ligands by NH_3 to produce a 3+ ion does not occur to any appreciable extent.

The reaction of *trans*-[Cr(1,3-pn)$_2$FNH$_3$](ClO$_4$)$_2$ with concentrated hydrobromic acid resulted, as anticipated, in the removal of the fluoro ligand and its replacement by water. The conclusion that the complex is not anated by the bromide ion is supported by the fact that the electronic spectrum of the reaction product resembles that of $[Cr(NH_3)_5(OH_2)]^{3+}$[15] very closely rather than resembling that of $[Cr(NH_3)_5Br]^{2+}$.[16]

Heating of solid *trans*-[Cr(1,3-pn)$_2$FNH$_3$]BrClO$_4$ at 120 °C for 3 days resulted in the loss of 1 mol of ammonia/formula weight of the complex. However, the electronic spectral data for this product do not match those of *trans*-[Cr(1,3-pn)$_2$FBr]ClO$_4$, one of the anticipated products of the deammination reaction, nor does the aqueous solution spectrum change rapidly with time. Rapid changes in the electronic spectrum would be anticipated if the product were *cis*- or *trans*-[Cr(1,3-pn)$_2$FBr]ClO$_4$. Thus, the deammination reaction is more complex than it would first appear. Identification and characterization of the products of this reaction are currently under way.

Registry No. *trans*-[Cr(1,3-pn)$_2$FNH$_3$](ClO$_4$)$_2$, 77462-46-5; *trans*-[Cr(1,3-pn)$_2$FNH$_3$]BrClO$_4$, 77462-45-4; *trans*-[Cr(1,3-pn)$_2$FBr]ClO$_4$, 19200-03-4; [Cr(1,3-pn)$_2$NH$_3$(OH$_2$)]Br$_2$ClO$_4$, 77462-43-2.

Supplementary Material Available: Listings of the observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry,
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Oxy and Thio Phosphorus Acid Derivatives of Tin. 7. Crystal and Molecular Structure of α-(Phenylphosphonato)trimethyltin(IV) at 138 K. A Unique, One-Dimensional, Helical $\{[(CH_3)_3Sn^+][C_6H_5(OH)P(O)OSn(CH_3)_3OP(O)(OH)C_6H_5]^-\}_n$ Polymer[1]

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α-(Phenylphosphonato)trimethyltin(IV) ($C_9H_{15}O_3PSn$) forms colorless crystals, mp = 201 °C dec, in the tetragonal space group $I4_1/acd$ with $a = b = 15.310$ (6) Å, $c = 42.620$ (59) Å, $V = 9989.96$ Å^3, $Z = 32$, and $\rho_{calcd} = 1.706$ g cm^{-3}. The structure was solved by the heavy-atom method to an R value of 0.046 for the 2578 reflections collected at 138 ± 2 K on an Enraf-Nonius CAD/4 automatic diffractometer with the use of Mo $K\bar{\alpha}$ radiation. The molecular units associate to form an infinite, one-dimensional polymer in which planar trimethyltin(IV) groups are axially bridged by –O–P–O– linkages of the phenylphosphonate ligand to yield an almost perfect trigonal bipyramid at tin. The chains are linear at the tin atoms but bent through a bite angle of 115.3 (3)° at phosphorus. The chains propagate helically through the crystal, and each phenylphosphonate P═O and P—OH group is hydrogen bonded, holding adjacent helixes, turning in opposite directions, into two-dimensional sheets. The phenyl groups point outward from the center of the propagating helixes, separating the sheets from one another. Tin atoms occupy two nonequivalent environments, alternating metal atoms forming either two short or two long bonds to oxygen, an arrangement best described as a combination of trimethyltin(IV) cations and bis(phenylphosphonato)trimethyltin(IV) anions, which alternate in the helical array.

We have been investigating the structures of organotin derivatives of thio phosphorus acids[2-4] which combine biocidal activity[5] in both halves of the molecule. The biocidal activity of the organotin moiety is now well established, and such species have found extensive commerical application in the fields of fungicides, insecticides, bacteriocides, and the protection of surfaces (ship hulls, pier pilings, etc.) from attack by marine organisms.[5] Particularly attractive is the idea of combining the organotin species with ligands which are themselves biocidally active with the potential for enhanced activity in the compounds thus formed. The importance of phosphorus acids in in vivo systems has thus led us to investigate the structures of organotin derivatives of ligands deriving from thio or oxy phosphorus acids.[2-4]

The possible structures such systems can adopt are depicted in A–E. The simplest is a monomeric structure containing a monodentate ligand and a four-coordinated tin atom as we have found in the solid (*O,O'*-diethyl dithiophosphato)triphenyltin(IV) $[(C_6H_5)_3SnSP(S)(OC_2H_5)_2]$[3] shown in A, but this configuration is virtually unique among the metal derivatives of such ligands.[6] Much more common is the chelated, five-coordinated monomer structure which can exist with anisobidentate or symmetrical chelation as shown in B and C, respectively. We have found severely anisobidentate chelation in the dimeric tin(II) derivative bis(*O,O'*-diphenyl dithiophosphato)tin(II) $([Sn[SP(S)(OC_6H_5)_2]_2]_2)$[7] as well as

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[1] For Part 6 of this series see: Molloy, K. C.; Hossain, M. B.; van der Helm, D; Zuckerman, J. J., Mullins, F. P. *Inorg. Chem.* **1981**, *20*, 2172.

[2] To whom correspondences should be addressed at the University of Oklahoma.

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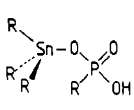
[8] The monomeric units in bis(*O,O'*-diphenyl dithiophosphato)tin(II) are held together in part by a weak bridging interaction between a sulfur atom of one chelate ligand and the adjacent tin atom to give the dimeric $[Sn[SP(S)(OC_6H_5)_2]_2]_2$ which contains three-coordinated bridging sulfur atoms in a planar Sn_2S_2 ring.[6]

0020-1669/81/1320-2402$01.25/0



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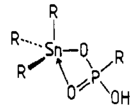

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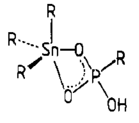

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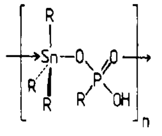
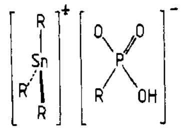


D



E

in the octahedral diorganotin(IV) derivative bis(dimethyldithiophosphinato)dimethyltin(IV) $[(CH_3)_2Sn[SP(S)(CH_3)_2]_2]$.[2] Bis(*O,O'*-diisopropyl dithiophosphato)diphenyltin(IV) $[(C_6H_5)_2Sn[SP(S)(OC_3H_7\text{-}i)_2]_2]$, on the other hand, forms a tightly packed, centrosymmetric structure containing *trans*-diorganotin(IV) units octahedrally coordinated by symmetrically chelating dithiophosphate ester ligands.[4] In these two latter diorganotin examples, we have noted that the tin atoms lie along a unit cell axis at a distance that could be easily spanned by a bridging dithiophosphate ester group to give a polymer. We have termed this situation a "virtual polymer"[2,4] whose synthesis must await the development of suitable methods to convert the assemblage of monomers actually found into the isomeric polymer yet unrealized.

When oxygen replaces sulfur in the phosphorus acids, bridging begins to predominate over chelation, and oligomeric and polymeric structures are found, as in D, which allow the more favorable axially most electronegative trigonal-bipyramidal structures to form. The more electronegative oxygen would tend to prefer axial sites where the p character of the orbital it draws from the tin atom is maximized. In addition, the chelate ring forms (B or C) become sterically less favorable because of the smaller M–O interatomic distrance and the increased difficulty of valence angle distortion.

The dimeric $[Cl_3SnPO_2Cl_2\cdot POCl_3]_2$ is such an example in which eight-membered centrosymmetric rings are formed by dichlorophosphate groups doubly bridging two $Cl_3Sn{\leftarrow}O{=}PCl_3$ units to form an octahedral geometry at tin.[9] In the divalent tin series, the tin(II) atoms in the hydrogen phosphate $(SnHPO_4)$[10–12] bis(dihydrogen phosphate) $[Sn(H_2PO_4)_2]$,[13] phosphite $(SnHPO_3)$,[12] $Sn_2(OH)PO_4$,[12,14] $Sn_3(PO_4)_2$,[12,15] $Sn_3(O)(OH)PO_3$,[12,16] the two halophosphites $Sn_3PO_4F_3$[12,17] and $SnFPO_3$,[12,18] and $ClSnH_2PO_2$[19] are all bridged by three-atom, –O–P–O– linkages. In addition, in the transition-metal series, the zinc(II) dialkylphosphinates are polymers containing alternating single and triple –O–P–O– bridges[20–27] as are the zinc(II) and cobalt(II) diarylthiophosphinates.[23] Molybdenum atoms are similarly bridged by ethylammonium phosphonate groups in substituted heteropolyanions[24] as are zinc(II) atoms by aminomethylphosphonate groups.[25] Beryllium atoms are alternately singly and triply bridged in the phosphinate polymers $[Be(R_2PO_2)_2]_2$.[26] Finally, tris[(dimethyltin(IV)] bis(orthophosphate) octahydrate $[[(CH_3)_2Sn]_3(PO_4)_2\cdot 8H_2O]$ consists of infinite ribbons in which octahedral, *trans*-dimethyltin(IV), *cis*-diaquo groups are cis linked by PO_4 tetrahedra to give eight-membered rings in chair conformations.[27]

At least in principle, an ionic form as shown in E is also possible. This latter possibility deserves mention since the onset of ionic character would in this associated system be detectable by the presence of long tin–ligand distances. Our 1978 review of the structural tin literature[28] or its update fail to reveal a demonstrated example of such a situation which would have important implications for certain solid-state physical properties such as electrical conductivity.

The title compound was prepared as in eq 1 by the action

$$(CH_3)_3SnCl + C_6H_5P(O)(OH)_2 \rightarrow \alpha\text{-}(CH_3)_3SnOP(O)(OH)C_6H_5 + HCl \quad (1)$$

of trimethyltin chloride on phenylphosphonic acid in water.[29] The same modification is obtained by refluxing trimethyltin acetate with the acid in water (eq 2). Rapid precipitation

$$(CH_3)_3SnO_2CCH_3 + C_6H_5P(O)(OH)_2 \rightarrow \alpha\text{-}(CH_3)_3SnOP(O)(OH)C_6H_5 + CH_3CO_2H \quad (2)$$

of the α form, however, yields a β modification whose X-ray powder diffraction patterns show no trace of the α form. The β modification is also exclusively obtained by reaction of the monosodium salt of the acid with trimethyltin chloride in a minimum of water solvent.[29]

The colorless, crystalline α product which can be crystallized from donor solvents such as methanol, acetone, THF, or pyridine without inclusion of solvent in the crystals, decomposes at 201 °C to release methane and form $(CH_3)_2SnPO_3C_6H_5$ and yields a proton NMR coupling constant, $|^2J(^{119}Sn\text{–}C\text{–}^1H)| = 69$ Hz, in solution. The doublet tin-119m Mössbauer spectrum with quadrupole splitting (QS) = 3.92 and isomer

Table I. Crystal Data

formula	$C_9H_{15}O_3PSn$	V, Å^3	9989.96
fw	320.90	Z	32
crystal class	tetragonal	ρ_{calcd}, g cm^{-3}	1.706
space group[a]	$I4_1/acd$	$F(000)$	5056
a, b,[b] Å	15.310 (6)	μ(Mo Kα), cm^{-1}	21.7
c,[b] Å	42.620 (59)	data cryst dimens, mm	0.17 × 0.15 × 0.17

[a] From systematic absences: hkl, $h + k + l = 2n + 1$; $hk0$, $h = 2n + 1$; $0kl$, $l = 2n + 1$; hhl, $2h + l \neq 4n$. [b] Based upon ±2θ values of 64 reflections and use of Mo Kα_1 radiation (λ = 0.709 26 Å).

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Table II. Data Collection Parameters for α-$(CH_3)_3SnOP(O)(OH)C_6H_5$

diffractometer	Enraf-Nonius CAD/4
radiation (λ, Å)	Mo $K\bar{\alpha}$ (0.710 69)
temp, K	138 ± 2
scan technique	θ-2θ
limit, deg	$0 \leqslant 2\theta \leqslant 53$
max scan time, s	40
scan angle, deg	$(0.7 + 0.20 \tan \theta)$
aperature width, deg	$(2.5 + 0.86 \tan \theta)$
aperature height, mm	6
aperature dist, mm	173
monitor reflctn	$\bar{4}08$
intens monitor frequency, s	3600
max fluctuation in monitor, %	<1.2
orientation monitors	200 reflctns
no. of unique data	2578
no. of obsd data[a]	2296
corrections	Lorentz, polarization, absorption, anomalous dispersion

[a] $I > 2\sigma(I)$.

Table III. Final Position (×10^4) Parameters for α-$(CH_3)_3SnOP(O)(OH)C_6H_5$[a]

atom	x	y	z
Sn(1)	5000	0	637.2 (2)
Sn(2)	2500	2156.9 (5)	1250
P(1)	4415 (1)	2143 (2)	792.9 (4)
O(1)	4310 (4)	1290 (4)	628 (1)
O(2)	3961 (3)	2211 (4)	1108 (1)
O(3)	5416 (4)	2334 (5)	852 (1)
C(1)	4033 (6)	2993 (5)	538 (2)
C(2)	3546 (6)	2769 (6)	273 (2)
C(3)	3236 (7)	3434 (6)	73 (2)
C(4)	3426 (7)	4298 (6)	135 (2)
C(5)	3925 (7)	4529 (6)	394 (2)
C(6)	4214 (6)	3864 (6)	604 (2)
C(7)	5000	0	1123 (3)
C(8)	3883 (7)	−527 (7)	410 (3)
C(9)	2500	3560 (9)	1250
C(10)	2139 (6)	1402 (7)	853 (2)

[a] Estimated standard deviations in parentheses.

shift (IS) = 1.35 mm s^{-1} [29] is consistent with five-coordinated tin in a conventional trigonal-bipyramidal environment, but neither the Mössbauer information derived for tin nor the infrared of the PO_3 system allows the four structural possibilities, B–E, discussed above, to be distinguished. The mass spectrum, however, contains ditin fragments at *m/e* 471 (17.9%), which can be assigned to the $[(CH_3)_5Sn_2PO_3C_6H_5]^+$ ion, and at 441 (5.1%), which would correspond to the further loss of two methyl groups from this species, suggesting a covalent oligomeric or polymeric situation (as in D) or an ionic array (as in E).

To test which of these possibilities exists, we have carried out a single-crystal X-ray diffraction study on the title compound, the results of which we now report.

Experimental Section

Crystal Data. Colorless crystals of the title compound were obtained over a period of 2 weeks by cooling a methanol solution and were stable to both atmospheric moisture[29] and X-rays. Crystal data are listed in Table I.

Details of our diffractometer and methods of data collection and data reduction have been outlined previously.[3] Specific parameters pertaining to the collection of the data set are summarized in Table II. The structure factors for each reflection were assigned individual weights.[3]

Structure Determination and Refinement

The positions of the tin atoms were obtained by direct methods using MULTAN.[30] It was found that the 32 tin atoms in the unit cell were comprised of 16 on each of the two types of special positions: $^1/_4$, *x*, $^1/_8$ (Wyckoff notation *e*, space group $I4_1/acd$) and 0, 0, *z* (*d*). This solution was confirmed by the successful use of these two positions to interpret the 28 largest peaks in a three-dimensional Patterson map.[31] Following two cycles of full-matrix, isotropic, least-squares refinement, a difference Fourier yielded the positions of the remaining nonhydrogen atoms. All atoms were refined anisotropically to a final *R* value of 0.046 (weighted *R* = 0.048). Final shifts in both positional and thermal parameters were less than one-fifth of their corresponding estimated standard deviation.

A final difference Fourier map contained areas of residual electron density of intensity, ca. 1 e Å^{-3}. Although these peaks correspond to probable hydrogen atom locations, no systematic attempt was made to assign the latter.

Final atomic parameters (both positional and thermal) and intramolecular distances and angles are listed in Tables III–VI. The asymmetric unit, with atomic labeling, is diagrammed in Figure 1.

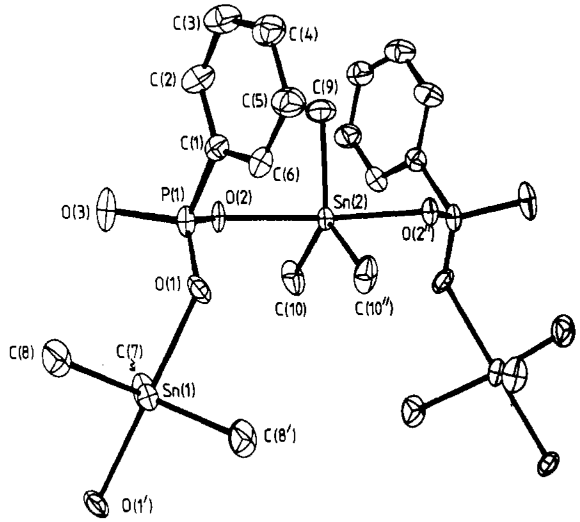

Figure 1. Asymmetric unit of α-(phenylphosphonato)trimethyltin(IV), showing the atom numbering scheme. Primed and doubly primed atoms are related to unprimed atoms by the twofold axes along Sn(1)–C(7) and Sn(2)–C(9), respectively.

Description and Discussion of the Structure

In gross feature, α-(phenylphosphonato)trimethyltin(IV) crystallizes in an infinite, one-dimensional, helical polymer as shown in Figure 1, in which planar trimethyltin(IV) units are axially bridged by three-atom, –O–P–O– linkages from the phenylphosphonate ligand.

The geometry at each tin atom is almost perfectly trigonal bipyramidal [O(1)–Sn(1)–O(1′) = 178.0 (2)°; O(2)–Sn(2)–O(2′) = 175.9 (2)°]. Within each of the two distinct trimethyltin groups, one tin–carbon bond lies on a twofold axis [Sn(1)–C(7) and Sn(2)–C(9)], establishing perfect planarity of the separate $[C_3Sn]$ moieties. This finding is in agreement with the infrared data from which it is possible to assign the tin–carbon $\nu_{asym}(SnC_3)$ stretching frequency at 532 cm^{-1}, but no lower frequency absorption band is available to assign to the $\nu_{sym}(SnC_3)$ mode. In the Raman spectrum, on the other hand, an intense absorption at 515 cm^{-1} can be assigned to this latter mode. Thus the trimethyltin(IV) group obeys the vibrational spectroscopic selection rules for the planarity confirmed in the structure.

Although the virtual linearity of the O–Sn–O bonds requires linearity of the polymer in the vicinity of the tin atoms, the chains are bent through the tetrahedrally coordinated phos-

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Table IV. Final Anisotropic (× 10^4) Thermal Parameters for α-$(CH_3)_3SnOP(O)(OH)C_6H_5$[a]

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn(1)	192 (4)	289 (4)	179 (4)	0	0	45 (3)
Sn(2)	142 (4)	260 (4)	173 (4)	0	−11 (3)	0
P(1)	94 (8)	377 (11)	176 (9)	−18 (8)	−4 (7)	−7 (8)
O(1)	218 (29)	281 (31)	411 (33)	−21 (26)	−45 (25)	106 (24)
O(2)	93 (24)	404 (33)	184 (25)	22 (23)	5 (20)	−9 (22)
O(3)	155 (29)	736 (50)	248 (28)	−44 (30)	−28 (23)	−85 (29)
C(1)	321 (43)	239 (41)	189 (35)	−7 (30)	72 (32)	−32 (33)
C(2)	260 (41)	302 (43)	236 (37)	5 (32)	−6 (32)	−57 (34)
C(3)	414 (53)	290 (46)	339 (47)	88 (36)	−35 (38)	−32 (40)
C(4)	453 (55)	327 (48)	311 (43)	43 (38)	88 (40)	3 (41)
C(5)	430 (55)	346 (50)	319 (43)	−59 (38)	127 (40)	3 (41)
C(6)	439 (51)	358 (47)	130 (33)	−49 (32)	36 (33)	−138 (40)
C(7)	54 (48)	737 (99)	343 (64)	0	0	59 (56)
C(8)	392 (57)	491 (62)	535 (59)	−185 (50)	−200 (48)	65 (47)
C(9)	434 (81)	294 (72)	683 (98)	0	102 (76)	0
C(10)	291 (46)	572 (63)	288 (42)	−206 (43)	−19 (36)	−78 (44)

[a] Estimated standard deviations in parentheses.

Table V. Final Interatomic Distances (Å) in α-$(CH_3)_3SnOP(O)(OH)C_6H_5$[a]

Sn(1)-O(1)	2.240 (6)	Sn(2)-O(2)	2.319 (5)
Sn(1)-C(7)	2.070 (13)	Sn(2)-C(9)	2.148 (14)
Sn(1)-C(8)	2.124 (11)	Sn(2)-C(10)	2.122 (9)
P(1)-O(1)	1.492 (6)	C(1)-C(2)	1.396 (12)
P(1)-O(2)	1.516 (5)	C(2)-C(3)	1.410 (13)
P(1)-O(3)	1.580 (6)	C(3)-C(4)	1.380 (13)
P(1)-C(1)	1.793 (9)	C(4)-C(5)	1.388 (13)
		C(5)-C(6)	1.426 (13)
		C(6)-C(1)	1.391 (12)

[a] Estimated standard deviations in parentheses.

Table VI. Final Interatomic Angles (Deg) in α-$(CH_3)_3SnOP(O)(OH)C_6H_5$[a]

O(1)-Sn(1)-O(1′)	178.0 (2)	O(1)-P(1)-O(2)	115.3 (3)
O(1)-Sn(1)-C(7)	91.0 (2)	O(1)-P(1)-O(3)	110.0 (3)
O(1)-Sn(1)-C(8)	87.0 (3)	O(1)-P(1)-C(1)	108.3 (4)
O(1)-Sn(1)-C(8′)	92.1 (3)	O(2)-P(1)-O(3)	106.9 (3)
C(7)-Sn(1)-C(8)	117.1 (3)	O(2)-P(1)-C(1)	109.7 (4)
C(8)-Sn(1)-C(8′)	125.8 (4)	O(3)-P(1)-C(1)	106.2 (4)
O(2)-Sn(2)-O(2″)	175.9 (2)	P(1)-C(1)-C(2)	119.1 (7)
O(2)-Sn(2)-C(9)	88.0 (2)	P(1)-C(1)-C(6)	120.6 (7)
O(2)-Sn(2)-C(10)	93.6 (3)	C(2)-C(1)-C(6)	120.4 (8)
O(2)-Sn(2)-C(10″)	88.6 (3)	C(1)-C(2)-C(3)	119.4 (8)
C(9)-Sn(2)-C(10)	123.0 (3)	C(2)-C(3)-C(4)	120.4 (9)
C(10)-Sn(2)-C(10″)	114.0 (4)	C(3)-C(4)-C(5)	120.8 (9)
Sn(1)-O(1)-P(1)	135.5 (3)	C(4)-C(5)-C(6)	119.2 (9)
Sn(2)-O(2)-P(1)	132.2 (3)	C(5)-C(6)-C(1)	119.7 (8)

[a] Estimated standard deviations in parentheses.

phorus atoms of the phosphonate ligand at an O(1)-P(1)-O(2) angle of 115.3 (3)°. The chains propogate through the crystal in a 4_1 helical fashion, with adjacent helixes turning in opposite directions. Adjacent helixes are, however, cross-linked by a network of hydrogen bonds to form two-dimensional sheets; an ORTEP representation of part of one sheet is shown in Figure 2. These hydrogen-bonding interactions, which we assume are binding the P—OH and O═P groups in each ligand, bring together the first and fourth phosphonate ligands of one helix (shown schematically in a, Figure 3), with the second and third phosphonate ligands of the second helix of opposite hand (b, Figure 3). The second and third ligand units of the first helix also form hydrogen bonds to the first and fourth phosphonate ligand groups of another helix adjacent to it (c, Figure 3) which is of the opposite hand. The stack of helixes, held at regular intervals by hydrogen bonds, creates infinite, two-dimensional sheets. As can be seen in Figure 4, the phenyl groups point outward from the center of the propagating helixes, separating the independent sheets of helixes from one another.

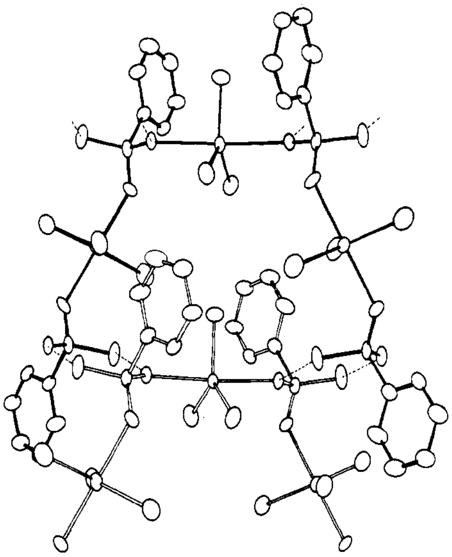


Figure 2. ORTEP drawing of two adjacent helixes, of opposite hand, linked by hydrogen bonds (- - -).

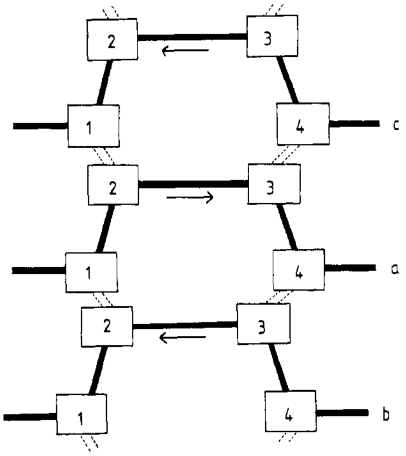


Figure 3. Schematic representation of the hydrogen bonding between adjacent helixes. Solid lines represent helixes propagating in a clockwise manner in the direction of the associated arrow; numbered boxes indicate PO_3 units within any given helix. Hydrogen-bonded PO_3 groups are linked by dotted lines (- - -).

Four pairs of helical chains, each pair consisting of two helixes of opposite hand, are found in the unit cell as seen in Figure 5. There are thus portions of four sheets propagating in the *ab* plane contained in each unit cell. The fourfold screw

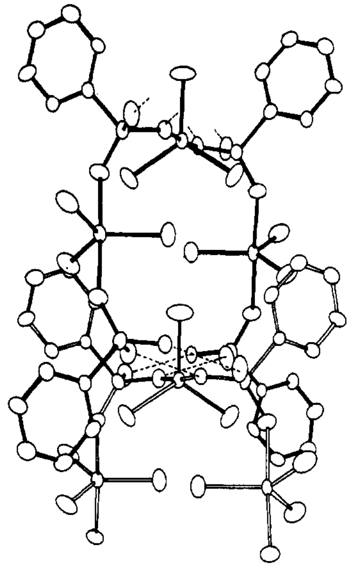


Figure 4. A pair of adjacent helixes, viewed along the axis of propagation. The upper (solid lines) and lower (double lines) helixes propagate out of the page in a counterclockwise and clockwise manner, respectively. Hydrogen bonds between helixes are dotted.

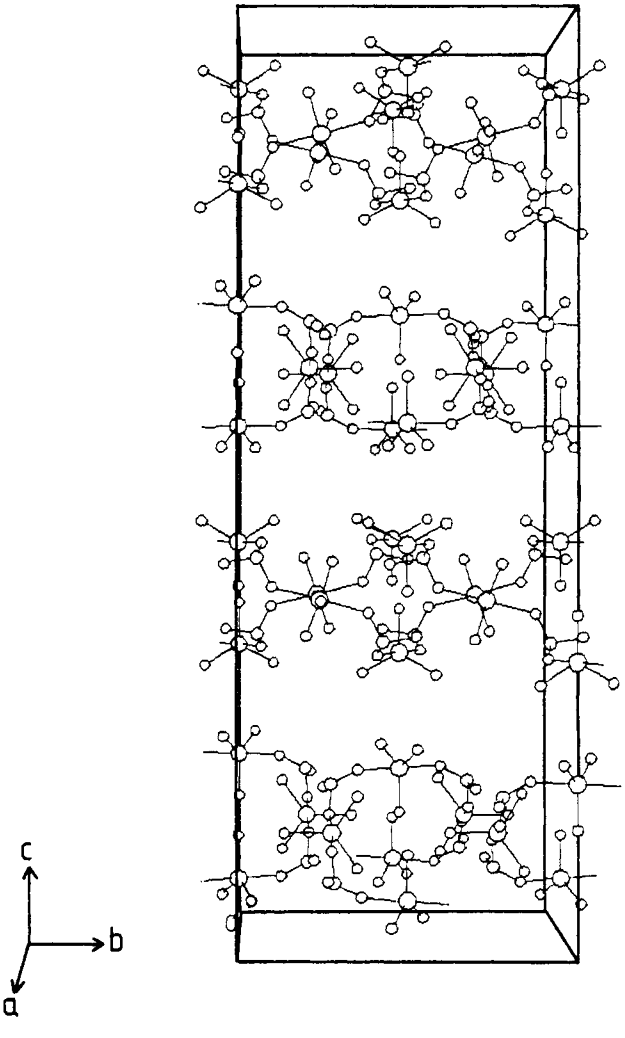
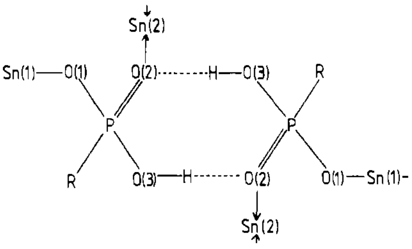


Figure 5. The unit cell, viewed along *a*.

axis along *c* dictates that the direction of propagation of helixes in adjacent sheets be at right angles (Figure 5), thereby producing a crosswise weave of one-dimensional helical polymers. We have previously noted a similar woven lattice structure adopted by trimethyltin(IV) glycinate (space group $P4_1$) in which the directions of propagation of the adjacent chains of the one-dimensional, amino-bridged polymers are also perpendicular.[32]

A more detailed description of the bonding within each chain requires the identification of the three different P–O bonds of each phosphonate group. We assume that the P=O and P—OH units bound together between adjacent chains by hydrogen bonding can be identified, despite our not having located the hydrogen atoms. Fortunately, structural data for the parent, phenylphosphonic acid $[C_6H_5P(O)(OH)_2]$ which also forms a hydrogen-bonded solid, are available. The P=O distance is, as expected, shortest at 1.496 Å, while the P—OH bond is at an average distance of 1.545 Å.[33] These distances change to 1.489 and 1.563 Å, respectively, in the singly ionized sodium acetyl phosphonate acetic acid solvate, $CH_3C(O)P(O)(OH)ONa$,[34] and to 1.500 and 1.569 Å, respectively, in the zwitterionic (2-aminoethyl)phosphonic acid (β-ciliatine).[35]

In the title compound, two of the oxygen atoms [O(2) and O(3)] lie within a hydrogen-bonding distance of the symmetry related oxygen atoms [O(3) and O(2), respectively] of an adjacent polymer chain. The hydrogen bonds thus formed are relatively short[36] (2.589 Å), essentially the same as the mean distance in the parent acid.[33] Since, according to the scheme in structure F, one must be the P=O and the other the P—OH system, the identification can be based upon the respective phosphorus–oxygen interatomic distances which specify P(1)=O(2) at 1.516 (5) Å as the double-bonded group and P(1)—O(3) at 1.580 (6) Å as the P—OH group. The remaining oxygen bonded to phosphorus [O(1)–P(1) = 1.492 (6) Å] is thus deprotonated and ester bound to tin [O(1)–Sn(1) = 2.240(6) Å]. The marked shortening of the P(1)–O(1) ester bond relative to the parent acid P–OH system (1.545 Å) is also seen in the $[PO_2Cl_2]^-$ anion which doubly bridges octahedral tin(IV) units in the $[Cl_3SnOPCl_3{\cdot}PO_2Cl_2]_2$ dimer[9] but not in $[trans\text{-}(CH_3)_2Sn]_3(PO_4)_2{\cdot}8H_2O$, where the double –O–P–O– bridges exhibit P–O ester distances in the range 1.52–1.56 Å.[27] The shortening of this P(1)–O(1) bond in the title compound possibly arises as a consequence of the mo-



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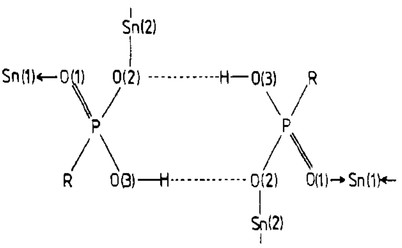

G

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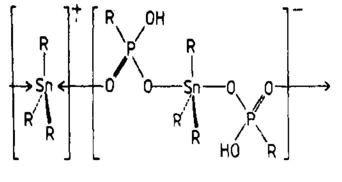
lecular packing which is dictated by the formation of interchain hydrogen bonding. The relative lengthening of the P(1)=O(2) bond, with respect to the parent acid, presumably arises because the O(2) atom engages in bifurcated coordination, forming both a dative bond to Sn(2) and a hydrogen bond to O(3). This has the effect of lengthening this bond so that its interatomic distance [1.516 (5) Å] becomes roughly comparable to the P(1)–O(1) distance at 1.492 (6) Å, which is different by only five standard deviations.

Confirmation for these assignments can come from a comparison of the respective distances these P–O units make with their tin bonding partners, where the doubly bonded phosphorus–oxygen linkage, assigned as P(1)=O(2), should be adjacent to a long, dative bond to tin [O(2)→Sn(2) = 2.319 (5) Å]. Likewise, the P(1)–O(1) bond is found contiguous to a relatively shorter covalent bond to tin [O(1)–Sn(1) = 2.240 (6) Å].

Reversing the assignments of the P(1)–O(1) and P(1)–O(2) systems to the P=O and P—O ester linkages, respectively, satisfies the criterion that the P=O bond be the shortest connection to phosphorus made by the oxygen atom, but that requires the hydrogen bonds to be established as in the less likely scheme G. In addition, the expectations that the P=O bond should make a longer, dative O→Sn bond to tin and that the O—Sn ester bond should be shorter are disappointed. For these reasons we prefer the first assignment (F) described above.

Comparison of the tin–oxygen bond distance contiguous to the P=O group [Sn(2)—O(2) = 2.319 (5) Å] can be drawn with the dative O→Sn interatomic distance of 2.29 Å in nitratotriphenyl(triphenylphosphine oxide)tin(IV) which also involves a trigonal-bipyramidal triorganotin(IV) center axially coordinated by oxygen.[37] A somewhat shorter connection is found in the octahedral anion, $[Cl_5Sn{\leftarrow}O{=}PCl_3]^-$, where the dative O→Sn interatomic distance is 2.27 Å,[38] and in the cis-octahedral complex $SnCl_4{\cdot}2O{=}PCl_3$ where the mean Sn–O distance is 2.28 Å.[39] Comparison of the ester tin–oxygen bond distance [Sn–O(1) = 2.240 (6) Å] with those in the $[Cl_3SnOPCl_3{\cdot}PO_2Cl_2]_2$ dimer where the bridging PO_2Cl_2 groups exhibit distances of 2.119 and 2.120 Å to the octahedral tin atoms[9] and with those in $[(CH_3)_2Sn]_3(PO_4){\cdot}8H_2O$ in which there are three tin environments[27] can be made. In the latter structure two aquated tin atoms whose geometries lie between trigonal bipyramidal and octahedral establish ester bridge bonds of 2.02 and 2.04 Å, while a *trans*-$(CH_3)_2Sn$ unit of octahedral structure makes ester bridge bonds of 2.17 and 2.18 Å.[27] The Sn–O ester bond in the title compound is thus longer than the corresponding bonds discussed above and is considerably longer than the single bond value of 2.10 Å.[27,36]

Because the two tin–oxygen distances at each tin center are symmetry related [by the twofold axes along Sn(1)–C(7) and Sn(2)–C(9)] and must, therefore, be equal, the conventional bridging arrangement, as in D, must be ruled out. Instead, we have in the title compound a situation in which there are two nonequivalent tin sites, with alternate tin atoms making two short [Sn(1)–O(1) = Sn(1)–O(1′) = 2.240 (6) Å] or two long [Sn(2)–O(2) = Sn(2)–O(2′) = 2.319 (5) Å] bonds to oxygen. An O(1)–Sn(1)–O(1′) angle of 178.0 (2)° is associated with the short Sn–O bonds, and an O(2)–Sn(2)–O(2′) angle of 175.9 (2)° is associated with the long Sn–O bonds. This is the only example of which we are aware of an associated organotin polymer in which the chains consist of alternating tin environments.[28,40] This arrangement is probably best described in terms of structure H as a combination of trimethyltin(IV) cations and bis(phenylphosphonato)trimethyltin(IV) anions $[[C_6H_5P(O)(OH)OSn(CH_3)_3OP(O)(OH)C_6H_5]^-]$ alternating in a helical array. The tin atoms are not sufficiently different to be distinguished by ^{119m}Sn Mössbauer spectroscopy, but this is not surprising since even the tin atoms in the five- and six-coordinated double salt $[(CH_3)_3Sn{\cdot}terpy]^+[(CH_3)_2SnCl_3]^-$ are barely distinguishable by Mössbauer spectroscopy.[43]



H

The phosphorus atoms, of which there is only one kind, are found at the center of a distorted tetrahedron with three oxygen atoms and a phenyl group as nearest neighbors. Contrary to the expectations of isovalent hybridization, the three O–P–C angles involving carbon are as an average (108.1°) smaller than the average of the three angles –O–P–O (110.7°). However, this value of the mean is mainly a result of the opening of the O(1)–P–O(2) angle, which involves the oxygen atoms connected to tin, to 115.3 (3)°. The comparable bite angle of the double –O–P–O– bridges between the octahedral tin(IV) atoms of bis[(phosphoryl trichloride)trichlorotin(IV)] $\{[(Cl_3SnOPCl_3)^+(PO_2Cl_2)^-]_2\}$ is 118.0°,[9] and a mean value of 111.4° is found in tris[dimethyltin(IV)] bis(orthophosphate) octahydrate, $[(CH_3)_2Sn]_3(PO_4)_2{\cdot}8H_2O$.[27] The comparable mean value for the singly bridged portion of the bis(diorganophosphinato)zinc(II) polymer is 116.8°.[22]

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Registry No. α-$(CH_3)_3SnOP(O)(OH)C_6H_5$, 77494-69-0.

Supplementary Material Available: A listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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(40) A similar situation has been noted in two determinations[41,42] of the structure of $(CH_3)_3SnO_2SCH_3$ which consists of two independent tin sites bridged by sulfinate ligands in an alternating, one-dimensional array. As in the title compound, each tin atom lies on a twofold axis and is bonded to two identical oxygen atoms that differ in the two sites. However, this difference between pairs of tin–oxygen bond distances was found to be only three standard deviations in one study[41] and zero in the other.[42] It is worth noting that these polymer chains also adopt a helical configuration, but the inability to form hydrogen bonds precludes the association of the helicies into sheets as in our structure.

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