The Molecular Structures of Triaminosilanes

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The structural chemistry of a series of triaminosilanes $XSi(NR_2)_3$ has been investigated in order to determine the ground-state configuration and conformation of these molecules. Theoretical studies and analogy with the isoelectronic $XP(NR_2)_3$ ($X = CH_2$, O, Se, $NSiMe_3$ etc.) and $P(NR_2)_3$ molecules suggest structures of C_s or C_3 symmetry, with small energy differences between them. The molecular structure of $HSi(NMe_2)_3$ (**1**) has been determined by a single-crystal X-ray diffraction study at low temperature. Surprisingly, the molecules have a non-standard conformation with an irregular orientation of the three NMe_2 groups. The hydrido-, chloro-, methyl-, and vinyltris(morpholino)silanes $XSi[N(CH_2CH_2)_2O]_3$ (X = H, Cl, Me, Vi; **2**–**5**) were prepared from the corresponding chlorosilanes and morpholine (**2**, **3**) or lithium morpholide (**4**, **5**). Their variable-temperature NMR spectra were studied and the molecular structures determined by single crystal X-ray diffraction. Compound **2** has a molecular geometry approaching mirror symmetry with one morpholino group significantly different from the other two. This structure resembles that of isoelectronic tris(amino)phosphines. Compounds **3**–**5** have structures with a propeller-like arrangement of the three morpholino rings approaching C_3 symmetry for this part of the molecules. The chloro compound **3** shows the shortest Si–N bond lengths (average 1.690 Å), followed by **2** (1.708 Å), **5** (1.709 Å) and **4** (1.712 Å). The configuration of all nitrogen atoms is almost planar, with sums of the angles close to 360°, and the morpholino rings adopt a chair conformation. According to the solution NMR spectra the ring inversion is slow at low temperature, but the rings rotate freely about the Si–N bonds on the NMR time scale. The molecular structures are discussed in terms of steric and electronic effects of the substituents. Other model compounds, including $(Me_2N)_3SiC_6H_4$-4-Br (**6**), $MeSi[N(CH_2CH_2)_2NMe]_3$ (**7**) and $PhSi[N(CH_2)_4]_3$ (**8**), could not be crystallized, but were characterized by their analytical and spectroscopic data.

Introduction

Ammonia and primary, secondary and tertiary *alkyl*-amines are pyramidal molecules[1,2]. In contrast, mono-, di- and tri*silyl*amines have ground-state molecular structures with "flat" nitrogen atoms. Trisilylamine $N(SiH_3)_3$, with its planar NSi_3 framework in all states of aggregation (gas, liquid, crystal), is the best known example. Its structure has been studied in great detail both experimentally and theoretically up to high levels of sophistication, and general agreement has been reached about the underlying principles of its chemical bonding[3,4]. Disilylamines are generally planar at the nitrogen atoms, the most prominent exception being the *N,N*-disilylhydroxylamines with slightly pyramidal N atoms[5,6]. For monosilylamines current knowledge is less satisfactory, since variations in oligomerization with temperature and state of aggregation [dimethyl(silyl)amine Me_2NSiH_3 is a pentamer in the crystal!][8,9] render generalizations rather difficult[7–17]. Generally, however, the nitrogen pyramids become flatter as the number of silyl substituents increases[6].

The situation is similar with the *polyaminosilanes*, where the structural information is limited to very few non-representative compounds (below). We became interested in the structural chemistry of *tri*aminosilanes $XSi(NR_2)_3$ when we were engaged in a reinvestigation of the molecular structures of triaminophosphines $P(NR_2)_3$ and the corresponding phosphonium salts $[RP(NR_2)_3]X$ and ylides $(R_2N)_3PCH_2$[18,19]. These molecules, cations and betaines, respectively, were found to exhibit unexpected structures with C_s symmetry and two distinctly different configurations of the amino groups: one almost planar, but two strongly pyramidal. The propeller structure with a threefold axis (point group C_3), which could intuitively be assumed to be the conformation of choice, was not encountered in any of the experimental investigations and was considered only in earlier theoretical calculations[18,20,21].

A systematic study of the molecular structures of triaminosilanes $XSi(NR_2)_3$ was therefore initiated with the aim of establishing if there are consistent similarities between the two related (isoelectronic) families of phosphorus and silicon compounds. A literature survey revealed that only very few $XSi(NR_2)_3$ structures had been determined experimentally[22–26], and state-of-the-art theoretical studies have been carried out only recently[27]. The triaminosilanes with simple groups X and R (e.g. X = R = H) are not stable, and most others are not available in crystalline form.

An important target molecule of this study was tris(dimethylamino)silane[28]. Although its crystal structure could now be determined, the molecules turned out not to adopt any of the expected configurations and conformations and thus did not fit into the picture drawn by experimental stud-

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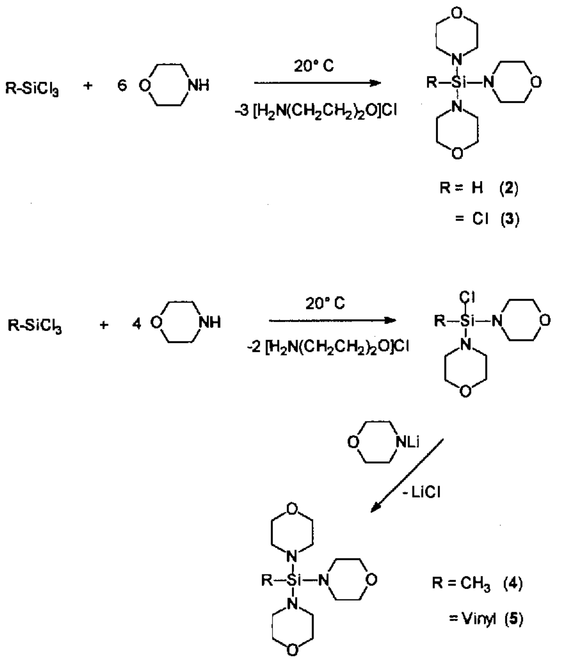
ies of the isoelectronic $P(NMe_2)_3$[18] and theoretical calculations of $HSi(NMe_2)_3$[27].

After a few further exploratory experiments, the tri*morpholino*silanes were chosen as substrates for the major part of the present study. This series includes a number of species still crystalline at room temperature, owing to the inherent polarity of the heterocycles. The morpholine unit represents a largely strain-free six-membered ring which does not impose major geometrical constraints on the amino function.

Preparation and Properties of the Compounds

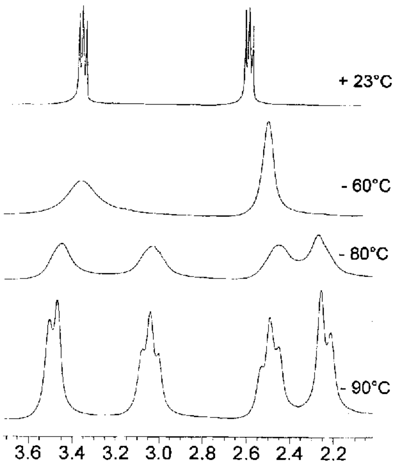
*Tri*chlorosilane $HSiCl_3$ is known to react with an excess of morpholine in diethyl ether at room temperature to give tris(morpholino)silane (**2**) and morpholinium hydrochloride[29]. The reaction of *tetra*chlorosilane with morpholine proceeds in toluene as solvent and affords a good yield of the monochloride **3**[30]. For complete conversion of trichloro(*methyl*)silane into the morpholine derivative **4**[31], the more strongly nucleophilic lithium morpholide is necessary; this is also the case for trichloro(*vinyl*)silane (to give **5**).



Compounds **2**–**5** are colourless crystalline products, slightly sensitive to atmospheric moisture (**3**) and oxygen (**2**). They are freely soluble in most common non-protic organic solvents without decomposition, but are degraded by water, acid and base. The compounds are readily identified by their analytical and spectroscopic data (see the Experimental Section).

The ^1H-NMR spectra of the compounds show a strong temperature dependence of the chemical shifts and multiplicities of the ring hydrogen atom signals. This behaviour resembles that of free morpholine, however, and is known to be a consequence of slow chair inversion at the low-temperature limit[32,33]. The geminal hydrogen atoms at the OCH_2 and NCH_2 groups become non-equivalent at low temperature, and four distinct multiplets are observed. At ambient temperature the $(ABXY)_2$ spin system reverts to the $(AA'XX')_2$ multiplet (Figure 1). The spectra were investigated in detail for **2** and **4** (see below and the Experimental Section).

Figure 1. Temperature-dependent ^1H-NMR spectra of compound **4** (in [D_8]toluene) in the methylene region (δ scale)



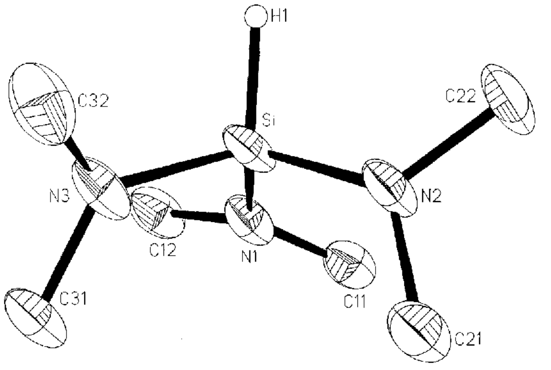
It should be noted that the $\{^1H\}^{13}C$-NMR spectra of the triaminosilanes show only two ring carbon resonances (O-bound and N-bound) over the whole temperature range. Thus the phenomena in the ^1H spectra cannot be ascribed to hindered morpholine rotation about the Si–N bond (and rapid ring inversion), which could result in a fixed propeller conformation with non-equivalent ring sides: The morpholine rings clearly spin freely on the NMR time scale in solution at the low-temperature limit (−90°C), ensuring full virtual three fold symmetry (point groups C_3 or even C_{3v}) for this part of the molecules.

The local symmetry of the substituents X in the molecules $XSi[N(C_2H_4)_2O]_3$ either makes the XSi units symmetrical tops ($C_{\infty v}$ for X = H, Cl) or impose mirror symmetry (C_s for Vi) or threefold symmetry (C_{3v} for X = Me). Threefold symmetry (C_{3v}) could thus be reached for X = H, Cl, Me, whereas mirror symmetry may be possible for X = Vi.

Molecular Structures

Tris(dimethylamino)silane (**1**) can be prepared following an established literature procedure[28]. The compound has a very low melting point (−93 to −88°C[34]), and single crystals were therefore grown from the melt in a capillary using microscale zone-melting technique (see the Experimental Section). The compound crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$. The individual molecules do not approach point groups C_3 or C_s (Figure 2). The configurations of the nitrogen atoms of the rather randomly orientated dimethylamino groups deviate only slightly from planarity, with sums of the angles of 358.8° (N1), 358.2° (N2) and 357.0° (N3). The Si–N bond lengths are equal within the standard deviations, whereas the N–Si–N angles are different and range from 106.6(1)° to as much as 115.3(1)°. As a consequence the H−Si−N angles also show large variations between the limits of 103.3(14)° and 113.7(14)°.

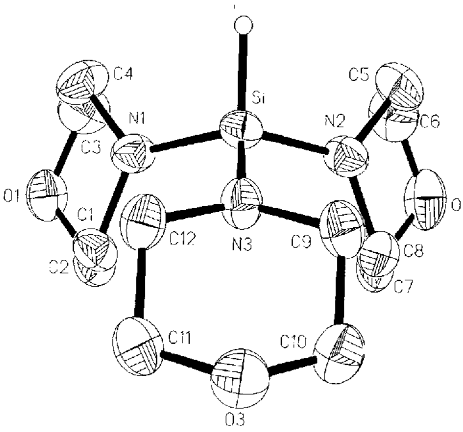
Figure 2. Molecular structure of compound **1** with atomic numbering (methyl hydrogen atoms omitted for clarity); selected bond lengths [Å] and angles [°]: Si−N1 1.706(3), Si−N2 1.708(2), Si−N3 1.708(3), Si−H1 1.38(4); N1−Si−N2 110.4(1), N1−Si−N3 106.6(1), N2−Si−N3 115.3(1), N1−Si−H1 114(1), N2−Si−H1 103(1), N3−Si−H1 108(2), C11−N1−Si 123.7(2), C12−N1−Si 122.7(3), C11−N1−C12 112.4(3), C21−N2−Si 121.4(2), C22−N2−Si 123.6(2), C21−N2−C22 113.2(3), C31−N3−Si 124.9(3), C32−N3−Si 118.9(2), C31−N3−C32 113.2(3)



By contrast the reported theoretical minimum-energy structure at the MP2/6-31G* level of theory has C_s symmetry and H−Si−N angles of 103.9 and 119.0°. The Si−N bond lengths, however, were calculated to be very similar (1.738 and 1.732 Å)[27]. According to our own calculation at the same level of theory, the energy difference between the C_s and C_3 structures is 4.1 kJ/mol, with the C_1 structure observed experimentally in the solid state probably being not much higher in energy. Assuming the MP2/6-31G* level of theory to be sufficiently high to provide us with the correct absolute minimum, the observed crystal structure appears to be the result of intermolecular forces in the crystal lattice, which give rise to a new, different energy minimum. Calculations with C_1 molecular symmetry gave no local or absolute energy minima for the free molecule[27].

Tris(morpholino)silane (**2**) crystallizes (from diethyl ether at low temperature) in the monoclinic space group *C*2/*c* with $Z = 8$. The structure of the individual molecules closely approaches C_s symmetry (Figure 3). The mirror plane contains the Si−H group and the nitrogen atom N3 and the oxygen atom O3 of the same morpholine ring. The remaining two morpholine rings are approximate mirror images. The configuration of the nitrogen atom N3 deviates slightly from planarity, with a sum of the angles of 356.9°. The two nitrogen atoms N1 and N2 have an essentially planar configuration, with sums of angles close to 360° (N1: 359.1°, N2: 359.2°). The three Si−N bonds are of equal length within the experimental standard deviations, but the N−Si−N angles at the silicon atom are grossly different: N1−Si−N2 is increased to as much as 120.23(8)°, while N1−Si−N3 and N2−Si−N3 are compressed to 106.15(7)° and 105.85(7)°, respectively. The set of H−Si−N angles shows a similar discrepancy, with H−Si−N3 = 116.9(8)° but H−Si−N2 = 104.3(7)° and H−Si−N1 = 104.1(7)°.

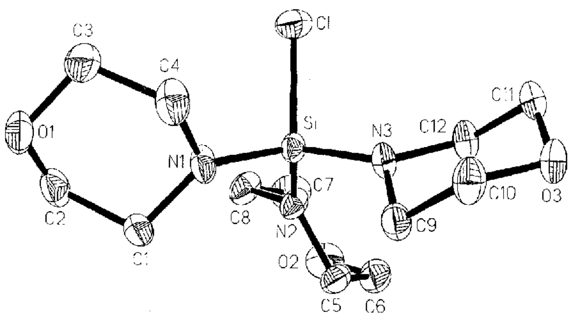
Figure 3. Molecular structure of compound **2** with atomic numbering (morpholine hydrogen atoms omitted for clarity); selected bond lengths [Å] and angles [°]: Si−N1 1.708(1), Si−N2 1.708(2), Si−N3 1.709(2), Si−H1 1.36(2); N1−Si−N2 120.2(1), N1−Si−N3 106.2(1), N2−Si−N3 105.9(1), N1−Si−H1 104.1(7), N2−Si−H1 104.3(7), N3−Si−H1 116.9(8), C1−N1−Si 124.4(1), C4−N1−Si 124.1(1), C1−N1−C4 110.6(1), C5−N2−Si 124.4(1), C8−N2−Si 124.4(1), C5−N2−C8 110.4(2), C9−N3−Si 123.9(1), C12−N3−Si 123.2(1), C9−N3−C12 109.8(1)



These structural details closely resemble those of P(NMe$_2$)$_3$ and indicate an analogous electronic situation, which is also borne out by theoretical calculations. With X = H, as the smallest possible substituent at the silicon atom, there is no significant steric effect that could overrule the inherent preference for a mirror-symmetry ground state.

Chlorotris(morpholino)silane (**3**) crystallizes (from toluene) in the triclinic space group $P\bar{1}$ with $Z = 2$. In this case the arrangement of the atoms is close to C_3 symmetry (Figure 4). The three morpholine rings are arranged like the blades of a threefold propeller, the axis of which passes through the Si−Cl atoms (Figure 5).

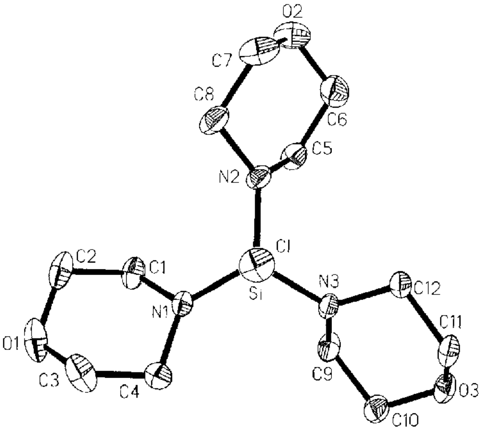
Figure 4. Molecular structure of compound **3** with atomic numbering (hydrogen atoms omitted for clarity); selected bond lengths [Å] and angles [°]: Si−N1 1.691(1), Si−N2 1.686(1), Si−N3 1.692(1), Si−Cl 2.092(1); N1−Si−N2 112.78(6), N1−Si−N3 111.37(6), N2−Si−N3 112.22(6), N1−Si−Cl 107.30(5), N2−Si−Cl 106.42(4), N3−Si−Cl 106.27(4), C1−N1−Si 125.3(1), C4−N1−Si 122.5(1), C1−N1−C4 111.8(1), C5−N2−Si 123.5(1), C8−N2−Si 124.2(1), C5−N2−C8 111.4(1), C9−N3−Si 124.8(1), C12−N3−Si 120.9(1), C9−N3−C12 111.1(1)



The geometrical parameters of the three heterocycles are similar, with all three nitrogen atoms in a planar or almost planar configuration: The sums of the angles amount to

359.6° at N1, 359.1° at N2 and 356.9° at N3. The angles at the silicon atom lie in the range 106.27(4)–112.78(6)°, and are thus within 3° of the ideal tetrahedral angle. The three Si–N distances are 1.691(1), 1.686(1) and 1.692(1) Å for Si–N1/N2/N3, respectively, and are thus significantly shorter than for the Si–H analogue **2**: The average Si–N bond length is 1.708 Å for **2**, but 1.690 Å for **3**. This shortening clearly reflects the electronic influence of the more electronegative chlorine atom in **3**, as is also observed for the series Me_3SiNMe_2[35], $H_2ClSiNMe_2$[36], HCl_2SiNMe_2[14], and Cl_3SiNMe_2[15].

Figure 5. View of the molecular structure of compound **3** along the Cl–Si bond, showing the C_3 arrangement of the three morpholino substituents

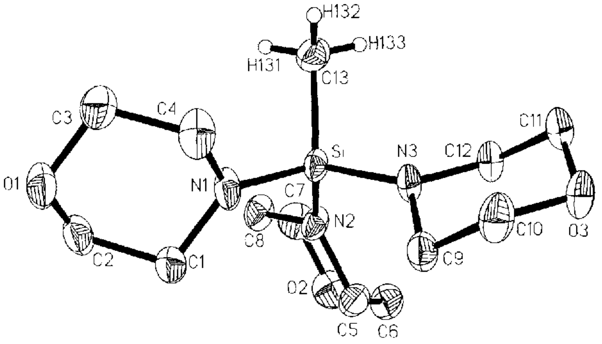


Although this bond shortening is not surprising, the change in overall symmetry from C_s to C_3 (**2** versus **3**) is unexpected at first sight, because the chlorine and the hydrogen atoms do not appear to have different symmetry requirements. It is likely that the change from mirror to propeller symmetry is caused by the greater electronegativity of the substituent (Cl > H). This is in keeping with the results of theoretical calculations for tris(amino)phosphines and their derivatives[18], where the electronegative oxygen atoms [e.g. in $O{=}P(NMe_2)_3$] are found to cause similar changes in structure. The energy differences between the conformers are small, however, and suggest that even minor influences can induce deviations from the ground-state geometry[23].

In this context it should also be remembered that on the NMR timescale the morpholine rings in compounds **2**–**5** rotate freely about their N–Si axes in solution, even at low temperatures, with estimated values for the activation energy of rotation lower than ca. 6 kcal/mole. Thus not only are the energy differences between rotamers small, but also the energy barriers separating these conformers.

Methyltris(morpholino)silane (**4**) also crystallizes (from diethyl ether at low temperature) in the triclinic space group $P\bar{1}$ with $Z = 2$. The dimensions of the unit cell are very similar to those of **3** (Table 1). The molecular structure again closely resembles that of a threefold propeller (point group C_3, Figure 6). The configurations of the nitrogen atoms are planar (N1: sum of the angles 359.9°) or nearly planar (N2: 357.5°, N3: 356.3°), and the angles at the silicon atom are close to the tetrahedral reference value by less than 1° [108.60(7)–110.31(6)°].

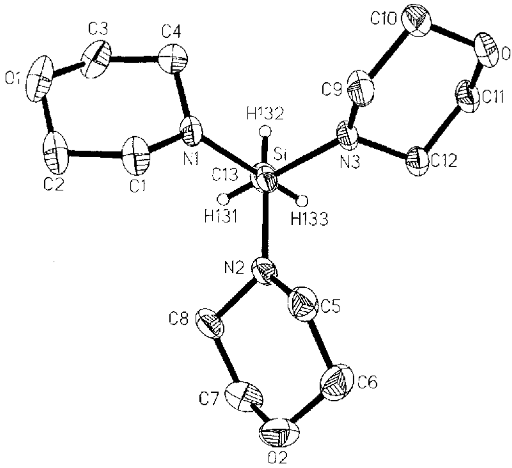
Figure 6. Molecular structure of compound **4** with atomic numbering (morpholine hydrogen atoms omitted for clarity); selected bond lengths [Å] and angles [°]: Si–N1 1.710(1), Si–N2 1.712(1), Si–N3 1.715(1), Si–C13 1.861(2); N1–Si–N2 110.31(6), N1–Si–N3 109.69(6), N2–Si–N3 109.85(6), N1–Si–C13 109.06(7), N2–Si–C13 106.42(4), N3–Si–C13 109.29(7), C1–N1–Si 125.9(1), C4–N1–Si 122.8(1), C1–N1–C4 111.3(1), C5–N2–Si 124.0(1), C8–N2–Si 123.0(1), C5–N2–C8 110.6(1), C9–N3–Si 124.7(1), C12–N3–Si 121.4(1), C9–N3–C12 110.3(1)



The average Si–N distance in compound **4** is 1.712(1) Å, which is larger than the average Si–N value in not only the Cl–Si but also the H–Si analogue (above), reflecting the electronegativity effects of the three substituents (Cl > H > Me).

The position of the methyl group relative to the three morpholino substituents is staggered (Figure 7). It is tempting to ascribe the reversion from C_s (**2**) to C_3 symmetry (**4**) to the conformational requirements of the threefold rotor H_3CSi, but the C_3 structure of the chloro compound **3** makes it clear that electronic factors are also important.

Figure 7. View of the molecular structure of compound **4** along the C13–Si axis, showing the staggered position of the methyl group relative to the three morpholino substituents



Superposition of the structures of **3** and **4** (Figure 8) shows the small geometrical differences between these two compounds. Since the unit cells of **3** and **4** are virtually isomorphous (Table 1), packing forces can also be assumed to be similar in the two lattices. If the C_s structure of the Si–H compound **2** is taken as the reference ground-state

Table 1. Crystal data, data collection, structure solution and refinement for compounds **1**–**5**

	1	**2**	**3**	**4**	**5**
Crystal data					
Formula	$C_6H_{19}N_3Si$	$C_{12}H_{25}N_3O_3Si$	$C_{12}H_{24}ClN_3O_3Si$	$C_{13}H_{27}N_3O_3Si$	$C_{14}H_{27}N_3O_3Si$
M_r	161.33	287.44	321.88	301.37	313.48
Crystal system	triclinic	monoclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	6.166(1)	14.981(2)	8.969(1)	8.968(1)	9.370(1)
b (Å)	7.577(1)	9.044(1)	9.502(1)	9.645(1)	9.551(1)
b (Å)	11.345(1)	22.475(3)	10.837(1)	10.833(1)	11.009(1)
α (°)	82.26(1)	90	81.52(1)	81.33(1)	82.77(1)
β (°)	76.10(1)	110.33(1)	68.55(1)	68.38(1)	69.51(1)
γ (°)	81.74(1)	90	66.34(1)	66.30(1)	62.82(1)
V (Å^3)	506.4(1)	2995.7(7)	787.3(1)	797.6(1)	820.3(1)
ρ_{calc} (gcm^{-3})	1.058	1.275	1.358	1.255	1.269
Z	2	8	2	2	2
$F(000)$ (e)	180	1248	344	328	340
μ(Mo-K_α) (cm^{-1})	1.78	1.66	3.30	1.59	1.57
Data collection					
Diffractometer	Enraf Nonius CAD4	Enraf Nonius CAD4	Enraf Nonius CAD4	Enraf Nonius CAD4	Enraf Nonius CAD4
Radiation	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α
λ(Mo-K_α) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
T (°C)	–152	–74	–68	–68	-74
Scan mode	ω–θ	ω	ω–θ	ω–θ	ω-θ
hkl range	$-7\rightarrow+7$ $-9\rightarrow+9$ $-14\rightarrow+9$	$-18\rightarrow+18$ $0\rightarrow+11$ $-28\rightarrow-16$	$-10\rightarrow+11$ $-11\rightarrow+12$ $0\rightarrow+13$	$-10\rightarrow+10$ $-11\rightarrow+11$ $0\rightarrow+12$	$0\rightarrow+11$ $-9\rightarrow+11$ $-12\rightarrow+13$
$\sin(\theta/\lambda)_{max}$ (Å^{-1})	0.64	0.64	0.64	0.62	0.64
Measured reflections	5216	5216	3272	3880	3032
Unique reflections	2116	3072	3269	2984	3032
Reflections used for refinement	2115	3068	3254	2984	3028
Refinement					
Refined parameters	168	176	181	181	202
H atoms (found/calculated)	19/0	1/24	0/24	0/27	3/24
Final R indices [$F > 4\sigma(F)$]					
R[a]	0.0797	0.0417	0.0285	0.0340	0.0336
$wR2$[b]	0.18.46	0.0997	0.0749	0.0925	0.0914
(shift/esd)$_{max}$	<0.001	<0.001	<0.001	<0.001	<0.001
ρ_{fin}(max/min) (eÅ^{-3})	0.691/–1.414	+0.204/–0.294	–0.269/–0.193	+0.326/–0.248	+0.232/-0.260

[a] $R = \Sigma(\|F_o|-|F_c\|)/\Sigma|F_o|$. – [b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; a = 0.0878 (**1**), 0.0480 (**2**), 0.0386 (**3**), 0.0556 (**4**), 0.0553 (**4**); b = 0.62 (**1**), 1.63 (**2**), 0.31 (**3**), 0.26 (**4**), 0.27 (**5**).

situation for molecules with a small, medium-electronegativity substituent (H), and if the C_3 structure of **3** is ascribed to the greater electronegativity of the chlorine atom (as supported by theoretical calculations)[18], then the electronegativity argument does not hold for the C_3 structure of the methyl homologue **4** and the conformational influence of the methyl group is the most plausible reason.

Tris(morpholino)vinylsilane (**5**) crystallizes (from diethyl ether) in the triclinic space group $P\bar{1}$ with $Z = 2$. The three morpholino substituents are in a propeller-type arrangement (Figure 9), but the details of the conformation of the $Si[N(CH_2CH_2)_2O]_3$ unit differ quite markedly from those of **3** and **4**. The Si–N bond lengths (average: 1.709 Å) are similar to those in **2** (Si–H) [i.e. shorter than in **4** (Si–Me), but longer than in **3** (Si–Cl), above], and the sums of the angles at the nitrogen atoms are all close to 360° (N1: 359.1°, N2: 357.3°, N3: 358.6°).

The most important result of the structure determination of **5** is the retention of the propeller conformation despite the preference of the vinyl group for overall mirror symmetry of the complete molecule. It thus appears that any substituent larger than hydrogen causes enough steric or electronic interaction to transform the C_s structure into a C_3 structure, regardless of the substituent symmetry [C_s (vinyl) or C_3 (methyl)].

Considering the structural data accumulated for the set of tris(morpholino)silanes, the almost random structure found for $HSi(NMe_2)_3$ is even more puzzling. While none of the four heterocyclic species **2**–**5** has a structure differing much from the reference geometries (C_s and C_3) suggested by calculations or analogies, the simple compound **1** adopts a geometry that is completely inconsistent with such symmetrical standards. It therefore appears that for such a simple silicon–nitrogen compound the energy profiles for N–Si–N and H–Si–N angle bending, Si–N rotation and nitrogen inversion are so flat (within limits) that changes in configuration and conformation are associated with only minute changes in energy. If packing forces are the major origin of the "distortion" found for the $HSi(NMe_2)_3$ molecule in the crystal, a gas-phase study should finally show the differences. Such a study, along with theoretical reinvestigations, will be initiated shortly.

Figure 8. A superposition of the structure of **3** and **4**, showing the small geometrical differences between these two nearly isomorphous compounds

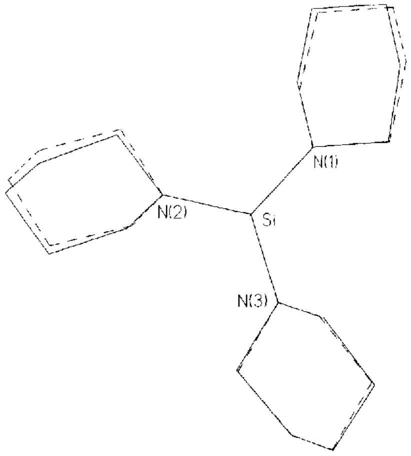
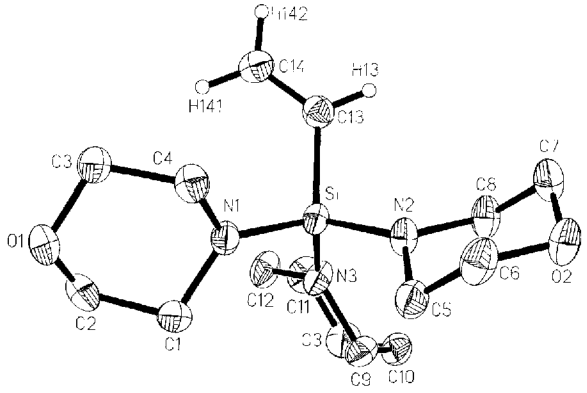


Figure 9. Molecular structure of compound **5** with atomic numbering (morpholine hydrogen atoms omitted for clarity); selected bond lengths [Å] and angles [°]: Si−N1 1.708(1), Si−N2 1.712(1), Si−N3 1.709(1), Si−C13 1.864(2), C13−C14 1.317(2); N1−Si−N2 111.17(6), N1−Si−N3 109.93(6), N2−Si−N3 109.98(6), N1−Si−C13 108.94(7), N2−Si−C13 107.44(7), N3−Si−C13 109.33(7), C1−N1−Si 124.7(1), C4−N1−Si 123.6(1), C1−N1−C4 110.8(1), C5−N2−Si 125.0(1), C8−N2−Si 121.7(1), C5−N2−C8 110.5(1), C9−N3−Si 124.9(1), C12−N3−Si 123.1(1), C9−N3−C12 110.6(1)



Supplementary Preparative Studies

During further attempts to gain access to crystalline triaminosilanes for structural studies, the following three compounds (**6**−**8**) were also prepared and characterized by analytical and spectroscopic techniques: 4-bromophenyltris(dimethylamino)silane [$(Me_2N)_3Si-C_6H_4$-4-Br, **6**], methyltris(4-methyl-1-piperazinyl)silane {$MeSi[N(CH_2CH_2)_2NMe]_3$, **7**} and phenyltris(1-pyrrolidinyl)silane [$PhSi[N(CH_2)_4]_3$, **8**]. Because none of them could be obtained as single crystals, details are given in the Experimental Section only.

The results of our structural studies of *tetraaminosilanes* will be reported in a forthcoming follow-up publication.

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Experimental Section

All experiments were carried out under dry purified nitrogen. Solvents and glassware were dried and kept under nitrogen. − NMR: Jeol GX 400 and Jeol GX 270, solutions in C_6D_6 at 23°C unless otherwise stated. − MS: GC/MS with mass-selective detector HP 5971 A (EI 70 eV). − IR: Perkin Elmer 1650 FT-IR.

Lithium Amides: In a typical reaction *n*-butyl lithium (1.7 M in hexane) was added dropwise to a solution of an excess of the amine in the appropriate solvent at room temperature. The reaction mixture was stirred for at least 1 h and was then used immediately in the following reactions.

Tris(dimethylamino)silane (**1**): This was prepared by following an established literature procedure[28].

Tris(morpholino)silane (**2**): The synthesis followed a literature procedure. Published analytical and spectroscopic data were confirmed[29]. − ^1H NMR (CD_2Cl_2, −30°C): δ = 2.86 (pseudo-t, $^3J_{H,H}$ = 5 Hz, 12H, NCH_2), 3.48 (pseudo-t, $^3J_{H,H}$ = 5 Hz, 12H, OCH_2), 4.15 (s, 1H, SiH). − ^1H NMR (CD_2Cl_2, −67°C): δ = 2.84 (m, 12H, NCH_2), 3.20−3.80 (m, br., 12H, OCH_2), 4.10 (s, 1H, SiH). − ^1H NMR (CD_2Cl_2, −91°C): δ = 2.80 (m, 12H, NCH_2), 3.25 and 3.64 (both m, 6H each, OCH_2), 4.06 (s, 1H, SiH). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −91°C): δ = 44.1 (s, NCH_2), 67.9 (s, OCH_2).

Chloro-tris(morpholino)silane (**3**): The synthesis followed a literature procedure[30]. − ^1H NMR: δ = 2.66 (pseudo-t, $^3J_{H,H}$ = 5 Hz, 12H, NCH_2), 3.34 (pseudo-t, $^3J_{H,H}$ = 5 Hz, 12H, OCH_2). − $^{13}C\{^1H\}$ NMR: δ = 45.3 (NCH_2), 67.9 (OCH_2). − $^{29}Si\{^1H\}$ NMR: δ = −35.0. − MS (EI, 70 eV) *m/z*: 321 [M^+], 235 [$M^+ - NC_4H_8O$], 149 [$235 - NC_4H_8O$], 86 [NC_4H_8O]. − $C_{12}H_{24}ClN_3O_3Si$ (321.88): calcd. C 44.8, H 7.5, N 13.1; found C 44.8, H 7.5, N 12.9.

Methyltris(morpholino)silane[31] (**4**): A solution of methyltrichlorosilane (5.86 ml, 0.05 mol) in 50 ml of toluene was added dropwise to a solution of morpholine (26.1 ml, 0.30 mol) in 250 ml of a toluene/hexane mixture (v/v 5:1) at room temperature. After stirring for 7 h at this temperature the precipitated salt was filtered off, and the solvent was removed in vacuo to leave a white solid that was shown by GC analysis to consist of 90% chloro(methyl)di(morpholino)silane. A suspension of lithium morpholide [0.05 mol, from 13.10 ml (0.05 mol) of morpholine and 34.4 ml (0.06 mol) of a 1.7 M solution of *n*-butyl lithium in hexane] in 100 ml of diethyl ether was added to the suspension of the crude chloro(methyl)di(morpholino)silane in 100 ml of pentane. After stirring for 6 h at room temperature the precipitate was filtered off and the solvent was evaporated from the filtrate. The crude product was recrystallized either from a toluene/pentane mixture or from diethyl ether at −20°C. Colourless crystals, 10.6 g (70%), m.p. 113°C. − ^1H NMR: δ = −0.14 (s, 3H, $SiCH_3$), 2.64 (pseudo-t, $^3J_{H,H}$ = 5 Hz, 12H, NCH_2), 3.42 (pseudo-t, $^3J_{H,H}$ = 5 Hz, 12H, OCH_2). − ^1H NMR ([D$_8$]toluene, 60°C): δ = −0.19 (s, 3H, $SiCH_3$), 2.59 (pseudo-t, $^3J_{H,H}$ = 5 Hz, 12H, NCH_2), 3.33 (pseudo-t, $^3J_{H,H}$ = 5 Hz, 12H, OCH_2). − ^1H NMR ([D$_8$]toluene, +23°C): δ = −0.21 (s, 3H, $SiCH_3$), 2.56 (pseudo-t, $^3J_{H,H}$ = 5 Hz, 12H, NCH_2), 3.33 (pseudo-t, $^3J_{H,H}$ = 5 Hz, 12H, OCH_2). − ^1H NMR ([D$_8$]toluene, −60°C): δ = −0.20 (s, 3H, $SiCH_3$), 2.52 (s, 12H, NCH_2), 3.38 (s, 12H, OCH_2). − ^1H NMR ([D$_8$]toluene, −80°C): δ = −0.31 (s, 3H,

$SiCH_3$), 2.31 and 2.49 (both m, 6H each, NCH_2), 3.06 and 3.48 (both m, 6H each, OCH_2). – ^{1}H NMR ([D_8]toluene, -90°C): $\delta = -0.29$ (s, 3H, $SiCH_3$), 2.27 and 2.49 (both m, 6H each, NCH_2), 3.07 and 3.52 (both m, 6H each, OCH_2). – $^{13}C\{^1H\}$ NMR: $\delta = -5.37$ ($SiCH_3$), 45.6 (NCH_2), 68.6 (OCH_2). – $^{13}C\{^1H\}$ NMR ([D_8]toluene, -90°C): 45.1 (s, NCH_2), 68.5 (s, OCH_2). – $^{29}Si\{^1H\}$ NMR: $\delta = -21.6$. – MS (EI, 70 eV) *m/z*: 301 [M^+], 286 [$M^+ - CH_3$], 215 [$M^+ - NC_4H_8O$], 129 [$215 - NC_4H_8O$]. – $C_{13}H_{27}N_3O_3Si$ (301.46): calcd. C 51.8, H 9.0, N 13.9; found C 51.5, H 8.9, N 13.8.

Tris(morpholino)vinylsilane (**5**): To a solution of trichlorovinylsilane (3.81 ml, 0.030 mol) in 150 ml of toluene, 8 equiv. of morpholine (19.83 ml, 0.240 mol) were added at room temperature. After stirring for 24 h a suspension of lithium morpholide [0.035 mol, from 10.0 ml (0.120 mol) of morpholine and 20.64 ml (0.035 mol) of a 1.7 M solution of *n*-butyl lithium in hexane] in 50 ml of toluene was added and the reaction mixture was stirred for 24 h. After filtration the solvent was removed in vacuo and the remaining white solid was extracted with diethyl ether. **5** crystallized from this solution at -30°C. Colourless crystals, 5.60 g (60%), m.p. 95°C. – ^{1}H NMR: $\delta = 2.70$ (pseudo-t, $^3J_{H,H} = 5$ Hz, 12H, NCH_2), 3.43 (pseudo-t, $^3J_{H,H} = 5$ Hz, 12H, OCH_2), 5.65–5.93 (vinyl-H, 3-H). – $^{13}C\{^1H\}$ NMR: $\delta = 45.6$ (NCH_2), 68.5 (OCH_2), 132.9 and 133.9 (vinyl-C). – $^{29}Si\{^1H\}$ NMR: $\delta = -32.3$. – MS (EI, 70 eV) *m/z*: 313 [M^+], 227 [$M^+ - NC_4H_8O$], 142 [$227 - NC_4H_8O$], 57 [$142 - NC_4H_8O$]. – $C_{14}H_{27}N_3O_3Si$ (313.47): calcd. C 53.6, H 8.7, N 13.4; found C 53.5, H 8.6, N 13.3.

4-Bromophenyltris(dimethylamino)silane (**6**): Tetrakis(dimethylamino)silane (1.02 ml, 7.20 mmol) was dissolved in 40 ml of toluene and cooled to 0°C. With stirring 2 equiv. of CF_3SO_3H (1.28 ml, 14.4 mmol), suspended in 10 ml of toluene, were added dropwise within 10 min[37]. The reaction mixture was stirred for 0.5 h at room temperature, filtered after cooling to 0°C and then used immediately in the following reaction.

To a solution of 1,4-dibromobenzene (1.70 g, 7.20 mmol) in 100 ml of diethyl ether were added dropwise at 0°C within 10 min 1.2 equiv. of a 1.7 M solution of *n*-butyl lithium in hexane (5.08 ml, 8.64 mmol). After stirring for 1.5 h at room temperature this reaction mixture was added dropwise at 0°C within 30 min to the suspension of tris(dimethylamino)silyl triflate (above). After the addition the reaction mixture was allowed to warm to room temperature and was then stirred for 2.5 h. After removing the solvent under reduced pressure the remaining oil was extracted with pentane. 4-Bromophenyltris(dimethylamino)silane was separated from the extract by distillation (65°C, 0.01 mbar). Colourless liquid 0.40 g (18%). – ^{1}H NMR: $\delta = 2.41$ (s, 18H, NCH_3), 7.30 and 7.36 (both d, $^3J_{H,H} = 9$ Hz, 4H, C_6H_4). – $^{13}C\{^1H\}$ NMR: $\delta = 38.1$ (NCH_3), 124.2 (C-4), 131.1 (C-3/5), 135.5 (C-2/6), 137.3 (C-1). – $^{29}Si\{^1H\}$ NMR: $\delta = -21.5$. – MS (EI, 70 eV) *m/z*: 317 [$M^+ + 2$], 315 [M^+], 271 [$M^+ - NMe_2$], 228 [$271 - NMe_2$], 185 [$228 - CH_2{=}NMe$]. – IR (film): $\tilde{\nu} = 3069$ w, 2970 m, 2836 s, 2789 s, 1571 m, 1480 m, 1288 s, 1175 s, 1067 s, 987 s, 810 m, 727 s, 623 m, 498 m [cm^{-1}].

Methyltris(4-methyl-1-piperazinyl)silane (**7**): A solution of methyltrichlorosilane (3.91 ml, 0.033 mol) in 100 ml of diethyl ether was added dropwise to a solution of *N*-methylpiperazine (22.2 ml, 0.20 mol) in 200 ml of diethyl ether within 0.5 h at room temperature. After stirring for 6 h at this temperature a suspension of lithium *N*-methylpiperazide [0.033 mol, from 3.70 ml (0.033 mol) of *N*-methylpiperazine and 19.4 ml (0.033 mol) of a 1.7 M solution of *n*-butyl lithium in hexane] in 50 ml of diethyl ether was added. After stirring for 10 h the precipitate was separated, the solvent removed from the filtrate in vacuo, and the remaining oil purified by sublimation (100°C/0.005 mbar). Colourless oil, 7.40 g (65%), m.p. ≈ -20°C. – ^{1}H NMR: $\delta = -0.04$ (s, 3H, $SiCH_3$), 2.08 (s, br., 21H, $SiNCH_2$ and NCH_3), 2.81 (pseudo-t, $^3J_{H,H} = 5$ Hz, 12H, CH_2NCH_3). – $^{13}C\{^1H\}$ NMR: $\delta = -4.58$ ($SiCH_3$), 45.2 (NCH_3), 47.2 ($SiNCH_2$), 57.3 (CH_2NCH_3). – ^{29}Si NMR: $\delta = -21.4$ (m). – MS (EI, 70 eV) *m/z*: 340 [M^+], 325 [$M^+ - CH_3$], 241 [$M^+ - NC_4H_8NCH_3$], 143 [$241 - HNC_4H_8NCH_3$]. – IR (film): $\tilde{\nu} = 2943$ s, 2876 m, 2830 s, 2781 s, 2733 w, 2685 w, 1448 s, 1370 s, 1287 s, 1154 s, 1100 s, 1067 m, 1006 s, 964 s, 788 s, 734 m [cm^{-1}]. – $C_{16}H_{36}N_6Si$ (340.58): calcd. C 56.4, H 10.7, N 24.7; found C 55.5, H 10.8, N 24.3.

Phenyltris(1-pyrrolidinyl)silane (**8**): A solution of phenyltrichlorosilane (3.20 ml, 0.02 mol) in 50 ml of toluene was added dropwise within 10 min to a suspension of lithium pyrrolidine [0.08 mol, from 6.61 ml (0.08 mol) of pyrrolidine and 55.3 ml (0.094 mol) of a 1.7 M solution of *n*-butyl lithium in hexane) in 250 ml of toluene. After stirring for 10 h the precipitate was separated, the solvent was removed from the filtrate in vacuo and the remaining oil was extracted with pentane. Filtration and evaporation of the solvent left a crude product, which was purified by distillation (110°C/0.01 mbar). Colourless liquid, 4.73 g (75%). – ^{1}H NMR: $\delta = 1.63$ (m, 12H, CCH_2), 3.09 (m, 12H, NCH_2), 7.24–7.31 (m, 3H, 3/4/5-H), 7.69 (dd, $^3J_{H,H} = 8$ Hz, $^4J_{H,H} = 1$ Hz, 2H, 2/6-H). – $^{13}C\{^1H\}$ NMR: $\delta = 27.2$ (CCH_2), 47.5 (NCH_2), 127.9 (C-4), 129.1 (C-3/5), 135.3 (C-2/6), 137.7 (C-1). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2, -90°C): 26.9 (s, CCH_2), 46.7 (s, NCH_2). – $^{29}Si\{^1H\}$ NMR: $\delta = -34.4$. – MS (EI, 70 eV) *m/z*: 315 [M^+], 245 [$M^+ - NC_4H_8$], 175 [$245 - NC_4H_8$], 105 [$175 - NC_4H_8$]. – IR (Nujol): $\tilde{\nu} = 3066$ w, 2958 s, 2867 s, 2820 s, 1428 w, 1346 w, 1198 m, 1112 s, 1071 s, 1006 s, 737 m, 701 m, 557 m, 517 m [cm^{-1}]. – $C_{18}H_{29}N_3Si$ (315.53): calcd. C 68.5, H 9.3, N 13.3; found C 68.6, H 9.6, N 13.1.

Crystal Structure Determinations: A single crystal of compound **1** was grown on the diffractometer from the melt at low temperature by zone melting of a seed crystal at -88°C, followed by cooling to -91°C within 5 min. Suitable single crystals of compounds **2**, **3**, **4**, and **5** were sealed in glass capillaries and used for measurement of precise cell constants and collection of intensity data. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for any compound. Diffraction intensities were corrected for Lorentz and polarization effects, but not for absorption. The structures were solved by direct methods and refined by full matrix least-squares refinement on F^2. The displacement parameters of all non-hydrogen atoms were treated anisotropically. All morpholino-hydrogen atoms of **4** were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic displacement parameters [$U_{iso(fix)} = 1.5 \cdot U_{eq}$ of the attached C atom]. The methyl-hydrogen atoms of **4** were found and included with fixed isotropic displacement parameters [$U_{iso(fix)} = 1.5 \cdot U_{eq}$ of the attached C atom]. The Si–*H* in **2**, the vinyl-*H* atoms in **5**, and all hydrogen atoms in **1** were found and refined isotropically. Further details of the crystal data, data collection, and structure refinement are summarized in Table 1. Selected interatomic distances and angles are shown in the corresponding figure captions.

Anistropic thermal parameters, tables of interatomic distances and angles, and atomic coordination have been deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request on quoting the depository numbers CSD-406434 (**1**), -406435 (**5**), 406436 (**3**), -406437 (**2**) and -406438 (**4**).

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