

A COMPARATIVE STUDY OF THE ^1H , ^{29}Si AND ^{119}Sn NMR SPECTRA OF COMPOUNDS OF THE TYPE $(\text{CH}_3)_n\text{MX}_{4-n}$ ($n=1, 2, 3$) WHERE $\text{M}=\text{Si}$ OR Sn AND $\text{X}=\text{Cl}, \text{Br}$ OR I

E. V. VAN DEN BERGHE and G. P. VAN DER KELEN

Laboratory for General and Inorganic Chemistry-B, University of Ghent, Krijgslaan 271, B-9000 Ghent (Belgium)

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SUMMARY

The ^1H , ^{29}Si and ^{119}Sn NMR parameters for methylsilicon halides and methyltin halides have been determined and compared with each other. It was found that the ^1H chemical shifts of the former compounds are governed by the extent of *s* hybridisation involving the $\text{C}\rightarrow\text{H}$ orbitals thus implying that it is not necessary to invoke major contributions arising from the diamagnetic anisotropic effect of the $\text{Si}-\text{X}$ bonds in order to explain the trends among the chemical shifts for these compounds.

With the methyltin halides, the ^1H chemical shifts are again strongly influenced by the extent of *s* hybridisation involving the $\text{C}\rightarrow\text{H}$ orbitals, but in this case contributions arising from the diamagnetic anisotropic effect of the $\text{Sn}-\text{X}$ bonds have to be invoked in order to explain the overall trend in the ^1H chemical shifts.

The increasing dependence of the ^{29}Si and ^{119}Sn chemical shifts on the electronegativity of the halogen and comparison with the ^{13}C chemical shifts in alkyl halides indicate that significant $p_{\text{X}}\rightarrow d_{\text{Si}}$ back-donation occurs which increases with increasing electronegativity of X and ultimately leads to ionic contributions being of major importance in $\text{Sn}-\text{X}$ bonds.

Several effects may contribute to this observed upfield displacement of the ^{29}Si and ^{119}Sn chemical shifts with increased halogen substitution. Thus it has been argued that σ^{E} and σ^{anis} contributions must play an important role in the observed shifts. In addition, intramolecular Van der Waals' interaction forces between the bulkier halogens and the CH_3 protons strongly affect the $\text{C}\rightarrow\text{H}$ rehybridisation as may be derived from values of the $^{13}\text{C}-\text{H}$ coupling constants in both organometallic halides. Finally, hyperconjugation effects may also possibly contribute to the observed behaviour.

The $^{29}\text{Si}-\text{C}-\text{H}$ coupling constants of trimethylsilicon halides have also been discussed using structural arguments. The inductive electron-withdrawing capacity of the halogens apparently dominates the observed trend in the $^{117,119}\text{Sn}-\text{C}-\text{H}$ coupling constants.

INTRODUCTION

A systematic study of the ^1H and ^{119}Sn NMR spectra of compounds of the type

$(\text{CH}_3)_n\text{SnX}_{4-n}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) ($n = 1, 2, 3$) has been reported previously^{1,2}. The observed inverse relationship between the ^1H chemical shifts and the electronegativity of the halogen was explained in terms of a major contribution by the diamagnetic anisotropic effect of the $\text{Sn}-\text{X}$ bond and by the influence of intramolecular Van der Waals forces involving the halogen substituents. The $^{117,119}\text{Sn}-\text{C}-\text{H}$ coupling constants, on the other hand, exhibited variations which were linearly dependent on the electronegativity and were readily explained in terms of a related change in the s character of the tin-carbon orbital in accordance with the theory of Bent³. The increasing non-additivity of these couplings as the extent of halogen substitution increases has been discussed.

No corresponding influence of the electronegativity on the $^{13}\text{C}-\text{H}$ coupling constants could be established probably due to limited experimental accuracy. For this reason a new determination of these constants appears justified and is reported in this paper. The data relating to the ^{119}Sn chemical shifts are explained in terms of inductive and possible back-donation effects of the halogens together with anisotropy contributions.

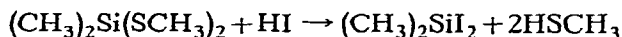
As far as organosilicon chemistry is concerned, no complete and systematic study of the ^1H and ^{29}Si NMR spectra of methylsilicon halides has been reported. Apart from the complete series $(\text{CH}_3)_n\text{SiCl}_{4-n}$, only $(\text{CH}_3)_3\text{SiBr}$ and $(\text{CH}_3)_3\text{SiI}$ have been investigated in this manner⁴⁻⁸. It has been established that the ^1H NMR data for $(\text{CH}_3)_3\text{SiHal}$ also exhibit an inverse relationship with respect to electronegativity. However, in this case this behaviour is quite unexpected in view of the observed dependencies of the $^{29}\text{Si}-\text{C}-\text{H}$ and $^{13}\text{C}-\text{H}$ coupling constants. An increased lone-pair back-donation to the empty silicon $3d$ orbitals for smaller and more electronegative halogen substituents has been suggested as an explanation of this trend⁷. This explanation has been subsequently questioned⁹ but to date no alternative interpretation has been proposed. The reported ^{29}Si chemical shifts for the $(\text{CH}_3)_3\text{SiX}$ compounds⁶ exhibit a linear dependence on the electronegativity.

In this study it is proposed to fill the gap in the ^1H and ^{29}Si NMR data for methylsilicon halides and hence to enable a comparative study to be made of all the ^1H , ^{29}Si and ^{119}Sn parameters in relation to the chemical bonding involved.

EXPERIMENTAL

Synthesis of compounds

The methyltin halides were prepared by standard methods. Methylsilicon chlorides could be obtained commercially while $(\text{CH}_3)_2\text{SiBr}_2$ and CH_3SiBr_3 were prepared by a Rochow synthesis¹⁰. $(\text{CH}_3)_2\text{SiI}_2$ and CH_3SiI_3 could not be prepared by this method, however, and although a synthesis¹¹ based on a substitution reaction between methyl(anilino)silanes and HI resulted in the formation of $(\text{CH}_3)_2\text{SiI}_2$ and CH_3SiI_3 , it was extremely difficult to isolate the pure compounds from the reaction mixture in reasonable yields. For this reason, a method was developed to prepare pure $(\text{CH}_3)_2\text{SiI}_2$ and CH_3SiI_3 in almost quantitative yield by means of a substitution reaction between the corresponding methyl(thiomethyl)silicon compounds and dry HI gas.



The thiomethylsilicon reactant was dissolved in dry benzene and a stream of dry N_2 saturated with HI was led into the solution. The course of the reaction was followed by NMR spectroscopy utilising the ^1H signal of $\text{Si}-\text{SCH}_3$. The products were isolated by fractional vacuum distillation.

NMR spectra

The NMR spectra were recorded by a frequency-sweep method using a Bruker-Physik HFX₅ spectrometer operating at a proton frequency of 90 MHz. The compounds were examined as solutions in benzene (20%) using 5 mm diameter NMR tubes, the benzene signal being used to lock the field signal. The INDOR technique was applied to record the ^{29}Si NMR spectra using the method previously employed for the ^{119}Sn NMR spectra² thus allowing an overall accuracy of ± 1 Hz in the shift determination.

Previous investigators^{6,8} have recorded silicon signals using the rapid passage dispersion mode, the error in the shift determination being estimated as ± 1 ppm. Under these conditions it was not possible to observe any multiplicity due to the CH_3 protons.

Some of the ^{29}Si NMR spectra obtained in this work are presented in Fig. 1

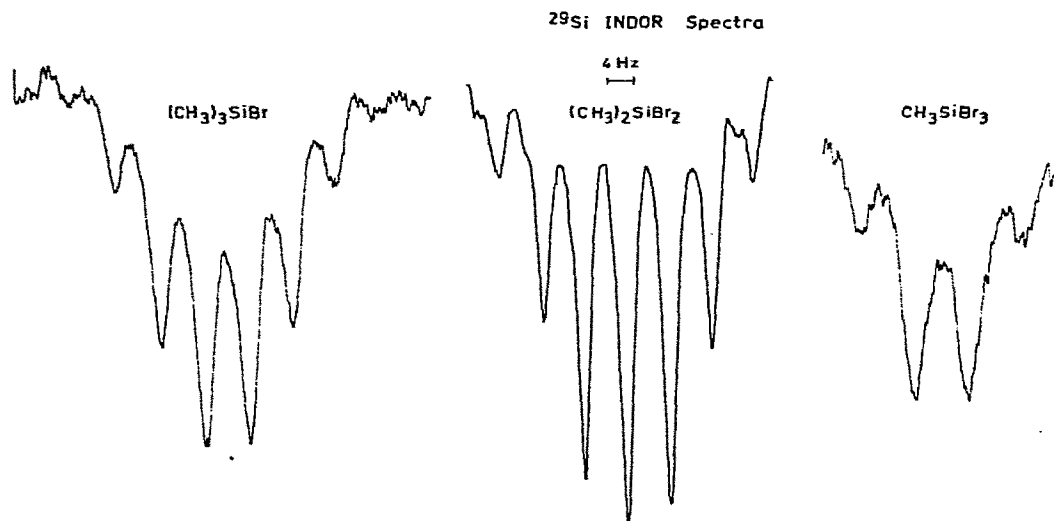


Fig. 1. ^{29}Si INDOR spectra of methylsilicon bromides.

TABLE I

CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR METHYLSILICON HALIDES

X	$\text{Si}(\text{CH}_3)_4$	$(\text{CH}_3)_3\text{SiX}$			$(\text{CH}_3)_2\text{SiX}_2$			CH_3SiX_3		
		Cl	Br	I	Cl	Br	I	Cl	Br	I
$\delta(^1\text{H})\text{ppm}$	0	+0.23	+0.36	+0.53	+0.43	+0.72	+1.09	+0.57	+1.02	+0.91
$\delta(^{29}\text{Si})\text{ppm}$	0	+30.21	+26.41	+8.72	+32.17	+19.86	-33.68	+12.47	-18.18	-17.96
$J(^{29}\text{Si}-\text{C}-\text{H})$	6.6	6.9	7.0	7.1	7.6	7.6	7.4	9.0	8.6	8.5
$J(^{13}\text{C}-\text{H})$	118.9	120.9	121.4	121.8	123.5	124.2	124.7	126.2	126.9	126.4

and as can be seen the $(\text{CH}_3)_3\text{Si}$ -, $(\text{CH}_3)_2\text{Si}$ - and CH_3Si - moieties are readily recognisable through their multiplicity.

RESULTS AND DISCUSSION

The various NMR parameters obtained in this work are recorded in Tables 1 and 2 and presented graphically in Figs. 2-5 along with NMR data for the methyltin halides obtained previously. Low-field shifts are expressed as positive ppm values and high-field shifts as negative ppm values relative to TMS (^1H , ^{29}Si shifts) or $\text{Sn}(\text{CH}_3)_4$ (^{119}Sn shifts).

1 ^1H , ^{29}Si and ^{119}Sn chemical shift data

1.1 Influence of electronegativity

The ^1H chemical shift data for methylsilicon halides (Fig. 2) as well as those for the methyltin halides exhibit an inverse dependency on the electronegativity of the halogen substituent. Such an inverse order, however, is not observed for the ^{29}Si chemical shifts nor for the ^{119}Sn chemical shifts (Fig. 3).

Spiesecke and Schneider¹² in a study of alkyl halides and Hunter and Reeves⁶

TABLE 2

^{13}C -H COUPLING CONSTANTS FOR METHYLTIN HALIDES

X	$\text{Sn}(\text{CH}_3)_4$	$(\text{CH}_3)_3\text{SnX}$			$(\text{CH}_3)_2\text{SnX}_2$			CH_3SnX_3		
		Cl	Br	I	Cl	Br	I	Cl	Br	I
$J(^{13}\text{C}-\text{H})$	127.5	131.6	131.8	132.1	136.2	136.8	136.8	141.2	141.2	141.2

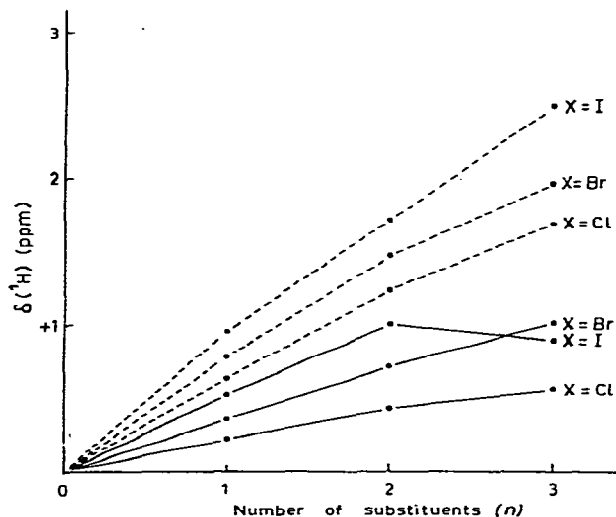


Fig. 2. ^1H chemical shifts of $(\text{CH}_3)_{4-n}\text{SnX}_n$ (—) and $(\text{CH}_3)_{3-n}\text{SnX}_n$ (----) compounds, respectively.

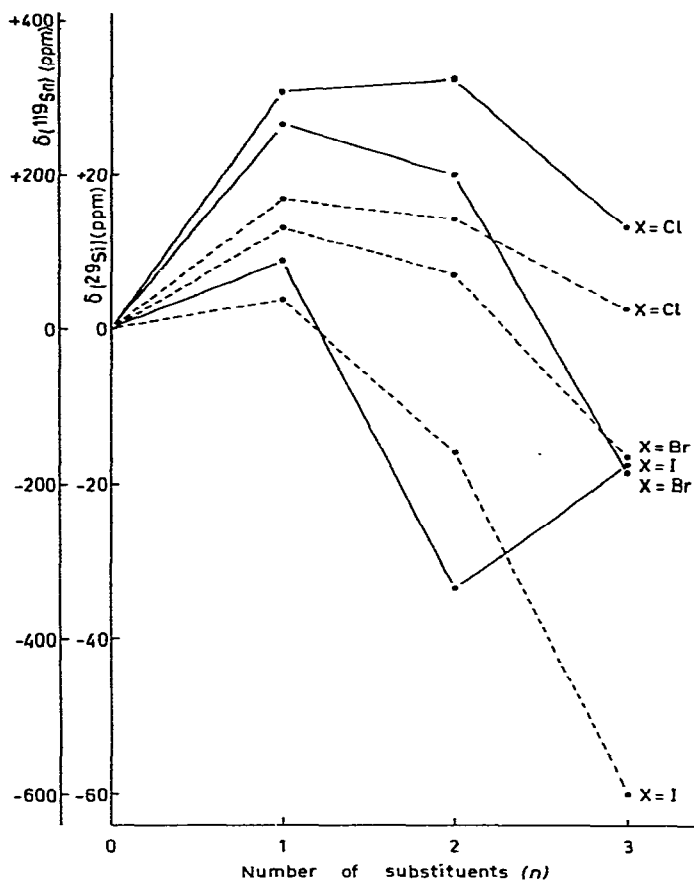


Fig. 3. ^{29}Si and ^{119}Sn chemical shifts of $(\text{CH}_3)_{4-n}\text{SiX}_n$ (—) and $(\text{CH}_3)_{4-n}\text{SnX}_n$ (---) compounds, respectively.

in a study of methylsilicon halides have established a linear dependency on the electronegativity for the ^{13}C and ^{29}Si chemical shifts. We have also previously established a similar dependency for the ^{119}Sn chemical shifts in trimethyltin halides and our present measurements on the corresponding silicon compounds confirm the observations of Hunter and Reeves.

Apparently the diamagnetic anisotropy of the Si-X bonds together with the Van der Waals' interactions of the halogens, which increase with increasing radius, may be advanced as an explanation of the shielding of the distant protons in methylsilicon halides (see Section 2.2 for further details on this point). A similar explanation has been put forward for the methyltin halides. The observed sequence in the ^{29}Si chemical shifts also eliminates the increasing back-donation effect of the halogen substituent with increasing electronegativity (such that the overall substitution effect of the halogen opposes the inductive effect) as an explanation of the ^1H NMR data. An alternative explanation will be presented in the discussion below of the different coupling constants.

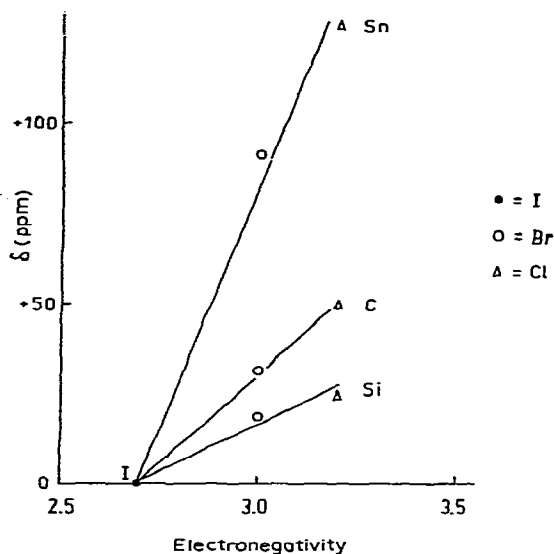


Fig. 4. ^{13}C , ^{29}Si and ^{119}Sn chemical shifts in CH_3X and $(\text{CH}_3)_3\text{MX}$ compounds ($\text{M} = \text{Sn}, \text{Si}$) plotted against the electronegativity (Allred) of X (I, Br, Cl), the data for $\text{X} = \text{I}$ being taken arbitrarily as zero.

In Fig. 4, the ^{13}C , ^{29}Si and ^{119}Sn chemical shifts in CH_3X and $(\text{CH}_3)_3\text{MX}$ ($\text{M} = \text{Si}, \text{Sn}$) compounds are plotted as a function of the electronegativity of X . The shift deviations are expressed in Δ ppm values relative to the value for the iodine compound which was arbitrarily taken as zero. The increasing sequence $\text{Si} > \text{C} > \text{Sn}$ for the slope of the line may be considered as a reflection of the increasing range of chemical shifts observed for these three nuclei which occur in the same order, *i.e.*, 140, 316 and 1852 ppm respectively, for ^{29}Si ⁸, ^{13}C ¹³ and ^{119}Sn ¹⁴. However, the restricted range of ^{29}Si chemical shifts relative to those observed for ^{13}C chemical shifts is unexpected for normally the range of chemical shifts increases with atomic number Z for a particular group of the Periodic Table and also increases with the value of Z in a given period¹⁵.

It has been suggested^{6,15} that the restricted range of ^{29}Si shifts may be explained in terms of $(p-d)\pi$ bonding. It is indeed possible that the reduced tendency for the removal of electron charge from the silicon atom in relation to that anticipated from the numerical value of the electronegativity of the halogen atom may result from $p_{\text{X}} \rightarrow d_{\text{Si}}$ back-donation and thus give rise to the rather small difference in value between the ^{29}Si chemical shift for a silicon atom in a strongly covalent $\text{Si}-\text{X}$ bond and in an almost ionic $\text{Si}-\text{X}$ bond.

The more extended shift range observed for ^{119}Sn may be interpreted in terms of increased ionic contributions to the $\text{Sn}-\text{X}$ bonds; further, the slope of the ^{13}C correlation line is primarily determined by the σ -electron-withdrawing capacity of the halogen substituent. In addition, the ionic character of the $\text{M}-\text{F}$ bond in binary fluorides has also been invoked in ^{19}F NMR spectroscopy by Gutowsky and Hoffman¹⁶ in order to explain the large range (625 ppm) of fluorine chemical shifts observed.

For these reasons we believe that the deviation in the upfield shift of the ^{29}Si correlation line may be explained by increased back-donation of the halogen atoms with increasing electronegativity. The considerably greater slope of the ^{119}Sn corre-

lation line can then be related to the considerably greater polarization of the Sn-X bond relative to that in Si-X, in agreement with Fajans' rule. Thus back-donation from the halogen atoms in the trimethyltin halides must therefore be very weak. Further, if such back-donation occurs it increases in the series $\text{I} > \text{Br} > \text{Cl}$. This is the opposite trend from that deduced for back-donation in the trimethylsilicon halides but in this respect it should be borne in mind that maximum overlap between the respective empty $3d$ Si and $5d$ Sn orbitals and filled np halogen orbitals should occur when the contributing orbitals are of the same principal quantum number *i.e.*, $3p(\text{Cl}) \rightarrow 3d(\text{Si})$ and $5p(\text{I}) \rightarrow 5d(\text{Sn})$. Conclusions drawn from quadrupole splitting data of alkyltin halides obtained by Mössbauer spectroscopy¹⁷ are also consistent with the very low back-donation effect of the halogens. Furthermore, molecular orbital calculations on $(\text{CH}_3)_3\text{SnX}$ ¹⁸ reveal small π -bond orders for $\text{X} = \text{F}, \text{Cl}$ and Br , increasing in this order in agreement with the above conclusions. Bond dissociation energy measurements on trimethylsilicon halides¹⁹ have been interpreted in terms of an increased $(p \rightarrow d)\pi$ bonding in going from chlorine to iodine, in contrast to the trend observed in this study. On the other hand, overlap integral calculations by Jaffé²⁰ also reveal decreasing $(p \rightarrow d)\pi$ overlap with the larger halogens.

1.2 Influence of halogen substitution

Increased halogen substitution causes a progressive low-field shift of the ^1H resonance irrespective of the nature of the halogen atom. This trend, which is opposite to the halogen electronegativity effect discussed above and is illustrated in Fig. 2, is maintained throughout the whole series of compounds with the exception of $\text{CH}_3\text{-SiI}_3$. (An explanation for this exception is presented in Section 2.2) On the other hand, the ^{29}Si and ^{119}Sn resonances exhibit a progressive upfield shift with the introduction of two or three halogen substituents into the molecule. The following considerations may be relevant to this observation.

(i) σ^p contributions. Calculations have shown^{15,21,22} that for nuclei other than hydrogen the paramagnetic term in the shielding expression of Ramsey should make the largest contribution to the total shielding. According to Jameson and Gutwosky¹⁵ this term may be written as expressed in eqn. (1).

$$\sigma^p = -(2e^2 h^2 / 3 \Delta m^2 e^2) (\langle 1/r^3 \rangle_p \text{Pu} + \langle 1/r^3 \rangle_d \text{Du}) \quad (1)$$

where

$$\langle 1/r^3 \rangle = \frac{1}{3} (Z_{\text{eff}} / n \cdot a_0)^3 \quad (2)$$

and where n is the principal quantum number and a_0 the Bohr radius. The values of $\langle a_0^3 / r^3 \rangle$ reflect approximately how the order of increasing chemical shift varies with increasing atomic number, the corresponding values derived for C, Si and Sn being 1.23^{23} , 2.31^{23} and 8.65^{15} (11.2^{23}), respectively.

The $(p \rightarrow d)\pi$ back-donation effects of the halogens which increase the electron density at the Si or Sn nucleus may reduce the paramagnetic term and lead to an upfield shift in the ^{29}Si and ^{119}Sn resonance. If this is correct, the observed increasing upfield shift could be explained by increased $(p \rightarrow d)\pi$ back-donation resulting from halogen substitution. However, in alkyl halides¹² where $(p \rightarrow d)\pi$ back-donation is generally accepted to be impossible, a similar upfield shift with increasing halogen substitution has been observed with the bromides and iodides. Furthermore, cal-

culated values for $\langle 1/r^3 \rangle_{np}$ and $\langle 1/r^3 \rangle_{nd}$ obtained by Jameson and Gutowsky¹⁵ imply that the *p*-electron contribution to σ^p must be at least one or two orders of magnitude larger than the *d*-electron contribution. These results suggest that the dependence of the rather unusual and drastic upfield displacement of the ²⁹Si and ¹¹⁹Sn chemical shifts solely on *dπ* orbital contributions caused by back-donation is highly doubtful.

Although it has been shown¹⁵ that variations in *dπ* contributions can be much greater than corresponding variations in *pπ* contributions, it is unlikely that within the same series of compounds the *dπ* contribution should vary significantly.

(ii) σ^d contributions. A discussion of σ^d contributions relative to ¹³C chemical shifts has been made in a recent paper by Mason²⁴ in which it has been claimed, on the basis of calculations for σ^d as proposed by Flygare and Goodisman²⁵, that diamagnetic shielding contributions to the ¹³C chemical shifts from highly polarisable substituents should play a significant role in the total shielding. Similar suggestions apply to ¹⁴N chemical shifts²⁶. A consequence of this is that in organotin and organosilicon halides the possibility of an increasing diamagnetic shielding contribution occurring with the increasing halogen size must also be taken into account. This however should imply a decreasing *d*-orbital contribution to the shielding since these orbitals make no direct contribution to σ^d .

(iii) σ^E and σ^{anis} contributions. Large contributions to the shielding of an atom in an X–Y bond in which X or Y is highly polarisable may also arise both from the electric-field effect due to permanent dipole moments in the molecule and from Van der Waals' interactions between the atoms²⁷. This effect can be generally expressed as:

$$\sigma^E = -AE_z - BE^2 \quad (3)$$

in which *E* is equal to the electric field at the nucleus and *E_z* is equal to the electronic-field component along the bond. The σ^E contribution thus depends on both the constants *A* and *B*. Values for these constants have been calculated by Buckingham³² for the case of proton resonance involving a C–H bond. A number of *A* and *B* values for ¹³C resonances in C–X bonds have also been calculated by Horsley and Sternlicht³³.

It has been suggested²⁷ that the considerable ¹³C high-field shifts observed in alkyl iodides may arise from important σ^E contributions. In Section 2.2, the importance of Van der Waals' interactions in the compounds investigated in this study is established from considerations of the individual coupling constants and it is therefore possible that the influence of such interactions on the σ^E values makes a major contribution to the observed ¹¹⁹Sn and ²⁹Si upfield shifts.

Another possible contribution which should be taken into account is the anisotropy contribution, σ_{AB}^{anis} , caused by the magnetic anisotropy, $\Delta\chi_B$, centered on atom B in an AB bond. These two quantities are related by eqn. (4):

$$\sigma_{AB}^{anis} = \frac{1}{3H_0 \cdot R_{AB}^3} \cdot \Delta\chi_B (1 - 3 \cos^2 \theta) \quad (4)$$

in which θ is the angle between the line joining the anisotropy site on the AB bond axis to the nucleus for which the σ_{AB}^{anis} contributions are calculated and the direction of the magnetic field *H₀*²⁸. In the case of the anisotropy contribution involving ²⁹Si or ¹¹⁹Sn resonance, A = Si or Sn, X = halogen and $\theta = 0$ so that σ_{AB}^{anis} is positive and an increased magnetic shielding of the ¹¹⁹Sn and ²⁹Si nuclei can be expected from the

increased diamagnetic anisotropy contribution of the Sn-X and Si-X bonds resulting from an increasing number of halogen substituents. On the other hand, a decrease in the value of R_{AB} (the interatomic distance in the AB bond) must significantly increase $\sigma_{AB}^{\text{anis}}$. Considerable decreases in such values for Sn-X or Si-X bonds have been measured in alkyltin or alkylsilicon halides with increasing halogen substitution²⁹.

From the considerations discussed in (i), (ii) and (iii), it follows that back-donation due to the halogen atoms is not the most important factor influencing the upfield shifts which occur with increasing halogen substitution. Although such factors cannot be entirely neglected, it is more likely that the major factors arise from σ^E and σ^{anis} contributions and that σ^d contributions must also be taken into account in the case of ^{13}C chemical shifts as demonstrated by Mason.

2. Coupling constants

2.1 $^{29}\text{Si-C-H}$ and $^{117,119}\text{Sn-C-H}$ couplings (see Fig. 5)

The $^{29}\text{Si-C-H}$ coupling constants in trimethylsilicon halides show an inverse

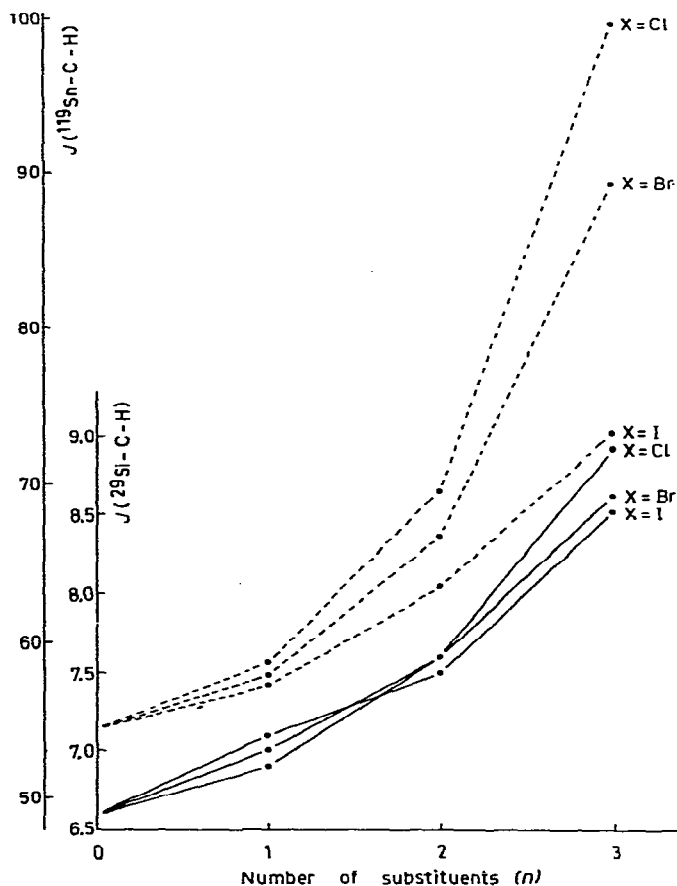


Fig. 5. $^{29}\text{Si-C-H}$ and $^{119}\text{Sn-C-H}$ coupling constants for $(\text{CH}_3)_{4-n}\text{SiX}_n$ (—) and $(\text{CH}_3)_{4-n}\text{SnX}_n$ (----) compounds, respectively.

dependence on the electronegativity of the halogen atom, whereas with the di- and tri-halides a gradual approach towards the predictions of Bent's rule may be discerned.

With all the methyltin halides, the variation of the $^{117,119}\text{Sn}-\text{C}-\text{H}$ coupling constants is directly related to the variation in electronegativity irrespective of the degree of halogen substitution. This behaviour again demonstrates that substitution effects on the Sn atom are dominated by the inductive effect of the substituents.

As mentioned above, the observed trend in the $^{29}\text{Si}-\text{C}-\text{H}$ coupling constants together with those of the $^{13}\text{C}-\text{H}$ coupling constants and ^1H chemical shifts in $(\text{CH}_3)_3\text{SiX}$ compounds has been ascribed by Schmidbauer⁷ to a reversal of the inductive effect of the halogen atoms caused by an increasing and ultimately dominating π -bonding effect of the halogens in going from iodine to chlorine. If the observed trend of the ^{29}Si chemical shifts is taken into account together with their interpretation as outlined in the previous sections, it is seen that Schmidbauer's suggestion is questionable and must be replaced by the alternative explanation given below.

If it is assumed that in these halogen-substituted compounds the variation of the $^{29}\text{Si}-\text{C}-\text{H}$ coupling constants is proportional to the percentage s character of Si atom in the $\text{Si}\rightarrow\text{C}$ orbital, it follows on the basis of the experimental results, that this variation increases in the trimethylsilicon halides in going from chlorine to iodine as substituents. This trend cannot be explained on the basis of Bent's rules.

An alternative explanation is that rehybridisation in the $\text{Si}\rightarrow\text{C}$ orbitals may be brought about by some structural change. Thus, if a small isovalent rehybridisation of the $\text{Si}\rightarrow\text{C}$ orbitals is assumed to occur which results in a small opening of the CSiC angle or a reduction of the CSiX angle on replacing Cl by I as the substituent, it is possible to explain the observed values of the $^{29}\text{Si}-\text{C}-\text{H}$ coupling constants. Unfortunately, insufficient accurate structural data on these compounds are available to test this hypothesis.

However, in methyl monohalides³¹ where a similar trend in the $^{13}\text{C}-\text{H}$ coupling constants to that observed with the trimethylsilicon halides occurs, a reduction in the HCX bond angle as predicted above for the $(\text{CH}_3)_3\text{SiX}$ compounds has been demonstrated (Table 3). This observation therefore supports the suggestions put forward above.

TABLE 3

OBSERVED HCX BOND ANGLES IN METHYL MONOHALIDES³¹

	HCX
CH_3F	$108^\circ 27'$
CH_3Cl	$108^\circ 00'$
CH_3Br	$107^\circ 14'$
CH_3I	$106^\circ 58'$

2.2 $^{13}\text{C}-\text{H}$ couplings (see Fig. 6)

For the methylsilicon halides, the trend in the $^{13}\text{C}-\text{H}$ coupling constants is opposite to the variation in the electronegativity over the whole range of compounds studied, with the exception of CH_3SiI_3 and CH_3SiBr_3 . Furthermore, in the methyltin halides a similar reverse trend to the electronegativity has been established for the

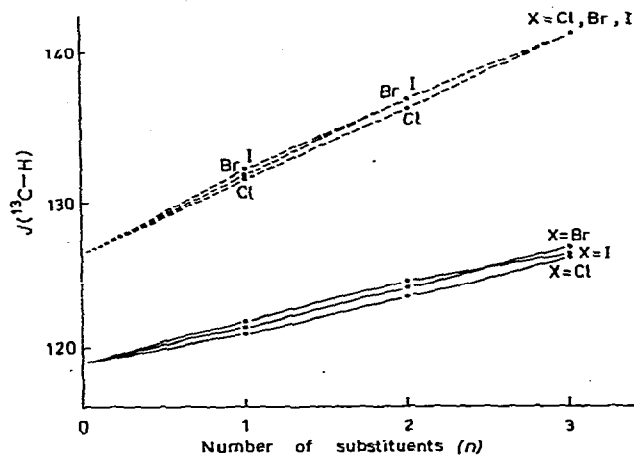
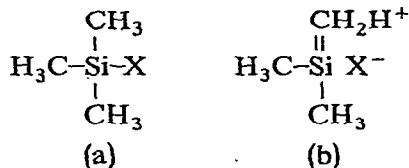


Fig. 6. ^{13}C -H coupling constants for $(\text{CH}_3)_{4-n}\text{SiX}_n$ (—) and $(\text{CH}_3)_{4-n}\text{SnX}_n$ (---) compounds, respectively.

monohalides. With the di- and tri-halides, the $J(^{13}\text{C}-\text{H})$ values approach each other and the effect is diminished. These variations in the $^{13}\text{C}-\text{H}$ coupling constants when compared with those of the $^{29}\text{Si}-\text{C}-\text{H}$ and $^{119}\text{Sn}-\text{C}-\text{H}$ coupling constants lead to the conclusion that $\text{C}\rightarrow\text{H}$ rehybridisation is not induced in a similar fashion to $\text{Si}\rightarrow\text{C}$ or $\text{Sn}\rightarrow\text{C}$ rehybridisation by halogen substitution in these compounds.

As an explanation, it is possible to suggest a valence bond resonance structure (b) whose contribution increases with decreasing halogen electronegativity relative to that of structure (a) and which strongly affects the hybridisation of the $\text{C}\rightarrow\text{H}$ orbitals.



This resonance may be induced by the hyperconjugation effect of the halogens, but it is more likely that it arises from Van der Waals' repulsion effects between the bulkier halogen atoms and the CH_3 protons. Increased electron delocalisation by increased halogen substitution should decrease the effect of structure (b) and this could provide an explanation for the observed trend of the $^{13}\text{C}-\text{H}$ coupling constants. In addition, the importance of the canonical form (b) is apparently greater for Si than for Sn. In the latter case, inductive effects are believed to be more important as has been most clearly established for the trimethyl compounds. Indeed, in structure (b), isovalent rehybridisation is not confined to the $\text{C}\rightarrow\text{H}$ orbitals alone but also occurs in the $\text{Si}\rightarrow\text{C}$ or $\text{Sn}\rightarrow\text{C}$ orbitals. The effect on the $\text{Si}\rightarrow\text{C}$ and $\text{Sn}\rightarrow\text{C}$ orbitals is however weaker because of the directly bonded halogen substituents. Nevertheless it may also be expected that the values of the $^{29}\text{Si}-\text{C}-\text{H}$ and $^{117,119}\text{Sn}-\text{C}-\text{H}$ coupling constants should increase as the importance of structure (b) increases *i.e.* with decreasing electronegativity of the halogen substituent. Since this is observed for the $^{29}\text{Si}-\text{C}-\text{H}$ coupling constants it must therefore be concluded that the importance of structure (b) is greater in the silicon compounds than in the corresponding tin compounds. The existence of such a re-

sonance structure should have a similar effect on the bond angles to that described in Section 2.1.

One other significant feature of this data is that the observed trend in the ^1H resonances with increasing halogen substitution in both Si and Sn compounds is opposite to that for the $J(\text{M}-\text{C}-\text{H})$ and $J(^{13}\text{C}-\text{H})$ values. The ^1H shifts therefore obviously decrease with increasing percentage s character of the $\text{C}\rightarrow\text{H}$ orbitals *i.e.* with increasing orbital electronegativity of the $\text{C}\rightarrow\text{H}$ bonding. Hence it is possible to interpret the apparently unusual ^1H chemical shift observed for CH_3SiI_3 in terms of the $^{29}\text{Si}-\text{C}-\text{H}$ and $^{13}\text{C}-\text{H}$ coupling constants. This also means that in the methylsilicon halides it is not necessary to invoke a diamagnetic anisotropy effect of the $\text{Si}-\text{X}$ bond in order to explain the trend in the ^1H chemical shifts relative to electronegativity. However, the possibility that such a contribution does not occur cannot be completely ignored, and it appears that at least in the case of the ^1H chemical shifts in methyltin halides it still plays a significant role. Although the trend of the ^1H chemical shifts in the $(\text{CH}_3)_3\text{SnX}$ compounds may be explained by reference to the variation of the $^{13}\text{C}-\text{H}$ coupling constants alone, anisotropy contributions must be accepted in the di- and trihalides since the observed $^{13}\text{C}-\text{H}$ coupling constants of these compounds, which establish a decreasing tendency for Van der Waals' interaction involving the halogen atoms, can no longer explain the persistent trend of the ^1H chemical shifts inverse to the electronegativity. It must also be taken into account that the Van der Waals' interactions between halogen atoms and CH_3 groups bonded to tin can be expected to be less than those in the corresponding silicon compounds due to the greater atomic radius of the Sn atom.

Finally, it is worth mentioning that the structural proposals made above for the trimethylsilicon halides also lead to a qualitative explanation for the unusual trend in their dipole moments which increase with decreasing electronegativity. The increasing s character of the $\text{Si}\rightarrow\text{C}$ orbitals as we proceed from $(\text{CH}_3)_3\text{SiCl}$ to $(\text{CH}_3)_3\text{SiI}$ which is induced by the corresponding increase in the CSiC angle decreases the magnitude of the $\text{C}\leftarrow\text{Si}$ moment which is opposite to the $\text{Si}\Rightarrow\text{X}$ moment.

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