Determination of Absolute Signs of $^{119}$Sn–$^{117}$Sn Spin–Spin Coupling Constants

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If for a given system two-dimensional (2D) $^{119}$Sn/$^1$H heteronuclear shift correlations can be established for long range coupling constants $J^{(119}\text{Sn},^1\text{H})$ ($n = 4$, 6), absolute signs of coupling constants $J$(Sn,Sn) are accessible by this technique for the first time. This has been demonstrated for tetrakis(trimethylstannyl)allene (1) with $J^{(119}\text{Sn},^1\text{H})$ ($>0$) and $J^{(117}\text{Sn},^1\text{H})$ ($<0$), and for tris(trimethylstannyl)phosphane (2) and bis(trimethylstannyl)sulfane (3) with $J^{(119}\text{Sn},^1\text{H})$ ($<0$).

There is a wealth of molecules containing two or more tin atoms and, consequently, numerous coupling constants $J$(Sn,Sn) have been measured from $^{119}$Sn NMR spectra [1]. The presence of the $^{117}$Sn isotope with $I = 1/2$ with an appreciable natural abundance (7.61%) makes it possible to measure $J^{(119}\text{Sn},^{117}\text{Sn})$ also for chemically equivalent tin atoms. However, the magnitude of $|J^{(119}\text{Sn},^{117}\text{Sn})|$ without knowing the coupling sign has only a limited diagnostic value. Except for a few examples with $n = 1$ [2] and 2 [3, 4], absolute signs of $J$(Sn,Sn) have not been determined. In the case of one-bond and geminal Sn–Sn couplings, it has been shown that the sign may easily change which points to the fact that the determination of the coupling sign is essential for a meaningful discussion of this parameter. Here we propose a simple approach to solve the problem of sign determination of many Sn–Sn coupling constants, by using 2D heteronuclear $^{119}$Sn/$^1$H shift correlations.

Considering the nuclear magnetic moment and the valence s electron density of $^{119}$Sn or $^{119}$Sn one can expect unresolved small long range coupling constants $J$(Sn,H) ($n > 3$) of the type $^{119}$Sn$\sim \sim$Sn$\sim$H in many organotin compounds. If 2D heteronuclear $^{119}$Sn/$^1$H shift correlations can be based on such long range $^{119}$Sn/$^1$H coupling constants, the desired information on the sign of coupling constants $J$(Sn,Sn) is becoming accessible by detecting the tilt of the cross peaks in both dimensions [5]. The principle is shown in Scheme 1, and an instructive example is given in Figure 1 for tetrakis(trimethylstannyl)allene (1). Further examples studied are tris(trimethylstannyl)phosphane (2) and bis(trimethylstannyl)sulfane (3).

Scheme 1. Relevant isotopomers of any compound containing two tin atoms for the comparison of signs of coupling constants $J^{(119}\text{Sn},^1\text{H})$ and $J^{(117}\text{Sn},^1\text{H})$, as indicated by the dashed lines; drawn lines mark the path of polarization transfer.

In the case of isotopomer A, the 2D $^{119}$Sn/$^1$H shift correlation is straight-forward since it is based on the fairly large coupling constants $J^{(119}\text{Sn},^1\text{H})$. However, only relative signs of $J^{(119}\text{Sn},^{117}\text{Sn})$ and $J^{(117}\text{Sn},^1\text{H})$ are obtained since the sign of the $J^{(117}\text{Sn},^1\text{H})$ is a priori unpredictable. Furthermore, the expected small values of $|J^{(n\geq 2)}(117\text{Sn},^1\text{H})|$ (<1.5 Hz) require a high digital resolution in $F_1$ ($^1$H) in order to identify the tilt of the corresponding cross peaks. In the case of A, the sign of $J^{(119}\text{Sn},^1\text{H})$ is known ($>0$, reduced coupling constant $\Delta K^{(119}\text{Sn},^1\text{H}) < 0$ [6], with very few and well defined exceptions [7]), and therefore, the comparison with the sign of $J^{(119}\text{Sn},^{117}\text{Sn})$ reveals the absolute sign of the latter coupling. This 2D experiment requires only a
low digital resolution in $F_1$ since the cross peaks are now separated by $2J(117\text{Sn},1\text{H})$ ($\approx 40$ to 80 Hz). However, it should be noted that the sensitivity of the 2D experiment for A is lower than for B owing to loss of transverse magnetization during the longer delays in the pulse sequence.

Tetrakis(trimethylstannyl)allene (1) is a very useful compound to demonstrate the meaningfulness of the 2D experiment involving the isotopomer A: (i) The principles of this approach are demonstrated both for $2J(119\text{Sn},1\text{H}) (+227.7\text{ Hz})$ and for $4J(119\text{Sn},117\text{Sn}) (-252.0\text{ Hz})$; (ii) the experiment shows that the signs of these coupling constants are opposite but the absolute magnitudes are comparable; (iii) it appears that long range couplings $6J(119\text{Sn},1\text{H})$ even for $n = 6$ can be exploited, although the allene system may be a special case. Figure 1 shows the result of the $119\text{Sn}/1\text{H}$ shift correlation for 1, based on an assumed coupling constant $4J(119\text{Sn},1\text{H}) = 1\text{ Hz}$, by using the most simple pulse sequence [8]. Figure 1 shows cross peaks for all possible $119\text{Sn},117\text{Sn}$ isotopomers. There are also same cross peaks for $119\text{Sn},13\text{C}$ isotopomers, but these are not shown in Figure 1. The apparently enhanced intensity of cross peaks with small tilt or no tilt arises from unsuppressed polarization transfer via the geminal coupling $2J(119\text{Sn},1\text{H})$. The tilt of all these cross peaks should be discussed with respect to the reduced coupling constants $K$ $[K(\text{A},\text{B}) = 4\pi^2 \cdot J(\text{A},\text{B}) (\gamma_A \cdot \gamma_B / \hbar)]$ because of the negative sign of $\gamma(117\text{Sn})$ and $\gamma(119\text{Sn})$. Cross peaks separated by $2J(119\text{Sn},1\text{H})$ in $F_1$ relate the signs of $2K(119\text{Sn},1\text{H})$ and $4K(119\text{Sn},117\text{Sn})$ (negative tilt), and of $2K(119\text{Sn},1\text{H})$ with $4K(119\text{Sn},117\text{Sn})$ (positive tilt), respectively. The intensity of the $117\text{Sn}$ satellites in the 1D $119\text{Sn}$ NMR spectrum [9] of 1 shows that the larger value $|J(\text{Sn},\text{Sn}))|$ belong to $4J(\text{Sn},\text{Sn})$. It turns out that $2J(119\text{Sn},117\text{Sn})$ has a positive sign, whereas the sign of $4J(119\text{Sn},117\text{Sn})$ is negative. Cross peaks relating $6K(119\text{Sn},1\text{H})$ and $4K(119\text{Sn},117\text{Sn})$ are probably not tilted since $6J(119\text{Sn},1\text{H})$ could not be resolved. The cross peaks arising from $4K(119\text{Sn},1\text{H})$ and $2K(119\text{Sn},117\text{Sn})$ show a negative tilt since $4J(119\text{Sn},1\text{H}) (1.2\text{ Hz})$ is slightly greater than the digital resolution in $F_1$ which, in this particular experiment, was set deliberately to a rather high value ($0.5\text{ Hz/pt}$). This proves that $4K(119\text{Sn},1\text{H})$ and $2K(119\text{Sn},117\text{Sn})$ are of opposite sign, and since $2K(119\text{Sn},117\text{Sn}) > 0$ it follows that $4K(119\text{Sn},1\text{H}) < 0$ $[4J(119\text{Sn},1\text{H}) > 0]$.

To give two further examples, we have examined P(SnMe$_3$)$_3$ (2) and S(SnMe$_3$)$_2$ (3), using $4J(119\text{Sn},1\text{H})$ in the $119\text{Sn}/1\text{H}$ heteronuclear shift correlations. This revealed in both cases that $2J(119\text{Sn},117\text{Sn}) < 0$ ($2: -315.4\text{ Hz}; 3: -206.2\text{ Hz}$) and that $1J(119\text{Sn},31\text{P}) > 0$ (+832.0 Hz) $[4K(119\text{Sn},31\text{P}) < 0]$, in agreement with the literature [10].

The large data set known in particular for geminal Sn–Sn coupling constants accumulated in the literature [1] can be extended by this method of

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**Fig. 1. 186.5 MHz 2D Heteronuclear $119\text{Sn}/1\text{H}$ shift correlation of tetrakis(trimethylstannyl)allene (1) [spectral windows were 600 Hz in $F_2$ ($117\text{Sn}$) for 2 K data points and 60 Hz in $F_1$ ($1\text{H}$) for 128 experiments each with 32 transients; recycle time 3 s; 6 h of spectrometer time; zero filling and Gaussian multiplication in both dimensions]. The $117\text{Sn}$ satellites in $F_1$ and $F_2$ are marked by arrows (an impurity is marked by an asterisk). The relative intensities of the $117\text{Sn}$ satellites in the 1D $119\text{Sn}$ NMR spectrum are almost opposite to those from the projection in $F_2$ and it is due to the delays in the 2D experiment [1/2 $J = 0.5\text{ s}$ and $0.11/J = 0.11\text{ s}$] which were based on the approximate magnitude of $4J(119\text{Sn},1\text{H})$ rather than on the presumably very small magnitude of $6J(119\text{Sn},1\text{H})$, making the polarization transfer via $6J(119\text{Sn},1\text{H})$ much less efficient.**
coupling sign determination, using standard NMR equipment and running the simple 2D heteronuclear $^{119}\text{Sn}/^1\text{H}$ shift correlations as routine measurements. This will stimulate the application of $^2J(\text{Sn,Sn})$ data to the assignment of molecular and electronic structure.

**Experimental**

The compound 1 [11], 2 [12] and 3 [13] were prepared as described elsewhere. Solutions in C$_6$D$_6$ (ca. 5–10%) in 5 mm tubes were used for the NMR measurements. All spectra were measured at 25 ± 1 °C using a Bruker AM 500 spectrometer equipped with with a 5 mm quadruple probe head ($^1\text{H}$, $^{13}\text{C}$, $^{31}\text{P}$, $^{15}\text{N}$). The range for $^{31}\text{P}$ was also tunable to $^{119}\text{Sn}$ (pulse widths for 90° pulses: $^1\text{H}$: 11 µs, $^{119}\text{Sn}$: 6.5 µs; see also Fig. 1).

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