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DIORGANOTIN HALIDE CARBOXYLATES, THIOCARBOXYLATES AND HALIDE HA--ETC(U)
AUG 78 W D HONNICK, J J ZUCKERMAN N00014-77-C-0432
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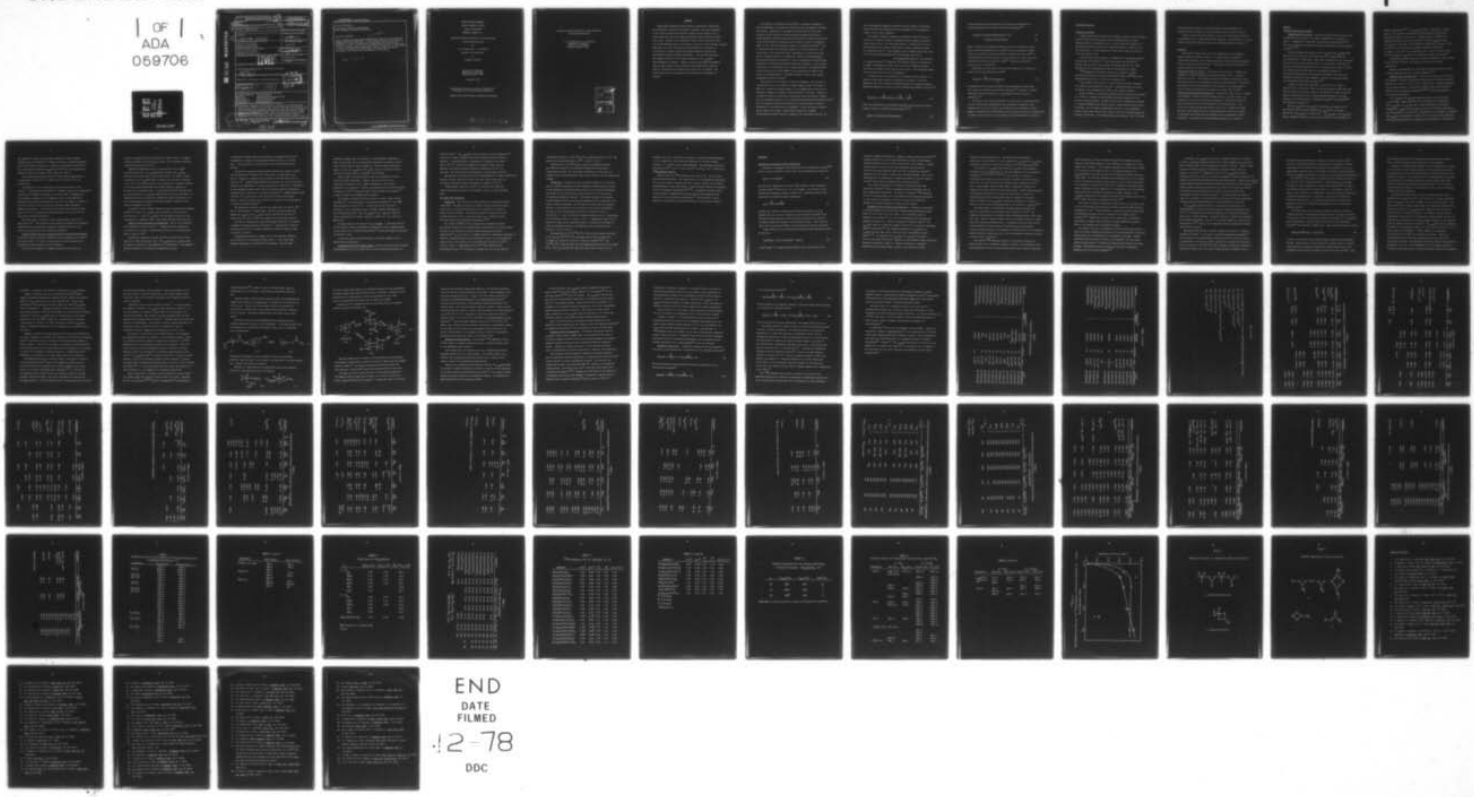

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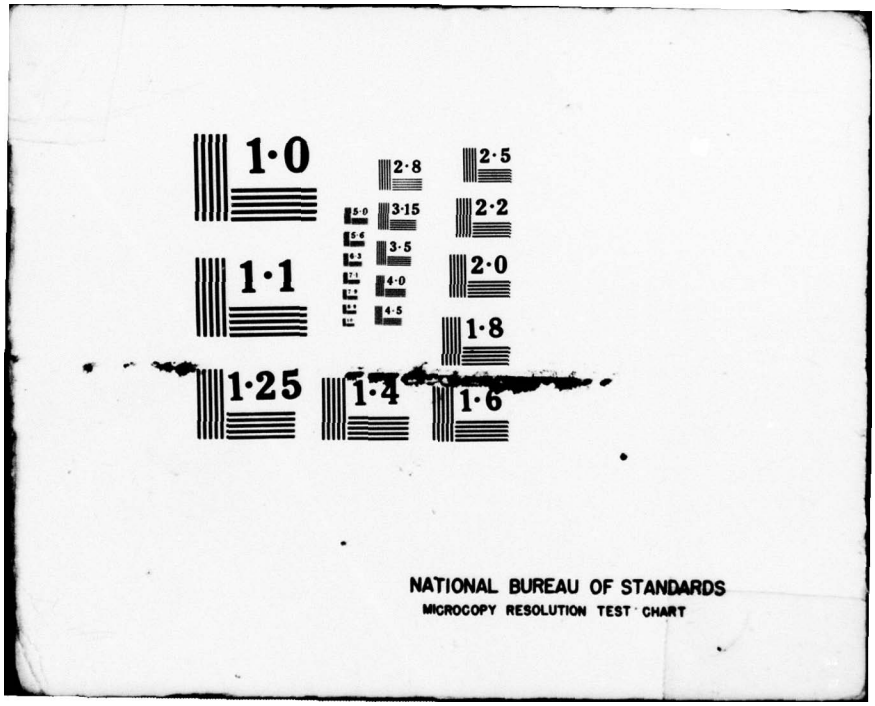
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Twenty-eight inorganotin halide acetates, thioacetates, haloacetates and carboxylates, eighteen not previously reported, have been synthesized by the reaction between the diorganotin oxides and acid halides, and by transacyloxylation reactions between diorganotin halide acetates and carboxylic acids. Infrared in the 2000-200cm^{-1} range, proton and carbon-13 nmr and tin-119m Mössbauer data are interpreted in terms of acetoxy-bridged, trigonal bipyramidal tin in the solid phase with depolymerization occurring in solution.

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where a dynamic equilibrium between diorganotin dihalide and dicarboxylate species is rapidly established. A new infrared absorption also appears at 100-125cm^{-1} to higher frequency of the $\nu_{asym}(CO_2)$ which disappears on heating. A dimeric structure based upon four-membered Sn_2O_2 or Sn_2OX rings in which carboxylate group oxygen atoms bridge tin atoms of a second molecule leaving the C=O group free is proposed. The halide thioacetates are associated in the solid state but monomeric in solution.

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Diorganotin Halide Carboxylates, Thiocarboxylates and Halide Haloacetates

by

W. D. Honnick and J. J. Zuckerman

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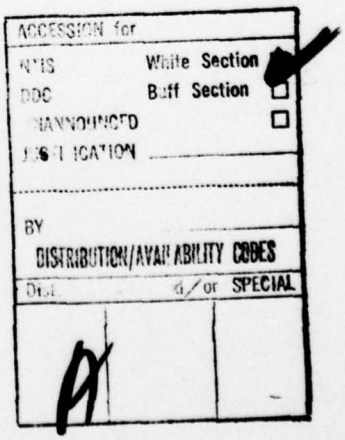
W. D. Honnick and J. J. Zuckerman
Department of Chemistry
University of Oklahoma
Norman, Oklahoma 73019



ABSTRACT

Twenty-eight inorganotin halide acetates, thioacetates, haloacetates and carboxylates, eighteen not previously reported, have been synthesized by the reaction between the diorganotin oxides and acid halides, and by transacyloxylation reactions between diorganotin halide acetates and carboxylic acids. Infrared in the 2000-200cm^{-1} range, proton and carbon-13 nmr and tin-119m Mössbauer data are interpreted in terms of acetoxy-bridged, trigonal bipyramidal tin in the solid phase with depolymerization occurring in solution where a dynamic equilibrium between diorganotin dihalide and dicarboxylate species is rapidly established. A new infrared absorption also appears at 100-125 cm^{-1} to higher frequency of the $\nu_{asym}(CO_2)$ which disappears on heating. A dimeric structure based upon four-membered Sn_2O_2 or Sn_2OX rings in which carboxylate group oxygen atoms bridge tin atoms of a second molecule leaving the C=O group free is proposed. The halide thioacetates are associated in the solid state but monomeric in solution.

The question of intermolecular association in organotin compounds, of interest generally,[1] is brought into sharp focus with the organotin chlorides and acetates. Examination of available structural data for short intermolecular contact distances and for potentially bridging atoms lying in stereochemically significant positions reveals the great ambiguity that exists in the interpretations of molecular structure data in terms of coordination number at tin. Data from gas phase studies of the methyltin halides[2-4] show no large deviations from tetrahedral geometry in the free molecules. The crystal data, on the other hand, show a progression of situations from the nearly tetrahedral geometry of triphenyltin chloride,[5] through diphenyl-[6] and bis(chloromethyl)tin dichloride[7] to that of dimethyltin dichloride[8] whose environment is substantially distorted toward the octahedral. We are clearly dealing here in an intermediate area, and the question of coordination number at the tin atom in the latter members of this series must be said at this writing to be indeterminate.[1] The same situation is found in the recently investigated diethyltin halides.[9]

The situation in the organotin acetates is analogous. The inclusion of a second donor site in the ligand X in R_3SnX compounds allows this moiety to behave as a bidentate chelating ligand or as a bridging group to give rise to associated oligomeric or polymeric chain structures in the solid. Binding in a unidentate fashion is found when a second donor group successfully competes for the coordination sites as in 2,2'-bipyridylbis(trifluoroacetato)divinyltin(IV),[10] when the chelating interaction would be weak or possibly impose a strained conformation on the molecule as in Cl_3SnCH_2Cl,[4] or when the organic groups at the tin atom are too bulky to permit either chelation or bridging. Tricyclohexyltin acetate[11] may be an example of the last-named situation, but

the stereochemically suggestive position and short distance of the second oxygen atom make this conclusion, and the assignment of the coordination number at the tin atom, ambiguous.

The simplest organotin carboxylate, trimethyltin formate,[12] forms a structure of formoxy- and planar trimethyltin groups arranged alternately along a helical chain. The carboxylate groups in trimethyltin acetate and trifluoroacetate also bridge in associated structures comprised of planar tin-carboxylate units.[13] Acetate groups in other examples bridge ditin units as in di-μ-acetatobis(diphenyltin)[14] and stannoxane units as in $\{[(n\text{-}C_4H_9)_2SnO_2CCCl_3]_2O\}_2$.[16] The structure of tribenzyltin acetate[17] exemplifies the crossover between the tendency for a bridged, one-dimensional polymer and the descrete, monomeric molecular form with an increase in steric bulk at the tin atom. The coordination number at the tin atom in this case is indeterminate.

In between these two situations lie the organotin halide acetates, for which no X-ray crystal structure information is available.[1] The first compound of this type, dimethyltin chloride acetate, was prepared in 1960 by Okawara and Rochow by the action of acetic anhydride and methyltin dichloride:[18]

$$(CH_3)_2SnCl_2 + (CH_3\overset{O}{\overset{\|}{C}})_2O \longrightarrow (CH_3)_2ClSn\overset{O}{\overset{\|}{O}}CCH_3 + CH_3\overset{O}{\overset{\|}{C}}Cl \qquad (1)$$

Later, the redistribution of dialkyltin dihalides and diacetates was used to prepare a variety of dialkyltin halide acetates:[19-22]

$$R_2SnX_2 + R_2Sn(O_2CCH_3)_2 \rightarrow 2R_2XSnO_2CCH_3 \qquad (2)$$

Another synthetically useful method is the reaction of tetraalkyl-1,3-dichlorodistannoxanes with acetic acid or acetic anhydride:[23]

$$2(R_2ClSn)_2O + 2CH_3CO_2H \rightarrow 2R_2ClSnO_2CCH_3 + H_2O \quad (3)$$

$$+ (CH_3CO)_2O \rightarrow 2R_2ClSnO_2CCH_3 \quad (4)$$

Other, in general less convenient, methods include the cleavage of tetra-n-butyl-1,2-diacetoxydistannane with bromine[24] to give di-n-butyltin bromide acetate, the reaction of di-n-butylchlorotin hydride with acetic acid[25] to give di-n-butyltin chloride acetate, and the cleavage of a methyl group from trimethyltin chloride by haloacetic acids[26,27] when heated together for several hours in a sealed tube.

Dimethyltin chloride acetate has also been prepared by the reaction of acetyl chloride with dimethyltin oxide:[28]

$$(CH_3)_2SnO + ClC(=O)CH_3 \rightarrow (CH_3)_2SnClO_2CCH_3 \quad (5)$$

An analogous reaction between diethyltin oxide and benzoyl chloride gives only diethyltin dichloride and diethyltin dibenzoate.[28] Attempts to prepare dimethyltin chloride benzoate via a redistribution reaction were also unsuccessful.[21]

We report in this paper the synthesis of twenty-eight triorganotin halide acetates, thioacetates, haloacetates, and carboxylates, eighteen of them reported here for the first time, and infrared, proton and carbon-13 nuclear magnetic resonance and tin-119m Mössbauer spectroscopic data which are interpretated in terms of the structures of these systems in the solid phase and in solution.

Experimental Section

Chemicals and Spectra

Reagent grade chemicals were used as received, except for acetyl bromide, which was distilled in the presence of N,N'-dimethylaniline to remove hydrogen bromide, and immediately used. Melting points were measured on a Thomas-Hoover Capillary Melting Point Apparatus (Arthur H. Thomas Co.) and were uncorrected. Tin was analyzed as tin(IV) oxide through the action of nitric and sulfuric acids.

Infrared spectra were recorded on a Beckman IR-12 infrared spectrometer as Nujol mulls from 600-200 cm^{-1} and as KBr pellets from 2000-300 cm^{-1}. Solution infrared spectra were obtained between KBr plates in the region 2000-400 cm^{-1} and in polyethylene cells for the 600-200 cm^{-1} region.

^{119m}Sn Mössbauer spectra were recorded on a cam-drive, constant acceleration spectrometer previously described,[29] using a $Ba^{119m}SnO_3$ source (New England Nuclear Corp.) as the zero of Isomer Shift.

^1H nmr spectra were recorded on a Varian A60-A spectrometer operating at an ambient probe temperature of ca. 39°. Deuterochloroform was used as the solvent, and tetramethylsilane (TMS) as the internal standard.

Natural abundance, proton noise-decoupled carbon-13 spectra were recorded at 25.1 MHz on a modified Varian HA-100D spectrometer equipped for fast Fourier transform operation. Carbon-13 nmr data were collected and processed by a Digilab FTS/NMR-3 pulse and data system. Deuterochloroform was used as the solvent, and the samples, approximately 50% (wt/v), were contained in 8 mm O.D. tubes which held 2 mm O.D. coaxial inner cells containing C_6F_6, the external lock material. Probe temperatures were maintained at ca. 40° during

proton-decoupled experiments utilizing the Digilab 50-80 decoupler by a continuous flow of nitrogen circulated through cooling coils held in Dry Ice.

Carbon chemical shifts were measured in parts per million (ppm) relative to internal TMS, positive values being to high frequency. A resolution of ± 1 Hz was achieved using 16384 (16K) data points and a sampling frequency of 12000 s^{-1}.

Syntheses

Two synthetic methods were used in the preparation of the diorganotin halide carboxylates listed in Table 1: by reaction between diorganotin oxides and acid halides, and by transacyloxylation reactions between diorganotin halide acetates and carboxylic acids. A description of each method used in a typical preparation is given below.

Di-n-butyltin Chloride Acetate. Di-n-butyltin oxide (3.00 g., 12 mmole) was suspended in carbon tetrachloride and acetyl chloride (0.94 g., 12 mmole) added with stirring. The mixture was heated and allowed to reflux ca. ½ hour, during which time all the suspended di-n-butyltin oxide dissolved. The solution was cooled, the carbon tetrachloride solvent removed by rotary evaporation, and the product recrystallized from hexane, m.p. 63-64° (lit.[25] 63-65°).

Di-n-butyltin Chloride Monochloroacetate. Di-n-butyltin oxide (3.00 g., 12 mmole) was suspended in toluene and acetyl chloride (0.94 g., 12 mmole) added. The temperature of the mixture was slowly increased, but kept below the boiling point of toluene, until all the di-n-butyltin oxide had dissolved. The solution was cooled and monochloroacetic acid (1.14 g., 12 mmole) was added. The acetic acid released during the transacyloxylation reaction was removed by azeotropic distillation and the remaining toluene was removed by rotary evaporation. The product was recrystallized from hexane, m.p. 68-69.5°.

Results

Infrared Spectra and Assignments

Diorganotin Halide Acetates. Solid-state infrared spectral data for the diorganotin halide acetates in the range of 2000-200 cm^{-1} are given in Table 2. Assignments are based upon the spectrum of sodium acetate.[30-33] The infrared spectrum of dimethyltin chloride acetate has also been previously reported.[21,27,34]

The most prominent bands arise from the $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ modes which occur as very strong, broad absorptions in the ranges 1560-1551 and 1422-1408 cm^{-1}, respectively. Other bands associated with the carboxylate group are the CO_2 scissor vibration which is a strong band at 689-679 cm^{-1}, the CO_2 out-of-plane deformation which is a medium band at 618-612 cm^{-1}, and the in-plane CO_2 deformation which is a weak band at 498-484 cm^{-1}. These CO_2 deformations have been previously identified. The lowest CO_2 deformation frequency has been assigned to the out-of-plane motion based upon the bending frequencies of acetone.[35,36]

A medium to strong band that occurs in the 287-271 cm^{-1} range is assigned to the ν(Sn-O) mode. While only few far infrared studies have been made on organotin carboxylates, bands in the 300-250 cm^{-1} region, which are absent in the infrared spectra of sodium formate and acetate, have been assigned to the ν(Sn-O) mode for triorganotin formates[37] and acetates[38-40] and dialkyltin diacetates.[41]

Both the ν_{asym}(Sn-C) and ν_{sym}(Sn-C) vibrations are observed for all the dialkyltin halide acetates studied with ν_{asym}(Sn-C) in the range 606-577 cm^{-1} and ν_{sym}(Sn-C) at 530-515 cm^{-1}. The ν_{asym}(Sn-C) and ν_{sym}(Sn-C) modes in phenyltin compounds are found in the 382-261 cm^{-1} and 249-225 cm^{-1}

regions, respectively.[42-45] The ν_{asym}(Sn-C) mode in diphenyltin chloride acetate is not observed, and probably coincides with the strong ν(Sn-O) band which overlaps it at 294 cm^{-1}. A shoulder appears at 280 cm^{-1} for diphenyltin bromide acetate, which may arise from the ν_{asym}(Sn-C) mode. The ν_{sym}(Sn-C) vibrations for the diphenyltin compounds are assigned to 238 and 224 cm^{-1} for the chloride and bromide compounds, respectively. Assignment of this band is not unambiguous since a band in the same region has been assigned to ν_{sym}(Sn-O) for trimethyltin formate and acetate.[46]

Tin-halogen stretching vibrations are easily observable as intense bands in the 335-326 and 242-227 cm^{-1} regions for ν(Sn-Cl) and ν(Sn-Br), respectively.

Benzene ring assignments for the diphenyltin halide acetates are based on comparisons made with other phenyltin compounds.[45,47]

Dialkyltin Halide Haloacetates. Solid-state infrared spectral data for the dimethyltin chloride and bromide haloacetates and di-n-butyltin chloride haloacetates are given in Tables 3 and 4, respectively. Complete assignments have not been attempted, but literature values for the sodium haloacetate salts[31] and the triorganotin haloacetates[38-40,48] allow some assignments to be made with confidence.

The $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ modes yield broad, very strong bands in the frequency ranges 1651-1580 cm^{-1} and 1408-1358 cm^{-1}, respectively. While $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ show a marked dependence on increasing halogenation, ν_{asym}(Sn-C) and ν_{sym}(Sn-C) show little variation, appearing in the ranges 586-580 and 528-522 cm^{-1}, respectively for the dimethyltin compounds. The ν_{asym}(Sn-C) mode appears at 603-595 cm^{-1} in the di-n-butyltin compounds. The CO_2 bending vibrations were assigned to the following: a strong band in

the 718-682 cm^{-1} range to the CO_2 scissor vibration, a weak to medium intensity band in the 639-615 cm^{-1} range to the CO_2 out-of-plane deformation, and the CO_2 in-plane deformation to a medium to strong band at 514-497 cm^{-1}. This band probably overlaps the ν_{sym}(Sn-C) absorption for the di-n-butyltin compounds, which is also found in this region (cf. Table 2).

The tin-halide stretching vibrations are again easily identifiable as a strong band at 350-314 cm^{-1} for ν(Sn-Cl) and at 241-236 cm^{-1} for the ν(Sn-Br) mode.

The assignment of the carbon-halogen stretching vibrations is more difficult. Strong bands in the 849-788 cm^{-1} frequency range for the chloroacetate derivatives can probably be assigned to the ν(C-Cl) mode. Assignments for the dimethyltin compounds are not unambiguous since a strong absorption arising from the Sn-CH_3 rocking mode also occurs in this region (cf. Table 2). This band is absent in the di-n-butyltin compounds, making assignments somewhat less difficult. The ν(C-Br) mode is easily identified as a strong band at 727 cm^{-1} for dimethyltin chloride bromoacetate and at 702 cm^{-1} for di-n-butyltin chloride bromoacetate.

The ν(Sn-O) mode is found as a weak to medium intensity band in the range 293-253 cm^{-1}. The frequency of this vibration increases with increasing halogenation for the dimethyltin compounds, although observation of the effect is less certain for the di-n-butyltin compounds.

Solution Infrared Spectra of Dialkyltin Halide Acetates and Haloacetates. The prominent absorption bands of dimethyltin halide haloacetates in solution are given in Table 5, and those of di-n-butyltin chloride haloacetate and di-n-butyltin bromide acetate are given in Table 6.

The tin-carbon asymmetric and symmetric stretching vibrations are

relatively unchanged from the solid-state (cf. Tables 2 and 3). Compared to their positions in the solid-state, however, the tin-halogen stretching frequencies increase by 10-35 cm^{-1}.

Significant changes also occur in the positions of the carbonyl stretching vibrations. The $\nu_{asym}(CO_2)$ modes increase, and $\nu_{sym}(CO_2)$ decrease from the solid-state to the solution phase. The shift to higher frequencies for the $\nu_{asym}(CO_2)$ mode is greatest for the acetate compounds (41-47 cm^{-1}), and relatively smaller for the haloacetate compounds, although in some cases precise measurement was difficult owing to asymmetry in the shape of the absorption band. In the dimethyltin halide chloroacetates and dichloroacetates the $\nu_{asym}(CO_2)$ absorption was split into two bands. No comparable splitting was observed in dimethyltin chloride bromoacetate, or in the corresponding di-n-butyltin chloride compounds, although the band showed some asymmetry in shape.

In solution all the compounds exhibited a higher frequency band generally 100-200 cm^{-1} higher than $\nu_{asym}(CO_2)$ that was absent in the solid state infrared spectra. Shifts in $\nu_{asym}(CO_2)$ with increasing halogenation were accompanied by a comparable shift in this higher frequency absorption band.

Dialkyltin Halide Benzoates and Thioacetates. Data for the dialkyltin halide benzoates are given in Table 7. Assignments and the numbering of the benzene ring vibrations are based upon the spectra of the alkali metal salts of benzoic acid.[49]

The observed frequencies and band intensities closely parallel those observed for these alkali metal salts. The $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ modes are found at 1575-1566 cm^{-1} and 1380-1366 cm^{-1}, respectively. The asymmetric carbonyl vibrations in the dimethyltin compounds are split;

in dimethyltin chloride benzoate the splitting is unresolved and the band is asymmetric in shape, but in dimethyltin bromide acetate it is clearly split. In CCl_4 solution, on the other hand, only one absorption peak is observed.

Characteristic benzene ring vibrations in benzoic acid include a strong band at 1609-1616 cm^{-1} arising from a ν(C-C) mode, a strong band at 725-720 cm^{-1} assigned to a benzene ring deformation, and a weak ν(C-C) mode at 1308-1305 cm^{-1}. Carbon-hydrogen deformation vibrations are found at 1179-1178, 1076-1071, and 1028-1025 cm^{-1}. The very sharp band at 1452-1451 cm^{-1} observed for all the compounds probably arises from a C-C skeletal vibration, although no comparable band is reported for the alkali metal salts.[49] A medium intensity band at 1135-1134 cm^{-1} is also absent in the spectra of the alkali metal salts; however, a medium intensity band at 1134 cm^{-1} is reported in the Raman spectra of lithium and sodium benzoate.[49]

The symmetrical deformation and CO_2 out-of-plane rock are found at 700-691 cm^{-1} and 568-550 cm^{-1}, respectively. The later absorption band lies between the ν_{asym}(Sn-C) and ν_{sym}(Sn-C) modes at 615-591 and 534-518 cm^{-1}, respectively, all three of which are broadened and in some cases overlap.

The ν(Sn-Cl) vibrations are found in the range 359-324 cm^{-1} and ν(Sn-Br) in dimethyltin bromide benzoate at 237-236 cm^{-1}. The positions of ν(Sn-Cl) is shifted by 20-30 cm^{-1} to higher frequencies in solution, however, there is no shift in ν(Sn-Br).

Surprisingly few spectral changes occur on dissolving the compounds. As was observed for the dialkyltin halide acetates, a new, sharp, high frequency band appears at 1701-1697 cm^{-1} in solution. The only other

significant changes occur in the spectra of the dimethyltin compounds, in which a band at 946 cm^{-1} in the solid-state disappears in solution, and the ν(Sn-Cl) mode shifts to higher frequencies. The most notable observation, however, is that the $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ modes in the halide acetates show only very small shifts, as compared to the acetates.

Table 8 gives the infrared spectral data for the dimethyl- and di-n-butyltin chloride thioacetates. Owing to the lack of data for the metal salts of thioacetic acid, complete assignments of the infrared absorptions are not possible. However, by comparison with the infrared spectra of thioacetic acid,[50] thioacetate esters,[51] and trialkyltin thioacetates,[52] a number of bands can be assigned with confidence.

The carbonyl stretching vibration is seen as a broad, intense band at 1612-1600 cm^{-1}, the ν(C-S) mode as a strong band at 965-963 cm^{-1}, and $\nu(\overset{O}{\overset{\|}{C}}-C)$ the strong band at 1139-1133 cm^{-1}. A strong band is also observed at 657-654 cm^{-1}, and is assigned to the out-of-plane skeletal deformation of the thiocarboxylate group. Both the ν_{asym}(Sn-C) and ν_{sym}(Sn-C) modes are found in the 610-500 cm^{-1} region, ν(Sn-Cl) at 340-321 cm^{-1}, and ν(Sn-S) at 386-378 cm^{-1}.

The band observed at 273-266 cm^{-1} is not assigned. It may arise from the ν(Sn-O) stretch of weakly coordinated tin-oxygen bond, since a comparable band is also found in the trialkyltin thioacetates,[52] in which tin-oxygen coordination is believed to exist.

As with the dialkyltin halide benzoates, no spectral changes occur on dissolving the thioacetates.

Di-n-butyltin Chloride Trimethylacetate. The data for di-n-butyltin chloride trimethylacetate as the neat liquid and in carbon tetrachloride solution are

listed in Table 9. The $\nu_{asym}(CO_2)$ stretch is split, as in the sodium salt,[31] and occurs at higher frequencies like other dialkyltin halide acetates in solution. A strong absorption, attributable to a carbonyl out-of-plane bend at 627 cm^{-1}, obscures the asymmetric tin-carbon stretch, but the symmetric tin-carbon stretching vibration is observed at 515 cm^{-1} as a weak band. The tin-chlorine stretch absorbs as a strong band at 330 cm^{-1}.

The spectrum of di-n-butyltin chloride trimethylacetate in carbon tetrachloride solution is nearly identical to that of the neat liquid, except that the tin-chlorine stretching vibration increases in frequency by 23 cm^{-1}.

A high frequency band near 1705 cm^{-1} for both the neat liquid and carbon tetrachloride solution is also observed, similar to those described above.

Nmr Spectra and Assignments

^{1}H Nmr Data. Table 10 lists the ^{1}H nmr data for the dimethyltin halide carboxylates. The general increase in chemical shifts of the acetate group protons with increasing halogen substitution is expected on the basis of simple electron withdrawal. The methyltin protons are similarly affected by halosubstitution, but in a much less drastic way. Comparable shifts have been observed for trimethyltin haloacetates.[29,38]

The two-bond $|^2J(^{119}Sn\text{-}C\text{-}^1H)|$ couplings for the dimethyltin halide haloacetates decrease with increasing halogen substitution on the acetate group. The data for the dimethyltin chloride haloacetates *vs.* group electronegativities,[53] χ_i, can be fit to a straight line with a correlation coefficient of 0.985 and a standard deviation of the calculated values of J from the measured values of 0.16. The equation of the calculated line is found to be $J^{119} = -3.84\ \chi_i + 83.61$. A least-squares fit of the ^{119}Sn J values *vs.* the Taft inductive factor σ^*[54] also gives a straight line, but in this case the

correlation coefficient is only 0.974 with a standard deviation of 0.21. The equation of the calculated line is $J^{119} = -0.90\,\sigma^* + 76.09$.

Similar plots of the ^{119}Sn data *vs.* group electronegativities and Taft inductive factors for the dimethyltin bromide haloacetates give unsatisfactory results. The correlation coefficients are less than 0.9, probably owing to the exceptionally high J values found for the monochloroacetate compound.

^{13}C Nmr Data. Carbon-13 nmr data are listed in Table 11 for the di-*n*-butyltin chloride haloacetates and the dimethyltin halide benzoates, but not for the dimethyltin halide haloacetates owing to their limited solubilities. The results for the di-*n*-butyltin compounds parallel the ^{1}H nmr data for the analogous dimethyltin compounds. The general increase in the acetate α-carbon chemical shifts with increasing halosubstitution is expected on the basis of electron withdrawal, and the *n*-butyltin carbon atoms are similarly affected. A least-squares fit of the shifts of the carbon atoms bonded to tin (C_1) *vs.* group electronegativities gives a straight line with a correlation coefficient of 0.903 and a standard deviation of 5.8. The equation of the calculated line is $\delta = 53.9\chi_i + 544.4$. A significantly better fit is obtained by using the Taft inductive factors, (a correlation coefficient of 0.959 and standard deviation of 3.8 obtained for the calculated line of equation $\delta = 14.1\sigma^* + 647.3$).

The magnitudes of the $|^{1}J(^{119}Sn-^{13}C)|$ values are much larger than those of the two bond $|^{2}J(^{119}Sn-C-^{1}H)|$ couplings, and are much more sensitive to changes in bonding and structure in organotin compounds.[55,56] The $|^{1}J(^{119}Sn-^{13}C)|$ values decrease with increasing halosubstitution on the acetate group. Their plot against Taft inductive factors give a better fit to a

straight line, with a correlation coefficient of 0.980 and standard deviation of 2.7 as compared to the correlation coefficient of 0.950 and standard deviation of 4.2 against group electronegativity. The resulting equations for each line are $\underline{J}^{119} = -14.3\sigma^* + 503.2$ and $\underline{J}^{119} = -56.4\chi_i + 611.7$, respectively.

^{119m}Sn Mössbauer Spectra.

Table 12 lists the ^{119m}Sn Mössbauer data taken at 77K. All the spectra are well-resolved doublets. The Isomer Shifts (I.S.) and Quadrupole Splittings (Q.S.) in each series of haloacetates show a general increase with increasing halosubstitution on the acetate group, a trend previously observed for analogous series of triorganotin haloacetates.[29,57,58] A pronounced saturation effect in the variation of Quadrupole Splitting with group electronegativity was observed for the tri-n-butyltin haloacetates.[29] The same effect is also observed for di-n-butyltin chloride haloacetates, as illustrated by Figure 1.

Discussion

Preparation of Diorganotin Halide Carboxylates.

Reactions of diorganotin oxide with metallic and organometallic halides[59-62] and with thionyl chloride[63] are well-known, and in general may be written as:

$$R_2SnO + X\text{-}Y \longrightarrow R_2XSnOY \qquad (6)$$

The reaction of dimethyltin oxide with acetyl chloride to give dimethyltin chloride acetate,[28] shown in Eq. (5), is an example. The reaction of acid halides with diorganotin oxides was found to be a convenient method for the preparation of diorganotin halide carboxylates:

$$R_2SnO + X\overset{O}{\overset{\|}{C}}R' \longrightarrow R_2XSn\overset{O}{\overset{\|}{O}}CR' \qquad (7)$$

Although only diethyltin dichloride and diethyltin dibenzoate could be isolated from the reaction of diethyltin oxide and benzoyl chloride,[28] the dialkyltin halide benzoates in this study were isolated from the reaction of benzoyl halides with dimethyl- and di-n-butyltin oxide. Acetyl chloride reacts with di-n-butyltin sulfide to give di-n-butyltin chloride thioacetate.

Other carboxylic acid derivatives were obtained through exchange reactions of the type:

$$R_2XSnO_2CCH_3 + HO_2CR' \longrightarrow R_2XSnO_2CR' + HO_2CCH_3 \qquad (8)$$

in which HO_2CR' is a higher boiling carboxylic acid, and the acetic acid

formed was removed by distillation. However, as noted in earlier studies,[64,65] relative volatility is not the controlling factor in these transformations. Although thioacetic acid (b.p. 93°) is more volatile, for example, it readily liberates acetic acid (b.p. 118°) from dimethyltin chloride acetate. Thioacetic acid also displaces acetic acid from tri-n-butyltin acetate,[66] suggesting that tin-sulfur is favored over tin-oxygen bonding. This is also demonstrated by the preparation of organotin mercaptans in aqueous alkaline solution[67] while organotin alkoxides react rapidly with water.

The structure and bonding of triorganotin carboxylates have been extensively discussed,[68] however, diorganotin halide carboxylates have not been as thoroughly investigated. The results of infrared, ^{119m}Sn Mössbauer, ^{1}H and ^{13}C nmr measurements for the diorganotin halide carboxylates prepared for this study are interpreted in terms of structure and bonding and compared with previous findings for closely-related systems.

Diorganotin Halide Acetates and Haloacetates. Triorganotin carboxylates are pentacoordinated in the solid-state through bridging carboxylate groups, unless the substituents at tin are bulky, or the carboxylate group is branched at the α-carbon,[69] and X-ray crystallographic data[1] confirms this suggestion originally put forward on the basis of infrared studies.[70] The $\nu_{asym}(CO_2)$ mode for trimethyltin acetate[34] at 1576 cm^{-1} is typical of associated organotin carboxylates.[68] The frequency separations of $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ have also been used to infer the type of carboxylate structure present.[71-73] The separations of $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ from Table 2 are all in the range 150-128 cm^{-1}, indicative of the expected bridging carboxylate structure illustrated in Figure 2a. Similar conclusions for organotin haloacetates are precluded owing to shifts in the carbonyl stretching

frequencies with halosubstitution. All the acetate and haloacetate derivatives listed in Tables 2, 3 and 4 exhibit both $\nu_{asym}(Sn-C)$ and $\nu_{sym}(Sn-C)$, indicating a nonlinear C-Sn-C moiety consistent with the proposed structure.

The increase in $\nu_{asym}(CO_2)$ and lowering of $\nu_{sym}(CO_2)$ with increasing halogenation on the acetate group has also been observed for the triorganotin haloacetates.[27,29,34,38,57,58,72,74,75] Many factors are involved in determining this frequency, such as inductive, resonance, and field effects, which alter the force constant of the carbonyl group, and physical factors such as phase changes, mass and angle effects, vibrational coupling, and changes in the force constants of the adjacent bonds. Substituting increasingly electronegative groups on the α-carbon atom would tend to increase the $\nu(CO_2)$ frequency, while the mass effect would be expected to decrease it. Thus the increases in the $\nu_{asym}(CO_2)$ frequency are dominated by inductive effects, while the mass effect predominates in the lowering of $\nu_{sym}(CO_2)$.[38,74]

The Isomer Shifts of organotin(IV) compounds measure changes in the density of s-electrons at the nucleus, mainly $|\Psi_{5s}(0)|^2$ for tin.[76] The progressive substitution of increasing electron withdrawing groups should lower this value. Table 12, however, shows a small, but monotonic increase of Isomer Shift with successive halosubstitution. In addition, while the Isomer Shifts of the dialkyltin chloride acetates are smaller than the corresponding dialkyltin bromide acetates as is predicted, the Isomer Shifts of the diorganotin halide acetates are larger than those of the corresponding trialkyltin acetates, opposite to what is predicted.

The observed ^{119m}Sn Mössbauer data may be interpreted, following our previous study of the trialkyltin acetates, as follows: the population of the empty 5d-orbitals of the tin atom by electron pairs from a carbonyl oxygen atom

would be expected to lower the effective $|\Psi_{5s}(0)|^2$ by shielding, and thus lower the Isomer Shift relative to the value found in a monomer with a free, organic ester structure. The subsequent weakening of the Lewis base strength of the carbonyl by the inductive pull of the halomethyl group in the $X_nH_{3-n}CCO_2$-system could thus account for the observed incremental increase in Isomer Shift. We previously predicted that halosubstitution at the tin atom, with its concomitant increase in Lewis acidity of the tin atom, would result in an increase in Isomer Shift,[29] and this is confirmed by the observed data. Another consequence of this suggestion is a strengthening of the tin-carbonyl oxygen bond with a concomitant lowering of the $\nu(CO_2)$ frequency. The $\nu_{asym}(CO_2)$ frequencies of the dimethyltin chloride and bromide acetates are ca. 20 cm^{-1} lower than those of trimethyltin acetate.[34,71]

The ratios of Quadrupole Splitting to Isomer Shift (σ), are greater than 2.1 for all the acetate and haloacetates studied, reflecting higher than four coordination at tin.[76] The observation of a spectrum at ambient temperatures for dimethyltin chloride acetate is indicative of a polymeric lattice structure.[76,78] Examination of Table 12 also reveals that the Quadrupole Splittings for dimethyl- and di-n-butyltin halide acetates are the same as those of the trimethyl- and tri-n-butyltin acetates.

The proposed structure for diorganotin chloride halide acetate shown in Figure 2a contains bridging acetoxy groups in the axial-positions, with the two organic groups and the halogen atom in the equatorial positions. Another associated, pentacoordinated structure is also possible, with the acetoxy groups bridging from axial- to equatorial- positions with halogen in the axial-position. Distinguishing these two isomers on the basis of infrared or Mössbauer data is at present impossible.[79]

In solution, the $\nu_{asym}(CO_2)$ modes shift to higher frequencies (cf. Tables 5 and 6), the greatest increases being for the acetate compounds (ca. 40-50 cm^{-1}). These increases suggest that depolymerization occurs in solution. Similar changes have been previously reported for dialkyltin chloride acetates, which are monomeric in solution.[23] Trimethyltin acetate, whose $\nu_{asym}(CO_2)$ frequency increases from 1570 to 1658 cm^{-1}, and which is monomeric in dilution solution,[77] is typical of a triortanotin carboxylate with an ester-type structure. However, the chelated structure shown in Figure 2b has also been proposed for the halide acetates in solution.[23,27] Similar carbonyl stretching vibrations at ca. 1600 cm^{-1} have also been observed for monomeric dialkyltin diacetates in solution, and bis-chelated, hexa-coordinated structures have been proposed.[41] The chelated structure shown in Figure 2b is analogous to that determined for the sulfur derivative, dimethyltin chloride N,N-dimethyldithiocarbamate, by X-ray diffraction of the solid.

The $\nu_{asym}(CO_2)$ absorption bands of the dimethyltin halide mono- and dichloroacetates in solution show splittings with frequency differences of ca. 24-37 cm^{-1}, indicating that rotational isomerism of the acetoxy chloromethyl group occurs in these compounds. Rotational isomerism, inferred from splittings with frequency differences of ca. 25 cm^{-1}, has been claimed for tri-n-butyltin chloroacetates,[74,81] however, the corresponding bands in di-n-butyltin chloride haloacetates are unsplit.

Nmr spectroscopy has been a valuable technique in the study of organotin compounds in solution. On the basis of isovalent hybridization arguments,[82] the s-character of the hybrid orbitals directed from the tin atom will tend to be concentrated in the bonds to carbon, leaving the tin-oxygen bond relatively more p- in character. The $|^2J(^{119}Sn\text{-}C\text{-}^1H)|$ couplings for methyltin compounds of coordination numbers four to six show a steady increase, presumably arising

through increased concentration of s-character in the tin-carbon bond.[83] Any removal of electron density by an inductive pull through the $-C-CO_2-Sn$ system would tend to enhance this concentration of s-character in the tin-carbon bonds, and should lead to an increase in tin-proton coupling constant values with halogen substitution as has been seen for trimethyltin haloacetates.[29]

The $|^2J(^{119}Sn-C-^1H)|$ values for dimethyltin halide haloacetates fall in the range 69-76 Hz in chloroform solution. These values are in the range attributed to pentacoordinated tin, and have been interpreted[27] in terms of the chelated acetoxy structure shown in Fig. 2b. The results in Table 10, however, show a decrease in the magnitude of tin-proton coupling constants with increasing halosubstitution, a trend that is opposite to that found for trimethyltin haloacetates. Tin-carbon coupling constants likewise show a monotonic decrease with increasing halosubstitution in the di-n-butyltin chloride compounds.

It has been noted that the carbon-13 chemical shifts and tin-carbon coupling constants for di-n-butyltin chloride acetate are merely the average of the values for neat di-n-butyltin dichloride and diacetate.[56] Comparison of the ^1H nmr parameters listed in Table 10 with data for neat dimethyltin dihalides[84] and diacetates[41] suggest that a dynamic equilibrium exists in solution:

$$2R_2XSnO_2CR' \rightleftharpoons R_2SnX_2 + R_2Sn(O_2CR')_2 \qquad (9)$$

in which the halide and acetoxy groups exchange rapidly between dimethyltin moieties. When solutions of either dimethyltin bromide acetate or chloride trichloroacetate are mixed with dimethyltin chloride acetate, the ^1H nmr parameters quickly become the average of those for the neat solutions. Thus,

nmr coupling constant data for diorganotin halide carboxylates cannot be used to assign the solution state structures of these compounds.

However, the averaged values measured in this investigation are related to the neat values, and the general decrease in the coupling constants may be rationalized in terms of the chelated acetoxy structure proposed for the dialkyltin diacetates. The inductive effect of halosubstitution is expected to be greatest on the adjacent carboxylate carbonyl oxygen, whose Lewis basicity is decreased with increasing halosubstitution. As the carbonyl oxygen becomes less effective in coordinating to the tin atom, the coupling constants decrease in magnitude.

The solution infrared spectra for all the acetate and haloacetate compounds show an additional band at ca. 100-125 cm^{-1} to higher frequencies than the $\nu_{asym}(CO_2)$ mode, which is absent in the solid-state spectra. The shifts in these higher frequency absorptions with increasing halosubstitution parallel the shifts in the $\nu_{asym}(CO_2)$ mode, suggesting that the band is associated with a carboxylate vibration. This higher frequency band was investigated in more detail for di-n-butyltin chloride acetate, where it is invariant with concentration, while the $\nu_{asym}(CO_2)$ absorption at ca. 1600 cm^{-1} shows the expected increases in intensity. The $\nu_{asym}(CO_2)$ mode is unaffected by addition of triethylamine; however, at a mole ratio of base above 1:10, the high frequency band disappears. Further addition of triethylamine precipitates the bis-adduct of di-n-butyltin dichloride. Addition of 1,10-phenanthroline to solutions of dimethyltin chloride acetate also precipitates the adduct with dimethyltin dichloride, results which confirm the equilibrium in Eq. (9). As the temperature of a cyclohexane solution of di-n-butyltin chloride acetate is raised, the higher frequency band disappears

reversibly. In contrast, no variation is observed in the $\nu_{sym}(CO_2)$ mode.

Figure 3 illustrates some of the carboxylate structures possible. Organotin compounds possessing the bridging structure (Figure 3a) generally exhibit the $\nu_{asym}(CO_2)$ mode in the range 1560-1540 cm^{-1}, whereas those possessing the free ester-type structure (Figure 3d), show the $\nu_{asym}(CO_2)$ mode at 1640-1660 cm^{-1}. Compounds containing a dimeric structure such as that shown in Figure 3b, which has been proposed for the neat liquid dialkyltin diacetates,[41] have the $\nu_{asym}(CO_2)$ mode in the same range as the bridging structures of the type shown in Figure 3a. Structures with a chelating acetate group, as in Figure 3c, would be expected to have the $\nu_{asym}(CO_2)$ absorb at frequencies between those of the bridging and the free-ester type structures.

Asymmetric carbonyl stretching frequencies for the acetate derivatives of the Group IV elements, M, recorded under conditions in which all the derivatives possess an ester-type structure, decrease with increasing atomic weight, as shown in Table 13. This trend is opposite to increasing the halosubstitution on the acetate group, where the mass effect does not predominate in determining the shifts of the asymmetric carbonyl frequencies. Although mass effects predominate in substitution of M, other effects must also be considered.

The observed shifts may be caused by changes in the degree of ionicity of the metal-oxygen bonds,[85] however, this suggestion assumes that only electronic effects occur, ignoring the rotational isomerism that has been observed for the mono- and dihaloacetate compounds.[74,81] In the case of the compounds listed in Table 13, only the rotational isomers of the cis-derivative should be observed, since steric considerations would rule out the trans-derivative. With the carbonyl oxygen in the cis-position, interaction

with the central element could be possible. Since Lewis acidities are in the order Sn>Ge>Si, the donor interactions of the carbonyl oxygen should follow that order, and a decrease in frequency with increasing interaction should be observed.

Trimethyltin acetate has been studied in detail.[77] In dilute solution the compound is monomeric, the $\nu_{asym}(CO_2)$ mode occurring at 1650 cm^{-1}. As the concentration is increased, a band at 1580 cm^{-1} attributable to the associated form grows. Upon heating, this band disappears while the band arising from the monomer grows at 1650 cm^{-1}. The same effect also occurs upon addition of trimethylamine. The two bond tin-proton coupling constants for trimethyltin acetate in dilute solution are comparable to those of trimethyltin chloride, suggesting tetracoordination at the tin atom.

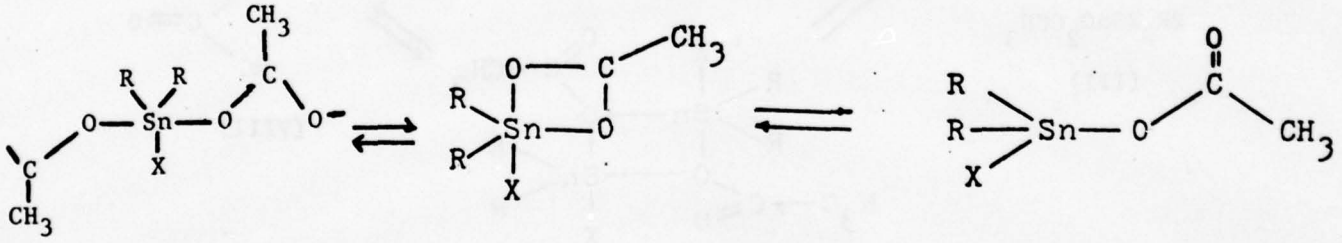
The question of interaction of the carbonyl oxygen in the presumably tetracoordinated monomeric tin compound is not unequivocal, however. While the infrared and nmr data indicate no appreciable interaction, the ^{119m}Sn Mössbauer data for tricyclohexyltin acetate is not consistent. The X-ray crystal structure shows tricyclohexyltin acetate to consist of discrete monomers in which the intramolecular tin-carbonyl oxygen distance is only 2.95 Å,[12] the $\nu_{asym}(CO_2)$ mode[12] occurring at 1645 cm^{-1} in the solid is nearly identical to that for trimethyltin acetate in dilute solution.[77] However, the Isomer Shift and Quadrupole Splitting values at 77K are 1.57 and 3.27 mm/s, respectively,[86] (ρ = 2.08), the latter being much larger than expected for tetracoordinated tin, and suggestive of considerable interaction.

Steric requirements in trimethyl- and tricyclohexyltin acetate prevent the carbonyl oxygen from being directed away from the tin atom. Compounds such as tin tetraacetate,[87,88] butyltin tricarboxylates,[89] and dimethyltin

oxalate monohydrate,[90] in which at least one carbonyl oxygen cannot be coordinated to tin, all exhibit a high frequency carboxylate absorption band.

Molecular models of di-n-butyltin chloride acetate and trimethylacetate suggest that rotation to the trans-isomer is possible for the former but not for the latter. However, the high frequency band is also observed for di-n-butyltin trimethylacetate, exhibiting the same temperature dependence as in the acetate. Rotational isomerism alone then cannot explain these results.

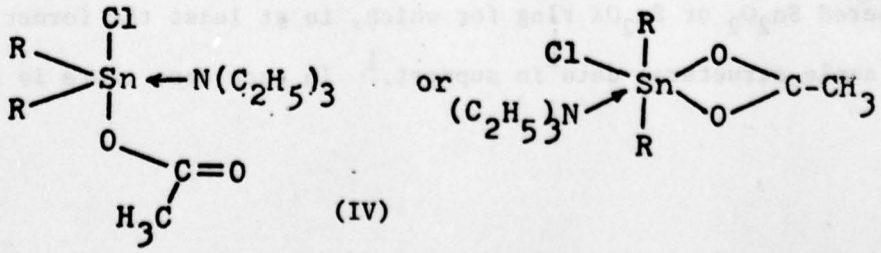
The Lewis acidity of tin in $R_2XSnO_2CCH_3$ toward coordination by the carbonyl oxygen will be greater than in $R_3SnO_2CCH_3$. If the high frequency band is attributed to an uncoordinated carboxylate oxygen, then an equilibrium could be established:



(I) (II) (III) (10)

Increasing the temperature would be expected to shift the equilibrium toward the right and result in an increase in the intensity of the high frequency band. However, the opposite is observed.

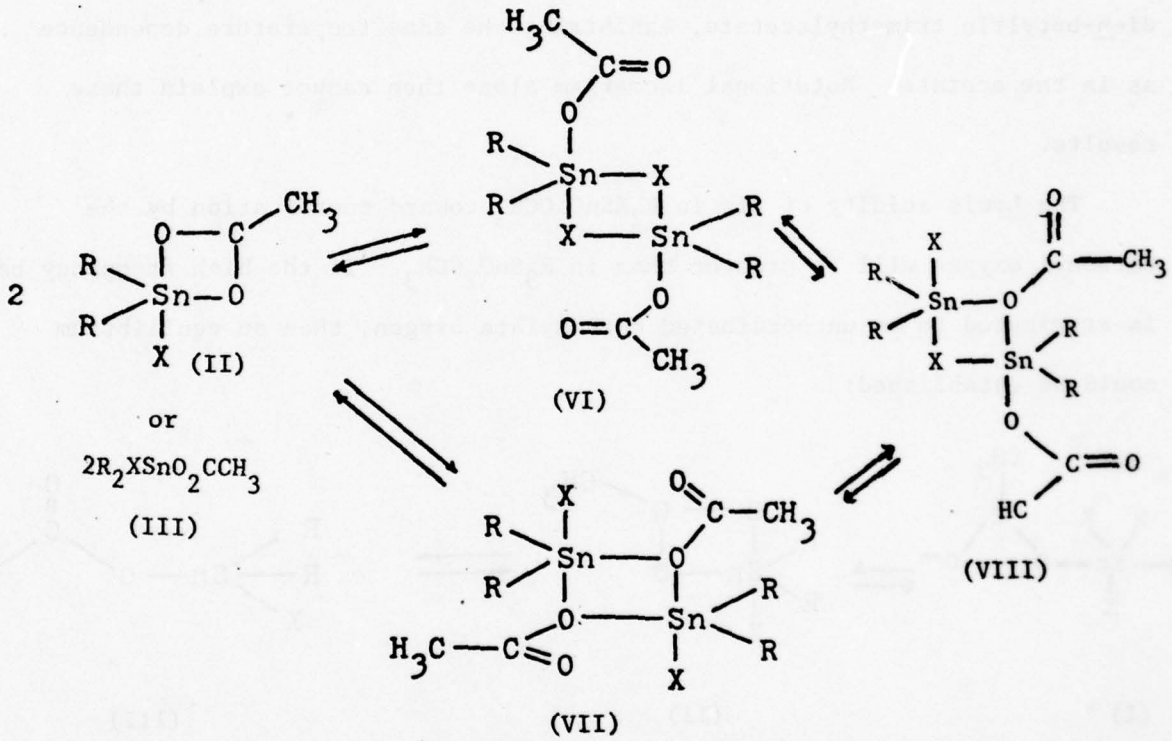
Addition of a Lewis base such as triethylamine which would coordinate with the tin atom producing either of the species



(IV) (V)

the first of which would exhibit in an enhanced intensity for the uncoordinated carboxylate oxygen band, again contrary to what is observed. Production of the second species is complicated by the fact that addition of even a small excess of triethylamine precipitates the bis-adduct with R_2SnX_2.

Association of the organotin species to give dimers must be considered. Possible equilibrium structures are:



(11)

Molecular weight data for diethyl- and di-n-propyltin chloride acetate, as determined cryoscopically in benzene, are about 5% higher than the monomeric molecular weights,[23] but those for dimethyltin chloride monoiodo- and dichloroacetate in chloroform[27] exceed the calculated values by about 25%.

The dimeric structures (VII) and (VIII) in the scheme are based upon a four-membered Sn_2O_2 or Sn_2OX ring for which, in at least the former case, there is ample structural data in support.[1] In each case there is an acetate

group with the carboxylate oxygen both bonded to a tin atom and coordinated to the tin atom of the second molecule in the dimer. This arrangement, which leaves the carbonyl group free, is seen in the X-ray crystal structures of the dimeric $\{[(H_2C{=}CH)_2SnO_2CCF_3]_2O\}_2$[15] and $\{[(\underline{n}\text{-}C_4H_9)_2SnO_2CCCl_3]_2O\}_2$,[16] molecules which include such a tricoordinated carboxylate oxygen and free carbonyl group. Such a system would be expected to exhibit a higher carbonyl stretching vibration than for a typical free-ester group, and strong absorptions at ca. 1700 and 1715 cm^{-1}, respectively, have been recorded for these two examples as well as at 1715 cm^{-1} for the dimeric $\{[(\underline{n}\text{-}C_4H_9)_2SnO_2CCH_nCl_{3-n}]_2O\}_2$ molecules.[91] Since the dynamic equilibria shown in Eq. (11) involve only dimers, their relative positions should be unaffected by concentration changes, but the addition of the Lewis base triethylamine would quickly shift the system to the bis-adduct of the monomer, which is observed to precipitate. Heating would also drive the system to the monomeric form.

Diorganotin Halide Benzoates. The infrared, ^{119m}Sn Mössbauer, ^{1}H and ^{13}C nmr results for dialkyltin halide benzoates, in general parallel those of the diorganotin halide acetates.

In the solid-state, the benzoate may act as a bridging group between dialkyltin halide units in a linear polymer. The carbonyl stretch at ca. 1570 cm^{-1} and the Quadrupole Splitting values of ca. 3.5 mm/s are very similar to those of the diorganotin halide acetates.

Unlike in the diorganotin halide acetates, however, the $\nu_{asym}(CO_2)$ modes do not shift to higher frequencies in solution, and except for the appearance of the high frequency absorption band at ca. 1700 cm^{-1}, the solution infrared spectra are nearly identical to the solid-state spectra. We interpret the high frequency band in the same way as above.

In the solid-state, the $\nu_{asym}(CO_2)$ mode of triphenyltin benzoate is found at 1620,[47] and at 1565 and ca. 1640 cm^{-1} in tri-n-propyl-[85] and tri-n-butyltin benzoate,[85,92] which are liquids. The $\nu_{asym}(CO_2)$ mode has also been reported for di-n-butyltin dibenzoate at 1560 in the solid-state and at 1568 cm^{-1} in chloroform solution. Since far less data are available, the assignment of a solid-state structure analogous to that of the corresponding acetate derivatives must be tentative. Since there is no shift toward higher frequencies in the $\nu_{asym}(CO_2)$ mode on dissolution, it is likely that structures adopted in both states contains chelated benzoate groups.

Again, two bond tin-proton nmr coupling constants measured for the dimethyltin halide benzoates are the average of those for dimethyltin dihalide[93] and dimethyltin dibenzoate,[21] and an equilibrium as in Eq. (9) must exist.

Dialkyltin Chloride Thioacetates. The physical and spectral data for diorganotin halide acetates suggest that in the solid-state they take an associated trigonal bipyramidal structure containing bridging acetate groups. Dialkyltin chloride thioacetates have considerably different properties, however. Dimethyltin chloride thioacetate is a low melting crystalline solid, and di-n-butyltin chloride thioacetate is a liquid at room temperature.

The solid-state infrared spectra of dimethyltin chloride thioacetate and of di-n-butyltin chloride thioacetate in a liquid film are similar to their spectra obtained in carbon tetrachloride solutions. In each state, the $\nu(C{=}O)$ mode is found in the range 1612-1604 cm^{-1}, similar to the dialkyltin halide acetates. This value is ca. 50 cm^{-1} lower than those observed for trialkyltin thioacetates.[52,94] Although the $\nu(C{-}O)$ mode for the sodium salt of thioacetic acid has not been assigned, a qualitative comparison may be made with that of sodium thiobenzoate,[51] which is found at 1557 cm^{-1}.

Trimethyltin thioacetate is monomeric in solution,[52] and its two bond tin-proton coupling constant values are in the range of those attributable to tetracoordinated tin atoms, as in trimethyltin acetate in dilute solution, which has a free-ester type structure. While both the ν_{asym}(Sn-C) and ν_{sym}(Sn-C) modes are observed, no bands attributable to the ν(C=S) mode are observed, indicating that the carbonyl oxygen is only weakly coordinating.

Proton nmr data are in the range of those expected for pentacoordinated tin, for the acetates, but exchanges as in Eq. (9) may also be occurring.

Evidence in support of a pentacoordinated structure comes from the Quadrupole Splitting data which for the trialkyltin thioacetates are in the range of those found for tetracoordinated tin,[52] but for the dimethyl- and di-n-butyltin chloride thioacetate are >3.00 mm/s. Unfortunately, no ^{119m}Sn Mössbauer data are available for any other organotin-sulfur compounds having a similar structure. The Mössbauer spectrum of the disulfur analogue dimethyltin chloride N,N-dimethyldithiocarbamate, whose chelating structure has been confirmed by X-ray crystallography[80] has not been measured.

Trialkyltin Thioacetates. Trimethyltin thioacetate has been prepared by the action of the potassium salt of thioacetic acid on trimethyltin chloride:[94]

$$(CH_3)_3SnCl + KS\overset{O}{\overset{\|}{C}}C_6H_5 \longrightarrow (CH_3)_3Sn\overset{O}{\overset{\|}{S}}CC_6H_5 + KCl \qquad (12)$$

The n-butyl derivative has been made by the action of thioacetic acid on bis(tri-n-butyltin)oxide:[95]

$$R_3SnOSnR_3 + 2HS\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow 2R_3Sn\overset{O}{\overset{\|}{S}}CCH_3 + H_2O \qquad (13)$$

or on tri-n-butyltin acetate:[66]

$$(n\text{-}C_4H_9)_3SnOCCH_3 + HSCCH_3 \longrightarrow (n\text{-}C_4H_9)_3SnSCCH_3 + HOCCH_3 \quad (14)$$

We have prepared the trimethyltin compound in high yield using sodium methoxide in a variation of a published method:

$$(CH_3)_3SnCl + HSCCH_3 + NaOCH_3 \longrightarrow (CH_3)_3SnSCCH_3 + NaCl + CH_3OH \quad (15)$$

The tri-n-butyl derivative was synthesized by the method depicted in Eq. 13.

The infrared spectra are given in Table 14 for the neat compounds and their solutions in carbon tetrachloride. The infrared spectra of tri-n-butyltin thioacetate as a liquid film and carbon tetrachloride solution, and the trimethyltin thioacetate in carbon tetrachloride solution are all very similar. The ν(C=O) modes are observed as intense absorption bands at ca. 1660 cm^{-1}. The ν(C=O) mode for trimethyltin thioacetate gives rise to an absorption band which is broad and split, at 1603 and 1575 cm^{-1}. This band for trimethyltin thioacetate has been previously reported[52] to occur at the same frequency observed in solution, 1667 cm^{-1}, however, no mention was made of whether the compound was dispersed in a potassium bromide disc or run as a Nujol mull. It was found in this investigation that when trimethyltin thioacetate was run in Nujol, the sharp band at ca. 1660 cm^{-1} appears together with a weaker band at ca. 1600 cm^{-1}.

The ^{119m}Sn Mössbauer data in Table 12 reveal that the value of the Quadrupole Splitting for trimethyltin thioacetate is significantly greater than that of tri-n-butyltin thioacetate, which is monomeric and tetracoordinated,[1]

but similar to the value found for the tri-n-butyltin compound in frozen pyridine solution, in which there is higher coordination at tin.[95] The infrared and Mössbauer data for trimethyltin thioacetate suggest that in the solid-state its structure contains a chelating thioacetoxy- group.

The Lewis acidity of a triorganotin group is less than that of a diorganochlorotin group, and in solution trimethyltin thioacetate is tetra-coordinated, the ν(C=O) mode moving to higher frequencies. In carbon tetrachloride, the $|J(^{119}Sn\text{-}C\text{-}^{1}H)|$ value is 58.0 Hz, similar to that for trimethyltin acetate in dilute solution, which is monomeric and generally considered to be tetracoordinated.[77]

A recent report[95] opens up a new dimension on these studies. During the annealing of a sample of $(C_6H_5)_3SnO_2CCCl_3$[58] at room temperature for five years a solid state monomer-polymer phase transition occurred. This new associated form could also be produced directly by changing the solvent of reaction from methanol[58] to ethanol.[95] The $\nu_{asym}(CO_2)$ mode absorbs at 1700 cm^{-1} in the monomer (Q.S. 2.97 mm/s) and at 1618 cm^{-1} in the polymer (Q.S. 3.90 mm/s) in the solid state, but the latter dissolves as the monomer in dilute carbon tetrachloride.[95]

TABLE 1

Diorganotin Halide Carboxylates

Compound	Preparative[a] Method	Recryst. Solvent	Yield, %	m.p.	% Sn (% Sn calc.)
$(CH_3)_2ClSnO_2CCH_3$	1	acetone	80	186-189°[b]	48.20(48.79)
$(CH_3)_2ClSnO_2CH_2Br$	2	hexane/$CHCl_3$	80	136-138°	35.24(36.84)
$(CH_3)_2ClSnO_2CCH_2Cl$	2	hexane/$CHCl_3$	76	123-126°[c]	43.16(42.74)
$(CH_3)_2ClSnO_2CCHCl_2$	2	CCl_4	80	123-125°[d]	37.84(38.02)
$(CH_3)_2ClSnO_2CCCl_3$	2	$CHCl_3$	55	186°[e]	34.13(34.25)
$(CH_3)_2ClSnO_2CC_6H_5$	1	hexane	67	73-76°	36.06(35.71)
$(CH_3)_2ClSnSC(O)CH_3$	2	pentane	64	62-63°	45.80(45.77)
$(CH_3)_2BrSnO_2CCH_3$	1	acetone	90	191-193°	40.76(41.25)
$(CH_3)_2BrSnO_2CCH_2Cl$	2	toluene	82	122-124°	37.24(36.84)
$(CH_3)_2BrSnO_2CCHCl_2$	2	CCl_4	72	72-75	33.48(33.28)
$(CH_3)_2BrSnO_2CCCl_3$	2	$CHCl_3$	81	175-176°	30.21(30.35)
$(CH_3)_2BrSnO_2CC_6H_5$	2	hexane		76-78°	32.47(33.93)
$(n\text{-}C_4H_9)_2ClSnO_2CCH_3$	1	hexane	93	63-64°[f]	

TABLE 1 (cont'd)

Compound	Preparative[a] Method	Recryst. Solvent	Yield,%	m.p.	% Sn (% Sn calc.)
$(\underline{n}\text{-}C_4H_9)_2ClSnO_2CCH_2I$	2	hexane	88	68-69.5°	25.89(26.18)
$(\underline{n}\text{-}C_4H_9)_2ClSnO_2CCH_2Br$	2	hexane	90	60-62°	29.58(29.21)
$(\underline{n}\text{-}C_4H_9)_2ClSnO_2CCH_2Cl$	2	hexane	93	68-69.5°	32.79(32.80)
$(\underline{n}\text{-}C_4H_9)_2ClSnO_2CCHCl_2$	2	hexane	92	75.5-77°	29.87(29.95)
$(\underline{n}\text{-}C_4H_9)_2ClSnO_2CCCl_3$	2	hexane	84	92.5-94°	27.38(27.55)
$(\underline{n}\text{-}C_4H_9)_2ClSnO_2CC(CH_3)_3$	1			g	32.83(32.12)
$(\underline{n}\text{-}C_4H_9)_2ClSnO_2CC_6H_5$	1	pentane	66	40-41.5°	30.03(30.47)
$(\underline{n}\text{-}C_4H_9)_2ClSnSC(O)CH_3$	1			h	35.54(34.56)
$(\underline{n}\text{-}C_4H_9)_2BrSnO_2CCH_3$	1	hexane	92	64[i]	
$(\underline{n}\text{-}C_8H_{17})_2ClSnO_2CCH_3$	1	pentane	32	73.5-75°	27.08(27.00)
$(\underline{n}\text{-}C_8H_{17})_2BrSnO_2CCH_3$	1	pentane	67	70-71.5°	24.40(24.52)
$(C_6H_5)_2ClSnO_2CCH_3$	1	pentane	79	92-95°	31.76(32.31)
$(C_6H_5)_2BrSnO_2CCH_3$	1	pentane	21	86-89°	28.44(28.82)

TABLE 1 (cont'd)

[a] 1- reaction between R_2SnO and R'COX; 2- reaction between $R_2XSnO_2CCH_3$ formed *in situ*, and $R'CO_2H$.

[b] Lit. values, 184-189° [18] and 187-188°.[27]

[c] Lit. values, 126.5-128° [21] and 129-130°.[27]

[d] Lit. value, 130-131°.[27]

[e] Lit. value, 196°.[27]

[f] Lit. values, 56.5-57.5°,[20] 60-61°,[22] 61°,[23] and 63-65°.[25]

[g] B.P. 106-109° at 0.25 torr.

[h] B.P. 96-99° at 0.25 torr.

[i] Lit. value, 67-68.5°.[24]

TABLE 2

Infrared Spectra of Diorganotin Halide Acetates, $R_2XSnO_2CCH_3$

Assignments	R= CH_3 X= Cl	CH_3 Br	$\underline{n}$-C_4H_9 Cl	$\underline{n}$-C_4H_9 Br	$\underline{n}$-C_8H_{17} Cl	$\underline{n}$-C_8H_{17} Br	C_6H_5 Cl	C_6H_5 Br
$\nu_{asym}(CO_2)$	1555 vs	1557 vs	1558 vs	1560 vs	1551 vs	1554 vs	1555 vs	1550 vs
$\nu(C\text{-}C)$[a]							1482 s	1483 s
$\delta_{asym}(C\text{-}CH_3)$	1453 s	1452 s	1465 s	1466 s	1467 s	1468 s	1447 s	1447 s
	1435 s	1434 s	1448 s	1445 s	1450 s	1450 s	1434 s	1435 s
$\nu_{sym}(CO_2)$	1408 s	1408 s	1417 s	1419 s	1410 s	1404 s	1413 s	1422 s
			1380 w	1379 w	1381 sh			
			1347 w	1347 w			1347 m	1351 w
							1335 w	1333 w
					1272 w	1270 w	1306 w	1306 w
					1257 w	1256 w		
$\delta_{sym}(Sr\text{-}CH_3)$	1212 w	1209 w			1212 w	1217 w		
	1199 w	1199 w	1194 w	1195 w			1194 w	1196 w
$\delta(C\text{-}H)$ i.p.[a]							1182 w	1183 w
							1158 w	1162 w

TABLE 2 (cont'd)

Assignment	CH_3 Cl	CH_3 Br	$\underline{n}$-C_4H_9 Cl	$\underline{n}$-C_4H_9 Br	$\underline{n}$-C_8H_{17} Cl	$\underline{n}$-C_8H_{17} Br	C_6H_5 Cl	C_6H_5 Br
			1161 m	1157 m	1155 m	1152 m		
					1114 m	1112 m		
			1081 m	1083 m				
δ (C-H) i.p.[a]							1076 m	1076 m
δ (O_2C-CH_3) rock	1052 w	1050 w	1049 w	1051 w	1048 w	1048 w	1046 w	1049 w
	1020 m	1019 m	1016 m	1016 m	1016 m	1015 m	1022 m	1023 m
ν (C-C)[a]							999 s	1000 s
δ (C-H) o.p.[a]							976 w	980 w
			967 w	970 w	988 w	988 w		
ν (O_2C-CH_3)	952 w	950 w	947 w	947 w	950 w	948 w	948 w	948 w
					910 w	909 w		
			874 m	875 m				
			854 sh	854 sh			848 w	852 w
				832 m	831 m			
δ (Sn-CH_3) rock	817 sh							
	798 s	798 s						

TABLE 2 (cont'd)

Assignment	CH_3 Cl	CH_3 Br	n-C_4H_9 Cl	n-C_4H_9 Br	n-C_8H_{17} Cl	n-C_8H_{17} Br	C_6H_5 Cl	C_6H_5 Br
			773 w	773 w		769 w		
δ(C-H) o.p.[a]							735 s	739 s
					725 m	724 m		
δ(C-H) o.p.[a]							696 s	697 s
$\delta(CO_2)$ scissor	689 s	687 s	678 s	679 s	683 s	682 s	688 sh	686 sh
					673 sh	673 sh		
$\delta(CO_2)$ o.p.	618 m	616 m	614 m	613 sh	615 m	615 m	612 m	616 m
ν_{asym}(Sn-C)	579 m	577 m	600 m	595 m	606 m	604 m		
					589 w			
ν_{sym}(Sn-C)	529 m	525 m	520 m	515 m	530 m	522 m		
$\delta(CO_2)$ i.p.	495 m	495 m	488 m	492 sh	484 m	485 m	498 w	496 w
16b(B_1)[a]							451 s	452 s
		420 w		415 w	432 w	430 w		
	396 w		396 w	395 w				
						350 m		
ν(Sn-Cl)	330 s		332 s		326 s		335 s	

TABLE 2 (Cont'd)

Assignment	CH_3 Cl	CH_3 Br	$\underline{n}$-C_4H_9 Cl	$\underline{n}$-C_4H_9 Br	$\underline{n}$-C_8H_{17} Cl	$\underline{n}$-C_8H_{17} Br	C_6H_5 Cl	C_6H_5 Br
ν(Sn-O) + ν_{asym}(Sn-C_6H_5)	287 m	287 m	275 m	280 m	271 m	275 s	295 s	294 s
								280 sh
ν(Sn-Br)		227 s		228 s		227 s		252 s
ν_{sym}(Sn-C_6H_5)							238 m	224 m
	207 w	205 w	207 w					

[a]Benzene ring vibrations in the phenyltin compounds.

TABLE 3

Infrared Spectra of Dimethyltin Halide Haloacetates, $(CH_3)_2XSnO_2CR$

Assignment	X= Cl R= CH_2Br	Cl CH_2Cl	Cl $CHCl_2$	Cl CCl_3	Br CH_2Cl	Br $CHCl_2$	Br CCl_3
$\nu_{asym}(CO_2)$	1612 vs	1601 vs	1630 vs	1645 vs	1607 vs	1628 vs	1653 vs
				1519 w			1512 w
				1407 m			1401 m
				1377 sh			1372 sh
		1414 sh					
$\nu_{sym}(CO_2)$	1400 vs	1402 vs	1395	1363 vs	1404 vs	1396 vs	1358 vs
						1367 vs	
	1361 s						
					1343 m		
	1218 s	1253 s			1251 s		
			1240 w			1238 m	
			1221 m		1229 m		
	1205 sh	1211 w			1208 w	1219 w	
			1200 m	1201 vw	1197 w	1199 m	
	1160 vw	1182 vw			1160 w		
	1131 w						
	1110 w	1020 vw	1019 vw				
	946 w						
ν(C-C)	899 m	939 m	956 w	970 w	935 m	950 w	967 m
	892 m						

TABLE 3 (cont'd)

Assignment	Cl CH_2Br	Cl CH_2Cl	Cl $CHCl_2$	Cl CCl_3	Br CH_2Cl	Br $CHCl_2$	Br CCl_3
ν_{asym}(C-Cl)			822 s	849 s 836 s		823 s	849 s 833 s
		820 sh			820 sh		
δ(Sn-CH_3) rock	802 s	792[a] s	793 s	805 s	788[a] s	801 s	804 m
ν_{sym}(C-Cl)				753 s		778 sh	754 s
ν(C-Br)	727 s						
			735 sh			734 sh	
δ(CO_2) scissor	695 s	682 s	718 s	688 s	685 s	712 s	685 s
			685 sh			680 m	
δ(CO_2) o.p.	637 m	615 w	637 m	636 m	639 w	629 m	635 w
ν_{asym}(Sn-C)	586 m	581 m	580 m	582 m	586 m	585 m	583 m
	564[b] w						
ν_{sym}(Sn-C)	522 w	525 sh	525 m	528 m	524 sh	525 m	528 m
δ(CO_2) i.p.	504 m	507 s	497 m	498 s	506 s	500 m	500 s
	448 m						
ρ(C-Cl_3)				433 w			434 w 348 m/s
ν(Sn-Cl)	323 s	339 s	350 s	337[c] s			

TABLE 3 (Cont'd)

Assignment	X= Cl R= CH_2Br	Cl CH_2Cl	Cl $CHCl_2$	Cl CCl_3	Br CH_2Cl	Br $CHCl_2$	Br CCl_3
			325 sh				
			314 m			315 m	
ν(Sn-O)	253 m	264 m	264 m	287 m	285 m	280 sh	288 m
			242 m				
ν(Sn-Br)					237 s	241 s	236 s
	215 w	225 w	222 w	227 m		219 m	205 w

[a] ν(C-Cl).

[b] May be low frequency band of a rotational isomer.

[c] ν($C-Cl_3$).

TABLE 4

Infrared Spectra of Di-n-butyltin Chloride Haloacetates, $(n\text{-}C_4H_9)_2ClSnO_2CR$

Assignment	R= CH_2I	CH_2Br	CH_2Cl	$CHCl_2$	CCl_3
$\nu_{asym}(CO_2)$	1580 vs	1588 vs	1604 vs	1634 vs	1646 vs
					1528 w
	1465 m	1467 m	1465 m	1468 m	1468 m
	1436 s	1435 s	1410 s		1407 m
					1381 sh
$\nu_{sym}(CO_2)$	1392 vs	1408 vs	1400 vs	1387 vs	1358 vs
		1380 sh	1346 sh		
	1294 m	1294 w	1292 w	1296 w	1296 w
	1270 w	1269 w		1270 w	1271 w
					1252 w
		1220 m	1249 s	1226 s	
	1195 w	1193 w	1195 sh	1195 w	1195 w
			1175 m		1181 w
	1157 m	1154 m	1159 m	1159 m	1158 m
		1120 m			
	1102 m				
	1082 m	1081 m	1084 m	1084 m	1082 m
	1022 m	1019 m	1025 m	1024 m	1023 m
	1003 w	1002 w		1002 w	1002 w

TABLE 4 (cont'd)

Assignment	R= CH_2I	CH_2Br	CH_2Cl	$CHCl_2$	CCl_3
	959 m	954 w	965 w	962 w	964 w
		935 w			
	889 sh				
	874 m	874 m	880 m	877 m	875 sh
	852 w		854 w		
ν_{asym}(C-Cl)				822 s	840 vs
				796 s	
ν(C-Cl)			795 s		
	779 m		774 sh		
ν_{sym}(C-Cl)				731 s	756 s
					749 s
ν(C-Br)		702 s			
	696 sh				
$\delta(CO_2)$ scissor	682 s	682 s	684 s	686 s	688 s
$\delta(CO_2)$ o.p.		615 sh	616 sh	622 w	
ν_{asym}(Sn-C)	599[a] m	597 m	603 m	600 m	595 m
		565[b] m	576 m	553 vw	576 m
$\nu_{sym}(CO_2)$, $\delta(CO_2)$ i.p.	514 m		504 s	506 m	507 m

TABLE 4 (cont'd)

Assignment	R=	CH_2I	CH_2Br	CH_2Cl	$CHCl_2$	CCl_3
		457 w	460 w			457 w
			415 w	418 w		435 w
		401 w	400 w	395 w	396 w	402 w
			350 sh			
ν(Sn-Cl)		314 s	319 s	339 s	336 s	334 s
		300 sh				
ν(Sn-O)		280 sh	278 sh	275 sh	280 w	293 w
			247 w	260 m	249 w	
		225 w	225 w	225 sh		227 w

[a] ν(C-I).

[b] May be a low frequency band of a rotational isomer.

TABLE 5

Selected Solution Infrared Absorptions of Dimethyltin Halide Haloacetates, $(CH_3)_2XSnO_2COR$

R		$\nu_{asym}(CO_2)$	$\nu_{sym}(CO_2)$	ν_{asym}(Sn-C)	ν_{sym}(Sn-C)	ν(Sn-X)
X = Cl						
CH_3	a	1715	1602	1388	572	528
	b				569	529 331
CH_2Br	a	1727	1623	1363	582	530
	b				580	528 358
CH_2Cl	a	1734	1637, 1600	1375	582	527
	b				580	528 359
$CHCl_2$	a	1749	1648, 1624	1370	582	526
	b				581	527 357
CCl_3	a	1760	1645	1325	582	525
	b				580	528 359
X = Br						
CH_3	a	1716	1603	1383	578	526
	b				581	524 254
CH_2Cl	a	1735	1637, 1600	1376	585	526
	b				585	526 253
$CHCl_2$	a	1750	1650, 1625	1372	582	523
	b				582	523 252
CCl_3	a	1759	1645	1325	583	523
					581	524 254

[a] $CHCl_3$ solution. [b] CCl_4 solution.

TABLE 6

Selected Solution Infrared Absorptions of Di-n-butyltin Halide Haloacetates, $(n\text{-}C_4H_9)_2XSnO_2CR$

R		$\nu_{asym}(CO_2)$	$\nu_{sym}(CO_2)$	ν_{asym}(Sn-C)	ν_{sym}(Sn-C)	ν(Sn-X)
X = Cl						
CH_3	a	1717	1602	1382	614	521	333
	b	1720	1598	1385	613		
CH_2I	a	1715	1611	1357	614	517	346
	b	1721	1608	1366	626	513	
CH_2Br	a	1728	1621	1369	612	520	352
	b	1731	1620	1367	628		
CH_2Cl	a	1737	1634	1376	613	520	352
	b	1737	1635	1378	626	521	
$CHCl_2$	a	1750	1629	1365	610	521	352
	b	1748	1641	1365	628	523	
CCl_3	a	1753	1646	1339		520	351
	b	1762	1658	1343	630	520	
X = Br						
CH_3	a	1716	1601	1380	606	538	253

[a] CCl_4 solution.

[b] $CHCl_3$ solution.

TABLE 7

Infrared Spectra of Dialkyltin Halide Benzoates, $R_2XSnO_2CC_6H_5$

Assignment	R_2X= $(CH_3)_2Cl$		$(CH_3)_2Br$		$(n\text{-}C_4H_9)_2Cl$	
	KBr Disc	CCl_4 Soln	KBr Disc	CCl_4 Soln	KBr Disc	CCl_4 Soln
	1697 m	1698 s		1699 m	1701 w	1698 m
a_1 fund, ν_{8a}, ν(C-C)	1623 sh	1623 sh	1624 sh	1624 sh		
b_1 fund, ν_{8b}, ν(C-C)	1606 s	1607 s	1605 s	1609 s	1606 a	1606 s
$\nu_{asym}(CO_2)$	1566 s	1573 s	1566 s	1575 s	1571 s	1572 s
			1549 s			
	1495 m	1495 m	1496 m	1496 m	1493 m	1496 m
	1452 s	1452 s	1451 s	1452 s	1452 s	1452 s
$\nu_{sym}(CO_2)$	1380 vs	1368 vs	1376 vs	1366 vs	1368 vs	1369 vs
		1319 w	1322 vw	1320 w		1319 w
b_1 fund, ν_{14} ν(C-C)	1305 m	1307 w	1306 m	1308 w	1308 w	1308 w
		1290 w		1291 w		1291 w
				1255 w	1250 w	1253 w
a_1 fund, ν_{9a} δ(CH)	1179 m	1178 m	1179 m	1177 m	1178 m	1177 m
					1158 w	1159 w
	1134 m	1135 m	1134 m	1133 m	1135 m	1134 m

TABLE 7 (cont'd)

Assignment	R_2X= $(CH_3)_2Cl$		$(CH_3)_2Br$		$(n\text{-}C_4H_9)_2Cl$	
	KBr Disc	CCl_4 Soln	KBr Disc	CCl_4 Soln	KBr Disc	CCl_4 Soln
					1082 w	1082 w
b_1 fund, ν_{15} δ(CH)	1073 m	1076 m	1073 m	1071 m	1072 m	1071 m
a_1 fund, ν_{18a} δ(CH)	1025 m	1028 m	1025 m	1026 m	1025 m	1028 m
						962 w
	946 m		946 m			
a_1 fund, ν_{6a}	866 m	873 m	867 m	871 m	870 m	870 m
δ(Sn-CH_3) rock	800 s	a	800 m	a	848 m	
					780 w	
b_2 fund, ν_4 ϕ(C-C)	725 s	721 vs	724 s	720 s	722 vs	722 vs
a_1 fund, CO_2 sym def.	691 s	700 m	691 s	697 m	690 s	698 s
b_1 fund, ν_{6b} α(C-C-C)	618 w	632 m		639 w		
ν_{asym}(Sn-C)	591 m		592 m		615 m	609 m
b_1 fund $\delta(CO_2)$ o.p. rock	550 m	568 m		565 m	558 m	555 m

TABLE 7 (cont'd)

Assignment	$R_2X=$ $(CH_3)_2Cl$		$(CH_3)_2Br$		$(n\text{-}C_4H_9)_2Cl$	
	KBr Disc	CCl_4 Soln	KBr Disc	CCl_4 Soln	KBr Disc	CCl_4 Soln
ν_{sym}(Sn-C)	518 sh	528 w	534 m	525 w	520 w	524 sh
b_2 fund, ν_{16b}	452 s	468 m	453 s	466 m	452 m	465 m
ν(Sn-Cl)	335 m	359 m			324 m	354 m
		295 w	285 w		286 w	
	242	234 w				
ν(Sn-Br)			237 m	236 m		

[a]Region masked by solvent.

TABLE 8

Infrared Spectra of Dialkyltin Chloride Thioacetates

Assignment	$(CH_3)_2ClSnSCCH_3$ (O)		$(\underline{n}\text{-}C_4H_9)_2ClSnSCCH_3$ (O)	
	KBr pellet	CCl_4 Soln	neat	CCl_4 Soln
	1704 w	1719 m	1716 vw	1720 vw
ν(C=O)	1600 vs	1612 vs	1607 vs	1610 vs
			1465 s	1468 s
	1417 m	1421 m	1417 m	1420 m
			1379 m	1382 m
	1354 m	1358 m	1356 m	1359 m
			1294 w	1296 w
			1250 w	1252 w
		1218 m		1219 w
	1175 m	1173 m	1177 m	1180 m
ν(C-C)	1133 s	1138 s	1136 s	1139 s
			1079 w	1078 w
			1026 vw	1025 vw
	1002 w	1011 vw		
ν(C-S)	965 m	965 m	963 m	963 m
			879 m	879 m
			870 sh	870 sh
			848 w	847 w
δ(Sn-CH_3) rock	787 vs	a		

TABLE 8 (cont'd)

Assignment	$(CH_3)_2ClSnSCCH_3$ (O) KBr pellet	$(CH_3)_2ClSnSCCH_3$ (O) CCl_4 Soln	$(n\text{-}C_4H_9)_2ClSnSCCH_3$ (O) neat	$(n\text{-}C_4H_9)_2ClSnSCCH_3$ (O) CCl_4 Soln
			773 vw	
			743 vw	
			708 m	707 m
			679 m	679 m
δ(COS) o.p. bend	657 s	655 s	654 s	655 s
ν_{asym}(Sn-C)	565 m	561 m	607 sh	606 w
ν_{sym}(Sn-C)	514 m	525 m	532 sh	531 sh
			518 m	516 m
			456 w	457 w
ν(Sn-S)	386 m	382 m	382 w	378 m
			345 sh	350 sh
ν(Sn-Cl)	321 m	340 m	325 m	336 m
	266 m	272 m	273 m	273 m

[a]Masked by solvent.

TABLE 9

Infrared Spectrum of Di-n-butyltin Chloride Trimethylacetate $(n\text{-}C_4H_9)_2ClSnO_2CC(CH_3)_3$, cm^{-1}

Assignment	Neat Liquid	CCl_4 Solution
	1706 m	1704 m
$\nu_a(CO_2)$	1596 s	1596 s
	1570 s	1570 s
$\delta_a(C\text{-}H_3)$	1484 s	1482 s
$\delta_a(C\text{-}H_3)$	1464 s	1465 s
	1403 s	1402 s
$\nu_s(CO_2)$	1357 s	1356 s
	1295 m	1296 m
$\delta_s(C\text{-}H_3)$	1252 m	1252 m
$\delta_s(C\text{-}H_3)$	1215 s	1215 s
	1183 m	1184 m
	1157 m	1157 m
	1081 m	1080 m
	1050 w	1051 w
	1031 m	1032 m
	1001 w	1000 w
	963 w	962 m
$\nu_a(C\text{-}CH_3)$	941 w	942 w
	911 m	909 m
$\nu_a(C\text{-}CH_3)$	881 m	881 m
	872 sh	871 sh
	851 w	850 w
$\nu_s(C\text{-}CH_3)$	818 m	820 m
	794 m	
	775 w	
	752 w	
	711 m	707 m
	685 m	682 m

TABLE 9 (cont'd)

Assignment	Neat Liquid	CCl_4 Solution
$\delta(CO_2)$ o.p. bend	627 s	627 s
	546 m	549 m
	526 w	
ν_s(Sn-C)	515 w	517 w
	438 s	439 m
	392 vw	
ν(Sn-Cl)	330 s	353 s
	298 sh	295 sh
	217 w	217

TABLE 10

^{1}H Nmr Data for $(CH_3)_2XSnO_2CR'$

R'	δ(Sn-C-H)[a]	δ(O_2C-C-H)[a]	$\lvert^2J(^{119}Sn\text{-}C\text{-}^1H)\rvert$[b]
X = Cl			
CH_3	1.08	2.09	76.0
CH_2Br	1.13	3.87	75.5
CH_2Cl	1.16	4.14	75.1
$CHCl_2$	1.18	5.96	74.1
CCl_3	1.20		73.8
C_6H_5	1.13		76.1
X = Br			
CH_3	1.18	2.10	74.0
CH_2Cl	1.22	4.11	74.8
$CHCl_2$	1.30	5.99	73.3
CCl_3	1.33		72.6
C_6H_5	1.29		70.5
$(CH_3)_2ClSnSC(O)CH_3$	1.06	2.04	71.8

[a]Ppm relative to internal TMS.

[b]In Hz.

TABLE 11

^{13}C Nmr Data for R_2XSnO_2CR'

Compound	$\delta(C_1)^a$	$\delta(C_2)^a$	$\delta(C_3)^a$	$\delta(C_4)^a$	$\delta(C_\alpha)^a$	$\delta(O_2C)^a$	$^1J^b$	$^2J^c$	$^3J^d$
$(\underline{n}\text{-}C_4H_9)_2ClSnO_2CCH_3$	25.56	26.27	25.80	13.03	19.63	178.87	506	34	92
$(\underline{n}\text{-}C_4H_9)_2ClSnO_2CCH_2I$	26.25	26.25	26.64	13.47		178.12	492	36	92
$(\underline{n}\text{-}C_4H_9)_2ClSnO_2CCH_2Br$	26.40	26.67	26.25	13.99	25.66	176.20	488	34	91
$(\underline{n}\text{-}C_4H_9)_2ClSnO_2CCH_2Cl$	26.51	26.71	26.27	13.46	40.82	175.81	485	34	92
$(\underline{n}\text{-}C_4H_9)_2ClSnO_2CCHCl_2$	26.85	26.64	26.25	13.44	64 57	172.50	474	36	91
$(\underline{n}\text{-}C_4H_9)_2ClSnO_2CCCl_3$	27.07	26.61	26.22	13.44	90.37	169.16	468	36	89
$(\underline{n}\text{-}C_4H_9)_2ClSnO_2CC_6H_5$	26.28	26.76	26.27	13.47	129.26	175.78	507		
$(\underline{n}\text{-}C_4H_9)_2BrSnO_2CC_6H_3$	26.46	26.12	27.16	13.47	20.14	181.02	482	34	88
$(CH_3)_2ClSnO_2CC_6H_5$	6.24				128.91	174.72	568		
$(CH_3)_2BrSnO_2CC_6H_5$	10.82				128.63	175.16	500		

[a] Ppm relative to internal TMS.

[b] $|^1\underline{J}(^{119}Sn\text{-}^{13}C)|$ in Hz.

[c] $|^2\underline{J}(^{119}Sn\text{-}C\text{-}^{13}C)|$ in Hz.

[d] $|^3\underline{J}(^{119}Sn\text{-}C\text{-}C\text{-}^{13}C)|$ in Hz.

TABLE 12

^{119m}Sn Mössbauer Data for R_2XSnO_2CR' at 77K

Compound	I.S.[a]	Q.S.[b]	Γ_1	Γ_2	(Q.S./I.S.)
$(CH_3)_2ClSnO_2CH_3$	1.39	3.52	1.46	1.41	2.53
$(CH_3)_2ClSnO_2CCH_2Br$	1.39	3.81	1.16	1.06	2.74
$(CH_3)_2ClSnO_2CCH_2Cl$	1.44	3.84	1.32	1.33	2.67
$(CH_3)_2ClSnO_2CCHCl_2$	1.44	3.87	1.34	1.37	2.69
$(CH_3)_2ClSnO_2CCCl_3$	1.49	3.94	1.04	1.10	2.64
$(CH_3)_2ClSnO_2CC_6H_5$	1.35	3.49	1.03	1.10	2.59
$(CH_3)_2ClSnSC(O)CH_3$	1.44	3.08	1.10	1.06	2.14
$(CH_3)_2BrSnO_2CCH_3$	1.44	3.58	1.07	1.03	2.49
$(CH_3)_2BrSnO_2CCH_2Cl$	1.52	3.87	1.02	1.09	2.55
$(CH_3)_2BrSnO_2CCHCl_2$	1.63	3.93	1.03	1.17	2.41
$(CH_3)_2BrSnO_2CCCl_3$	1.48	3.98	0.96	1.01	2.69
$(CH_3)_2BrSnO_2CC_6H_5$	1.40	3.57	0.89	0.98	2.55
$(\underline{n}\text{-}C_4H_9)_2ClSnO_2CCH_3$	1.42[c]	3.58[a]	1.09	1.20	2.52
$(\underline{n}\text{-}C_4H_9)_2ClSnO_2CCH_2I$	1.60	3.84	1.11	1.00	2.40
$(\underline{n}\text{-}C_4H_9)_2ClSnO_2CCH_2Br$	1.63	3.95	1.19	1.15	2.42
$(\underline{n}\text{-}C_4H_9)_2ClSnO_2CCH_2Cl$	1.59[c]	3.91[a]	1.10	1.13	2.46
$(\underline{n}\text{-}C_4H_9)_2ClSnO_2CCHCl_2$	1.58[c]	3.90[a]	1.06	1.16	2.47
$(\underline{n}\text{-}C_4H_9)_2ClSnO_2CCCl_3$	1.62[c]	3.90[a]	1.04	1.16	2.41
$(\underline{n}\text{-}C_4H_9)_2ClSnO_2CC_6H_5$	1.59	3.53	1.08	1.12	2.22
$(\underline{n}\text{-}C_4H_9)_2ClSnSC(O)CH_3$	1.60	3.22	0.93	1.11	2.01

TABLE 12 (cont'd)

Compound	I.S.[a]	Q.S.[b]	Γ_1	Γ_2	(Q.S./I.S.)
$(\underline{n}\text{-}C_4H_9)_2BrSnO_2CCH_3$	1.56	3.67	1.07	1.19	2.35
$(\underline{n}\text{-}C_8H_{17})_2ClSnO_2CCH_3$	1.50	3.59	1.00	1.03	2.39
$(\underline{n}\text{-}C_8H_{17})_2BrSnO_2CCH_3$	1.54	3.63	1.04	1.12	2.36
$(C_6H_5)_2ClSnO_2CCH_3$	1.38	3.37	1.27	1.36	2.44
$(C_6H_5)_2BrSnO_2CCH_3$	1.44	3.44	1.03	1.05	2.39
$(CH_3)_3SnO_2CCH_3$[d]	1.31	3.57	1.10	1.16	2.73
$(\underline{n}\text{-}C_4H_9)_3SnO_2CCH_3$[d]	1.38	3.71	1.33	1.05	2.69
$(CH_3)_3SnSC(O)CH_3$	1.34	2.86	1.28	1.14	2.13
$(\underline{n}\text{-}C_4H_9)_3SnSC(O)CH_3$	1.48	2.39	1.20	1.05	1.61

[a] ± 0.06 mm/s.

[b] ± 0.12 mm/s.

[c] ± 0.03 mm/s.

[d] Reference 52.

TABLE 13

$\nu(CO_2)$ Frequencies for the Acetate Derivatives of Group IV Elements, $(CH_3)_3MO_2CCH_3$, cm^{-1}

M	$\nu_{asym}(CO_2)$	$\nu_{sym}(CO_2)$	Reference
Si	1725	1267	31
Ge	1692	1280	3
Sn	1650[a]	1380	77

[a]Recorded in dilute solution in which the compound is monomeric.

TABLE 14

Infrared Spectra of Triorganotin Thioacetates, $R_3SnSC(O)CH_3$

	R = CH_3		R = $\underline{n}$-C_4H_9	
Assignment	KBr Disc	CCl_4 Soln.	Liquid Film	CCl_4 Soln.
(C=O)	1603 vs,br	1664 vs	1663 vs	1661 vs
	1575 vs,br			
			1465 m	1466 m
				1458 sh
			1419 m	1419 m
	1370 m		1378 m	1378 m
	1356 m	1354 m	1351 m	1352 m
			1294 w	1294 w
		1254 w	1250 w	1251 w
	1193 w	1194 w		
			1181 w	1182 w
(C-C)	1158 m	1140 s	1138 s	1138 s
	1115 m,br	1110 s	1109 s	1110 s
			1075 m	1076 m
			1047 w	1048 w
			1023 w	1025 w
			1004 w	1004 w
(C-S)	957 m	955 m	953 s	954 s
			878 m	877 m
			868 sh	868 sh
(C-CH_3) rock	777 vs,br			
			771 w	
			748 w	
			696 m	694 m
	673 sh		675 m	674 m
(COS) o.p.	650 m	637 m	637 s	637 s

TABLE 14 (cont'd)

Assignment	R = CH_3 KBr Disc	R = CH_3 CCl_4 Soln.	R = $\underline{n}$-C_4H_9 Liquid Film	R = $\underline{n}$-C_4H_9 CCl_4 Soln.
ν_{asym}(Sn-C)	555 m	543 m	603 m	602 m
ν_{sym}(Sn-C)	512 w	513 m	493 m	498 m
	499 w			
			453 w	457 w
(Sn-S)	390 m	391 m	390 m	396 m
	260 sh			
	248 m	262 m	261 m	261 m

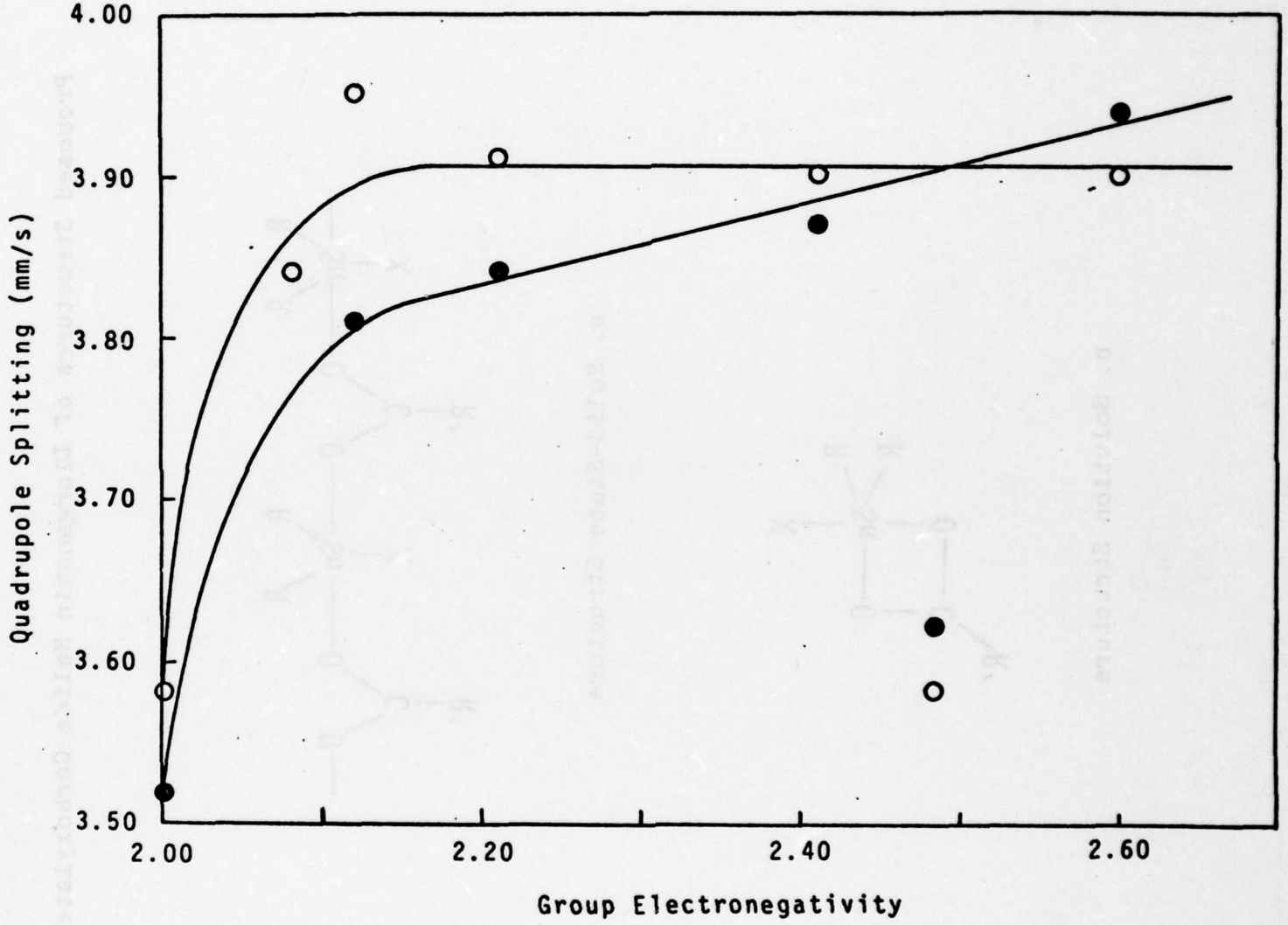
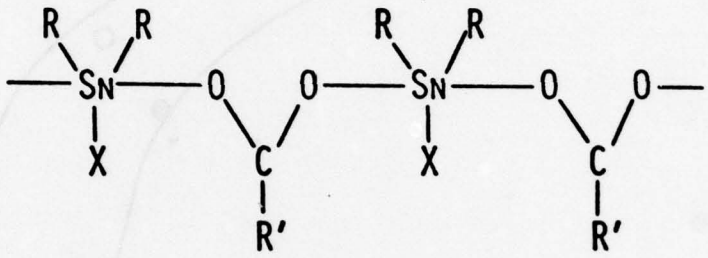


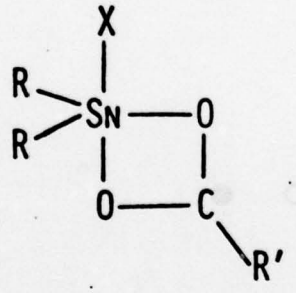
Figure 1 . The Quadrupole Splitting of $R_2ClSnO_2CCH_nX_{3-n}$ <u>vs</u>. the Group Electronegativity of CH_3X_{3-n}.

Figure 2

Proposed Structures of Diorganotin Halide Carboxylates



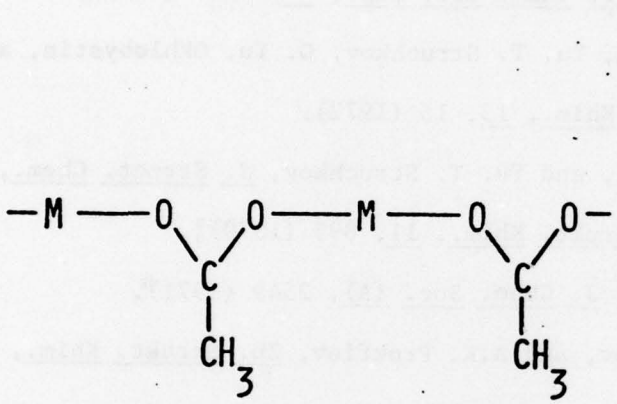
a. Solid-State Structure



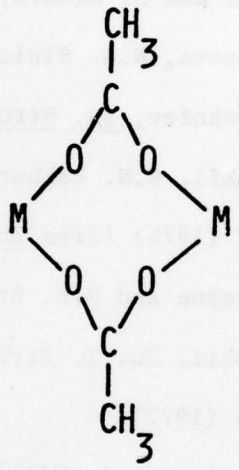
b. Solution Structure

Figure 3

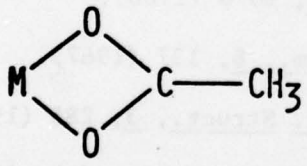
Possible Organometal Acetate Structures



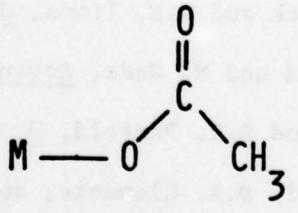
a.



b.



c.



d.

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78. The recent observation of ambient-temperature tin-119m Mössbauer spectra for certain molecular solids such as tetraphenyltin (m.p. 229°)[79] does not affect our conclusion which is based upon a variety of physical evidence and upon close analogies with other associated tin(IV)-oxygen and sulfur solids whose structures are known.[1]

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