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Synthesis, characterization and crystal structures of triorganotin(IV) complexes of 4-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]- and 4-{(*E*)-4-hydroxy-3-[(*E*)-4-(aryl)iminomethyl]phenyldiazenyl}-benzoic acids and toxicity studies of their tri-*n*-butyltin(IV) derivatives on the *Aedes aegypti* and *Anopheles stephensi* mosquito larvae

Tushar S. Basu Baul[1]*, Keisham Surjit Singh[1], Antonin Lyčka[2], Anthony Linden[3], Xueqing Song[4], Alejandra Zapata[4] and George Eng[4]

[1]Department of Chemistry, North-Eastern Hill University, NEHU Permanent Campus, Umshing, Shillong 793 022, India
[2]Research Institute for Organic Syntheses, Rybitvi 296, CZ-532 18 Pardubice 20, Czech Republic
[3]Institute of Organic Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland
[4]Department of Chemistry and Physics, University of the District of Columbia, Washington DC 20008, USA

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Triorganotin(IV) complexes of 4-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]- and 4-{(*E*)-4-hydroxy-3-[(*E*)-4-(aryl)iminomethyl]phenyldiazenyl}-benzoic acids (aryls = 4-CH_3, 4-Br, 4-Cl, 4-OCH_3) have been synthesized. The structures have been characterized by ^{1}H, ^{13}C, ^{119}Sn NMR, IR and ^{119m}Sn Mössbauer spectroscopies. The crystal structures of $Ph_3Sn[O_2CC_6H_4\{N{=}N(C_6H_3\text{-}4\text{-}OH[C(H){=}NC_6H_4CH_3\text{-}4]\}\text{-}p]$ and $^{n}Bu_3Sn[O_2CC_6H_4\{N{=}N(C_6H_3\text{-}4\text{-}OH[C(H){=}NC_6H_4Br\text{-}4]\}\text{-}p]$ are also reported. The ^{119}Sn Mössbauer and ^{119}Sn NMR data indicate that the tri-*n*-butyltin(IV) and triphenyltin(IV) complexes have a tetrahedral geometry in the solid state as well as in solution. Toxicity studies of the tri-*n*-butyltin(IV) complexes on the second larval instar of the *Aedes aegypti* and *Anopheles stephensi* mosquito larvae indicated that the complexes are effective larvicides. The LC_{50} values range from 1.21 to 3.38 μM for the *Ae. aegypti* and from 0.83 to 2.31 μM for the *An. stephensi*.

KEYWORDS: tri-*n*-butyltins; triphenyltins; carboxylates; 4-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid; 4-{(*E*)-4-hydroxy-3-[(*E*)-4-(aryl)iminomethyl]phenyldiazenyl}benzoic acid; crystal structure; *Aedes aegypti*; *Anopheles stephensi*; mosquito; larvicide and larvae

INTRODUCTION

Organotin(IV) complexes of 2-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]-[1–5] and 2-{(*E*)-4-hydroxy-3-[(*E*)-4-(aryl)iminomethyl]phenyldiazenyl}benzoic acids[3,5–8] have been studied in great detail due to their various structural motifs (**I**–**III**, Scheme 1) as well as for their important role in understanding Sn(IV) coordination chemistry in solution as well as in the solid state. In addition, this class of compounds has shown promise as larvicides against various species of mosquito. For example, azo-butyltin(IV) carboxylates, viz., tri-*n*-butyltin(IV) 5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoates and tri-*n*-butyltin(IV) 2-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoate have been investigated for their toxicites against both the *Aedes aegypti* (*Ae. aegypti*) and *Anopheles stephensi* (*An. stephensi*) mosquito larvae. The results indicated that these

*Correspondence to: Tushar S. Basu Baul, Department of Chemistry, North-Eastern Hill University, NEHU Permanent Campus, Umshing, Shillong 793 022, India.
E-mail: basubaul@hotmail.com
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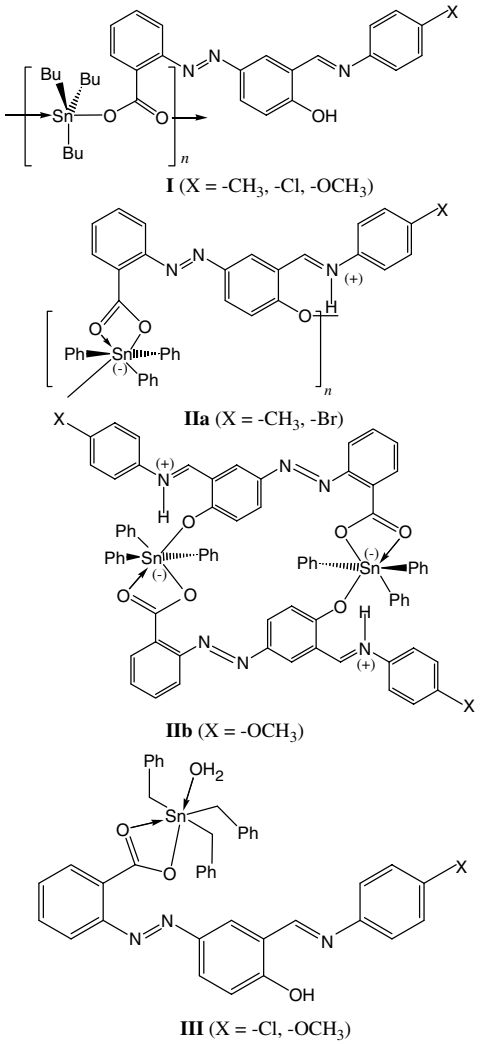

Scheme 1. Structural motifs in $R_3Sn[O_2CC_6H_4\{N=N(C_6H_3\text{-}4\text{-}OH[C(H)=NC_6H_4X\text{-}4])\}-o]$ complexes.

compounds have moderate[9] to good[3] activities, respectively. The latter compounds were further condensed with primary aromatic amines to obtain the tri-*n*-butyltin(IV) 2-{(*E*)-4-hydroxy-3-[(*E*)-4-(aryl)iminomethyl]phenyldiazenyl}-benzoates. The activities for these compounds were found to be lower and to correlate with the size of the molecules.[6]

In view of this, and in search of better candidates for the control of various mosquito larvae, the present study details the synthesis and characterization of the pre-ligand i.e. 4-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid [LHH′, Fig. 1(a)] and the triorganotin(IV) complexes of the corresponding condensed ligands, i.e. 4-{(*E*)-4-hydroxy-3-[(*E*)-4-(aryl)iminomethyl]phenyldiazenyl}benzoic acids [L^{1-4}HH′, Fig. 1(b)]. We are also reporting the toxicity studies of the tri-*n*-butyltin(IV) complexes $^nBu_3SnLH$ (**1**), $^nBu_3SnL^1H$ (**2**), $^nBu_3SnL^2H$ (**3**), $^nBu_3SnL^3H$ (**4**) and $^nBu_3SnL^4H$ (**5**) against the second larval instar of *Ae. aegypti* and *An. stephensi* mosquito.

EXPERIMENTAL

Materials

$(^nBu_3Sn)_2O$ (Merck), salicylaldehyde (Lancaster) and the substituted anilines (reagent grade) were used without further purification. Ph_3SnOH was prepared from Ph_3SnCl (Fluka) following the literature method.[10] The solvents used in the reactions were of AR grade and dried using standard procedures. Toluene was distilled from sodium benzophenone ketyl.

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 ligand 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,

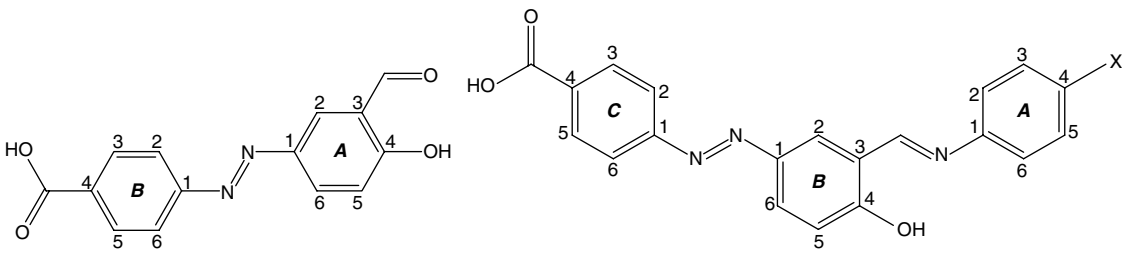

Figure 1. Generic structure of the ligand. Abbreviations: (a) LHH′ (pre-ligand), (b) L^1HH': X = $-CH_3$; L^2HH', –Br, L^3HH', –Cl, L^4HH' and $-OCH_3$ (condensed ligands), where H and H′ represent hydroxy and carboxylic acid H atoms, respectively. Complex numbers are included underneath the ligands for convenience.

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$CDCl_3$ at 77.0 ppm and Me_4Sn at 0.00 ppm, respectively. The Mössbauer spectra of the complexes in the solid state were recorded using a Ranger Model MS-900 spectrometer in the acceleration mode with a moving source geometry. A 10 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. 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.

Syntheses of ligands

Preparation of 4-[(E)-2-(3-formyl-4-hydroxy-phenyl)-1-diazenyl]benzoic acid (LHH′)

The ligand, LHH′ [Fig. 1(a)] was prepared by reacting *para*-carboxybenzenediazonium chloride with salicylaldehyde in an alkaline solution under cold conditions following the method described earlier for the *ortho*-analog.[1] The amounts of concentrated HCl and water used for the dissolution of the *para*-aminobenzoic acid were 8 and 32 ml, respectively. The crude LHH′ was obtained after acidification with dilute acetic acid. The light yellow precipitate was filtered, washed with water until the filtrate became neutral and then dried *in vacuo*. The resultant brown product was then washed thoroughly with hexane to remove any tarry materials and dried. The brown LHH′ was insoluble in all common organic solvents and water, and consequently could not be recrystallized. The brown precipitate was then re-dissolved in a hot aqueous sodium bicarbonate solution. It was filtered to remove any undissolved particles and re-precipitated using dilute acetic acid. The precipitate was filtered, washed with water and dried, which afforded a bright brown product in 56% yield; m.p.>275 °C. Anal found: C, 61.38; H, 3.73; N, 10.26%; calcd for $C_{14}H_{10}N_2O_4$: C, 62.22; H, 3.70; N, 10.37%. IR (cm^{-1}) 1679 $\nu(OCO)_{asym}$. ^{1}H-NMR (DMSO-d_6); δ_H: 7.24 [d,1H, (A) H5], 7.95 [m (part of AA′BB′ system), 2H, (B) H2 and H6], 8.14 [dd, 1H, (A) H6], 8.16 [m (part of AA′BB′ system), 2H, (B) H3 and H5], 8.25 [d, 1H, (A) H2], 10.38 [s, 1H, C(H)═O], ppm. Signals for –OH and –COOH were not observed due to exchange. ^{13}C-NMR (DMSO-d_6); δ_C: 118.7 [(A) C5], 122.4 [(B) C2 and C6], 122.8 [(A) C3], 124.5 [(A) C2], 129.9 [(A) C6], 130.7 [(B) C3 and C5], 132.5 [(B) C4], 144.8 [(A) C1], 154.3 [(B) C1], 164.2 [(A) C4], 166.8 [CO_2H)], 190.5 [C(H)═O], ppm.

Preparation of 4-{(E)-4-hydroxy-3-[(E)-4-(aryl) iminomethyl]phenyldiazenyl}benzoic acid (L^{1-4} HH′)

Unlike the *ortho*-analog,[3] the *para*-carboxylic acid ligands (L^{1-4}HH′) [Fig. 1(b)] could not be prepared by the condensation of LHH′ with the appropriately substituted aniline, owing to the insolubility of the LHH′ in common organic solvents. However, the ligand frameworks, i.e. L^{1-4}HH′, were generated by the reaction of ^{n}Bu_3SnLH with the appropriate *para*-substituted anilines.

Syntheses of triorganotin(IV) complexes

*Preparation of ^{n}Bu_3SnLH (**1**)*

The compound was synthesized by reacting LHH′ (0.90 g, 3.33 mmol) and (^{n}$Bu_3Sn)_2O$ (1.0 g, 1.67 mmol) in 50 ml anhydrous toluene. The reaction mixture was refluxed using a Dean–Stark moisture trap and water cooled condenser for 7 h. It was then filtered while still hot. The filtrate was collected and the volatiles were removed using a rotary evaporator. The pasty mass was dried *in vacuo*, cooled in ice, triturated with a minimum amount of hexane and filtered. The yellow-orange coloured powder was dissolved in hexane and filtered to remove any unreacted LHH′. The orange crystals of the desired product were obtained after evaporation of the hexane solution. Yield (0.26 g, 26%); m.p. 89–92 °C. Anal. found: C, 55.78; H, 6.36; N, 5.46%; calcd for $C_{26}H_{36}N_2O_4Sn$: C, 55.84; H, 6.48; N, 5.00%. IR (cm^{-1}): 1639 $\nu(OCO)_{asym}$. ^{1}H-NMR ($CDCl_3$/400.13 MHz); δ_H, 7.92 [d, 1H, (A) H5], 8.18 [dd, 2H, (A) H2 and H6], 8.23 [m, 4H, (B) H2 and H6 and H3 and H5], 10.0 [s, 1H, C(H)═O], 11.4 [brs, 1H, OH]; Sn-^{n}Bu skeleton: 0.93 [t, 9H, H4*], 1.39 [m, 12H, H2* and H3*], 1.69 [m, 6H, H1*], ppm. ^{13}C-NMR ($CDCl_3$/100.62 MHz); δ_C, 118.8 [(A) C5], 122.5 [(B) C2 and C6], 128.9 [(A) C3], 129.9 [(A) C2], 130.8 [(A) C6], 131.3 [(B) C3 and C5], 134.3 [(B) C4], 146.0 [(A) C1], 154.5 [(B) C1], 164.3 [(A) C4], 170.9 [CO_2)], 196.7 [C(H)═O]; Sn-^{n}Bu skeleton: 13.8 [C4*], 16.8 [C1*], 27.2 [C3*], 28.0 [C2*], ppm.

*Preparation of ^{n}Bu_3SnL^{2}H (**3**)*

^{n}Bu_3SnLH (**1**) (0.58 g, 1.03 mmol) in absolute ethanol (45 ml) was added drop-wise to a hot stirred ethanolic solution (20 ml) containing *para*-bromoaniline (0.18 g, 1.03 mmol). The reaction mixture was then refluxed using a Dean–Stark moisture trap and water cooled condenser for 3 h and then filtered while still 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 hexane and filtered. The crude product was obtained after evaporation. It was then recrystallized from a chloroform–hexane mixture (1:3, v/v) to yield orange crystals of the desired product. Yield (0.22 g, 29.7%); m.p. 83–84 °C. Anal. found: C, 57.40; H, 6.19; N, 6.20; calcd for $C_{32}H_{40}BrN_3O_3Sn$: C, 57.43; H, 6.02; N, 6.27%. IR (cm^{-1}): 1619 $\nu(OCO)_{asym}$. ^{1}H-NMR ($CDCl_3$); δ_H, ligand skeleton: 7.13 [d,1H, (B) H5], 7.21 [d, 2H, (A) H2 and H6], 7.58 [d, 2H, (A) H3 and H5], 7.90 [d, 2H, (C) H2 and H6], 8.08 [d, 2H, (B) H2 and H6], 8.18 [d, 2H, (C) H3 and H5], 8.73 [s, 1H, C(H)═N], 13.64 [brs, 1H, OH], Sn-^{n}Bu skeleton: 0.93 [t, 9H, H4*], 1.39 [m, 12H, H2* and H3*], 1.66 [m, 6H, H1*], ppm. ^{13}C-NMR ($CDCl_3$); δ_C: ligand skeleton: 162.6 [C(H)═N], 164.4 [C–OH], 171.1 [CO_2], other carbons: 118.5, 118.9, 121.1, 122.4, 123.0, 128.0, 128.6, 131.3, 132.8, 133.9, 145.8, 146.9, 154.7; Sn-^{n}Bu skeleton: 13.8 [C4*], 16.8 [C1*], 27.2 [C3*], 28.0 [C2*], ppm.

The other tri-n-butyltin(IV) complexes were prepared by reacting ^{n}Bu_3SnLH with the appropriate *para*-substituted anilines using an analogous procedure. The characterization and spectroscopic data of the complexes are given below.

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*$^{n}Bu_3SnL^1H$ (**2**)*

An orange crystalline compound was obtained from a chloroform-hexane mixture (1 : 3, v/v). Yield: 45.7%. M. p.: 82–83 °C. Anal. Found: C, 61.23; H, 6.70; N, 6.54%. Calc. for $C_{33}H_{43}N_3O_3Sn$: C, 61.10; H, 6.68; N, 6.47%. IR (cm^{-1}): 1619 $\nu(OCO)_{asym}$. ^{1}H-NMR ($CDCl_3$); δ_H: ligand skeleton: 2.40 [s, 3H, CH_3], 7.14 [d, 1H, (B) H5], 7.20 [d, 4H, (A) H2, H3, H5 and H6], 7.90 [d, 2H, (C) H2 and H6], 8.03 [d, 1H, (B) H6], 8.06 [d, 1H, (B) H2], 8.18 [d, 2H, (C) H3 and H5], 8.75 [s, 1H, C(H)═N], 14.12 [brs, 1H, OH], Sn-^{n}Bu skeleton: 0.93 [t, 9H, H4*], 1.39 [m, 12H, H2* and H3*], 1.66 [m, 6H, H1*], ppm. ^{13}C-NMR ($CDCl_3$); δ_C: ligand skeleton: 21.3 [CH_3], 161.1 [C(H)═N], 164.8 [C–OH], 171.1 [CO_2], other carbons: 118.5, 119.2, 121.2, 121.4, 127.6, 128.4, 130.3, 131.3, 133.8, 137.7, 145.1, 145.7, 154.8; Sn-^{n}Bu skeleton: 13.8 [C4*], 16.8 [C1*], 27.2 [C3*], 28.0 [C2*], ppm.

*$^{n}Bu_3SnL^3H$ (**4**)*

An orange crystalline compound was obtained from a chloroform-hexane mixture (1 : 3, v/v). Yield: 41.8%; m.p. 99–102 °C. Anal. found: C, 57.49; H, 6.11; N, 6.34%; calcd for $C_{32}H_{40}ClN_3O_3Sn$: C, 57.46; H, 6.02; N, 6.28%. IR (cm^{-1}): 1617 $\nu(OCO)_{asym}$. ^{1}H-NMR ($CDCl_3$); δ_H: ligand skeleton: 7.15 [d, 1H, (B) H5], 7.26 [d, 2H, (A) H2 and H6], 7.42 [d, 2H, (A) H3 and H5], 7.90 [d, 2H, (C) H2 and H6], 8.07 [d, 2H, (B) H2 and H6], 8.19 [d, 2H, (C) H3 and H5], 8.73 [s, 1H, C(H)═N], 13.66 [brs, 1H, OH], Sn-^{n}Bu skeleton: 0.93 [t, 9H, H4*], 1.38 [m, 12H, H2* and H3*], 1.64 [m, 6H, H1*], ppm. ^{13}C-NMR ($CDCl_3$); δ_C: ligand skeleton: 162.4 [C(H)═N], 164.3 [C–OH], 170.9 [CO_2], other carbons: 118.3, 118.8, 122.2, 122.5, 127.8, 128.4, 129.6, 131.1, 133.0, 133.7, 145.7, 146.3, 154.6; Sn-^{n}Bu skeleton: 13.7 [C4*], 16.7 [C1*], 27.8 [C3*], 27.9 [C2*], ppm.

*$^{n}Bu_3SnL^4H$ (**5**)*

An orange crystalline compound was obtained from hexane. Yield: 39%; m.p. 79–81 °C. Anal. found: C, 59.76; H, 6.54; N, 6.53. Calc. for $C_{33}H_{43}N_3O_4Sn$: C, 59.63; H, 6.52; N, 6.32%. IR (cm^{-1}): 1618 $\nu(OCO)_{asym}$. ^{1}H-NMR ($CDCl_3$); δ_H: ligand skeleton: 3.85 [s, 3H, OCH_3], 6.96 [d, 2H, (A) H2 and H6], 7.13 [d, 1H, (B) H5], 7.32 [d, 2H, (A) H3 and H5], 7.91 [d, 2H, (C) H2 and H6], 8.02 [d, 1H, (B) H6], 8.05 [d, 1H, (B) H2], 8.18 [d, 2H, (C) H3 and H5], 8.73 [s, 1H, C(H)═N], 14.16 [brs, 1H, OH], Sn-^{n}Bu skeleton: 0.93 [t, 9H, H4*], 1.39 [m, 12H, H2* and H3*], 1.69 [m, 6H, H1*], ppm. ^{13}C-NMR ($CDCl_3$); δ_C: ligand skeleton: 55.7 [OCH_3], 159.8 [C(H)═N], 164.6 [C–OH], 171.1 [CO_2], other carbons: 114.9, 118.4, 119.3, 122.4, 122.6, 127.5, 128.1, 131.3, 133.8, 140.7, 145.8, 154.9, 159.4; Sn-^{n}Bu skeleton: 13.8 [C4*], 16.8 [C1*], 27.6 [C3*], 28.1 [C2*], ppm.

*Synthesis of Ph_3SnLH (**6**)*

Compound **6** was synthesized by reacting LHH′ (0.36 g, 1.33 mmol) with Ph_3SnOH (0.50 g, 1.33 mmol) in 50 ml of anhydrous toluene in a 100 ml flask equipped with a Dean–Stark moisture trap and water-cooled condenser. The reaction mixture was refluxed for 7 h and filtered while still 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 benzene and filtered. The crude product was obtained after evaporation and then recrystallized from benzene to yield orange crystals of the desired product. Yield (0.27 g, 32.9%); m.p. 179–182 °C. Anal. found: C, 62.58; H, 4.12; N, 4.70; calcd for $C_{32}H_{24}N_2O_4Sn$: C, 62.41; H, 3.90; N, 4.52%. IR (cm^{-1}): 1659 $\nu(OCO)_{asym}$. ^{1}H-NMR ($CDCl_3$); δ_H: ligand skeleton: 7.14 [d, 1H, (B) H5], 7.93 [d, 2H, (B) H2 and H6], 8.21 [d, 1H, (A) H6], 8.24 [d, 1H, (A) H2], 8.30 [d, 2H, (B) H3 and H6], 10.08 [s, 1H, C(H)═O], 11.40 [brs, 1H, OH], Sn–Ph skeleton: 7.49 [m, 9H, H3* and H4*], 7.83 [m, 6H, H2*], ppm. ^{13}C-NMR ($CDCl_3$); δ_C: ligand skeleton: 118.7 [(A) C5], 120.4 [(A) C3], 122.4 [(B) C2 and C6], 129.8 [(A) C2], 130.7 [(A) C6], 131.7 [(B) C3 and C5], 132.7 [(B) C4], 126.0 [(A) C1], 154.8 [(B) C1], 164.3 [(A) C4], 171.9 [CO_2], 196.4 [C(H)═O]; Sn–Ph skeleton ($^{n}J(^{13}C–^{119}Sn$, Hz)): 129.0 (60) [C3*], 130.3 (nd) [C4*], 136.9 (47) [C2*], 138.3 (nd) [C1*], ppm.

*Synthesis of Ph_3SnL^1H (**7**)*

Ph_3SnLH (**6**) (0.53 g, 0.85 mmol) in absolute ethanol (55 ml) was added drop-wise to a hot stirred ethanolic solution (25 ml) containing *para*-toluidine (0.091 g, 0.85 mmol). The reaction mixture was refluxed using a Dean–Stark moisture trap and 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 benzene and filtered. The crude product was obtained after evaporation and then recrystallized from benzene to yield orange crystals of the desired product. Yield (0.45 g, 74.2%); m.p. 183–184 °C. Anal. found: C, 66.18; H, 4.51; N, 5.98; calcd for $C_{39}H_{31}N_3O_3Sn$: C, 66.13; H, 4.41; N, 5.93%. IR (cm^{-1}): 1622 $\nu(OCO)_{asym}$. ^{1}H-NMR ($CDCl_3$); δ_H: ligand skeleton: 2.40 [s, 3H, CH_3], 7.14 [d, 1H, (B) H5], 7.27 [d, 4H, (A) H2, H3, H5 and H6], 7.90 [d, 2H, (C) H2 and H6], 8.06 [d, 2H, (B) H2 and H6], 8.28 [d, 2H, (C) H3 and H5], 8.76 [s, 1H, C(H)═N], 14.10 [brs, 1H, OH], Sn-Ph skeleton: 7.47 [m, 9H, H3* and H4*], 7.79 [m, 6H, H2*], ppm. ^{13}C-NMR ($CDCl_3$); δ_C: ligand skeleton: 21.0 [CH_3], 160.8 [C(H)═N], 164.8 [C–OH], 172.1 [CO_2], other carbons: 118.3, 118.9, 121.0, 122.2, 127.4, 128.3, 131.6, 132.1, 144.9, 145.5, 155.1; Sn-Ph skeleton ($^{n}J(^{13}C–^{119}Sn$, Hz)): 128.9 (60) [C3*], 130.1 (13) [C4*], 136.8 (46) [C2*], 137.5 (nd) [C1*], ppm.

X-ray crystallography

Orange plate crystals of **3** and **7** suitable for an X-ray crystal-structure determination were obtained from their hexane and benzene solutions, respectively. All measurements were made at 160(1) K on a Nonius Kappa-CCD diffractometer[11] fitted with graphite-monochromated MoK_α radiation (λ = 0.71073 Å) and an Oxford Cryosystems Cryostream 700 cooler. Data reduction was performed with HKL Denzo and Scalepack.[12] The intensities were corrected for *Lorentz* and polarization effects, and empirical absorption correction based on the multi-scan method[13] were applied. Equivalent

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Table 1. Crystallographic data and structure refinement parameters for **3** and **7**

	3	**7**
Empirical formula	$C_{32}H_{40}BrN_3O_3Sn$	$C_{39}H_{31}N_3O_3Sn$
Formula weight	713.19	708.29
Crystal dimensions (mm)	0.03 × 0.15 × 0.25	0.05 × 0.25 × 0.38
Colour and morphology	Orange, plate	Orange, plate
Temperature (K)	160(1)	160(1)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	C2
a (Å)	26.7487(9)	34.7582(4)
b (Å)	13.5648(6)	6.6423(1)
c (Å)	18.4337(7)	29.0970(5)
β (deg)	106.521(2)	104.9867(9)
V (Å^3)	6412.4(4)	6489.3(2)
Z	8	8
D_{calc} (g cm^{-3})	1.477	1.450
Linear absorption coefficient (mm^{-1})	2.081	0.830
Transmission factors (min, max)	0.677, 1.000	0.817, 0.960
$2\theta_{max}$ (deg)	50	50
Reflections measured	86 236	51 237
Independent reflections (R_{int})	11 183 (0.183)	11 403 (0.069)
Reflections with $I > 2\sigma(I)$	5732	8612
Number of parameters	764	870
Number of restraints	67	169
$R(F)$ [$I > 2\sigma(I)$ reflns]	0.088	0.040
$wR(F^2)$ (all data)	0.163	0.091
GOF(F^2)	1.096	1.020
max, min $\Delta\rho$(e Å^{-3})	1.14, −0.92	1.17, −0.62

reflections were merged, except for the Friedel pairs for **7**. The data collection and refinement parameters are given in Table 1. The structures were solved by direct-methods using *SHELXS97*[14] and the non-hydrogen atoms were refined with anisotropic atomic displacement parameters. There are two symmetry-independent molecules in the asymmetric unit of each structure. The atomic coordinates were tested carefully for a relationship from a higher symmetry space group using the program *PLATON*,[15] but none could be found.

For **3**, the terminal propyl segment of one butyl group in one of the symmetry-independent molecules is disordered over two conformations. Two sets of overlapping positions were defined for the disordered atoms and the site occupation factor of the major conformation refined to 0.67(2). Bond length and similarity restraints were applied to the chemically equivalent bonds and angles involving all disordered C atoms, while neighbouring atoms within and between each conformation were restrained to have similar atomic displacement parameters.

For **7**, the 4-methylphenyl ring in one of the symmetry independent molecules is disordered through a rotation of the ring plane about its 1,4-axis. Two sets of positions were defined for the 1,3,5,6-atoms of this ring and the site occupation factor of the major orientation of the ring refined to 0.58(1). Similarity restraints were applied to the lengths of the chemically equivalent bonds involving all disordered C atoms, while neighbouring atoms within and between each conformation of the disordered ring were restrained to have similar atomic displacement parameters.

For **3**, the phenoxy H atoms were placed in the positions indicated by a difference *Fourier* map and their positions were allowed to refine together with individual isotropic displacement parameters. Although the hydroxy H-atoms in **7** were initially located in a difference *Fourier* map, their positions were subsequently optimized. All of the remaining H atoms in both structures 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 1.2 U_{eq} of its parent atom (1.5U_{eq} for the methyl and hydroxy groups).

The refinement of each structure was carried out on F^2 using a full-matrix least-squares procedure, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. Corrections for secondary extinction were not applied. For **7**, one reflection, whose intensity was considered to be an extreme outlier, was omitted from the final refinement, while refinement of the absolute structure parameter[16,17] yielded a value of −0.08(2), thereby confirming that the model represents the true absolute structure. All calculations were performed using the SHELXL97 program.[18]

Biological tests

Preparation of the organotin stock solution

Stock solutions of the tri-*n*-butyltin compounds **1–5**, were prepared by dissolving the complexes in 95% ethanol. The dissolution of the compounds **1–5** in the organic media was to facilitate the dispersion of the compounds in water.

Mosquito larvae

Dried *Ae. aegypti* mosquito eggs and *An. Stephensi* larvae were obtained from the Entomology Department at the Walter Reed Army Institute of Research, Washington, DC. *Ae. aegypti* eggs were hatched in a tray of tap water and after 2–3 days the second larval instar stage was attained. The larvae were maintained in an environmental chamber at 27–28 °C with a humidity of 60–90%. The *An. stephensi* larvae were kept in the same environment chamber under the same conditions. Both species of larvae were fed with ground dog food.

Larval toxicity studies

The toxicity studies were performed in 100 × 15 mm disposable Petri dishes using 10 larvae in the second

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instar stage. The *Ae. aegypti* or *An. stephensi* larvae were transferred into the Petri dishes using a 100 μl micro-pipette. An additional 15 ml of deionized water were then added. No turbidity was observed upon the addition of the water. Aliquots of the tri-*n*-butyltin(IV) solution were then added to the Petri dish containing the larvae along with deionized water to give the desired concentration of the tri-*n*-butyltin(IV) compounds. The total assay volume in each case was 20 ml. Both positive and negative controls were used in the assays. The larvae were exposed to the tri-*n*-butyltin(IV) 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. A minimum of three trials was used for each assay. Probit analyses[19] were used to determine the LC_{50} (concentration at which the test compounds killed 50% of the tested organisms).

RESULTS AND DISCUSSION

Synthetic aspects

The 4-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid ligand [LHH′, Fig. 1(a)] was prepared by the diazo-coupling reaction between the *para*-aminobenzoic acid and salicylaldehyde in an alkaline medium under cold conditions. The 4-{(*E*)-4-hydroxy-3-[(*E*)-4-(aryl)iminomethyl]phenyldiazenyl}benzoic acid ligand ($L^{1-4}HH'$) could not be prepared by the condensation of LHH′ with appropriate substituted anilines owing to the insolubility of the pre-ligand in common organic solvents and water. However, the deprotonated $L^{1-4}HH'$ frameworks were generated during the reaction of R_3SnLH (R = ^{n}Bu or Ph) with the appropriate *para*-substituted anilines. The basic ligand framework is shown in Fig. 1, along with the abbreviations and numbering scheme for the spectroscopic analyses. The details of their synthesis and characterization are presented in the experimental section.

$^n Bu_3SnLH$ and Ph_3SnLH were obtained from the reaction of LHH′ with $(^n Bu_3Sn)_2O$ and Ph_3SnOH, respectively, in anhydrous toluene. These compounds were then condensed with the appropriate *para*-substituted anilines in absolute ethanol to obtain the other tri-*n*-butyltin(IV) and triphenyltin(IV) compounds. 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 soluble in all common organic solvents.

Spectroscopy

The diagnostically important infrared absorption frequencies for the carboxylate antisymmetric [ν_{asym}(OCO)] stretching vibration of the ligands and their complexes with triorganotin(IV) 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 comparisons with the spectra of the free ligands (LHH′). The antisymmetric [ν_{asym}(OCO)] stretching vibration for the uncomplexed pre-ligand (LHH′) occurs at 1679 cm^{-1}. In the triorganotin(IV) complexes with the pre-ligand (**1** and **6**), the carbonyl stretching frequency appears at $\sim 1647 \pm 8$ cm^{-1}, while in the other complexes (**2–5** and **7**) this frequency was found to be shifted further to ~ 1620 cm^{-1}. The shift of the band relative to its position for the free pre-ligand is ascribed to the carboxylate coordination in accordance with earlier reports.[3,20,21]

The ^1H and ^{13}C NMR data of LHH′ are given in the experimental section. The signals were assigned by the use of correlated spectroscopy (COSY), heteronuclear single-quantum correlation (HSQC) and heteronuclear multiple-bond connectivitiy (HMBC) experiments using gradient coherence selection. The conclusions drawn from the pre-ligand assignments were then subsequently extrapolated to complexes **1** and **6** owing to their data similarity. The ^1H NMR integration values were completely consistent with the formulation of the products. The assignments of the individual ^{13}C NMR signals (except for a few) could not be made, since the data for the free ligands (L^1HH'–L^4HH') are unavailable and hence cannot be compared. Moreover, the ^{13}C NMR spectra of the complexed ligands, which were generated *in situ*, are rather complex. However, the number of ^{13}C signals corresponds with the proposed formulations of the products. The ^1H and ^{13}C chemical shift assignment of the triorganotin(IV) moiety is straightforward from the multiplicity patterns, resonance intensities and also by examining the $^nJ(^{13}C–^{119/117}Sn)$ coupling constants.[20–22] The ^{119}Sn NMR chemical shifts of the triorganotin(IV) complexes (**1–7**) in $CDCl_3$ solution are listed in Table 2. Both the tri-*n*-butyltin(IV) (**1–5**) and triphenyltin(IV) (**6, 7**) complexes exhibit a single sharp resonance at around 115 and −107 ppm, respectively. Their ^{119}Sn NMR values fall within the ranges specified for tetrahedral tri-*n*-butyltin(IV) compounds[23] and triphenyltin(IV) compounds,[20,22,24] respectively. This is further supported by our recent work on the tri-*n*-butyltin(IV)[3] and triphenyltin(IV)[8] carboxylates which were derived from the *ortho*-analogs of the ligands.

Table 2. ^{119}Sn NMR data (δ, ppm) and ^{119}Sn Mössbauer parameters (mm s^{-1}) for the triorganotin(IV) complexes

Compound	^{119}Sn NMR data[a]	^{119}Sn Mössbauer data[b]		
		δ	Δ	$\rho = \Delta/\delta$
1	116.5	1.41	3.42	2.42
2	114.7	1.37	2.75	2.0
3	115.1	1.38	2.82	2.0
4	114.9	1.39	2.88	2.07
5	114.3	1.33	2.62	1.97
6	−107.7	1.22	2.28	1.87
7	−107.9	1.15	2.39	2.08

[a] In $CDCl_3$ solution.
[b] Parameters: δ, isomer shifts; Δ, quadrupole splitting.

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In order to obtain further structural evidence, the ^{119}Sn Mössbauer spectra were recorded for the triorganotin(IV) complexes in the solid state (Table 2). The ratio of the quadrupole splitting to the isomer shift value ($\rho = \Delta/\delta$) can be used to distinguish between the different geometries of the central tin atom.[25] Tin compounds which are four coordinated have ρ values less than 1.8 while ρ values larger than 2.1 would indicate compounds with a greater than 4 coordination. As can be seen in Table 2, complexes **2–5** have $\rho \leq 2.1$ suggesting that the complexes have a coordination number of 4. This was subsequently confirmed by the determination of the crystal structure of the representative complex **3**. On the other hand, complex **1** has a ρ value of 2.42 which is indicative of a coordination number greater than 4. Similar ρ values were recently observed for the polymeric tri-*n*-butyltin(IV) compounds possessing a *trans*-Bu_3SnO_2 trigonal bipyramidal geometry.[3] Furthermore, complex **1** exhibited a higher quadrupole splitting (Δ) value of ca. 3.42 mm s^{-1} compared to complexes **2–5**. Similar Δ values were also encountered in its ortho-analogue, which has been characterized crystallographically. This value is within the range 3.0–4.1 mm s^{-1}, which is consistent with a *trans*-Bu_3SnO_2 trigonal bipyramidal geometry with ^{n}Bu groups in the equatorial plane and two axial carboxylate oxygen atoms.[26] Such a structural configuration has also been noted for trialkyltin(IV) *para*-carboxylates.[2,27] Thus, it may be inferred that complex **1** has a trigonal bipyramidal geometry, while rest of the tri-*n*-butyltin(IV) complexes (**2–5**) are tetrahedral (see the crystal structure discussion, below). Furthermore, the triphenyltin(IV) complexes (**6–7**) exhibited Δ and ρ values of ~2.30 mm s^{-1} and ~2.0, respectively, which correspond to a tetrahedral geometry around the tin atom[8,26,28,29] and is in agreement with the crystal structure of complex **7**.

X-ray crystallography

Compound **7** crystallizes with two symmetry-independent monomeric molecules in the asymmetric unit (molecules A and B). The primary coordination sphere of the Sn atom is best described as 4-coordinate with a distorted C_3O tetrahedral geometry involving one of the carboxylate O atoms and the C atoms from the three phenyl ligands (Table 3, Fig. 2). The other carboxylate O atom of the benzoate ligand also coordinates weakly to the Sn atom with the Sn···O distances being 2.773(4) and 2.579(4) Å for molecules A and B, respectively. This interaction is the cause of the distortion of the tetrahedral primary coordination sphere, but the Sn···O distance is considered to be too long for the Sn atom to be described as truly 5-coordinate. In

Table 3. Selected bond lengths (Å) and angles (deg) for the two symmetry-independent molecules of **7**

	Molecule A	Molecule B
Sn1–O1	2.061(3)	2.115(4)
Sn1···O2	2.773(4)	2.579(4)
Sn1–C22	2.120(6)	2.132(5)
Sn1–C28	2.132(5)	2.129(6)
Sn1–C34	2.113(5)	2.117(5)
O1–C1	1.324(7)	1.233(7)
O2–C1	1.214(6)	1.256(9)
N1–N2	1.260(5)	1.245(6)
O1–Sn1···O2	51.8(1)	53.6(2)
O1–Sn1–C22	113.7(2)	124.6(2)
O1–Sn1–C28	99.1(2)	93.2(2)
O1–Sn1–C34	105.9(2)	103.9(2)
O2···Sn1–C22	82.8(2)	86.8(2)
O2···Sn1–C28	150.6(2)	145.4(2)
O2···Sn1–C34	83.0(2)	89.6(2)
C22–Sn1–C28	110.9(2)	109.1(2)
C22–Sn1–C34	114.1(2)	113.9(2)
C28–Sn1–C34	112.2(2)	110.1(2)
Sn1–O1–C1	109.3(4)	104.5(4)
Sn1–O2–C1	78.3(4)	81.7(4)
O1–C1–O2	120.6(6)	120.2(6)

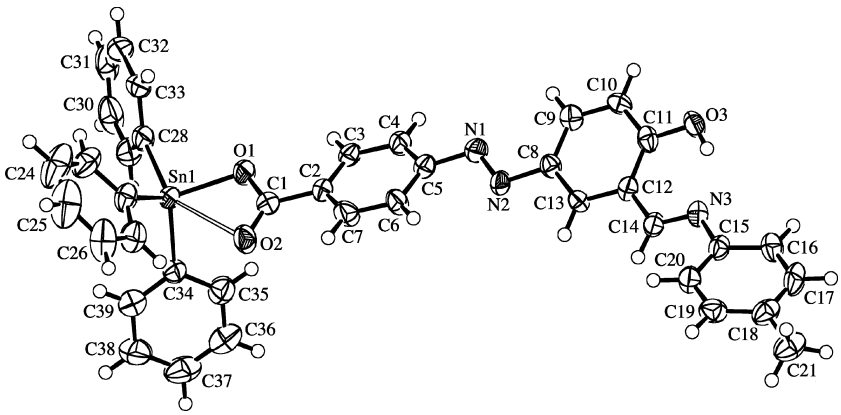

Figure 2. A view of the one of the symmetry-independent molecules (molecule A) of Ph_3SnL^1H (**7**) showing the atom-labeling scheme (50% probability ellipsoids).

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addition, the bond angles around the Sn atom in **7** are more consistent with a tetrahedral environment than with a trigonal bipyramidal five-coordinate environment. If the longer of the Sn · · · O interactions is interpreted as a significant bonding interaction, then the geometry about the tin atom would be described as *cis*-R_3SnO_2 trigonal bipyramidal with, for molecule A, atoms C22, C34 and O2 defining the trigonal plane. In this description, the Sn atom lies 0.636(1) Å out of the equatorial plane in the direction of atom C28. The corresponding displacement in molecule B is 0.518(1) Å. These significant displacements suggest that a trigonal bipyramidal description of the coordination environment, in which the carboxylate ligand is chelating asymmetrically, may be less appropriate than assigning the coordination as tetrahedral. The displacements are comparable with those described for related triphenyltin carboxylate complexes for which the 4-coordinate tetrahedral description of the coordination geometry was also favoured.[21,22] While the overall geometry of the two symmetry-independent molecules of **7** is similar, there is a notable difference at the carboxylate group. Whereas the carboxylate C–O distances in molecule A suggest the presence of distinct carbonyl and carboxyl O atoms (Table 3), the corresponding distances in molecule B are more in keeping with a fully delocalized carboxylate group. As a direct and consistent reflection of this difference, the bonding Sn–O distance in molecule A is shorter than that in molecule B, while the Sn · · · O distance is significantly shorter in molecule B than in molecule A.

The coordination motif in the structure of **7** is often found for compounds of this type.[21,30,31] The monomeric motif contrasts with the polymeric motifs shown in Scheme 1 that are found for the triorganotin(IV) complexes with the related *ortho*-substituted benzoate ligands.[1–8] This difference may relate to the synthetic route to the complexes. Whereas the complete *ortho*-ligand was synthesized first and then reacted with trialkyltin(IV), it was necessary to prepare the trialkyltin(IV) complexes of the *para*-pre-ligand initially and then perform the condensation reaction to give the extended ligands (see Experimental section).

As a result of difficulty in obtaining high-quality crystals of compound **3**, despite repeated attempts, the quality of the results for **3** is less than optimal, so that a fine analysis of the geometric parameters is not warranted. Compound **3** also crystallizes with two symmetry-independent monomeric molecules in the asymmetric unit and the coordination geometry of the Sn atom in each independent molecule (Fig. 3) is essentially identical with that of molecule A of compound **7**. In the structures of **3** and **7**, the phenoxy H atom forms an intramolecular hydrogen bond with the imine N atom.

Larval toxicity studies

The LC_{50} values (μM) and their standard deviations for the complexes (**1**–**5**) screened against the second larval instar stage of the *Ae. aegypti* and *An. stephensi* mosquitoes are given in Table 4. They ranged from 1.21 to 3.38 μM for the *Ae. aegypti* and from 0.83 to 2.31 μM for the *An. stephensi*. The observed toxicity data for this series of compounds indicated that their toxicity values are in the range of other tributyl-,[3,6,9,32] triphenyl-[9,32–34] and tricyclohexyltins.[32–34]

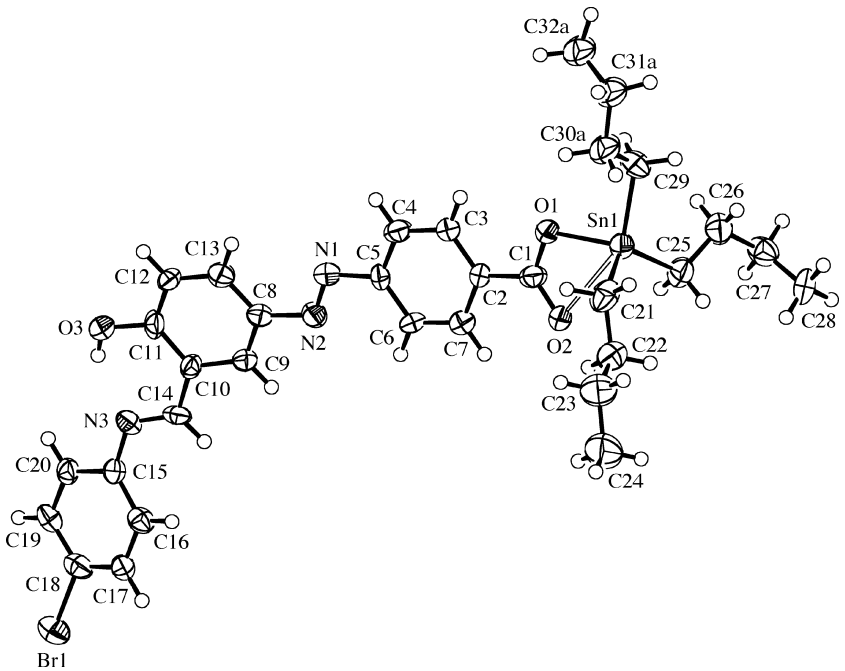

Figure 3. A view of the one of the symmetry-independent molecules (molecule A) of $^{n}Bu_3SnL^2H$ (**3**) showing the atom-labeling scheme (50% probability ellipsoids) and only one conformation of the disordered ^{n}Bu group.

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Table 4. LC_{50} value (in μM) of the tri-*n*-butyltin(IV) complexes against the second instar larval stage of the *Ae. aegypti* and *An. stephensi* mosquito larvae

Compound[a]	*Ae. aegypti*	*An. stephensi*
1	2.57 ± 0.05 (0.48 ± 0.04[9])[b]	1.11 ± 0.05 (0.84 ± 0.02)[b]
2	3.38 ± 0.08 (0.85 ± 0.06)[b]	2.31 ± 0.06 (1.80 ± 0.02)[b]
3	1.21 ± 0.11 (0.50 ± 0.03)[b]	1.14 ± 0.07 (1.15 ± 0.03)[b]
4	2.47 ± 0.21 (1.03 ± 0.02)[b]	0.83 ± 0.13 (1.50 ± 0.03)[b]
5	1.67 ± 0.02 (0.86 ± 0.05)[b]	1.40 ± 0.08 (1.32 ± 0.06)[b]

[a] Refer to Fig. 1 for the ligand framework (LHH′ and L^1HH' to L^4HH').
[b] Values in parentheses are for the respective tri-*n*-butyltin(IV) compounds derived from *ortho*-carboxy analogs. Data was taken from Basu Baul *et al*.[6] for comparison.

A comparison of the toxicity effects of the compounds of the two species of mosquito larvae indicates that the *Ae. aegypti* larvae were more tolerant to this set of compounds. In the earlier *ortho* analogs, the *An. stephensi* larvae were more tolerant. The observation that there is a difference in toxicities of two similar series of compounds towards two different species of mosquito larvae is not atypical. This phenomenon has been reported previously.[33,34] Even the same compound has shown differences in tolerance to different strains of the same mosquito larvae.[32,35] Thus, these results give further support to the conclusion that the toxicity of triorganotin compounds towards mosquito larvae is dependent on both the compound and the species of mosquito larvae.[33]

It has been reported that the triorganotin cation, R_3Sn^+, is responsible for the toxicity of triorganotin compounds against these two species of mosquito larvae[32,33] as well as on *Ceratocystis ulmi* (*C. ulmi*.), the fungus responsible for Dutch elm disease.[36–38] Comparison of the toxicities of the current series of complexes **1**–**5** (*para* derivatives) with those of their analogs (*ortho* derivatives) indicated that, in general, the *ortho* complexes were more toxic to the mosquito larvae. Assuming that the toxicity is caused by the R_3Sn^+ cation, it would then appear that the *ortho* derivatives are more able to dissociate into the triorganotin cation once the complex has been transported into the active site. It appears that the role of the ligand may be one of transporting the complex into the active site or imparting increased water solubility to the compounds. Both of these factors have been cited, in the literature, as increasing the toxicity of triorganotin complexes.[39,40]

For the current series of compounds, a common order of activity was not observable accross both species of mosquito larvae as a function of the X group on the ligand. The X substituent is far removed from the tin center, its influence on the dissociation of the ligand to give the R_3Sn^+ cation can only be minimal at best. A similar conclusion was drawn for a series of triorganotin dithiocarbamates screened against these two species of mosquito larave.[33] This line of reasoning was used to explain the inhibition of *C. ulmi* by a series of N-alkylsalicylideneimines.[38]

Any further modification of the organotin molecules in the hopes of increasing their activity against these two species of mosquito larvae should focus on compounds that would enhance the formation and stabilization of the triorganotin cation. Triorganotins have an advantage over currently used pesticides since organotin compounds are known to biodegrade in the environment to non-toxic inorganic tin compounds.[41]

Supplementary Material

CCDC-604932 and 604933 contain the supplementary crystallographic data for complexes **3** and **7**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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