Synthesis, characterization and catalytic properties of diorganotin derivatives. Crystal and molecular structure of the first complex of 2-(2-methyl-3-nitroanilino)benzoic acid of 1,2:3,4-di-µ2-2-(2-methyl-3-nitroanilino)benzoato-O,O-1,3-bis-2-(2-methyl-3-nitroanilino)-benzoato-O-1,2,4:2,3,4-di-µ3-oxo-tetrakis[di-methyltin(IV)]

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ABSTRACT

The complexes [Me$_2$(MNAB)SnOSn(MNAB)Me$_2$]$_2$ (**2**) and [Me$_2$Sn(MNAB)$_2$] (**3**), where HMNAB is 2-(2-methyl-3-nitroanilino)benzoic acid, (**1**), have been prepared and structurally characterized by means of vibrational, ^{1}H and ^{13}C NMR spectroscopies. The crystal structure of [Me$_2$(MNAB)SnOSn-(MNAB)Me$_2$]$_2$ has been determined by X-ray crystallography. Three distannoxane rings are present to the dimeric tetraorganodistannoxane of planar ladder arrangement. The structure is centro-symmetric and features a central rhombus Sn$_2$O$_2$ unit with two additional tin atoms linked at the O atoms. Six-coordinated tin centers are present in the dimmer distannoxane. This structure is self-assembled in one dimensional infinite chain *via* intermolecular hydrogen bonds, $\pi \to \pi$ and C–H $\to \pi$ stacking interactions. The polar imino hydrogen atom participates in intramolecular hydrogen bonds. The catalytic activity of the prepared complexes in transesterification reactions has been studied. The diorganotin complexes efficiently catalyze the transesterification reaction of 2-phenylethanol without addition of free ligand or any promoting additive.

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1. Introduction

Diorganotin carboxylates derived from carboxylic acids are among the most extensively studied class of compounds owing to their rich structural chemistry. The diverse structural motifs known in this family of compounds are attributed to the ambidentate character of the carboxylate ligands. Steric and electronic attributes of organic substituents on tin and/or the carboxylate moiety impart significant influence on the structural characteristics in tin carboxylates. Information on the structures of organotin carboxylates continues to accumulate, and at the same time new applications of such compounds are being discovered in industry, ecology and medicine. Recently, much attention has also been focused on their use as metal-based drugs [1–3].

Tin derivatives are used as homogeneous catalysts in esterification and transesterification reactions [4]. Acylation of alcohols is one of the most important manipulations in organic synthesis and transestrification by using of esters as acylating reagents is

another important and versatile means. The acetyl ester plays an important role for protection of the hydroxyl group in organic synthesis. Consequently, numerous methodologies have so far been put forth for the acetylation of alcohols [4].

Dimeric organotin cations [5] and neutral dimeric tetraorganodistannoxanes of the type [R$_2$XSnOSnXR$_2$]$_2$ (X = Cl, OH, R'COO, NCS; R, R' = alkyl, aryl) have been found to be efficient catalysts for transesterifications and for the highly selective acylation of alcohols [6,7]. The catalytic activity of distannoxanes in this type of reaction was reported to be the result of their dimeric structure [7] in solution. 2-(2-Methyl-3-nitroanilino)benzoic acid (Scheme 1), HMNAB (**1**), resembles mefenamic, tolfenamic, flufenamic acids and other fenamates in clinical use, it was thought of interest to explore the chemistry of organotin/anilinobenzoic acid compounds, as a continuation of our studies on organotin chemistry [8–10] and to study the catalytical activity of the prepared diorganotin derivatives.

2-(2-Methyl-3-nitroanilino)benzoic acid (**1**), and the novel complexes [Me$_2$(MNAB)SnOSn(MNAB)Bu$_2$]$_2$ (**2**) and [Me$_2$Sn-(MNAB)$_2$] (**3**), where HMNAB is 2-(2-methyl-3-nitroanilino)benzoic acid (**1**), have been prepared and structurally characterized

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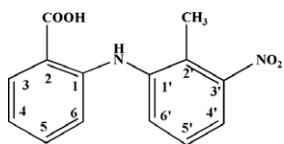
Scheme 1.

by means of vibrational, ^{1}H and ^{13}C NMR. The crystal and molecular structure of **2** is described. Also, the transesterification reactions of **2** and **3** are described.

2. Experimental

2.1. General and instrumental

2.1.1. General

The reagents (Aldrich, Merck) were used as supplied while the solvents were purified according to standard procedures [11c]. Elemental analyses (C, H and N) were carried out by the microanalytical service of the University of Ioannina. Melting points were determined in open capillaries and are uncorrected. Infrared and far-infrared spectra were recorded on a Perkin–Elmer Spectrum GX Fourier transform spectrophotometer using KBr pallets (4000–400 cm^{-1}) and nujol mulls dispersed between polyethylene disks (400–40 cm^{-1}). The ^{1}H (250.13 MHz), ^{13}C (62.90 MHz) NMR spectra were recorded on a Bruker AC-250 and on a Bruker AMX-400 spectrometers. Samples were dissolved in CDCl$_3$ and spectra were obtained at room temperature with the signal of the free CDCl$_3$ at 7.24 ppm. GC analysis was performed using a Shimadzu GC-17A gas chromatograph coupled with a GCMS-QP5000 mass spectrometer with the following temperature program: initial temperature, 80 °C (starting time 5 min); heating rate, 10 °C/min; final temperature, 150 °C (final time 5 min); injector temperature, 230 °C. The yields of products were estimated from the peak areas based on the internal standard technique [11d].

2.2. Synthesis

2-(2-Methyl-3-nitroanilino)benzoic acid (HMNAB) (**1**), was synthesized according to published procedure, the Ullmann–Goldberg condensation [11a,b]. 2-Methyl-3-nitro-benzenamine (11.26 g, 0.074 mol), potassium 2-bromobenzoate (18.17 g, 0.076 mol), 4-ethylmorpholine (9.5 ml, 0.076 mol) and 0.8 g of anhydrous copper acetate in 30 ml of distilled N,N-dimethylformamide under nitrogen atmosphere were refluxed at 145 °C for 4 h. In the resulting solution 20 ml of distilled N,N-dimethylformamide was added, and 30 ml of 12% hydrochloric acid. The aqueous layer was decanted and methanol was added. The solid was collected and recrystallized three times from acetone. M.p. 222–223 °C. Yield 24.35% (2.70 g). IR (KBr): 3323sh v(NH), 1597 v_{as}(COO), 1425 v_{sym}(COO); ^{1}H NMR (CDCl$_3$): δ 9.30 (s, 1H, NH), 8.07 (dd, H3), 6.83 (t, H4), 7.65 (d, H5), 6.81 (t, H6), 7.57 (d, H4′), 7.37 (t, H5′), 7.35 (d, H6′) 3.49/2.17 (s, CH3), ^{13}C NMR: δ 174.1 (COOH), 147,7 (C1), 111.4 (C2), 131.6 (C3), 114.2 (C4), 135.8 (C5), 118.8 (C6), 135.5 (C1′), 132.2 (C2′), 141.4 (C3′), 120.2 (C4′), 130.4 (C5′). Anal. Calc. for C$_{14}$H$_{13}$N$_2$O$_4$ (272.3 g mol^{-1}): C, 61.77; H, 4.44; N, 10.29. Found: C, 61.25; H, 4.10; N, 10.05%.

[Me$_2$(MNAB)SnOSn(MNAB)Me$_2$]$_2$ (**2**). Dimethyl-tin(IV) oxide (0.1977 g, 1.2 mmol), HMNAB (0.2723 g, 1.0 mmol) and 30 ml of benzene were refluxed overnight with azeotropic removal of water via a Dean-Stark trap. The resulting clear solution was rotary evap-

orated under vacuum to a small volume (2 ml), chilled and triturated with acetone to give a yellow solid. The yellow powder was recrystallized from CH$_2$Cl$_2$ and was dried in vacuo over silica gel. M.p. 219–221 °C; yield 26%. IR (KBr, cm^{-1}): 3324, 3290 v(NH), 1614, 1590 v_{as}(COO), 1373, 1457 v_{sym}(COO); 569, 522 v(Sn–C); 440, 411 v(Sn–O)$_2$; 281, 225, 218 v(Sn–O); ^{1}H NMR (CDCl$_3$): δ 9.57 (s, 1H, NH), 7.89 (d, H3), 6.89 (d, H4), 7.57 (t, H5), 6.77 (t, H6), 7.65 (dt, H4′), 7.37 (t, H5′), 7.34 (d H6′), 3.31/2.45(s, CH3), ^{13}C NMR: δ 175.7 (COOH), 152.4 (C1), 114.4 (C2), 132.9 (C3), 118.3 (C4), 134.6 (C5), 115.5 (C6), 148.0 (C1′), 120.0 (C2′), 142.0 (C3′), 127.6 (C5′) 127.3 (C6′) 14.5 (CH3) 10.4/7.80 (·R–Sn) Anal. Calc.: C, 44.90; H, 4.00; N, 6.15. Found: C, 44.50; H, 4.14; N, 5.90%. Crystals of **2** suitable for X-ray analysis were obtained by slow evaporation of a CHCl$_3$/CH$_3$CN solution.

[Me$_2$Sn(MNAB)$_2$] (**3**). Dimethyl tin(IV) oxide (0.1649 g, 1.0 mmol), HMNAB (0.5989 g, 2.20 mmol) and 30 ml of benzene were refluxed for 24 h with azeotropic removal of water via a Dean-Stark trap. The resulting clear solution was rotary evaporated under vacuum to a small volume (2 ml), chilled and triturated with acetone to give a bright yellow solid. The yellow powder was recrystallized from CH$_2$Cl$_2$ and dried in vacuo over silica gel. M.p. 165–166 °C; yield 77%. IR (KBr): 3318 v(NH), 1666 v_{as}(COO), 1404 v_{sym}(COO); 569, 545 v(Sn–C); 280, 217 v(Sn–O). ^{1}H NMR (CDCl$_3$): δ 9.29 (s, 1H, NH), 8.15 (dd, H3), 6.92 (d, H4), 7.60 (t, H5), 6.85 (t, H6), 7.60 (t, H4′), 7.31 (t, H5′), 7.35 (d, H6′); 3.49/2.17(s, CH3), ^{13}C NMR: δ 177.6 (COOH), 151.9 (C1), 112.3 (C2), 133.4 (C3), 118.2 (C4), 135.0 (C5), 113.9 (C6), 147.7 (C1′), 119.7 (C2′), 141.4 (C3′), 121.2 (C4′), 127.3 (C5′), 126.7 (C6′) 13.6 (CH3). Anal. Calc. for C$_{30}$H$_{28}$SnN$_4$O$_8$ (691.2 g mol^{-1}): C, 52.10; H, 4.10; N, 8.10. Found: C, 52.10; H, 4.07; N, 8.26%.

2.3. Catalytic reactions

2-Phenylethanol (1 mM) was slowly added to a solution of ethylacetate (5 ml). As an internal standard acetophenone was used. Catalytic reaction was started by adding 10 µM of **2** or **3**. The ratio of catalyst: 2-phenylethanol was 1:100. The reaction mixture was refluxed at 77 °C and the progress of the reaction was monitored by GC–MS, by removing small samples of the reaction mixture.

To establish the identity of the products unequivocally, the retention times and spectral data were compared to those of commercially available compounds. Thus, 2-phenylethanol, 2-phenylethyl acetate and acetophenone were purchased in their highest commercial purity, stored at 5 °C and purified by passage through a column of basic alumina prior to use.

2.4. X-ray crystallography

Slow evaporation of a dilute 1:1 by volume CH$_3$CN/CHCl$_3$ solution provided a yellow prismatic crystal of **2**, which was mounted on a sealed tube and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 25 reflections in the range 1.34 < θ < 26.30° on a Bruker Smart Apex diffractometer. Data were collected at 293 K using Mo Kα radiation (λ = 0.71073 Å) and the ω-scan technique, and corrected for Lorentz and polarization effects [12]. A semi-empirical absorption correction (Ψ-scans) was made. The structure was solved by direct methods (program SHELXS97) and refined by the full-matrix least-squares method on all F^2 data using the WinGX version of SHELXL97 programs [13]. All hydrogen atoms were located in their calculated positions (C–H 0.93–0.97 Å) and refined using a riding model. Molecular graphics were performed using PLATON2001 [14]. A summary of the crystal data, experimental details and refinement results are listed in Table 1.

Table 1
Crystal data and structure refinement

	2
Empirical formula	$C_{64}H_{72}N_8O_{20}Sn_4$
Formula weight	1748.04
Temperature (K)	293(2)
Wavelength (Å)	Mo Kα 0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	8.504(2)
b (Å)	14.760(3)
c (Å)	16.761(3)
α (°)	65.786(3)
β (°)	83.109(4)
γ (°)	85.074(4)
Volume (Å^3)	1903.4(7)
Z	4
D_c (mg m^{-3})	1.525
Absorption coefficient, μ (mm^{-1})	1.367
$F(000)$	872
Crystal size (mm)	$0.30 \times 0.40 \times 0.50$
θ range for data collection (°)	1.34, 26.37
Ranges of h, k, l	$-10 \leqslant h \leqslant 10, -18 \leqslant k \leqslant 18, -20 \leqslant l \leqslant 20$
Reflections collected/unique [$R_{(int)}$]	15429/7686 [0.0505]
Data/parameters	7686/0/434
Goodness-of-fit (F^2)	1.001
Final R_1/wR_2 indices ($I > 2\sigma_1$)	$R_1 = 0.0613$, $wR_2 = 0.1504$
Largest diff. peak/hole (e Å^{-3})	1.334 and -0.765

3. Results and discussion

3.1. Synthetic aspects

Compound **1** was synthesized according to *Ullmann–Goldberg* condensation from 2-methyl-3-nitro-benzenamine (11.26 g, 0.074 mol), potassium 2-bromobenzoate in the presence of 4-ethylmorpholine and Cu(OAc)$_2$, scheme 2. Adducts **2** and **3** were obtained by azeotropic removal of H$_2$O from the reaction (in benzene) between the dimethylorganotin oxide and HMNAB in a molar ratio of 1:1 and 1:2 for 2 and 3, respectively, scheme 3.

3.2. Crystal structure of **2**

The molecular structure of **2** is shown in Fig. 1 and selected interatomic parameters are collected in Table 2. Compound **2** is a centrosymmetric dimmer distannoxane built up around the planar cyclic Sn$_2$O$_2$ unit. The two oxygen atoms of this unit are tridentate as they link three Sn centres, two endo-cyclic and one exo-cyclic. The distance between the endocyclic and exocyclic tin atoms is 3.6306(10) and the distance between the two endocyclic tin centers is 3.2660(11). The additional links between the endo- and exo-cyclic Sn atoms are provided by bidentate carboxylate ligands that form nearly symmetrical bridges (Sn(1)–O(2) 2.242(6) Å and Sn(2a)–O(3) 2.294(5) Å). Each exocyclic Sn atom is also coordi-

nated by an anisobidentate chelating carboxylate ligand (Sn(2)–O(4) 2.177(5) Å and Sn(2)–O(5) 2.865 (6) Å). The distance Sn(1)–O(4) is 2.781(5) Å. The Sn–O distances 2.865 and 2.781 Å are considered long to indicate strong bonding interactions, however, the range of distances Sn–O of 2.61–3.02 Å, has been confidently reported for intramolecular bonds [15]. In this case the O(5) acts as monoatomic bridge and connects the endocyclic and exocyclic tin centers.

The phenyl rings are planar. The dihedral angles between the planes of the phenyl rings for 2 are 59.5(4) and 56.5(5)° for the bidentate bridging and the anisobidentae chelating ligands, respectively. The aminobenzoate portion of each carboxylato ligand is effectively planar which presumably facilitates the formation of intramolecular N(18)–H″···O(3) and N(38)–H···O(5) interactions of 2.660(9) and 2.675(10) Å, respectively. The monomers of **2** form hydrogen-bonded dimers linked by two hydrogen bonds involving the C(28)H hydrogen atom and the adjacent O(25) atom, and vice versa, of centro-symmetrically related pairs of molecules. The observed hydrogen-bonding pattern is of the DA = AD type, Fig. 2. The crystal structure of **2** shows ring stacking interactions. The monomers are stacked by a strong $\pi \rightarrow \pi$ interaction and weaker C–H $\rightarrow \pi$ interactions. The monomers are stacked to a chain by a strong $\pi \rightarrow \pi$ interaction, the phenyl rings C(39)–C(40)–C(41)–C(42)–C(43)–C(47) are at a distance of 3.579(6) (symmetry operation; $1 - x, 1 - y, -z$). In this case **2** is self-assembled *via* inter-molecular hydrogen bonds, C–H $\rightarrow \pi$ and $\pi \rightarrow \pi$ stacking interactions. C–H $\rightarrow \pi$, $\pi \rightarrow \pi$ stacking, intra- and inter-molecular hydrogen interactions stabilize this structure, Table 3. The structures of dimeric distannoxane of anthranilic acid, [Me$_2$(NH$_2$-o-H$_{46}$CO$_2$)SnOSn(NH$_2$-o-H$_4$C$_6$CO$_2$)Me$_2$]$_2$ [16] and of [Bu$_2$(DMPA) SnOSn(DMPA)Bu$_2$]$_2$ HDMPA is 2-[bis(2,6-dimethylphenyl)amino]-benzoic acid [10b] have solid state structure closely resembling **2** both in the geometry of the central core (Sn$_2$O$_2$)$_2$, the coordination mode of anthranilic acid and the presence of weaker interactions 2.736(9)–2.918(6) Å.

3.3. Spectroscopy

3.3.1. Infrared spectroscopy

As the carboxylic hydrogen is more acidic than the imino hydrogen the deprotonation occurs in the carboxylic group. This is confirmed by the IR spectra of the complexes, showing the characteristic bands for the secondary amino groups and for the coordinated carboxylate group [17]. The band at ~3300 cm^{-1}, which appears in the IR spectra of the ligand, is assigned to the NH stretching motion and the broad band at ~3000–2900 cm^{-1} is taken to represent the v(NH···O) mode, due to intramolecular hydrogen bonding [3,8–10,17]. The absence of large systematic shifts of the v(NH) and δ(NH) bands in the spectra of the complexes compared with those of the ligand indicates that there is no interaction between the NH group and the metal ions, which is also confirmed
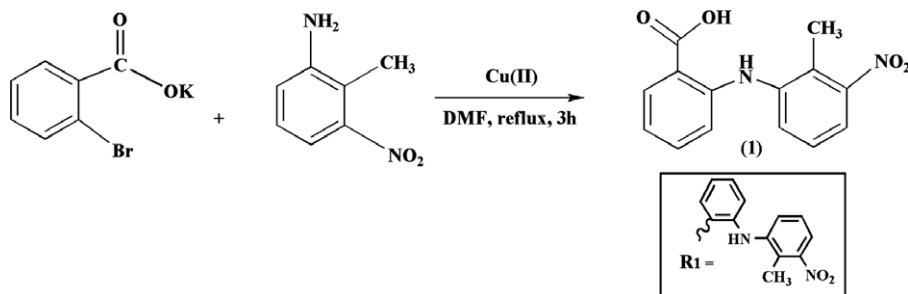
Scheme 2. The reaction scheme for synthesis of **1**.
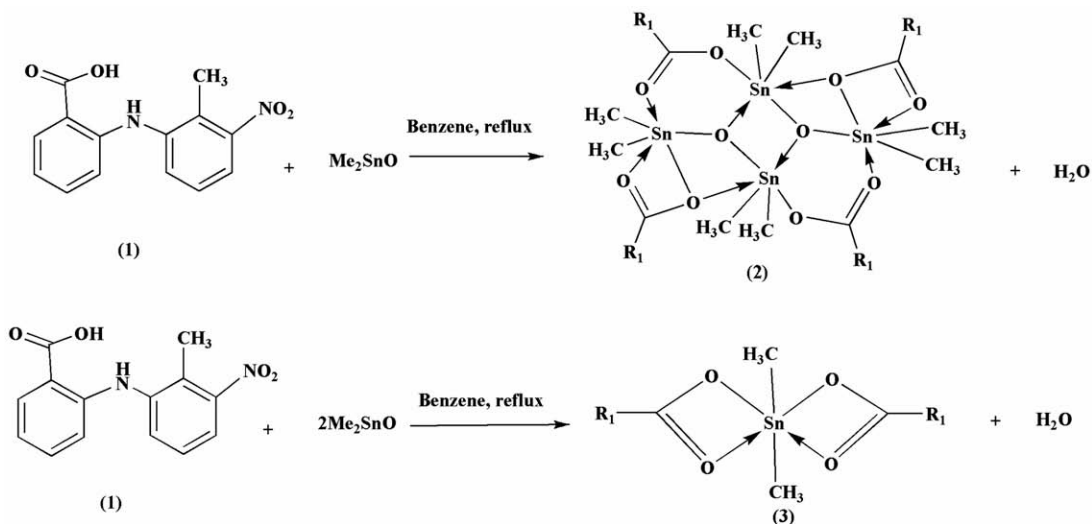
Scheme 3. The reaction scheme for synthesis of **2** and **3**.
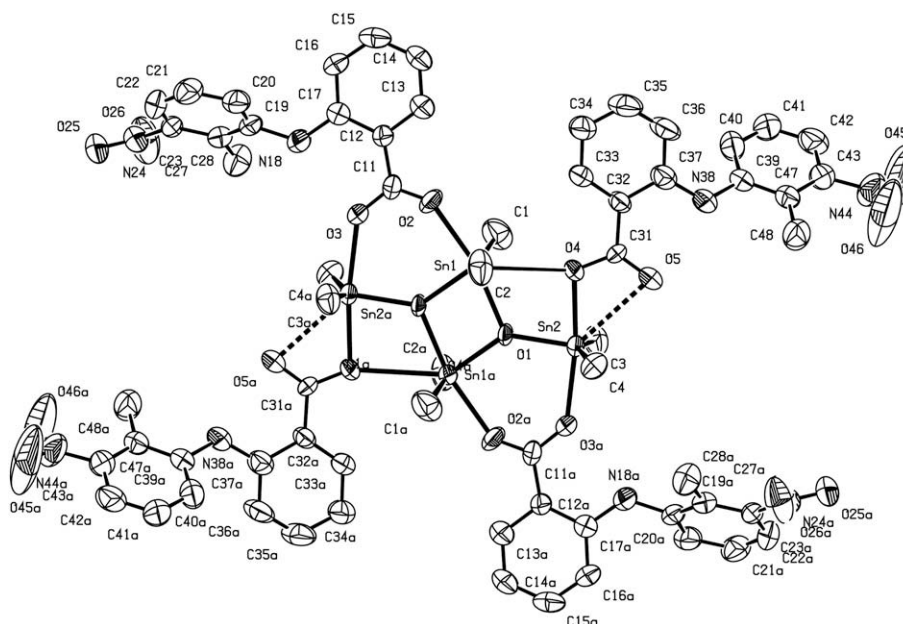
Fig. 1. Perspective view of **2** showing the atomic numbering scheme.

by X-ray analysis. The v_{as}(COO) bands appear at 1614 and 1590 and v_{sym}(COO) at 1373 and 1459 cm^{-1} for 2. The difference, $\Delta[v_{as^-}$ (COO)–v_{sym}(COO)] between these frequencies for **2** (241, 133 cm^{-1}) is close to that found for anisobidentate chelate mode (241 cm^{-1}) and bridging bidentate carboxylato groups (133 cm^{-1}). This is totally consistent with the X-ray structure of **2**. The v_{asym}(COO) and v_{sym}(COO) bands appear at 1666 and 1404 cm^{-1} for **3**. The difference $\Delta[v_{asym}$(COO)–v_{sym}(COO)] between these frequencies is 262 cm^{-1}, which is close to that found for the anisobidentate chelate carboxylato group [7–10,17]. Two bands at 440–410 for 2, are assigned to $v_{as,sym}$(SnO)$_2$, indicating non-linear O–Sn–O moieties, while the bands at 280–210 cm^{-1} are assigned to the tin-oxygen (COO) stretching modes [8–10,17].

3.3.2. NMR spectra

^{1}H and ^{13}C NMR chemical shifts of ligand and its complexes were recorded in CDCl$_3$ solution. The existence of the HN reso-

nance in the ^{1}H NMR spectra of complexes indicates that the nitrogen atom remain protonated and the downfield chemical shift for this group indicates that this proton is involved in an intramolecular hydrogen bond between the HN group and the carbonyl oxygen of the carboxylato group. Deshielding of protons H(3) and H(4) is observed in complexes, which should be related to the electrophilicity of the tin. A σ-charge donation from the COO-donor to the tin center removes electron density from the ligand and produces this deshielding which will attenuate at positions remote from the metal. All shifts are downfield except for that due to H(5) which is shifted upfield. The upfield shift observed for H(5) and its corresponding carbon atom C5, *para* to the tin center, could be due to the flow of charge from the tin into the aromatic ring. The ^{13}C NMR spectra of **2** and **3** reveal resonance assignable to the CO$_2$ nucleus and coordination is confirmed by the fact that this resonance exhibits a downfield shift. Involvement of the carboxyl group in bonding to tin is confirmed by the resonance ascribed

Table 2
Bond lengths [Å] and angles [°] for **2**

Sn(1)–O(1)[a]	2.023(4)
Sn(1)–C(1)	2.078(9)
Sn(1)–C(2)	2.089(8)
Sn(1)–O(1)	2.145(4)
Sn(1)–O(2)[a]	2.242(6)
Sn(1)–Sn(1)[a]	3.2661(11)
Sn(2)–O(1)	2.011(4)
Sn(2)–C(3)	2.080(8)
Sn(2)–C(4)	2.090(7)
Sn(2)–O(4)	2.177(5)
Sn(2)–O(3)	2.294(5)
O(2)–Sn(1)[a]	2.242(6)
O(1)[a]–Sn(1)–C(1)	107.2(3)
O(1)[a]–Sn(1)–C(2)	103.4(3)
C(1)–Sn(1)–C(2)	148.5(4)
O(1)[a]–Sn(1)–O(1)	76.86(17)
C(1)–Sn(1)–O(1)	99.9(3)
C(2)–Sn(1)–O(1)	93.9(3)
O(1)[a]–Sn(1)–O(2)	91.5(2)
C(1)–Sn(1)–O(2)[a]	87.4(4)
C(2)–Sn(1)–O(2)[a]	84.7(3)
O(1)–Sn(1)–O(2)[a]	167.6(2)
O(1)[a]–Sn(1)–Sn(1)	39.76(12)
C(1)–Sn(1)–Sn(1)[a]	107.2(3)
C(2)–Sn(1)–Sn(1)[a]	100.9(3)
O(1)–Sn(1)–Sn(1)[a]	37.11(11)
O(2)[a]–Sn(1)–Sn(1)	131.11(16)
O(1)–Sn(2)–C(3)	104.4(3)
O(1)–Sn(2)–C(4)	107.7(3)
C(3)–Sn(2)–C(4)	147.2(3)
O(1)–Sn(2)–O(4)	79.97(17)
C(3)–Sn(2)–O(4)	97.1(3)
C(4)–Sn(2)–O(4)	95.1(3)
O(1)–Sn(2)–O(3)	92.36(18)
C(3)–Sn(2)–O(3)	87.8(3)
C(4)–Sn(2)–O(3)	84.1(3)
O(4)–Sn(2)–O(3)	171.70(18)
Sn(2)–O(1)–Sn(1)[a]	134.9(2)
Sn(2)–O(1)–Sn(1)	121.7(2)
Sn(1)[a]–O(1)–Sn(1)	103.14(17)

Symmetry transformations used to generate equivalent atoms.
[a] −x + 2, −y + 2, −z+.

to C(2) and C(3), which exhibit the greatest shift upon coordination [3,8–10].

3.4. Catalysis

The catalytic activity of **2** and **3** were assessed for acetylation of 2-phenylethanol by ethylacetate (Table 4). Ethylacetate was used as solvent, while the molar ratio of catalyst: substarte was 1:100.
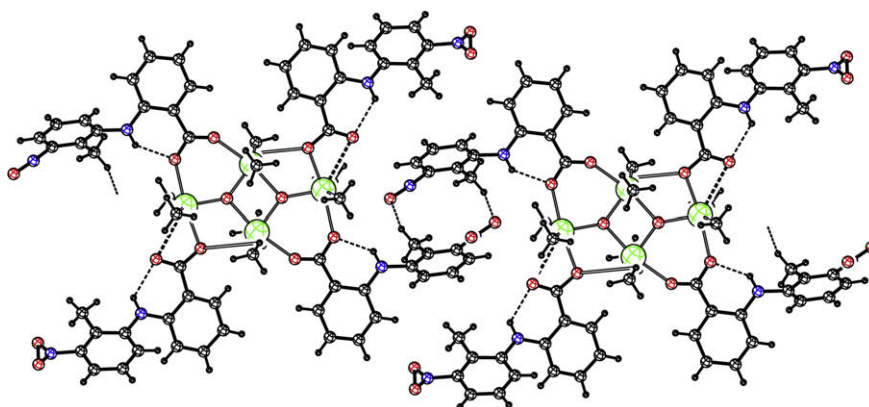
Table 3
Distances (Å) and angles (°) of C–H–π, π–π interactions and intramolecular hydrogen bonds for 2 and

| C	H	Cg	H···Cg	C···Cg	∠(C–H···Cg)
C–H/π					
C(2)[i]	H(2A)	Cg(2) [a]	2.967	3.680(9)	132.13
C(2)[ii]	H(2A)	Cg(2)[a]	3.088	3.657(9)	121.09
		Cg–Cg[b]	β[c]	CgI-Perp[d]	CgJ-Perp[d]
Cg(8)[iv]	Cg(8)	3.579(6)	3.98	3.570	3.570
H-bonds					
N(18)	H(18)	O(3)	2.01	2.660(9)	131
N(38)	H(38)	O(5)	2.12	2.675(10)	122
C(28)[iv]	H(28A)	O(5)	2.42	3.175(13)	135

[a] Cg(8) and Cg(2) refer to the centroids C(39)···C(47), and Sn(1)–O(1)–Sn(1a)–O(1a).
[b] Cg–Cg is the distance between ring centroids; symmetry transformations, (i) *x, y, z*; (ii) −*x, −y*, 1 − *z*; (iii) 1 − *x*, 1 − *y*, −*z*; (iv) −1 − *x, −y*, 2 − *z*.
[c] Where *β* is the angle Cg(I) → Cg(J).
[d] CgI-Perp or CgJ-Perp is the perpendicular distance of Cg(I) on ring J.

The reaction mixture was refluxed at 77 °C under aerobic conditions and the progress of the reaction was monitored by GC–MS, by removing small samples of the reaction mixture. Under these conditions, the transesterification catalysed by **2** was normally progressed and quantitative yields were obtained after 6 h. When the monomeric catalyst **3** was used, low yields of 25% were obtained within 6 h. However, after 22 h, **3** was able to give quantitative yields as well. In all cases, the only reaction product which has been detected was 2-phenylethylacetate.

To identify the active catalytic species involved in the present reaction, small liquots of the reaction mixture were studied by LC–MS method and the analysis was performed in the negative ion mode. For reactions catalysed by **2**, after 0, 2, 4 and 22 h, LC–MS spectroscopy always revealed one major product, with a very intense anion at *m/z* 853.5 tentatively assigned to a dianion of **2**. When the catalyst **3** was used, sample analysis after 0, 2, 4 and 6 h reaction time, exhibited characteristic ions at *m/z* 565.4, which is the major one, and one less intense at *m/z* 853.5. The first anion assigned to **3** after the cleavage of the peripheral CH_3^- and NO_2^- groups of the organic ligand. The analysis of an aliquot of the reaction mixture after 22 h, interestingly, showed a very intense anion at *m/z* 853.5 and only a small one at *m/z* 565.4. The appearance of the peak at *m/z* 853.5 clearly indicates the formation of a dimeric species analogous to **2**. This was possibly generated after several hours into the refluxed catalytic reaction, it seems to be the active catalyst and it is directly correlated to the quantitative yields obtained after 22 h.

Fig. 2. Inter- and intra molecular hydrogen bonding pattern of **2**.

Table 4
Acetylation of 2-phenylethyl alcohol catalyzed by **2** and **3**[a]
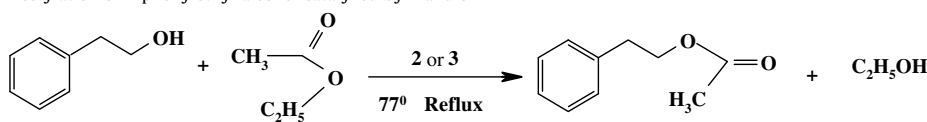
| 2-Phenylethanol | Ethylacetate | 2-Phenylethylacetate | Ethanol |

Cat (conc./mol%)	Reaction time (h)	Yield[b] (%)
2 (0.01)	1	38.8
2 (0.01)	4	88.5
2 (0.01)	6	100
2 (0.01)	22	100
3 (0.01)	1	21.3
3 (0.01)	4	25.1
3 (0.01)	6	25.7
3 (0.01)	22	100

[a] Reaction conditions: ROH (1 mmol); ethylacetate (5 ml); catalyst (10 μmol).
[b] Yields were based on alcohol and determined by GC–MS.

The present findings are in accordance and further support previously proposed mechanism, whereas the fundamental aspects is the existence of an active core which involves a dimeric distannoxane [4]. In this context, transesterification catalysed by **2**, which bears such distannoxane centre, evolved progressively, and resulted in a 100% yield within 6 h. The reaction catalysed by monomeric **3** slowed down, however, when active distannoxane core formed, it was able to function as an efficient catalyst leading finally to quantitatively yields too.

In conclusion, the present air and moisture stable diorganotin complexes efficiently catalyze the transesterification reaction of 2-phenylethanol without addition of free ligand or any promoting additive. Moreover, we have demonstrated that for the development of efficient catalytic systems, a distannoxane core should be involved into the catalyst molecule.

Supplementary material

CCDC 671218 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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