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Oxy- and thio-phosphorus acid derivatives of tin(IV). The crystal and molecular structure of *O*-methylmethylphosphatotriphenyltin(IV) *

J.G. Masters **, **F.A.K. Nasser, M.B. Hossain, A.P. Hagen** ★, **D. van der Helm, and J.J. Zuckerman**

Department of Chemistry and Biochemistry, The University of Oklahoma, Norman, OK 73019-0370 (U.S.A.)

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Abstract

O-Methylmethylphosphatotriphenyltin(IV) (II) is synthesized by treating stoichiometric amounts of *O*,*O*′-dimethylmonothiophosphatotriphenyltin(IV) (I) with mercury. The negative ^{119}Sn chemical shift in solution relative to tetramethyltin for I corresponds to higher than four coordination (at tin) in solution. The values of the ^{119}Sn Mössbauer isomer shift for I and II confirm the presence of tin as tin(IV). The magnitudes of the quadrupole splitting and the ratios of the *QS* to the *IS* of both compounds reveal that tin is higher than four coordinated. The solid state structure of II was determined by X-ray diffraction. The compound crystallized in the trigonal space group $R\bar{3}$ with a, b 31.433(15), c 10.259(3) Å, V 8778.2 Å^3, $Z = 18$, D_x 1.56 g cm^{-3} at 138 K. In the solid state compound II exists as a highly symmetric cyclic hexamer in which planar trimethyltin(IV) groups are axially bridged by O–P–O linkages. The geometry about tin is trigonal bipyramidal with an axial O–Sn–O angle of 177.1(2)° and average C–Sn–C angle of 120.0(2)°. The structure of the hexameric ring is linear at tin but bent at phosphorus with an O–P–O angle of 117.1(2)°.

Introduction

Organotin(IV) compounds have been used as marine antifouling agents, agricultural fungicides, miticides and surface disinfectants. An interesting development is the synthesis of organometallic compounds in which the organotin moiety is bonded

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* This paper is dedicated to the memory of Professor J.J. Zuckerman.

** Present Address: Department of Chemistry, the University of Pennsylvania, Philadelphia, PA 19104 (U.S.A.)

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to ligands which exhibit biocidal activity. One such ligand system involves (thio) and (oxy)phosphorus acids [1–6] which form complexes in which either an oxygen or sulfur bridges the tin and the phosphorus atoms. The incorporation of organotin and phosphorus portions in one molecule leads to the possibility that each fragment may make a contribution to the compound's overall biocidal activity. Moreover, specific evidence for the activity of miscellaneous organotin derivatives of phosphorus acids is available yielding incentive for further study [7–9]. Specifically, in order to answer questions concerning the relationship which structure has with reactivity, reliable solid-state data are needed. Herein we report the conversion of *O,O′*-dimethylmonothiophosphatotriphenyltin(IV) (I) to and the molecular structure of *O*-methylmethylphosphatotriphenyltin(IV) (II).

Experimental

All manipulations were carried out under argon or nitrogen. All solvents were distilled and dried by conventional methods prior to use. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc.; Knoxville, TN. The melting points listed were uncorrected.

Infrared spectra (PE-283B) were recorded as KBr pellets or as Nujol mulls on CsI and KBr plates. Tin-119m Mössbauer spectra at 77 ± 2 K were recorded on a Ranger Engineering spectrometer fitted with a NaI scintillation counter using $Ca^{119m}SnO_3$ (New England Nuclear Corp.) as the source and reference standard material for zero velocity. The velocity was calibrated using β-tin and natural iron. Standard, non-linear, least-squares techniques were used to fit the data to Lorentzian curves. NMR data were recorded on IBM NR-80 and Varian XL-300 MHz spectrometers.

Sodium O,O′-dimethylmonothiophosphate [10,11], $Na[OP(S)(OCH_3)_2]$. Sodium (9.2 g, 0.40 mol) was dissolved in 150 ml methanol. After the reaction had ceased, *O,O′*-dimethylphosphite (44 g, 0.40 mol) in 30 ml methanol was added. To this solution was added 150 ml of diethyl ether and the mixture was allowed to stir for 20 min. As the sulfur (12.8 g, 0.40 mol) was slowly added in 2 g portions a vigorous reaction took place and the mixture was allowed to reflux. Unreacted sulfur was filtered using a glass frit. Ether (50 ml) was added at 0 °C and the solution placed in the refrigerator and let stand for 2 h. Colorless fine, silky needles of $Na[OP(S)(OCH_3)_2]$ formed. Additional fractions were obtained (49.70 g, 63%), m.p. 195–197 °C. The salt was very soluble in ethanol, methanol and H_2 but insoluble in ether and chloroform.

O,O′-Dimethylmonothiophosphatotriphenyltin(IV) [11] $(C_6H_5)_3SnOP(S)(OCH_3)_2$ (I). To 225 ml of dried methanol was added triphenyltin (IV) chloride (3.85 g, 10 mmol). The mixture was stirred for 10 min after which sodium *O,O′*-dimethylmonothiophosophate (1.64 g, 10 mmol) in 25 ml of methanol was added via syringe. The mixture was refluxed for 2.5 h and allowed to cool. The NaCl was filtered with a glass frit and the supernatant was cooled to −78 °C. Colorless crystals of I were obtained, m.p. 219–221 °C (lit. [11] 215–222 °C) Anal. Found C, 50.09, H, 4.30, Sn, 24.21. $C_{20}H_{21}O_3PSn$ calc.: C, 48.93, H, 4.31, Sn 24.17%. IR: 1160s, 1050m, 1000s, 985s, 705m, 700s, 484w, 447w cm^{-1}.

O-Methylmethylphosphatotriphenyltin(IV) $(C_6H_5)_3SnOP(O)(CH_3)OCH_3$ (II). Acetone (25 ml) and I (4.93 g, 0.01 mol) were combined in a three-necked flask and allowed to stir. Mercury (2 g, 0.01 mol) was added and the solution stirred at room temperature for two days. A black powder was separated by filtration. Upon cooling in dry ice II separated as colorless crystals (4.20 g, 91.4%) m.p. 222–225 °C. IR: 1183vs, 1086s, 1015m, 454w cm^{-1}.

Preparation of crystals

A pure sample of II was dissolved in a minimum of absolute ethanol. Diethyl ether was allowed to slowly diffuse into this concentrated solution. The two solutions were kept below 0 °C for several days. Single, colorless cubic-shaped crystals were obtained and one was selected and used for the X-ray diffraction study.

Crystal data. All measurements were performed on an Enraf–Nonius CAD-4 automatic counter diffractometer controlled by a PDP8/e computer and fitted with a low-temperature device. The Laue group was determined as $\bar{3}$ and the structure

Table 1

Crystal data and data collection parameters for $(C_6H_5)_3SnOP(O)(OCH_3)(CH_3)$ (II)

Formula	$C_{20}H_{21}O_3PSn$
Crystal system	trigonal
Systematic absences	$-h+k+l \neq 3n$
F_w	459.89
Space group	$R\bar{3}$
a, Å	31.433(15) [a]
b, Å	31.433(15) [a]
c, Å	10.259(3) [a]
α	90
β	90
γ	120
V, $Å^3$	8778.2
Z	18
R factor	0.0394
$F(000)$	4032
ρ_{calcd}, g cm^{-3}	1.56
μ, cm^{-1}	12.84
Crystal dimensions	0.20 × 0.20 × 0.25 mm
Radiation	Mo-$K_{\bar{\alpha}}$ (λ 0.71069 Å)
Temp., K	138 ± 2
Scan technique	θ–2θ
2θ limit, deg	43°
Max scan time, s	60
Scan angle, deg	$1.0 + 0.2 \tan\theta$
Aperture width, mm	$3.0 + 0.86 \tan\theta$
Aperture height, mm	6
Aperture distance, mm	173
Monitor reflector/ orientation monitors	3/200
No. of unique data	4032
No. of observed data	3064 [b]

[a] Determined on the basis of $\pm 2\theta$ values of 48 reflections and with Mo-K_{α_1}, radiation (λ 0.70926 Å).
[b] $I > 2\sigma(I)$.

determination proved the trigonal space group to be $R\bar{3}$. Crystal data and intensity data collection parameters are listed in Table 1.

The unscaled intensity data were calculated as $I = [P - 2(LB + RB)]$ and were scaled by monitor intensities. In all, 4032 independent reflections were measured. Intensities were corrected for Lorentz and polarization effects, but no absorption correction was applied (ratio of max. and min. transmission factor was 1.53). The structure factor for each reflection was assigned a weight given by $W_F = 1/\sigma_F^2$, where σ_F was obtained from counting statistics.

Structure determination and refinement

The structure was determined by the heavy-atom method and refined by full-matrix least-squares methods [12]. All the hydrogen atoms except the methyl hydrogens were located and refined isotropically. Final refinements were carried out using anisotropic thermal parameters for all non-hydrogen atoms. Refinement was discontinued when the maximum parameter shift was less than one-quarter of the corresponding standard deviation. The final R factor ($R = (\Sigma \| F_o - F_c \| / \Sigma | F_o |)$ was 0.0394 for 3064 reflections. The final difference map was featureless with peaks ranging between ± 0.3 e/Å^3. The scattering factors for all atoms were taken from ref. 13.

Results and discussion

The coordination of oxy and thiophosphorus acids to tin are not the same. A very common mode of coordination in triorganotindithiophosphate derivatives is intramolecular chelation. When an oxygen atom is substituted for sulfur in the dithiophosphate series, the chelating ability of sulfur toward tin is weakened, creating a greater chance for the monothiophosphate ligand to form unidentate complexes [14]. In the oxygenated series chelation is less favored than bridged species where the planar triorganotin(IV) units are axially bridged by oxygen atoms forming a trigonal configuration at tin [3].

Compound II is synthesized by reacting equimolar amounts of I and metallic mercury in acetone at room temperature. The first step involves abstraction of a sulfur atom by mercury forming HgS. Once the first step is complete, there is ample precedent for the intermediate to undergo an Arbusov rearrangement producing II which contains a P–C single bond. A similar rearrangement is also known in the silicon series, as well as the rearrangement which produces a triorganotin phosphate linked by acetylene in the tin series [15].

The tin-119m Mössbauer data (Table 2) for compounds I and II are consistent with other triorganotin(IV) phosphate esters which contain higher than four coordination about the tin center [3,11]. The magnitudes of the isomer shift (IS) for both compounds fall below the 2.65 mm^{-1} dividing line between the two tin valences, thus confirming the presence of a tin(IV) oxidation state [16,17]. The high quadrupole splitting values for I and II along with high magnitudes of their ρ values (the ratio of the QS to the IS) reveal a higher coordination at tin than tetrahedral.

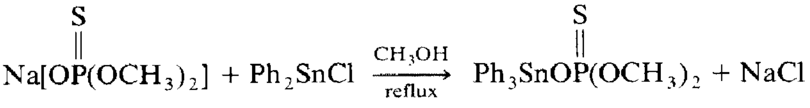
The ^{1}H NMR spectrum of II (Table 6) shows three groups of resonances, one group arising from the phenyl protons and two separate doublets corresponding to the methyl and methoxy protons. The magnitudes of the coupling constants for the methyl and methoxy groups, viz. $|^2J(^{31}\text{P–C–}^1\text{H})|$ 6.1 Hz and $|^2J(^{31}\text{P–O–C–}^1\text{H})|$

Table 2

Comparison of tin-119m Mössbauer data for I and II with other organotin(IV) monothiophosphates and phenyl phosphoric acid esters.

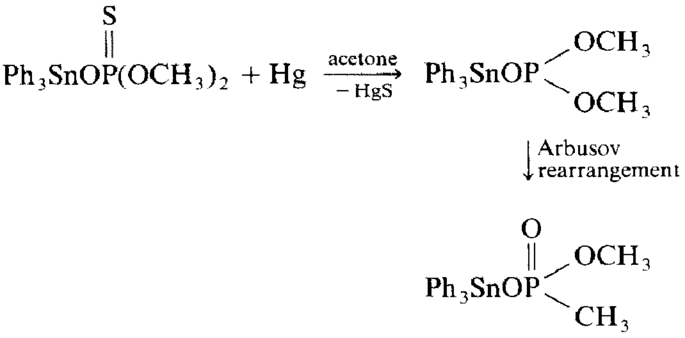
Compound	$IS \pm 0.03$ (mm sec^{-1})	$QS \pm 0.06$ (mm sec^{-1})	$\Gamma_{av} \pm 0.03$	$\rho = \frac{QS}{IS}$	Ref.
I	1.23	3.63	1.09	2.97	
II	0.96	3.38	1.28	3.52	
$(CH_3)_3SnOP(S)(OCH_3)_2$	1.32	3.90	1.32	2.00	11
$(n\text{-}C_4H_9)_3SnOP(S)(OCH_3)_2$	1.44	3.87	1.23	2.69	11, 21
$(C_6H_5)_3SnOP(S)(OC_6H_5)_2$	1.30	3.13	1.38	2.41	11
$(C_6H_5CH_2)_3SnOP(S)(OC_6H_5)_2$	1.81	2.97	1.28	1.64	11
$(CH_3)_3SnOP(O)(C_6H_7)(OC_6H_5)$	1.33	3.78	1.27	2.84	3
$(C_6H_5)_3SnOP(O)(C_6H_5)(OC_6H_5)$	1.32	3.69	1.29	2.73	3
$(n\text{-}C_4H_9)_3SnOP(O)(C_6H_5)(OC_6H_5)$	1.47	4.12	1.61	2.80	3

11.18 Hz, are consistent with 2 and 3 bond coupling to a phosphorus atom, respectively [18]. The ^{13}C NMR spectrum also exhibits two signals at 52.86 ppm and 33.6 ppm which lie in the chemical shift region for attached methoxy and methyl



$$Na[O\overset{\overset{S}{\|}}{P}(OCH_3)_2] + Ph_2SnCl \xrightarrow[\text{reflux}]{CH_3OH} Ph_3SnO\overset{\overset{S}{\|}}{P}(OCH_3)_2 + NaCl \qquad (1)$$

(I)



(2)

(II)

groups. The ^{31}P NMR spectrum of I (δ 56.52 ppm) and II (δ 22.68 ppm) are consistent with values of other di- and tri-organotin monophosphate esters [11].

In the ^{119}Sn NMR spectrum, the tin-119 NMR chemical shift for I relative to tetramethyltin corresponds to higher coordinated species in this medium, dissimilar to its tri-n-butyl tin analog, $(n\text{-}C_4H_9)_3SnOP(S)(OCH_3)_2$, which is four-coordinated in $CDCl_3$ [11]. Compound II which has a five coordinated tin center in the solid state exhibits higher than four coordination in solution as well [19]. When the coordination number at the tin center is increased, the tin resonance is shifted upfield with respect to the tetramethyltin reference, while attachment of electronegative atoms will result in a downfield shift in resonance [20].

Final atomic parameters for all non-hydrogen atoms are listed in Table 3. Figure 1 shows the coordination geometry about the tin and phosphorus atoms, and the atom numbering scheme. Table 4 lists the bond angles about the tin, phosphorus

Table 3

Final positional parameters for $(C_6H_5)_3SnOP(O)OCH_3)(CH_3)($ $(\times 10^4)$ [a]

Atom	x	y	z
Sn	456.0(1)	8299.0(1)	9647.0(4)
P	−875.8(5)	7428.1(5)	9480(2)
O(1)	1248(1)	8834(1)	9711(4)
O(2)	−334(1)	7750(1)	9485(4)
O(3)	−1017(2)	6905(2)	9985(6)
C(1)	492(2)	8421(2)	7594(6)
C(2)	923(2)	8561(2)	6900(6)
C(3)	940(2)	8649(3)	5569(7)
C(4)	536(3)	8606(3)	4924(7)
C(5)	113(3)	8469(3)	5587(7)
C(6)	87(2)	8376(2)	6920(7)
C(7)	599(2)	7761(2)	10461(6)
C(8)	335(3)	7487(3)	11526(8)
C(9)	437(3)	7150(3)	12137(9)
C(10)	806(3)	7087(3)	11634(9)
C(11)	1067(2)	7343(2)	10559(8)
C(12)	967(2)	7684(2)	9991(7)
C(13)	282(2)	8717(2)	10941(6)
C(14)	−118(2)	8499(2)	11785(5)
C(15)	−234(2)	8782(2)	12603(6)
C(16)	60(2)	9290(2)	12573(7)
C(17)	453(2)	9514(2)	11732(8)
C(18)	566(2)	9230(2)	10926(7)
C(19)	−741(3)	6671(3)	9511(11)
C(20)	−1053(4)	7325(3)	7746(10)
O(1′)	−1166(1)	7586(1)	10289(4)

[a] Estimated standard deviations in parentheses. O(1′) is related by symmetry to O(1) (x, y, z) by ($y-1$), ($-x+y$), ($2-z$).

and oxygen atoms. Bond distances and angles of the phenyl rings are listed in Table 9 (Supplementary). Figure 2 shows the cyclic hexameric structure of II.

In the solid state, compound II exists as a cyclic hexamer (Fig. 2) in which planar trimethyltin(IV) moieties are axially bridged by O–P–O linkages. The overall structural features of II resemble those of the related diphenyl analog, $(C_6H_5)_3SnOP(O)(OC_6H_5)_2$ [21], though the two hexameric structures show some significant differences.

The coordination geometry about the tin atom is close to a perfect trigonal bipyramid, with average C–Sn–C angles of 120.0(2)° and an axial O–Sn–O angle of 177.1(1)°. The two axial Sn–O distances are almost identical, Sn–O(1) 2.201(3) Å and Sn–O(2) 2.209(3) Å, and they are noticeably shorter than the average Sn–O(axial) distance of 2.234(9) Å observed in the diphenyl analog or distances of 2.319(5) and 2.240(6) Å observed for similar bonds in the analogous helical structure, (α-phenylphosphinato trimethyltin(IV) [22]. The two P–O distances, of the bridging O–P–O′ moieties are also essentially equal, (P(1)–O(1)′ 1.489(3) Å and P–O(2) 1.487(7) Å, indicating the presence of extensive π delocalization of the P=O double bond, as seen in the related diphenyl analog, where the average P–O distance is 1.487 Å. The almost equal Sn–O distances (and corresponding P–O distances) in II make it even harder than in the case of its diphenyl analog, to

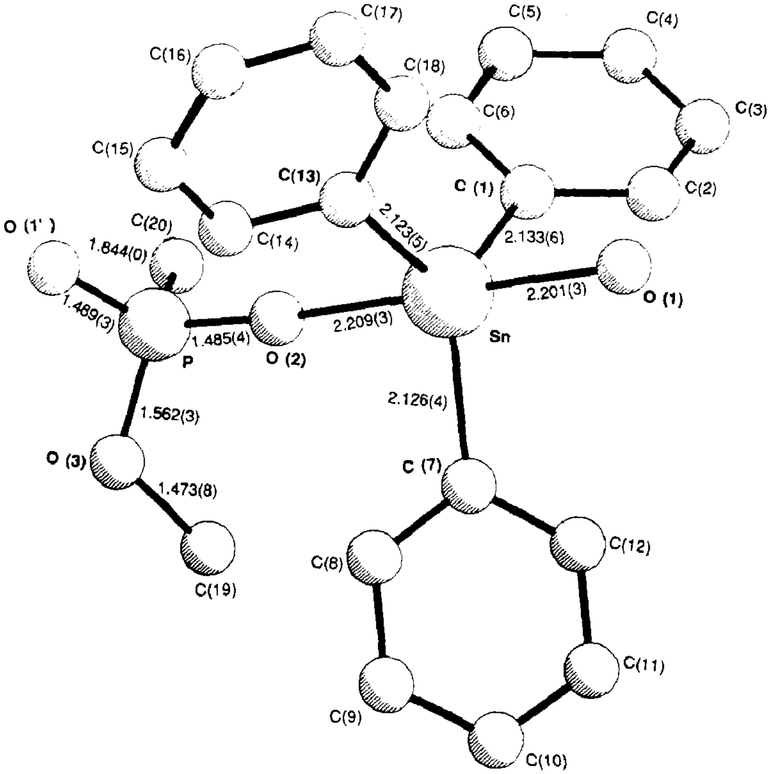


Fig. 1. Coordination geometry at the tin and phosphorus atoms in triphenyltin(IV) methylmethoxyphosphate shown with the atomic numbering. Internuclear bond distances are shown.

Table 4

Bond angles of hexameric ring (deg) in $(C_6H_5)_3SnOP(O)(OCH_3)(CH_3)$ [a]

O(1)-Sn-O(2)	177.1(2)
O(1)-Sn-C(1)	87.4(2)
O(1)-Sn-C(7)	89.3(2)
O(1)-Sn-C(13)	92.9(2)
C(1)-Sn-C(7)	121.2(2)
C(7)-Sn-C(13)	118.0(2)
C(13)-Sn-C(1)	120.9(2)
O(2)-Sn-C(1)	90.3(2)
O(2)-Sn-C(7)	90.6(2)
O(2)-Sn-C(13)	89.7(2)
Sn-O(2)-P	172.3(2)
O(2)-P-O(3)	109.9(2)
O(2)-P-C(20)	105.4(4)
O(2)-P-O(1')	117.1(2)
O(3)-P-C(20)	103.5(3)
O(3)-P-O(1')	105.5(2)
C(19)-O(3)-P	119.3(5)
O(1')-P-C(20)	114.5(3)
Sn-O(1)-P'	147.8(2)

[a] Estimated standard deviations in parentheses.

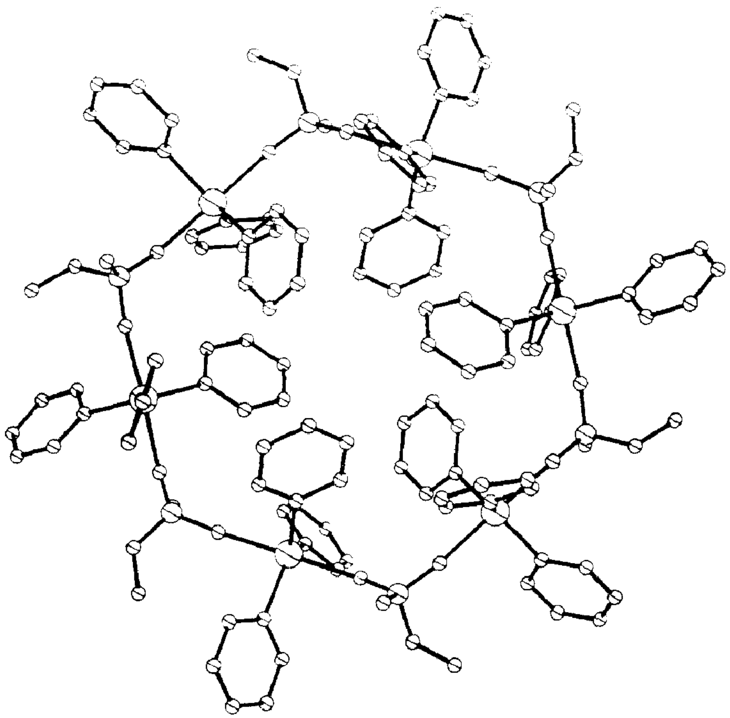


Fig. 2. The cyclic, hexameric triphenyltin(IV) methylmethoxyphosphate viewed down the z-axis.

distinguish which one of the two P–O–Sn connections is double bonding and dative and which one is single bonding as an ester linkage. The phosphorus to methoxy oxygen distance, P–O(3) 1.562(3) Å, is, as expected, longer than the two P–O–Sn distances but it is shorter than the phosphorus–phenoxy distance of 1.585(4) Å observed in the diphenyl analog.

The geometry about the phosphorus atom is that of a distorted tetrahedron with bond angles ranging from 103.5(3) (O(3)–P–C) to 117.1(2) (O(2)–P–O(1)′). The corresponding angular spread in the diphenyl analog structure is 104.5° to 118.5° (Table 5).

Table 5

Geometrical features of various [O–Sn–O–P–O] systems

Compound [a]	Overall Structure	Sn–O (Å)	P–O (Å)	O–Sn–O (°)	O–P–O (°)	Sn–O–P (°)
1	monomer	2.29(2)	1.47(2)	174.1(7)	–	153(1)
2	helical	2.240(6)	1.492(6)	178.0(2)	115.3(3)	135.5(3)
		2.319(5)	1.516(5)	175.9(2)	–	132.2(3)
3	hexamer	2.241(8) [b]	1.486(8)	177.0(3)	118.5(5)	151.8(5)
		2.228(8)	1.488(8)	–	–	148.8(5)
4 (II)	hexamer	2.201(3)	1.489(3)	177.1(2)	117.1(2)	147.8(2)
		2.209(3)	1.485(4)	–	–	172.3(2)

[a] (Nitratotriphenyl(triphenylphosphineoxide)tin(IV) [23] (**1**); α-(phenylphosphonato)trimethyltin(IV) [22] (**2**); triphenyltin(IV)diphenylphosphate [21] (**3**); compound **II** (present work) (**4**). [b] Average of three independent values.

Table 6

NMR data [a] for $(C_6H_5)_3SnOP(S)(OCH_3)_2$ (I) and $(C_6H_5)_3SnOP(O)(OCH_3)CH_3$ (II)

	I	II
^1H NMR		
$\delta(POCH_3)$ [a]	3.27 ppm	3.27 ppm
$\lvert ^3J(^{31}P\text{–}O\text{–}C\text{–}^1H)\rvert$	11.18 Hz	11.18 Hz
$\delta(PCH_3)$	–	1.10 ppm
$\lvert ^2J(^{31}P\text{–}C\text{–}^1H)$	–	6.10 Hz
^{13}C NMR [c]		
$\delta(POCH_3)$	52.77 ppm	52.86 ppm
$\lvert ^2J(^{31}P\text{–}O\text{–}^{13}C)\rvert$	4.90 Hz	4.90 Hz
$\delta(PCH_3)$	–	15.19 Hz
^{31}P NMR [d]	56.52 ppm	22.68 ppm
^{119}Sn NMR [e]	−81.78 ppm	−80.87 ppm

[a] Ref. 11, 16,18, 24, 25 present ^{31}P and ^{119}Sn comparison NMR data. [b] Recorded in C_6D_6 at room temperature with TMS as reference. [c] In $(CD_3)_2CO$ at room temperature with TMS as reference. [c] In C_6D_6 relative to phosphoric acid at room temperature. [e] In C_6D_6 at 37 °C relative to tetramethyltin.

The two Sn–O–P angles in the present structure are different. The Sn–O(1)–P′ angle of 147.8(2)° in II is slightly smaller but close to the average Sn–O–P angle observed in the hexameric diphenyl analog (150.3°) and that in the monomer, (nitrato)triphenyl(diphenyl)phosphine oxide)tin(IV) (153°) [23], the Sn–O(2)–P angle of 172.3(2) in II indicates an almost linear Sn–O–P at O(2). In contrast, in the helical structure of the analog (α-phenylphosphonato)trimethyltin(IV) [22], the two Sn–O–P angles are similar and smaller, 135.5° and 132.2°, respectively. Such a wide variation in M–O–P angles has also been observed for other metal-phosphate complexes [22] and is suggestive that the tetrahedral angle at P may not be the only deciding factor for the chain formation. In fact, a close look at some of the geometrical parameters of the four known O–P–O bridged trigonal bipyramidal tin(IV) structures (Table 5) shows that the geometry at the phosphorus atom does not change significantly from one structure to another. The change in P–O distances is almost negligible and even O–P–O angle changes are small. The two most variant parameters appear to be the Sn–O distance and the Sn–O–P angle of which the latter is most flexible and probably plays a major role in shaping the chain conformation.

The $\bar{3}$ symmetry of the macrocycle causes the methyl groups on the phosphorus atoms to alternate in location, above and below the ring. The 24-membered hexameric ring in the present structure is more symmetric than the one in the analogous structure of $(C_6H_5)_3SnOP(O)(OC_6H_5)_2$ ($\bar{3}$ as compared to $\bar{1}$) and the projected hexameric ring of II has the appearance of a regular hexagon with P atoms at the corners (Fig. 2). In II, such a hexagon defined by the P atoms only, has a chair conformation with a substantial ring puckering, $|\tau|$ 28.8°, while the corresponding hexagon in the analogous structure is virtually planar, $|\tau|$ 3.0°. The disposition of the six tin atoms in the two hexameric structures are closely similar: the hexagon with six tin atoms at the corners has a $|\tau|$ of 22.7° for compound II and 21.5° for the analog. The methoxy group on each phosphorus atom is pointed away from the ring center, and, as in the diphenyl analog structure, one of the phenyl groups at each tin atom is directed toward the center of the ring.

Supplementary material available: Table (SVII) of hydrogen atomic positions, (SVIII) of anisotropic parameters and SIX and SX listing of phenyl ring distances and angles for $(C_6H_5)_3SnOP(O)(OCH_3)CH_3$ (4 pages); listings of final observed and calculated structure factors for II (13 pages). See NAPS document No. 04741 for 38 pages of supplementary material. Order from NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10163-3513. Remit in advance, in U.S. Funds only, \$ 13.15 for photocopies or \$ 4.00 for microfiche. Outside the U.S. and Canada, add postage of \$ 4.50 for the first 20 pages and \$ 1.00 for each of 10 pages of material thereafter, or \$ 1.50 for microfiche postage.

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