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Synthesis, structural and larvicidal studies of some triorganotin 2-(*p*-chlorophenyl)-3-methylbutyrates

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Abstract

A series of triorganotin 2-(*p*-chlorophenyl)-3-methylbutyrates, ($R_3SnO_2CCH(CH(CH_3)_2)C_6H_4Cl$-4), where R = methyl, ethyl, *n*-propyl, *n*-butyl, phenyl and *cyclo*-hexyl, have been synthesized. Elemental analyses, Mössbauer, Infrared and NMR spectroscopies have been used to characterize their structures. Based on the spectroscopic results, all the complexes with the exception of the tricyclohexyl compound were found to be five-coordinated in the solid state while the tricyclohexyltin derivative was determined to be four-coordinated. Structural assignments based on spectroscopic data are supported by the crystallographic results of four of the triorganotin butyrates (trimethyl-, tri-*n*-propyl-, tri-*n*-butyl- and tricyclohexyltin 2-(*p*-chlorophenyl)-3-methylbutyrate). Multinuclear NMR spectroscopy studies indicated that all the complexes were tetrahedral in solution. Larvicidal activities of the complexes were evaluated against the 2nd instar stage of the *Anopheles stephensi*, *Aedes aegypti* and *Culex pipiens quinquefasciatus* mosquitoes. The toxicity data indicate that there does not appear to be any significant differences of the compounds towards the different mosquito species based on their averaged toxicity values. In addition, the toxicity of the triorganotin compounds towards the mosquito larvae was concluded to be dependent on both the compound and the species of mosquito larvae.

Keywords: *Aedes aegypti*; *Anopheles stephensi*; *Culex pipiens quinquefasciatus*; Larvae; Mosquito; Toxicity; Triorganotins

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1. Introduction

Organotins, especially triorganotin complexes, comprise an important class of compounds which exhibit a wide range of biological activities. Organotin compounds [1–3] have been used as the active agent in various agrochemicals, antifoulants and anticancer drugs. For example, triphenyltins [1–5] are useful in treating fungal diseases and pests in crops while tributyltins [1–3,6] have been incorporated into marine paints as the active agent. Gielen [7] has reported that various organotins have been found active against a host of cell lines. Triorganotins [8,9] as well as pyrethroids [10,11] have been shown to be effective against mosquito larvae as well as adult mosquitoes. It is hypothesized that incorporating a triorganotin moiety into a pyrethroid molecule will have synergistic effects, thereby reducing the amount of chemicals needed for the task. A more potent compound will also reduce the amount of toxicants that would be discharged into the environment. Other advantages of this class of insecticides/larvicides are the fact that triorganotins

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are known to biodegrade into non-toxic species in the environment [2], and there are no known reports of these species of mosquitoes being tolerant to triorganotins. Tsushima and his co-workers [12] have taken a step in this direction, by synthesizing a series of trimethylstanniomethyl ethers using several pyrethroidal alcohols. This series of ethers showed high activities against rice stem borers, houseflies and German cockroaches [12]. A series of triorganotin 2-(*p*-chlorophenyl)-3-methylbutyrates have been synthesized by introducing 2-(*p*-chlorophenyl)-3-methylbutyric acid as the modification of the acid moiety of the pyrethroid. Their syntheses, structural characterization and larvicidal activities are reported herein.

2. Experimental

2.1. Material and elemental analyses

2-(*p*-Chlorophenyl)-3-methylbutyric acid was obtained from Aldrich Chemical Co. Inc., Milwaukee, WI, USA and the triorganotin chloride, oxide or hydroxide were purchased from Gelest Inc., Tullytown, PA, USA. The starting materials were used as received. All the solvents were obtained from Fisher Scientific Inc., Pittsburgh, PA, USA and used without further purification.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY, USA.

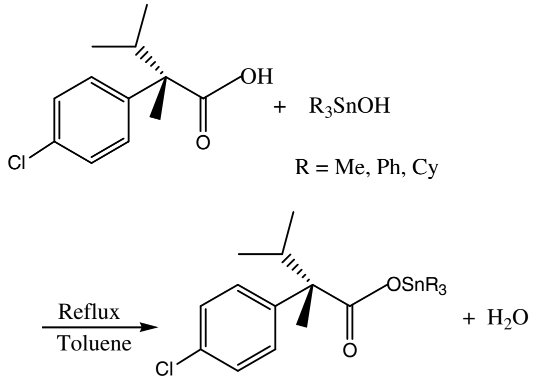
2.2. Spectral studies

The IR spectra in the 400–4000 cm^{-1} region were recorded as KBr pellets on a Nicolet Magna-IR 760 spectrometer. All NMR measurements were made on a Varian Unity Inova 500 MHz spectrometer with a carbon frequency of 125.684 MHz. Sample and instrument temperatures were controlled at 298 K. Proton-decoupled ^{13}C and ^{119}Sn spectra were acquired with WALTZ decoupling. ^{1}H and ^{13}C chemical shifts were referenced to internal TMS while ^{119}Sn chemical shifts were referenced to tetramethyltin externally. The Mössbauer spectra of the solid compounds were measured at 80 K on a Ranger Mössbauer Model MS-900 spectrometer in the acceleration mode with a moving-source geometry using a liquid nitrogen cryostat. The source was 10 mCi $Ca^{119m}SnO_3$ and the velocity was calibrated at ambient temperatures using a composition of $BaSnO_3$ and tin foil (splitting 2.52 $mm\,s^{-1}$).

2.3. Syntheses of the complexes

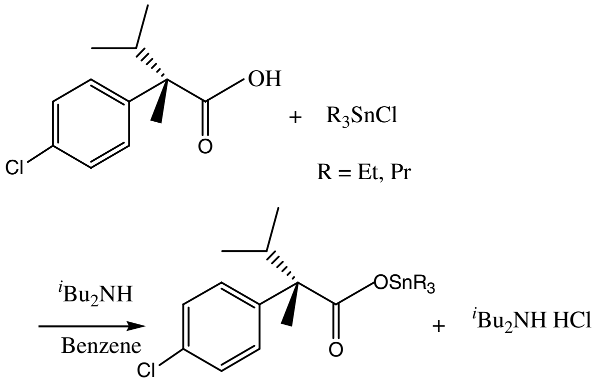
The complexes were synthesized using 2-(*p*-chlorophenyl)-3-methylbutyric acid and the appropriate triorganotin according to the procedures given below.

2.3.1. Preparation of complexes **1**, **5**, **6** [trimethyltin-, triphenyltin- and tricyclohexyltin-2-(p-chlorophenyl)-3-methylbutyrates]



Triorganotin hydroxide [$(CH_3)_3SnOH$ (2 mmol; 0.361 g) for complex **1**, $(C_6H_5)_3SnOH$ (2 mmol; 0.733 g) for complex **5** and $(C_6H_{11})_3SnOH$ (2 mmol; 0.770 g) for complex **6**] was dissolved in 20 mL of hot toluene in a 100 mL round-bottom flask fitted with a Dean-Stark trap. To this was added, with stirring, an equal molar amount of 2-(*p*-chlorophenyl)-3-methylbutyric acid dissolved in 20 mL toluene. The mixture was refluxed for 2 h and upon cooling, the reaction mixture was filtered. The solvent was removed using a rotor evaporator resulting in a crude oil and upon refrigeration, a white solid formed. Recrystallization from 95% ethanol gave the desired product.

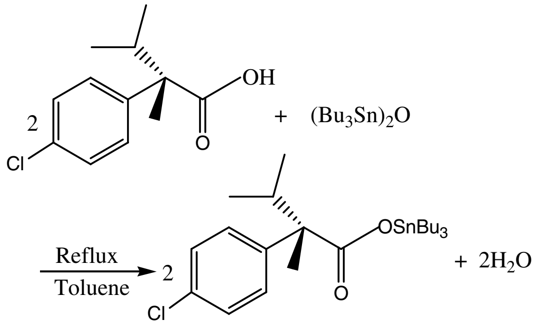
2.3.2. Preparation of complexes **2** and **3** [triethyltin- and tri-n-propyltin-2-(p-chlorophenyl)-3-methylbutyrates]



2 mmole (0.26 g) of di-*iso*butyl amine in 10 mL of benzene was added dropwise to a mixture of the appropriate triorganotin chloride [$(C_2H_5)_3SnCl$ (2 mmol; 0.413 g) for complex **2** and $(n\text{-}C_3H_7)_3SnOH$ (2 mmol; 0.480 g) for complex **3**] and 2-(*p*-chlorophenyl)-3-methylbutyric acid (2 mmol) dissolved in 30 mL of benzene under a nitrogen atmosphere. A cloudy white solution formed immediately which turned cleared upon refluxing for 1 h. The solvent was removed partially under reduced pressure until approximately 20 mL of solution was left. A white solid formed upon refrigeration overnight.

Recrystallization from a mixture of chloroform and pet ether afforded fine crystals.

*2.3.3. Preparation of complex **4** [tri-n -butyltin-2-(p-chlorophenyl)-3-methylbutyrate]*



A suspension of *bis*(tri-*n*-butyltin) oxide and 2-(*p*-chlorophenyl)-3-methylbutyric acid in a 1:2 molar ratio (1 mmol; 0.697 g and 2 mmol; 0.425 g, respectively) was suspended in 50 mL of toluene in a 100 mL round-bottom flask fitted with a Dean-Stark moisture trap. The reaction mixture was refluxed for 4 h. The solution was then filtered off and the clear filtrate was concentrated to dryness using a rotary evaporator to give a white solid. Fine crystals of complex **4** were obtained by recrystallizing the crude product in 95% ethanol.

The melting points and the elemental analyses for the complexes are given in Table 1.

2.4. X-ray crystallography

Crystal structure data were collected using a Bruker SMART Apex II X-ray diffractometer with an Oxford Cryosystream low temperature device using graphite-monochromated Cu Kα radiation. The data were corrected for Lorentz and polarization effects. The structure was solved by the direct method (SHELXS-97; [13]) and refined by the full-matrix least squares method on all F^2 data (SHELXL-97 [13]). Non-hydrogen atoms were refined with anisotropic thermal parameter and the hydrogen atoms included from the geometry of the molecules were refined isotropically.

Table 1
Melting points and elemental analysis of triorganotin 2-(*p*-chlorophenyl)-3-methylbutyrates ($R_3SnO_2CCH(CH(CH_3)_2)C_6H_4Cl$-4)

Complex	R	MP (°C)	Elemental analysis found (Calc.)		
			%C	%H	%Sn
1	Me	162–164	44.79(45.02)	5.64(5.51)	31.61(31.18)
2	Et	97–99	49.26(48.90)	6.23(6.52)	28.12(28.43)
3	*n*-Pr	82–84	52.38(52.26)	7.56(7.24)	26.00(25.82)
4	*n*-Bu	78–80	55.06(55.33)	7.84(7.93)	23.66(23.76)
5	Ph	88–90	62.01(61.91)	4.73(4.84)	21.22(21.33)
6	Cy	81–83	60.07(60.23)	7.82(7.95)	20.47(20.96)

2.5. Toxicity studies

The mosquito larvae [*Anolphes stephensi* (*An. stephensi*), *Aedes aegypti* (*Ae. aegypti*) and *Culex pipiens quinquefasciatus* (*Cx. p. quinquefasciatus*)] were obtained from the Laboratory of Malaria and Vector Research of the National Institutes of Health. The protocols for the larvicidal studies have been previously reported [8].

3. Results and discussion

3.1. Infrared spectra

Absence of the broad band due to the OH absorption (3200–2800 cm^{-1}) in the infrared spectra of the compounds confirms the deprotonation of the acid group. The mode of coordination of the carboxylate group to metals including tin has been deduced using the differences of the asymmetric and symmetric OCO vibrations [$\Delta v = v_{asy}(OCO) - v_{as}(OCO)$]. If the Δv difference is smaller than 250 cm^{-1}, then the carboxylate moiety is considered to act as bidentate ligand [14,15] forming a five-coordinated complex. Values less than 150 cm^{-1} have been assigned to chelated structures [14] while differences between 150 cm^{-1} and 250 cm^{-1} have been assigned as bridged structures [14]. On the other hand, differences greater than 250 cm^{-1} would indicate a monodentate behavior for the ligand [14,16] and result in a four-coordinated compound. As can been seen in Table 2, the Δv values for complexes **1**–**5**, in the solid state, were observed to be between 146 and 204 cm^{-1} indicating a bidentate bridged coordination mode for the carboxylate groups. However, the Δv value for the tricyclohexyltin derivative (complex **6**) was 281 cm^{-1}. This would indicate the carboxylate group for this compound acts as a monodentate ligand. Based on the infrared data, all the complexes are pentacoordinated with a bridged carboxylate ligand with the exception of the tricyclohexyl derivative which is four coordinated and monodentate.

3.2. Mössbauer spectra

The ^{119m}Sn Mössbauer parameters [isomer shift (δ) and quadruple splitting (Δ)] of the triorganotin 2-(*p*-chlorophenyl)-3-methylbutyrate are also listed in Table 2. The ratio of the quadrupole splitting to isomer shift values ($\rho = \Delta/\delta$) has been used to determine the coordination number of the central tin atom [17]. Tin compounds which are four coordinated have ρ values smaller than 1.8 while ρ values larger than 2.1 are indicative of compounds which are greater than four coordinated [17]. As can be seen in Table 2, the ρ values for complexes **1**–**5** ranged from 2.44 to 2.64, indicating a coordination number greater than four for these complexes. On the other hand, the ρ value for complex 6 [tricyclohexyl derivative] is 1.84, indicative of a four-coordinated structure.

Table 2
Selected infrared (cm^{-1}) and ^{119}Sn Mössbauer data for triorganotin 2-(*p*-chlorophenyl)-3-methylbutyrates ($R_3SnO_2CCH(CH(CH_3)_2)C_6H_4Cl$-4)

Complex	R	γ (OCO)as	γ (OCO)s	$\Delta\nu$	δ (mm s^{-1})	Δ (mm s^{-1})	$\rho = \Delta/\delta$
1	Me	1567	1385	182	1.398	3.702	2.64
2	Et	1581	1390	191	1.510	3.691	2.44
3	*n*-Pr	1580	1376	204	1.446	3.587	2.48
4	*n*-Bu	1561	1387	174	1.513	3.733	2.47
5	Ph	1552	1376	146	1.288	3.371	2.62
6	Cy	1642	1361	281	1.581	2.911	1.84

Quadruple splitting values are often used to distinguish between trigonal bipyramidal and tetrahedral configurations. Values between 3.0 and 4.4 mm s^{-1} are associated with trigonal bipyramidal structures and tetrahedral structures tend to have lower values [18]. All the Δ values for complexes **1**–**5** are larger than 3.0 mm s^{-1}, while the tricyclohexyl complex is below 3.0 mm s^{-1}, supporting the assignments based on the ρ values. These results are also in agreement with the earlier structural assignments based on the infrared data that all the complexes with the exception of the tricyclohexyl complex are pentacoordinated.

3.3. Solution studies

The ^{1}H NMR parameters of the complexes recorded in $CDCl_3$ are given in Table 3. Assignment of the proton resonances were based on their intensity, multiplicity pattern and coupling constants. The number of protons calculated from the integration values in the spectra is in agreement with those calculated for the molecule. In addition, a 1:1 tin to ligand stoichiometry was observed from the integrated intensities of the spectra and is in agreement with the analytical data for the solid samples. Two methyl signals were observed for the isopropyl group. This is in agreement with isopropyl groups that are attached to chiral carbons [19]. Absence of the carboxylic proton signal at 11.93 ppm in all the complexes indicates that the carboxylate group is involved with bonding to the tin atom.

As can be seen from Table 3, a $^2J(^1H–^{119}Sn)$ value of 58.5 Hz was observed for the methyl derivative. This would indicate that the tin atom has approximately 25% s-character. The value of the $^2J(^1H–^{119}Sn)$ coupling constants have been related to the percent s-character of tin-methyl orbitals [20]. Furthermore, a C–Sn–C bond angle of 111.3° was calculated using the Lockhart equation [21], suggesting that the methyl derivative is four-coordinated in solution. While triorganotin carboxylates are commonly pentacoordinated in the solid state they have been reported to dissociate, in solution, into tetrahedral structures [22]. Thus, it would be reasonable to assume that the other compounds would act similarly.

Table 3
^{1}H NMR chemical shifts and coupling constants of 2-(*p*-chlorophenyl)-3-methylbutyric acid and the triorganotin derivatives ($R_3SnO_2CCH(CH(CH_3)_2)C_6H_4Cl$-4)[a,b,c]

Complex	R	$ClC_6\mathbf{H}_4$–	ClC_6H_4–**CH**	$(CH_3)_2$**CH**–	**CH$_3$**	**R**
1	Me	7.25(2H, d) [8.5] 7.29(2H, d) [8.5]	3.12(1H, d) [10.5]	2.15–2.25(1H, m)	0.67(3H, d) [7.0] 1.06(3H, d) [6.0]	0.5(9H, s) {58.5/56.0}
2	Et	7.24(2H, d) [8.5] 7.30(2H, d) [8.5]	3.12(1H, d) [10.5]	2.15–2.25(1H, m)	0.67(3H, d) [7.0] 1.06(3H, d) [6.0]	
3	*n*-Pr	7.24(2H, d) [8.7] 7.29(2H, d) [8.7]	3.12(1H, d) [10.5]	2.20–2.30(1H, m)	0.68(3H, d) [6.5] 1.04(3H, d) [6.5]	0.85(9H, t) [7.5] 1.19(6H, t) [8.0] 1.55–1.65(6H, m)
4	*n*-Bu	7.24(2H, d) [8.5] 7.29(2H, d) [8.5]	3.12(1H, d) [11.0]	2.25–2.35(1H, m)	0.68(3H, d) [6.5] 1.04(3H, d) [6.0]	0.92(9H, t) [7.3] 1.20(6H, t) [8.5] 1.25–1.35(6H, m) 1.45–1.55(6H, m)
5	Ph	7.20(2H, d) [8.5] 7.26(2H, d) [8.5]	3.27(1H, d) [10.5]	2.25–2.40(1H, m)	0.67(3H, d) [7.0] 0.92(3H, d) [6.5]	7.60–7.65(6H, m) 7.35–7.45 (9H, m)
6	Cy	7.23(2H, d) [8.5] 7.30(2H, d) [8.5]	3.14(1H, d) [11.0]	2.25–2.40(1H, m)	0.70(3H, d) [6.5] 1.06(3H, d) [6.5]	1.25–1.95(33H,m)
Acid		7.18(2H, d) [9.0] 7.33(2H, d) [9.0]	3.06(1H, d) [10.5]	2.20–2.30(1H, m)	0.67(3H, d) [7.0] 1.00(3H, d) [6.0]	11.92(1H, br) COOH

[a] s, singlet; d, doublet; t, triplet; m, multiplet; br, broad.
[b] Numbers in [ ] are the ^2J(HH) coupling constants in Hz.
[c] Numbers in {} are the $^2J(^1H–^{119}Sn)/^2J(^1H–^{117}Sn)$ coupling constants in Hz.

Listed in Table 4 are the ^{13}C NMR spectral data. In organotin compounds, the $^{1}J(^{119}Sn–^{13}C)$ coupling constants have been used to infer the coordination number of the tin atom [1,23]. As can be seen in Table 4, the $^{1}J(^{119}Sn–^{13}C)$ coupling constants range from 338 Hz to 397 Hz for the alkyl compounds and 642 Hz for the triphenyltin derivative. These values are consistent with values for similar compounds [22,24–26]. In addition, a C–Sn–C bond angle of 111.6° was calculated using the $^{1}J(^{119}Sn–^{13}C)$ coupling constant of 397 Hz for the methyl derivative [21] supporting the previous assignment of a four-coordinated geometry for this compound.

^{119}Sn chemical shifts have also been correlated with the coordination number of the tin atom. The ^{119}Sn chemical shifts range for four-coordinated alkyltin compounds is approximately between +200 ppm and −60 ppm [27]. As evident from Table 4, all the ^{119}Sn chemical shifts for the compounds [17.5–137.3 ppm] except the phenyl derivative are within the range for four-coordinated structures. The ^{119}Sn chemical shifts of the triphenyltin complex in $CDCl_3$ solution exhibited a single sharp resonance at −106.9 ppm, similar to those reported values for other four-coordinated triphenyltin carboxylates [22,25,28]. Thus, the ^{119}Sn NMR results also indicate that the complexes are four-coordinated in solution. In conclusion, the multinuclear NMR results indicate that the complexes are four-coordinated in solution.

3.4. Crystal structure of tri-n-butyltin 2-(p -chlorophenyl)-3-methylbutyrate

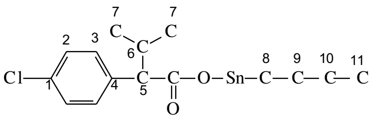
Listed in Table 5 are the crystal data and structure refinement for tri-*n*-butyltin 2-(*p*-chlorophenyl)-3-methylbutyrate. Selected bond lengths and angles are given in Table 6. Shown in Fig. 1 is the crystal structure of the complex. The central pairs of carbon atoms in two of the butyl groups exhibited disorder and were modeled and refined using partial occupancies. The analyses indicate that the complex exists as a polymer in the solid state. The geometry around the tin atom is essentially trigonal bipyramid with three butyl groups occupying the equatorial positions. One axial position is occupied by one of the ester oxygen atoms, O(1), forming a Sn–O bond length of 2.4127(19) Å while the other site is occupied by an oxygen atom from a second carboxylate molecule with a Sn–O bond length of 2.2071(19) Å. The sum of the equatorial angles was found to be 359.4° while the O(1)–Sn–O(2) angle was 173.37°(7). These values are close to the ideal values for a trigonal bipyramidal (tbp) structure of 360° and 180°, respectively. Since the carboxylate C–O bond lengths are not equal [C–O1 1.247(3), C–O2 1.279(3)], it would indicate that the C–O1 bond has some double bond character.

Crystal structures for three of the other analogs of this series of compounds have been reported [29,30]. The crystal structures for the trimethyl- [29] and tri-*n*-propyl- [30]

Table 4
^{13}C NMR chemical shifts of 2-(*p*-chlorophenyl)-3-methylbutyric acid and ^{13}C chemical shifts, coupling constants and ^{119} Sn NMR chemical shifts for the triorganotin derivative ($R_3SnO_2CCH(CH(CH_3)_2)C_6H_4Cl$-4)[a,b,c]

Complex	R	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C=O	^{119}Sn NMR
1	Me	132.52	129.84	128.34	138.18	60.23	32.47	21.58 20.15	−2.46 [397/379]				178.86	137.3
2	Et	132.38	129.86	128.24	138.64	60.86	32.13	21.67 20.18	7.95 [374/348]	9.77 {26.9}			178.98	110.2
3	*n*-Pr	132.42	129.85	128.23	138.41	60.61	32.07	21.63 20.16	19.36 [356/340]	19.15 {20.6}	18.44 [64.0/61.4]		178.66	112.7
4	*n*-Bu	132.52	129.84	128.34	138.47	60.64	32.09	21.63 20.17	16.48 [d]	27.76 {21.0}	26.96	13.61	178.69	112.9
5	Ph	132.68	129.93	128.37	137.52	59.57	32.40	21.44 20.12	138.09 [642/614]	130.08 {13.5}	128.84 [64.0/61.4]	136.71	179.87	−106.9
6	Cy	132.44	129.86	128.25	138.69	60.99	31.63	21.74 20.18	33.79 [338/323]	30.97	28.86 [64.0/61.4]	26.87	178.50	17.5
Acid		133.27	129.88	128.66	136.45	59.69	31.59	21.32 20.02					179.73	

[a] Numbering scheme for carbons in the complexes:



[b] Numbers in [] are the $^{n}J(^{119}Sn- -^{13}C)/^{n}J(^{117}Sn–^{13}C)$ coupling constants in Hz.

[c] Numbers in { } are the averages of $^{n}J(^{119}Sn–^{13}C)$ and $^{n}J(^{117}Sn–^{13}C)$ coupling constants in Hz.

[d] $^{n}J(^{119}Sn–^{13}C)/^{n}J\ (^{117}Sn–^{13}C)$ is not observed due to overlapping.

Table 5
Crystal data and structure refinement for tri-*n*-butyltin 2-(*p*-chlorophenyl)-3-methylbutyrate

Empirical formula	$C_{23}H_{39}ClO_2Sn$
Formula weight	501.68
Crystal size (mm)	0.48 × 0.38 × 0.21
Temperature (K)	200(2)
Crystal system	Monoclinic
Space group	$P2(1)/n$
a (Å)	14.0212(5)
b (Å)	10.1982(4)
c (Å)	18.0514(6)
β (°)	101.6180(10)
V (Å^3)	2528.30(16)
Z	4
D_x (g cm^{-3})	1.318
F(000)	1040
Transmission factors (max, min)	0.2508, 0.0971
Absorption coefficient (mm^{-1})	9.104
Reflections collected	27875
Independent reflection (R_{int})	4527(0.0330)
Data/restraints/parameters	4527/4/289
Final R indices [$I > 2\sigma(I)$]	0.0288
$wR(F^2)$ (all data)	0.0313
Goodness-of-fit (F^2)	1.071
Maximum, minimum $\Delta\rho$ (e/Å^{-3})	0.543, −0.402

derivatives are similar to the tri-*n*-butyl- compound being reported in this paper. All the three compounds are polymeric with a tbp configuration. On the other hand, the tricyclo- derivative was reported to be a distorted tetrahedron [29]. Thus, the crystal data is in agreement with the assignments based on the infrared and Mössbauer data.

Table 6
Selected bond lengths and bond angles for tri-*n*-butyltin 2-(*p*-chlorophenyl)-3-methylbutyrate

Sn(1)–C(16)	2.141(3)	C(16)–Sn(1)–C(12)	124.80(12)
Sn(1)–C(12)	2.148(3)	C(16)–Sn(1)–C(20)	119.29(13)
Sn(1)–C(20)	2.149(3)	C(12)–Sn(1)–C(20)	115.35(13)
Sn(1)–O(2)#1	2.2071(19)	C(16)–Sn(1)–O(2)#1	93.98(11)
Sn(1)–O(1)	2.4127(19)	C(12)–Sn(1)–O(2)#1	94.49(10)
Cl(1)–C(9)	1.752(3)	C(20)–Sn(1)–O(2)#1	88.71(12)
O(1)–C(1)	1.247(3)	C(16)–Sn(1)–O(1)	86.82(10)
O(2)–C(1)	1.279(3)	C(12)–Sn(1)–O(1)	90.44(9)
O(2)–Sn(1)#2	2.2071(19)	C(20)–Sn(1)–O(1)	85.16(11)
C(1)–C(2)	1.534(4)	O(2)#1–Sn(1)–O(1)	173.37(7)
C(2)–C(6)	1.527(4)	C(1)–O(1)–Sn(1)	146.11(18)
C(2)–C(3)	1.547(4)	C(1)–O(2)–Sn(1)#2	120.72(17)
C(3)–C(5)	1.521(5)	O(1)–C(1)–O(2)	123.0(2)
C(3)–C(4)	1.526(5)	O(1)–C(1)–C(2)	121.2(2)
C(6)–C(7)	1.381(4)	O(2)–C(1)–C(2)	115.8(2)
C(6)–C(11)	1.387(4)	C(6)–C(2)–C(1)	109.8(2)
C(7)–C(8)	1.389(4)	C(6)–C(2)–C(3)	112.4(2)
C(8)–C(9)	1.365(5)	C(1)–C(2)–C(3)	111.3(2)
C(9)–C(10)	1.380(5)	C(5)–C(3)–C(4)	110.3(3)
C(10)–C(11)	1.386(5)	C(5)–C(3)–C(2)	111.5(3)
C(12)–C(13)	1.522(4)	C(4)–C(3)–C(2)	111.2(3)
C(13)–C(14)	1.520(4)	C(7)–C(6)–C(11)	118.6(3)
C(14)–C(15)	1.521(5)	C(7)–C(6)–C(2)	121.6(3)
		C(11)–C(6)–C(2)	119.8(3)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1/2$, $y+1/2$, $-z+1/2$ #2 $-x+1/2$, $y-1/2$, $-z+1/2$.

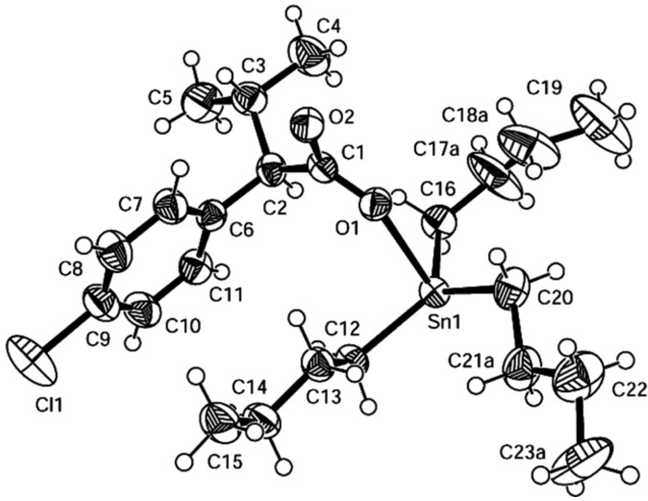


Fig. 1. ORTEP drawings of tri-*n*-butyltin 2-(*p*-chlorophenyl)-3-methylbutyrate with the atom labels. Displacement ellipsoids are shown at 50% level.

3.5. Toxicity

The complexes were screened against the second larval stage of three species of mosquitos (*Anolphes stephensi*, *Aedes aegypti*, and *Culex pipiens quinquefasciatus*). The individual toxicity as well as the averages in parts per million along with their standard deviations, are listed in Table 7. The data indicate that there does not appear to be any significant differences in toxicity of the compounds towards the different species of mosquito larvae based on their averaged values. This was confirmed by an ANOVA analysis single factor method. The observed screening data indicate that the toxicities for this series of compounds are better or similar to other triorganotins tested [8,9]. Furthermore, no common order of activity based on the organic group attached to the tin atom was observed. These two observations would suggest that the toxicity of the triorganotin compounds towards these mosquito larvae is dependent on both the compound and the species of mosquito larvae. This conclusion has been previously reported [9]. While no definitive order of toxicity was observed for this series of triorganotins, their high activities toward various mosquito larvae would make this series of compounds

Table 7
LC_{50} values in ppm of triorganotin-2-(*p*-chlorophenyl)-3-methylbutyrates against the 2nd instar stage of the *Anopheles stephensi*, *Aedes aegypti* and *Culex pipiens quinquefasciatus* mosquito larvae

R	*An. stephensi*	*Ae. aegypti*	*Cx. P. quinquefasciatus*
Me	1.10 ± 0.02	3.13 ± 0.05	0.72 ± 0.07
Et	5.87 ± 0.02	1.15 ± 0.04	3.21 ± 0.08
n-Pr	1.99 ± 0.02	0.78 ± 0.04	0.68 ± 0.07
n-Bu	0.31 ± 0.01	0.32 ± 0.01	0.39 ± 0.03
Ph	0.33 ± 0.01	1.02 ± 0.03	0.43 ± 0.06
Cy	0.16 ± 0.01	0.42 ± 0.01	0.57 ± 0.06
Ave	1.63 ± 0.02	1.14 ± 0.03	1.00 ± 0.06

good candidates as a possible larvicide against these three species of mosquito larvae.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.11.030.

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