Tin-119 Nuclear Magnetic Resonance Study of Trimethylstannylhydrazines †

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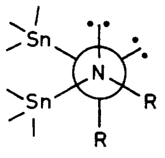
$\delta(^{119}Sn)$ and $^{2,3}J(SnSn)$ data for trimethylstannylhydrazines $(Me_3Sn)_{4-n}N_2Me_n$ (n = 0—2) as well as of $(Me_3Sn)_3N_2Ph$ are reported. The $^{2,3}J(SnSn)$ values appear to be highly sensitive to lone-pair interactions, with $^2J(SnSn)$ covering a large range (>500 Hz). The temperature dependence of the ^{119}Sn parameters indicates changes in the population of the contributing conformations.

Our continuing interest in the n.m.r. parameters of trimethylstannyl Group 3—5 compounds [1-4] led us to study trimethylstannylhydrazines. These highly reactive compounds are excellent reagents,[5] however, little is known about their structure and bonding.

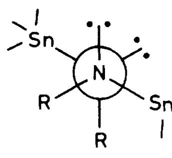
Some information concerning bonding and molecular motion in hydrazines may be obtained by n.m.r. spectroscopy as has been shown by ^{13}C [6] and ^{15}N n.m.r. [7] studies of alkylhydrazines. In the case of stannylhydrazines, ^{119}Sn n.m.r. spectroscopy is expected to become a valuable tool for the following reasons: (*i*) the presence of a second magnetically active isotope ^{117}Sn (both ^{117}Sn and ^{119}Sn have $I = \frac{1}{2}$ and 7.61 and 8.58% natural abundance, respectively) allows the direct measurement of the spin–spin coupling constants $J(SnSn)$ between tin nuclei in equivalent chemical surroundings; (*ii*) previous studies [1-4] suggest that both chemical shift values, $\delta(^{119}Sn)$, and coupling constants, $J(^{119}Sn^{119}Sn)$ and $J(^{119}Sn^{13}C)$, will be sensitive even to small changes in the bonding; (*iii*) the expected sensitivity of the ^{119}Sn n.m.r. parameters should allow the recognition of conformational changes with temperature.

It is well known that non-cyclic hydrazines prefer the *gauche* conformation which leads to minimum interaction between the nitrogen lone electron pairs (dihedral angle $\varphi \approx 90°$).[8] However, the conformers (I) and (II) may be of unequal energy depending upon the nature of R. Therefore, different conformational populations may be expected depending on the temperature.

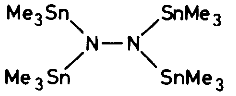
The trimethylstannylhydrazines (1)—(5) were studied by ^{119}Sn n.m.r. spectroscopy and compound (6) was included for the purpose of comparison.



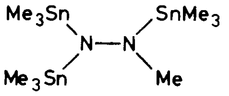
(I)



(II)



(1)



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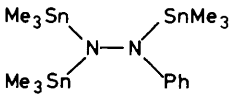

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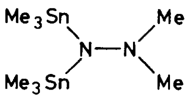

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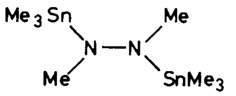

(5)

$Me_3Sn{-}CH_2{-}SnMe_2{-}NEt_2$

(6)

Experimental

Tin-119 (74.631 MHz) and ^{13}C (50.3 MHz) n.m.r. spectra were recorded with a Bruker WP 200 PFT n.m.r. spectrometer equipped with a multinuclear probe head. A thermocouple element placed directly underneath the sample served for the temperature control (±2 °C). Several measurements were made at each temperature for reproducibility and constancy of $\delta(^{119}Sn)$ and $J(SnSn)$ values. The compounds (1)—(6) were dissolved (10—25%) in [$^2H_8$]toluene (distilled and stored over a molecular sieve) in 5 mm (outside diameter) tubes, degassed by several freeze–pump–thaw cycles, and sealed *in vacuo*.

The hydrazine derivatives (1)—(5) were prepared *via* transamination reactions similar to the procedure reported for (1) [9a] starting from diethyl(trimethylstannyl)amine [9b] and the pure hydrazines. Diethylamine was distilled off at normal pressure by heating the mixtures to 120 °C. The residues were purified by fractional distillation in high vacuum. Yields were in general between 70 and 90%.

Methyltris(trimethylstannyl)hydrazine (2) (77%), b.p. 75 °C (30 Torr), colourless liquid (Found: C, 22.3; H, 5.65; N, 5.40. $C_{10}H_{30}N_2Sn_3$ requires C, 22.45; H, 5.65; N, 5.25%). Phenyltris(trimethylstannyl)hydrazine (3) (91%), b.p. 145 °C (0.5 Torr), colourless waxy solid [9c] (Found: C, 30.45; H, 5.45; N, 4.50. $C_{15}H_{32}N_2Sn_3$ requires C, 30.2; H, 5.40; N, 4.70%). 1,1-Dimethyl-2,2-bis(trimethylstannyl)hydrazine (4) (91%), b.p. 72 °C (1 Torr), colourless liquid [9c] (Found: C, 25.25; H, 6.25; N, 7.25. $C_8H_{24}N_2Sn_2$ requires C, 24.9; H, 6.25; N, 7.05%). 1,2-Dimethyl-1,2-bis(trimethylstannyl)hydrazine (5) (82%), b.p. 61 °C (1.5 Torr), colourless liquid (Found: C, 25.2; H, 6.30; N, 7.25. $C_8H_{24}N_2Sn_2$ requires C, 24.9; H, 6.25; N, 7.05%).

(Diethylaminodimethylstannyl)(trimethylstannyl)methane (6) was isolated as a second product from the preparation of $NEt_2(SnMe_3)$. From the oily residue which is left after $NEt_2(SnMe_3)$ had been distilled off, compound (6) was obtained as a colourless liquid by fractional distillation in high vacuum: b.p. 146 °C (10^{-3} Torr) (Found: C, 30.9; H, 7.05;

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† *Non-S.I. unit employed*: Torr = 101 325/760 Pa.

Table. Carbon-13 and ^{119}Sn n.m.r. data [a] of trimethylstannylhydrazines at ambient temperature (33 °C)

Compound	$\delta(^{119}Sn)$	$\delta[^{13}C(SnMe_3)]$	$\delta[^{13}C(Me,Ph)]$	$^1J(^{119}Sn^{13}C)$	$^nJ(^{119}Sn^{13}C)$	$^2J(^{119}Sn^{119}Sn)$ [b]	$^3J(^{119}Sn^{119}Sn)$ [b]
(1)	+65.3	−5.2	—	349.6	—	972.0	42.0
(2)	+61.5 (Sn_2)	−4.6 (Sn_2)	50.5	340.0 (Sn_2)	<2 (^3J)	833.0	50.2
	+56.7 (Sn)	−6.4 (Sn)		369.0 (Sn)	57.0 (^2J)		
(3)	+79.5 (Sn_2)	−4.6 (Sn_2)	158.8 (*i*) 111.2 (*o*)	348.0 (Sn_2)	5.0 (^3J)	640.5	21.0
	+49.8 (Sn)	−4.7 (Sn)	129.4 (*m*) 114.4 (*p*)	385.2 (Sn)	14.0 (^2J)		
(4)	+49.0	−3.2	53.4	351.4	16.6 (^3J)	486.0	—
(5)	+49.0	−6.8	40.2	362.0	<2 (^3J) 47.0 (^2J)	—	244.0

[a] Chemical shifts (+) to high frequency of internal $SiMe_4$ [$\delta(^{13}C)$] and external $SnMe_4$ [$\delta(^{119}Sn)$], coupling constants in Hz. [b] By multiplying $^{2,3}J(^{119}Sn^{117}Sn)$ by $\gamma(^{119}Sn)/\gamma(^{117}Sn) = 1.0465 \pm 1.5$.

N, 3.80. $C_{10}H_{27}NSn_2$ requires C, 30.1; H, 6.85; N, 3.5%). N.m.r.: $\delta(^{119}Sn)$ +20.6 [$Sn(CH_3)_3$], +75.0 [$Sn(CH_3)_2$], $^2J(^{119}Sn^{119}Sn)$ 244.0 Hz; $\delta(^{13}C)$ [$J(^{119}Sn^{13}C)$ in parentheses]: −12.9 (307.6, 261.2) ($SnCH_2Sn$), −7.9 (332.0, 12.0) (Sn^1-CH_3), −5.4 (371.1, 5.0) (Sn^2CH_3), 17.5 (14.6) (CH_3), and 46.2 (17.3) (CH_2).

Compounds (1)—(6) are extremely sensitive to moisture and should be stored in the dark.

Results and Discussion

The n.m.r. data obtained are summarized in the Table.

^{119}Sn *Chemical Shifts.*—The nuclear shielding of the tin atoms in compounds (1)—(5) is similar to that of the trimethylstannylamines.[1] The relationship found for stannylamines that the shielding of tin increases when a $(CH_3)_3Sn$ group in geminal position is replaced by a phenyl or a methyl group also holds for the stannylhydrazines. However, the phenyl group in compound (3) causes a large deshielding of the tin nuclei of the $[(CH_3)_3Sn]_2N$ group with respect to $\delta(^{119}Sn)$ in (1). In contrast, the methyl group in compound (2) provokes a shielding with respect to $\delta(^{119}Sn)$ in (1) as well as in (4) and (5) as compared to $\delta(^{119}Sn)$ in (2).

The temperature dependence of the $\delta(^{119}Sn)$ data for compounds (1), (2), and (4)—(6) is shown in Figure 1. The graphs indicate an approximately linear increase of the nuclear shielding of ^{119}Sn for compounds (1), (2) (CH_3NSn group), and (4) as well as for both tin atoms in (6). However, the temperature dependences of $\delta(^{119}Sn)$ of the $[(CH_3)_3Sn]_2N$ group in (2) and of $\delta(^{119}Sn)$ for compound (5) are definitely not linear. Since the shielding of the tin atoms increases with increasing temperature, significant intermolecular association at lower temperatures can be excluded.

Considering the similar environments at the tin atoms in compounds (1), (2), and (4) (Sn_2N group) or in (2) and (5) (CH_3NSn group) a comparison of the trends seems justified. Fairly regular changes in the $\delta(^{119}Sn)$ values with temperature for compounds (1) and (4) would be in accord with the expectation that conformational changes of the hydrazine framework are unlikely to effect the surroundings at the tin atoms provided there is no change in hybridization at the nitrogen atoms. The same holds for compound (2) (CH_3NSn group). In contrast, a change in conformation should influence the shielding of the two tin atoms in compound (2) and the tin atom in (5). We therefore take the non-linear behaviour of $\delta(^{119}Sn)$ as evidence for the presence of conformations which are of unequal energy.

A quantitative assessment of the data is difficult considering the many factors contributing to the temperature dependence of chemical shifts, *e.g.* rotation, vibration, and solvent-solute interactions.[10]

Coupling Constants.—The most striking feature in the Table is the astonishingly large values for the geminal tin-tin coupling constants $|^2J(^{119}Sn^{119}Sn)|$ as well as the large range (486—972 Hz). The distinction between ^2J(SnSn) and ^3J(SnSn) is straightforward as shown in Figure 2. The relative intensities of the ^{117}Sn satellites due to $^2J(^{119}Sn^{117}Sn)$ and $^3J(^{119}Sn^{117}Sn)$ in the ^{119}Sn n.m.r. spectrum of compound (1) are 1 : 2 corresponding to one geminal tin and two vicinal tin atoms. The increase in the magnitude of $|^2J(^{119}Sn^{119}Sn)|$ in compounds (1)—(4) as compared to bis(trimethylstannyl)amines [1] (0—200 Hz) indicates strongly that this is due to lone pair–lone pair interactions in these hydrazines. These interactions will depend on the relative population of conformations of unequal energy as well as on the number of stannyl groups at the nitrogen atom adjacent to the $[(CH_3)_3Sn]_2N$ group.

Hybridization and therefore the nature of the lone pair at the intervening nitrogen is an important contributing factor [1] for the geminal coupling constants. In this context the values of $^2J(^{119}Sn^{13}C)$ for compounds (2), (3), and (5) are interesting. The absolute values $|^2J(^{119}Sn^{13}C)|$ [57 Hz for (2) and 47 Hz for (5)] are significantly larger than observed for the corresponding stannylamines [*e.g.* 12.2 Hz in $NMe(SnMe_3)_2$ [1]]. Interestingly, $|^2J(^{119}Sn^{13}C)|$ for compound (3) is only 14.0 Hz, and this matches the 14.6 Hz in $NPh(SnMe_3)_2$.[1] We take this as evidence for the interaction of the nitrogen lone pair with the phenyl group, and this is substantiated by the low-frequency shift of the *para*-carbon resonance relative to $\delta(^{13}C)$ in benzene (Δ −14.1 p.p.m.). This indicates a planar or approximately planar nitrogen in the $N(C_6H_5)SnR_3$ group while all others are more likely to be trigonal pyramidal.

It is well known that the magnitude of vicinal coupling constants is sensitive to changes in dihedral angles.[11] The angle between the N–Sn bonds in compounds (1)—(5) will depend on the dihedral angle φ between the nitrogen lone-pair orientations. Assuming the presence of a *gauche* or an

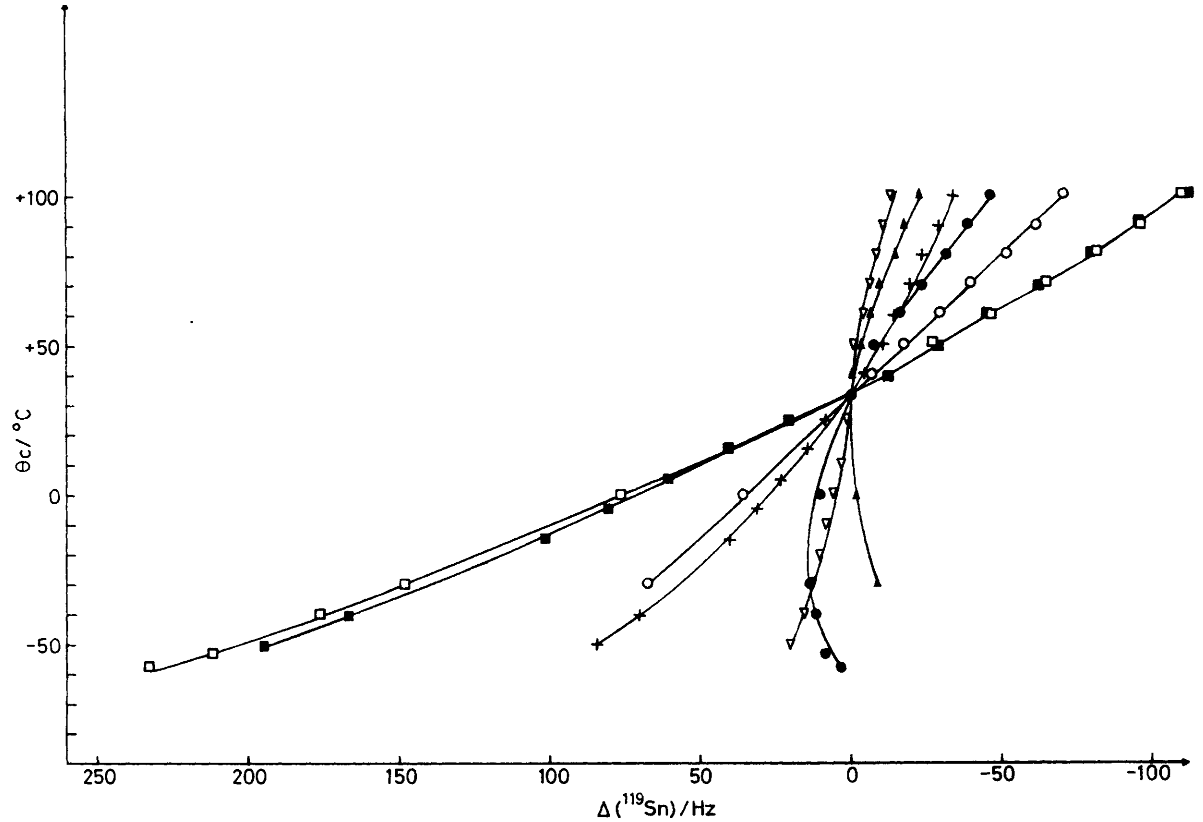

Figure 1. Temperature dependence of δ(^{119}Sn) for stannylhydrazines (1) (○); (2) $[(CH_3)_3Sn]_2N$ group (●), $[(CH_3)_3Sn]NMe$ group (□); (4) (▽); (5) (▲); and the stannylamine (6) $(CH_3)_3Sn$ group (+), $(CH_3)_2Sn$ group (■). The Δ (^{119}Sn) data are given with respect to the δ (^{119}Sn) data at 33 °C (Table)

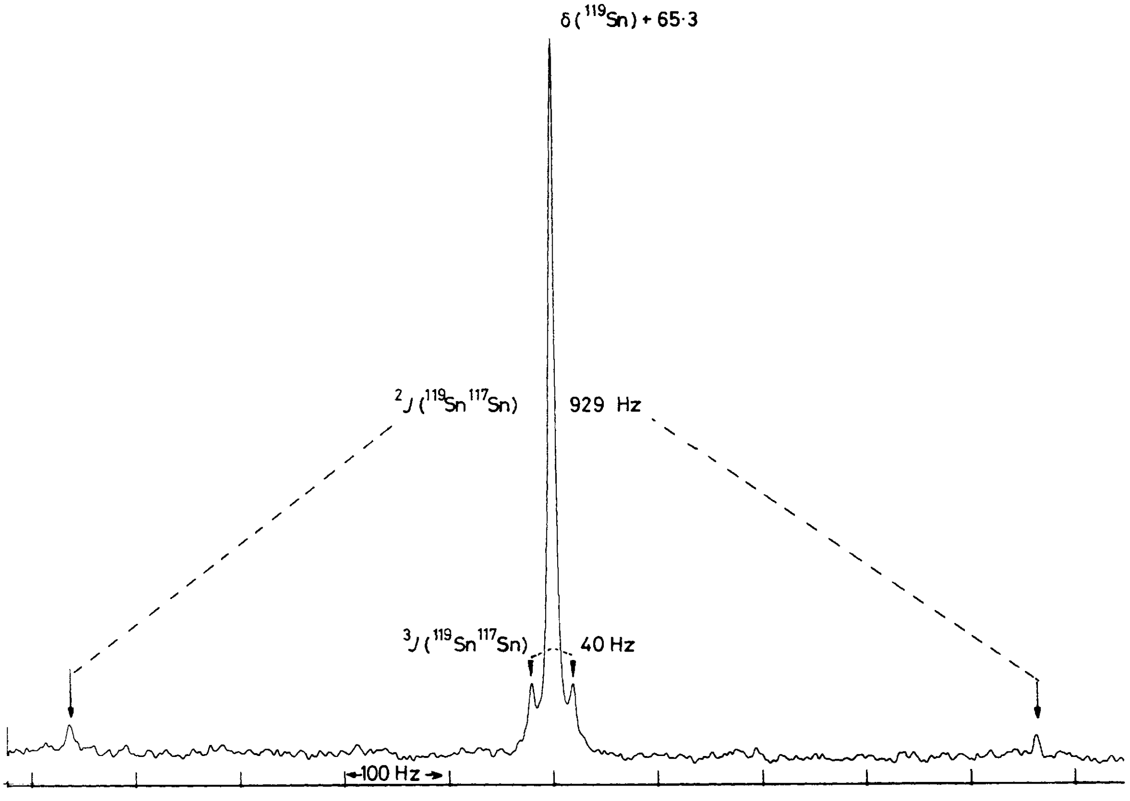

Figure 2. 74.631-MHz ^{119}Sn-{^{1}H} n.m.r. spectrum of compound (1) in [$^2H_8$]toluene (30% v/v) at 33 °C (1 000 scans, pulse angle 45° = 8 μs, acquisition time 2 s)

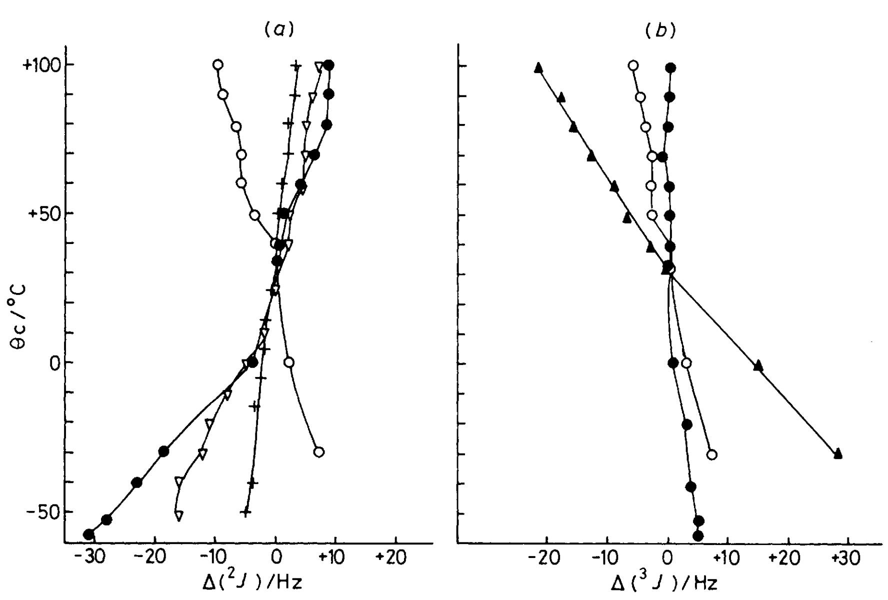

Figure 3. Temperature dependences of (*a*) $^2J(^{119}Sn^{119}Sn)$ and (*b*) $^3J(^{119}Sn^{119}Sn)$ for compounds (1) (○), (2) (●), (4) (▽), (5) (▲), and (6) (+). The Δ *J* data are given with respect to the $^{2,3}J$ data at 33 °C (Table)

approximate *gauche* conformation it is obvious that the mean relative orientation of the trimethylstannyl groups depends on the population of various conformers which will be influenced by temperature.

The smallest coupling constant $|^3J(^{119}Sn^{119}Sn)|$ is found for compound (3), again indicating the influence of the phenyl group. Since all vicinal coupling constants represent average values it is suggested that the fairly small values for $|^3J(^{119}Sn\text{-}^{119}Sn)|$ for compounds (1) and (2) result from contributions of opposite sign (*e.g.* from stannyl groups in *anti* and *gauche* positions, respectively). This would also explain the fairly large value for $|^3J(^{119}Sn^{119}Sn)|$ for compound (5) resulting from a large contribution of a *gauche* conformation (II) with *anti* arrangement of the stannyl groups.

The temperature dependence of $^{2,3}J(^{119}Sn^{119}Sn)$ as shown in Figure 3 reflects also the conformational changes. For instance $|^2J(^{119}Sn^{119}Sn)|$ for compound (6) increases only by 8 Hz between −50 and 100 °C in contrast to the stannylhydrazines. This again indicates strong lone-pair interactions. The data also indicate that the low-temperature equilibrium conformation of compound (1) is different to that of (2) and (4) as evidenced by $|^2J(^{119}Sn^{119}Sn)|$ and its temperature dependence. Higher temperatures result in smaller $|^3J(^{119}Sn^{119}Sn)|$ constants for compounds (1), (2), and (5). There is a change of 5—6 Hz for compound (2) between −58 and 33 °C, in contrast to 13 Hz between −30 and 100 °C for (1). The largest change (50 Hz) has been observed for (5) between −30 and 100 °C. This can be explained by a higher contribution of the *gauche* conformer (II) for compound (5) at low temperature (large dihedral angle between the N–Sn bonds). At higher temperatures conformation (I) with *gauche* arrangement of the stannyl groups seems to become increasingly populated.

Conclusions

This first study of the ^{119}Sn n.m.r. data of stannylhydrazines clearly indicates conformational changes with temperature. The equilibrium conformations at low temperature are different for the various stannylhydrazines. However, due to a lack of direct structural information, it is not yet possible to derive quantitative relationships between $\delta(^{119}Sn)$ and $|^nJ(^{119}Sn^{119}Sn)|$ and the dihedral angle as well as the absolute configuration. Therefore, studies on cyclic stannylhydrazines and the determination of crystal structures[12] should be included in further work. We are continuing our efforts in this direction.

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