analyzed, but its ready flammability on exposure to air suggested that it was the desired $(CH_3)_3Si(C_2H_4)BCl_2$ (63.3% yield).

To 5.3 g. of this chloroborane (0.029 mole) in 25 ml. of toluene under nitrogen at −40° was added slowly during 1 hr. 10.8 g. (0.108 mole) of aniline in 40 ml. of toluene. Subsequently 2 ml. of triethylamine was added. The reaction mixture was allowed to warm to room temperature, then was stirred for 1 hr. and for another hour at 70°. The precipitated solids (9.0 g.) were filtered, and the filtrate was distilled to give: (a) 4.5 g., b.p. 128–132° (0.03 mm.), presumed to be $(CH_3)_3Si(C_2H_4)B(NHC_6H_5)_2$; (b) 0.65 g., b.p. 160–170° (0.02 mm.); (c) 1.10 g., residue. Fraction (a) was pyrolyzed at 320–340° under nitrogen in a Claisen distilling flask during 8 hr. A highly viscous liquid residue remained. Methanol was added. After this mixture had stood overnight, 0.82 g. of white, crystalline solid had formed. Several recrystallizations from ether–methanol gave crystalline fractions melting at 132–133° and at 139–146°. The former fraction was analyzed.

Anal. Calcd. for $C_{33}H_{54}N_3B_3Si_3$: C, 65.02; H, 8.93. Found: C, 65.35; H, 8.94.

The infrared spectrum of this fraction was almost identical with that of $[(CH_3)_3SiCH_2CH_2BNC_6H_5]_3$,[10] showing bands due to the trimethylsilyl group at 1250, 832, 860, and 740 cm.$^{-1}$ and to the borazine ring around 1385 cm.$^{-1}$.

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CONTRIBUTION FROM NOYES CHEMICAL LABORATORY,
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Infrared and Nuclear Magnetic Resonance Spectra of Methyltin Compounds

BY THEODORE L. BROWN AND GEORGE L. MORGAN

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The infrared and n.m.r. spectra of a number of methyltin compounds containing tin–tin bonds have been studied. Polydimethyltin, $[Sn(CH_3)_2]_x$, prepared from the reaction of dimethyltin dichloride and sodium in liquid ammonia, consists of linear chains containing from 12 to 20 catenated tin atoms. A second form of polydimethyltin has been characterized as possessing a cyclic, six-membered ring of tin atoms (dodecamethylcyclohexatin). Observation of the ^{117}Sn and ^{119}Sn–proton couplings reveals that increasing catentation results in a decrease in J_{Sn-CH_3} and an increase in $J_{Sn-Sn-CH_3}$. An empirical relationship between J_{Sn-CH_3} and both the symmetric and asymmetric tin–carbon stretching modes for a series of methyltin compounds is proposed, employing data taken from the literature. The infrared and n.m.r. data for hexamethylditin and linear polydimethyltin fit the empirical relationship.

This paper reports the results of an investigation of some methyltin compounds containing tin–tin bonds. Although catenated organotin compounds have been known since the early work of Löwig and Frankland more than a century ago,[1,2] neither their chemical nor physical properties are well known. The report by Kraus and Sessions[3] that hexamethylditin is largely dissociated in solution has not been substantiated by more recent work on this simplest member of the series,[3,4] but the possibility of a facile dissociation has nevertheless been described recently as still a matter of uncertainty.[5]

The dehydrogenation of dialkyl- or diaryltin dihydrides to yield the corresponding dialkyl- or diaryltin recently has been developed and exploited for synthetic purposes.[6,7] Diethyltin prepared in this manner is reported to be a cyclic heptamer in benzene solution; the proton n.m.r. spectrum reveals an apparent equivalence of the ethyl groups.[8] Dimethyltin, obtained as a yellow solid from the decomposition of hexamethylditin in the presence of diborane,[9] possesses an empirical formula $(CH_3)_3Sn[Sn(CH_3)_2]_{7-8}Sn(CH_3)_3$ based on elemental analysis.

Experimental

Materials.—Trimethyltin chloride and dimethyltin dichloride were purchased from Metal and Thermit Co., Rahway, N. J. Although usually employed without further purification, they occasionally were sublimed before use. Anhydrous liquid ammonia was obtained from the Matheson Co. Reagent grade benzene was stored over sodium wire, and diethyl ether was dried with Linde Type 4A Molecular Sieve before use. All procedures in the syntheses were carried out under an inert atmosphere of nitrogen or argon. Preparation of samples for spectral analysis and other operations involving the purification and handling of the compounds were conducted in an inert atmosphere box under a nitrogen atmosphere.[10]

Tetramethyltin was prepared as described by Edgell and Ward.[11]

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(1) C. Löwig, *Ann.*, **84**, 308 (1852).

(2) E. Frankland, *ibid.*, **85**, 329 (1853).

(3) C. A. Kraus and W. V. Sessions, *J. Am. Chem. Soc.*, **47**, 2361 (1925).

(4) H. Morris and P. W. Selwood, *ibid.*, **63**, 2509 (1941).

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

(6) H. G. Kuivila, A. K. Sawyer, and A. G. Armour, *J. Org. Chem.*, **26**, 1426 (1961).

(7) W. P. Neumann and K. König, *Angew. Chem.*, **74**, 215 (1962).

(8) W. P. Neumann, *ibid.*, **74**, 122 (1962). NOTE ADDED IN PROOF.–In a recent paper, *Angew. Chem.*, **75**, 225 (1963), Neumann concludes that the product commonly obtained from $(C_2H_5)_2SnH_2$ is a cyclic hexamer.

(9) A. B. Burg and J. R. Spielman, *J. Am. Chem. Soc.*, **83**, 2667 (1961).

(10) T. L. Brown, D. W. Dickerhoof, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instr.*, **33**, 491 (1962).

(11) W. F. Edgell and C. H. Ward, *J. Am. Chem. Soc.*, **76**, 1169 (1954).

Hexamethylditin was prepared by addition of 9.90 g. (0.05 mole) of trimethyltin chloride to 1.15 g. (0.05 g.-atom) of sodium in 100 ml. of anhydrous ammonia. A white solid was filtered off, and the residual ammonia removed by pumping. Diethyl ether was added, and the resulting solution was filtered. A clear oil remained after removal of the ether by pumping off.

Octamethyltritin was prepared by two different methods. In the first, 2.3 g. (0.10 g.-atom) of sodium was dissolved in 100 ml. of ammonia. The alkali metal solution was added to a slurry of 5.50 g. (0.025 mole) of dimethyltin dichloride in 100 ml. of ammonia. A greenish yellow dimethyltin disodium solution resulted. To this was added 9.90 g. (0.050 mole) of trimethyltin chloride. The color changed to grayish white with formation of a precipitate. The solid filtrate was worked up as described above for hexamethylditin to obtain a straw-yellow oil. The n.m.r. spectrum revealed the presence of hexamethylditin in varying amounts in all preparations.

In the second method of preparation, 2.75 g. (0.0125 mole) of dimethyltin dichloride was added to 100 ml. of ammonia containing 0.025 mole of dimethyltin disodium, with the intention of producing 1,3-disodiumhexamethyltritin, $Na[Sn(CH_3)_2]_3Na$. Then 3.55 g. (0.025 mole) of methyl iodide was added with stirring. The yellow color of the solution disappeared, and a white precipitate formed. After working up the product as described above, a straw-yellow oil was obtained. On the basis of its n.m.r. spectrum in benzene solution, the oil appears to be a mixture of methyltin polymers containing from two to perhaps six tin atoms in a chain (see Fig. 1a, and text).

Polydimethyltin[12] was prepared by the method of Kraus and Greer,[13] and purified by a variety of methods. The usual method involved extraction of the yellow solid with warm benzene, with subsequent concentration of the combined solutions. Vacuum sublimation of the crude reaction product at 100–115° over a period of 4 days yielded a sublimate varying from yellow whiskers to a viscous oil.

In an alternate synthesis of polydimethyltin, 10.4 g. (0.047 mole) of dimethyltin dichloride was placed in a 500-ml. flask with 50 ml. of ether. Ten ml. of dry triethylamine then was added to form the amine adduct of the tin compound. A slurry of 2.8 g. of lithium aluminum hydride in 225 ml. of ether then was added through a dropping funnel over a period of 45 min., while maintaining the reaction flask at ice temperature. After further stirring for 2 hr., a yellow solution over a gray solid resulted. After filtration the ether was pumped off the solution, leaving a yellow oil. Upon standing the product formed two distinct phases, a colorless oil and a bright yellow solid. The yellow material was separated, washed with cold benzene, and dissolved in warm benzene. The n.m.r. spectrum of the benzene solution was essentially identical with that assigned to the cyclic, six-membered ring form of polydimethyltin, Fig. 1c. The colorless phase was not investigated in detail, but it was noted that it is extremely reactive with both air and moisture; it may be trimethylaluminum, or a partially halogenated methylaluminum compound.

Cyclic Polydimethyltin (Dodecamethylcyclohexatin).—In one preparation of polydimethyltin by reaction of dimethyltin dichloride with sodium in ammonia, a product resulted which was finely powdered, in contrast to the rather amorphous character of the solid usually obtained. It was found to have only a slight solubility in hydrocarbon solvents. The n.m.r. spectrum of a benzene extract of this product (Fig. 1c) disclosed that it consisted principally of a component of polydimethyltin which, although present in other preparations, was generally a minor contaminant. On the basis of its proton n.m.r. spectrum, and other observations described below, the structure of the compound is assigned as a six-membered ring of tin atoms, each of which is bonded to two methyl groups.

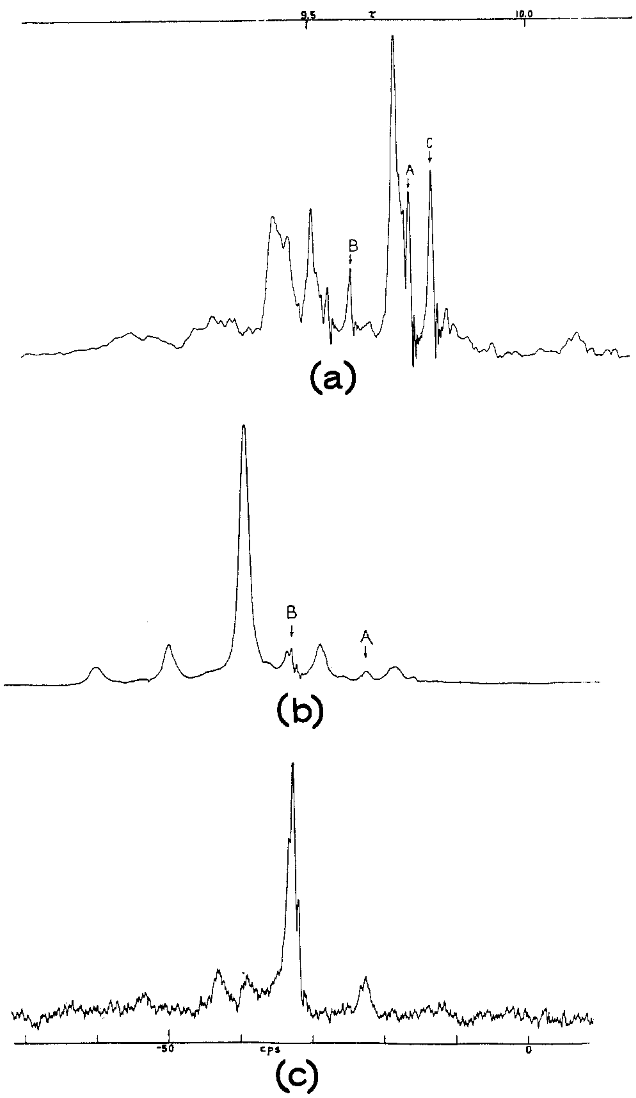

Fig. 1.—Proton n.m.r. spectra of: (a) mixture of hexamethylditin, octamethyltritin, and higher tin–tin bonded compounds; (b) linear polydimethyltin; (c) dodecamethylcyclohexatin.

Molecular Weight Measurement.—A solution of the presumed cyclic component was made up in benzene. Aliquots of the solution were added to weighed Vycor crucibles, and the crucibles wese reweighed. The solvent was removed by pumping, and the crucibles again were weighed to obtain the amount of dimethyltin. The solid was decomposed by the method of Gilman and Rosenberg[14] to obtain the weight of tin as tin(IV) oxide. The analytical data thus obtained (Table I) were in agreement with the empirical formula $Sn(CH_3)_2$, and provided a measure of the molality of the solution in terms of dimethyltin groups.

The freezing point lowerings of the benzene solutions were measured using a high sensitivity thermistor bridge. The freezing point cell is stirred mechanically with a solenoid-operated stirrer. The output of the thermistor bridge is amplified in a d.c. amplifier; the output of the amplifier is displayed by a recorder. N.m.r. spectra were taken of the solutions used in the freezing point lowering experiments to furnish a basis for correcting for the quantity of linear polydimethyltin present. In two separate determinations, apparent molalities corresponding to an average of 6.87 dimethyltin units per molecule were obtained.

The area under the proton absorption at $\tau = 9.45$ was 3.7 times the area under the absorption appearing at 9.35. If it is assumed that the cyclic component contains six dimethyltin

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[12] The name polydimethyltin would seem to be more appropriate than simply dimethyltin, since it is evident that there is extensive catenation in the compound, or rather series of compounds, which pass by the name. No evidence exists for a divalent alkyltin compound.

[13] C. A. Kraus and W. N. Greer, *J. Am. Chem. Soc.*, **47**, 2568 (1925).

[14] H. Gilman and S. D. Rosenberg, *J. Am. Chem. Soc.*, **75**, 3592 (1953).

TABLE I

ANALYTICAL DATA EMPLOYED IN MOLECULAR WEIGHT DETERMINATIONS

	I	II
Wt. of solution	8.524	7.565
Wt. of solute[a]	0.163	0.143
Wt. of tin(IV) oxide	$.165_5$	$.147_0$
Calcd. wt. of $Sn(CH_3)_2$ based on SnO_2 wt.	$.163_4$	$.145_0$
Molality in terms of $Sn(CH_3)_2$ groups	$.131_5$	$.131_5$
Observed molality	.0191	.0191
$\bar{n}$	6.87	6.87

[a] The weight of solute, obtained as described in the text, is precise to no better than ±1 mg. It is sufficiently accurate, however, for determining the weight of solute. The agreement with the calculated weight of dimethytin based on the SnO_2 weight is satisfactory.

units, the observed number average of 6.87 units requires that the linear form have an average of 15 dimethyltin units. This is in the range of the chain lengths commonly observed in samples of the linear form. The assumption that the cyclic form is a pentamer cannot be accommodated to the data for any chain length of the linear form. A cyclic heptamer is likewise not consistent with the data.

If the cyclic component were a heptamer, the average number of dimethyltin groups in the linear form would need to be less than seven to fit the data. No samples of linear polydimethyltin with chain lengths this short were observed among many preparations. Further, a linear hexamer would in all likelihood exhibit a τ value higher than the 9.35 value observed for the contaminant. Thus the combined results of the n.m.r. and molecular weight studies would appear to demonstrate conclusively that the component of polydimethyltin appearing at 9.45 in the proton resonance spectrum is dodecamethylcyclohexatin.

Infrared and N.m.r. Spectra.—Infrared spectra in the range 650–4000 cm.$^{-1}$ were obtained with a Beckman IR-7 spectrophotometer. Spectra in the range 300–650 cm.$^{-1}$ were obtained with a Beckman IR-5A spectrophotometer fitted with cesium bromide optics. All of the samples reported upon were examined as smears between cesium bromide plates.

Nuclear magnetic resonance spectra were obtained on a Varian Associates Model A-60 spectrometer, except in two instances: (a) Spectra of hexamethylditin were examined at a number of temperatures in the range 6 to 70° on a Varian Associates Model 4300-B spectrometer fitted with a variable temperature probe. (b) In order to ascertain the nature of the closely spaced side bands on either side of the major proton absorption in dodecamethylcyclohexatin (Fig. 1c), the proton resonance spectrum of a benzene solution was obtained at both 40 and 60 Mc. using a Varian Associates Model 4300-B spectrometer. The frequency separation of the bands was not observed to change, thus establishing that the bands arise from spin–spin interactions.

The values of chemical shifts and coupling constants reported in Table I are based upon several determinations on separately prepared samples for each compound. The τ values, $10 - \delta$, where δ is the chemical shift in p.p.m. relative to tetramethylsilane, are precise to ±0.01; the coupling constants are accurate to 0.3 c.p.s.

Results

N.m.r. Results.—The study of catenated methyltin compounds is greatly facilitated by the existence of two tin nuclides, ^{117}Sn and ^{119}Sn (in 7.67 and 8.67% abundances, respectively) with spin 1/2. Thus, in addition to the unsplit proton resonances of the methyl groups, spin–spin couplings between protons and tin atoms may be observed. In order to simplify the notation, the following symbols will be employed for the various coupling situations encountered

$\mathit{Sn}\text{–CH}_3\text{:H-}\alpha$ $\qquad$ $\mathit{Sn}\text{–Sn–C}\mathit{H}_3\text{:}\mathit{H}\text{-}\beta$

$\mathit{Sn}\text{–Sn–Sn–C}\mathit{H}_3\text{:}\mathit{H}\text{-}\gamma$

A further designation is required to distinguish protons bonded through carbon to a tin atom at the end of a chain (H_t) from those bonded through carbon to an internal tin atom in the chain (H_i).

A. Hexamethylditin.—The proton magnetic resonance spectrum of hexamethylditin has been reported by Kaesz.[15] Our results, which are in excellent agreement with his, are listed in Table II for comparison purposes. As a matter of incidental interest, the n.m.r. spectrum unambiguously fixes the structure of the compound as two trimethyltin groups bonded through a tin–tin bond. Furthermore, the appearance of an H-β spin–spin coupling rules out the possibility of a rapid rate of dissociation of the tin–tin bond. Spectra obtained at 6.5 and 69° were identical.[16]

B. Octamethyltritin.—The proton magnetic resonance spectrum of octamethyltritin is characterized by major absorptions at τ values of 9.73 and 9.60, due to the methyl groups bonded to terminal and internal tins, respectively. It is noteworthy that $J_{H_t\text{-}\alpha}$ is larger than $J_{H_i\text{-}\alpha}$, and that $J_{H_t\text{-}\beta}$ is on the other hand smaller than $J_{H_i\text{-}\beta}$ (Table II).

TABLE II

NUCLEAR MAGNETIC RESONANCE DATA FOR METHYLTIN COMPOUNDS[b]

	Sn-$(CH_3)_4$	Sn_2-$(CH_3)_6$	Sn_3-$(CH_3)_8$	[Sn-$(CH_3)_2]_x$[a] (linear)	Sn_6-$(CH_3)_{12}$[a] (cyclic)
	Methyl bonded to terminal tin				
τ	9.94	9.78	9.73	9.63	
$J_{^{117}Sn\text{–}CH_3}$	51.8	46.4	45.8	46.0	
$J_{^{119}Sn\text{–}CH_3}$	54.1	48.4	47.6	48.0	
$J_{Sn\text{–}Sn\text{–}CH_3}$	. . .	16.0	15.6	15.7	
	Methyl bonded to internal tin				
τ			9.60	9.35	9.45
$J_{^{117}Sn\text{–}CH_3}$			42.8	40.4	41.2
$J_{^{119}Sn\text{–}CH_3}$			44.3		
$J_{Sn\text{–}Sn\text{–}CH_3}$			20.2	20.6	20.6
$J_{Sn\text{–}Sn\text{–}Sn\text{–}CH_3}$			. . .	. . .	1.3

[a] Spectra in benzene solution. [b] τ values are all referred to tetramethylsilane. Coupling constants in c.p.s.

The spectrum characteristic of octamethyltritin was determined from observation of a number of different sample preparations. It was not found possible to obtain a sample free of contamination from other tin–tin bonded compounds. These gave rise to absorptions in the ranges τ = 9.73 to 9.68 and 9.56 to 9.42. Absorptions due to spin–spin splitting appear on either side of these absorptions just as for octamethyltritin, and with values for the coupling constants similar to those observed in octamethyltritin. The indication is, therefore, that the absorptions are due

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(15) H. D. Kaesz, "Nuclear Magnetic Resonance Spectral Data," API Research Project 44, Serial No. 53.

(16) Mr. R. Meinzer of these Laboratories has very kindly examined a sample of hexamethylditin for the appearance of an electron spin resonance signal. None was observed.

to tin–tin bonded compounds containing four or more tin atoms in a chain. Figure 1a shows the spectrum of one of the more complex mixtures. A and B are due to octamethyltritin, and C is the central absorption due to hexamethylditin.

C. Polydimethyltin.—Figure 1b shows a typical spectrum of polydimethyltin, as isolated from the synthesis of Kraus and Greer.[13] The major absorption at $\tau = 9.35$ is ascribed to methyl groups bonded to internal tin atoms. The absorption at $\tau = 9.63$ (A) is ascribed to methyl groups bonded to a terminal tin atom. These assignments are substantiated by the values obtained for the various coupling constants in Table II. The component giving rise to absorption at B is a cyclic, six-membered ring form of polydimethyltin, dodecamethylcyclohexatin, a previously unreported compound (*vide supra*). The proton resonance spectrum of a benzene solution of the cyclic compound, contaminated with only a small amount of the linear form of polydimethyltin, is shown in Fig. 1c. The relevant coupling constants are listed in Table II. It is of interest that the H_1-γ couplings are clearly observable in this compound, but not in the linear form. It is clear that only one central proton resonance is present in the spectrum of Fig. 1c, aside from the absorption at $\tau = 9.35$, identifiable as due to the linear form of polydimethyltin. From the chemical shift of the central absorption it may be inferred that the methyl groups are bonded to internal tin atoms in a chain (Table II). This conclusion is borne out by the observation that the area under the H-β spin-coupled side bands is twice the area under the H-α side bands. The absence of an absorption characteristic of methyl groups bonded to terminal tin atoms suggests a cyclic structure.

Linear polydimethyltin obtained in various preparations varies considerably in chain length, as evidenced by the ratio of absorption intensity at $\tau = 9.35$ to that at 9.63. Chain lengths as estimated in this manner for a number of samples varied from 12 to perhaps 20.[17] In one preparation, however, the estimated chain length was 70. The high molecular weight of the material also is evidenced by the relative broadness of the absorptions; the isotopic doubling of the spin-coupled absorptions was not seen clearly in any of the samples. The broadening may, however, also be due in some measure to the presence of species of widely differing molecular weights, since the samples are almost certainly heterogeneous in this respect.

Decomposition of polydimethyltin occurs in the presence of light. A metallic mirror deposits on the wall of the sample tube. The absorption at $\tau = 9.63$ increases, while that at 9.35 decreases. Some tetramethyltin also is formed.

Infrared Spectra.—Table III lists the absorption frequencies observed for samples of polydimethyltin (linear) and hexamethylditin. Data for tetramethyltin have been included for comparison. The partial assignment of absorptions is based largely on the study by Edgell and Ward.[18]

TABLE III

INFRARED ABSORPTIONS OF METHYLTIN COMPOUNDS, CM.$^{-1}$

Poly-dimethyltin[a]	Hexa-methylditin	Tetramethyltin[18]	Assignments[18]
497	499	504 (Raman)	Sn–C sym. stretch
510	520	524	Sn–C asym. stretch
	700 m	680 ?	
713 vvs[b]	759 vvs	764 vvs	Sn–CH_3 rocking
773 s	1014 vw		
1026 w	1026 vw	1029 w	
1175 sh		1050 vw	
1183 m	1186 sh		
1192 sh	1192 m	1190 s	CH_3 sym. deformation
1262 vw		1348 m	
1382 mb	1385 wb	1412 m	
1459 mb	1455 mb	1445 s	CH_3 asym. deformation
1490			
1649 vw	1645 w	1697 m	
1674 w	1679 wsh		
	1692 w	1717 m	
		1861 vw	
1939 vw	1937 vw		
1948 m	1945 m	1962 w	
2016 w	2015 vw	2131 vw	
		2216 vw	
2340 m	2349 m	2363 m	
2370 m	2349 m	2363 m	
2370 wsh			
2859 sh			
2908 s	2908 s	2914 s	CH_3 sym. stretch
2978 s	2978 s	2982 s	CH_3 asym. stretch

[a] Spectrum of a viscous liquid fraction obtained in the vacuum sublimation of polydimethyltin. [b] w, weak; m, medium; s, strong; v, very; sh, shoulder; b, broad.

Because of difficulties encountered in obtaining a pure sample of octamethyltritin, the only absorption bands for which a good frequency assignment can be made are those occurring at 768 and 730 cm.$^{-1}$.

Discussion

Holmes and Kaesz have recently presented arguments for correlating J_{Sn-CH_3} in methyltin halides and related compounds with per cent s character in the tin orbital employed in bonding to carbon.[19] When our observed coupling constants are applied to the relationship the following values are obtained for per cent s character in the tin–carbon bonds: hexamethylditin, 22.5%; octamethyltritin (internal tin), 20.8%; linear polydimethyltin (internal tins) 19.3%. The lowering in per cent s character in the tin–carbon bonds with increasing catenation is reflected in a corresponding increase in per cent s character in the tin–tin bonds. One might expect, therefore, an increase in the H-β coupling constant in the same series, as observed. Of course, the arguments relating per cent s character and coupling constant are based on the assumption that the only variable of importance in the Fermi contact term is the contribution of the s orbitals to the atomic wave functions. Juan and Gutowsky

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(17) The estimations were based on the assumption that each terminal tin atom is bonded to three methyl groups, and that each internal tin atom is bonded to two.

(18) W. F. Edgell and C. H. Ward, *J. Mol. Spectry.*, **8**, 343 (1962).

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

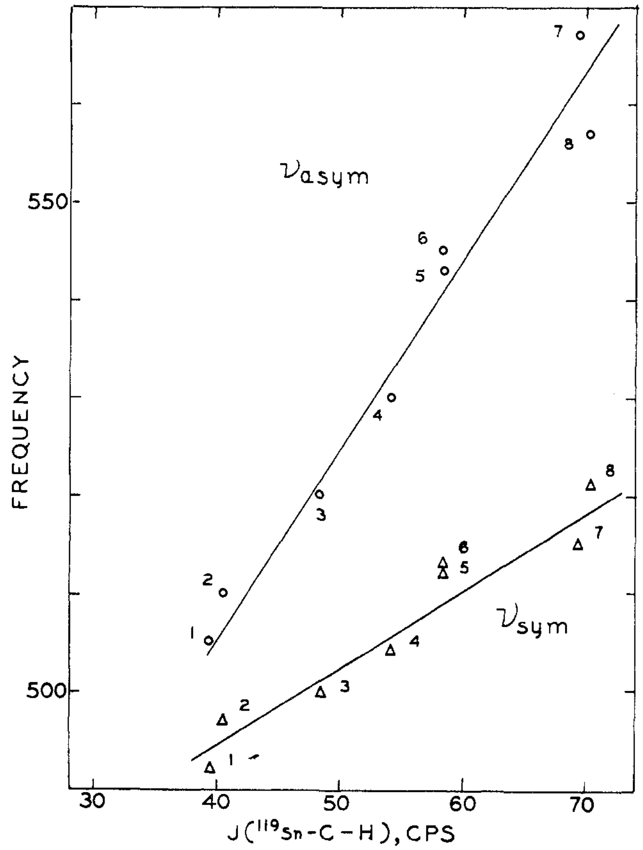

Fig. 2.—$J_{(^{119}Sn-CH_3)}$ *vs.* Sn–C stretching frequencies for some methyltin compounds: 1, trimethyltin lithium (G. L. Morgan, Ph.D. Thesis, University of Illinois, 1962); 2, dimethyltin; 3, hexamethylditin; 4, tetramethyltin; 5, trimethyltin bromide[21,22]; 6, trimethyltin chloride[21,22]; 7, dimethyltin dichloride[23,24]; 8, trimethyltin chloride (aqueous).[21,22]

recently have presented evidence that the variation in ionic character of the bond may be of importance in affecting the Si–H coupling constant in substituted silanes.[20] The relative constancy of the C^{13}–H coupling constants[21] in the compounds examined by Holmes and Kaesz does provide some assurance, however, that in the methyltin series hybridization change is of principal importance.

There is an interesting relationship between the observed Sn–CH_3 coupling constants and the symmetric and asymmetric (or degenerate) tin–carbon stretching frequencies, shown in Fig. 2. Data for methyltin halides are included.[18,21,22] A linear relationship is evident for both vibrational modes.[23] Thus, the tin–carbon stretching frequencies are linearly related to the per cent s character in the tin orbital used in the bond, as measured by J_{Sn-CH_3}. The observed relationship provides strong indication that the Sn–C stretching force constant increases with increasing s character in the tin orbital. An analogous relationship between carbon orbital hybridization and the C–H force constant is well known.

The Sn–CH_3 rocking frequencies in the same series of compounds also increase with increasing value of the Sn–CH_3 coupling constant. The relationship is not, however, linear; the frequencies approach a constant upper limit with increasing value for the coupling constant.

Acknowledgment.—This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

[20] C. S. Juan and H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2198 (1962).

[21] G. P. Van der Kelen, *Nature*, **193**, 1069 (1962).

[22] H. Kriegsmann and S. Pischtschan, *Z. anorg. allgem. Chem.*, **308**, 212 (1961).

[23] Interestingly, the line for the symmetric stretching frequency passes on extrapolation through the point 540 cm.$^{-1}$, 98.5 c.p.s., the experimentally observed values for methyltin trichloride.[21,24]

[24] R. Okawara, D. E. Webster, and E. G. Rochow, *J. Am. Chem. Soc.*, **82**, 3287 (1960).

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Trimethyltin Perchlorate, Trimethyltin Nitrate, and their Infrared Spectra

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Anhydrous trimethyltin perchlorate and trimethyltin nitrate have been prepared and both are volatile solids. The infrared spectrum of the perchlorate suggests that it is composed of planar trimethyltin groups bridged by partially covalent perchlorate groups to form chains. Trimethyltin nitrate, on the basis of its infrared spectrum, appears to contain a nitrato group linked to a non-planar trimethyltin group. Both the perchlorate and nitrate form diammonia adducts, which on the basis of their infrared spectra can best be formulated as $[(CH_3)_3Sn(NH_3)_2]^+X^-$, the tin atom having a trigonal bipyramidal configuration.

Recently, there has been considerable interest in the nature and constitution of organotin compounds and particularly of trialkyltin derivatives. Among the trialkyltin halides, interest arises from the marked physical and chemical differences between, say, trimethyltin fluoride and the remaining trimethyltin halides. Thus, such differences are taken to indicate that trimethyltin fluoride has a salt-like constitution, $(CH_3)_3Sn^+F^-$, while trimethyltin chloride, bromide, and iodide are thought to be molecular, crystalline solids.