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Synthesis and characterization of tributyltin(IV) complexes of 2-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid and 4-[((*E*)-1-{2-hydroxy-5-[(*E*)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}methylidene)amino]aryls – crystal structures of polymeric $(Bu_3Sn[O_2CC_6H_4\{N{=}N(C_6H_3\text{-}4\text{-}OH\text{-}5\text{-}CHO)\}\text{-}o])_n$ and $(Bu_3Sn[O_2CC_6H_4\{N{=}N(C_6H_3\text{-}4\text{-}OH(C(H){=}NC_6H_4Cl\text{-}4))\}\text{-}o])_n$ – toxicity studies on the second instar of *Aedes aegypti* mosquito larvae

Tushar S. Basu Baul [a,*], Keisham Surjit Singh [a], Xueqing Song [b], Alejandra Zapata [b], George Eng [b], Antonin Lycka [c], Anthony Linden [d,**]

[a] *Department of Chemistry, North-Eastern Hill University, NEHU Permanent Campus, Umshing, Shillong 793 022, India*
[b] *Department of Chemistry and Physics, University of the District of Columbia, 4200 Connecticut Avenue, NW Washington, DC 20008, USA*
[c] *Research Institute for Organic Syntheses, Rybitvi 296, CZ-532 18 Pardubice 20, Czech Republic*
[d] *Institute of Organic Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland*

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Abstract

The tri-*n*-butyltin(IV) complexes of 2-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid and 4-[((*E*)-1-{2-hydroxy-5-[(*E*)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}methylidene)amino]aryls (aryls = 4-CH_3, 4-Br, 4-Cl, 4-OCH_3) have been synthesized and characterized by ^1H, ^{13}C, ^{119}Sn NMR, IR and ^{119m}Sn Mössbauer spectroscopic techniques in combination with elemental analysis. The crystal structures of two compounds, $(Bu_3Sn[O_2CC_6H_4\{N{=}N(C_6H_3\text{-}4\text{-}OH\text{-}5\text{-}CHO)\}\text{-}o])_n$ and $(Bu_3Sn[O_2CC_6H_4\{N{=}N(C_6H_3\text{-}4\text{-}OH(C(H){=}NC_6H_4Cl\text{-}4))\}\text{-}o])_n$, are reported.The crystallographic and ^{119}Sn Mössbauer data both indicate that the tributyltin complexes form single-stranded polymeric structures in which the carboxylate O atoms of each aryl ligand bridge two Sn atoms. The Sn atoms have a slighly distorted trigonal bipyramidal coordination geometry with equatorial butyl groups and carboxylate O atoms occupying axial positions. The ^{119}Sn NMR spectroscopic data and the $^1J(^{13}C\text{–}^{119/117}Sn)$ coupling constant indicate a tetrahedral coordination geometry in non-coordinating solvents. The results of a toxicity study of a tributyltin compound on the second larval instar of *Aedes aegypti* mosquito larvae are reported.

Keywords: Tributyltin; Carboxylates; 2-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid; 4-[((*E*)-1-{2-hydroxy-5-[(*E*)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}methylidene)amino]aryls; NMR; Mössbauer; Crystal structure; Toxicity study

1. Introduction

Salicylaldehyde and their metal derivatives are well established [1–3]. More useful organic reagents having the properties of salicylaldehyde together with other

* Corresponding authors. Tel.: +91 364 272 2626; fax: +91 364 2550486/2721000.
** Tel.: +41 44 635 4228; fax: +41 44 635 6812.
E-mail addresses: basubaul@nehu.ac.in, basubaul@hotmail.com (T.S. Basu Baul), alinden@oci.unizh.ch (A. Linden).

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desired features, e.g., having an intense light absorption in the visible region for colorimetric applications, have also been reported. These organic reagents are commonly known as 5-(arylazo)salicylaldehyde (AAS) and were used by several workers in order to characterize U(VI) [4], Pd(II) [4], Co(II) [5], Cu(II) [6,7], Ni(II) [8], Mn(II) [9], Sn(II) [10] and Sn(IV) [11] complexes in both solid and solution states. A few transition metal complexes also show semi conducting properties in the temperature range 310–340 K [9]. Later, AAS were condensed with mono aromatic amine which resulted in 5-phenylazosalicylidene aniline (PASA) Schiff base and its metal complexes, viz., Fe(III), Co(II), Ni(II) and Cu(II) were prepared and characterized [12]. Recently, a few Cu(II) complexes of some Schiff bases obtained by condensation of AAS with di- and tri-amine have also been reported and in one case the structure of the complex was determined using single crystal X-ray crystallography [13]. Although PASA type ligands have been known for a long time, the extant literature contains no report of the isolation and characterization of metal or organometallic complexes of 4-[((*E*)-1-{2-hydroxy-5-[(*E*)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}-methylidene)amino]aryls. These ligands contain a carboxylate group in the *ortho*-position of the diazo-forming aryl moiety of the ASA unit, which provides an opportunity for synthesising a wide variety of complexes of the hetero-functional ligand.

In addition, tributyltin in the form of halides, oxides and acetates, displays a large array of biocidal properties and is used extensively in wood preservatives and in marine anti-fouling paints [14], although there has been considerable environmental concern about their latter use [15]. However, the tributyltin compounds have not been shown to be neurotoxins, mutagens, teratogens, or carcinogens in humans [16]. Recently, some tributyltin 5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoates have shown moderate activity towards the second larval instar stage of the *Aedes aegypti* mosquito [17]. In addition to their commercial applications, triorganotin carboxylates present an interesting variety of structural possibilities [18,19]. In line with these developments and as part of a wider study designed to ascertain

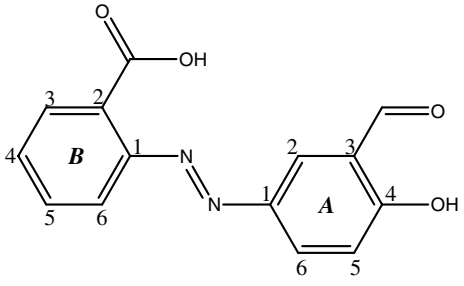


Fig. 1. Generic structure of the ligand, L^1HH'.

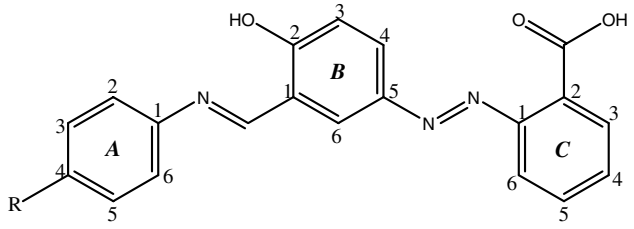


Fig. 2. Generic structure of the ligand $L^{2-5}HH'$. *Abbreviations.* L^2HH': R = 4-CH_3; L^3HH': 4-Br, L^4HH': 4-Cl, L^5HH': 4-OCH_3, where H and H′ represent hydroxyl and carboxyl protons, respectively.

the reasons for the structural variation found in these systems, we now describe some tri-*n*-butyltin(IV) complexes derived from (i) 2-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid (L^1HH') and, (ii) 4-[((*E*)-1-{2-hydroxy-5-[(*E*)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}methylidene)amino]aryls ($L^{2-5}HH'$). The generic structures of the ligand framework are shown in Figs. 1 and 2.

2. Experimental

2.1. Materials

$(Bu_3Sn)_2O$ (Merck), salicylaldehyde (Lancaster) and the substituted anilines (reagent grade) were used without further purification. The solvents used in the reactions were of AR grade and dried using standard procedures. Toluene was distilled from sodium benzophenone ketyl.

2.2. Physical measurements

Carbon, hydrogen and nitrogen analyses were performed with a Perkin–Elmer 2400 series II instrument. IR spectra in the range 4000–400 cm^{-1} were obtained on a BOMEM DA-8 FT-IR spectrophotometer with samples investigated as KBr discs. The ^1H and ^{13}C NMR spectra of the ligands were acquired on a Bruker Avance 500 spectrometer operating at 500.13 and 125.76 MHz, respectively. For the organotin compounds, the ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Bruker AMX 400 spectrometer and measured at 400.13, 100.62 and 149.18 MHz, respectively. The ^1H, ^{13}C and ^{119}Sn chemical shifts were referred to Me_4Si set at 0.00 ppm, $CDCl_3$ set at 77.0 ppm and Me_4Sn set at 0.00 ppm, respectively. The Mössbauer spectra of the complexes in the solid state were recorded using a Model MS-900 (Ranger Scientific Co., Burleson, TX) spectrometer in the acceleration mode with a moving source geometry. A 5 mCi $Ca^{119m}SnO_3$ source was used, and counts of 30 000 or more were accumulated for each spectrum. The spectra were measured at 80 K using a

liquid-nitrogen cryostat (CRYO Industries of America, Inc., Salem, NH). The velocity was calibrated at ambient temperature using a composition of $BaSnO_3$ and tin foil (splitting 2.52 mm s^{-1}). The resultant spectra were analyzed using the Web Research software package (Web Research Co., Minneapolis, MN).

2.3. Synthesis of ligands

2.3.1. Preparation of 2-[(E)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid (L^1HH')

The ligand, L^1HH' was prepared by reacting 2-carboxybenzenediazonium chloride with salicylaldehyde in alkaline solution under cold conditions by the method described in our earlier report [20]. The product was purified by recrystallization from toluene; m.p.: 177–179 °C. Anal. Found. 62.20; H, 3.65; N, 10.35. Calc. for $C_{14}H_{10}N_2O_4$: C, 62.22; H, 3.70; N, 10.37%.

2.3.2. Preparation of 4-[((E)-1-{2-hydroxy-5-[(E)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}methylidene)amino]aryls ($L^{2-5}HH'$)

A typical procedure is described below.

2.3.2.1. Preparation of 4-[((E)-1-{2-hydroxy-5-[(E)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}methylidene)amino]chlorobenzene (L^4HH').

An equimolar amount of *p*-chloroaniline (0.42 g, 3.36 mmol) in hot absolute ethanol solution (15 ml) was added to hot toluene (30 ml) containing L^1HH' (0.91 g, 3.36 mmol) and the reaction mixture was refluxed for 5 h. The water formed during the reaction was removed using a Dean-Stark apparatus. The reaction mixture was concentrated to half of the initial solvent volume on a hot plate, cooled to room temperature and was kept overnight in a refrigerator whereupon a dark brown solid precipitated. The precipitate was filtered, washed with absolute ethanol (3×5 ml) followed by diethyl ether (2×5 ml), and then dried in air. The crude product was washed with hexane to remove any tarry materials and recrystallized from ethanol to yield pure orange crystalline L^4HH' (0.78 g, 56%); m.p.: 225–226 °C. Anal. Found. 63.20; H, 3.65; N, 11.13. Calc. for $C_{20}H_{14}N_3O_3Cl$: C, 63.24; H, 3.71; N, 11.06%. IR (cm^{-1}): 1725 $\nu(OCO)_{asym}$. ^1H NMR (DMSO-d_6/500.13 MHz); δ_H: 7.21 [d, 1H, (B) H3], 7.53 [part of AA′BB′ system, 2H, (A) H3 and H5], 7.57 [part of AA′BB′ system, 2H, (A) H2 and H6], 7.60 [m, 1H, (C) H6], 7.61 [m, 1H, (C) H4], 7.69 [m, 1H, (C) H5], 7.83 [m, 1H, (C) H3], 7.99 [dd, 1H, (B) H4], 8.31 [d, 1H, (B) H6], 9.16 [s, 1H, C(H)=N], 12.97 [br s, 1H, CO_2H], 13.59 [br s, 1H, OH] ppm. ^{13}C NMR (DMSO-d_6/125.76 MHz); δ_C: 118.1 [(B) C3], 118.4 [(C) C6], 119.4 [(B) C1], 123.4 [(A) C2 and C6], 126.9 [(B) C4], 128.7 [(B) C6], 129.3 [(C) C3], 129.5 [(A) C3 and C5], 129.9 [(C) C4], 130.2 [(C) C2], 131.6 [(A) C4], 131.7 [(C) C5], 145.1 [(B) C5], 146.6 [(A) C1], 150.9 [(C) C1], 163.1 [C(H)=N], 163.8 [(B) C2], 168.5 [CO_2H)] ppm.

The other 4-[((E)-1-{2-hydroxy-5-[(E)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}methylidene)amino]aryls, viz., L^2HH', L^3HH' and L^5HH' were prepared analogously by reacting L^1HH' with the appropriate anilines. The characterization and spectroscopic data are presented below.

2.3.2.2. Preparation of 4-[((E)-1-{2-hydroxy-5-[(E)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}methylidene)amino]methylbenzene (L^2HH').

Recrystallized from absolute ethanol to give reddish brown precipitate in 70% yield; m.p.: 199–201 °C. Anal. Found. 69.95; H, 4.65; N, 11.58. Calc. for $C_{21}H_{17}N_3O_3$: C, 70.20; H, 4.76; N, 11.69%. IR (cm^{-1}): 1725 $\nu(OCO)_{asym}$. ^1H NMR (DMSO-d_6/500.13 MHz); δ_H: 2.38 [s, 3H, CH_3], 7.18 [d, 1H, (B) H3], 7.32 [part of AA′BB′ system, 2H, (A) H3 and H5], 7.43 [part of AA′BB′ system, 2H, (A) H2 and H6], 7.60 [m, 1H, (C) H4], 7.61 [m, 1H, (C) H6], 7.69 [m, 1H, (C) H5], 7.84 [m, 1H, (C) H3], 7.98 [dd, 1H, (B) H4], 8.29 [d, 1H, (B) H6], 9.16 [s, 1H, C(H)=N], 12.91 [br s, 1H, CO_2H], 14.16 [br s, 1H, OH] ppm. ^{13}C NMR (DMSO-d_6/125.76 MHz); δ_C: 20.7 [CH_3], 118.3 [(B) C3], 118.33 [(C) C6], 119.2 [(B) C1], 121.4 [(A) C2 and C6], 126.5 [(B) C4], 129.2[(B) C6], 129.3 [(C) C3], 129.9 [(C) C4], 130.1 [(A) C3 and C5], 130.2 [(C) C2], 131.7 [(C) C5], 137.1 [(A) C4], 144.5 [(A) C1], 144.9 [(B) C5], 150.9 [(C) C1], 161.7 [C(H)=N], 164.5 [(B) C2], 168.5 [CO_2H] ppm.

2.3.2.3. Preparation of 4-[((E)-1-{2-hydroxy-5-[(E)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}methylidene)amino]bromobenzene (L^3HH').

Recrystallized from absolute ethanol to give an orange precipitate in 49% yield; m.p.: 213–214 °C. Anal. Found. 56.50; H, 3.30; N, 10.01. Calc. for $C_{20}H_{14}N_3O_3$ Br: C, 56.60; H, 3.32; N, 9.90%. IR (cm^{-1}): 1723 $\nu(OCO)_{asym}$. ^1H NMR (DMSO-d_6/500.13 MHz); δ_H: 7.21 [d, 1H, (B) H3], 7.48 [part of AA′MM′ system, 2H, (A) H2 and H6], 7.60 [m, 1H, (C) H6], 7.61 [m, 1H, (C) H4], 7.70 [m, 1H, (C) H5], 7.71 [part of AA′MM′ system, 2H, (A) H3 and H5], 7.84 [m, 1H, (C) H3], 7.99 [dd, 1H, (B) H4], 8.31 [d, 1H, (B) H6], 9.16 [s, 1H, C(H)=N], 12.99 [br s, 1H, CO_2H], 13.57 [br s, 1H, OH] ppm. ^{13}C NMR (DMSO-d_6/125.76 MHz); δ_C: 118.2 [(B) C3], 118.4 [(C) C6], 119.4 [(B) C1], 120.4 [(A) C4], 123.7 [(A) C2 and C6], 126.9 [(B) C4], 128.8 [(B) C6], 129.3 [(C) C3], 129.9 [(C) C4], 130.2 [(C) C2], 131.7 [(C) C5], 132.5 [(A) C3 and C5], 145.1 [(B) C5], 147.0 [(A) C1], 150.9 [(C) C1], 163.1 [C(H)=N], 163.8 [(B) C2], 168.5 [CO_2H] ppm.

2.3.2.4. Preparation of 4-[((E)-1-{2-hydroxy-5-[(E)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}methylidene)amino]methoxybenzene (L^5HH').

Recrystallized from absolute ethanol to give a dark red precipitate in 54%

yield; m.p.: 174–176 °C. Anal. Found. 67.25; H, 4.60; N, 11.18. Calc. for $C_{21}H_{17}N_3O_4$: C, 67.21; H, 4.56; N, 11.19%. IR (cm^{-1}): 1723 $\nu(OCO)_{asym}$. ^1H NMR (DMSO-d_6/500.13 MHz); δ_H: 3.84 [s, 3H, OCH_3], 7.08 [part of AA′MM′ system, 2H, (A) H3 and H5], 7.17 [d, 1H, (B) H3], 7.53 [part of AA′MM′ system, 2H, (A) H2 and H6], 7.60 [m, 1H, (C) H4], 7.61 [m, 1H, (C) H6], 7.70 [m, 1H, (C) H5], 7.83 [m, 1H, (C) H3], 7.96 [dd, 1H, (B) H4], 8.26 [d, 1H, (B) H6], 9.16 [s, 1H, C(H)=N], 12.90 [br s, 1H, CO_2H], 14.24 [br s, 1H, OH] ppm. ^{13}C NMR (DMSO-d_6/125.76 MHz); δ_C: 55.5 [OCH_3], 114.8 [(A) C3 and C5], 118.2 [(B) C3], 118.3 [(C) C6], 119.3 [(B) C1], 122.9 [(A) C2 and C6], 126.3 [(B) C4], 128.9 [(B) C6], 129.3 [(C) C3], 129.8 [(C) C4], 130.2 [(C) C2], 131.7 [(C) C5], 139.8 [(A) C1], 144.9 [(B) C5], 150.9 [(C) C1], 158.9 [(A) C4], 160.4 [C(H)=N], 164.3 [(B) C2], 168.5 [CO_2H] ppm.

2.4. Synthesis of the tributyltin complexes

Two typical methods are described below.

2.4.1. Synthesis of Bu_3SnL^1H (1)

The compound was synthesized by mixing L^1HH' (0.90 g, 3.33 mmol) and $(Bu_3Sn)_2O$ (1.0 g, 1.67 mmol) in 50 ml of anhydrous toluene in a 100 ml flask equipped with a Dean-Stark moisture trap and a water cooled condensor. The reaction mixture was refluxed for 7 h. The solvent was then distilled off to dryness and the residue was dried in vacuo. The solid mass was washed with hexane (2 × 5 ml) under cold conditions and was recrystallized from hexane to yield orange crystals of the desired product. Yield (0.74 g, 79%); m.p.: 63–64 °C. Anal. Found: C, 55.76; H, 6.39; N, 5.20. Calc. for $C_{26}H_{36}N_2O_4Sn$: C, 55.84; H, 6.48; N, 5.00%. IR (cm^{-1}): 1660 $\nu(OCO)_{asym}$.

2.4.2. Synthesis of Bu_3SnL^4H (4)

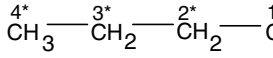
Bu_3SnL^1H (0.79 g, 1.41 mmol) in absolute ethanol (30 ml) was added dropwise to a hot stirred ethanolic solution (20 ml) containing *p*-chloroaniline (0.18 g, 1.41 mmol). The reaction mixture was then refluxed using a Dean-Stark moisture trap and a water cooled condenser for 3 h and filtered while hot. The filtrate was collected and the volatiles were removed using a rotary evaporator. The residue was dried in vacuo, washed with hexane (2 × 1 ml), extracted into chloroform and filtered. The crude product was obtained after evaporation and this was then recrystallized from a chloroform-hexane mixture (1:1, v/v) to yield orange crystals of the desired product. Yield (0.83 g, 82.4%); m.p.: 88–90 °C. Anal. Found: C, 57.40; H, 6.19; N, 6.20. Calc. for $C_{32}H_{40}ClN_3O_3Sn$: C, 57.43; H, 6.02; N, 6.27%. IR (cm^{-1}): 1616 $\nu(OCO)_{asym}$.

The other tributyltin complexes of the ligands, viz., L^2HH', L^3HH' and L^5HH' were prepared by reacting

Table 1
^1H NMR data (δ, ppm) for the tributyltin complexes in $CDCl_3$

Ring[a] /Other/Sn–Bu[b] protons	Proton number	Compound				
		1	**2**	**3**	**4**	**5**
A	2	8.20	7.24	7.19	7.25	7.32
	3	–	7.24	7.56	7.25	6.97
	5	7.10	7.24	7.56	7.25	6.97
	6	8.14	7.24	7.19	7.25	7.32
B	3	7.84	7.15	7.12	7.12	7.11
	4	7.49	7.99	8.01	8.01	7.98
	5	7.49	–	–	–	–
	6	7.49	8.04	8.05	8.04	8.02
C	3	–	7.82	7.82	7.82	7.82
	4	–	7.53	7.52	7.42	7.51
	5	–	7.44	7.44	7.42	7.43
	6	–	7.53	7.52	7.51	7.51
Other	C(H)=O/C(H)=N	10.02	8.73	8.69	8.71	8.71
	OH	11.35	14.0	13.6	13.6	14.0
	CH_3/OCH_3	–	2.40	–	–	3.85
Sn–Bu	1*	1.68	1.62	1.61	1.61	1.61
	2*	1.34	1.30	1.31	1.31	1.32
	3*	1.34	1.30	1.31	1.31	1.32
	4*	0.88	0.87	0.87	0.86	0.86

[a] Refer to Fig. 1 (for compound **1**) and Fig. 2 (for compounds **2**–**5**) for the numbering scheme of the ligand skeleton (Ring A, B and/or C).
[b] Numbering scheme for Sn–Bu skeleton as shown below:



Bu_3SnL^1H with the appropriate anilines by following analogous procedures. The characterization data of the complexes are given below while the spectroscopic data are presented in Tables 1–3.

*2.4.3. Bu_3SnL^2H (**2**)*

Yield: 80%; m.p.: 89–91 °C. Anal. Found: C, 61.20; H, 6.75; N, 6.53. Calc. for $C_{33}H_{43}N_3O_3Sn$: C, 61.10; H, 6.68; N, 6.47%. IR (cm^{-1}): 1622 $\nu(OCO)_{asym}$.

*2.4.4. Bu_3SnL^3H (**3**)*

Yield: 78%; m.p.: 86–88 °C. Anal. Found: C, 53.80; H, 5.60; N, 5.98. Calc. for $C_{32}H_{40}BrN_3O_3Sn$: C, 53.86; H, 5.65; N, 5.88%. IR (cm^{-1}): 1618 $\nu(OCO)_{asym}$.

*2.4.5. Bu_3SnL^5H (**5**)*

Yield: 93%; m.p.: 84–86 °C. Anal. Found: C, 59.73; H, 6.49; N, 6.50. Calc. for $C_{33}H_{43}N_3O_4Sn$: C, 59.63; H, 6.52; N, 6.32%. IR (cm^{-1}): 1619 $\nu(OCO)_{asym}$.

2.5. X-ray crystallography

Crystals of compounds **1** and **4** suitable for an X-ray crystal-structure determination were obtained from hexane and $CHCl_3$/hexane, respectively. All measurements were made at low temperature on a Nonius Kappa CCD diffractometer [21] with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and an Oxford Cryosystems Cryostream 700 cooler. Data reduction was performed with HKL Denzo and Scalepack [22]. The intensities were corrected for *Lorentz* and polarization effects, and an empirical absorption correction based on the multi-scan method [23] was applied. Equivalent reflections were merged. The data collection and refinement parameters are given in Table 4, and views of segments of the polymeric structures are shown in Figs. 3–5. The structure of **1** was solved by employing heavy-atom Patterson methods [24], followed by the Fourier expansion routine of DIRDIF94 [25], while that of **4** was solved by direct methods using SIR92 [26]. In each structure, the non-hydrogen atoms were refined anisotropically, while employing restraints when necessary as described below.

In **1**, there are two symmetry-independent fragments of the polymer in the asymmetric unit, with each fragment being comprised of four repeats of the principle chemical unit. The root-mean-square fit of the atoms of one fragment to those of the other is 0.17 Å. This close fit, plus the equivalence of the unit cell parameters β and γ, and the similarity of the unit cell parameters b

Table 2
^{13}C NMR data (δ, ppm) for the tributyltin complexes in $CDCl_3$

Ring[a]/Other Sn–Bu[b]carbon	Carbon number	Compound				
		1	**2**	**3**	**4**	**5**
A	1	164.1	145.2	147.0	146.5	140.7
	2	120.5	121.0	122.8	122.5	122.4
	3	129.9	130.2	132.7	129.7	114.8
	4	146.4	137.5	120.9	131.6	159.3
	5	118.7	130.2	132.7	129.7	114.8
	6	130.2	121.0	122.8	122.5	122.4
B	1	131.9	118.9	118.7	118.7	119.0
	2	151.7	164.3	164.0	164.0	164.2
	3	130.8	117.8	117.7	117.7	117.8
	4	131.2	127.3	127.6	127.6	127.0
	5	130.3	145.9	146.0	146.0	146.0
	6	117.7	128.6	128.9	127.6	128.5
C	1	–	152.0	151.9	151.9	152.0
	2	–	130.9	130.9	130.9	130.9
	3	–	129.2	129.3	129.3	129.2
	4	–	129.9	129.9	129.9	129.9
	5	–	131.5	131.6	133.1	131.5
	6	–	118.1	118.1	118.1	117.9
Other	C(H)=O/C(H)=N	196.6	161.0	162.5	162.4	159.7
	CH_3/OCH_3	–	21.1	–	–	55.6
	COO	172.7	172.5	172.4	172.6	172.7
Sn–Bu	1*	16.8 (336)	16.8 (342)	16.8 (362)	16.8 (362)	16.8 (342)
	2*	27.8 (20)	27.9 (20)	27.9 (20)	27.9 (20)	27.9 (20)
	3*	27.3 (64)	27.1 (64)	27.1 (64)	27.1 (64)	27.1 (64)
	4*	13.8 (–)	13.6 (–)	13.6 (–)	13.6 (–)	13.6 (–)

[a] Refer to Fig. 1 (for compound **1**) and Fig. 2 (for compounds **2-5**) for the numbering scheme of the ligand skeleton (Ring A, B and/or C).
[b] Numbering scheme for Sn–Bu skeleton as shown in Table 1. $^nJ(^{13}C–^{119/117}Sn)$ mean values are given in parentheses.

Table 3
^{119}Sn NMR data (δ, ppm) and ^{119}Sn Mössbauer parameters (mm s^{-1}) for the tributyltin complexes

Compound	^{119}Sn NMR data[a]	^{119}Sn Mössbauer data				
		δ	Δ	$\rho = \Delta/\delta$	Γ_1	Γ_2
1	116.6	1.44	3.84	2.7	1.53	1.62
2	116.0	1.50	3.79	2.5	1.00	1.01
3	116.2	1.52	3.77	2.5	0.95	0.96
4	116.1	1.53	3.83	2.5	0.96	0.98
5	116.0	1.50	3.80	2.5	1.05	1.05

Parameters: δ, isomer shifts; Δ, quadrupole splitting; Γ_1 and Γ_2, line widths.
[a] In $CDCl_3$ solution.

Table 4
Crystallographic data and structure refinement parameters for the tributyltin complexes **1** and **4**

	1	**4**
Empirical formula	$C_{26}H_{36}N_2O_4Sn$	$C_{32}H_{40}ClN_3O_3Sn$
Formula weight	559.18	668.74
Crystal size (mm)	$0.05 \times 0.15 \times 0.22$	$0.17 \times 0.25 \times 0.27$
Crystal shape	Plate	Prism
Temperature (K)	160(1)	160(1)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	20.4071(4)	14.1136(2)
b (Å)	23.8710(4)	9.9787(1)
c (Å)	26.1342(4)	23.2971(3)
α (°)	86.3718(9)	90
β (°)	66.9966(8)	105.3959(7)
γ (°)	67.0400(7)	90
V (Å^3)	10730.4(3)	3163.31(7)
Z	16	4
Dx (g cm^{-3})	1.384	1.404
μ (mm^{-1})	0.983	0.927
Transmission factors (min, max)	0.711, 0.969	0.780, 0.860
$2\theta_{max}$ (°)	50	60
Reflections measured	176976	71033
Independent reflections (R_{int})	37789 (0.121)	9248 (0.062)
Reflection with $I > 2\sigma(I)$	21227	7081
Number of parameters	2619	390
Number of restraints	2805	18
$R(F)$ ($I > 2\sigma(I)$ reflns)	0.056	0.034
$wR(F^2)$ (all data)	0.148	0.082
$GOF(F^2)$	1.02	1.01
max., min. $\Delta\rho$ (e/Å^3)	1.07, −0.74	1.08, −0.59

and *c*, suggests that the independent fragments are almost related by a superstructure. If parameters *b* and *c* were identical, the structure could be defined in the higher symmetry space group *C*2/*c*, where only one fragment would need to be defined in the asymmetric unit. However, the difference between the unit cell parameters *b* and *c* means that the superstructure relationship is only approximate. This was confirmed in a test of the atomic coordinates for a relationship from a higher symmetry space group using the program PLATON [27], which indicated that additional crystallographic symmetry was not present. Nine of the 24 unique butyl groups in the structure are disordered over two conformations. Two sets of

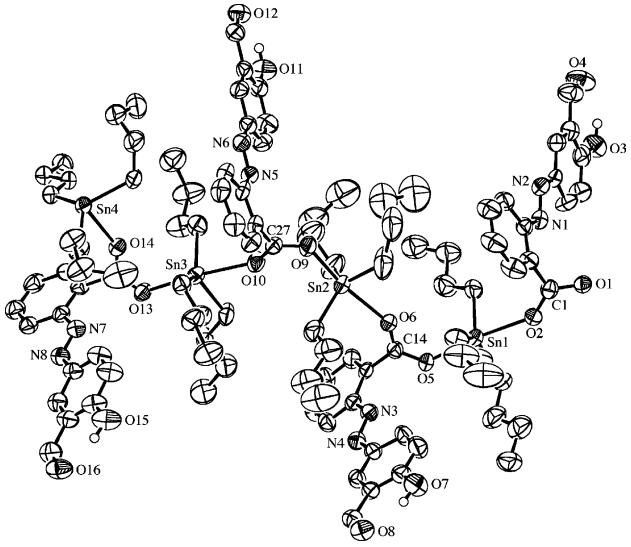


Fig. 3. One of the two symmetry-independent three-unit segments of the polymeric $[Bu_3SnL^1H]_n$ chain in the asymmetric unit of **1** (50% probability ellipsoids).

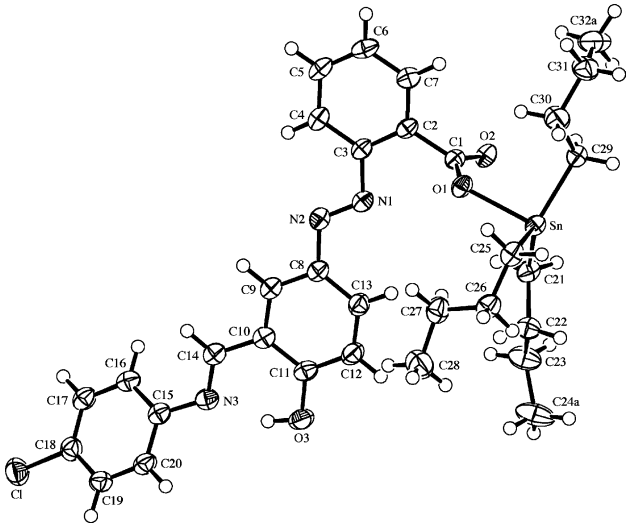


Fig. 4. The asymmetric unit of $[Bu_3SnL^4H]_n$ **4** showing the atom-labelling scheme (50% probability ellipsoids).

overlapping positions were defined for all atoms of one butyl group, for the terminal propyl segment of five butyl groups and for the terminal ethyl segment of another

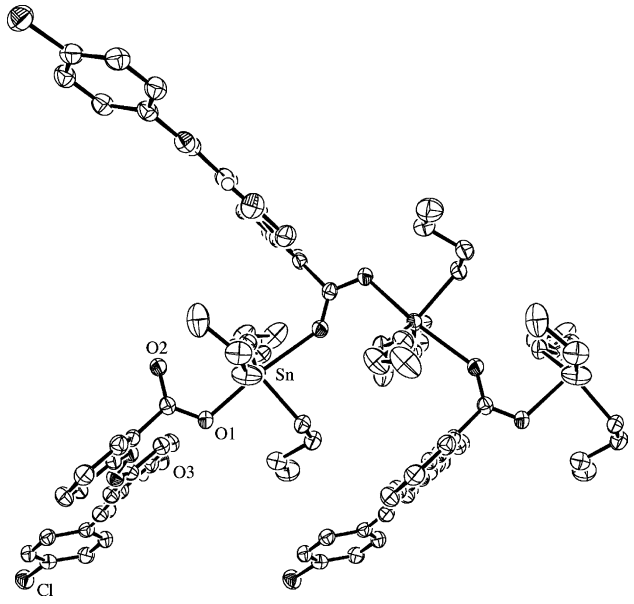


Fig. 5. A three-unit segment of the polymeric $[Bu_3SnL^4H]_n$ chain in **4** (50% probability ellipsoids).

three butyl groups. Refinement of the site occupation factors of the disordered groups indicated that most disordered conformations are approximately equally occupied. Similarity restraints were applied to the chemically equivalent bond lengths and angles within all butyl groups, including the ordered ones. Bond length restraints were also applied to any Sn–C bonds involving a disordered butyl C atom. Furthermore, neighbouring atoms within and between each conformation of the disordered butyl groups and within the ordered butyl groups were restrained to have similar atomic displacement parameters.

In **4**, the terminal methyl groups in two of the butyl ligands are disordered over two conformations. The refinement of constrained site occupation factors for the two orientations yielded values of 0.63(3) and 0.61(1) for the major conformation of each disordered group. Similarity restraints were applied to the chemically equivalent bond lengths involving disordered C atoms and neighbouring disordered atoms were restrained to have similar atomic displacement parameters.

The hydroxy H atom in **4** was placed in the position indicated by a difference electron density map and its position was allowed to refine together with an isotropic displacement parameter. All of the remaining H atoms in both **1** and **4** were placed in geometrically calculated positions and refined using a riding model where each H atom was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent atom ($1.5U_{eq}$ for the methyl and hydroxy groups). The orientation of each hydroxy O–H vector in **1** was optimised to correspond with the direction that would bring the H atom closest to the nearest hydrogen bond acceptor. Refinement of each structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\sum w(F_o^2 - F_c^2)^2$. Corrections for secondary extinction were not applied. One reflection, whose intensity was considered to be an extreme outlier, was omitted from the final refinement in the case of **1**. All calculations were performed using the SHELXL97 [28] program.

2.6. Biological tests

2.6.1. Preparation of the organotin stock solution

A stock solution (360 ppm) of the tributyltin compound, **1**, was prepared by dissolving the compound in 95% ethanol. The dissolution of the organotin compound in the organic media was to facilitate the dispersion of the compounds in water.

2.6.2. Hatching of the mosquito eggs

Dried *Aedes aegypti* (*Ae. aegypti*) mosquito eggs were obtained from the laboratory of Dr. Daniel Strickman, Entomology Department at the Walter Reed Army Institute of Research, Washington, DC. Approximately 0.01 g of the *Ae. aegypti* eggs were placed in a stainless steel tray (30 cm × 20 cm × 5 cm) containing approximately 1l of deionized water. After 24 h, finely-ground dog food (0.2–0.5 g) was added as the nutrient. The container was kept at 25–29 °C with a humidity of 80%. The second instar stage was attained after 2–3 days.

2.6.3. Larval toxicity studies

The toxicity studies were performed in 100×15 mm^2 disposable Petri dishes using ten *Ae. aegypti larvae* in the second instar stage. The *Ae. aegypti* larvae were transferred into the Petri dishes using a 100 μl micro-pipetter. An additional 15 ml of water was added. No turbidity was observed upon the addition of the water. Aliquots of the organotin solution and deionized water were then added to the Petri dish containing the larvae to give the desired concentration. The total assay volume in each case was 20 ml. Both positive and negative controls were used in the assay. Each assay was done in triplicate. The larvae were exposed to the organotin compounds for 24 h and the mortality rates for the mosquito larvae were determined by visual counting. Mosquito larvae that showed a slight reflex to disturbance were considered alive. Probit analyses [29] were used to determine the LC_{50} values (concentration at which the test compound killed 50% of the tested organisms).

3. Results and discussion

3.1. Syntheses

The 2-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]-benzoic acid ligand (L^1HH') was prepared by the diazo-coupling reaction between the anthranilic acid and

salicylaldehyde in alkaline medium under cold conditions. The 4-[((*E*)-1-{2-hydroxy-5-[(*E*)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}methylidene)amino]aryls ligand frameworks were usually generated by the reaction of Bu_3SnL^1H with the appropriate *para*-substituted aniline. The free ligands ($L^{2-5}HH'$) were also prepared by condensation of L^1HH' with the appropriate substituted aniline in an anhydrous toluene-ethanol mixture. The basic ligand framework is shown in Figs. 1 and 2 along with the abbreviations and numbering schemes for spectroscopic analyses. The details of their synthesis and characterization are presented in the experimental section.

Bu_3SnL^1H was obtained from the reaction of L^1HH' with $(Bu_3Sn)_2O$ in anhydrous toluene in a 2:1 molar ratio. The compound, Bu_3SnL^1H was used as the starting materials for synthesizing the rest of the tributyltin compounds. The other tributyltin derivatives, $Bu_3SnL^{2-5}H$, were synthesized by condensing Bu_3SnL^1H with the appropriate the *para*-substituted aniline in absolute ethanol. However, $Bu_3SnL^{2-5}H$ could also be prepared by reacting the appropriate 4-[((*E*)-1-{2-hydroxy-5-[(*E*)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}methylidene)amino]aryl (Fig. 2) with $(Bu_3Sn)_2O$ and the yield of the product was found to be lower. Synthetic convenience led to the choice of the former procedure. The characterization data of the complexes are given in the experimental section. The complexes were obtained in good yield and purity. They are stable in air and are soluble in all common organic solvents.

3.2. Infrared data

Diagnostically important infrared absorption frequencies for the carboxylate antisymmetric [ν_{asym}(OCO)] stretching vibration of the ligands and the complexes are given in the experimental section. The assignment of the symmetric [ν_{sym}(OCO)] stretching vibration band could not be made owing to the complex pattern of the spectra. The assignment of the band is based on comparison with the spectra of the free ligands (LHH′). The antisymmetric [ν_{asym}(OCO)] stretching vibrations for the uncomplexed ligands have been detected at 1733 cm^{-1} in L^1HH' and around the 1725 cm^{-1} region for $L^{2-5}HH'$. In the complexes, the carbonyl stretching frequencies are found to be shifted to lower wavenumber which is ascribed to carboxylate coordination in accordance with earlier reports [30,31].

3.3. ^1H, ^{13}C and ^{119}Sn NMR data

The ^1H and ^{13}C NMR data of L^1HH' were reported in our earlier [20] and the signals were assigned by the use of correlated spectroscopy (COSY), heteronuclear single-quantum correlation (HMQC) and heteronuclear multiple-bond connectivities (HMBC) experiments. The conclusions drawn from the ligand assignments were then subsequently extrapolated to the complexes owing to the data similarity. The ^1H and ^{13}C chemical shift assignment (Tables 2 and 3, respectively) of the tributyltin moiety is straightforward from the multiplicity patterns, resonance intensities and also by examining the $^nJ(^{13}C–^{119/117}Sn)$ coupling constants [30–32]. The ^1H NMR integration values were completely consistent with the formulation of the products.

Four-coordinated tributyltin compounds, however, exhibit couplings $^1J(^{13}C–^{119/117}Sn)$ in the range 325–390 Hz, and five-coordinated ones in the range 440-540 Hz [33–36]. The tributyltin complexes of the present investigation exhibit $^1J(^{13}C–^{119/117}Sn)$ coupling satellites in the range 336–362 Hz in $CDCl_3$ solution, suggesting that the tin atom is four-coordinate in solution. In contrast, a polymeric structure with five-coordinate tin atoms is found in the solid state (see Sections 3.4 and 3.5); this is possibly lost in solution to generate a monomeric four-coordinated tetrahedral structure [32]. The ^{119}Sn NMR chemical shifts of tributyltin complexes in $CDCl_3$ solution are listed in Table 3. The complexes exhibit a single sharp resonance at around 116 ppm, consistent with the range specified for tetrahedral triorganotin compounds [35]. This is further supported by our recent work on analogous triorganotin azocarboxylates [30–32].

3.4. ^{119}Sn Mössbauer data

The Mössbauer spectra of the complexes are listed in Table 3. The ratio of the quadrupole splitting value to isomer shift value ($\rho = \Delta/\delta$) can be used to distinguish between the different coordination states of the central tin atom [37]. Tin compounds which are four coordinate have ρ values less than 1.8 while ρ values larger than 2.1 would indicate compounds with greater than four coordination. As can be seen in Table 3, all the complexes have ρ values greater than 2.1 suggesting that the complexes have a coordination number greater than four. Furthermore, the tributyltin complexes exhibited quadrupole splitting (QS) values of approximately 3.80 mm s^{-1}. These values are within the range 3.0–4.1 mm s^{-1}, which are consistent with a *trans*-trigonal bipyramidal geometry with a planar Bu_3Sn unit and two axial carboxylate oxygen atoms [38]. Further, the QS data for complexes **1**–**5** matches closely with the data of complexes having a *trans*-trigonal bipyramidal geometry in a polymeric structure [31,32], which was subsequently also found here from the crystal structures (see Section 3.5). The QS values for the complexes are in the same order of magnitude, suggesting that they adopt the same structural motif.

3.5. X-ray crystallography

The crystal structures of two of the tributyltin complexes (**1** and **4**) have been determined. The two structures conform to the same motif in which the carboxylate O atoms of a single aryl ligand bridge two Sn atoms and the pattern then repeats itself to give a continuous single-stranded polymeric structure, as illustrated in Figs. 3–5. The Sn atoms in each structure have a slightly distorted *trans*-R_3SnO_2 trigonal bipyramidal coordination geometry with equatorial butyl groups and carboxylate O atoms occupying axial positions, one being from each of two aryl ligands. The carboxylate C–O bond lengths are not equivalent, which shows some distinction between the carbonyl and carboxylic acid O atoms. Correspondingly, the Sn–O bond lengths involving these O atoms are also not equivalent, with the Sn–O bond to the carbonyl O atom being the longer, as would be expected on electronic grounds. Selected geometric parameters for **4** are given in Table 5 and the corresponding parameters for **1** are equivalent. The length of the intramolecular Sn···O(2) separation in **4** is 3.138(2) Å, and is similar for the corresponding interactions in **1**. Although these distances are well inside the sum of the van der Waals radii of the Sn and O atoms (ca. 3.6 Å), there does not appear to be any significant distortion of the trigonal bipyramidal coordination geometry as a result of this contact.

In **4**, the asymmetric unit of the crystal structure contains just one of the principle chemical units, which then repeats to form the polymeric structure. By contrast, the asymmetric unit in **1** contains two symmetry-independent fragments of the polymer, with each fragment being comprised of four repeats of the principle chemical unit. Thus there are eight symmetry-independent Sn atoms in the structure.

The hydroxy group in each ligand forms an intraligand hydrogen bond with the adjacent aldehyde O atom in **1** and with the adjacent imino N atom in **4**. Some of the butyl groups in each structure are disordered, as is common for complexes involving the Bu_3Sn core (see Section 2).

The structures of **1** and **4** correspond with the type **II** polymeric motif described by Willem et al. for related R_3SnO_2CR' compounds [32] and the general description of the structure of $[Me_3Sn(O_2CR')]_n$ (R′ = 2-[(*E*)-2-(2-hydroxy-5-methylphenyl)-1-diazenyl]benzoate) given there applies equally well to **1** and **4**. As in the earlier report [32], the polymeric chain in the structures of both **1** and **4** propagates in a 2_1 screw fashion, with this being a crystallographic 2_1 screw axis in the case of **4** and a non-crystallographic pseudo-2_1 screw axis in **1**. In **4**, the repeat Sn···Sn distance is 5.2601(2) Å, which agrees very well with the mean repeat distance found in other type **II** carboxylate-bridged triorganotin species of 5.19 ± 0.21 Å [39], i.e., the repeat distance is independent of the nature of the tin-bound substituents and carboxylate residues. In **1**, the eight symmetry-independent Sn···Sn distances range from 5.1288(9) to 5.548(1) Å.

Table 5
Selected bond lengths (Å) and angles (°) for **4**[a]

Sn–O(1)	2.213(2)	Sn–C(21)	2.143(2)
Sn–O(2)^{i}	2.454(2)	Sn–C(25)	2.147(2)
Sn ··· O(2)	3.138(2)	Sn–C(29)	2.134(2)
O(1)–Sn–O(2)^{i}	173.19(5)	O(2)^{i}–Sn–C(25)	84.55(7)
O(1)–Sn–C(21)	96.25(7)	O(2)^{i}–Sn–C(29)	86.19(7)
O(1)–Sn–C(25)	89.68(8)	C(21)–Sn–C(25)	120.58(9)
O(1)–Sn–C(29)	93.12(7)	C(21)–Sn–C(29)	122.68(9)
O(2)^{i}–Sn–C(21)	89.80(7)	C(25)–Sn–C(29)	115.88(9)

[a] Atom labels with superscript ^{i} refer to atoms from the next symmetrically-related ligand in the polymeric chain.

3.6. Larval toxicity studies

Compound **1** and the ligand were screened against the second larval instar stage of the *Ae. aegypti* mosquito. The LC_{50} for compound **1** is 0.27 mg l^{-1} while the ligand had a 100-fold decrease (greater than 20 mg l^{-1}) in toxicity. These results clearly indicate that the toxicity of the compound is due to the tributyltin moiety of the molecule. This is not surprising since it is known that tributyltins have various biocidal activities [40] including those against various mosquitoes [17,41].

The toxicities for a series of tributyl- and triphenyltin-azocarboxylates previously screened against the second larval instar stage of the *Ae. aegypti* mosquito [17] and compound **1** were compared since the ligand structures of the two systems are somewhat similar. The results indicated that compound **1** is more effective in its activity than either the tributyl- (0.53–1.23 mg l^{-1}) or triphenyltin (1.82–3.50 mg l^{-1}) azocarboxylates reported earlier [17]. As the results indicated, the toxicity of compound **1** is significant when compared with the triphenyl derivative. This observation is in agreement with the work of Nguyen et al. [42] in which several series of triorganotins were screened against this same species of mosquito.

The toxicity of compound **1** is not as effective as organophosphorus insecticides [43] in their larvicidal capabilities; however, it should not be excluded as a possible larvicidal candidate. Its advantages lie in its biodegradability and lack of known resistance by this species of mosquitoes. For example, many strains of *Ae. aegypti* have shown some resistance to several organophosphorus insecticides [43,44], with that to Malathion being the highest [43]. It has also been established that highly toxic triorganotins biodegrade in the environment [45] to non-toxic inorganic tin species through the progressive removal of the organic groups attached to the tin atom. These are important aspects for an insecticide. Furthermore, some countries have banned the use of organophosphorus compounds for the control of mosquitoes due to their toxic side effects [46]. In view of

these two advantages over organophosphorus insecticides, in addition to the overall effectiveness of compound **1** against the *Ae. aegypti* larvae, this compound can be considered a good candidate for the control of this species of mosquito larvae.

4. Supplementary material

CCDC-244249 and CCDC-244250 contain the supplementary crystallographic data for complexes **1** and **4**, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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References

[1] L.E. Maley, D.P. Mellor, Nature 159 (1974) 370.
[2] M. Calvin, K.W. Wilson, J. Am. Chem. Soc. 67 (1945) 2003.
[3] D.G. Vartak, K.R. Menon, J. Inorg. Nucl. Chem. 31 (1969) 3341.
[4] P.N. Mohan Das, C.P. Trivedi, J. Indian Chem. Soc. 49 (1972) 739.
[5] K.G. Deshmukh, R.A. Bhobe, Curr. Sci. 46 (1977) 67.
[6] K.G. Deshmukh, R.A. Bhobe, J. Indian Chem. Soc. 54 (1977) 375.
[7] A.A. Khandar, Z. Rezvani, Polyhedron 18 (1998) 129.
[8] K.G. Deshmukh, R.A. Bhobe, J. Inorg. Nucl. Chem. 40 (1978) 135.
[9] L. Pardeshi, A. Rasheed, R.A. Bhobe, J. Indian Chem. Soc. 57 (1980) 388.
[10] K.K. Sarma, T.S. Basu Baul, D.D. Mishra, Synth. React. Inorg. Met-Org. Chem. 23 (1993) 1277.
[11] K.K. Sarma, T.S. Basu Baul, E. Rivarola, R.P. Agrawal, Polyhedron 13 (1994) 2217.
[12] M.A. Pujar, T.D. Bharamagoudar, J. Indian Chem. Soc. 57 (1980) 462.
[13] A.A. Khandar, K. Nejati, Polyhedron 19 (2000) 607.
[14] S.J. de Mora, in: S.J. de Mora (Ed.), Tributyltin: Case Study of an Environmental Contaminant, Cambridge University Press, London, 1996, pp. 1–20.
[15] P.E. Gibbs, G.W. Bryan, in: S.J. de Mora (Ed.), Tributyltin: Case Study of an Environmental Contaminant, Cambridge University Press, London, 1996, pp. 212–236.
[16] R.F. Bennett, in: S.J. de Mora (Ed.), Tributyltin: Case Study of an Environmental Contaminant, Cambridge University Press, London, 1996, pp. 21–61.
[17] T.S. Basu Baul, S. Dhar, E. Rivarola, F.E. Smith, R. Butcher, X. Song, M. McCain, G. Eng, Appl. Organomet. Chem. 17 (2003) 261.
[18] E.R.T. Tiekink, Appl. Organomet. Chem. 5 (1991) 1.
[19] E.R.T. Tiekink, Trends Organomet. Chem. 1 (1994) 71.
[20] T.S. Basu Baul, S.P. Pyke, K.K. Sarma, E.R.T. Tiekink, Main Group Met. Chem. 19 (1996) 807.
[21] R. Hooft, Kappa CCD Collect Software, Nonius BV, Delft, The Netherlands, 1999.
[22] Z. Otwinowski, W. Minor, in: C.W. CarterJr., R.M. Sweet (Eds.), Methods in Enzymology, Macromolecular Crystallography, Part A, vol. 276, Academic Press, New York, 1997, pp. 307–326.
[23] R.H. Blessing, Acta Crystallogr., Sect. A 51 (1995) 33.
[24] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. Garcia-Granda, R.O. Gould, J.M.M. Smits, C. Smykalla, PATTY: The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992.
[25] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, J.M.M. Smits, DIRDIF94: The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994.
[26] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, SIR92, J. Appl. Crystallogr. 27 (1994) 435.
[27] A.L. Spek, PLATON, Program for the Analysis of Molecular Geometry, University of Utrecht, The Netherlands, 2003.
[28] G.M. Sheldrick, SHELXL97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
[29] D.J. Finney, Probit Analysis: A Treatment of the Sigmoid Curve Response, third ed., Cambridge University Press, UK, 1971.
[30] T.S. Basu Baul, S. Dhar, N. Kharbani, S.M. Pyke, R. Butcher, F.E. Smith, Main Group Met. Chem. 22 (1999) 413.
[31] T.S. Basu Baul, S. Dhar, S.M. Pyke, E.R.T. Tiekink, E. Rivarola, R. Butcher, F.E. Smith, J. Organomet. Chem. 633 (2001) 7.
[32] R. Willem, I. Verbruggen, M. Gielen, M. Biesemans, B. Mahieu, T.S. Basu Baul, E.R.T. Tiekink, Organometallics 17 (1998) 5758.
[33] J. Holeček, M. Nadvornik, K. Handlir, A. Lycka, J. Organomet. Chem. 241 (1983) 177.
[34] M. Nadvornik, J. Holeček, K. Handlir, A. Lycka, J. Organomet. Chem. 275 (1984) 43.
[35] A. Lycka, J. Holeček, M. Nadvornik, K. Handlir, J. Organomet. Chem. 280 (1985) 323.
[36] J. Holeček, K. Handlir, M. Nadvornik, A. Lycka, J. Organomet. Chem. 258 (1983) 147.
[37] J.J. Zuckerman, in: F.G.A. Stone, R. West (Eds.), Advances in Organometallic Chemistry, vol. 9, Academic Press, New York, 1970, p. 21.
[38] R. Barbieri, F. Huber, L. Pellerito, G. Ruisi, A. Silvestri, in: P.J. Smith (Ed.), Chemistry of Tin: ^{119}Sn Mössbauer Studies on Tin Compounds, Blackie, London, 1998, pp. 496–540.
[39] S.W. Ng, C. Wei, V.G. Kumar Das, J. Organomet. Chem. 345 (1988) 59.
[40] A.G. Davis, P.J. Smith, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 2, Pergamon, New York, 1982, p. 519.
[41] G. Eng, X. Song, Trends Organomet. Chem. 4 (2002) 81.
[42] T.T. Nguyen, N. Ogwuru, G. Eng, Appl. Organomet. Chem. 14 (2000) 345.
[43] S.C. Rawlins, J.O.H. Wan, J. Am. Mosq. Control Assoc. 11 (1995) 59.
[44] S. Mohiuddin, Z. Ahmed, S.A. Qureshi, Pak. J. Sci. Ind. Res. 34 (1991) 356.
[45] S.J. Blunden, A. Chapman, in: P.J. Craig (Ed.), Organometallic Compounds in the Environment, John Wiley, New York, 1986, p. 111.
[46] B. Sinniah, Trans. R. Soc. Trop. Med. Hyg. 77 (1983) 35.