formed by overlap of p orbitals lying in a plane parallel to the benzene ring, rationalizing the rather long tin–carbon distance.[43] This scheme contrasts with the generally accepted bonding model for transition-metal aromatic complexes where metal d orbitals are directed toward the carbon atoms. In the tin(II) case, only the $5p_x$ and $5p_y$ orbitals are available for interaction with the benzene e_1 electrons.

Our derivative is unusual and different from the materials discussed above in two ways: to our knowledge we have here, first, the only example of an η^6-C_6H_5 main-group π interaction and, second, the only known example of such an interaction contributing to the formation of a dimer from the constituent monomers.

The two phenyl rings that appear overlayed in the center of the cell in Figure 2 in fact occupy front and back regions and are separated by more than 12 Å.

The phosphorus atoms in the dithiophosphate ester ligands are found at the center of a distorted tetrahedral system with two oxygen atoms and two sulfur atoms, one of the latter double bonded. As we have found in other dithiophosphate ester derivatives of tin(IV),[25,26] the angles involving the more electronegative oxygen atoms are, as expected on the basis of isovalent hybridization arguments, smaller than those involving the sulfur atoms. We find that in both the chelating and bridging ligands $\angle$S–P–S > $\angle$S–P–O(mean values) > $\angle$O–P–O.

Of the tin(II) dithiophosphate esters, only the phenoxy derivative is stable to air oxidation. The other analogues we have prepared turn orange on exposure to air, and the surface oxidation to produce an unidentified tin(IV) product, presumably of the $[(RO)_2PS_2]_2SnO$ variety, can be followed by Mössbauer spectroscopy. The structure–reactivity relation that can rationalize the chemical stability of the phenoxy ester derivative must have to do either with additional lattice energy provided by the η^6-C_6H_5 bonding interaction with the tin(II) atom or with the protection of the tin(II) lone pair of electrons by the steric bulk of the phenyl ring, or with both.

Our observation, discussed above, that the magnitude of the QS values remains unchanged in going from the tin(II) dithiophosphate esters to their bipyridyl adducts can now be understood in terms of the structure we have solved. If the coordination number at the tin(II) center is the same in the bipyridyl adduct as in the parent solids from which they are derived, then with the presumption that the bipyridyl donor is itself bidentate, one of the dithiophosphate ester ligands must be monodentate in these adducts to produce the ψ-6 situation. Such a monodentate ligand is found in the structure of triphenyltin(IV) diethyl dithiophosphate.[11] The more reasonable ψ-7 alternative, employing all ligands in a bidentate manner, is known for tin(II) in the structure η^6-$C_6H_6Sn(AlCl_4)_2{\cdot}C_6H_6$.[43]

Acknowledgment. Our work is supported by the Office of Naval Research and by the National Science Foundation through Grant CHE-78-26548 (J.J.Z.) and by the National Cancer Institute through Grant CA-17562 (D.v.d.H.). We thank the University of Oklahoma for providing computer time.

Registry No. $Sn[S_2P(OCH_3)_2]_2$ (salt form), 80301-45-7; $Sn[S_2P(OCH_3)_2]_2$ (coordination form), 80327-00-0; $Sn[S_2P(OC_2H_5)_2]_2$ (salt form), 80301-46-8; $Sn[S_2P(OC_2H_5)_2]_2$ (coordination form), 80327-01-1; $Sn[S_2P(OC_3H_7\text{-}i)_2]_2$ (salt form), 80301-47-9; $Sn[S_2P(OC_3H_7\text{-}i)_2]_2$ (coordination form), 80327-09-9; $Sn[S_2P(OC_6H_5)_2]_2$ (salt form), 73286-41-6; $Sn[S_2P(OC_6H_5)_2]_2$ (coordination form), 73296-25-0; $Sn[S_2P(OC_3H_7\text{-}i)_2]_2{\cdot}C_{10}H_8N_2$, 80327-68-0; $Sn[S_2P(OCH_3)_2]_2{\cdot}C_{10}H_8N_2$, 80327-67-9; $Sn[S_2P(OC_2H_5)_2]_2{\cdot}C_{10}H_8N_2$, 80327-66-8; $Sn[S_2P(OC_6H_5)_2]_2{\cdot}C_{10}H_8N_2$, 80327-69-1.

Supplementary Material Available: Analytical and physical (Table I), infrared (Table IV), and mass spectral data (Table V) for the tin(II) dithiophosphate esters and positional and isotropic thermal parameters for hydrogen atoms (Table IX), anisotropic thermal parameters for nonhydrogen atoms (Table X), carbon–carbon distances (Table XII), intramolecular angles involving only carbon (Table XIV), and a listing of structure factor amplitudes for $Sn[S_2P(OC_6H_5)_2]_2$ (32 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, University College, Galway, Ireland,
and University of Oklahoma, Norman, Oklahoma 73019

Oxy and Thio Phosphorus Acid Derivatives of Tin. 11. Synthesis and Properties of Di- and Triorganotin(IV) Derivatives of Phenylphosphonic Acid Phenyl Ester[1]

D. CUNNINGHAM,*[2a] L. A. KELLY,[2b] K. C. MOLLOY,[2b] and J. J. ZUCKERMAN*[2b]

Received March 25, 1981

Seven di- and triorganotin(IV) phenylphosphonic acid phenyl esters, $R_2Sn[O_2P(C_6H_5)OC_6H_5]_2$, where R = CH_3, n-C_4H_9, n-C_8H_{17}, or C_6H_5, and $R_3SnO_2P(C_6H_5)OC_6H_5$, where R = CH_3, n-C_4H_9, or C_6H_5, are synthesized in quantitative yield by the action of the corresponding organotin(IV) chlorides or acetates upon the free acid in water or methanol, respectively. The products are colorless, insoluble solids. The diorganotin(IV) derivatives are infusible. In the mass spectra no ions having mass greater than the parent or containing more than one tin atom are detected, but parent molecular ions are found in the spectra of the trimethyl- and triphenyltin(IV) derivatives. The ion of highest abundance arises in all the triorganotins from loss of an organo group from the tin, while for the triphenyl derivative the triphenyltin fragment is most abundant. Successive loss of organic groups from tin is seen, and even-electron ions are preferred. The identity of the phenyl groups lost from the ligands in both series is unknown. No monoorganotin fragments are seen in the spectra of the diorganotin(IV) derivatives. Infrared and Raman data in the ν(Sn–C) region are used to assign a linear C–Sn–C configuration and a planar SnC_3 configuration in the di- and trimethyltin(IV) derivatives, respectively. Bands at 1080–1063 and 1000–993 cm^{-1} are also assigned to the ν_{asym}- and $\nu_{sym}(PO_2)$ modes, respectively. Tin-119m Mössbauer isomer shift (IS) values (1.12–1.47 mm s^{-1}) confirm the presence of tetravalent tin; the ρ [ratio of quadrupole splitting (QS) to IS] values (2.73–3.74) and QS values (3.60–4.66 mm s^{-1}) specify higher than four-coordination at tin. The particularly high QS values for the diorganotin(IV) series suggest a six-coordinated, trans-octahedral geometry. Ambient-temperature Mössbauer spectra for this series indicate intermolecular association, while the absence in the triorganotin analogues suggests an oligomeric structure where five units are the minimum for ring formation accommodating trigonal-bipyramidal and –O–P–O–bridges.

Previous reports in this series have described the syntheses of the di-[3] and triorganotin(IV) dithiophosphate[4] and diphenyl phosphate[1] esters. These studies are directed toward developing the basis for more powerful biocidal activity[5] through

0020-1669/82/1321-1416$01.25/0 © 1982 American Chemical Society

Table I. Di- and Triorganotin(IV) Derivatives of Phenylphosphonic Acid Phenyl Ester, $R_nSn[OP(O)(C_6H_5)OC_6H_5]_{4-n}$ ($n = 3, 2$)

	%C		%H			
compd	found	calcd	found	calcd	mp °C	prepn
$(CH_3)_3SnOP(O)(C_6H_5)OC_6H_5$	45.85	45.35	4.89	4.83	147	5
$(n\text{-}C_4H_9)_3SnOP(O)(C_6H_5)OC_6H_5$	57.97	55.08	5.54	7.14	78-80	5
$(C_6H_5)_3SnOP(O)(C_6H_5)OC_6H_5$	61.45	61.78	4.46	4.33	209-210	6
$(CH_3)_2Sn[OP(O)(C_6H_5)OC_6H_5]_2$	50.65	50.76	4.26	4.23	>230	5
$(n\text{-}C_4H_9)_2Sn[OP(O)(C_6H_5)OC_6H_5]_2$	55.26	54.96	5.58	5.44	>230	5
$(n\text{-}C_8H_{17})_2Sn[OP(O)(C_6H_5)OC_6H_5]_2$	59.44	59.49	6.77	6.25	>230	6
$(C_6H_5)_2Sn[OP(O)(C_6H_5)OC_6H_5]_2$	58.28	58.48	4.18	4.10	>230	5

dual-acting compounds incorporating both organotin and organophosphorus moieties in the same molecule. In this paper we describe the preparation and properties of the di- and triorganotin(IV) derivatives of phenylphosphonic acid phenyl ester.

Experimental Section

Organotin starting materials were of commercial grade and were used without further purification. Infrared spectra were recorded on a Beckman 4250 spectrometer as Nujol mulls on KBr plates and polyethylene film. Raman spectra were recorded on the neat solids with use of a Spex Ramalog 5 laser Raman system. Mass spectra were recorded on a Hewlett-Packard 5985B mass spectrometer at 70 eV. Tin-119m Mössbauer spectra were recorded on a Ranger Engineering constant-acceleration spectrometer equipped with an NaI scintillation counter and using $Ca^{119m}SnO_3$ (New England Nuclear Corp.) as the source and $Ca^{119}SnO_3$ at room temperature as the standard reference material for zero velocity. Velocity calibration was based upon β-tin and natural iron. Standard, nonlinear, least-squares techniques were used to fit the data to Lorentzian curves. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

The phenyl ester of phenylphosphonic acid was prepared by the action of phenol on the dichloride

$$C_6H_5P(O)Cl_2 + C_6H_5OH \rightarrow C_6H_5P(O)(OC_6H_5)Cl + HCl \quad (1)$$

followed by hydrolysis[6]

$$C_6H_5P(O)(OC_6H_5)Cl + H_2O \rightarrow C_6H_5P(O)(OC_6H_5)OH + HCl \quad (2)$$

or by the action of dicyclohexylcarbodiimide on phenylphosphonic acid

$$2C_6H_5P(O)(OH)_2 + (C_6H_{11}N)_2C \rightarrow [C_6H_5P(O)OH]_2O + (C_6H_{11}NH)_2CO \quad (3)$$

followed by esterification by phenol

$$[C_6H_5P(O)OH]_2O + C_6H_5OH \rightarrow C_6H_5P(O)(OC_6H_5)OH + C_6H_5P(O)(OH)_2 \quad (4)$$

The phenylphosphonic acid is returned to the reaction cycle until the conversion to the monoester is complete.[7]

The compounds studied are listed with the method of preparation used and their melting points and microanalytical data in Table I. Tin-119m Mössbauer data are listed in Table II, and mass spectral, infrared, and Raman data in Tables III–V. The preparations are described below.

(Phenyl phenylphosphonato)trimethyltin(IV), $(CH_3)_3SnO_2P(C_6H_5)OC_6H_5$. A solution of the phenyl ester of phenylphosphonic acid (0.94 g, 4.0 mmol) in distilled water (30 mL) was added to a solution of trimethyltin chloride (1.10 g, 4.0 mmol) in distilled water (30 mL). The solution was concentrated on a rotary evaporator, producing the solid product in quantitative yield (mp 147 °C), which was filtered and washed with cold methanol.

(Phenyl phenylphosphonato)tri-*n*-butyltin(IV), $(n\text{-}C_4H_9)_3SnO_2P(C_6H_5)OC_6H_5$. Most attempts to prepare this compound, for example, from tri-*n*-butyltin chloride or acetate and the phosphorus acid, yielded only oily materials. The following method yields a solid. Tri-*n*-butyltin chloride (0.71 g, 2.0 mmol) in benzene (a suspected carcinogen) and the acid (0.51 g, 2.0 mmol) also in benzene (total volume ca. 50 mL) were stirred together at ambient temperature overnight. The resulting solution was filtered to remove traces of solid and concentrated in vacuo, leaving an oil, which was stirred with petroleum ether (30 mL) to form a white solid, which was filtered, washed with the same solvent, and dried (0.31 g, 27% yield; mp 78–80 °C). The compound does not analyze well, and purification has proved impossible. (Anal. Calcd: C, 55.08; H, 7.14. Found: C, 57.97; H, 5.54.) The waxy product does not grind, and its immiscibility with Nujol prevented the obtainment of a strong infrared spectrum.

(Phenyl phenylphosphonato)triphenyltin(IV), $(C_6H_5)_3SnO_2P(C_6H_5)OC_6H_5$. A solution of sodium acetate (0.71 g, 5.0 mmol) in methanol (30 mL) was added to a solution of triphenyltin chloride (2.00 g, 5.0 mmol) in methanol (30 mL). A solution of the phenyl ester of phenylphosphonic acid (1.22 g, 5.0 mmol) in methanol (20 mL) was then added to the above-prepared solution of triphenyltin acetate. The solution was concentrated on a rotary evaporator and allowed to stand at 0 °C 1 week. Crystals of the product formed in quantitative yield (mp 209–210 °C). The crystals were filtered and washed with cold methanol followed by ether.

Bis(phenyl phenylphosphonato)dimethyltin(IV), $(CH_3)_2Sn[O_2P(C_6H_5)OC_6H_5]_2$. A solution of the phenyl ester of phenylphosphonic acid (1.00 g, 4.0 mmol) in distilled water (30 mL) was added in a 2:1 ratio to a stirred solution of dimethyltin dichloride (0.47 g, 2.0 mmol) in distilled water (30 mL) to form a white product in quantitative yield (mp >230 °C), which was filtered and washed with cold methanol.

Bis(phenyl phenylphosphonato)diphenyltin(IV), $(C_6H_5)_2Sn[O_2P(C_6H_5)OC_6H_5]_2$. The phenyl ester of phenylphosphonic acid (1.00 g, 4.0 mmol) in methanol (30 mL) was added in a 2:1 ratio to a stirring solution of diphenyltin dichloride (2.94 g, 2.0 mmol) in methanol (30 mL) to give an immediate white precipitate in quantitative yield. The solid was washed in cold methanol followed by ether (mp >230 °C).

Bis(phenyl phenylphosphonato)di-*n*-butyltin(IV), $(n\text{-}C_4H_9)_2Sn[O_2P(C_6H_5)OC_6H_5]_2$. A solution of sodium acetate (0.89 g. 6.0 mmol) in methanol (20 mL) was added to a solution of di-*n*-butyltin dichloride (1.00 g, 3.0 mmol) in methanol (30 mL). A solution of the phenyl ester of phenylphosphonic acid (1.54 g, 6.0 mmol) in methanol (20 mL) was added to the above-prepared solution of di-*n*-butyltin diacetate. A white solid precipitated in quantitative yield and was filtered and washed with cold methanol followed by ether (mp >230 °C).

Bis(phenyl phenylphosphonato)di-*n*-octyltin(IV), $(n\text{-}C_8H_{17})_2Sn[O_2P(C_6H_5)OC_6H_5]_2$. A solution of sodium acetate (0.82 g, 6.0 mmol) in ethanol (20 mL) was added to a solution of di-*n*-octyltin dichloride (1.25 g, 3.0 mmol) in ethanol (30 mL). A solution of the phenyl ester of phenylphosphonic acid (1.54 g, 6.0 mmol) in ethanol (20 mL) was added to the above-prepared solution of di-*n*-octyltin diacetate. Upon the addition of 15 mL of methanol, a white precipate formed immediately in quantitative yield. The solid was filtered and washed with cold methanol followed by ether (mp >230 °C).

Results and Discussion

The di- and triorganotin(IV) phenylphosphonic acid phenyl

---

(1) For the previous paper in this series see: Molloy, K. C.; Nasser, F. A. K.; Barnes, C. L.; van der Helm, D.; Zuckerman, J. J. *Inorg. Chem.* **1982**, *21*, 960.

(2) (a) University College. (b) University of Oklahoma.

(3) Lefferts, J. L.; Molloy, K. C.; Zuckerman, J. J.; Haiduc, I.; Curtui, M.; Guta, C.; Ruse, D. *Inorg. Chem.* **1980**, *19*, 2861.

(4) Lefferts, J. L.; Molloy, K. C.; Zuckerman, J. J.; Haiduc, I.; Guta, C.; Ruse, D. *Inorg. Chem.* **1980**, *19*, 1662.

(5) Zuckerman, J. J.; Reisdorf, R. P.; Ellis, H. V., III; Wilkinson, R. R. In "Chemical Problems in the Environment: Occurrence and Fate of the Organoelements"; Bellama, J. M., Brinckman, F. E., Eds.; American Chemical Society: Washington, D.C., 1978; ACS Symp. Ser. No. 82, p 388.

(6) Michaelis, A. *Justus Liebigs Ann. Chem.* **1876**, *181*, 275.

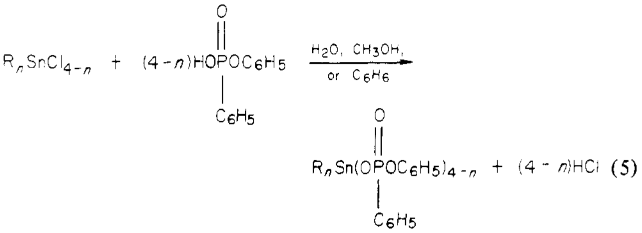
(7) Burger, A.; Anderson, J. J. *J. Am. Chem. Soc.* **1957**, *79*, 3575.

Table II. Tin-119m Mossbauer Data for $R_nSn[OP(O)(C_6H_5)OC_6H_5]_{4-n}$ ($n = 3, 2$) at 77 K

compd	$IS^{a,b}$	$QS^{a,c}$	$\Gamma_{av}{}^{a,b}$	ρ^d
$(CH_3)_3SnOP(O)(C_6H_5)OC_6H_5$	1.33	3.78	1.27	2.84
$(n\text{-}C_4H_9)_3SnOP(O)(C_6H_5)OC_6H_5$	1.47	4.12	1.61	2.80
$(C_6H_5)_3SnOP(O)(C_6H_5)OC_6H_5$	1.32	3.60	1.29	2.73
$(CH_3)_2Sn[OP(O)(C_6H_5)OC_6H_5]_2$	1.32	4.66	1.22	3.53
$(n\text{-}C_4H_9)_2Sn[OP(O)(C_6H_5)OC_6H_5]_2$	1.47	4.61	1.46	3.14
$(n\text{-}C_8H_{17})_2Sn[OP(O)(C_6H_5)OC_6H_5]_2$	1.46	4.60	1.32	3.15
$(C_6H_5)_2Sn[OP(O)(C_6H_5)OC_6H_5]_2$	1.12	4.19	1.20	3.74

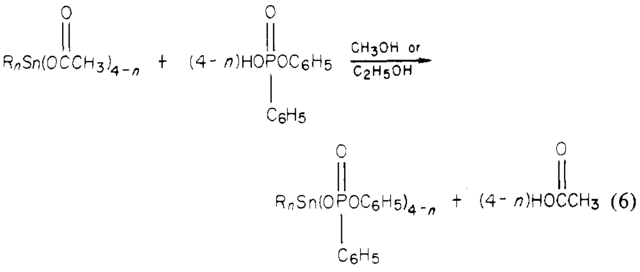
[a] In mm s^{-1}. [b] ± 0.03 mm s^{-1}. [c] ± 0.06 mm s^{-1}. [d] ρ = QS/IS.

ester derivatives can be synthesized in quantitative yield by the action of the organotin(IV) chlorides upon the free acid



$n = 3$; R = CH_3, $n\text{-}C_4H_9$
$n = 2$; R = CH_3, C_6H_5

or from the organotin(IV) acetates



$n = 3$; R = C_6H_5
$n = 2$; R = $n\text{-}C_4H_9$, $n\text{-}C_8H_{17}$

The di- and triorganotin(IV) derivatives of phenylphosphonic acid phenyl ester are air- and moisture-stable, colorless solids that are largely insoluble in water or organic solvents. The triorganotin derivatives are slightly more soluble and have lower melting points.

The possible structures for the triorganotin(IV) derivatives include a four-coordinated, $R_3SnO_2P(C_6H_5)OC_6H_5$ configuration (A) containing monodentate phenylphosphonato ligands. Indeed, this rare form is adopted by (*O,O'*-diethyl dithiophosphato)triphenyltin(IV), $(C_6H_5)_3SnS_2P(OC_2H_5)_2$, whose structure we have recently reported,[8] but chelation is far more

Table III. Mass Spectral Data for $R_3SnO_2P(C_6H_5)OC_6H_5$[a]

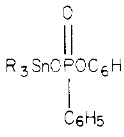
m/e (rel abund)			
R = CH_3	R = $n\text{-}C_4H_9$	R = C_6H_5	assignt
		584 (2.0)	$(C_6H_5)_3SnO_2P(C_6H_5)OC_6H_5{}^+$
		507 (45.3)	$(C_6H_5)_2SnO_2P(C_6H_5)OC_6H_5{}^+$
	467 (100.0)		$(n\text{-}C_4H_9)_2SnO_2P(C_6H_5)OC_6H_5{}^+$
		429 (86.2)	$(C_6H_5)_2SnO_2P(C_6H_5)OC_6H_5 - C_6H_6{}^+$
398 (2.7)			$(CH_3)_3SnO_2P(C_6H_5)OC_6H_5{}^{+\cdot}$
383 (100.0)			$(CH_3)_2SnO_2P(C_6H_5)OC_6H_5{}^+$
367 (5.4)			$(CH_3)_2SnO_2P(C_6H_5)OC_6H_5 - CH_4{}^+$
353 (11.4)	353 (59.5)	353 (42.3)	$SnO_2P(C_6H_5)OC_6H_5{}^+$
		352 (50.5)	$(C_6H_5)_2SnO_2P(C_6H_5)OC_6H_5 - C_6H_5{}^{+\cdot}$
		351 (100.0)	$(C_6H_5)_3Sn^+$
		337 (25.3)	$C_6H_5SnO_2PC_6H_5{}^+$
		309 (9.2)	?
305 (8.0)			$(n\text{-}C_4H_9)_2SnO_2P(C_6H_5)OC_6H_5 - C_6H_6{}^+$
		289 (36.9)	$C_6H_5SnOC_6H_5 - H^+ \equiv (C_6H_5)_2SnO - H^+$
		274 (2.5)	$(C_6H_5)_2Sn^+$
248 (3.9)			$(CH_3)_3SnOC_6H_5{}^+$
213 (10.9)	213 (52.8)	213 (20.9)	$SnOC_6H_5{}^+$
	197 (8.1)	197 (64.5)	$C_6H_5Sn^+$
183 (7.3)			SnO_2P^+
	177 (13.3)		$n\text{-}C_4H_9Sn^+$
165 (41.2)			$(CH_3)_3Sn^+$
150 (8.3)			$(CH_3)_2Sn^{+\cdot}$
	137 (6.2)	137 (5.3)	$SnOH^+$
	121 (10.3)		SnH^+
120 (6.3)	120 (6.9)	120 (34.6)	$Sn^{+\cdot}$

[a] Tin-bearing fragments only; mass numbers are based upon ^{120}Sn, ^{31}P, ^{16}O, ^{12}C, and ^{1}H.

Table IV. Mass Spectral Data for $R_2Sn[O_2P(C_6H_5)OC_6H_5]_2$[a,b]

m/e (rel abund)			
R = CH_3	R = $n\text{-}C_4H_9$	R = $n\text{-}C_8H_{17}$	assignt
	607 (4.6)		$(n\text{-}C_4H_9)_2Sn[O_2P(C_6H_5)OC_6H_5]O_2PC_6H_5{}^+$
		579 (3.4)	$(n\text{-}C_8H_{17})_2SnO_2P(C_6H_5)OC_6H_5{}^+$
523 (7.7)			$(CH_3)_2Sn[O_2P(C_6H_5)OC_6H_5]O_2PC_6H_5{}^+$
	467 (21.0)		$(n\text{-}C_4H_9)_2SnO_2(C_6H_5)OC_6H_5{}^+$
		439 (3.9)	$(n\text{-}C_8H_{17})_2SnOC_6H_5{}^+$
383 (64.3)			$(CH_3)_2SnO_2P(C_6H_5)OC_6H_5{}^+$
353 (13.8)	353 (73.1)	353 (43.2)	$SnO_2P(C_6H_5)OC_6H_5{}^+$
213 (16.8)	213 (27.5)	213 (19.2)	$SnOC_6H_5{}^+$
	155 (7.1)		?
	120 (3.3)	120 (1.7)	$Sn^{+\cdot}$

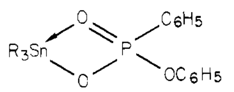
[a] Tin-bearing fragments only; mass numbers are based upon ^{120}Sn, ^{31}P, ^{16}O, ^{12}C, and ^{1}H. [b] The diphenyltin derivative was too involatile for a mass spectrum to be obtained.



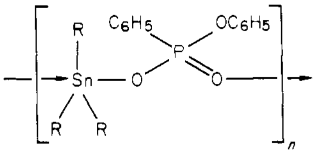
$R_3SnO\underset{C_6H_5}{\overset{O}{\overset{\|}{P}}}OC_6H_5$

A

common among these sulfur ligands.[9] Furthermore, chelation in the dithiophosphorus series gives way to bridging in the oxygenated ligands. Thus we expect that chelated forms such as B will be less favored than bridged forms (C), in which planar triorganotin(IV) units adopt an axially most electronegative trigonal-bipyramidal configuration. The more intense pull of the oxygen on the p component of the orbital on tin would maximize in the axial position. Also, the chelated forms will tend to become less favorable because of the increased difficulty of valence angle distortion arising from the smaller tin–oxygen internuclear distance. In the related triphenyltin(IV) diphenyl phosphate, $(C_6H_5)_3SnO_2P(OC_6H_5)_2$, a cyclic hexameric structure (n = 6 in C) is adopted.[1]

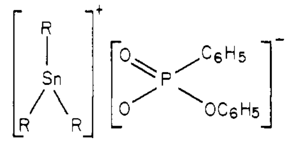


B

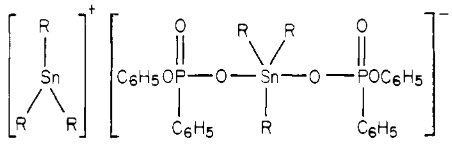


C

An ionic form D is also possible. Moreover, in the structure of α-(phenylphosphonato)trimethyltin(IV), $(CH_3)_3SnO_2P(C_6H_5)OH$, the tin atoms occupy two nonequivalent environments, alternating tins forming either two long or two short bonds to oxygen, an arrangement that can be interpreted in terms of a combination of triorganotin(IV) cations and bis(phosphorus acid)triorganotin(IV) anions.[10] This would suggest structure of the type E for the title compounds.



D

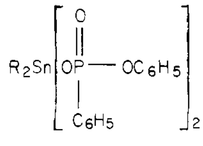


E

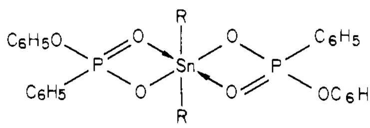
Table V. Infrared Frequencies (cm^{-1}) for the $R_nSn(OP(O)(C_6H_5)OC_6H_5)_{4-n}$ Derivatives in the Range of 1600–500 cm^{-1}

$C_6H_5O(C_6H_5)PO_2H$	3200 b, 1595 m, 1215 m, 1160 w, 1145 m, 1070 w, 1045 w, 1025 w, 920 m, 897 m, 692 m, 535 m
$(CH_3)_3SnO_2P(C_6H_5)OC_6H_5$	1595 m, 1492 s, 1220 s, 1206 vs, 1190 vs, 1163 m, 1145 vs, 1027 m, 1000 w, 908 s, 896 m, 775 s, 752 m, 740 m, 722 sh, 695 m, 548 s, 532 m, sh
$(n\text{-}C_4H_9)_3SnO_2P(C_6H_5)OC_6H_5$	1595 m, sh, 1590 m, 1490 vs, 1305 w, br, 1265 w, sh, 1240 s, 1212 m, sh, 1200 vs, 1195 vs, 1186 s, sh, 1160 m, 1129 m, 1115 m, sh, 1073 m, 1030 m, sh, 1020 m, sh, 1010 m, 993 s, 978 s, 940 vs, 930 vs, 905 m, 845 w, br, 777 m, 758 m, 740 m, 717 m, 717 m, 690 m, 670 w, 655 w, 590 w, br, 528 w, 510 w
$(C_6H_5)_3SnO_2P(C_6H_5)OC_6H_5$	1590 m, 1490 m, 1430 m, 1305 w, 1222 s, 1198 m, 1175 m, sh, 1163 vs, 1139 s, 1080 m, 1068 m, 1047 s, 1021 s, 995 w, 922 m, 904 m, 779 m, 752 w, 742 m, 730 s, 690 s, 617 w, 540 m, 450 w
$(CH_3)_2Sn[O_2P(C_6H_5)OC_6H_5]_2$	1594 m, 1490 m, 1215 m, 1195 m, sh, 1178 vs, 1142 vs, 1141 vs, 1065 vs, 1027 m, 998 w, 917 s, 891 m, 800 m, br, 773 s, 750 m, 740 m, 722 m, sh, 693 m, sh, 685 m, 580 w, br, 538 m, 522 m
$(n\text{-}C_4H_9)_2Sn[O_2P(C_6H_5)OC_6H_5]_2$	1595 m, 1491 s, 1224 s, 1192 vs, 1163 vs, 1145 s, 1085 s, sh, 1070 vs, 1026 m, 1004 m, sh, 974 w, 920 s, 898 m, 773 s, 754 m, sh, 742 m, 710 m, sh, 690 s, 545 m, sh, 530 s
$(n\text{-}C_7H_{18})_2Sn[O_2P(C_6H_5)OC_6H_5]_2$	1590 w, 1490 m, 1235 w, 1220 m, 1188 vs, 1160 m, sh, 1140 s, 1106 w, 1063 s, 1020 m, 920 m, 892 w, 768 m, 700 w, sh, 737 w, 717 w, 686 m, 544 w, sh, 526 w, br
$(C_6H_5)_2Sn[O_2P(C_6H_5)OC_6H_5]_2$	1595 w, 1492 m, 1328 s, 1316 sh, w, 1220 m, 1175 1175 vs, 1145 s, 1098 w, sh, 1080 s, 1026 w, 1000 w, 926 m, 899 w, 774 m, 743 w, sh, 735 w, 723 w, sh, 710 w, sh, 690 m, 653 w, 590 w, sh, 580 w, 578 w, sh, 545 m, 528 m

The analogous structures for the diorganotin(IV) derivatives include a monomeric form (F) with monodentate phenylphosphonic acid phenyl ester ligands, but an increased coordination number at tin is more likely. For example, the octahedrally chelated form G, which we write in the *trans*-diorganotin(IV) configuration, is analogous to the structure of the similar sulfur-containing bis(dimethyldithio-



F



G

---

(8) Molloy, K. C.; Hossain, M. B.; van der Helm, D.; Zuckerman, J. J.; Haiduc, I. *Inorg. Chem.* **1979**, *18*, 3507.

(9) Wasson, J. R.; Woltermann, G. M.; Stoklosa, H. J. *Fortschr. Chem. Forsch.* **1973**, *35*, 65.

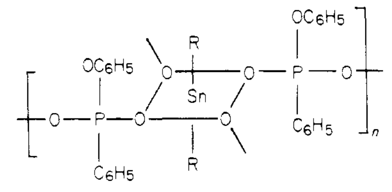
(10) Molloy, K. C.; Hossain, M. B.; van der Helm, D.; Cunningham, D.; Zuckerman, J. J. *Inorg. Chem.* **1981**, *20*, 2402.

Table VI. Selected Assignments in the Infrared Spectra of $R_nSn[OP(O)(C_6H_5)OC_6H_5]_{4-n}$ (n = 2, 3) in cm^{-1}

n, R							
3, CH_3	3, n-C_4H_9	3, C_6H_5	2, CH_3	2, n-C_4H_9	2, n-C_8H_{17}	2, C_6H_5	assignt
1070 vs	1073 m	1080 m	1065 vs	1070 vs	1063 s	1080 s	$\nu_{asym}(PO_3)$
1000 w	993 s	995 w	998 w	1004 m, sh	. . .	1000 w	$\nu_{sym}(PO_3)$
548 s			538 m				$\nu_{asym}(SnC)$
514 m (R)[a]			522 m (?)				ν_{sym}(Sn–C)

[a] R = Raman band.

phosphinato)dimethyltin(IV),[11] $(CH_3)_2Sn[S_2P(CH_3)_2]$, but oligomeric bridged forms (H) cannot be ruled out, and ionic forms are also possible. On the basis of the available structural data,[12] and our recent X-ray results on analogous compounds, we would expect axially bridged trigonal-bipyramidal structures for the triorganotin derivatives and *trans*-diorganotin bridged-octahedral structures for the diorganotin derivatives.


H

Mass Spectra. The mass spectral data listed in Tables III and IV for the tri- and diorganotin derivatives, respectively, are quite similar within their respective series. No ions of mass higher than the parent are detected, nor are there fragments containing more than one tin atom, ruling out gas-phase association of these species. Parent molecular ions in low abundance are detected for the trimethyl- and triphenyltin derivatives. The most abundant tin-bearing ions arise in the trialkyltin examples from the loss of an alkyl group from the tin atom, to give even-electron ions, and similar behavior is observed in the triorganotin(IV) diphenyl phosphate derivatives.[13] Successive loss of organic groups from the tin in the triorganotin series is also a feature of these data, and the triphenyltin ion is the most abundant ion in the triphenyltin derivative. The preference for the formation of even-electron ions is manifested in the loss of neutral CH_4, C_6H_6, etc. fragments from the even-electron R_2SnL^+ [L = $O_2P(C_6H_5)OC_6H_5$] rather than elimination of CH_3, C_6H_5, etc. radicals. In both series the ligand loses phenyl groups, but it is not possible to identify whether it is the phenoxy or phenylphosphorus moiety that is being lost.

Even-electron ions again dominate the mass spectra of the diorganotin(IV) derivatives. The odd-electron parent is never seen, but the loss of either $C_6H_5O\cdot$ or $L\cdot$ yields the even-electron $R_2Sn(O_2PC_6H_5)L^+$ or R_2SnL^+ fragment. No monoorganotin fragments RSnL, $RSnL_2$, etc. are seen even though a $P^+\cdot$–$R\cdot$ process would produce an even-electron ion. Instead, the even-electron ions lose the neutral alkane (C_2H_5, C_8H_{20}, $C_{16}H_{38}$, etc.) fragment R_2 to give SnL^+. The most abundant ion in these spectra is a non-tin-containing fragment at m/e = 357, which could be assigned to $[C_6H_5O(C_6H_5)PO_2PO_2(C_6H_5)OC_6H_5C_6H_5O_2]^+$.

Infrared and Raman Spectra. The ν_{asym}- and ν_{sym}(Sn–C) modes can be used to assign the geometries of the di- and trimethyltin derivatives. The vibrational spectroscopic selection rules dictate that for a linear dimethyl- or a planar trimethyltin system the ν_{asym} will be infrared active but Raman inactive, and vice versa for the ν_{sym}(Sn–C) mode, which is found generally ca. 30 cm^{-1} to lower energy. We observe in the infrared spectrum of the trimethyltin derivative $\nu_{asym}(Sn–C_3)$ at 548 cm^{-1}, but no band at lower energy assignable to the symmetric mode. In the Raman spectrum, however, a medium band appears at 514 cm^{-1}, presumably $\nu_{sym}(Sn–C_3)$, as well as a very weak feature at 548 cm^{-1}. Hence, we conclude that the trimethyltin group must be very close to planarity in its solid phenylphosphonic acid phenyl ester. The Raman spectrum of the dimethyl derivative contains only one band at 521 cm^{-1}, which, however, also appears in the infrared at 522 cm^{-1} and is assignable to the ν_{sym} mode. The $\nu_{asym}(Sn–C_2)$ mode absorbs at 538 cm^{-1} only in the infrared. Thus the evidence in this case apparently is conflicting, unless the band at 522 cm^{-1} in the infrared has an origin different from $\nu_{sym}(Sn–C_2)$. This possibility cannot be ruled out, since the usual ratio of intensities in the infrared, $\nu_{asym} > \nu_{sym}$, is reversed in our spectrum. On the basis of the Raman, but not the infrared, data we therefore conclude that the dimethyltin group in the solid ester is most likely linear.

In addition, modes that can be assigned to the ν_{asym}- and $\nu_{sym}(PO_3)$ are found at 1088–1070 and 1022–1000 cm^{-1}, respectively,[14] in $R_2SnOP(O)OH$, where R = CH_3, C_2H_5, or n-C_4H_9, at 1075 and 995–990 cm^{-1}, respectively,[15] in $[R_2SnOP(O)(R)O–]$, and at 1056–1050 and 977–972 cm^{-1}, respectively,[15] in $[R_2SnO]_2P(O)R$. Corresponding to these absorptions, which are separated by $\Delta = \nu_{asym} - \nu_{sym}$ = 80–66 cm^{-1}, our assignments for the title compounds are listed in Table VI.

Mössbauer Spectra. The isomer shift (IS) data (1.12–1.47 mm s^{-1}) in Table II specify tin in the four-valent state, and the magnitude of the quadrupole splitting (QS 3.60–4.66 mm s^{-1}) to the IS (ρ value 2.73–3.74) is indicative in all cases of a higher than four-coordinated situation at the tin atom.[16] The extremely high QS values for the diorganotin series (4.19–4.66 mm s^{-1}) specify a *trans*-diorganotin configuration in an octahedral geometry for those systems.

We have previously linked the magnitude of the QS values with the C–Sn–C angle in six-coordinated diorganotin(IV) compounds[3,12] by use of a treatment based upon a point-charge model.[17] In this treatment it is assumed that the partial QS values of the donor ligands will be small compared with those for the R groups and that the splitting will reach ca. 4.0 mm s^{-1} in a linear C–Sn–C array. Lately, however, we have examined several series of diorganotin(IV) derivatives, including the $R_2Sn[O_2P(OC_6H_5)_2]_2$[13] and $R_2Sn[O_2P(C_6H_5)OH]_2$[18] systems analogous to the compounds reported here, which exhibit QS values much above 4.0 mm s^{-1}. The partial QS values of the oxygenated ligands in these cases obviously cannot be ignored, and the underlying basis of the model breaks down. However, the extremely large splittings observed for these

---

(11) Molloy, K. C.; Hossain, M. B.; van der Helm, D.; Zuckerman, J. J.; Mullins, F. P. *Inorg. Chem.* **1981**, *20*, 2172.

(12) Zubieta, J. A.; Zuckerman, J. J. *Prog. Inorg. Chem.* **1978**, *24*, 251.

(13) Molloy, K. C.; Nasser, F. A. K.; Zuckerman, J. J. *Inorg. Chem.*, in press.

(14) Chivers, T.; van Roode, J. H. G.; Ruddick, J. N. R.; Sares, J. R. *Can. J. Chem.* **1973**, *51*, 3702.

(15) Ridenour, R. E.; Flagg, E. E. *J. Organomet. Chem.* **1969**, *16*, 393.

(16) Zuckerman, J. J. *Adv. Organomet. Chem.* **1970**, *9*, 21.

(17) Sham, T. K.; Bancroft, G. M. *Inorg. Chem.* **1975**, *14*, 2281.

(18) Molloy, K. C.; Cunningham, D.; Kelly, L. A.; van der Helm, D.; Zuckerman, J. J. "Abstracts of Papers", 2nd Chemical Congress of the North American Continent, Las Vegas, Nev., Aug 1980; American Chemical Society: Washington, D.C., 1980.

diorganotin derivatives must correspond to linear or nearly linear C–Sn–C moieties in the solids.

The dimethyl- and diphenyltin(IV) derivatives exhibit Mössbauer spectra at ambient temperatures, the former yielding quite a strong spectrum. While there are several monomeric molecular solids of known structure for which spectra can be recorded at these temperatures,[19] we interpret this observation in the light of the physical properties of these compounds in terms of a lattice composed of intermolecularly associated units extending in at least one dimension.[15]

The trimethyl- and triphenyltin(IV) derivatives, on the other hand, fail to produce resolvable spectra even after long counting times at ambient temperatures. We interpret this negative evidence as ruling out an intermolecularly associated extended lattice, and this conclusion is corroborated by the reduced melting points (Table I) and enhanced solubilties of these species in comparison with those of their diorganotin analogues (vide supra).

Structural Conclusions

The vibrational spectra of the dimethyltin(IV) derivatives in the $\nu(SnC_2)$ region obey the selection rules for a linear C–Sn–C system. The magnitude of the Mössbauer QS and ρ values specify a higher than four-coordinated situation at the tin atom, and the very large QS values corroborate a *trans*-diorganotin(IV) geometry seen for the dimethyl derivative in the infrared and Raman spectra. Structure F is thus eliminated, and the question of chelation vs. bridging is answered with respect to the ambient-temperature Mössbauer resonances observed for the dimethyl and diphenyl derivatives, which rule out structure G. Use of –O–P–O– bridges to link *trans*-diorganotin(IV) units as depicted in structure H is seen in solid tris[dimethyltin(IV)] bis(orthophosphate) octahydrate in which octahedral, *trans*-dimethyltin(IV) units are linked by PO_4 tetrahedra.[20] Our conclusion is consistent with the infusible, insoluble and nonvolatile nature of these solids.

The vibrational spectra in the $\nu(SnC_3)$ region of the trimethyltin(IV) derivative obey the selection rules for a planar SnC_3 system. The magnitude of the Mössbauer QS and ρ values specify a higher than four-coordinated situation at the tin atom. Structures A and B are thus eliminated because the former contains four-coordinated tin and the latter would not accommodate a planar R_3Sn unit. Thus the bridged form C would seem to be favored, but the trimethyl- and triphenyltin(IV) derivatives fail to show a Mössbauer spectrum at ambient temperatures. Considering the strong spectra developed by the diorganotin(IV) analogues, this negative evidence suggests that *n* in structure C is finite. A related compound, $(C_6H_5)_3SnO_2P(OC_6H_5)_2$, forms a cyclic hexamer in the solid,[1] rather than the helical polymer formed by $(CH_3)_3SnO_2P(C_6H_5)OH$.[10] The pentamer is the smallest structure capable of accommodating planar triorganotin(IV) units axially bridged by –O–P–O– linkages. The value of *n* in structure C must, therefore, be at least 5.

Acknowledgment. Our work is supported by the Office of Naval Research and by the National Science Foundation through Grant CHE-78-26548. We thank M&T Chemicals, Inc., for the donation of organotin starting materials and Mr. D. C. Teeters for help with the Raman spectra. We thank the National Science Foundation Undergraduate Research Participation Program for a stipend (to L.A.K.).

Registry No. $(CH_3)_3SnOP(O)(C_6H_5)OC_6H_5$, 80243-52-3; $(n\text{-}C_4H_9)_3SnOP(O)(C_6H_5)OC_6H_5$, 80243-54-5; $(C_6H_5)_3SnOP(O)(C_6H_5)OC_6H_5$, 80243-56-7; $(CH_3)_2Sn[OP(O)(C_6H_5)OC_6H_5]_2$, 80243-58-9; $(n\text{-}C_4H_9)_2Sn[OP(O)(C_6H_5)OC_6H_5]_2$, 80243-60-3; $(n\text{-}C_8H_{17})_2Sn[OP(O)(C_6H_5)OC_6H_5]_2$, 80243-62-5; $(C_6H_5)_2Sn[OP(O)(C_6H_5)OC_6H_5]_2$, 80243-64-7; $C_6H_5P(O)(OC_6H_5)OH$, 2310-87-4; $(CH_3)_3SnCl$, 1066-45-1; $(n\text{-}C_4H_9)_3SnCl$, 1461-22-9; $(C_6H_5)_3SnCl$, 639-58-7; $(CH_3)_2SnCl_2$, 753-73-1; $(C_6H_5)_2SnCl_2$, 1135-99-5; $(n\text{-}C_4H_9)_2SnCl_2$, 683-18-1; $(n\text{-}C_8H_{17})_2SnCl_2$, 3542-36-7.

---

(19) Bancroft, G. M.; Butler, K. D.; Sham, T. K. *J. Chem. Soc., Dalton Trans.* **1975**, 1483.

(20) Ashmore, J. P.; Chivers, T.; Kerr, K. A.; van Roode, J. H. G. *Inorg. Chem.* **1977**, *16*, 191.

Contribution from the Departments of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003,
and University of Oklahoma, Norman, Oklahoma 73019

Synthesis and Characterization of Novel Penta- and Hexacoordinated Sulfur-Containing Spirocyclic Tin(IV) Complexes

ARJUN C. SAU, ROBERT R. HOLMES,* KIERAN C. MOLLOY, and J. J. ZUCKERMAN

Received August 25, 1981

Reactions of bis(toluene-3,4-dithiolato)tin(IV), $Sn(TDT)_2$ (**2**), with the bases dimethyl sulfoxide (Me_2SO), hexamethylphosphoramide (HMPA), and triphenylphosphine oxide (Ph_3PO) yield hexacoordinated spirocyclic neutral adducts. Hydroxide ion with **2** gives a hexacoordinated dianionic product. Various reactions of **2** with a variety of halide salts yield new spirocyclic pentacoordinated monoanionic compounds, $[XSn(TDT)_2]^-[R_4M]^+$ (M = N, P, As). Large cations tend to stabilize the complexes. Reversible color changes take place on heating the pentacoordinated derivatives. The substances are characterized by ^1H NMR and tin-119m Mössbauer spectroscopy. The isomer shift of the monohalo anions shows a decrease with halogen electronegativity consistent with electron withdrawal at the tin center. The quadrupole splitting (QS) values are in the range 1.06–1.44 mm s^{-1} for the pentacoordinated monoanions investigated. These low values, lower than many QS values for tetracoordinate tin(IV) compounds, are associated with rectangular-pyramidal geometries around tin, as found by X-ray diffraction studies on representative members.

Introduction

Comprehensive information is now available concerning the synthesis and stereochemical nonrigidity of pentacoordinated phosphorus compounds.[1-3] We have recently turned our attention to group 4A elements[4-10] to ascertain the extent to which structural principles for the pentacoordinated state are transferable from phosphorus chemistry. As with some five-

---

* To whom correspondence should be addressed at the University of Massachusetts.

(1) Holmes, R. R. *Acc. Chem. Res.* **1979**, *12*, 257.

(2) Holmes, R. R. "Pentacoordinated Phosphorus—Structure and Spectroscopy"; American Chemical Society: Washington, D.C., 1980; ACS Monogr. Ser. No. 175.

(3) Holmes, R. R. "Pentacoordinated Phosphorus—Reaction Mechanism"; American Chemical Society: Washington, D.C., 1980; ACS Monogr. Ser. No. 176.

© 1982 American Chemical Society