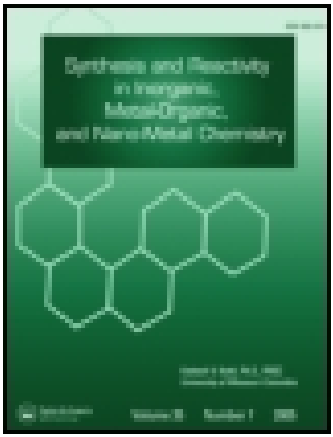

Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

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^{1}H, ^{13}C, ^{119}Sn NMR, ^{119m}Sn Mössbauer, Infrared and Mass Spectrometric Studies of Organotin Carboxylates of 2-(2,3-dimethylphenyl)Aminobenzoic Acid and their Effect on Microorganisms.

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^{1}H, ^{13}C, ^{119}Sn NMR, ^{119m}Sn MÖSSBAUER, INFRARED AND MASS SPECTROMETRIC STUDIES OF ORGANOTIN CARBOXYLATES OF 2-(2,3-DIMETHYLPHENYL)AMINOBENZOIC ACID AND THEIR EFFECT ON MICROORGANISMS.

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ABSTRACT

The synthesis of a new series of organotin carboxylates of 2-(2,3-dimethylphenyl)aminobenzoic acid is reported. Multinuclear NMR (^{1}H, ^{13}C,

^{119}Sn) data have been used as a tool for determining their structures in non-coordinating solvents. Solid state structures have been proposed on the basis of IR and Mössbauer parameters. 2D NMR has been used for the assignments of high-spin systems. Screening tests of these compounds showed that they are highly active against various bacteria and fungi.

INTRODUCTION

The broad spectrum of organotin chemistry extends right from architecture[1] through agriculture[2] to medicine and aircrafts[3]. Although R_3SnL derivatives (L = monodentate or bidentate ligand) possess acute toxicity[4-9] yet diorganotin derivatives like diethyltin(IV) and dibutyltin(IV) carboxylates are known anti-tumor agents[10-13]. Various studies have shown that replacement of the ligand changes the toxicity effect of the organotin moiety[4-9]. In order to explore the effect of ligands on the biological activity of organotin compounds we have prepared a series of organotin carboxylates of 2-(2,3-dimethylphenyl)aminobenzoic acid, HL, Fig. 1, commonly known as ponstan, one of the most frequently used analgesic, antipyretic and anti-inflamatory drugs[14].

These compounds have been characterized by multinuclear NMR, IR, mass spectrometry and Mössbauer spectroscopy. Their biological activity tests showed that they are potent candidates against various bacteria and fungi.

EXPERIMENTAL

Most organotin halides and their carboxylate derivatives are air and moisture sensitive, hence all the glassware was completely dried at 140° C. All reactions were carried out under argon in dried solvents.

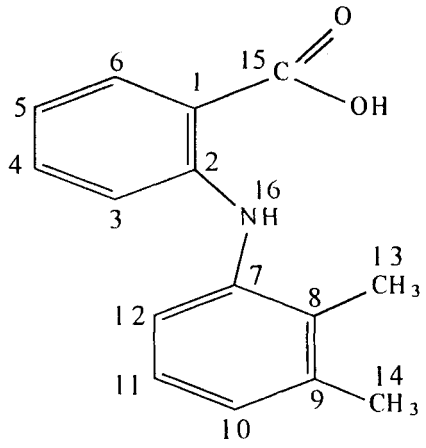


Fig. 1. *HL – 2-(2,3-Dimethylphenyl)aminobenzoic Acid*

Synthesis of Triorganotin Carboxylates

3.48g (0.01 mole) of the silver salt of 2-(2,3-dimethylphenyl)aminobenzoic acid was suspended in dry chloroform (100 mL) in a 250 mL two-necked round bottom flask equipped with a water condenser and magnetic stirring bar. The appropriate triorganotin chloride (0.01 mol) in dry chloroform (50 mL) was added to the suspension dropwise with constant stirring. The reaction mixture was refluxed for 6-8 h. The reaction mixture was allowed to stand overnight. Silver chloride formed during reaction was filtered off using a convensional Schlenk apparatus and solvent removed under reduced pressure. The solid mass left was recrystallized from suitable solvents.

Synthesis of Diorganotin Dicarboxylates

6.96g (0.02 mole of) 2-(2,3-dimethylphenyl)aminobenzoic acid and diorganotin oxide (0.01 mole) were refluxed in 150 mL toluene (eq. 2) for 4-6 hr. Water

formed during reaction was continuously removed using a Dean-Stark apparatus. Toluene was then completely removed under reduced pressure on a membrane pump or a high vacuum pump. The residue was given activated charcoal treatment in 100 mL dry dichloromethane and filtered. The filtrate was concentrated and kept at low temperature. Crystals or solid mass thus obtained was recrystallized from appropriate solvent or mixture.

Synthesis of Dimeric Tetraorganodicarboxylato Stannoxanes

3.48g (0.01 mole) of 2-(2,3-dimethylphenyl)aminobenzoic acid and 0.01 mole diorganotin oxides were refluxed in 100 mL toluene for 4-6 h. using a conventional Dean-Stark apparatus for continuous removal of water formed during condensation. Toluene was then completely removed under reduced pressure on a membrane pump or a high-vacuum pump. The residue was treated with activated charcoal in 100 mL dry dichloromethane and filtered. The filtrate was concentrated and kept at low temperature. Crystals or a solid mass thus obtained was recrystallized from an appropriate solvent or mixture.

Physical parameters of the organotin carboxylates are given in Table 1.

Instrumentation

Melting points were determined in a capillary tube using electrothermal melting point apparatus model MP-D Mitamura Riken Kogyo (Japan) and are uncorrected. Infrared absorption spectra were recorded in the KBr pellets on a Hitachi 270-50 Spectrophotometer (Japan). ^{119m}Sn Mössbauer spectra were obtained with a constant acceleration microprocessor-controlled spectrometer (Cryoscopic Ltd, Oxford U.K); a barium stannate

Table I. Physical Parameters

Compound	Recrystallization Solvents	MW	Yield %	Mp. °C	Elemental Composition (Cal.) / Exp		
					%C	%H	%N
(I) $C_{18}H_{23}NO_2Sn$	$CHCl_3$	405	75	123-125	(53.33) 53.39	(5.68) 5.70	(3.46) 3.44
(II) $C_{32}H_{34}N_2O_4Sn$	CH_2Cl_2/n-C_6H_{14}	630	84	154-155	(60.95) 60.50	(5.40) 5.39	(4.44) 4.46
(III) $C_{68}H_{80}N_4O_{10}Sn_4$	CH_2Cl_2/n-C_6H_{14}	1602	92	124	(51.26) 51.20	(5.03) 5.05	(3.52) 3.50
(IV) $C_{27}H_{41}NO_2Sn$	CH_2Cl_2/n-C_6H_{14}	531	60	135 (dec.)	(61.02) 61.05	(7.72) 7.68	(2.64) 2.65
(V) $C_{38}H_{46}N_2O_4Sn$	CH_2Cl_2/n-C_6H_{14}	714	80	100	(63.86) 63.80	(6.44) 6.40	(3.92) 3.90
(VI) $C_{92}H_{128}N_4O_{10}Sn_4$	CH_2Cl_2 at -20° C	1928	90	63	(57.26) 57.30	(6.64) 6.68	(2.90) 2.88
(VII) $C_{33}H_{29}NO_2Sn$	$CHCl_3$	591	68	158-160	(67.01) 67.05	(4.91) 4.88	(2.37) 2.40
(VIII) $C_{33}H_{47}NO_2Sn$	$CHCl_3$	609	70	144 (dec.)	(65.02) 65.10	(7.72) 7.75	(2.30) 2.28

source was used at room temperature and samples were packed in perspex discs and cooled to -193° C. Isomer data are relative to SnO_2. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 500 spectrometer (Germany), using $CDCl_3$ as an internal reference [δ $^1H(CDCl_3)$ = 7.24: δ $^{13}C(CDCl_3)$ = 77.0]. ^{119}Sn NMR spectra were obtained on Bruker 250 ARX spectrometer (Germany) with Me_4Sn[(Sn) = 37.290665 MHz] as an external reference. Mass spectral data were measured on a MAT 8500 Finnigan, (Germany).

RESULTS AND DISCUSSION

Preparation of Complexes

Triorganotin carboxylates were prepared by the reaction of silver salt of the ligand acid with an appropriate triorganotin chloride in dry chloroform in 1:1 molar ratio.

$$R_3SnCl + AgL \longrightarrow R_3SnL + AgCl \qquad (1)$$

R = Me **(I)**, n-Bu **(IV)**, Ph **(VII)**, Cyclohexyl **(VIII)**

Diorganotin dicarboxylates were prepared by the condensation of carboxylic acid and diorganotin oxide in 2:1 molar ratio

$$R_2SnO + 2HL \longrightarrow R_2SnL_2 + H_2O \qquad (2)$$

R = Me **(II)**, n-Bu **(V)**.

whereas dimeric tetraorganodicarboxylato stannoxanes were obtained by

the condensation of carboxylic acid and the diorganotin oxide in 1:1 molar ratio.

$$4R_2SnO + 4HL \longrightarrow [(R_2SnL)_2O]_2 + 2H_2O \quad \textbf{(3)}$$

R = Me **(III)** and n-Bu **(VI)**; HL = $(CH_3)_2C_6H_3NHC_6H_4COOH$

Multinuclear NMR

Multinuclear NMR data are given in Tables II-VI. In the ^{1}H NMR spectra, the resonances of the ligand protons have been assigned on the basis of their intensity and multiplicity pattern. 2D heteronuclear shift correlations (HETCOR) of the type $^{13}C/^{1}H$ [based on $^{1}J(^{13}C\text{-}^{1}H)$ = 170-180 Hz] were used to confirm these assignments which were made according to the numbering given in Fig. 1.

The aromatic carbon resonances were assigned by comparison of the experimental chemical shifts with those calculated from the incremental method[15]. For the trimethyltin derivative, $^{2}J[^{119/117}Sn\text{-}^{1}H]$ = 58.2 Hz falls in the range of a tetrahedral environment[16] around the tin atom which is further supported by the C-Sn-C angle (111°) (Table VI), which was calculated using Lockhart's equation[16]. In case of n-butyl, phenyl and cyclohexyl derivatives, the $^{n}J[^{119/117}Sn\text{-}^{1}H]$ couplings are not visible due to a complex multiplet pattern. The ^{13}C NMR data (Table IV) of the triorganotin carboxylates confirm the proposed tetrahedral structure in non-coordinating solvents.

Various literature methods[17,18] have been applied to calculate C-Sn-C angles (Table VI) based on $^{1}J[^{119/117}Sn\text{-}^{13}C]$ in the solution phase.

The chemical shifts $\delta^{119}Sn$ (Table VIII) are comparable with earlier reports describing tetrahedral geometry[19,20]. The NH resonance occurs at 9.3±0.2

Table II. ^{1}H NMR Data of Triorganotin Carboxylates[a-c]

Proton	(I) R = methyl	(IV) R = n-butyl	(VII) R = phenyl	(VIII) R = cyclohexyl
3	6.8 (d, 9.44)	6.8 (d, 9.35)	6.8 (d, 8.45)	6.8 (d, 8.50)
4	7.2 (dd, 8.65, 8.60)	7.3 (dd, 7.85, 7.70)	7.2 (dd, 7.90, 7.80)	7.2 (dd, 7.39, 7.20)
5	6.6 (dd, 8.13, 8.04)	6.7 (dd, 8.10, 8.20)	6.6 (dd, 8.00, 8.20)	6.7 (dd, 8.10, 8.20)
6	8.0 (d, 9.69)	8.2 (d, 8.00)	8.1 (d, 7.80)	8.0 (d, 7.90)
10	6.9 (d, 9.40)	6.9 (d, 8.47)	6.8 (d, 8.78)	6.9 (d, 9.00)
11	7.0 (dd, 7.52, 7.50)	7.1 (dd, 7.50, 7.49)	7.1 (dd, 7.50, 7.49)	7.0 (dd, 7.50, 7.48)
12	7.2 (dd, 8.65, 8.60)	7.3 (dd, 7.85, 7.70)	7.2 (dd, 7.90, 7.80)	7.2 (dd, 7.39, 7.20)
13	2.3 (s)	2.5 (s)	2.3 (s)	2.3 (s)
14	2.2 (s)	2.3 (s)	2.2 (s)	2.2 (s)
16	9.3 (s)	9.3 (s)	9.5 (s)	9.5 (s)
α	0.63 ^{2}J[58.20]	1.9 - 1.8 (m)	-----	2.0 - 1.9 (m)
β	-----	1.6 - 1.5 (m)	7.98 (m)	1.76 - 1.67 (m)
γ	-----	1.6 - 1.5 (m)	7.62 (m)	1.76 - 1.67 (m)
δ	-----	1.1 (t, 7.20)	7.57 (m)	1.37 - 1.29 (m)

[a] Chemical shift (δ) in ppm, $^{3}J(^{1}H\text{-}^{1}H)$ in Hz, $^{2}J[^{119,117}Sn\text{-}^{1}H]$ in Hz in parentheses [b] Multiplicity is given by: s singlet, d doublet t triplet and m multiplet.

Table III. ^{1}H NMR Data of Diorganotin Dicarboxylates and Dimeric Stannoxanes[a,b,c]

Proton	(II) R = methyl	III R = methyl	(V) R = n-butyl	(VI) R = n-butyl
3	6.8 (d, 9.33)	6.8 (d, 9.34)	6.9 (d, 9.34)	6.8 (d, 8.30)
4	7.3 (dd, 6.93, 6.50)	7.2 (dd 6.75, 6.70)	7.3 (dd, 6.75, 7.00)	7.3 (dd, 7.48, 7.45)
5	6.7 (dd, 8.19, 8.04)	6.6 (dd, 8.15, 8.00)	6.7 (dd, 8.20, 8.00)	6.6 (dd, 8.19, 8.10)
6	8.1 (d, 9.69)	8.0 (d, 9.70)	8.2 (d, 7.60)	8.0 (d, 7.4)
10	7.0 (d, 9.50)	6.9 (d, 8.47)	7.0 (9.30)	7.0 (d, 8.50)
11	7.1 (dd, 7.53, 9.49)	7.0 (dd, 7.59, 7.50)	7.1 (dd, 7.58, 7.48)	7.0 (dd, 7.60, 7.50)
12	7.3 (dd, 6.93, 6.50)	7.2 (dd, 6.75, 6.70)	7.3 (dd, 6.75, 7.00)	7.3 (dd, 7.48, 7.45)
13	2.3 (s)	2.4 (s)	2.3 (s)	2.4 (s)
14	2.2 (s)	2.3 (s)	2.2 (s)	2.3 (s)
16	9.1 (s)	9.3 (s)	9.3 (s)	9.4 (s)
α	1.20 ^{2}J[83.3]	1.10, 1.00 ^{2}J[89.5], ^{2}J[86.0]	1.80 - 1.70 (m)	1.90 - 1.80 (m)
β	-----	-----	1.54 - 1.45 (m)	1.50 - 1.40 (m)
γ	-----	-----	1.54 - 1.45 (m)	1.50 - 1.40 (m)
δ	-----	-----	0.96 (t, 7.00)	0.96 (t, 7.00), 0.94 (t, 7.00)

*[a] Chemical shift (δ) in ppm, $^{3}J(^{1}H\text{-}^{1}H)$ in Hz, $^{2}J[^{119/117}Sn\text{-}^{1}H]$ in Hz in parentheses [b] Multiplicity is given by s singlet, d doublet, t triplet and m multiplet. [c] **(III)** and **(VI)** are stannoxanes.*

Table IV. ^{13}C NMR Data of Triorganotin Carboxylates[a]

Carbon	(I) R = methyl	(IV) R = n-butyl	(VII) R = phenyl	(VIII) R = cyclohexyl
1	113.0	113.2	113.1	113.1
2	148.9	148.8	149.2	148.9
3	113.5	113.2	113.5	113.4
4	133.4	133.2	134.2	133.2
5	115.9	115.8	116.0	115.8
6	132.8	132.9	133.5	133.0
7	139.4	139.3	140.0	139.5
8	131.9	131.7	132.0	131.9
9	138.0	137.7	138.5	138.0
10	126.0	126.0	126.5	126.1
11	125.7	125.6	126.0	125.7
12	122.4	122.4	122.9	122.7
13	14.0	13.8	13.5	13.9
14	20.6	20.5	20.5	20.6
15	173.5	173.5	177.5	173.3
α	-2.17 ^{1}J[399.2]	16.6 ^{1}J[352.6]	139.0 ^{1}J[650.0]	33.9 ^{1}J[341.2]
β	-----	27.7 ^{2}J[21.4]	136.5 ^{2}J[50.0]	31.1 ^{2}J[14.6]
γ	-----	26.9 ^{3}J[64.7]	129.0 ^{3}J[70.0]	28.9 ^{3}J[65.3]
δ	-----	13.7	130.0 ^{4}J[13.5]	26.9 ^{4}J[7.5]

[a] *Chemical shifts (δ) in ppm, "$J[^{119/117}Sn\text{-}^{13}C]$ in Hz in parentheses*

Table V. ^{13}C NMR Data of Diorganotin Dicarboxylates and Dimeric Stannoxanes[a,b]

Carbon	(II) R = methyl	(III) R = methyl	(V) R = n-butyl	(VI) R = n-butyl
1	111.0	113.6	111.3	113.4
2	149.4	149.2	149.3	149.3
3	113.6	113.8	113.4	113.9
4	134.5	133.6	134.5	133.4
5	116.2	116.0	116.2	115.8
6	133.2	132.4	133.3	132.5
7	138.8	139.1	138.9	139.2
8	132.0	131.9	131.9	132.3
9	138.2	138.1	138.1	138.1
10	126.5	126.4	126.4	126.5
11	125.8	125.9	125.8	125.9
12	122.6	122.8	122.6	123.2
13	13.9	14.1	13.9	14.0
14	20.6	20.6	20.7	20.6
15	177.3	175.2	177.4	175.1
α	5.0 ^{1}J[659.8]	10.2 ^{1}J[794.0] 7.50 ^{1}J[759.9]	25.9 ^{1}J[589.0]	27.7 ^{1}J[695.9] 25.3 ^{1}J[589.7]
β	-----	------	26.9 ^{2}J[19.7]	27.9 ^{2}J[36.0] 26.9 ^{2}J[31.3]
γ	-----	-----	26.6 ^{3}J[98.7]	26.6 ^{3}J[100.0] 26.3 ^{3}J[68.0]
δ	-----	-----	13.6	13.5

[a] *Chemical shifts (δ) in ppm, "$J[^{119/117}Sn$-$^{13}C]$ in Hz in parentheses.*
[b] ***(III)** and **(VI)** are stannoxanes.*

Table VI. C-Sn-C Angles (°) Based on NMR Parameters

Compound	$^{1}J[^{119}Sn-^{13}C]$ (Hz)	$^{2}J[^{119}Sn-C-^{1}H]$ (Hz)	θ (°) ^{1}J	θ (°) ^{2}J
(I)	399.2	58.2	111.8	111.0
(II)	659.8	83.3	134.6	135.0
(III)	794.0 759.9	89.5 86.0	146.4 143.4	144.2 138.9
(IV)	352.6	-	110	-
(V)	589.0	-	133.6	-
(VII)	695.9	-	116.3	-

Where θ is the C-Sn-C angle.

Table VII. Characteristic Infrared Vibrations (cm^{-1})

Compound	$\nu(COO)_{asym}$	$\nu(COO)_{sym}$	Δν	ν(Sn-C)	ν(Sn-O)	ν(Sn-O-Sn)
Acid	1660 b	1334 s	326	----	----	----
Ag salt	1608 s	1368 s	240	----	----	----
(I)	1614 s	1356 s	258	549 s	477 sh	----
(II)	1608 s	1368 s	240	522 s	453 s	----
(III)	1610	1362	248	545	440	736
(IV)	1602	1348	254	550	450	----
(V)	1600	1350	250	555	450	----
(VI)	1605	1345	260	560	455	700
(VII)	1617 s	1362 s	255	525 s	441 s	----
(VIII)	1641 s	1392 s	249	504 s	405 sh	----

Table VIII. ^{119m}Sn Mössbauer and ^{119}Sn NMR Parameters[a]

Compound	δ (mm s^{-1})	Δ (mm s^{-1})	Γ_1	Γ_2	^{119}Sn (δppm)
(I)	1.31	3.59	0.89	0.89	133.4
(II)	1.22	3.26	0.88	0.99	-119.3
(VII)	1.15	2.35	0.94	0.94	-116.5
(VIII)	1.42	2.67	0.88	0.88	12

[a] *$\delta \pm 0.02$, $\Delta \pm 0.04$, $\Gamma \pm 0.02$ mm s^{-1} where Γ is line width at half height.*

ppm in all these carboxylates which reveals that the NH group does not show intra- or intermolecular interactions.

In the diorganotin dicarboxylates where R = Me, the $|^{2}J[^{119/117}Sn\text{-}^{1}H]|$ and $|^{1}J[^{119/117}Sn\text{-}^{13}C]|$ coupling constants (Tables II and V) have been used to calculate C-Sn-C angles (Table VI). These values lie in-between penta- and hexa-coordinated tin[19,20].

There is a difference of more than 250 ppm in the $\delta^{119}Sn$ chemical shifts of these compounds as compared to triorganotin carboxylates which suggest a coordination number greater than 5 for tin[19], as proposed in Fig. 2.

However, diorganotin dicarboxylates prepared by the reaction of organotin oxides with the acid in 1:1 molar ratio adopt a characteristic dimeric tetraorganodicarboxylato stannoxane structural mode (Fig. 3).

This has been reflected by two sets of signals in the ^{1}H and ^{13}C NMR spectra. Such types of signals are due to R groups attached with the endo- and exocyclic tin atoms. Similarly, two signals were observed in the ^{119}Sn NMR spectra supporting different tin environments in the same molecule [20-23].

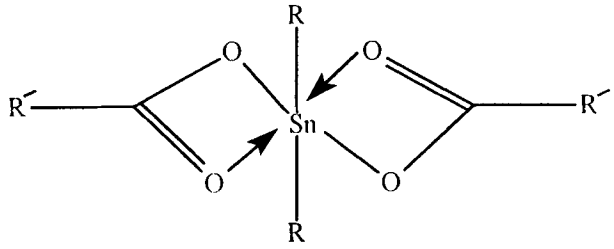


Fig. 2. *Proposed Structure for Diorganotin Dicarboxylates*

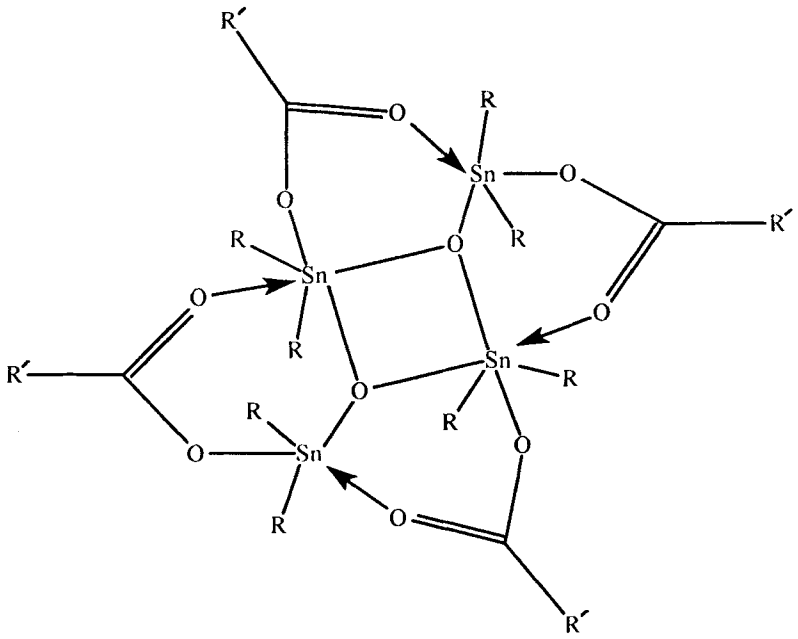


Fig. 3. *Proposed Structure for Dimeric Tetraorganodicarboxylato Stannoxanes*

Infrared Spectroscopy

Because of the low symmetry of the carboxylate ion, the different types of carboxylate interactions cannot be identified easily. However, attempts have been made to correlate the values of characteristic vibrations like $\nu(CO_2)$, ν(Sn-C), ν(Sn-O), ν(Sn-Cl) and ν(Sn-O-Sn), with their precursors, and literature reports for the elucidation of the polyhedra around the tin atom. IR spectra were recorded in the range 4000-400 cm^{-1} and the data are given in Table VII. The broad band in the range 3050 cm^{-1} due to ν(OH) present in the spectrum of the ligand is absent in the spectra of its silver salt and the corresponding organotin derivatives, thus showing complex formation.

The $\nu(CO_2)$ frequencies are shifted far from the free acid (1660 and 1334 cm^{-1}) and occur at 1620±20 and 1370±20 cm^{-1}. In R_3SnL, the vibrations $\nu(CO_2)$ are comparable to that of the silver salt, thus indicating a bidentate bridging nature of the carboxylate ion[24] (Fig. 4.)

The vibrations ν(Sn-C) and ν(Sn-O) are observed in the range 549-504 cm^{-1} and 477-405 cm^{-1} respectively[25,26]. The vibration ν(Sn-Cl) is alltogether absent in these compounds. A strong band at 3316-3268 cm^{-1}, characteristic for an NH group and observed in the spectrum of the ligand, also persists in the spectra of these complexes which shows that the NH group does not participate via intra- or intermolecular modes of interaction. This observation is parallel with the NMR results.

In the case of diorganotin dicarboxylates, the most important bands arising from $\nu(CO_2)_{asym}$ and $\nu(CO_2)_{sym}$ occur at 1641-1602 and 1392-1350 cm^{-1}, respectively (Table VII). The $\Delta\nu$ value [$\Delta\nu = \nu(CO_2)_{asym} - \nu(CO_2)_{sym}$] has been used to predict the mode of carboxylate interaction. According to

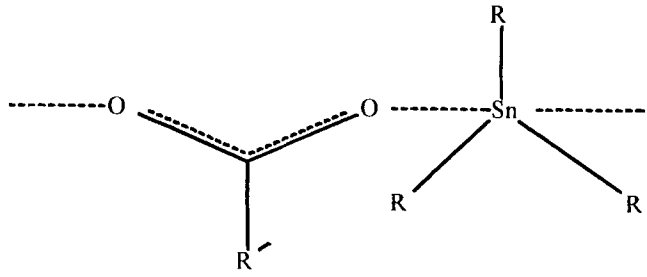


Fig. 4. *Proposed Polymeric Structure for Triorganotin Carboxylates*

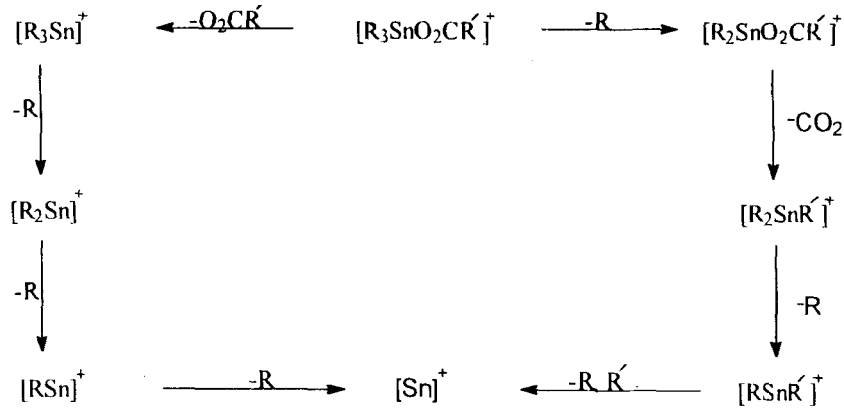
earlier reports, if this value is comparable to that of the silver salt of the ligand acid, then the carboxylate ion is acting as a bidentate chelate group. It is, therefore, proposed that the carboxylate group in these compounds is acting as a bidentate chelate ligand[24,27,28].

The IR spectra of dimeric tetraorganodicarboxylato stannoxanes are almost similar to those observed for diorganotin dicarbdxylates except for a very sharp band in the range 736-700 cm^{-1} characteristic for the Sn-O-Sn-O ring in these compounds[23,29].

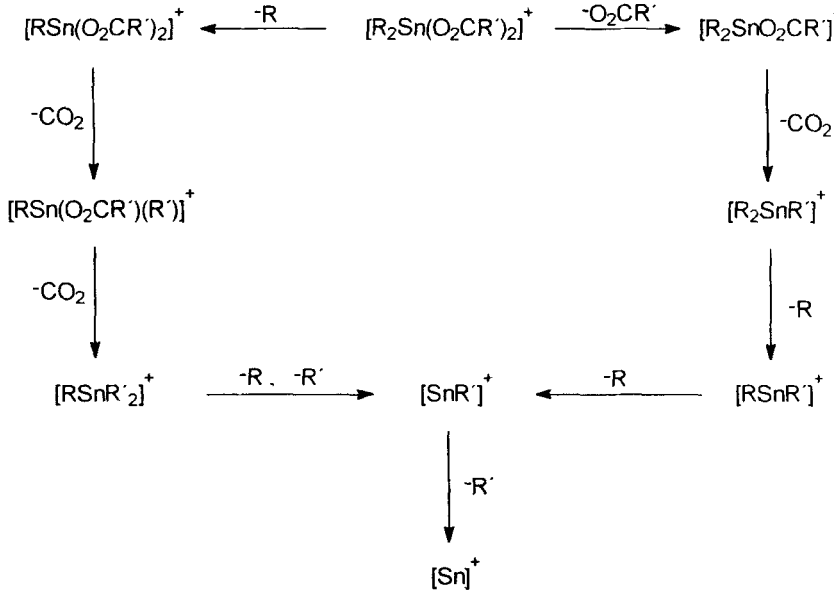
In the absence of crystallographic data, IR studies cannot be taken as an unequivocal criterion for the coordination state of the tin atom in such systems, hence, these results are supported by Mössbauer spectroscopy.

Mössbauer Spectroscopy

Mössbauer parameters of the representative compounds are given in Table VIII. The QS value (Δ), which is a consequence of the geometry around the tin atom, falls in the range of >3.5 mm s^{-1} for compounds having a *trans*-R_3SnO_2 arrangement with bridging carboxylate groups[29]. A comparison of



Scheme 1. *Fragmentation Pattern of Triorganotin Carboxylates*



Scheme 2. *Fragmentation Pattern of Diorganotin Dicarboxylates*

Table IX. Antibacterial Activity[a]

Bacterium	Acid	(I)	(II)	(VII)	(VIII)
Gram Positive					
B. anthracis	+++	-	+	+++	+++
S. aureus	-	-	++	+++	+
Micrococci	-	-	-	+++	+
S. epidermis	-	-	-	+++	++
S. faecalis	-	-	-	-	-
C. dephtheriae	++	-	-	++	+
Gram Negative					
C. hoffmani	-	-	-	-	-
E. coli	-	-	-	-	-
P. aeruginosa	-	-	-	-	-
P. pseudomalliae	-	-	-	-	-
A. sobriae	-	-	-	-	-

[a] = *200 mg ml*$^{-1}$.

+ = *low activity*, ++ = *good activity*, +++ = *high activity, and* – = *no activity*.

the Mössbauer parameters with earlier reports shows that **(I)** is polymeric in the solid state, however, **(VII)** and **(VIII)** are probably monomeric, **(II)** having a Δ value of 3.26 mm s^{-1} possesses a *trans*-R_2SnO_4 geometry around the tin atom[30-35].

Mass Spectrometry

The mass fragmentation patterns of the triorganotin carboxylates and diorganotin dicarboxylates are given in Schemes 1 and 2, respectively.

Table X. Antifungal Activity[a]

Fungus	Acid	(I)	(II)	(VII)	(VIII)
Candida Albicans	-	+	-	+	-
Penicillium Notatum	+	+++	-	-	-
Curvularis Lunata	++	+++	+	++	++
Alternaria Solani	x	+++	++	++	++
Fusarium Solani	++	+++	-	-	+
Epdermofloccosum	+++	+++	+	+++	-
Candida Tropicalis	+	++	-	+	++
Aspergillus Niger	++	+++	-	-	-
Ascomycetes	++	+++	+	++	-
Dutarium rotatum	x	+++	-	++	+

[a] $= 250\ mg\ mL^{-1}$

+ = *low activity,* **++** = *good activity,* **+++** = *high activity,* **–** = *no activity and* x = *not checked.*

A molecular ion peak of very low intensity was only observed for **(VII)**. In the triorganotin derivatives the primary fragmentation is due to the loss of the R group. The secondary fragment is a consequence of loss of either the R group or CO_2. However, the latter is more frequent and a more probable pathway. In case of the diorganotin derivatives, the primary fragmentation is mostly the loss of one ligand and CO_2 is eliminated in a second step. However, if the primary fragmentation is due to loss of the R group, then there is a successive elimination of two CO_2 molecules . Dimeric stannoxanes show a fragmentation pattern similar to that of diorganotin dicarboxylates, except for very weak peaks for $[R_2SnO]^+$ and $[RSnO]^+$.

Peaks for $[R_3Sn]^+$ $[R_2Sn]^+$ and $[RSn]^+$ have either very low intensities or are absent, thus indicating that fragmentation through these species is not favourable [24,36]

Biological Testing

Biological activity tests for some of the compounds were carried out against various bacteria and fungi by the "agar well diffusion" method[37] These results are given in Tables IX and X, respectively.

Triphenyltin and tricyclohexyltin derivatives are highly active against gram-positive bacteria while none of the others were found active against gram-negative bacteria. Furthermore, the extent of activity decreases with a decrease in the number of R groups which is in accordance with earlier reports[2,20]

The antifungal activity tests show that the effect of these compounds varies with the fungi and the nature and number of R groups, **(I)** is highly active in this series. The activity decreases in the following order; **(I) > (VII) > (II) = (VIII).**

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