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Triphenyltin Esters of *N*-(2-Carboxybenzylidene)anilines: Synthesis, Spectroscopic Characterization, X-ray Structure Analysis and Fungicidal Activity*

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Four triphenyltin carboxylates formulated as *o*-$Ph_3SnOCOC_6H_4CH{=}N{-}Ar$ ($Ar = C_6H_5$; *p*-$CH_3C_6H_4$; *o*-$CH_3C_6H_4$; *o*-HOC_6H_4) were prepared and spectroscopically characterized. The crystal structure of *o*-$Ph_3SnOCOC_6H_4CH{=}NC_6H_5$ indicates that the tin atom, in each of the two molecules comprising the asymmetric unit, exists in a distorted tetrahedral geometry owing to an intramolecular acyl O...Sn contact. These new triphenyltin carboxylates display marked toxicity against the fungus *Ceratocystis ulmi*.

Keywords: triphenyltin; carboxylate; spectroscopy; crystal structure; fungitoxicity; *Ceratocystis ulmi*

INTRODUCTION

In recent years, triphenyltin compounds (Ph_3SnX), including triphenyltin acetate, have achieved commercialization as agricultural fungicides.[1-5] The effect of the anionic group (X) is not clear, as reports[1,3,6,7] cite both the insignificance and importance of this group. In addition to their fungicidal properties, triphenyltin carboxylates (X= substituted benzoic acids) present an interesting structural investigation. They have been reported to have various structural possibilities with either a tetrahedral or a trigonal bipyramidal geometry for the tin atom.[8] Therefore we describe here the synthesis of several triphenyltin derivatives of *N*-(2-carboxybenzylidene)anilines. These new carboxylates with the formula *o*-$Ph_3SnOCOC_6H_4CH{=}NAr$ [$Ar = C_6H_5$ (**1**); $Ar =$ *p*-$CH_3C_6H_4$ (**2**); $Ar =$ *o*-$CH_3C_6H_4$ (**3**); $Ar =$ *o*-HOC_6H_4 (**4**)] were spectroscopically characterized and screened *in vitro*, using a shake culture method against the fungus *Ceratocystis ulmi*, the causative agent of Dutch elm disease. An X-ray crystal structure analysis of triphenyltin 2-phenyliminomethylbenzoate (**1**) is also reported.

EXPERIMENTAL

The starting materials were of reagent or analytical grade and used as received. Bis(triphenyltin) oxide and 2-carboxybenzaldehyde were purchased from Aldrich Chemicals, Milwaukee, WI, USA. The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Model AM 500 spectrometer using tetramethylsilane (TMS) as the reference. Infrared spectra were recorded as KBr pellets in a Perkin–Elmer Model 1725FT-IR spectrometer. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY, USA, and at the School of Chemical Sciences, Universiti Sains Malaysia, Malaysia. The Mössbauer spectra were measured at 80 K on a Mössbauer spectrometer, Model MS-900 (Ranger Scientific Co.,

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* Atomic coordinates for the title structure have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK.

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Burelson, TX, USA) in the acceleration mode with a moving-source geometry using a liquid-nitrogen cryostat (CYRO Industries of America Inc., Salem, NH, USA). The samples were mounted in Teflon holders. The source was 15 mCi $Ca^{119m}SnO_3$, and the velocity was calibrated at ambient temperature using a composition of $BaSnO_3$ and tinfoil (splitting -2.52 mm s^{-1}). The resultant spectra were analysed by a least-squares fit to Lorenzian-shaped lines.

Preparation of triphenyltin 2-aryliminomethylbenzoates: Method A

To a suspension of 2-carboxybenzaldehyde (0.75 g, 5 mmol) and bis(triphenyltin) oxide (1.8 g, 2.5 mmol) in 50 ml of benzene or toluene was added the appropriate substituted aniline (5 mmol). The stirred mixture was refluxed and the water formed was removed azeotropically using a Dean–Stark apparatus. After all the water had been removed from the reaction mixture (5–6 h) the solvent was evaporated with a rotary evaporator. On cooling, *ca* 10 ml of petroleum ether (b.p. 30–75 °C) was added to the concentrated solution before putting it in the freezer overnight. The product was then filtered off and purified by recrystallization from ligroin or petroleum ether. The elemental analyses and the melting points are given in Table 1, below.

Preparation of triphenyltin 2-formylbenzoate: Method B

A mixture of 2-carboxybenzaldehyde (3 g, 20 mmol) and bis(triphenyltin) oxide (7.16 g, 10 mmol) in 150 ml of benzene was refluxed for *ca* 4 h and the water formed was removed azeotropically using a Dean–Stark apparatus. The mixture was concentrated on a rotary evaporator and, on cooling, petroleum ether (b.p. 30–75 °C) was added to induce precipitation. The product (9.2 g, yield 92%), isolated by filtration, was purified in petroleum ether to afford colourless crystals of triphenyltin 2-formylbenzoate, m.p. 114 °C. Analysis: Calcd for $C_{26}H_{20}O_3Sn$: C, 62.56; H, 4.05. Found: C, 62.32; H, 3.97%. IR (KBr; ν, cm^{-1}): 1667, 1646 (CO_{asym}); 1350, 1323 (OCO_{sym}). ^1H NMR ($CDCl_3$; δ, ppm): 10.77 (s, CH=O); 7.20–8.15 (m, aromatic).

A mixture of triphenyltin 2-formylbenzoate (1.0 g, 2 mmol) and the appropriate substituted aniline (2 mmol) in 50 ml of benzene was refluxed for 3–4 h and the water formed was removed azeotropically. On cooling, the mixture was concentrated under reduced pressure and petroleum ether was added to the mixture before allowing it to stand in the freezer overnight. The product was filtered off and recrystallized from petroleum ether. Melting points and analytical data are summarized in Table 1, below.

Preparation of stock organotin solutions and fungicidal activity determination

The preparation of the organotin stock solutions and fungus for the toxicity studies has been previously described.[9] A stock suspension (1.0 ml) of cells of *Ceratocystis ulmi* (concentration$=10^6$ cells ml^{-1}), strain 32437, obtained from the American Type Culture Collection, Rockville, MD 20852, USA, was added to amended potato dextrose broth, and the resulting suspension was then shaken for seven days in an incubator–shaker (22 °C). The contents of the flask were then filtered and rinsed with distilled water. The fungal growth was dried and weighed until a constant weight was obtained. Three replicates were used for each concentration tested.

The inhibitory concentration value was obtained by plotting the percentage growth of the fungus versus the concentration of organotin compound (parts per million) added. The concentration at which 50% of the fungus is inhibited is taken as the inhibitory concentration value (IC_{50}).

X-ray crystallography of *o*-$Ph_3SnOCOC_6H_4CH{=}NC_6H_5$ (1)

Crystal data: $C_{32}H_{25}NO_2Sn$, *Mr* 574.2, triclinic, space group $P\bar{1}$,

$a=9.680(2)$ Å, $b=14.580(4)$ Å,
$c=19.796(5)$ Å, $\alpha=101.68(2)°$,
$\beta=94.21(2)°$, $\gamma=96.27(2)°$,
$V=2706.6(11)$ $Å^3$, $Z=4$,
$D_{cal}=1.409$ Mg m^{-3} and $F(000)=1160$.

A selected crystal of dimensions 0.30 mm×0.25 mm×0.20 mm was used. Diffraction data ($3.0°<2\Theta>50.0°$, 9609 unique reflections) collected on a Siemens R3M/V

Table 1 Analytical, physical and IR data of triphenyltin 2-aryliminomethylbenzoates, *o*-$Ph_3SnOCOC_6H_4CH{=}NAr$

					Elemental analysis (%): Found (calcd.)			IR(cm^{-1})		
								ν(O–C=O)		
Compound	Ar	Preparation method	Yield (%)	Melting point (°C)	C	H	N	Asym.	Sym.	$\Delta\nu$
1	C_6H_5	B	75	106–108	67.05 (66.93)	4.55 (4.39)	2.34 (2.44)	1626	1339	287
2	*p*-$CH_3C_6H_4$	B	65	98–100	67.21 (67.38)	4.75 (4.63)	2.38 (2.38)	1626	1344	282
3	*o*-$CH_3C_6H_4$	A	80	102–103	67.15 (67.38)	4.82 (4.63)	2.34 (2.38)	1622	1363	259
4	*o*-HOC_6H_4	B	70	148–150	65.65 (65.12)	4.54 (4.27)	2.39 (2.37)	1621	1348	273

Table 2 ^1H and ^{13}C NMR, Mössbauer data and IC_{50} values against *Ceratocystis ulmi* for triphenyltin 2-aryliminomethylbenzoates

	^1H NMR, δ(ppm)			^{13}C NMR, δ(ppm)				Mössbauer (mm s^{-1})		
Compound	CH=N	CH_3	Aromatic	CH_3	COO	CH=N	Aromatic	Quadrupole splitting ±0.02	Isomer shift ±0.01	IC_{50} (mg dm^{-3})
1	9.36		7.2–8.3		173.21	166.70	152.03; 138.3–115.1	2.35	1.22	0.8
2	9.38	2.40	7.1–8.2	21.07	173.30	159.70	149.42; 138.1–115.4	2.32	1.23	0.4
3	9.29	2.38	6.9–8.3	17.87	173.29	159.78	151.17; 138.1–118.1	2.40	1.21	0.6
4	9.62		6.9–8.2		173.45	157.14	152.50; 138.3–114.9	2.55	1.26	0.8

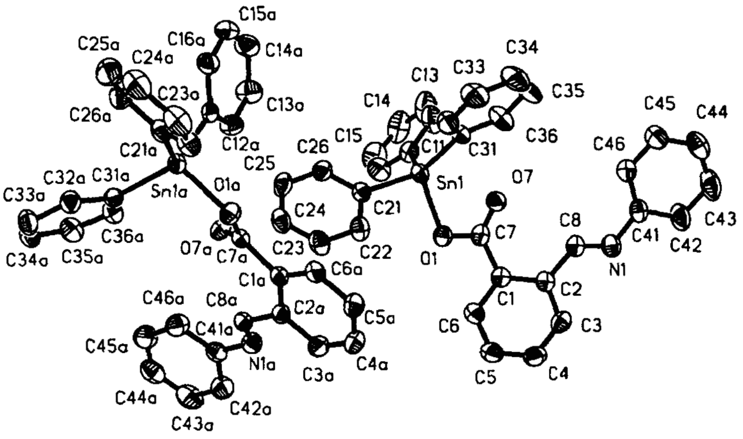

Figure 1 Molecular structure and crystallographic numbering scheme for o-$Ph_3SnOCOC_6H_4CH{=}NH_6H_5$.

diffractometer using the ω-scan mode (2.49–29.30° min^{-1}) were reduced and corrected for Lorentz and polarization factors using the applied programs. Semi-empirical absorption corrections were applied ($m\mu = 0.972\ mm^{-1}$, transmission factors 0.8066–0.8609). A total of 7209 observed reflections with $|F|>4\sigma|F|$ were used in the structure analysis. The structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically.[10] All hydrogen atoms were placed at calculated positions (C–H = 0.96 Å) and included in structure-factor calculations with fixed isotropic thermal parameters. Final R and R_w values are 0.0269 and 0.0362, data to parameter ratio = 11.1 : 1 and the weight scheme $w=[\sigma^2(|F_o|)+0.0010\ |F_o|^2]^{-1}$. The residual electron density peaks in the final difference map are in the range of +0.40 to $-0.33\ e\ Å^{-3}$.

RESULTS AND DISCUSSION

The triphenyltin carboxylates, o-$Ph_3SnOCOC_6H_4CH{=}NAr$, listed in Table 1 can be prepared by refluxing a mixture of bis(triphenyltin) oxide, 2-carboxybenzaldehyde and the appropriate aniline in benzene/toluene as shown by Eqn [1] below (Method A)

$$(Ph_3Sn)_2O + 2\ o\text{-}HOOCC_6H_4CHO + 2H_2N\text{-}Ar \rightarrow o\text{-}Ph_3SnOCOC_6H_4CH{=}N\text{-}Ar + 2H_2O \qquad [1]$$

Alternatively, the carboxylates can be synthesized through the intermediate, triphenyltin 2-formylbenzoate, as shown in Eqn [2] (Method B):

$$o\text{-}Ph_3SnOCOC_6H_4CHO + H_2N\text{–}Ar \rightarrow o\text{-}Ph_3SnOCOC_6H_4CH{=}N\text{–}Ar + H_2O \qquad [2]$$

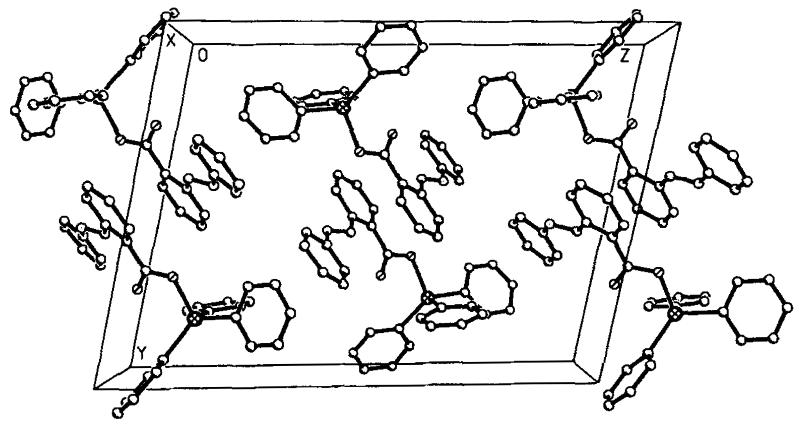

Figure 2 The packing view of the unit cell of o-$Ph_3SnOCOC_6H_4CH{=}NC_6H_5$.

The yields for the two methods are comparable and in the range of 65–80%. The melting points and analytical data for the range of carboxylates synthesized are shown in Table 1. All the carboxylates listed in Table 1 were isolated as yellowish solids (except **4**, dark brown) that were stable in air.

The ^{1}H and ^{13}C NMR signals for the triphenyltin carboxylates, **1**–**4**, are recorded in Table 2. A singlet located at $\delta = 9.29-9.62$ ppm is recorded for the azomethine proton of **1**–**4**. The absence of the spin–spin coupling between the azomethine proton and the tin nucleus, ^3J(SnN=CH), which would confirm the presence of a tin–nitrogen coordination,[11] indicates that the azomethine nitrogen is *not* involved in coordination with the tin atom.

The observed infrared absorption frequencies for the carboxylic antisymmetric [ν_{asym}(OCO)] and symmetric [ν_{sym}(OCO)] stretching vibrations are shown in Table 1. The assignment of the ν_{asym}(OCO) band is complicated by the presence of the ν(C=N) stretching vibration, which is observed in the region 1611–1620 cm^{-1}. Nevertheless, the magnitude of the ν_{asym}(OCO) − ν_{sym}(OCO) separation (i.e. $\Delta\nu$) is of interest. The observed values of $\Delta\nu$, which are in the range 259–287 cm^{-1}, indicate a unidentate

Table 3 Atomic coordinates (×10^4) for *o*-$Ph_3SnOCOC_6H_4CH{=}NC_6H_5$

Molecule **a**				Molecule **b**			
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Sn(1)	3535(1)	1770(1)	8472(1)	Sn(1A)	1422(1)	2018(1)	3600(1)
N(1)	6599(3)	4405(2)	11382(2)	N(1A)	−1337(3)	4245(2)	6193(1)
O(1)	3048(3)	3004(2)	9063(1)	O(1A)	2117(2)	3363(2)	4181(1)
O(7)	4539(3)	2621(2)	9828(1)	O(7A)	592(2)	2786(1)	4806(1)
C(1)	3481(3)	4035(2)	10165(2)	C(1A)	1752(3)	4351(2)	5253(2)
C(2)	4455(3)	4480(2)	10726(2)	C(2A)	803(3)	4658(2)	5724(2)
C(3)	4104(4)	5253(3)	11189(2)	C(3A)	1191(4)	5479(2)	6222(2)
C(4)	2839(4)	5577(3)	11105(2)	C(4A)	2498(4)	5980(3)	6262(2)
C(5)	1908(4)	5156(3)	10545(2)	C(5A)	3424(4)	5685(3)	5797(2)
C(6)	2222(4)	4388(3)	10073(2)	C(6A)	3058(3)	4878(2)	5289(2)
C(7)	3753(4)	3168(3)	9677(2)	C(7A)	1436(3)	3442(2)	4728(2)
C(8)	5868(4)	4199(2)	10809(2)	C(8A)	−650(3)	4171(2)	5670(2)
C(11)	2779(4)	639(3)	8925(2)	C(11A)	2219(3)	1007(2)	4112(2)
C(12)	3701(5)	109(3)	9203(3)	C(12A)	1889(4)	911(2)	4765(2)
C(13)	3202(7)	−605(4)	9515(3)	C(13A)	2399(5)	228(3)	5067(2)
C(14)	1819(7)	−804(4)	9560(3)	C(14A)	3207(5)	−370(3)	4724(2)
C(15)	829(6)	−343(4)	9250(3)	C(15A)	3548(4)	−295(3)	4080(2)
C(16)	1372(5)	384(3)	8925(2)	C(16A)	3061(4)	392(2)	3773(2)
C(21)	2223(3)	1871(2)	7583(2)	C(21A)	2555(3)	2152(2)	2735(2)
C(22)	2011(4)	2743(3)	7452(2)	C(22A)	3503(3)	2943(3)	2738(2)
C(23)	1113(4)	2813(3)	6889(2)	C(23A)	4224(4)	3024(3)	2174(2)
C(24)	424(4)	2030(3)	6458(2)	C(24A)	4024(4)	2338(4)	1559(2)
C(25)	607(4)	1158(3)	6580(2)	C(25A)	3111(5)	1542(4)	1570(2)
C(26)	1508(4)	1071(3)	7140(2)	C(26A)	2375(4)	1444(3)	2140(2)
C(31)	5677(3)	1892(2)	8305(2)	C(31A)	−754(3)	1783(2)	3285(2)
C(32)	6060(4)	2033(3)	7670(2)	C(32A)	−1239(3)	1854(3)	2624(2)
C(33)	7432(5)	2125(3)	7543(2)	C(33A)	−2653(4)	1660(3)	2396(2)
C(34)	8455(5)	2067(4)	8043(3)	C(34A)	−3582(4)	1388(3)	2823(2)
C(35)	8112(4)	1927(4)	8670(3)	C(35A)	−3124(4)	1314(3)	3487(2)
C(36)	6730(4)	1866(3)	8819(2)	C(36A)	−1719(3)	1515(2)	3719(2)
C(41)	7963(4)	4218(3)	11426(2)	C(41A)	−2751(3)	3817(2)	6114(2)
C(42)	8878(5)	4603(4)	11964(2)	C(42A)	−3612(4)	4207(3)	6590(2)
C(43)	10229(5)	4396(5)	12043(3)	C(43A)	−5005(5)	3828(4)	6543(3)
C(44)	10654(5)	3686(4)	11599(3)	C(44A)	−5537(4)	3054(3)	6036(3)
C(45)	9764(5)	3194(4)	11065(3)	C(45A)	−4702(4)	2675(3)	5569(3)
C(46)	8406(5)	3413(3)	10973(3)	C(46A)	−3292(4)	3039(3)	5608(2)

Table 4 Selected bond distances (Å) and angles (deg) for *o*-$Ph_3SnOCOC_6H_4CH{=}NC_6H_5$

Molecule a		Molecule b	
Atoms	Distance	Atoms	Distance
Sn(1)-O(1)	2.059(2)	Sn(1A)-O(1A)	2.075(2)
Sn(1)-C(11)	2.119(4)	Sn(1A)-C(11A)	2.129(3)
Sn(1)-C(21)	2.133(3)	Sn(1A)-C(21A)	2.130(3)
Sn(1)-C(31)	2.117(3)	Sn(1A)-C(31A)	2.123(3)
O(1)-C(7)	1.314(4)	O(1A)-C(7A)	1.301(4)
O(7)-C(7)	1.224(5)	O(7A)-C(7A)	1.230(4)
C(1)-C(7)	1.488(5)	C(1A)-C(7A)	1.495(4)
N(1)-C(8)	1.256(4)	N(1A)-C(8A)	1.263(4)
Atoms	Angle	Atoms	Angle
O(1)-Sn(1)-C(11)	108.1(1)	O(1A)-Sn(1A)-C(11A)	109.0(1)
O(1)-Sn(1)-C(21)	93.7(1)	O(1A)-Sn(1A)-C(21A)	96.1(1)
O(1)-Sn(1)-C(31)	110.9(1)	O(1A)-Sn(1A)-C(31A)	114.0(1)
C(11)-Sn(1)-C(21)	112.6(1)	C(11A)-Sn(1A)-C(21A)	110.1(1)
C(11)-Sn(1)-C(31)	116.7(1)	C(11A)-Sn(1A)-C(31A)	116.1(1)
C(21)-Sn(1)-C(31)	112.5(1)	C(21A)-Sn(1A)-C(31A)	109.8(1)
Sn(1)-O(1)-C(7)	109.3(2)	Sn(1A)-O(1A)-C(7A)	105.2(2)
O(1)-C(7)-O(7)	121.0(3)	O(1A)-C(7A)-O(7A)	120.6(3)
O(1)-C(7)-C(1)	115.0(3)	O(1A)-C(7A)-C(1A)	116.8(3)
O(7)-C(7)-C(1)	124.0(3)	O(7A)-C(7A)-C(1A)	122.5(3)

bonding mode for the carboxylate moiety.[12] For a bridging or chelating carboxylate group,[13] $\Delta\nu$ would be expected to be $\leqslant 150\ cm^{-1}$, as is widely observed in the infrared spectra of triorganotin carboxylates.[14] However, the Mössbauer quadrupole splitting values for **1**–**4** range from 2.32 to 2.55 mm s^{-1} (Table 2), which is in the range commonly observed for tetrahedral triorganotin compounds.[5] Thus the spectroscopic data suggest a tetrahedral geometry for the tin atom in these triphenyltin carboxylates. This conclusion was confirmed by the results of an X-ray structural analysis for triphenyltin 2-phenyliminomethylbenzoate (**1**).

The molecular structure of **1**, together with the numbering scheme employed, is shown in Fig. 1 and the packing view of the unit cell is presented in Fig. 2. The fractional atomic coordinates are listed in Table 3 and the selected bond lengths and bond angles are given in Table 4. There are two molecules in the crystallographic asymmetric unit, labelled **a** and **b**, and there are no significant intermolecular contacts in the lattice.

The geometry at the tin atom is a tetrahedron that is distorted owing to an intramolecular acyl O. . .Sn contact of 2.774(2) Å and 2.645(2) Å for **a** and **b**, respectively. The C–Sn–C angles are opened up [112.6(1)°, 116.7(1)°, 112.5(1)° for **a** and 110(1)°, 116.1(1)°, 109.8(1)° for **b**] whereas the O–Sn–C angles are compressed [93.71(1)°, 108.1(1)°, 110.9(1)° for **a** and 96.1(1)°, 109.0(1)°, 114.0(1)° for **b**]. The Sn–O–C=O fragment is coplanar in both **a** and **b** and the phenyl rings attached to the azomethine bond, together with the C=N atoms, are in another plane [0.074(3) Å for **a** and 0.091(3) Å for **b**] and at −25.9(3)° for **a** and 25.8(3)° for **b** to the former plane. It is interesting to note that in *o*-$Ph_3SnOCOC_6H_4N{=}NC_6H_3BrN(Me)_2$, the phenyl rings associated with the diazo moiety, the Br, and the three N atoms are coplanar and at 90° to the Sn–O–C=O plane.[15]

The toxicity results for **1**–**4** against *Ceratocystis ulmi* are listed in Table 2. The IC_{50} values for the triphenyltin carboxylates in this study fall below the 1 mg dm^{-3}, indicating that these compounds possess a higher fungitoxicity than commercially available triphenyltins such as triphenyltin hydroxide (2 mg dm^{-3})[9] and triphenyltin acetate (3 mg dm^{-3}).[9] This observed increase in toxicity for the triphenyltin carboxylates may be a result of a synergistic effect between the triphenyltin and Schiff base moieties in the molecule. Schiff bases are known to possess biological activity[16] and triphenyltin compounds have been found to be effective inhibitors of *Ceratocystis ulmi*.[9,17] Varying the substituents on the Schiff base portion of the molecule did not significantly increase the activity of the compound. This would suggest that the substitution site is too far removed from the tin atom to have any significant effect on the inhibition. Thus, any further modifications of the molecule in hopes of increasing its activity against *Ceratocystis ulmi* should be focused on varying the groups directly attached to the tin atom.

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