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SPIN COUPLING THROUGH OXYGEN. INFLUENCE OF STRUCTURE AND SOLVENT ON $^2J(^{119}Sn,^{117}Sn)$ IN THE ^{119}Sn NMR OF HEXAORGANODISTANNOXANES

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Summary

Sn,Sn spin coupling though oxygen, $^2J(^{119}Sn,^{117}Sn)$, has been measured for seven hexaorganodistannoxanes $[(R_3Sn)_2O]$. The magnitude of the coupling constant depends strongly on the organic ligand, varying over the range 421 to 651 Hz in benzene solution. The substituent effect on ^2J is interpreted as arising from changes in the Sn–O–Sn bond angle, which should strongly influence the magnitude of the Fermi contact term contribution to the coupling constant. A pronounced solvent effect on $^2J(^{119}Sn,^{117}Sn)$ was also observed; solvent studies with $(n\text{-}Bu_3Sn)_2O$ indicate that the electron acceptor strength of the solvent determines the magnitude of the interaction. The utility of the coupling constant as a means of distinguishing between distannoxanes and related compounds is noted.

Introduction

Relatively few examples of spin coupling through oxygen have been reported [1], yet this NMR parameter may provide useful insight into the occurrence and structure of M–O–M linkages in certain organometal catalysts, cluster compounds, and ceramic precursors. Using ^{119}Sn FT NMR, we have examined Sn,Sn spin coupling through oxygen $[^2J(^{119}Sn,^{117}Sn)]$ in a series of hexaorganodistannoxanes, $(R_3Sn)_2O$ [2], compounds which have important applications as biocides in commerce and agriculture [3]. The data reveal a pronounced influence of solvent and organic substituent on the magnitude of the spin coupling, which may arise from changes in the Sn–O–Sn bond angle.

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Results and discussion

The ^{119}Sn NMR data for benzene solutions of seven hexaorganodistannoxanes with substituents of varied steric and electronic character are compared in Table 1. In addition, one of these compounds [hexa-n-butyldistannoxane, $(n\text{-}Bu_3Sn)_2O$] has been examined in several solvents and at several concentrations (Table 2). As seen in Fig. 1, the ^{117}Sn satellites are a pronounced feature of the ^{119}Sn NMR spectra and are easily distinguished from the ^{13}C satellites [$^1J(^{119}Sn,^{13}C)$] by their greater natural abundance (7.6 vs. 1.1%; the presence of three organic substituents gives a 2.3/1 ratio of $^{117}Sn/^{13}C$ satellite intensities).

Unlike substituted distannoxanes [4], $(R_nX_{3-n}Sn)_2O$ (X = electronegative group), the following observations suggest that intermolecular association of hexaorganodistannoxanes is insignificant under the NMR conditions: (1) Line widths were < 8 Hz for all compounds (the line width for Me_4Sn = 4 Hz in the same solutions). (2) Experiments with $(n\text{-}Bu_3Sn)_2O$ in benzene solution showed the coupling constants [$^2J(^{119}Sn,^{117}Sn)$, $^1J(^{119}Sn,^{13}C)$], ^{119}Sn chemical shift, and line width to be insensitive to changes in concentration below about 30% (v/v); $^1J(^{119}Sn,^{13}C)$ and line widths were also insensitive to changes in solvent (Table 2). (3) $^1J(^{119}Sn,^{13}C)$ is extremely

TABLE 1

^{119}Sn NMR DATA FOR HEXAORGANODISTANNOXANES IN BENZENE [a]

$(R_3Sn)_2O$ R =	Chemical shift (ppm)	$^2J(^{119}Sn, ^{117}Sn)$ (Hz)	$^1J(^{119}Sn, ^{13}C)$ (Hz)
n-Pr	83.7	446.8	368.7
n-Bu	84.8	451.7	368.7
Neophyl [b]	57.7	532.1	362.9
i-Pr	20.7	615.4	370.9
s-Bu	24.7	650.7	361.0
Benzyl	9.2	617.9	319.3
Ph	−83.1	420.6	625.8

[a] Digital resolution ≤ 1.5 Hz, peak widths (W 1/2) ≤ 5 Hz for all compounds. Chemical shifts relative to Me_4Sn internal standard. [b] Neophyl = $C_6H_5(CH_3)_2CCH_2$.

TABLE 2

INFLUENCE OF SOLVENT, CONCENTRATION ON ^{119}Sn NMR SPECTRUM OF $(n\text{-}Bu_3Sn)_2O$ [a]

Solvent	Conc. (% v/v)	Chemical shift (ppm)	$^2J(^{119}Sn, ^{117}Sn)$ (Hz)	$^1J(^{119}Sn, ^{13}C)$ (Hz)	Acceptor number [b]
n-Heptane	8	79.5	471.8	372.3	0.0
Benzene	5	84.8	451.7	368.7	8.2
	10	84.7	452.3	368.7	
	20	84.5	452.9	369.3	
	30	84.3	454.7	369.9	
Pyridine	8	85.1	435.2	369.9	14.2
CH_2Cl_2 [c]	10	86.8	402	366	20.4
$CDCl_3$ [c]	10	92.0	377	[d]	23.1

[a] Digital resolution 0.6 Hz/pt. Line widths (W 1/2) ≤ 6 Hz. Chemical shifts relative to Me_4Sn internal standard. [b] Ref. 14. [c] Digital resolution 2.1 Hz/pt. [d] Unresolved from $^2J(^{119}Sn,^{117}Sn)$.

sensitive to changes in the coordination number of alkyltins [5]; the alkyl-substituted distannoxanes investigated had ^1J values between 361 and 371 Hz, typical [5] for tetracoordinate trialkyltin. (4) The X-ray crystal structures show hexaphenyl- [6] and hexabenzyldistannoxane [7] to be monomeric in the solid state, where the chance for intermolecular interaction should be greatest.

The synthesis and identification of distannoxanes has been hindered by the difficulty of distinguishing between distannoxanes and their frequent impurities, triorganostannols, R_3SnOH, and bis(triorganotin) carbonates, $(R_3Sn)_2CO_3$ [8,9]. The large spin coupling to ^{117}Sn in distannoxanes and the absence of spin coupling to Sn in stannols makes this parameter very useful for discriminating between the two structures. Sn,Sn spin coupling in bis(triorganotin) carbonates, $^4J(^{119}Sn,^{117}Sn)$, is not generally observable [10], although we have recently detected [9] Sn,Sn spin coupling in the sterically congested $(neophyl_3Sn)_2CO_3$ (neophyl = $C_6H_5(CH_3)_2$-CCH_2). The spin coupling of this carbonate, $^4J(^{119}Sn,^{117}Sn)$ 44 Hz, is an order of magnitude smaller than those we observe for hexaorganodistannoxanes.

To understand the large substituent effect on the ^{119}Sn,^{117}Sn coupling constant, we note that the structural data available for several hexaorganodistannoxanes shows that the Sn–O–Sn bond angle, θ, is sensitive to the nature of the organic substituent: for R = phenyl, θ is 137.1° [6]; for R = methyl, 140.8° (determined by gas phase electron diffraction) [11]; for benzyl, 180.0° [7]. Glidewell [12] has attributed the large difference between these distannoxane Sn–O–Sn bond angles to electronic factors, and has suggested that in general, for molecules of the type M–X–M, increased electron donation by ligands on M will increase the size of θ.

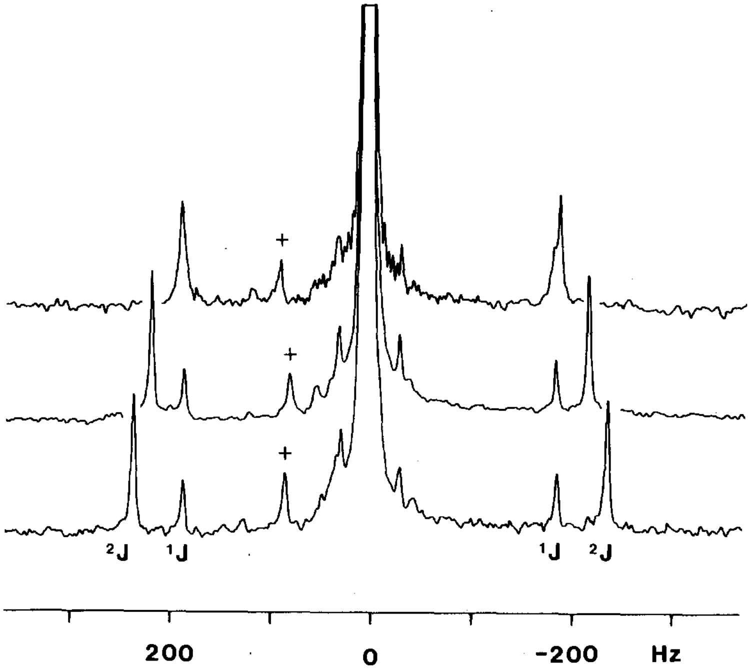


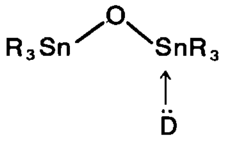
Fig. 1. Solvent effect on $^2J(^{119}Sn,^{117}Sn)$ of $(n\text{-}Bu_3Sn)_2O$. Upper spectrum, $CDCl_3$; middle, pyridine; lower, n-heptane solvent. $^1J(^{119}Sn,^{13}C)$ and $^2J(^{119}Sn,^{117}Sn)$ labelled for bottom spectrum; side band marked with (+).

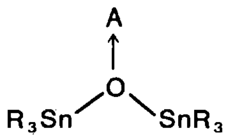
Comparison of the magnitude of Sn,Sn spin coupling in hexaphenyl- and hexabenzyldistannoxane suggests a correlation of the coupling constant with the size of the Sn–O–Sn bond angle (the distannoxanes were examined in a common, nonpolar solvent in order to minimize the influence of solvent on the Sn–O–Sn bond angle). The similar magnitude of $^2J(^{119}Sn,^{117}Sn)$ of the hexa-n-alkyldistannoxanes and the phenyl-substituted compound is consistent with this correlation if $(n\text{-}Pr_3Sn)_2O$ and $(n\text{-}Bu_3Sn)_2O$ are assumed to have Sn–O–Sn bond angles comparable to $(Me_3Sn)_2O$.

Further support for a bond angle/spin coupling correlation is provided by the series of alkyl-substituted distannoxanes. Branching of the alkyl group at the α and β carbons produces greater electron donation to Sn; reflecting this, the ^{119}Sn chemical shift progresses to higher field in the ligand series n-Pr $\cong$ n-Bu $<$ neophyl $<$ i-Pr $<$ s-Bu. Following Glidewell's arguments [12], substitution at tin with increasingly electron-donating ligands should produce a corresponding increase in the Sn–O–Sn bond angle. Notably, the magnitude of $^2J(^{119}Sn,^{117}Sn)$ also increases in the series, the linear relationship between the chemical shift and the coupling constant having a correlation coefficient of 0.98.

A simple Fermi contact term model [13] may account for the correlation of $^2J(^{119}Sn, ^{117}Sn)$ with θ. That is, the magnitude of the coupling constant should depend strongly on the *s* character of the oxygen bond to tin. Since the %*s* character will decrease as the Sn–O–Sn bond angle decreases from 180° (*sp*-hybridized oxygen), the magnitude of $^2J(^{119}Sn,^{117}Sn)$ should also decrease. The strong correlation between the ^{119}Sn chemical shift and the magnitude of the spin coupling in the alkyl-substituted distannoxanes suggests that hybridization at oxygen is the dominant factor in determining the magnitude of $^2J(^{119}Sn,^{117}Sn)$. Other factors such as differences in the Sn–O bond length or the Sn–Sn through-space distance may also contribute to the differences in $^2J(^{119}Sn,^{117}Sn)$, but the limited structural data on these compounds prevents a more detailed analysis (of the four structurally uncharacterized compounds studied, three are liquids; the fourth, $(neophyl_3Sn)_2O$, because of disorder in the crystal, has resisted our attempts to carry out an X-ray analysis).

The ^{119}Sn chemical shift and the magnitude of the $^{119}Sn,^{117}Sn$ coupling constant of the n-alkyl- and benzyl-substituted distannoxanes were found to be extremely sensitive to changes in solvent (Table 2, Fig. 1). A priori, several solvent–distannoxane interactions may be proposed to account for the solvent effect: Because of the dipolar Sn–O function, a solvent may interact with the distannoxane at tin (as an electron donor solvent [14]) or at oxygen (as an electron acceptor solvent [14]). Alternately, a less specific interaction, perhaps related to a bulk solvent parameter such as dielectric constant or dipole moment, may be responsible for the observed effects.





D = donor solvent,

A = acceptor solvent

To determine which of these mechanisms might be operative, $(n\text{-}Bu_3Sn)_2O$ was examined in several solvents (Table 2). $^2J(^{119}Sn,^{117}Sn)$ showed a strong, inverse dependence on the acceptor strength of the solvent, the hydrogen bonding solvents CH_2Cl_2 and $CDCl_3$ producing the smallest values of the spin coupling. The relatively large changes in ^{119}Sn chemical shift observed for $(n\text{-}Bu_3Sn)_2O$ also support this picture: strong acceptor solvents produced the greatest deshielding of tin. In contrast, the magnitude of $^2J(^{119}Sn,^{117}Sn)$ does not show a simple dependence on solvent dipole moment or dielectric strength (the dielectric constant of pyridine > CH_2Cl_2 > $CDCl_3$ > benzene > n-heptane).

While pyridine is an acceptor solvent of moderate strength, it is a very strong electron donor solvent. Nevertheless, both the ^{119}Sn chemical shift and $^2J(^{119}Sn,^{117}Sn)$ observed suggest that it behaves only as an electron acceptor toward $(n\text{-}Bu_3Sn)_2O$. The absence of significant electron donation by pyridine to the distannoxane is most strongly indicated by the observation that the magnitude of $^1J(^{119}Sn,^{13}C)$, which should increase markedly in the event of increased coordination at Sn [5], remained unchanged in pyridine.

Large solvent effects may be observed when the interaction between solvent and an organotin substrate produces a change in the coordination number of tin (a chemical change, resulting from solvent complexation or a difference in the extent of self-association). The magnitude of the solvent effect reported here (a difference in $^2J(^{119}Sn, ^{117}Sn)$ of 95 Hz between n-heptane and $CDCl_3$ solvent) is, to our knowledge, one of the largest observed in the absence of such a compositional change [13].

Although only speculative, it is tempting to ascribe the influence of solvent on $^2J(^{119}Sn,^{117}Sn)$ to changes induced in the Sn–O–Sn bond angle. For the distannoxanes with bulky substituents, only modest changes in $^2J(^{119}Sn, ^{117}Sn)$ (< 25 Hz) were observed. The smaller solvent influence on these distannoxanes may arise either from hindered approach of solvent to oxygen as a consequence of the steric bulk of the ligand, or because steric interactions between ligands on the different tin atoms may prevent a significant decrease in the bond angle.

Experimental

NMR experiments. ^{119}Sn NMR spectra were collected (90° pulse, 4 s repetition rate) with a Bruker WM 400 at 149.212 MHz and at 304 K, with proton decoupling at 400 MHz gated on only during data acquisition in order to minimize the negative nuclear Overhauser effect (NOE). Solutions of distannoxanes were prepared using deuterated or protio solvents (the latter with a concentric tube containing a deuterated lock solvent), with a small amount (ca. 1%) of Me_4Sn as internal standard (0 ppm). Control experiments with $(n\text{-}Bu_3Sn)_2O$ in several solvents showed that small volumes of added Me_4Sn had no influence on the position or shape of the distannoxane resonance. Analysis of different solutions of several of the compounds showed excellent reproducibility of the coupling constants and chemical shift. The uncertainty in the values of J is about the same as the digital resolution (listed in the Tables) and the chemical shifts are precise to 0.1 ppm.

Materials. The solvents employed in the NMR studies were dried over freshly activated molecular sieves for several days prior to use. Contact of NMR solutions with humid air was minimized by use of a nitrogen sweep during sample preparation. The distannoxanes used in this study were either obtained from commercial sources or prepared by standard methods [15] (several were provided by generous loan). The compounds studied were judged, by ^{119}Sn NMR, to be better than 95% pure, with the exception of the i-propyl and s-butyl compounds which were only about 75 and 50% pure, respectively. Addition of small amounts of water to solutions of the distannoxanes produced the hydrolysis product, R_3SnOH, which gave a broad resonance somewhat downfield of the distannoxane signal. The presence of R_3SnOH had no observable effect on the distannoxane resonance in dilute solution.

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