NMR spectra and isotope analysis of hexaethyldistannane

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The $^{13}C—\{^1H\}$ and $^{119}Sn—\{^1H\}$ NMR spectra of hexaethyldistannane were measured and analyzed using an iteration program for the calculation of the complete line shape with correction of a residual inhomogeneity of the magnetic field and phase distortions. Signals of 22 isotopomers containing magnetic isotopes of tin and carbon in different pairwise and triple combinations were identified, and their spectral parameters were determined. The content of isotopes ^{119}Sn, ^{117}Sn, and ^{115}Sn in the molecule was determined with a high accuracy sufficient for the study of isotope effects in chemical reactions.

Key words: organotin compounds, isotope analysis, NMR spectroscopy, isotope effects.

To study magnetic isotope effects on tin nuclei ^{119}Sn, ^{117}Sn, and ^{115}Sn in photolysis reactions of organotin compounds (Eq. (1)), we developed a procedure of highly precise determination of the isotope composition of organotin molecules from high-resolution NMR spectra on ^{13}C and ^{1}H nuclei.**1**

$$2\,RSnR'_3 \rightarrow R—R + R'_3Sn—SnR'_3, \qquad (1)$$

where R = Ar, CH_2Ar; R′ = Me, Et.

High (by absolute value) direct spin coupling constants (SCC) of magnetic tin isotopes with ^{13}C nuclei, which are distinctly seen in spectra, make it possible to easily reveal changes in the isotope composition in reaction products and starting compounds. However, the accuracy of standard procedures of computer integration on modern NMR spectrometers, being about 1—2% for nonoverlapping signals if their integral intensities differ by at most an order of magnitude, turned out to be insufficient for our purposes. Applying the INSPECT2 iteration program for analysis of the complete line shape in spectra, which has been developed by us previously and allows the efficient correction of a residual inhomogeneity of the magnetic field and phase distortions of spectral lines to perform,**2** we showed that accuracy and reproducibility of results of isotope analysis are not worse than 0.05% at a high signal/noise ratio (S/N ≥ 10000) in the ^{13}C NMR spectra of model organotin compounds. The problem becomes more complicated for analysis of spectra of distannanes that are photolysis products. Their spectra manifest long-range constants of spin coupling of ^{13}C nuclei with magnetic tin isotopes through two and three bonds $^2J(C—Sn—Sn)$ and $^3J(C—C—Sn—Sn)$, which can be low by absolute value. As a result, the corresponding signals of isotopomers with magnetic tin isotopes in the form of doublets fall on the base of signals belonging to isotopomers containing no magnetic tin isotopes and overlap with them, thus decreasing the accuracy of iteration analysis. Taking into account these satellites, one has to determine independently long-range SCC from NMR spectra on tin nuclei. In this report, we present the spectral parameters of hexaethyldistannane obtained by the complete analysis of the ^{13}C and ^{119}Sn NMR spectra of this compound.

Experimental

Spectra were recorded on a Bruker AVANCE-600 spectrometer at a working frequency of 150.902 MHz for ^{13}C and on a Bruker DPX-300 spectrometer at 111.82 MHz for ^{119}Sn. A 30% solution of hexaethyldistannane (Aldrich) in benzene-d_6 (Merck) with a deuterium content of 99.9% was used. The substance and solvent were distilled prior to measurements, distilled in a vacuum line into a measuring NMR sample tube, and thoroughly degassed by a multiply repeated cycle of freezing with liquid nitrogen—evacuation—thawing out, after which the sample tube was sealed *in vacuo*. Measurements were carried out without sample spinning to avoid the appearance of spinning side bands. Chemical shift values are presented relatively to Me_4Si (^{13}C) and Me_4Sn (^{119}Sn). Pulses of 90° were used, and the pulse dura-

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tion was 10 and 9 μs for ^{13}C and ^{119}Sn nuclei, respectively. The signal/noise ratio for accumulation was 7200 : 1 for the main signal and 390 : 1 for ^{13}C—^{119}Sn satellites in ^{13}C NMR spectra and 8200 : 1 in ^{119}Sn NMR spectra. In both cases, a WALZ-16 pulse sequence was used for the broad-band proton decoupling.

Results and Discussion

The ^{13}C—{^{1}H} NMR spectrum of hexaethyldistannane (Fig. 1, *a*) contains a signal of the carbon atoms of the methylene group in a high field, and the most intense

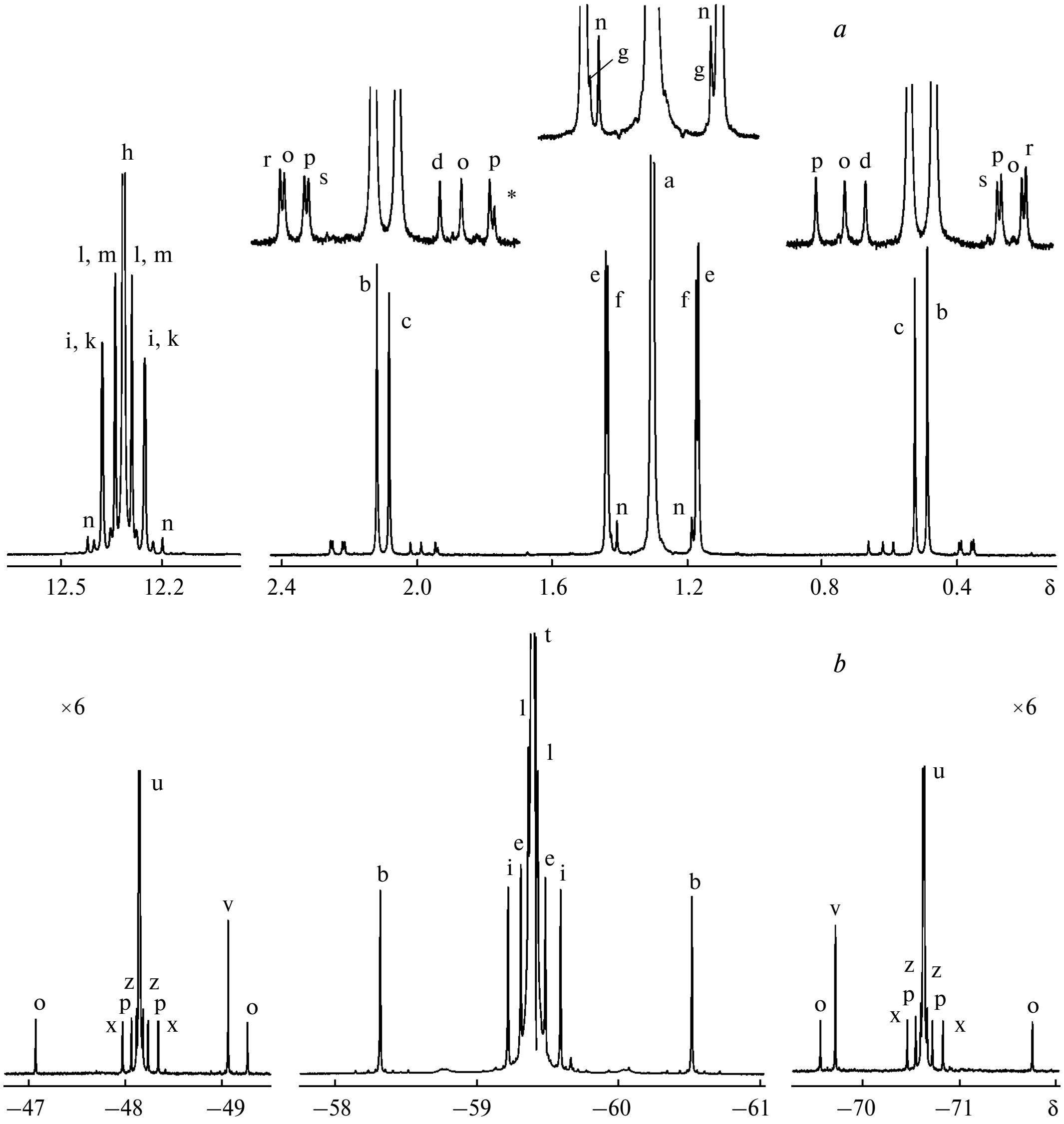

Fig. 1. ^{13}C—{^{1}H} (*a*) and ^{119}Sn—{^{1}H} (*b*) NMR spectra of hexaethyldistannane.

Symbol	Isotopomer
a	C—$^{13}\underline{C}$—Sn—Sn—C—C
b	C—$^{13}\underline{C}$—$^{119}\underline{Sn}$—Sn—C—C
c	C—$^{13}\underline{C}$—$^{117}\underline{Sn}$—Sn—C—C
d	C—$^{13}\underline{C}$—$^{115}\underline{Sn}$—Sn—C—C
e	C—$^{13}\underline{C}$—Sn—$^{119}\underline{Sn}$—C—C
f	C—$^{13}\underline{C}$—Sn—$^{117}\underline{Sn}$—C—C
g	C—$^{13}\underline{C}$—Sn—$^{115}\underline{Sn}$—C—C
h	$^{13}\underline{C}$—C—Sn—Sn—C—C
i	$^{13}\underline{C}$—C—$^{119}\underline{Sn}$—Sn—C—C
k	$^{13}\underline{C}$—C—$^{117}\underline{Sn}$—Sn—C—C
l	$^{13}\underline{C}$—C—Sn—$^{119}\underline{Sn}$—C—C
m	$^{13}\underline{C}$—C—Sn—$^{117}\underline{Sn}$—C—C
n	$^{13}\underline{C}$—$^{13}\underline{C}$—Sn—Sn—C—C
o	C—$^{13}\underline{C}$—$^{119}\underline{Sn}$—$^{117}\underline{Sn}$—C—C
p	C—$^{13}\underline{C}$—$^{117}\underline{Sn}$—$^{119}\underline{Sn}$—C—C
r	C—$^{13}\underline{C}$—$^{119}\underline{Sn}$—$^{119}\underline{Sn}$—C—C
s	C—$^{13}\underline{C}$—$^{117}\underline{Sn}$—$^{117}\underline{Sn}$—C—C
t	C—C—$^{119}\underline{Sn}$—Sn—C—C
u	C—C—$^{119}\underline{Sn}$—$^{117}\underline{Sn}$—C—C
v	C—C—$^{119}\underline{Sn}$—$^{115}\underline{Sn}$—C—C
x	$^{13}\underline{C}$—C—$^{119}\underline{Sn}$—$^{117}\underline{Sn}$—C—C
y	C—C—$^{119}\underline{Sn}$—$^{117}\underline{Sn}$—C—$^{13}\underline{C}$
*	

Note. Letter symbols designate signals of isotopomers; asterisk designates the signal of the admixture.

singlet in its center belongs to isotopomers containing no magnetic tin isotopes. Three pairs (e, f, g) of doublet satellites closest to this signal belong to isotopomers containing magnetic tin isotopes in a remote position and appear due to the SCC ^2J(C—Sn—Sn). The fourth pair (n) belongs to isotopomers containing no magnetic tin isotopes but having two ^{13}C isotopes in adjacent positions. Three pairs of most remote doublets appear due to the SCC ^1J(C—Sn) and are accompanied, in turn, by satellites belonging to molecules containing two magnetic tin isotopes in different combinations.

The signal of the carbon atoms of the methyl groups in a lower field (δ ~1.23) has a more complex shape due to line overlapping. However, this signal can easily be analyzed and all parameters can be determined with high accuracy using the SCC obtained from the ^{119}Sn NMR spectrum (see Fig. 1, *b*). For the indicated signal/noise ratios, signals of 22 isotopomers containing magnetic tin and carbon isotopes in different pairwise and triple combinations can be identified reliably in both spectra. The assignment of these signals are presented in Fig. 1. The chemical shifts and SCC are given in Table 1.

It should be mentioned that the isotope chemical shifts of the ^{13}C nuclei of the methylene groups are low, being upfield and about 0.02 Hz (0.033 ppb) per mass unit. Since the central signal is a superposition of the spectra of all isotopomeric molecules containing non-magnetic tin isotopes (^{112}Sn, ^{114}Sn, ^{116}Sn, ^{118}Sn, ^{120}Sn, ^{122}Sn,^{124}Sn), its position cannot be used unambiguously to determine isotope shift values. Therefore, the above estimate was obtained by a comparison of the chemical shifts of isotopomers containing the ^{119}Sn nuclei with the chemical shifts of isotopomers with the ^{117}Sn and ^{115}Sn nuclei. A low natural content of ^{115}Sn decreases an estimation accuracy in this case. The geminal isotope shift of the carbon atom of the methyl groups is still lower and, most likely, negative, as we found for tetraethyltin**[1]** and the authors**[3]** mentioned for geminal isotope effects on other nuclei. The isotope shift of the ^{13}C nuclei of the methylene groups is more pronounced when carbon in the methyl group is substituted by the ^{13}C isotope (see Table 1).

Table 1. Chemical shifts and spin-spin coupling constants in the ^{13}C NMR spectrum of hexaethyldistannane

δ_C	SCC	J_{C-Sn}/Hz	Δ*/Hz
1.30 (CH$_2$)	^1J(C—^{119}Sn)	246.16 (0.02), 246.18 (0.02)**	
	^1J(C—^{117}Sn)	235.23 (0.02), 235.24***	$^{117}\Delta = 0.09 \pm 0.04$
	^1J(C—^{115}Sn)	215.99 (0.02), 216.00***	$^{115}\Delta = 0.04 \pm 0.04$
	^2J(C—^{119}Sn)	41.45 (0.02)**, 41.46 (0.02)	
	^2J(C—^{117}Sn)	39.61***, 39.62 (0.02)	$^{117}\Delta = -0.01 \pm 0.04$
	^2J(C—^{115}Sn)	36.37***, 36.40 (0.02)	$^{115}\Delta = 0.02 \pm 0.04$
	^1J(C—C)	33.44 (0.02)	$\Delta = -1.01 \pm 0.03$
12.31 (CH$_3$)	^2J(C—^{119}Sn)	19.40 (0.02)**	
	^2J(C—^{117}Sn)	18.53***	
	^2J(C—^{115}Sn)	17.02***	
	^3J(C—^{119}Sn)	7.59 (0.02)**	
	^3J(C—^{117}Sn)	7.25***	
	^3J(C—^{115}Sn)	6.66***	

* Isotope shifts were determined with respect to ^{119}Sn.

** From the ^{119}Sn NMR spectrum.

*** Determined through the gyromagnetic ratio.

Table 2. Chemical shift and spin-spin coupling constants in the ^{119}Sn NMR spectrum of hexaethyldistannane

δ_{Sn}	SCC	J_{Sn-Sn}/Hz	Δ/Hz
−59.40	^1J(^{115}Sn—^{119}Sn)	2310.45 (0.02)	$^{115}\Delta = 0.04 \pm 0.04$**
	^1J(^{117}Sn—^{119}Sn)	2516.08 (0.02)	
	^1J(^{119}Sn—^{119}Sn)	2633.1*	

* Determined through the gyromagnetic ratio.

** With respect to ^{117}Sn.

Table 3. Content of magnetic isotopes ^{119}Sn, ^{117}Sn, and ^{115}Sn in a hexaethyldistannane molecule according to the data of iteration analysis of the ^{13}C NMR spectra

Isotope	Content (%)
^{115}Sn	0.3 (0.1)
^{117}Sn	7.4 (0.1)
^{119}Sn	8.2 (0.1)
Other isotopes	84.1 (0.4)

The ^{119}Sn—{^{1}H} NMR spectrum of hexaethyldistannane (see Fig. 1, *b*) makes it possible to determine easily all SCC J(^{13}C—^{119}Sn) (see Table 1), as well as the direct SCC ^1J(^{119}Sn—^{117}Sn) and ^1J(^{119}Sn—^{115}Sn). The SCC J(^{13}C—^{119}Sn) values, determined experimentally and calculated by gyromagnetic constants for different magnetic isotopes with a high accuracy, coincide. This indicates that noticeable isotope effects do not affect these SCC. The spectral parameters are presented in Table 2.

The obtained values of the NMR spectral parameters of hexaethyldistannane made it possible to take into account all satellites in the iteration analysis of the complete form of multiplet lines and determine the content of magnetic isotopes ^{119}Sn, ^{117}Sn, and ^{115}Sn in the compound with a high accuracy (Table 3) necessary for subsequent observation of magnetic isotope effects in photolysis of organotin compounds. The values obtained are close to the tabulated values of the natural content of tin magnetic isotopes (8.59 for ^{119}Sn, 7.68 for ^{117}Sn, and 0.34% for ^{115}Sn).

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