

MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1963-A

OFFICE OF NAVAL RESEARCH

Contract N00014-77-C-0432

Task No. NR 053-636

TECHNICAL REPORT NO. 25

9

11

LEVEL III

14 TR-25

AD A092239

Oxy- and Thio Phosphorus Acid Derivatives of Tin.
VI. The Crystal and Molecular Structures of Bis(dimethyl dithiophosphinato)dimethyltin(IV) and Bis(diethyl dithiophosphinato)diiodotin(IV) at 138K

by

15 N00014-77-C-0432

10

K. C. Molloy, M. B. Hossain, D. van der Helm and J. J. Zuckerman

F. P. Mullins

Department of Chemistry

University of Oklahoma

Norman, OK 73019

and

F. P. Mullins

Department of Chemistry

Mount St. Vincent University

Halifax, Nova Scotia B3M 3J6

Canada

Prepared for Publication

in

Inorganic Chemistry

Reproduction in whole or in part is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited

8011 20 005

403980

DTIC ELECTED NOV 23 1980

BDC FILE COPY

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 25 ✓	2. GOVT ACCESSION NO. AD-A092239	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Oxy- and Thio-Phosphorus Acid Derivatives of Tin. VII. The Crystal and Molecular Structures of Bis(dimethyldithiophosphinato)dimethyltin(IV) and Bis(diethyl dithiophosphinato)diiodotin(IV)		5. TYPE OF REPORT & PERIOD COVERED
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) K.C. Molloy, M.B. Hossain, D. van der Helm, J.J. Zuckerman and F.P. Mullins		8. CONTRACT OR GRANT NUMBER(s) N00014-77-C-0432 ✓
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Oklahoma Department of Chemistry Norman, OK 73019		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 053-636
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		12. REPORT DATE 15 November 1980
		13. NUMBER OF PAGES 29
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. 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, if different from Report) Prepared for Publication in Inorganic Chemistry		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Organotin, Dimethyltin(IV), Diiodotin(IV), Phosphoric Acids, Dithiophosphoric Acids, X-ray Diffraction, Crystal Structure, Molecular Structure, Dithio- phosphophatinate Ester Ligands, Monomers, <u>trans</u> -Dimethyltin(IV), <u>cis</u> - Diiodotin(IV), Octahedron, Anisobidentate Chelation, Sulfur Intermolecular Contacts, Virtual Polymers.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Bis(dimethyl dithiophosphinato)dimethyltin(IV), C ₆ H ₁₈ P ₂ S ₄ Sn, forms colorless crystals, mp=215-217°C, in the orthorhombic space group C222 ₁ with a=6.218(2), b=11.001(4) and c=22.347(20) Å, v=1528.6 Å ³ , Z=4 and ρ _{calc} =1.73 g cm ⁻³ . The structure was solved by three-dimensional Patterson and difference Fourier techniques from 914 reflections measured at 138±2 K on an Enraf-Nonius CAD/4 automatic diffractometer using monochromated MoK _α radiation to a final R value of 0.029 for the 786 reflections included in the least squares sums. The molecule is six-coordinated in a distorted octahedral geometry with the four		

DD FORM 1473

1 JAN 73

EDITION OF 1 NOV 68 IS OBSOLETE
S/N 0102-LF-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

4. at 138 K.

20. sulfur atoms of the anisobidentate chelating dithiophosphinato ligands lying in a plane with the central tin atom while the dimethyltin system makes a trans- C-Sn-C angle of $122.6(8)^\circ$ (127.5° predicted from the tin-119m Mössbauer Quadrupole Splitting value of 3.00 mm s^{-1}). The ester (shorter) and dative (longer) pairs of Sn-S bonds are found on opposite sides of the girdle of the molecule, cis-oriented. The tin atoms stack in a linear array along the a-axis at a distance of $6.218(2) \text{ \AA}$, well within the bridging range of a dithiophosphinate ligand.

Bis(diethyl dithiophosphinato)diiodotin(IV), $\text{C}_8\text{H}_{20}\text{I}_2\text{P}_2\text{S}_4\text{Sn}$, forms red crystals, $\text{mp}=174\text{--}176^\circ\text{C}$, in the monoclinic space group $\text{P}2_1/a$ with $a=14.817(4)$, $b=11.223(3)$, $c=13.170(5) \text{ \AA}$, $\beta=115.53(3)^\circ$, $V=1976.2 \text{ \AA}^3$, $Z=4$ and $\rho_{\text{calc}}=2.28 \text{ g cm}^{-3}$. The structure was solved by three-dimensional Patterson and difference Fourier techniques from 4073 reflections measured at 138.2 K on the above automatic diffractometer using monochromated MoK α radiation to a final R value of 0.058 for the 3746 reflections included in the least squares sums. This molecule is octahedral at tin with a cis-diiodotin system. Opposite each tin iodine bond lies a longer Sn-S dative bond, while the sulfur atoms of the ester system are in a trans-arrangement in contrast to the cis-orientation of the corresponding atoms in the structure of the first title compound. The phosphorus atoms in the dithiophosphinate ligands are found at the center of a distorted tetrahedral system in both structures.

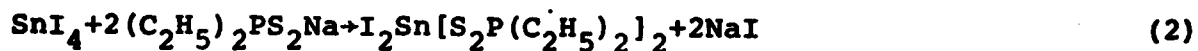
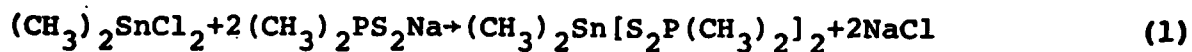
Accession For	
NTIS CAA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Special

A

A series of diorgano- and dihalotin(IV) dithiophosphinates was prepared by us (F.P.M.) who brought to bear tin-119m Mössbauer, electric dipole moment and infrared data on the question of the geometry about tin in these complexes.² Comparison with the analogous and better known dithiocarbamatotin(IV) complexes led to the view that the tin atom adopts a distorted octahedral geometry in the title compounds. The very large electric dipole moments in the dihalo derivatives require aniscbidentate phosphinate ligand chelation and a cis-arrangement of both the halogen atoms as well as the Sn←S dative bonds. Similarly, the dipole moments of the diorganotin derivatives, $R_2Sn[S_2PR'_2]_2$, were interpreted as demanding non-equivalent Sn-S bonds in a cis- arrangement of Sn-S ester and Sn←S dative bonds with trans-diorganotin groups. The difference in the infrared ν_{asym} (P-S) and ν_{sym} (P-S) stretching frequencies was used to infer the presence of non-equivalent P-S and, therefore, non-equivalent Sn-S bonds in these complexes. Tin-119m Mössbauer Isomer Shift (I.S.) and Quadrupole Splitting (Q.S.) values for the diorganotin dithiophosphinates are similar to those for the analogous trans-diorganotin(IV) dithiophosphato, $S_2P(OR')_2$, and dithiocarbamato, $S_2CNR'_2$, complexes, suggesting a similar anisobidentate character in the chelating ligands, and consequent distortion from 180° in the C-Sn-C bond angle, as is seen in, for example, $(CH_3)_2Sn[S_2CN(CH_3)_2]_2$.³ The Q.S. values for the dimethyltin derivatives of the dithio-phosphinato, phosphato and carbamato ligands are 3.00,² 3.35⁴ and (3.14⁵ or 3.04⁶), respectively. The Mössbauer data for the dihalo complexes (I.S. = ca. 0.90 mm s⁻¹; Q.S. = 0.0 mm s⁻¹) are consistent with a six-coordinated geometry at tin with cis-halogen atoms.

Specific physical and spectroscopic properties for the title compounds are listed in Table I. The compounds were prepared from the

reaction of the sodium salt of the dithiophosphinic acid and a diorganotin dihalide or tin(IV) halide in a 2:1 ratio:



Pursuing our interest in the structural chemistry⁷ of biocidal organotin compounds,⁸ and in particular the derivatives of thio- and oxyphosphorus acids,^{1,4,9-11} we have investigated representatives of the diorgano- and dihalodithiophosphinatotin(IV) complexes to test whether the predicted geometries² would in fact be found.

Experimental Section

Crystal Data. Data were obtained at $138 \pm 2\text{K}$ with an Enraf-Nonius CAD-4 automatic counter diffractometer controlled by a PDP-8/e computer and fitted with a low temperature apparatus. Crystal data are listed in Table II.

Details of our diffractometer, method of data collection and data reduction have been outlined previously.¹ Specific parameters pertaining to the collection of the two data sets are summarized in Table III. For both compounds, the structure factors for each reflection were assigned individual weights.¹

Structure Determination and Refinement

Bis(dimethyl dithiophosphinato)dimethyltin(IV), $(\text{CH}_3)_2\text{Sn}[\text{S}_2\text{P}(\text{CH}_3)_2]_2$.

From an inspection of the three-dimensional Patterson map the tin atom was found to occupy the special position $x, 0, 0$ (that is, lying on a 2-fold axis). The Patterson map was interpreted to yield the positions of all the remaining non-hydrogen atoms. Following three cycles of least squares isotropic refinement¹² the atomic thermal parameters were allowed to vary anisotropically and refinement continued for a further four cycles. At this point anomalous dispersion corrections for tin, phosphorus and sulfur were included and anisotropic refinement continued for six additional cycles, to give a final R value of 0.029 for the 786 reflections included in the least squares sums

and 0.038 over all data.

A final difference Fourier indicated some residual electron density (ca. $1 \text{ e } \text{\AA}^3$) in the vicinity of the tin atom and several smaller peaks (ca. $0.5 \text{ e } \text{\AA}^3$), corresponding to the probable positions of hydrogen atoms, although no systematic attempt was made to locate the latter.

Final atomic parameters (positional and thermal) are given in Tables IV and V; final interatomic distances and angles are given in Tables VI and VII, respectively. The asymmetric unit (with atom numbering scheme) is shown in Figure 1, and the arrangement of molecules within the unit cell in Figure 2.

Bis(diethyl dithiophosphinato)diodotin(IV), $\text{I}_2\text{Sn}[\text{S}_2\text{P}(\text{C}_2\text{H}_5)_2]_2$.

The positions of the three heavy atoms [Sn(1), I(1), I(2)] were located from a three-dimensional Patterson map and were used to phase the initial structure factor calculations. Sequential refinement¹² followed by difference Fourier syntheses was used to locate the positions of the non-hydrogen light atoms. All atoms were refined first isotropically and then anisotropically to an R factor of 0.060 for the 3742 reflections included in the least squares sums. Since a difference Fourier synthesis indicated areas of electron density remaining about the tin, iodine, sulfur and phosphorus atoms, an anomalous dispersion correction was made for each of these atom types. Anisotropic least squares refinement was continued to a final R factor of 0.058 for the 3746 reflections included in the least squares sums and 0.064 over all data.

A final difference Fourier synthesis still contained large areas of electron density (ca. $2.5 \text{ e } \text{\AA}^3$) in the proximity of the three heavy atoms. No attempt was made to locate hydrogen atoms.

Final positional and thermal atomic parameters and intermolecular distances and angles are given in Tables VIII, IX, X and XI, respectively. The asymmetric unit (with atom numbering) and unit cell contents are shown in Figures 3 and 4, respectively.

The scattering factors used in both determinations were for neutral atoms and were taken from references 13 (Sn, C, P, S and I) and 14 (H).

Description and Discussion of the Structures

The predictions on the basis of previous physical and spectroscopic data² are entirely borne out in the structures of the title compounds. Both are six-coordinated, distorted octahedral in geometry with chelating anisobidentate dithiophosphinato ligands. The diorganotin derivative shown in Figure 1 has trans-dimethyl groups while the diiodo analogue in Figure 3 has a cis-SnI₂ system. The respective molecules in their unit cells are shown in Figures 2 and 4.

Understanding these and related chelated structures involves first an analysis to determine the identity of the sulfur atoms, that is, whether belonging to the covalently bound ester system, $\text{>P}^{\text{S}}\text{-S-Sn}$, or to the datively bound $\text{>P}^{\text{S}}=\text{S}\rightarrow\text{Sn}$ system. In the analogous dithiophosphate ester derivatives of the metals, it has been noted that the more tightly the sulfur atom is bound to the metal atom, then the longer is its bond with phosphorus.¹⁵ Put the other way around, the shorter bonds to phosphorus can be written in each case as P=S, and are associated with the longer, coordinate covalent sulfur-tin interaction. These shorter, P=S distances are found for the dithiophosphate ester complexes to lie in the range 1.85-1.95 Å, with the corresponding single-bonded, P-S distances at 1.99-2.19 Å.¹⁵ Direct comparison can be made to three recent molecular structure determinations of dithiophosphate ester derivatives of tin(II)⁹ and di-¹ and tri-phenyltin(IV)¹⁰ from this laboratory, plus another from the literature.¹⁶

The internuclear distances in the ester P-S-Sn and dative P=S→Sn linkages are listed in Table XII. Except for bis(O,O'-diisopropyl dithiophosphato)diphenyltin(IV), $[(i-C_3H_7O)_2PS_2]_2Sn(C_6H_5)_2$, which contains symmetrically chelating ligands, and must, therefore, involve extensive electron delocalization within the $-S^{\ominus}-P^{\oplus}-S$ system, it is easy to distinguish the ester from the dative portion of these chelating ligands.

Comparison of the tin-sulfur interatomic distances in the dimethyltin derivative with the analogous chelated systems listed in Table XII, reveals that the dative S→Sn bonds in the title compound are the longest, while the covalent S-Sn bonds are the shortest [excluding $(C_2H_5O)_2PS_2Sn(C_6H_5)_3$ in which the dithiophosphato ligand is monodentate]. In addition, the short ester S-Sn bond is associated with a contiguous P-S bond which is the longest observed, again with the exception of the monodentate $(C_2H_5O)_2PS_2Sn(C_6H_5)_3$. The distances found for the P-S and S-Sn bonds do not seem to be affected by the change of substituent at the phosphorus atom from the alkoxy and phenoxy groups of the dithiophosphates to the aliphatic methyl- and ethyl-residues of the title compounds. The P=S bond in the monodentate $(C_2H_5O)_2PS_2Sn(C_6H_5)_3$ is shorter than in the title compounds since the dative S-Sn bond is longer, or non-existent, but the P=S bond in the more closely related octahedral $(C_2H_5O)_2PS_2Sn(C_6H_5)_2$ is also shorter, while the dative S→Sn bond in the latter is shorter than in our dimethyltin derivative as well.

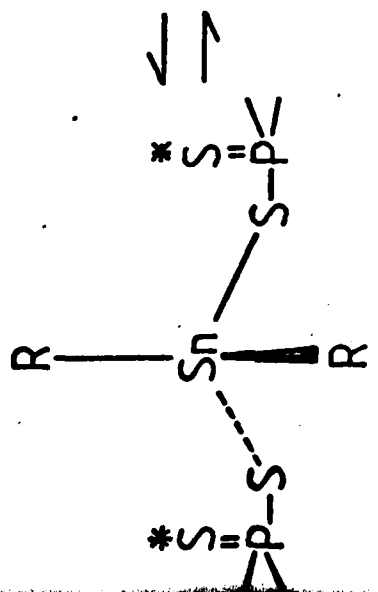
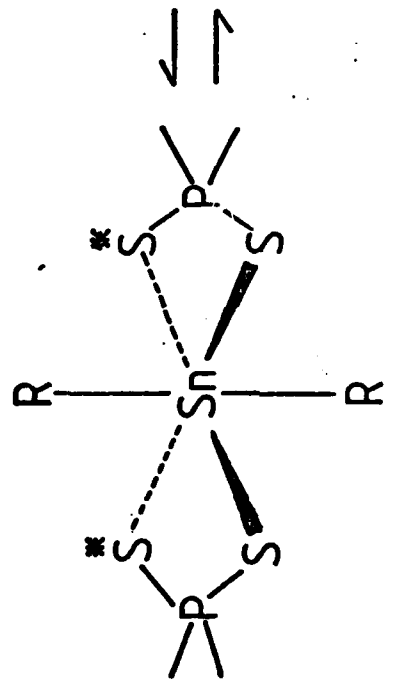
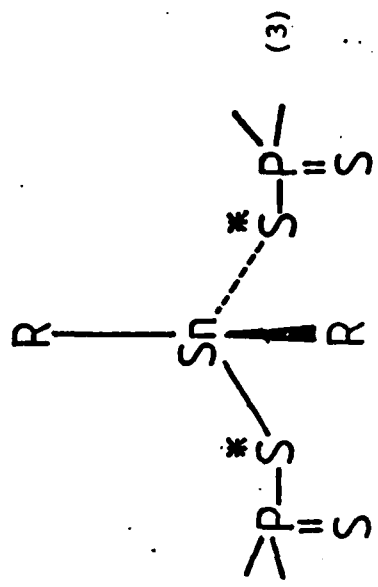
In the severely anisobidentate bis(O,O'-diethyl dithiophosphato)-diphenyltin(IV), $[(C_2H_5O)_2PS_2]_2Sn(C_6H_5)_2$, the ester and dative pairs of S-Sn bonds are found on opposite sides of the girdle of the molecule, cis-oriented.¹⁶ This is also the case for the title compound, bis-

(dimethyl dithiophosphinato)dimethyltin(IV), $[(\text{CH}_3)_2\text{PS}_2]_2\text{Sn}(\text{CH}_3)_2$. The geometry at the tin atom can be described as a badly distorted tetrahedron in which the C-Sn-C angle made by the dimethyltin system has opened to $122.6(8)^\circ$, while the angle at tin between the two ester-bound sulfur atoms [S(1)-Sn(1)-S(1')] has closed to $79.2(2)^\circ$. The compound is, however, unambiguously six-coordinated, with the four sulfur atoms about the central tin atom around the girdle of the molecule lying in a plane defined by the equation $-11.001y + 0.110z = 0.000$. The maximum deviation from the plane is $\pm 0.009 \text{ \AA}$ for the S(1) and S(1') atoms. The sum of the four relevant S-Sn-S angles [S(1)-Sn(1)-S(2) = S(1')-Sn(1)-S(2') = $68.9(1)^\circ$; S(1)-Sn(1)-S(1') = $79.9(2)^\circ$; S(2)-Sn(1)-S(2') = $142.3(1)^\circ$] is 360.0° .

Alternatively, it is possible to think of the structure as a frozen intermediate in the intramolecular exchange reaction which would scramble the tin-sulfur linkages:¹⁷

Equation 3

Our structural studies thus far conducted on dithiophosphatotin systems have elucidated a four-coordinated, monodentate starting material,¹⁰ the diorganotin(IV) title complex on its way toward the exchange depicted in Eqn. 3 and the symmetrical system lying almost precisely between starting material and product in the complex bis(O,O'-diisopropylidithiophosphato)diphenyltin(IV).¹ The usual nomenclature of kinetics is confusing for this process. Equilibrations of the kind depicted in Eq. 3 would retain configuration. If one S* enters as one S leaves the tin atom coordination sphere, then the reaction would be considered an S_N2 rearrangement. However, since both S and S* belong to the same molecule, first-order kinetics would be followed, and in



this sense the reaction is S_N1 . The process reflected in the structure of the title compounds is the simultaneous addition of two ligand atoms, S^* , to a tetrahedral R_2SnS_2 molecule to give the octahedral intermediate for a disubstitution reaction. Dunitz has termed this double addition-elimination an S_N3 reaction,¹⁷ but since both S^* atoms belong to the same molecule, first-order kinetics would again be followed. Sommer discussed long ago the mechanisms and intermediates in reactions of organosilyl derivatives which lead to retention of configuration in terms of frontside attack.¹⁸

The Mössbauer Q.S. value measured for the dimethyltin derivative is 3.00 mm/s.² A simple point charge model can be used to rationalize the changes in the magnitude of the Q.S. values as a function of the C-Sn-C angle in six-coordinated, $(CH_3)_2Sn(IV)$ structures.¹⁹ According to this treatment, the splitting is generated by the $(CH_3)_2Sn(IV)$ unit only, the contribution of the other ligands being negligible, and it is assumed that there will be no sign inversion over the range of systems compared. Nevertheless, the relationship:

$$|Q.S.| = 4\{CH_3\}[1-3 \sin^2\theta \cos^2\theta]^{1/2} \quad (4)$$

where $\{CH_3\}$ is $1/2e^2Q[CH_3]$, the partial Q.S., taken as -1.03 mm/s, and the angle C-Sn-C is $(180-2\theta)^\circ$,¹⁹ is supported by abundant structural data for six-coordinated, dimethyltin(IV) compounds.⁷ The Q.S. value of 3.00 mm/s for our dimethyltin(IV) derivative gives a C-Sn-C angle of 127.5° vs. the angle of $122.6(8)^\circ$ observed. We consider this result as further support for the concept of using Q.S. values to predict structure in the diorganotin(IV) systems.

The diiodotin(IV) derivative, being cis-oriented, is a special case and must be discussed separately. Here the question of which type of S-Sn bond is found trans- to the Sn-I linkage is of interest,

As can be seen in Figure 3, in each it is a long, dative S→Sn bond [Sn(1)-S(2) = 2.621(2); Sn(1)-S(4) = 2.593(2) Å] that is so located. The arrangement of atoms about the tin atom describes a distorted octahedron in which the cis- angle I(1)-Sn(1)-I(2) is 93.32(2)°, and the angle at the tin atom between the sulfur atoms of the ester system, S(1)-Sn(1)-S(3), is 167.30(7)°, describing a trans-arrangement in contrast to the cis- orientation of the corresponding atoms in the dimethyltin derivative. The mean trans-angle is 168.38° and the mean cis-angle is 90.38°. Clearly, this structure represents a position further along the pathway of the sulfur atom scrambling reaction analogous to Eqn. 3 than in the dimethyltin case, but now involving a cis-oriented intermediate.

The phosphorus atoms in the dithiophosphate ligands are found at the center of a distorted tetrahedral system in each case with two carbon and two sulfur atom nearest neighbors, one of the latter double bonded. In the analogous dithiophosphate ligand the angles involving the more electronegative oxygen atoms are, as expected on the basis of isovalent hybridization, smaller than those involving the double-bonded P=S sulfur atoms.^{1,10} In the dimethyltin dithiophosphate case the relative magnitudes of the angles at phosphorus are: S-P-S > C-P-S > C-P-C, except for the S(2)-P(1)-C(1) angle which is greatest. In the diiodo case: S-P-C > S-P-S > C-P-C. Hence, in the dimethyltin case sulfur is behaving in a weakly electronegative fashion, that is, less electronegative than carbon. Thus it is perhaps not surprising that the dative bonds it forms to tin are relatively long. Identifying the relative electronegativities of carbon and sulfur in the diiodotin case is less straightforward, but it appears from the similarity in the S-P-S and C-P-C angles that the electronegativities are approximately equal. This is reflected in rather similar dative and covalent S-Sn

bond lengths (Table XII), arising from a relatively strong coordinate S Sn interaction.

In bis(dimethyl dithiophosphinato)dimethyltin(IV) the molecules stack along the a-axis. Figure 2 shows the arrangement of the molecules in the unit cell which produces a linear tin-tin array with an intermetallic distance of 6.218(2) Å along the a-axis. Figure 5 shows the dithiophosphate ligand systems about two adjacent tin atoms along this axis, with the shortest intermolecular contacts (excluding carbon). The shortest intermolecular sulfur-sulfur contact [S(1)-S(2'') and S(1')-S(2''')] is 3.594 Å which occurs above and below the tin-tin axis of propagation. The van der Waals radius of sulfur has been quoted as 1.73 Å,²⁰ and thus these intermolecular contact distances can at best only reflect a weak interaction between the sulfur atoms of adjacent molecules.

We have recently noted a similar situation in the corresponding bis(O,O'-diisopropyl dithiophosphato)diphenyltin(IV) where the tin atoms lie at 6.341 Å intervals along the c-axis, and the sulfur atoms of adjacent molecules are brought within 3.46 Å above and below this axis. In this case, however, the P-Sn-P vector is not normal to the c-axis, but instead the ligand system is rotated somewhat about the tin atom to bring pairs of sulfur atoms on opposite sides of alternating molecules together at 3.30 Å.¹

In both cases, however, the relatively short tin-tin intermetallic distances along the axes is within the expected bridging capability for a dithiophosphorus ligand. This means that the four sulfur and two phosphorus atoms that chelate each tin atom in these structures could be rearranged to lie between instead of about the

tin atoms, thus linking the diorganotin(IV) units together at an equivalent distance into an isomeric polymer of equal dimensions and density to the assemblage of monomers actually found. In the analogous bis(O,O'-diisopropyl dithiophosphato)diphenyltin(IV) system referred to above, we termed this structure a virtual polymer. The metal complexes of the parent phosphinates themselves generally adopt bridged structures to give actual polymers,^{21,22} and the zinc(II) and cobalt(II) diethyl dithiophosphinates are dimers in which there are both terminal, chelating and bridging dithiophosphinate ligands. In the zinc(II) solid, however, the metal-metal distance is 4.25 Å (mean) and the S-P-S angle in the bridging ligand opens to 115.7° (mean) compared to the 109.6° (mean) value for the terminal, chelating ligands. However, this angle opening is apparently accompanied by a twist in the bridging ligands which has the effect of bringing the zinc atoms closer together.²³

The realization of the true polymeric isomer of the dimethyltin(IV) title compound must await the discovery of methods capable of directing synthesis and separation toward this end.

We conclude by noting that the unstructured iodine atom substituent with its longer bond to the central tin atom [2.8088 Å mean] can be accommodated in the cis-configuration which is preferred in these octahedral, SnX_4B_2 systems, whenever possible,⁷ while the structured methyl group which is held closer to the central tin atom [2.132(8) Å] is forced into a less-favorable trans-configuration.

Acknowledgement. Our work is supported by the Office of Naval Research and the National Science Foundation through Grant CHE-78-26548 (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.

References and Notes

- (1) For Part V of this series see Molloy, K. C.; Hossain, M. B.; van der Helm, D.; Zuckerman, J. J.; Haiduc, I. Inorg. Chem. 1980, 19, 0000.
- (2) Mullins, F. P. J. Inorg. Nucl. Chem. 1979, 41, 633.
- (3) Kimura, T.; Yasuoka, N.; Kasai, N.; Kakudo, M. Bull. Chem. Soc. Japan 1972, 45, 1649.
- (4) Lefferts, J. L.; Molloy, K. C.; Zuckerman, J. J.; Haiduc, I.; Curtui, M.; Guta, C.; Ruse, D. Inorg. Chem., 1980, 19, 0000.
- (5) Fitzsimmons, B. W.; Owusu, A. A.; Seely, N. J.; Smith, A. W. J. Chem. Soc. (A) 1970, 935.
- (6) DeVries, J. L. K. F.; Herber, R. H. Inorg. Chem. 1972, 11, 2458.
- (7) Zubieta, J. A.; Zuckerman, J. J. Prog. Inorg. Chem. 1978, 24, 251.
- (8) Zuckerman, J. J.; Reisdorf, R. P.; Ellis, H. V., III; Wilkinson, R. R. Chemical Problems in the Environment: Occurrence and Fate of the Organoelements, ed. by Bellama, J. M.; Brinkman, F. E. ACS Symposium Series No. 82. American Chemical Society, Washington, DC, 1978, 388.
- (9) Lefferts, J. L.; Hossain, M. B.; Molloy, K. C.; van der Helm, D.; Zuckerman, J. J. Angew. Chem. Int. Ed. Engl. 1980, 19, 0000.
- (10) Molloy, K. C.; Hossain, M. B.; van der Helm, D.; Zuckerman, J. J.; Haiduc, I. Inorg. Chem. 1979, 18, 3507.
- (11) Lefferts, J. L.; Molloy, K. C.; Zuckerman, J. J.; Haiduc, I.; Guta, C.; Ruse, D. Inorg. Chem. 1980, 19, 0000.
- (12) Ahmed, F. R., SFLS Program NCR-10, National Research Council, Ottawa, Canada, 1966.

- (13) "International Tables for X-ray Crystallography"; Kynoch Press, Birmingham; England, 1974; Vol. IV, p. 72.
- (14) Stewart, R. F.; Davidson, E. R.; Simpson, W. J. J. Chem. Phys. 1965, 42, 3175.
- (15) Wasson, J. R.; Woltermann, G. M.; Stoklosa, H. J. Fortschr. Chem. Forsch. 1973, 35, 65.
- (16) Lieblich, B. W.; Tomassini, M. Acta Crystallogr. Sect. B 1978, 34, 944.
- (17) D. Britton and J. D. Dunitz, private communication, 1980.
- (18) L. H. Sommer, Stereochemistry, Mechanism and Silicon, McGraw-Hill Book Co., 1965.
- (19) Sham, T. K.; Bancroft, G. M. Inorg. Chem. 1975, 14, 2281.
- (20) van der Helm, D.; Lessor, A. E., Jr.; Merritt, L. L., Jr. Acta Crystallogr. 1962, 15, 1227.
- (21) Giancotti, V.; Giordano, F.; Radnaccio, L.; Ripamonti, A. J. Chem. Soc. (A), 1968, 757.
- (22) Giordano, F.; Randaccio, L.; Ripamonti, A. J. Chem. Soc., Chem. Commun. 1968, 1014.
- (23) Calligaris, M.; Nardin, G.; Ripamonti, A. J. Chem. Soc., (A), 1970, 714.

Table I. Physical and Spectroscopic Data for the Two Title Compounds²

<u>Compound</u>	<u>Color</u>	<u>Mp°C</u>	ν_{asym} (P-S)	ν_{sym} (P-S)	<u>Q.S.^a</u>	$\frac{\nu_D}{\nu_D}$
$(\text{CH}_3)_2\text{Sn}[\text{S}_2\text{P}(\text{CH}_3)_2]_2$	colorless	215-217°	601, 593 cm^{-1}	484 cm^{-1}	3.00 mm/s	3.53
$\text{I}_2\text{Sn}[\text{S}_2\text{P}(\text{C}_2\text{H}_5)_2]_2$	red	174-176°	581, 569 cm^{-1}	503, 484 cm^{-1}	0.00 ^b	8.1

^a $\pm 0.05 \text{ mm s}^{-1}$

^bThe width at half-height Γ , is 0.93 mm/sec

Table II. Crystal Data for the Two Title Compounds

	$(\text{CH}_3)_2\text{Sn}[\text{S}_2\text{P}(\text{CH}_3)_2]_2$	$\text{I}_2\text{Sn}[\text{S}_2\text{P}(\text{C}_2\text{H}_5)_2]_2$
formula	$\text{C}_6\text{H}_{18}\text{P}_2\text{S}_4\text{Sn}$	$\text{C}_8\text{H}_{20}\text{I}_2\text{P}_2\text{S}_4\text{Sn}$
fw	399.11	678.97
crystal system	orthorhombic	monoclinic
a, Å ^a	6.218(2)	14.817(4)
b, Å ^a	11.001(4)	11.223(3)
c, Å ^a	22.347(20)	13.170(5)
β, deg ^a	90	115.53(3)
v, Å ³	1528.6	1976.2
space group	$\text{C}222_1^b$	$\text{P}2_1/a^c$
z	4	4
F(000)	792	1272
D _{calcd} , gm cm ⁻³	1.73	2.28
μ, cm ⁻¹	23.8	50.0
Dimensions of Data Crystal	0.25x0.25x0.10 mm	0.15x0.30x0.35 mm

^aFrom ±2θ values of 48 reflections, using MoKα₁ radiation (λ=0.70926 Å).

^bBased upon systematic absences: $h\bar{k}l$, $h+k=2n+1$; $00l$, $l=2n+1$.

^cBased upon systematic absences: $h0l$, $h=2n+1$; $0k0$, $k=2n+1$.

Table III. Data Collection Parameters for $(\text{CH}_3)_2\text{Sn}[\text{S}_2\text{P}(\text{CH}_3)_2]_2$ and $\text{I}_2\text{Sn}[\text{S}_2\text{P}(\text{C}_2\text{H}_5)_2]_2$

	$(\text{CH}_3)_2\text{Sn}[\text{S}_2\text{P}(\text{CH}_3)_2]_2$	$\text{I}_2\text{Sn}[\text{S}_2\text{P}(\text{C}_2\text{H}_5)_2]_2$
Diffractometer	Enraf-Nonius CAD/4	Enraf-Nonius CAD/4
Radiation	MoK_α ($\lambda=0.7121 \text{ \AA}$)	MoK_α ($\lambda=0.7121 \text{ \AA}$)
Temperature	138±2K	138±2K
Scan Technique	θ - 2θ	θ - 2θ
2θ Limit	$0 \leq 2\theta \leq 53^\circ$	$1 \leq 2\theta \leq 53$
Scan Time	50 sec	50 sec
Scan Angle	$(0.8+0.2 \tan \theta)$	$(0.8+0.2 \tan \theta)$
Aperture Width	$(3.5+0.86 \tan \theta)$	$(3.0+0.86 \tan \theta)$
Aperture Height	6 mm	6 mm
Aperture Distance	173 mm	173 mm
Monitor Reflection	3 1 4	$\bar{4}$ 0 8
Intensity Monitor	3600 s	2500 s
Max. Fluctuation in Monitor	<2.5%	<3.5%
Orientation Monitors	200 reflections ^a	200 reflections ^b
Number of Unique Data	914	4073
Number of Observed Data ^c	805	3816
Corrections	Lorentz Polarization Anomalous Dispersion	Lorentz Polarization Absorption Anomalous Dispersion

^aNew orientation matrix if angular change greater than 0.1° . Orientation matrix based upon 17 reflections.

^bNew orientation matrix if angular change greater than 0.1° . Orientation matrix based upon 15 reflections.

^c $I > 2\sigma(I)$

Table IV. Final Positional ($\times 10^4$) Parameters for $(\text{CH}_3)_2\text{Sn}[\text{S}_2\text{P}(\text{CH}_3)_2]_2^{\text{a}}$

<u>Atom</u>	<u>X</u>	<u>Y</u>	<u>Z</u>
Sn(1)	249.3(8)	0(0)	0(0)
P(1)	1664(3)	13(10)	1506(1)
S(1)	3310(3)	16(10)	713(1)
S(2)	-1484(3)	12(11)	1412(1)
C(1)	2689(14)	1280(9)	1912(4)
C(2)	2660(16)	-1306(9)	1923(4)
C(3)	-1397(12)	1698(7)	48(20)

^aEstimated standard deviations in parentheses.

Table V. Final Anisotropic Thermal Parameters^a ($\times 10^4$) for
 $(\text{CH}_3)_2\text{Sn}[\text{S}_2\text{P}(\text{CH}_3)_2]_2$ ^b

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn(1)	108(4)	129(4)	192(4)	-16(4)	16(26)	2(21)
P(1)	147(8)	205(9)	218(8)	40(40)	3(6)	24(47)
S(1)	150(8)	380(12)	235(8)	-91(30)	-7(6)	122(34)
S(2)	135(8)	412(10)	299(8)	28(56)	2(6)	-55(60)
C(1)	197(44)	321(48)	281(43)	41(39)	18(37)	-101(38)
C(2)	302(52)	267(46)	415(51)	167(42)	-23(44)	143(41)
C(3)	171(31)	180(34)	336(121)	59(26)	4(70)	191(99)

^aAnisotropic thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

^bEstimated standard deviations in parentheses.

TABLE VI. Final Intramolecular Distances (Å) in $(\text{CH}_3)_2\text{Sn}[\text{S}_2\text{P}(\text{CH}_3)_2]_2$ ^a

Sn(1)-S(1) 2.482(2)

Sn(1)-S(2) 2.334(2)

Sn(1)-C(3) 2.132(8)

P(1)-S(1) 2.047(2)

P(1)-S(2) 1.969(2)

P(1)-C(1) 1.781(13)

P(1)-C(2) 1.832(13)

^aEstimated standard deviations in parentheses.

Table VII. Final Intramolecular Angles (deg.) in $(\text{CH}_3)_2\text{Sn}[\text{S}_2\text{P}(\text{CH}_3)_2]_2^{\text{a}}$

S(1)-Sn(1)-S(2)	68.9(1)	S(1)-P(1)-S(2)	113.8(3)
S(1)-Sn(1)-S(2')	148.8(1)	S(1)-P(1)-C(1)	105.1(4)
S(1)-Sn(1)-S(1')	79.9(2)	S(1)-P(1)-C(2)	105.8(4)
S(1)-Sn(1)-C(3)	109.2(5)		
S(1)-Sn(1)-C(3')	114.0(5)	S(2)-P(1)-C(1)	114.2(4)
		S(2)-P(1)-C(2)	113.0(4)
S(2)-Sn(1)-S(2')	142.3(1)		
S(2)-Sn(1)-C(3)	78.1(5)	C(1)-P(1)-C(2)	103.9(5)
S(2)-Sn(1)-C(3')	84.0(5)		
C(3)-Sn(1)-C(3')	122.6(8)		
Sn(1)-S(1)-P(1)	99.9(2)		
Sn(1)-S(2)-P(1)	77.3(2)		

^aEstimated standard deviations in parentheses.

Table VIII. Final Positional Parameters ($\times 10^4$) for $\text{I}_2\text{Sn}[\text{S}_2\text{P}(\text{C}_2\text{H}_5)_2]_2^{\text{a}}$

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>
Sn(1)	2700.4(3)	-194.4(5)	2514.3(4)
I(1)	3499.4(4)	1821.2(5)	1928.4(4)
I(2)	790.8(3)	834.2(5)	1708.5(4)
P(1)	2600(2)	-851(2)	4805(2)
P(2)	3575(2)	-1949(2)	1268(2)
S(1)	3379(2)	520(2)	4536(2)
S(2)	2157(2)	-1942(2)	3450(2)
S(3)	2134(1)	-1358(2)	695(2)
S(4)	4320(2)	-1366(2)	2879(2)
C(1)	1528(6)	-264(8)	4956(7)
C(2)	932(7)	-1249(8)	5206(9)
C(3)	3391(6)	-1633(8)	6099(7)
C(4)	3644(7)	-848(9)	7131(7)
C(5)	3652(6)	-3564(8)	1213(7)
C(6)	3195(8)	-4210(9)	1902(9)
C(7)	4095(6)	-1371(8)	342(7)
C(8)	5188(6)	-1717(9)	713(9)

^aEstimated standard deviations in parentheses.

Table IX. Final Anisotropic Thermal Parameters^a ($\times 10^4$) for $\text{I}_2\text{Sn}[\text{S}_2\text{P}(\text{C}_2\text{H}_5)_2]_2^{\text{b}}$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn(1)	158(2)	107(3)	140(2)	-2(2)	64(2)	-6(2)
I(1)	216(3)	155(3)	228(3)	-24(2)	95(2)	32(2)
I(2)	157(2)	166(3)	215(2)	11(2)	63(2)	-2(2)
P(1)	209(9)	144(11)	165(10)	6(8)	88(8)	0(8)
P(2)	170(9)	144(10)	177(9)	12(8)	75(8)	4(8)
S(1)	245(9)	156(10)	180(9)	-45(8)	80(8)	-13(8)
S(2)	292(10)	157(10)	220(10)	-49(8)	130(8)	-28(8)
S(3)	170(8)	174(10)	182(9)	10(8)	67(7)	-22(8)
S(4)	193(9)	193(11)	203(9)	19(8)	51(8)	-11(9)
C(1)	266(40)	182(43)	220(41)	37(33)	145(34)	24(35)
C(2)	344(48)	170(45)	508(60)	59(38)	305(46)	89(44)
C(3)	243(40)	205(44)	178(39)	25(34)	75(33)	26(35)
C(4)	296(43)	277(52)	147(38)	7(36)	83(34)	17(36)
C(5)	254(40)	151(42)	233(41)	22(33)	114(34)	31(35)
C(6)	457(57)	227(53)	412(58)	21(43)	242(49)	96(46)
C(7)	219(38)	227(47)	273(44)	-10(33)	139(35)	75(38)
C(8)	201(40)	320(54)	389(53)	-18(36)	171(40)	-10(44)

^aAnisotropic thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^{*} + 2U_{13}hla^*c^{*} + 2U_{23}klb^*c^*)]$.

^bEstimated standard deviations in parentheses.

Table X. Final Intramolecular Distances (Å)^a in I₂Sn[S₂P(C₂H₅)₂]₂^a

Sn(1)-I(1)	2.8110(8)		
Sn(1)-I(2)	2.8065(7)		
Sn(1)-S(1)	2.537(2)		
Sn(1)-S(2)	2.621(2)		
Sn(1)-S(3)	2.533(2)		
Sn(1)-S(4)	2.593(2)		
P(1)-S(1)	2.043(3)	P(2)-S(3)	2.044(3)
P(1)-S(2)	2.026(3)	P(2)-S(4)	2.032(3)
P(1)-C(1)	1.808(10)	P(2)-C(5)	1.820(9)
P(1)-C(3)	1.824(9)	P(2)-C(7)	1.820(10)
C(1)-C(2)	1.538(14)	C(5)-C(6)	1.529(15)
C(3)-C(4)	1.524(13)	C(7)-C(8)	1.526(13)

^aEstimated standard deviations in parentheses.

Table XI. Final Intramolecular Angles (deg) in $I_2Sn[S_2P(C_2H_5)_2]_2^a$

I(1)-Sn(1)-I(2)	92.32(2)	Sn(1)-S(3)-P(2)	87.17(10)
I(1)-Sn(1)-S(1)	93.60(5)	Sn(1)-S(4)-P(2)	85.81(10)
I(1)-Sn(1)-S(2)	169.23(6)	S(3)-P(2)-S(4)	106.96(13)
I(1)-Sn(1)-S(3)	99.34(5)	S(3)-P(2)-C(5)	112.48(32)
I(1)-Sn(1)-S(4)	89.62(5)	S(3)-P(2)-C(7)	108.29(32)
I(2)-Sn(1)-S(1)	98.39(5)	S(4)-P(2)-C(5)	110.30(32)
I(2)-Sn(1)-S(2)	91.24(5)	S(4)-P(2)-C(7)	112.85(33)
I(2)-Sn(1)-S(3)	89.16(5)	C(5)-P(2)-C(7)	106.05(43)
I(2)-Sn(1)-S(4)	168.60(6)	P(2)-C(5)-C(6)	113.41(69)
S(1)-Sn(1)-S(2)	78.83(7)	P(2)-C(7)-C(8)	113.10(68)
S(1)-Sn(1)-S(3)	167.30(7)		
S(1)-Sn(1)-S(4)	92.82(7)		
S(2)-Sn(1)-S(3)	90.87(7)		
S(2)-Sn(1)-S(4)	88.89(7)		
S(3)-Sn(1)-S(4)	79.44(7)		
Sn(1)-S(1)-P(1)	86.89(10)		
Sn(1)-S(2)-P(1)	85.00(10)		
S(1)-P(1)-S(1)	107.20(14)		
S(1)-P(1)-C(1)	109.47(32)		
S(1)-P(1)-C(3)	109.93(31)		
S(2)-P(1)-C(1)	110.48(32)		
S(2)-P(1)-C(3)	111.47(32)		
C(1)-P(1)-C(3)	108.27(43)		
P(1)-C(1)-C(2)	112.05(66)		
P(1)-C(3)-C(4)	111.55(64)		

^aEstimated standard deviations in parentheses.

Table XII. Phosphorus-Sulfur and Sulfur-Tin Internuclear Distances in Dithiophosphate Ester Derivatives and the Title Compounds, Å.

Compound	<u>Ester</u> ^a		<u>Dative</u> ^a		Ref.
	P—S—Sn	P—S—Sn	P—S—Sn	P—S—Sn	
$[(C_6H_5O)_2PS_2]_2Sn(II)$ ^b	2.0016	2.6230	1.9670	2.8300	9
$(C_2H_5O)_2PS_2Sn(C_6H_5)_3$ ^c	2.054	2.4582	1.931	5.326	10
$[(C_2H_5O)_2PS]_2Sn(C_6H_5)_2$ ^d	2.04	2.48	1.92	3.20	16
	2.03	2.49	1.94	3.23	
$[(i-C_3H_7O)_2PS_2]_2Sn(C_6H_6)_2$ ^d	2.006	2.678	1.998	2.689	1
$[(CH_3)_2PS_2]_2Sn(CH_3)_2$ ^d	2.047	2.482	1.969	3.334	<u>e</u>
$[(C_2H_5)_2PS_2]_2SnI_2$ ^f	2.043	2.537	2.026	2.621	<u>e</u>
	2.044	2.533	2.032	2.593	

^aThe first number listed in each case is the P-S distance and the second is the S-Sn distance.

^bDistorted ψ -6 octahedron.

^cThis compound is a rare example of a monodentate dithiophosphate ligand system.

^dTrans-diorganotin groups.

^eThis work.

^fCis-diiodotin configuration.

Figure Captions

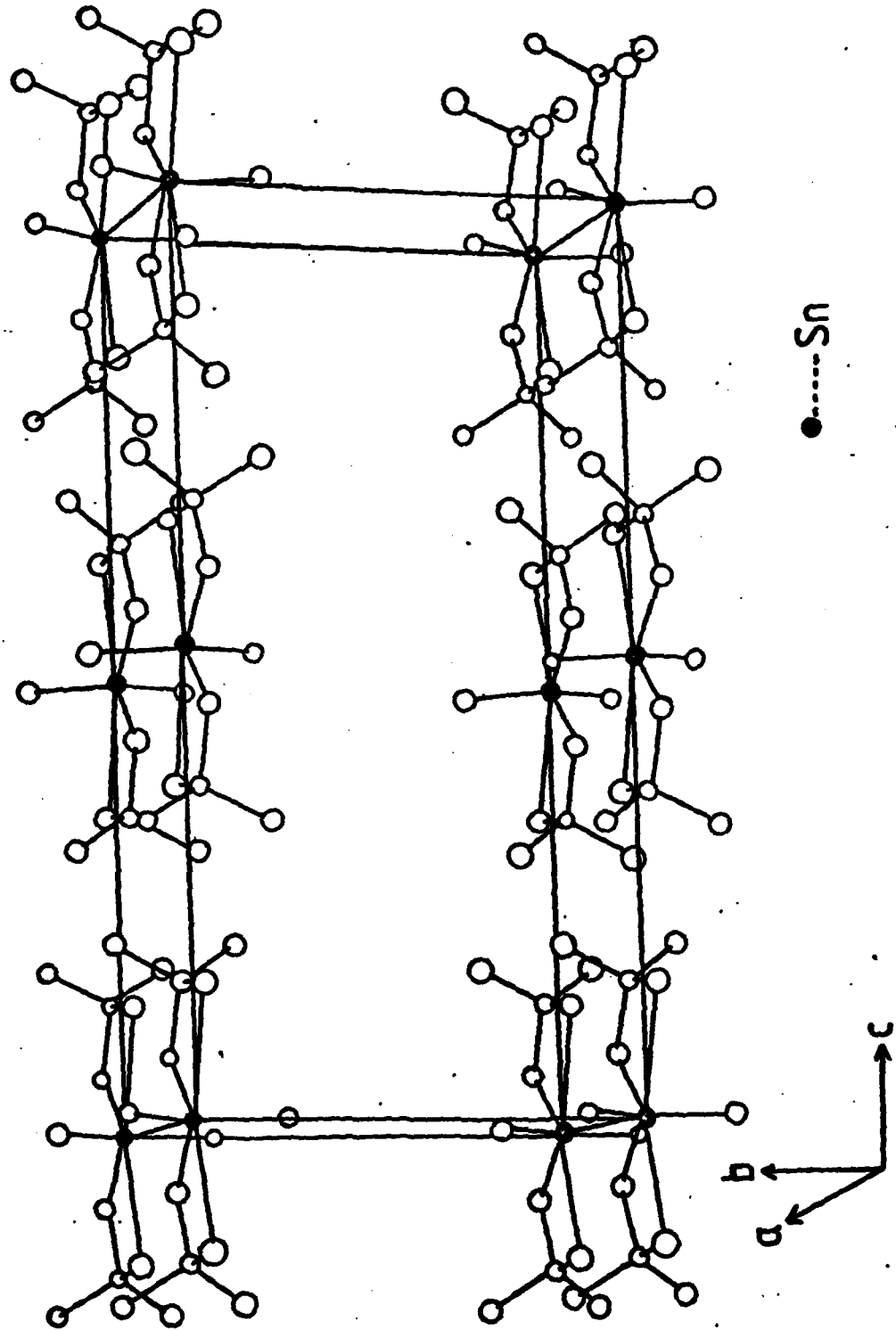
Figure 1. The asymmetric unit of bis(dimethyl dithiophosphinato) dimethyltin(IV) showing the atomic labeling. Primed atoms are related to the corresponding unprimed atoms by a two-fold axis passing through the tin atom and lying along the a-axis of the unit cell.

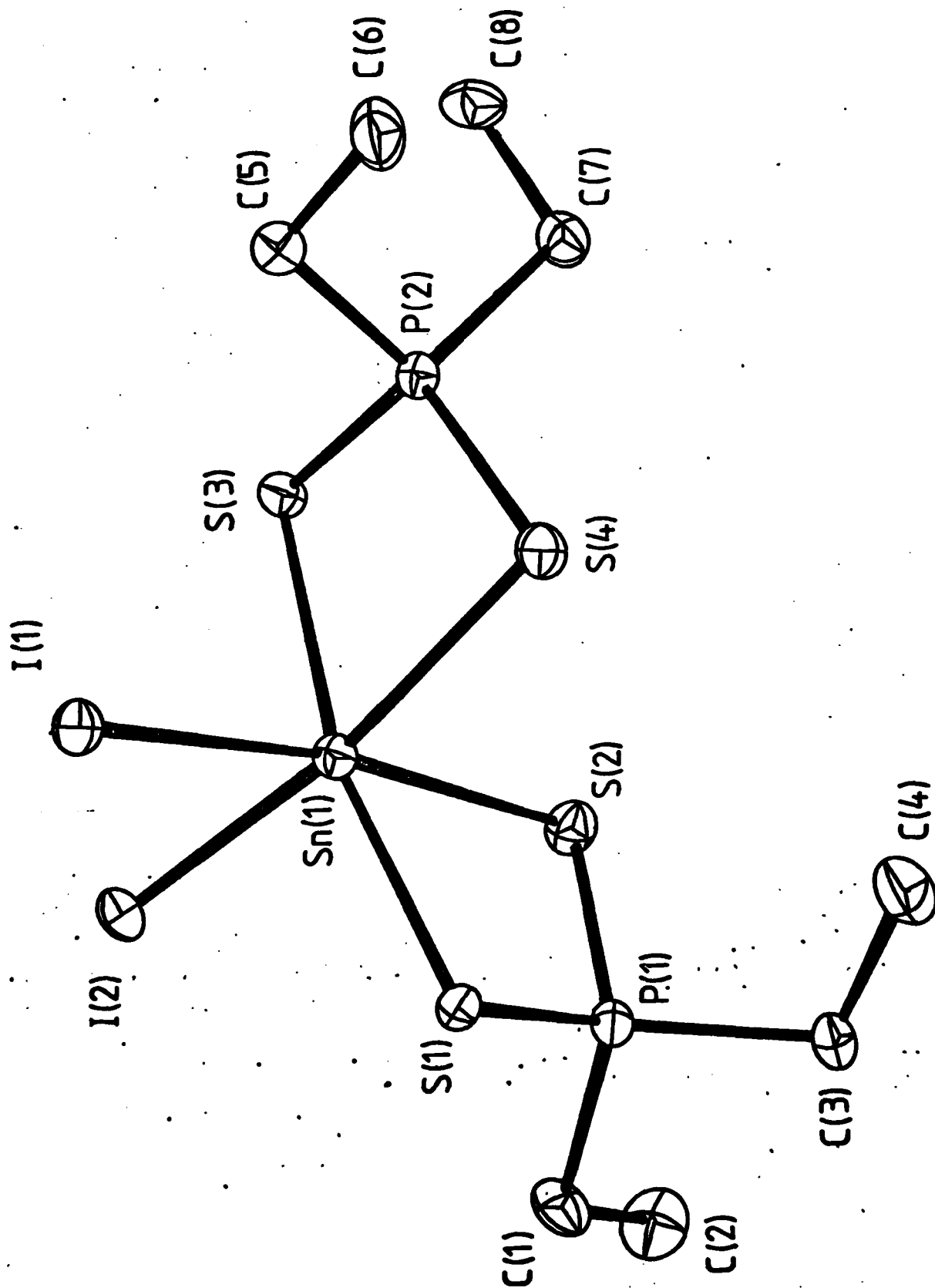
Figure 2. The unit cell contents of bis(dimethyl dithiophosphinato) dimethyltin(IV).

Figure 3. The molecular structure of bis(diethyl dithiophosphinato) diiodotin(IV) showing the atomic labeling.

Figure 4. The unit cell contents of bis(diethyl dithiophosphinato) diiodotin(IV).

Figure 5. A view of the close packing of molecules along the a-axis, showing the closest intermolecular distances (methyl-groups have been omitted for clarity). Singly-primed atoms are related to unprimed atoms by the 2-fold axis along a. Doubly-primed atoms are related to unprimed atoms by a translation of $1/2$; the same translation relates singly- and triply-primed atoms.





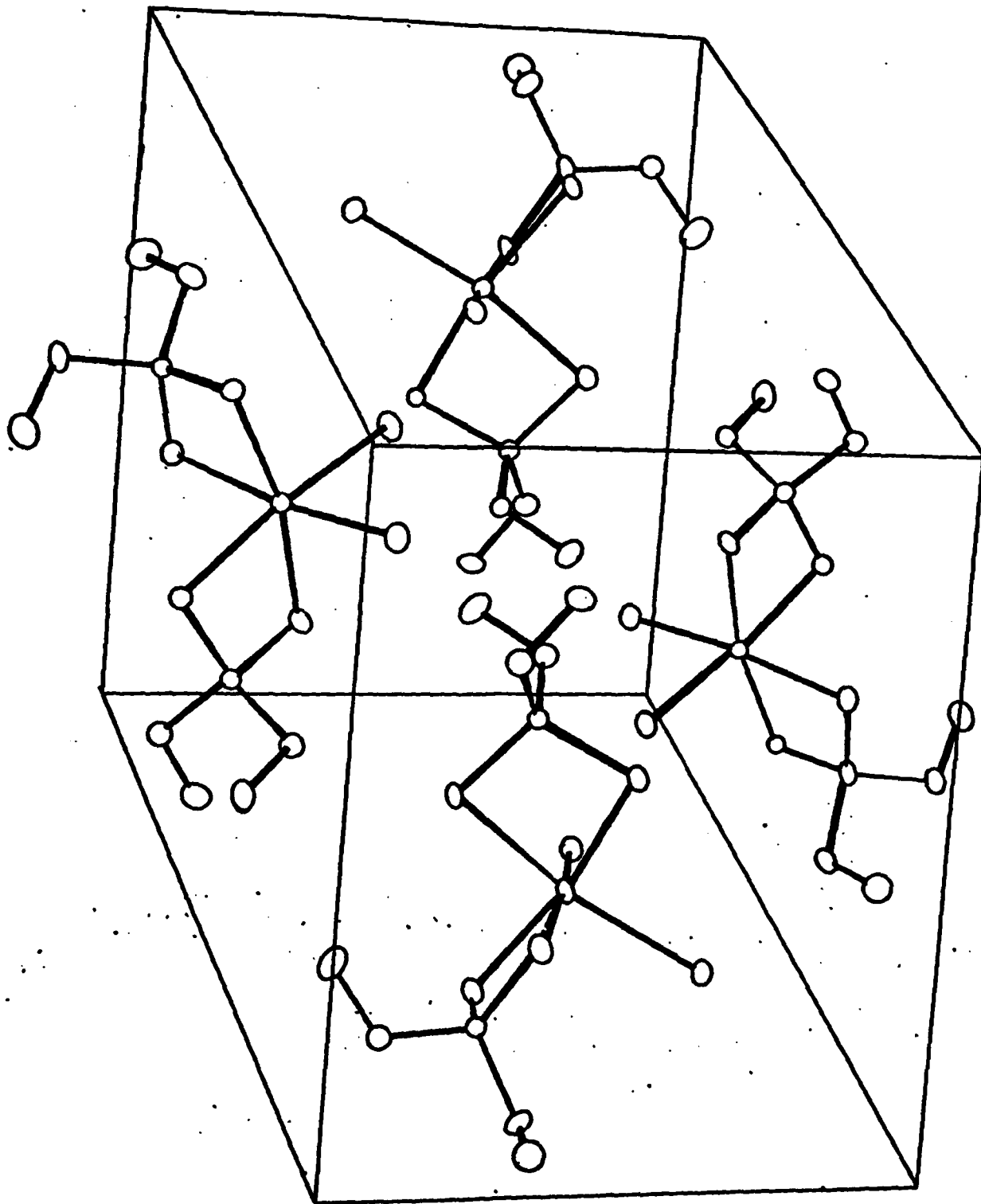


Figure 5

