

THE PROTON MAGNETIC RESONANCE SPECTRA AND ELECTRICAL DIPOLE MOMENTS OF METHYLTIN HALIDES

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For substituted methanes, CHXYZ, Malinowski¹ has derived an additivity relation for the ¹³C–proton coupling in nuclear magnetic resonance. A theoretical study of this relation was made by Juan and Gutowsky² and later several authors showed that the additivity parameters are inappropriate when such substituents as F^{3,4,5} or OCH₃⁴ are bonded on carbon. The direct coupling constants between ²⁹Si and protons in silicon hydrides, measured by Ebsworth and Turner⁶, also fail to fit into an additivity scheme. In a valence bond treatment of the theory for ¹³C–H and ²⁹Si–H coupling constants, Juan and Gutowsky⁷ presented an interpretation for the additivity of substituent effects. Thus, for carbon the distribution of s-character among the carbon orbitals in accord with the relative s-affinities of the four substituents, leads to the observed additivity relation provided that the total s-character is conserved. The ²⁹Si–H coupling constants, however, exhibit systematic and large deviations. The ¹³C–fluorine coupling constants also present systematic positive deviations from additivity^{3,8}. Douglas⁹ showed that for ¹³C–H couplings the consistent deviations from additivity of the substituent, for highly electronegative substituents, could be accounted for by the introduction of pair-wise interaction terms. Similarly, pair-wise interaction terms were derived by Malinowski and Vladimiroff for ²⁹Si–H and ¹³C–¹⁹F couplings¹⁰ and even for indirectly bonded tin–proton couplings¹¹. In the latter case, however, their calculations were restricted to the methylstannanes and the methyltin chlorides.

Because this correlation should be of prime interest from a theoretical standpoint, a complete study is made in this paper of the PMR data of the methyltin halides. Since the substituents are bulky, the results might be affected by steric hindrance and, therefore, the electrical dipole moments were also measured. These data are also useful in discussing chemical bonding.

EXPERIMENTAL

The methyltin compounds were synthesized in our laboratory by standard methods. They were purified by distillation or sublimation and the purity was checked by m.p. or b.p. determinations, analysis of halogen content and the PMR spectrum. The PMR spectra were recorded with a Varian high resolution NMR dual-purpose spectrometer V-4300 B at 56,44 Mc. The experimental techniques were the same as those mentioned in our earlier papers¹².

TABLE I

CHEMICAL SHIFT AND COUPLING CONSTANTS OF METHYL TIN HALIDES

	$(CH_3)_4Sn$			$(CH_3)_3SnX$			$(CH_3)_2SnX_2$			CH_3SnX_3		
		Cl	Br	I	Cl	Br	I	Cl	Br	I		
$J(^{117}Sn-C-H)$	52	56	56	56	67	63.5	60	95.5	85	70		
$J(^{119}Sn-C-H)$	54.3	58.5	58.5	58.5	70	66	62.5	98	89	73		
$J(^{13}C-H)$	128	134	134	134	138	138	138	143	143	143		
$J(TMS)$		37	45	55	70	83	97	95	110	140		

The chemical shift data, expressed in cps downfield of the TMS signal and the coupling constants $J(^{117}Sn-C-H)$, $J(^{119}Sn-C-H)$ and $J(^{13}C-H)$ are shown in Table I. The electrical dipole moments were calculated by the classical method from the data gained from measurements of the dielectric constant, the refractive index and the density of dilute solutions in benzene. The techniques of measuring and the method of calculation have been published previously¹³. The experimental values found are listed in Table 2, column 2, as μ_{exp} . and are expressed in Debye units.

TABLE 2

DIPOLE MOMENTS OF METHYL TIN HALIDES

	μ_{exp} .	μ_{theor} .	$\mu_{exp} - \mu_{theor}$.
$(CH_3)_3SnCl$	3.50	3.50	0
$(CH_3)_2SnCl_2$	4.10	4.06	+0.04
CH_3SnCl_3	3.64	3.50	+0.14
$(CH_3)_3SnBr$	3.45	3.45	0
$(CH_3)_2SnBr_2$	3.80	4.00	-0.14
CH_3SnBr_3	3.24	3.45	-0.21
$(CH_3)_3SnI$	3.37	3.37	0
$(CH_3)_2SnI_2$	3.76	3.91	-0.15
CH_3SnI_3	2.52	3.37	-0.85

RESULTS AND DISCUSSION

Chemical shifts

The graphical presentation of the chemical shift data (Fig. 1) shows two important features. First, there is the increasing downfield shift of the methyl resonances with increasing number of halogen substituents. This is the usual pattern, which is also observed in the halomethanes. The relative downfield shifts for an equal number of chlorine, bromine or iodine atoms bonded on tin, however, do not follow the expected trend according to the electronegativity of these atoms. The inductive effect term would yield negative shifts decreasing in the order $\Delta(Cl) > \Delta(Br) > \Delta(I)$. This anomaly of the experimental data can be explained in accordance with the arguments put forward by Spiesscke and Schneider¹⁴ for the shifts of the β -protons in the ethyl halides and by one of us¹⁵ in an earlier paper on the ethyltin chloride spectra.

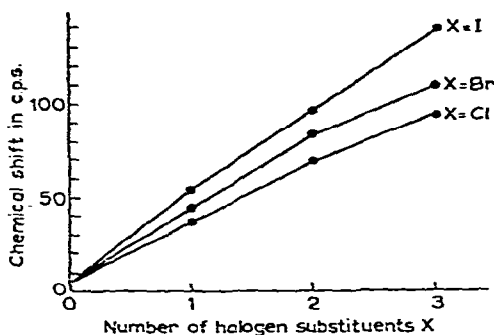
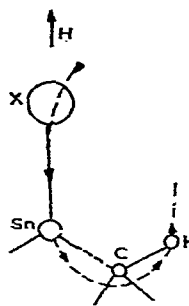


Fig. 1. Chemical shift data of methyltin halides.

Fig. 2. Spatial configuration and diamagnetic anisotropy in $XSnCH_3$ groups.

If an increasing contribution of the diamagnetic anisotropy term acting along the Sn-X bond, in going from Sn-Cl to Sn-I (Fig. 2) is accepted, the anomalous sequence observed could be a result of overcompensation of the inductive effect term. This situation is schematically presented in Fig. 3.

Coupling constants

The ^{13}C -proton coupling constants in these spectra increase only slightly with progressive halogenation and they are obviously independent of the electronegativity of the halogen atom. This means that changes in the carbon atomic orbital in the respective Sn-C bonds are weak, the main change in these bonds being the result of the isovalent rehybridization of the tin atom. The indirect tin-proton coupling constant values are plotted against the number of halogen atoms in Fig. 4. For trimethyltin halides the coupling constants for the chloride, bromide and iodide are of the same value.

It can be seen that an additivity relation as proposed by Malinowski¹ for substituted methanes, is not satisfied (dotted line in Fig. 4). We observe an increasing

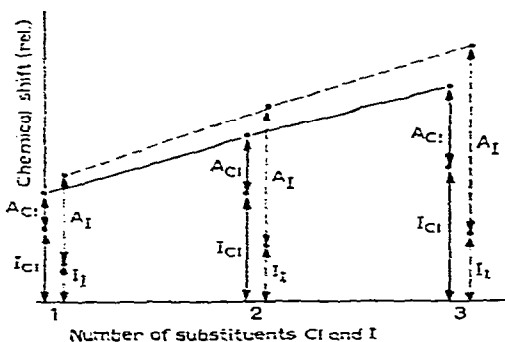


Fig. 3. Relative importance of anisotropy contribution (A) and inductive shielding contribution (I) in methyltin halides.

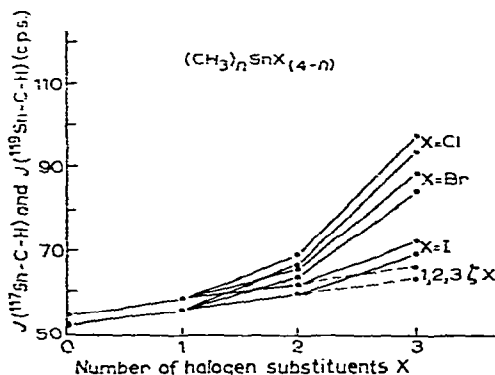


Fig. 4. Coupling constants of methyltin halides and deviation from Malinowski's additivity rule.

deviation in going from dihalides to trihalides and the deviation increases also with the electronegativity of the halogen atom. These deviations from direct additivity can be correlated with the pair-wise interaction equation derived by Vladimiroff and Malinowski¹¹ for indirect as well as for direct couplings. Using the symbols proposed by these authors we find for the interaction parameters in monosubstituted products (for ¹¹⁷Sn couplings only)

$$\eta(\text{CH}_3\text{-Cl}) = \eta(\text{CH}_3\text{-Br}) = \eta(\text{CH}_3\text{-I}) = 19.00$$

and for di- and tri-substituted products $\eta(\text{Cl-Cl}) = 31.68$, $\eta(\text{Br-Br}) = 28.33$ and $\eta(\text{I-I}) = 23.33$.

The direct coupling constants, $J(^{13}\text{C-H})$ and $J(^{29}\text{Si-H})$, measured on $\text{CH}_n\text{X}_{(4-n)}$ and $\text{SiH}_n\text{X}_{(4-n)}$ compounds are plotted in Fig. 5, a and b. Apparently, no distinction depending on the electronegativity of X can be observed for monosubstituted compounds, MH_3X . With disubstitution, there is a deviation from additivity for the direct coupling constants (C, Si) as well as for the indirect. For carbon, this deviation is only notable with fluorine substituents; for silicon, Cl and Br yield stronger deviations than I, and for tin it is evident that the deviation is a function of the electronegativity of X. These observations show that such deviations, for which Douglas⁹ developed his interaction parameters, increase with increasing atomic number of the central element.

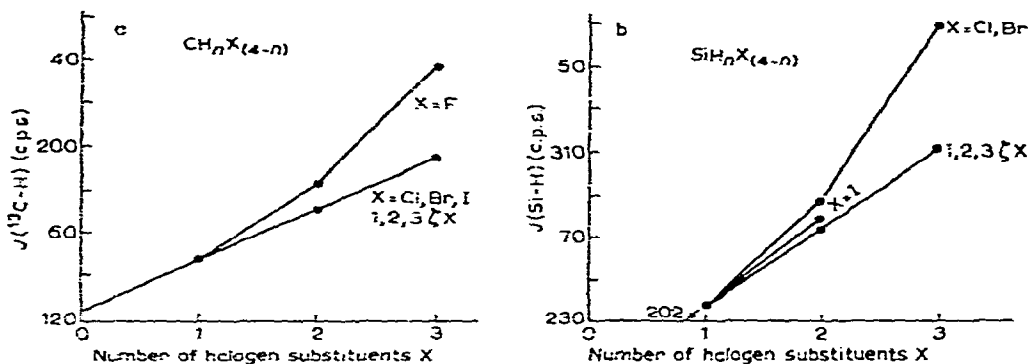


Fig. 5. a and b. Direct M-X coupling constants for halomethanes and halosilanes.

According to Juan and Gutowsky⁷, the direct coupling constants $J(\text{M-H})$ ($\text{M} = \text{C, Si, Ge, Sn}$) and the indirect coupling constants $J(\text{M-C-H})$ ($\text{M} = \text{Si, Sn}$) are proportional to the Fermi contact term value in the Ramsey equation for coupling constants. Smith¹⁶ has pointed out that J expressed by this equation is extremely sensitive to changes in Z , the effective nuclear charge, and to α_0 and r_m , respectively, the first Bohr orbit radius and the radius of the maximum in the radial wave function. Craig and Zauli¹⁷, on the other hand, have calculated that for elements with principal quantum number $n = 5, 6$, there is considerable distortion of the atomic orbitals when strongly electronegative substituents are bonded to them. Increase in the value of n and of the electronegativity of the substituents, results in an increase in the effective nuclear charge parameter and a decrease in the equilibrium internuclear distances. These considerations may explain the deviations cited in our data. For

carbon the distortion will be only effective with the highest electronegative substituent, F; for silicon, Cl and Br will both be sufficiently strong; whereas for tin, starting from disubstitution, Cl, Br and I each yield deviations in agreement with their electronegativity values.

These observations are in agreement with the isovalent rehybridization theory of Bent¹⁸. In these molecules, $J(\text{Sn-C-H})$ increases with increasing percentage of *s*-character of the tin orbital, *i.e.*, with increasing electron density in the Sn-C-H bond. The deviations from linear increase of J with the number of X substituents, however, are to be accounted for by the mechanisms explained above.

In view of this reasoning it is interesting to examine the trend in the value of the symmetrical stretching frequency $\nu_s(\text{Si-C})$ and $\nu_s(\text{Sn-C})$, in the methylsilyl and the methyltin halides. These values are plotted in Fig. 6, a and b, using literature data¹⁹⁻²³. The parallelism between this graph and the plot of $J(\text{Sn-C-H})$ vs. number of X atoms (X = Cl, Br, I) is very close. Apparently, the bond strength of the Sn-C bonds increases with increasing number of substituents and the electronegativity of X. This is further evidence for the theory developed above.

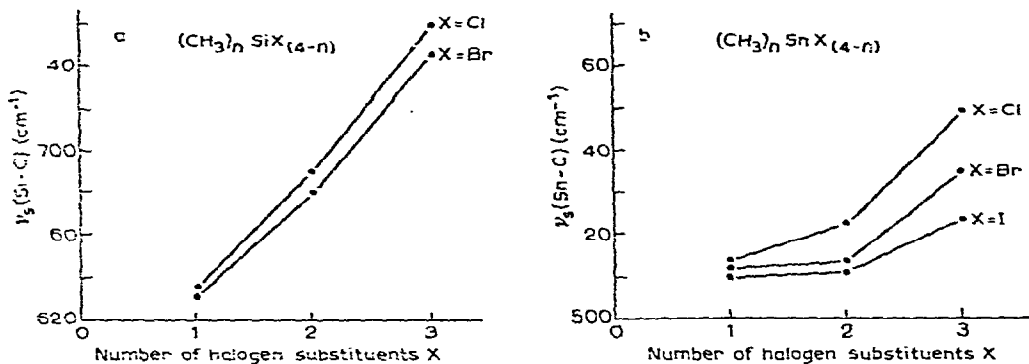


Fig. 6, a and b. Symmetrical stretching frequencies $\nu(\text{Si-C})$ and $\nu(\text{Sn-C})$, for methylhalosilanes and methylhalostannanes.

Dipole moments

On the assumption that the inter-bond angles in the compounds are tetrahedral and that the partial moments remain constant within each halide series, the following relations should be valid.

$$\frac{\mu(\text{Me}_2\text{SnX})}{\mu(\text{MeSnX}_2)} = 1 \quad \text{and} \quad \frac{\mu(\text{Me}_2\text{SnX}_2)}{\mu(\text{Me}_3\text{SnX})} = 1.16$$

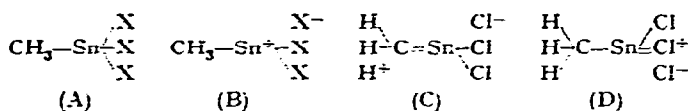
Starting with the experimental values for the trimethyl compounds, we calculated the theoretical values for the mono- and di-methyl compounds. These are listed in column 3 of Table 2. Because the first of the above assumptions is fulfilled for these molecules, as shown by the X-ray data of Skinner and Sutton²⁴, the differences noted in column 4 must be ascribed to changes in the partial moments, $\mu(\text{Sn} \leftarrow \text{C})$ and $\mu(\text{Sn} \rightarrow \text{X})$.

The interatomic distance Sn-C is almost constant for all these molecules. The Sn-X distance, however, decreases going from the mono- to the trihalides. Moreover,

since the electronegativity difference between tin and carbon is less than that between tin and the halogens, we can assume, to a first approximation, that the Sn-C partial moment is practically invariable. These considerations applied to the data of Table 2 indicate that $\mu(\text{Sn} \rightarrow \text{Cl}) < \mu(\text{Sn} \rightarrow \text{Br}) < \mu(\text{Sn} \rightarrow \text{I})$ as would be expected.

The differences between the experimental and theoretical values of column 4 can then be explained as follows. For the chloride series, positive deviations are obtained; this reveals an increase of the partial Sn-Cl electric moment with increasing number of chlorine atoms. The corresponding data for bromides and iodides are parallel to the observations of Van de Vondel²⁵ for the methylgermanium chlorides and suggest a decrease of the metal-to-halogen bond moment with increasing number of halogen atoms. This effect is more pronounced for iodides than for bromides.

Four types of resonance structures can be considered for these molecules.



Increase in importance of resonance contributions of type D will decrease the M-X partial moment. The relative importance of resonance contributions of types C and D will increase with increasing electronegativity and increasing number of substituents, X. The resonance contributions of type C will be favoured in order of polarizability of the central atom: $\text{C} < \text{Si} < \text{Ge} < \text{Sn}$. Contributions of type C resonance *vs.* type D, will become more effective the more electronegative is X. For tin compounds, this structure should thus be even more prominent than in the corresponding germanium compounds. The combined action of these effects will be to make the partial moments Sn-X decrease with progressive halogenation for $\text{X} = \text{Br}$ and I , and this trend should obviously be stronger for iodides than for bromides.

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SUMMARY

The PMR spectra and electric moments of $(\text{CH}_3)_n\text{SnX}_{4-n}$ compounds have been studied for $\text{X} = \text{Cl}$, Br and I . The trend of the chemical shifts is opposite to the inductive effect of the substituent, X, and can be explained by a diamagnetic anisotropy effect acting along the Sn-X bond. Also, the Sn-C-H coupling constants do not agree with any additivity rule as a function of progressive halogenation, the deviations being higher for chlorides than for bromides or iodides. This has been ascribed to a strong distortion of the atomic orbitals of tin, increasing with electronegativity of the substituent. The electric moments can be explained by assuming resonance structures with a double-bond character in the Sn-X or the Sn-C bond.

REFERENCES

- 1 E. R. MALINOWSKI, *J. Am. Chem. Soc.*, 83 (1961) 4479.
- 2 H. S. GUTOWSKY AND C. S. JUAN, *J. Am. Chem. Soc.*, 84 (1962) 307.
- 3 G. P. VAN DER KELEN AND Z. EECKHAUT, *J. Mol. Spectry.*, 10 (1963) 141.
- 4 N. MULLER AND P. I. ROSE, *J. Am. Chem. Soc.*, 84 (1962) 3973.
- 5 S. G. FRANKIS, *J. Phys. Chem.*, 67 (1963) 752.
- 6 E. A. V. EBSWORTH AND J. J. TURNER, *J. Chem. Phys.*, 36 (1962) 2628.
- 7 C. JUAN AND H. S. GUTOWSKY, *J. Chem. Phys.*, 17 (1962) 2198.
- 8 R. K. HARRIS, *J. Phys. Chem.*, 66 (1962) 768.
- 9 A. W. DOUGLAS, *J. Chem. Phys.*, 40 (1964) 2413.
- 10 E. R. MALINOWSKI AND T. VLADIMIROFF, *J. Am. Chem. Soc.*, 86 (1964) 3575.
- 11 T. VLADIMIROFF AND E. R. MALINOWSKI, *J. Chem. Phys.*, 42 (1965) 440.
- 12 E. V. VAN DEN BERGHE AND G. P. VAN DER KELEN, *Z. Elektrochem.*, 68 (1964) 652.
- 13 E. G. CLAEYS AND G. P. VAN DER KELEN, *Bull. Soc. Chim. Belges*, 70 (1961) 462.
- 14 H. SPIESECKE AND W. G. SCHNEIDER, *J. Chem. Phys.*, 35 (1962) 722.
- 15 L. VERDONCK AND G. P. VAN DER KELEN, *Z. Elektrochem.*, 69 (1965) 478.
- 16 G. W. SMITH, *J. Chem. Phys.*, 39 (1963) 2031.
- 17 D. P. CRAIG AND C. ZAULI, *J. Chem. Phys.*, 37 (1962) 609.
- 18 H. A. BENT, *J. Inorg. Nucl. Chem.*, 19 (1961) 43.
- 19 C. H. WARD, *Dissertation abstr.*, 14 (1954) 456.
- 20 H. KRIEGSMANN AND S. PISCHTSCHAN, *Z. Anorg. Allgem. Chem.*, 308 (1961) 212.
- 21 A. OKAWARA, D. E. WEBSTER AND E. G. ROCHOW, *J. Am. Chem. Soc.*, 82 (1960) 3287.
- 22 E. R. LIPPINCOTT, P. MERCIER AND MCTOBIN, *J. Phys. Chem.*, 57 (1953) 939.
- 23 H. KRIEGSMANN, *Z. Anorg. Allgem. Chem.*, 229 (1959) 138.
- 24 H. A. SKINNER AND L. E. SUTTON, *Trans. Faraday Soc.*, 40 (1944) 164.
- 25 D. F. VAN DE VONDEL AND G. P. VAN DER KELEN, *Bull. Soc. Chim. Belges*, 74 (1965) 618.