(5) The intense infrared absorption of the Cd or vacuum treated samples (yielding blue crystals) decreases between 300 and 77°K. but is identical at 77 and 6°K. It is essentially the same for all conductivity-producing dopants.

(6) The visible phosphorescence and thermoluminescence are very similar with all conductivity-producing dopants. They are both yellow to yellow-green, and the phosphorescent lifetimes are of the order of seconds.

(7) The electron-donor levels and impurity conduction levels can be associated with an electron shared by the 12 Cd nearest neighbors to the substituted M^{+3}. Then charge transfer between the Cd "impurity" levels can account for the intense infrared absorption observed in the conducting crystals.

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Mössbauer Spectra of Tin Dithiolates[1a]

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The Mössbauer spectra of several compounds of Sn(IV) with 1,2-ethanedithiolate (EDT) and 3,4-toluenedithiolate (TDT) were measured. Evidence was obtained for a nontetrahedral configuration for $Sn(EDT)_2$ and a polymeric structure for $Sn(TDT)_2$. The mixed compounds of dimethyl- and diphenyltin(IV) with EDT and TDT show large quadrupole splittings. The formation of an adduct, for example with pyridine or 1,10-phenanthroline, which increases the coordination number of the tin, in all cases results in a more negative isomer shift, indicating a lower s electron density on the tin. EDT and TDT form equally covalent bonds with Sn(IV). Methyl tin compounds have larger quadrupole splittings than the corresponding phenyl compounds.

Introduction

A number of compounds containing Sn(IV) combined with a 1,2-dithiol were examined using Mössbauer spectroscopy. One of our objectives was a comparison of the two bis(dithiolates), $Sn(EDT)_2$ and $Sn(TDT)_2$, where EDT indicates the 1,2-ethanedithiolate anion, $^-SC_2H_4S^-$, and TDT indicates the 3,4-toluenedithiolate anion, $CH_3C_6H_3S_2{}^{2-}$. The latter tin compound has two unusual properties: a bright red color (useful for analytical purposes[2,3]) and very low solubility in any nonreacting solvent. These properties have been attributed to a polymeric structure achieved *via* intermolecular bonding by bridging sulfur atoms, giving tin a coordination number of six.[4] It was our purpose to clarify further the nature of the bonding to tin in this compound. In the course of this work a number of other compounds containing EDT or TDT along with various other ligands were examined.

The Mössbauer absorption spectra of all the compounds studied are simple doublets. The splitting, Δ, is due to a nuclear quadrupole interaction and is thus a direct measure of the electric field gradient at the tin nucleus or, in qualitative terms, a measure of the deviation of the surrounding electron cloud from cubic symmetry. The average line position, δ, also called the center, or isomer, shift is a measure of the s electron density at the tin nucleus. All numerical values of δ and Δ are given in velocity units, mm./sec. The source used in this work was Mg_2Sn at room temperature, and all δ values are referred to it.

The isomer shifts of tin compounds cover a range of over 4 mm./sec. At the positive end of the range are the ionic Sn(II) salts, the tin having about two s electrons (*i.e.*, $5s^2$), and at the negative end the ionic Sn(IV) salts. (Positive velocity, corresponding in tin to large s electron density, means the source and absorber are approaching each other.) In about the center of the range is gray tin which has four completely covalent sp^3 bonds, corresponding roughly to one s electron, there being some 5p shielding. (We ignore in this discussion the first four electron shells which constitute a core essentially unaffected by bond formation.) In Mg_2Sn the tin has a slightly lower electron density than gray tin. For comparison, the closest approximation to a bare Sn^{4+} core occurs in SnF_4, which is about 2.4 mm./sec. negative with respect to Mg_2Sn. Covalent compounds of four-coordinated tin, such as SnI_4, $SnBr_4$, and $Sn(C_6H_5)_4$, fall in the range 0.1 to 0.5 mm./sec. negative with respect to Mg_2Sn.

In this paper we will be concerned mostly with δ values between 0.4 and 1.0 mm./sec. negative with respect to Mg_2Sn, corresponding to essentially covalent

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[1] (a) Presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 5, 1965; (b) Westinghouse Electric Corporation; (c) University of Pittsburgh.

[2] M. Farnsworth and J. Pekola, *Anal. Chem.*, **26**, 735 (1954).

[3] R. E. D. Clark, *Analyst*, **83**, 396 (1958).

[4] R. C. Poller, *Proc. Chem. Soc.*, 312 (1963).

bonding. If there is no π bonding, a greater electron density on the tin indicates greater covalency of the tin bonds, so that the less negative the δ value we observe, the more covalent the bonds.

Experimental

Mössbauer Spectra.—Methods for observing Mössbauer spectra have been described in detail in the literature.[5,6] A velocity scan method was used throughout this work. In the beginning the base-line input method along with a normalizing "form" was used; later the time mode was used. A 400-channel analyzer was employed and the dispersion was 0.04 mm./sec. per channel in the earlier work and 0.015 mm./sec. per channel in the later work. In the earlier work a computerized curve-fitting procedure was available for determining the true line positions; later a manual numerical method was used to find the apparent line positions, which were corrected for overlap where necessary using a separately computed general table of corrections. With few exceptions, samples were observed at liquid nitrogen temperature, using a simple brass sample holder with its lower end immersed in liquid nitrogen and its upper end, holding the sample, encased in styrofoam. A metallic iron absorber and Co-57 source were used to calibrate the scale in both modes of operation. In the time mode, in order to avoid disturbing the drive between calibration and measurement, both the iron and tin sources were mounted on the same drive shaft, using a shutter to choose between them.

Preparation of Compounds. **$\mathrm{Sn(EDT)_2}$.**—A mixture of 10.0 g. (0.107 mole) of 1,2-ethanedithiol and 13 g. (0.23 mole) of potassium hydroxide in about 10 ml. of water was slowly poured, with stirring, into a solution of 18.7 g. (0.053 mole) of $\mathrm{SnCl_4 \cdot 5H_2O}$ in about 20 ml. of water. Heat was evolved and an immediate white precipitate formed. After stirring about 10 min., the mixture was filtered and the product washed twice with 50 ml. of water, air-dried, then recrystallized from methylene chloride. The colorless, air-dried crystals melted at 180–181° (lit.[4,7,8] 181–183°).

$\mathrm{Sn(EDT)_2 \cdot 2py}$.—This adduct formed in large colorless crystals when $\mathrm{Sn(EDT)_2}$ was recrystallized from hot pyridine. The crystals were washed with pentane and air-dried.

Anal. Calcd. for $\mathrm{SnC_{14}H_{18}N_2S_4}$: N, 6.1. Found: N, 5.9.

$\mathrm{Sn(EDT)_2 \cdot}$*o*-phen.—A mixture of 0.30 g. (0.0010 mole) of $\mathrm{Sn(EDT)_2}$ in about 5 ml. of methylene chloride was treated with 0.18 g. (0.0010 mole) of 1,10-phenanthroline. The solid completely dissolved to give a clear pale yellow solution, then very quickly a crystalline precipitate formed. The sulfur-yellow powder was collected, washed with methylene chloride, and air-dried. The material did not melt below 260°.

Anal. Calcd. for $\mathrm{SnC_{16}H_{16}N_2S_4}$: N, 5.8. Found: N, 5.4.

$\mathrm{Sn(TDT)_2}$.—A mixture of 5.0 g. (0.032 mole) of 3,4-toluenedithiol and 3.6 g. (0.064 mole) of potassium hydroxide in about 10 ml. of water was poured with stirring into a solution of 5.6 g. (0.016 mole) of $\mathrm{SnCl_4 \cdot 5H_2O}$ in about 20 ml. of water. The red precipitate was collected, washed with water, and air dried.

$\mathrm{Sn(TDT)_2 \cdot 2py}$.—This adduct was precipitated by addition of pentane to a solution of $\mathrm{Sn(TDT)_2}$ in pyridine. The yellow powder was dried in air.

$\mathrm{Sn(TDT)_2 \cdot}$*x*DMSO.—This was prepared, in the same way as the pyridine adduct, using dimethyl sulfoxide. The yellow powder was not analyzed. The value of x is assumed to be 2, as in the very similar pyridine complex.

$\mathrm{Sn(TDT)_2 \cdot 2(C_2H_5)_3N}$.—A suspension of 1.0 g. of $\mathrm{Sn(TDT)_2}$ in about 20 ml. of methylene chloride was treated with triethylamine until the red solid had completely dissolved to give a clear yellow solution. The solution was filtered, evaporated to about one-half its initial volume, and pentane was added. The supernatant liquid was decanted and the yellow oil triturated with several portions of pentane until it had completely solidified. The yellowish green powder was air-dried. The compound decomposes before melting.

Anal. Calcd. for $\mathrm{SnC_{20}H_{27}S_4N}$: N, 2.65. Calcd. for $\mathrm{SnC_{26}H_{42}S_4N_2}$: N, 4.52. Found: N, 3.32.

$\mathrm{Sn(TDT)_2 \cdot}$*o*-phen.—A mixture of 0.43 g. (0.0010 mole) of $\mathrm{Sn(TDT)_2}$ and 0.22 g. (0.0012 mole) of 1,10-phenanthroline in 55–60 ml. of methylene chloride was heated with stirring until complete solution took place. The orange solution was filtered and evaporated until orange crystals formed. These were collected, washed with a small amount of methylene chloride, and air-dried. The crystals did not melt below 260°.

Anal. Calcd. for $\mathrm{SnC_{26}H_{20}N_2S_4}$: N, 4.6. Found: N, 4.5.

$\mathrm{Sn(TDT)_2 \cdot bipy}$.—This was prepared in the same manner as the 1,10-phenanthroline complex, using 0.20 g. (0.0013 mole) of 2,2′-bipyridine. The orange crystals did not melt below 260°.

Anal. Calcd. for $\mathrm{SnC_{24}H_{20}N_2S_4}$: N, 4.8. Found: N, 4.7.

$\mathrm{(CH_3)_2Sn(EDT)}$.—A mixture of 2.5 g. (0.027 mole) of 1,2-ethanedithiol and 3.3 g. (0.059 mole) of potassium hydroxide in about 10 ml. of water was added with stirring to 5.8 g. (0.025 mole) of $\mathrm{(CH_3)_2SnCl_2}$ dissolved in about 20 ml. of water. A colorless oil precipitated which crystallized upon cooling. The crystals were washed with water, dried, and recrystallized from methylene chloride. They melted at 81.5–82° (lit.[8,9] 82–83°).

Anal. Calcd. for $\mathrm{SnC_4H_{10}S_2}$: C, 19.9; H, 4.18. Found: C, 19.8; H, 4.09.

$\mathrm{(CH_3)_2Sn(TDT)}$.—A mixture of 1.56 g. (0.010 mole) of 3,4-toluenedithiol and 1.12 g. (0.020 mole) of potassium hydroxide in 10 ml. of water was added to a solution of 2.4 g. (0.010 mole) of $\mathrm{(CH_3)_2SnCl_2}$ in 20 ml. of water. After stirring for several minutes, the mixture was filtered and the white precipitate washed with water. Recrystallization from methylene chloride afforded white crystals melting at 137°.

Anal. Calcd. for $\mathrm{SnC_9H_{12}S_2}$: C, 35.7; H, 3.99. Found: C, 35.7; H, 3.87.

$\mathrm{(CH_3)_2Sn(TDT) \cdot py}$.—This adduct was precipitated from a pyridine solution of $\mathrm{(CH_3)_2Sn(TDT)}$ by addition of pentane. The semisolid precipitate was triturated with several portions of pentane until complete crystallization had occurred. The air-dried white crystals melted at 106–108°.

Anal. Calcd. for $\mathrm{SnC_{14}H_{17}NS_2}$: N, 3.7. Found: N, 3.5.

$\mathrm{(CH_3)_2Sn(TDT) \cdot}$*o*-phen.—A solution of 0.30 g. (0.0010 mole) of $\mathrm{(CH_3)_2Sn(TDT)}$ in 3 ml. of methylene chloride was treated with 0.18 g. (0.0010 mole) of 1,10-phenanthroline. The yellow solution was filtered and allowed to evaporate until crystals formed. The air-dried yellow crystals were not analyzed.

$\mathrm{(C_6H_5)_2Sn(EDT)}$.—A mixture of 2.5 g. (0.027 mole) of 1,2-ethanedithiol and 3.3 g. (0.059 mole) of potassium hydroxide in 10 ml. of water was added with stirring to a mixture of 9.1 g. (0.026 mole) of $\mathrm{(C_6H_5)_2SnCl_2}$ in 30 ml. of water. Stirring was continued for at least 30 min. until the reaction was complete. The white precipitate was collected by filtration, washed with water, dried, and recrystallized from methylene chloride. The white crystals melted at 109–110° (lit.[4] 108–109°).

$\mathrm{(C_6H_5)_2Sn(EDT) \cdot}$*o*-phen.—Yellow crystals of this compound were obtained by evaporating a solution of 0.36 g. (0.0020 mole) of 1,10-phenanthroline and 0.73 g. (0.0020 mole) of $\mathrm{(C_6H_5)_2Sn(EDT)}$ in about 5 ml. of methylene chloride.

Anal. Calcd. for $\mathrm{SnC_{26}H_{22}N_2S_2}$: N, 5.1. Found: N, 4.7.

$\mathrm{(C_6H_5)_2Sn(TDT)}$.—To 3.4 g. (0.010 mole) of $\mathrm{(C_6H_5)_2SnCl_2}$ in 20 ml. of water was added, with stirring, a mixture of 1.56 g. (0.010 mole) of 3,4-toluenedithiol and 1.1 g. (0.020 mole) of potassium hydroxide in water. The mixture was stirred for 30 min. until reaction was complete. After recrystallization from methylene chloride the white crystals melted at 151–152° (lit.[3] 155°).

$\mathrm{(C_6H_5)_2Sn(TDT) \cdot py}$.—This compound formed when $\mathrm{(C_6H_5)_2}$-

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(5) H. Frauenfelder, "The Mössbauer Effect," W. A. Benjamin, Inc., New York, N. Y., 1962.

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(7) H. J. Backer and W. Drenth, *Rec. trav. chim.*, **70**, 559 (1951).

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Sn(TDT) was recrystallized from hot pyridine. After washing with pentane, the air-dried crystals melted at 105–106°.

Anal. Calcd. for $SnC_{24}H_{21}NS_2$: N, 2.8. Found: N, 3.0.

Results

The isomer shifts (δ) and quadrupole splittings (Δ) of the 19 tin compounds studied in this work are given in Table I. Values of δ cover the range -0.4 to -0.9 mm./sec., except for the 2,2′-bipyridine and the unusual triethylamine complexes of $Sn(TDT)_2$. In all cases, δ becomes more negative when the coordination number of the tin increases from four to five or six. This change in δ may be due to the fact that the covalent radius of Sn(IV) increases with increase in coordination number; Pauling indicates that the octahedral radius of Sn(IV) is greater than the tetrahedral radius by a factor of 1.03.[10]

The range in Δ values is from 0.8 to 2.6 mm./sec. The splitting is much greater for the mixed (*i.e.*, the dimethyl- and diphenyltin) compounds than it is for the bis(dithiolates), as is expected because of their inherently less symmetrical structures. The largest splitting is found for $(CH_3)_2Sn(TDT)$.

Table I

Isomer Shifts and Quadrupole Splitting Constants for Tin–Sulfur Compounds at Liquid Nitrogen Temperature Relative to Mg_2Sn Source[a]

Compound	δ, mm./sec.	Δ, mm./sec.
$Sn(EDT)_2$	−0.48	0.98
$Sn(EDT)_2 \cdot 2py$	−0.77	1.84
$Sn(EDT)_2 \cdot$ *o*-phen	−0.86	1.00
$Sn(TDT)_2$	−0.61	1.52
$Sn(TDT)_2$	−0.56[b]	1.37[b]
$Sn(TDT)_2 \cdot 2py$	−0.86	1.69
$Sn(TDT)_2 \cdot 2DMSO$	−0.87	1.62
$Sn(TDT)_2 \cdot 2(C_2H_5)_3N$	−1.32	0.84
$Sn(TDT)_2 \cdot$ *o*-phen	−0.81	1.26
$Sn(TDT)_2 \cdot bipy$	−1.00	0.92
$(CH_3)_2Sn(EDT)$	−0.47	2.33
$(CH_3)_2Sn(EDT) \cdot py$	−0.57	2.25
$(CH_3)_2Sn(TDT)$	−0.46	2.62
$(CH_3)_2Sn(TDT) \cdot py$	−0.56	2.28
$(CH_3)_2Sn(TDT) \cdot$ *o*-phen	−0.82	2.05
$(C_6H_5)_2Sn(EDT)$	−0.46	1.69
$(C_6H_5)_2Sn(EDT) \cdot py$	−0.60	1.76
$(C_6H_5)_2Sn(EDT) \cdot$ *o*-phen	−0.82	1.76
$(C_6H_5)_2Sn(TDT)$	−0.49	1.93
$(C_6H_5)_2Sn(TDT) \cdot py$	−0.58	1.76

[a] Abbreviations: EDT, 1,2-ethanedithiolate; TDT, 3,4-toluenedithiolate; py, pyridine; *o*-phen, 1,10-phenanthroline; DMSO, dimethyl sulfoxide; bipy, 2,2′-bipyridine. [b] Measured at room temperature.

Discussion

(A) Bis(dithiolate) Tin Compounds. $Sn(EDT)_2$.—The isomer shift for this compound (see Table I) when compared with that of tetraphenyltin, −0.57 mm./sec., indicates that the dithiol–tin bonds are slightly more covalent than the phenyl–tin bonds.

No quadrupole splitting is expected for a tetrahedral Sn(IV) compound; the magnitude of Δ for $Sn(EDT)_2$ indicates considerable distortion from cubic symmetry of the electric field gradient around the tin. This supports the work of Arbousow, who measured the dipole moment of $Sn(EDT)_2$ and the silicon analog, $Si(EDT)_2$, and found values for μ of 0.98 and 1.03 D., respectively.[11] Arbousow could explain the moment of 0.98 D. for $Sn(EDT)_2$ by assuming a structure requiring a SSnS angle (within the chelate ring) of 100° (rather than the tetrahedral angle of 109°).

$Sn(TDT)_2$.—Both δ and Δ were larger for this compound than for the corresponding EDT compound. As will be shown later for the mono(dithiolate) tin compounds, the sulfur–tin bonds in EDT and TDT compounds are about equally covalent, so that the more negative δ of $Sn(TDT)_2$ is an indication of an increase in the coordination number of the tin.

Additional evidence for the polymeric structure suggested by Poller[4] was the large Mössbauer resonant fraction at room temperature, the intensity being about 40% of that observed at liquid nitrogen temperature. This indicates that the crystal lattice is quite rigid. For $Sn(EDT)_2$, the intensity at room temperature was only 12% of that at liquid nitrogen temperature.

The increase in Δ can be ascribed primarily to the presence of two bonds (those of the bridging sulfur atoms) sufficiently different from the four other bonds to induce a field gradient larger than that in $Sn(EDT)_2$, in which there are just four equal bonds. Also, the deviation of the SSnS angle (within the chelate ring) from the tetrahedral value is greater with TDT than with EDT (*i.e.*, the SSnS angle in Sn–TDT is smaller than in Sn–EDT) because the sulfur atoms in TDT are on aromatic carbon atoms only 1.39 Å. apart, while in EDT the sulfur atoms are on aliphatic carbon atoms 1.54 Å. apart.

Adducts of $Sn(EDT)_2$ and $Sn(TDT)_2$. Isomer Shifts.—In the seven cases investigated, the formation of an adduct caused δ to become more negative. In the case of $Sn(EDT)_2$ this reflects the increase in coordination number of the tin; for $Sn(TDT)_2$, it appears that the bridging sulfur–tin bonds are more covalent than the substituting ligand (*e.g.*, pyridine, dimethyl sulfoxide, etc.)–tin bonds.

The formation of the pyridine and dimethyl sulfoxide adducts of $Sn(TDT)_2$ resulted in identical changes in δ and Δ. One must conclude that the pyridine–tin bond is electronically identical with the sulfoxide–tin bond.

Triethylamine caused the greatest change in δ (and gave the smallest Δ) of any of the ligands; a steric effect may be operative in this case, but in the absence of more data no definite conclusions are possible.

The addition of two molecules of pyridine to $Sn(EDT)_2$ caused less of a change in δ than the addition of one molecule of 1,10-phenanthroline. The formation of the 2,2′-bipyridine adduct of $Sn(TDT)_2$, which one might naïvely expect to have an effect on δ intermediate between that of pyridine and 1,10-phenanthroline, caused an unusually large change in δ. (In Fe(II)

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(10) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 251.

(11) B. A. Arbousow, *Bull. soc. chim. France*, 1311 (1960).

complexes, the effect is in the opposite direction, 2,2′-bipyridine giving a greater s electron density than 1,10-phenanthroline.[12])

Quadrupole Splittings.—In all cases in which bidentate ligands were added to the bis(dithiolate), the quadrupole splitting was substantially less than that obtained with two monodentate ligands, triethylamine excepted. Two possible explanations can be advanced for this observation, one based on the necessarily *cis* configuration of the nitrogen atoms in the bidentate ligands, and the other based on the possibility of stronger π bonding for the bidentate ligands. If six atoms (two of one kind and four of another) were attached to the tin in perfect octahedral geometry, the resultant field gradient could be approximated by two point charges in either *cis* or *trans* positions. It can be readily shown that quadrupole splitting is larger for the *trans* configuration than it is for the *cis*. It is not unlikely that the monodentate ligands went on *trans*, whereas the bidentate ligands must give a *cis* arrangement. The difference in Δ could be due in part to this geometric difference. Also, there should be more π-bonding character in the nitrogen–tin bonds with the bidentate ligands and the smaller splitting may be the result of the greater diffuseness of such bonds compared to nitrogen–(or oxygen)–tin bonds with the monodentate ligands.

The bidentate adducts of $Sn(TDT)_2$ had smaller Δ values than $Sn(TDT)_2$ itself, suggesting that, if the structure of the latter is indeed close to octahedral, the bridging sulfur bonds occupy the *trans* positions.

(B) Mono(dithiolate) Tin Compounds. Pyridine Adducts.—The spectra of $(CH_3)_2Sn(TDT)\cdot py$ and $(C_6H_5)_2Sn(TDT)\cdot py$ were obtained both on the frozen pyridine solution of the uncomplexed tin compound and on the isolated and analyzed solid. No significant differences were found. The values of δ and Δ listed in Table I for the (assumed monoadducts), $(CH_3)_2Sn(EDT)\cdot py$ and $(C_6H_5)_2Sn(EDT)\cdot py$, are for the nonisolated adducts. (A recently isolated sample of $(C_6H_5)_2Sn(EDT)\cdot py$ gave an isomer shift of -0.55 mm./sec.)

The addition of one molecule of pyridine caused an average change in δ of -0.11 mm./sec.; the addition of two molecules (as in the case of $Sn(EDT)_2$), a change of -0.29 mm./sec. The effect on δ is not simply additive.

The changes in Δ upon forming the pyridine adducts appear inconsistent on first consideration. On further inspection it is seen that the addition of pyridine tends to reduce the range of Δ values: from 2.62–1.69 mm./sec. for $(CH_3)_2Sn(TDT)$ and $(C_6H_5)_2Sn(EDT)$, respectively, to 2.25–1.76 mm./sec. for $(CH_3)_2Sn(EDT)\cdot py$ and $(C_6H_5)_2Sn(EDT)\cdot py$, respectively; see Table I. The greatest change, -0.34 mm./sec., and the smallest change, $+0.07$ mm./sec., occur with $(CH_3)_2Sn(TDT)$ and $(C_6H_5)_2Sn(EDT)$, respectively, exactly those compounds having the largest and smallest Δ values initially.

1,10-Phenanthroline Adducts.—Addition of one molecule of 1,10-phenanthroline caused an average change in δ of -0.37 mm./sec. This relatively large change in δ, compared with -0.11 mm./sec. for one pyridine and -0.29 mm./sec. for two pyridines, may be due to π bonding, which tends to reduce electron density on the tin.

Just as with pyridine, the addition of 1,10-phenanthroline made the greatest reduction in Δ for $(CH_3)_2Sn(TDT)$.

Comparison of EDT and TDT.—In the four cases listed in Table I in which the only change was the replacement of EDT by TDT, little, if any, change took place in δ. Except when masked by pyridine, TDT caused larger splittings than EDT, probably because the SSnS angle is smaller in TDT.

Comparison of Methyl with Phenyl.—In the four cases listed in Table I in which methyl was replaced by phenyl, δ for the phenyl compound was, on the average, more negative by 0.02 mm./sec. This is too close to experimental error to be conclusive; the weight of evidence in related studies by Russian workers on tetraalkyl- and tetraphenyltins[13] and dialkyl- and diaryltin oxides[14] also indicates that the phenyl group makes a slightly more negative contribution to the isomer shift in Sn(IV) compounds than does the methyl group, although again the difference barely exceeds the experimental error.

The situation is much more definite with regard to Δ. The methyl compounds had much greater splittings, even in the presence of pyridine, than the phenyl compounds. The carbon atom in $Sn-CH_3$ is sp^3-hybridized, and thus the bond is more directed (less diffuse) than the $Sn-C_6H_5$ bond, in which the carbon atom bonded to tin is sp^2-hybridized. A similar result was found by Goldanskii, *et al.* in the R_2SnO series[14] (even though the bonding is much more ionic): when R was aliphatic, Δ was 0.3–0.4 mm./sec. greater than when R was aromatic.

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