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FOURIER TRANSFORM NMR INVESTIGATIONS OF ^{13}C LABELED SILYL AND STANNYL ACETYLENES

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Summary

The ^{13}C NMR spectra of ^{13}C labeled mono- and di-substituted silyl- and stannyl-acetylenes have been studied. It was found that the values of $^1J(CC)$ coupling constants between acetylenic carbons decrease very sharply in the series $Alk_3SiC{\equiv}CH$, $Alk_3SnC{\equiv}CH$, $Alk_3SiC{\equiv}CSiAlk_3$ and $Alk_3SnC{\equiv}CSnAlk_3$. These results and the observed changes in the geminal hetero-atom —β-acetylenic carbon couplings suggest a very strong p_π—d_π interaction between the π-electrons of the triple bond and the vacant d orbitals of silicon and tin.

Introduction

The character of the bonding between carbon and the Group IV elements, and the electron distribution changes in an organic molecule upon substitution with silicon or tin containing groups are the subjects of a rapidly growing number of investigations [1] and theoretical calculations [2]. For the investigation of the metal—carbon interactions in acetylenic compounds various techniques have been used, in particular electron diffraction [3,4] and IR [5], UV [6] and NMR [7—10] spectroscopy. The NMR studies have been limited to the investigation of the chemical shifts and/or carbon—proton and carbon—metal spin—spin couplings, and no data on ^{13}C—^{13}C coupling constants have been reported.

To provide information on the electron distribution in the silicon and tin derivatives of acetylene, Fourier transform NMR studies have been carried out in ^{13}C enriched mono- and bis-(triethylsilyl)acetylenes and their tributylstannyl analogues. The results presented below show that there is a very strong delocalization of the π electrons of the triple bond towards the silicon or tin atoms. This is manifested by a very large decrease in the ^{13}C—^{13}C coupling between the

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carbon atoms of the triple bond when the acetylenic hydrogens are replaced by an Alk_3M substituent. The most striking is the case of bis(tributylstannyl)-acetylene, where the value of $^1J(CC)$ viz. 80 Hz falls in the range typical of coupling across a double bond.

Results

Mono- and bis-(triethylsilyl)acetylenes and their tributylstannyl analogues labeled in the acetylenic fragment with carbon-13 have been synthesized, and their FT-NMR spectra measured and analysed. The results are presented in Tables 1 and 2 and Fig. 1 and 2.

In all the syntheses, acetylene-$^{13}C_2$-1,2 of 90% isotopic enrichment was used as the starting material. Consequently, the samples studied consisted of 81% of $^{13}C_2$-labeled acetylenes and ~18% of monolabeled ones. The amount of non-labeled compound was 1%.

The interpretation of the spectra of triethylsilylacetylene-$^{13}C_2$-1,2 (I) and tributylstannylacetylene-$^{13}C_2$-1,2 (II) presented no problems. The acetylenic fragments of these compounds represent an AB system, and the $^1J(CC)$ coupling through the triple bond can be derived directly from the spectrum (Fig. 1) without further calculations. The chemical shifts of the α(C2) and β(C1) acetylenic carbons can also be easily determined for this system, and the values are confirmed by the positions of the strong singlets belonging to the monolabeled compounds $Alk_3M\overset{*}{C}{\equiv}CH$ and $Alk_3MC{\equiv}\overset{*}{C}H$ (9% of each in the isotopic mixture). M—^{13}C spin—spin couplings were observed as ^{29}Si, ^{117}Sn and ^{119}Sn satellites in the ^{13}C spectra of the non-labeled compounds. Additionally, in the spectrum

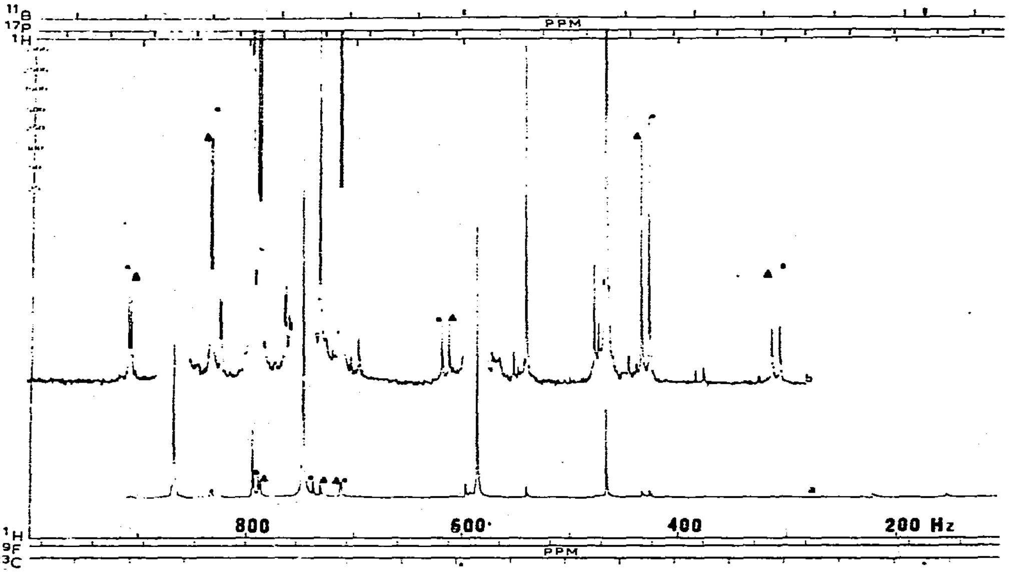

Fig. 1. The $-\overset{*}{C}{\equiv}\overset{*}{C}-$ portion of the ^{13}C NMR spectrum of tributylstannylacetylene-$^{13}C_2$-1,2 (in acetone); (a) 500 TN; (b) 7000 TN; ▲ signals of $^{117}Sn^{13}C{\equiv}^{13}C$ satellite ABX spectrum (AB part); ● signals of $^{119}Sn^{13}C{\equiv}^{13}C$ satellite ABX spectrum (AB part).

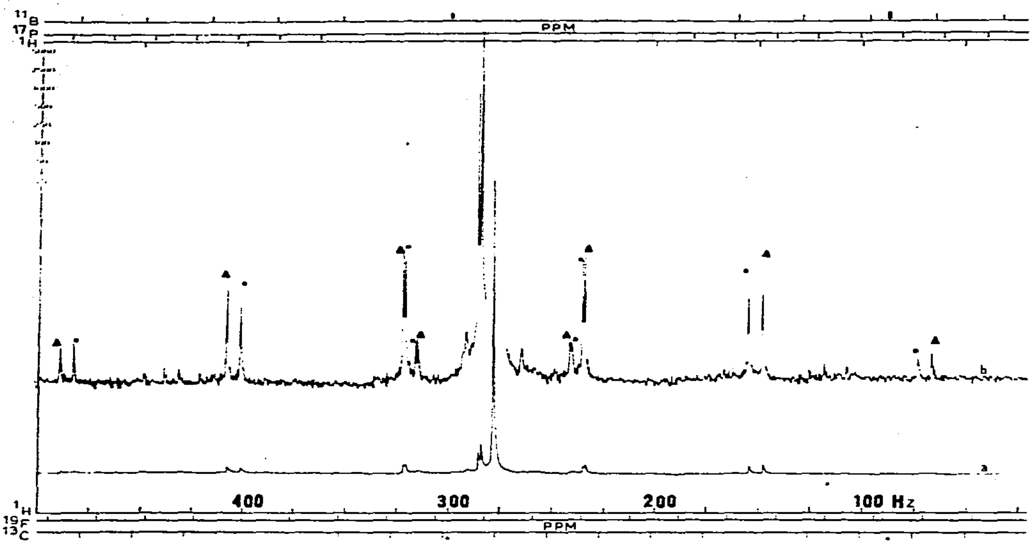

Fig. 2. The $-\overset{\star}{C}\equiv\overset{\star}{C}-$ portion of the ^{13}C NMR spectrum of bis(tributylstannyl)acetylene-$^{13}C_2$-1,2 (in acetone); (a) 500 TN; (b) 7000 TN; ▲ signals of $^{117}Sn^{13}C\equiv^{13}C$ satellite AA′X spectrum (AA′ part); ● signals of $^{119}Sn^{13}C\equiv^{13}C$ satellite AA′X spectrum (AA′ part).

of the tributylstannylacetylene-$^{13}C_2$-1,2 (II) (Fig. 1) two superimposed satellite spectra of the ABX type arising from coupling between two ^{13}C-acetylenic nuclei (AB) and ^{117}Sn or ^{119}Sn atoms (X) have also been observed. The analysis of the AB parts of these spectra again gave ^{1}J(C1C2), ^{1}J(SnC2), and ^{2}J(SnC1) constants. The values were in excellent agreement with those found from the main AB spectrum (^{1}J(C1C2)) and from the satellite spectrum of the non-labeled compound (^{1}J(SnC2) and ^{2}J(SnC1)).

The resonance assignments for acetylenic carbons (C1and C2) were based on the magnitudes of the ^{13}C—M couplings, the larger one-bond coupling being observed for the higher field signal in both I and II.

The situation in the bis(triethylsilyl)- and bis(tributylstannyl)-acetylenes is more complex. Both equivalent ^{13}C acetylenic atoms give only one, very strong signal (Fig. 2). The ^{13}C—^{13}C coupling constant can be found only from a weak satellite spectrum of AA′X type, where AA′ denotes two carbon nuclei in the acetylenic fragment and X is the corresponding hetero atom. In order to find all the lines of the AA′ part including the weakest, a long cumulation time (7600 TN for III and 7000 TN for IV) had to be used. The analysis of these spectra gave the ^{1}J(C1C2) and both ^{1}J(MC2) and ^{2}J(MC1) in III and IV (Table 1). No attempt was made to determine the signs of the coupling constants.

Discussion

Perhaps the most important result concerns the magnitude of the ^{13}C—^{13}C spin—spin couplings between the two acetylenic carbons. Even in triethylsilylacetylene (I) the value of the ^{13}C—^{13}C coupling constant is as low as 130.9 Hz (in acetone), and in III (a disubstituted silyl derivative) diminishes to 101.4 Hz,

TABLE 1

COUPLING CONSTANTS IN ^{13}C LABELED SILYL- AND STANNYL-ACETYLENES $\overset{6}{C}—\overset{5}{C}—\overset{4}{C}—\overset{3}{C}—M—\overset{2}{C}\equiv\overset{1}{C}$

Compound	No.	Solvent	^1J(C1C2) (Hz)	^1J(MC2) (Hz)	^2J(MC1) (Hz)	^1J(MC3) (Hz)	^2J(MC4) (Hz)	^3J(MC5) (Hz)
$(CH_3CH_2)_3{}^{29}Si\overset{*}{C}\equiv\overset{*}{C}H$	I	CD_3COCD_3	130.9	75.0	18.6	57.0	*a*	
$(CH_3CH_2CH_2CH_2)_3{}^{119}Sn\overset{*}{C}\equiv\overset{*}{C}H$	IIa	CD_3COCD_3	119.8	327.6	61.5	388.0	24.2	58.8
		C_6D_{12}	122.0	350.0	64.7	*b*	*b*	*b*
$(CH_3CH_2CH_2CH_2)_3{}^{117}Sn\overset{*}{C}\equiv\overset{*}{C}H$	IIb	CD_3COCD_3	119.8	313.1	58.8	370.0	24.2	56.8
		C_6D_{12}	122.0	334.3	64.9	*b*	*b*	*b*
$(CH_3CH_2)_3{}^{29}Si\overset{*}{C}\equiv\overset{*}{C}SiEt_3$	III	CD_3COCD_3	101.4	74.8	11.5	56.0	*a*	
$(CH_3CH_2CH_2CH_2)_3{}^{119}Sn\overset{*}{C}\equiv\overset{*}{C}SnBu_3$	IVa	CD_3COCD_3	81.0	319.6	28.2	*b*	*b*	*b*
		C_6D_{12}	82.1	336.8	28.9	380.0	23.4	55.2
$(CH_3CH_2CH_2CH_2)_3{}^{117}Sn\overset{*}{C}\equiv\overset{*}{C}SnBu_3$	IVb	CD_3COCD_3	81.0	305.4	27.0	*b*	*b*	*b*
		C_6D_{12}	82.1	320.7	32.3	363.2	23.4	53.3
$(CH_3CH_2CH_2CH_2)_4{}^{119}Sn$	*c*					310	25	52

[a] Not observed. [b] Not measured. [c] Ref. 13.

TABLE 2

CARBON-13 CHEMICAL SHIFTS IN ^{13}C-LABELED SILYL- AND STANNYL-ACETYLENES MEASURED IN ACETONE $\overset{6}{C}—\overset{5}{C}—\overset{4}{C}—\overset{3}{C}—M\overset{2}{C}\equiv\overset{1}{C}$

Compound	No.	δ(C1) (ppm)		δ(C2) (ppm)	δ(C3) (ppm)	δ(C4) (ppm)	δ(C5) (ppm)	δ(C6) (ppm)
$(CH_3CH_2)_3Si\overset{*}{C}\equiv\overset{*}{C}H$	I	96.1		86.9	4.7	7.5		
$(CH_3CH_2CH_2CH_2)_3Sn\overset{*}{C}\equiv\overset{*}{C}H$	II	97.4		87.5	11.2	29.2	27.1	13.8
$(CH_3CH_2)_3Si\overset{*}{C}\equiv\overset{*}{C}SiEt_3$	III		112.5		4.9	7.6		
$(CH_3CH_2CH_2CH_2)_3Sn\overset{*}{C}\equiv\overset{*}{C}SnBu_3$	IV		115.4		11.0	29.0	27.2	13.8
$(CH_3CH_2CH_2CH_2)_4Sn$	*a*				9.1	29.6	27.6	13.7
$CH_3CH_2CH_2CH_2C\equiv CH$	*b*	67.4		82.8				
$CH_3CH_2C\equiv CCH_2CH_3$	*b*		79.9 [c]					

[a] Ref. 13. [b] Ref. 11. [c] Chemical shift of C3, C4.

i.e., much below the values previously observed for a coupling through a triple bond (viz. 150—180 Hz [11]). This feature is still more pronounced in stannylacetylenes. The magnitudes of the coupling constants measured under similar conditions (acetone solutions of the same concentration) for tributylstannylacetylene (II) and bis(tributylstannyl)acetylene (IV) are 119.8 and 81.0 Hz, respectively. The latter value is not much higher than the J(CC) coupling constant in ethylene (67.6 Hz). These results can be interpreted in terms of a strong $p_\pi - d_\pi$ interaction, i.e. a very large contribution of the mesomeric form B.

$$\underset{\text{(A)}}{\mathrm{Alk_3M{-}C{\equiv}CH}} \longleftrightarrow \underset{\text{(B)}}{\mathrm{Alk_3\overset{-}{M}{=}C{=}\overset{+}{C}H}}$$

The s character of the carbon atoms in III and IV, calculated from the Frei—Bernstein relationship [12], are 46.3 and 38.3%, respectively. The corresponding values for acetylene and ethylene are 55.1 and 35.1%, respectively.

The one-bond coupling constants ^{29}Si—^{13}C2, ^{119}Sn—^{13}C2 and ^{117}Sn—^{13}C2 * accross a single bond are almost insensitive to the effective increase in the electron density on the hetero atom and the changes in the hybridization of the linked atoms. A comparison of $^1J(^{29}\mathrm{Si}{-}^{13}\mathrm{C2})$ in I and III and $^1J(^{119}\mathrm{Sn}{-}^{13}\mathrm{C2})$ and $^1J(^{117}\mathrm{Sn}{-}^{13}\mathrm{C2})$ in II and IV shows that the attachment of a second Alk$_3$M group to the acetylenic bond has practically no influence on these ^1J values. (Thus $^1J(\mathrm{I})/^1J(\mathrm{III}) = 1.00$, $^1J(\mathrm{IIa})/^1J(\mathrm{IVa})$ and $^1J(\mathrm{IIb})/^1J(\mathrm{IVb}) = 1.02$ in acetone).

In contrast the changes in the spin—spin coupling between the hetero atom and acetylenic carbon β(C1) through two bonds are very large ($^2J(\mathrm{I})/^2J(\mathrm{III}) = 1.6$ and $^2J(\mathrm{II})/^2J(\mathrm{IV})$ in all cases >2). This confirms that the density of π-electrons in the triple bond diminishes drastically upon substitution with Alk$_3$Si and Alk$_3$Sn groups, and indicates that the ^2J(MC) coupling constants, like ^1J(CC), are valuable guides to these changes. The corresponding ^2J(CH) values remain practically constant in the series $(\mathrm{CH_3})_3\mathrm{SiC{\equiv}CH}$, $(\mathrm{C_6H_5})_3\mathrm{SiC{\equiv}CH}$, $(\mathrm{C_2H_5})_3\mathrm{GeC{\equiv}CH}$ and $(\mathrm{C_6H_5})_3\mathrm{SnC{\equiv}CH}$ (41.0—42.5 Hz [8]).

Features of the chemical shifts of the acetylenic carbon atoms are also in a good agreement with conclusions drawn from the ^1J(C1C2) and ^2J(MC1) changes. Monosubstitution of the triple bond with trialkylsilyl and trialkylstannyl groups results in a downfield shift for the α- and β-acetylenic carbons; an especially large shift (>28 ppm) is observed for the β carbon when the resonances in I and II are compared with analogous signals in hexyne-1 (Table 2). Upon introduction of the second Alk$_3$M group, a further shift of acetylenic carbon resonance towards lower field is observed (deshielding of 32.6 and 35.5 ppm in III and IV, respectively, relative to the analogous signal in hexyne-3). A similar deshielding of acetylenic carbons in mono- and di-substituted trimethylsilyldiynes was observed by Hearn [9], and attributed to $p_\pi - d_\pi$ interaction between the carbon—carbon triple bond and the silicon atom.

It should be noted that our conclusions are the opposite of those drawn by

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* Two separate sets of lines arising from the coupling between carbon-13 and tin-119 and -117 isotopes were observed for all but one case. Since the differences between the corresponding coupling constants were quite marked. the values for both $J(^{119}\mathrm{Sn}{-}^{13}\mathrm{C})$ and $J(^{117}\mathrm{Sn}{-}^{13}\mathrm{C})$ are reported and discussed separately.

Mitchell [10] for stannyl acetylenes of the type $Me_3Sn(C{\equiv}CR)_{4-n}$ with varyin n and R. Mitchell's conclusion that $p_\pi - d_\pi$ interaction between tin and the acetylenic bond are not important was based on the substituent chemical shift (SCS) in the R fragment, but Hearn has shown that these electronic influences are only poorly transmitted to more distant nuclei [9].

Finally we comment briefly on the chemical shifts and coupling constants i the alkyl chains of the compounds studied. Assignment of the α and β carbons (C3 and C4) in triethylsilylacetylenes I and III is easy; the higher field signal with a large ^{13}C—^{29}Si coupling constant (57 Hz) arises from the α carbon and that at the lower field from the β carbon. Assignments in the butyl group of stannylacetylenes II and IV follow those made by Mitchell for tetrabutyltin (Table 2). Examination of the results for both of these sets of compounds reve that only the α-carbon (C3) is influenced by the changes in the structure of the molecule, the chemical shifts and coupling constants for carbons β, γ and δ (C4 C5 and C6) being very similar to those in the compound studied by Mitchell (Tables 1 and 2).

It is noteworthy that in both mono- and bis-(tributylstannyl)acetylenes the coupling of the tin nuclei with the $sp^3\alpha$ (C3) carbon in an alkyl chain is larger than that with a neighbouring sp acetylenic carbon; whereas the exactly opposit result would be expected if the Frei—Bernstein correlation of $^1J(CC)$ with the s-character of bonding orbital [12] were valid for J(C—Sn) couplings. Our observation confirms that by Mitchell [10] for other tin compounds, viz. that the hybridization of the carbon nucleus cannot be considered as the only factor governing the changes in the J(C—Sn) coupling constants.

Experimental

The synthesis of the investigated compounds will be described in a separate paper [14].

The spectra were recorded on a XL-100 Varian NMR spectrometer in a Fourie transform mode with XL = 100's pulse - Fourier Transform Control Module and Varian Data 620 L computer, with proton-noise decoupling. Either CD_3COCD_3 or C_6D_{12} was used as lock. The number of pulses ranged from 500—8000, and the resolution was 0.1 Hz. The chemical shifts are expressed in ppm relative to internal TMS and are believed to be accurate to 0.1 ppm. The compounds were examined as 10% solutions in acetone-d_6 and cyclohexane-d_{12}. Either 5 or 12 mm NMR tubes were used depending on the amount of the compound available. The analysis of the spectra was performed by the Garbisch Jr. method [15] and the results checked by means of the LAOCOON III program.

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