nearly tetrahedral C–Sn–C angle is suggested by the tin–proton coupling constants observed by McGrady and Tobias.[2] Martin and co-workers had postulated a *trans* arrangement of the methyl groups based on their interpretation of the infrared spectrum[3] and their inability to resolve optical isomers.[4] Okawara[5] also preferred the *trans* structure. The observed C–Sn–C angle (110.7 ± 0.8°) is remarkably close to the tetrahedral angle and lends support to the suggested relationship between tin–proton coupling constants and tin orbital hybridization.[18]

An interesting qualitative MO approach to the bonding in tin compounds with coordination number greater than four, not requiring the use of the 5d orbitals, has been postulated.[2,19] For all cases where more than four atoms are bonded to the tin atom by bonds with covalent character, three-center, two-electron bonds can be postulated. For $(CH_3)_2Sn(C_9H_6NO)_2$ the bonding could involve sp^3 hybrid orbitals on the tin participating in normal covalent bonds to the methyl groups and three-center bonds to the oxinate groups. Molecular orbitals constructed from a tin sp^3 hybrid orbital and σ-type orbitals from both nitrogen and oxygen would result in bonding, nonbonding, and antibonding combinations. The four ligand electrons would occupy the bonding and nonbonding orbitals. The angles between the center point of the line connecting N(1) and O(1), the tin atom, and the atoms C(10) and C(20) are 129.8 and 95.8°, respectively. The angles between the center point of the line connecting N(2) and O(2), the tin atom, and the atoms C(10) and C(20) are 94.0 and 133.4°, respectively. The angle between the center point of the line connecting N(1) and O(1), the tin atom, and the center point of the line connecting N(2) and O(2) is 97.5°. The fact that these angles describe a distorted tetrahedral coordination of the tin atom lends some support to the above bonding theory. The fact that the Sn–C bond distances are the same as those observed for tetrahedral tin compounds also lends support to the theory. A larger coefficient for the oxygen orbital in the bonding molecular orbital could account for the shorter Sn–O than Sn–N bond distances and the distortion from tetrahedral coordination observed for the above bond angles. The shorter Sn–C bond in $(CH_3)_2SnF_2$ (Table IV) could be explained by the use of sp hybrid orbitals on the tin for the Sn–C bonds with any covalent bonding to fluorine atoms involving the use of the other two tin p orbitals. The bonds to the fluorine atoms are, however, probably primarily ionic. It is possible that there is some d-orbital contribution to the bonding in $(CH_3)_2Sn(C_9H_6NO)_2$, but the extent of involvement is uncertain. It is also probable that the bonding to the oxinate groups is somewhat ionic. The author plans to examine a complex of the type $R_3Sn(C_9H_6NO)$ as a further test of the above bonding approach and of the relationship between tin–proton coupling constants and the C–Sn–C bond angle.

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Electric Dipole Moments and Mössbauer Spectra of Complexes of *o*-Phenanthroline with Di-*n*-butyltin dihalides

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Isomer shifts reveal an order of bond polarity Sn–Cl > Sn–Br > Sn–I in complexes of dibutyltin dihalides with *o*-phenanthroline and with α,α-dipyridyl. The electric dipole moments of the *o*-phenanthroline complexes are 11.3, 12.7, and 12.9 D. for the dichloride, dibromide, and diiodide, respectively, indicating that a portion of the latter two moments is associated with asymmetry in the distribution of unshared halogen electrons. The large moments obtained for these complexes indicate a *trans* arrangement for the butyl groups.

Isomer shifts of compounds of the type R_2SnX_2 and its complexes with donor compounds give an indication of the relative polarity of the Sn–Cl, Sn–Br, and Sn–I bonds and the relative changes in polarity on complex formation. A comparison of the electric dipole moments of these complexes with their Mössbauer spectra offers a means of illustrating the contribution of unshared halogen electrons to the dipole moments.

Bidentate ligands are preferred to monodentate in dipole moment studies because in the event of chelation—the formation of monomer complexes—the number of possible isomers is reduced and the resultant of the dipoles associated with the dative bond is fixed.

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Table I

Isomer Shifts (δ) Relative to a Palladium–Tin Alloy Source, Quadrupole Splittings (ΔE_Q), Polarizations, and Electric Moments at 25°

Compound	δ, mm/sec	ΔE_Q, mm/sec	$1000(wf)_2$	$\Delta\epsilon/(wf)_2$	$\Delta d/(wf)_2$, g/ml	$P_{2\infty}$, ml	MR_D, ml	μ, D.	μ_H, D.
$(C_4H_9)_2SnCl_2$	$(+0.1)^{a,b}$	3.25^b	21–44	7.0	0.34	463	66	4.37	4.37
$(C_4H_9)_2SnBr_2$	$(+0.2)^{a,b}$	3.15^b	32–46	4.9		397	72	4.15	4.15
$(C_4H_9)_2SnI_2$	$(+0.3)^{a,b}$	2.9^b	50–71	3.5		270	83	3.84	3.87
$(C_4H_9)_2SnCl_2 \cdot$phen	+0.07	4.07	1.3–4.1	29.2	0.51	2726	118	11.3	11.3
$(C_4H_9)_2SnBr_2 \cdot$phen	+0.11	3.94	2.9–6.1	31.0	0.48	3427	131	12.7	12.8
$(C_4H_9)_2SnI_2 \cdot$phen	+0.17	3.75	2.8–4.8	27.2	0.41	3532	136	12.9	12.9
$(C_4H_9)_2SnCl_2 \cdot$dipy	+0.04	3.83							
$(C_4H_9)_2SnBr_2 \cdot$dipy	+0.10	3.95							
$(C_4H_9)_2SnI_2 \cdot$dipy	+0.18	3.82							

[a] Values obtained by adding 1.52 to the isomer shifts reported[b] using stannic oxide as source. [b] A. Aleksandrov, N. Delyagin, K. Mitrofanov, L. Polak, and V. Shpinel', *Soviet Phys. JETP*, **16**, 879 (1963).

Because of solubility limitations, few, if any, dipole moments of complexes of *o*-phenanthroline with metal halides or alkylmetal halides have been reported. Fortunately the complexes of this ligand with di-*n*-butyltin dihalides are sufficiently soluble for dielectric constant measurements. Complexes of these halides with α,α-dipyridyl are also soluble in benzene, but dielectric constant data indicate appreciable dissociation of the complexes in solution, in line with the conclusions of Tanaka, *et al.*[2]

Experimental Section

Preparation of Compounds.—Di-*n*-butyltin dichloride was obtained from Alfa Inorganics, Inc., and was purified by recrystallization from benzene.

Di-*n*-butyltin dibromide was prepared according to Alleston and Davies,[3] by keeping a mixture of tetra-*n*-butyltin (0.1 mole) and tin tetrabromide (a slight excess over 0.1 mole) at about 220° for 3 hr. The brown liquid so obtained was distilled through a packed column; mp 20°; $n^{25}D$ 1.5412 (lit.[3] 1.5400); d^{25} 1.7214.

Anal. Calcd for $C_8H_{18}SnBr_2$: C, 24.46; H, 4.62. Found: C, 24.18; H, 4.48.

Di-*n*-butyltin diiodide was prepared by allowing di-*n*-butyltin dichloride to react with sodium iodide (in excess) using acetone as the solvent. The mixture was refluxed for several hours and filtered; the solvent was evaporated, and the remaining liquid was washed with petroleum ether (bp 35–60°) and distilled; $n^{25}D$ 1.6040 (lit.[3] 1.6042); d^{25} 2.0126.

Anal. Calcd for $C_8H_{18}SnI_2$: C, 19.74; H, 3.73. Found: C, 19.70; H, 3.63.

The chelate complexes of α,α-dipyridyl and *o*-phenanthroline were prepared from the di-*n*-butyltin dihalides (chloride, bromide, iodide) by the method of Alleston and Davies,[3] using absolute ethanol in minimum amounts as the solvent, by adding with stirring a solution of the di-*n*-butyltin dihalide to an equivalent amount of the solutions of the ligand. The complexes separated immediately, were recrystallized from absolute ethanol, and were washed with absolute ethanol and petroleum ether. The infrared spectra showed complexes were formed in each case.

Anal. Calcd for $(C_4H_9)_2SnCl_2 \cdot C_{10}H_8N_2$: C, 47.01; H, 5.70. Found: C, 47.15; H, 5.87. Calcd for $(C_4H_9)_2SnBr_2 \cdot C_{10}H_8N_2$: C, 39.38; H, 4.77. Found: C, 39.66; H, 4.93. Calcd for $(C_4H_9)_2SnI_2 \cdot C_{10}H_8N_2$: C, 33.63; H, 4.08. Found: C, 33.67; H, 4.12. Calcd for $(C_4H_9)_2SnCl_2 \cdot C_{12}H_8N_2$: C, 49.63; H, 5.41. Found: C, 49.49; H, 5.38. Calcd for $(C_4H_9)_2SnBr_2 \cdot C_{12}H_8N_2$: C, 41.92; H, 4.57. Found: C, 41.69; H, 4.80. Calcd for $(C_4H_9)_2SnI_2 \cdot C_{12}H_8N_2$: C, 36.02; H, 3.93. Found: C, 36.15; H, 3.99.

Dielectric constant and density measurements and calculations of electric moments were carried out as in previous investigations,[4] using an oscillator similar to that described by Estok.[5] For the two liquids, di-*n*-butyltin dibromide and diiodide, the equation of Estok was used.[6] The polarizations and electric moments are listed in Table I. $\Delta\epsilon/(wf)_2$ and $\Delta d/(wf)_2$ are the changes in dielectric constant and density, respectively, with weight fraction of solute. Extrapolated values of $\Delta\epsilon/(wf)_2$ were used for the complexes of *o*-phenanthroline with di-*n*-butyltin dichloride and dibromide; average values were used in all other calculations. The distortion polarizations were taken as 1.10 MR_D for the dibutyltin dihalides and as 1.15 MR_D for the complexes. The moments of the dibutyltin dihalides are considered to be accurate to 0.04 and the complexes to 0.1 D. The moments were also calculated by the method of Higasi,[7] using a value of 0.8481 for β.[8]

Mössbauer Spectra.—These were obtained with a Nuclear Science and Engineering Model AM-1 transducer-type spectrometer, a Reuter-Stokes Model RSG-30A counting tube with xenon–nitrogen fill gas, a Victoreen preamplifier and single-channel analyzer, a modified Tektronix oscilloscope, Model RM 503, which obviated the need for a time base generator, a Nuclear Data 180-M 512 channel analyzer, and a Teletype readout. A Pd–Sn^{119m} source, containing 12% tin by weight, obtained from New England Nuclear Corp., was used at room temperature. The absorber consisted of 0.2–0.3 g of finely divided solid sample placed between two sheets of collodion-coated aluminum foil covered with a thin film of silicone grease. The sample thus prepared, with a cross-sectional area of 2.9 cm², was mounted in a copper block suspended from a glass dewar and placed in an evacuated chamber with aluminum foil windows. The dewar was kept filled with liquid nitrogen. At least 40,000 counts were collected in each channel, requiring from 8 to 12 hr for each spectrum. A computer program[9] was designed to process output data according to a least-squares method developed by Wentworth.[10] By an iterative process parameters are adjusted to fit better the theoretical Lorentzian curve to the experimental points using an 1107 computer. The parameters determined in these cases of quadrupole splitting describe component single absorptions. The isomer shifts and quadrupole splittings were obtained from the computer analysis.

The AM-1 spectrometer was calibrated with anhydrous stannous chloride, β-tin, and stannic oxide. The isomer shifts for these substances were determined with an NSEC Model B Mössbauer spectrometer, using an RIDL preamplifier, single-channel analyzer, scaler, and timer. The dial velocities for this instrument are indicated as being precise to 1%. The velocities were

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determined under experimental conditions, using a vernier caliper and timer, to a precision of 0.5%; the small corrections noted were applied to the dial readings. The isomer shifts obtained from the plotted curves and from the computer analysis,[11] assuming Lorentzian-type curves, agreed within 0.02 mm/sec. The isomer shifts relative to the palladium–tin source are for $SnCl_2$ 2.53 ± 0.04 mm/sec, for β-tin 1.05 ± 0.03 mm/sec, and for SnO_2 −1.52 ± 0.03 mm/sec.

Discussion of Results

The dipole moments, isomer shifts relative to the palladium–tin source, and quadrupole splittings obtained for the compounds studied are listed in Table I. The moments obtained by the calculations of Higasi indicate that density and index of refraction measurements are unnecessary. The moments of the dibutyltin dihalides compare with the values of 4.10, 3.86, and 3.76 D. reported[12] for dimethyltin dichloride, dibromide, and diiodide, respectively.

Moments were calculated for the *o*-phenanthroline complexes for configurations having the butyl groups in *trans* and *cis* positions. As tin and cadmium have similar electronegativities and as the octahedral radius of tin is close to the tetrahedral radius of cadmium, $\mu_{\mathrm{N-Sn-X}}$ was considered to be equal to $\mu_{\mathrm{N-Cd-X}}$, 0.5 less than $\mu_{\mathrm{N-Zn-X}}$.[13] Assuming 90° bond angles, the moment of *trans*-$(C_4H_9)_2SnCl_2 \cdot$phen is $\mu_{\mathrm{phen}} - 1.41\mu_{\mathrm{py}} + (1.414/1.16)(\mu_{\mathrm{ZnCl_2 \cdot 2py}} - 0.6) = 11.6$ D. ($\mu_{\mathrm{phen}} = 4.1$[14] and $\mu_{\mathrm{ZnCl_2 \cdot 2py}} = 9.20$[15]). Considering the moments of the dibutyltin dihalides, the moments of the Sn–Br and Sn–I bonds were taken as 0.15 and 0.4 D. less than the Sn–Cl moment, yielding 11.4 and 11.0 as the moments of the *trans*-$(C_4H_9)_2SnBr_2 \cdot$phen and $(C_4H_9)_2SnI_2 \cdot$phen. For calculating the moments of the complexes in the *cis* configuration, the portions of $\mu_{\mathrm{N-Sn-X}}$ due to $\mu_{\mathrm{Sn-X}}$ are needed. It is generally agreed that the Sn–Cl moment is about 3.0 D. in tetrahedral compounds.[16] Considering the Sn–X moments to be increased by 0.4 D. on complex formation (and a corresponding decrease in the C–Sn moment), the moments calculated for the *cis* complexes (which change by less than 0.1 D. as the Sn–Cl moment is varied from 3.0 to 4.0) are 10.2, 10.0, and 9.7 D., compared to the experimental values of 11.3, 12.7, and 12.9. This comparison strongly suggests that the butyl groups are *trans* to each other. Clark and Wilkins[17] have concluded from infrared measurements that the alkyl groups in $R_2SnX_2 \cdot$dipy complexes are *trans*. The similar quadrupole splittings obtained for the two sets of complexes also indicate similar configurations for these complexes.

The increase in the dipole moments of the *o*-phenanthroline complexes from chloride to bromide to iodide parallels that found for zinc halide complexes with pyridine and with hexamethylphosphoramide, and for cobalt(II) halide complexes with hexamethylphosphoramide.[4] The isomer shifts for the complexes of both *o*-phenanthroline and dipyridyl indicate that the *order* of bond polarity, Sn–Cl > Sn–Br > Sn–I, does not change on complex formation. The reverse order of dipole moments for the *o*-phenanthroline complexes reveals that a portion of the increase in dipole moments of the dibromide and of the diiodide on complex formation is associated with an increase in the asymmetry of the distribution of the unshared halogen electrons. As the polarity of the tin–halogen bond is increased on complex formation, the repulsion between the shared pair and the unshared electrons shifts the cloud of the latter away from the bond. This shift is greater for the more polarizable bromine and iodine atoms, resulting in greater dipole moments than that for the complex of the dichloride.

The large quadrupole splittings obtained for these complexes compared to the lack of quadrupole splitting in $SnCl_4 \cdot$dipy and $SnBr_4 \cdot$dipy[18] indicate that whereas the tin share of the bonding electrons of the Sn–Cl bond is about the same as that of the N–Sn dative bond, it is much less than that of the Sn–C bond.

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