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A STUDY OF THE ^{1}H AND ^{119}Sn NMR SPECTRA OF $(CH_3)_{4-n}Sn(NR_2)_n$ COMPOUNDS ($R=CH_3$, C_2H_5)

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SUMMARY

The ^{1}H and ^{119}Sn NMR spectra of the aminostannanes, $(CH_3)_{4-n}Sn(NR_2)_n$ ($R=CH_3$ and C_2H_5; $n=1$–4) have been studied. The previously undetected ^{117,119}Sn–N–C–H coupling in the methylaminostannanes was observed in these experiments thus making the proposal of a fast exchange of amine groups made by other authors difficult to sustain.

From considerations of the ^{119}Sn chemical shifts and the coupling constants ^{117,119}Sn–C–H, ^{117,119}Sn–N–C–H, it has been shown that back-donation from the nitrogen lone pair to the vacant *d* orbitals of Sn is of little or no importance. On the other hand a significant intermolecular association via N—H bridges apparently occurs in solutions of $(CH_3)_3SnN(CH_3)_2$ and $(CH_3)_2Sn[N(CH_3)_2]_2$.

It is suggested that weaker van der Waals interactions than these occur in other $(CH_3)_{4-n}SnX_n$ compounds which contain bulky X substituents and that these interactions explain the low ^{117,119}Sn–C–H coupling constants of the compounds studied.

The percentage *s* character is both $Sn \rightarrow CH_3$ and $Sn \rightarrow NR_2$ orbitals increases with increasing NR_2 substitution. The percentage *s* character increases in the $Sn–CH_3$ orbitals in the order $N(CH_3)_2 > N(C_2H_5)_2$ while a corresponding decrease occurs in the $Sn \rightarrow NR_2$ orbitals with the same substitution sequence.

INTRODUCTION

In previous ^{1}H NMR investigations of $(CH_3)_{4-n}Sn(NR_2)_n$ compounds[1-3] in which $R=CH_3, C_2H_5$, ^{117,119}Sn–N–C–H coupling could only be detected when $R=C_2H_5$ and not when $R=CH_3$. Low temperature studies of $(CH_3)_3SnN(CH_3)_2$[2,3] also failed to detect ^{117,119}Sn–N–C–H satellite lines and a fast exchange of $N(CH_3)_2$ groups was proposed as an explanation of this observation. It was also concluded that exchange would be favoured with increasing NR_2 substitution[3].

This unexpected apparent difference in the NMR behaviour of such closely related aminostannanes has prompted us to undertake a further study of their ^{1}H NMR spectra and to supplement this with ^{119}Sn NMR spectral studies. In addition, it is also possible to discuss the different NMR parameters obtained in relation to those for other $(CH_3)_{4-n}SnX_n$ compounds with different X substituents.

EXPERIMENTAL

The compounds were synthesized according to the method described by Jones and Lappert[4,5]:

$$(CH_3)_{4-n}SnCl_n + nLiNR_2 \rightarrow (CH_3)_{4-n}Sn(NR_2)_n + nLiCl$$

The NMR spectra were recorded on a Bruker-Physik HFX5 spectrometer operating for protons at 90 MHz, using a frequency sweep method. Normally the compounds were examined as 25% (v/v) solutions in benzene. The ^1H resonance line of this solvent was used as the lock signal.

The ^{119}Sn NMR spectra were recorded by means of the INDOR technique irradiating a $^{119}Sn-C-H$ and/or a $^{119}Sn-N-C-H$ satellite line with the ^{119}Sn resonance frequency, the nitrogen quadrupole moment causing a significant broadening of the lines. It was established that the extent of line broadening depends on the nature of the alkyl group in the NR_2 substituent, the greatest broadening appearing with $R=CH_3$ (Fig. 1(a) and (b)). Under such circumstances, additional line splitting

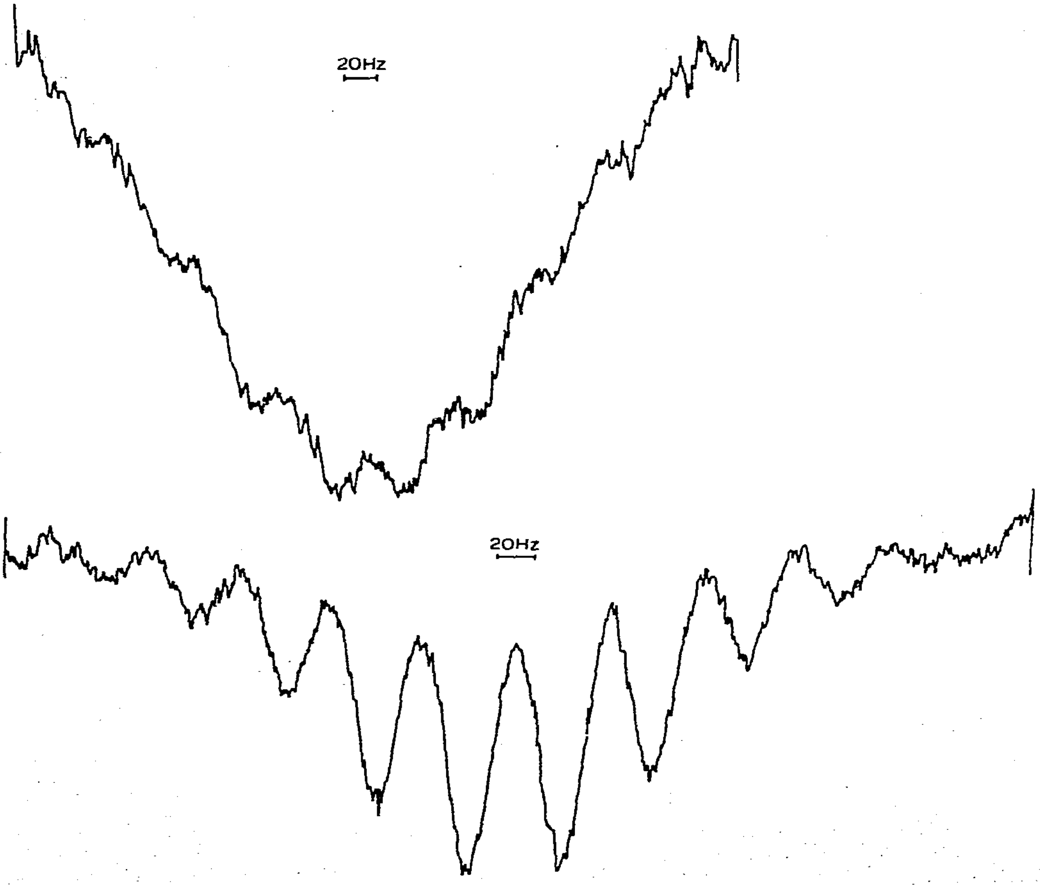


Fig. 1. ^{119}Sn INDOR NMR spectrum of (a) $(CH_3)_3SnN(CH_3)_2$ and (b) $(CH_3)_3SnN(C_2H_5)_2$.

due to ^{119}Sn–N–C–H coupling was not observed. However, with the corresponding thiomethyltin compounds, splitting in the ^{119}Sn NMR spectra due to ^{119}Sn–S–C–H coupling was easily recognised[6]. Increasing line broadening and complete line collapse occurred with increasing NR_2 substitution.

RESULTS AND DISCUSSION

The values of the different NMR parameters obtained are recorded in Table 1 where ^{1}H and ^{119}Sn chemical shifts are expressed in δ p.p.m. values to the ^{1}H signal of TMS and to the ^{119}Sn resonance frequency of $Sn(CH_3)_4$. Negative and positive signs indicate shifts to higher and lower field respectively. The variation of the ^{1}H chemical shifts and coupling constants of $(CH_3)_3SnN(CH_3)_2$ for varying concentrations in benzene are listed in Table 2. In this table the ^{1}H chemical shifts are expressed in Hz because of the rather small differences which occur.

TABLE 1

CHEMICAL SHIFTS (ppm) AND COUPLING CONSTANTS IN THE COMPOUNDS $(CH_3)_{4-n}Sn(NR_2)_n$

$(CH_3)_{4-n}Sn(NR_2)_n$ *n*	1		2		3		4
R	CH_3	C_2H_5	CH_3	C_2H_5	CH_3	C_2H_5	CH_3
$\delta(^1H)$ of CH_3–Sn	+ 0.05	+ 0.11	+ 0.10	+ 0.17	+ 0.12	+ 0.25	
δ(1H) of CH_3–N	+2.70		+ 2.75		+ 2.76		+ 2.77
$\delta(^1H)$ of CH_3–CH_2–N		+ 2.92		+ 2.98		+ 2.98	
$\delta(^1H)$ of CH_3–CH_2–N		+ 0.97		+ 1.04		+ 1.02	
$\delta(^{119}Sn)$	+75	+60	+58.8	+45	−15.1	−24	−118
$J(^{117}Sn–C–H)$	53	52.9	58.2	57	65.6	65	
$J(^{119}Sn–C–H)$	55.3	55.2	61	59.4	68.7	68	
$J(^{117}Sn–N–C–H)$	42	44	43	45	43.9	47	51
$J(^{119}Sn–N–C–H)$					45.6		53
$J(^1H–^1H)$		7		7		7	

TABLE 2

THE EFFECT OF CONCENTRATION ON THE NMR PARAMETERS OF $(CH_3)_3SnN(CH_3)_2$ IN BENZENE

	Percentage of $(CH_3)_3SnN(CH_3)_2$ *in benzene*		
	80	40	10
$\delta(^1H)$ of CH_3–Sn (Hz)	5	6	8
$\delta(^1H)$ of CH_3–N (Hz)	231	237	244
$\delta(^{119}Sn)$ ppm	+74.7	+75	+75.5
$J(^{117}Sn–C–H)$	53	53	53
$J(^{119}Sn–C–H)$	55.3	55.3	55.3
$J(^{117,119}Sn–N–C–H)$	—	—	42

Chemical shifts

^{1}H chemical shifts

The proton resonances of both the Sn–CH_3 and $N(CH_3)_2$ protons move to lower field as *n* increases. This can be readily explained in terms of the increased amount of *s* character and the corresponding increase in the electronegativity of the Sn→CH_3 and Sn→$N(CH_3)_2$ orbitals as may also be inferred from the increase in the ^{117,119}Sn–C–H and ^{117,119}Sn–N–C–H coupling constants. The regularity of this decreasing trend is not as well established for $N(C_2H_5)_2$ protons as for $N(CH_3)_2$ protons.

The shielding of the Sn–CH_3 protons decreases on replacing R=CH_3 by R=C_2H_5 in the NR_2 group. This may be due to a diamagnetic anisotropy of the C–C bond in the C_2H_5 group which gives rise to a deshielding effect for the distant Sn–CH_3 protons. In addition, a greater van der Waals interaction involving the bulkier C_2H_5 group may contribute to this effect.

^{119}Sn chemical shifts

From a comparison of the ^{119}Sn chemical shifts in $N(CH_3)_2$ substituted aminostannes relative to the corresponding $N(C_2H_5)_2$ substituted compounds, it may be seen that the ^{119}Sn chemical shifts decreases in going from $N(CH_3)_2$ to $N(C_2H_5)_2$. Since ^{119}Sn chemical shifts are apparently dependent upon the relative electronegativity or electron-withdrawing capacity of X substituents derived from the same Group in the Periodic Table [6,8], the above observation may be easily explained on the basis of the greater electron-releasing ability of the ethyl group. Thus on the Taft scale $\sigma^*(C_2H_5) = -0.100$ while $\sigma^*(CH_3) = 0$[9].

A more detailed discussion of the influence of NR_2 substitution on ^{119}Sn chemical shifts, together with a comparison with other X substituents and with the influence of similar substituent effects on ^{13}C chemical shifts, is made in the following paragraphs.

Monosubstitution and electronegativity

In carbon chemistry a linear dependence of the ^{13}C chemical shifts on electronegativity is observed in CH_3X compounds[10] when X=CH_3, NO_2, OH and F. The ^{13}C chemical shifts in $CH_3X(R)$ compounds are known to be rather insensitive to the nature of the substituent R attached to the X atom when X=O, N. For this reason, it is possible to compare the data for CH_3NO_2 with those obtained for dimethylaminostannanes.

A similar correlation to that mentioned above is found in stannanes if one CH_3 group in $Sn(CH_3)_4$ is replaced by $N(CH_3)_2$ and OCH_3 (substitution of fluorine into the molecule leads to the formation of virtually insoluble polymeric $(CH_3)_3SnF$). To compare the electron-withdrawing capacity of a nitrogen-containing group substituted on carbon and tin, the two correlation lines obtained are presented together in Fig. 2 where the ^{13}C and ^{119}Sn chemical shifts of CH_4 and $Sn(CH_3)_4$ respectively are taken as the common origin of the graph. From this figure it may be seen that substitution of an NR_2 group on Sn leads to a much greater shift to lower field relative to the ^{119}Sn resonance than does substitution of an NO_2 group in CH_4 relative to the ^{13}C resonance. This indicates that it is not necessary to invoke extra shielding of the Sn atom, *e.g.* originating from a possible N→Sn *pπ–dπ* back-donation. If such back-donation does occur it will be completely obscured by the inductive electron-

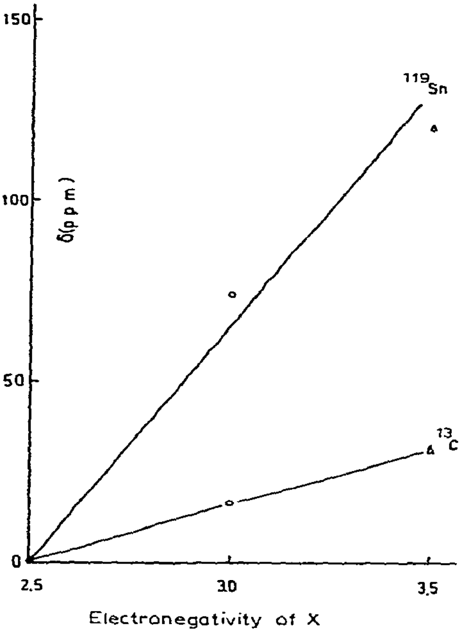


Fig. 2. Variation of ^{13}C and ^{119}Sn NMR chemical shifts with the electronegativity of X for CH_3X and $(CH_3)_3SnX$, respectively. ●: $X=CH_3$; ○: $X=N(CH_3)_2$ and ▲, $X=OCH_3$.

withdrawing capacity of the nitrogen atom. The same conclusions are valid for OCH_3 substitution.

Increased substitution

Increasing NR_2 substitution (increasing n) leads to a corresponding upfield shift of the ^{119}Sn resonances. A similar trend is observed for the ^{119}Sn chemical shifts in methyltin halides[6]. The chemical shifts observed in going from $n=1$ to $n=3$ are however less in the $(CH_3)_{4-n}Sn(NR_2)_n$ compounds than in the methyltin halides. In the latter compounds, an increase in the ^{119}Sn chemical shift increments is observed in the sequence I > Br > Cl. The simplest explanation of this increasing upfield shift is that there is a progressive increase in the nitrogen lone-pair back-donation into the empty *d* orbitals of Sn. However it has been argued that in the case of the methyltin halides[11] the most likely explanation of the upfield trend of the ^{119}Sn chemical shifts is the increasing dominance of σ^E and σ^{anis} effects. In our opinion, this latter explanation most probably applies to $(CH_3)_{4-n}Sn(NR_2)_n$ compounds also, the increasing increments in the ^{119}Sn chemical shift in the sequence I > Br > Cl > $N(CH_3)_2$ on increasing substitution being attributable to a large extent on an increase in the sum $\sigma^E+\sigma^{anis}$ during this sequence.

Coupling constants

^{117,119}Sn–C–H coupling constants (^2J)

The ^{117,119}Sn–C–H coupling constants of the compounds $(CH_3)_{4-n}Sn(NR_2)_n$ show an expected increase upon the introduction of more NR_2 substituents. The increasing +I effects of the C_2H_5 group relative to CH_3, already mentioned in the discussion of the ^{119}Sn chemical shift, is also involved in the observed trend for ^2J values since lower values are observed for $R=C_2H_5$ than for $R=CH_3$. When a comparison is made of ^2J values for $(CH_3)_3SnX$ ($X=N(CH_3)_2$, Cl, Br, I)[6], the somewhat surprising result is obtained that although nitrogen is the more electronegative substituent the value of ^2J for the methylaminostannane is the lowest. In addition it is found that the increase of ^2J with increasing values of n is much lower in the aminostannanes than in the corresponding halides.

These observations obviously cannot be explained solely on the basis of electronegativity. On the other hand, the assumption that a significant back-donation contribution in the Sn–N bond explains the low coupling constants is not justified because of the following reasons.

In a previous study of $(CH_3)_{4-n}MX_n$ compounds where M = Sn, Si and X = Cl, Br, I[11], the occurrence of strong intramolecular van der Waals forces giving rise to through-space halogen-orbital interactions involving mainly the C–H but also to a certain extent the M–C orbitals was established. It was proposed that this phenomenon together with possible contributions of hyperconjugation effects would lead to a slight increase in the $\widehat{HCH}$ angle and to a lesser extent in the $\widehat{CMC}$ intervalence and interorbital angles. Thus the amount of s character in the C→H and M→C orbitals would increase together with the values of the corresponding coupling constants.

On this basis, it may be argued that the reduction in the ^{117,119}Sn–C–H coupling constants in the compounds $(CH_3)_{4-n}Sn\{N(CH_3)_2\}_n$ relative to those for the methyltin halides arises from a decrease in the van der Waals interaction of the nitrogen atom (which is less bulky than the halogen atoms) with the C–H and Sn–C orbitals of the CH_3–Sn moiety.

This view is strongly supported by the fact that in monosubstituted methanes a similar decrease in the ^{13}C–H coupling constants is observed in the presence of similar X substituents. Indeed, the ^{13}C–H coupling constants in CH_3NH_2 and $CH_3N(CH_3)_2$, *i.e.* 133 and 131 Hz respectively, are considerably lower than the ^{13}C–H coupling constants in alkyl halides which lie between 149 and 152 Hz.

The smaller difference between the ^2J values for $(CH_3)_3SnN(CH_3)_2$ (^2J 55.3 Hz) and for a trimethyltin halide (^2J 57.2–58.8 Hz) in comparison with the difference observed between the $J(^{13}C\text{–}H)$ values in CH_3NH_2 and an alkyl halide respectively may be attributed to the increasing influence of electronegativity on the highly polarisable Sn atom together with the decreasing influence of van der Waals interaction around this bulky metal atom.

^{117,119}Sn–N–C–R coupling constants (^3J)

As mentioned above in the introduction, no ^{117,119}Sn–N–C–H couplings were observed in previous ^{1}H NMR investigations of $(CH_3)_{4-n}Sn[N(CH_3)_2]_n$ compounds.

The ^{1}H NMR data reported here, which were obtained by measurements on benzene solutions, reveal that detection of these satellite lines in some solutions of these compounds is dependent on a concentration effect which influences the line shape of the $N(CH_3)_2$ proton signals. This effect is illustrated in Fig. 3 (a) and (b). In an 80% solution, a very broad resonance signal corresponding to the $N(CH_3)_2$ protons is observed in contrast to the sharp resonance line of the $(CH_3)_3Sn$ protons (Fig. 3(a)). Under these conditions, no ^{117,119}Sn–N–C–H satellite lines may be detected but

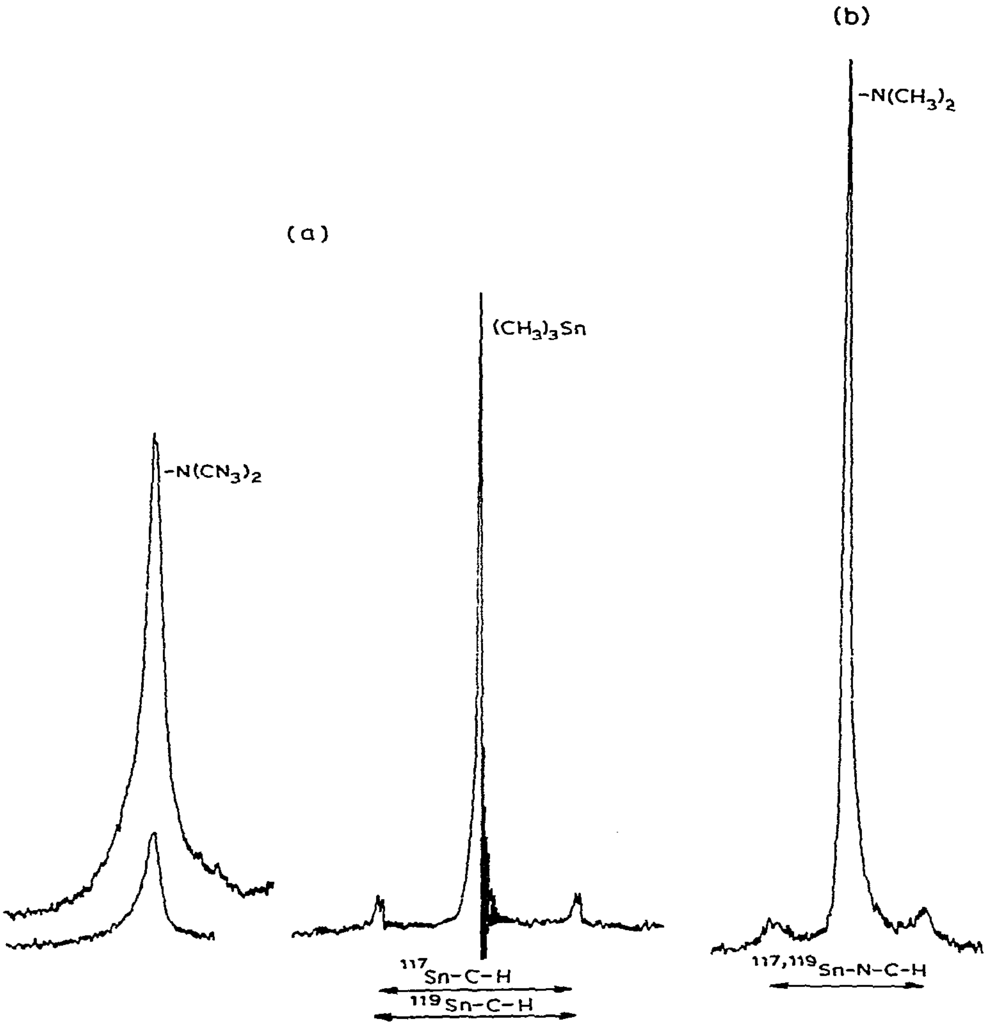


Fig. 3. ^1H NMR spectrum of $(CH_3)_3SnN(CH_3)_2$ in benzene solution (a) 80% (v/v): (b) 10% (v/v).

$^{117,119}Sn-C-H$ coupling may however be readily observed around the sharp $(CH_3)_3$-Sn proton resonance line. In more dilute solutions, the $N(CH_3)_2$ ^1H resonance is narrowed and at the same time in 10% solutions the $^{117,119}Sn-N-C-H$ satellites become visible (Fig. 3(b)). However, even under these conditions the signal remains rather broad and the $^{117}Sn/^{119}Sn$ satellites remain unresolved. Similar observations were made for the $(CH_3)_2Sn[N(CH_3)_2]_2$ compound. In contrast, solutions of CH_3Sn-$[N(CH_3)_2]_3$ and $Sn[N(CH_3)_2]_4$ exhibit sharp ^1H signals and well-resolved $^{117,119}Sn$-$-C-H$ satellite lines possessing the characteristic doublet structure even in concentrated solution (Fig. 4). Identification of the observed satellite lines was achieved by recording the ^{119}Sn INDOR spectrum of the compound using the satellite line ascribed to the $^{119}Sn-N-C-H$ coupling.

From these observations it follows that only increased line broadening of signals

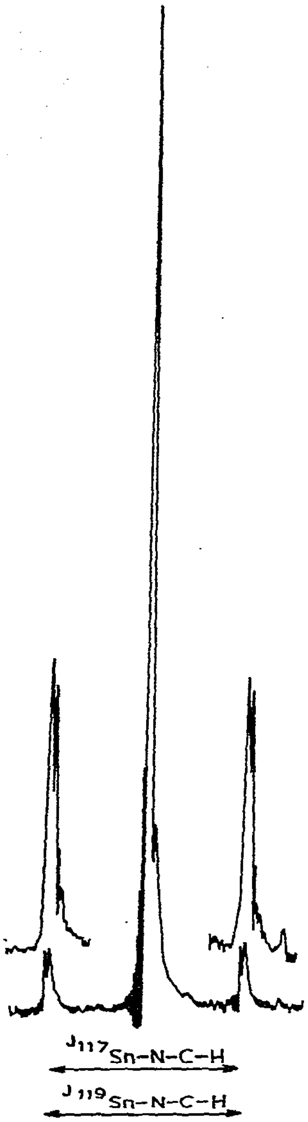
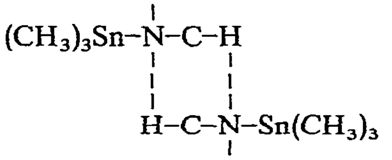


Fig. 4. ^{1}H NMR spectrum of $Sn[N(CH_3)_2]_4$.

corresponding to the $N(CH_3)_2$ protons in more concentrated solutions prevented the detection of ^{117,119}Sn–N–C–H satellites in some of the compounds studied, these satellites being readily observed in dilute solutions. Hence the suggestion that a rapid exchange of amine groups occurs in these compounds is difficult to sustain.

Previous investigators[3] have also suggested that the rate of exchange should increase with an increasing number of NR_2 substituents. Even if a slow rate of exchange were assumed for methylaminostannanes, this conclusion would be untenable for the ^{117,119}Sn–N–C–H satellite lines are more readily detected in $Sn[N(CH_3)_2]_4$ relative to $(CH_3)_3SnN(CH_3)_2$.

The very broad ^1H resonance line of the $N(CH_3)_2$ protons in $(CH_3)_3SnN(CH_3)_2$ and $(CH_3)_2Sn[N(CH_3)_2]_2$ may in fact be attributed to the presence of significant intermolecular association involving hydrogen bridges which occurs in concentrated solutions:



In such an arrangement, the $N(CH_3)_2$ protons can undergo a quadrupole relaxation effect with the nitrogen atom which leads to a corresponding broadening of the ^1H resonance signal. In more dilute solutions, the extent of association and N—H interaction become less and this leads to a sharpening of the ^1H signal.

The proposed structural behaviour implies the absence of intermolecular association via Sn–N···Sn bridges and this in turn explains the very small variation of the ^{119}Sn chemical shifts on dilution (Table 2). It also suggests that nitrogen lone-pair back-donation to Sn should not be significant, in agreement with conclusions derived from other NMR parameters as discussed in the foregoing sections.

Finally, it is necessary to consider the general trend in the values of the $^{117,119}Sn–N–C–H$ (^3J) coupling constants upon increasing NR_2 substitution and upon altering the nature of the alkyl group R. From the data recorded in Table 1, it follows that increasing NR_2 substitution leads to an increase in ^3J values, the values for $R=CH_3$ being slightly less than those for $R=C_2H_5$. This implies that as the extent of NR_2 substitution increases this leads not only to an increasing amount of s character in the $Sn \rightarrow CH_3$ orbital but also an increase is the percentage s character of the $Sn \rightarrow NR_2$ orbital, the increase in s character being a function of the nature of the group R, following the sequence $CH_3 < C_2H_5$. This is accompanied by a greater increase in the percentage s character of the $Sn \rightarrow CH_3$ orbital in the reverse sequence $CH_3 > C_2H_5$.

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