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Isotope $^{13/12}C$ effects on ^{119}Sn nucleus shielding in ethynylstannanes

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Abstract

Isotope shifts in ^{119}Sn NMR spectra caused by the replacement of ^{12}C by ^{13}C in the acetylenylstannanes $(CH_3)_{3-n}(t\text{-}C_4H_9)_nSnC_\alpha{\equiv}C_\beta X$ were shown to be interrelated as indicated by a set of correlations between individual isotope shifts. Linear correlations were found between isotope shifts and the coupling constants $^nJ(^{119}Sn-^{13}C)$. The different best-fitting lines observed for compounds with $n = 0$–3 as well as for $(R'CH_2)_3Sn$ derivatives are explained by $\mathrm{H}\overset{\curvearrowright}{-\mathrm{C}-}\mathrm{Sn}\overset{\curvearrowright}{-\mathrm{C}\equiv}$ hyperconjugation.

Introduction

Extensive introduction into multinuclear NMR practice of spectrometers with high-intensity magnets and polarization transfer methods provides rapid information about isotope shifts in the shielding of "heavy" nuclei and permits examination of the influence of different substituents on their reactions. So far, the theory of isotope shifts (IS) only works satisfactorily in the case of diatomic molecules [1]. However, Jameson and Osten have shown [2,3] that the same notions may apply to terminal groups in the molecule. According to this theory and within the Born–Oppenheimer approximation, the isotope substitution has its chemical effect because the vibrational and rotational effects of the bond depend upon its isotopic mass. The most important theoretical investigations of IS for various resonances were carried out on hydrides $AH_{4-n}D_n$ [4]. Replacement of hydrogen by deuterium leads to a significant upfield shift of the central atom resonance that can be approximated by eq. 1:

$$\begin{aligned} {}^1\Delta A(^{2/1}H) &\cong (\delta\sigma^A/\delta\Delta r_{AH})_e[\langle\Delta r_{AH}\rangle - \langle\Delta r_{AD}\rangle] \\ &\cong (\delta\sigma^A/\delta\Delta r_{AH})_e(\tfrac{1}{4}\langle\Delta r_{AH}\rangle), \end{aligned} \qquad (1)$$

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where $\langle \Delta r_{AH} \rangle$ is the mean extension of the A–H bond (roughly equal to 15–20 × 10^{-3} Å [5]).

The reasons for changes in isotope shifts are not yet completely clear. According to equation 1, they can be attributed both to changes in the first derivative of the magnetic shielding surface $(\delta\sigma^A/\delta\Delta r_{AH})_e$ and in the value $[\langle \Delta r_{AH} \rangle - \langle \Delta r_{AD} \rangle]$ caused by variation of nuclear charge in the central atom. The IS ${}^1\Delta A({}^{2/1}H)$ is significantly influenced by the charge on the central atom [6]: an increase in the positive charge decreases the IS. However, when uncharged molecules are investigated and when the substitution occurs far from the central atom, changes in the $(\delta\sigma^A/\delta\Delta r_{AH})_e$ term can be considered as insignificant for a given bond. Then the main source of changes in the isotope shift must arise from differences in the geometric characteristics of bonds. There is no doubt that a more thorough analysis of isotope shifts on σ^A must also take into account the quadratic terms for rotational corrections and the mean bond angle deformations. However, it has been shown [2,3–5,7] that the terms $(\delta^2\sigma^A/\delta\Delta r^2_{AH})_e\langle(\Delta r_{AH})^2\rangle$ and $(\delta\sigma^A/\delta\Delta\alpha)_e[\langle\Delta\alpha\rangle_{\text{light}} - \langle\Delta\alpha\rangle_{\text{heavy}}]$ are too small and therefore can be neglected. An increase in reduced bond mass causes some decrease in the bond length. Usually, decreased bond length is associated with decreased chemical shift [8–10]. Therefore ${}^{13/12}C$ isotope shift over one bond calculated from equation (2):

$$ {}^1\Delta A({}^{13/12}C) = \sigma^A(A{-}{}^{12}C) - \sigma^A(A{-}{}^{13}C) \qquad (2) $$

will have a negative sign. Isotope shifts for the ${}^{13/12}C$ substitution on "heavy" central atom resonances are large enough to be easily mesured. Recently, ${}^{13/12}C$ isotope shifts have been measured in NMR spectra of ${}^1H$, ${}^{13}C$, ${}^{15}N$, ${}^{19}F$, ${}^{29}Si$, ${}^{31}P$, ${}^{59}Co$, ${}^{77}Se$, ${}^{111}Cd$, ${}^{119}Sn$, ${}^{125}Te$, ${}^{199}Hg$, ${}^{207}Pb$ [11–33]. ${}^{13/12}C$ isotope shifts for the ${}^{77}Se$ nucleus are directly correlated with the length of the Se–C bond [16]. This accords with the hypothesis advanced above, that only negligible changes in the nucleus shielding derivative in uncharged molecules of similar structure result from the influence of remote substituents. Wrackmeyer et al. [21] explain the ${}^{13/12}C$ isotope shifts measured on ${}^{29}Si$, ${}^{119}Sn$ and ${}^{207}Pb$ NMR resonances as consisting of two components: (1) the upfield shift that is as usually ascribed to the shortening of the M–C bond in the heavier isotopomer compared to the lighter one, and (2) the additional electronic effects that operate more effectively in the heavier isotopomer leading to a less pronounced polarization of the M–C bond. The latter effect produces a downfield shift of the central atom resonance. These two effects explain the situation occurring with highly electronegative substituents at the central atom when the ${}^{13/12}C$ isotope shifts approach zero values or even become positive. Thus investigation of isotopic shifts creates a unique possibility for establishing a relationship between the geometric and electronic structure of the molecule. Total quantitative analysis of isotopic shifts in polyatomic molecules requires the examination of changes in vibration–rotational levels not only for a particular bond but also for the entire molecule. At present such analysis is impossible. However, one can hope to reveal at least some of the reasons for differences in isotopic shifts if the shielding of nuclei is analysed in structurally similar molecules. In this connection, acetylene derivatives of the type $(CH_3)_{3-n}(t\text{-}Bu)_nSnC_\alpha{\equiv}C_\beta X$ appear very attractive. The remote location of substituent X relative to the indicator centre (${}^{119}Sn$ nucleus) and the linearity of the MC≡CX fragment allow one to neglect the conformational nonhomogeneity and anisotropy of this substituent. In acetylenes, the π- and σ-electronic effects of substituent X are more pronounced compared with those associated with single or double bonds. Therefore these effects can be observed more easily.

Results and discussion

Values for the isotope shifts in ^{119}Sn NMR spectra, resulting from the replacement on ^{12}C by ^{13}C isotopes in the $(CH_3)_{3-n}(t\text{-}Bu)_nSnC_\alpha{\equiv}C_\beta X$ skeleton of the molecules, are summarized in Table 1. For convenience these data are supplemented with the coupling constants $^nJ(^{119}Sn-^{13}C)$. The ^{119}Sn and ^{13}C chemical shifts of these compounds have been discussed previously [34,35].

The data in the table show that the properties of the Sn–C(sp) single bond are markedly different from those of Sn–C(sp^3). For the former bond $^{13/12}$C isotope shift has a negative sign, whereas for the latter the sign is positive. Interpretation of positive isotope shifts generally meets with certain difficulties, because the theory does not account for such positive values. In principle, this may be due to either (1) changes in vibrational surface asymmetry for the $^{119}Sn-^{13}C$ bond compared to $^{119}Sn-^{12}C$, or (2) differences in the magnetic shielding surface of these two bond types. The first explanation implies a departure from the Born–Oppenheimer approximation, therefore it appears more reasonable that the positive sign of isotope shifts for the Sn–C(sp^3) bond would be associated with the properties of isoshielding surfaces. It should be noted that positive $^{13/12}$C isotope shifts have been found for the ^{199}Hg resonance in RHgX [19,20]. It cannot be ruled out that dynamic processes may affect $^{13/12}$C isotope shift sign determination for heavy metal resonances, e.g. differences in hyperconjugation of the ^{13}C–M and ^{12}C–M bonds and subsequent changes in rotational equilibrium around these bonds. Such processes are quite common for the C–D and C–H bonds in allylic type compounds and carbonium ions [36,37]. Positive isotope shifts can occur in response to an increase in the positive charge on the observed nucleus [38]. However, comparison of the $^{13/12}$C isotope shifts with ^{119}Sn or ^{13}C chemical shifts shows that no linear relationships have yet been formed between these values.

As the number of t-Bu groups at the tin atom increases, the coupling constants $^{119}Sn-^{13}C$ and the isotope shifts for all Sn–C bonds decrease, can be probably because all Sn–C bonds are lengthened, and the valency angles around the tin atom change [39].

The more positive value of isotope shifts for the Sn–C(t-Bu) bond compared to Sn–C(CH_3) ($n = 1$) apparently suggests that the former bond is not so strong which accords with its greater length [39]. On the other hand, the more pronounced variation of isotope shifts in the Sn–C(t-Bu) bonds (as compared to Sn–C(CH_3) or Sn–C_α) as the number of t-Bu groups increases is probably associated with more dramatic changes in the strength of the first type of bonds. However, these differences can be also due to greater changes in the shielding derivatives $(\delta\sigma^{Sn}/\delta\Delta r_{SnC})_e$ for the surfaces of isomagnetic shielding in Sn–C(t-Bu) bonds as compared to Sn–C(CH_3) and Sn–C_α.

Changes in the mass of substituent in compounds of the type $(CH_3)_{3-n}(t\text{-}Bu)_nSnC_\alpha{\equiv}C_\beta X$ have a nominal effect on the vibrational levels of Sn–C bonds because of the relatively great distance between them. Therefore changes in isotope shifts under the influence of substituent X must be due mainly to the electronic

Table 1

Isotope shifts $^{n}\Delta^{119}Sn(^{13/12}C)$ (10^3 ppm) ^{a} and $^{n}J(^{119}Sn-^{13}C)$ coupling constants in NMR spectra ^{119}Sn of ethynylstannanes $(CH_3)_{3-n}(t\text{-}C_4H_9)_nSnC_\alpha{\equiv}C_\beta X$ in C_6D_6

No.	X	n	$^{1}\Delta^{119}Sn(C_\alpha)$	$^{1}J(^{119}Sn-^{13}C_\alpha)$ (Hz)	$^{1}\Delta^{119}Sn(C_{CH_3})$	$^{1}J(^{119}Sn-^{13}CH_3)$ (Hz)	$^{1}\Delta^{119}Sn(C-C{\equiv})$	$^{1}J(^{119}Sn-^{13}C{\equiv})$ (Hz)	$^{2}\Delta^{119}Sn(C_\beta)$	$^{2}J(^{119}Sn-^{13}C_\beta)$ (Hz)
1	H	0	−58.2	423.1	+3.3	406.5	–	–	−17.5	87.1
		1	−59.4	352.5	+0.6	350.0	+15.8	502.5	−17.4	67.3
		2	−60.9	274.0	+0.5	290.9	+10.5	437.9	−15.5	46.7
		3	−61.8	207.6	–	–	+3.8	371.4	−10.1	30.7
2	CH_3	0	−49.3	498.1	+1.4	405.1	–	–	−10.9	105.7
		1	−49.6	424.3	+0.6	351.0	+14.7	502.4	−10.4	85.6
		2	−50.4	344.6	−2.2	293.3	+9.8	439.8	−9.8	65.1
		3	−52.6	276.0	–	–	+2.7	374.6	−8.9	48.6
3	$C(CH_3)_3$	0	−51.2	496.5	+1.1	403.4	–	–	−11.4	98.2
		1	−50.0	421.5	0.0	350.7	+14.7	501.0	−10.4	76.4
		2	−51.2	341.3	−1.6	293.5	+8.8	438.8	−10.0	59.4
		3	−55.4	270.8	–	–	+0.9	373.9	−9.1	42.0
4	$Si(CH_3)_3$	0	−57.3	403.6	+2.3	402.5	–	–	−16.3	64.4
		1	−59.1	330.3	+2.3	346.8	+15.0	497.9	–	46.4
		2	−61.8	256.0	+1.5	289.0	+9.2	434.8	–	30.1
		3	−62.7	198.5	–	–	+3.7	370.1	–	18.2
5	$Si(C_2H_5)_3$	0	−56.7	399.6	+2.5	402.2	–	–	−16.3	63.4
6	$Ge(CH_3)_3$	0	−54.1	413.5	+2.3	401.8	–	–	−13.2	60.6
		1	−57.2	339.8	0.0	346.9	+14.7	498.1	−16.3	42.0
		2	−57.1	269.3	−0.5	289.7	+10.5	435.3	−13.2	26.3
7	$Ge(C_2H_5)_3$	0	−54.2	411.8	+2.6	401.3	–	–	−14.2	59.7
8	$Sn(CH_3)_3$	0	−54.4	404.4	+2.6	400.3	–	–	–	49.9
		3	−59.0	201.3	–	–	+1.5	369.3	–	4.0

9	$Sn(C_2H_5)_3$	3	−59.2	200.4	–	–	+2.9	369.7	–	0
10	$Sn(t\text{-}C_4H_9)_3$	0	−53.2	405.5	+1.5	400.3	–	–	–	49.7
		3	−58.9	204.7	–	–	+2.2	370.0	–	0
11	$Sn(t\text{-}C_4H_9)\text{-}(CH_3)_2$	1	−54.4	330.0	+1.5	345.5	+14.6	496.5	−14.9	30.6
12	Cl	0	−63.2	399.4	+4.4	406.9	–	–	−19.1	80.3
		1	−62.1	322.3	+2.8	348.4	+16.9	503.4	−17.4	55.6
		2	−63.0	238.3	+0.8	287.7	+11.4	436.5	−15.1	31.2
		3	−64.0	164.5	–	–	+4.5	368.3	−11.1	10.7
13	Br	1	–	304.5	–	346.9	–	501.8	–	41.3
		2	–	223.0	–	286.1	–	435.0	–	19.5
		3	−65.2	155.4	–	–	+4.5	367.4	–	0
14	I	3	−65.2	145.5	–	–	+4.5	365.8	–	0
15	C_6H_5	0	−58.5	443.2	+2.1	404.1	–	–	−16.1	93.0
		1	−57.7	370.4	+0.8	348.6	+16.0	500.2	−14.5	73.1
		2	−58.5	291.1	0.0	290.0	+10.1	437.2	−13.3	53.8
16	SC_2H_5	0	−58.5	432.0	+3.0	404.4	–	–	−17.3	84.0
		2	−58.8	278.6	0.0	289.9	+11.1	436.7	−13.0	41.9
		3	−62.6	211.6	–	–	+4.5	370.4	−10.7	24.5
17	OCH_3	0	−46.5	533.1	+0.9	407.0	–	–	−8.3	128.4
18	CF_3	0	−76.5	274.6	+6.8	406.4	–	–	−26.5	54.6
19	CH_2Br	0	−60.5	415.8	+3.8	405.3	–	–	–	85.1
20	$\underset{CH_3}{\underset{\vert}{C}}=CH_2$	3	−56.1	232.9	–	–	+3.3	372.9	–	37.3
21	C_6F_5	0	−65.5	356.6	+5.4	405.8	–	–	−16.7	76.4
22	$P(=O)(OCH_3)_2$	0	–	–	+6.5	412.1	–	–	–	–

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[a] The accuracy of measurements: ±0.5×10^3 ppm.

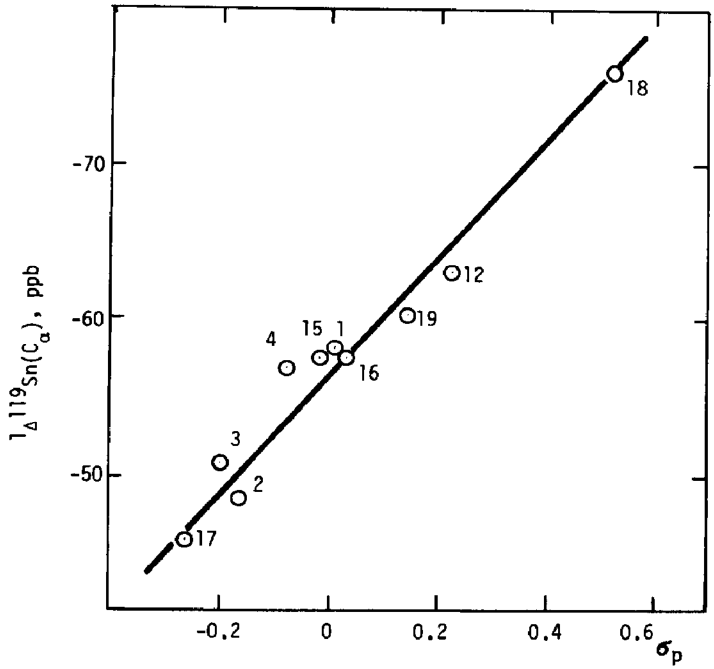

Fig. 1. Correlation between isotope shifts $^{1}\Delta^{119}Sn(C_\alpha)$ and σ_p constants for substituent X in ethynylstannanes $(CH_3)_3SnC{\equiv}CX$. Numeration of compounds as in Table 1.

effects exerted by the latter on the shielding surface profile and/or the length of the Sn–C bond. The substituent exerts the greatest effect on isotope shifts in the Sn–C_α bond ($^{1}\Delta^{119}Sn(C_\alpha)$) and on isotope shifts over the two Sn–$C_\alpha{\equiv}C_\beta$ bonds ($^{2}\Delta^{119}Sn(C_\beta)$) (Table 1). As already shown above, the isotope shift $^{n}\Delta^{119}Sn(^{13/12}C)$ according to eq. 1 is proportional to the product of the first magnetic shielding derivative $(\delta\sigma^{Sn}/\delta\Delta r_{SnC})_e$ and the change in the length of the Sn–C bond when going from the lighter to heavier isotopomer. If one assumes that the magnetic shielding term is constant for any particular type of bond in eq. 1, then changing isotope shifts would reflect differences in bond energies in the two isotopomers. As Sn–C bond lengths increase their energies in the isotopomers differ less markedly, and the same applies to their vibrational levels. On the other hand, potentional function anharmonicity for vibrational movements becomes less pronounced with increasing bond length [3,8]. Both these factors contribute to a decrease in isotope shifts $^{1}\Delta^{119}Sn(^{13/12}C)$ as Sn–C bond length increases.

As follows from the correlation between the isotope shifts $^{1}\Delta^{119}Sn(C_\alpha)$ and substituent X σ_p-constants (Fig. 1), an increase in the electron-acceptor strength of substituent X leads to an increase in the isotope shifts for the Sn–C_α bond. This reflects an increase in the order of the Sn–C_α bond and decrease of its length as the σ_p-values for substituent X become more positive. Thus these changes in $^{1}\Delta^{119}Sn(C_\alpha)$ can be also explained by variability of the $(\delta\sigma^{Sn}/\delta\,\Delta r_{SnC})_e$ term in eq. 1. However, experimental and theoretical data suggest that an increase in the negative electronic charge over the central atom leads to increased negative isotope shifts [40,41]. Therefore the increase in isotope shifts in the series $X = OCH_3 < CH_3 < C(CH_3)_3 < SiMe_3 < Ph \approx H < Cl < Br < CF_3$ (i.e. with the increasing electron-acceptor strength of substituent X) is incompatible with the electronic effect of substituent X,

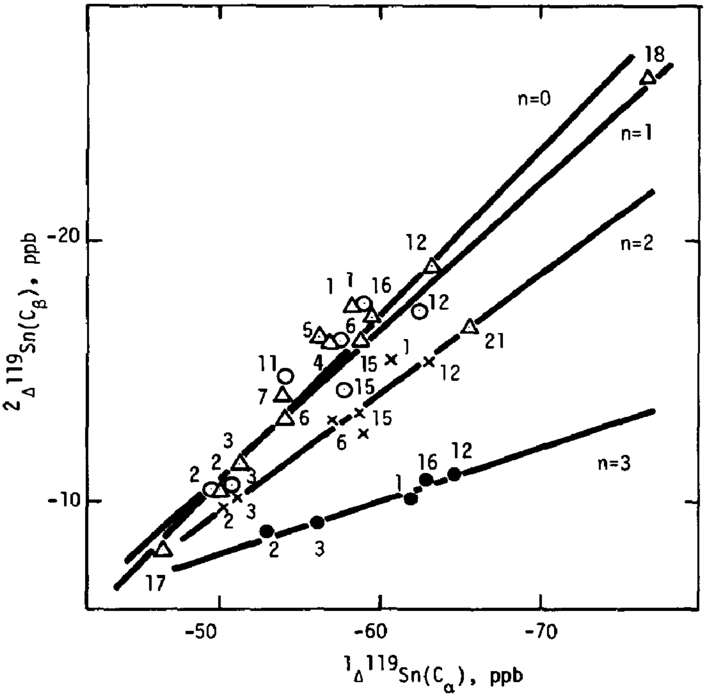

Fig. 2. Correlation between isotope shifts ${}^{1}\Delta^{119}Sn(C_\alpha)$ and the isotope shifts over two bonds ${}^{2}\Delta^{119}Sn(C_\beta)$ in ethynylstannanes $(CH_3)_{3-n}(t\text{-}C_4H_9)_nSnC_\alpha{\equiv}C_\beta X$. Numeration of compounds as in Table 1.

but must be connected with variation in vibrational characteristics and hence the length of Sn–C bond. This is in keeping with the results of normal coordinate analysis [42–44] showing that the replacement of ethynic hydrogen by a chlorine atom in the $(CH_3)_3SnC{\equiv}CH$ molecule slightly increases the stretching constant of the Sn–C≡ bond but the shape of the potential energy surface for vibrations of that bond becomes significantly mixed with the vibrations $\nu(C{\equiv}C)$ and $\nu({\equiv}C{-}Cl)$.

The isotope shift over the two bonds ${}^{2}\Delta^{119}Sn(C_\beta)$ is, apparently, also influenced by changes in the state of the neighbouring C≡C bond because there is a similar change in ${}^{2}\Delta^{119}Sn(C_\beta)$ and ${}^{1}J(C{\equiv}C)$, when n changes from 0 to 3. The s-character of the $C_\alpha{\equiv}C_\beta$ bond grows with the electronegativity of substituents attached to this bond [45,46]. However, upon transition from $(CH_3)_3SnC{\equiv}CH$ to $(CH_3)_3SnC{\equiv}CCl$ the force constant $K(C{\equiv}C)$ decreases and the vibrational function changes in shape from characteristic to mixed with $\nu({\equiv}C{-}Cl)$ [47,48].

Substituent X elicits similar alterations in the isotope shifts over one ${}^{1}\Delta^{119}Sn(C_\alpha)$ and two bonds ${}^{2}\Delta^{119}Sn(C_\beta)$, as shown clearly in Fig. 2 by the correlations between these two values. Interestingly, compounds bearing a different number of CH_3 groups attached to the tin atom show best-fitting lines with different slopes:

$$n = 0 \quad {}^{2}\Delta^{119}Sn(C_\beta) = 18.74 + 0.60\,{}^{1}\Delta^{119}Sn(C_\alpha) \tag{3}$$

$r = 0.987$

$n = 12$ (except for $X = C_6F_5$)

$$n = 1 \quad {}^2\Delta^{119}\mathrm{Sn}(\mathrm{C}_\beta) = 19.2 + 0.60\,{}^1\Delta^{119}\mathrm{Sn}(\mathrm{C}_\alpha) \tag{4}$$

$$r = 0.950$$

$$n = 7$$

$$n = 2 \quad {}^2\Delta^{119}\mathrm{Sn}(\mathrm{C}_\beta) = 13.55 + 0.46\,{}^1\Delta^{119}\mathrm{Sn}(\mathrm{C}_\alpha) \tag{5}$$

$$r = 0.975$$

$$n = 7$$

$$n = 3 \quad {}^2\Delta^{119}\mathrm{Sn}(\mathrm{C}_\beta) = 1.12 + 0.19\,{}^1\Delta^{119}\mathrm{Sn}(\mathrm{C}_\alpha) \tag{6}$$

$$r = 0.967$$

$$n = 5$$

The influence of substituent X on the vibrational characteristics of the Sn–C_α bond therefore depends substantially on the ratio of $SnCH_3$ and Sn-t-Bu groups at the tin atoms. Thus, contrary to substituent X effect, an increase in the number of Sn-t-Bu groups in the molecule in the series $n = 0$–3 is followed by dissimilar changes in the isotope shifts ${}^1\Delta^{119}Sn(C_\alpha)$ and ${}^2\Delta^{119}Sn(C_\beta)$ (Table 1). If one assumes the above interpretation of the theory of isotope shifts, the simultaneous increase in ${}^1\Delta^{119}Sn(C_\alpha)$ and ${}^2\Delta^{119}Sn(C_\beta)$ brought about by changes in the more electronegative substituent X would reflect decreased Sn–C_α and Sn–C_β distances. At the same time, an increase in the number of Sn-t-Bu groups at the atom insignificantly changes the Sn–C_α distance but lengthens Sn–C_β, i.e., increases the C≡C bond length.

Isotope shifts for the Sn–C_α and Sn–CH_3 bonds in compounds with $n = 0$ show a linear relationship with negative slope (Fig. 3). Thus, substituent X has different electronic effects on the strengths of these two bonds. The strengthening of the Sn–C_α bond is accompanied by the weakening of Sn–CH_3 and vice versa. Obviously, such correlations can be also found for compounds with different n.

Difference in the Sn–C_α bond length and bond order caused by the electronic effects of substituent X essentially affect the polarization of s-electrons in the bond.

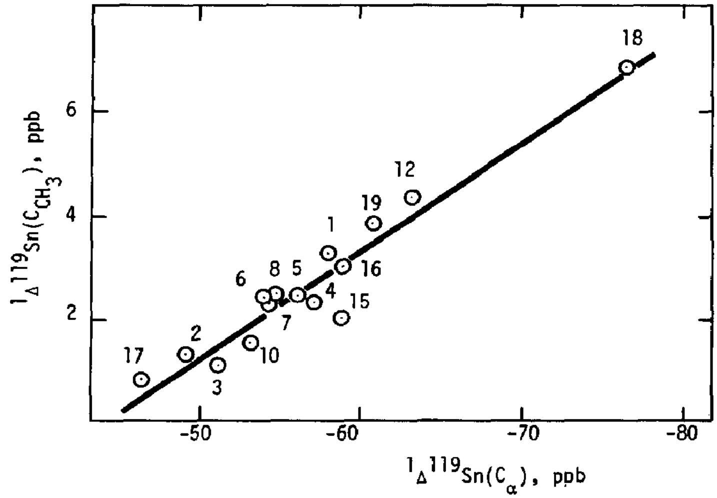

Fig. 3. Correlation between isotope shifts ${}^1\Delta^{119}Sn(C_{CH_3})$ and ${}^1\Delta^{119}Sn(C_\alpha)$ in ethynylstannanes $(CH_3)_3SnC_\alpha{\equiv}C_\beta X$. Numeration of compounds as in Table 1.

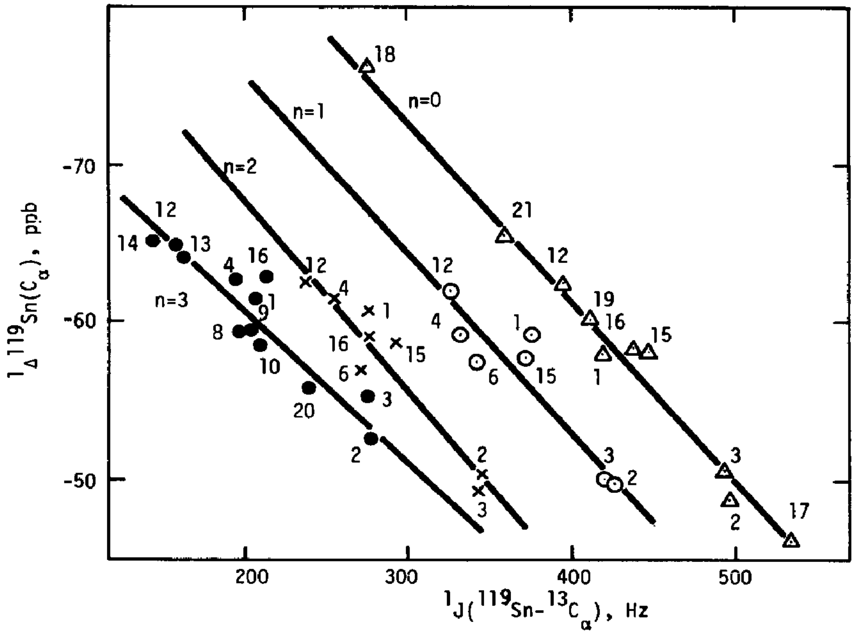

Fig. 4. Correlation between isotope shifts ($^1\Delta^{119}Sn(C_\alpha)$) and $^1J(^{119}Sn-^{13}C_\alpha)$ coupling constants in ethynylstannanes $(CH_3)_{3-n}(t\text{-}C_4H_9)_nSnC_\alpha{\equiv}C_\beta x$. Numeration of compounds as in Table 1.

This leads to significant changes in the coupling constants $^1J(^{119}Sn-^{13}C\alpha)$ (Table 1). Correlations exist between the isotope shifts $^1\Delta^{119}Sn(C_\alpha)$ and the coupling constants $^1J(^{119}Sn-^{13}C_\alpha)$, differing for every n (Fig. 4):

$$n = 0 \quad {}^1\Delta^{119}Sn(C_\alpha) = -108.1 + 0.12\,{}^1J\left({}^{119}Sn-{}^{13}C_\alpha\right) \tag{7}$$

$r = 0.993$

$n = 10$

(except for X = $SiMe_3$, $SiEt_3$, $GeMe_3$, $GeEt_3$, $SnMe_3$, $Sn(t\text{-}Bu)_3$)

$$n = 1 \quad {}^1\Delta^{119}Sn(C_\alpha) = -96.42 + 0.10\,{}^1J\left({}^{119}Sn-{}^{13}C_\alpha\right) \tag{8}$$

$r = 0.954$

$n = 7$

(except for X = $Sn(t\text{-}Bu)Me_2$)

$$n = 2 \quad {}^1\Delta^{119}Sn(C_\alpha) = -93.34 + 0.12\,{}^1J\left({}^{119}Sn-{}^{13}C_\alpha\right) \tag{9}$$

$r = 0.987$

$n = 7$

(except for X = $GeMe_3$)

$$n = 3 \quad {}^1\Delta^{119}Sn(C_\alpha) = -79.2 + 0.09\,{}^1J\left({}^{119}Sn-{}^{13}C_\alpha\right) \tag{10}$$

$r = 0.950$

$n = 11$

As can be deduced from the equations, the more negative isotope shifts correspond to the smaller coupling constants. The same sequence has been observed for other isotope shifts and coupling constants [15,33,49]. However, theoretical interpre-

Table 2

Isotope shifts ${}^{n}\Delta^{119}Sn({}^{13/12}C)$ (10^3 ppm) and ${}^{n}J({}^{119}Sn-{}^{13}C)$ coupling constants in NMR spectra ${}^{119}Sn$ of ethynylstannanes $R_3SnC_\alpha \equiv C_\beta X$ in C_6D_6

R	X	${}^{1}\Delta^{119}Sn(C_\alpha)$	${}^{1}J({}^{119}Sn-{}^{13}C_\alpha)$ (Hz)	${}^{2}\Delta^{119}Sn(C_\beta)$	${}^{2}J({}^{119}Sn-{}^{13}C_\beta)$ (Hz)	${}^{1}\Delta^{119}Sn(C_R)$	${}^{n}J({}^{119}Sn-{}^{13}C_R)$ (Hz)
n-C_4H_9	H	−64.5	339.1	–	–	−1.0(α-CH_2)	383.5(α-CH_2)
n-C_4H_9	(t-C_4H_9)$_3$	−59.0	325.4	–	–	0	379.4(α-CH_2)
C_2H_5	SC_2H_5	−63.9	338.0	−16.3	56.9	+0.3(CH_2)	388.8(CH_2)
						+3.6(CH_3)	27.9(CH_3)
C_2H_5	Ge(CH_3)$_3$	−60.7	328.6	−17.5	39.1	−0.5(CH_2)	387.5(CH_2)
						+4.0(CH_3)	27.4(CH_3)
C_2H_5	CF_3	−85.8	185.4	–	34.1	+3.3(CH_2)	384.5(CH_2)
C_2H_5	(t-C_4H_9)$_3$	−59.9	321.1	–	26.0	−3.7(CH_2)	390.1(CH_2)
n-C_3H_7	CF_3	−85.1	186.9	–	33.1	+2.9(α-CH_2)	377.7(α-CH_2)

tation of such slopes for these correlation equations meets with some difficulties. Firstly, a large body of experimental data shows that a decrease in bond length as a result of substituent effect is connected with increased coupling constant values over that bond. On the other hand, decreased bond length leads to more negative isotope shifts. On these grounds similar changes of isotope shifts and coupling constants would be anticipated. Theoretical calculations for methane, ethylene and acetylene molecules unexpectedly revealed that the shortening of the C–H bond is accompanied by decreased $^1J(^{13}\mathrm{C}{-}^1\mathrm{H})$ values, provided the type of hybridization of the carbon atom is unchanged [50].

Therefore it must be assumed that the opposite direction of isotope shift and coupling constant changes caused by substituents X is associated with two mutally independent phenomena: (1) isotopic substitution exerts too slight an effect to change the hybridization of atoms involved in bond formation; (2) on the contrary, changes in the coupling constants are mainly related to marked changes in hybridization of both atoms owing to substituent X effects.

Hybridization changes in the bonded atoms are accompanied by changes in valency angles and bond lengths as well as by the redistribution of electronic charge in the bond. The latter feature can substantially influence the profile of the magnetic isoshielding surface of the bond in question which is apparently responsible for the opposite trends in isotope shift and coupling constant variation.

Interestingly, correlations between $^1J(^{119}\mathrm{Sn}{-}^{13}\mathrm{C}_\alpha)$ and $^1\Delta^{119}\mathrm{Sn}(\mathrm{C}_\alpha)$ are proportional to the number of hydrogen atoms in SnR_3 substituents and their distance from the tin atom. Therefore we observe different correlation lines for different n. At the same time, $\mathrm{Sn(CH_2R')_3}$ substituents build up a separate correlation (Table 2) different from that of the $\mathrm{(CH_3)_2(t\text{-}C_4H_9)Sn}$ group, though the number of hydrogens in substituents at the tin atom in both series of compounds is identical. This fact, in our view, provides evidence of the exceptionally important role of hyperconjugation $\mathrm{H}\overset{\curvearrowright}{-\mathrm{C}-}\mathrm{Sn}\overset{\curvearrowright}{-\mathrm{C}}{\equiv}$ in determining coupling constants, i.e., the state of hybridized orbitals in the $\mathrm{Sn{-}C_\alpha}$ bond. Isotopic shifts in this case change insignificantly. Obviously, this type of hyperconjugation induces only minor changes in $\mathrm{Sn{-}C_\alpha}$ bond length. Our calculations of the vibrational spectra of $\mathrm{(CH_3)_3M{-}X}$ molecules, where M = Sn, Ge, Si; X = Hal, $\mathrm{C{\equiv}CX}$, show that the rotational motion of the $\mathrm{CH_3}$ group around the $\mathrm{Sn{-}C{\equiv}}$ bond is significantly restricted [48]. These facts can apparently be regarded as a confirmation that such hyperconjugation occurs.

The electronic effects of substituent X only slightly influence hyperconjugation, as the plots of $^1\Delta^{119}\mathrm{Sn}(\mathrm{C}_\alpha)$ against $^1J(^{119}\mathrm{Sn}{-}^{13}\mathrm{C}_\alpha)$ have practically the same slopes notwithstanding the number n. The $\mathrm{SnR_3}$, $\mathrm{GeR_3}$, $\mathrm{SiR_3}$ substituents for $n = 0, 1, 2$ but not for $n = 3$ do not satisfy equations 7–9. Such deviations probably indicate a complete hyperconjugation between these substituents and the triple bond resulting in lowered coupling constant values $^1J(^{119}\mathrm{Sn}{-}^{13}\mathrm{C}_\alpha)$.

Isotope shifts $^2\Delta^{119}\mathrm{Sn}(\mathrm{C}_\beta)$ over two bonds, like $^1\Delta^{119}\mathrm{Sn}(\mathrm{C}_\alpha)$ are correlated with $^2J(^{119}\mathrm{Sn}{-}^{13}\mathrm{C}_\beta)$. Again there are lines with different slopes for compounds differing as to the number of t-Bu groups at the tin atom (Fig. 5):

$$n = 0 \quad ^2\Delta^{119}\mathrm{Sn}(\mathrm{C}_\beta) = -38.24 + 0.25\,^2J\left(^{119}\mathrm{Sn}{-}^{13}\mathrm{C}_\beta\right) \tag{11}$$

$$r = 0.948$$
$$n = 9$$

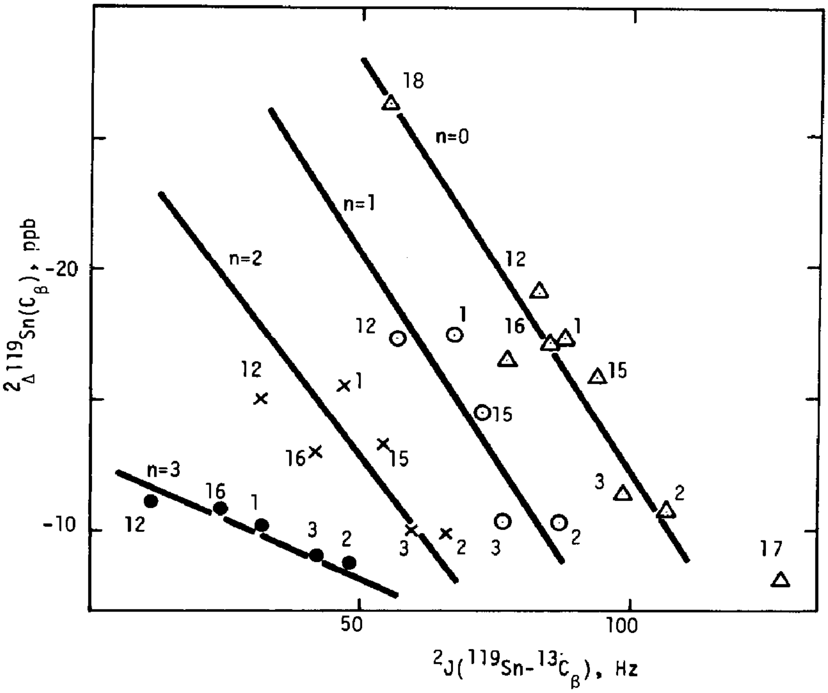

Fig. 5. Correlation between isotope shifts ($^2\Delta^{119}$Sn(C$_\beta$)) and ^2J(^{119}Sn–^{13}C$_\beta$) coupling constants in-ethynylstannanes $(CH_3)_{3\text{-}n}(t\text{-}C_4H_9)_nSnC_\alpha{\equiv}C_\beta X$. Numeration of compounds as in Table 1.

(except for X = SiMe$_3$, SiEt$_3$, GeMe$_3$, GeEt$_3$)

$$n = 1 \quad {}^2\Delta^{119}\mathrm{Sn}(\mathrm{C}_\beta) = -33.65 + 0.27\,{}^2J\left({}^{119}\mathrm{Sn}\text{–}{}^{13}\mathrm{C}_\beta\right) \tag{12}$$

$r = 0.870$

$n = 5$

(except for X = GeMe$_3$, SnMe$_2$(t-Bu))

$$n = 2 \quad {}^2\Delta^{119}\mathrm{Sn}(\mathrm{C}_\beta) = -23.3 + 0.20\,{}^2J\left({}^{119}\mathrm{Sn}\text{–}{}^{13}\mathrm{C}_\beta\right) \tag{13}$$

$r = 0.799$

$n = 6$

(except for X = GeMe$_3$)

$$n = 3 \quad {}^2\Delta^{119}\mathrm{Sn}(\mathrm{C}_\beta) = -11.97 + 0.06\,{}^2J\left({}^{119}\mathrm{Sn}\text{–}{}^{13}\mathrm{C}_\beta\right) \tag{14}$$

$r = 0.978$

$n = 5$

As explained above, the slope differences in eq. 11–14, unlike those in eq. 7–10 possibly stem from additional electronic effects of substituent X on the order and strength of the triple bond $C_\alpha{\equiv}C_\beta$.

The insufficient accuracy of measurements and the negligible changes of isotope shifts in the Sn–C(CH$_3$) and Sn–C(t-Bu) bonds prevented us from establishing a reliable correlation between the isotope shifts and ^1J(^{119}Sn–^{13}C) over these bonds affected by substituents X. However, it should be noted that an increase of number of Sn(t-Bu) groups in the molecules leads to slope changes for the above types of correlations both for the Sn–C(CH_3) and Sn–C(t-Bu) bonds. Thus, substituent X slightly influences the vibrational characteristics of the latter bonds, the degree of influence being controlled by substituents located at the tin atom.

Experimental

^{119}Sn NMR spectra were recorded on a Bruker WM-360 instrument (134.29 MHz) using 20% solution in deuterobenzene at 30 ° C. Digital resolution was ±0.04 Hz. Isotope shifts were measured as differences between the position of the ^{119}Sn–^{12}C resonance signal and the centre of the ^{119}Sn–^{13}C doublet.

The synthesis of compounds is described elsewhere [34,35].

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