

# Synthesis of a cyclic dinuclear organotin carboxylate via simultaneous debenzoylation and decarbonylation reactions: X-ray crystal structure of $[(\text{PhCH}_2)_2\{\text{O}_2\text{CC}_6\text{H}_4\{\text{N}(\text{H})-\text{N}=(\text{C}_6\text{H}_3-4(=\text{O})-5-\text{O})\}-o\}\text{Sn}]_2$

Tushar S. Basu Baul<sup>a,\*</sup>, Keisham Surjit Singh<sup>a</sup>, Antonín Lyčka<sup>b</sup>,  
Michal Holčápek<sup>c</sup>, Anthony Linden<sup>d,\*</sup>

<sup>a</sup> Department of Chemistry, North-Eastern Hill University, NEHU Permanent Campus, Umshing, Shillong 793 022, India

<sup>b</sup> Research Institute for Organic Syntheses, Rybitví 296, CZ-532 18 Pardubice 20, Czech Republic

<sup>c</sup> University of Pardubice, Faculty of Chemical Technology, Department of Analytical Chemistry, nám. Čs. legii 565, 53210 Pardubice, Czech Republic

<sup>d</sup> Institute of Organic Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland

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## Abstract

The complex,  $[(\text{PhCH}_2)_2\{\text{O}_2\text{CC}_6\text{H}_4\{\text{N}(\text{H})-\text{N}=(\text{C}_6\text{H}_3-4(=\text{O})-5-\text{O})\}-o\}\text{Sn}]_2$  (**1**), is obtained as the exclusive reaction product from the reaction of sodium 2-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoate and  $(\text{PhCH}_2)_3\text{SnCl}$ . The reaction possibly proceeds via Dakin type rearrangements where arylazosalicylaldehyde is oxidized to arylazocatechol, followed by facile Sn–C bond cleavage. Complete assignments were achieved by <sup>1</sup>H, <sup>13</sup>C, 2D <sup>1</sup>H–<sup>119</sup>Sn HMQC (<sup>119</sup>Sn chemical shift), 1D gs <sup>1</sup>H–<sup>15</sup>N HMQC (<sup>1</sup>J(<sup>15</sup>N, <sup>1</sup>H) coupling constant) NMR and ESI-MS. The crystal structure of compound **1** as determined by X-ray diffraction analyses shows a cyclic centrosymmetric dinuclear moiety linked into extended chains by pairs of long Sn···O contacts of approximately 3.2 Å. Two polymorphs were identified and their structures differ primarily in the packing arrangement afforded by the benzyl groups. In one polymorph, when viewed along the Sn···Sn vector, the benzyl groups at each Sn-atom are oriented to form an S-shape, while they form a U-shape in the second polymorph.

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## 1. Introduction

Investigation of the organotin compounds  $\text{R}_n\text{SnX}_{(4-n)}$  ( $n = 1-4$ ) is of interest because of their biological activity, reactivity, and industrial applications

[1–4]. Several organostannoxanes have been shown to be extremely versatile catalysts for polyurethane, RTV silicone polymerisation and for *trans* esterification reactions [5–9]. Some dibenzyltin dicarboxylates have also been used as catalysts for the synthesis of urethanes [10]. Owing to these applications, the structure and mechanisms of action of these organotin compounds remain a matter of great interest [6,11–17]. In view of this, in recent years there have been constant efforts to develop new synthetic strategies and consequently dearylation and dealkylation [18–24] reactions proved to be useful for synthesizing new organotin clusters. The reaction of  $(\text{PhCH}_2)_3\text{SnCl}$  with sodium

\* Corresponding authors. Tel.: +91 364 272 2626; fax: +91 364 2550486/2721000 (T.S. Basu Baul); Tel.: +41 44 635 4228; fax: +41 44 635 6812 (A. Linden).

E-mail addresses: basubaul@nehu.ac.in, basubaul@hotmail.com (T.S. Basu Baul), alinden@oci.unizh.ch (A. Linden).

2-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoate proceeded effectively via debenylation and subsequent oxidative decarbonylation reactions, and affords the cyclic dinuclear dibenzyltin complex **1**, in contrast to the carboxylate-bridged polymeric structures obtained for the Me<sub>3</sub>Sn (**2**) [25] and Bu<sub>3</sub>Sn (**3**) [26] analogues and the monomeric complex with the Ph<sub>3</sub>Sn (**4**) [27] analogue. In this communication, the synthesis, characterization, and the tin coordination of the novel cyclic and pseudo-polymeric moiety that crystallized as the two polymorphs **1a** and **1b** are reported.

## 2. Experimental

### 2.1. Materials

The solvents used in the reactions were of AR grade and dried using standard procedures. (PhCH<sub>2</sub>)<sub>3</sub>SnCl [28] and LHN<sub>a</sub> [25] were prepared by following the reported methods.

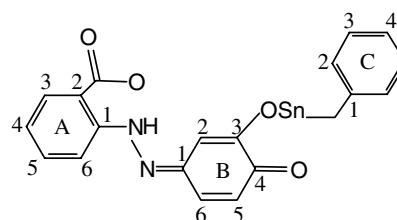
### 2.2. Physical measurements

Elemental analyses were performed with a Perkin-Elmer 2400 series II instrument. IR spectra in the range 4000–400 cm<sup>-1</sup> were obtained on a BOMEM DA-8 FT-IR spectrophotometer with samples investigated as KBr discs. The <sup>1</sup>H-, <sup>13</sup>C NMR and <sup>119</sup>Sn NMR spectra were acquired on a Bruker Avance 500 spectrometer operating at 500.13, 125.76 and 186.46 MHz, respectively. The <sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn chemical shifts were referred to Me<sub>4</sub>Si set at 0.00 ppm, CDCl<sub>3</sub> set at 77.0 ppm and tetramethyltin set at 0.00 ppm, respectively. 2D gs (gradient selected)-H,H-COSY, gs <sup>1</sup>H-<sup>13</sup>C HSQC (optimized for <sup>1</sup>J(<sup>13</sup>C, <sup>1</sup>H) ca. 150 Hz) and gs <sup>1</sup>H-<sup>13</sup>C HMBC (optimized for <sup>3</sup>J(<sup>13</sup>C, <sup>1</sup>H) ca. 5–10 Hz) were determined using microprogrammes (Bruker: XWINNMR 3.5). 2D <sup>1</sup>H-<sup>119</sup>Sn HMQC (optimized for J(<sup>119</sup>Sn, <sup>1</sup>H) = 100 Hz) and 1D gs <sup>1</sup>H-<sup>15</sup>N HMQC (optimized for <sup>1</sup>J(<sup>15</sup>N, <sup>1</sup>H) = 100 Hz) were used for the measurement of the <sup>119</sup>Sn chemical shift and <sup>1</sup>J(<sup>15</sup>N, <sup>1</sup>H) coupling constants, respectively. Positive- and negative-ion electrospray ionization mass spectra (ESI-MS) were measured on an Esquire 3000 (Bruker Daltonics) in the range *m/z* 50–1500. Compound **1** was dissolved in acetonitrile and analysed by direct infusion at a flow rate of 1 μl/min. The selected precursor ions were further analysed by MS/MS analyses (isolation width *m/z* = 8 for ions containing one tin atom and *m/z* = 12 for ions containing more tin atoms, collision amplitude: 0.8–1.0 V, ion source temperature: 300 °C, tuning parameter compound stability 20%, flow rate and the pressure of nitrogen 4 l/min and 10 psi, respectively).

### 2.3. Synthesis of [(PhCH<sub>2</sub>)<sub>2</sub>{O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>-*N*(H)-N=(C<sub>6</sub>H<sub>3</sub>-4(=O)-5-O)}<sub>2</sub>Sn]<sub>2</sub> (**1**)

A warm solution of (PhCH<sub>2</sub>)<sub>3</sub>SnCl (0.71 g, 1.66 mmol) in anhydrous methanol (ca. 30 ml) was added slowly to a solution of LHN<sub>a</sub> (0.50 g, 1.67 mmol) in hot anhydrous methanol (ca. 70 ml) under stirring conditions. The dark red solution was refluxed for 8 h. It was then evaporated to dryness and the residue was dried in vacuo. The dried mass was washed with hot petroleum ether (60–80 °C, 4 × 5 ml), dried in vacuo, extracted by boiling in anhydrous benzene (ca. 60 ml) and filtered while hot. The filtrate was then concentrated to one-sixth of initial solvent volume, precipitated with petroleum ether (60–80 °C), filtered and the crude product was dried in vacuo. The dark red solid was dissolved by boiling in benzene, filtered to remove any undissolved particles and the filtrate was left to evaporate slowly at room temperature for 3 days to afford dark red crystals (prism and needle types) of the title compound **1**, 0.53 g yield (43%); m.p.: 205–208 °C. Anal. Found: C, 58.25; H, 4.01; N, 5.00. Calc. for C<sub>54</sub>H<sub>44</sub>N<sub>4</sub>O<sub>8</sub>Sn<sub>2</sub>: C, 58.21; H, 3.90; N, 5.02. IR (KBr, cm<sup>-1</sup>): 1589 ν(OCO)<sub>asym</sub>. <sup>1</sup>H NMR (CDCl<sub>3</sub>/500.13 MHz) <sup>1</sup>: δ<sub>H</sub>: 12.26 [br s, 1H, NH], 8.01 [m, 1H, (A) H3], 7.85 [m, 1H, (A) H6], 7.55 [m, 1H, (A) H5], 7.36 [dd, J(H,H) = 9.0) and 2.4 Hz, 1H, (B) H6], 7.19 [m, 1H, (A) H4], 7.02 [m, 1H, (C) H2], 6.91 [m, 1H, (C) H3], 6.80 [tt, 1H, (C) H4], 6.59 [d, J(H,H) = 2.4 Hz, 1H, (B) H2], 6.51 [d, J(H,H) = 9.0 Hz, 1H, (B) H5], 3.09 and 3.06 [AB system of prochiral methylene group, 2H, CH<sub>2</sub>], ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>/125.76 MHz) <sup>1</sup>: δ<sub>C</sub>: 182.5 [(B) C4], 173.1 [CO<sub>2</sub>], 157.5 [(B) C3], 143.9 [(B) C6], 142.5 [(A) C1], 139.9 [(B) C1], 137.3 [(C) C1], 133.8 [(A) C5], 132.5 [(A) C3], 128.9 [(C) C2], 128.0 [(C) C3], 124.8 [(C) C4], 124.3 [(A) C4], 120.5 [(B) C5], 117.9 [(A) C2], 115.6 [(A) C6], 98.3 [(B) C2], 34.2 [CH<sub>2</sub>], ppm. <sup>119</sup>Sn NMR (CDCl<sub>3</sub>, 186.46 MHz); δ<sub>Sn</sub>: -256.1, ppm. ESI-MS: (a) Positive-ion MS: *m/z* 1155 (42%); 1139 (100%); 597 (62%); 581 (48%). MS/MS of 1155: *m/z* 973; 791; 597; 415. MS/MS of 1139: *m/z* 1047; 955; 937; 775; 671; 581; 489; 399. MS/MS of 597: *m/z* 399. MS/MS of 581: *m/z* 415. Suggested interpretation of observed ions: *m/z* 1155 [M + K]<sup>+</sup>; 1139 [M + Na]<sup>+</sup>; 1047 [M + Na - CH<sub>3</sub>C<sub>6</sub>H<sub>5</sub>]<sup>+</sup>; 973 [M + K - 2\*CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>]<sup>+</sup>; 955 [M + Na - 2\*CH<sub>3</sub>C<sub>6</sub>H<sub>5</sub>]<sup>+</sup>; 937 [M + Na - 2\*CH<sub>3</sub>

<sup>1</sup> Refer to the following figure for the numbering scheme for <sup>1</sup>H and <sup>13</sup>C NMR.



$C_6H_5 - H_2O]^+$ ; 791  $[M + K - 7*CH_3C_6H_4]^+$ ; 775  $[M + Na - 2*CH_3C_6H_4 - 2*CH_3C_6H_4]^+$ ; 671  $[M + Na - CH_3C_6H_5 - 376]^+$ ; 597  $[M_B + K]^+$ ; 581  $[M_B + Na]^+$ ; 489  $[M_B + Na - CH_3C_6H_5]^+$ ; 415  $[M_B + K - 2*CH_3C_6H_4]^+$ ; 399  $[M_B + Na - 2*CH_3C_6H_4]^+$ ,  $M_B$  corresponds to the fragment ion  $HOOC_6H_4N-NC_6H_5O(O)Sn(CH_2C_6H_5)_2$  with  $m/z = 558$ . (b) Negative-ion MS:  $m/z$  1137 (3%); 1115 (16%); 933 (2%); 723 (5%); 557 (6%); 257 (100%); 213 (39%). Negative-ion MS/MS of 1137:  $m/z$  953; 771; 727. Negative-ion MS/MS of 1115:  $m/z$  933; 751; 723; 557. Negative-ion MS/MS of 933:  $m/z$  751; 707; 677; 557. Negative-ion MS/MS of 723:  $m/z$  679; 633; 257; 213. Negative-ion MS/MS of 557:  $m/z$  513. Negative-ion MS/MS of 257:  $m/z$  213. Negative-ion MS/MS of 213:  $m/z$  183. Suggested interpretation of observed ions:  $m/z$  1137  $[M - 2H + Na]^-$ ; 1115  $[M - H]^-$ ; 953  $[M - 2H + Na - 2*CH_3C_6H_5]^-$ ; 933  $[M - H - 2*CH_3C_6H_4]^-$ ; 771  $[M - 2H + Na - 2*CH_3C_6H_5 - 2*CH_3C_6H_4]^-$ ; 751  $[M - H - 4*CH_3C_6H_4]^-$ ; 727  $[M - 2H + Na - 2*CH_3C_6H_5 - 2*CH_3C_6H_4 - CO_2]^-$ ; 723  $[M - Sn(CH_2C_6H_5)_3]^-$ ; 707  $[M - 4*CH_3C_6H_4 - CO_2 - H]^-$ ; 679  $[M - Sn(CH_2C_6H_5)_3 - CO_2]^-$ ; 677  $[M - H - 2*CH_3C_6H_4 - 256]^-$ ; 633  $[M - H - Sn(CH_2C_6H_5)_2 - 2*CH_3C_6H_3]^-$ ; 557  $[M_B - H]^-$ ; 513  $[M_B - H - CO_2]^-$ ; 257  $[M_B + H - Sn(CH_2C_6H_5)_2]^-$ ; 213  $[M_B + H - Sn(CH_2C_6H_5)_2 - CO_2]^-$ .

#### 2.4. X-ray crystallography

Crystals of polymorphs **1a** and **1b** suitable for an X-ray crystal structure determination were initially obtained from the same benzene solution, although the reported data for **1b** are for a crystal obtained from chloroform. All measurements were made at low temperature on a Nonius KappaCCD diffractometer [29] with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and an Oxford Cryosystems Cryostream 700 cooler. Data reduction was performed with HKL Denzo and Scalepack [30]. The intensities were corrected for Lorentz and polarization effects, and empirical absorption corrections based on the multi-scan method [31] were applied. Equivalent reflections were merged. The data collection and refinement parameters are given in Table 1. Each structure was solved by employing heavy-atom Patterson methods [32] followed by the Fourier expansion routine of DIRDIF94 [33]. The non-hydrogen atoms were refined anisotropically. The protonated amine H atom in each structure was placed in the position indicated by a difference electron density map and its position was allowed to refine together with an isotropic displacement parameters. All remaining H atoms were placed in geometrically calculated positions and refined using a riding model where each H atom was assigned a fixed isotropic displacement parameter with a value equal to  $1.2U_{eq}$  of its parent

Table 1  
Crystallographic data for polymorph **1a** and **1b**

	<b>1a</b>	<b>1b</b>
Empirical formula	$C_{54}H_{44}N_4O_8Sn_2$	$C_{54}H_{44}N_4O_8Sn_2$
Formula weight	1114.16	1114.16
Crystal size (mm)	$0.10 \times 0.13 \times 0.25$	$0.12 \times 0.17 \times 0.35$
Crystal shape	Prism	Prism
Temperature (K)	160(1)	160(1)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
<i>a</i> (Å)	10.5488(3)	12.9401(2)
<i>b</i> (Å)	11.3805(3)	14.7264(4)
<i>c</i> (Å)	11.8873(3)	12.6837(3)
$\alpha$ (°)	112.727(2)	90
$\beta$ (°)	110.373(2)	100.008(1)
$\gamma$ (°)	99.154(2)	90
<i>V</i> (Å <sup>3</sup> )	1160.63(6)	2380.24(9)
<i>Z</i>	1	2
<i>D<sub>x</sub></i> (g cm <sup>-3</sup> )	1.594	1.554
( $\mu$ ) (mm <sup>-1</sup> )	1.137	1.109
Transmission factors (min., max.)	0.745, 0.895	0.683, 0.772
$2\theta_{max}$ (°)	55	60
Reflections measured	27,801	59,159
Independent reflections ( <i>R</i> <sub>int</sub> )	5306 (0.074)	6924 (0.065)
Reflection with <i>I</i> > 2σ( <i>I</i> )	4239	5309
Number of parameters	312	311
<i>R</i> ( <i>F</i> ) ( <i>I</i> > 2σ( <i>I</i> ) reflections)	0.039	0.038
<i>wR</i> ( <i>F</i> <sup>2</sup> ) (all data)	0.095	0.085
GOF( <i>F</i> <sup>2</sup> )	1.081	1.045
max., min. Δρ (e/Å <sup>3</sup> )	1.53, -1.08	1.28, -0.91

atom. The refinement of each structure was carried out on  $F^2$  using full-matrix least-squares procedures, which minimized the function  $\sum w(F_o^2 - F_c^2)^2$ . A correction for secondary extinction was applied only for **1a**. Neutral atom scattering factors for non-hydrogen atoms were taken from Maslen et al. [34] and the scattering factors for H-atoms were taken from Stewart et al. [35]. The values of the mass attenuation coefficients are those of Creagh and Hubbel [36]. All calculations were performed using the SHELXL97 [37] program.

### 3. Results and discussion

#### 3.1. Synthesis

Triorganotin(IV) carboxylates are normally prepared by simple metathesis reactions, and in a similar way, the complexes  $R_3Sn[O_2CC_6H_4\{N=N(C_6H_3-4-OH-5-CHO)\}-o]$  were obtained in one step reactions between (i) sodium 2-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoate (LHNa) and  $R_3SnCl$  in methanol (*R* = Me (**2**)) [25], (ii) 2-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid [27] (LHH', where H and H' refer to phenolic and carboxylic protons, respectively) and  $(R_3Sn)_2O$  (*R* = *n*Bu (**3**)) [26] and  $R_3SnOH$  in toluene (*R* = Ph (**4·OH<sub>2</sub>**)) [27] under different experimental



mass spectra provide other abundant fragment ions. The suggested fragment ions are in a good correlation with the cyclic moiety elucidated from the X-ray crystal structure data (vide infra). The typical neutral losses are the subsequent losses of benzyl or toluene. Another important neutral loss is CO<sub>2</sub> as a typical fragmentation path in the negative-ion ESI mass spectra of carboxylic acids.

The <sup>1</sup>H-, <sup>13</sup>C- and <sup>119</sup>Sn chemical shifts for **1** are given in Section 2. The proton–proton connectivity was determined from a correlated spectroscopy (H,H-COSY) experiment. The <sup>13</sup>C chemical shift assignments were straightforward and have been achieved from heteronuclear single quantum correlation (HSQC) and heteronuclear multiple-bond connectivity (HMBC) spectra. The solubility of compound **1** in deuteriochloroform was very low and, thus, 2D <sup>1</sup>H–<sup>119</sup>Sn heteronuclear multiple quantum correlation (HMQC) had to be used for the measurement of the <sup>119</sup>Sn chemical shift. The <sup>119</sup>Sn resonance was found at –256.1 ppm, which corresponds to the value found for dibenzyltin(IV) dibenzoate (–252.5 ppm) [41] in deuteriochloroform. In dibenzyltin(IV) dibenzoate, two benzyl groups and all four oxygen atoms (bidentate carboxylates) are bound to the tin atom analogously to the situation in compound **1**. The 1D gs <sup>1</sup>H–<sup>15</sup>N HMQC (optimized for <sup>1</sup>J(<sup>15</sup>N, <sup>1</sup>H) = 100 Hz) technique was used to determine the <sup>1</sup>J(<sup>15</sup>N, <sup>1</sup>H) coupling constant, which is 96.0 Hz. Such a value is typical of a hydrazone form (*keto*-) [42,43] in deuteriochloroform. This indicates that complex **1** retains its dinuclear cyclic solid-state structure in solution, although there may be a breakdown of the

polymeric linkages (see Section 3.3). Further, the existence of the *keto*- form of the compound **1** is also reflected clearly in the <sup>13</sup>C chemical shift of C4 (182.5 ppm) of the ring B [42,43].

### 3.3. X-ray crystallography

Compound **1** crystallizes as two polymorphs, **1a** and **1b**. The structure of the principal centrosymmetric cyclic dinuclear moiety in each polymorph is depicted in Figs. 1 and 2, respectively, while selected geometric parameters are given in Table 2. Each Sn-atom is coordinated by two benzyl groups and the opposite ends of two azo ligands. Each azo ligand coordinates to two Sn-atoms via bidentate coordination of the carboxylate group to one Sn-atom and bidentate coordination of the adjacent O-atoms of the *o*-substituted ring to the other Sn-atom. One of the azo N-atoms is protonated to compensate for the deprotonation of the original hydroxy group in the ligand and the bond lengths within the *o*-substituted ring show a quinoline pattern (see Scheme 1). The coordination of the Sn-atom leaves one face of the coordination sphere quite open. This space is filled by a long Sn···O(1)<sup>i</sup> contact of 3.248(2) Å in **1a** and 3.199(2) Å in **1b** from an adjacent cyclic moiety to give a distorted pentagonal bipyramidal coordination geometry about the Sn-atom. These Sn···O(1)<sup>i</sup> distances are well inside the sum of the van der Waals radii of these atoms, so represent significant secondary interactions. The long Sn···O contacts link dinuclear moieties across a centre of inversion to form

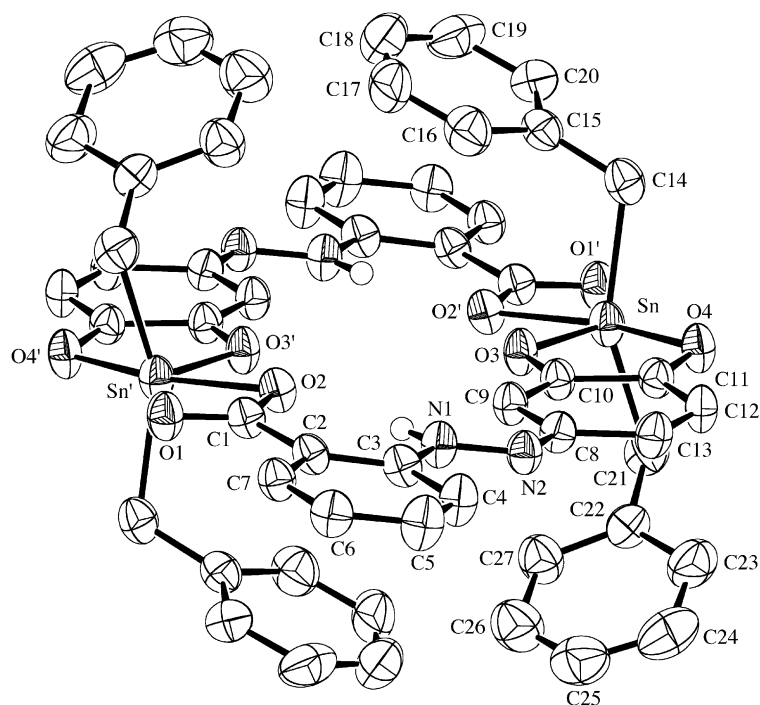


Fig. 1. The cyclic dinuclear moiety of polymorph **1a** with the atom-labelling scheme (50% probability ellipsoids).

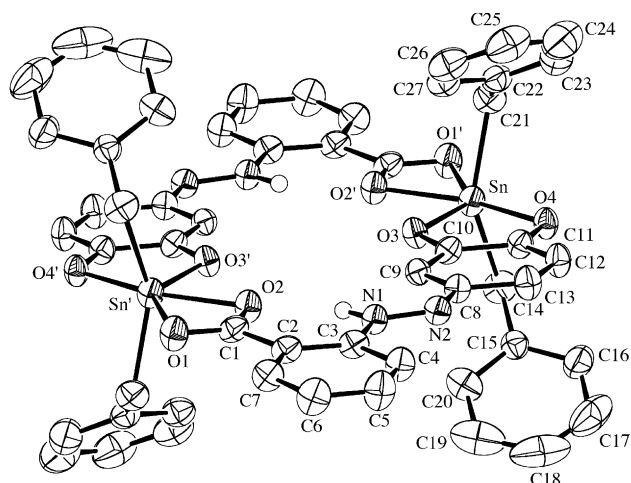


Fig. 2. The cyclic dinuclear moiety of polymorph **1b** with the atom-labelling scheme (50% probability ellipsoids).

Table 2

Selected bond lengths (Å) and angles (°) for polymorphs **1a** and **1b**<sup>a</sup>

	<b>1a</b>	<b>1b</b>
Sn–O(1) <sup>i</sup>	2.635(2)	2.612(2)
Sn–O(1) <sup>ii</sup>	3.248(2)	3.199(2)
Sn–O(2) <sup>i</sup>	2.170(2)	2.203(2)
Sn–O(3)	2.066(2)	2.071(2)
Sn–O(4)	2.235(2)	2.231(2)
Sn–C(14)	2.150(4)	2.142(3)
Sn–C(21)	2.138(4)	2.137(8)
O(3)–C(10)	1.331(4)	1.327(3)
O(4)–C(11)	1.278(4)	1.272(3)
N(2)–C(8)	1.334(4)	1.339(3)
N(1)–N(2)	1.295(4)	1.308(3)
O(1) <sup>i</sup> –Sn–O(1) <sup>ii</sup>	67.89(7)	67.48(6)
O(1) <sup>i</sup> –Sn–O(2)	53.55(7)	53.69(6)
O(1) <sup>i</sup> –Sn–O(3)	138.57(8)	135.68(6)
O(1) <sup>i</sup> –Sn–O(4)	145.06(7)	148.10(6)
O(1) <sup>i</sup> –Sn–C(14)	83.7(1)	80.65(9)
O(1) <sup>i</sup> –Sn–C(21)	82.1(1)	81.74(9)
O(1) <sup>ii</sup> –Sn–O(2) <sup>i</sup>	121.34(7)	121.17(6)
O(1) <sup>ii</sup> –Sn–O(3)	153.34(7)	156.72(6)
O(1) <sup>ii</sup> –Sn–O(4)	77.19(7)	80.63(6)
O(1) <sup>ii</sup> –Sn–C(14)	81.7(1)	71.36(9)
O(1) <sup>ii</sup> –Sn–C(21)	70.6(1)	74.21(8)
O(2) <sup>i</sup> –Sn–O(4)	161.35(8)	158.14(6)
O(2) <sup>i</sup> –Sn–O(3)	85.02(8)	82.05(6)
O(2) <sup>i</sup> –Sn–C(14)	94.4(1)	97.9(1)
O(2) <sup>i</sup> –Sn–C(21)	96.5(1)	95.42(9)
O(3)–Sn–O(4)	76.35(8)	76.22(6)
O(3)–Sn–C(14)	101.7(1)	106.13(9)
O(3)–Sn–C(21)	105.0(1)	107.47(9)
O(4)–Sn–C(14)	90.4(1)	90.4(1)
O(4)–Sn–C(21)	87.6(1)	88.89(9)
C(14)–Sn–C(21)	151.9(1)	145.2(1)

<sup>a</sup> Atom labels with superscript 'i' refer to atoms from the centrosymmetrically related ligand in the dinuclear moiety, while those with superscript 'ii' refer to atoms from the next dinuclear moiety in the polymeric chain.

a cooperative four-membered Sn–O···Sn–O loop. As the same pair of interactions occurs at each end of the dinuclear moiety, these moieties are linked into extended chains which run along the [101] (in **1a**) and [100] (in **1b**) directions (Figs. 3 and 4). The protonated amine group forms an intramolecular hydrogen bond with the adjacent carboxylate O-atom in the same ligand.

The two polymorphs of **1** were found in the same batch of crystals, so had apparently crystallized simulta-

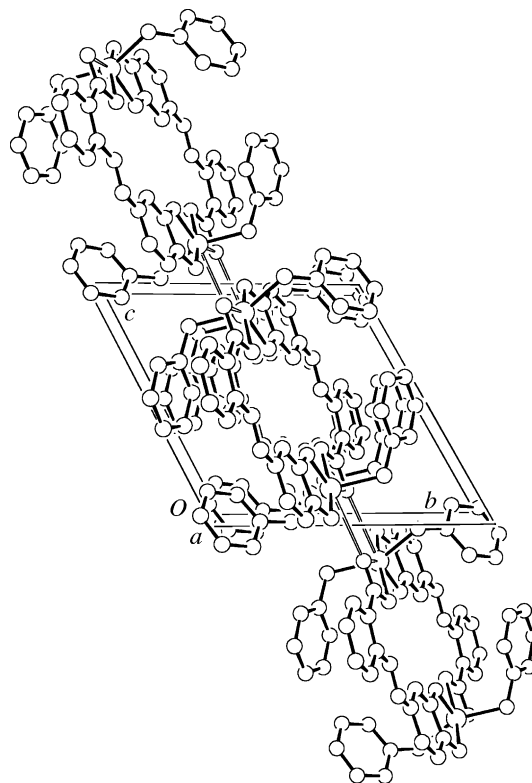


Fig. 3. The molecular packing of **1a** showing the links between the cyclic dinuclear moieties to form a polymeric chain.

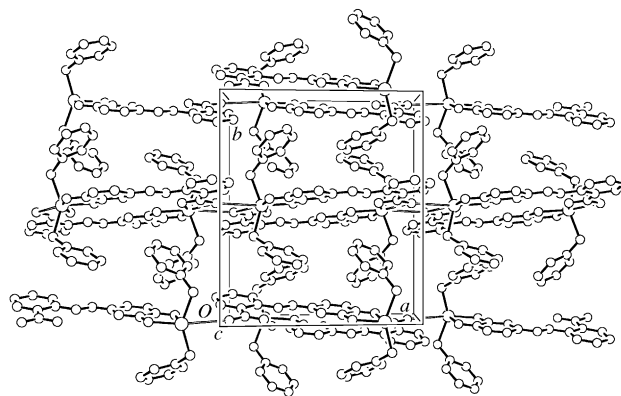


Fig. 4. The molecular packing of **1b** showing the links between the cyclic dinuclear moieties to form a polymeric chain.

neously. The structures of the polymorphs differ primarily in the arrangement of the benzyl groups, which apparently allows different, but energetically similar, packing motifs to be adopted. In **1a**, when viewed along the Sn···Sn vector, the benzyl groups at each Sn-atom are oriented such that they appear to form an S-shape through the Sn-atom and those from the front Sn-atom directly eclipse those from the rear Sn-atom. In **1b**, the benzyl groups at each Sn-atom are oriented such that they appear to form a U-shape through the Sn-atom and those from the front Sn-atom point in the opposite direction to those from the rear Sn-atom in an up–down relationship.

#### 4. Supplementary material

CCDC-253636 (**1a**) and CCDC-253637 (**1b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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