

Solvent Effects on Two-Bond  $^{119}\text{Sn}$ - $^{117}\text{Sn}$  Spin Coupling in  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  and  $(\text{Me}_3\text{Sn})_2\text{O}$ 

Thomas P. Lockhart\*

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Profound solvent effects on the tin-tin spin coupling constant,  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$ , of the hexaorganodistannoxanes  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  and  $(\text{Me}_3\text{Sn})_2\text{O}$  have been investigated for a large number of solvents. For both compounds, a good correlation has been found with the empirical acceptor number solvent scale, implicating a principal interaction of solvent with oxygen. Evidence consistent with a halogen-bonding interaction in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and  $\text{CCl}_4$  solutions was found for  $(n\text{-Bu}_3\text{Sn})_2\text{O}$ . This effect is absent, or strongly reduced, for  $(\text{Me}_3\text{Sn})_2\text{O}$ . While no evidence of a coordinative interaction of solvent with tin was found for the *n*-butyl derivative, changes in  $^1J(^{119}\text{Sn}, ^{13}\text{C})$  and the  $^{119}\text{Sn}$  chemical shift for  $(\text{Me}_3\text{Sn})_2\text{O}$  provide evidence of a secondary interaction of strongly coordinating solvents with tin. A structural basis for the solvent effect on  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$  has been proposed on the basis of recent empirical correlations of  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$  with the Sn-O-Sn angle.

## Introduction

Two-bond tin-tin spin coupling interactions through oxygen and other chalcogenides,  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$ , have received considerable attention recently.<sup>1-11</sup> Within a few years of the first reports,<sup>1,2</sup> observations of  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$  have been extended to numerous hexaorganoditin chalcogenides,  $(\text{R}_3\text{Sn})_2\text{X}$  (X = O, S, Se, Te),<sup>4,5,8,9</sup> unsymmetrically substituted hexaorganoditin chalcogenides of the type  $\text{R}_3\text{Sn-X-SnR}'_3$  (X = O, S),<sup>7</sup> various cyclic diorganotin chalcogenides,<sup>3,8,9</sup> and miscellaneous other systems.<sup>1,2,10,11</sup> The large number of derivatives  $(\text{R}_3\text{Sn})_2\text{X}$  and related compounds accessible synthetically has provided an experimentally flexible system for studying the influence of structural and electronic factors on *J* coupling through chalcogenides. From such studies, evidence of a direct relationship between  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$  and the magnitude of the angle  $\angle\text{Sn-X-Sn}$  has been obtained.<sup>4,8,9</sup> The Sn-Sn spin coupling constant has also proven to be useful for the often recalcitrant problem of distinguishing between hexaorganodistannoxanes and their hydrolysis products, triorganostannols, in solution.<sup>6,7,9</sup>

The remarkable influence of solvent on  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$  for several hexaorganodistannoxanes has been noted in a preliminary report.<sup>4</sup> In the present article results of a systematic study of solvent effects on  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$  of  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  are described. The parent hexaorganodistannoxane,  $(\text{Me}_3\text{Sn})_2\text{O}$ , for which limited NMR data have been available,<sup>9,12</sup> has also been examined; this distannoxane shows some interesting contrasts to the behavior of  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  in solution.

## Experimental Section

Solvents from the highest quality commercial sources were dried over the appropriate activated commercial sieves (3A or 4A) for several days prior to use. A fresh sample of  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  (Alfa) was further purified by fractional distillation under vacuum and stored under  $\text{N}_2$  over 4A sieves in a flask covered against light. To minimize the possible influence of moisture on the NMR spectra of  $(n\text{-Bu}_3\text{Sn})_2\text{O}$ , solutions were prepared in oven-dried NMR tubes cooled under an  $\text{N}_2$  flush. Solvent and  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  were added to the 10-mm NMR tubes by syringe under an  $\text{N}_2$  blanket. For measurements in nondeuterated solvents, desiccator-dried Teflon inserts and a  $\text{C}_6\text{D}_6$ -filled lock tube (5 mm) were added (concentric geometry) and the whole apparatus was capped securely. With this method, no complications attributable to spurious hydrolysis of  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  were encountered. In order to avoid possible complications from self-association of  $[(n\text{-Bu}_3\text{Sn})_2\text{O}]$ , its concentration was kept <8 vol % in all experiments.<sup>4</sup>  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  was found to be chemically unstable in all solvents with AN values comparable to or higher than that of  $\text{CHCl}_3$  (including alcohol solvents of varying steric bulk and *N*-methylacetamide); this prevented the determination of  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$  in high AN solvents.

The preparation of  $(\text{Me}_3\text{Sn})_2\text{O}$  has been described previously.<sup>9</sup> NMR solutions that were 2-4 vol % in  $(\text{Me}_3\text{Sn})_2\text{O}$  were prepared as for  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  above. A pronounced tendency to line broadening was observed for this compound and was more serious in nonpolar solvents such as *n*-heptane (line width at half-height (LW) = 20 Hz), than in  $\text{CDCl}_3$  (LW = 4 Hz). The line width observed in the nonpolar solvents was

Table I.  $^{119}\text{Sn}$  NMR Data for  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  in Solvents of Varying Acceptor Number (AN)

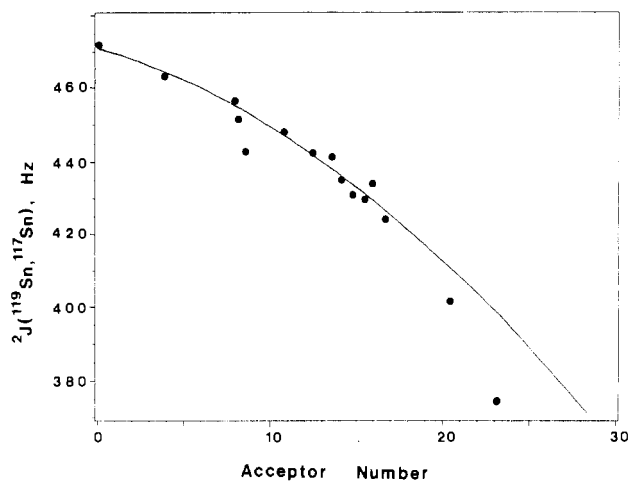
solvent <sup>a</sup>	$^2J(^{119}\text{Sn}, ^{117}\text{Sn})$ , Hz	$^1J(^{119}\text{Sn}, ^{13}\text{C})$ , Hz	$^{119}\text{Sn}$ chem shift, ppm	AN <sup>b</sup>
<i>n</i> -heptane	471.8	372.3	79.5	0.0
triethylamine	470.0	371.1	80.0	
diisopropylamine	466.3	371.7	80.4	
diethyl ether	463.3	372.3	79.5	3.9
di- <i>n</i> -butylamine	461.4	370.5	80.9	
tetrahydrofuran	456.5	372.9	79.2	8.0
toluene	455.9	369.3	83.7	
benzene	451.7	368.7	84.8	8.2
<i>p</i> -dioxane	448.0	371.1	81.3	10.8
chlorobenzene	443.7	370.5	85.4	
$\text{CCl}_4$	443.1	369.3	85.1	8.6
acetone	442.5	372.9	80.8	12.5
DMA	441.3	374.8	78.5	13.6
pyridine	435.2	369.9	85.1	14.2
DMF	434.0	374.2	78.9	16.0
nitrobenzene	430.9	368.0	85.9	14.8
benzonitrile	429.7	369.9	86.3	15.5
1,2-dichloro- ethane	424.2	369.3	84.4	16.7
$\text{CH}_2\text{Cl}_2$	402.0	366.2	86.8	20.4
$\text{CDCl}_3$	376.6	365 <sup>c</sup>	92.1	
$\text{CHCl}_3$	374.6	<i>c</i>	92.4	23.1

<sup>a</sup> Abbreviations: DMF, *N,N*-dimethylformamide; DMA, *N,N*-dimethylacetamide. <sup>b</sup> AN = acceptor number.<sup>14</sup> AN for *n*-heptane is assumed to be the same as that for *n*-hexane (0.0). <sup>c</sup> Tin-carbon coupling constant partially obscured by  $^{117}\text{Sn}$  satellites.

reduced significantly by the presence of a small amount of NaH, which converts<sup>9</sup>  $\text{Me}_3\text{SnOH}$  to  $(\text{Me}_3\text{Sn})_2\text{O}$ , suspended in the sample tube. This result suggests that the line broadening observed arises from a dynamic process involving the interaction of  $(\text{Me}_3\text{Sn})_2\text{O}$  with  $\text{Me}_3\text{SnOH}$ , small amounts of which may have been formed by spurious hydrolysis of  $(\text{Me}_3\text{Sn})_2\text{O}$  during sample preparation. Experiments with  $\text{CDCl}_3$  showed no influence of  $(\text{Me}_3\text{Sn})_2\text{O}$  concentration on the LW or other NMR

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\* Address correspondence to the author at Eniricerche S.p.A., 20097 San Donato Milanese, Italy.



**Figure 1.**  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$  plotted against AN for  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  in 15 solvents. Line drawn is calculated from quadratic regression (eq 2 in text) for the 12 non- or monochlorinated solvents.

parameters between 2 and 4% concentration (v/v), indicating that self-association of  $(\text{Me}_3\text{Sn})_2\text{O}$  is unimportant at the concentrations employed in the NMR measurements.

The NMR equipment and method have been described elsewhere.<sup>4</sup> All spectra (149.212 MHz for  $^{119}\text{Sn}$ ) were obtained at 304 K except as noted.  $\text{Me}_4\text{Sn}$  (<1 vol %) was present as an internal standard in all solutions except that for  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  in  $\text{CH}_2\text{Cl}_2$  in which the  $^{119}\text{Sn}$  chemical shift was determined by reference to the lock channel.

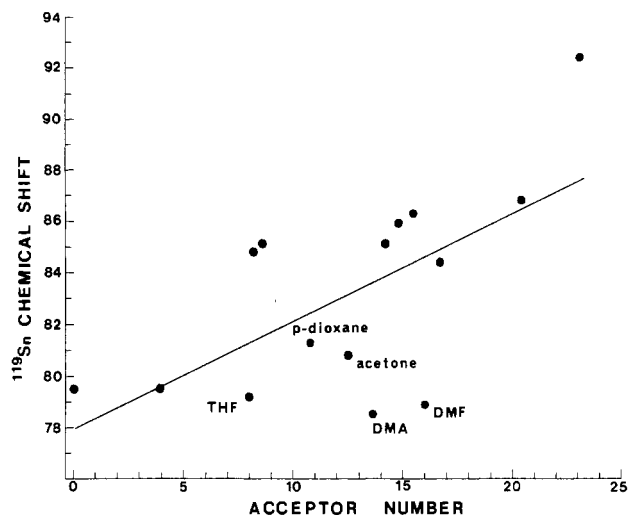
### Results and Discussion

**$^{119}\text{Sn}$  NMR Study of  $(n\text{-Bu}_3\text{Sn})_2\text{O}$ .** NMR results for  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  in 21 solvents are given in Table I. Particularly striking is the influence of solvent on the magnitude of  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$ , which varies over 97 Hz in the noncoordinating solvents *n*-heptane and  $\text{CHCl}_3$ . A modest solvent effect on the  $^{119}\text{Sn}$  chemical shift, which varies over 13.9 ppm, was also observed.

Molecules of the type  $(\text{R}_3\text{Sn})_2\text{O}$  contain two possible sites for a strong interaction with solvent, and three distinct mechanisms for the influence of solvent on the NMR spectrum of  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  can be suggested: (1) a general dipolar effect to stabilize the separation of charge in the Sn–O–Sn system; (2) a nucleophilic interaction of solvent with tin; (3) an electrophilic interaction with the distannoxane oxygen atom.

These possibilities have been evaluated by analyzing the NMR data with various solvent parameter systems.<sup>13,14</sup> An unsatisfactory correlation of the NMR data with the bulk dielectric constants of the solvents weighs strongly against the dipolar mechanism. Similarly, neither  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$  nor the  $^{119}\text{Sn}$  chemical shift correlates significantly with the donor number (DN) scale of Gutmann,<sup>14</sup> which describes solvent nucleophilicity. In contrast, a smooth curve (Figure 1) was obtained from a plot of  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$  against the acceptor numbers (AN)<sup>14</sup> available for 15 of the solvents. The empirical AN scale was developed by Gutmann as a probe of the electrophilic properties of solvents, and the correlation of  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$  with this parameter strongly implies that interaction of the solvent with the distannoxane oxygen gives rise to the observed changes in the NMR spectra. In the last part of this article, it is proposed that the influence of solvent on  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$  is connected with a specific conformational change of the Sn–O–Sn moiety.

A quadratic regression of  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$  versus AN gave only a modest fit for the data shown in Figure 1 (correlation coefficient 0.96). In particular, the  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$  value for  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  in  $\text{CCl}_4$  was substantially lower than that expected given its AN. Peculiar solvent effects (halogen bonding) are well-known for organic oxides in  $\text{CCl}_4$  and other halogenated solvents.<sup>15</sup> The possibility that such an effect might be operative for  $\text{CCl}_4$  and the other halogenated solvents was evaluated by carrying out a



**Figure 2.**  $^{119}\text{Sn}$  chemical shift plotted against AN for  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  in 15 solvents. Line drawn was obtained from linear regression.

**Table II.** Temperature Effects on  $^{119}\text{Sn}$  NMR Data for  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  in Toluene

temp, K	$^2J(^{119}\text{Sn}, ^{117}\text{Sn})$ , Hz	$^{119}\text{Sn}$ chem shift, ppm	$^1J(^{119}\text{Sn}, ^{13}\text{C})$ , Hz
345	470.6	81.8	369.3
330	465.7	82.4	369.3
317	460.8	83.0	369.9
304	455.9	83.7	369.3
253	435.8	86.0	369

quadratic regression for the data obtained for the 12 non-chlorinated solvents plus 1,2-dichloroethane. The curve obtained (eq 1; correlation coefficient 0.97) is shown in Figure 1, and was

$$^2J(^{119}\text{Sn}, ^{117}\text{Sn}) = -0.074(\text{AN})^2 - 1.42(\text{AN}) + 471 \quad (1)$$

judged to fit much better the data for the 12 solvents; the exceptional behavior of the more heavily chlorinated solvents is evident from inspection of this plot. Hydrogen bonding to the distannoxane oxygen might be offered as an alternate explanation for the particularly strong influence of  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  on  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$ .<sup>15</sup> The unremarkable data (Table I) obtained in *i*- $\text{Pr}_2\text{NH}$  solution (AN not available), however, do not favor this argument.

The specific solvent effects for the more heavily chlorinated solvents and the slight curvature of the  $^2J(^{119}\text{Sn}, ^{117}\text{Sn})/\text{AN}$  plot for the remaining solvents serves to emphasize that the empirical AN solvent scale, which was derived from the influence of various solvents on the  $^{31}\text{P}$  chemical shift of triethylphosphine oxide, is not independent of the identity of the donor molecule (in this case the distannoxane).<sup>16</sup>

A very weak correlation of  $^{119}\text{Sn}$  chemical shift with AN was found (Figure 2), implying that there is only an indirect, probably inductive, effect of the solvent on tin. It may be of interest to note that, for the oxygen atom containing donor solvents acetone, THF, 1,4-dioxane, DMF, and DMA, the  $^{119}\text{Sn}$  chemical shift falls well below the line obtained from linear regression for all the data (shown in the figure). Pyridine, the strongest donor solvent examined, however, gives a "normal" value, which implies that the effect is not due to a direct coordinative interaction between the oxygenated solvents and tin. Additional evidence against direct interaction of solvent with tin comes from the observation that  $^1J(^{119}\text{Sn}, ^{13}\text{C})$ , which is strongly sensitive to changes in the coordination at tin,<sup>17</sup> shows no systematic variation with the more nucleophilic solvents.

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**Table III.**  $^{119}\text{Sn}$  NMR Results for  $(\text{Me}_3\text{Sn})_2\text{O}$  in Various Solvents

solvent	temp °C	$^2J(^{119}\text{Sn},^{117}\text{Sn})^a$ Hz	$^1J(^{119}\text{Sn},^{13}\text{C})^a$ Hz	$^{119}\text{Sn}$ chem shift, ppm	AN <sup>b</sup>
<i>n</i> -heptane	300	400 ± 10	395 ● 10	109.8	0.0
benzene	300	347.3	394.3	114.1	8.2
pyridine	300	326.5	402.8	104.8	14.2
	270	319	409	99.9	
1,2-dichloroethane	300	317	394	115.9	16.7
$\text{CH}_2\text{Cl}_2$	304	308.2	393.7	118.9	20.4
$\text{CDCl}_3$	304	291.1	391.2	125.7	23.1
triethylamine	300	353	398	109.9	

<sup>a</sup> For solutions where line broadening was a problem (line width at half-height > 7 Hz), coupling constants were determined to only three significant figures. In addition, for *n*-heptane the near-superposition of the tin-tin and tin-carbon satellites led to additional uncertainty in the coupling constants. <sup>b</sup> Same as Table I; value used for  $\text{CDCl}_3$  is that for  $\text{CHCl}_3$ .

Limited NMR studies of  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  solutions at variable temperature have been carried out. The results obtained for a toluene solution are given in Table II and show that  $^2J(^{119}\text{Sn},^{117}\text{Sn})$  and to a lesser extent the  $^{119}\text{Sn}$  chemical shift vary significantly with temperature between 345 and 253 K. In contrast,  $^1J(^{119}\text{Sn},^{13}\text{C})$  was independent of changes in temperature over the range investigated. The stronger interaction between  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  and toluene at lower temperature is typical of many solute-solvent systems.<sup>13</sup> An interesting feature here is that the  $^2J(^{119}\text{Sn},^{117}\text{Sn})$  values observed in toluene at the limiting temperatures studied correspond approximately to those observed at 304 K for  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  in solvents ranging from AN = 0 to 14. The monotonic dependence of  $^{119}\text{Sn}$  chemical shift on temperature in toluene is in pronounced contrast to the scattered chemical shifts observed for  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  in solvents of varying AN (shown in Figure 2).

**$^{119}\text{Sn}$  NMR Study of  $(\text{Me}_3\text{Sn})_2\text{O}$ .** A limited series of  $^{119}\text{Sn}$  NMR measurements have been carried out on the moisture-sensitive parent hexaorganodistannoxane,  $(\text{Me}_3\text{Sn})_2\text{O}$  (Table III). An even wider range of  $^2J(^{119}\text{Sn},^{117}\text{Sn})$  values, ranging from 400 Hz in *n*-heptane to 291 Hz in  $\text{CDCl}_3$ , was found for this distannoxane than for  $(n\text{-Bu}_3\text{Sn})_2\text{O}$ . The relationship between  $(\text{Me}_3\text{Sn})_2\text{O}$   $^{119}\text{Sn}$  chemical shift,  $^1J(^{119}\text{Sn},^{13}\text{C})$ , and  $^2J(^{119}\text{Sn},^{117}\text{Sn})$  values and the AN for six solvents is shown in Figure 3. As for  $(n\text{-Bu}_3\text{Sn})_2\text{O}$ ,  $^2J(^{119}\text{Sn},^{117}\text{Sn})$  is found to correlate with AN; a linear regression gives eq 2 (correlation coefficient 0.975). Once

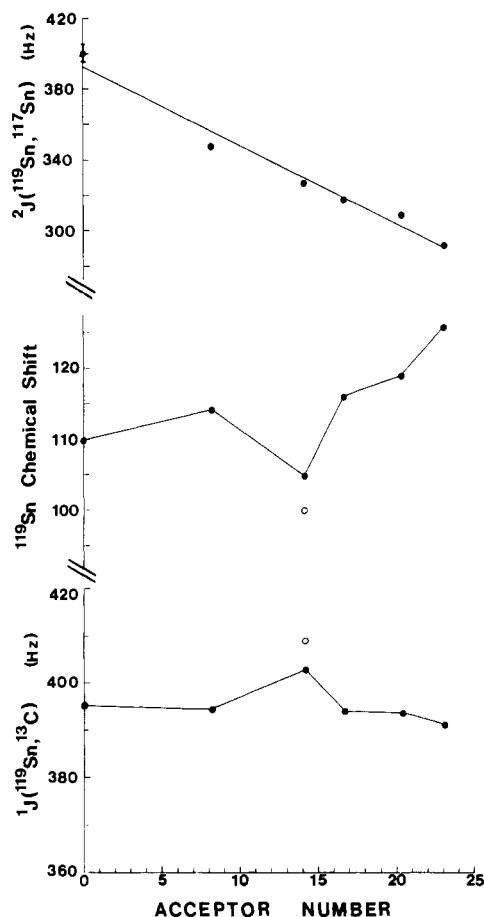
$$^2J(^{119}\text{Sn},^{117}\text{Sn}) = -4.46(\text{AN}) + 393 \quad (2)$$

again, the bridging oxygen atom is indicated as the principal site of interaction of solvent with the distannoxane. While the plot of  $^2J(^{119}\text{Sn},^{117}\text{Sn})$  against AN for  $(\text{Me}_3\text{Sn})_2\text{O}$  provides no evidence of a significant halogen-bond interaction with  $\text{CH}_2\text{Cl}_2$  or  $\text{CDCl}_3$ , the  $^{119}\text{Sn}$  chemical shift in  $\text{CDCl}_3$  is somewhat higher than expected by extrapolation from values for the other solvents (Figure 3, middle plot). Reduced halogen bonding to  $(\text{Me}_3\text{Sn})_2\text{O}$  seems reasonable in view of the lower electron-donating character of the alkyl ligands in this distannoxane relative to  $(n\text{-Bu}_3\text{Sn})_2\text{O}$ .

The NMR data for  $(\text{Me}_3\text{Sn})_2\text{O}$  in pyridine provide another contrast to the behavior of  $(n\text{-Bu}_3\text{Sn})_2\text{O}$ . The anomalously high value of  $^1J(^{119}\text{Sn},^{13}\text{C})$  and the low  $^{119}\text{Sn}$  chemical shift found for  $(\text{Me}_3\text{Sn})_2\text{O}$  in pyridine (see the middle and lower plots of Figure 3) provide evidence of a coordinative interaction of pyridine with tin. These effects are further enhanced at lower temperature. It is interesting that the nucleophilic interaction of pyridine with tin does not appear to interfere with the smooth variation of  $^2J(^{119}\text{Sn},^{117}\text{Sn})$  as a function of solvent AN.

Results for  $\text{Et}_3\text{N}$  (AN not available) also suggest a coordinative interaction with tin. Judging from the relative  $^{119}\text{Sn}$  chemical shift and  $^1J(^{119}\text{Sn},^{13}\text{C})$  values, however,  $\text{Et}_3\text{N}$  appears to interact less strongly with tin than does pyridine, notwithstanding its substantially greater DN value (61 for  $\text{Et}_3\text{N}$  versus 33.1 for pyridine<sup>14</sup>). This difference may indicate that the coordinative interaction is sensitive to steric crowding at tin.

The greater sensitivity to donor solvents of tin in  $(\text{Me}_3\text{Sn})_2\text{O}$  relative to the *n*-butyl derivative suggests enhanced Lewis acidity, which seems reasonable given the lower electron-donating ability of the methyl ligands. The reduced steric congestion around tin in  $(\text{Me}_3\text{Sn})_2\text{O}$  relative to  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  may also facilitate inter-



**Figure 3.**  $^2J(^{119}\text{Sn},^{117}\text{Sn})$  (top),  $^{119}\text{Sn}$  chemical shift (middle) and  $^1J(^{119}\text{Sn},^{13}\text{C})$  (bottom) plotted against AN for  $(\text{Me}_3\text{Sn})_2\text{O}$  in six solvents at either 300 or 304 K (filled circles). Open circles are for  $(\text{Me}_3\text{Sn})_2\text{O}$  in pyridine at 270 K.

action with nucleophilic solvents.

Another indication that the solvent-distannoxane interaction may be sensitive to steric factors comes from a comparison of the results obtained for  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  and  $(\text{Me}_3\text{Sn})_2\text{O}$  in  $\text{Et}_3\text{N}$ . For  $(\text{Me}_3\text{Sn})_2\text{O}$ ,  $^2J(^{119}\text{Sn},^{117}\text{Sn})$  is 47 Hz smaller in  $\text{Et}_3\text{N}$  than in *n*-heptane (AN = 0), and is close to the value observed in benzene (AN = 8.2). In contrast,  $^2J(^{119}\text{Sn},^{117}\text{Sn})$  for  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  is virtually the same in  $\text{Et}_3\text{N}$  as in *n*-heptane, suggesting that the steric congestion in the *n*-butyl-substituted distannoxane reduces the strength of the interaction between oxygen and this bulky solvent.

**Structural Basis for the  $^2J(^{119}\text{Sn},^{117}\text{Sn})/\text{AN}$  Correlation.** The evidence for a direct relationship between  $^2J(^{119}\text{Sn},^{117}\text{Sn})$  and  $\angle\text{Sn-O-Sn}$  for hexaorganoditin chalcogenides<sup>4,8,9</sup> suggests a structural basis for the effect of acceptor solvents on  $^2J(^{119}\text{Sn},^{117}\text{Sn})$  in  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  and  $(\text{Me}_3\text{Sn})_2\text{O}$ : changes in  $^2J(^{119}\text{Sn},^{117}\text{Sn})$  observed for different solvents reflect changes in the Sn-O-Sn angle. An empirical relationship relating  $^2J(^{119}\text{Sn},^{117}\text{Sn})$  and  $\angle\text{Sn-O-Sn}$  has been derived<sup>9</sup> from data for hexaorganodistannoxanes and

cyclic hexaorganotristannoxanes (eq 3) and can be used to estimate

$$\angle \text{Sn-O-Sn} = 0.087[{}^2J({}^{119}\text{Sn}, {}^{117}\text{Sn})] + 98.6 \quad (3)$$

the  $\angle \text{Sn-O-Sn}$  angle of  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  and  $(\text{Me}_3\text{Sn})_2\text{O}$  in solution.<sup>18</sup> From eq 3,  $\angle \text{Sn-O-Sn}$  of  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  is estimated to be about  $142^\circ$  in *n*-heptane and  $133^\circ$  in  $\text{CHCl}_3$  at 304 K, a difference of  $9^\circ$ . The estimate for  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  in *n*-heptane, the most weakly interacting solvent, seems reasonable in light of the structural data for  $(\text{Me}_3\text{Sn})_2\text{O}$  and  $(\text{Ph}_3\text{Sn})_2\text{O}$  ( $\angle \text{Sn-O-Sn} = 141$  and  $137.1^\circ$ , respectively<sup>19,20</sup>). The angle estimated for  $(\text{Me}_3\text{Sn})_2\text{O}$  in *n*-heptane,  $135^\circ$ , is  $6^\circ$  smaller than that determined by gas-phase electron diffraction.<sup>19</sup> The disagreement between  $\angle \text{Sn-O-Sn}$  estimated for  $(\text{Me}_3\text{Sn})_2\text{O}$  in solution and that in the gas phase could arise either from a medium effect on  $\angle \text{Sn-O-Sn}$ , a partial failure of the  ${}^2J({}^{119}\text{Sn}, {}^{117}\text{Sn})/\angle \text{Sn-O-Sn}$  relationship for this compound or, possibly, inaccuracy of the gas-phase structure determination. The pronounced solvent effect on  ${}^2J({}^{119}\text{Sn}, {}^{117}\text{Sn})$  of  $(\text{Me}_3\text{Sn})_2\text{O}$  corresponds to a decrease of  $\angle \text{Sn-O-Sn}$  of  $10^\circ$  on going from *n*-heptane to  $\text{CDCl}_3$ .

The suggestion that  $\angle \text{Sn-O-Sn}$  could be susceptible to changes on the order of  $10^\circ$  in different solvents appears reasonable in view of the large (345 Hz) decrease in  ${}^2J({}^{119}\text{Sn}, {}^{117}\text{Sn})$  of hexabenzylidistannoxane on going from the crystalline solid (where  $\angle \text{Sn-O-Sn} = 180^\circ$ <sup>21</sup>) to benzene solution (estimated  $\angle \text{Sn-O-Sn} = 155^\circ$ ).<sup>9</sup> Indeed, the available evidence suggests that the barrier to bending of the Sn-O-Sn bond is quite low in hexaorganodistannoxanes, at least in compounds where steric interactions are not limiting.

An interesting question is whether or not the smaller angles  $\angle \text{Sn-O-Sn}$  indicated for certain solvents are consistent with the physical limit imposed by the tin-tin nonbonded interaction. Glidewell has proposed<sup>20,22</sup> a hard-atom radius of 1.82 Å for tin, which would limit the approach of the two tin atoms,  $D(\text{Sn}\cdots\text{Sn})$ , to 3.64 Å. It can be shown that for this limiting tin-tin distance and an estimated  $\angle \text{Sn-O-Sn}$  of  $125^\circ$ , the distance  $D(\text{Sn-O})$  of  $(\text{Me}_3\text{Sn})_2\text{O}$  would have to increase from 1.94 (gas-phase electron diffraction) to 2.05 Å in  $\text{CDCl}_3$ , a value well outside the range

known from crystallographic studies on hexaorganodistannoxanes (1.893–1.955 Å<sup>8,9,20,21</sup>). Structural data reported recently for cyclic  $[(\text{mesityl})_2\text{SnO}]_3$ <sup>23</sup> indicate a much lower hard-atom radius for tin (1.70 Å), although in this molecule the close approach of the tins may be an extraordinary response to the steric crowding. For this lower nonbonded limit of approach,  $\angle \text{Sn-O-Sn}$  of both hexaorganodistannoxanes would be free to vary over the entire interval estimated from the solution NMR data without requiring an increase in  $D(\text{Sn-O})$  beyond the range found for hexaorganodistannoxanes in structural studies.

Glidewell has developed a theoretical model<sup>24</sup> to account for the preference of compounds containing the moiety M-O-M (where M = Si, Ge, Sn, and others) for adopting a linear or bent M-O-M skeleton. A linear configuration is predicted when  $R_3M$  is of low electronegativity (i.e., an electron donor) relative to the bridging oxygen. Although the theory was not developed in order to account for the *relative degree of bending* of related families of molecules, we have noted previously<sup>4,9</sup> that substitution of tin with increasingly electron-donating substituents leads to progressively less positive  ${}^{119}\text{Sn}$  chemical shift values (lower electronegativity of Sn) and larger values of  ${}^2J({}^{119}\text{Sn}, {}^{117}\text{Sn})$  (larger  $\angle \text{Sn-O-Sn}$ ), encouraging the cautious extrapolation of Glidewell's arguments.

The solvent effects reported in this paper resemble the substituent effects just described. That is, a trend between decreasing (positive)  ${}^{119}\text{Sn}$  chemical shift and increasing  ${}^2J({}^{119}\text{Sn}, {}^{117}\text{Sn})$  (increasing  $\angle \text{Sn-O-Sn}$ ) has been identified for both  $(n\text{-Bu}_3\text{Sn})_2\text{O}$  and  $(\text{Me}_3\text{Sn})_2\text{O}$ . It is difficult, however, to connect the apparent influence of the solvent acceptor strength on structure with the previous model. Solvents of increasing acceptor strength should stabilize electron density on oxygen, further increasing its electronegativity; this should lead to an increased electronegativity difference between Sn and oxygen and result in a more nearly linear Sn-O-Sn skeleton. An alternate explanation for the smaller  $\angle \text{Sn-O-Sn}$  angles apparently adopted in solvents of greater acceptor strength is that the energetically favorable interaction between solvent and the distannoxane oxygen is enhanced for a more highly bent geometry, which renders oxygen more accessible to the solvent.

**Registry No.**  ${}^{119}\text{Sn}$ , 14314-35-3;  $(n\text{-Bu}_3\text{Sn})_2\text{O}$ , 56-35-9;  $(\text{Me}_3\text{Sn})_2\text{O}$ , 1692-18-8.

(18) Note that the observed values of  ${}^2J({}^{119}\text{Sn}, {}^{117}\text{Sn})$  must be multiplied by 1.045 before applying eq 3.

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