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A Raman spectroscopic study of the rotational isomerism of linear permethylated stannylsilanes $Me_3Sn(SiMe_2)_nSnMe_3$ with $n = 1, 2, 3, 4$

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Abstract

The IR and Raman vibrational spectra of the methyl(trimethylstannyl)silanes $Me_3Sn(SiMe_2)_nSnMe_3$ with $n = 1$ (**1**), 2 (**2**), 3 (**3**) and 4 (**4**) were recorded at various temperatures. Compound **2** consists of a mixture of two conformers, *gauche* (G) and *anti* (A), in the liquid state. By variable temperature Raman spectroscopy, the enthalpy difference $\Delta H = H_{gauche} - H_{anti}$ was determined from the relative intensities of the symmetric SiSn stretching bands as 0.8 ± 0.3 kJ mol^{-1}. In the Raman spectrum of the crystalline solid, the lines of the G conformer disappear completely, facilitating the assignment of the fundamental vibrations for the A form. No indication of the presence of a third (*ortho*) conformer could be detected. HF-SCF ab initio calculations using electron core potentials for the heavy atoms predict the existence of three conformers on the potential surface. In the Raman spectra of **3**, the symmetric SiSn stretching vibration splits into three components, which can be assigned to the G^+G^+, GA and AA conformers. The G^+G^- rotamer could not be observed. As its energy is significantly larger than that for the other conformations due to repulsive four bond interactions between the $SnMe_3$ groups (pentane effect), the concentration in the equilibrium mixture is negligibly small. For **4**, eight (2^3) spectroscopically distinct (classical) conformations are possible. In the room temperature Raman spectrum, the SiSn stretching vibration consists of a line at 330 cm^{-1} with a broad shoulder at 320 cm^{-1}. In the solid (−60°C), a single rotamer (probably the all *anti* form) survives. Upon heating, several conformational states with higher energies are populated which could not be resolved by Raman spectroscopy. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Raman spectroscopy; Stannylsilanes; Rotational isomerism

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1. Introduction

Because of the potential use of peralkylated polysilanes as photoresists, precursors for ceramic materials or as materials with nonlinear optical properties, the conformations of peralkylated linear Si_n-chains have been the subject of numerous studies. A compilation of relevant literature is contained in the excellent reviews on polysilanes by Miller and Michl in 1989 [1] and by West in 1995 [2]. Decamethyl-*n*-tetrasilane, $Me_3SiSiMe_2SiMe_2SiMe_3$ is the shortest peralkylated chain expected to show rotational isomerism of the SiSi bond. From a Raman and IR vibrational study [3] it was concluded that two conformers, a planar *anti* form and a twisted *gauche* form are present in the liquid state, with the *anti* rotamer being more stable by 2.26 ± 0.15 kJ mol^{-1}. Recent extensive work of Michl and his group [4] on conformational properties of tetrasilanes yielded the surprising prediction that, according to HF/6-31G* and MP2/6-31-G* ab initio calculations, *n*-Si_4Me_{10} should comprise a mixture of three spectroscopically distinct conformers with dihedral angles ± 53° (*gauche*), ± 91° (termed *ortho* by the authors) and ± 162° (*anti*). The origin of the splitting of the usual single twisted minimum into a pair of minima (which is also observed for C_4F_{10} [5]) has been attributed to 1,4-substituent interactions. The authors were not able to identify all three conformers in the

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matrix-IR spectra, although the wavenumbers for the SiSi stretching vibrations were calculated to differ by up to 5 cm^{-1} for the three conformers. The spectra could be decomposed into those of the *anti* form and those of the *gauche* form by annealing. No experimental evidence for the presence of the *ortho* form could be found. During the present work we also reinvestigated the Raman spectra of liquid *n*-Si_4Me_{10}, accurately reproducing the results reported in Ernst et al. [3]. No indication of a third conformer could be detected, probably a consequence of the fact that two conformers, which are interconverted by a rotation of only 30–60°, cannot coexist in the gaseous phase because for all normal torsional force constants the barrier between the two forms will be so low that the lowest torsional vibrational level would lie above it [6]. In the liquid state, a stabilization of the conformers could occur through intermolecular forces, but the lowest torsional level is likely to lie near the top of the barrier, resulting in a rapid interconversion of the conformers on the time scale of vibrational spectroscopy ($\approx 10^{-13}$ s). In this case also, no distinct conformers would be observed in the vibrational spectra.

Here we report on the general features of the vibrational spectra and the conformational properties of the title compounds, which differ from linear permethylated Si_n-chains by the substitution of the end-Si atoms with Sn.

2. Experimental

2.1. Materials

The stannylsilanes $Me_3Sn(SiMe_2)_nSnMe_3$ with $n = 1$ (**1**), 2 (**2**), 3 (**3**) and 4 (**4**) were prepared by reaction of the fluorosilanes $F(SiMe_2)_nF$ with $NaSnMe_3$ as described in the literature [7] and purified by careful fractional distillation. The purity of the samples was checked with ^{1}H-, ^{29}Si- and ^{119}Sn-NMR spectroscopy.

2.2. Vibrational spectra

Room temperature (r.t.) IR spectra of the neat liquids were recorded on a Bruker IFS28 IR spectrometer in the range 4000–280 cm^{-1} as films between CsBr plates. Frequencies were calibrated with the absorptions of a polystyrole film.

Raman spectra of the neat solids and liquids sealed in Kimax capillaries were observed with a T64000 spectrometer of Jobin–Yvon equipped with a triple monochromator. The spectra were excited with the green line (514 nm) of an Ar-laser of Coherent, employing a 90° scattering geometry. Frequencies were calibrated with the lines of S_8. Intensity measurements were made over the -100 to $+100$°C temperature range. For that purpose, the capillary was mounted on a copper block that was cooled with liquid nitrogen and heated resistively, resulting in identical sample setups for low and high temperatures. The temperature was monitored by a thermocouple. To avoid any deposition of ice, the copper block was placed in an evacuated chamber equipped with quartz windows.

Deconvolution of overlapping bands was accomplished with the PEAKFIT program package, and relative band intensities were obtained by numerical integration of the band areas.

2.3. Method for calculating ΔH

The equilibrium constant K for the interconversion *anti*↔*gauche* can be written as $K = C_g/C_a = I_g\alpha_a/I_a\alpha_g$, where C_i, I_i and α_i are the rotamer concentrations, vibrational band intensities and the scattering coefficients, respectively. From the definition of $\Delta G°$, it follows

$$\ln(I_g/I_a) = -\Delta H°/RT + \text{const.}$$

$$\text{const.} = \Delta S°/R - \ln(\alpha_a/\alpha_g)$$

If $\Delta H°$ and the ratio of the scattering coefficients are independent of temperature, a linear van't Hoff plot of $\ln(I_g/I_a)$ versus $1/T$ will result.

3. Ab initio calculations

For **3**, HF-SCF calculations of equilibrium geometries, harmonic frequencies and harmonic force constants were performed employing the GAMESS software package. To keep the costs at an affordable level, a fairly simple computational scheme was used. For the heavy atoms, effective core potentials of Stevens et al. [8,9] and a valence double zeta basis with a single set of Cartesian polarization functions [10] was chosen (CEP-N1G**/SCF, $N = 3$ or 4). For the hydrogen atoms, an unscaled -31G basis was used.

Geometry optimizations were performed for three conformers (*anti*, *ortho* and *gauche*) of **2** assuming C_2-symmetry in all cases. Stationary points were located for all conformers, representing minima on the potential surface as all frequencies were real. Relevant geometrical parameters are summarized in Table 1. The optimized values for the dihedral angles of the conformers of **2** are 165 (*anti*), 91° (*ortho*) and 59° (*gauche*), which compare well with the ab initio values for Si_4Me_{10} (162.1, 93.4 and 52.7°, respectively [4]). With all conformers, the terminal $SnMe_3$ groups are rotated with respect to an *anti* SiSiSnC arrangement (dihedral angle SiSiSnC of 180°) by roughly 10–20°. It is highly probable that there are other conformational minima differing by rotations of the methyl groups. We made no attempt to investigate the existence of these conformers, as the calculated wavenumbers for the SiSi and SiSn stretching vibrations are only marginally supposed to depend on the dihedral angles of the methyl groups. Also, because of the prohibitive costs, we did not investigate additional points on the potential curve for the internal rotation of the SiSi bond.

4. Infrared and Raman spectra

The vibrational spectra of stannylsilanes have not been examined very thoroughly in the past. Schuhmann and co-workers reported on the IR spectra of $Me_3SiSnMe_3$ [11], assigning the strong band at 322 cm^{-1} as ν(SiSn). Bürger and Götze [12] discussed the Raman and IR spectra of $(Me_3Si)_4Sn$ with the help of a simplified normal coordinate analysis using a point mass model for the methyl group. They reported a SiSn stretching force constant of 166N/m. The totally symmetric SiSn stretching vibration appears as a strong Raman band at 328 cm^{-1}. To the best knowledge of the authors, no further studies of vibrational spectra of SiSn compounds exist in the literature, and also no studies of the rotational isomerism of such molecules.

Table 2 summarizes the wavenumbers that have been measured for **1**, **2**, **3** and **4** in the range 900–290 cm^{-1} (Ir) and 900–50 cm^{-1} (Ra). The vibrations of the methyl groups with wavenumbers > 900 cm^{-1} (ν_{as}, ν_s, δ_{as} and δ_s CH_3) have been omitted for clarity and simplicity, as they do not depend on molecular conformations. We also were not interested in force constants of the methyl groups. Because of the large differences in the masses of the Si and Sn atoms, the vibrations in the range 900 — 300 cm^{-1} can be divided into those involving essentially displacements of the Si atoms and those involving the Sn atoms. ρCH_3 (Si) vibrations fall into the range 850–760 cm^{-1}, ρCH_3 (Sn) modes into the much smaller range 760 — 740 cm^{-1}, an effect of the

Table 1
Important ab initio geometrical parameters (pm, deg) for *anti*, *ortho* and *gauche* $Me_3Sn(SiMe_2)_2SnMe_3$

Parameter	*Anti*	*Ortho*	*Gauche*
r(SiSn)	261.9	261.8	261.9
r(SiSi)	238.3	238.9	238.5
∠SiSiSn	112	113	115
τ(SnSiSiSn)	165	91	59
τ(SiSiSnC)	166	171	161

Table 2
Wavenumbers in the IR and Raman spectra of the stannylsilanes $Me_3Sn(SiMe)_nSnMe_3$ with $n = 1$, 2, 3 and 4

$n = 1$		$n = 2$			$n = 3$			$n = 4$			assignment
Ra(l)	Ir(l)	Ra(l)	Ra(s)	Ir(l)	Ra(l)	Ra(s)	Ir(l)	Ra(l)	Ra(s)	Ir(l)	
845vvw	842s		846vvw	836s	841vvw	846vvw	835s	842vvw	846w	835s	
808vvw	810sh	811vvw	811vw			818vvw		815vvw	816vw		$\rho(Si)CH_3$
				805sh	800vvw	802vvw			792vw	800sh	
766vvw	757vs,b	763vvw	768vvw	756vs,b	760vvw	763vvw	757vs,b	760vvw	760vvw	756vs	$\rho(Sn)CH_3$
744w		739vvw	741vvw	730sh	739vvw	740vvw		738vw	743vw		
694w	693m	684mw	690w	693mw	684mw	685m	691m	683mw	687w	690w	$\nu_{as}SiC_2$
644ms	642m	649ms	653ms	640mw	654ms	655s	658w	655ms	663s	668w	ν_sSiC_2
					630w	632vvw	635mw	633w		634w	
517s	517ms	511s	516ms	516s	511s	514s	516s	511s	516vs	516s	$\nu_{as}SnC_3$
508vs	503ms	503vs	507s	504ms	501vs	504vs	502ms	502vs	507vs	503m	ν_sSnC_3
					462mw	466w		471mw	475ms		
		439m	443m					425mw			
					390w,b	393vw,b		365mw	370s		νSiSi
369mw		340vw			325ms	327s		320ms	329vs		νSnSi
		314ms	318s		317m	318m		310m,b			
					308m	308mw					
284ms	280mw	293m		287w			289mw			290mw	
	266m			266s			277mw			280w	
	260m			258s			256vs			268mw	
	246vs			246vs	240vw	243vvw	245vs	246vvw		246vs	
							235s			229ms	
	224m	228w	233vw	224s			224s			218ms	
										211ms	δSiC_2
181ms			188w		183m,sh				187s		δSnC_3
		172m	152vw		166m,sh	174w,sh		174m,sh			
148ms		140m	140w		142ms	144m		142ms	147m		
113ms		97mw	98m		96mw	97w		95w	103w		
		66mw			73mw	76s		76w	88w		
									77s		
								53w	59w		

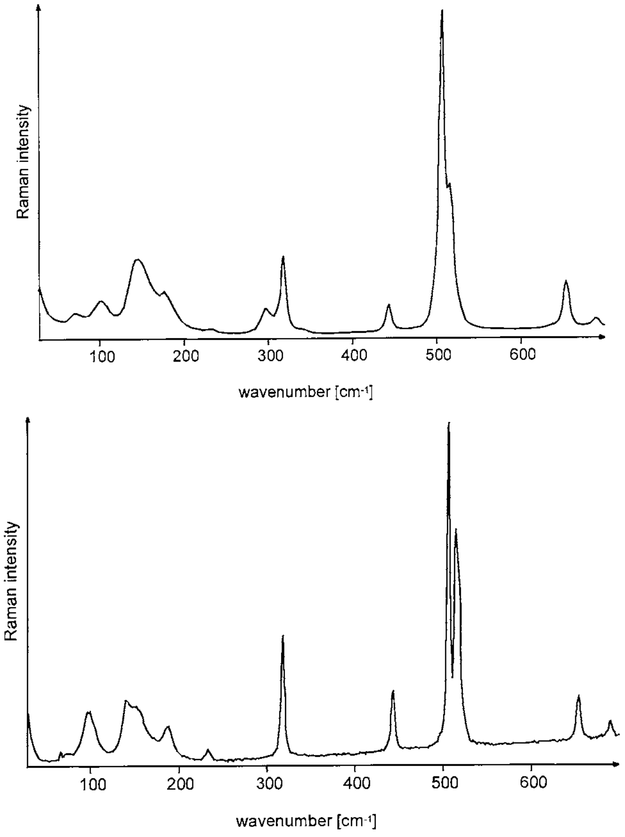

Fig. 1. Raman spectrum of liquid (22°C, top) and solid (−100°C, bottom) 1,2-bis(trimethylstannyl)tetramethyldisilane.

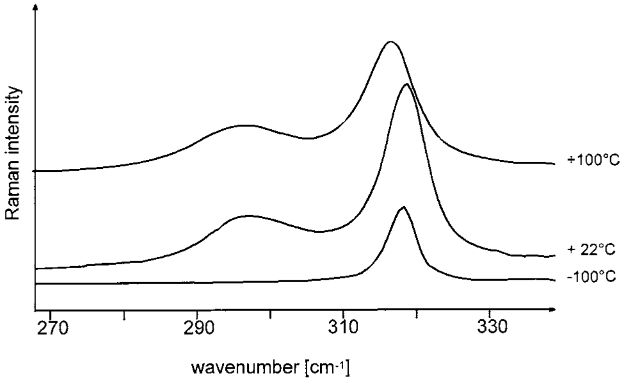

Fig. 2. Intensity variation with temperature for the SnSi stretching vibration of $Me_3Sn(SiMe_2)_2SnMe_3$.

increased mass of the Sn atom. All ρCH_3 (Si) and ρCH_3 (Sn) vibrations have very low Raman intensities but appear as strong IR absorptions.

Then follow the SiC stretching vibrations $\nu_{as}SiC_2$ (720–690 cm^{-1}) and ν_sSiC_2 (660 cm^{-1}) and the SnC stretching modes $\nu_{as}SnC_3$ and ν_sSnC_3 (500–510 cm^{-1}). Here again, the large mass of the Sn atom acts as an effective barrier between the SnC bonds. The antisymmetric and symmetric stretching modes are separated by merely 10 cm^{-1}, and these two groups of vibrations are also highly degenerate. For instance, four antisymmetric SnC_3 stretching modes are expected for **1**, **2**, **3** and **4**, but only one line is observed in each case.

The SiSi and SiSn stretching vibrations appear in the range 480–280 cm^{-1}, which can be assigned for **1** and **2** using symmetry arguments (selection rules), as they are hardly influenced by vibrations involving C- or H-atoms. For **1**, ν_{as} and ν_sSiSn_2 are observed as medium (ν_{as}) and strong (ν_s) Raman bands at 369 and 284 cm^{-1}, respectively. Their IR intensities are very low, $\nu_{as}SiSn_2$ even escaping the observation. For the disilane **2**, the vibrations of the *anti* rotamer are expected to obey the rule of mutual exclusion largely, as the SnSiSiSn dihedral angle is close to 180°, with ν_sSiSn and $\nu SiSi$ being Raman active. They appear at 314 and 439 cm^{-1} with strong and medium intensity, respectively. $\nu_{as}SiSn$, which should be IR active, has not been observed because of its low intensity. All three vibrations ($\nu_{as}SiSn$, ν_sSiSn and $\nu SiSi$) of the *gauche* rotamer are expected to be Raman and IR active, but only ν_sSiSn could be observed at 293 cm^{-1} in the Raman spectrum. The SiSi stretching vibration coincides with $\nu SiSi$ of the *anti* rotamer, and the IR intensities are again very small.

The increased SiSi chain length of **3** and **4** increases the number of SiSi stretching vibrations in the range 370–480 cm^{-1}, which may be broadened because of the larger number of rotational isomers present in the liquid state. The difference in the wavenumbers for the two SiSn vibrations on the other hand becomes smaller, as they are separated by an increased number of Si atoms. They fall into the same narrow range 290–330 cm^{-1}, making an assignment without the support of ab initio calculations very speculative.

The low frequency region of the spectra < 260 cm^{-1} cannot be assigned unambiguously, even with the help of the ab initio calculations. The large number of deformation modes of the SiC_n and SnC_n groups, which are crowded between 260 and 100 cm^{-1}, cannot be resolved, resulting in rather broad barely structured bands. The presence of rotational isomers as well as extensive vibrational couplings further complicate matters, making an assignment and description of the bands as group vibrations almost meaningless.

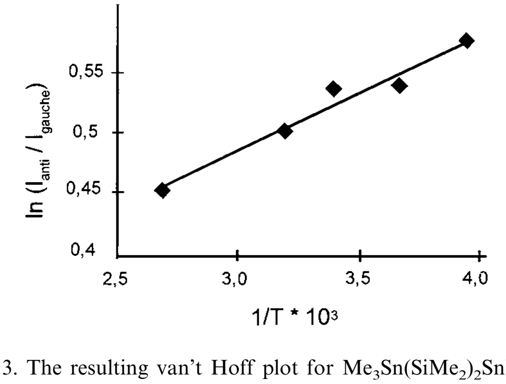

Fig. 3. The resulting van't Hoff plot for $Me_3Sn(SiMe_2)_2SnMe_3$.

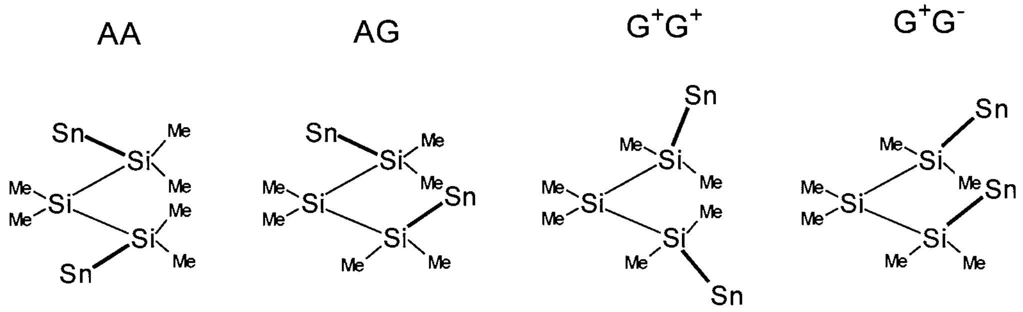

Fig. 4. Schematic drawings of the four conformers of **3**.

5. Rotational isomerism

5.1. $Me_3Sn(SiMe_2)_2SnMe_3$ (**2**)

The two intense Raman bands at 293 cm^{-1} (*gauche*) and 314 cm^{-1} (*anti*) were selected for a determination of the relative populations with the method described in the Section 2. Fig. 1 presents the Raman spectra of the liquid (top) and the solid (bottom) between 50 and 700 cm^{-1}, and Fig. 2 displays the Raman spectra between 270 and 330 cm^{-1} for three different temperatures. The resulting van't Hoff plot is displayed in Fig. 3. A $\Delta H°$ for the *anti–gauche* interconversion of 0.8 ± 0.3 kJ mol^{-1} was obtained. The error limit of ± 0.3 kJ mol^{-1} is an estimated value larger than the statistical error, reflecting the inherent difficulties of the method which are discussed in an excellent review of Klaboe [13].

5.2. $Me_3Sn(SiMe_2)_3SnMe_3$ (**3**)

For the trisilane **3**, four spectroscopically distinct conformers with SnSiSiSi dihedral angles of ca. ±180 and ±60° may be expected within the framework of classical conformational analysis. They are presented in Fig. 4 below with the notation AA, AG, G^+G^+ and G^+G^-.

The AA, AG, G^+G^+ conformers constitute the low energy forms. It is reasonable to expect that the relative energy of the G^+G^- rotamer is considerably higher. For instance, the G^+G^- state of $Me_3Si(SiMe_2)_3SiMe_3$ is calculated to lie above the other conformational states by as much as 160 kJ mol^{-1}, using empirical force field methods [14]. In the temperature range selected for the present work, states that high in energy are populated to a negligible degree.

The Raman spectrum of **3** confirms this expectation. The SiSn stretching vibration at 320 cm^{-1} splits into three components displaying a clear temperature dependence of the relative intensities as illustrated in Fig. 5.

We were not able to obtain satisfactory bilinear plots and reliable ΔH data, but it can be safely concluded from the relative peak heights that the rotamer corresponding to the vibration with the highest wavenumber (330 cm^{-1}) is the most stable one and that the conformational energies of the other two rotamers are nearly the same. As ab initio calculations of the normal vibrations for these molecules could not be performed because of the prohibitive costs, a simpler computational scheme was chosen as an aid for the assignment of the lines to the individual rotamers. It is described in Section 6 (Normal Coordinate Analysis). As can be seen from Table 5 presented in Section 6, the wavenumbers of the SnSi stretching vibrations that fall into the totally symmetric representation A (assuming point group C_2 for the AA and G^+G^+ rotamers) decrease in the series $AA > G^+G^+$ supporting the prediction that

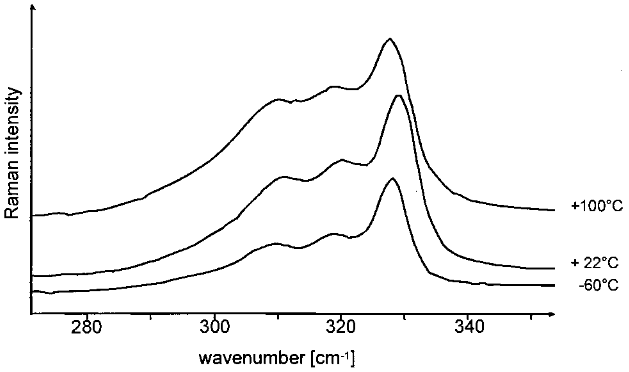

Fig. 5. Temperature dependence of the Raman spectrum of **3** in the range 280–340 cm^{-1}.

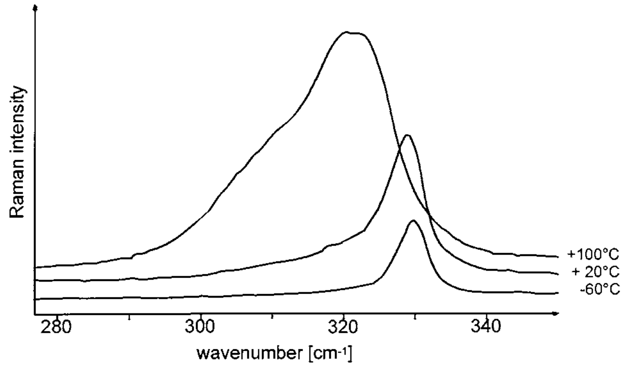

Fig. 6. Temperature dependence of the Raman spectrum of **4** in the range 280–350 cm^{-1}.

Table 3
Wavenumbers for the observed and calculated (scaled by 0.92) SiSi and SiSn stretching vibrations for the *anti*, *ortho* and *gauche* conformers of $Me_3Sn(SiMe_2)_2SnMe_3$

Vibration	Species	*Anti*		*Ortho*	*Gauche*	
		Calc.	Exp.	Calc.	Calc.	Exp.
ν_sSiSn	A	300	314	288	275	293
ν_{as}SiSn	B	302	–	324	333	340
νSiSi	A	432	439	432	434	439

it is the all *anti* rotamer (AA) which has the lowest energy in the liquid state and that the energies of the AG and G^+G^+ conformers do not differ significantly. Again, no indications for non-classical conformations with dihedral angles around 90° could be observed in the Raman spectra of the liquid.

5.3. $Me_3Sn(SiMe_2)_4SnMe_3$ (4)

For **4**, eight (2^3) conformational states are expected, again assuming a classical conformational behaviour. Fig. 6 displays the SiSn stretching vibration of **4** for three temperatures. At low temperatures, a single line is observed. It is tentatively assigned to the all *anti* isomer, because ν_s(SiSn) of the A and AA conformers of **2** and **3**, respectively also possess the highest wavenumber of all rotamers. Upon heating, a broad shoulder at the low-frequency side develops, indicating the population of several high energy states which cannot be resolved.

6. Normal coordinate analysis

The assignments of the normal modes which are included in Table 2 are based upon HF-SCF ab initio calculations (described in Section 3), which were performed for **2**. Through numerical differentiation at the calculated equilibrium geometries, harmonic wavenumbers and harmonic force constants were calculated. The force constants, which were initially defined with Cartesian coordinates (Hessian matrix), were then converted into symmetry force constants defined by symmetry coordinates which themselves were linear combinations of internal coordinates (bond lengths, bond angles and torsion angles). The symmetry coordinates were chosen by assuming local C_{2v} symmetry for the $SiMe_2$ groups and local C_{3v} symmetry for the $SnMe_3$ groups. This particular choice ensures the transferability of the force fields to other stannylsilanes, for instance **3**.

The Cartesian coordinates of the equilibrium geometries for the *anti*, *ortho* and *gauche* conformers of **2**, the Hessian matrices and the symmetry coordinates were then used to calculate the G and F-matrices according to Wilson [15], as well as the potential energy distributions for the normal modes, employing the program ASYM40 in an enlarged version [16]. Table 3 summarizes the observed and scaled ab initio wavenumbers for the SiSn and SiSi stretching vibrations of the *anti*, *ortho* and *gauche* conformers of **2**. With decreasing SnSiSiSn dihedral angle (*anti* > *ortho* > *gauche*), ν_sSiSn of species A, which possesses the highest Raman intensity, also decreases, whereas ν_{as}SiSn of species B increases. Here, ν_sSiSn and ν_{as}SiSn denote in phase and out of phase distortions of the two SiSn bonds, respectively. The SiSi stretching vibration is barely affected by conformational impacts.

The ab initio force constants of the SiSn and SiSi bonds do not differ significantly for the three conformers, with scaled (0.92^2) values for f(SiSi) and f(SiSn) between 148–149 and 116–117 N/m, respectively. Table 4 presents scaled theoretical symmetry force constants for the vibrations of the SnC_3 groups, which can be used as a set of transferable force constants for other stannylsilanes containing the group. Again, the differences between the three conformers are negligibly small. The notation of the symmetry coordinates as used in Table 4 is described in [17], with the index 1 denoting symmetry coordinates with the linear combination $2/-1/-1$ of internal coordinates and the index 2 the combination $0/1/-1$. Detailed force fields for all three conformers can be obtained from the authors upon request.

For **3**, a reasonable geometry and force field was chosen by assuming transferability of bond lengths,

Table 4
Theoretical symmetry force constants (N/cm, scaled by $0.92^2 = 0.8464$) for the internal vibrations of a SnC_3 group

	Symmetry force constants							
ν_sSnC_3	1.99	0.06	0	0	0	0	0	0
δ_sSnC_3		0.51	0	0	0	0	0	0
$\nu^1_{as}SnC_3$			1.89	0.08	−0.07	0	0	0
ρ^1SnC_3				0.38	−0.07	0	0	0
$\delta^1_{as}SnC_3$					0.48	0	0	0
$\nu^2_{as}SnC_3$						1.89	0.08	−0.07
ρ^2SnC_3							0.37	−0.04
$\delta^2_{as}SnC_3$								0.46

Table 5
Calculated SiSi and SiSn stretching vibrations for the AA and G^+G^+ conformers of $Me_3Sn(SiMe_2)_3SnMe_3$

Vibration	Species	Conformer	
		AA	G^+G^+
ν_sSiSn	A	309	294
ν_{as}SiSn	B	297	336
ν_sSiSi	A	416	426
ν_{as}SiSi	B	497	479

bond angles, torsion angles and force constants from **2**, and a normal coordinate analysis was performed with these parameters for the AA and G^+G^+ conformers assuming C_2-symmetry with dihedral angles of 180°/180° and 60°/60°, respectively. The vibrations of the methyl groups were initially included, but later removed by a method described by Wilson [15], except the ρCH_3-modes as these can influence the vibrations of the heavy-atom skeleton via kinetic coupling. The calculated wavenumbers for the SiSi and SiSn stretching vibrations are presented in Table 5. With decreasing SnSiSiSi-dihedral angles ν_sSiSn is shifted to lower, ν_{as}SiSn to larger wavenumbers as is also the case for **2**. For the AG conformer, which belongs to point group C_1, no normal coordinate analysis was carried out because of the large dimensions of the G- and F-matrices involved (128 × 128). With some confidence, which is supported by the ab initio results for **2**, one can conclude that ν_sSiSn of the AG conformer will have a value in between those for the AA and G^+G^+ conformers. This assumption leads to the prediction that it is the AA rotamer which possesses the lowest energy in the liquid state.

7. Conclusions

The present Raman spectrocopic study proves that the permethylated stannylsilanes $Me_3Sn(SiMe_2)_nSnMe_3$ with $n = 2$ (**2**), 3 (**3**) and 4 (**4**) exist as mixtures of rotamers in close analogy with the permethylsilanes $Me_3Si(SiMe_2)_nSiMe_3$. The value for ΔH of 0.8 ± 0.3 kJ mol^{-1} for **2** can be compared with 2.26 ± 015 kJ mol^{-1} for liquid n-Si_4Me_{10}. For both molecules, the *anti* rotamers are favoured energetically. In comparison with n-Si_4Me_{10}, the *gauche* conformer of **2** is stabilized (with respect to the *anti* conformation), which can be attributed to smaller non-bonding repulsive interactions between the methyl groups due to the longer SiSn bond. HF-SCF ab initio calculations predict the existence of three conformers for **2** (also in close analogy with n-Si_4Me_{10}), but only two conformers were detected in the liquid by Raman spectroscopy.

In the Raman spectra of $Me_3Sn(SiMe_2)_3SnMe_3$ (**3**), three conformers (AA, AG and G^+G^+) can be observed. The G^+G^- rotamer is missing because it is destabilized by the pentane effect. The AA conformer seems to be lowest in energy, in contrast with $Me_3Si(SiMe_2)_3SiMe_3$ for which the G^+G^+ conformer is predicted to constitute the low-energy form by empirical force field calculations [14].

At r.t., **4** probably adopts the all-*anti* conformation as a single line is observed for the SiSn stretching vibration. Upon heating, several other conformational states are populated leading to a broadening of the Raman line, which corresponds to the SiSn stretching vibration.

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