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OXY- AND THIO-PHOSPHORUS ACID DERIVATIVES OF TIN

XIII *. DI- AND TRIORGANOTIN(IV) MONOTHIOPHOSPHATE ESTERS

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Summary

Eleven di- and triorganotin(IV) *O,O′*-diorganomonothiophosphate esters, $R_nSn[OP(S)(OR')_2]_{4-n}$ where $n = 2$, $R = CH_3$, C_2H_5, n-C_4H_9, n-C_8H_{17}, C_6H_5 and $R' = CH_3$ and where $R = C_6H_5$ and $R' = C_6H_5$ and where $n = 3$, $R = CH_3$, n-C_4H_9, C_6H_5 and $R' = CH_3$ and where $R = C_6H_5$, $C_6H_5CH_2$ and $R' = C_6H_5$, are synthesized in high yield by the reaction of the corresponding organotin(IV) chlorides with the sodium salt of the $R' = CH_3$ acid and the triethylammonium salt of the $R' = CH_3$ acid and the triethylammonium salt of the $R' = C_6H_5$ acid in ethanol. The products are colorless crystalline solids or oils, soluble in organic solvents. Vibrational spectroscopic band assignments can be made for the ν(P–O) (1220–1050 cm^{-1}), ν(P–OR) (1000–900 cm^{-1}), ν(P=S) (700–600 cm^{-1}), ν(Sn–C) (600–500 cm^{-1}), and ν(Sn–O) (500–400 cm^{-1}).

The tin-119m Mössbauer isomer shift (IS) values confirm tin as tin(IV), but the quadrupole splitting (QS) values fall into two groups with the tribenzyl- and di-n-octyltin derivatives exhibiting small magnitudes typical of four-coordination, with unidentate ligands. The other diorganotins exhibit very large QS values, corresponding to six-coordination with *trans*-R_2Sn groups. From a point-charge model calculation, the dimethyltin group is linear, and the diphenyltin angles are 173.2 and 139.4° for $(C_6H_5)_2Sn[OP(S)(OR)_2]_2$ where $R = CH_3$ and C_6H_5, respectively. However, the observation of both ν_{asym} and ν_{sym}(Sn–C) in both the infrared and Raman spectra of the dimethyltin derivative rules out a strictly linear array. The strong Mössbauer spectra exhibited by the $R_2Sn[OP(S)(OCH_3)_2]_2$ derivatives at room temperature where $R = CH_3$ and C_2H_5 suggest intermolecular association, and variable-temperature data for the $R = C_6H_5$ derivative yield a slope of $d\ln A/dT = -0.972 \times 10^{-2} K^{-1}$, reflecting a tightly-bound lattice as well, probably containing bridging ligands. No fragments of mass greater than the parent ion or containing more than one tin atom are seen in the mass spectra of any of the compounds

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* For part XII see ref. 1.

studied, however. The triorganotins, other than the tribenzyl-derivative, exhibit large QS values signifying five-coordination, and the NMR $|^2J(^{119}\mathrm{Sn{-}C{-}}^1\mathrm{H})|$ of 74.0 Hz for the trimethyltin derivative in solution is corroboratory. However, the negative tin-119 NMR chemical shift relative to tetramethyltin for the tri-n-butyltin derivative corresponds to four-coordination in solution. Bis(*O*,*O'*-diphenylthiophosphato)diphenyltin(IV) hydrolyzes on the benchtop or in wet ether to give the intermediate, dimeric hydrolysis product, $[(C_6H_5)_2SnOP(S)(OC_6H_5)_2OH]_2$.

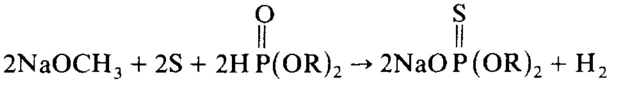
Introduction

We have reported in this series of papers on the synthesis and properties of organotin(IV) [2–6] and inorganic tin(II) [7] derivatives of oxy and thiophosphorus acids which contain the structures $\mathrm{Sn{-}O{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}\lessdot$ and $\mathrm{Sn{-}S{-}}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{P}}\lessdot$. Bringing the phosphorus and tin portions together in the same molecule opens the way to the intriguing possibility that each part will make its contribution to the biocidal activity of the whole substance, which could then find use as an agricultural and marine pesticide [8–10]. Specific evidence for the activity of organotin(IV) derivatives of the phosphorus acids is available [11,12] and provides the impetus for more detailed studies.

From structural studies we have determined that the dithio and dioxophosphorus derivatives adopt contrasting configurations. In particular, the sulfur derivatives with tin are monodentate [13] or chelating [7,14,15], while the oxygen derivatives bridge tin atoms into associated cyclic [16] or helical [17] structures. For this reason we thought it interesting to prepare the intermediate species, the *O*,*O'*-diorganomonothiophosphate ester derivatives to determine which configurations these mixed systems would adopt. We report in this paper the preparation and physical and spectroscopic properties of eleven di- and triorganotin(IV) derivatives of these phosphorus acid esters.

Experimental

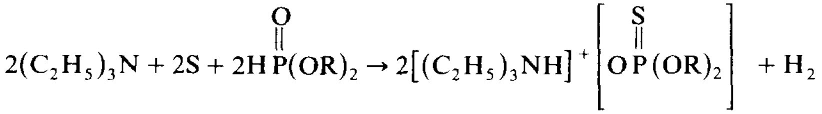
Organotin starting materials were of commercial grade and were used without further purification. Sodium *O*,*O'*-dimethylmonothiophosphate and triethylammonium *O*,*O'*-phenylmonothiophosphate were prepared by reacting hydrogen *O*,*O'*-diorganophosphite with sodium methoxide and elemental sulfur in ether:



$$2NaOCH_3 + 2S + 2H\overset{\overset{O}{\|}}{P}(OR)_2 \rightarrow 2NaO\overset{\overset{S}{\|}}{P}(OR)_2 + H_2 \qquad (1)$$

$(R = CH_3)$

or triethylamine under the same conditions:



$$2(C_2H_5)_3N + 2S + 2H\overset{\overset{O}{\|}}{P}(OR)_2 \rightarrow 2[(C_2H_5)_3NH]^+\left[O\overset{\overset{S}{\|}}{P}(OR)_2\right]^- + H_2 \qquad (2)$$

$(R = C_6H_5)$

Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are listed uncorrected.

Infrared spectra were recorded on a Beckman 4250 spectrometer as Nujol mulls on CsI plates. Mass spectra were recorded on a Hewlett-Packard 5985B mass spectrometer at an exciting voltage of 70 eV. Tin-119m Mössbauer spectra were recorded on a Ranger Engineering spectrometer equipped with a NaI scintillation counter and using $Ca^{119m}SnO_3$ as both source (New England Nuclear Corp.) and as standard reference material for zero velocity. Velocity calibration was based upon β-tin and natural iron. Standard, non-linear, least-squares techniques were used to fit the data to Lorentzian curves. Raman data were recorded on a Spex Ramalog 5 laser Raman Spectrometer.

The compounds studied are listed with their yields, melting points, and microanalytical data in Table 1. Tin-119m Mössbauer data are listed in Table 2, mass spectral data in Tables 3 and 4, and infrared and Raman data in Tables 5 and 6, respectively.

Sodium O-O'-dimethylmonothiophosphate [18], $Na^+\ [OP(S)(OCH_3)_2]^-$. Sodium (4.60 g, 0.200 mol) was dissolved in distilled methanol (60 ml). After the reaction was completed, *O,O'*-dimethylphosphite (22.0 g, 0.200 mol) and ether (60 ml) were added. Sulfur (6.4 g, 0.20 mol) was added in portions. The reaction took place vigorously on reflux. Excess sulfur was filtered, and the colorless sodium di-*O*-methylmonothiophosphate was separated, which is insoluble in ether and chloroform, but readily soluble in pyridine (22.9 g, 58%); m.p. 195–197°C.

Triethylammonium O,O'-diphenylmonothiophosphate [19,20], $[HNEt_3]^+\ [(C_6H_5O)_2P(S)O]^-$. To an ether suspension (100 ml) of sulfur (6.4 g, 0.20 mol), *O,O'*-diphenylphosphite (46.8 g, 0.200 mol) was added, triethylamine (21.0 g, 0.200 mol) was added dropwise to give an oil layer which was extracted with ether (50 ml). Removal of the ether under reduced pressure left the product as a colorless oil (63.1 g, 87%).

O,O'-Dimethylmonothiophosphatotrimethyltin(IV), $(CH_3)_3SnOP(S)(OCH_3)_2$. To an

TABLE 1

PHYSICAL DATA FOR THE $R_nSn[OP(S)(OR')_2]_{4-n}$ (n = 2,3) DERIVATIVES

Compound	M.p. (°C)	Analyses (Found(calcd.)(%)) C	H	Yield (%)
$(CH_3)_3SnOP(S)(OCH_3)_2$	oil	19.60 (19.70)	4.90 (4.92)	76
$(n\text{-}C_4H_9)_3SnOP(S)(OCH_3)_2$	oil	39.07 (38.93)	7.41 (7.64)	57
$(C_6H_5)_3SnOP(S)(OCH_3)_2$	215–222	49.91 (48.93)	4.56 (4.31)	82
$(C_6H_5)_3SnOP(S)(OC_6H_5)_2$	oil	56.76 (58.6)	4.54 (4.09)	73
$(C_6H_5CH_2)_3SnOP(S)(OC_6H_5)_2$	145–148	58.02 (60.31)	5.12 (4.75)	27
$(CH_3)_2Sn[OP(S)(OCH_3)_2]_2$	249–250	15.18 (16.71)	4.23 (4.20)	95
$(C_2H_5)_2Sn[OP(S)(OCH_3)_2]_2$	205–210	21.14 (20.93)	4.91 (4.83)	92
$(n\text{-}C_4H_9)_2Sn[OP(S)(OCH_3)_2]_2$	178–188	22.46 (23.97)	6.72 (5.86)	55
$(C_6H_5)_2Sn[OP(S)(OCH_3)_2]_2$	247–250	28.50 (29.61)	3.72 (3.99)	90
$(C_6H_5)_2Sn[OP(S)(OC_6H_5)_2]_2$	123–126	52.85 (53.80)	3.81 (3.76)	46
$(n\text{-}C_8H_{17})_2Sn[OP(S)(OCH_3)_2]_2$	> 250	37.73 (38.29)	6.91 (7.39)	80
$[(C_6H_5)_2SnOP(S)(OC_6H_5)_2OH]_2$ [a]	128–129	53.59 (51.87)	3.70 (3.78)	61

[a] Tin % 21.70(21.38).

TABLE 2

TIN-119m MÖSSBAUER DATA FOR THE ORGANOTIN(IV) *O,O′*-DIPHENYL- AND DIMETHYLMONOTHIOPHOSPHATES (at 77 K in mm s^{-1})

Compound	IS ± 0.03	QS ± 0.06	Γ_1 ± 0.03	Γ_2 ± 0.03	ρ = QS/IS
$(CH_3)_3SnOP(S)(OCH_3)_2$	1.32	3.89	1.31	1.33	2.99
$(n\text{-}C_4H_9)_3SnOP(S)(OCH_3)_2$	1.44	3.87	1.17	1.30	2.69
$(C_6H_5)_3SnOP(S)(OCH_3)_2$	1.23	3.63	1.09	1.09	2.97
$(C_6H_5)_3SnOP(S)(OC_6H_5)_2$	1.30	3.13	1.35	1.42	2.41
$(C_6H_5CH_2)_3SnOP(S)(OC_6H_5)_2$	1.81	2.97	1.34	1.22	1.64
$(CH_3)_2Sn[OP(S)(OCH_3)_2]_2$	1.26	4.54	1.08	1.08	3.62
	1.31[a]	4.31[a]	0.92[a]	0.86[a]	3.29[a]
$(C_2H_5)_2Sn[OP(S)(OCH_3)_2]_2$	1.51	4.39	1.53	1.05	2.91
	1.84[a]	4.48[a]	1.54[a]	1.60[a]	2.43[a]
$(n\text{-}C_4H_9)_2Sn[OP(S)(OCH_3)_2]_2$	1.41	4.49	1.21	1.27	3.19
$(C_6H_5)_2Sn[OP(S)(OCH_3)_2]_2$	1.29	3.78	2.18	1.24	2.94
$(C_6H_5)_2Sn[OP(S)(OC_6H_5)_2]_2$	1.23	3.14	1.30	1.61	2.55
$(n\text{-}C_8H_{17})_2Sn[OP(S)(OCH_3)_2]_2$	1.81	2.97	1.34	1.22	1.64
$[(C_6H_5)_2SnOP(S)(OC_6H_5)_2OH]_2$	1.28	2.98	2.20	1.26	2.33

[a] Ambient-temperature data.

ethanol solution (150 ml) of trimethyltin(IV) chloride (2.05 g, 10.0 mmol), sodium *O,O′*-dimethylmonothiophosphate (1.64 g, 10.0 mmol) was added and the mixture refluxed for 1 h to form a clear solution. Solvent was removed under reduced pressure yielding a pale, oily product (2.0 g, 76%).

O,O′-Dimethylmonothiophosphatotri-n-butyltin(IV), $(n\text{-}C_4H_9)_3SnOP(S)(OCH_3)_2$. To an ethanol solution (150 ml) of tri-n-butyltin(IV) chloride (3.25 g, 10.0 mmol), sodium *O,O′*-dimethylmonothiophosphate (1.64 g, 10.0 mmol) was added and the mixture refluxed for 1 h. Solvent was removed under reduced pressure and the precipitate was separated by filtration yielding a pale, oily product (2.45 g, 57.0%).

O,O′-Dimethylmonothiophosphatotriphenyltin(IV), $(C_6H_5)_3SnOP(S)(OCH_3)_2$. To an ethanol solution (150 ml) of triphenyltin(IV) chloride (3.85 g, 10.0 mmol), sodium *O,O′*-dimethylmonothiophosphate (1.64 g, 10.0 mmol) was added, and the mixture refluxed for 1 h and allowed to cool. The resulting precipitate of sodium chloride was separated by filtration, and the filtrate after cooling overnight gave the product as colorless crystals (4.0 g, 82%), m.p. 215–222°C.

O,O′-Diphenylmonothiophosphatotriphenyltin(IV), $(C_6H_5)_3SnOP(S)(OC_6H_5)_2$. To an ethanol solution (150 ml) of triphenyltin(IV) chloride (3.85 g, 10.0 mmol), triethylammonium *O,O′*-diphenylmonothiophosphate (3.67 g, 10.0 mmol) was added and the mixture refluxed for 1 h. Triethylammonium chloride was separated by filtration and solvent was removed under reduced pressure yielding a pale, oily product (4.5 g, 73%).

O,O′-Diphenylmonothiophosphatotribenzyltin(IV), $(C_6H_5CH_2)_3SnOP(S)(OC_6H_5)_2$. To an ethanol solution (100 ml) of tribenzyltin(IV) chloride (2.14 g, 5.00 mmol), triethylammonium *O,O′*-diphenylmonothiophosphate (1.84 g, 5.00 mmol) was added and the mixture refluxed for 1 h. The resulting precipitate of triethylammonium chloride was separated by filtration. The filtrate after cooling overnight gave the product (0.88 g, 27%), m.p. 145–148°C.

Bis(O,O′-dimethylmonothiophosphato)dimethyltin(IV), $(CH_3)_2Sn[OP(S)(OCH_3)_2]_2$. To an ethanol solution (150 ml) of dimethyltin(IV) dichloride (2.20 g, 10.0 mmol), sodium *O,O′*-dimethylmonothiophosphate (3.28 g, 20.0 mmol) was added and the mixture refluxed for 1 h. The resulting precipitate was separated by filtration and sodium chloride removed by washing several times with distilled water to give the product as a white powder (4.1 g, 95%), m.p. 249–250°C.

Bis(O,O′-dimethylmonothiophosphato)diethyltin(IV), $(C_2H_5)_2Sn[OP(S)(OCH_3)_2]_2$. To an ethanol solution (150 ml) of diethyltin(IV) dichloride (2.47 g, 10.0 mmol), sodium *O,O′*-dimethylmonothiophosphate (3.28 g, 20.0 mmol) was added and the mixture refluxed for 1 h. The resulting precipitate was separated by filtration and sodium chloride was removed by washing several times with distilled water to give the product as a white powder (4.2 g, 92%), m.p. 205–210°C.

Bis(O,O′-dimethylmonothiophosphato)di-n-butyltin(IV), $(n\text{-}C_4H_9)_2Sn[OP(S)(OCH_3)_2]_2$. To an ethanol solution (150 ml) of a di-n-butyltin(IV) dichloride (3.04 g, 10.0 mmol), sodium *O,O′*-dimethylmonothiophosphate (3.28 g, 20.0 mmol) was added and the mixture refluxed for 1 h. The resulting precipitate was separated by filtration and sodium chloride removed by washing several times with distilled water to give the product as a white powder (2.85 g, 55.0%), m.p. 178–188°C.

Bis(O,O′-dimethylmonothiophosphato)di-n-octyltin(IV), $(n\text{-}C_8H_{17})_2Sn[OP(S)(OCH_3)_2]_2$. To an ethanol solution (150 ml) of di-n-octyltin(IV) dichloride (2.08 g, 5.00 mmol), sodium *O,O′*-dimethylmonothiophosphate (3.28 g, 20.0 mmol) was added and the mixture refluxed for 1 h. The resulting precipitate was separated by filtration and sodium chloride removed by washing several times with distilled water to give the product as a white powder (2.5 g, 80%), m.p. 255–260°C.

Bis(O,O′-dimethylmonothiophosphato)diphenyltin(IV), $(C_6H_5)_2Sn[OP(S)(OCH_3)_2]_2$. To an ethanol solution (50 ml) of diphenyltin(IV) dichloride (3.44 g, 10.0 mmol), sodium *O,O′*-dimethylmonothiophosphate (3.28 g, 20.0 mmol) was added and the mixture refluxed for 1 h. The resulting precipitate was separated by filtration and sodium chloride was removed by washing the compound several times with distilled water to give the product as a white powder (5.00 g, 90.0%), m.p. 247–250°C.

Bis(O,O′-diphenylmonothiophosphate)diphenyltin(IV), $(C_6H_5)_2Sn[OP(S)(OC_6H_5)_2]_2$. To an ethanol solution (50 ml) of diphenyltin(IV) chloride (4.01 g, 5.00 mmol), triethylammonium *O,O′*-diphenylmonothiophosphate (3.67 g, 10.0 mmol) was added and the mixture refluxed for 1 h. The resulting precipitate of triethylammonium chloride was separated by filtration, excess solvent was removed under reduced pressure yielding a pale, oily product which was recrystallized from methanol and filtered. The filtrate, after cooling overnight gave the product as colorless crystals (1.85 g, 46.0%), m.p. 123–126°C.

Results and discussion

The di- and triorganotin(IV) derivatives were synthesized by four routes:

$$R_3SnCl + NaOP(S)(OCH_3)_2 \xrightarrow{C_2H_5OH} R_3SnOP(S)(OCH_3)_2 + NaCl \qquad (3)$$

$(R = CH_3, n\text{-}C_4H_9, C_6H_5)$

(Continued on p. 26)

TABLE 3

MASS SPECTRAL DATA FOR THE $R_3SnOP(S)(OR')_2$ DERIVATIVES[a,b]

m/e	$(CH_3)_3SnOP(S)(OCH_3)_2$	$(n\text{-}C_4H_9)_3SnOP(S)(OCH_3)_2$	$(C_6H_5)_3SnOP(S)(OC_6H_5)_2$	$(C_6H_5)_3SnOP(S)(OCH_3)_2$
567				
492				$[(C_6H_5)_3SnOP(S)(OCH_3)_2]^{+\cdot}(1.1)$
460				$[(C_6H_5)_3SnOP(OCH_3)_2]^{+\cdot}(2.0)$
415				$[(C_6H_5)_2SnOP(S)(OCH_3)_2{}^{+}(18.0)$
399				$[(C_6H_5)_2SnP(S)(OCH_3)_2]^{+}(6.9)$
385				
383				$[(C_6H_5)_2SnOP(OCH_3)_2]^{+}(100.0)$
375		$[(C_4H_9)_2SnOP(S)(OCH_3)_2]^{+}(32.8)$		
351				$[(C_6H_5)_3Sn]^{+}(36.9)$
343		$[(C_4H_9)_2SnOP(OCH_3)_2]^{+}(100.0)$		
309			$[(C_6H_5)_2SnPH_4]^{+}(75.5)$	
306	$[(CH_3)_3SnOP(S)(OCH_3)_2]^{+\cdot}(2.8)$			
291	$[(CH_3)_2SnOP(S)(OCH_3)_2]^{+}(2.8)$			
272			$[(C_6H_5)_2Sn{-}2H]^{+\cdot}(1.1)$	
261		$[SnOP(S)(OCH_3)_2]^{+}(46.9)$		
259	$[SnOP(S)(OCH_3)_2 - H_2]^{+}(86.8)$			
245	$[Sn(S)P(OCH_3)_2]^{+}(100.0)$			
229	$[SnOP(OCH_3)_2]^{+}(70.0)$	$[SnOP(OCH_3)_2]^{+}(85.9)$		
213	$[(CH_3)_2SnSP]^{+}(63.4)$	$[SnOP(O)(OCH_2)]^{+}(24.2)$		
			$(C_6H_5)_3SnOP(S)(OCH_3)_2$	$(C_6H_5CH_2)_3SnOP(S)(OC_6H_5)_2$
199		$[HSnOP(OCH_3)]^{+}(32.8)$		
197	$[(CH_3)SnP(S)-H]^{+}(78.0)$		$[SnC_6H_5]^{+}(22.4)$	
183	$[Sn(S)P]^{+}(23.2)$			
177		$[n\text{-}C_4H_9Sn]^{+}(53.4)$		
165	$[(CH_3)_2SnO\text{-}H]^{+}(87.9)$			
155				

154			$[\mathrm{Sn(OH)_2}]^{+\cdot}$(100.0)	
151	$[\mathrm{CH_3SnO}]^+$(66.3)	$[\mathrm{CH_3SnO}]^+$(44.9)		
135	$[\mathrm{CH_3Sn}]^+$(83.1)			
120	$\mathrm{Sn}^{+\cdot}$(33.1)	$\mathrm{Sn}^{+\cdot}$(18.2)	$\mathrm{Sn}^{+\cdot}$(17.5)	
567				$[(\mathrm{C_6H_5})_2\mathrm{SnOP(S)(OC_6H_5)_2OP(S)(OC_6H_5)}]^+$ (22.5)
492				
460				
415				
399				
385				$[\mathrm{SnOP(S)(OC_6H_5)_2}]^+$(100.0)
375				
351				
343				
309				
306				
291				$[(\mathrm{C_6H_5})_2\mathrm{SnOP(S)(OC_6H_5)OP(S)} - 3\mathrm{H}]^+$(26.2)
273			$[(\mathrm{C_6H_5})_2\mathrm{Sn} - \mathrm{H}]^+$(28.7)	
272				
261			$[\mathrm{SnOP(S)(OCH_3)_2}]^+$(11.0)	
259				
245			$[\mathrm{SnP(S)(OCH_3)_2}]^+$(1.8)	
229			$[\mathrm{SnOP(OCH_3)_2}]^+$(19.5)	
211				$[(\mathrm{C_6H_5})\mathrm{SnO{-}H_2}]^+$(79.6)
213				
199				
197			$[\mathrm{C_6H_5Sn}]^+$(87.8)	
155				$[\mathrm{Sn(OH)_2} - \mathrm{H}]^+$(69.1)
120		$\mathrm{Sn}^{+\cdot}$(51.1) $\mathrm{Sn}^{+\cdot}$(28.3)		

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[a] Relative abundance values in parentheses. [b] Only tin-bearing fragments are listed; mass numbers are based upon $^{120}\mathrm{Sn}$, $^{32}\mathrm{S}$, $^{31}\mathrm{P}$, $^{16}\mathrm{O}$, $^{12}\mathrm{C}$ and $^{1}\mathrm{H}$.

TABLE 4

MASS SPECTRAL DATA FOR $R_2SnOP(S)(OR')_2$ DERIVATIVES[a]

m/e	$(CH_3)_2Sn[OP(S)OCH_3)_2]_2$	$(C_2H_5)_2Sn[OP(S)(OCH_3)_2]_2$	$(n\text{-}C_4H_9)_2Sn[OP(S)(OCH_3)_2]_2$	$(C_6H_5)_2Sn[OP(S)(OCH_3)_2]_2$
539				
461				
459			$[(C_4H_9)_2SnOP(S)(OCH_3)]$ $[SP(O)H_5]^+$ (15.3)	
427			$[C_4H_9)_2SnOP(S)(OCH_3)]$ $[OPH_5]^+$ (17.9)	
385				
383				$[(C_6H_5)_2SnOP(OCH_3)_2]^+$ (10.1)
381				
355			$[(C_4H_9)_2SnP(S)(OCH_3)-4H]^+$ (16.3)	
351				$[(C_6H_5)_2SnPS]^+$ (16.3)
341				
321		$[(C_2H_5)_2SnSPO(OCH_3)_2H_2]^+$ (9.9)	$[C_4H_9SnOP(S)(OCH_3)PH_3]^+$ (22.8)	
309				$[C_6H_5SnOP(OCH_3)_2H_3]^+$ (40.7)
303				
291	$[(CH_3)_2SnOP(S)(OCH_3)_2]^+$ (24.3)			
281			$[(C_4H_9)_2SnOP]^+$ (26.2)	
275	$[(CH_3)_2SnP(S)(OCH_3)_2]^+$ (14.1)			
268				
265				
261			$[SnOP(S)(OCH_3)_2]^+$ (58.0)	
259	$[CH_3SnP(S)(OCH_3)_2-H]^+$ (45.8)			
245	$[SnP(S)(OCH_3)_2]^+$ (15.8)		$[SnP(S)(OCH_3)_2]^+$ (22.8)	
229	$[SnOP(OCH_3)_2]^+$ (40.7)	$[SnOP(OCH_3)_2]^+$ (100.0)	$[SnOP(OCH_3)_2]^+$ (100.0)	$[SnOP(OCH_3)_2]^+$ (20.9)
215		$[Sn(S)P(OCH_3)H]^+$ (32.5)		
213	$[(CH_3)_2SnPS]^+$ (15.0)		$[SnOP(S)(OCH_3)-H]^+$ (19.7)	
200				

199		$[HSnOP(OCH_3]^+$(34.5)		
197	$[(CH_3)SnSP-H]^+$(43.2)			$[C_6H_5Sn]^+$(48.8)
183	$[SnPS]^+$(23.2)			
167		$[SnOP]^+$(23.6)	$[SnOP]^+$(60.1)	
165	$[(CH_3)_2SnO-H]^+$(36.2)			
155				
154				$[SnSH_2]^+$(67.6)
151	$[CH_3SnO]^+$(33.3)	$[CH_3SnO]^+$(40.4)	$[CH_3SnO]^+$(26.7)	
135	$[CH_3Sn]^+$(37.6)			
120	$Sn^{+\cdot}$(21.2)	$Sn^{+\cdot}$(13.3)	$Sn^{+\cdot}$(32.7)	
79	$[C_6H_5+H_2]^+$(100.0)			
77				$[C_6H_5]^+$(100.0)
71				

m/e	$(C_6H_5)_2Sn[OP(S)(OC_6H_5)_2]_2$	$(n\text{-}C_8H_{17})_2Sn[OP(S)(OCH_3)_2]_2$
539	$[(C_6H_5O)_2P(S)$ $OSn(C_6H_5)_2]^+$(40.7)	
461	$[(C_6H_5O)_2P(S)$ $OSn(C_6H_5)-H]^+$(10.1)	
385	$[SnOP(S)(OC_6H_5)_2]^+$(10.1)	
381		$[C_8H_{17})_2SnSH_3]^+$(8.0)
351	$[(C_6H_5O)_2P(O)Sn-SH]^+$(20.6)	
303		$[(C_8H_{17})SnC_5H_{10}]^+$(9.4)
268		$[(C_8H_{17})SnSH_3]^+$(24.5)
265	$[HSn(C_6H_5)_2]^+$(8.6)	
200		$[H_2SnOPOCH_3]^+$(26.1)
197	$[SnC_6H_5]^+$(100.0)	
167		$[CH_3SnS]^+$(15.8)
155		$[SnSH_3]^+$(37.7)
154	$[SnSH_2]^{+\cdot}$(23.9)	
120	$Sn^{+\cdot}$(60.1)	$Sn^{+\cdot}$(5.0)
71		$[PO(S)H_2]^+$(100.0)

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[a] Relative abundance values in parentheses. [b] Only tin-bearing fragments are listed; mass numbers are based upon ^{120}Sn, ^{32}S, ^{31}P, ^{16}O, ^{12}C and ^{1}H.

TABLE 5

INFRARED SPECTRAL FREQUENCIES OF $Na[OP(S)(OCH_3)_2]$, $[HN(C_2H_5)_3]^+[OP(S)(OC_6H_5)_2]^-$ AND THE TRIORGANOTIN(IV) *O,O'*-DIMETHYL- AND DIPHENYLMONOTHIOPHOSPHATE, $R_3SnOP(S)(OR')_2$, DERIVATIVES (in Nujol)

Compound	Infrared absorptions (cm^{-1}) [a]
$Na[OP(S)(OCH_3)_2]$	3360bs, 2968vs, 2929vs, 2842s, 2360s, 1650w, 1445vw, 1309s, 1200vs, 1050vs, 1000vs, 945vs, 780vs, 585vw, 550m, 500m, 475sh, 435vw, 390s, 275m.
$[HN(C_2H_5)_3][OP(S)(OC_6H_5)_2]$	3020sh, 2848vs, 2620s, 2450s, 1938vw, 1861vw, 1780vw, 1720vw, 1442vs, 1390m, 1368m, 1352w. 1277w. 1225s, 1200s, 1140s, 1060s, 1030m, 992s, 905s, 880s, 840m, 825w, 765s, 750s, 715s, 682s, 622m, 560m, 490s, 440m, 310s, 278w.
$(CH_3)_3SnOP(S)(OCH_3)_2$	2950vs, 2930vs, 2845s, 2335m, 1490vw, 1450ah, 1430sh, 1309m, 1185s, 1080s, 1055s, 1032sh, 1000m, 894m, 780s, 700vw, 588m, 550m, 495vw, 445vw, 390m, 298m, 278m.
$(n\text{-}C_4H_9)_3SnOP(S)(OCH_3)_2$	3360bs, 2950vs, 2920vs, 2870s, 2850s, 2360m, 1650vw, 1418vw, 1385sh, 1375m, 1340vw, 1302m, 1200vs, 1085vs, 1052vs, 1000vw, 974m, 946m, 890m, 878m, 852w, 790s, 700vw, 665w, 600vw, 545m, 500vw, 470vw, 386m, 272w.
$(C_6H_5)_3SnOP(S)(OCH_3)_2$	3065sh, 8044w, 2920vs, 2858vs, 2389vw, 1590vw, 1483m, 1410s, 1335vw, 1308vw, 1212vw, 1183s, 1170sh, 1108sh, 1093s, 1080sh, 1050s, 1025m, 1000m, 912vw, 899w, 806m, 790w, 735s, 700s, 663vw, 585vw, 540vw, 500vw, 450w, 370m, 353m, 338vw, 299w.
$(C_6H_5)_3SnOP(S)(OC_6H_5)_2$	3060w, 3040w, 2950s, 2922s, 2850m, 2680vw, 2486s, 1428s, 1330vw, 1300vw, 1220sh, 1200s, 1160m, 1110m, 1072m, 1020m, 1002sh, 998w, 910s, 890s, 832vw, 775s, 730s, 695s, 660s, 650vw, 498w, 448w.
$(C_6H_5CH_2)_3SnOP(S)(OC_6H_5)_2$	3090vw, 3068w, 3030w, 2925vs, 2862vs, 1604m, 1496m, 1470s, 1382m, 1212w, 1186vw, 1119vw, 1055w, 908vw, 802w, 762s, 700s, 540vw, 450w, 385s.

[a] s = strong, b = broad, v = very, w = weak, m = medium, sh = shoulder.

$$R_2SnCl_2 + 2NaOP(S)(OCH_3)_2 \xrightarrow{C_2H_5OH} R_2Sn[OP(S)(OCH_3)_2]_2 + 2NaCl \qquad (4)$$

$$(R = CH_3, C_2H_5, n\text{-}C_4H_9, C_6H_5, n\text{-}C_8H_{17})$$

$$R_3SnCl + [HNEt_3][OP(S)(OC_6H_5)_2] \xrightarrow{C_2H_5OH} R_3Sn[OP(S)(OC_6H_5)]_2 + HNEt_3Cl \qquad (5)$$

$$(R = C_6H_5, C_6H_5CH_2)$$

$$R_2SnCl_2 + 2[HNEt_3][OP(S)(OC_6H_5)_2] \xrightarrow{C_2H_5OH} R_2Sn[OP(S)(OC_6H_5)_2]_2 + 2HNEt_3Cl \qquad (6)$$

$$(R = C_6H_5)$$

The sodium or triethylammonium chlorides are precipitated and separated by

TABLE 6

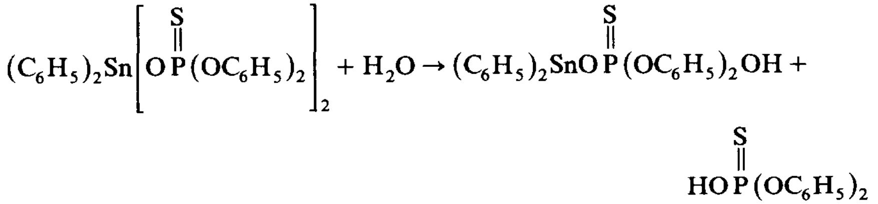
INFRARED SPECTRAL FREQUENCIES OF THE DIORGANOTIN(IV) BIS(*O*,*O*′-DIMETHYL- AND DIPHENYLMONOTHIOPHOSPHATE), $R_2Sn[OP(S)(OR')_2]_2$, DERIVATIVES

Compound	Infrared absorptions (cm^{-1}) [a]
$(CH_3)_2Sn[OP(S)(OCH_3)_2]_2$	2920vs, 2852vs, 2390w, 1364sh, 1308w, 1175s, 1075s, 1048s, 1020sh, 1000m, 898w, 790s, 585m, 540vw, 390m, 298m, 278vw.
$(C_2H_5)_2Sn[OP(S)(OCH_3)_2]_2$	2920vs, 2860vs, 2395vw, 1368sh, 1310vw, 1180m, 1085m, 1050m, 1022m, 1000m, 965m, 898vw, 800m, 788m, 695w, 585w, 550vw, 392w, 298w, 278vw.
$(n\text{-}C_4H_9)_2Sn[OP(S)(OCH_3)_2]_2$	3460bm, 2920vs, 2858vs, 2390vw, 1635vw, 1415s, 1365sh, 1308vw, 1184s, 1160s, 1080s, 1048s, 990w, 970vw, 880vw, 785m, 690w, 582m, 390m, 294m, 275m.
$(C_6H_5)_2Sn[OP(S)(OCH_3)_2]_2$	3420s, 3035vw, 3025w, 2880sh, 2860sh, 2860vs, 2825vs, 2400w, 1640w, 1580vw, 1486w, 1432s, 1368sh, 1310m, 1268vw, 1220sh, 1170vs, 1090vs, 1055vs, 1020w, 1000w, 985vw, 840vw, 800s, 735s, 697s, 668vw, 585m, 535vw, 458m.
$(C_6H_5)_2Sn[OP(S)(OC_6H_5)_2]_2$	3050m, 2990m, 2950m, 2858w, 2640m, 2445w, 1595s, 1490vs, 1434m, 1393w, 1286vw, 1222sh, 1200vs, 1164s, 1088s, 1068s, 1025s, 1008m, 915vs, 985sh, 835vw, 776vs, 735s, 694s, 670sh, 654sh, 550vw, 499m, 445vw, 389s, 370s, 350s, 330m.
$(n\text{-}C_8H_{17})_2Sn[OP(S)(OCH_3)_2]_2$	2925vs, 2860vs, 2296w, 1470s, 1420sh, 1368sh, 1308m, 1185s, 1152s, 1085s, 1050s, 1000s, 914vw, 899m, 835w, 801s, 790s, 742w, 690m, 585m, 550w, 475vw, 420sh, 392m, 296m, 278vw.
$[(C_6H_5)_2SnOP(S)(OC_6H_5)_2OH]_2$	3335m, 3025s, 2998vs, 2795m, 2599s, 2500m, 1590m, 1490vs, 1458sh, 1436vs, 1400s, 1230sh, 1205vs, 1168vs, 1110vs, 1074vs, 1030vs, 1010s, 1005sh, 900vs, 840vw, 780vs, 740vs, 700vs, 658s, 560w, 500m, 450w, 390vs, 375vs, 353vs, 334m, 285vw.

[a] s = strong, b = broad, v = very, w = weak, m = medium, sh = shoulder.

filtration. The products which are listed in Table 1 with their melting points and yields are colorless oils or solids sparingly soluble in organic solvents.

Substitution of the more electronegative oxygen for sulfur in the dithiophosphate derivatives would be expected to weaken the donor ability of the sulfur atom toward tin in the O–P=S → Sn system. Thus there should be a greater tendency for the monothiophosphate ligand to form unidentate complexes [21]. Indeed, we have recently solved the structure of the intermediate hydrolysis product of bis(*O*,*O*′-diphenylthiophosphato)diphenyltin(IV):



$$(C_6H_5)_2Sn\left[O\overset{\overset{S}{\|}}{P}(OC_6H_5)_2\right]_2 + H_2O \rightarrow (C_6H_5)_2SnO\overset{\overset{S}{\|}}{P}(OC_6H_5)_2OH + HO\overset{\overset{S}{\|}}{P}(OC_6H_5)_2 \qquad (7)$$

a product of the action of air and moisture on the benchtop, or the result of refluxing a stoichiometric amount of the parent bis-ligand compounds with water in ether. Sensitivity to hydrolysis is not a feature of the chemistry of either the phosphate [5] or dithiophosphate [2,3] ester derivatives of tin. The hydrolysis product exists as a doubly-hydroxide bridged, centrosymmetric Sn_2O_2-ring dimer in the solid. The tin atoms are five-coordinated in badly-distorted trigonal bipyramidal geometries with equatorial diphenyltin moieties. The sulfur to tin distance of 3.947 Å is outside the range of dative S → Sn interactions by at least half an Ångstrom unit, and hence the ligand is unidentate rather than chelated. Hydrogen bonding links each ligand sulfur atom to one of the hydroxide groups [22]. This structure confirms that the products of eqs. 3–6 are bonded through the oxygen of the ligand, as expected, and that no rearrangement has occurred in the course of these syntheses to produce the sulfur-bonded $Sn{-}S{-}\overset{O}{\overset{\|}{P}}$ derivatives.

Table 2 lists the ^{119m}Sn Mössbauer data for the products. The isomer shift (IS) data confirm that the materials contain tin(IV) [23], but the magnitudes of the quadrupole splittings (QS) and the ratios of QS to IS ($\rho = QS/IS$) fall into two groups. The tribenzyl and di-n-octyl derivatives exhibit data typical of four-coordinated tin atoms, and these compounds presumably contain unidentate ligands. At the other extreme are the dimethyl-, diethyl-, di-n-butyl- and diphenyl-derivatives which exhibit very large QS values and ρ ratios. These data point to six-coordination at tin with *trans*-diorgano groups. Using a treatment based upon a point-charge model [24] to link the magnitudes of the QS values with the carbon–tin–carbon angle in octahedral diorganotin(IV) derivatives, it is possible to calculate dimethyl- and diphenyl-tin [3,24] angles. The treatment assumes that the contribution of the donor ligands to the QS will be negligible compared with that of the R groups and that the magnitude of the QS will reach 4.0 mm s^{-1} when the R_2Sn system becomes linear. The values above 4.0 mm s^{-1} for the dialkyltin derivatives in Table 2 must then reflect a breakdown in the model. Other diorganotin derivatives whose QS values also exceed 4.0 mm s^{-1} include the $R_2Sn[O\overset{O}{\overset{\|}{P}}(OC_6H_5)_2]_2$, [5], $R_2Sn[O\overset{O}{\overset{\|}{P}}(C_6H_5)OH]_2$ [17] and $R_2Sn[O\overset{O}{\overset{\|}{P}}(C_6H_5)OC_6H_5]_2$ [4] systems analogous to the compounds reported here. The extremely high splittings observed must correspond to nearly linear C–Sn–C arrays in the dialkytin series.

For the two diphenyltin derivatives, on the other hand, the QS values can be used to calculate phenyl–tin–phenyl angles of 173.2 and 139.4° for $(C_6H_5)_2Sn[OP(S)(OR)_2]_2$ where $R = CH_3$ and C_6H_5, respectively.

Additional information can be derived from the temperature-dependence of the Mössbauer recoil-free fraction, f, which reflects the binding strength of the lattice, since it is a function of the mean-square-displacement, $\langle x^2 \rangle$, of the tin atom from its equilibrium position:

$$f = \exp\left[-\frac{\langle x^2 \rangle}{2\lambda}\right] \tag{8}$$

where λ is the wavelength of the Mössbauer γ-ray. Two of our products, $R_2Sn[OP(S)(OCH_3)_2]_2$ where $R = CH_3$ and C_2H_5 exhibit quite strong Mössbauer spectra at room temperature. While there are monomeric molecular organotin solids which yield room temperature spectra [25], the observation generally arises in cases in which the lattice is composed of intermolecularly associated units extending in at least one dimension [23]. For thin absorbers free of saturation effects, using the Debye model, f is related linearly to the area under the resonance, A_T, and its temperature-dependence is given by:

$$A_T \propto f = \exp\left[-\frac{6E_R T}{k\theta_M^2}\right] \text{ for } T \gg \frac{\theta_M}{2} \tag{9}$$

where E_R is the Mössbauer recoil energy, and θ_M is a Mössbauer atom-probed lattice temperature, similar to θ_D for a Debye solid. Thus in the high-temperature limit, plots of $\ln A_T$ vs. T are linear. It is found that the more tightly-bound the lattice, the slower will be the fall in the f value, and hence A_T, as T is raised. A number of broad generalizations can be made concerning the slope of the temperature dependence of A and the question of association in organotin solids. For molecular solids $d\ln A/dT$ is generally above -1.6×10^{-2} K^{-1}, while for associated solids the values are -1×10^{-2} K^{-1} or less.

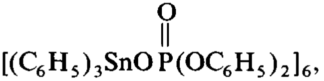
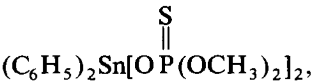
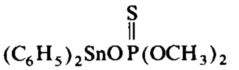
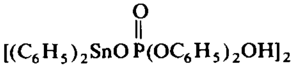
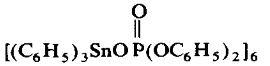
Variable-temperature Mössbauer data are listed in Table 7 for three related organotin phosphate compounds of increasing molecular complexity, and $\ln(A_T/A_{77})$ normalized to the area under the resonance at 77 K are plotted for each vs. T in Fig. 1. From the systematics developed above, the cyclic, hexameric,  $[(C_6H_5)_3SnO\overset{\overset{O}{\|}}{P}(OC_6H_5)_2]_6$, whose structure we have recently solved [16], exists as a molecular unit in its solid as corroborated by our X-ray study. The dimeric, μ-$(OH)_2$,  $[(C_6H_5)_2SnO\overset{\overset{S}{\|}}{P}(OC_6H_5)_2OH]_2$, whose structure we have also solved [22], exists in its solid as discrete molecular units as well. The slope of the third compound,  $(C_6H_5)_2Sn[O\overset{\overset{S}{\|}}{P}(OCH_3)_2]_2$, on the other hand, suggests a lattice in

TABLE 7

VARIABLE-TEMPERATURE MÖSSBAUER DATA FOR THREE ORGANOTIN(IV) PHOSPHATE ESTERS

Compound	$d\ln A/dT \times 10^{-2}$ K^{-1} [a]	r [b]	Intercept	Number of points	T range (K)
 $(C_6H_5)_2SnO\overset{\overset{S}{\|}}{P}(OCH_3)_2$	−0.972	0.9659	0.661	6	77–170
 $[(C_6H_5)_2SnO\overset{\overset{O}{\|}}{P}(OC_6H_5)_2OH]_2$	−1.76	0.9947	1.443	6	77–160
 $[(C_6H_5)_3SnO\overset{\overset{O}{\|}}{P}(OC_6H_5)_2]_6$	−1.37	0.9841	0.932	6	77–170

[a] Normalized to 77 K for ease of comparison. [b] Correlation coefficient.

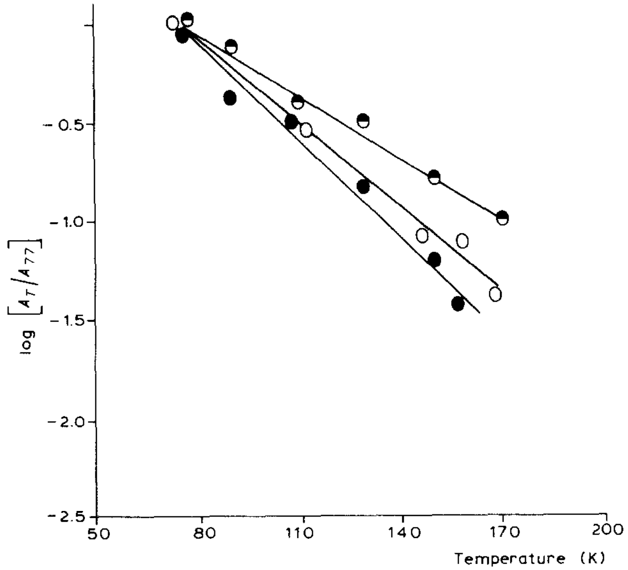


Fig. 1. Temperature dependence of the normalized area under the resonance curve for three organotin(IV) phosphate esters in order of increasing relative steepness: $(C_6H_5)_2Sn[O\overset{\overset{S}{\|}}{P}(OCH_3)_2]_2$ (-0.972×10^{-2} K^{-1} for $T = 77$–170 K), $[(C_6H_5)_3SnO\overset{\overset{O}{\|}}{P}(OC_6H_5)_2]_6$ (-1.37×10^{-2} K^{-1} for $T = 77$–170 K) and $[(C_6H_5)_2SnO\overset{\overset{S}{\|}}{P}(OC_6H_5)_2OH]_2$ (-1.76×10^{-2} K^{-1} for $T = 77$–160 K).

which the tin atom is tightly bound. This could arise through bridging sulfur–tin bonding, Sn–O–P=S → Sn, or from a very tightly-bound lattice of monomers with short intermolecular contacts. Direct comparison can be drawn with the data for the $(C_6H_5)_2SnS_2P(OR)_2$ analogues in which the $R = i\text{-}C_3H_7$ derivative crystallizes in a centrosymmetric lattice of strongly-held monomers [14], and exhibits a slope of -1.06×10^{-2} K^{-1} [3]. The $R = C_2H_5$ and $n\text{-}C_3H_7$ derivatives, on the other hand, exhibit slopes of -1.92 and -2.19×10^{-2} K^{-1}, respectively, characteristic of conventional monomer packing [3]. The X-ray structure of the $R = C_2H_5$ derivative [26] is corroboratory.

Thus the Mössbauer QS data for our $(C_6H_5)_2Sn[OP(S)(OR)_2]_2$ compounds where $R = CH_3$ and C_6H_5 are consistent with six-coordination, but cannot distinguish between chelated and bridged, *trans*-diphenyl, octahedral structures for these solids. But the strong, ambient-temperature spectra for the dimethyl- and diethyltin derivatives, and the apparent lack of preference for chelation as shown in the structure of the $[(C_6H_5)_2SnOP(S)(OC_6H_5)OH]_2$ dimer [22], point to bridged structures for all except the di-n-octyltin derivative which contains four-coordinated tin atoms.

For the $R_3SnOP(S)(OR)_2$ series the large QS values and QS/IS ratios indicate higher than four-coordination for all except the tribenzyltin derivative which presumably contains four-coordinated tin atoms. The absence of ambient-temperature spectra cannot alone be used to rule out bridging structures for these derivatives.

In the mass spectra there are no peaks of mass greater than the parent, and no fragments containing more than one tin atom. In both the di- and triorganotin series successive loss of the organic group attached to the tin atom is seen. Among the triorganotin derivatives listed in Table 3 the most abundant fragments for the tri-n-butyl- and triphenyltin compounds has the general formula $[R_2SnOP(OCH_3)_2]^+$, but no such fragments appear in the spectra of the trimethyl- and tribenzyltin compounds where the most abundant peaks are the $[SnP(S)(OCH_3)_2]^+$ and $[SnOP(S)(OC_6H_5)_2]^+$, respectively. Among the diorganotin

TABLE 8. SOME IR AND RAMAN [a] SPECTRAL FREQUENCIES OF $R_nSn[OP(S)(OR')_2]_{4-n}$

Compound	ν(Sn–O)	ν(P–O)	ν(P–S)	ν(POR)	ν(SnC)
$(CH_3)_3SnOP(S)(OCH_3)_2$	445vw	1080s		1000vw	550m
		1185s			588m
					(518s)
					(554w, 556sh)
$(n\text{-}C_4H_9)_3SnOP(S)(OCH_3)_2$	470vw	1053vs	665w	974m, 1000vw	
		1085vs			
		1200vs			
$(C_6H_5)_3SnOP(S)(OCH_3)_2$	450w	1080sh	663vw	1000m	
		1093s	(618m)		
		1170sh	(575w)		
		1183s			
$(C_6H_5)_3SnOP(S)(OC_6H_5)_2$	448w	1072m	660s	998w, 1002sh	
	498w	1110m			
		1160m			
		1200s			
$(C_6H_5CH_2)_3SnOP(S)(OC_6H_5)_2$	450vw	1119vw		908vw	
		1186vw			
		1212w			
$(CH_3)_2Sn[OP(S)(OCH_3)_2]_2$		1075s		1000m	540vw
		1175s			585m
					(528w)
$(C_2H_5)_2Sn[OP(S)(OCH_3)_2]_2$		1185m	695w	965m, 1000m	
		1180m			
$(n\text{-}C_4H_9)_2Sn[OP(S)(OCH_3)_2]_2$		1080s	690w	970vw, 990w	
		1160s			
		1184s			
$(C_6H_5)_2Sn[OP(S)(OCH_3)_2]_2$	458m	1090s	668vw	985vw, 1000w	
		1170vs	697s		
		1220sh	(645m,566m)		
$(C_6H_5)_2Sn[OP(S)(OC_6H_5)_2]_2$	445vw	1068s	654sh	1000s	
		1088s	670sh		
		1164s	694s		
		1200vs			
$(n\text{-}C_8H_{17})_2Sn[OP(S)(OCH_2)_2]_2$	420sh	1085s	690m	1000s	
	475vw	1152s			
		1185s			
$[(C_6H_5)_2SnOP(S)(OC_6H_5)_2OH]_2$ [b]	450w	1074vs	658s	1005sh	
		1110vs			
		1168vs			

[a] Raman data are in parentheses. [b] The ν(O–H) frequencies are 3180sh, 3070s, and 3048s cm^{-1}.

TABLE 9

^{31}P[a] AND ^{119}Sn[b] NMR DATA FOR ORGANOTIN(IV) *O,O'*-DIMETHYL- AND DIPHENYLMONOTHIOPHOSPHATE DERIVATIVES IN HEXADEUTEROBENZENE AND DEUTEROCHLOROFORM, RESPECTIVELY (ppm)[c]

P-31	
$(CH_3)_2Sn[OP(S)(OCH_3)_2]_2$	−23.03, −30.76
$(C_2H_5)_2Sn[OP(S)(OCH_3)_2]_2$	+2.99, +1.18
$(n\text{-}C_4H_9)_2Sn[OP(S)(OCH_3)_2]_2$	+3.45, +1.57, −16.08, −20.37
$(C_6H_5)_2Sn[OP(S)(OCH_3)_2]_2$	−3.31, −9.19, −24.20
$(C_6H_5)_2Sn[OP(S)(OC_6H_5)_2]_2$	−47.91
Sn-119	
$(n\text{-}C_4H_9)_3SnOP(S)(OCH_3)_2$	68.4
$(C_6H_5)_2Sn[OP(S)(OC_6H_5)_2]_2$	58.9

[a] Relative to 85% phosphoric acid. [b] Relative to tetramethylstannane. [c] Negative shifts are to high field of the standard.

derivatives listed in Table 4 the most abundant fragment for both the diethyl- and di-n-butyltin compounds is $[SnOP(OCH_3)_2]^+$, a fragment which also appears in the spectra of the dimethyl- and diphenyltin compounds as well as in the spectra of the trimethyl-, tri-n-butyl and triphenyltin derivatives. Non-tin bearing fragments are the most abundant in the spectra of the dimethyl- and di-n-octyltin derivatives.

Infrared and Raman spectra of the tri- and dimethyltin derivatives contain bands arising from the ν_{asym} and ν_{sym}(Sn–C) modes, ruling out the high-symmetry planar and linear configurations, respectively (see Table 8). For the presumably *trans*-dimethyltin octahedron, these vibrational data contradict the conclusion drawn from the very high Mössbauer QS value (4.54 ± 0.06 mm s^{-1} at 77 K) which would suggest a completely linear array. In this case, apparently the point-charge model breaks down (see above). It is of course not known precisely how much of a deviation from perfect linearity is necessary to generate observable infrared ν_{sym}(Sn–C) and Raman ν_{asym}(Sn–C).

The proton NMR resonance of $(CH_3)_3SnOP(S)(OCH_3)_2$ at δ 0.31 ppm exhibited a $|^2J(^{119}Sn\text{–}C\text{–}^1H)|$ value of 74.0 Hz, corresponding to a higher coordinated tin atom [27] in the concentrated $CDCl_3$ solution used for the measurement. However, the tin-119 NMR chemical shifts relative to tetramethyltin (TMT) for $(n\text{-}C_4H_9)_3SnOP(S)(OCH_3)_2$ and $(C_6H_5)_2Sn[OP(S)(OC_6H_5)_2]_2$ in concentrated $CDCl_3$ solution to low field of TMT correspond to four-coordinated, and hence monomeric species in this medium (see Table 9). Raising the coordination number at tin moves the chemical shift upfield of TMT, while attaching electronegative atoms moves the resonance downfield [28].

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