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Di- and tri-organotin(IV) derivatives of (*Z*)-3-(4-nitrophenyl)-2-phenyl-2-propenoic acid: spectroscopic characterization and biocidal studies. Crystal structure analysis of tetrameric tri-*n*-butyltin(IV) (*Z*)-3-(4-nitrophenyl)-2-phenyl-2-propenoate

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Seven new organotin(IV) compounds containing the carboxylate ligand (*Z*)-3-(4-nitrophenyl)-2-phenyl-2-propenoate (L) have been synthesized with formulations of R_2SnL_2 (R = Me, Et, *n*-Bu, *n*-Oct) and R_3SnL, (R = Me, *n*-Bu, Ph). All compounds have been studied in solution by multinuclear (^1H, ^{13}C, ^{119}Sn) magnetic resonance spectroscopy. The solid-state structures have been investigated by means of FT-IR spectroscopy and the molecular structure of one example, namely *n*-Bu_3SnL, has been determined by X-ray crystallography. The novel structure of *n*-Bu_3SnL is tetrameric owing to the presence of bidentate bridging carboxylate ligands. The solution studies show collapse of the intermolecular interactions observed in the solid state to yield monomeric species. Some of the new compounds were found to display significant biocidal activities. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: organotin(IV); carboxylates; X-ray crystal structure; tetrameric structure; biocidal activity

INTRODUCTION

The chemistry of organotins continues to attract significant attention owing to their potential biological[1,2] and industrial[3–6] applications. Organotin(IV) compounds have also been extensively screened for anti-tumour activity.[7,8] Recently, particular attention has again been paid to triorganotin(IV) derivatives owing to their high *in vitro* anti-fungal activities against some medically important fungi.[9,10] In view of the well-known biocidal properties of organotin(IV) compounds, and on the basis of our previous experience in this area,[11–16] we have prepared a series of organotin(IV) carboxylates with the carboxylate ligand derived from (*Z*)-3-(4-nitrophenyl)-2-phenyl-2-propenoic acid, shown in Fig. 1. The spectroscopic characterization of these compounds and their *in vitro* biological activities are presented.

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RESULTS AND DISCUSSION

Compounds **1**–**7** were obtained by heating at reflux the stoichiometric amount of (*Z*)-3-(4-nitrophenyl)-2-phenyl-2-propenoic acid or its silver salt with the corresponding

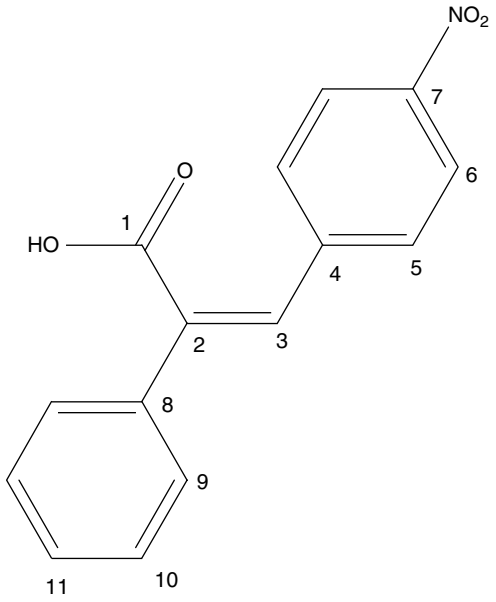

Figure 1. The structure of the ligand (*Z*)-3-(4-nitrophenyl) -2-phenyl-2-propenoic acid (L) showing numbering scheme for spectroscopic analysis.

organotin chloride in chloroform or organotin oxide in toluene (Eqns (1)–(4)) solutions.

$$R_2SnCl_2 + 2AgL \longrightarrow R_2SnL_2 + 2AgCl \quad (1)$$

R = Me (**1**), Et (**3**)

$$R_3SnCl + AgL \longrightarrow R_3SnL + AgCl \quad (2)$$

R = Me (**2**), Ph (**7**)

$$R_2SnO + 2LH \longrightarrow R_2SnL_2 + H_2O \quad (3)$$

R = *n*-Bu (**4**), *n*-Oct (**6**)

$$(R_3SnO)_2O + 2LH \longrightarrow 2R_3SnL + H_2O \quad (4)$$

R = *n*-Bu (**5**)

All compounds synthesized are stable and soluble in common organic solvents; their physical characteristics are collected in Table 1.

IR data

The coordinating mode of (*Z*)-3-(4-nitrophenyl)-2-phenyl-2-propenoate towards the di- and tri-organotin(IV) moieties can be inferred by comparing the IR spectra of the free acid, its silver salt and the organotin compound. Frequencies assigned to ν_{asym}(COO) and ν_{sym}(COO) have been identified for all species and are reported together with bands assigned to ν(Sn–C) and ν(Sn–O) in Table 2. The most significant differences in the spectra were found in the regions between 1700 and 1350 cm^{-1} and between 600 and 400 cm^{-1}.[17] In all organotin compounds the $\Delta\nu$ values [$\Delta\nu = \nu_{asym}(COO) - \nu_{sym}(COO)$] were under 200 cm^{-1}, which indicates a bidentate coordination mode for the carboxylate ligand. These results suggest that the tin atom in each of the di- and tri-organotin species approaches six- and five-coordination, respectively. Referring to the considerable crystallographic evidence in the literature,[18,19] it is likely that the coordination geometry for the tin atom in the diorganotin species is based on a skew-trapezoidal bipyramidal geometry. In this description,

Table 2. IR data (cm^{-1}) for organotin(IV) derivatives of (*Z*)-3-(4-nitrophenyl)-2-phenyl-2-propenoic acid[a]

	ν(COO)				
Compound	Asym	Sym	$\Delta\nu$	ν(Sn–C)	ν(Sn–O)
1	1593 s	1406 s	187	563 w	480 w
2	1576 s	1379 m	197	555 w	478 w
3	1560 s	1393 s	167	545 m	464 w
4	1561 s	1393 m	168	544 w	480 w
5	1584 s	1392 s	192	557 m	475 w
6	1575 s	1381 s	194	592 w	490 m
7	1595 s	1397 m	198	—	449 m
LH	1686 s	1415 s	271	—	—
AgL	1591 s	1375 s	216	—	—

[a] s = strong; m = medium; w = weak.

Table 1. Physical data for organotin(IV) derivatives of (*Z*)-3-(4-nitrophenyl)-2-phenyl-2-propenoic acid

					Analysis (%)		
Compound	Molecular formula	(Formula weight)	M.p. (°C)	Yield (%)	C Calc. (Found)	H Calc. (Found)	N Calc. (Found)
1 Me_2SnL_2	$C_{32}H_{26}N_2O_8Sn$	685	179–181	85	56.06 (56.08)	3.80 (3.99)	4.09 (4.20)
2 Me_3SnL	$C_{18}H_{19}NO_4Sn$	432	123–125	90	50.00 (49.92)	4.40 (4.19)	3.24 (3.15)
3 Et_2SnL_2	$C_{34}H_{30}N_2O_8Sn$	713	136–139	85	57.22 (57.32)	4.21 (4.30)	3.93 (3.96)
4 *n*-Bu_2SnL_2	$C_{38}H_{38}N_2O_8Sn$	769	116–118	80	59.30 (59.39)	4.94 (5.04)	3.64 (3.71)
5 *n*-Bu_3SnL	$C_{27}H_{37}NO_4Sn$	558	82–84	83	58.06 (58.10)	6.63 (6.48)	2.51 (2.42)
6 *n*-Oct_2SnL_2	$C_{46}H_{54}N_2C_8Sn$	881	Viscous liquid	60	62.66 (62.70)	6.13 (6.04)	3.18 (3.20)
7 Ph_3SnL	$C_{33}H_{25}NO_4Sn$	618	73–75	70	64.08 (63.98)	4.05 (4.10)	2.27 (2.30)

the carboxylate ligands coordinate in an asymmetric fashion and the tin-bound organo groups lie over the weaker Sn···O interactions. Unfortunately, single crystals of **1**, **3**, **4** and **6** could not be obtained to verify this assignment. In the same way,[18,19] it is likely that the triorganotin species are linear polymers, as commonly found for triorganotin carboxylates with bidentate ligands leading to *trans*-R_3SnO_2 geometry for tin. Although the X-ray crystal structures of **2** and **7** were not obtained, again due to the lack of crystals, to verify this assignment, the structure of **5** was obtained. Rather than the expected polymeric structure, a rare example of a tetrameric structure, but still featuring *trans*-R_3SnO_2 geometries, was found as described in detail below.

NMR data

NMR spectra for the new compounds and free acid have been recorded in $CDCl_3$ solution and are reported in Tables 3 (for ^1H) and 4 (for ^{13}C) and are consistent with expectation.[20,21]

The methyl protons of dimethyl- (**1**) and trimethyltin(IV) (**2**) derivatives appear as sharp singlets at 1.14 ppm and 0.62 ppm respectively, both with well-defined satellites; coupling constants are included in Table 3. The α-CH_2 protons of diethyltin(IV) compound (**3**) resonate as a quartet at 1.75–1.79 ppm and the β-CH_3 protons resonate as a triplet at 1.35–1.38 ppm with $^3J[^1H, ^1H] = 8.0$ Hz. Similarly, the α-CH_2 protons of di-*n*-butyltin appear as a triplet in the range 1.77–1.79 ppm with $^2J[^{119}Sn, ^1H] = 72.9$ and $^3J[^1H, ^1H] = 8.0$ Hz; the β-CH_2 and γ-CH_2 protons appear as multiplets, and δ-CH_3 appears as a triplet with $^3J[^1H, ^1H] = 7.30$ Hz. In the tri-*n*-tributyltin(IV) complex, δ-CH_3 resonates as a triplet at 0.89–0.93 ppm with $^3J[^1H, ^1H] = 7.3$ Hz, γ-CH_2 as a pseudo-quintet at 1.26–1.36 ppm with $^3J[^1H, ^1H] = 7.4$ Hz, and the α-CH_2 and β-CH_2 protons appear as multiplets at 1.61–1.64 ppm and 1.57–1.61 ppm respectively.

The methylene protons (CH_2) of the *n*-octyltin(IV) moiety exhibit a somewhat different behaviour compared with the *n*-butyl groups of the respective complexes. The α-CH_2, β-CH_2 and the γ-CH_2 to γ'-CH_2 protons give broad signals at 1.71 ppm and 1.17 ppm respectively, which are consistent with the values calculated by the incremental method.[21] However, the δ'-CH_3 protons appear as a triplet at 0.74–0.77 ppm with $^3J[^1H, ^1H] = 6.2$ Hz. The *meta* and *para* proton resonances in the triphenyltin(IV) derivative also give broad signals centred at 7.46 ppm.

The ^{13}C NMR spectral data for the R groups attached to the tin atom, where R = CH_3, C_2H_5, *n*-Bu, *n*-Oct and Ph, were assigned by comparison with related analogues as model compounds.[12–16] The assignment of the ^{13}C resonances associated with the carboxylate ligand is based on comparison with the results obtained from incremental methods.[22] The positions of the phenyl and olefinic carbon signals undergo minor variations in the complexes compared with those observed in the free acid. The carboxylate carbon shifts to a lower field region in all the complexes, indicating participation of the carboxylic group in coordination to tin(IV).[23]

The possibility of detecting the presence of coordinatively different organotin(IV) moieties was explored by acquisition of ^{119}Sn NMR spectra for all compounds investigated. The ^{119}Sn chemical shifts usually cover a range of 600 ppm, quoted relative to tetramethyltin, with increasing coordination number of tin producing a large upfield shift for $\delta(^{119}Sn)$.[24] With this in mind, the ^{119}Sn NMR spectra were recorded in $CDCl_3$ solution, a non-coordinating solvent. The chemical shift values obtained for the triorganotin(IV) derivatives lie in the range expected for a tetrahedral geometry, whereas the diorganotin(IV) compounds show higher coordination, probably five (Table 4).[25]

In order to gain further information about the possible coordination geometries in solution, a close examination of the $^1J[^{119}Sn, ^{13}C]$ and $^2J[^{119}Sn, ^1H]$ coupling constants was undertaken, as structural details, such as the determination of C–Sn–C bond angles, can be enumerated by use of the literature methods.[26,27] Data are summarized in Table 5. As indicated by Nadvornik and co-workers[27,28] the $^2J[^{119}Sn, ^1H]$ in *n*-Bu_3Sn(IV) carboxylates alter very little with a change in coordination, being the smallest among such couplings. The $^1J[^{119}Sn, ^{13}C]$ coupling constant is, instead, quite amenable for making predictions about the geometry around the tin atom. For the *n*-tributyltin(IV) derivative, with the $^1J[^{119}Sn, ^{13}C]$ value being 350.6 Hz and by the use of the Holeček and Lycka equation,[23] a C–Sn–C value of 111.6° was calculated, which corresponds to a quasi-tetrahedral geometry in $CDCl_3$ solution. The geometric data calculated, as just described, are consistent with tetrahedral geometries for the triorganotin(IV) species, i.e. monomers in solution. For the diorganotin(IV) species, for which earlier results indicate five-coordination, the calculated C–Sn–C angles are consistent with the skew-trapezoidal bipyramidal geometries, with the lower apparent coordination number arising from the asymmetric coordination mode of the carboxylate ligands.

X-ray crystal structure of *n*-Bu_3SnL (5)

The molecular structure of **5** is shown in Fig. 2 and selected geometric parameters are collected in Table 6. The structure of **5** is an isolated cyclotetrameric 16-membered ring that is located about a crystallographic centre of inversion so that two independent *n*-Bu_3SnL units comprise the asymmetric unit. This aggregation arises as the carboxylate ligands are bidentate bridging, albeit forming asymmetric bond distances of approximately 2.2 and 2.6 Å. The individual tin atom coordination geometry is based on a *trans*-R_3SnO_2 trigonal bipyramid with the above-mentioned disparity in the Sn–O bond distances not withstanding. The axial angle of 171.19(10)° for the Sn1 atom is more significantly distorted from the ideal angle compared with the Sn2 atom, for which the equivalent angle is 177.62(11)°. It is noted that the intramolecular Sn1···O2 distance of 3.191(3) Å is shorter than the Sn2···O6 distance of 3.327(3) Å, which may explain the different *trans* angles. Certainly, the relative close approach of the O2 atom has the result of opening up the C16–Sn1–C24 angle to 131.1(2)°, whereas for the Sn2 atom, where the

Table 3. ^{1}H NMR data for organotin(IV) derivatives of (*Z*)-3-(4-nitrophenyl)-2-phenyl-2-propenoic acid[a,b,c,d]

^{1}H No.	LH Acid	**1** Me_2SnL_2	**2** Me_3SnL	**3** Et_2SnL_2	**4** *n*-Bu_2SnL_2	**5** *n*-Bu_3SnL	**6** *n*-Oct_2SnL_2	**7** Ph_3SnL
3	7.11 (s)	7.01 (s)	6.88 (s)	6.99 (s)	6.97 (s)	6.87 (s)	7.08 (s)	6.93 (s)
5	8.02 (d, 8.8)	8.01 (d, 8.8)	7.99 (d, 8.9)	8.01 (d, 8.8)	8.01 (d, 8.9)	7.98 (d, 8.9)	7.87 (d, 8.8)	7.98 (d, 10.0)
6	8.23 (d, 8.7)	8.20 (d, 8.6)	8.19 (d, 8.8)	8.19 (d, 8.8)	8.19 (d, 8.6)	8.18 (d, 8.8)	8.07 (d, 7.86)	7.96 (d, 8.8)
9	7.39–7.42 (m)	7.38–7.43 (m)	7.34–7.35 (m)	7.38–7.41 (m)	7.38–7.40 (m)	7.32–7.34 (m)	7.27–7.38 (m)	7.32–7.36 (m)
10	7.39–7.42 (m)	7.38–7.43 (m)	7.34–7.35 (m)	7.38–7.41 (m)	7.38–7.40 (m)	7.32–7.34 (m)	7.27–7.38 (m)	7.32–7.36 (m)
11	7.20–7.23 (m)	7.19–7.22 (m)	7.16–7.21 (m)	7.19–7.22 (m)	7.19–7.22 (m)	7.16–7.19 (m)	7.11–7.16 (m)	7.16–7.20 (m)
α	—	1.14 (s); ^{2}J[78.5]	0.62 (s); ^{2}J[58.0]	1.77 (q, 8.0); ^{2}J[74.5]	1.78 (t, 8.0); ^{2}J[72.9]	1.61–1.64 (m)	1.71 (bs)	—
β	—	—	—	1.37 (t, 8.0)	1.68–1.74 (m)	1.57–1.61 (m)	1.71 (bs)	7.68–7.73 (m)
γ	—	—	—	—	1.40 (ps, 7.4)	1.32 (pq, 7.4)	—	7.46 (bs)
δ	—	—	—	—	0.91 (t, 7.3)	0.91 (t, 7.3)	—	7.46 (bs)
γ to γ'						—	1.17 (bs)	—
δ'							0.75 (t, 6.2)	

[a] Chemical shifts (δ) in ppm; ^{2}J[^{119}Sn, ^{1}H] and ^{3}J(^{1}H, ^{1}H) in hertz are listed in square brackets and parentheses respectively. Multiplicity is given as s = singlet, bs = broad signal, d = doublet, q = quartet, pq = pseudoquintet, ps = pseudosextet, m = multiplet.
[b] Numbering is according to Fig. 1.
[c] γ to γ' = 1.17 [$(CH_2)_5$ = 10 H, bs].

d

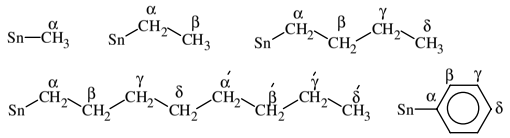

Table 4. ^{13}C NMR data for organotin(IV) derivatives of (*Z*)-3-(4-nitrophenyl)-2-phenyl-2-propenoic acid[a,b,c]

^{13}C No.	LH Acid	**1** Me_2SnL_2	**2** Me_3SnL	**3** Et_2SnL_2	**4** n-Bu_2SnL_2	**5** n-Bu_3SnL	**6** n-Oct_2SnL_2	**7** Ph_3SnL
1	171.85	176.18	173.53	176.58	176.48	173.46	175.99	173.12
2	130.79	128.97	128.94	129.23	129.18	129.06	128.90	130.30
3	139.5	139.11	142.08	138.88	141.25	136.16	140.98	137.86
4	142.05	142.53	141.15	141.24	142.68	142.31	142.53	142.58
5	129.58	129.46	129.63	129.56	129.51	129.62	129.28	129.74
6	123.42	123.30	123.27	123.44	123.36	123.29	123.04	123.29
7	147.7	147.46	147.12	147.56	147.50	147.10	147.01	147.27
8	137.61	136.19	136.48	136.69	136.06	138.80	136.36	137.14
9	128.89	128.82	128.62	128.09	129.00	128.68	128.59	128.83
10	131.18	130.91	130.76	131.07	130.98	130.80	130.74	130.86
11	126.96	126.56	126.50	126.87	126.79	128.01	126.47	126.58
α	—	4.70[d]	−2.25 [394.8]	17.91 [545.8]	25.60[d]	16.75 [350.6]	25.76 [462.8]	141.81[d]
β	—	—	—	9.07	26.72	27.86[20.3]	24.42	136.76
γ	—	—	—	—	26.35	27.02[62.4]	33.06	129.00
δ	—	—	—	—	13.51	13.65	28.87	128.27
α'	—	—	—	—	—	—	29.17	—
β'	—	—	—	—	—	—	31.57	—
γ'	—	—	—	—	—	—	22.40	—
δ'	—	—	—	—	—	—	13.87	—
$\delta^{119}Sn$	—	−118.2	145.0	−150.8	−144.7	130.9	−147.2	−108.6

[a] Chemical shifts (δ) in ppm; $^nJ[^{119}Sn, ^{13}C]$ in hertz are listed in square brackets.
[b] Numbering is according to Fig. 1.
[c] See footnoted of Table 3 for meanings of α, β, γ, δ, α', β', γ', δ'.
[d] Coupling not observed.

Table 5. C–Sn–C angles (°) calculated from NMR parameters

Compound	$^1J[^{119}Sn-^{13}C]$ (Hz)	$^2J[^{119}Sn-^1H]$ (Hz)	C–Sn–C angles (°) calculated from ^1J	C–Sn–C angles (°) calculated from ^2J
Me_2SnL_2	—	78.5	—[a]	129.0
Me_3SnL	394.8	58.0	111.4	111.0
Et_2SnL_2	545.8	74.5	124.6	124.4
n-Bu_2SnL_2	—	72.9	—[a]	122.7
n-Bu_3SnL	350.6	—	111.6	—[a]
n-Oct_2SnL_2	462.8	—	122.1	—[a]

[a] Coupling not observed

intramolecular contact is weaker, the trigonal C–Sn2–C angles span a relatively narrow range of 117.2(3) to 122.2(3)°. As can be noted from the torsion angle data included in Table 6, within the carboxylate ligands the aromatic rings are each significantly twisted with respect to the central chromophore. Of particular interest is the mode of molecular aggregation in **5**.

As alluded to above, there are a considerable number of crystal structure determinations for compounds of the general formula $R_3Sn(O_2CR')$, and these are known to adopt a variety of coordination geometries.[18,19] The overwhelming majority of structures are monomeric; these may be described as *cis*-R_3SnO_2, depending on the magnitude of the intramolecular Sn···O interaction, or *trans*-R_3SnO_2, which is polymeric as the carboxylate ligands are bidentate bridging. Indeed, a model exists in the literature rationalizing the appearance of the monomeric or polymeric species based on steric factors associated with the tin- and carboxylate-bound R groups and global crystal packing considerations.[29] Such considerations are also known to be important for related

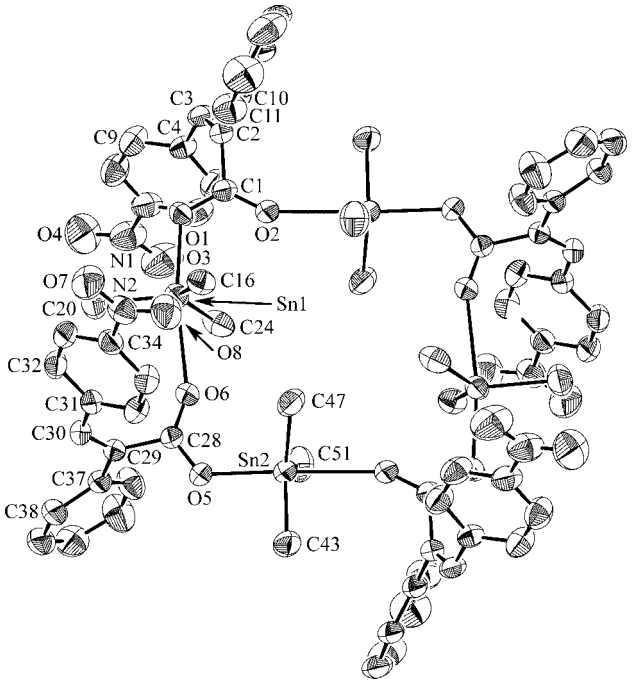

Figure 2. Molecular structure and crystallographic numbering scheme for cyclotetrameric *n*-Bu_3SnL (**5**). Hydrogen atoms have been removed for reasons of clarity.

diorganotin carboxylates[30] and indeed for the zinc-triad 1,1-dithiolates.[31–33] However, there are two $R_3Sn(O_2CR')$ structures in the literature that adopt the tetrameric motif reported here for **5**.[34,35] The rationalization of the appearance of these cyclotetrameric structures, which may be thought of as being intermediate between the monomeric and polymeric extremes described above, remains elusive.

Biological studies

The observed bactericidal activities of the compounds synthesized are given in Table 7. The results demonstrate that diorganotin(IV) derivatives show good activity against various bacteria. The triorganotin(IV) derivatives, including ligand acid, exhibit low activity, with the only exception being compound **7** (Table 7). This contradicts the assessment that an increase in the number of R groups augments the antimicrobial activity of the organotin(IV) compounds reported earlier.[14,36] Thus, the results obtained indicate that the anionic ligand may also play some important role in the biocidal activity of organotin(IV) compounds.

The fungicidal screening data for the compounds tested are listed in Table 8. The investigation shows that triorganotin compounds are generally more active than diorganotin derivatives, particularly against *T. longifusus* and *A. flavus*, which are human pathogens. The importance of the organotin moiety present is seen when one considers that the free acid has poor biocidal activity.

Finally, the brine-shrimp lethality bioassay studies demonstrate that all of the compounds are non-toxic.

EXPERIMENTAL

Chemicals and instrumentation

All reactants and solvents used in this study were reagent grade and were supplied by Fluka/Aldrich, except for

Table 6. Selected geometric parameters (Å; °) for *n*-Bu_3SnL (**5**)[a]

Sn1–O1	2.160(3)	Sn2–O5	2.171(3)
Sn1–O6	2.640(3)	Sn2–$O2^i$	2.599(3)
Sn1–C16	2.123(5)	Sn2–C43	2.107(5)
Sn1–C20	2.139(5)	Sn2–C47	2.121(5)
Sn1–C24	2.141(5)	Sn2–C51	2.125(6)
O1–Sn1–O6	171.19(10)	O5–Sn2–$O2^i$	177.62(11)
O1–Sn1–C16	93.64(16)	O5–Sn2–C43	91.56(17)
O1–Sn1–C20	96.89(18)	O5–Sn2–C47	98.35(17)
O1–Sn1–C24	95.81(18)	O5–Sn2–C51	95.42(18)
O6–Sn1–C16	83.10(15)	$O2^i$–Sn2–C43	86.70(17)
O6–Sn1–C20	91.92(18)	$O2^i$–Sn2–C47	83.91(16)
O6–Sn1–C24	80.41(17)	$O2^i$–Sn2–C51	84.16(18)
C16–Sn1–C20	112.2(2)	C43–Sn2–C47	118.3(3)
C16–Sn1–C24	131.1(2)	C43–Sn2–C51	122.2(3)
C20–Sn1–C24	114.0(2)	C47–Sn2–C51	117.2(3)
Sn1–O1–C1	121.0(3)	Sn2–O5–C28	125.4(3)
Sn1–O6–C28	154.9(3)	Sn2–$O2^i$–$C1^i$	153.6(3)
C1–C2–C3–C4	−4.7(7)	C28–C29–C30–C31	−3.8(7)
C4–C3–C2–C10	−0.7(4)	C31–C30–C29–C37	−1.5(4)
C2–C3–C4–C5	−53.8(8)	C29–C30–C31–C32	146.2(5)
C1–C2–C10–C11	−36.1(6)	C28–C29–C37–C38	157.5(4)

[a] Symmetry operation *i*: $-x, -y, -z$.

Table 7. Anti-bacterial activity for organotin(IV) derivatives of (*Z*)-3-(4-nitrophenyl)-2-phenyl-2-propenoic acid[a,b]

Bacterium	Clinical implication	Zone of inhibition (mm)								Ref. drug
		LH	**1**	**2**	**3**	**4**	**5**	**6**	**7**	
Escherichia coli	Infection of wounds, urinary tract and dysentery	5	8	10	7	10	12	5	10	30
Bacillus subtilis	Food poisoning	—	11	5	12	8	5	8	5	31
Shegella flexenari	Blood diarrhoea with fever and severe prostration	—	8	—	6	12	—	5	8	33
Staphylococcus aureus	Food poisoning, scaled skin syndrome, endocarditis	5	15	—	5	10	10	12	12	43
Pseudomonas aeruginosa	Infection of wounds, eyes, septicaemia	—	—	5	—	—	—	—	—	25
Salmonella typhi	Typhoid fever, food poisoning, localized infection	—	5	10	—	10	—	—	14	41

[a] *In vitro*, agar well diffusion method, conc. 1 mg ml^{-1} of dimethylsulfoxide (DMSO).
[b] Reference drug, Imipenum.

Table 8. Anti-fungal activity for organotin(IV) derivatives of (*Z*)-3-(4-nitrophenyl)-2-phenyl-2-propenoic acid[a]

Fungus	Inhibition[b] (%)								Standard drug	Inhibition (%)	MIC[c] (μg ml^{-1})
	LH	**1**	**2**	**3**	**4**	**5**	**6**	**7**			
Trichophyton longifusus	50	50	75	50	60	70	75	60	Miconazole	100	70
Candida albicans	10	30	25	20	—	—	65	—	Miconazole	100	110.8
Aspergillus flavus	—	35	70	—	60	50	—	35	Amphotericin B	100	20
Microsporum canis	—	—	—	—	30	30	—	—	Miconazole	100	98.4
Fusarium solani	—	—	35	20	—	—	35	45	Miconazole	100	73.25
Candida glaberata	10	—	—	—	—	—	—	10	Miconazole	100	110.8

[a] Concentration: 200 μg ml^{-1} of DMSO.
[b] Dashes indicate no activity.
[c] Minimum inhibitory concentration.

di-*n*-octyltin oxide and diethyltin dichloride, which were provided by Alfa-Aesar. The ligand (*Z*)-3-(4-nitrophenyl)-2-phenyl-2-propenoic acid was synthesized by the Perkin condensation method in the laboratory.[37]

Melting points were determined in a capillary tube using an MPD Mitamura Riken Koggyo (Japan) electrothermal melting point apparatus. IR spectra were registered, as KBr pellets, on a Bio-Rad *excaliber* FT-IR, model FTS 300 MX spectrophotometer (USA). Multinuclear magnetic resonance (^{1}H, ^{13}C, ^{119}Sn) spectra were recorded with a Bruker ARX 250 FT-NMR instrument (operating at 250 MH_3, 63 MH_3 and 93 MHz respectively) using $CDCl_3$ as the internal reference [δ ^{1}H = 7.25 and δ ^{13}C = 77.0 ppm]. ^{119}Sn NMR spectra were obtained with Me_4Sn as external reference [Ξ(Sn) = 37.290 665].

General procedure for synthesis

Methyl-, ethyl- and phenyltin(IV) derivatives (compounds **1–3** and **7**) were prepared by heating at reflux for 6–8 h the corresponding diorganotin dichloride (10.64 mmol) or triorganotin chloride (5.32 mmol) with the silver salt of (*Z*)-3-(4-nitrophenyl)-2-phenyl-2-propenoic acid (2.0 g, 5.32 mmol) in 1 : 2 and 1 : 1 molar ratio, respectively; see Eqns (1) and (2). The solvent used was dry chloroform (70 ml) contained in a 250 ml two-necked round-bottom flask equipped with a water condenser and a magnet bar. This was placed overnight at room temperature; the silver chloride (AgCl) formed was filtered off and the solvent was evaporated under reduced pressure.

Di-*n*-butyl, di-*n*-octyl- and tri-*n*-butyltin(IV) carboxylates (compounds **4–6**) were synthesized by the condensation of (*Z*)-3-(4-nitrophenyl)-2-phenyl-2-poropenoic acid (2.0 g, 7.44 mmol) and the corresponding diorganotin oxides (14.87 mmol) and bis(tri-*n*-butyltin) oxide (7.44 mmol) in 2 : 1 molar ratio by heating at reflux temperature for 8–10 h in toluene (80 ml), using a Dean and Stark apparatus; see Eqns (3) and (4). All the products obtained were recrystallized from a chloroform and *n*-hexane (4 : 1) mixture *via* slow evaporation at room temperature.

Crystal structure determination

Data were collected at 223(2) K on a Bruker AXS SMART CCD for a pale-yellow block of dimensions 0.23 × 0.29 × 0.52 mm^3. $C_{27}H_{37}NO_4Sn$, M = 558.27, triclinic, $P\bar{1}$, a = 14.5526(9), b = 14.8181(10), c = 15.5621(10) Å, α = 91.867(2), β = 109.335(2), γ = 117.040(2)°, V = 2752.7(3) Å^3, Z = 4(= 1 cyclotetramer), 15 624 unique data (θ_{max} 30.1°), 8274 data with $I \geq 2\sigma(I)$, R = 0.060 (obs. data), wR = 0.166 (all data). Programs used: teXsan, DIRDIF, SHELXL-97 and ORTEP. CCDC deposition number: 234260.

Biocidal studies

Biological activity tests for the free acid and all compounds synthesized were carried out against various bacteria and fungi by the agar well diffusion method[38] and the tube diffusion test,[39] respectively. The toxicity of these compounds was determined by a brine-shrimp method.[40]

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