Preparative, Spectroscopic, and Structural Studies on Some New Silylamines

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The synthesis and characterization of two complete series of benzyl(phenylsilyl)amines $(PhH_2Si)_x(PhH_2C)_{3-x}N$, benzyl(*p*-tolylsilyl)amines $(p\text{-}H_3CC_6H_4H_2Si)_x(PhH_2C)_{3-x}N$, and of bis(*p*-tolylsilyl)amine are described. The compounds have been prepared from the corresponding amines and chlorosilanes with triethylamine as the auxiliary base. Bis(phenylsilyl)(trimethylsilyl)amine, $(PhH_2Si)_2NSiMe_3$ (**10**), was obtained by the reaction of lithium bis(phenylsilyl)amide with chlorotrimethylsilane. Crystal structure analyses reveal that dibenzyl(*p*-tolylsilyl)amine (**7**) and **10** contain planar nitrogen atoms. Heteronuclear NMR spectra (^1H, ^{13}C, ^{15}N, and ^{29}Si) have been measured for all compounds. The ^{15}N chemical shifts are shown to be sensitive to variations of the geometry at the nitrogen atom. The coupling constants $^1J(^{15}N^{29}Si)$ show a linear correleation with the N–Si bond lengths.

The planarity of nitrogen coordination in silylamines continues to be a frequently discussed issue[1]. This unique structural feature – as compared to the carbon analogs – was first discovered for trisilylamine, $(H_3Si)_3N$, in a gas-phase electron diffraction study by Hedberg[2] in 1955 and confirmed for the crystalline state by Barrow and Ebsworth in 1984[3]. All doubly and triply silylated amines whose structures have been elucidated are planar at nitrogen[4]. It is only for selected monosilylated amines, like dimethylsilylamine, $(H_3C)_2NSiH_3$, that pyramidal nitrogen has been observed in the gas phase[5]. In the crystalline phase, $(H_3Si)_2NCH_3$ is associated to give pentamers with tetrahedral coordination at nitrogen and trigonal-bipyramidal coordination at silicon[6]. These results have prompted a large number of theoretical studies[7,8]. In a series of calculations the configurational effect in the Si_3N, Si_2NC, and $SiNC_2$ units has been interpreted initially in terms of d-orbital participation [(p→d)π bonding], but a more sophisticated treatment has shown that such contributions should be only marginal. Other approaches have focused on σ/π-hyperconjugative effects and on electrostatic effects originating from the special force field for longer bond distances and higher polarity of SiN as compared to CN linkages, and on steric effects. All of these studies agree with the prediction that the inversion barrier at nitrogen – if any – should be flat and that only a few kJ/mol are necessary for nitrogen inversion in silylamines. Recent findings that tertiary amines with bulky alkyl groups are also flat at nitrogen[9], and that silylated primary amines R_3SiNH_2 appear to be pyramidal[10], have added to the current uncertainties, if not confusion.

In an attempt to contribute to the discussion with more experimental data, we have described in preceding papers the synthesis and structure of tris(phenylsilyl)amine[11,12]. In contrast to the pyramidal benzylamine analog[19], this molecule has been shown to be completely planar at nitrogen. Since there is no reason to invoke steric effects for $(PhH_2Si)_3N$ with six small hydrogen substituents at the silicon atoms and virtually free rotation of the SiH_2Ph groups, it has been concluded that Si_3N planarity is indeed a silicon-based effect.

This work has now been extended to include two complete series of related compounds with the emphasis on spectroscopic data in the hope of obtaining structural information also from techniques other than diffraction methods.

These studies are complemented by work on related silylhydrazines[13,14] and on amines with bulky trimethylsilyl groups.

Synthesis of the Silylamines

Benzylbis(phenylsilyl)amine (**2**), *dibenzyl(phenylsilyl)amine* (**3**), *benzylbis(p-tolylsilyl)amine* (**6**), *and dibenzyl(p-tolylsilyl)amine* (**7**) (for numbering of compounds see Table 2) have been prepared by silylating benzylamine or dibenzylamine with chloro(phenyl)silane and chloro(*p*-tolyl)silane, respectively (Eqs. 1, 2). Triethylamine has proved to be an efficient auxiliary base in these reactions, which are both carried out in toluene.

$$PhH_2CNH_2 + 2\ R{-}SiH_2Cl + 2\ NEt_3 \rightarrow PhH_2CN(SiH_2{-}R)_2 + 2\ [HNEt_3]Cl \qquad (1)$$

$$\mathbf{2}\text{: } R = Ph$$

$$\mathbf{6}\text{: } R = p\text{-}C_6H_4CH_3$$

$$(PhH_2C)_2NH + R{-}SiH_2Cl + NEt_3 \rightarrow (PhH_2C)_2NSiH_2{-}R + [HNEt_3]Cl \qquad (2)$$

$$\mathbf{3}\text{: } R = Ph$$

$$\mathbf{7}\text{: } R = p\text{-}C_6H_4CH_3$$

All four compounds can be purified by distillation in vacuo. The pure products are stable in dry air for short periods of time, but are readily hydrolyzed.

Bis(p-tolylsilyl)amine (**8**) has been synthesized by passing a stream of dry ammonia through a hexane/THF solution of chloro(*p*-tolyl)silane heated to 50°C (Eq. 3).

$$2\,p\text{-}H_3CC_6H_4{-}H_2SiCl + 3\,NH_3 \rightarrow \underset{\mathbf{8}}{(p\text{-}H_3CC_6H_4{-}H_2Si)_2NH} + 2\,[NH_4]Cl \qquad (3)$$

After filtration of the ammonium chloride and evaporation of the solvents only traces of tris(*p*-tolylsilyl)amine (**5**) are detectable in the product. Distillation gives pure **8** in high yield.

Tris(p-tolylsilyl)amine (**5**): Even at elevated temperatures the direct silylation of ammonia with chloro(*p*-tolyl)silane leads only to **8**. Treatment of **8** with the chlorosilane and NEt_3 (Eq. 4) results in low yield of **5** mixed with the starting compound **8**. However, the reaction can be brought to completion in one day if carried out in pentane as solvent in a sealed glass tube at 140°C in the presence of triethylamine.

$$\underset{\mathbf{8}}{(p\text{-}H_3CC_6H_4\text{–}H_2Si)_2NH} + p\text{-}H_3CC_6H_4\text{–}H_2SiCl + NEt_3 \rightarrow \underset{\mathbf{5}}{(p\text{-}H_3CC_6H_4\text{–}H_2Si)_3N} + [HNEt_3]Cl \qquad (4)$$

Bis(phenylsilyl)(trimethylsilyl)amine (**10**): Bis(phenylsilyl)amine (**9**) does not undergo a reaction with chlorotrimethylsilane due to steric hindrance. This is somewhat surprising, because hexamethyldisilazane is known to react with chloro(phenyl)silane at elevated temperatures to give (phenylsilyl)bis(trimethylsilyl)amine (**11**) in good yields[11]. Under carefully controlled conditions (−110°C), compound **9** can be lithiated with methyllithium to give lithium bis(phenylsilyl)amine (**13**), and this is allowed to react further with chlorotrimethylsilane to give **10** (Eq. 6).

$$\underset{\mathbf{9}}{(PhH_2Si)_2NH} + H_3CLi \rightarrow \underset{\mathbf{13}}{(PhH_2Si)_2NLi} + CH_4 \qquad (5)$$

$$\mathbf{13} + Me_3SiCl \rightarrow \underset{\mathbf{10}}{(PhH_2Si)_2NSiMe_3} + LiCl \qquad (6)$$

Compound **10** can be purified by fractional distillation and finally by crystallization from pentane at −20°C.

Crystal Structures of 7 and 10

Single crystals of 7 (and 10) are grown by cooling the melt of the individual compound slowly to room temperatur (−20°C).

Compound 7 crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$ formula units in the unit cell. No intermolecular Si-N interactions are detectable in the lattice. The molecular structure of 7 is shown in Figure 1, with selected bond lengths and angles given in the figure caption. There is no crystallographic symmetry in the molecule. The nitrogen atom deviates only 11.9 pm from the C20—C30—Si plane [sum of angles at nitrogen: 358.2(6)°]. This deviation from planarity falls in the range found for other silylamines (see Table 1), but there is no correlation between the number of silicon atoms bound to nitrogen and the extent of the deviation of the nitrogen atom from planarity. Molecule 7 should be viewed as a homolog of dimethylsilylamine with phenyl-substituted methyl groups and a *p*-tolyl-substituted silyl group. While dimethylsilylamine crystallizes in a pentameric structure with tetracoordinated nitrogen and pentacoordinated silicon, its homolog 7 is monomeric in the crystal.

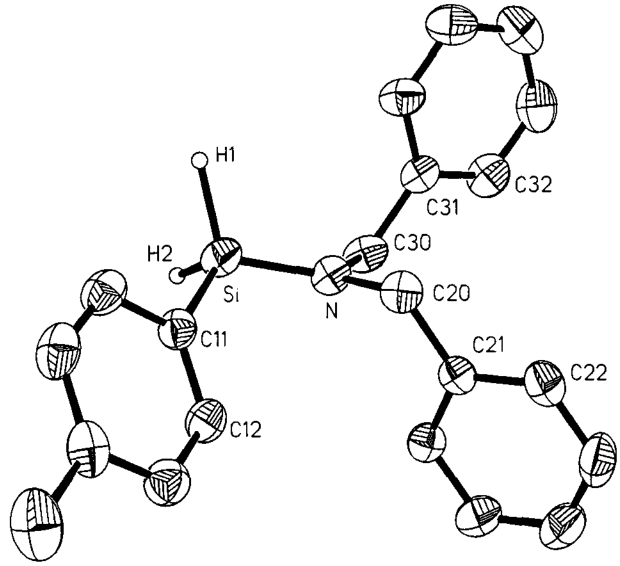

Figure 1. Molecular Structure of dibenzyl(*p*-tolylsilyl)amine (7) with atomic numbering. Hydrogen atoms have been omitted for clarity. — Selected bond distances [pm] and angles [°]: N—Si1 170.4(2), N—C20 146.0(4), N—C30 146.3(3), Si—C11 184.8(2), C20—C21 150.9(3), C30—C31 150.4(3); Si—N—C20 123.7(2), Si—N—C30 120.7(2), C20—N—C30 113.8(2), N—Si—C11 111.1(1), N—C20—C2 115.0(2), N—C30—C31 115.6(2)

Table 1. Selected structural parameters of several silylamines. Abbreviations: av = average, gas = gas phase, *p*-tol = *p*-$H_3CC_6H_4$, s = solid

Compound	Sum of angles at N [°]	d(Si^a-N) [pm]	d(Si^b-N) [pm]
$(PhH_2Si)_3N$ (**1**)	358.3(3)	173.5(1)	
(p-tol$H_2Si)_3N$ (**5**)[26]	359.3	173.3 (av)	
$(H_3Si)_3N$ (s)	360.0(9)	172.9 (av)	
$(PhH_2Si^a)_2NSi^bMe_3$ (**10**)	359.9(3)	172.9 (av)	175.8(2)
$PhH_2Si^aN(Si^bMe_3)_2$ (**11**)	359.7(3)	172.3 (2)	175.1(av)
$(Me_3Si)_3N$ (gas)	360.0	175.5 (3)	
p-tol$H_2SiN(CH_2Ph)_2$ (7)	358.2(6)	170.4(2)	
H_3SiNMe_2 (gas)	354.6(7)	171.3(5)	
$(Me_3Si)NMe_2$ (s)	357.78(18)	171.94(12)	

The Si—N bond length of 7 is the shortest in Table 1 [170.4(2) pm]. Shorter Si—N bonds are observed only if electronegative substituents are attached to silicon, e.g. in $ClSiH_2NMe_2$ [168.9(4) pm in the gas phase[15]]. The CNSi angles in 7 are widened at the expense of the angle C20—N—C30.

Crystals of *compound* **10** are monoclinic and belong to space group $P2_1/c$ with $Z = 4$ formula units in the unit cell. The molecular geometry is presented in Figure 2, with selected bond lengths and angles given in the figure caption. The NSi_3 skeleton of **10** is completely planar as indicated by the sum of angles at the N atom of 359.9(3)°. The bulky trimethylsilyl group is bound to nitrogen with a bond length Si—N of 175.8(2) pm, i.e. significantly longer than the remaining two Si—N bonds. This value is very close to that found for tris(trimethylsilyl)amine[16] in the gas phase [175.7(3) pm]. The difficulties in obtaining silylamines with bulky substituents are clearly reflected by these structural data. Dimethyl(trimethylsilyl)amine, which is available by an ambient-temperature condensation reaction, shows a markedly shorter Si—N bond [171.0(5) pm][17]. The Si2—N—Si3 bond angle in **10** is compressed to 116.5(1)°, leaving the remaining two Si—N—Si angles expanded. In the absence of major electronic differences for the three silyl substituents, this may be attributed to the bulk of the Me_3Si group. The completely isoelectronic silylated phosphonium ylide $Me_3P^+{-}C^-(SiH_2Ph)_2$ shows a similar structure[11] with a virtually planar carbanionic center (isoelectronic to N). The conformations of the molecules **10** (as judged from the orientation of the phenyl rings) and of the above phosphorus ylide, and a related molecule, $Me_3P^+{-}C^-(SPh)(SePh)$[18] (another isoelectronic species), are different and appear to be dependent on the dipole contributions of the substituents and on packing forces.

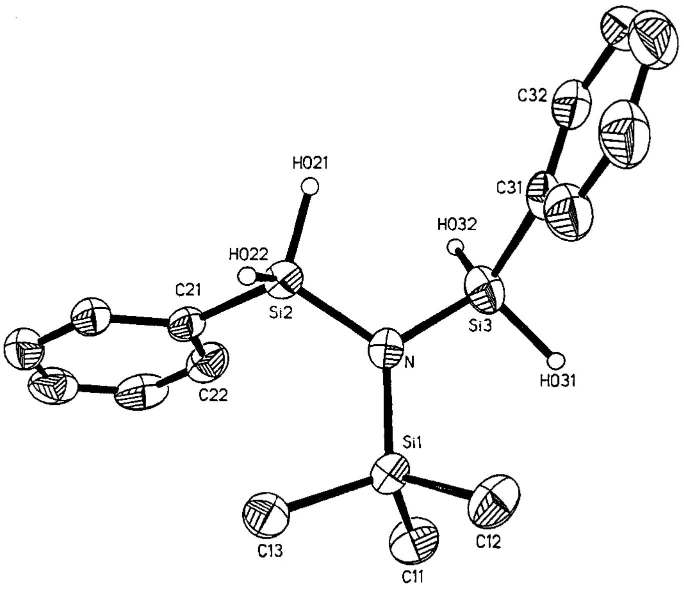

Figure 2. Molecular structure of bis(phenylsilyl)(trimethylsilyl)amine (**10**) in the crystal. Hydrogen atoms bound to carbon have been omitted for clarity. – Selected bond distances [pm] and angles [°]: N—Si1 175.8(2), N—Si2 172.8(2), N—Si3 173.0(2), Si1—C11 185.5(2), Si2—C21 186.8(2), Si3—C31 186.6(2); Si1—N—Si2 122.1(1), Si1—N—Si3 121.3(1), Si2—N—Si3 116.5(1), N—Si1—C11 110.8(1), N—Si2—C21 112.4(1), N—Si3—C31 113.1(1)

NMR Spectroscopy

NMR spectra of all nuclei with spin-½ isotopes contained in the compounds described above have been measured. The complete data sets are listed in the experimental section, and selected data of ^{15}N and ^{19}Si parameters are compiled in Table 2.

The *chemical shifts* $\delta^{29}Si$ are found to increase as the replacement of phenylsilyl groups (*p*-tolylsilyl groups) by benzyl groups is progressing in the two series of compounds **1**, **2**, **3** (**5**, **6**, **7**). The *coupling constants* $^1J(^{29}Si^1H)$ are decreasing following the same order of substitution. Replacement of phenylsilyl by trimethylsilyl groups results in a decrease of $\delta^{29}Si$ for $PhH_2{}^{29}Si$ and an increase for $Me_3{}^{29}Si$ in the series **1**, **10**, **11**, **12**, while the $^1J(^{29}Si^1H)$ coupling constants are showing an inverse trend.

Table 2. Selected ^{15}N- and ^{29}Si-NMR data of silylamines. Abbreviations: *p*-tol = *p*-$H_3CC_6H_4$

	Compound	$\delta(^{29}Si)$	$^1J(SiH)$	$\delta(^{15}N)$	$^1J(NSi)$
1	$(PhH_2Si)_3N$	-23.6	210.3	-376.8	8.8
2	$(PhH_2Si)_2NCH_2Ph$	-21.8	208.8	-365.2	14.3
3	$PhH_2SiN(CH_2Ph)_2$	-19.4	205.9	-355.1	21.2
4	$(PhH_2C)_3N$	------	------	-327.7	------
5	$(p\text{-tolH}_2Si)_3N$	-24.1	209.7	-386.0	8.9
6	$(p\text{-tolH}_2Si)_2NCH_2Ph$	-22.1	207.8	-374.7	14.2
7	$p\text{-tolH}_2SiN(CH_2Ph)_2$	-19.5	205.0	-364.7	20.9
8	$(p\text{-tolH}_2Si)_2NH$	-28.8	207.1	-389.3	13.8
9	$(PhH_2Si)_2NH$	-28.6	207.8	-389.7	13.9
10	$(PhH_2Si^a)_2NSi^bMe_3$	-28.8^a -9.7^b	208.0	-367.4	9.0^a 7.3^b
11	$PhH_2Si^aN(Si^bMe_3)_2$	-35.9^a 6.1^b	205.1	-358.4	9.4^a 7.8^b
12	$N(SiMe_3)_3$	2.4[27]	------	-346.1	7.6

The *chemical shifts* $\delta^{15}N$ appear to reflect the different substitution pattern and the coordination geometry. In Figure 3 the values of $\delta^{15}N$ of the silylamines $(PhH_2Si)_x$-$N(SiMe_3)_{3-x}$ (with $x = 0, 1, 2, 3$; for compounds **12**, **11**, **10**, **1**) are plotted versus x, which results in a linear relationship with negative slope. In Figure 4 the correlation between the coordination geometry at nitrogen and $\delta^{15}N$ is presented. For both series $(PhH_2Si)_xN(CH_2Ph)_{3-x}$ (with $x = 0, 1, 2, 3$; compounds **4**, **3**, **2**, **1**) and $(p\text{-}H_3CC_6H_4{-}H_2Si)_xN(CH_2Ph)_{3-x}$

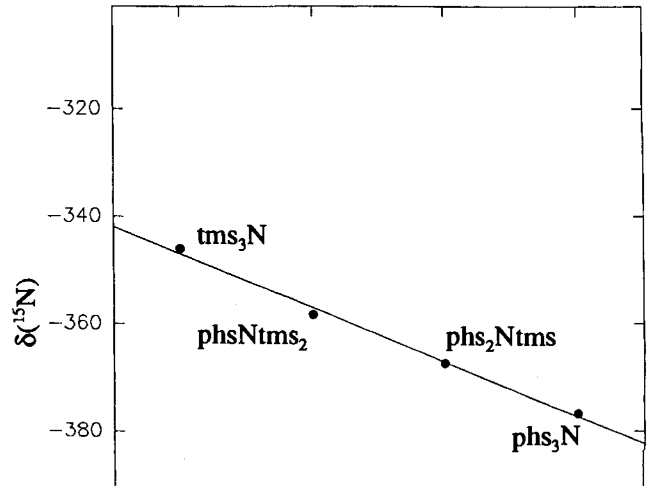

Figure 3. $\delta^{15}N$ of the trimethylsilyl-substituted amines $(PhH_2Si)_xN(SiMe_3)_{3-x}$ plotted against x. Abbreviations: phs = PhH_2Si, tms = $(H_3C)_3Si$

(with $x = 0, 1, 2, 3$; compounds **4**, **7**, **6**, **5**) there is a clear linear relationship between $\delta^{15}N$ and x. It is only for tribenzylamine (**4**), the only unsilylated amine and the only one with a pyramidal nitrogen atom (shown in an X-ray crystallographic study by Iwasaki et al.[19]) that a clear deviation of $\delta^{15}N$ occurs. Deviations of the ^{15}N chemical shift of an individual compound in a series of successively substituted silylamines may therefore be taken as an indication of structural non-conformity, especially in cases where diffraction methods are not applicable. The slope of the diagram in Figure 4 suggests that benzyl groups exhibit more pronounced electron withdrawing properties than phenylsilyl groups, as expected from the different electronegativities of carbon and silicon.

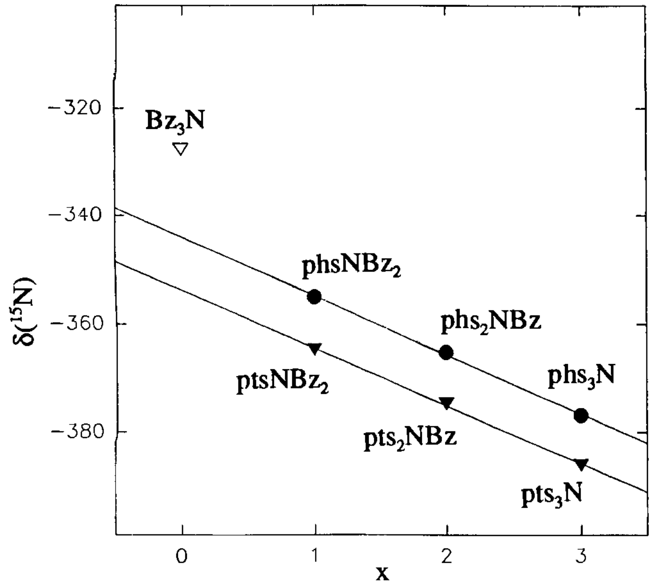

Figure 4. $\delta^{15}N$ of the silylated benzylamines $(ArH_2Si)_xN(CH_2Ph)_{3-x}$ plotted against x. Abbreviations: Ar = Aryl, Bz = PhH_2C, phs = PhH_2Si, pts = p-$H_3CC_6H_4H_2Si$

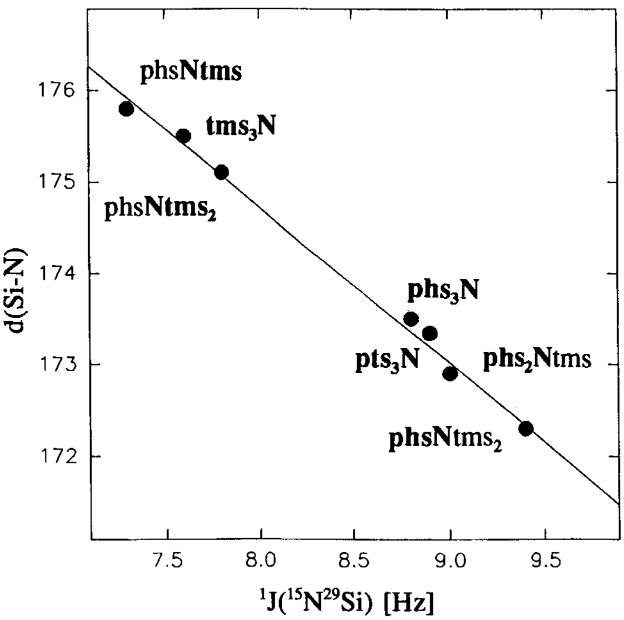

Figure 5. Bond distances d_{Si-N} [pm] in trisilylamines plotted against the coupling constants $^1J(^{15}N^{29}Si)$ [Hz]. If an individual molecule has two different Si—N bonds, the data are taken from the part printed in bold face. Abbreviations: phs = PhH_2Si, pts = p-H_3C-$C_6H_4H_2Si$, tms = $(H_3C)_3Si$

The *coupling constants $^1J(^{15}N^{29}Si)$* can be expected to be a direct probe for the nitrogen-silicon bond. $^1J(^{15}N^{29}Si)$ values have previously been shown to be directly correlated with stretching frequencies νNH[20] and to exhibit a linear relation to the Si—N bond s-character[21]. These results have led to the prediction that $^1J(^{15}N^{29}Si)$ values should be applicable to the solution of structural problems, but no attempts have been made to actually verify such a correlation by a series of structural parameters deduced from diffraction methods. For all silylamines described in this paper these constants could be measured by using the polarization transfer techniques INEPT and DEPT in their proton-decoupled modifications with samples present in high concentrations. Fortunately, the published[22] and later revoked[23] opinion that polarization transfer techniques are applicable only to compounds bearing NH functions owing to the low values of ^{15}N-^1H long-range couplings has turned out to be not valid for the systems studied in this paper. $^2J(^{15}NSi^1H)$ couplings have been assumed to be in the order of 6 Hz and used for polarization transfer. The results are listed in Table 2. There is a clear dependence of the $^1J(^{15}N^{29}Si)$ coupling constant of the number of silicon atoms attached to nitrogen. The lowest values (7 – 10 Hz) are those of trisilylamines (**1**, **5**, **10**, **11**, **12**), while disilylated amines have larger coupling constants (13 – 15 Hz). The largest values are obtained for the monosilylamines (**3**, **7**). Of much greater interest is the correlation between $^1J(^{15}N^{29}Si)$ and the Si—N bond lengths as shown in Figure 5 for some *tri*silylamines (see also Table 1). In this group of compounds a striking linear dependence is observed within the limits of error, according to equation (7).

$$d_{Si-N}[pm] = 188.4 - 1.71 \cdot |^1J(^{15}N^{29}Si)| \qquad (7)$$

The literature data for trisilylamine, the only compound besides **12** which has previously been studied by diffraction methods and by heteronuclear NMR spectroscopy [d_{Si-N} = 172.9 pm, $^1J(^{15}N^{29}Si)$ = 6 Hz][24], are not in accord with this correlation, and we can offer no simple explanation for this failure. Clearly a modified picture arises for each individual series of compounds.

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Experimental

The experiments were carried out under dry purified nitrogen. Solvents were dried and distilled prior to use. All glassware was heated to 150°C, evacuated and filled with dry nitrogen several times. — NMR: Jeol GX 400 spectrometer (samples were 50% [vol] dissolved in C_6D_6, kept at 25°C; internal TMS as reference). For ^{15}N NMR external 50% $C_6H_5{}^{15}NH_2$ in C_6D_6 was used as a reference ($\delta = -333.60$) and converted to CH_3NO_2 ($\delta = 0$). ^1H NMR (399.78

MHz), ^{13}C NMR (100.54 MHz), ^{29}Si NMR (79.43 MHz), ^{15}N NMR (40.51 MHz). – IR: films between KBr plates, Perkin-Elmer 1650 FT-IR. – MS: MAT 311 (EI). – GC-MS Hewlett Packard HP 5890 with mass selective detector 5971 A.

Reagents: Chloro(phenyl)silane was obtained by chlorination of phenylsilane[25], and chloro(*p*-tolyl)silane by an analogous procedure from *p*-tolylsilane. **9** was prepared as described[11].

General Procedure for the Synthesis of Silylamines **2**, **3**, **6**, **7**: The alkylamine and triethylamine were dissolved in 100 ml of toluene. The chlorosilane was added in portions, and the resulting mixture was heated to reflux for 2 h. The precipitated ammonium salt was filtered off, the toluene was evaporated from the filtrate under reduced pressure and the residue subjected to fractional distillation.

Benzylbis(phenylsilyl)amine (**2**):Benzylamine (8.35 ml, 76 mmol), triethylamine (21.2 ml, 150 mmol), chloro(phenyl)silane (20.0 ml, 150 mmol); yield 21.5 g of **2** (88%), b.p. 142–144°C/0.02 mbar. – ^{1}H NMR: $\delta = 3.85$ (s, 4H, H_2C), 5.34 (s, 2H, SiH_2), 7.07–7.19 (m, 13H, H_5C_6C and (*m,p*)-H_5C_6Si), 7.61–7.65 (m, 2H, *o*-H_5C_6Si). – $^{13}C\{^{1}H\}$ NMR: $\delta = 51.5$ (s, CH_2), 127.0 (s, *p*-C_6H_5C), 128.3 (s, *o*-C_6H_5Si), 128.4 (s, *o*-C_6H_5C), 128.5 (s, *m*-C_6H_5C), 130.3 (s, *p*-C_6H_5Si), 134.5 (s, *i*-C_6H_5Si), 135.3 (s, *m*-C_6H_5Si), 140.0 (s, *i*-C_6H_5C). – $^{15}N\{^{1}H\}$ NMR (INEPT): $\delta = -355.0$ [s, ^{1}J(NSi) = 14.3 Hz]. – ^{29}Si NMR (INEPT): $\delta = -19.4$ [tm, ^{1}J(SiH) = 205.9 Hz]. – IR (film): $\tilde{\nu} = 2143$ cm^{-1} s (νSiH), 952 m (ν_{as}SiNSi). – MS (GC-coupled), *m/z*: 303 [M$^+$], 226 [M$^+$ – Ph], 212 [M$^+$ – CH_2Ph], 183, 134, 107, 91 (100%).

Dibenzyl(phenylsilyl)amine (**3**): Dibenzylamine (14.7 ml, 76 mmol), triethylamine (10.6 ml, 76 mmol), chloro(phenyl)silane (10.0 ml, 76 mmol); yield 18.3 g of **3** (79%), b.p. 145°C/0.02 mbar, m.p. 54–56°C. – ^{1}H NMR: $\delta = 3.99$ (s, 2H, CH_2), 5.19 (s, 4H, SiH_2), 7.03–7.16 [m, 13H, H_5C_6C and (*m,p*)-H_5C_6Si], 7.48–7.50 (m, 2H, *o*-H_5C_6Si). – $^{13}C\{^{1}H\}$ NMR: $\delta = 51.4$ (s, CH_2), 127.1 (s, *p*-C_6H_5C), 128.1 (s, *o*-C_6H_5C), 128.1 (s, *o*-C_6H_5Si), 128.3 (s, *m*-C_6H_5C), 130.2 (s, *p*-C_6H_5Si), 133.9 (s, *i*-C_6H_5Si), 135.0 (s, *m*-C_6H_5Si), 140.4 (s, *i*-C_6H_5C). – $^{15}N\{^{1}H\}$ NMR (INEPT): $\delta = -365.2$ [s, ^{1}J(NSi) = 14.3 Hz]. – ^{29}Si NMR (INEPT): $\delta = -21.8$ [ttm, ^{1}J(SiH) = 208.8, ^{3}J(SiCCH) = 6.2 Hz]. – IR (film): $\tilde{\nu} = 2141$ cm^{-1} s (νSiH). – MS (GC-coupled), *m/z*: 319 [M$^+$], 318 [M$^+$ – H], 240 (100%) [M$^+$ – Ph – 2 H], 226 [M$^+$ – H – CH_2Ph], 210 [M$^+$ – H – SiH_2Ph], 183, 163, 150, 107, 105, 91.

Benzylbis(p-tolylsilyl)amine (**6**): Benzylamine (5.4 ml, 49 mmol), triethylamine (13.7 ml), chloro(*p*-tolyl)silane (15.0 ml, 99 mmol); yield of **6** 15.6 g (92%), b.p. 164–167°C/0.01 mbar. – ^{1}H NMR: $\delta = 2.07$ (s, 6H, CH_3), 3.87 (s, 2H, CH_2), 5.33 (s, 4H, SiH_2), 7.01–7.23 and 7.56–7.58 (m, 13H, HC_{ar}). – $^{13}C\{^{1}H\}$ NMR: $\delta = 21.4$ (s, CH_3), 51.3 (s, CH_2), 127.0 (s), 128.3 (s), 128.3 (s), 128.4 (s), 129.1 (s), 130.8 (s), 135.4 (s), 140.0 (s). – $^{15}N\{^{1}H\}$ NMR (DEPT): $\delta = -374.7$ [s, ^{1}J(NSi) = 14.2 Hz]. – ^{29}Si NMR (DEPT): $\delta = -22.1$ [tm, ^{1}J(SiH) = 207.8 Hz]. – IR (film): $\tilde{\nu} = 2137$ cm^{-1} s (νSiH). – MS (GC-coupled), *m/z*: 347 [M$^+$].

Dibenzyl(p-tolylsilyl)amine (**7**): Dibenzylamine (12.7 ml, 66 mmol), triethylamine (9.2 ml, 66 mmol), chloro(*p*-tolyl)silane (10.0 ml, 66 mmol); yield of **7** 19.4 g (93%), b.p. 165–170°C/0.01 mbar, m.p. 39°C. – ^{1}H NMR: $\delta = 2.09$ (s, 3H, H_3C), 3.86 (s, 4H, H_2C), 5.36 (s, 2H, H_2Si), 7.00–7.24 and 7.56–7.58 (m, 14H, H_{ar}). – ^{13}C NMR: $\delta = 21.4$ (s, CH_3), 51.3 (s, CH_2), 127.0 (s, *p*-C_6H_5), 128.3 (s, *o*-C_6H_5), 128.4 (s, *m*-C_6H_5), 129.1 (s, *o*-C_6H_4), 130.8 (s, *p*-C_6H_4), 135.4 (s, *m*-C_6H_4), 140.1 (s, *i*-C_6H_5 and *i*-C_6H_4). – $^{15}N\{^{1}H\}$ NMR (DEPT): $\delta = -364.7$ [s, ^{1}J(NSi) = 20.9 Hz]. – ^{29}Si NMR (DEPT): $\delta = -19.5$ [tm, ^{1}J(SiH) = 205.0 Hz]. – MS (GC-coupled), *m/z*: 317 [M$^+$]. – IR (Film): $\tilde{\nu} = 2139$ cm^{-1} s (νSiH).

Bis(p-tolylsilyl)amine (**8**): A slow stream of dry ammonia is admitted at 50°C into a warm, vigorously stirred solution of 25.0 ml of chloro(*p*-tolyl)silane (0.165 mol) in 250 ml of THF/hexane (1:2). Gas admission was discontinued as soon as the absorption of ammonia was completed. The mixture was then heated to reflux for several minutes and the resulting suspension cooled to ambient temperature and filtered. Evaporation of the solvents from the filtrate under reduced pressure afforded an oil which was distilled to give 18.3 g (86%) of **8**, b.p. 115°C/0.01 mbar, m.p. 4°C. – ^{1}H NMR: $\delta = 0.25$ (s, broad, 1H, NH), 2.11 (s, 6H, H_3C), 5.04 [d, ^{3}J(HSiNH) = 4.0 Hz, 4H, H_2Si], 6.99 [d, ^{3}J(HCCH) = 7.8 Hz, 4H, *o*-H], 7.43 [d, ^{3}J(HCCH) = 7.8 Hz, 4H, *m*-H]. – $^{13}C\{^{1}H\}$ NMR: $\delta = 21.4$ (s, CH_3), 129.0 (s, *o*-C), 131.5 (s, *p*-C), 134.7 (s, *m*-C), 139.9 (s, *i*-C). – ^{15}N NMR (DEPT): $\delta = -389.3$ [d quin, ^{1}J(NH) = 70.6, ^{2}J(NSiH) = 5.2, ^{1}J(NSi) = 13.8 Hz]. – ^{29}Si NMR (DEPT): $\delta = -28.8$ [tm, ^{1}J(SiH) = 207.1 Hz]. – IR (film): $\tilde{\nu} = 3357$ cm^{-1} w (νNH), 2140 s (νSiH). – MS (GC-coupled), *m/z*: 257 [M$^+$], 164 (100%) [M$^+$ – 2 H – $CH_3C_6H_4$].

Tris(p-tolylsilyl)amine (**5**): A mixture of 5.09 g of bis(*p*-tolylsilyl)amine (**8**, 19 mmol), 2.75 ml of triethylamine (19 mmol), 3.0 ml of chloro(*p*-tolyl)silane (19 mmol), and 15 ml of pentane was sealed in a thick-walled glass tube and heated to 130°C for 36 h in a pentane-filled autoclave. After slow cooling to ambient temp. the ampoule was opened and the suspension filtered. The precipitated ammonium salt was washed with several small portions of pentane, the combined filtrate and washings were concentrated in vacuo, and the residue was distilled in vacuo to yield 5.71 g of **5** (80%), b.p. 165°C/0.01 mbar. – ^{1}H NMR: $\delta = 2.06$ (s, 9H, H_3C), 5.30 (s, 6H, H_2Si), 6.93 [d, ^{3}J(HCCH) = 8.4 Hz, 6H, *m*-H], 7.41 [d, ^{3}J(HCCH) = 8.4 Hz, 6H, *o*-H]. – $^{13}C\{^{1}H\}$ NMR: $\delta = 21.5$ (s, CH_3), 129.0 (s, *o*-C), 130.5 (s, *p*-C), 135.5 (s, *m*-C), 140.2 (s, *i*-C). – ^{15}N NMR (DEPT): $\delta = -386.0$ [sept, ^{2}J(NSiH) = 4.9, ^{1}J(NSi) = 8.9 Hz]. – ^{29}Si NMR (DEPT): $\delta = -24.1$ [tm, ^{1}J(SiH) = 209.7 Hz]. – IR (film): $\tilde{\nu} = 2142$ cm^{-1} s (νSiH). – MS (GC-coupled), *m/z*: 377 [M$^+$], 285 [M$^+$ – H – $CH_3C_6H_4$], 193 [100%, M$^+$ – 2 H – 2 $CH_3C_6H_4$], 162 [M$^+$ – 3 H – 2 $CH_3C_6H_4$ – Si].

Bis(phenylsilyl)(trimethylsilyl)amine (**10**): 16.5 ml of a 1.6 M solution of methyllithium (26 mmol) in diethyl ether was added dropwise to a solution of 6.0 ml of bis(phenylsilyl)amine (26 mmol) in 50 ml of diethyl ether, and the mixture was cooled to –110°C by a THF/liquid nitrogen slush. It was then stirred at this temp. for 30 min. Then 3.3 ml of chlorotrimethylsilane (26 mmol) was added dropwise, and the solution was warmed to –78°C, stirred for 1 h and subsequently warmed to ambient temp. The solvent was removed under reduced pressure and replaced by the same volume of pentane. The resulting suspension was filtered, the pentane evaporated, and the residue subjected to fractional distillation to yield 3.2 g (40%) of **10**, b.p. 107–109°C, m.p. –1°C. – ^{1}H NMR: $\delta = 0.23$ (s, 1H, H_3C), 5.18 (s, 4H, H_2Si), 7.16–7.19 (m, 6H, *m,p*-H), 7.60–7.63 (m, 4H, *o*-H). – $^{13}C\{^{1}H\}$ NMR: $\delta = 2.1$ (s, CH_3), 128.3 (s, *o*-C), 130.2 (s, *p*-C), 134.7 (s, *m*-C), 135.3 (s, *i*-C). – $^{15}N\{^{1}H\}$ NMR (INEPT): $\delta = -387.4$ [s, ^{1}J(NSi-Ph) = 9.0, ^{1}J(NSi-Me$_3$) = 7.3 Hz]. – ^{29}Si NMR (INEPT): $\delta = -28.8$ [ttt, ^{1}J(HSi) = 208.0, ^{3}J(SiCCH) = 5.6, ^{3}J(SiNSiH) = 5.6 Hz, SiH_2], –9.69 [dez quin, ^{2}J(SiCH) = 6.6, ^{3}J(SiNSiH) = 3.3 Hz, $SiMe_3$]. – MS (GC-coupled), *m/z*: 302 [M$^+$], 286 [M$^+$ – H – CH_3], 240, 222, 208 (100%).

Crystallographic Structure Determinations of 7 *and* 10

Specimens of suitable quality of both compounds were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection. Diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å) with $\Theta-\Theta$ scan mode at −56 and −75°C for **7** and **10**, respectively. During data collection three standard relections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for both compounds. Lp corrections were applied, but intensity data were not corrected for absorption effects. The structures were solved by direct methods (SHELXS-86) and completed by difference Fourier syntheses (SHELXTL-PLUS). The final atomic positions and isotropic equivalent displacement factors are listed in Tables 3 (**7**) and 4 (**10**).

7: $C_{21}H_{23}NSi$, M_r = 317.51, monoclinic, a = 17.667(3), b = 5.922(1), c = 19.296(2) Å, β = 115.17(1)°, space group $P2_1/n$, $Z = 4$, $D_{\text{calcd.}}$ = 1.154 g cm^{-1}, $F(000)$ = 680, μ(Mo-K_α = 1.2 cm^{-1}. 4520 intensity data were measured up to $(\sin\Theta/\lambda)_{\max}$ = 0.639 Å^{-1}. After merging of equivalent data (R_{int} = 0.033), 2876 of the remaining 3488 independent structure factors were considered "observed" $[F_o \geq 3\sigma(F_o)]$ and used for refinement. All hydrogen atoms could be located and were refined isotropically. The non-H atoms were refined with anisotropic displacement parameters. The function minimized was $\Sigma w(\mid F_o \mid - \mid F_c \mid)^2/\Sigma WF_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$. The final R and R_w values were 0.050 and 0.057, respectively (number of refined parameters: 300). Residual electron density: +0.31/−0.29 eÅ^3.

10: $C_{15}H_{23}NSi_3$, M_r = 301.62, monoclinic, a = 13.454(2), b = 6.145(1), c = 21.426(2) Å, β = 92.30(1)°, space group $P2_1/c$, $Z = 4$, $D_{\text{calcd.}}$ = 1.132 g cm^{-1}, $F(000)$ = 648, μ(Mo-K_α) = 2.6 cm^{-1}. 3520 intensity data were measured up to $(\sin\Theta/\lambda)_{\max}$ = 0.595 Å^{-1}. After merging of equivalent data (R_{int} = 0.015), 2477 of the remaining 2856 independent structure factors were considered "observed" $[F_o \geq 4\sigma(F_o)]$ and used for refinement. All hydrogen atoms could be located, the H atoms bound to Si were refined isotropically, the remaining ones were included in the refinement with fixed isotropic displacement parameters (U_{iso} = 0.05 and 0.075 for phenyl and methyl H atoms, respectively). The non-H atoms were refined with anisotropic displacement parameters. The function minimized was $\Sigma w(\mid F_o \mid - \mid F_c \mid)^2/\Sigma WF_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$. The final R and R_w values were 0.034 and 0.041, respectively (number of refined parameters: *0.034* and 0.041, respectively (number of refined parameters: 188). Residual electron density: +0.30/0.21 eÅ^3.

Further information on the X-ray structure determinations can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-57286, the names of the authors, and the journal citation.

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