

correct the MP4 calculations, the average difference in the relative energies is less than 2 kcal/mol. In HOCH<sub>2</sub>CH<sub>2</sub>, the barriers for the [1,3] shift to form ethoxy radical and for the loss of H to form vinyl alcohol are close in energy, but slightly higher than decomposition to HO + C<sub>2</sub>H<sub>4</sub>; the [1,2] shift is the least favorable reaction. The three lowest energy pathways for unimolecular decomposition of HOCHCH<sub>3</sub> are nearly equal in energy: isomerization to ethoxy radical, loss of H to form acetaldehyde, and loss of H to form vinyl alcohol (not shown, ca. 1.5 kcal/mol relative to OH + C<sub>2</sub>H<sub>4</sub>). The other [1,2]-shift transition state to form

HOCH<sub>2</sub>CH<sub>2</sub> is at least 10 kcal/mol higher. Decomposition of ethoxy radical occurs via loss of CH<sub>3</sub>. The loss of H, the [1,2] shift, and the [1,3] shift require substantially more energy.

**Acknowledgment.** This work was supported by a grant from the National Science Foundation (Grant No. CHE-83-12505).

**Registry No.** HO•, 3352-57-6; C<sub>2</sub>H<sub>4</sub>, 74-85-1; HOCH<sub>2</sub>CH<sub>2</sub>•, 4422-54-2; CH<sub>3</sub>CH<sub>2</sub>O•, 2154-50-9; HOCHCH<sub>3</sub>, 2348-46-1; CH<sub>2</sub>=CHOH, 557-75-5; H, 12385-13-6; CH<sub>2</sub>O, 50-00-0; CH<sub>3</sub>•, 2229-07-4; CH<sub>3</sub>CHO, 75-07-0.

## Solid-State <sup>13</sup>C NMR Investigation of Methyltin(IV) Compounds. Correlation of NMR Parameters with Molecular Structure

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Received November 10, 1986

**Abstract:** Solid-state <sup>13</sup>C NMR data are reported for 52 methyltin(IV) compounds. The dependence of NMR parameters (chemical shift and tin-carbon *J* coupling, <sup>1</sup>*J*(<sup>119</sup>Sn,<sup>13</sup>C)) on molecular structure has been investigated with reference to the X-ray structures known for many of the compounds. <sup>13</sup>C chemical shifts of the tin-methyls generally increase (are more deshielded) in the series tetra- < penta- < hexa- < heptacoordinated methyltin(IV) and tri- < di- < monomethyltin(IV) compounds, although there is considerable overlap between several of these groups. <sup>1</sup>*J*(<sup>119</sup>Sn,<sup>13</sup>C) values were determined for 29 compounds whose X-ray structures are known; a linear regression of the data for 28 compounds yields the equation <sup>1</sup>*J*(<sup>119</sup>Sn,<sup>13</sup>C) = 10.7 (Me-Sn-Me angle) - 778 (*r* = 0.975). A Fermi contact term-tin hybridization model is used to rationalize the general behavior; changes in the effective nuclear charge of tin may be responsible for the several poorly behaved compounds that have been identified. Cases have been found in which more than one <sup>1</sup>*J*(<sup>119</sup>Sn,<sup>13</sup>C) value exists for the methyls in di- and trimethyltin(IV) compounds. This appears to arise in cases where the tin atom bonds to different methyls with substantially different hybrid orbitals.

We have suggested<sup>2</sup> that solid-state NMR provides a powerful means for discovering and for evaluating relationships between NMR and structural parameters. In a preliminary communication we reported<sup>3</sup> our finding that the magnitude of tin-carbon *J* coupling, <sup>1</sup>*J*(<sup>119</sup>Sn,<sup>13</sup>C) (<sup>1</sup>*J*), measured for structurally characterized methyltin(IV) compounds by solid-state <sup>13</sup>C NMR, is linearly related to the Me-Sn-Me angle for di- and trimethyltin(IV)s. To account for this simple behavior we have offered a hypothesis that depends on the contribution of the Fermi contact term, FCT (commonly assumed to dominate *J* coupling interactions of organotin(IV) compounds), to <sup>1</sup>*J*.<sup>4-7</sup> The FCT depends strongly on the *s* character of the bonding orbitals of the coupled nuclei, as should the Me-Sn-Me angle (larger angles in organotin(IV) compounds are believed<sup>8</sup> to reflect increased *s* character in the bonding orbitals); therefore, changes in the angle should be accompanied by corresponding changes in <sup>1</sup>*J*.

The data for most methyltin(IV) compounds are well-behaved and the empirical <sup>1</sup>*J*/angle relationship provides a useful tool for the structural analysis of uncharacterized methyltin(IV) compounds.<sup>9,10</sup> <sup>1</sup>*J* can also be determined for many methyltin(IV) polymers, and it provides one of the few probes of molecular structure for amorphous or microcrystalline methyltin(IV) compounds.<sup>11</sup> Because <sup>1</sup>*J* can be measured in solution, the solid-state NMR-derived relationship also can be used to estimate molecular structures in solution and to evaluate medium effects on the structure of methyltin(IV) compounds.<sup>10,12</sup>

Given the potential utility of the empirical relationship between <sup>1</sup>*J* and the Me-Sn-Me angle, it is important that its accuracy and limitations be broadly investigated. The physical basis for the simple empirical relationship is also of interest and, it is hoped,

may be elucidated in part by the identification of compounds displaying exceptional behavior. In this paper we report solid-state <sup>13</sup>C NMR data for a large number of methyltin(IV) compounds. Data for several fall outside the simple relationship and raise interesting questions about the mechanism of tin-carbon *J* coupling in these molecules.

### Results and Discussion

**NMR of Methyltin(IV) Solids. Structure Correlations.** Solid-state <sup>13</sup>C NMR data for 52 compounds are reported in Table I (along with solution data for Me<sub>4</sub>Sn). For 41 of these compounds one or, usually, both of the tin-carbon *J* coupling satellites were visible and <sup>1</sup>*J* could be determined. The major difficulty encountered in observing the <sup>117,119</sup>Sn satellites and determining <sup>1</sup>*J*

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**Table I.** Solid-State  $^{13}\text{C}$  NMR Data for Methyltin(IV) Compounds

compound, structure type <sup>a</sup>	Sn-methyl chemical shift <sup>b</sup> (ppm)	LW <sup>c</sup> (Hz)	$ ^1J(^{119}\text{Sn}, ^{13}\text{C}) ^d$ (Hz)	X-ray structure data	
				Me-Sn-Me angle (deg)	ref
tetraordinated					
$\text{Me}_4\text{Sn}$ (1)	0		336 <sup>e</sup>	109.5 <sup>f</sup>	
$[\text{Me}_2\text{SnS}]_3$ (2)	12.2, 8.3, 7.5	<10	430 (av)	118 (av)	46
$\text{Me}_2\text{SnPh}_2 \cdot 2\text{Cr}(\text{CO})_3$ (3)	-6.7	40	380	115.5	47
$\text{MeSnPh}_3$ (4)	-8.8, -6.9	14	510 <sup>g</sup>		
pentacoordinated					
$\text{Me}_2\text{Sn}[\text{ON}(\text{Ph})\text{COPh}]$ (5)	5.6	35	410	109.7 (av)	48
$\text{Me}_3\text{SnCl}$ (6)	4.1	160	470	117.2	<sup>h</sup>
$\text{Me}_2\text{SnNO}_2 \cdot \text{H}_2\text{O}$ (7)	1.0	27	490	120 (av)	49
$\text{Me}_2\text{Sn}[\text{O}_2\text{C}(1\text{-Np})]$ (8)	3.9, 1.8	20	490	119.6 (av)	38
$\text{Me}_2\text{SnNO}_3$ (9)	0.9	30	500		
$\text{Me}_2\text{Sn}[\text{O}_2\text{C}(\text{c-C}_6\text{H}_{11})]$ (10)	2.2, 0.1	20	510 (av)	119.6 (av)	38
$\text{Me}_2\text{Sn}[\text{O}_2\text{C}(p\text{-C}_6\text{H}_4\text{NH}_2)]$ (11)	1.5	30	530	119.5 (av)	38
$\text{Me}_2\text{SnOAc}$ (12)	1.7, -0.1	<10	540	120	65
$\text{Me}_2\text{SnF}$ (13)	2.3	120	550		
$[(\text{Me}_2\text{Sn})_2\text{CO}_3]_n$ (14)	0.4	45	590		
$\text{Me}_2\text{SnOH}$ (15)	6.2, 3.5	18	600		
$\text{Me}_2\text{Sn}(\text{S}_2\text{CNMe}_2)$ (16)	3.5	90			
$\text{Me}_2\text{PhSnOAc}$ (17)	2.1	12	610	128.1	50
$\text{Me}_2\text{Sn}(\text{Cl})(\text{S}_2\text{CNMe}_2)$ (18)	13.3	130	580	128	51
$\text{Me}_2\text{Sn}(\text{Cl})(\text{cysteine ethyl ester})$ (19)	10.1	130	600	119.5	22
$\text{Me}_2\text{Sn}(\text{glycylmethioninate})$ (20)	-0.1	<10	640	123.8	23
$\text{Me}_2\text{Sn}(\text{NO}_3)(\text{OH})$ (21)	9.6	15	730	139.9	24
$\text{Me}_2\text{Sn}(\text{Cl})(o\text{-C}_6\text{H}_4\text{NMe}_2)$ (22)	1	100			
$[\text{Me}_2\text{SnO}]_n$ (23)	6.4	21	660		
hexacoordinated					
$\text{Me}_2\text{Sn}(\text{S}_2\text{PMe}_2)_2$ (24)	16.9	<10	470	122.6	20
$\text{Me}_2\text{Sn}(\text{S}_2\text{COEt})_2$ (25)	9.9	<10	570	130.1	21
$\text{Me}_2\text{Sn}[\text{ON}(\text{H})\text{COCH}_3]_2$ (26)	7.3	30	600	109.1	17
$\text{Me}_2\text{Sn}(\text{oxinate})_2$ (27)	10.7, 7.5	30	630	110.7	18
$\text{Me}_2\text{Sn}(\text{OAc})_2$ (28)	4.0	<10	660		
$\text{Me}_2\text{Sn}(\text{NCS})_2$ (29)	14.1	17	670	147.4	26
$\text{Me}_2\text{Sn}(\text{S}_2\text{CNMe}_2)_2$ (30)	17.9	<10	670	136	52
$\text{Me}_2\text{Sn}(\text{S}_2\text{CNEt}_2)_2$ (31)	15.2, 16.5	<10	680	135.6	12
$[\text{Me}_2\text{SnCl}_2\text{-salicylaldehyde}]_2$ (32)	14.6	150	680	131.4	19
$\text{Me}_2\text{Sn}[\text{S}_2\text{CN}(\text{CH}_2)_4]_2$ (33)	18.0	20	705	137.4	9
$\text{Me}_2\text{Sn}(\text{laurate})_2$ (34)	5.2	<10	720		
$\text{Me}_2\text{SnPO}_4\text{H}$ (35)	13.0, 11.5, 10.6	20	780		
$[\text{Me}_2\text{SnCl}_2\text{-lutN-O}]_2$ (36)	19.0	150	810	145.3	53
$[\text{Me}_2\text{Sn}(\text{O}_2\text{CCH}_2\text{Cl})_2\text{O}]$ (37)	11.7	40	820	152 (av)	54
$\text{Me}_2\text{SnCl}_2 \cdot 2\text{DMF}$ (38)	24.2	<i>i</i>	990	165.0	55
$\text{Me}_2\text{SnCl}_2 \cdot 2\text{DMSO}$ (39)	28.5, 23.5	14	1060	170	56
$\text{Me}_2\text{SnCl}_2 \cdot 2\text{pyrN-O}$ (40)	19.6	90	1120	180.0	57
$\text{Me}_2\text{Sn}(\text{acac})_2$ (41)	11.4	<10	1175	180.0	58
$\text{Me}_2\text{SnF}_2$ (42)	11.9	250			
$\text{Me}_2\text{SnCl}_2$ (43)	16.8	200			
$\text{Me}_2\text{SnCl}_2 \cdot 2\text{pyr}$ (44)	26	110			
$\text{Me}_2\text{SnCl}_2 \cdot \text{bpy}$ (45)	29	150			
$[\text{Me}_2\text{SnCl}_2\text{-diphenylcyclopropanone}]_2$ (46)	17.5	142			
$[\text{Me}_2\text{SnCl}_2\text{-dibenzyl sulfoxide}]_2$ (47)	16.1	70			
$\text{Me}_2\text{SnCl}_2 \cdot \text{salenH}_2$ (48)	25.1	60			
$\text{MeSn}(\text{Cl})(\text{S}_2\text{CNMe}_2)_2$ (49)	31.6	90	950 ± 50		
$[\text{MeSn}(\text{O})\text{OH}]_n$ (50)	16.2, 10.0	70	1160, 1030		
heptacoordinated					
$\text{MeSn}(\text{S}_2\text{CNEt}_2)_3$ (51)	37.1	17	1015		

<sup>a</sup> Abbreviations: 1-Np = 1-naphthyl; c-C<sub>6</sub>H<sub>11</sub> = cyclohexyl; OAc = acetate; oxinate = 8-oxyquinoline; lutN-O = 2,6-lutidine *N*-oxide; DMF = dimethylformamide, DMSO = dimethyl sulfoxide; pyrN-O = pyridine *N*-oxide; acac = acetylacetonate; pyr = pyridine; bpy = 2,2'-bipyridine; salenH<sub>2</sub> = bis(salicylaldehyde)ethylenediimine. <sup>b</sup> Chemical shifts relative to internal secondary standard delrin [89.1 ± 0.3 ppm (Me<sub>4</sub>Si = 0 ppm)]. <sup>c</sup> LW = line-width at half-height. <sup>d</sup>  $|^1J|$  values rounded off to nearest decade and are ±10 Hz. Exceptions are 33, 41, 51 (±5), and 49 (±50) Hz. <sup>e</sup> Average solution value in ref 35a. <sup>f</sup> Tetrahedral geometry assumed. <sup>g</sup>  $J$  coupling constant of tin to phenyl carbon (C<sub>1</sub>). <sup>h</sup> Lefferts, J. L.; Molloy, K. C.; Hossain, M. B.; van der Helm, D.; Zuckerman, J. J. *J. Organomet. Chem.* **1982**, *240*, 349. <sup>i</sup> Could not be measured due to partial overlap with adjacent resonance.

arose in compounds containing halogen or nitrogen since the presence of these high-abundance, spin-active nuclei causes substantial line broadening.<sup>13</sup> In this context we mention the striking observation that the line width at half-height, LW, of one dimethyltin(IV) dihalide, bis(DMSO) complex **39**, was 14 Hz,

whereas for all the other halide complexes, including the other coordination complexes, LW's from 60 to 250 Hz were found.

X-ray structures have been reported for 29 of the compounds whose  $|^1J|$  values were measured, and a plot of  $|^1J|$  versus the Me-Sn-Me angle was constructed (Figure 1). Visual inspection of the plot reveals that data for the majority of tetra-, penta-, and hexacoordinated di- and trimethyltin(IV) compounds closely define a linear relationship. A least-squares linear regression with data for all compounds except hexacoordinated *cis*-dimethyltin(IV)

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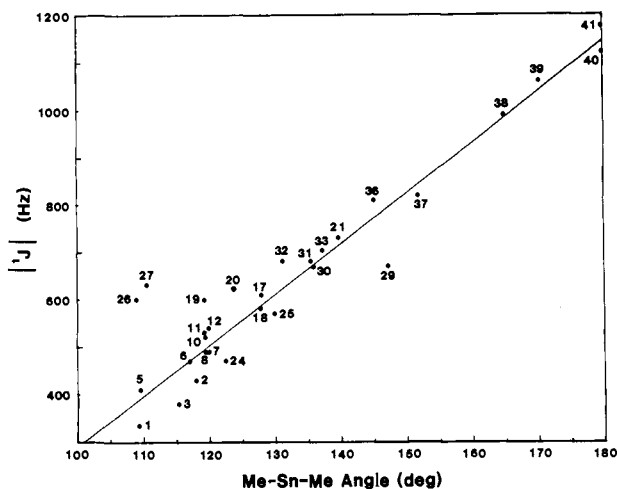


Figure 1. Plot of Me-Sn-Me angle versus  $|^1J|$  ( $^{119}\text{Sn}$ ,  $^{13}\text{C}$ ) for 30 methyltin(IV) compounds (numbers defined in Table I). Least-squares line based on 28 points (excluding 26 and 27, see text).

26 and 27 (which lie some 200 Hz above the line) gives eq 1, where  $|^1J|$  is in Hz, and the Me-Sn-Me angle is in degrees. The average

$$|^1J| = (10.7 \pm 0.5)(\text{Me-Sn-Me angle}) - (778 \pm 64) \quad (1)$$

$(r = 0.975, n = 28)$

deviation between C-Sn-C angles predicted and found was  $3.3^\circ$  (standard deviation  $2.1^\circ$ ). The error between predicted and actual Me-Sn-Me angles is  $\leq 5^\circ$  for 68% and  $\leq 3^\circ$  for 83% of the 28 compounds used in calculating eq 1. Equation 1 agrees well with that reported in a preliminary communication<sup>3</sup>  $|^1J| = 11.3(\text{Me-Sn-Me angle}) - 875$ ; the predicted  $|^1J|$  values and angles at both ends of the likely range of bond angles ( $90$  and  $180^\circ$ )<sup>14</sup> agree within 34 Hz, or about  $3^\circ$ . The difference between the two equations results largely from the new data for 19, 20, and 29, which together reduce the slope by 4% ( $r$  for the remaining 25 points is 0.990). The unusual behavior of these three compounds and 26 and 27 will be considered further below.

It has long been recognized<sup>15</sup> that there is a general trend between  $|^1J|$  and the tin coordination number. This reflects the fact that the Me-Sn-Me angle increases in going from tetra-coordinated tetrahedral to pentacoordinated trigonal bipyramidal to hexacoordinated skew or trans octahedral methyltin(IV) configurations. It is clear from the data, however, that a crossover of  $|^1J|$  values can occur for certain tetra-, penta-, and hexacoordinated methyltin(IV) geometries. For this reason, ligand structure and possible medium effects on coordination must be taken into account when assigning coordination number or molecular configuration with eq 1.

The data in the table can be used to examine the relationship of the  $^{13}\text{C}$  chemical shift of methyls bonded to tin to the tin coordination number or to the nature of the substituents at tin. The tetra-coordinated methyltin(IV) compounds have tin-methyl chemical shifts from  $-8.8$  to  $+12$  ppm, pentacoordinated trimethyltin(IV) compounds from  $-0.1$  to  $+6.2$  ppm, pentacoordinated dimethyltin(IV) compounds from  $-0.1$  to  $+13.3$  ppm, hexacoordinated dimethyltin(IV) bis(chelate) compounds from 4 to 18.0 ppm, and hexacoordinated  $\text{Me}_2\text{SnCl}_2$  compounds from 14.6 to 29 ppm. The largest tin-methyl  $^{13}\text{C}$  chemical shifts were found for monomethyl, hexacoordinated 49, 31.6 ppm, and monomethyl, heptacoordinated 51, 37.1 ppm. These shifts are consistent with the idea that the methyl group becomes increasingly deshielded as additional electronegative substituents are brought into the coordination sphere of tin, although there is a surprisingly large range of  $^{13}\text{C}$  chemical shifts within each

class of compounds. Only a modest correlation of  $^{13}\text{C}$  chemical shift with  $|^1J|$  (or the Me-Sn-Me angle) is found:  $^{13}\text{C}$  shift (in ppm) =  $0.063(|^1J|) - 32$  ( $r = 0.70, n = 41$  points).

If  $|^1J|$  depends largely on the percent s character of the bonding orbitals, then one would expect  $|^1J|$  to correlate with the Sn-C distance,  $D_{\text{Sn-C}}$ , as well as with the Me-Sn-Me angle. However, no systematic trend is found:  $D_{\text{Sn-C}}$  values for the tetra-coordinated compounds lie in the middle of the range defined by the penta-coordinated compounds ( $2.10$ – $2.19$  Å), which is nearly coincident with that of the hexacoordinated dimethyltin(IV) compounds ( $2.09$ – $2.23$  Å). The accuracy of this analysis is limited by the fact that the average uncertainty in the  $D_{\text{Sn-C}}$  values for the compounds in Table I is between  $0.01$  and  $0.02$  Å, about 10% of the total range of  $D_{\text{Sn-C}}$  observed ( $D_{\text{Sn-C}}$  varies from  $2.09$  to  $2.23$  Å).

**Methyltin(IV) Compounds That Deviate from the NMR-Structure Correlation.** It should be emphasized that the  $|^1J|/\text{Me-Sn-Me angle}$  correlation, independent of its success<sup>9,12</sup> in predicting bond angles of methyltin(IV) compounds, is wholly empirical and without an explicit theoretical basis.<sup>16</sup> To the extent that significant deviations from eq 1 will not be anticipated, the utility of the correlation is lessened. Our expanded investigation has turned up several compounds which lie significantly far from the empirical line.

We noted earlier that data for 26 and 27 fall far above the line in Figure 1. These two compounds are structurally unique, having the smallest Me-Sn-Me angles ( $110.7^\circ$ <sup>17</sup> and  $109.1^\circ$ <sup>18</sup> respectively) known for hexacoordinated dimethyltin(IV) compounds. Twelve of the thirteen other hexacoordinated dimethyltin(IV) compounds examined lie within  $6^\circ$  of the line [ $\text{Me}_2\text{Sn}(\text{NCS})_2$  lies  $12^\circ$  below the line], suggesting that the unusual configuration and relatively large  $|^1J|$  values of 26 and 27 may be related. Several lines of evidence suggest that substituent electronegativity is also an important parameter in deviations from the empirical relationship. For example, hexacoordinated  $[\text{Me}_2\text{SnCl}_2\text{-salicylaldehyde}]_2$  (32) bears both strongly electronegative substituents (Cl and oxygen) and adopts a relatively small Me-Sn-Me angle ( $131.4^\circ$ <sup>19</sup>); it lies somewhat farther than average ( $5^\circ$ ) above the line in Figure 1 [four other hexacoordinated  $\text{Me}_2\text{SnCl}_2$  complexes examined (36 and 38–40), all with larger Me-Sn-Me angles, adhere closely to the relationship]. However, two other hexacoordinated dimethyltin(IV) compounds with similar, small Me-Sn-Me angles,  $\text{Me}_2\text{Sn}(\text{S}_2\text{PMe}_3)_2$  and  $\text{Me}_2\text{Sn}(\text{S}_2\text{COEt})_2$  (24 and 25, Me-Sn-Me angles  $124^\circ$ <sup>20</sup> and  $130^\circ$ <sup>21</sup> respectively), do follow the empirical relationship closely. These two compounds differ from 32 (and also 26 and 27) in having chelating ligands bonded to tin through less electronegative atoms (sulfur rather than oxygen and nitrogen).

Two of the pentacoordinated dimethyltin(IV) compounds, 19<sup>22</sup> and 20,<sup>23</sup> also have estimated Me-Sn-Me angles significantly greater ( $9^\circ$  and  $7^\circ$ , respectively) than found by X-ray. These compounds, too, bear strongly electronegative substituents and have relatively small Me-Sn-Me angles ( $<124^\circ$ ). In contrast, two other pentacoordinated dimethyltin(IV) compounds, one having less electronegative substituents (18) and the other a large Me-Sn-Me angle (21<sup>24</sup>), are well behaved.

(16) See, however, an attempt of Holmes and Kaesz [Holmes, J. R.; Kaesz, H. D. *J. Am. Chem. Soc.* **1965**, *83*, 3902] to relate  $[^2J(^{119}\text{Sn}, ^1\text{H})]$  to the tin-carbon bond percent s character (a relevant cautionary note has been published: Grant, D. M.; Litchman, W. M. *J. Am. Chem. Soc.* **1965**, *87*, 3994).

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The apparent influence of ligand electronegativity on  $|^1J|$ , indicated by the examples discussed above, can be rationalized within the FCT model by considering that the FCT depends not only on the hybridization of the orbitals bonding the coupled nuclei but also on their effective nuclear charge.<sup>25</sup> More electronegative substituents on an atom tend to increase orbital electron density at the nucleus and lead to a decrease in the magnitude of the FCT contribution to the  $J$  coupling of that atom. The electronegative substituent effects described above, and the fact that these compounds fall *above* the empirical line, are consistent with a role of the effective nuclear charge of tin in producing the unusually large values of  $|^1J|$ . Alternately, it can be postulated that the  $|^1J|$ -structure correlation depends principally on the FCT but that the scatter derives from small changes in the other spin coupling mechanisms, induced by structure or substituent effects.

$\text{Me}_2\text{Sn}(\text{NCS})_2$  is unique among the compounds studied in having a Me-Sn-Me angle<sup>26</sup> substantially smaller ( $12^\circ$ ) than that predicted from its  $|^1J|$  value. Notably, whereas all the other ligands employed in this study are hard bases (and  $\text{R}_2\text{Sn}^{\text{IV}}$  is a hard acid),  $\text{NCS}^-$  is a soft base.<sup>27</sup> With  $\text{NCS}^-$  there is also a possibility of  $p(\pi)$ - $d(\pi)$  back-bonding from nitrogen to tin which would reduce the effective nuclear charge of tin and  $|^1J|$ . The three tetra-coordinated methyltin(IV) compounds examined (1-3) have estimated angles  $5$ - $7^\circ$  below the empirical line. This could also reflect the low number of electronegative substituents and a lower effective nuclear charge of tin.

The data for pentacoordinated  $\text{Me}_3\text{SnX}$  compounds 6-15 (which are coordinative polymers owing to bridging of the ligand X in the solid state), however, do not fit easily with the picture drawn above. While the deviation is slight ( $<3^\circ$ ) for seven compounds (6-12), data for three (13-15) indicate angles  $4^\circ$  or more above the line (9,<sup>28</sup> 13,<sup>29</sup> 14, and 15<sup>30</sup> happen to be poorly characterized, or uncharacterized, by X-ray; nevertheless, for a trimethyl-substituted tin the maximum average Me-Sn-Me angle cannot exceed  $120^\circ$ ). The relative group electronegativities of hard basic ligands can be crudely estimated by comparing their basicities ( $\text{p}K_a$ ) toward the proton.<sup>31</sup> The  $K_a$ 's (electronegativities) of these ligands decrease in the order  $\text{HCl} > \text{HNO}_3 > \text{HF} > \text{RCO}_2\text{H} > \text{HCO}_3^- > \text{H}_2\text{O}$ . With the inversion only of HF and the carboxylic acids, this order is the reverse of the magnitude of the deviations from eq 1 observed for  $\text{Me}_3\text{SnX}$  compounds.

The experimental results discussed above suggest that both structural and substituent effects may influence the magnitude of  $J$  coupling in methyltin(IV) compounds. To some extent, consideration of the electronegativity of substituents bonded to tin and how acute is the magnitude of the predicted bond angle provides a means of estimating the reliability of Me-Sn-Me angles derived from  $|^1J|$ . Alternate hypotheses which invoke the other (orbital-dipole and magnetic dipole-dipole)  $J$  coupling terms or other effects (such as the varying involvement of  $d$  orbitals in the tin-methyl bonds) might also be proposed to account for scatter in the  $J$  coupling-structure correlation; however, their poorly developed theoretical basis for heavy nuclei makes them difficult to apply.

**Comparison of  $|^1J|$  and  $|^2J|$ .** Equation 1 will be most useful for making structure determinations if it is possible to identify those methyltin(IV) compounds that are likely to deviate from the NMR/structure relationship. From the data in Table I it is

clear that predicted Me-Sn-Me angles must be treated as suspect for dimethyltin(IV) compounds which are likely to be hexacoordinated, have  $|^1J|$  values less than about 650 Hz, and bear three or four strongly electronegative atoms (O, N, Cl) bonded to tin. Also, data for 19 and 20 indicate that pentacoordinated dimethyltin(IV) complexes with a strongly electronegative atom in the trigonal plane also tend to have Me-Sn-Me angles that are overestimated.<sup>32</sup>

Interestingly, comparison of  $|^1J|$  and  $|^2J|$  ( $^{19}\text{Sn}, ^1\text{H}$ ) ( $|^2J|$ ) values measured in solution may provide a means for determining which compounds may deviate from the correlations. We have described<sup>33</sup> the construction of a plot of  $|^2J|$  versus Me-Sn-Me angle (the latter derived from  $|^1J|$ ) using data obtained from solution  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectroscopy. This analysis revealed some interesting features of the relationship between  $|^2J|$  and the Me-Sn-Me angle; most notably, a nonlinear  $|^2J|/\text{angle}$  relationship (eq 2) was found for di- and trimethyltin(IV) compounds [dimethyltin(IV) dihalides and their complexes describe a distinct, second curve]. Surprisingly, Me-Sn-Me angles for hexa-

$$\text{Me-Sn-Me angle (deg)} = 0.0161(|^2J|)^2 - 1.32(|^2J|) + 133.4 \quad (2)$$

coordinated cis dimethyltin(IV) complexes appear to be much better described by eq 2, using  $|^2J|$  values, than by eq 1 (i.e., much smaller Me-Sn-Me angles are indicated by  $|^2J|$ ). Thus, while the difference between Me-Sn-Me angles predicted by the two equations is less than  $3^\circ$  for most compounds, the difference between the predicted angles is much larger for the cis dimethyltin(IV) complexes. For example, the solution  $|^1J|$  and  $|^2J|$  values for  $\text{Me}_2\text{Sn}(\text{oxinate})_2$  (27) give estimated Me-Sn-Me angles differing by  $11^\circ$ . Similarly, differences of  $12^\circ$  and  $5^\circ$  are predicted for  $\text{Me}_2\text{Sn}[\text{ON}(\text{H})\text{COCH}_3]_2$  (26) and  $\text{Me}_2\text{Sn}(\text{Cl})$  (cysteine ethyl ester)<sup>34</sup> (19), respectively (the solid-state structures of 19, 26, and 27 are believed to be retained in solution, since the solid-state and solution  $|^1J|$  values differ by less than 10 Hz for 19 and 27, and about 60 Hz for 26). These examples suggest that compounds for which the Me-Sn-Me angles predicted from solution  $|^1J|$  and  $|^2J|$  values differ by more than about  $5^\circ$  may not be well-behaved and that estimates of their Me-Sn-Me angles from solid-state or solution  $^{13}\text{C}$  NMR are unreliable.

The better overall adherence of compounds to eq 2 than eq 1, in spite of the former being an indirectly derived relationship and relying on a long-range  $J$  coupling constant, is curious. Petrosyan and Roberts<sup>35</sup> have argued that non-FCT factors are more important for the direct coupling  $|^1J|$  than for  $|^2J|$ . Since it is difficult to see why changes in the tin effective nuclear charge should influence  $|^2J|$  differently than  $|^1J|$  in cis hexacoordinated dimethyltin(IV) compounds, these data may point to a non-FCT role in the deviation of these compounds.

**Methyltin(IV) Compounds with Multiple  $|^1J|$  Values.** A clear conclusion from this structural investigation is that  $|^1J|$  and the Me-Sn-Me angle are closely related. This relationship, however, must have its basis in a co-dependence on some other factor(s). After all,  $|^1J|$  and  $|^2J|$  values are observed for monomethyltin(IV) compounds, and they are comparable to those of dimethyltin(IV) compounds of the same coordination number [cf. 49 and 50 in Table I, and solution NMR data in ref 36]. As stated previously,

(32) This suggests, for example, that the Me-Sn-Me angle estimated from the  $|^1J|$  value for  $[\text{Me}_2\text{SnO}]_n$  (ref 11), a pentacoordinated compound with oxygen in the trigonal plane, may be as much as  $5$ - $10^\circ$  too large.

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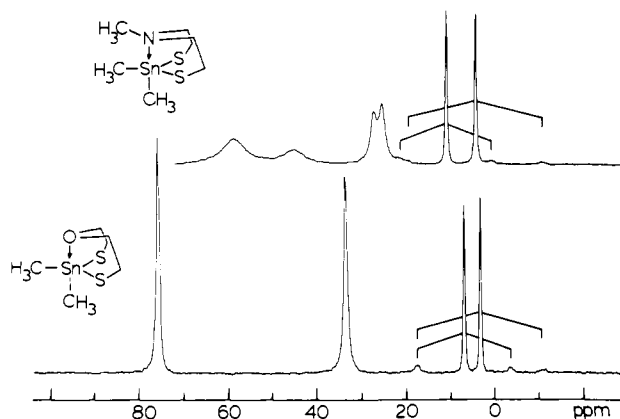
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**Figure 2.** Solid-state magic angle spinning  $^{13}\text{C}$  NMR spectra of **52** and **53** (15.08 MHz).  $J$  coupling interactions ( $|^1J|$ ) indicated for resonances of methyl groups bonded to tin. Broad resonances in the upper spectrum arise from coupling to quadrupolar  $^{14}\text{N}$  nucleus.

**Table II.** Solid-State  $^{13}\text{C}$  NMR for  $\text{Me}_2\text{Sn}(\text{SCH}_2\text{CH}_2)_2\text{X}$

compd	X	chemical shift, <sup>a</sup>	$ ^1J(^{119}\text{Sn}, ^{13}\text{C}) $ , <sup>b</sup>
		ppm	Hz
<b>52</b>	NCH <sub>3</sub>	4.8	465
		11.4	325
<b>53</b>	O	3.3	430
		7.0	315

<sup>a</sup> Relative to Delrin internal standard (89.1 ± 0.3 ppm). <sup>b</sup> Calculated from  $|^1J(^{117,119}\text{Sn}, ^{13}\text{C})|$  observed.

the hybridization of tin orbitals directed toward carbon should largely determine both the magnitude of the Me–Sn–Me angle and the magnitude of the FCT contribution to  $|^1J|$ . If, in a di- or trimethyltin(IV) compound, tin does not employ identical orbitals in bonding to each (inequivalent) methyl, then each methyl ought to have a unique value of  $|^1J|$ . Although the methyl groups are inequivalent in most of the compounds in Table I (as indicated by the tin–methyl  $^{13}\text{C}$  chemical shift multiplicity, and X-ray crystal structure), only for one compound, trimethyltin(IV) cyclohexanoate (**10**), was more than one  $|^1J|$  value clearly observed.<sup>37</sup> From X-ray the three methyl groups in **10** are known to reside in different environments and the Me–Sn–Me angles are 116.9 (4), 117.6 (4), and 124.2 (4)°.<sup>38</sup> In the solid-state  $^{13}\text{C}$  NMR spectrum an approximately 2:1 ratio of methyl signals is observed, with  $|^1J|$  values of ca. 485 and 550 Hz, respectively. This corresponds to Me–Sn–Me angles of 118 and 124°, in good agreement with the X-ray result.

This result encouraged us to look for methyltin(IV) compounds in which the methyls are even more markedly unique. The synthesis of one such compound, **52**, was recently reported by Tzschach and co-workers.<sup>39,40</sup> In the modestly distorted trigonal-bipyramidal conformation,<sup>41</sup> one methyl group clearly resides in the equatorial plane and the other in an apical position [Me–Sn–Me angle = 107°, Me(apical)–Sn–N angle = 167°;<sup>40</sup> see drawing in Figure 2]. Solution NMR data,<sup>39</sup> in fact, hint at the unusual character of this compound: two  $^{13}\text{C}$  methyl resonances are observed, each with a distinct  $|^1J|$  value (472 and 341 Hz).

(37) At the field strength employed in the present study (1.4 T, 15.08 MHz for  $^{13}\text{C}$ ), small differences in  $|^1J|$  values are not resolved. We have recently observed inequivalencies of 20–40 Hz in  $|^1J|$  values for the methyls in a hexacoordinated dimethyltin(IV) at higher field strengths (7.0 T, 75.5 MHz). In general,  $|^1J|$  values for different methyls in a compound appear to be very similar; eq 1 should apply to averaged values of  $|^1J|$  in these cases.

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The solid-state  $^{13}\text{C}$  NMR spectrum of crystalline **52** (Figure 2)<sup>42</sup> also contains two  $^{13}\text{C}$  resonances, with coupling constants of 465 and 325 Hz, respectively (similarly for the oxygen analogue **53**, Table II).

The data for **10**, **52**, and **53** demand the conclusion that tin employs dissimilar orbitals in bonding to methyls which reside in dissimilar environments in a molecule and that they can have distinct, resolvable  $|^1J|$  values. A further, striking conclusion for **52** and **53** is that tin must not employ (nearly) pure p or dp orbitals to bond to the apical methyl carbon in these compounds: the  $|^1J|$  values, 325 and 315 Hz, are not substantially different from  $\text{sp}^3$ -hybridized  $\text{Me}_4\text{Sn}$  (336 Hz<sup>35a</sup>)! It appears that a simple  $\text{sp}^3\text{d}$  hybridization description is inappropriate for these compounds.

## Conclusions

Determining the solid-state  $^{13}\text{C}$  NMR spectra of a number of structurally characterized methyltin(IV) compounds has made it possible to examine in greater detail the dependence on structural parameters of  $|^1J|$  and the chemical shift of methyls bonded to tin. In particular, the large data base has provided more insight into the occurrence of exceptions to the simple, linear relationship between  $|^1J|$  and the Me–Sn–Me angle. For dimethyltin(IV) compounds with Me–Sn–Me angles greater than 140°, only compound **29** is poorly behaved. For  $|^1J|$  less than about 650 Hz estimated angles may be too large if the other ligands are bonded to tin through three or four highly electronegative atoms. It appears that the comparison of Me–Sn–Me angles estimated from solution  $|^1J|$  and  $|^2J|$  values may provide an indication of compounds that strongly disobey eq 1. In cases where discrepancies of 5° or more in the estimated solution angles are found, the estimated angles (from solution or solid-state NMR data) should be used with caution.

It has been proposed that the dependence of  $|^1J|$  on the Me–Sn–Me angle reflects the dominant contribution of the FCT to tin–carbon  $J$  coupling. However, this model is only partly successful in rationalizing the sometimes large scatter observed in the empirical  $|^1J|$ –structure plot. In the absence of a sophisticated theoretical treatment of tin–carbon  $J$  coupling, for which the NMR–structure data set reported here should provide a unique resource, it may be difficult to develop a model with more predictive power.

Perhaps the most remarkable thing about the empirical NMR–structure correlation is that the large difference in type and number of substituents at tin have such a modest effect on  $|^1J|$ . Comparison may be made to a correlation that has been drawn between the  $^{119}\text{mSn}$  Mössbauer quadrupole splittings and Me–Sn–Me angles of hexacoordinated dimethyltin(IV) complexes. Although a concise theoretical basis for the Mössbauer–structure correlation has been developed,<sup>43</sup> large, apparent substituent effects substantially limit the reliability of the structural estimates thus derived.<sup>43–45</sup>

The finding that methyl groups in a di- or trimethyltin(IV) compound can have individual  $J$  coupling values, if they reside in sufficiently dissimilar bonding environments, indicates that the hybridization of the orbitals used by tin in bonding to methyl largely determines  $|^1J|$ . This provides further insight into the basis of the  $|^1J|$ /Me–Sn–Me angle correlation and suggests that the correlation of  $|^1J|$  with Me–Sn–Me angle is in some sense fortuitous: it works only because, for most compounds, tin bonds to different methyls in a molecule with similarly hybridized orbitals, and because the Me–Sn–Me angle and  $|^1J|$  depend on common factors (i.e., Sn orbital hybridization).

## Experimental Section

**Materials.** Compounds **1**, **2**, **4**, **6**, **15**, **23**, **34**, **42**, **43**, and **50** were obtained from commercial sources. Crystals of **4** were obtained upon slow evaporation of a saturated methanol solution at room temperature.

(42) Samples of **52** and **53** were kindly provided by Prof. A. Tzschach (Martin-Luther-Universität, GDR).

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The purification of **15** and **50** has been described previously.<sup>11</sup> Crystalline samples of **2**,<sup>46</sup> **3**,<sup>47</sup> **5**,<sup>48</sup> **7**,<sup>49</sup> **8**, **10**, and **11**,<sup>38</sup> **17**,<sup>50</sup> **18**,<sup>51</sup> **19**,<sup>34</sup> **20**,<sup>23</sup> **21**,<sup>24</sup> **25**,<sup>21</sup> **26**,<sup>17</sup> **27**,<sup>18</sup> **29**,<sup>26</sup> **30**,<sup>52</sup> **31**,<sup>12</sup> **32**,<sup>19</sup> **33**,<sup>9</sup> **36**,<sup>53</sup> **37**,<sup>54</sup> **38**,<sup>55</sup> **39**,<sup>56</sup> **40**,<sup>57</sup> **41**,<sup>58</sup> **44** and **45**,<sup>59</sup> **46**,<sup>60</sup> **48**,<sup>61</sup> **49**,<sup>62</sup> and **51**<sup>63</sup> were obtained by using the methods described in the papers reporting their X-ray structures or syntheses.

The syntheses of **9**,<sup>64</sup> **12**,<sup>65</sup> **13**,<sup>66</sup> **14**,<sup>67</sup> **22**,<sup>68</sup> **24**,<sup>69</sup> **28**,<sup>10</sup> **35**,<sup>11b</sup> and **47**<sup>70</sup>

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have been described. Compound **12** was recrystallized from acetone, **13** from hot methanol, and **24** from CHCl<sub>3</sub>. Compound **32**<sup>19</sup> was prepared by the combination of benzene solutions containing equimolar amounts of Me<sub>2</sub>SnCl<sub>2</sub> and salicylaldehyde. Concentration of the solution gave pale yellow crystals (mp 55 °C) of **32**. Compound **16** was prepared from Me<sub>3</sub>SnCl and NaS<sub>2</sub>CNMe<sub>2</sub>·2H<sub>2</sub>O with the method Bonati and Ugo<sup>71</sup> described for the synthesis of Et<sub>3</sub>Sn(S<sub>2</sub>CNEt<sub>2</sub>). Recrystallization from acetone-hexane solution gave needles with mp 58-61 °C (lit.<sup>72</sup> mp 63 °C).

The unit cells of crystalline **19** and **29** were determined to confirm their identification.

**NMR Spectroscopy.** Solid-state <sup>13</sup>C NMR spectra were obtained on ca. 0.4 g of polycrystalline or amorphous methyltin(IV) compounds at 15.08 MHz with 60 MHz high-power proton decoupling. Magic angle spinning at 2300 Hz in an Andrew-type rotor and spin-locking cross-polarization with the <sup>1</sup>H and <sup>13</sup>C fields matched at 57 kHz for 2 ms were used to obtain high-resolution solid-state spectra. With dwell times of 50 μs and repetition rates of 3-20 s, generally 3 to 20 k scans were required to determine [1J]. Chemical shifts (±0.3 ppm) are referenced to the internal secondary standard, delrin [89.1 ppm (Me<sub>4</sub>Si = 0 ppm)]. The solution <sup>13</sup>C NMR spectrum of **26** was obtained on a DMSO-*d*<sub>6</sub> solution at 100 MHz on a Bruker WM-400 spectrometer (400 MHz for <sup>1</sup>H). [1J] was 691.1 Hz and [2J] was 76.7 Hz at 304 K.

**Acknowledgment.** We thank Professors R. R. Holmes, F. Huber, F. P. Mullins, A. Tzschach, and J. J. Zuckerman for kindly providing us with several of the compounds employed in this study, Professors Holmes, Huber, and Zuckerman for communicating details of X-ray structures prior to their publication, and Professor E. M. Holt, who determined the unit cells of several compounds.

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## Microwave Spectrum, Inversion, and Molecular Structure of Monofluoramine, FNH<sub>2</sub>

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**Abstract:** Microwave spectra of a new molecule, monofluoramine, and its deuteriated isotopomers have been recorded and analyzed, yielding data on the molecular structure, dipole moment, quadrupole coupling, and barrier to inversion. The results are the following:  $A = 263\,271.534$  MHz,  $B = 26\,357.357$  MHz,  $C = 25\,329.428$  MHz,  $\mu_a = 1.58$  D,  $\mu_c = 1.63$  D,  $\mu_{\text{total}} = 2.27$  D,  $\chi_{aa} = 7.16$  MHz,  $\chi_{bb} = -0.61$  MHz,  $\chi_{cc} = -6.55$  MHz for the protonated species. The structural parameters are as follows:  $r_{\text{NF}} = 143.29$  pm,  $r_{\text{NH}} = 102.25$  pm,  $\angle\text{FNH} = 101.08^\circ$ ,  $\angle\text{HNH} = 106.27^\circ$ ,  $H_{\text{INV}} = 5200$  cm<sup>-1</sup>.

In recent years the investigation of substituted ammonia has aroused considerable interest due to an increased understanding of the effect of the inversion motion on the molecular spectra. As to the elucidation of the electronic properties that govern the inversion motion in a double minimum potential, one hopes that the analysis of the molecular spectra of simple amines will provide a better understanding.

Many of the simple amines, however, possess additional large amplitude motions ( $\lambda$ am), which can considerably complicate the microwave spectra and blur the meaning of the inversion motion,

as in H<sub>2</sub>NNH<sub>2</sub><sup>1</sup> or H<sub>2</sub>NCN.<sup>2</sup> There are cases, however, where these complications apparently do not arise, as in H<sub>2</sub>NOH,<sup>3</sup> H<sub>2</sub>NNO<sub>2</sub>,<sup>4</sup> and H<sub>2</sub>NNC.<sup>5</sup> but in order to isolate the inversion motion, only molecules with one H atom substituted by another atom should be considered. Until now, the only member of this

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