$^nJ(^{29}Si-^{13}C)$ coupling constants and $^{13/12}C$ isotope shifts in ^{29}Si NMR spectra of ethynylsilanes

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Abstract

The coupling constants $^nJ(^{29}Si-^{13}C)$ and isotope shifts $^n\Delta\ ^{29}Si(^{13/12}C)$ in the ^{29}Si NMR spectra of the ethynylsilanes $(CH_3)_3SiC\equiv CX$ (X = H, Br, I, SCH_3, SC_2H_5, SC_6F_5, CH_3, CH_2Cl, $CH_2OC_2H_5$, $CH_2N(C_2H_5)_2$, $CH_2Si(CH_3)_3$, $CH_2Ge(CH_3)_3$, $CH_2C(CH_3)_3$, CF_3, CN, C_6H_5, C_6F_5, $Si(CH_3)_3$, $Ge(CH_3)_3$, $Ge(C_2H_5)_3$, $Sn(CH_3)_3$, $Sn(t-C_4H_9)_3$) have been examined. There is a linear correlation between the isotope shifts and coupling constants. Compounds with X = MR_3 (M = Si, Ge, Sn; R = Alk) deviate from these correlations, probably because the concurrent hyperconjugation falls in the order M = Sn > Ge > Si. The data are compared with the ^{119}Sn NMR spectral data of the isostructural ethynylstannanes.

Introduction

In recent years, much attention has been devoted to studies of isotope shifts in NMR spectra caused by the replacement of ^{12}C isotopes with ^{13}C in the molecule. For instance, $^{13/12}C$ isotope shifts have been studied in ^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 NMR spectra [1–24]. In the case of ^{77}Se nuclei it has been found that $^{13/12}C$ isotope shifts are linearly correlated with the length of the appropriate Se–C bond [6]. Hence, an increase in bond order as well as the shortening of the Se–C bond increases the $^{13/12}C$ isotope shifts.

As for the ethynylsilanes, the $^{13/12}C$ isotope shifts in the ^{29}Si NMR spectra have so far been determined only for three derivatives [24]. Therefore, in order to study this phenomenon more thoroughly we synthesized a wide range of ethynylsilanes: $(CH_3)_3SiC\equiv CX$, where X = H, Br, I, SCH_3, SC_2H_5, SC_6F_5, CH_3, CH_2Cl, $CH_2OC_2H_5$, $CH_2N(C_2H_5)_2$, $CH_2Si(CH_3)_3$, $CH_2Ge(CH_3)_3$, $CH_2Sn(t-C_4H_9)_3$, CF_3,

CN, C_6H_5, C_6F_5, $Si(CH_3)_3$, $Ge(CH_3)_3$, $Ge(C_2H_5)_3$, $Sn(CH_3)_3$, $Sn(t-C_4H_9)_3$ and examined their ^{29}Si NMR spectra. The data were compared with the ^{119}Sn NMR spectral data of the analogous tin derivatives $(CH_3)_3SnC{\equiv}CX$ reported previously [25].

Experimental

The ^{29}Si NMR spectra were recorded at 70.5 MHz on a WM-360 Bruker spectrometer at 30°C for ~ 20% solutions in $CDCl_3$. The isotope shifts were measured as the difference

$$^n\Delta\,^{29}Si(^{13/12}C) = \delta(^{29}Si)_{Si-^{12}C} - \delta(^{29}Si)_{Si-^{13}C} \tag{1}$$

The accuracy of measurements was ± 0.5 ppb (10^{-3} ppm) for the isotope shifts and ± 0.04 Hz for the coupling constants.

The compounds were synthesized as described elsewhere [26,27].

Results and discussion

The isotope shifts $^n\Delta\,^{29}Si(^{13/12}C)$ measured in the ^{29}Si NMR spectra of ethynylsilanes are listed in Table 1. The ^1H, ^{13}C and ^{29}Si chemical shifts of these compounds have been discussed previously [28]. For some of these ethynylsilanes the coupling constants $^nJ(^{29}Si-^{13}C)$ have been reported [29–32] but not discussed.

The values of the $^1J(^{29}Si-^{13}C_\alpha)$ coupling constants largely depend on the electronic properties of substituent X:

$$^1J(^{29}Si-^{13}C_\alpha) = 82.9 - 21.7\,\sigma_p \qquad (r = 0.98,\ n = 12) \tag{2}$$

Coupling constants over two bonds—$^2J(^{29}Si-^{13}C_\beta)$—are influenced similarly by substituent X. This is demonstrated by the correlation between $^1J(^{29}Si-^{13}C_\alpha)$ and $^2J(^{29}Si-^{13}C_\beta)$:

$$^2J(^{29}Si-^{13}C_\beta) = -3.44 + 0.23\,^1J(^{29}Si-^{13}C_\alpha) \qquad (r = 0.94,\ n = 15) \tag{3}$$

Thus, an increase in the electron-accepting ability of substituent X leads to a decrease in the coupling constant. A correlation similar to that in eq. 3 has been found by us for the coupling constants $^nJ(^{119}Sn-^{13}C)$ in the ethynylstannanes $(CH_3)_3SnC{\equiv}CX$ [25]. The slope of this correlation for tin derivatives (0.28) is very close to that found for the ethynylsilanes (0.23), which indicates that the transmission of electronic effects of substituent X through the triple bond is very similar for both classes of compounds.

It is noteworthy that the points obtained for ethynylsilanes with $X = Si(CH_3)_3$, $Ge(CH_3)_3$, $Sn(CH_3)_3$ deviate strongly from correlations 2 and 3. In the case of the relationship 2 one can speculate that the σ_p-values for $X = M(CH_3)_3$ (M = Si, Ge, Sn) substituents inadequately describe the electronic effects in ethynylsilanes, however the analogous deviations in the case of correlation 3 make this explanation questionable. These effects may be connected both with the violation of the nonlinearity of $R_3MC{\equiv}CM'R_3$ acetylenides [33,34] and/or with the existing additional concurrent hyperconjugation effect $H_3{\equiv}C-M-C{\equiv}$ in these molecules [35]. The latter effect must affect the state of π- and σ-electrons in the triple bond,

Table 1

$^n J(^{29}\text{Si}-^{13}\text{C})$ coupling constants (Hz) and $^{13/12}\text{C}$ isotope shifts (ppb) in the ^{29}Si NMR spectra of ethynylsilanes $(\text{CH}_3)_3\text{SiC}_\alpha\equiv\text{C}_\beta\text{X}$

No.	X	$^1\Delta^{29}\text{Si-}$ $(^{13/12}\text{C}_\alpha)$	^1J- $(^{29}\text{Si}-^{13}\text{C}_\alpha)$	$^2\Delta^{29}\text{Si-}$ $(^{13/12}\text{C}_\beta)$	^2J- $(^{29}\text{Si}-^{13}\text{C}_\beta)$	$^1\Delta^{29}\text{Si-}$ $(^{13/12}\text{C}_{\text{CH}_3})$	^1J- $(^{29}\text{Si}-^{13}\text{C}_{\text{CH}_3})$
1	H	−16.4	81.47	−5.2	15.41	−1.2	56.28
2	CH_3	−14.8	85.75	−4.2	15.74	−1.3	56.28
3	$\text{CH}_2\text{Si}(\text{CH}_3)_3$	−13.3	89.54	−3.1	17.86	−1.8	56.06
4	$\text{CH}_2\text{Ge}(\text{CH}_3)_3$	−12.9	88.31	−3.0	17.69	−2.0	56.01
5	$\text{CH}_2\text{Sn}(\text{t-C}_4\text{H}_9)_3$	−13.5	90.80	−3.1	18.02	−1.8	55.91
6	$\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$	−15.0	83.84	−4.3	15.75	−1.1	56.24
7	$\text{CH}_2\text{OC}_2\text{H}_5$	−15.3	80.57	−4.0	15.49	−1.1	56.41
8	CH_2Cl	−16.7	80.77	−5.0	15.42	−1.1	56.53
9	SCH_3	−16.2	82.63	−4.8	15.54	−1.0	56.44
10	SC_6F_5	−17.2	78.50	−4.9	14.61	−0.1	56.70
11	SC_2H_5	−16.2	82.73	−4.5	16.67	−0.9	56.39
12	C_6H_5	−15.6	83.12	−4.7	16.01	−1.1	56.28
13	C_6F_5	−19.0	77.62	−6.2	14.00	−0.8	56.57
14	Br	−16.7	80.22	−5.5	15.05	−1.0	56.68
15	I	−17.9	77.73	−5.5	13.15	−0.8	56.49
16	CN	−21.8	68.10	−7.6	13.14	−0.5	57.27
17	CF_3	−20.9	71.77	a	a	−0.2	57.33
18	$\text{Si}(\text{CH}_3)_3$	−16.1	76.75	−4.2	12.37	−1.4	56.13
19	$\text{Ge}(\text{CH}_3)_3$	−15.4	78.25	−4.1	12.20	−1.3	56.09
20	$\text{Ge}(\text{C}_2\text{H}_5)_3$	−15.0	78.30	−4.3	12.30	−1.3	55.99
21	$\text{Sn}(\text{CH}_3)_3$	−15.3	78.83	a	a	−1.3	55.92
22	$\text{Sn}(\text{t-C}_4\text{H}_9)_3$	−14.3	78.66	a	a	−1.3	55.79

^{a} Not recorded.

which are involved in the transmission of spin information between the various nuclei.

In contrast to the $^1J(^{29}\text{Si}-^{13}\text{C}_\alpha)$ and the $^2J(^{29}\text{Si}-^{13}\text{C}_\beta)$, the $^1J(^{29}\text{Si}-^{13}\text{CH}_3)$ coupling constants increase with increasing acceptor properties of substituent X. Such changes can be attributed to the occurrence of the same hyperconjugation effect. However, this shows that both types of Si–C bond are interrelated: a change in the properties of substituent X strengthens the Si–C_α and weakens the Si–CH_3 bond and vice versa. However, the data in Table 1 show that the $^1J(^{29}\text{Si}-^{13}\text{CH}_3)$ values are subject to minor variations, thus making a more detailed discussion impossible.

The $^n J(^{29}\text{Si}-^{13}\text{C})$ coupling constants measured in ethynylsilane $(\text{CH}_3)_3\text{SiC}_\alpha\equiv\text{C}_\beta\text{X}$ were compared with the $^n J(^{119}\text{Sn}-^{13}\text{C})$ couplings in the analogous tin derivatives $(\text{CH}_3)_3\text{SnC}_\alpha\equiv\text{C}_\beta\text{X}$ [25,31,36]. We found the following correlations:

$$^1J\left(^{29}\text{Si}-^{13}\text{C}_\alpha\right) = 49.6 + 0.07\ ^1J\left(^{119}\text{Sn}-^{13}\text{C}_\alpha\right) \qquad (r = 0.964,\ n = 13) \qquad (4)$$

$$^2J\left(^{29}\text{Si}-^{13}\text{C}_\beta\right) = 5.57 + 0.11\ ^2J\left(^{119}\text{Sn}-^{13}\text{C}_\beta\right) \qquad (r = 0.997,\ n = 8) \qquad (5)$$

The nearly equal slopes in correlations 4 and 5 are indicative of a similar mechanism for transmission of spin information across one or two bonds in both types of compound. The slope values in expressions 4 and 5 must be related to the ratio of valence s-electron densities for silicon and tin atoms, if the main mechanism for transmission of spin information in ethynyl derivatives is due to Fermi contact [37].
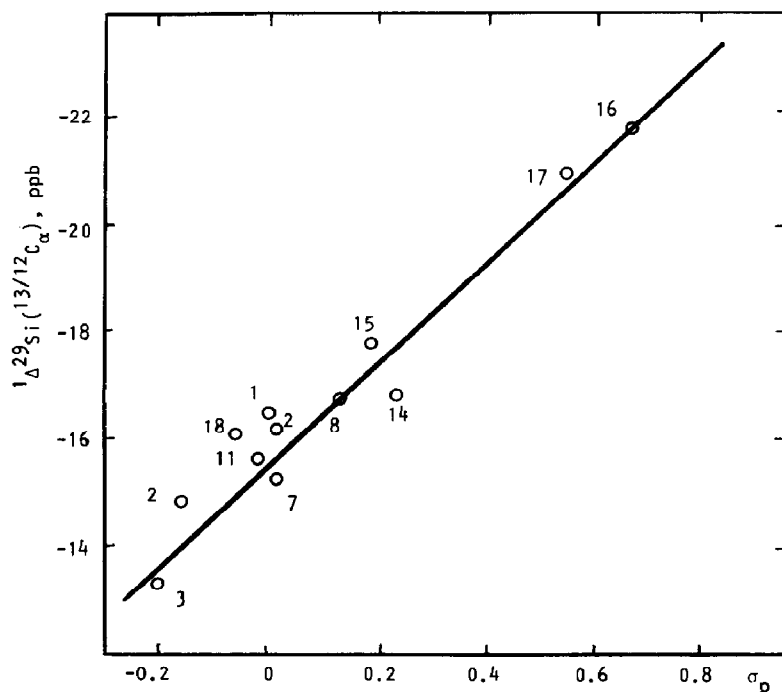
Fig. 1. Correlation between the isotope shifts $^1\Delta\,^{29}\text{Si}(^{13/12}\text{C}_\alpha)$ and the σ_p-constants of substituent X in the ethynylsilanes $(\text{CH}_3)_3\text{SiC}{\equiv}\text{CX}$. The numbering of the compounds corresponds to that in Table 1.

However, the values obtained from 4 and 5 after calibration with gyromagnetic constants for the ratios $K(^{29}\text{Si}-^{13}\text{C})/K(^{119}\text{Sn}-^{13}\text{C}) \approx 0.15-0.20$ are much lower than the expected value of 4.6 [37]. This shows that contributions other than those by Fermi-contact determine the $^nJ(\text{M}-^{13}\text{C})$ values in ethynylsilanes and -stannanes.

The isotope shifts in the NMR spectra indicate that theoretically an increase in the bond's isotope mass within the Born–Oppenheimer approximation leads to some shortening of the corresponding bond length. The shortening of bonds usually leads to decreased chemical shifts for the nuclei involved [38–41]. Therefore the $^{13/12}\text{C}$ isotope shifts calculated by equation 1 are negative (Table 1).

From the isotope shifts (Table 1) it can be deduced that the Si–C(sp) bond length differs substantially from that of Si–C(sp^3). The larger $^1\Delta\,^{29}\text{Si}(^{13/12}\text{C})$ isotope shifts in the first case must be indicative of a shorter Si–C(sp) bond, compared with Si–C(sp^3), which is consistent with the available structural data [42].

An increase in the acceptor properties of substituent X also enhances the $^1\Delta\,^{29}\text{Si}(^{13/12}\text{C}_\alpha)$ values (Fig. 1):

$$^1\Delta\,^{29}\text{Si}\!\left(^{13/12}\text{C}_\alpha\right) = -15.9 - 8.8\,\sigma_p \qquad (r = 0.966,\ n = 13) \tag{6}$$

At the same time, the $^1\Delta^{29}\text{Si}(^{13/12}\text{C}_{\text{CH}_3})$ values decrease (Table 1). This means that the Si–C_α bond strengthening and Si–CH_3 bond weakening occur simultaneously, which is consistent with the conclusions based on the analysis of the coupling constants $^1J(^{29}\text{Si}-^{13}\text{C})$.

Changes in the Si–C bond order and length caused by the electronic effects of substituent X must influence the polarizability of the s electrons in silicon and carbon atoms. The latter effect is connected with changes in the coupling constants
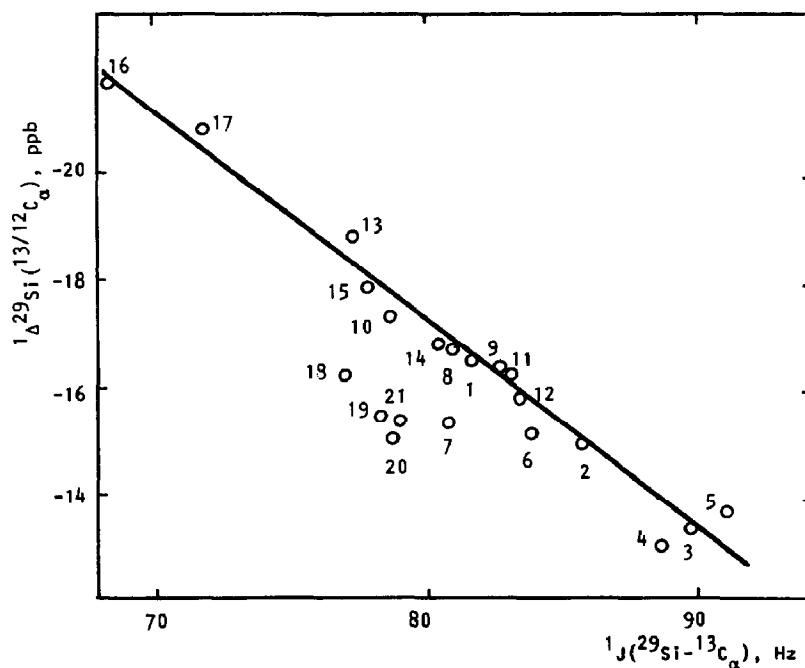
Fig. 2. The relationship between the isotope shifts $^1\Delta\,^{29}\mathrm{Si}(^{13/12}C_\alpha)$ and coupling constants $^1J(^{29}\mathrm{Si}-^{13}C_\alpha)$ in the ethynylsilanes $(CH_3)_3SiC_\alpha{\equiv}C_\beta X$. The numbering of the compounds corresponds to that in Table 1.

$^nJ(^{29}\mathrm{Si}-^{13}C)$. Thus we found linear correlations between $^1\Delta\,^{29}\mathrm{Si}(^{13/12}C_\alpha)$ and $^1J(^{29}\mathrm{Si}-^{13}C_\alpha)$ as well as $^2\Delta\,^{29}\mathrm{Si}(^{13/12}C_\beta)$ and $^2J(^{29}\mathrm{Si}-^{13}C_\beta)$ values, respectively (Fig. 2, 3):

$$^1\Delta\,^{29}\mathrm{Si}\left(^{13/12}C_\alpha\right) = -49.69 + 0.41\;^1J\left(^{29}\mathrm{Si}-^{13}C_\alpha\right) \qquad (r = 0.971,\; n = 16) \qquad (7)$$

$$^2\Delta\,^{29}\mathrm{Si}\left(^{13/12}C_\beta\right) = -17.60 + 0.82\;^2J\left(^{29}\mathrm{Si}-^{13}C_\beta\right) \qquad (r = 0.93,\; n = 16) \qquad (8)$$
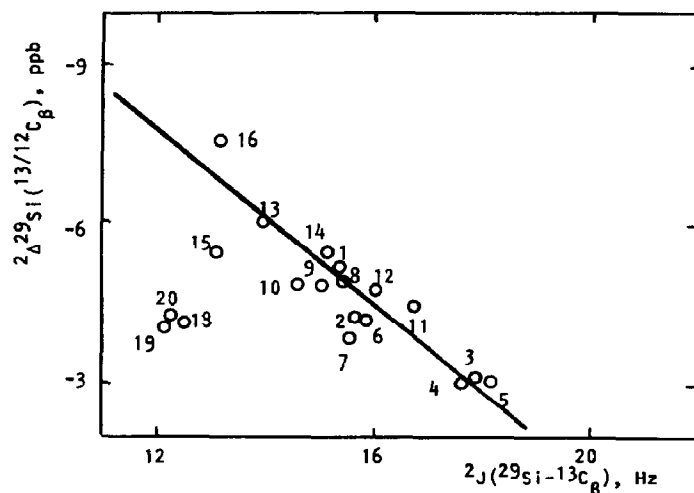

Fig. 3. The relationship between the two-bond isotope shifts $^2\Delta\,^{29}\mathrm{Si}(^{13/12}C_\beta)$ and coupling constants $^2J(^{29}\mathrm{Si}-^{13}C_\beta)$ in the ethynylsilanes $(CH_3)_3SiC_\alpha{\equiv}C_\beta X$. The numbering of the compounds corresponds to that in Table 1.

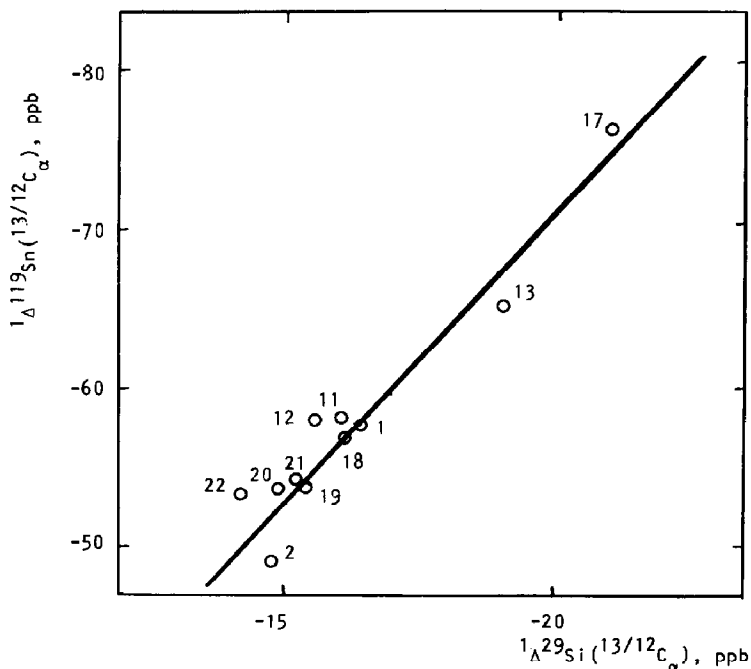Fig. 4. The correlation between one-bond $^1\Delta$ M$(^{13/12}$C) isotope shifts in the ^{29}Si and ^{119}Sn NMR spectra of isostructural acetylenes $(CH_3)_3MC_\alpha{\equiv}C_\beta X$ (M $= ^{29}$Si, ^{119}Sn). The numbering of the compounds corresponds to that in Table 1.

The increase in the $^nJ(^{29}$Si$-^{13}$C) coupling constants is associated with the decrease in the $^n\Delta$ ^{29}Si$(^{13/12}$C) isotope shifts. That the isotope shifts and the coupling constants, under the influence of substituent X, are inversely related has also been found previously [25].

The points for the compounds with X = MR$_3$ (M = Si, Ge, Sn) do not obey relationships 7 and 8. An analogous phenomenon in the ethynylstannanes has been explained in terms of concurrent hyperconjugation of MR$_3$ substituents with the triple bond [28]. For instance, the disubstituted Group IVB acetylenides R$_3$MC≡CM′R$_3$ form a separate class of compounds whose properties differ considerably from those of other studied acetylenides. These differences fall in the sequence: Sn > Ge > Si, which corresponds to the probable order of decreasing hyperconjugation.

As has been already found for ethynylstannanes [25], substituent X in ethynylsilanes elicits similar changes in isotope shifts both across one $^1\Delta$ ^{29}Si$(^{13/12}$C$_\alpha)$ and two $^2\Delta$ ^{29}Si$(^{13/12}$C$_\beta)$ bonds:

$$^1\Delta\ ^{29}\mathrm{Si}\left(^{13/12}\mathrm{C}_\alpha\right) = -7.63 + 1.8\ ^2\Delta\ ^{29}\mathrm{Si}\left(^{13/12}\mathrm{C}_\beta\right) \qquad (r = 0.973,\ n = 19) \qquad (9)$$

Isotope shifts $^1\Delta$ ^{29}Si$(^{13/12}$C$_\alpha)$ in the ^{29}Si NMR spectra of ethynylsilanes reveal the same tendencies as the $^1\Delta$ ^{119}Sn$(^{13/12}$C$_\alpha)$ values in the ^{119}Sn NMR spectra of ethynylstannanes (Fig. 4):

$$^1\Delta\ ^{119}\mathrm{Sn}\left(^{13/12}\mathrm{C}_\alpha\right) = 0.59 + 3.61\ ^1\Delta\ ^{29}\mathrm{Si}\left(^{13/12}\mathrm{C}_\alpha\right) \qquad (r = 0.966,\ n = 11) \qquad (10)$$

The latter correlation suggests that the changes in the isotope shifts are uniform regardless of the type of resonance of the central atom in the Group IVB acetylenides.

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