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A09071 SECURITY CLASSIFICATION OF THIS PAGE (When De READ INSTRUCTIONS **REPORT DOCUMENTATION** BEFORE COMPL FCR 1. REPORT NUMBER RECIPIENT'S CA 4. TIXLE (and Sublitie) YPE OF REPOR Oxy- and Thio Phosphorus Acid Derivatives of Tine VII. The Crystal and Molecular Structure of Alpha PERFORMING ORG. REPORT NUMBER A-Phenylphosphonatotrimethyltin(IV) at 138 K Unique, One-dimensional, Helical CONTRACT OR GRANT NUMBER(+) K.C. Mollov M.B. Hossain TD. van der Helm J. J. AD A 09157 Zuckerman 👥 D. Cunningham NØØØ14-77-C-0432 PERFORMING ORGANIZATION NAME AND ADDRESS PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS University of Oklahoma 1 Nov 20 Department of Chemistry NR 053-636 Norman, Oklahoma 73019 11. CONTROLLING OFFICE NAME AND ADDRESS 12. REPORT DATE 1 November, 1980. Office of Naval Research 13. NUMBER OF PAGES Department of the Navy Arlington, Virginia 22217 MONITORING AGENCY NAME & ADDRESS(II different from Controlling Office) 15. SECURITY CLASS. (of this report) Unclassified chrisal ports 154. DECLASSIFICATION/DOWNGRADING SCHEDULE 16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release, Distribution Unlimited 17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, Il different from Rep. Nov 0 5 1980 Prepared for Publication in Inorganic Chemistry 18. SUPPLEMENTARY NOTES E 19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Organotin, Trimethyltin(IV), Phosphoric Acids, Phenyl Phosphoric Acid, X-ray Diffraction, Crystal Structure, Molecular Structure, Esters, Ligands, a-Phenylphosphonatotrimethyltin(IV), Trigonal bipyramidal trimethyltin, Planar trimethyltin, One-dimensional polymer, Association, Polymer, Phenylphosphonate A.pla -Ligand, Bridging phenylphosphonate, Helix, Hydrogen Londing, Layer structure 20. ABSTRACT (Continue on reverse side if necessery and identity by block number) COL -Phenylphosphonatotrimethyltin(IV), CgH1503PSn, forms colorless crystals, mp=201<sup>3</sup> decomp., in the tetragonal space group I41/acd with a=b=15.310(6), c=42.620(50) Å, V=9989.96 Å<sup>3</sup>, Z=32 and  $\rho_{calc}=1.71$  g cm<sup>-3</sup>. 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 using  $(MoK_{\overline{\alpha}})$  radiation. The molecular units associate to form an infinite, one-dimensional polymer in which planar trimethyltin(IV) groups are axiallybridged by -O-P-O- linkages of the phenylphosphonate ligand to yield an. DD 1 JAN 73 1473 EDITION OF I NOV 65 IS OBSOLETE Unclassified 5/N 0102-LF-014-6601 SECURITY CLASSIFICATION OF THIS PAGE (When Date Entre mskan 110 3.180 8011 03 027 and the second second

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4.

 $\{[(CH_3)_3Sn]^+[C_6H_5]_{OH}^{H} - O-Sn(CH_3)_3 - O-H_{OH}^{H} - C_6H_5]^-\}_n$  Polymer. DEG.

20. almost perfect trigonal bipyramid at tin. The chains are linear at the tin atoms, but bent through a bite angle of  $115.4(3)^{\textcircled{0}}$  at phosphorus. The chains propogate helically through the crystal, and each phenylphosphonate P=O and P-OH group is hydrogen bonded, holding adjacent helicies, turning in opposite directions, into two-dimensional sheets. The phenyl groups point outward from the center of the propogating helicies, separating the sheets from one another. Tin atoms occupy two non-equivalent environments, alternating metal atoms forming either two short or two long bonds to oxygen.



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OFFICE OF NAVAL RESEARCH Contract N00014-77-C-0432 Task No. NR 053-636 TECHNICAL REPORT NO. 24

Oxy- and Thio Phosphorus Acid Derivatives of Tin. VII. The Crystal and Molecular Structure of a-Phenylphosphonatotrimethyltin(IV) at 138 K.

A Unique, One-dimensional, Helical  $\left[ [CH_3]_3 Sn \right]^+ \left[ C_6 H_5 \frac{p}{DH} - O - Sn (CH_3)_3 - O - \frac{p}{DH} - C_6 H_5 \right]^- \right]_n$ Polymer<sup>1</sup>

by

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Inorganic Chemistry

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This document has been approved for public release and sale; its distribution is unlimited We have been investigating the structures of organo in derivatives of thio phosphorus acids<sup>1-3</sup> which combine biocidal activity<sup>4</sup> in both halves of the molecule. The biocidal activity of the organotin moiety is now well-established, and such species have found extensive commercial application in the fields of fungicides, insecticides, bacteriocides and the protection of surfaces (ship hulls, pier pilings, etc.) from attack by marine organisms.<sup>4</sup> Particuarly 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 <u>in vivo</u> systems has thus led us to investigate the structures of organotin derivatives of ligands deriving from thio- or oxy-phosphorus acids.<sup>1-3</sup>

The possible structures this system can adopt are depicted in <u>A</u> to <u>E</u>. The simplest is a monomeric structure containing a monodentate ligand and a four-coordinated tin atom as we have found in the solid  $(\underline{0}, \underline{0}'$ -diethyl dithiophosphato)triphenyltin(IV),  $(C_{6}H_5)_3 \text{SnSP}(OC_2H_5)_2$ ,<sup>2</sup> shown in <u>A</u>, but this configuration is virtually unique among the metal derivatives of such ligands.<sup>5</sup> Much more common is the chelated, five-coordinated monomer structure which can exist with anisobidentate or symmetrical chelation as shown in <u>B</u> and <u>C</u>, respectively. We have found severely anisobidentate chelation in the dimeric tin(II) derivative bis( $\underline{0}, \underline{0}'$ -diphenyl dithiophosphato)tin(II),  $\{\text{Sn}[\text{SP}(OC_6H_5)_2]_2\}_2$ ,<sup>6</sup> as well as in the octahedral diorganotin(IV) derivative, bis(dimethyl dithiophosphinato) dimethyltin(IV),  $(CH_3)_2 \text{Sn}[\text{SP}(CH_3)_2]_2$ .<sup>1</sup> Bis( $\underline{0}, \underline{0}'$ -diisopropyl dithiophosphato)diphenyltin(IV),  $(C_6H_5)_2 \text{Sn}[\text{SP}(OC_3H_7-i)_2]_2$ , on the other hand, forms a tightly packed, centrosymmetric structure containing <u>trans</u>- diorganotin(IV) units octahedrally coordinated by symmetrically chelating dithiophosphate ester ligands.<sup>3</sup> 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"<sup>1,3</sup> whose synthesis must await the development of suitable methods to convert the assemblage of monomers actually found into the isomeric polymer yet unrealized.<sup>7</sup>

When oxygen replaces sulfur in the phosphorus acids, bridging begins to predominate over chelation, and oligomeric and polymeric structures are found, as in <u>D</u>, which allow the more favorable axially-most-electronegative trigonal bipyramidal structures to form. The more electronegative oxygen would tend to prefer <u>axial</u>sites where the <u>p</u>-character of the orbital it draws from the tin atom is maximized. In addition, the chelate ring forms (<u>B</u> or <u>C</u>) become sterically less favorable because of the smaller M-O interatomic distance 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  $Cl_3Sn+O=PCl_3$  units to form an octahedral geometry at tin.<sup>8</sup> In the divalent tin series the tin(II) atoms in the hydrogen phosphate  $(SnHPO_4)$ , <sup>9-11</sup> bis(dihydrogen phosphate)  $[Sn(H_2PO_4)_2]$ , <sup>12</sup> phosphite  $(SnHPO_3)$ , <sup>11</sup>  $Sn_2(OH)PO_4$ , <sup>11,13</sup>  $Sn_3(PO_4)_2$ , <sup>11,14</sup>  $Sn_3(O)(OH)PO_3$ , <sup>11,15</sup> the two halophosphites  $Sn_3PO_4F_3$ , <sup>11,16</sup> and  $SnFPO_3$ , <sup>11,17</sup> and  $ClSnH_2PO_2$  are all bridged by three-atom, -O-P-O- linkages. In addition, in the transition metal series, the zinc(II) dialkyl

phosphinates are polymers containing alternating single and triple -O-P-O- bridges<sup>19-21</sup> as are the zinc(II) and cobalt(II) diaryl monothiophosphinates.<sup>22</sup> Molybdenum atoms are similarly bridged by ethyl ammonium phosphonate groups in substituted heteropolyanions<sup>23</sup> as are zinc(II) atoms by aminomethylphosphonate groups.<sup>24</sup> Berylium atoms are alternately singly and triply bridged in the phosphinate polymers,  $[Be(R_2PO_2)_2]_2$ .<sup>25</sup> 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<sub>4</sub> tetrahedra to give eightmembered rings in chair conformations.<sup>26</sup>

At least in principle, an ionic form as shown in  $\underline{E}$  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<sup>27</sup> or its update<sup>28</sup> 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 of 'trimethyltin chloride on phenylphosphonic acid in water:<sup>29</sup>

$$(CH_3)_3 SnC1 + C_6^{H_5^{P}(OH)}_2 + \alpha - (CH_3)_3 SnOP - C_6^{H_5} + HC1$$
(1)

The same modification is obtained by refluxing trimethyltin acetate . with the acid in water:

[J( Sn-C- H)] = 69 HZ in solution and exhibits a doublet

$$(CH_3)_3 SnO_2 CCH_3 + C_6 H_5 P(OH)_2 \rightarrow \alpha - (CH_3)_3 SnOPC_6 H_5 OH + CH_3 CO_2 H$$

(2)

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Rapid precipitation of the  $\alpha$ -form, however, yields a  $\beta$ -modification whose X-ray powder diffraction patterns show no trace of the  $\alpha$ -form. The  $\beta$ -modification is also exclusively obtained by reaction of the monosodium salt of the acid with trimethyltin chloride in a minimum of water solvent.<sup>29</sup>

The colorless, crystalline  $\alpha$ -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° to release methane and form (CH<sub>3</sub>)<sub>2</sub>SnPO<sub>3</sub>C<sub>6</sub>H<sub>5</sub>, and yields a proton nmr  $|^{2}H(^{119}Sn-C-^{1}H)| = 69$  Hz in solution. The doublet tin-119m Mössbauer spectrum with Quadrupole Splitting (Q.S.) = 3.92 and Isomer Shift (I.S.) = 1.35 mm s<sup>-1</sup>.<sup>29</sup> These data are 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<sub>3</sub> system allow the four structural possibilities, <u>B-E</u>, 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 the former 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

<u>Crystal Data</u>. Colorless crystals of the title compound were obtained over a period of two weeks by cooling a methanol solution, and were stable to both atmospheric moisture<sup>29</sup> and X-rays. Crystal data are listed in Table I.

Details of our diffractometer, method of data collection and data reduction have been outlined previously.<sup>2</sup> 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.<sup>2</sup>

## Structure Determination and Refinement

The positions of the tin atoms were obtained by direct methods using MULTAN.<sup>30</sup> It was found that the 32 tin atoms in the unit cell were comprised of 16 on each of two special positions: 1/4,  $\underline{x}$ , 1/8 (Wyckoff notation <u>e</u>, space group  $I4_1/acd$ ) and  $0,0,\underline{z}$  (<u>d</u>). This solution was confirmed by the successful use of these two positions to interpret the 28 most intense peaks in a three-dimensional Patterson map.<sup>31</sup> Following two cycles of full matrix, isotropic, least-squares refinement, a difference Fourier yielded the positions of the remaining non-hydrogen 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 onefifth of their corresponding estimated standard deviation.

A final difference Fourier map contained areas of residual electron density of intensity, <u>ca</u>. le  $\mathbb{A}^3$ . 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, respectively. The asymmetric unit, with atomic labeling, is diagramed in Figure 1.

7

# Description and Discussion of the Structure

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

The geometry at each tin is almost perfectly trigonal bipyramidal  $[O(1)-Sn(1)-O(1') = 178.0(2)^\circ; O(2)-Sn(2)-O(2') = 175.9(2)^\circ]$ . Within each of the two distinct trimethyltin groups, one tin-carbon bond lies on a two-fold axis [Sn(1)-C(7) or 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  $v_{asym}(SnC_3)$  stretching frequency at 532 cm<sup>-1</sup>, but no lower frequency absorption band is available to assign to the  $v_{sym}(SnC_3)$  mode. In the Raman spectrum, on the other hand, an intense absorption at 515 cm<sup>-1</sup> 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 phosphorus atoms of the phosphonate ligand at an -O(1)-P(1)-O(2) angle of 115.3(3)°. The chains thus propogate through the crystal in a helical fashion, with adjacent helicies turning in opposite directions.

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 Figure 2a), with the second and third phosphonate ligands of the second helix of opposite hand (Figure 2b). 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 (Figure 2c) which is of the opposite hand. The stack of helicies held at regular intervals by hydrogen bonds creates infinite, two-dimensional sheets. An ORTEP representation of part of one sheet is shown in Figure 3. As can be seen in Figure 4, the phenyl groups point outward from the center of the propogating helicies, separating the independent sheets of helicies from one another.

Four pairs of helical chains, each pair consisting of two helicies of opposite hand, are found in the unit cell as seen in Figure 5. There are thus portions of four sheets propogating in the <u>ab</u>-plane contained in each unit cell. Within any sheet two he cal chains are contained in the b-dimension of the unit cell.

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,  $C_6H_5^{P}(OH)_2$ , 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.<sup>32</sup> These distances change to 1.489 and 1.563 Å, respectively, in the singly-ionized sodium acetylphosphonate acetic acid solvate,  $CH_3^{O}C-P(OH)ONa$ , <sup>33</sup> and to 1.500 and 1.569 Å, respectively, in the zwitterionic 2-aminoethylphosphonic acid ( $\beta$ -ciliatine).<sup>34</sup>

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  $^{35}$  (2.589 Å), essentially the same as the mean distance found in the parent acid.  $^{32}$  Sinc 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<sub>2</sub>Cl<sub>2</sub>] anion which doubly bridges octahedral tin(IV) units in the [Cl<sub>3</sub>SnOPCl<sub>3</sub>·PO<sub>2</sub>Cl<sub>2</sub>]<sub>2</sub> dimer,<sup>8</sup> but not in the  $[\underline{trans}-(CH_3)_2Sn]_3(PO_4)_2\cdot 8H_2O$  where the double -O-P-O- bridges exhibit P-O ester distances in the range 1.52-1.56 Å.<sup>26</sup> The shortening of this P(1)-O(1) bond in the title compound possibly arises as a consequence of the molecular 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  $[O(2) \rightarrow Sn(2) = 2.319(5)$  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 <u>G</u>. In addition, the expectation 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 (<u>F</u>) 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.<sup>36</sup> A somewhat shorter connection is found in the octahedral anion,  $[Cl_5Sn+O=PCl_3]^-$ , where the dative O+Sn interatomic distance is 2.27 Å,<sup>37</sup> and in the <u>cis</u>-octahedral complex  $SnCl_4 \cdot 20=PCl_3$  where the mean Sn-O distance is 2.28 Å.<sup>38</sup>

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 bridge  $PO_2Cl_2$  groups exhibit distances of 2.119 and 2.120 Å to the octahedral tin atoms,<sup>8</sup> and with those in  $[(CH_3)_2Sn]_3(PO_4) \cdot 8H_2O]$  in which there are three tin environments.<sup>26</sup> In the latter structure two aquated tin atoms whose geometries lie between tetrahedral and

octahedral establish ester bridge bonds of 2.02 and 2.04 Å, while a  $\underline{\text{trans}}$ -(CH<sub>3</sub>)<sub>2</sub>Sn unit of octahedral structure makes ester bridge bonds of 2.17 and 2.18 Å.<sup>26</sup> 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.<sup>26,35</sup>

Because the two tin-oxygen distances at each tin center are symmetry related [by the two-fold 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 non-equivalent 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. $^{27-8}$ , 3 This arrangement is probably best described in terms of structure H as a combination of trimethyltin(IV) cations and bis-(phenylphosphonato) trimethyltin(IV) anions,  $[C_6H_5]_{1.1}^{H_1}$  OSn(CH<sub>3</sub>)<sub>3</sub>O<sub>4.1</sub><sup>H\_2</sup>C<sub>6</sub>H<sub>5</sub>], alternating · in a helical array. The tin atoms are not sufficiently different to be distinguished by <sup>119m</sup>Sn Mössbauer spectroscopy, but this is not surprising since even the tin atoms in the five- and six-coordinated double salt [(CH<sub>3</sub>)<sub>3</sub>Sn·terpy]<sup>+</sup>[(CH<sub>3</sub>)<sub>2</sub>SnCl<sub>3</sub>]<sup>-</sup> are barely distinguishable by Mössbauer spectroscopy. 42

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 di(phosphoryl trichloride) hexachloroditin(IV),  $[(Cl_3SnOPCl_3)^+$ (PO<sub>2</sub>Cl<sub>2</sub>)<sup>-</sup>]<sub>2</sub>, is 118.0°,<sup>8</sup> and a mean value of 111.4° is found in tris[dimethyltin(IV)bis(orthophosphate) octahydrate,  $[(CH_3)_2Sn]_3$ (PO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O.<sup>26</sup> The comparable mean value for the singly-bridged portion of the bis(diorganophosphinato)zinc(II) polymer is 116.8°.<sup>21</sup> <u>Acknowledgement</u>. Our work is supported by the Office of Naval Research and the National Science Foundation through Grant CHE-78-17562 J.J.Z.) and the National Cancer Institute, DHEW through Grant CA-17562 (d.v.d.H). We thank the University of Oklahoma for providing computer time, and the M&T Chemicals, Inc. for the donation of organotin starting materials.

Table I. Crystal Data	
formula	C9 <sup>H</sup> 15 <sup>O</sup> 3 <sup>PSn</sup>
fw	320.90
crystal class	tetragonal
spage group <mark>a</mark>	14 <sub>1</sub> /acd
a,b <sup>b</sup>	15.310(6) Å
c <sup><u>b</u></sup>	42.620(59) Å
v	9989.96 Å <sup>3</sup>
Z	32
F(000)	5056
μMOK	21.7 $cm^{-1}$
data crystal dimensions	0.17x0.15x0.17 mm

 $\underline{a}_{From systematic absences:}$  <u>hkl</u>, <u>h+k+l</u> = 2n+l; <u>hk0</u>, <u>h</u> = 2n+l; <u>0k1</u>, <u>l</u> = 2n+l; <u>hhl</u>, 2<u>h+l</u>  $\neq$  4n.

 $\frac{b}{Based}$  upon ±29 values of 64 reflections, and using MoK<sub>a</sub> radiation ( $\lambda = 0.70926$  Å).

Table III.	Final Position	(x10 <sup>4</sup> ) Parameters for	$\alpha \sim (CH_3)_3 SnOP(OH) C_6 H_5^{\underline{a}}$
Atom	<u>×</u>	· ¥	<u>z</u>
Sn(1)	5000(0)	. 0(0)	637.2(2)
Sn(2)	2500(0)	2156.9(5)	1250(0)
P(1)	4415(1)	2143(2)	792.9(4)
0(1)	4310(4)	1290(4)	628(1)
0(2)	3961(3)	2211(4)	1108(1)
O(3)	5416(4)	2334 (5)	85. (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)	0(0)	1123(3)
C(8)	3883(7)	-527(7)	410(3)
C(9)	2500(0)	3560(9)	1250(0)
C(10)	2139(6)	1402(7)	853(2)

 $\underline{a}_{Estimated standard deviations in parentheses.}$ 

Table II. Data Collection Parameters for  $\alpha - (CH_3)_3 SnOP(OH)C_6H_5$ 

	•
Diffractometer	Enraf-Nonius CAD/4
Radiation	мок-α (0.7121 Å)
Temperature	138±2 K
Scan Technique	θ-2θ
Limit	0 <u>&lt;</u> 20 <u>&lt;</u> 53°
Scan Time	40s
Scan Angle	(0.7+0.20 tan0)
Aperature Width	(2.5+0.86 tan0)
Aperature Height	6 mm
Aperature Distance	173 mm
Monitor Reflection	<b>4</b> 0 8
Intensity Monitor	2500s
Max. Fluctuation in Monitor	<1.2%
Orientation Monitors	200 reflections
Number of Unique Data	2578
Number of Observed Data <sup>a</sup>	2296
Corrections	Lorentz Polarization Absorption

 $\frac{a}{1>2\sigma}$ (I)

$a - (CH_3)_3 SnOP(OH) C_6 H_5 = \frac{a}{100}$							
Atom	<u> </u>	<u>U</u> 22	U <sub>33</sub>	<u>U23</u>	<u> </u>	<u> </u>	
Sn(1)	192(4)	289(4)	179(4)	0(0)	0(0)	45(3)	
Sn(2)	142(4)	260(4)	173(4)	0(0)	-11(3)	0(0)	
P(1)	94 (8)	377(11)	176(9)	-18(8)	-4 (7)	-7(8)	
0(1)	218 (29)	281(31)	411 (33)	-21(26)	-45(25)	106(24)	
0(2)	93 (24)	404 (33)	184(25)	22(23)	5(20)	-9(22)	
0(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)	238(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)	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(0)	102(76)	0(0)	
C(10)	291(46)	572(63)	288(42)	-206(43)	-19(36)	-78(44)	

**Table IV.** Final Anisotropic  $(x10^4)$  Thermal Parameters for  $Q = (CH_2)_2 \sin OP(OH) C_c H_z^{\frac{a}{2}}$ 

**Estimated** standard deviations in parentheses

Table V. Fi	nal Interatomic	Distances (Å) in $\alpha$ -	- (CH <sub>3</sub> ) $_{3}$ SnOP (OH) C <sub>6</sub> H <sub>5</sub> <sup>a</sup>
Sn(1)-O(1)	2.240(6)	P(1)-O(1)	1.492(6)
Sn(1)-O(1')	2.240(6)	P(1)-O(2)	1.516(5)
Sn(1) - C(7)	2.070(13)	P(1) ∸O(3)	1.580(6)
Sn(1)-C(8)	2.124(11)	P(1)-C(1)	1.793(9)
Sn(l)-C(8')	2.124(11)		
Sn(2) - O(2)	2.319(5)	C(1)-C(2)	1.396(12)
Sn(2)-0(2')	2.319(5)	C(2)-C(3)	1.410(13)
Sn(2)-C(9)	2.148(14)	_ C(3)-C(14)	1.380(13)
Sn(2) - C(10)	2.122(9)	C(4)-C(5)	1.388(13)
Sn(2)-C(10')	2.122(9)	C(5)-C(6)	1.426(13)
		C(6)-C(1)	1.391(12)

and the second

v

Δ

**Estimated standard deviations in parentheses.** 

Table VI. Final I	nteratomic Angles	(deg.) in $\alpha$ -(CH <sub>3</sub>	$\frac{0}{3}$ snop (OH) C <sub>6</sub> H <sub>5</sub> <sup>a</sup>
O(1)-Sn(1)-O(1')	178.0(2)	Sn(1)-O(1)-P(1)	135.5(3)
O(1) - Sn(1) - C(7)	91.0(2)	Sn(2)-O(2)-P(1)	132.2(3)
O(1) - Sn(1) - C(8)	87.0(3)		
O(1)-Sn(1)-C(8')	92.1(3)	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)	92.1(3)	O(1)-P(1)-C(1)	108.3(4)
O(1')-Sn(1)-C(8')	87.0(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(7) - Sn(1) - C(8')	117.1(3)	O(3)-P(1)-C(1)	106.2(4)
C(8) - Sn(1) - C(8')	125.8(4)		
		P(1)-C(1)-C(2)	119.1(7)
0(2)-Sn(2)-O(2')	175.9(2)	P(1)-C(1)-C(6)	120.6(7)
O(2) - Sn(2) - C(9)	88.0(2)	C(2)-C(1)-C(6)	120.4(8)
0(2) - Sn(2) - C(10)	93.6(3)	C(1)-C(2)-C(3)	119.4(8)
O(2)-Sn(2)-C(10')	93.6(3)	C(2)-C(3)-C(4)	120.4(9)
O(2)-Sn(2)-C(10')	88.6(3)	C(3)-C(4)-C(5)	120.8(9)
O(2')-Sn(2)-C(9)	88.0(2)	C(4)-C(5)-C(6)	119.2(9)
O(2')-Sn(2)-C(10)	88.6(3)	C(5)-C(6)-C(1)	119.7(8)
$O(2^{\circ}) - Sn(2) - C(10^{\circ})$	93.6(3)		•
C(9)-Sn(2)-C(10)	123.0(3)		
C(9)-Sn(2)-C(10")	123.0(3)	•	

<sup>a</sup>Estimated standard deviations in parentheses

C(10)-Sn(2)-C(10') 114.0(4)

#### References and Notes

(1) For Part VI of this series see Molloy, K. C.; Hossain, M. B.; van der Helm, D.; Zuckerman, J. J., Mullins, F. P. <u>Inorg. Chem</u>. submitted.

Molloy, K. D.; Hossain, M. B.; van der Helm, D.; Zuckerman, J. J.;Haiduc, I. <u>Inorg. Chem. 1979, 18, 3507.</u>

Molloy, K. C.; Hossain, M. B.; van der Helm, D.; Zuckerman, J. J.;
Haiduc, I. <u>Inorg. Chem</u>. <u>1980</u>, <u>19</u>, 0000.

(4) Zuckerman, J. J.; Reisdorf, R. P.; Ellis, H. V., III; Wilkinson,
R. R. <u>Chemical Problems in the Environment: Occurrence and Fate of</u> <u>the Organoelements</u>, ed. by Bellama, J. M.; Brinkman, F. E. ACS
Symposium Series No. 82. American Chemical Society, Washington, DC, <u>1978</u>, 388.

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

(6) Lefferts, J. L.; Hossain, M. B.; Molloy, K. C.; van der Helm, D.;
Zuckerman, J. J. Angew Chem. Int. Ed. Engl. <u>1980</u>, <u>19</u>, 309.

(7) The monomeric units in bis(0,0'-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  $\{Sn[SP(OC_6H_5)_2]_2\}_2$  which contains three-coordinated bridging sulfur atoms in a planar  $Sn_2S_2$  ring.<sup>6</sup>

(8) Moras, D.; Mitschler, A.; Weiss, R. J. Chem. Soc. Chem. Commun.,
1968, 26; Acta Crystallogr. 1969, B25, 1720.

(9) Berndt, A. F.; Lamberg, R. <u>Acta Crystallogr. 1971</u>, <u>B27</u>, 1092.
(10) Schroeder, L. W.; Prince, E. <u>Acta Crystallogr. 1976</u>, <u>B32</u>, 3309.
(11) McDonald, R. C.; Ericks, K. <u>Inorg. Chem.</u>, <u>1980</u>, <u>19</u>, 1237 and references therein.

(12) Herak, R.; Prelesnik, B.; Curic, M. J. Chem. Soc. Dalton Trans. 1978, 566. (13) Jordan, T. H.; Schroeder, L. W.; Dickens, B.; Brown, W, E. 1976, 15, 1810. Inorg. Chem. (14) Mathew, M.; Schroeder, L. W.; Jordan, T. H. Acta Crystallogr. 1977, B33, 1812. (15) Jordan, T. H.; Dickens, B.; Schroeder, L. W.; Brown, W. E. quoted in ref. 11. (16) Berndt, A. F. J. Deut. Res. 1972, 51, 53. (17) Berndt, A. F. Acta Crystallogr. 1974, B30, 529. (18) Weakley, T. J. R.; Watt, W. W. L. Acta Crystallogr. 1979, B35, 3023. (19) Giordano, F.; Randaccio, L; Ripamonti, A. J. Chem. Soc. Chem. Commun. 1967, 19. (20) Giancotti, V.; Giordano, F.; Randaccio, L.; Ripamonti, A. J. Chem. Soc. (A) 1968, 757. (21) Giordano, F.; Randaccio, L.; Ripamonti, A. Acta Crystallogr. 1969, B25, 1057. (22) Brückner, S.; Calligaris, M.; Nardin, G.; Randaccio, L.; Ripamonti, A. J. Chem. Soc. Chem. Commun. 1969, 474. (23) Stalick, J. K.; Quicksall, C. O. Inorg. Chem., 1976, 15, 1577. (24) Fenot, P.; Darriet, J.; Garrigout-Lagrange, C.; Cassaigne, A. J. Mol. Struct. 1978, 43, 49. (25) Gemiti, F.; Giancotti, V.; Ripamonti, A. J. Chem. Soc., (A) 1968, 763. (26) Ashmore, J. P.; Chivers, T.; Kerr, K. A.; van Roode, J. H. G. J. Chem. Soc. Chem. Commun. 1974, 653; Inorg. Chem. <u>1977, 16, 191.</u> (27) Zubieta, J. A.; Zuckerman, J. J. Prog. Inorg. Chem. 1978, 24, 251.

(28) Molloy, K. C.; Zuckerman, J. J. unpublished work.

(29) Cunningham, D.; Molloy, K. C.; Zuckerman, J. J. submitted for publication.

(30) Germain, G.; Main, P.; Woolfson, M. M. <u>Acta crystallogr</u>. 1971, A27, 368.

(31) All computations were made using the SHELX program. [Sheldrick,
G. M. <u>1976</u>, SHELX-76. Program for crystal structure determination,
University of Cambridge, England]. Scattering factors were for neutral atoms, and were used as listed in SHELX-76.

(32) Weakley, T. J. R. Acta Crystallogr. 1976, B32, 2889.

(33) Jones, P. G.; Kennard, O. <u>Acta Crystallogr</u>. <u>1978</u>, <u>B34</u>, 2309.
(34) Okaya, Y. <u>Acta Crystallogr</u>. <u>1966</u>, <u>20</u>, 712.

(35) L. Pauling, The Nature of the Chemical Bond, 3rd Ed., Cornell University Press, Ithaca, NY, 1960.

(36) Nardelli, M.; Pelizzi, C.; Pelizzi, G. <u>J. Organomet. Chem</u>. <u>1976</u>, <u>112</u>, 263.

(37) Banister, A. J.; Durrant, J. A.; Rayment, I.; Shearer, H. M. M.
 <u>J. Chem. Soc. Dalton Trans.</u> 1976, 928.

(38) Brandon, C. I. Acta Chem. Scand. 1963, 17, 759.

(39) A similar situation has been noted in two independent determinations<sup>40,44</sup> of the structure of  $(CH_3)_3SnO_2SCH_3$  which consists of crystallographically independent tin sites bridged by sulfinate ligands in an alternating one-dimensional array. As with the title compound, each tin atom lies on a two-fold axis, and is bonded to two identical oxygen atoms, but these 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 determination,<sup>40</sup> and zero in the other.<sup>41</sup> It is (39). A similar situation has been noted in two determinations<sup>40,4+</sup> 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 two-fold axis and is bonded to two identical oxygen atoms which 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,  $^{40}$  and zero in the other. <sup>41</sup> 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.

(40) Sheldrick, G. M.; Taylor, R. <u>Acta Cryst</u>. <u>1977</u>, <u>B33</u>, 135.
(41) Hengel, R.; Kunze, U.; Strähle, J. <u>Z. Anorg. Chem</u>. <u>1976</u>, <u>423</u>, 35.

(42) Debye, N. W. G.; Rosenberg, E.; and Zuckerman, J. J. <u>J. Am</u>.
 <u>Chem.</u> Soc. 1968, <u>90</u>, 3234.

## Figure Captions

- Figure 1. The asymmetric unit of  $\alpha$ -phenylphosphonatotrimethyltin(IV), showing the atom numbering scheme. Primed and doubly primed atoms are related to unprimed atoms by the two-fold axes Sn(1)-C(7) and Sn(2)-C(9), respectively.
- Figure 2. Schematic representation of the hydrogen bonding between adjacent helicies. Solid lines ( ) represent helices propagating in a clockwise manner in the direction of the associated arrow; numbered boxes indicate PO<sub>3</sub> units within any given helix. Hydrogen bonded PO<sub>3</sub> groups are linked by dotted lines ( ).
- Figure 3. ORTEP drawing of two adjacent helices, of opposite hand, linked by hydrogen bonds ( ).
- Figure 4. A pair of adjacent helices, viewed along the axis of propagation. The upper ( ) and lower ( ) helices propagate out of the page in an anti-clockwise and clockwise manner, respectively. Hydrogen bonds between helices are dotted.











<u>C</u>



E





H







