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PHOSPHORIC ACID DERIVATIVES OF TIN. I. TRIORGANOTIN(IV) DITHIOP--ETC(U)

SEP 79 J L LEFFERTS , K C MOLLOY

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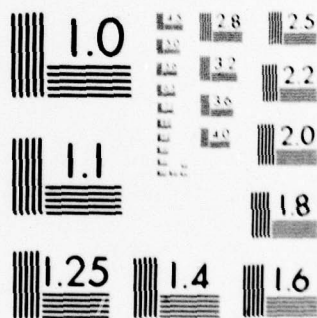
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Twelve triorganotin dithiophosphate esters, $R_3SnS_2P(OR')_2$, where $R=C_6H_5$ and
 $R'=CH_3$, C_2H_5 , $n-C_3H_7$, $i-C_3H_7$, $n-C_4H_9$, $i-C_4H_9$ and C_6H_5 ; and $R=CH_3$ and
 $R'=CH_3$, C_2H_5 , $n-C_3H_7$ and $i-C_3H_7$; and $R=C_6H_{11}$ and $R'=i-C_3H_7$ were
synthesized in high yield by the condensation of the organotin hydroxide with
the O,O'-diorganodithiophosphoric acid to release water which was distilled
azeotropically, or taken up in an alcohol solvent corresponding to the phos-
phoric acid ester group, or by the reaction of the triorganotin chlorides with
an alkali metal salt of the dithiophosphoric acid. The products are colorless.

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crystalline solids except for the trimethyltin derivatives which are oils. The synthesis of the diisopropyl ester in the trimethyltin series was accompanied by protodemetalation to yield the bis-compound, $(C_6H_5)_2Sn[S_2P(OC_3H_7-12)]_2$. Infrared spectral bands were assigned to the $\nu CO(1170-1095)$, $\nu_{asym} PS_2(675-635)$, and $\nu_{POR}(1015-965) \text{ cm}^{-1}$, but the $\nu_{sym} PS_2$ absorption obscures the $\nu_{sym} SnC_3$ modes. Nmr $[^2J(^{119}Sn-C-^1H)]$ coupling constants for the methyltin series are consistent with four-coordinated tin in solution, and mass spectral data with monomers. Tin-119m Mössbauer data, on the other hand, specify a five-coordinated structure for the methyltins, but four-coordinated for the cyclohexyl- and phenyltins. The triphenyltin ethoxy and isopropoxy derivatives behave identically in a variable-temperature Mössbauer study, where the slope of the temperature-dependence of the log of the resonance area is consistent with a monomeric structure packed in the solid into a rather tight lattice. Using low-energy, lattice-mode Raman data in the effective vibrating mass treatment, the molecularity of the vibrating unit is found to be monomeric. The predicted monomeric, monodentate structure for these two esters is unique among dithiophosphate-metal systems.

(1015-965) cm⁻¹

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⁹ TECHNICAL REPORT NO. 11

⁶ Phosphoric Acid Derivatives of Tin. I.
Triorganotin(IV) Dithiophosphate Esters.

by

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Phosphoric Acid Derivatives of Tin. I. Triorganotin(IV) Dithiophosphate Esters.

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ABSTRACT

Twelve triorganotin dithiophosphate esters, $R_3SnS_2P(OR')_2$, where $R=C_6H_5-$ and $R'=CH_3-$, C_2H_5- , $n-C_3H_7-$, $i-C_3H_7-$, $n-C_4H_9-$, $i-C_4H_9-$ and C_6H_5- ; and $R=CH_3-$ and $R'=CH_3-$, C_2H_5- , $n-C_3H_7-$ and $i-C_3H_7-$; and $R=C_6H_{11}-$ and $R'=i-C_3H_7-$ were synthesized in high yield by the condensation of the organotin hydroxide with the 0,0'-diorganodithiophosphoric acid to release water which was distilled azeotropically, or taken up in an alcohol solvent corresponding to the phosphoric acid ester group, or by the reaction of the triorganotin chlorides with an alkali metal salt of the dithiophosphoric acid. The products are colorless, crystalline solids except for the trimethyltin derivatives which are oils. The synthesis of the diisopropyl ester in the triphenyltin series was accompanied by protodemetalation to yield the bis-compound, $(C_6H_5)_2Sn[S_2P(OC_3H_7-i_2)]_2$. Infrared spectral bands were assigned to the $\nu_{CO}(1170-1095)$, $\nu_{asym} PS_2(675-635)$, and $\nu_{POR}(1015-965) cm^{-1}$, but the $\nu_{sym} PS_2$ absorption obscures the $\nu_{sym} SnC_3$ modes. Nmr $|^2J(^{119}Sn-C-^1H)|$ coupling constants for the methyltin series are consistent with four-coordinated tin in solution, and mass spectral data with monomers. Tin-119m Mössbauer data, on the other hand, specify a five-coordinated structure for the methyltins, but four-coordinated for the cyclohexyl- and phenyltins. The triphenyltin ethoxy and isopropoxy derivatives behave identically in a variable-temperature Mössbauer study, where the slope of the temperature-dependence of the log of the resonance area is consistent with a monomeric structure packed in the solid into a rather tight lattice. Using low-energy, lattice-mode Raman data in the effective vibrating mass treatment, the molecularity of the vibrating unit is found to be monomeric. The predicted monomeric, monodentate structure for these two esters is unique among dithiophosphate-metal systems.

Organotin compounds are powerful biocides, and have found wide application as agricultural fungicides and miticides, surface disinfectants, anthelmintics and marine antifouling agents.^{1,2} A particularly intriguing idea is to combine the triorganotin moieties which show the strongest biocidal activity with organophosphorus moieties which are also known for their potent biocidal effect. The combination of the two kinds of biological activity in a single molecule could produce a still more powerful and lasting effect, and prevent the problems associated with the development of tolerance to each kind.

Several model organotin dithiophosphorus systems suggest themselves as subjects for study. We initiate this series of papers with a description of the synthesis of the triorganotin dithiophosphate esters. This class of compounds was first introduced in 1964³, and has been the subject of several patents describing applications as bactericides, insecticides, fungicides, etc.,⁴⁻¹⁵ but a satisfactory answer to the question of the structure-function relationships in the known systems¹⁶⁻¹⁹ has not yet been given. The systems are also of interest structurally²⁰ since several modes of attachment of the dithiophosphate ester ligand are in principle possible, including as a monodentate, bidentate, bridging in an oligomeric form as in a dimer or as a bridging ligand in an associated polymer chain. The X-ray crystallographic results for certain key examples will be published as a part of this series.

We report here the synthesis of 12 compounds, nine not reported before, by two preparative methods.⁴³

Experimental Section

Reagent grade chemicals and solvents were used as received, except for triphenyltin chloride (M&T) which was recrystallized from chloroform before use. Trimethyltin hydroxide was prepared from the chloride. Infrared spectra were recorded as KBr discs or Nujol mulls on KBr plates and polyethylene film on Beckman 4250 or IR-12 spectrometers. Tin-119m Mössbauer spectra were recorded at 77K on a Ranger Engineering constant acceleration spectrometer equipped with scintillation counting and with $\text{Ca}^{119\text{m}}\text{SnO}_3$ (New England Nuclear Corp.) used both as source and zero isomer shift (I.S.) reference standard. Mass spectra were recorded on a Hewlett Packard 5985 GC/MS System at 70 ev. Raman spectra were recorded on a Spex Ramalog 5 system. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc.

The compounds studied are listed with the preparatory method used, their yields, melting points, and microanalytical data in Table I. Tin-119m Mössbauer data are listed in Table II.

Preparation of the 0,0'-Dialkylphosphorodithioic Acids, HS(S)P(OR)'_2 .

Tetraphosphorus decasulfide (444.5g, 1 mole) was treated with the corresponding anhydrous alcohol (4 moles), added dropwise with magnetic stirring. Hydrogen sulfide was evolved, and the solid dissolved completely with formation of the crude acid. The reaction was exothermic and external cooling was applied at initial stages. Toward the end of the reaction, gentle warming with a water bath (ca. 60-80°C) was necessary to speed up the reaction. The crude acid was distilled in vacuo (as fast as possible to avoid decomposition) at the following temperatures: $\text{R}=\text{CH}_3^{21,22}$, b. 62-4°/0.5; $\text{C}_2\text{H}_5^{21,22}$, b. 75-8°/0.3; $\text{n-C}_3\text{H}_7^{21,22}$, b. 112°/0.5; $\text{i-C}_3\text{H}_7^{21-23}$, b. 72-4°/0.7; $\text{n-C}_4\text{H}_9^{22,23}$, b. 120°/0.8-1; $\text{i-C}_4\text{H}_9^{24}$, b. 75°-84°C/0.08-0.1 torr; $\text{C}_6\text{H}_5^{25}$, m.p. 60-61°C.

Preparation of the Sodium Salts, NaS(S)P(OR)'_2 .²⁶

Sodium 0,0'-dialkyldithiophosphates were prepared via sodium ethoxide, formed by dissolving the stoichiometric amount of metallic sodium in absolute ethanol (excess) and treating the solution with an equivalent amount of dialkyldithiophosphoric acid. The solutions were used immediately without isolation of the salt.

Preparation of Ammonium Dialkyldithiophosphates, $\text{NH}_4\text{S}_2\text{P}(\text{OR}')_2$.²⁷

Phosphorous decasulfide (88.9g, 0.2 moles) was treated with anhydrous alcohol (0.8 moles) added dropwise. After all the phosphorus decasulfide had dissolved the mixture was heated gently on a water bath until the reaction was completed. The acid thus obtained was diluted with 3-400 ml of dry benzene and a stream of anhydrous ammonia bubbled through the solution. The ammonium dialkyldithiophosphate precipitated was filtered, washed with benzene and dried. The yields were as follows: $\text{R}' = \text{CH}_3$, 46%; C_2H_5 , 61%; $n\text{-C}_3\text{H}_7$, 61%; $i\text{-C}_3\text{H}_7$, 70%; $n\text{-C}_4\text{H}_9$, 58%.

Preparation of Triphenyltin Dithiophosphate Esters.

0,0'-Dimethyldithiophosphatotriphenyltin, $(\text{C}_6\text{H}_5)_3\text{SnS}_2\text{P}(\text{OCH}_3)_2$.

Triphenyltin chloride (7.70g, 0.02 mole) was treated with $\text{NaS}_2\text{P}(\text{OCH}_3)_2$ (3.6g, 0.02 mole) in methanol. The mixture was heated on a water bath for 1h, filtered and concentrated to give 3.6g (35.6%) of the product, m.p. 83° (lit. 86°C^3).

Alternatively, a suspension of triphenyltin hydroxide (1.22g, 0.0033 mole) in methanol was heated with dimethyldithiophosphoric acid (0.61g, 0.004 mole) on a water bath until a clear solution was obtained, which on cooling deposited 1.2g (71.7%) of the crystalline product. m.p. 83° (lit. 86°C^3).

0,0'-Diethyldithiophosphatotriphenyltin, $(\text{C}_6\text{H}_5)_3\text{SnS}_2\text{P}(\text{OC}_2\text{H}_5)_2$.

Triphenyltin chloride (7.7g, 0.02 mole) was similarly treated with sodium diethyldithiophosphate (4.16g, 0.02 mole) to give 6.4g of the product (60% yield), mp 105° (lit. 105°C^3).

Alternatively, a suspension of triphenyltin hydroxide (18.3g, 0.05 mole) in absolute ethanol was treated with diethyldithiophosphoric acid (9.3g, 0.05 mole) diluted with absolute ethanol and allowed to reflux for 2h. on a water bath until a clear solution was obtained. The solution was concentrated and cooled to give 21.5g (88.5% yield) product. m.p. 105° (lit. 105°C^3).

0,0'-Di-n-propyldithiophosphatotriphenyltin, $(\text{C}_6\text{H}_5)_3\text{SnS}_2\text{P}(\text{OC}_3\text{H}_7\text{-}n)_2$.

Triphenyltin chloride (3.88g, 0.02 mole) was treated in the same way with sodium di-n-propyldithiophosphate (2.36g, 0.02 mole) to yield 1.3 g of the

product (23%), mp 63° (lit. 63°C.³).

Alternatively, a suspension of triphenyltin hydroxide (5.0g, 0.014 mole) in n-propanol was heated with di-n-propyldithiophosphoric acid (2.9g, 0.014 mole) until a clear solution was formed. After concentration and cooling 5.1g (65.1% yield) of product, m.p. 63° (lit. 63°C³) was obtained.

0,0'-Diisopropyldithiophosphatotriphenyltin, (C₆H₅)₃SnS₂P(OC₃H₇-i)₂

A solution of the sodium salt of diisopropyldithiophosphoric acid (0.01m) in absolute ethanol (20 mL) was added dropwise to a stirred solution of triphenyltin chloride (0.01m) in freshly distilled diethylether (70 mL). After 24 h. the white ppt. was separated by filtration through diatomaceous earth, and the filtrate concentrated to dryness on a rotary evaporator. The resulting white solid was dissolved in a minimum of warm toluene, filtered, and allowed to crystallize at 0°C, yielding white, prismatic crystals (2.93 gms. 52% yield) of the title compound. m.p. 73.5-74.5°C.

A second crop of needle-like crystals separated after several days, identified as bis-(0,0'-diisopropyldithiophosphato)diphenyltin (m.p. 110°C.) Anal.: Found: C, 41.78; H, 5.37%, C₂₄H₃₈O₄P₂S₄Sn requires: C, 41.20; H, 5.49%.

0,0'-Di-n-butyldithiophosphatotriphenyltin, (C₆H₅)₃SnS₂P(OC₄H₉-n)₂

A suspension of triphenyltin hydroxide (4.0g, 0.011 mole) in n-butanol was allowed to reflux for 3h. with di-n-butyldithiophosphoric acid (2.6g, 0.011 mole). The solution was concentrated and cooled, to give 6.1g (94.3% yield) of the product, m.p. 68-9°C (lit. 69.05°C³).

0,0'-Diisobutyldithiophosphatotriphenyltin, (C₆H₅)₃SnS₂P(OC₄H₉-i)₂

Equimolar quantities (0.02m) of triphenyltin hydroxide and diisobutyldithiophosphoric acid were allowed to reflux together in benzene (100 mL) and the water formed azeotropically distilled into a Dean and Stark trap. Concentration of the resulting solution yielded a colorless oil, from which crystallization was induced by the addition of n-hexane at 0°C. The product was purified by recrystallization from a hexane/benzene (10:1) mixture (8.74 gms, 63%) m.p. 52-4°C.

0,0'-Diphenyldithiophosphatotriphenyltin, $(C_6H_5)_3SnS_2P(OC_6H_5)_2$

Triphenyltin hydroxide and diphenyldithiophosphoric acid in 0.02 molar quantities were allowed to reflux together in benzene (100 mL) and the water formed azeotropically distilled into a Dean and Stark separator. After 2 h. the requisite amount of water had been collected and the resulting solution was allowed to cool, filtered and concentrated to ca. 10mL on a rotary evaporator. The white precipitate that formed was taken up in a minimum amount of warm toluene and allowed to crystallize 0°C., yielding a white crystalline product (9.8 gms, 77% yield), identified as 0,0'-diphenyldithiophosphatotriphenyltin, m.p. 121-2°C.

0,0'-Dimethyldithiophosphatotrimethyltin, $(CH_3)_3SnS_2P(OCH_3)_2$

Metallic sodium (1.20g, 0.052 mol) was dissolved in 30mL absolute ethanol and dimethyldithiophosphoric acid (8.24g, 0.052 mol) added. Trimethyltin chloride (9.50g, 0.048 mol) in absolute ethanol was added with stirring, sodium chloride filtered, and the filtrate concentrated to give the crude product as an oil. This was distilled (b.p. 75-80° C/0.01mm) to give pure product (6.35g, 42%).

0,0'-Diethyldithiophosphatotrimethyltin, $(CH_3)_3SnS_2P(OC_2H_5)_2$

Method A.

Trimethyltin hydroxide (3.77g, 20.9 mmol) and diethyldithiophosphoric acid (3.94g, 21.2 mmol) were mixed in benzene (65 ml), and the solution heated at reflux for 3 h. Water produced in the reaction was collected by a Dean and Stark trap. After removal of benzene under vacuum, the product was vacuum distilled to give 4.64g (13.3 mmol, 64% yield) of the product, b.p. 112-115°C/0.2mm.

Method B.

Potassium hydroxide (0.28g, 5 mmol) was dissolved in ethanol and trimethyltin chloride (0.995g, 5 mmol) added to give a precipitate. Diethyldithiophosphoric acid (0.93g, 5 mmol) was added, and the mixture refluxed for 1h. The solution was filtered and the filtrate evaporated to give 1.3g (80% yield) of the product as an oil.

0,0'-Di-n-propyldithiophosphatotrimethyltin, $(\text{CH}_3)_3\text{SnS}_2\text{P}(\text{OC}_3\text{H}_7\text{-n})_2$

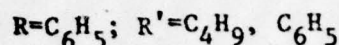
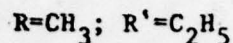
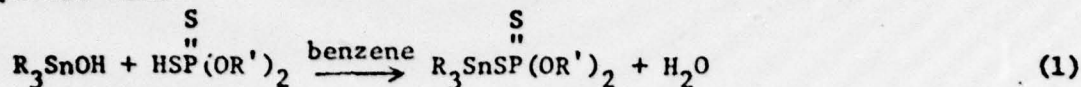
Potassium hydroxide (0.28g, 5 mmol) in ethanol was treated with trimethyltin chloride (0.995g, 5 mmol). After the addition of di-n-propyldithiophosphoric acid (1.02g, 4.8 mmol) the mixture was refluxed for 1 h., then filtered and the solvent evaporated to give an oil (1.37g, 75% yield).

0,0'-Diisopropyldithiophosphatotrimethyltin, $(\text{CH}_3)_3\text{SnS}_2\text{P}(\text{OC}_3\text{H}_7\text{-iso})_2$

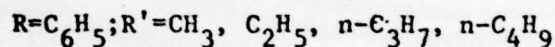
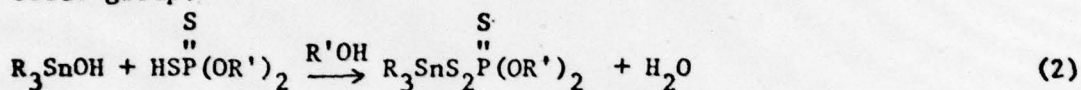
To a solution of trimethyltin chloride (3.98g, 20 mmol) in diethyl ether (30 ml) was added a solution of the sodium salt of diisopropyldithiophosphoric acid (4.86g, 20.5 mmol) in anhydrous ethanol. Formation of a white precipitate began immediately. The mixture was heated at reflux for 1 h., cooled and filtered through diatomaceous earth. Solvent was removed under vacuum on the rotary evaporator. The residual oil was purified by vacuum distillation to yield 5.65g of the product (15 mmol, 75% yield), b.p. 105-109°C/0.4mm.

Results and Discussion

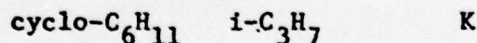
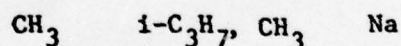
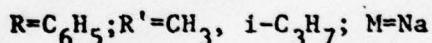
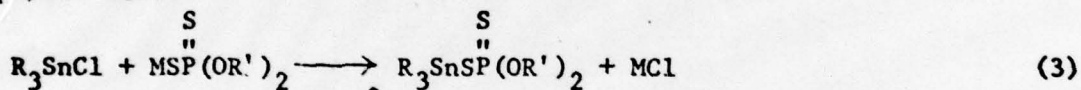
The synthesis of the triorganotin dithiophosphate esters proceeds in high yield from the reaction of a triorganotin hydroxide with the 0,0'-diorganodithiophosphoric acid:



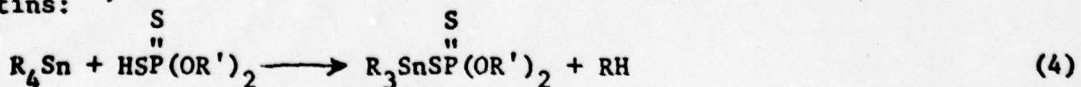
The released water is azeotropically distilled to drive the reaction. The above reaction also proceeds in a solvent of the alcohol corresponding to the phosphoric acid ester group:



In addition, triorganotin chlorides react with the alkali metal salts of the dithiophosphoric acid:



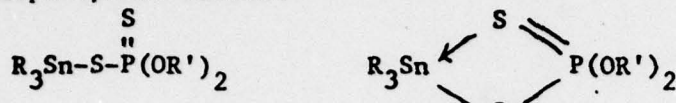
These derivatives have also been synthesized by the protodemetalation of tetraorganotins:^{16,18}



The organotin dithiophosphate esters listed in Table I are colorless, crystalline solids, soluble in polar and non-polar solvents, except for the trimethyltin derivatives which are liquids or oils in the case of the higher esters. The synthesis of 0,0'-diisopropyldithiophosphatetriphenyltin from the sodium salt of the dithiophosphoric acid was accompanied by the cleavage of the phenyl-tin bond to produce the

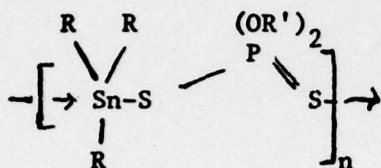
bis-compound.

Three different covalent structures (A-C) must be considered for the triorganotin dithiophosphate esters:



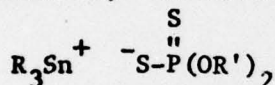
A

B



C

In addition, an ionic form (D) is also possible:



D

The ionic form, D, and the polymeric form, C, are improbable in view of the good solubility of the species in non-polar organic solvents. The dithiophosphate group is known to act as a bidentate ligand through sulfur in many transition metal chelate complexes, but monodentate behavior as in A is apparently unknown.²⁸

Infrared data cannot distinguish between the various possibilities since it is impossible to assign with confidence the P-S and P=S stretching frequencies. Thus for the free acids $(\text{RO})_2\text{PSH}$ and their esters $(\text{RO})_2\text{PSR}$ the P-S stretching bands appear in the same region as for the transition metal complexes $\text{M}[\text{S}_2\text{P}(\text{OR})_2]_n$ which contain bidentate dithiophosphate ligands.²⁹ The P-S absorptions appear in the range $560\text{--}530$ and $670\text{--}630 \text{ cm}^{-1}$,³⁰ and can probably best be described as $\nu_{\text{sym}} \text{PS}_2$ and $\nu_{\text{asym}} \text{PS}_2$, respectively. There seems to be little sensitivity on the part of these frequencies to the groups connected to sulfur.^{30,31}

The infrared spectral assignments for our compounds are listed in Table III.

It is possible to assign with confidence only the ν_{CO} , $\nu_{\text{asym}} \text{PS}_2$ and ν_{POR} bands.

The $\nu_{\text{asym}} \text{PS}_2$ absorption is found in the range 675-635 for our compounds with ν_{CO} at 1170-1095 and ν_{POR} at 1015-965 cm^{-1} .³² The $\nu_{\text{sym}} \text{PS}_2$ absorptions apparently obscure the $\nu_{\text{sym}} \text{SnC}_3$ region, thus denying us important information on the configuration of the triorganotin skeleton. The assignment of the ν_{PS_2} modes is done by analogy with those reported for the corresponding organolead,³³ thallium³¹ and mercury³⁴ derivatives.

Proton nmr data are listed in Table IV. The spectra exhibit the resonances arising from the aromatic protons in the range 7.00-8.30 ppm, and for the organic ester groups attached to phosphorus through oxygen with the expected integrated areas and spin-spin coupling constants. Thus, in the spectrum of $(\text{C}_6\text{H}_5)_3\text{SnSP}(\text{OCH}_3)_2$, the methoxy group signal appears as a doublet arising from the coupling $|^3J(^{31}\text{P}-\text{O}-\text{C}-^1\text{H})| = 15.5\text{Hz}$, and in the ethoxy derivative the methylene protons appear as a doublet of quartets arising from the coupling $|^3J(^{31}\text{P}-\text{O}-\text{C}-^1\text{H})| = 10\text{Hz}$ and the coupling $|^3J(^1\text{H}-\text{C}-\text{C}-^1\text{H})| = 7.0\text{Hz}$ with the terminal methyl protons. The methyltin $|^2J(^{119}\text{Sn}-\text{C}-^1\text{H})| = 57.5\text{Hz}$ couplings are in the range expected for four-coordinated, triorganotin species in the neat liquid or dilute solutions in which they were measured.³⁵ The magnitude of this coupling increases from 57.5 to 70.0 Hz for the isopropyl ester in pyridine solution, indicative of the formation, in situ, of a five-coordinated complex with the pyridine solvent, and establishing the lower J value as corresponding to the four-coordinated situation.

The mass spectra of the three trimethyltin dithiophosphate esters show certain similarities, but the cracking pattern is very different for the 0,0'-dimethyldithiophosphate compound. In all three spectra the highest mass fragment observed arises from the loss of one methyl group from tin. In none of the spectra were there any fragments of higher mass than the monomeric species should give, nor any arising from polytin species, thus ruling out any gas phase association of these molecules. All three compounds also give prominent species at m/e 165 $[(\text{CH}_3)_3\text{Sn}^+]$; in fact, this is the base peak (relative abundance 100%) for the methyl and ethyl esters.

The major pathway for decomposition of the isopropyl ester appears to be by sequential loss of the alkene from the dithiophosphate group after initial loss of $\text{CH}_3\cdot$ from tin.

This pathway is also important for the ethyl ester, but not for the methyl since the latter has no available β -hydrogen for abstraction. Thus, for the isopropyl ester, prominent fragments arise from m/e 321 $[(CH_3)_2SnS_2P(OH)(OC_3H_7)^+]$ and m/e 279 $[(CH_3)_2SnS_2P(OH)_2^+]$, base peak] owing to loss of $CH_3CH=CH_2$ twice; and for the ethyl ester, fragments at m/e 307 and 279 arise from sequential loss of $CH_2=CH_2$.

On the other hand, the dimethyldithiophosphate cannot eliminate alkene, and, therefore, appears to fragment by loss of methyl radicals from tin to give m/e 277 $[SnS_2P(OCH_3)_2^+]$ and by loss of the entire dithiophosphate group to give m/e 165 $[(CH_3)_3Sn^+]$, base peak].

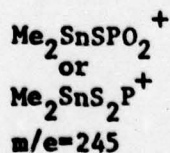
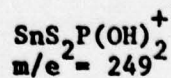
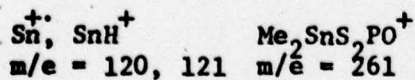
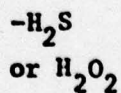
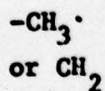
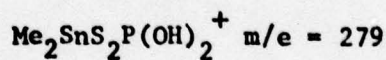
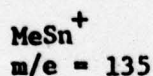
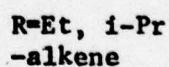
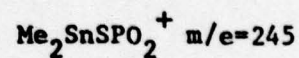
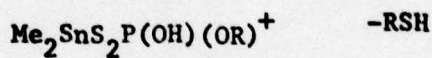
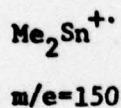
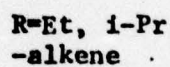
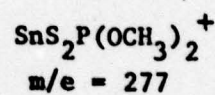
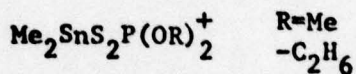
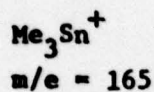
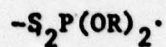
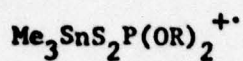
a large background due to impurities arising from thermal decomposition which could not be separated by gas chromatography.

Most of the high abundance fragments are even electron ions. Odd electron ions fragment to give high abundance even electron ion by loss of radicals such as $CH_3\cdot$ or $(RO)_2PS_2\cdot$. Even electron species, where possible, lose neutral alkenes to give other even electron fragments (see Scheme and Table V).

The tin-119m Mössbauer data found in Table II are consistent with triorganotin(IV) compounds in a four-coordinated form (ρ values <1.8)³⁶ for the triphenyl- and tricyclohexyltin derivatives. The trimethyltin compounds studied display larger quadrupole splitting (QS) values which indicates that the tin atom is in a higher than four-coordinated state. This suggests, along with the nmr $|^2J(^{119}Sn-C-^1H)|$ coupling constant data, a monomeric, weakly bidentate chelate arrangement for the solid trimethyltins at 77K as in structure B as one possible configuration, with the triphenyl-, tricyclohexyl- and methyltin derivatives (the latter in the liquid state) adopting the A structure.

Two compounds have been subjected to variable-temperature Mössbauer study, and the results are depicted in Figure 1. The Mössbauer recoil-free fraction, f , is a function of the mean-square-displacement, $\langle x^2 \rangle$ of the tin atom from its equilibrium position:

SCHEME



$$f = \exp \left[- \frac{\langle x^2 \rangle}{\lambda^2} \right] \quad (5)$$

where λ is the wavelength of the Mössbauer gamma ray. The parameter f thus reflects the binding strength of the lattice. For thin absorbers, the recoil-free fraction is linearly related in a Debye model to the area under the resonance, A_T , and its temperature dependence is given by:

$$A_T \left\{ f = \exp \left[\frac{-6E_R T}{k\theta_D^2} \right] \right. \quad (6)$$

for $T > \frac{\theta_D}{2}$ where E_R is the Mössbauer recoil energy and θ_D is the Debye temperature of the solid. In the high temperature limit plots of $\ln A_T$ vs. T should be linear, and the results for the two compounds studied bear this out. For $(C_6H_5)_3SnSP(OC_2H_5)_2$ between 77 and 150K the slope of $-1.43 \times 10^{-2} K^{-1}$ is based upon seven points with intercept at 1.113 and a correlation coefficient of 0.999. For $(C_6H_5)_3SnSP(OC_3H_7-i)_2$ between 77 and 155K the slope of $-1.40 \times 10^{-2} K^{-1}$ is based upon nine points with intercept at 1.075 and a correlation coefficient of 0.998. These slopes are within experimental error identical, and with the isomer shift (IS) and QS data specify that we are dealing here with very similar lattice dynamics in the two cases.

The more tightly bound the tin atoms are in a lattice, the slower the decrease in f , and hence A_T , is found as the temperature is raised. The slope of the plot of $\ln A$ vs. T is thus characteristic of the lattice packing of molecules. Non-interacting, monomeric molecules exhibit slopes of ca. $-1.8 \times 10^{-2} K^{-1}$ no matter what the coordination number at tin. A lattice held in part by weak intermolecular interactions such as hydrogen bonding reduces this value to ca. $-1.7 \times 10^{-2} K^{-1}$. A more complex system of hydrogen bonds can further reduce the slope to ca. $-1.3 \times 10^{-2} K^{-1}$. Lattices which are strongly hydrogen bonded or in which the tin atom participates in one-, two- or three dimensional association exhibit slopes of ca. $-1.0 \times 10^{-2} K^{-1}$. Tin(II) oxide exhibits the most gentle slope yet reported ($-0.23 \times 10^{-2} K^{-1}$).^{37,38} Against this background, the slope of ca. $-1.40 \times 10^{-2} K^{-1}$

found for both the ethoxy and isopropoxy derivatives indicates a monomeric structure packed in a rather tight lattice. Comparison should be drawn with the corresponding slope data for tetraphenyltin, $-1.659 \times 10^{-2} \text{K}^{-1}$,^{39,30} for which a spectrum at ambient temperatures can be resolved.⁴¹

The effective vibrating mass model developed by Herber can be used to obtain the mass of the vibrating unit in the solid from the variation of the recoil-free fraction with temperature and the low energy ($<200 \text{cm}^{-1}$) lattice mode absorptions in the Raman spectrum.⁴² The molecularity of the vibrating unit is calculated from:

$$M_{\text{eff}} = - \frac{3E_{\gamma}^2 k}{(hc)^2 \omega_L^2} \left(\frac{dT}{d \ln A} \right) \quad (7)$$

where $\frac{d \ln A}{dT}$ is the slope of the plot of the normalized area under the Mössbauer resonance vs. temperature ($\sim -1.40 \times 10^{-2} \text{K}^{-1}$ for the compounds considered in Figure 1), and E_{γ} is the energy of the Mössbauer gamma-ray. The low-energy Raman spectrum which should contain the lattice mode frequency ω is shown in Figures 2 and 3 for the ethyl and isopropyl esters, while Table VI lists the correlation between the ω frequencies and the M_{eff} values. We are aware of no data in the literature which could serve as a guide for the assignment of the Raman-active bands below 50cm^{-1} . The molecular weights of the ethyl and isopropyl ester monomers are 535 and 563, respectively. Thus no band in either spectrum above those found at 34 and 37cm^{-1} , respectively, can correspond to the unique intermolecular, intra-unit cell vibration sought in this treatment. These bands correspond to the monomer. None of the other Raman frequencies observed correspond to a reasonable integer unit above the monomer, thus ruling out structure C. This finding corroborates the Mössbauer IS and QS data which specify four coordination at tin which rules out structure B, and the magnitude of the slope of the plot of area vs. temperature which also rules out a polymeric lattice as in structure C. Thus we are forced to conclude that the triphenyltin dithiophosphate esters adopt a unique, monomeric, monodentate structure such as A.

Acknowledgement.

Our work is supported by the Office of Naval Research (J.J.Z.). We thank the M&T Chemicals, Inc. for the donation of organotin starting materials, and Professor R.E. Frech for help with the Raman spectra.

Table I. Triorganotin Dithiophosphate Esters

$R_3SnS_2P(OR'_2)_2$					ΣC		ΣH	
<u>R</u>	<u>R'</u>	<u>Prep</u> ^a	<u>Yield</u> .%	<u>mp/bp</u> .°C.	<u>calcd</u>	<u>found</u>	<u>calcd</u>	<u>found</u>
C ₆ H ₅	CH ₃ ^c	2,3	72	83°	6.12 ^b	6.00 ^b		
	C ₂ H ₅ ^d	2,3	89	105°	5.80 ^b	5.65 ^b		
	n-C ₃ H ₇ ^e	2,3	65	63°	5.51 ^b	5.40 ^b		
	i-C ₃ H ₇	2,3	52	73.5-74.5°	51.16	51.01	5.20	5.27
	n-C ₄ H ₉ ^f	2	94	68-9°	5.26 ^b	5.10 ^b		
	i-C ₄ H ₉	1	63	52-54°	58.80	52.95	5.64	5.68
	C ₆ H ₅	1	77	121°-122°	57.07	57.10	4.00	4.17
CH ₃	CH ₃	3	25	g	18.71	20.34	4.71	5.08 ^h
	C ₂ H ₅	1,3	64	112°-115°/0.2 torr	24.09	23.89	5.49	5.41
	n-C ₃ H ₇	3	75	oil				
	i-C ₃ H ₇	3	75	105°-109°/ 0.4 torr	28.67	28.73	6.15	6.28
C ₆ H ₁₁	i-C ₃ H ₇	4		43-44°				

^a Numbers 1,2 and 3 correspond to the syntheses described by Eqs. 1, 2 and 3; 4 was used as received from the Stauffer Chemical Company. Its preparation was described in ref. 15 from the potassium salt of the acid (7.6g, 0.03 moles) and tricyclohexyltin chloride (10.1 g, 0.025 moles).

^b Analysis for phosphorus.

^c Ref. 3 reports a mp of 86°C.

^d Ref. 3 reports a mp of 105°; ref. 16 of 90°-91°C.

^e Ref 3 reports a mp of 63°C.

^f Ref. 3 reports a mp of 69.1°C.

^g This compound distilled over a wide temperature range, indicating some thermal decomposition. Purification could not be affected by gas chromatography. The composition is based upon n.m.r. and mass spectral data.

^h Molecular weight: calculated, 321; found (in benzene), 300.

Table II. ^{119}mSn Mössbauer Data at 77K

	IS, mm/s^a	QS, mm/s^b	$\Gamma_1 \text{ mm/s}^c$	$\Gamma_2 \text{ mm/s}^d$	ρ^e
$(\text{C}_6\text{H}_5)_3\text{SnS}_2\text{P}(\text{OCH}_3)_2$	1.27	2.07	1.12	1.22	1.63
$(\text{C}_6\text{H}_5)_3\text{SnS}_2\text{P}(\text{OC}_2\text{H}_5)_2$	1.26	2.08	1.10	1.24	1.65
$(\text{C}_6\text{H}_5)_3\text{SnS}_2\text{P}(\text{OC}_3\text{H}_7\text{-i})_2$	1.28	2.03	1.09	1.23	1.59
$(\text{C}_6\text{H}_5)_3\text{SnS}_2\text{P}(\text{OC}_3\text{H}_7\text{-n})_2$	1.26	2.03	1.08	1.22	1.61
$(\text{C}_6\text{H}_5)_3\text{SnS}_2\text{P}(\text{O-C}_4\text{H}_9\text{-i})_2$	1.28	1.94	1.08	1.50	1.52
$(\text{C}_6\text{H}_5)_3\text{SnS}_2\text{P}(\text{OC}_6\text{H}_5)_2$	1.31	2.32	1.08	1.30	1.77
$(\text{CH}_3)_3\text{SnS}_2\text{P}(\text{OC}_2\text{H}_5)_2$	1.38	3.09	1.38	1.55	2.24
$(\text{CH}_3)_3\text{SnS}_2\text{P}(\text{OC}_3\text{H}_7\text{-i})$	1.35	2.92	1.21	1.28	2.16
$(\text{cyclo-C}_6\text{H}_{11})_3\text{SnS}_2\text{P}(\text{OC}_3\text{H}_7\text{-i})_2$	1.52	2.56	1.08	1.32	1.68

$\underline{a}$ $\pm 0.02 \text{ mm/s}$.

$\underline{b}$ $\pm 0.03 \text{ mm/s}$.

$\underline{c}$ High velocity resonance, $\pm 0.04 \text{ mm/s}$.

$\underline{d}$ Low velocity resonance, $\pm 0.05 \text{ mm/s}$.

$\underline{e}$ QS/IS.

Table III. Infrared Spectral Data of the Triorganotin Dithiophosphate Esters, $R_3\text{SnSP}(\text{OR}')_2$, cm^{-1}

<u>$R=\text{C}_6\text{H}_5$; $R'=\text{CH}_3$</u>	<u>C_2H_5</u>	<u>$n\text{-C}_3\text{H}_7$</u>	<u>$i\text{-C}_3\text{H}_7$</u>	<u>$i\text{-C}_4\text{H}_9$</u>	<u>C_6H_5</u>	
	3065w 2995w 2990w 2935vw 2900vw 2370vw					
			1575vw	1574vw	1592sh 1587m 1575w 1484vs	
	1485m 1445vw 1433s 1390m			1428m	1429s	
					1364vw 1350vw 1330w 1300w 1261vw 1240w 1199s 1190m 1178vs	
1328w 1295w	1336w 1310w	1295w	1328vw 1295w 1254vw	1330vw 1295w	1330w 1300w 1261vw 1240w 1199s 1190m 1178vs	
			1185sh 1174m 1155w 1135m 1095m	1185vw 1155w(br) 1124w	1157vs	$\nu(\text{P}-\text{O}-\text{C})^a$
1166m	1160m	1145m(br)				
1154sh	1102w 1095w					
1065m	1075s 1044s(br)	1069s 1048m(br)	1069m 1060sh 1018vw	1070m 1046sh 1019w	1060vw 1022m 1004m 995m(?)	$\nu(\text{P}-\text{O}-\text{C})^a$
1007vs 990s	1015vs 998s	990s	990vs	991s		
	956vs 935s 924sh	967s(br)	970sh 965vs 932sh	959w 908w	981w 965w 933vs 912vs 901s 894vs 858vw	
		906vw	883m			
		832m 810w	846vw	860m 850m 818vw	825w(br)	
809s 794sh	805w 796sh 790s 770m				775vs	

Table III. (continued)

		748s	767s		764vs	
	740s		741w		747m	
722vs	732s	722s	723s	723s	737s	
	700s		691s	692s	729s	
633s(br)	655vs	655m	663s	655s	720sh	
		639m	648sh		695s	
					689m	
					675vs	$\nu_{\text{asym}}(\text{PS}_2)$
					660w	
					648vw	
					610vw	
486m	540m	514m(br)	505s	545w(br)	564m	
	515w			521m	525s	$\nu_{\text{sym}}(\text{PS}_2)$
			480w			
432m	446m	435s	435s	437m	489m	
					437s	

R = CH₃; R' = CH₃C₂H₅i-C₃H₇R = C₆H₁₁; R' = i-C₃H₇

2985m
2940s
2910m
2920m

2990vs
2940m
2910m
2880w

2975s
2930m
2920sh
2870w

1460sh
1452m
1438m

2780vw
1480m
1455sh
1446m
1393s
1370sh

1462m
1447m
1381s
1370s
1348w

1442s
1370m
1362sh
1349w
1340vw
1325vw
1292w
1263w

1294m(br)
1268vw
1190w

1173s

1164s

1175m
1138m
1102s

1175sh
1168m
1137m
1103s

 $\nu((\text{P})-\text{O}-\text{C})^{\text{a}}$

1100s

1040sh
1018vvs(br)

1045vs
1025vs
955vs(br)

985vs
962vs(br)
935sh
883s

1080w
1060vw
1038w
987vs
965vs
905w
880m
835w
800vw

 $\nu(\text{P}-\text{O}-(\text{C}))$

780vs(br)

788vs(br)

785sh
765vs

768s

 $\rho(\text{Sn}-\text{C})$

Table III. (continued)

745s	730sh	750sh	752w	
700s			719vw	
685sh	675sh	660w	665m	
655vs	658vs	645s	650s	$v_{\text{asym}}(\text{PS}_2)$
530s	540vs	538s		$v_{\text{asym}}(\text{Sn-C})$
510sh	508s	503m	541m	$v_{\text{asym}}(\text{PS}_2)$
495s				$v_{\text{sym}}(\text{Sn-C})$
			512w	
390w	380w	380w	480w	
				$v(\text{Sn-S})$

^asee Ref. 32.

Table IV. Proton Magnetic Resonance Data for the Triorganotin Dithiophosphate $\text{R}_3\text{SnP}(\text{OR})_2$

R	R'	$(\text{C}_6\text{H}_5)_3\text{Sn}^{\text{a}}$	$(\text{CH}_3)_3\text{Sn}^{\text{a}}$	$(\text{C}_6\text{H}_{11})_3\text{Sn}^{\text{a}}$	$\text{H}_{\text{a,b}}$	$\text{H}_{\text{a,b}}$	$\text{H}_{\text{a,b}}$
C_6H_5	CH_3	7.1-7.8m(15)			$ ^3\text{J}(^3\text{P}-\text{O}-\text{C}-^1\text{H}) = 15.5$		
C_6H_5	CH_2CH_3	7.2-7.8m (15)			$ ^3\text{J}(^3\text{P}-\text{O}-\text{C}-^1\text{H}) = 10.0$ $ ^3\text{J}(^1\text{H}-\text{C}-\text{C}-^1\text{H}) = 7.0$	$1.09\text{c}(6)$ $ ^3\text{J}(^3\text{P}-\text{O}-\text{C}-^1\text{H}) = 7.0$	
C_6H_5	$\text{CH}_2\text{CH}_2\text{CH}_3$	7.2-7.8m (15)			$ ^3\text{J}(^3\text{P}-\text{O}-\text{C}-^1\text{H}) = 9.5$ $ ^3\text{J}(^1\text{H}-\text{C}-\text{C}-^1\text{H}) = 6.5$	$0.7-1.7\text{m}(10)^{\text{c,d}}$ $ ^3\text{J}(^1\text{H}-\text{C}-\text{C}-^1\text{H}) = 6.0$	
C_6H_5	$\text{CH}(\text{CH}_3)_2$	7.12-7.87 (15)			$ ^3\text{J}(^3\text{P}-\text{O}-\text{C}-^1\text{H}) = 12.0$ $ ^3\text{J}(^1\text{H}-\text{C}-\text{C}-^1\text{H}) = 6.0$	$1.15\text{d}(12)$ $ ^3\text{J}(^1\text{H}-\text{C}-\text{C}-^1\text{H}) = 6.0$	
C_6H_5	$\text{CH}_2\text{CH}(\text{CH}_3)_2$	7.23-7.93m (15)			$ ^3\text{J}(^3\text{P}-\text{O}-\text{C}-^1\text{H}) = 9.0$ $ ^3\text{J}(^1\text{H}-\text{C}-\text{C}-^1\text{H}) = 6.5$	$3.64\text{m}(4)$ $ ^3\text{J}(^1\text{H}-\text{C}-\text{C}-^1\text{H}) = 6.5$	$1.4-2.0\text{m}(2)^{\text{d}}$ $0.79\text{d}(12)$
C_6H_5	C_6H_5	7.0-8.2m (25)					
CH_3	CH_3		$0.66\text{s}(9)$ $ ^2\text{J}(^{119}\text{Sn}-\text{C}-^1\text{H}) = 57.0$		$3.65\text{d}(6)$ $ ^3\text{J}(^3\text{P}-\text{O}-\text{C}-^1\text{H}) = 15.0$		
CH_3	CH_2CH_3		$0.68\text{s}(9)$ $ ^2\text{J}(^{119}\text{Sn}-\text{C}-^1\text{H}) = 57.5$		$4.16\text{m}(4)$ $ ^3\text{J}(^3\text{P}-\text{O}-\text{C}-^1\text{H}) = 10.0$ $ ^3\text{J}(^1\text{H}-\text{C}-\text{C}-^1\text{H}) = 7.5$	$1.36\text{c}(6)$	
CH_3	$\text{CH}(\text{CH}_3)_2$		$0.68\text{s}()$ $ ^2\text{J}(^{119}\text{Sn}-\text{C}-^1\text{H}) = 57.5$		$4.83\text{m}(2)$ $ ^3\text{J}(^3\text{P}-\text{O}-\text{C}-\text{H}) = 13.0$ $ ^3\text{J}(^1\text{H}-\text{C}-\text{C}-^1\text{H}) = 6.5$	$1.36\text{d}(12)$	

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Table IV. (continued)

R	R'	$(C_6H_5)_3Sn^a$	$(CH_3)_3Sn^a$	$(C_6H_{11})_3Sn^a$	$H_{\alpha}^{a,b}$	$H_{\beta}^{a,b}$	$H_{\gamma}^{a,b}$
CH_3^e	$CH(CH_3)_2$		1.00s(9) $ ^2J(^{119}Sn-C-^1H) = 70.0$		5.02m(2) $ ^3J(^{31}P-O-C-^1H) = 13.0$ $ ^3J(^1H-C-C-^1H) = 6.5$	1.38d(12) $ ^3J(^1H-C-C-^1H) = 6.5$	
C_6H_{11}	$CH(CH_3)_2$		1.00-2.50m(33) ^d	4.93m(2)	1.28d(12)		
				$ ^3J(^{31}P-O-C-^1H) = 12.0$	$ ^3J(^1H-C-C-^1H) = 6.0$		
					$ ^3J(^1H-C-C-^1H) = 6.0$		

^aShifts in ppm; coupling constants in Hz; the number of protons in resonance is given in parentheses; s=singlet; d=doublet; t=triplet; m=multiplet; dq=doublet of quartets. All spectra are recorded as CDCl₃ solutions, unless otherwise indicated.

^b $H_{\alpha}, \beta, \gamma$ refer to $R_3SnS_2P[O(CH_{\alpha})_x(CH_{\beta})_y(CH_{\gamma})_z]_2$

^cBoth H_{α} and H_{β} .

^dSatellites unresolvable.

^eSpectrum recorded as a dilute solution in pyridine.

Table V. Mass Spectral Data for $(\text{CH}_3)_3\text{SnS}_2\text{P}(\text{OR})_2$

<u>R = i-C₃H₇</u>	<u>Mass Number^a</u>	<u>Rel. Abund.</u>	<u>Assignment</u>
	363	29.7	$(\text{CH}_3)_2\text{SnS}_2\text{P}(\text{OC}_3\text{H}_7)_2^+$
	321	21.9	$(\text{CH}_3)_2\text{SnS}_2\text{P}(\text{OH})(\text{OC}_3\text{H}_7)^+$
	279	100.0	$(\text{CH}_3)_2\text{SnS}_2\text{P}(\text{OH})_2^+$
	261	14.2	$(\text{CH}_3)_2\text{SnS}_2\text{PO}^+$
	249	10.7	$\text{SnS}_2\text{P}(\text{OH})_2^+$
	245	19.6	$(\text{CH}_3)_2\text{SnSPO}_2^+$ (or $(\text{CH}_3)_2\text{SnS}_2\text{P}^+$)
	214	12.2	$\text{HS}_2\text{P}(\text{OC}_3\text{H}_7)_2^+ ?$
	183	43.0	$(\text{CH}_3)_2\text{SnSH}^+$
	165	47.5	$(\text{CH}_3)_3\text{Sn}^+$
	153	19.8	SnSH^+
	150	15.0	$(\text{CH}_3)_2\text{Sn}^+$
	135	24.2	$(\text{CH}_3)\text{Sn}^+$

<u>R = C₂H₅</u>			
	335	97.2	$(\text{CH}_3)_2\text{SnS}_2\text{P}(\text{OC}_2\text{H}_5)_2^+$
	307	19.7	$(\text{CH}_3)_2\text{SnS}_2\text{P}(\text{OH})\text{OC}_2\text{H}_5^+$
	279	63.0	$(\text{CH}_3)_2\text{SnS}_2\text{P}(\text{OH})_2^+$
	261	27.2	$(\text{CH}_3)_2\text{SnS}_2\text{PO}^+$
	249	13.1	$\text{SnS}_2\text{P}(\text{OH})_2^+$
	245	29.3	$(\text{CH}_3)_2\text{SnSPO}_2^+$ (or $(\text{CH}_3)_2\text{SnS}_2\text{P}^+$)
	229	14.5	$(\text{CH}_3)_2\text{SnSPO}^+$
	214	21.7	?
	211	28.6	?
	185	95.1	SnS_2H^+ or SnPSH_2^+
	165	100.0	$(\text{CH}_3)_3\text{Sn}^+$
148-157			overlapping clusters

Table V. (continued)

	135	61.7	$(\text{CH}_3)\text{Sn}^+$
	121	33.8	$(\text{CH}_3)\text{Sn}^+$
	120	23.7	Sn^+
R = CH_3	307	47.5	$(\text{CH}_3)_2\text{SnS}_2\text{P}(\text{OCH}_3)_2^+$
	277	39.0	$\text{SnS}_2\text{P}(\text{OCH}_3)_2^+$
	209-212	12.0-20.0	overlapping clusters
	200	32.7	? (no Sn)
	197	45.8	$(\text{CH}_3)\text{Sn}(\text{OCH}_3)_2^+$ or $(\text{CH}_3)\text{SnP}(\text{OCH}_2)^+$
	185	99.0	SnS_2H^+
	172	40.0	?
	165	100.0	$(\text{CH}_3)_3\text{Sn}^+$
	146-155	13.0-40.6	overlapping clusters
	135	58.6	$(\text{CH}_3)\text{Sn}^+$
	125	47.3	?
	121	22.1	SnH^+
	120	28.9	Sn^+

^aRepresents most intense peak for clusters containing tin, based on ^{120}Sn , ^{32}S , ^{16}O , ^{12}C , ^1H , ^{31}P .

Table VI. The Effective Vibrating Mass Model. Low Energy Lattice Mode Raman Frequencies and M_{eff} Values.

	ω	M_{eff}	Molecular Weight Multiple
$\overset{\text{S}}{\parallel}$ $(\text{C}_6\text{H}_5)_3\text{SnSP}(\text{OC}_2\text{H}_5)_2$	22	1487	2.78
	34	623	1.16
$\overset{\text{S}}{\parallel}$ $(\text{C}_6\text{H}_5)_3\text{SnSP}(\text{OC}_3\text{H}_7-1)_2$	23	1390	2.47
	33	675	1.20
	37	537	0.954
	50	294	0.522

Figure Captions

Figure 1. The plot of $\ln A$ (normalized to the area under the resonance curve at 77K) vs. temperature in K. The slopes are $-1.43 \times 10^{-2} \text{ K}^{-1}$ for the ethyl and $-1.40 \times 10^{-2} \text{ K}^{-1}$ for the isopropyl ester.

Figure 2. The low-energy, lattice-mode Raman spectrum of 0,0'-diethyldithiophosphatetriphenyltin.

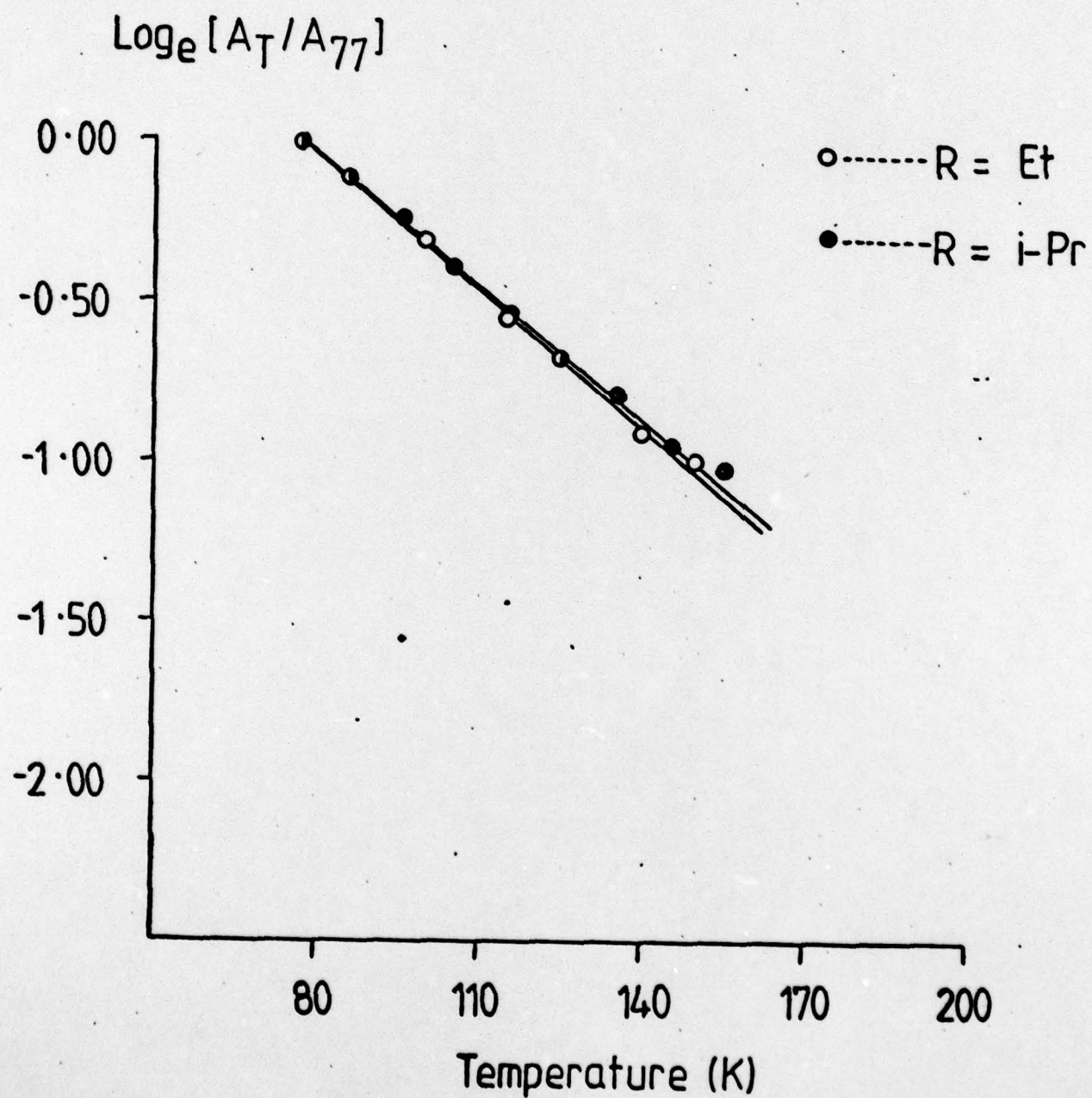
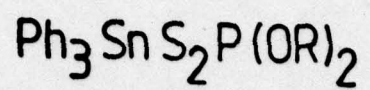
Figure 3. The low-energy, lattice-mode Raman spectrum of 0,0'-di-iso-propyldithiophosphatetriphenyltin, (a) $\lambda_0 = 4880$ @ 100 mw, (b) $\lambda_0 = 5145$ @ 200 mw.

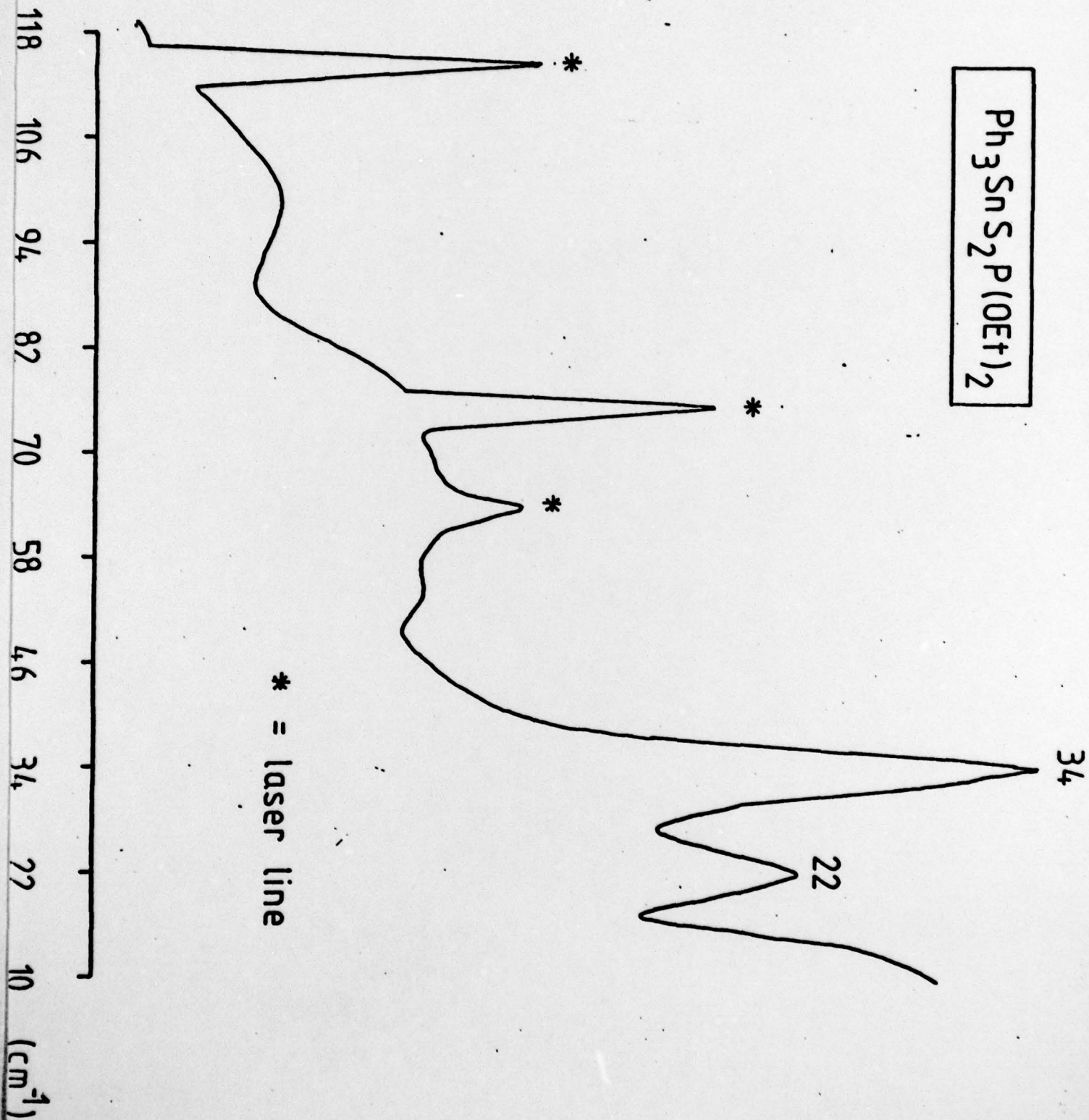
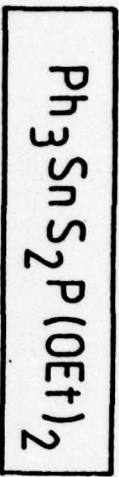
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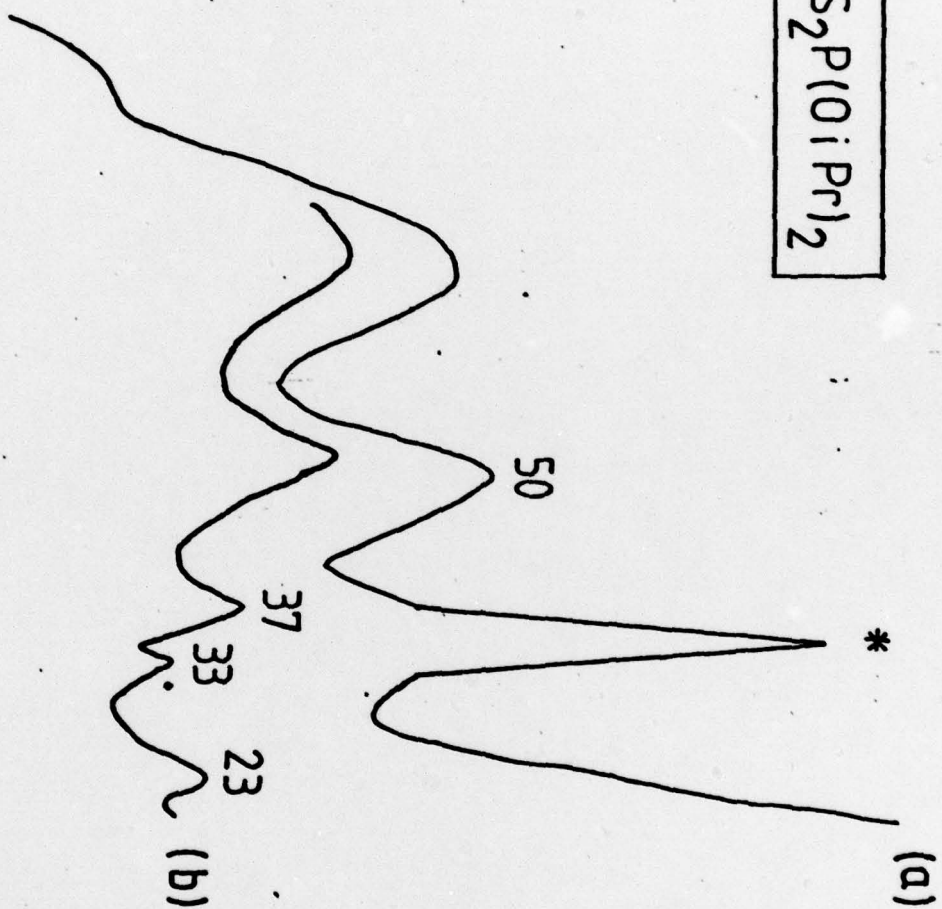
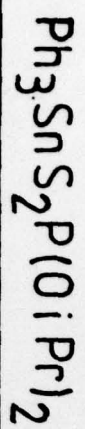
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* = laser line

88 76 64 52 40 28 16 (cm^{-1})