(14) G. Beall and W. O. Milligan, unpublished results.

(15) $M^{II}_3[Co(CN)_6]_2 \cdot xH_2O$ and $Cs_2LiCo(CN)_6$ all crystallize in the space group *Fm*3*m* with the $Co(CN)_6^{3-}$ moiety occupying the 4a site. In the Prussian Blues the M^{II} ion occupies the other O_h site, 4b, while Li^+ occupies this site in $Cs_2LiCo(CN)_6$. In $Cs_2LiCo(CN)_6$ the Cs^+ ions occupy the tetrahedral holes while in the Prussian Blues water occupies this site.

(16) B. I. Swanson, *Appl. Spectrosc.*, **27**, 382 (1973).

(17) B. I. Swanson, *Appl. Spectrosc.*, **27**, 235 (1973).

(18) Dehydration was also followed using x-ray crystallography. The crystals were placed in Lindemann capillaries and heated to 70°C while evacuating the capillary. No further change was observed in the lattice constant after dehydrating for 24 hr; the overall change was significant (ca. 0.2 Å): G. Beall, W. O. Milligan, and B. I. Swanson, unpublished results.

(19) For scan $(101)[(101)(10\bar{1})^s](010)$ the intensity for E_g modes is predicted to be 2.5 times as great as for scan $(10\bar{1})[(101)(101)^s](010)$; see ref 16.

(20) B. I. Swanson and J. R. Rafalko, *Inorg. Chem.*, preceding article in this issue.

(21) L. Sacconi, A. Sabatini, and P. Gans, *Inorg. Chem.* **3**, 1772 (1964).

(22) G. Ron, A. Ludi, and P. Engel, *Chimia*, **27**, 77 (1973).

(23) J. H. Schachtschneider, "Vibrational Analysis of Polyatomic Molecules. III," Technical Report No. 263-62, Shell Development Co., Emeryville, Calif., 1962.

(24) One obvious problem in comparing $F^{\nu}_{MN,MN}$ of $Cs_2MgFe(CN)_6$ and $Mn_3[Co(CN)_6]_2 \cdot xH_2O$ is the different oxidation states of the iron and cobalt atoms. Clearly, it would be more valid to compare Mn–N and Mg–N interactions where the TM hexacyanides were in the same oxidation state. However, the Mg–$[NCM'(CN)_5]$ interaction would be weaker if M' were trivalent than if M' were divalent in view of the overall charge on the $M'(CN)_6^{n-}$ moiety, and the disparity between $F^{\nu}_{MnN,MnN}$ and $F^{\nu}_{MgN,MgN}$ would be even greater. Thus, the comparison made here is on the conservative side.

(25) The close agreement between the change calculated for f_{CN} in the A_{1g} and E_g blocks (0.46 and 0.30 mdyn/Å, respectively) is reassuring (for the isolated ion $F^{A_{1g}}_{CN,CN} = f_{CN} + 4f^{cis}_{CN,C'N'} - f^{trans}_{CN,C'N'}$ and $F^{E_g}_{CN,CN} = f_{CN} - 2f^{cis}_{Cn,C'N'} - f^{trans}_{CN,C'N'}$). This merely implies that a change in $F^{\nu}_{CN,CN}$ results primarily from a change in f_{CN}.

(26) W. O. Milligan, private communication.

(27) The $Cs_2LiM(CN)_6$ salts are always observed to be less soluble than the $K_3M(CN)_6$ salts.

(28) K. Maer, Jr., M. L. Beasley, R. L. Collins, and W. O. Milligan, *J. Am. Chem. Soc.*, **90**, 3201 (1968).

(29) A. Ito, M. Suenaga, and K. Ono, *J. Chem. Phys.*, **48**, 3597 (1968).

(30) J. F. Duncan and P. W. R. Wigley, *J. Chem. Soc.*, 1120 (1963).

(31) L. M. Epstein, *J. Chem. Phys.*, **36**, 2731 (1962).

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Iodine-129 and Tin-119 Mössbauer Studies of Methyltin Iodides. Tin–Ligand Bond Character and the Failure of the Point-Charge Model

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The results of a ^{119}Sn Mössbauer study of $(CH_3)_3SnI$, CH_3SnI_3, $(C_6H_5)_3SnCl$, and $C_6H_5SnCl_3$ are reported for the neat compounds as well as for frozen solutions of these compounds in an inert solvent at liquid nitrogen temperature. The ^{129}I Mössbauer spectra of frozen solutions of the above two iodides in an inert solvent at liquid helium temperature are also reported. Molecular weight measurements indicate that the two iodides are monomers in solution. The combined study, in which NMR coupling constants along with the Mössbauer spectra of two different atoms bonded to each other in the same molecule are investigated, offers much more information than obtained from the study of only one atom in a molecule and allows checks of consistency in interpretation not offered by investigations of a single atom. The ^{119}Sn and ^{129}I Mössbauer parameters are both used to test proposed interpretations of earlier results from ^{119}Sn Mössbauer data alone which, in order to account for a p- or d-orbital imbalance, have led to much speculation about the bonding in these compounds. Furthermore, the results are used to show how and why the simple point-charge model is inadequate for interpretation of the quadrupole splitting in the ^{119}Sn Mössbauer spectra of these compounds.

Introduction

In recent years, several different models have been proposed to account for the origin of the quadrupole hyperfine interaction in ^{119}Sn Mössbauer spectra. Some of these models invoke only a p-orbital population imbalance,[2-4] whereas in other descriptions of the bonding, a d-orbital population imbalance—arising from a p_π–d_π bonding interaction—is cited[5-7] as being a major contributing factor to the magnitude of the observed quadrupole splitting.

In order to examine in greater detail which of these models (if any) do, in fact, lead to a self-consistent description of the bonding in organotin compounds, a detailed study of methyltin(IV) triiodide and trimethyltin(IV) iodide, as well as some related molecules, was undertaken. These compounds were chosen for several reasons: (a) they are symmetry related in terms of a point-charge model calculation since they both have C_{3v} symmetry with the symmetry axis coincident with the metal atom–unique ligand bond axis; (b) the ^{119}Sn quadrupole splitting is well resolved in both compounds; (c) it is possible to study the nature of the metal–ligand bonding interaction by both ^{119}Sn and ^{129}I Mössbauer effect spectroscopy, and thus the data extracted from one spectroscopic study can be used to interpret the data extracted from the other, and vice versa, thus leading ultimately to a self-consistent description; and (d) these compounds have chemical properties (e.g., stability, solubility in inert solvents, relative ease of preparation and purification, etc.) which make them suitable for such an investigation.

In addition to the Mössbauer data, it is also possible to gain some insight into the nature of the metal–ligand interactions via the tin–proton ($J_{^{117}Sn-H}$ and $J_{^{119}Sn-H}$) coupling constant extracted from nuclear magnetic resonance data, and such information can be used to estimate the electron density at the metal atom.[8] The methyltin iodides have proton NMR resonances which consist of a sharp singlet peak with symmetrical tin–proton coupling peaks on either side.

The third possible methyltin(IV) iodide, $(CH_3)_2SnI_2$, was not included in the present study since the absence of a threefold symmetry axis in this compound makes the interpretation of the ^{119}Sn Mössbauer spectra considerably more complex, especially in the absence of detailed crystallographic data related to bond angles and bond distances in this molecule.

Experimental Section

The ^{119}Sn Mössbauer spectra were obtained using a constant-acceleration spectrometer described earlier.[9] Spectrometer calibration was determined using the four inner lines of the magnetically split ^{57}Fe Mössbauer resonance in 0.8-mil NBS SRM standard iron foil at room temperature.[10] All ^{119}Sn isomer shifts are reported with respect to the center of a room-temperature $BaSnO_3$ absorption spectrum using the same $Ba^{119}SnO_3$ Mössbauer source as employed for the sample spectra.

Neat solid samples [e.g., CH_3SnI_3, $(C_6H_5)_3SnCl$, etc.] were supported between aluminum foils in a copper sample holder which in turn was attached to the tail section of a standard liquid nitrogen dewar mounted vertically, and the spectra were obtained in normal transmission geometry. Neat liquids [$(CH_3)_3SnI$, $C_6H_5SnCl_3$] and solutions of the compounds in *n*-butylbenzene were transferred by means of a hypodermic syringe to a standard copper sample holder which had been fitted with Mylar windows attached by means of a thermoplastic adhesive[11] coating at ~140°C. The filled cells were immediately cooled to 78 K and maintained at this temperature until being mounted in the precooled liquid nitrogen dewar just prior to spectroscopic examination.

n-Butylbenzene was chosen as a solvent for these experiments since the exceptionally large temperature dependence of the viscosity of this material[12] significantly reduces diffusional processes, which might otherwise lead to microcrystalline solid formation by the solutes. Hence, it is assumed that the solute molecules are trapped as isolated entities in a matrix of inert solvent molecules and that the structures and conformations adopted by the experimental compounds in the frozen glassy matrix are essentially those of free (unconstrained) molecules (vide infra).

Experimental temperatures during the time required for the Mössbauer data accumulation (4–24 hr) were monitored with a precalibrated thermocouple attached directly to the sample support and were constant within ±1° of the values quoted in the table.

The ^{119}Sn Mössbauer spectra were analyzed using a matrix inversion least-squares computer-fitting program[13] in which intensities, line position, and line widths of the (presumed) Lorentzian resonance maxima were allowed to vary independently. The ^{119}Sn Mössbauer spectra (with the exception of the $BaSnO_3$ singlet used in the isomer shift–zero point calibration) consisted of well-resolved doublets with line widths of 0.87–1.00 mm/sec, indicating the absence of unresolved hyperfine interactions in these diamagnetic, essentially covalent solids.

The ^{129}I **Mössbauer spectra** were obtained in a manner analogous to that used for the ^{119}Sn Mössbauer spectra except that the velocity calibration was determined from the ^{57}Fe Mössbauer spectrum of Fe_2O_3. The source used in these experiments was $Zn^{129m}Te$. All ^{129}I isomer shifts are reported with respect to the $Zn^{129m}Te$ source. The spectra were obtained in a standard transmission geometry. The multichannel analyzer operated in the time mode.

The samples, dissolved in methylcyclohexane, were placed in cylindrical nylon holders, with a bottom window thickness of about 0.01 in., about 1 cm in diameter. The volume was approximately 1.5 ml. After the solutions were pipetted into the sample holder, the sample holder was sealed in a polyethylene envelope to protect the instrument against possible leakage. The samples were then quick frozen at liquid nitrogen temperature and remained at that temperature until they were mounted in the precooled cryostat. The spectra were recorded with both the source and the absorber at liquid helium temperature.

Methylcyclohexane was chosen as a solvent for these studies because of its inert character and the ease with which it forms glasses at low temperatures. This solvent was not used for the ^{119}Sn Mössbauer spectra only because methyltin triodide crystallized out of methylcyclohexane solution at the concentrations needed to observe the Mössbauer effect for ^{119}Sn. The ^{129}I Mössbauer spectra were analyzed using a computer program similar to that described for the data reduction of the ^{119}Sn Mössbauer spectra.

The **concentrations** of the solutions used to obtain all the Mössbauer spectra were determined from the weight of the neat compound and the volume of solvent used, except for the solution of $(CH_3)_3SnI$ used for the ^{129}I Mössbauer spectrum. The concentration of this solution was determined by comparison of the intensity of the peak at 780 cm^{-1} in the infrared spectrum of this solution to the intensity of this peak in solutions of $(CH_3)_3SnI$ of known concentration. The infrared spectra were recorded on a Perkin-Elmer 457 grating infrared spectrophotometer in 0.5-mm NaCl solution cells at room temperature.

The **molecular weight** of CH_3SnI_3 in a 0.023 *M* cyclohexane solution was determined by osmometry in the microanalytical laboratory of the School of Chemical Sciences at the University of Illinois. The molecular weight of $(CH_3)_3SnI$ in a 0.025 *M* cyclohexane solution was determined by freezing point depression in an apparatus previously described.[14]

$(CH_3)_3SnI$ was prepared by mixing $(CH_3)SnCl$ and NaI in acetone solution.[15] Being insoluble in acetone, NaCl precipitates out of solution leaving a solution of $(CH_3)_3SnI$ in acetone which may be purified by distillation (60°C at 12 mmHg). Precautions were taken to exclude oxygen from the system bacause the iodide is easily oxidized in acetone solution or as a neat liquid. $(CH_3)_3Sn^{129}I$ was prepared from a $Na^{129}I$ solution in aqueous Na_2SO_3 obtained from Oak Ridge National Laboratory on a scale too small for distillation to be practicable. This small-scale preparation has been previously described in detail.[14]

CH_3SnI_3 was prepared in a manner similar to Pfeiffer's procedure[16] and this method has already been described in detail.[14] $CH_3Sn^{129}I_3$ was prepared similarly using the $Na^{129}I$ solution described above.

Table I. ^{119}Sn Mössbauer Measurements

Absorber	Form	*T*, K	IS,[a] mm/sec	QS,[b] mm/sec	Γ_{av},[c] mm/sec	*R*[d]
$(CH_3)_3SnI$	Neat liquid[f]	81.5	1.43	2.91		1.06
$(CH_3)_3SnI$	0.86 *M* BuBz[e]	82.5	1.42	2.69	0.88	0.97
CH_3SnI_3	Neat solid	86	1.58	1.68	0.94	
CH_3SnI_3	0.46 *M* BuBz[e]	83	1.56	1.61	0.94	0.96
$(C_6H_5)_3SnCl$	Neat solid	83	1.39	2.48	0.93	0.96
$(C_6H_5)_3SnCl$	0.82 *M* BuBz[e]	83	1.30	2.40	0.87	0.94
$(C_6H_5)SnCl_3$	Neat liquid[g]	83.5	1.19	1.73	0.97	0.91
	1:1 v/v BuBz[e]	82	1.21	1.69	1.03	0.97

[a] Isomer shift with respect to the center of a room-temperature $BaSnO_3$ absorption spectrum; ±0.02 mm/sec. [b] Quadrupole splitting; ±0.02 mm/sec. [c] Average line width, uncorrected for thickness broadening. [d] Intensity ratio; $R = I_+/I_-$, where I is the total area under each component of the resonance doublet; ±0.03. [e] BuBz = *n*-butylbenzene. [f] For earlier results, see G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.*, 15 (1972). [g] For an earlier result, see H. A. Stockler and H. Sano, *Trans. Faraday Soc.*, 64, 577 (1968).

Table II. ^{129}I Mössbauer Measurements

Absorber	Form	*T*, K	IS,[a] mm/sec	$e^2 q^{127}Q$,[b] MHz	Γ,[c] mm/sec	η,[d] mm/sec
$(CH_3)_3SnI$	0.03 *M* in methylcyclohexane	4.2	−0.15	−740	0.80	0.02
$(CH_3)SnI_3$	0.037 *M* in methylcyclohexane	4.2	+0.26	−1270	0.84	0.02

[a] Isomer shift with respect to the $Zn^{129m}Te$ source; ±0.05 mm/sec. (This error includes an estimate of systematic errors). [b] Quadrupole splitting; QS = $e^2q^{129}Q$; ±20 MHz, including systematic errors. The values of $e^2q^{127}Q$ were obtained by dividing the values of $e^2q^{129}Q$ by 0.969. See ref 17 for a discussion on the appropriate units. [c] Average line width; ±0.04 mm/sec, including systematic errors. [d] Asymmetry parameter; ±0.02 mm/sec, including systematic errors.

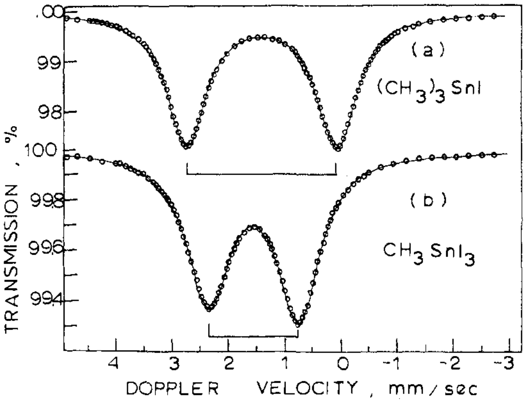

Figure 1. ^{119}Sn Mössbauer spectra of $(CH_3)_3SnI$ and CH_3SnI_3 in frozen *n*-butylbenzene solutions: (a) 0.86 *M* solution at 82.5 K; (b) 0.46 *M* solution at 83 K. The data have been normalized to 100% transmission at $V = V_\infty$. The Doppler velocity scale is based on the resonance maximum for a room-temperature $BaSnO_3$ absorber using the same ^{119}Sn source.

Results

The results of the ^{119}Sn Mössbauer spectra are summarized in Table I and those of the ^{129}I Mössbauer spectra are summarized in Table II. The ^{119}Sn Mössbauer spectra of $(CH_3)_3SnI$ and CH_3SnI_3 are shown in Figure 1. The ^{129}I Mössbauer spectra of these two compounds are shown in Figure 2.

No resonance effect was observed for the ^{119}Sn Mössbauer spectrum of CH_3SnI_3 in a 0.15 *M* methylcyclohexane solution

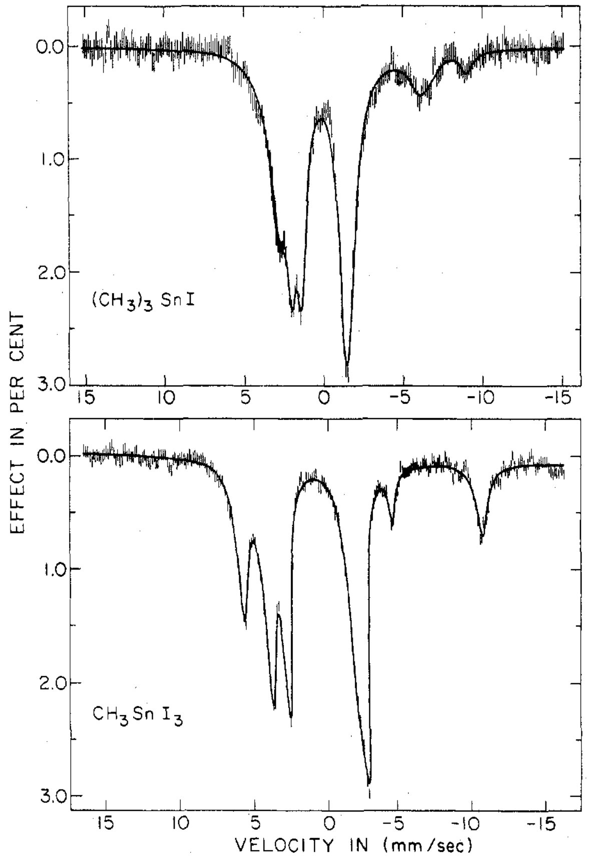

Figure 2. ^{129}I Mössbauer spectra of $(CH_3)_3SnI$ and CH_3SnI_3 in frozen methylcyclohexane solutions: (a) 0.03 *M* solution at 4.2 K; (b) 0.037 *M* at 4.2 K.

presumably because of the relatively small isotopic abundance of ^{119}Sn (8.58%) combined with the large nonresonant scattering of the 23.38-keV Mössbauer γ radiation by the heavy iodine atoms. With more concentrated solutions, crystallization occurs at liquid nitrogen temperatures. Therefore, *n*-butylbenzene was used as the solvent for the ^{119}Sn Mössbauer spectra. The ^{119}Sn Mössbauer spectra of the neat compounds were recorded as well.

The molecular weight of $(CH_3)_3SnI$ in a 0.025 *M* cyclohexane solution was found to be 316.9. This value is within experimental error[39] of the monomer molecular weight of 290.7.

The molecular weight of CH_3SnI_3, as determined by osmometry, in 0.023 *M* cyclohexane solution was 528 compared to a monomer molecular weight of 514.4.

Discussion

^{119}Sn Mössbauer Spectra. The Mössbauer parameters for the neat solid samples and for the frozen solutions of CH_3SnI_3 suggest that there are no major structural differences in the two different environments; that is, solvation and polymerization effects are negligible or absent. As has been pointed out in a previous study[18] of $(C_6H_5)_2SnCl_2$, the ^{119}Sn Mössbauer parameters (especially the magnitude of the quadrupole hyperfine interaction (QS)) are sensitive to the presence of intermolecular stacking forces in crystalline solids. In this context, it is inferred that the difference in the QS parameter for the same compound in the two different matrices is largely due to the release of such forces when the neat compound is dissolved in an inert amorphous environment. Consistent with this view is the observation that the QS difference between neat solid and frozen solution is 0.22 mm/sec for $(CH_3)_3SnI$ and only 0.07 mm/sec for CH_3SnI_3. Similarly, this difference amounts to 0.08 mm/sec for $(C_6H_5)_3SnCl$ and 0.03 mm/sec (possibly not significant in terms of the standard error of ±0.015 mm/sec associated with each value) for $C_6H_5SnCl_3$. In each case, equivalent crystal stacking forces would be expected to deform the triorganotin halide to a larger extent than the corresponding organotin trihalide molecule, in agreement with the data summarized above.

On this basis, it is inferred that all of the compounds for which data are given in Table I can be considered as having a distorted tetrahedral structure with four metal–ligand bonds and that intermolecular bonding forces—even for the neat solid samples—in these predominantly covalent molecules are negligibly small. The essential validity of this assumption for a wide variety of organotin(IV) halides has recently been discussed in detail.[19] Further evidence to support this assumption can also be drawn from infrared studies,[20–22] x-ray diffraction crystallographic data,[23–25] and the trends in properties such as melting point and solubility[15] using various types of alkyltin halides. In particular, for $(CH_3)_3SnI$ and CH_3SnI_3, the molecular weight studies described above show conclusively that these two compounds are monomers in solutions of inert solvents.

The asymmetry parameter, η, is zero for all the compounds listed in Table I due to the presence of a threefold axis of symmetry through the tin atom in each of these compounds.

^{129}I Mössbauer Spectra. The empirical relationship shown in eq 1 has been reported to relate the isomer shift in ^{129}I

$$\delta = -8.20h_s + 1.50h_p - 0.54 \qquad (1)$$

Mössbauer spectra to electron density. Here δ is the isomer shift relative to a $Zn^{129m}Te$ source in mm/sec; and h_s and h_p are the numbers of s- and p-electron holes, respectively, from the closed-shell configuration $5s^25p^6$ (I^-). For many iodine compounds (especially iodides), it is believed[27,28] that the iodine employs mainly p orbitals in the bonding in which case h_s will be zero and the isomer shift will be given by

$$\delta = 1.50h_p - 0.54 \qquad (2)$$

The isomer shifts in Table II indicate that the electron density at the iodine nucleus is greater for CH_3SnI_3 than for $(CH_3)_3SnI$ (i.e., the ^{129}I isomer shift of CH_3SnI_3 is greater than that for $(CH_3)_3SnI$). This result is consistent with the fact that two electronegative iodine atoms in CH_3SnI_3 are replaced by two electropositive methyl groups in $(CH_3)_3SnI$. Using the values of δ given in Table II, in eq 2, one can calculate a value of 0.26 ± 0.04 electron for h_p in $(CH_3)_3SnI$ and a value of 0.53 ± 0.04 electron for h_p in CH_3SnI_3.

The quadrupole splitting parameters of these two compounds are consistent with the iodine nucleus in $(CH_3)_3SnI$ being in a more symmetrical environment than the iodine nuclei in CH_3SnI_3. The iodine quadrupole splitting in $(CH_3)_3SnI$ is much smaller than those which have been previously reported for covalent compounds of iodine.[17] The quadrupole splittings also indicate a more ionic bond in $(CH_3)_3SnI$ than in CH_3SnI_3.

The asymmetry parameter in $(CH_3)_3SnI$ is taken as zero since the threefold cylindrical symmetry axis is coincidental with the tin–iodine bond axis. In CH_3SnI_3, where the tin–iodine bond does not coincide with an axis of threefold or higher symmetry, the experimental value of η indicates that the departure from cylindrical symmetry is very small.

An alternative approach to the interpretation of the ^{129}I Mössbauer spectra employs[17] the empirical relationship given in eq 3.[40] Here h_s is defined as in eq 1, U_z is the population

$$\delta = -8.2h_s - 3U_p - 4.5U_z + 8.46 \text{ (mm/sec)} \qquad (3)$$

of electrons in the p_z iodine orbital, and U_p is the ratio of the molecular quadrupole coupling constant to the atomic quadrupole coupling constant ($e^2q_{atom}Q$ for the ^{127}I atom is 2293 MHz[17]).

The population of electrons in the $5p_x$ and $5p_y$ orbitals is given by eq 4.[17] Assuming pure p bonding ($h_s = 0$) results

$$\begin{aligned} U_x &= U_z + U_p\,(1 + \eta/3) \\ U_y &= U_z + U_p\,(1 - \eta/3) \end{aligned} \tag{4}$$

in values of U_x and U_y that are greater than 2. By assuming that the bond is primarily $5p_\sigma$, we set $U_x = 2.00$ and estimate h_s. Using eq 3 and 4, we find $U_x = 2.00$, $U_y = 2.00$, $U_z = 1.68$, and $h_s = 0.01$ for $(CH_3)_3SnI$ and $U_x = 2.00$, $U_y = 2.00$, $U_z = 1.45$, and $h_s = 0.07$ for $(CH_3)SnI_3$. The number of 5p-electron holes in the $5s^25p^6$ configuration, h_p', is $h_p' = 6 - 3U_z - 2U_p$. Thus, $h_p' = 0.32$ and 0.55 for $(CH_3)_3SnI$ and $(CH_3)SnI_3$ respectively. This interpretation is vastly oversimplified,[29] but the values of h_p yield the expected result of more electron density on the iodine atom in $(CH_3)_3SnI$ than on the iodine atoms in CH_3SnI_3.

There have been several models offered to correlate and interpret the Mössbauer parameters of tin compounds and we are now in a position to evaluate some of these.

Point-Charge Model. The point-charge model is an approximate treatment frequently applied to correlate and interpret the quadrupole splitting parameter in ^{129}Sn Mössbauer spectra[4,7,29] and in NQR spectral studies. In this approach, the atoms (or groups of atoms) bonded directly to the tin atom are approximated by point charges. The z component of the electric field gradient tensor, V_{zz}, due to distant point charges is given by eq 5 where r_i is the distance between the charge

$$V_{zz} = \sum_i q_i \frac{\langle 3\cos^2\theta_i - 1\rangle}{\langle r_i^3\rangle} \tag{5}$$

q_i and the origin and θ_i is the angle between the z axis and a line connecting q_i to the origin, i.e., the ^{119}Sn nucleus in question. There are two types of contributions to V_{zz} for each ligand (or charge) around the tin atom: the geometric term $(3\cos^2\theta_i - 1)$ and q_i/r_i^3 (q_i represents the charge removed from or donated to the tin atom and r_i is the mean radius of the electrons in the valence orbital concerned). It is further assumed[29] that each ligand, L, makes a fixed contribution, [L], to the quadrupole splitting (i.e., has a constant "effective charge"), regardless of the structure of the compound and the nature of the other ligands attached.

Using this model, it can be shown[4] that the quadrupole splitting for compounds of the type $RSnX_3$ should be equal in magnitude but opposite in sign to that for compounds of the type R_3SnX, where X is a halide atom and R is an alkyl group, when tetrahedral geometry is assumed. However, there are many reported examples[3,4,30–32] in which the quadrupole splitting for the R_3SnX compound is much greater than that for the $RSnX_3$ compound (for a given R and X group). The results reported in Table I follow the same trend as these reported examples both in the neat state and in solution. These differences in the ^{119}Sn quadrupole splitting cannot be accounted for by the small deviations from T_d symmetry in the unassociated molecules. A change of 0.1 Å in the tin–carbon bond length of these compounds would result in only a 14% change in the "q_i/r_i" term in eq 5 while a 0.1-Å change in the tin–iodine bond length would result in only a 5% change in this term. The quadrupole splitting is more sensitive to changes in bond angles. A change in the bond angle by 5.5° from the tetrahedral angle would result in a 24% change in the "$3\cos^2\theta_i - 1$" term of eq 5 when the angle is decreased to 104°. When the bond angle is increased to 115°, the change in this term would be almost 30%. However, the bond angles[33] in the series of compounds $(CH_3)_nSnX_{4-n}$ (where $n = 0$–4) in the gaseous state are expected to be within 3° of the tetrahedral angle. Thus, the observed differences in the ^{119}Sn quadrupole splitting between R_3SnX and $RSnX_3$ compounds cannot be explained by the small deviations from tetrahedral geometry expected in these types of compounds. Furthermore, if our $RSnX_3$ compounds are not associated, it must be concluded that the prediction by the point-charge model of equal magnitude quadrupole splittings in R_3SnX and $RSnX_3$ compounds (for a given R and X) is obviously untenable.

The results of the ^{129}I Mössbauer spectra (Table II) also indicate other breakdowns in the assumptions of the point-charge model. The ^{129}I Mössbauer results show that the iodine atom in $(CH_3)_3SnI$ is different from the iodine atom in CH_3SnI_3. The assumption that [L] is constant for a given ligand regardless of the structure of the compound or the nature of the other ligands in the compound is seen not to be valid in the system. This assumption will probably not be valid in general for compounds in which the ligands differ considerably in their bond type because the assumption that the "effective charge" of a particular ligand is independent of the nature of the other ligands bonded to the central atom will not hold.

Simultaneous Interpretation of the Tin and Iodine Mössbauer Spectra. The main objective of this study has been to resolve some of the ambiguities in interpretation of tin Mössbauer results by having information pertaining to more than one type of nucleus in the molecule. It has been suggested[5–7] that a large quadrupole splitting in the ^{119}Sn Mössbauer spectrum of a compound can be associated with a high p_π–d_π bond order between the ligand and the central tin atom. The quadrupole splitting is postulated to arise from the d-orbital imbalance created by the formation of π bonds with some of the ligands but not with others. If the ^{119}Sn quadrupole splittings in the iodides studied here are rationalized by this model, then it would be concluded that there is a greater d-orbital imbalance in $(CH_3)_3SnI$ than in CH_3SnI_3 because the former compound has the larger ^{119}Sn quadrupole splitting. In the absence of significant p_π–d_π interactions from the methyl groups, we would be forced to conclude that there must be more p_π–d_π bonding between the iodine and tin atoms in $(CH_3)_3SnI$ than in CH_3SnI_3. This conclusion is quite unlikely because the d-orbital energies are lower in CH_3SnI_3 and consequently more likely to be involved in π bonding than those in $(CH_3)_3SnI$. Furthermore, the greater p_π–d_π bonding in $(CH_3)_3SnI$ would drain electron density from the iodine atom, but the ^{129}I Mössbauer spectra of $(CH_3)_3SnI$ and CH_3SnI_3 clearly indicate that there is more electron density on the iodine atom in $(CH_3)_3SnI$ than on the iodine atoms in CH_3SnI_3. More effective π back-bonding in CH_3SnI_3 is eliminated for this effect would cause a greater quadrupole splitting in the ^{119}Sn Mössbauer spectrum of CH_3SnI_3 than in that of $(CH_3)_3SnI$. Since this result is contrary to the observed trend of quadrupole splittings, the postulate that the quadrupole splitting in the ^{119}Sn Mössbauer spectra of these compounds results primarily from a d-orbital imbalance must be rejected. This does not mean that there is *no* contribution to the observed ^{119}Sn quadrupole splitting from a d-orbital imbalance, only that the d-orbital imbalance, if it does exist, does not make a major contribution to it.

To summarize the above discussion, the ^{129}I Mössbauer spectra indicate a larger electron density on the iodine atom in $(CH_3)_3SnI$ than in those of CH_3SnI_3. If p_π–d_π bonding were the dominant mechanism, the following trends in the ^{119}Sn Mössbauer parameters would have to be observed to be consistent with the ^{129}I Mössbauer results: $\delta((CH_3)_3SnI) \geq \delta(CH_3SnI_3)$; $|QS((CH_3)_3SnI)| < |QS(CH_3SnI_3)|$. The observed trends in these parameters are $\delta((CH_3)_3SnI) \approx \delta(CH_3SnI)$ and $|QS((CH_3)_3SnI)| > |QS(CH_3SnI_3)|$. Thus, the p_π–d_π-bonding mechanism is not consistent with the observed results.

It has been proposed[2a,3,4] that the magnitude of the quadrupole splitting in ^{119}Sn Mössbauer spectra is governed primarily by imbalance in the polarity of the tin–ligand σ bonds, and, contrary to earlier suggestions,[5,6] π bonding is of little, if any, consequence in accounting for the results. Watanabe and Niki[3] have used this model proposed originally by Hill, Drago, and Herber[2a] to explain the fact that the ^{119}Sn quadrupole splitting in $(C_2H_5)_3SnI$ is larger than that in $C_2H_5SnI_3$. In compounds of the type $RSnX_3$ where R is an alkyl group and X is a halogen atom, the four molecular orbitals used in bonds to the tin atom, Ψ_j, are expressed as functions of ϕ_R and ϕ_X, the valence atomic orbitals of carbon and the halogen atoms, respectively, and as functions of i_R and i_X, their coefficients in the appropriate molecular orbital.

Using the expectation value of the field gradient operator ($\hat{H}_q = \langle 3\cos^2\theta - 1\rangle/\langle r^3\rangle$) and neglecting the two-center and three-center integrals as too small, the field gradient, *eq*, is

$$eq(\mathrm{RSnX_3}) = 2V_{p(z)}\,\frac{1 - C_R^{\,2}}{1 - i_R^{\,2}} + 3\frac{1 - C_X^{\,2}}{1 - i_X^{\,2}}\;\frac{3\cos^2\alpha - 1}{2} \tag{6}$$

where $V_{p(z)} = \int \phi_{p(z)}\hat{H}_q\phi_{p(z)}\,d\tau$, C_R and C_X are the s characters of the hybrid tin orbitals directed toward the alkyl group and halogen atoms, respectively, and α is the angle between the tin–carbon bond and the tin–halogen bond. From the orthogonality conditions of the four valence hybrid orbitals of the tin atom, it can be shown that

$$\cos^2\alpha = \frac{C_R^{\,2}C_X^{\,2}}{(1 - C_R^{\,2})(1 - C_X^{\,2})}$$

and

$$C_X^{\,2} = \frac{1 - 3\cos^2\alpha}{3\sin^2\alpha}$$

Using these orthogonality conditions in eq 6 yields

$$eq(\mathrm{RSnX_3}) = (1 - C_R^{\,2})(I_R - I_X)V_{p(z)} \tag{7}$$

where the bond ionic characters are expressed as

$$I_X = \frac{1 - i_X^{\,2}}{1 + i_X^{\,2}} \tag{8}$$

$$I_R = \frac{1 - i_R^{\,2}}{1 + i_R^{\,2}} \tag{9}$$

An analogous calculation for R_3SnX yields

$$eq(\mathrm{R_3SnX}) = (1 - (C_X')^2)(I_X' - I_R')V_{p(z)} \tag{10}$$

using primed quantities for R_3SnX and unprimed quantities for $RSnX_3$. Combining eq 7 and 10 yields

$$\frac{eq(\mathrm{RSnX_3})}{eq(\mathrm{R_3SnX})} = -\frac{(1 - C_R^{\,2})(I_X - I_R)}{(1 - (C_X')^2)(I_X' - I_R')} \tag{11}$$

Since I_R and I_R' are small, we have

$$\frac{I_X - I_R}{I_X' - I_R'} \approx \frac{I_X}{I_X'} \tag{12}$$

Substitution of eq 12 into eq 11 results in the relationship

$$\frac{eq(\mathrm{RSnX_3})}{eq(\mathrm{R_3SnX})} = -\frac{(1 - C_R^{\,2})I_X}{(1 - (C_X')^2)I_X'} \tag{13}$$

A test of the validity of this model can be obtained by using the isomer shifts in the ^{129}I Mössbauer spectra to estimate I_X and I_X', and the previously published[34] NMR spin–spin coupling constants between the ^{119}Sn nuclei and the methyl protons to estimate C_R and C_X'.

Table III. Fractional s Character and Ionicity of Tin–Carbon Bonds

	$(CH_3)_3SnI$	CH_3SnI_3
$J_{^{119}\mathrm{Sn-C-H}}$	58.5 Hz	73.0 Hz
C_R (Sn–C s character)	0.266	0.355
$C_X{}^b$ (Sn–X s character)	0.202	0.215
h_p (p-electron holes)	0.26	0.53
I_X (formal charge on I)	0.74–	0.47–
$U_z,{}^a$	1.68	1.45
$h_s{}^a$	0.01	0.07
$h_p'{}^a$	0.32	0.55
$I_X''{}^b$	–0.68	–0.45

[a] See eq 3 and the discussion that follows it. [b] Calculated from the equation $I_X'' = h_p' - 1$. This value results from the alternate treatment of the ^{129}I Mössbauer parameters similar to that of Greenwood and Gibb.[17]

Calculated values of the percent ionic character in a bond frequently vary, for the same molecule, by more than 10% (for example, see Table 13 in ref 14). The percent ionic character in a bond and the charge on an atom can be estimated in favorable cases from a crude interpretation of the Mössbauer spectrum of the compound. The net formal charge on the iodine atom, I_X, can be estimated by

$$I_X = h_p - 1 \tag{14}$$

where h_p is calculated from eq 2, assuming that a pure p orbital is used by iodine in bonding to tin. The isomer shift in the ^{129}I Mössbauer spectrum of $(CH_3)_3SnI$ leads to a value of h_p for the iodine atom in $(CH_3)_3SnI$ of ~0.26 electron or a charge on the iodine atom of ~–0.74. This result implies that the tin–iodine bond in $(CH_3)_3SnI$ is about 75% ionic.

For CH_3SnI_3, the value of h_p calculated from the isomer shift in the ^{129}I Mössbauer spectrum of that compound is ~0.5 electron leading to a charge on the iodine atoms of ~–0.5, a tin–iodine bond which is about 50% ionic (significantly less ionic than $(CH_3)_3SnI$).

Linear relationships between the NMR spin–spin coupling constant, $J_{^{119}\mathrm{Sn-C-H}}$, and the percent s character that the tin atom uses in the tin–carbon bond have been reported in the literature previously.[35-37] The percent s character employed by the tin atom in the tin–carbon bonds in $(CH_3)_3SnI$ and CH_3SnI_3 can be interpolated from reported graphs. Ideally, the values employed for $J_{^{119}\mathrm{Sn-C-H}}$ should be obtained in a noninteracting solvent, such as cyclohexane, at the same concentrations that the molecular weight studies and the Mössbauer studies (vide supra) were performed. Unfortunately, the proton resonances arising from alkane solvents interfere with the methyl peaks from methyltin halides. However, it has been found[38] that for both $(CH_3)_3SnCl$ and CH_3SnCl_3, the coupling constants measured in several noncoordinating solvents and at several different concentrations are similar. The same trend would be expected for the iodides, as well. The values of the coupling constants used for $(CH_3)_3SnI$ and CH_3SnI_3 in our analysis are those measured in $CHCl_3$ solution by Van Den Berghe and Van Der Kelen[34] and are given in Table III. The interpolated values of the percent s character of the tin atomic orbital in the tin–carbon bond are also reported in Table III, along with the fractional s character of the tin atomic orbital in the tin–iodide bond C_X and the ionicity of the tin–iodide bond I_X. The values of C_X are obtained by assuming that the four tin bonds in both $(CH_3)_3SnI$ and CH_3SnI_3 employ hybrid orbitals composed of 5s and 5p atomic orbitals; i.e., there are no contributions from d orbitals. For $(CH_3)_3SnI$, C_X is given by

$$C_X = 1.00 - 3C_R \tag{15}$$

while for CH_3SnI_3, C_X is given by

$$C_X = (1.00 - C_R)/3 \tag{16}$$

Substituting the values of I_X, C_R, and C_X that are shown in Table III into eq 13 results in

$$\frac{eq(CH_3SnI_3)}{eq((CH_3)_3SnI)} = -0.58$$

Substituting the values of I_X'', C_R, and C_X that are given in Table III into eq 13 results in

$$\frac{eq(CH_3SnI_3)}{eq((CH_3)_3SnI} = -0.60$$

From the values of the quadrupole splitting in the ^{119}Sn Mössbauer spectra of these two compounds (see Table I), the above ratio is 0.58 ± 0.01 for the neat compounds and 0.60 ± 0.01 for the compounds in *n*-butylbenzene solution. (It should be noted that only the absolute magnitude of the quadrupole splitting can be obtained from the ^{119}Sn Mössbauer spectra shown in Figure 1.) Considering the approximate nature of some of the relationships used, these results are in excellent agreement.

It can be concluded that the quadrupole splitting in the ^{119}Sn Mössbauer spectra of these alkyltin iodides can be explained entirely on the basis of a p-orbital imbalance. The results indicate that the tin $5p_z$ orbital in $(CH_3)_3SnI$ (where the z axis is along the tin–iodine bond) has a very small electron population relative to those of the tin $5p_x$ and $5p_y$ orbitals, whereas, in CH_3SnI_3 (where the z axis is along the tin–carbon bond), the $5p_x$ and $5p_y$ orbitals have electron populations closer to the electron population of the tin $5p_z$ orbital.

The isomer shifts in the ^{119}Sn Mössbauer spectra of $(CH_3)_3SnI$ and CH_3SnI_3 are very similar. This can also be explained in terms of isovalent hybridization and bond ionicities. Consider the tin orbital used in the tin–iodine bond in $(CH_3)_3SnI$ and compare it to a tin orbital used in a tin–iodine bond in CH_3SnI_3. More of the bonding electron density is found on the iodine atom in the former bond, but, as shown by NMR, the tin atom employs a slightly higher percent s character in the bond to iodine in CH_3SnI_3. Furthermore, there are three such tin–iodine bonds in the latter compound. These trends go in the opposite direction indicating that the amount of s-electron density in the tin atomic orbitals of these two compounds will be more similar than simple electronegativity or ionic character alone would predict. Accordingly, similar isomer shifts in the ^{119}Sn Mössbauer spectra are found.

We thus see how a combination of ^{119}Sn and ^{129}I Mössbauer coupled with NMR tin-proton coupling constants has provided us with a consistent interpretation of the data which can be checked because, for the first time, we have available more experimental data than there are unknowns. It can be concluded from this study that the quadrupole splitting in the ^{119}Sn Mössbauer spectra of alkyltin iodides (and, perhaps, other alkyltin halides, as well) can be explained, semiquantitatively, by the imbalance in the tin p-orbital framework, without the necessity of invoking a π-bonding interaction between the metal atom and its halogen ligands.

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References and Notes

(1) (a) Abstracted in part from the Ph.D. Thesis of A. P. Marks, University of Illinois, Urbana, Ill., 1973. To whom correspondence should be addressed at Rohm and Haas Co., Philadelphia, Pa., 19137. (b) School of Chemical Sciences, University of Illinois, Urbana, Ill., 61801. (c) Department of Chemistry, Rutgers University, New Brunswick, N.J., 08903. (d) Department of Physics, University of Illinois, Urbana, Ill., 61801.

(2) (a) J. C. Hill, R. S. Drago, and R. H. Herber, *J. Am. Chem. Soc.*, **91**, 1644 (1969); (b) D. E. Williams and C. W. Kocher, *J. Chem. Phys.*, **52**, 1480 (1970).

(3) N. Watanabe and E. Niki, *Bull. Chem. Soc., Jpn.*, **45**, 1 (1972).

(4) R. V. Parish and R. H. Platt, *J. Chem. Soc. A*, 2145 (1969).

(5) T. C. Gibb and N. N. Greenwood, *J. Chem. Soc. A*, 43 (1966).

(6) N. N. Greenwood, P. G. Perkins, and D. H. Wall, *Discuss. Faraday Soc.*, **1**, 90 (1968).

(7) J. J. Zuckerman, *Adv. Organomet. Chem.*, **9**, 21 (1971).

(8) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance", McGraw-Hill, New York, N.Y., 1959.

(9) R. L. Cohen, P. G. McMullin, and G. K. Wertheim, *Rev. Sci. Instrum.*, **34**, 671 (1963); see also Y. Hazony and R. H. Herber in "Physical Methods of Chemistry", Vol. 1, A. Weissberger and B. W. Rossiter, Ed., Wiley-Interscience, New York, N.Y., 1972, part III.

(10) J. J. Spijkerman, J. R. deVoe, and J. C. Travis, *Natl. Bur. Stand. (U.S.), Spec. Publ.*, **No. 260-20** (1970).

(11) G. T. Schjeldahl Co., Northfield, Minn., Type GT-300.

(12) A. C. Ling and J. E. Willard, *J. Phys. Chem.*, **72**, 1918, 3349 (1968).

(13) Developed by R. P. Bell, Boston University, and modified appropriately to run on the Rutgers IBM 360/67 computer by J. Fischer and M. F. Leahy.

(14) A. P. Marks, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1973.

(15) R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, **60**, 459 (1960).

(16) P. Pfeiffer, *Ber. Dtsch. Chem. Ges.*, **37**, 4618 (1904).

(17) N. N. Greenwood and T. C. Gibb, "Mössbauer Spectroscopy", Chapman and Hall, London, 1971.

(18) R. H. Herber, *J. Inorg. Nucl. Chem.*, **35**, 67 (1973).

(19) R. H. Herber, J. Fischer, and Y. Hazony, *J. Chem. Phys.*, **58**, 5185 (1973); Y. Hazony and R. H. Herber, *Mössbauer Eff. Methodol.*, **8**, 107–126 (1974); R. H. Herber, M. F. Leahy, and Y. Hazony, *J. Chem. Phys.*, **60**, 5070 (1974).

(20) R. J. H. Clark, A. G. Davies, and R. J. Puddephatt, *J. Chem. Soc. A*, 1828 (1968).

(21) H. Kriegsmann and S. Pischtschan, *Z. Anorg. Allg. Chem.*, **308**, 212 (1969).

(22) I. R. Beattie and G. P. McQuillan, *J. Chem. Soc.*, 1519 (1963).

(23) V. P. Brand and H. Sackmann, *Acta Crystallogr.*, **16**, 446 (1963).

(24) F. Meller and I. Fankuchen, *Acta Crystallogr.*, **8**, 343 (1955).

(25) A. G. Davies, H. J. Milledge, D. C. Puxley, and P. J. Smith, *J. Chem. Soc. A*, 2862 (1970).

(26) M. Pasternak and T. Sonnino, *J. Chem. Phys.*, **48**, 1997 (1968).

(27) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969.

(28) R. V. Parish and R. H. Platt, *Inorg. Chim. Acta*, **4**, 65 (1969).

(29) D. White and R. S. Drago, *J. Chem. Phys.*, **52**, 4717 (1970).

(30) R. H. Herber, H. A. Stöckler, and W. T. Reichle, *J. Chem. Phys.*, **42**, 2447 (1965).

(31) H. A. Stöckler and H. Sano, *Trans. Faraday Soc.*, **64**, 577 (1968).

(32) R. V. Parish and R. H. Platt, *Chem. Commun.*, 1118 (1968).

(33) Structural data on the gaseous compounds are found in the following sources: (a) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 11** (1958); (b) O. Kennard and D. G. Watson, Ed., "Complexes and Organometallic Structures", Vol. 2, International Union of Crystallography, 1970; (c) B. Y. K. Ho and J. J. Zuckerman, *J. Organomet. Chem.*, **49**, 1 (1973).

(34) E. V. Van Den Berghe and G. P. Van Der Kelen, *J. Organomet. Chem.*, **6**, 515 (1966).

(35) J. R. Holmes and H. D. Kaesz, *J. Am. Chem. Soc.*, **83**, 3903 (1961).

(36) N. Flitcroft and H. D. Kaesz, *J. Am. Chem. Soc.*, **85**, 1377 (1963).

(37) T. F. Bolles and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 5730 (1966).

(38) T. L. Brown and K. Stark, *J. Phys. Chem.*, **69**, 2679 (1965).

(39) This measurement was performed in the presence of biphenyl, which was used as a standard to calibrate the apparatus. (The concentration of biphenyl was about 0.03 *M*; i.e., the mole ratio of $(CH_3)_3SnI$ to biphenyl was close to unity.) Possible intermolecular interactions between biphenyl and $(CH_3)_3SnI$ would have resulted in a measured molecular weight significantly higher than the monomer molecular weight.

(40) This equation relates the isomer shift of ^{129}I relative to the $Zn^{129m}Te$ source to the iodine electron density.