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A STUDY OF THE CHEMICAL BOND IN $(CH_3)_nSn(SCH_3)_{4-n}$ (n=0, 1, 2, 3) BY NMR (^1H, ^{119}Sn, ^{13}C) SPECTROSCOPY

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SUMMARY

The ^{119}Sn and ^{13}C NMR spectra of $(CH_3)_nSn(SCH_3)_{4-n}$ (n=0, 1, 2, 3) compounds are presented. From the observed chemical shifts and by comparison with other groups of compounds, inductive and magnetic anisotropy effects seem to govern the shifts of the nuclei studied.

I. INTRODUCTION

In a previous report[1] the chemical bond in methyl(methylthio)stannanes, $(CH_3)_nSn(SCH_3)_{4-n}$ (n = 1, 2, 3) was studied by means of the PMR spectra of these compounds.

Now further information is presented about the variation of the electron density around the different nuclei from the ^{119}Sn and ^{13}C chemical shifts obtained by ^1H–^{119}Sn and ^1H–^{13}C double resonance experiments procuring high-resolution INDOR* spectra.

II. EXPERIMENTAL

(1) *Synthesis of compounds*

The compounds $(CH_3)_nSn(SCH_3)_{4-n}$ (n = 1, 2, 3), were obtained from aqueous solutions of the corresponding organotin chloride and CH_3SH as described by Abel and Brady[2].

Mehrotra *et al.*[3] prepared several tetrakis(alkylthio)stannanes $Sn(SR)_4$ ($R = C_2H_5$, n-C_3H_7, i-C_3H_7, n-C_4H_9):

$$SnCl_4 + 4\,RSH + 4\,NH_3 \xrightarrow{\text{Benzene}} Sn(SR)_4 + NH_4Cl\downarrow$$

In this way it was possible to prepare tetrakis(methylthio)stannane, $Sn(SCH_3)_4$, in a yield of 60%.

An excess of CH_3SH was bubbled through the benzene solution of $SnCl_4$ cooled to 0°, in order to obtain maximum resorption of the gas. Then, NH_3 gas was

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* INDOR = internuclear double resonance.

introduced into the solution resulting in an exothermic reaction with the formation of NH_4Cl. After the reaction mixture had cooled to room temperature, the addition of NH_3 gas was stopped and the NH_4Cl removed by filtration. The solvent was then evaporated until precipitation occurred and the precipitate was filtered off. The precipitated $Sn(SCH_3)_4$ was further purified by recrystallisation from petroleum ether. The purity was checked by melting point (34.6°), and the identity by mass and NMR spectrum. From the mass spectrum, a monomeric structure was established.

On complete evaporation of benzene from the solution another white compound was isolated which was insoluble in organic solvents and H_2O and decomposed above 150°. The IR spectrum of this compound shows broad absorption bands at 310, 555, 1415 and 3200 cm^{-1}. The 310 cm^{-1} band can be attributed to a Sn–S–Sn vibration. The remaining absorptions are situated in the region of $\rho(CH_3)$, $\delta(CH_3)$ and $\nu(CH_3)$ vibrations. Most probably this compound is a dimeric or polymeric species e.g. $[Sn(SCH_3)_4]S$. The analogeous Si derivative $\{Si(SCH_3)_4\}S$ is known[4]; it is formed by the reaction of $Si(SCH_3)_4$ with S.

2. *Spectra*

The NMR spectra were recorded in frequency-sweep mode with a Bruker-Physik HFX4 instrument operating at a proton frequency of 90 MHz. The ^{119}Sn and ^{13}C resonance frequencies were measured by recording the ^{119}Sn and ^{13}C INDOR spectra sweeping with either the ^{119}Sn or the ^{13}C frequency at a level H_2 [$\nu^0(^{119}Sn)$ 33.54 MHz, $\nu^0(^{13}C)$ 22.62 MHz] while the observing r.f. field (H_1) was set on a ^{119}Sn or ^{13}C satellite line.

These satellite lines were brought to maximum intensity avoiding saturation by properly adjusting the power level H_1 while the level of H_2 was set to obtain a maximum value of the signal-to-noise ratio and an optimum resolution of separated lines in the INDOR spectrum. The frequency differences between the observed lines and the lock signal of benzene were followed with the inner frequency counter of the NMR instrument. By means of an external counter-timer (Monsanto Model 1500 A) we also measured the frequency values of the ^{119}Sn and ^{13}C resonance frequencies. The extreme values of the ^{119}Sn resonance frequencies for the methyl methylthio stannanes were found in $(CH_3)_3SnSCH_3$ and $CH_3Sn(SCH_3)_3$, resp. 33.560418 and 33.562995 MHz. For the ^{13}C chemical shifts the lowest value was observed in $Sn(CH_3)_4$, *i.e.* 22.630198 and the highest in $Sn(SCH_3)_4$ *i.e.* 22.630562 MHz. The ^1H resonance of the lock signal, benzene, occurred at 89.999765 MHz.

The spectra of all the compounds were investigated as 3–20% solutions in C_6H_6 or $CHCl_3$ and in 5 mm probes. For recording the ^{119}Sn INDOR spectra either a ^{119}Sn–C–H or ^{119}Sn–S–C–H satellite line could be used. In both cases a well resolved INDOR spectrum was obtained allowing practically the complete theoretical multiplicity to be observed taking into account the number of the protons in the surrounding CH_3 and SCH_3 groups and the different spacings $J(^{119}Sn\text{–C–H})$, and $J(^{119}Sn\text{–S–C–H})$. An example of the theoretical and observed spectrum of a compound studied is presented in Fig. 1. The ^{13}C INDOR spectra of the CH_3 and SCH_3 groups in either compound shows the expected 1/3/3/1 quadruplet but the obtained resolution was not as good as in the case of the ^{119}Sn INDOR spectra.

The ^{119}Sn spectra of the methyltin halides mentioned in this report were measured in order to compare the variation of the ^{119}Sn chemical shift in the series,

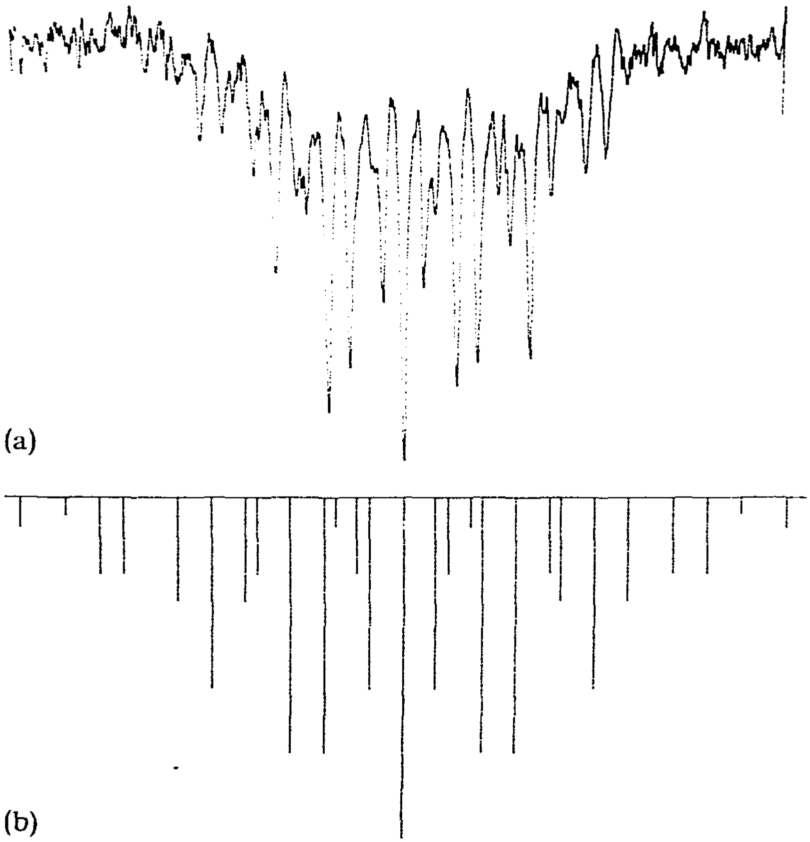

Fig. 1. (a). Experimental ^{119}Sn INDOR spectrum of $(CH_3)_2Sn(SCH_3)_2$. (b). Most intense lines of the theoretical spectrum.

$(CH_3)_nSnX_{4-n}$ ($n = 1, 2, 3$) caused by various substituents ($X = Cl, Br, I, SCH_3$) and the effect of increasing n.

In the course of this investigation, the ^{119}Sn chemical shifts of some methyltin-halides have been published by Davies *et al.*[5]; These are mentioned in Table 2 (in parentheses). The difference between both sets of values most probably are to be ascribed to concentration effects. Indeed, we find that twofold dilution could cause downfield shifts up to 3 ppm. In the light of some of our results[6] on the concentration effect on the ^{119}Sn chemical shifts of molecules showing association in solution, the downfield shifts on dilution could be ascribed to partial association of the methyltin halide molecules in the more concentrated solutions.

For the methylthio tin compounds, however, only shifts of ca. 0.13 ppm were observed at the same dilution. Moreover the different solvent effects of $CHCl_3$ and C_6H_6 could cause shifts up to 4 ppm. On the other hand it should be noted that the ^{119}Sn INDOR spectra of the $(CH_3)_2SnX_2$ and CH_3SnX_3 compounds could only be observed as very broad bands. For the trimethyltin halides the best resolved INDOR spectrum was obtained for $(CH_3)_3SnI$ showing however only six relatively broad lines out of the expected multiplicity.

An increased broadening is observed for $(CH_3)_3SnBr$ while in the spectrum of $(CH_3)_3SnCl$ the lines collapse to a great extent. No absorption could be found for the CH_3SnI_3 compound. Most probably the shift exceeds the sweep width of the instrument. Indeed if we take into account the sequence of the chemical shifts for other organotin halides a value can be expected at about ±600 ppm in Sn units (Fig. 2) and the maximum range of our instrument is 597 ppm for ^{119}Sn.

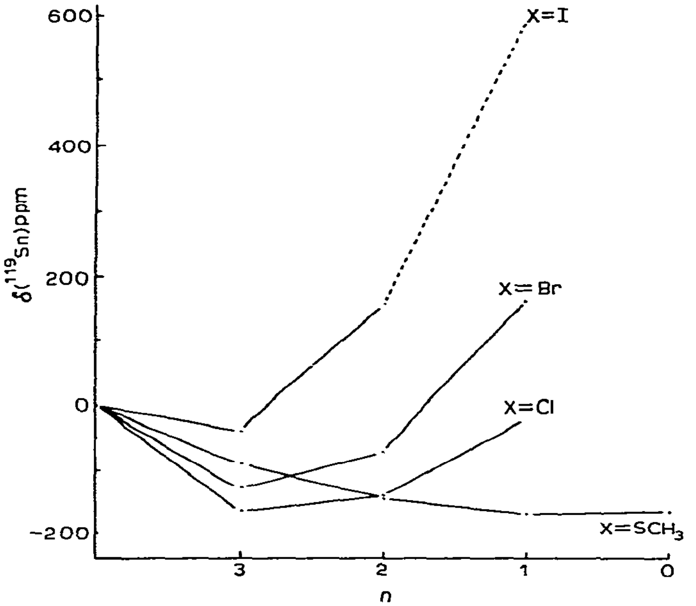

Fig. 2. ^{119}Sn chemical shifts in the series $(CH_3)_nSnX_{4-n}$ ($n=1, 2, 3, 4$) for X = Cl, Br, I and $(CH_3)_nSnX_{4-n}$ ($n=0, 1, 2, 3, 4$) for $X=SCH_3$.

The results of the ^{119}Sn and ^{13}C chemical shifts are summarised in Tables 1 and 2, and graphically represented in Fig. 2. In Table 1, the ^1H chemical shifts are also included in order to have a complete picture of the screening of the different nuclei. In Table 2, the ^{119}Sn chemical shifts (in parentheses) of the SnX_4 (X = Cl, Br, I) compounds are taken from ref. 12.

TABLE 1

^1H, ^{119}Sn AND ^{13}C CHEMICAL SHIFTS IN THE SERIES $(CH_3)_nSn(SCH_3)_{4-n}$ ($n=0, 1, 2, 3$)

Compound	$\tau(CH_3)$	$\tau(SCH_3)$	$\delta(^{119}Sn)$ (ppm)	$\delta(^{13}C)$ of CH_3 (ppm)	$\delta(^{13}C)$ of SCH_3 (ppm)
$(CH_3)_4Sn$	9.96		0	0	
$(CH_3)_3SnSCH_3$	9.65	7.99	−90	−3.9	−18.7
$(CH_3)_2Sn(SCH_3)_2$	9.35	7.87	−144	−6.7	−19.0
$CH_3Sn(SCH_3)_3$	9.06	7.75	−167	−10.3	−20.0
$Sn(SCH_3)_4$		7.66	−165		−20.0

TABLE 2

^{119}Sn CHEMICAL SHIFTS *vs.* $Sn(CH_3)_4$ IN $(CH_3)_nSnX_{4-n}$ ($n=0, 1, 2, 3$; X=Cl, Br, I)

Compound	δ(^{119}Sn) (ppm)					
	X=Cl		X=Br		X=I	
$(CH_3)_3SnX$	−164.2	(−166)	−128	(−128)	− 38.6	
$(CH_3)_2SnX_2$	−140	(−137)	− 70		+159	
CH_3SnX_3	− 21	(− 19)	+165	(+170)	+600?	(extr.)
SnX_4	(+150)		(+638)		(+1701)	

III. RESULTS AND DISCUSSION

(1) *^{119}Sn resonance data.* From the graphical presentation of the data in Fig. 2 a common trend is observed for the chemical shift values in methyltin halides. For the thiomethylmethylstannanes however there results a different pattern; starting from $Sn(CH_3)_4$ a nearly monotonous decrease of the ^{119}Sn resonance is seen and only for $Sn(SCH_3)_4$ is there a very slight upfield shift.

The sequence observed for the ^{119}Sn chemical shift in the trimethyltin halides with X = Cl, Br, I and the low-field position of these ^{119}Sn resonances parallel the trend to be expected due to the inductive effect of the electronegative substituents. $(CH_3)_3$-$SnSCH_3$ seems to follow more or less this general trend. In order to explain the upfield shifts from $(CH_3)_3SnX$ to CH_3SnX_3 (X=Cl, Br, I) one might suppose, in agreement with a proposal made by Davies *et al.*[5] that the observed high field shift could be caused by a back-donation of the halogen *p*-lone pair electrons into an empty 5*d* orbital of Sn having π-symmetry, resulting in a $(p\rightarrow d)\pi$ overlap between these two orbitals. On the other hand Ebsworth[13] has forwarded the argument that any $(p\rightarrow d)\pi$ bonding will influence the *d* orbitals of the central atom and might cause an increase in the energy of the *d* orbitals, thereby decreasing the contribution of the paramagnetic term to the shielding and subsequently contributing to the observed high-field shift.

In this case $(p\rightarrow d)\pi$ bonding in the methyltin halides should not decrease but remain constant or even increase with each additional chlorine atom, and this should, in the view of the whole series here presented, increase in the sequence: Cl→Br→I.

In this respect it is noteworthy that for Si compounds where the π bonding ability in certain Si–X bonds has been more clearly established, π bonding contribution from chlorine to silicon in $(CH_3)_2SiCl_2$ is estimated to be insufficient to exceed the inductive effect and that in alkyl alkoxy silanes for which the presence of $(p\rightarrow d)\pi$ bonding has been fully demonstrated the maximum observed shielding *i.e.* for $Si(OC_2H_5)_4$ has a value of +59 ppm[10].

In general the ability of $(p\rightarrow d)\pi$ bonding should be determined by an optimum geometrical arrangement of the two contributing orbitals.

In the studies of Craig and Zauli[11] it has been established that the *d* orbitals which are diffused in the atomic state must be contracted to a greater extent to take part in a σ bond and also to some extent for taking part in π bonding. This however, depends on the quantum number *n* of the *d* orbitals of the central metal, the electronegativity of the substituent and the quantum number *n'* of the atomic orbitals containing the lone pair of electrons. As yet the influence of these different factors on the $(p \rightarrow d)\pi$ bonding ability is not clear. On the other hand the paramagnetic term certainly contributes to the shielding for the heavier elements such as the tin atom.

Calculations however, of its contribution as a function of the amount of *d* oribtal participation in π bonding and the atomic number of the metal have not been reported.

Furthermore, if the *d* orbitals are sufficiently contracted by the influence of electronegative substituents and so can be mixed with the bonding *s* and *p* orbitals to form additional σ bonds, they also could be used to form the σ bonds of the parent compound. So the bonds of tetrahedral molecules of heavy metals substituted by sufficient electronegative substituents apparently can have a considerable *d* character. This is another factor which may influence the shielding of the central metal.

In view of these arguments we believe that more experimental data and quantum-mechanical considerations are necessary to draw more specific conclusions about the ^{119}Sn chemical shifts of the methyltin halides.

Considering, however, the trend of the ^{119}Sn chemical shift of the compounds $(CH_3)_nSn(SCH_3)_{4-n}$ ($n=2, 3, 4$) an entirely different pattern is found. Therefore the explanations tentatively given for the upfield shifts in the methyltin halides need some reconsideration in the case of the thiomethyl derivatives.

An explanation could be found in the assumption that on further introduction of SCH_3 substituents both the inductive effect and the $(p \rightarrow d)\pi$ bonding effect "per SCH_3 group" decrease; the decrease, however, of the $(p \rightarrow d)\pi$ bonding effect exceeding the decrease of the inductive effect.

Only for $Sn(SCH_3)_4$ could the total π bonding effect be slightly more important than the total inductive effect, when the data of this compound are compared with those of $CH_3Sn(SCH_3)_3$.

(2) *^{1}H and ^{13}C shifts in methylthio compounds.* Let us now consider the ^{1}H and ^{13}C chemical shifts of the CH_3 groups attached to tin in the same series of compounds. Should these shifts be determined by the same parameters as those governing the electron density on the Sn atom, a trend analogous to that for the ^{119}Sn chemical shifts would be expected. However a continuously increasing downfield shift versus $Sn(CH_3)_4$ is observed with increasing SCH_3 substitution. So it seems that electron withdrawal or donation by the neighbouring atom(s) does not play the most important role in the shielding or deshielding of the nuclei in the CH_3 groups. Obviously a diamagnetic anisotropy contribution[7,8] of the Sn–S bond and/or dispersion effects[9] of the SCH_3 substituents determine also to a greater extent the observed trend for ^{13}C and ^{1}H chemical shifts of the CH_3 group.

For the chemical shifts of the ^{13}C and ^{1}H nuclei in the SCH_3 group we first note the influence of the inductive effect of the sulfur atom shifting the ^{13}C and ^{1}H resonances to a lower field than that observed for these resonances in the CH_3 group. Moreover there is also but a slight downfield shift with increasing SCH_3 substitution. This is not what would be expected from the observed ^{119}Sn resonances. Indeed, in view of the downfield shift of the ^{119}Sn resonance an increase in the electron density on the S atom of the SCH_3 group(s) should be expected in going from $(CH_3)_2Sn(SCH_3)_2$ to $CH_3Sn(SCH_3)_3$, which would have yielded a high field shift of the ^{13}C and ^{1}H resonances. In $Sn(SCH_3)_4$ these resonances should practically equal those in

$CH_3Sn(SCH_3)_3$. The trends shown in the graph therefore reveal that the electron withdrawing capacity of the SCH_3 group(s) does not play the most important role in the variation of the chemical shifts of the ^{13}C and ^1H nuclei in the SCH_3 group(s).

Apparently a weak contribution to the deshielding of these nuclei can originate from the increasing electronegativity of the tin atom by the increasing number of SCH_3 groups. However, since the angular position of the ^{13}C and ^1H nuclei of the SCH_3 group with respect to the Sn–S bond is nearly the same as that of the ^{13}C and ^1H nuclei of the CH_3 groups, also a deshielding effect arising from a diamagnetic anisotropy of the Sn–S bond must be taken into account.

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