$^{13}C\{^1H$, SELECTIVE $^{119}Sn\}$ NMR EXPERIMENT AS A TOOL FOR DETERMINATION AND ASSIGNMENT OF $^nJ(^{119}Sn, ^{13}C)$ COUPLING CONSTANTS

Antonín LYČKA[a1] and Jaroslav HOLEČEK[b]
[a]Research Institute for Organic Syntheses, CZ–532 18 Pardubice,
[b]Department of General and Inorganic Chemistry,
The University of Pardubice, CZ–532 10 Pardubice

$^{13}C\{^1H$, selective $^{119}Sn\}$ NMR experiment is an effective one-dimensional technique for determination and assignment of $^nJ(^{119}Sn, ^{13}C)$ coupling constants in organotin compounds containing two or more tin atoms in a molecule. Signals of ^{119}Sn satellites are decoupled and, thus, "removed" from the ^{13}C NMR spectra. For one-bond tin-carbon coupling constants, only $^1J(^{117}Sn, ^{13}C)$ coupling constants are visible while for much smaller long-range tin-carbon coupling constants, for which ^{119}Sn and ^{117}Sn satellites are not separated, relative integral intensities are reduced approximately to a half with respect to those carbons for which selective ^{119}Sn decoupling is not effective.

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[1] To whom correspondence should be addressed.

Introduction

NMR spectroscopy is undoubtedly a very important tool for characterisation of organotin(IV) derivatives due to very favourable NMR properties of two most frequently measured nuclei: ^{119}Sn and ^{117}Sn. It is, thus, not surprising that ^{1}H and ^{119}Sn NMR spectra of organotin compounds have been studied successfully for many years [1,2]. Early reviews published by Petrosyan [3], Smith [4,5] and Kennedy [6] were focussed on ^{1}H and ^{119}Sn chemical shifts, and also $^nJ(^{119}$Sn,^{1}H) coupling constants in simple (preferably methyl) compounds were reported. In line with a considerable improvement of NMR spectrometers sensitivity and resolution it started to be possible to measure NMR spectra of less abundant and low sensitive nuclei and, consequently, due to the relatively high natural abundance of ^{119}Sn and ^{117}Sn isotopes, to determine various $^nJ(^{119}$Sn, X) coupling constants (e.g., X = ^{119}Sn, ^{13}C, ^{31}P, ^{15}N, etc., for n being. 1-5). Typical values of both ^{119}Sn chemical shifts in more complicated compounds as well as various $^nJ(^{119}$Sn, X) coupling constants can be found in review paper [7]. Application of more sophisticated two-dimensional heteronuclear correlation experiments allowed determining both relative and absolute sign of various coupling constants. The data are collected in a review published by Wrackmeyer [8], who, with his co-workers, has determined most of known data using wide variety of 2D NMR techniques. Willem and co-workers [9] have published a review on application of gradient-selected ^{1}H-^{119}Sn HMQC spectra in organotin compounds studies.

A huge amount of ^{119}Sn chemical shifts and various $^nJ(^{119}$Sn, X) coupling constants can be found in the literature. It is very difficult to estimate an exact proportion but, undoubtedly, strongly predominant part of these data have been determined by measuring organotin compounds containing only one tin atom in a molecule. In molecules having *several* tin atoms in a molecule, there is a custom to publish a list of ^{119}Sn chemical shifts without any assignment or with a tentative assignment of tin resonances only. It would be desirable to have techniques for an undoubted assignment of tin resonances as well as various $^nJ(^{119}$Sn, X) coupling constants in compounds containing two or more tin atoms per molecule. For example, there are only two papers [10,11] utilising ^{13}C-^{119}Sn HMQC spectra for differentiation of tin resonances and $^nJ(^{119}$Sn, ^{13}C) coupling constants in relatively simple compounds where other NMR techniques failed. 3D ^{1}H-^{13}C-^{119}Sn NMR spectra were also measured [12] for the same purpose.
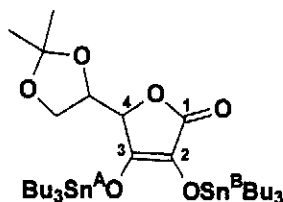
Experimental

Tetramethylstannane and tributylstannyl chloride were commercial products. Bis(tributylstannyl(IV)) *O*-5,6-isopropylidene-L-(+)-ascorbate (*1*) was prepared as described previously [11].

The ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Bruker AVANCE 500 spectrometer at 500.13, 125.76 and 186.52 MHz, respectively, using 5 mm triple ^{1}H/^{13}C/broad band probe. WALTZ-16 decoupling was used for protons and continuous-wave decoupling for ^{119}Sn (35 dB attenuation). The compounds were dissolved in deuteriochloroform (ca 30 % solutions) and NMR spectra were measured at room temperature.

Results and Discussion

An application of gradient-selected one- and two-dimensional ^{1}H-^{119}Sn HMQC spectra in organotin compounds studies can be used for the assignment of tin resonances in mixtures of organotin compounds as shown in an excellent review by Willem and co-workers [9] This technique allows to determine appropriate $^nJ(^{119}$Sn, ^{1}H) coupling constants. ^{1}H-^{119}Sn J-HMBC experiment [13] provides spectroscopists with the possibility to determine $^nJ(^{119}$Sn, ^{1}H) coupling constants lower than 1 Hz.

Gradient-selected one- and two-dimensional ^{1}H-^{119}Sn HMQC spectra can also be used for the assignment of tin resonances in organotin compounds containing two and more tin atoms per molecule. We applied successfully this technique in differentiation of two tin resonances in bis(tributylstannyl(IV)) O-5,6-isopropylidene-L-(+)-ascorbate (1) [11]. The tin resonances at 146.0 (Sn^A) and 118.6 (Sn^B) ppm were assigned [11].

Most carbons in compound 1 possess $^nJ(^{119}$Sn, ^{13}C) and $^nJ(^{117}$Sn, ^{13}C) coupling constants with both Sn^A and Sn^B atoms. For an unambiguous assignment of $^nJ(^{119}$Sn, ^{13}C) coupling constants in compound 1, two-dimensional ^{13}C-^{119}Sn HMQC experiment with proton-noise decoupling was used. The application of this experiment was successful, however, the necessary time for accumulation was about 80 hours [11] regardless of the fact that we used only 8 increments in F1 (with appropriate folding along F1 in order to improve digital resolution). This technique is, however, not applicable for molecules with higher molecular mass or molecules having low solubility.

We propose to use a simple one-dimensional ^{13}C{^{1}H, selective ^{119}Sn} NMR experiment to solve the problem in a considerably shorter experimental time since

only one experiment per one tin can be used instead of several experiments (increments) in F1 domain. In principle, this experiment is an analogy, e.g., with ^{13}C{^{1}H, selective ^{31}P} one[14], however, a considerable difference between these techniques consists in the fact that phosphorus-31 is the only naturally abundant nucleus and an appropriate doublet observable in a standard ^{13}C NMR spectrum due to J(^{31}P, ^{13}C) coupling constant collapses completely into a singlet in ^{13}C{^{1}H, selective ^{31}P} experiment while in organotin compounds ^{13}C signal bound to NMR non-active tin nuclei (tin has ten naturally abundant isotopes[15]) as well as satellites due to $J(^{117}$Sn, ^{13}C) coupling constant are retained and only doublet due to $J(^{119}$Sn, ^{13}C) coupling constant collapses and, thus, the measurement is much more time consuming compared with that for organophosphorus compounds, and interpretation of results is more complicated.

Figure 1 shows a standard ^{13}C NMR spectrum (bottom trace) of tetramethyl-stannane, where $^1J(^{119}$Sn, ^{13}C) and $^1J(^{117}$Sn, ^{13}C) coupling constants are very well separated and ^{13}C{^{1}H, selective ^{119}Sn} (upper trace) NMR spectrum in which $^1J(^{119}$Sn, ^{13}C) is decoupled and, thus, "removed" from the ^{13}C NMR spectrum and only $^1J(^{117}$Sn, ^{13}C) is visible since ^{117}Sn nucleus behaves as a real passive one.
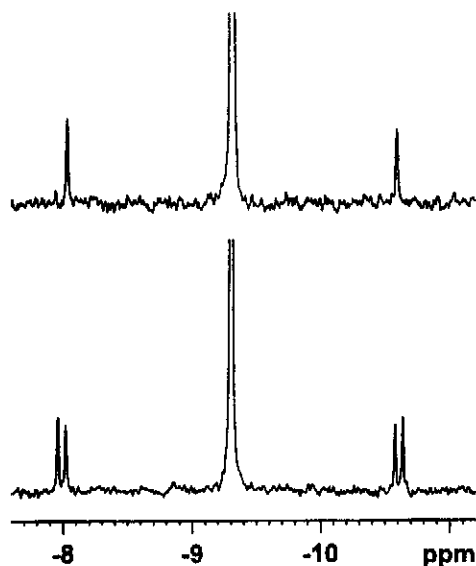

Fig. 1 Standard ^{13}C NMR spectrum (bottom trace) and ^{13}C{^{1}H, selective ^{119}Sn} NMR spectrum (upper trace) of tetramethylstannane

For much smaller long-range tin-carbon coupling constants in tributylstannyl chloride (Fig. 2), for which ^{119}Sn and ^{117}Sn satellites are not separated for C-2 carbon, relative integral intensities of satellites with respect to the central line are about 4 –

5 % (within an experimental error) compared with ca 8-9 % (within experimental error) in standard ^{13}C NMR spectrum due to the natural abundance of ^{119}Sn (8.6%) and ^{117}Sn (7.6%) nuclei. The two above-mentioned model compounds have only one tin atom in a molecule.

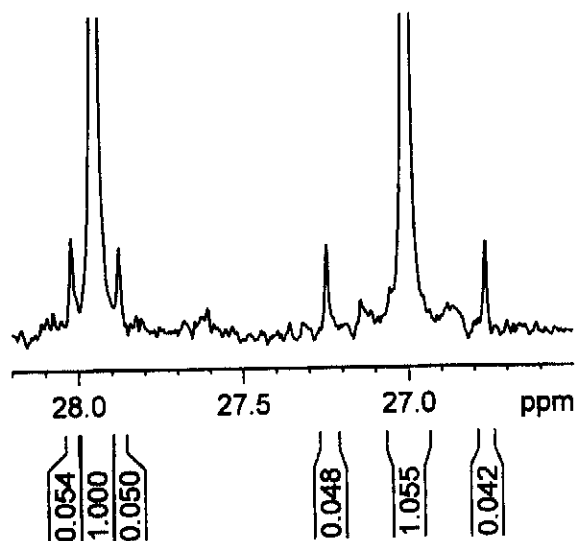Fig. 2 ^{13}C{^{1}H, selective ^{119}Sn} NMR spectrum of SnCH$_2$ *CH$_2$* and SnCH$_2$ CH$_2$ *CH$_2$* groups in tributylstannyl chloride and integral intensities of tin satellites

Figure 3 shows signals of SnCH$_2$ groups in ^{13}C{^{1}H, selective ^{119}Sn^{B}} NMR spectrum of bis(tributylstannyl(IV)) O-5,6-isopropylidene-L-(+)-ascorbate (*I*) having Sn^{A} and Sn^{B} atoms in which $^{1}J(^{119}$Sn^{B}, ^{13}C) is decoupled ($\delta(^{13}$C) = 17.71) and, thus, only $^{1}J(^{117}$Sn, ^{13}C) is visible for C-Sn^{B} while both $^{1}J(^{119}$Sn, ^{13}C) and $^{1}J(^{117}$Sn, ^{13}C) coupling constants can be seen for C-Sn^{A} ($\delta(^{13}$C) = 17.80).

The differentiation of Sn^{A}CH$_2$ *CH$_2$* vs. Sn^{B}CH$_2$ *CH$_2$* ($\delta(^{13}$C) = 27.44 vs. 27.67) Sn^{A}CH$_2$ CH$_2$ *CH$_2$* vs. Sn^{B}CH$_2$ CH$_2$ *CH$_2$* ($\delta(^{13}$C) = 26.83 vs. 26.94) groups follows from Fig. 4. The intensity of tin satellites for carbons belonging to selectively decoupled Sn^{B} tin atom is approximately a half compared with that for non-decoupled Sn^{A} one and this effect is clearly visible in the spectrum even without integration. The time necessary for performing this experiment compared with ^{13}C-^{119}Sn HMQC experiment with proton-noise decoupling [11] was reduced ca ten times.

The ^{13}C{^{1}H, selective^{119}Sn} NMR technique is an one-dimensional experiment with direct detection having disadvantages and advantages of such a type of experiments, i.e., low sensitivity (which can be easily improved by implementing selective ^{119}Sn decoupling into experiments with polarisation transfer (INEPT or DEPT)), and, on the other hand, good digital resolution (it is possible to distinguish
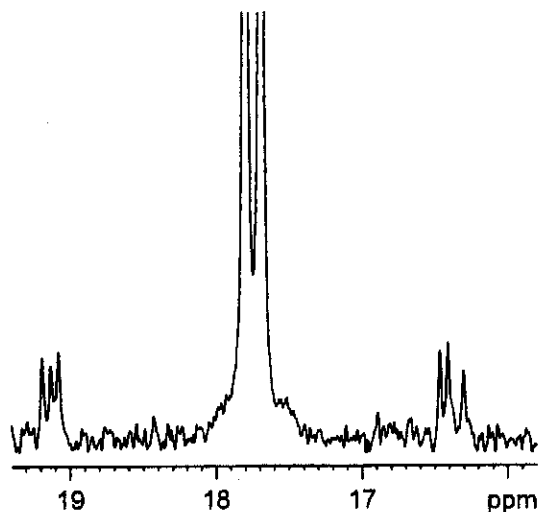
Fig. 3 $^{13}C\{^1H, \text{selective } ^{119}Sn^B\}$ NMR spectrum of $SnCH_2$ groups in bis(tributylstannyl(IV) O-5,6-isopropylidene-L-(+)-ascorbate (1)

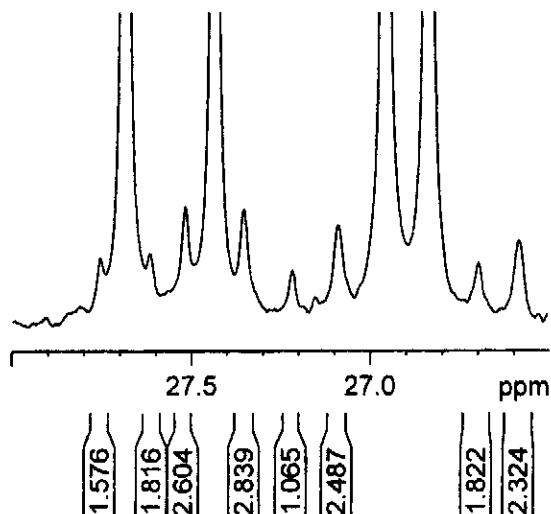Fig. 4 $^{13}C\{^1H, \text{selective } ^{119}Sn^B\}$ NMR spectrum of $SnCH_2$ CH_2 and $SnCH_2$ CH_2 CH_2 groups in bis(tributylstannyl(IV) O-5,6-isopropylidene-L-(+)-ascorbate (1) and integral intensities of tin satellites

carbons of $SnCH_2$ groups in $^{13}C\{^1H, \text{selective } ^{119}Sn\}$ NMR spectrum of bis(tributyl-stannyl(IV)) O-5,6-isopropylidene-L-(+)-ascorbate (1) differing in 0.09 ppm only (see Fig. 4).

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The $^{13}C\{^1H$, selective $^{119}Sn\}$ NMR experiments shown in Figs 1-4 were performed using a standard 5-mm triple $^1H/^{13}C$/broad band probe for which the sensitivity of selective ^{13}C channel for direct observation of ^{13}C NMR spectrum is not too high. A higher sensitivity would be achievable the experiment being performed using either $^1H/^{119}Sn$/broad band probe or, even better, a probe allowing ^{13}C direct detection and proton-noise and selective ^{119}Sn decoupling.

The $^{13}C\{^1H$, selective $^{119}Sn\}$ NMR experiment can be used for assignment of carbon atoms and $^nJ(^{119}Sn, ^{13}C)$ in compounds containing two or more tin atoms in a molecule or in a mixture of organotin compounds having approximately the same population. Good digital resolution in this experiment allows to distinguish undoubtedly carbons differing by several hundredth in ^{13}C chemical shifts only, which can hardly be possible in 2D experiments.

Acknowledgements

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