Simple Silylhydrazines as Models for Si–N β-Donor Interactions in SiNN Units

Norbert W. Mitzel*

Dedicated to Professor Wolfgang A. Herrmann on the occasion of his 50th birthday

Abstract: Two simple silylhydrazines, $H_3SiMeNNMe_2$ and $(H_3Si)_2NNMe_2$, have been prepared by the reaction of bromosilane with the corresponding NH-functional hydrazine in the presence of a base and the appropriate lithiated hydrazine. The intermolecular attractive interactions (β-donor–acceptor interaction) between the silicon and β-nitrogen atoms of $H_3SiMeNNMe_2$ and $(H_3Si)_2NNMe_2$ has been demonstrated by low-temperature X-ray crystallography and ab initio calculations (MP2/6-311G). The contributions to the strength of this two-bond interaction are discussed in the light of a new series of calculations on $RSiH_2NR'NR''_2$ molecules (R = H, F; R′ = H, Me, SiH_3; R″ = H, Me), which show electronegative substituents at the silicon acceptor center to exert the largest effect, while the electronic nature of the substituent at the β-nitrogen atom is also important. As the resulting structures cannot be described satisfactorily by either the VSEPR concept or Bartell's two-bond radius model, a two-bond interatomic attraction has to be taken into account in addition; this leads to an extension of the common models for empirical structure prediction.

Keywords: ab initio calculations · donor–acceptor systems · molecular modeling · silylhydrazines · structure elucidation

Introduction

We have recently proved the occurrence of β-donor bonding in the chemistry of p-block elements. Interactions between donor and acceptor centers separated by one atom only (two classical bonds) are well established in the chemistry of transition metal compounds, for example in the eight-coordinate systems $[Ti(ONR_2)_4]$ with side-on-coordinated hydroxylamino ligands.[1,2] Our examples from p-block chemistry so far include systems containing SiON[3,4] and SiNN units,[5,6] both of which have relatively short Si⋯N distances and small Si-X-N angles (with X = O, NR). To date, the strongest of these interactions has been detected in $H_2Si(ONMe_2)_2$, in which the Si-O-N angle is as small as 95.2° and the Si⋯N distance is only 2.30 Å. Although predictably weak, such β-donor interactions can lead to a partial enlargement of the coordination sphere of the central atom and consequently change its reactivity and reaction kinetics.[6]

So far, we have been able to show β-donor interactions to be operative in two SiNN systems: $Cl_2Si(NMeNMe_2)_2$ (SiNN angle: 108.7°) and the heterocyclic silylhydrazine $(H_2CSiH_2)_2NNMe_2$, which has (solid-state) Si-N-N angles of 115.0(1)° and 129.1(1)°. In contrast, the isoelectronic compound $(H_2SiCH_2)_2NCHMe_2$ is unable to form β-donor interactions and the corresponding (gas-phase) Si-N-C angles are 122.6(6)° and 125.5(6)°.

In order to exclude any contributions that are difficult to predict, such as ring strain (as in $(H_2CSiH_2)_2NNMe_2$) or the electronic effects of electronegative ligands (as in $Cl_2Si(NMeNMe_2)_2$), we decided to examine the simplest systems capable of forming β-donor interactions in SiNN atom sequences. As the most basic silylhydrazines without any alkyl substituents, $H_3SiNHNH_2$ and $(H_3Si)_2NNH_2$, are probably not isolable or are unstable at the temperatures necessary at present for detailed studies, we prepared the simplest N-methylated derivatives, $H_3SiMeNNMe_2$ and $(H_3Si)_2NNMe_2$, which can serve as model compounds for most silylhydrazines. A wide variety of silylhydrazines have already been synthesized and studied structurally,[7] but most of these compounds either bear silicon substituents at both nitrogen atoms or have peralkylated silicon substituents and are therefore unsuitable as models for the study of β-donor–acceptor interactions.

---

[*] Dr. N. W. Mitzel
Anorganisch-chemisches Institut
der Technischen Universität München
Lichtenbergstrasse 4, D-85747 Garching (Germany)
Fax: (+49)89-289-13125
E-mail: N.Mitzel@lrz.tu-muenchen.de

0947-6539/98/0404-0692 $ 17.50+.50/0

Results

Preparation of $H_3SiMeNNMe_2$ and $(H_3Si)_2NNMe_2$ (1 and 2): Condensation reactions [Eqs. (1) and (2)] of bromosilane with the corresponding NH-functional hydrazines in the presence

$$\mathrm{Me_2NNHMe + H_3SiBr + 2,6\text{-}Me_2C_5H_5N \rightarrow H_3SiMeNNMe_2\ (\mathbf{1}) + 2,6\text{-}Me_2C_5H_5N \cdot HBr} \tag{1}$$

$$\mathrm{Me_2NNH_2 + 2\,H_3SiBr + 2\,2,6\text{-}Me_2C_5H_5N \rightarrow (H_3Si)_2NNMe_2\ (\mathbf{2}) + 2\,2,6\text{-}Me_2C_5H_5N \cdot HBr} \tag{2}$$

of the auxiliary base 2,6-lutidine were found to give better results than those with triethylamine or an excess of the hydrazine itself. The yields of these reactions, however, were never higher than 12%.

Although we found slightly higher yields (15%) in an alternative procedure, reaction of bromosilane with lithium trimethylhydrazide (prepared according to Equation (3)) in dimethyl ether as a solvent [Eq. (4)], separation of the desired

$$\mathrm{Me_2NNHMe} + n\mathrm{BuLi} \rightarrow \mathrm{Me_2NNLiMe} \tag{3}$$

$$\mathrm{Me_2NNLiMe + H_3SiBr \rightarrow H_3SiMeNNMe_2\ (\mathbf{1}) + LiBr} \tag{4}$$

product from the $H_3SiBr \cdot OMe_2$ adduct proved difficult. Yields of the product were not satisfactory, however, with low-boiling hydrocarbons as solvents.

Compounds **1** and **2** are both very sensitive to hydrolysis and spontaneously ignite in moist air. In pure form they can be stored in a sealed tube at ambient temperature.

The compounds have been characterized by gas-phase IR and solution NMR (^{1}H, ^{13}C, ^{15}N, ^{29}Si) spectroscopy and by mass spectrometry. Under high-resolution conditions, the proton-coupled ^{13}C NMR signals show the typical splitting into a quartet (^{1}J(C,H)) of quartets (^{3}J(C,H)), the ^{3}J coupling being much larger for the Me_2N units in **1** (4.6 Hz) and **2** (5.0 Hz) than for the H_3CNSiH_3 unit (2.2 Hz) in **1** or the corresponding ^{3}J(Si,H) coupling in the $(H_3Si)_2N$ group in **2**. All the ^{15}N NMR chemical shifts are found in a very narrow range of the spectrum and do not provide direct information about the bonding situation. The ^{29}Si NMR chemical shift of **1** is $\delta = -52.2$, which is 6.7 ppm higher than that of **2**, reflecting the slightly higher electron-withdrawing ability of an H_3CN group compared with an H_3SiN group in **2**. The ^{1}H NMR resonance of the two different silyl groups of **2** does not split into two signals down to −110 °C in 2-methylbutane as solvent (400 MHz). This indicates rapid topomerization of the molecule by internal rotation about the N–N bond and/or by inversion of the $NNMe_2$ group.

Abstract in German: *Die beiden einfachen Silylhydrazine $H_3SiMeNNMe_2$ und $(H_3Si)_2NNMe_2$ wurden aus Bromsilan und den entsprechenden NH-funktionellen Hydrazinen in Gegenwart einer Base oder den lithiierten Hydrazinen hergestellt. $H_3SiMeNNMe_2$ und $(H_3Si)_2NNMe_2$ bilden intermolekulare Wechselwirkungen zwischen ihren Silicium- und β-Stickstoffatomen (β-Donor-Acceptor-Wechselwirkung). Dies wurde durch Tieftemperatur-Kristallographie und Ab-initio-Rechnungen (MP2/6-311 G**) nachgewiesen. Die Beiträge, welche die Stärke dieser Zwei-Bindungs-Wechselwirkung bestimmen, werden anhand einer Serie von Rechnungen an Molekülen der Formel $RSiH_2NR'NR''_2$ (R = H, F; R' = H, Me, SiH_3; R'' = H, Me) diskutiert, wobei sich zeigt, daß elektronegative Substituenten an den Silicium-Acceptor-Zentren den bedeutendsten Einfluß haben und der elektronischen Natur der Substituenten am β-Stickstoffatom ebenfalls eine bedeutende Rolle zukommt. Die resultierenden Strukturen können mit dem VSEPR-Konzept genausowenig befriedigend beschrieben werden, wie mit dem Zwei-Bindungs-Radienmodell von Bartell. Attraktive interatomare Wechselwirkungen über zwei Bindungen hinweg müssen deshalb zusätzlich in die Beschreibung einbezogen werden, was eine Erweiterung der gängigen Modelle zur Strukturvorhersage bedeutet.*

Experimental and theoretical studies on the molecular structures of 1 and 2: The main goal of this study was to obtain structural information about the two simple silylhydrazines **1** (Figure 1) and **2** (Figure 2). Both compounds are liquids at ambient temperature and solidify at very low temperatures (**1** at ca. −115 °C; **2** at ca. −85 °C). However, we were successful in growing single crystals of both compounds from the melt sealed in glass capillaries, by using the cryostream of a diffractometer and the technique of microscale zone refinement for the production of a suitable seed crystal, then slowly decreasing the temperature.

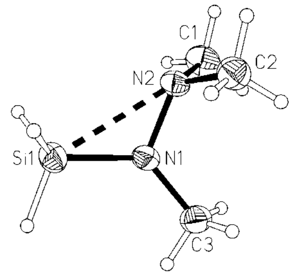

Figure 1. Molecular structure of $H_3SiMeNNMe_2$ (**1**).

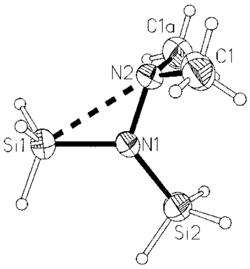

Figure 2. Molecular structure of $(H_3Si)_2NNMe_2$ (**2**).

Compound **1** crystallizes in the triclinic space group $P\bar{1}$, but **2** forms a crystal belonging to the hexagonal system, space group $P6_3/m$, with a crystallographic plane of symmetry passing through the Si_2NN skeleton of the molecule. This means that **2** has an exactly planar coordination geometry at the silylated nitrogen atom (an example of the N-planarity in silylamines imposed by crystal symmetry), whereas **1** shows a slight deviation from planarity. Both coordination geometries are in very good agreement with ab initio calculations at the MP2/6-311 G** level of theory (see Table 1 for a comparison). Theory levels at which electron correlation is not considered predict a planar nitrogen geometry for **1** and it is only at the MP2/6-31 G* level that frequency calculations show these planar arrangements not to correspond with minima on the potential hypersurface.

The main focus of interest is the Si-N-N angles in **1** and **2**, because they reflect the strength of β-donor bonding in such

Table 1. Molecular geometries of $H_3SiMeNNMe_2$ (**1**) and $(H_3Si)_2NNMe_2$ (**2**) as determined by low-temperature X-ray crystallography and calculated by using ab initio methods at the MP2/6-311G** level of theory (distances in [Å], angles in [°]).

	$H_3SiMeNNMe_2$ (**1**)		$(H_3Si)_2NNMe_2$ (**2**)	
	XRD	MP2/6-311G**	XRD	MP2/6-311G**
Si–N	1.693(1)	1.730	1.714(2)	1.746
Si/C–N	1.448(2)	1.455	1.719(2)	1.753
N–N	1.432(2)	1.425	1.461(3)	1.449
N–C	1.452-8(2)	1.460	1.451(3)	1.459
Si-N-N	108.2(1)	109.1	106.0(2)	104.0
Si/C-N-N	119.4(1)	118.9	124.5(2)	124.7
Si-N-Si/C	130.3(1)	128.3	129.5(1)	131.3
C-N-N	112.6/111.5(1) 112.5/111.1	110.5(2)	110.5	
C-N-C	111.5(1)	111.6	111.6(3)	111.9
Si⋯N	2.540(2)	2.577	2.537(2)	2.545

compounds. For **1** the Si-N-N angle was refined to 108.2(1)°, which is as much as 11.1° smaller than the N-N-C angle at the same nitrogen atom, indicating the amount of distortion exerted by the weak Si–β-N interaction.

One of the Si-N-N angles in **2**, which includes the silicon atom oriented *cis* to the lone pair of electrons at the β-N atom, is only 106.0(2)°, whereas the other Si-N-N angle is as much as 18.5° larger [124.5(2)°] and on that side of the molecule which does not allow the formation of β-donor interactions. The resulting intramolecular Si⋯N distances are 2.537(2) Å in **1** and 2.540(2) Å in **2**, which are much shorter than the sum of the van der Waals radii of Si and N (3.54 Å).[8] In each case the conformation of the NMe_2 group relative to the silicon atom involved in secondary bonding is such that a maximum interaction between the lone pair of electrons (lp) and the acceptor silicon atom becomes possible, to give an arrangement where Si-N-N-lp is coplanar. In the present cases, this geometry is also favored by the minimization of the repulsive forces between the lone pairs of electrons at the two nitrogen atoms, which is achieved in orthogonal orientation.

There are no strong intermolecular interactions in the crystal packing of the molecules of either compound **1** or **2** (Figures 3 and 4). The most likely interactions would be those between the dimethylamino-nitrogen atom of one molecule and one H_3Si group of another. However, the shortest intermolecular Si⋯N distances are 4.873 Å (**1**) and 4.949 Å (**2**) (see Figures 3 and 4). This is surprising if considered with respect to the structures of comparable silylamines such as Me_2NSiH_3[9] and Me_2NSiH_2Cl,[10] in the crystals of which pentamers and dimers, respectively, are formed by enlargement of the coordination spheres of their silicon and nitrogen centers. The basicity of the α-nitrogen lone pairs in **1** and **2** is quite low because of the silicon substituents, which generally reduce the nitrogen basicity and lead to geometries with planar nitrogen coordination.[11] However, in **1** and **2** non-silylated nitrogen atoms are present in the Me_2N groups and these can be expected to have high donor ability, as has been shown, for example, by the formation of H_3B adducts of the cyclic silylhydrazines such as $(H_2CSiH_2)_2NNMe_2(BH_3)$.[12] The absence of intermolecular interactions in **1** and in **2** is therefore consistent with the interpretation that the lone pair of the Me_2N groups is involved in β-donor interactions and is consequently not available for intermolecular secondary bonding.

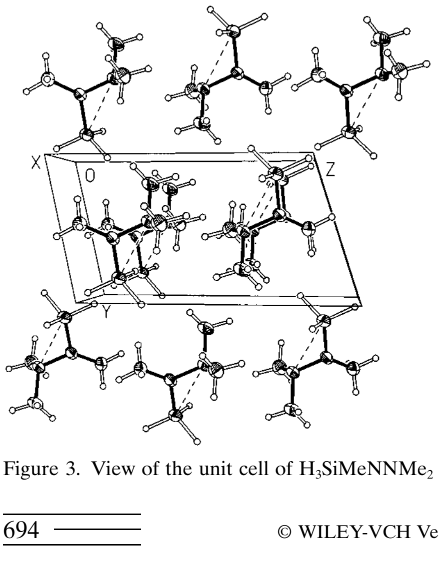

Figure 3. View of the unit cell of $H_3SiMeNNMe_2$ (**1**) down the *x* axis.

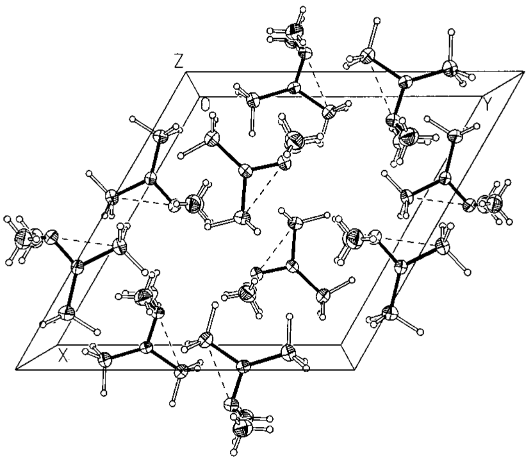

Figure 4. View of the unit cell of $(H_3Si)_2NNMe_2$ (**2**) down the *z* axis.

Theoretical studies of the effects influencing the strength of the β-donor interactions: The excellent agreement between calculated and crystallographically determined geometric parameters of simple silylhydrazines encouraged us to perform calculations on even simpler silylhydrazines in order to gauge the effect of the methyl substituents on the experimentally observed structures. For this purpose a carefully graded series of ab initio geometry optimizations was performed on $H_3SiNHNH_2$. The results are listed in Table 2 and show that it is necessary to take electron correlation into consideration in order to obtain reliable geometry predictions by means of quantum-chemical calculations. On the other hand, comparison of the values at the MP2/6-31G* level of theory with those calculated at higher levels indicates that the geometry optimizations almost converge at these levels. The use of basis sets larger than 6-31G* changes the results only slightly. The inclusion of diffuse functions (6-311+G** basis set) could be shown to have only a marginal effect.

The calculations predict a much weaker Si⋯N β-donor interaction for $H_3SiNHNH_2$ than those that were observed and predicted for **1** and **2**. The Si-N-N angle in $H_3SiNHNH_2$ is

Table 2. Molecular geometry of $H_3SiNHNH_2$ calculated by using ab initio methods at different levels of theory (distances in [Å], angles in [°], energies in hartrees).

	SCF		MP2			QCISD		
	3-21G*	6-31G*	6-31G*	6-311G**	6-311 + G**	6-31G*	6-311G**	6-311 + G**
Si–N	1.711	1.723	1.739	1.729	1.737	1.743	1.730	1.737
N–N′	1.446	1.405	1.430	1.422	1.424	1.434	1.426	1.427
Si-N-N	114.3	117.5	113.5	114.5	114.7	113.7	114.8	115.1
Si-N-H	128.6	123.3	121.3	122.5	122.1	120.8	122.0	121.6
N′-N-H	117.1	116.4	115.8	116.2	115.6	115.4	115.8	115.2
N-Si-H	106.4	105.8	105.5	105.5	105.7	105.5	105.5	105.7
N-Si-H	112.9	111.4	110.3	110.6	109.9	110.2	110.6	109.9
N-Si-H	112.9	113.6	114.4	114.2	113.5	114.5	114.3	113.6
E	−399.2321553	−401.267414	−401.6728278	−401.8038897	−401.8121176	−401.7110697	−401.8434185	−401.85129336

114.5° (MP2/6-311 G**), which is much larger than the corresponding ones in **1** and **2**. This implies that the greater basicity of an Me_2N group compared with that of an H_2N group leads to stronger interactions in **1** and **2**. Despite its weakness the β-donor interaction in $H_3SiNHNH_2$ leads to a distortion of the geometry of the H_3Si group. The H atom on the side opposite the β-donating N atom encloses a smaller N-Si-H angle (105.7° at QCISD/6-311 + G**), whereas the position of the one closest to the β-N atom is defined by an N-Si-H angle of 113.6°. The silylated nitrogen atom in this compound is predicted to be slightly pyramidal (sum of angles at N = 351.9°).

The geometries of a series of other compounds have been optimized at the MP2/6-311 G** level of theory. The molecular structures are presented in Figure 5 and the values of the geometrical parameters are listed in Table 3. Three contributions to the strength of the β-donor interaction in SiNN units have been probed: the effect of an alkylated nitrogen donor center compared with an unsubstituted one; the effect of substitution of the α-nitrogen atom; and the effect of electronegative substitution at the silicon acceptor center.

Comparison of the Si-N-N angles in **1**, **2**, and **3** (with β-NMe_2 groups) with those of **1a**, **2a**, and **3a** (with β-NH_2 groups) shows that **1**, **2**, and **3** have equal or slightly smaller angles. This implies a strengthening of the β-donor interaction with alkyl substitution, due to the higher basicity of alkylated amino functions. In this context it is also worth mentioning the structure of tetrasilylhydrazine, $(H_3Si)_2NN(SiH_3)_2$, which has D_{2d} symmetry and shows no sign of the β-donor interaction, exhibited also by most of the silylated hydrazines studied so far. The complete silyl substitution leaves no nitrogen atom with significant donor ability which could exert donor bonding towards a silicon acceptor center.

The contribution of the substituent at the α-nitrogen atom also has a marked effect. The β-donor interactions become stronger in the order **3**→**1**→**2**, **3a**→**1a**→**2a**, and **3b**→**1b**→**2b**; that is, as R in the SiNRN unit changes from H to C to Si (steps of < SiNN are about 4–5°). The differences in angle between the molecules with R = C and R = Si are most easily explained. The smaller electron-withdrawing ability of Si allows the electron cloud of the Si′–N bond to get closer to the nitrogen atom than in the corresponding C–N bond. According to the VSEPR model this leads to Si′-N-N and Si′-N-Si angles which are larger than the corresponding C-N-N and C-N-Si angles. As the silylated nitrogen atoms are always almost planar, the Si-N-N angle describing the β-donor interaction must become smaller if R = Si.

The most pronounced effect on the strength of the β-donor interaction was predicted for the substitution on the acceptor silicon atom of electronegative elements, thus increasing its electrophilicity. Each of the three compounds **1b**, **2b**, and **3b** bears one fluorine substituent on its silicon atom. Compared with the nonfluorinated compounds **1**, **2**, and **3**, the compounds **1b**, **2b**, and **3b** have Si-N-N angles that are smaller by more than 7°. The most extreme case is that of **2b**, which has an Si-N-N angle of only 93.9° according to the calculations. In the compounds **1b**, **2b**, and **3b** the geometry of the FH_2Si group is slightly distorted because of the close proximity of the NMe_2 group on the side of the two hydrogen atoms. For instance, in the simplest of these compounds (**3b**) the N-Si-H angles are calculated to be 110.2° and 114.1°, whereas the N-Si-F angle is 106.1°. The F atom in these compounds is always at the maximum distance from the β-donor nitrogen atom.

Calculations on $FH_2SiNHNH_2$ (**4**) give an Si-N-N angle that is slightly larger than that of $FH_2Si-NH-NMe_2$ (**3b**); this is consistent with the contribution of β-nitrogen substitution discussed above. Surprisingly, however, a calculation on $F_3SiNHNH_2$ (**5**) predicts the Si-N-N angle to be 114.5°, which is exactly the same as predicted for $H_3SiNHNH_2$ (**3a**). This

Table 3. Molecular geometry of various silylhydrazines R^s-NR^α-NR^β_2 calculated by using ab initio methods at the MP2/6-311G** level of theory (the geometries are shown in Figure 5). R^s = silyl group, R^α = substituent at the α-N atom, R^β = substituents at the β-N atom (distances in [Å], angles in [°]).

	1	**1a**	**1b**	**2**	**2a**	**2b**	**3**	**3a**	**3b**	**4**	**5**
R^s	H_3Si	H_3Si	FH_2Si	H_3Si	H_3Si	FH_2Si	H_3Si	H_3Si	FH_2Si	FH_2Si	F_3Si
R^α	Me	Me	Me	H_3Si	H_3Si	H_3Si	H	H	H	H	H
R^β	Me	H	Me	Me	H	Me	Me	H	Me	H	H
symmetry	C_1	C_1	C_1	C_s	C_s	C_s	C_1	C_1	C_1	C_1	C_1
N–Si	1.730	1.737	1.708	1.746	1.740	1.725	1.731	1.729	1.718	1.718	1.680
N–N′	1.425	1.424	1.421	1.449	1.448	1.449	1.418	1.422	1.425	1.425	1.417
N–R	1.455	1.451	1.449	1.753	1.737	1.746	1.019	1.011	1.017	1.012	1.010
Si⋯N	2.577	2.600	2.457	2.515	2.590	2.328	2.656	2.655	2.540	2.587	2.608
Si-N-N	109.1	110.3	103.1	104.0	108.3	93.9	114.7	114.5	109.1	109.1	114.5
Si-N-R	128.3	115.1	135.4	131.3	117.7	139.1	123.6	122.5	125.4	125.4	126.4
N-N-R	118.9	125.1	121.5	124.7	134.0	127.0	114.2	116.2	116.8	116.8	119.1

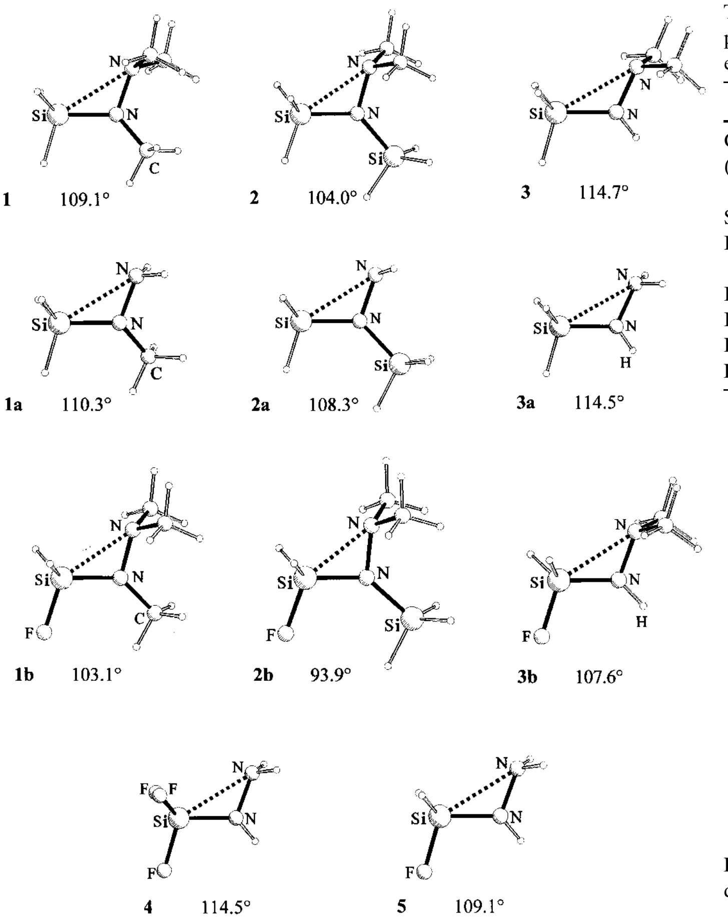

Figure 5. Calculated molecular structures (MP2/6-311 G**) of each silylhydrazine described in Table 3 with its Si-N-N angle.

Table 4. Comparison of values of the geometrical parameters in compounds with β-donor interactions (XRD = X-ray diffraction, GED = gas electron diffraction, av = average)

	Method	Si-X-N [°]	Si$\cdots$N [Å]	Ref.
$Cl_2Si(NMeNMe_2)_2$	XRD	108.7(av)	2.514(4)	[5]
$(CH_2SiH_2)_2NNMe_2$	XRD	115.0(1)		[6]
	GED	116.4(6)	2.678(7)	[6]
$Si(ONMe_2)_4$	XRD	109.1(av)	2.537(av)	[3]
$H_3SiONMe_2$	XRD	102.6(1)	2.453(2)	[4]
	MP2/6-311G**	102.5	2.454	[3]
$H_2Si(ONMe_2)_2$	XRD	95.2(av)	2.318(av)	[14]
$HSi(ONMe_2)_3$	XRD	103.5(av)	2.442(av)	[13]
$FH_2SiONMe_2$	MP2/6-311G**	90.0	2.229	[3]
$F_3SiONMe_2$	MP2/6-311G**	93.8	2.281	[3]

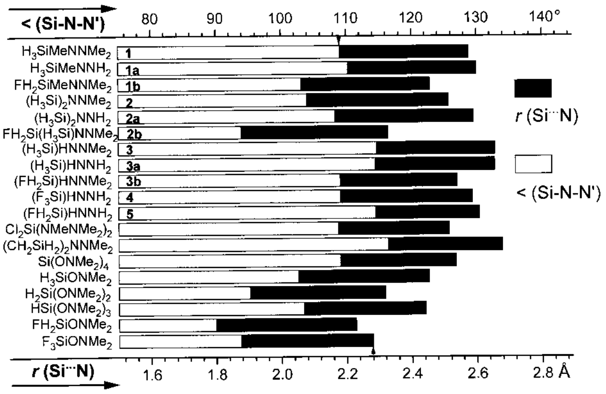

Figure 6. Graphical comparison of Si-X-N angles and Si$\cdots$N β-donor distances for selected hydrazinosilanes and hydroxylaminosilanes.

shows that backbonding from the fluorine lone pairs of electrons towards the silicon compensates for the effect of electronegative substitution.

These results point to new goals for the synthesis of compounds with very strong Si$\cdots$N β-donor interactions, which could be achieved if NR_2 groups with stronger basicity are involved. Alternatively, a strengthening of the interactions could also be achieved by making the Si acceptor center more electrophilic. The extreme bonding situations in these hydrazines could lead to unexpected reactivity.

Comparison with other SiNN and SiON compounds: Table 4 lists a number of compounds in which Si-N β-donor interactions have been detected. A graphical representation including the results of Table 3 is presented in Figure 6. A comparison of compounds **1** and **2** and the silylhydrazines in Table 4 with the silylhydroxylamines in this table shows that stronger Si–N β-donor bonds are generally formed by hydroxylaminosilanes than by hydrazinosilanes. The maximum strength of such interactions has been predicted for $FH_2SiONMe_2$ (Si-O-N 90.0° at MP2/6-311 G**). The corresponding hydrazines $FH_2SiNRNMe_2$ have larger Si-N-N angles, although that in $(FH_2Si)(H_3Si)NNMe_2$ (**4**, 93.6°) is close to the latter Si-O-N angle in magnitude. The bis(hydrazino) compound $Cl_2Si(NMeNMe_2)_2$ (Si-N-N 108.7°) has a far weaker β-donor interaction than the bis(hydroxylamino) compound $H_2Si(ONMe_2)_2$ (Si-O-N 95.2°), although the hydrazino compound bears electronegative substituents on the silicon atom which should increase its electrophilicity.

Discussion

β-Donor interactions make a significant contribution to the molecular structures of compounds that have acceptor and donor centers separated by two bonds only. However, so far a more detailed discussion of the interaction between atoms in the β-position to one another has been widely neglected in empirical models for structure prediction, and has only been treated in calculations, which often do not give a simple description of the nature of the bonding. The presence of those interactions has to be taken into account in the prediction of molecular structures; this is in addition to semiquantitative models such as the VSEPR concept, which was introduced by Gillespie and Nyholm,[14] and was recently extended[15] and newly rationalized by comparing the predictions of the model with those from ab initio calculations and (where possible) with experimental values for an array of simple molecules $(H_nX)_nE$ (X = main group element). According to the VSEPR method, only interelectron repulsions are considered, whereas internuclear repulsions or interatomic attractions over two-bond distances are neglected. An attempt to address the effect of internuclear repulsion was made by Bartell[16] and later by Glidewell,[17] who defined two-bond radii which can be used to predict bond angles by simple trigonometry involving the standard covalent radii. Using the average crystallographic values for Si–N and N–N bond lengths in **1** and **2** (1.704 Å and 1.447 Å) and the two-bond radius for Si$\cdots$N (2.69 Å), a trigonometric calculation predicts 117.0° for the Si-N-N angle. This can be regarded as the angle that would be adopted by SiNN units in the absence of other geometry-distorting effects. A similar calculation of a standard Si-O-N angle gives 120°, which shows by consideration of the values given in Table 4 that *O*-silylhydroxylamines have stronger β-donor interactions than comparable silylhydrazines. Angles that are much smaller than these estimated values indicate the presence of β-donor interactions in strain-free molecules. The two-bond radii therefore have to be modified if they are used to describe XMY systems with a large difference in the atomic charges of X and Y, which can be approximated by the difference between the effective nuclear charges.

Consideration of three effects, interelectron repulsion, two-bond internuclear repulsion, and two-bond interatomic attractions, thus leads to a more complete description of electronic and electrostatic contributions to molecular geometries.

Conclusion

Two model compounds, which are at present among the most basic known examples of silylhydrazines, have been prepared successfully. Their molecular structures have been determined by low-temperature X-ray crystallography and by theoretical calculations. The results show that silylhydrazines with one nonsilylated nitrogen atom adopt molecular structures with a significant contribution from β-donor interactions between Si and β-N atoms. There is evidence that the formation of intramolecular β-donor interactions is preferred over the alternative formation of intermolecular Si$\cdots$N contacts in crystals, which are observed in many systems not capable of forming β-donor interactions.

At least three major contributions to the strength of those β-donor interactions could be derived from comparative theoretical studies on simple model compounds: the nucleophilicity of the β-N atom, which is influenced by its substituents; the electrophilicity of the silicon center, which can be increased by electronegative substituents, but decreased by backbonding from substituents bearing lone pairs of electrons; and the nature of the substituent at the β-N atom, which influences the ease and extent of deformation of the coordination geometry at this N atom.

Comparison of compounds containing SiNN units with those containing SiON units shows silylhydrazines to form weaker β-donor interactions than *O*-silylhydroxylamines.

Neither the VSEPR method nor the model of two-bond radii, which takes two-bond internuclear repulsion into account, is appropriate to describe the molecular geometry of systems having acceptor and donor centers in a geminal position to one another. A third contribution, β-donor interactions or two-bond interatomic attractions, has to be considered in addition.

So far, only a few systems capable of formation of β-donor interactions have been synthesized, structurally characterized, and tested for their reactivity. Systems involving other kinds of donor centers (for example, P or S) and acceptor groups (such as B, Al, Ge, or PF_2) as well as α-atoms could be envisaged as new goals for more detailed studies. The enlargement of both donor and acceptor atoms in β-donor-bonded systems, such as the (4+1)-coordinate silicon in SiNN and SiON compounds, could lead to changes in reaction kinetics. These are the areas of our present research.

Experimental Section

General: All experiments were carried out in a vacuum line with greaseless stopcocks (Young taps), which is directly attached to the gas cell in an FTIR spectrometer (Midac Prospect FTIR). Bromosilane was prepared from phenylsilane and liquid HBr,[18] and trimethylhydrazine was obtained as previously described.[19] Me_2O and 2,6-lutidine were dried over CaH_2. All NMR spectra were recorded at 21 °C on a JEOL JNM-LA400 spectrometer in sealed tubes with C_6D_6 as the solvent, directly condensed onto the sample from K/Na alloy.

$H_3SiMeNMe_2$ (1): *n*BuLi solution in hexane (22.8 mL, 1.8 M) was added to trimethylhydrazine (3.04 g, 41 mmol) in a 500 mL bulb at −78 °C. For completion of the reaction the mixture was warmed to 0 °C for 15 min. The volatiles were removed in vacuo at ambient temperature, the bulb containing the lithium hydrazide was cooled to −196 °C, and dimethyl ether (5 mL) and bromosilane (4.56 g, 41 mmol) were condensed into it. The mixture was brought to −78 °C, and held there for 2 h then at −50 °C for 0.5 h. The contents were distilled through a series of traps held at −78, −96, and −196 °C. The first and second traps retained the product and $H_3SiBr \cdot OMe_2$ adduct. These were separated by four sequential distillations through −78, −86, −96, and −196 °C traps with the product condensing in the first two. The final distillation gave pure $(H_3Si)MeNMe_2$ (0.65 g) in the −78 and −86 °C traps (15 %). ^1H NMR: $\delta = 2.17$ (s, 6H; H_3C), 2.24 (s, 3H; H_3C), 4.58 (s, 3H; H_3Si); ^{13}C NMR: $\delta = 24.4$ (qq, $^1J(C,H) = 134.2$, $^3J(C,H) = 1.2$ Hz; CNSi), 42.0 (qq, $^1J(C,H) = 135.0$, $^3J(C,H) = 4.6$ Hz; C_2N); ^{15}N NMR: $\delta = -326.1$ (NC_2), −320.0 (NSi); ^{29}Si NMR: $\delta = -52.2$ (qq, $^1J(Si,H) = 207.7$, $^3J(C,H) = 3.5$ Hz); MS: $m/z = 104$.

$(H_3Si)_2NNMe_2$ (2): 2,6-Lutidine (1.62 g) and *N,N*-dimethylhydrazine (1.62 g, 27 mmol) were placed in a 1 L bulb and cooled to −196 °C before bromosilane (6.0 g, 54 mmol) was condensed onto them. The bulb was closed and brought to −78 °C for 0.5 h, then allowed to warm to 0 °C within 2 h. After traces of noncondensable gases had been pumped off, the mixture was repeatedly condensed from trap to trap to remove the lutidinium salts and then fractionated through a series of traps held at −30, −78, −96, and −198 °C. The −96 °C trap contained the product and some H_3SiBr, which was removed by another distillation through traps at −78, −96, and −196 °C. The −96 °C trap contained $(H_3Si)_2NNMe_2$ (0.39 g, 12 %). ^1H NMR: $\delta = 2.28$ (s, 6H; H_3C), 4.40 (s, 6H; H_3Si); ^{13}C NMR: $\delta = 46.4$ (qq, $^1J(C,H) = 134.3$, $^3J(C,H) = 5.0$ Hz); ^{15}N NMR: $\delta = -324.1$ (NC_2), −316.4 (NSi_2); ^{29}Si NMR: $\delta = -58.9$ (qq, $^1J(SiH) = 211.2$, $^3J(CH) = 2.2$ Hz); MS: $m/z = 120$.

Crystal structure determinations of 1 and 2: 1: Crystal system triclinic, space group $P\bar{1}$, $Z = 2$, $a = 6.238(1)$ Å, $b = 6.315(1)$ Å, $c = 10.158(1)$ Å, $V = 341.18(8)$ Å^3 at 110 K, cell from 25 reflections in the θ range 19–22°. Diffractometer: Enraf–Nonius Turbo-CAD4. $Mo_{K\alpha}$ radiation, graphite monochromator, $2\theta_{max.} = 52°$, ω scan, 1342 independent reflections of which 1264 have $F_0 > 4\sigma(F_0)$. No absorption correction. Solution by direct methods (SHELXTL[20]), refinement using SHELXL-93;[21] 103 parameters, $R(F)$ (obs.) = 0.0381, $wR(F) = 0.1043$, maximum residual electron density 0.46 and −0.28 e Å^{-1}. All non-H atoms were refined by applying anisotropic thermal displacement parameters; all hydrogen atoms were located in difference Fourier maps and refined by applying isotropic thermal displacement parameters. **2**: Crystal system hexagonal, space group $P6_3/m$, $Z = 6$, $a = b = 11.974(2)$ Å, $c = 9.343(3)$ Å, $V = 1154.9(5)$ Å^3 at 145 K, cell from 23 reflections in the θ range 19–22°. Diffractometer: Enraf–Nonius Turbo-CAD4. $\mathrm{Mo}_{\mathrm{K}\alpha}$ radiation, graphite monochromator, $2\theta_{\mathrm{max.}} = 52°$, ω scan, 567 independent reflections ($R_{\mathrm{int.}} = 0.044$) of which 566 have $F_0 > 4\sigma(F_0)$. No absorption correction. Solution by direct methods (SHELXTL[20]), refinement using SHELXL-93;[21] 60 parameters, $R(F)$ (obs.) $= 0.0315$, $wR(F) = 0.0852$, maximum residual electron density 0.25 and -0.14 e Å^{-1}. All non-H atoms were refined by applying anisotropic thermal displacement parameters; all hydrogen atoms were located in difference Fourier maps and refined by applying isotropic thermal displacement parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100678. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Ab initio calculations: Ab initio molecular orbital calculations were carried out using the Gaussian 94 program.[22] Geometry optimizations and vibrational frequency calculations were performed from analytic first and second derivatives at the SCF and MP2 levels of theory. Calculations were undertaken at the SCF level using the standard 3-21 G*,[25,26] 6-31 G*,[27–29] and 6-311 G**[30,31] basis sets; the two larger basis sets were used for calculations at the MP2 level of theory. Additional geometry optimizations for $H_3SiNHNMe_2$ were performed at the MP2/6-311 G**, QCISD/6-31 G*, QCISD/6-311 G**, and QCISD/6-311 + G** levels to test the effects of a more complete description of electron correlation and the inclusion of diffuse functions in the basis set.

Acknowledgments: This work was supported by the Bayerischer Staatsminister für Unterricht, Kultus, Wissenschaft und Kunst (Bayerischer Habilitationsförderpreis, 1996), the Deutsche Forschungsgemeinschaft, and the Leonhard-Lorenz-Stiftung; the Leibniz-Rechenzentrum-München provided computational resources. I am grateful to Professor H. Schmidbaur for his generous support and thank J. Riede for collection of the diffraction data.

Received: September 5, 1997 [F 814]

---

[1] K. Wieghardt, I. Tolksdorf, J. Weiss, W. Swiridoff, *Z. Anorg. Allg. Chem.* **1982**, *490*, 182–190.

[2] N. W. Mitzel, A. J. Blake, S. Parsons, D. W. H. Rankin, *J. Chem. Soc. Dalton Trans.* **1996**, 2089–2093.

[3] N. W. Mitzel, A. J. Blake, D. W. H. Rankin, *J. Am. Chem. Soc.*, **1997**, *119*, 4143–4148.

[4] N. W. Mitzel, U. Losehand, *Angew. Chem.* **1997**, *109*, 2897–2899; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2807–2809.

[5] N. W. Mitzel, B. A. Smart, A. J. Blake, S. Parsons, D. W. H. Rankin, *J. Chem. Soc. Dalton Trans.* **1996**, 2095–2100.

[6] N. W. Mitzel, H. Schmidbaur, B. A. Smart, D. W. H. Rankin, M. Hofmann, P. von R. Schleyer, *Inorg. Chem.* **1997**, *36*, 4360–4368.

[6] C. Chuit, R. J. P. Corriu, C. Reyé, J. C. Young, *Chem. Rev.* **1993**, *93*, 1371–1448.

[7] Examples: a) C. Drost, U. Klingebiel, M. Noltemeyer, *J. Organomet. Chem.* **1991**, *414*, 307 –310; b) F. Höfler, U. Wannagat, *Monatsh. Chem.* **1966**, *97*, 1598–1610.

[8] J. Emsley, *The Elements*, Clarendon Press, Oxford, **1989**.

[9] a) R. Rudmann, W. C. Hamilton, S. Norvick, T. D. Goldfarb, *J. Am. Chem. Soc.* **1967**, *89*, 5157–5160; b) A. J. Blake, E. A. V. Ebsworth, A. J. Welch, *Acta Crystallogr. Sect. C* **1984**, *40*, 895–897.

[10] D. G. Anderson, A. J. Blake, S. Cradock, E. A. V. Ebsworth, D. W. H. Rankin, A. J. Welch, *Angew. Chem.* **1986**, *98*, 97–98; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 107–108.

[11] E. A. V. Ebsworth, *Acc. Chem. Res.* **1987**, *20*, 295–301.

[12] N. W. Mitzel, M. Hofmann, K. Angermaier, A. Schier, P. von R. Schleyer, H. Schmidbaur, *Inorg. Chem.* **1995**, *34*, 4840–4845.

[13] N. W. Mitzel, U. Losehand, unpublished results.

[14] R. J. Gillespie, *Chem. Soc. Rev.* **1992**, 59–69.

[15] a) R. J. Gillespie, S. A. Johnson, *Inorg. Chem.* **1997**, *36*, 3031–3039; b) R. J. Gillespie, E. A. Johnson, *Angew. Chem.* **1996**, *108*, 539–560; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 495–514.

[16] L. S. Bartell, *J. Chem. Phys.* **1960**, *32*, 827–831.

[17] C. Glidewell, *Inorg. Chim. Acta* **1975**, *12*, 219–227.

[18] L. G. L. Ward, *Inorg. Synth.* **1968**, *11*, 159–162.

[19] J. B. Class, J. G. Aston, T. S. Oakwood, *J. Am. Chem. Soc.* **1953**, *75*, 2937–2939.

[20] G. M. Sheldrick, SHELXTL/PC v5.03, Siemens Analytical X-Ray Instrumentation, Madison (WI), **1995**.

[21] G. M. Sheldrick, SHELX-93, Universität Göttingen, **1993**.

[22] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian 94, Revision C.2, Gaussian, Pittsburgh (PA), **1995**.

[23] J. S. Binkley, J. A. Pople, W. J. Hehre *J. Am. Chem. Soc.* **1980**, *102*, 939–947.

[24] M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, W. J. Hehre *J. Am. Chem. Soc.* **1982**, *104*, 2797–2803.

[25] W. J. Pietro, M. M. Francl, W. J. Hehre, D. J. Defrees, J. A. Pople, J. S. Binkley *J. Am. Chem. Soc.* **1982**, *104*, 5039–5048.

[26] W. J. Hehre, R. Ditchfield, J. A. Pople *J. Chem. Phys.* **1972**, *56*, 2257–2261.

[27] P. C. Hariharan, J. A. Pople *Theor. Chim. Acta*, **1973**, *28*, 213–222.

[28] M. S. Gordon *Chem. Phys. Lett.* **1980**, *76*, 163–168.

[29] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople *J. Chem. Phys.* **1980**, *72*, 650–654.

[30] A. D. McLean, G. S. Chandler *J. Chem. Phys.* **1980**, *72*, 5639–5648.