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Syntheses, Raman and Infrared Vibrational Spectra, Normal Coordinate Analyses and  $^{29}Si$ -NMR-Spectra of Halogenated Trisilanes Me<sub>n</sub>Si<sub>3</sub>X<sub>8-n</sub> and (H<sub>m</sub>X<sub>3-m</sub>Si)<sub>2</sub>SiMe<sub>2</sub> (X = F, Cl, Br,I)

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## 1. INTRODUCTION

Methylated trisilanes  $Me_nSi_3X_{8-n}$  or  $Me_nSi_3X_{8-n-m}H_m$  (n, m = 1,2 .....8) are useful low molecular weight compounds for the study of properties of the SiSi bond. The results such as correlations between structures and <sup>29</sup>Si chemical shifts or <sup>29</sup>Si<sup>29</sup>Si coupling constants, bond strengths and bond lengths as determined by vibrational spectroscopy [1-4] and electron diffraction [5,6] and energies involved in rotational isomerism facilitate the understanding of polymeric silanes. For this purpose, we have prepared a large number of trisilanes and studied their properties

## 2. SYNTHESES

All compounds were synthesized from appropriate phenyltrisilanes in a first step

 $Ph_{n}Si_{3}Me_{8-n} + n HX/AIX_{3} \longrightarrow X_{n}Si_{3}Me_{8-n} + n C_{6}H_{6} \qquad X = CI, Br, I$ 

followed by fluorination with ZnF2

 $Br_nSi_3Me_{8-n} + n/2 ZnF_2 - F_nSi_3Me_{8-n} + n/2 ZnBr_2$ 

Trisilanes of the type  $(XH_2Si)_2SiMe_2$  and  $(X_2HSi)SiMe_2$  (X = F, Cl, Br, I) were synthesized from  $(Ph_3Si)_2SiMe_2$  [7] and triflic acid, followed by reduction with LiAlH<sub>4</sub> and subsequent removal of the phenyl groups as described above

 $(Ph_3Si)_2SiMe_2 + CF_3SO_3H (= TfH) \longrightarrow (Ph_{3-n}Tf_nSi)_2SiMe_2 + n C_6H_6$  n = 1, 2

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 $\begin{array}{rcl} (\mathrm{Ph}_{3-n}\mathrm{Tf}_{n}\mathrm{Si})_{2}\mathrm{SiMe}_{2} & + & \mathrm{LiAlH}_{4} & & & & & & & & & \\ (\mathrm{Ph}_{3-n}\mathrm{H}_{n}\mathrm{Si})_{2}\mathrm{SiMe}_{2} & + & n & \mathrm{LiTf} \\ (\mathrm{Ph}_{3-n}\mathrm{H}_{n}\mathrm{Si})_{2}\mathrm{SiMe}_{2} & + & n & \mathrm{C}_{6}\mathrm{H}_{6} & \mathrm{X} = \mathrm{CI}, \ \mathrm{Br}, \ \mathrm{I} \\ (\mathrm{Br}_{3-n}\mathrm{H}_{n}\mathrm{Si})_{2}\mathrm{SiMe}_{2} & + & n/2 \ \mathrm{ZnF}_{2} & & & & \\ (\mathrm{F}_{3-n}\mathrm{H}_{n}\mathrm{Si})_{2}\mathrm{SiMe}_{2} & + & n/2 \ \mathrm{ZnBr}_{2} \end{array}$ 

#### 3. VIBRATIONAL SPECTRA AND ROTATIONAL ISOMERISM

The infrared and Raman spectra of all trisilanes are quite easily interpreted using the group character of the methyl vibrations  $v_{as}$ ,  $v_s$ ,  $\delta_{as}$ ,  $\delta_s$  and  $\rho$ CH<sub>3</sub>. With fluorocompounds, v(SiF) usually is overlapped by the  $\rho$ CH<sub>3</sub> vibrations in the infrared spectra, but can be observed in the Raman spectra quite clearly. Chloro, bromo and iodotrisilanes have their skeletal stretching vibrations in the range between 720 and 620 cm<sup>-1</sup> (v(SiC)) and 550 - 300 cm<sup>-1</sup> (SiSi and SiX stretchings).

The skeletal stretching vibrations are sensitive to molecular conformations, giving rise to doubling of bands. As an example, the temperature dependence of v(SiCI) of CIMe<sub>2</sub>SiSiMe<sub>2</sub>SiMe<sub>3</sub> is depicted in Fig. 1. The rotamer which is faintly more stable is trans, v(SiCI) of the gauche rotamer disappearing in the solid.



Fig. 1: Temperature dependence of v(SiCI) of  $CIMe_2SiSiMe_2SiMe_3$ 

#### 4. NORMAL COORDINATE ANALYSES

Using a local symmetry force field for the methyl groups, normal coordinate calculations have been carried out for many trisilanes. As can be seen from Table 1, the SiSi valence force constants increase with increasing sum of the electronegativities of the substituents. There is a good linear correlation between  $29Si^{2}9Si$ -coupling constants <sup>1</sup>J(SiSi) (see section 29Si-NMR) and SiSi valence force constants f(SiSi) (Fig.2), as is also observed for <sup>1</sup>J(CC) and f(CC) [8].

molecule	f/Nm <sup>-1</sup>	molecule	f/Nm <sup>-1</sup>	
(Me <sub>3</sub> Si) <sub>4</sub> Si	130	Me <sub>2</sub> Si(SiCl <sub>3</sub> ) <sub>2</sub>	200	
Me2Si(SiMe3)2	150	Me <sub>2</sub> Si(SiBr <sub>3</sub> ) <sub>2</sub>	190	
F <sub>2</sub> Si(SiMe <sub>3</sub> )2	163	Me <sub>2</sub> Si(SiOMe <sub>3</sub> ) <sub>2</sub>	200	

Table 1: Si-Si valence force constants for some selected trisilanes





o f(SiSi) calculated by NCA, o (SiSi) estimated by interpolation

# 5. 29Si-NMR-SPECTRA

Table 2 summarizes <sup>29</sup>Si<sup>29</sup>Si coupling constants of selected trisilanes, including some two bond couplings. Generally, <sup>1</sup>J(SiSi) increases with increasing sum of the electronegativites of the substituents. The <sup>29</sup>Si chemical shift data (not included in Table 3) can be used to develop a model for the prediction of  $\delta$ (<sup>29</sup>Si) values based on mutual interaction terms [9]. The advantage of using trisilanes over disilanes is that influences of substituents that are two SiSi bonds away can be included.

• • • • • • • • • • • • • • • • • • •	x	δ( <b>S</b> i)	δ( <b>*S</b> i)	δ(** <b>S</b> i)	1 <sub>J(Si*Si)</sub>	<sup>1</sup> J(*Si**Si)	<sup>2</sup> J(Si**Si)
X <sub>2</sub> MeSi*SiMe <sub>2</sub> **SiMe <sub>3</sub>	н	-64.6	-47.6	-16.0	68.3	75.3	7.9
	F	17.4	-52.0	-16.7	99.4	75.1	9.4
	СІ	37.8	-39.9	-16.2	83.1	75.6	11.2
	Br	26.9	-36.8	-16.2	74.6	75.4	11.8
	1	-22.4	-34.7	-16.0	64.4	74.7	12.2
	OMe	-5.0	-52.6	-16.6	106.0	74.2	5.9
	Ph	-18.9	-47.9	-15.6	73.5	72.7	7.6
(XMe <sub>2</sub> Si) <sub>2</sub> *SiMeX	н	-40.2	-76.4		70.4		
	F	30.2	24.2	i	96.8		
	СІ	19.8	-0.3		89.3		
	Br	11.9	-11.0		84.4		
		-12.7	-38.9		76.8		
	OMe	14.0	+6.5		94.9		
	Ph	-18.6	-46.4		72.1		
(X <sub>3</sub> Si) <sub>2</sub> *SiMe <sub>2</sub>	F	-59.7	-60.2				
	СІ	13.0	-25.7		121.1		
	Br	-16.5	-19.4		105.7		
	I	-135.2	-33.9		82.2		
	OMe	-61.5	-40.2		143.7		
	Ph	-16.6	-45.7		74.4		

Table 2:29Si Chemical Shifts [ppm, TMS] and 29Si29Si Coupling Constantsof Methylated Trisilanes XnSi3Me8-n

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