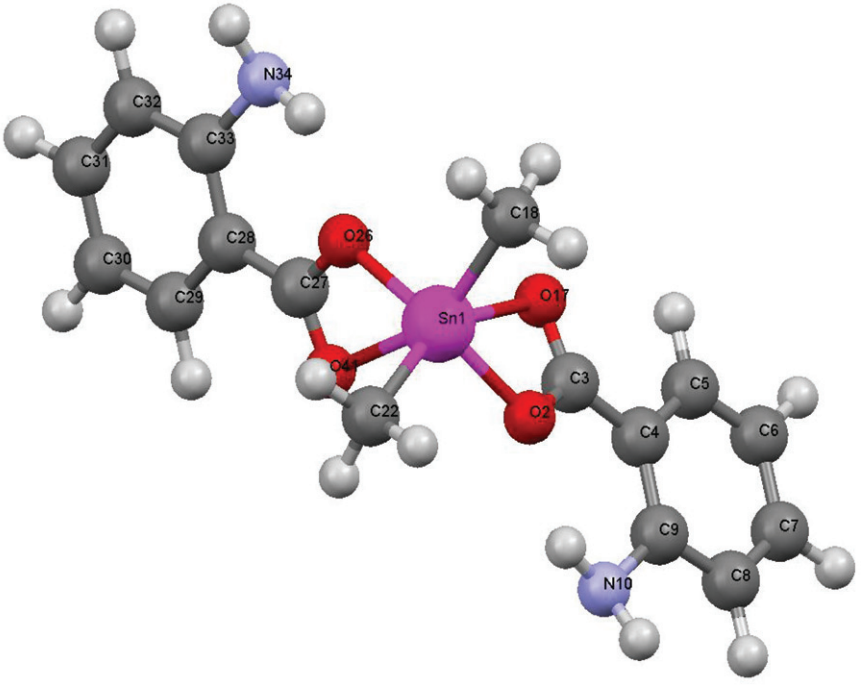



Figure 1. Geometry optimized structure of **1**.

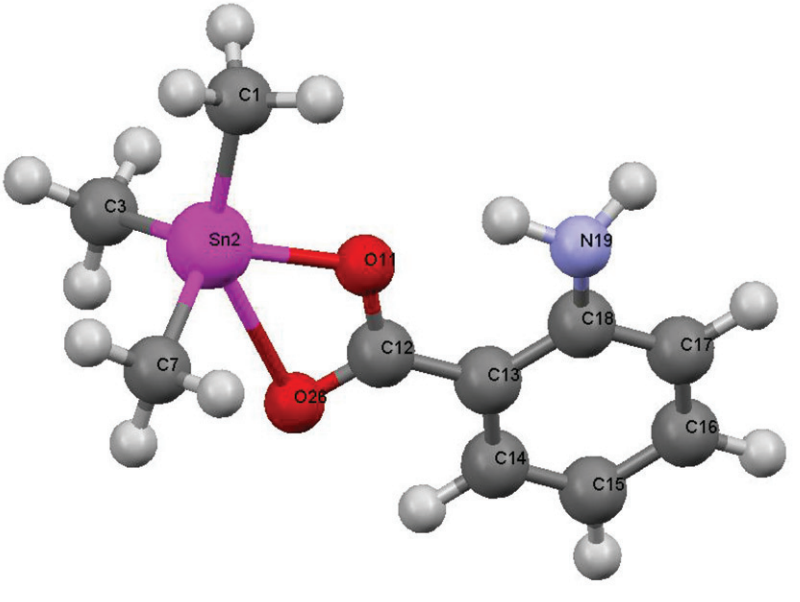



Figure 2. Geometry optimized structure of **3**.

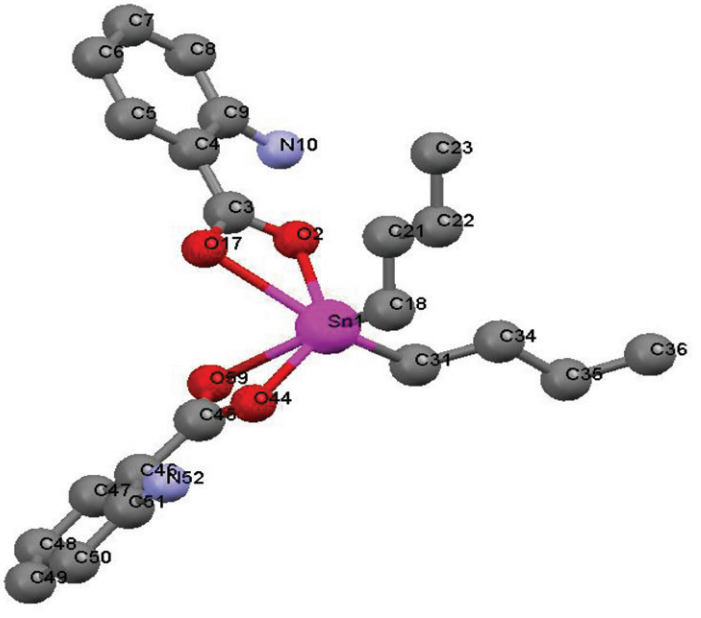



Figure 3. Geometry optimized structure of **5**.

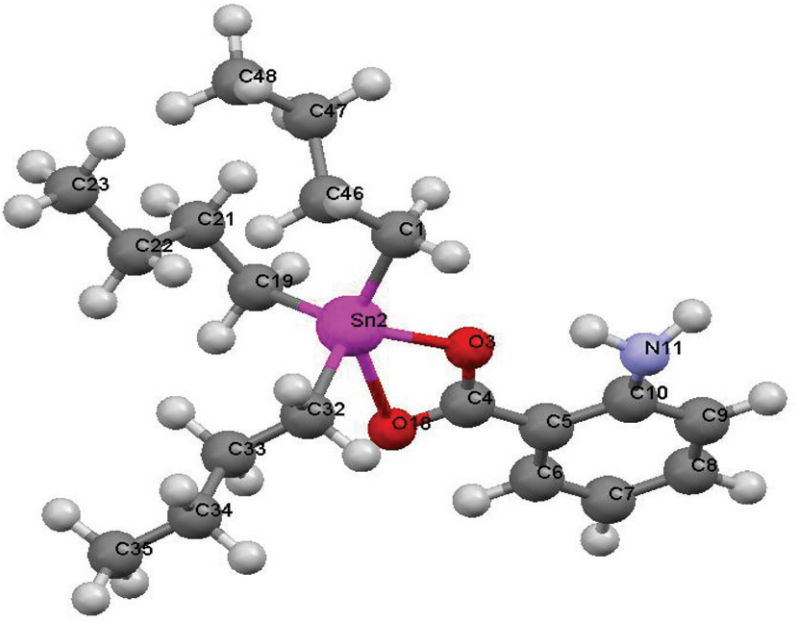



Figure 4. Geometry optimized structure of **7**.

Table 8. Antibacterial and antifungal activities of organotin carboxylates.

| Bacterium | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | Standard drug |
|---|---|---|---|---|---|---|---|---|---|
| Bacillus subtilius | + | ++ | ++ | ++ | ++ | +++ | +++ | ++++ | +++ |
| *Staphylococcus aureus* | + | ++ | ++ | +++ | +++ | ++++ | +++ | ++++ | +++ |
| *Escherichia coli* | + | ++ | + | +++ | +++ | ++++ | +++ | ++++ | ++++ |
| *Salmonella typhi* | + | ++ | ++ | +++ | +++ | ++++ | +++ | ++++ | +++ |
| Fungus | | | | | | | | | |
| *Aspergillus niger* | + | + | ++ | +++ | +++ | ++++ | +++ | ++++ | ++ |
| *Penicillium notatum* | ++ | ++ | + | +++ | +++ | ++++ | +++ | ++++ | ++ |

++++ = highly active, +++ = moderately active, ++ = low active, + = very low active.
Standard drug: Miconazole and Amphotericin B (antifungal agents); Imipenem (antibacterial agent).

triphenylphosphine further enhances their activity. There is a direct relation between the activity and the coordination environment of the metal. The ligand supports transport of the organotin moiety to the site of action where it is released by hydrolysis [39]. The anionic ligand also plays an important role in determining the degree of the activity of organotin compounds. All complexes show tetrahedral geometry in solution and few exceptions show significant activity, which is consistent with species generating tetrahedral geometry in solution being more active [39].



## 4. Conclusions

Organotin carboxylates of 2-aminobenzoic acid have been synthesized with and without triphenylphosphine and their coordination is interpreted from semi-empirical results and spectroscopy. FT-IR spectra demonstrate bidentate coordination for **1**, **3**, **5**, and **7** while monodentate in **2**, **4**, **6**, and **8**. In solid state, **1**, **2**, **5**, and **6** are six coordinate whereas **3**, **4**, **7**, and **8** are five coordinate. NMR data reveal the complexes are four coordinate in solution. Biological activities show that tributyltin carboxylates are potent antibacterial and antifungal agents, and triphenylphosphine enhances their activity; these complexes show potential as drugs in the pharmaceutical field.

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