

*Dedicated to Professor Alexandru T. Balaban on his 85 anniversary,
with best wishes for a long, scientifically productive life*

AN INORGANIC HELIX IN THE SUPRAMOLECULAR STRUCTURE OF TRIMETHYLTIN DIPHENYLARSINATE, $[\text{Me}_3\text{Sn}(\text{O}_2\text{AsPh}_2)]_n$: A STRUCTURAL COMPARISON OF TRIORGANOTIN ARSINATES AND PHOSPHINATES

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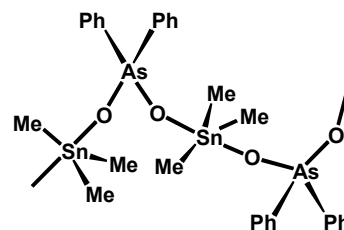
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The crystallographic structure analysis of $[\text{Me}_3\text{Sn}(\text{O}_2\text{AsPh}_2)]_n$ reveals supramolecular association owing to symmetric bridges between Me_3Sn centres afforded by O_2AsPh_2 groups. The resulting polymer has a helical topology. A systematic analysis of triorganotin arsinato and phosphinato analogues indicates a role for the remote substituents on aggregations patterns.



INTRODUCTION

Since the discovery of the DNA the helical structures are fascinating the chemists and numerous are now known as supramolecular architectures, formed by self-assembly. Supramolecular chemistry is defined as the “**chemistry of intermolecular bond**” and “**generalized coordination chemistry**”.¹ Intermolecular forces which can hold together the associated molecules in a supramolecular structure can be dative-coordinate (Lewis acid-base interactions),² hydrogen bonding,³ secondary bonds,⁴ metal lone pair- π (arene) interactions,⁵ and other non-covalent

interactions. As a result of a self-assembly process based upon molecular recognition and structural complementarity, many organometallic compounds form supramolecular architectures.² When organometallic compounds containing both potentially donor and acceptor sites crystallize from nonpolar solvents, the inorganic part of the molecules tend to self-assemble into a central core which is externally surrounded by the organic groups. The later form a lipophylic “sleeve”, compatible with the organic (hydrocarbon) environment. This type has been underscored by H. Bock *et al.*⁶ for some alkali metal derivatives of organophosphoric anions. The

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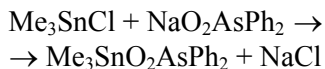
same principle is at work in many organometallic derivatives of organophosphorus ligands and in related organoarsenic derivatives.⁷

Among main group organometallic compounds organotin carboxylates are probably the best investigated supramolecular architectures, characterized by a broad compositional and structural variety,⁸ in which mono-, di- and triorganotin moieties can form very different types of mononuclear and polynuclear compounds. Equally attractive could be the organotin derivatives of element-organic oxoacids, *e.g.* organophosphoric and organoarsenic, as demonstrated by the already existing examples. However, their number is still limited. Thus, triorganotin derivatives of organophosphorus oxoacids are known to self-assemble with formation of supramolecular chain-like (linear and helical) arrays or discrete cyclic supermolecules, like the tetrameric trimethyltin diphenylphosphinate, $[\text{Me}_3\text{SnO}_2\text{PPh}_2]_4$. Organotin derivatives of organoarsenic oxoacids are much less investigated. For comparison, we found of interest to examine the solid state structure of the arsenic analogue the related trimethyltin diphenylarsinate, $\text{Me}_3\text{SnO}_2\text{AsPh}_2$. The examination of the literature reveals that most attention was paid to organotin derivatives of dimethylarsinic acid, $\text{Me}_2\text{As}(\text{O})\text{OH}$,⁹ and only one study was made on an organotin derivative of phenylarsonic acid, $\text{PhAs}(\text{O})(\text{OH})_2$, namely $\{\text{Me}_3\text{Sn}[\text{O}_2\text{As}(\text{Ph})\text{OH}]\}_n$.¹⁰

We report here the solid state of trimethyltin diphenylarsinate, which unlike its diphenylphosphinic analogue (a tetramer) was found to be a chain-like supramolecular polymer.

RESULTS

Trimethyltin diphenylarsinate, $\text{Me}_3\text{SnO}_2\text{AsPh}_2$ (**1**), has been prepared from trimethyltin chloride and sodium diphenylarsinate in benzene:



and crystals suitable for X-ray diffraction analysis deposited from this solution on slow evaporation. The compound has been obtained earlier by two different other procedures (oxidation of $\text{Me}_3\text{SnAsPh}_2$ and condensation of $\text{Me}_3\text{SnOSnMe}_3$ with $\text{Ph}_2\text{As}(\text{O})\text{OH}$) and reported as tetrameric in benzene solution.¹¹

The X-ray structure determination reveals $[\text{Me}_3\text{Sn}(\text{O}_2\text{AsPh}_2)]_n$ to be a coordination polymer with the asymmetric unit comprising one formula unit, Fig 1(a). The diphenylarsinato anion is μ_2 -bridging, linking two tin centres in a coordination

polymer propagating along the crystallographic *b*-axis, *i.e.* being generated by a 2_1 -screw symmetry so that the chain has the topology of a helix, Fig. 1(b). The Sn–O1, O2 bond lengths are experimentally equivalent at 2.224(2) and 2.225(2) Å, an observation related to the equivalence of the As–O1, O2¹ bond lengths [1.658(2) and 1.661(2) Å for *i*: 1-*x*, -1/2+*y*, 1/2-*z*]. The tin atom is penta-coordinate within a *trans*-C₃O₂ donor set. The computed value of τ is 0.90 which compares with $\tau = 0.0$ and 1.0 for ideal square pyramidal and trigonal bipyramidal coordination geometries, respectively.¹² The deviation of the *trans* angle, *i.e.* 174.99(9)°, for the ideal 180° is only minor. Similarly, the trigonal C–Sn–C angles span a narrow range [118.6(2) to 121.2(2)°] as do the O–Sn–C angles [87.18(15) to 93.75(13)°]. The supramolecular chains assemble in the crystal without directional intermolecular interactions between them in accord with the geometric criteria assumed in PLATON,¹³ Fig. 1(c).

DISCUSSION

A search of the Cambridge Structural Database (CSD)¹⁴ was undertaken to seek literature precedents for triorganotin compounds with diorganarsinato ligands. This revealed some related compounds, *e.g.* $[\text{Me}_3\text{Sn}(\text{O}_2\text{AsMe}_2)]_n$ ^{9a} and $[\text{Ph}_3\text{Sn}(\text{O}_2\text{AsMe}_2)]_n$.^{9c} Simplified illustrations for these coordination polymers are shown in Fig. 2, and selected geometric parameters are given in Table 1. As mentioned above, the title compound, $[\text{Me}_3\text{Sn}(\text{O}_2\text{AsPh}_2)]_n$, is a helical polymer. Similar but non-identical helical chains are found in trimethyltin derivative $[\text{Me}_3\text{Sn}(\text{O}_2\text{AsMe}_2)]_n$ ^{9a}; in this compound two independent formulae units comprise the asymmetric unit and non-systematic differences in key geometric parameters are apparent, Table 1. Further, while helical, the helix is somewhat stretched in this chain with disparate pitches. In $\{\text{Me}_3\text{Sn}[\text{O}_2\text{As}(\text{Ph})\text{OH}]\}_n$,¹⁰ the R' groups are distinct, *i.e.* methyl and hydroxyl. This introduces asymmetry in the Sn–O bond lengths if not for electronic reasons, this is due to hydrogen bonding interactions between neighbouring chains. In this scheme, chains are linked into a two-dimensional array *via* eight-membered $\{\dots\text{HOAsO}\}_2$ synthons. The bridging-O atom involved in this hydrogen bonding interaction forms the longer of the Sn–O bonds. A quite distinctive chain is found in the crystal structure of $[\text{Ph}_3\text{Sn}(\text{O}_2\text{AsMe}_2)]_n$ [9c] which is strictly linear. By contrast to the pitches observed for the three trimethyltin compounds, the pitch in

$[\text{Ph}_3\text{Sn}(\text{O}_2\text{AsMe}_2)]_n$ ^{9c} has elongated to 7.00 Å, and this gives a clue for the observed distinct topology in this structure. As often invoked in the structural chemistry organotin carboxylates (see INTRODUCTION), steric effects can influence

structural motifs, at least in the solid-state.⁸ In the present circumstances, the presence of three (relatively) bulky phenyl rings about the tin atom precludes the adoption of the helical chain.

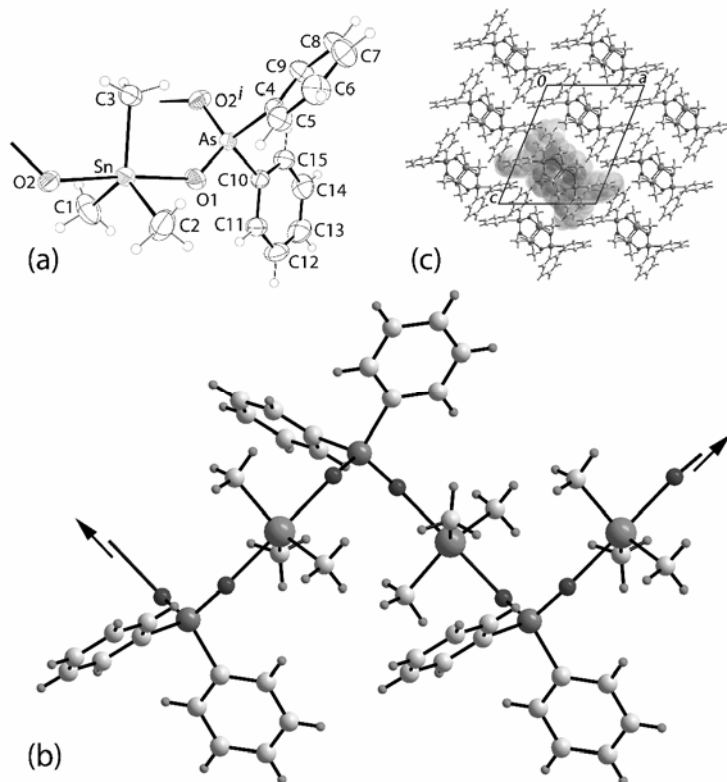


Fig. 1 – (a) Molecular structure diagram of the asymmetric unit in $[\text{Me}_3\text{Sn}(\text{O}_2\text{AsPh}_2)]_n$, extended to show the immediate coordination environment of the arsenic atom, and showing the atom labelling and displacement ellipsoids at the 35% probability level; $i: 1-x, -1/2+y, 1/2-z$. (b) A side-on view of the coordination polymer. (c) The unit cell contents viewed in projection down the b -axis, the axis of propagation of the coordination polymer shown in (b).

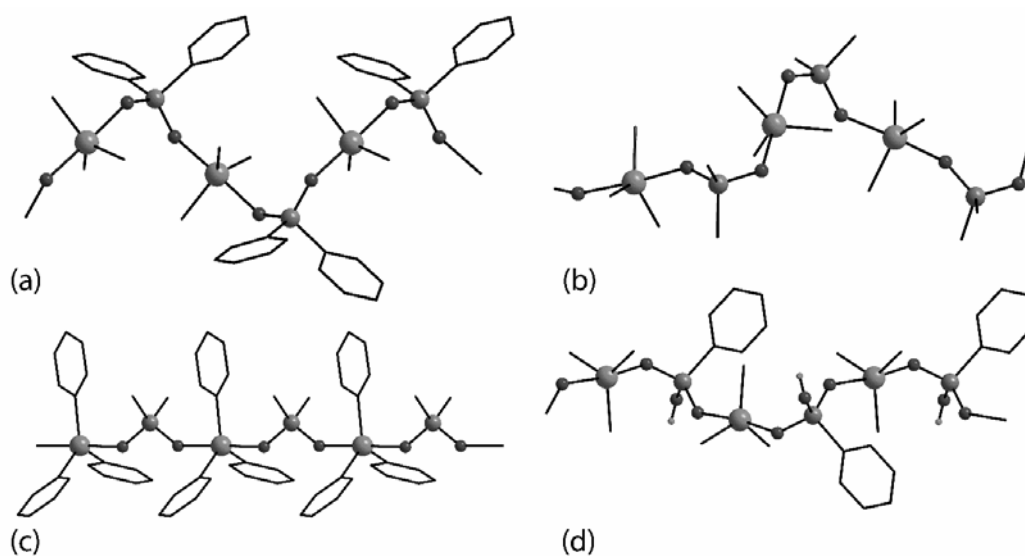


Fig. 2 – Images of coordination polymers for (a) $[\text{Me}_3\text{Sn}(\text{O}_2\text{AsPh}_2)]_n$, (b) $[\text{Me}_3\text{Sn}(\text{O}_2\text{AsMe}_2)]_n$, (c) $[\text{Ph}_3\text{Sn}(\text{O}_2\text{AsMe}_2)]_n$ and (d) $\{\text{Me}_3\text{Sn}[\text{O}_2\text{As}(\text{Ph})\text{OH}]\}_n$. For reasons of clarity, non-acidic hydrogen atoms have been removed and carbon-containing residues illustrated in (black) stick form. Colour code: orange, tin; olive-green, arsenic; red, oxygen; green, hydrogen.

Table 1
Selected geometric data (Å, °) for $[R_3Sn(O_2AsR'_2)]_n$ and $[R_3Sn(O_2PR'_2)]_n$ compounds

Compound	Sn–O1, Sn–O2	O1–Sn–O2	O1–As–O2	Pitch	Ref.
$[Me_3Sn(O_2AsPh_2)]_n$	2.224(2) 2.225(2)	174.99(9)	116.97(14)	4.86	this work
$[Me_3Sn(O_2AsMe_2)]_n$	2.196(2) 2.219(2) 2.2067(19) 2.277(2)	174.49(9) 176.48(7)	110.92(11) 111.95(11)	5.04 5.48	[9a]
$[Ph_3Sn(O_2AsMe_2)]_n$	2.165(4) 2.170(4)	178.38(13)	106.35(17)	7.00	[9c]
$\{Me_3Sn[O_2As(Ph)OH]\}_n$	2.168(2) 2.3577(1)	173.03(7)	114.16(9)	5.23	[10]
$[Me_3Sn(O_2PMe_2)]_n$	2.208(10) 2.208(10)	174.2(4)	115.0(6)	5.35	[15]
$[n-Bu_3Sn(O_2PMe_2)]_n$	2.220(7) 2.241(7)	176.2(3)	117.4(4)	5.91	[16]
$[Me_3Sn(O_2PPh_2)]_4$	2.250(6) 2.250(6) 2.238(6) 2.238(6) 2.224(6) 2.245(7)	178.1(3) 178.6(3) 176.2(2)	117.4(5) 117.2(5) 117.2(5)	– – –	[17]
$\{n-Bu_3Sn[O_2P(CMe_2C(H)Me)CMe_2]\}_4$	2.209(4) 2.268(4)	176.20(14)	116.5(2)	–	[18]
$[(Ph_2PO_2)Sn(CH_2)_3Sn(O_2PPh_2)]_2$	2.205(4) 2.237(4) 2.215(3) 2.246(3)	175.18(15) 176.26(12)	115.9(3) 116.3(3)	– –	[19]

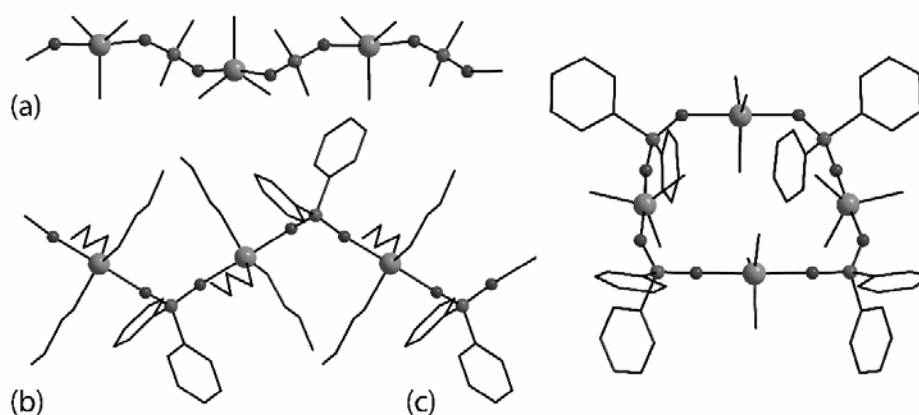


Fig. 3 – Images of coordination polymers and an oligomer for (a) $[Me_3Sn(O_2PMe_2)]_n$, (b) $[n-Bu_3Sn(O_2AsPh_2)]_n$ and (c) $[Me_3Sn(O_2PPh_2)]_4$. For reasons of clarity, all hydrogen atoms have been removed and carbon-containing residues illustrated in (black) stick form. Colour code: orange, tin; pink, arsenic; red, oxygen.

Discussion is now extended to include triorganotin phosphinate derivatives for which only five structures are available in the CSD.¹⁴ Two of the derivatives adopt chain motifs, one of which has the topology of a zigzag chain, *i.e.*

$[Me_3Sn(O_2PMe_2)]_n$,¹⁵ Fig. 3(a), and the other, *i.e.* $[n-Bu_3Sn(O_2PMe_2)]_n$,¹⁶ having a helical topology, Fig. 3(b). The direct analogue of the title compound, *i.e.* $[Me_3Sn(O_2PPh_2)]_4$,¹⁷ is a cyclic tetramer with mirror symmetry (*i.e.* three

independent tin atoms) bisecting the molecule. Similar oligomeric structures are found for each of $\{n\text{-Bu}_3\text{Sn}[\text{O}_2\text{P}(\text{CMe}_2\text{C}(\text{H})\text{MeCMe}_2)]\}_4$,¹⁸ which has crystallographic 4-fold symmetry (*i.e.* one independent tin atom), and $[(\text{Ph}_2\text{PO}_2)\text{Sn}(\text{CH}_2)_3\text{Sn}(\text{O}_2\text{PPh}_2)]_2$,¹⁹ which is located about a centre of inversion (*i.e.* two independent tin atoms).

Direct analogues available for comparison are found in the crystal structures of $[\text{Me}_3\text{Sn}(\text{O}_2\text{AsMe}_2)]_n$ ^{9a} and $[\text{Me}_3\text{Sn}(\text{O}_2\text{PMe}_2)]_n$.¹⁵ While both adopt supramolecular chain, the former is extended helical and the latter zigzag. The pitch in $[\text{Me}_3\text{Sn}(\text{O}_2\text{PMe}_2)]_n$ ¹⁵ is intermediate between the two independent pitches in $[\text{Me}_3\text{Sn}(\text{O}_2\text{AsMe}_2)]_n$,^{9a} Table 1. The three other triorganotin phosphinate structures, with either or both bulky tin- or phosphorus-bound substituents have tetrameric motifs.

Clearly, even for this small series of compounds, great structural diversity is observed, seemingly related to the steric bulk of the tin- or arsenic-/phosphorus-bound groups.

EXPERIMENTAL

Preparation of $[\text{Me}_3\text{Sn}(\text{O}_2\text{AsPh}_2)]_n$

Sodium diphenylarsinate, $\text{Na}[\text{O}_2\text{AsPh}_2]$, was prepared by treating 0.262 g (1 mmol) $\text{Ph}_2\text{As}(\text{O})\text{OH}$ with NaOH (0.04 g, 1 mmol) in benzene and to the resulting suspension was added a solution of Me_3SnCl (0.20 g, 1 mmol) in benzene. The

mixture was stirred for 3 hrs, then filtered and the solvent evaporated on a rotavap. Yield: 65.7 % $(\text{Me}_3\text{Sn})\text{O}_2\text{AsPh}_2$.

M.p. 160°C. IR Spectrum (cm^{-1}): **552, 541** ($\nu_{\text{Sn-C}}$), **601, 604** ($\nu_{\text{As-C}}$), **761, 742** ($\nu_{\text{As-O}}$), **857** ($\nu_{\text{As=O}}$),

Crystals for X-ray analysis deposited from the benzene filtrate on standing.

Crystal Structure Determination

Intensity data were measured at 293 K on a Bruker SMART APEX I CCD with $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. Data processing and absorption corrections were accomplished with SMART,²⁰ SAINT²¹ and SADABS.²² The structure was solved with SIR-2014²³ and refined (SHELXL-2014/6²⁴) on F^2 by full-matrix least-squares with anisotropic displacement parameters for all non-hydrogen atoms, and with hydrogen atoms included in the riding model approximation with $U_{\text{iso}} = 1.2\text{--}1.5U_{\text{eq}}$ (carrier atom). A weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (0.038P)^2 + 0.264P]$ where $P = (F_o^2 + 2F_c^2)/3$ was introduced. Details of unit cell data, X-ray data collection and structure refinement are given in Table 2. The programs ORTEP-3 for Windows,²⁵ PLATON¹³ and DIAMOND²⁶ were also used in the analysis.

CONCLUSIONS

The status of triorganotin compounds of both arsinato and phosphinato ligands is still in its infancy. Already, several quite distinct structural motifs are apparent and early evidence suggests a dependency upon the tin- and/or arsenic-/phosphorus-bound substituents.

Table 2
Crystallographic data and refinement details for (1)

Formula	$\text{C}_{15}\text{H}_{19}\text{AsO}_2\text{Sn}$
Formula weight	424.91
Crystal colour, habit	Colourless prism
Crystal size/mm	0.13 x 0.14 x 0.26
Crystal system	monoclinic
Space group	$P2_1/c$
$a/\text{\AA}$	11.9615(10)
$b/\text{\AA}$	9.7260(9)
$c/\text{\AA}$	15.660(2)
$\beta/^\circ$	112.244(9)
$V/\text{\AA}^3$	1686.3(3)
Z/Z'	4/1
$D_c/\text{g cm}^{-3}$	1.674
$F(000)$	862
μ (MoK α)/ mm^{-1}	3.458
Measured data	3082
θ range/ $^\circ$	1.8 – 25.0
Unique data	2961
Rint	0.032
Observed data ($I \geq 2.0 \sigma(I)$)	2303
R , obs. data; all data	0.023; 0.064
R_w , obs. data; all data	0.044; 0.0704
$\Delta\rho_{\text{max, min}}/\text{e \AA}^{-3}$	0.40; 0.53
CCDC deposition no.	1452012

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