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Trisilylamines, a ^{13}C, ^{15}N and ^{29}Si NMR study in solution—evidence for Si—Br—Si bridging†

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ABSTRACT: Trisilylamines $(Me_3Si)_3N$ (**1**), $[Me_2(HC{\equiv}C)Si]_3N$ (**2**), $[Me_2(HC{\equiv}C)Si]_2NSiMe_2Br$ (**3**), $[Me_2(Br)Si]_2NSiMe_2C{\equiv}CH$ (**4**) and $[Me_2(Br)Si]_3N$ (**5**) were studied by ^{13}C, ^{15}N and ^{29}Si NMR spectroscopy. The trends in their chemical shifts, in particular of $\delta^{15}N$, coupling constants $^1J(^{29}Si, ^{13}C)$ and $^1J(^{29}Si, ^{15}N)$ and isotope-induced chemical shifts $^1\Delta^{28/29}Si(^{15}N)$ point towards a different bonding situation in **5** to that in **1**–**4**. It can be assumed that Si—Br—Si bridging in **5** leads to a fluxional structure in which the bromine atoms, and in turn a methyl group and the nitrogen atom, occupy pseudo-axial positions in the distorted trigonal planar surroundings of the silicon atom. © 1998 John Wiley & Sons, Ltd.

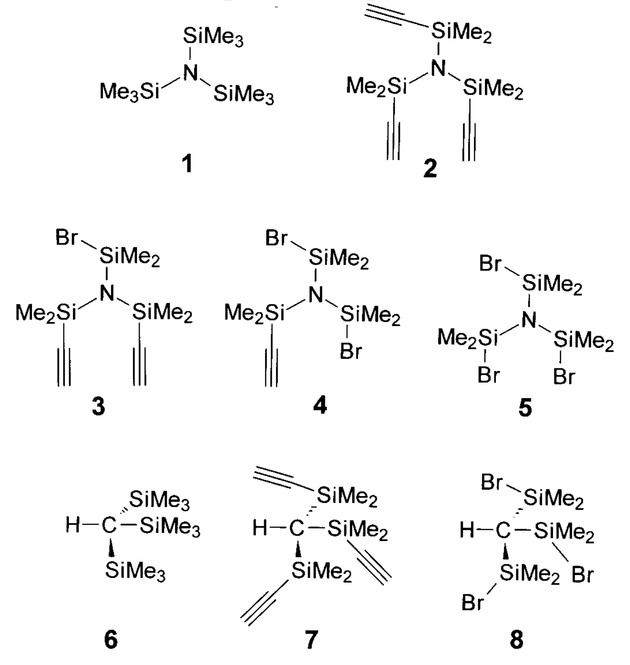
KEYWORDS: NMR; ^{13}C NMR; ^{15}N NMR; ^{29}Si NMR; silylamines; coupling constants; sign determination; isotope-induced shifts

INTRODUCTION

Trisilylamines are known to possess a planar NSi_3 skeleton.[1] If one or more halogen atoms are linked to the silicon atoms, Si—halogen—Si bridging is conceivable. Although this type of interaction has been well established in the case of tin,[2] only a few examples for silicon bridging have been described, mainly for anionic species,[3] and in hexakis(fluorodimethylsilyl)benzene.[4] In the absence of direct structural evidence, NMR spectra may be useful to detect Si—halogen—Si bridging, reflected by unusual trends in chemical shifts or coupling constants. In this context, we have studied the ^{13}C, ^{15}N and ^{29}Si NMR spectra of a series of trisilylamines **1**–**5**, derived from tris(trimethylsilyl)amine (**1**) in which one methyl group in each Me_3Si unit is replaced by either an ethynyl group or a bromine atom (Scheme 1).

RESULTS AND DISCUSSION

The ^{13}C, ^{15}N and ^{29}Si NMR data for the trisilylamines **1**–**5** and for trisilylmethanes **6**–**8** for comparison are given in Table 1. The ^{13}C NMR spectra were measured normally, whereas the ^{15}N and ^{29}Si NMR spectra were measured by using the refocused INEPT pulse sequence[7] with ^{1}H decoupling. The coupling constants $^1J(^{29}Si, ^{15}N)$ were determined with high accuracy from ^{29}Si satellites in the ^{15}N NMR spectra (Fig. 1). These experiments also gave the isotope-induced chemical shifts $^1\Delta^{28/29}Si(^{15}N)$. Only very few examples of such data can be found in the literature.[8] Under conditions corresponding to ultra-high resolution,[9] the ^{15}N resonance signal of the ^{15}N–^{30}Si isotopomer is well resolved. As expected,[10] the $^1\Delta^{28/30}Si(^{15}N)$ values are greater by a factor of two compared with $^1\Delta^{28/29}Si(^{15}N)$. The largest negative value $^1\Delta^{28/29}Si(^{15}N) = -3.9$ ppb in the series **1**–**5** belongs to **5**, pointing towards a different bonding situation in **5** (see below). The absolute positive sign of the coupling constants $^1J(^{29}Si, ^{15}N)$ in **2** and **5** was determined by observing the cross peaks for the ^{29}Si satellites in a 2D $^{15}N/^1H$ heteronuclear shift correlation following the procedure reported for **1**.[11]



Scheme 1. Trisilylamines (**1**–**5**) studied and trisilylmethanes (**6**–**8**) for comparison.

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Table 1. ^{13}C, ^{15}N and ^{29}Si NMR data[a] for the trisilylamines **1–5** and of some corresponding trisilylmethanes **6**,[5] **7**[6] and **8**[6] for comparison.

Compound	δ^{13}C [$^1J(^{29}$Si, ^{13}C)] SiMe$_2$R	δ^{13}C [$^1J(^{29}$Si, ^{13}C)] SiMe$_2$Br	δ^{15}N {$^1J(^{29}$Si, ^{15}N)}	$^1\Delta^{28/29}$Si(^{15}N)	δ^{29}Si
1	5.6 [56.1]	—	−346.9 {+7.7}	−3.5	2.6
6	3.7 [50.6][b]	—	—	—	0.5
2	5.3 [66.4][c]	—	−350.7 {+10.7}	−3.1	−17.2
7	2.5 [58.0][d]	—	—	—	−18.4
3	5.1 [64.7][e]	2.5 [67.9]	−342.5 {(+)11.3}[f]	−3.0	−19.3
					1.8 (SiBr)
4	4.9 [65.4][g]	2.8 [67.6]	−334.7 {(+)11.9}[f]	−3.0	−21.2
					3.1 (SiBr)
5	—	9.6 [56.2]	−317.0 {+5.0}	−3.9	11.5
8	—	7.5 [63.0][h]	—	—	22.0

[a] In C$_6$D$_6$ (*ca.* 10%) at 25 ± 1 °C; coupling constants in Hz: $J(^{29}$Si, ^{13}C) in square brackets (±0.2 Hz) and $^1J(^{29}$Si, ^{15}N) in braces (measured from ^{15}N NMR spectra, ±0.02 Hz); isotope-induced shifts $^1\Delta^{28/29}$Si(^{15}N) are given in ppb (±0.05) and the negative sign indicates that the ^{15}N resonance of the more heavy isotopomer (^{15}N—^{29}Si) is shifted to lower frequency with respect to that of the lighter isotopomer (^{15}N—^{28}Si).

[b] Other ^{13}C NMR data: 4.0 [38.7] (CH).

[c] Other ^{13}C NMR data: 91.8 [87.1] (Si—C≡), 95.6 [16.7) (≡CH).

[d] Other ^{13}C NMR data: 91.4 [80.3] (Si—C≡), 95.4 [15.3] (≡CH), 2.1 [42.0] (CH).

[e] Other ^{13}C NMR data: 92.1 [86.8] (Si—C≡), 94.9 [16.7] (≡CH).

[f] Only one type of ^{29}Si satellite was observed; the relative intensities of the ^{29}Si satellites correspond to three silicon atoms bonded to nitrogen.

[g] Other ^{13}C NMR data: 92.5 [86.5] (Si—C≡), 94.1 [16.7] (≡CH).

[h] Other ^{13}C NMR data: 15.1 [52.0] (CH).

The data in Table 1 show smooth changes for the trisilylamines **1–4**. Thus, δ^{13}C, δ^{15}N and δ^{29}Si data change in a regular way, and the increase in the magnitude of the coupling constants $|^1J(^{29}$Si, ^{13}C)$|$ and $|^1J(^{29}$Si, ^{15}N)$|$ in **2–4** with respect to **1** is in full agreement with expectations based on the concept of rehybridization.[12] In contrast, all data for **5** change to a much larger extent than expected taking into account the data set for **2–4**. The chemical shifts δ^{13}C, δ^{15}N and δ^{29}Si of **5**, compared with those of **3** and **4**, suggest a difference bonding situation in **5**. This is supported by the magnitude of both coupling constants $|^1J(^{29}$Si, ^{13}C)$|$ and $|^1J(^{29}$Si, ^{15}N)$|$ in **5**, which is markedly smaller than that in **3** or **4**. Table 1 indicates that such apparently irregular changes of the NMR data are not observed for corresponding trisilylmethanes. One explanation is to assume Si—Br—Si bridging in **5**, whereas this does not play a significant role in **3**, **4** and **8**.

There is only a small change in the isotope-induced shifts $^1\Delta^{29/28}$Si(^{15}N) if one compares **5** with **1–4**. This

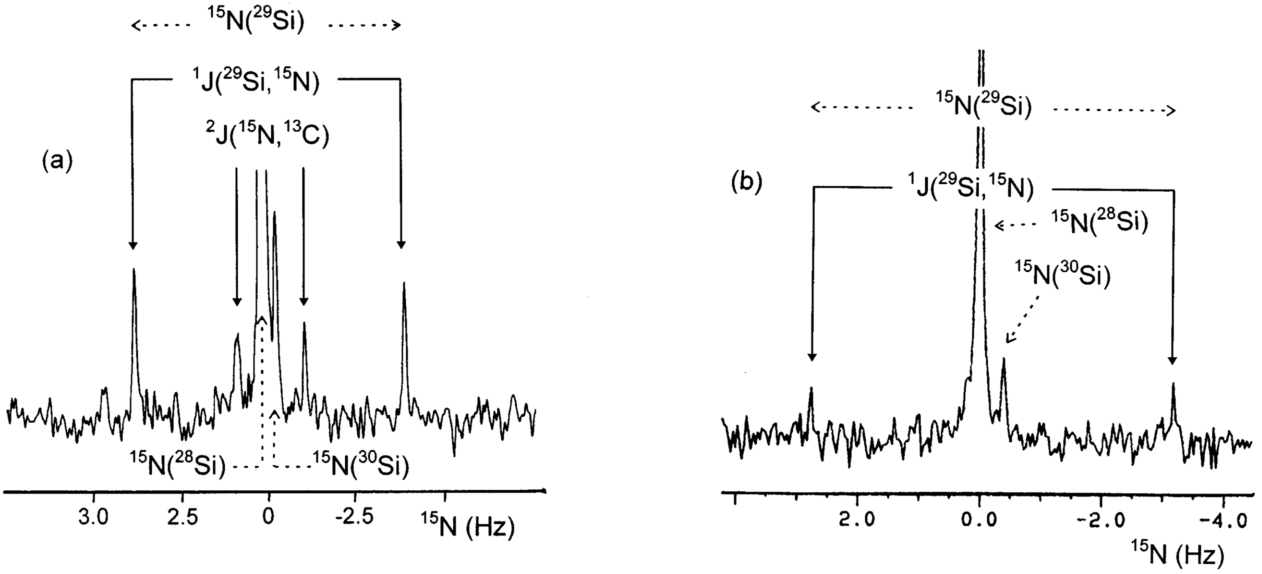

Figure 1. 50.7 MHz ^{15}N{^{1}H) NMR spectra of (a) N(SiMe$_3$)$_3$ (**1**) and (b) N(SiMe$_2$Br)$_3$ (**5**) recorded by the refocused INEPT pulse sequence with ^{1}H decoupling [7](result of 256 transients each). ^{29}Si satellites are indicated, in addition to ^{13}C satellites in (a). In both (a) and (b) the ^{15}N NMR signal of the ^{15}N—^{30}Si isotopomer is clearly resolved. The full linewidth at half height of the ^{15}N NMR signal is (a) 0.05 Hz and (b) 0.09 Hz.

small effect cannot be used as a strong argument for Si—Br—Si bridging in **5**. Similarly, at first glance, the decrease in ^{29}Si nuclear shielding in **5** (δ^{29}Si = 11.5) compared with that in **3** or **4** [δ^{29}Si(SiBr) = 1.8, 3.1] is not in line with an increase of the coordination number of the silicon atoms.[13] However, considering the roughly linear correlation between δ^{29}Si and δ^{119}Sn values,[14] it should be noted that ^{119}Sn nuclear shielding in tristannylamines analogous to **5** is also low for tin with coordination number 5 [e.g. δ^{119}Sn = 83.5 for $N(SnMe_2Cl)_3$ in solution, slightly increased in the solid state, δ^{119}Sn not given[2a]], although x-ray structural analysis has proved the Sn—Cl—Sn bridging with the chlorine atoms in pseudo-axial positions.[2a]

Stronger arguments for Si—Br—Si bridging are based on the coupling constants $^1J(^{29}\text{Si}, ^{13}\text{C})$ and $^1J(^{29}\text{Si}, ^{15}\text{N})$. The small magnitude of both coupling constants $|^1J(^{29}\text{Si}, ^{13}\text{C})|$ and $|^1J(^{29}\text{Si}, ^{15}\text{N})|$ in **5** is in line with contributions from fluxional structures with a distorted trigonal bipyramidal geometry at the three silicon atoms. In Fig. 2 it is indicated that not only the bromine atoms but also on average the nitrogen atom and the methyl groups are forced to move into pseudo-axial positions which would lead on average to smaller coupling constants. This has been found, e.g., for $^1J(^{119}\text{Sn}, ^{13}\text{C}_{\text{axial}})$ in pentacoordinate organotin compounds.[15] An alternative explanation for the abrupt changes in the NMR parameters of **5** compared with those in **1**–**4** would have to invoke marked and also abrupt changes in the Si—N and Si—C bond lengths as a result of the presence of three bulky Me_2SiBr groups in **5**. This is unlikely, and it is not supported by AM1[16] calculations, which suggest that the molecule with threefold Si—Br—Si bridging is more stable.

EXPERIMENTAL

All compounds were synthesized and handled under a nitrogen atmosphere, using carefully dried glassware and dry solvents. Compounds **1**[17] and **5**[18] were prepared following literature procedures. Compounds **2**, **3** and **4** were obtained either as a mixture or in the pure state (**2**) by treatment of **5** with ethynylmagnesium bromide as described for the corresponding trisilylmethanes.[6]

NMR spectra were measured from samples (*ca.* 10% in C_6D_6 at 25 °C) in 5 mm o.d. tubes using Bruker ARX 250, AC 300 and AM 500 spectrometers. Chemical shifts are given relative to Me_4Si [δ^1H (C_6D_5H) = 7.15, δ^{13}C (C_6D_6) = 128.0, δ^{29}Si = 0 for $\Xi(^{29}\text{Si})$ = 19.867184 MHz], neat $MeNO_2$ [δ^{15}N = 0 for $\Xi(^{15}\text{N})$ = 10.136767 MHz]. Delays for 2D ^{15}N/^{1}H heteronuclear shift correlations were optimized in the usual way by 1D polarization transfer experiments. Acquisition times of the order of 10 s for a frequency window of 100–200 Hz were used for the 50.7 MHz ^{15}N NMR spectra [refocused INEPT pulse sequence with ^{1}H decoupling;[7] $\pi/2(^1\text{H}) = 7$ μs; $\pi/2(^{15}\text{N}) = 18.5$ μs] in order to measure $^1J(^{29}\text{Si}, ^{15}\text{N})$ and isotope-induced shifts. The pulse repetition delays were set between 20 and 30 s; this allows for complete ^{1}H relaxation, and effects induced by dielectric heating of the sample due to ^{1}H decoupling are compensated for during the long pulse repetition delay when pressurized air of constant temperature passes through the probe head, ensuring that there are negligible temperature gradients in the sample.[9]

2: Waxy colorless solid; m.p. 45–50 °C; ^{1}H NMR (C_6D_6), δ^1H = 2.14 s, 3H $^3J(^{29}\text{Si}, ^1\text{H})$ = 3.5 Hz, $^1J(^{13}\text{C}, ^1\text{H})$ = 237.5 Hz (HC≡), 0.55 s, 18H (Me_2Si).

3: ^{1}H NMR (C_6D_6), δ^1H = 2.14 s, 2H (HC≡), 0.47 s, 12H (Me_2SiC), 0.25 s, 6H (Me_2SiBr).

4: ^{1}H NMR (C_6D_6), δ^1H = 2.14 s, 1H (HC≡), 0.40 s, 6H (Me_2SiC), 0.32 s, 12H (Me_2SiBr).

5:[18] ^{1}H NMR (C_6D_6), δ^1H = 0.78 s, $^2J(^{29}\text{Si}, ^1\text{H})$ = 7.0.

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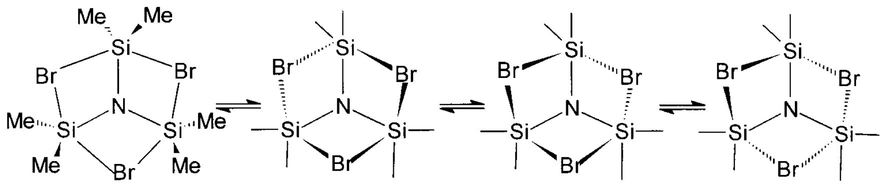

Figure 2. Proposed fluxional structures of **5**.

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