Hydroxylaminosilanes: Compounds with β-Donor−Acceptor Bonds

Udo Losehand and Norbert W. Mitzel*

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4,
85747 Garching, Germany

Received December 2, 1997

Two series of compounds, $H_xSi(ONMe_2)_{4-x}$ (**3a**, **2a**, **1a**) and $H_xSi(ONEt_2)_{4-x}$ (**3b**, **2b**, **1b**) (with $x = 1, 2, 3$), have been prepared by either the condensation of *N*,*N*-dialkylhydroxylamines with halogenosilanes in the presence of 2,6-lutidine as an auxiliary base or by the more selective reaction of the *O*-lithiohydroxylamines with halogenosilanes at low temperatures. The compounds are very sensitive to hydrolysis, but are not pyrophoric, and are stable at ambient temperature to a potentially very exothermic rearrangement into aminosilanoles. The compounds have been characterized by gas-phase IR and solution NMR spectroscopy (^{1}H, ^{13}C, ^{15}N, ^{17}O, ^{29}Si) and by mass spectrometry. The IR frequencies of the simplest compound $H_3SiONMe_2$ (**1a**) have been assigned by comparison with *ab initio* frequencies. The NMR data are discussed in the light of β-donor interactions. The ^{29}Si NMR shifts of the series $H_xSi(ONMe_2)_{4-x}$ are compared with those of the isoelectronic isopropoxysilanes, $H_xSi(OCHMe_2)_{4-x}$, which have been prepared for this purpose. Single crystals of $H_3SiONMe_2$ (**1a**), $H_3SiONEt_2$ (**1b**), $H_2Si(ONMe_2)_2$ (**2a**), and $HSi(ONMe_2)_3$ (**3a**) have been grown by *in situ* methods, and their structures have been determined by X-ray diffraction. All compounds have small Si−O−N angles, with the minimum of 95.2° occurring with $H_2Si(ONMe_2)_2$ (**2a**). The crystallographic data are compared with the results of *ab initio* calculations (MP2/6-311G**) and the crystal structure of the isoelectronic $H_3SiOCHMe_2$, which has now been determined, and the earlier reported $Si(OCHMe_2)_4$. $H_3SiOCHMe_2$ crystallizes in a transition state geometry according to MP2/6-311G** calculations and has a Si−O−C angle of 118.4(1)°. The data show clearly the large differences between Si−O−N and Si−O−C angles, which are attributed to the occurrence of β-donor interactions in Si−O−N units. The strength of this interaction has been estimated to be 15 kJ mol^{-1} from *ab initio* calculations.

Introduction

We have recently established the existence of weak secondary bonds between p-block donor and acceptor atoms in β-position to one another.[1] Examples of such compounds include hydroxylaminosilanes[2] and hydrazinosilanes,[3,4] with a β-donor interaction between the silicon atom and the nitrogen center. Such interactions are well known for transition metal acceptor atoms bound to μ^2-coordinating ligands, *e.g.* in the eight-coordinate $Ti(ONR_2)_4$ complexes,[5] but the 4+4 coordination in the analogous compound $Si(ONMe_2)_4$ was established only recently.[2] The scarce examples of β-donor interactions in main group systems other than hydroxylamino- and hydrazinosilanes include a few reports on lithiated hydrazines,[6] with the lithium atoms coordinated to both nitrogen centers of the hydrazine unit.

The small angles in Si−O−N units are surprising in the light of numerous established molecular structures, which contain Si−O linkages with almost always substantially widened angles at the oxygen atom.[7] After almost half a century of controversial discussion, negative hyperconjugation is often quoted (but not generally accepted) as the reason for the large differences in bonding of the first-row element compounds and the homologues of the second row of the periodic table,[8] *e.g.* the differences between the pyramidal $N(CH_3)_3$ and the planar $N(SiH_3)_3$ and the large difference between the bond angles at the oxygen atoms in $O(CH_3)_2$ (111.4°)[9] and $O(SiH_3)_2$ (144°).[10] Even in H_3COSiH_3 (120°)[11] the angle at oxygen is markedly widened as compared with $O(CH_3)_2$. In this respect, hydroxylaminosilanes form an important class of compounds, which do not follow the expectation that all silicon-substituted oxygen atoms must have wide bond angles.

The interest in weak interactions of the outlined type arose because of various reports on the high reactivity of hydroxylaminosilanes. The patent literature contains numerous claims for new cross-linking agents and cold curing catalysts for silicone polymers on the basis of hydroxylaminosilanes,[12] but the literature does not provide information why such compounds

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S0020-1669(97)01508-5 CCC: $15.00

have these properties and how to optimize them for a maximum of reactivity. Furthermore, catalytic action of hydroxylamines on the alcoholysis of Si−H functions in polyphenylsilane has recently been found.[13] We have postulated a mechanism to rationalize the role of hydroxylamine in these reactions.[2] As a key step, a silicon center with an O-bound hydroxylamine unit is thought to enlarge its coordination sphere by weakly coordinating the nitrogen atom in β-position. This would explain the acceleration of the hydrolysis because five-coordinate silicon (or better 4+1 in this case) is known to show largely increased reactivity in substitution reactions.

As there was almost nothing known about simple model systems containing the Si−O−N unit, we aimed to synthesize the compounds of this type. Structural information on this class of compounds was almost completely unavailable, which encouraged us to investigate these model compounds in detail. Thus we present here the synthesis, spectroscopic data, and structural and theoretical information on two series of compounds, $H_xSi(ONMe_2)_{4-x}$ and $H_xSi(ONEt_2)_{4-x}$ ($x = 1, 2, 3$). Others have investigated these and comparable systems, but reports of the explosive nature of hydroxylaminosilanes[14] have obviously been deterrents to extensive investigations.

Experimental Procedures

General. The experiments were carried out by using a standard Schlenk line or, when H_3SiBr or H_2SiCl_2 were involved, 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,[15] *N,N*-dimethylhydroxylamine according to ref 16. 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 a solvent directly condensed onto the sample from K/Na alloy. The high volatility and sensitivity of the compounds did not allow us to obtain elemental analyses in all cases.

***N,N*-Dimethylhydroxylaminosilane, $H_3SiONMe_2$ (1a).** *n*-Butyllithium (28 mmol, 1.8 M in hexane) was added dropwise to a stirred solution of dimethylhydroxylamine (2.0 mL, 28 mmol) in pentane (50 mL) at 0 °C, allowed to reach ambient temperature, and stirred for 1 h. The solvents were removed under reduced pressure, and dimethyl ether (*ca.* 5 mL, bp −24.7 °C) and bromosilane (3.1 g, 28 mmol) were condensed onto the residue at −196 °C. The reaction mixture was allowed to warm to −30 °C and was stirred for 2 h. The volatiles were collected in a trap held at −196 °C and then passed through a series of traps held at −50, −78, −100, −196 °C, with the product being retained in the −78 °C trap. The fractional condensation was repeated to achieve better purity. Yield: 1.45 g (56%), mp −60 °C. ^{1}H NMR: δ 2.32 (s, 6H, H_3C), 4.58 (s, 3H, H_3Si). ^{13}C NMR: δ 49.1 (qq, $^1J_{CH} = 135.4$ Hz, $^3J_{CNCH} = 5.4$ Hz, CH_3). $^{15}N\{^1H\}$ NMR: δ −234.0 (s). $^{17}O\{^1H\}$ NMR: δ 112.1 (s). ^{29}Si NMR: δ −49.5 (q, $^1J_{SiH} = 219.3$ Hz, SiH_3). IR (gas phase): 2177 s (ν(SiH)).

Bis(*N,N*-dimethylhydroxylamino)silane, $H_2Si(ONMe_2)_2$ (2a). Methyllithium (113 mmol, 1.60 M in diethyl ether) was added dropwise to a solution of *N,N*-dimethylhydroxylamine (8.0 mL, 113 mmol) in diethyl ether (25 mL) at 0 °C and was stirred at ambient temperature for 1 h. Dichlorosilane (5.7 g, 56 mmol) was condensed onto this mixture at −196 °C, which was then warmed to −78 °C and stirred for 1 h. The mixture was allowed to warm to ambient temperature, and the volatiles were collected in a trap held at −196 °C. They were fractionally condensed through a series of traps held at −35, −35, −78, and −196 °C, with the desired product being retained in the −35 °C traps. Yield: 4.2 g of bis(*N,N*-dimethylhydroxylamino)silane (28.2 mmol, 50%), colorless liquid, mp 0 °C). Anal. Calcd (found) for $C_4H_{14}N_2O_2Si$: H, 9.39 (9.44); C, 31.98 (31.51); N, 18.64 (18.73). ^{1}H NMR: δ 2.42 (s, 12H, H_3C), 4.70 (s, 2H, H_2Si). ^{13}C NMR: δ 49.7 (qq, $^1J_{CH} = 135.4$ Hz, $^3J_{CNCH} = 5.4$ Hz, CH_3). $^{15}N\{^1H\}$ NMR: δ −249.2 (s). $^{17}O\{^1H\}$ NMR: δ 141.1 (s). ^{29}Si NMR: δ −49.8 (t, $^1J_{SiH} = 256.2$ Hz, SiH_2). IR (gas phase): 2193 s (ν(SiH)). MS (CI): *m/z* 149 ($M^+ - 1$).

Tris(*N,N*-dimethylhydroxylamino)silane $HSi(ONMe_2)_3$ (3a). Methyllithium (113 mmol, 1.60 M in diethyl ether) was added dropwise to a solution of *N,N*-dimethylhydroxylamine (8.0 mL, 113 mmol) in diethyl ether (50 mL) at 0 °C and was stirred at ambient temperature for 1 h. Trichlorosilane (3.8 mL, 38 mmol) was added at −196 °C, and the mixture was allowed to warm slowly to ambient temperature. All material volatile at −10 °C was removed under vacuum. The residue consists of 5.09 g of tris(*N,N*-dimethylhydroxylamino)silane (24.4 mmol, 64%). Colorless liquid, mp −8 °C. Anal. Calcd (found) for $C_6H_{19}N_3O_3Si$: H, 9.15 (8.92); C, 34.43 (33.96); N, 20.07 (19.98). ^{1}H NMR: δ 2.51 (s, 18H, H_3C), 4.87 (s, 1H, HSi). ^{13}C NMR: δ 50.2 (qq, $^1J_{CH} = 134.9$ Hz, $^3J_{CNCH} = 5.5$ Hz, CH_3). $^{15}N\{^1H\}$ NMR: δ −248.1 (s, $J_{SiN} = 1.4$ Hz). ^{15}N NMR: −248.1 (sep, $^2J_{NCH} = 2.0$ Hz). $^{17}O\{^1H\}$ NMR: δ 141.1 (s). ^{29}Si NMR: δ −58.2 (d, $^1J_{SiH} = 318.2$ Hz, SiH). IR (gas phase): 2220 cm^{-1} s (ν(SiH)).

***N,N*-Diethylhydroxylaminosilane, $H_3SiONEt_2$ (1b).** *n*-Butyllithium (11 mL, 1.6 M solution in hexane, 18 mmol) was added dropwise to a solution of diethylhydroxylamine (2.0 rnL) in diethyl ether (25 mL). The mixture was stirred for 1 h at ambient temperature. After removal of the solvents in vacuo, the residue was suspended in diethyl ether (100 mL). Bromosilane (2.2 g, 20 mmol) was condensed onto the mixture at −196 °C, which was stirred and warmed slowly to ambient temperature. *N,N*-Diethylhydroxylaminosilane was isolated as a colorless airsensitive liquid (yield 1.48 g, 63%, mp −55 °C) by repeated fractional condensation. ^{1}H NMR: δ 0.94 (t, $^3J_{HCCH} = 7.1$ Hz, 6H, H_3C), 2.56 (m, 4H, H_2C), 4.66 (s, 3H, H_3Si). ^{13}C NMR: δ 12.0 (q t, $^1J_{CH} = 126.2$ Hz, $^2J_{CCH} = 3.1$ Hz, CH_3), 54.0 (t q, $^1J_{CH} = 134.3$ Hz, $^2J_{CCH} = 3.7$ Hz, CH_2), $^{15}N\{^1H\}$ NMR: δ −210.0 (s). $^{17}O\{^1H\}$ NMR: $\delta = 94.7$ (s). ^{29}Si NMR: $\delta = 36.8$ (q, $^1J_{SiH} = 218.7$ Hz, SiH_3). IR (gas): 2181 s (ν(SiH)).

Bis(*N,N*-diethylhydroxylamino)silane $H_2Si(ONEt_2)_2$ (2b) and Tris(*N,N*-diethylhydroxylamino)silane $HSi(ONEt_2)_3$ (3b). Dichlorosilane (4.9 g, 49 mmol) was condensed onto a frozen solution (−196 °C) of *N,N*-diethylhydroxylamine (8.7 g, 98 mmol) and 2,6-lutidine (10.5 g, 98 mmol) in pentane (100 mL). The mixture was allowed to warm to −78 °C and was stirred for 1 h. After slowly warming to ambient temperature, the suspension was filtered and the solvent removed by distillation over a Vigreux column (20 cm). 1.58 g of bis(*N,N*-diethylhydroxylamino)silane (7.7 mmol, 16%), bp 65 °C (40 mbar) and 2.21 g of tris(*N,N*-diethylhydroxylamino)silane (7.5 mmol, 15%), bp 83 °C (10^{-2} mbar) were isolated by distillation of the residue at reduced pressure.

Data for 2b. Anal. Calcd (found) for $C_8H_{22}N_2O_2Si$: H, 10.75 (10.81); C 46.56 (46.21); N, 13.57 (13.37). ^{1}H NMR: δ 1.00 (t, $^3J_{HCCH} = 7.3$ Hz, 12H, H_3C), 2.68 (m, 8H, H_2C), 4.73 (s, 2H, H_2Si). ^{13}C NMR: δ 11.4 (q t, $^1J_{CH} = 126$ Hz, $^2J_{CCH} = 3$ Hz, CH_3), 52.8 (t q t, $^1J_{CH} = 134$ Hz, $^2J_{CCH} = 4$ Hz, $^3J_{CNCH} = 4$ Hz). $^{15}N\{^1H\}$ NMR: δ −225.6 (s). $^{17}O\{^1H\}$ NMR: δ 122.6 (s). ^{29}Si NMR: δ −44.1 (t, $^1J_{SiH} = 257.9$ Hz, SiH_2). IR (film): 2184 m (νSiH). MS (CI): *m/z* 205 [$M^+ - 1$].

Data for 3b. Anal. Calcd (found) for $C_{12}H_{31}N_3O_3Si$: H, 10.65 (10.54); C, 49.11 (48.72); N, 14.32 (14.43). ^{1}H NMR: δ 1.09 (t, $^3J_{HCCH} = 7.5$ Hz, 6H, H_3C), 2.74 (m, 4H, H_2C), 4.90 (s, 1H, HSi). ^{13}C NMR: δ 12.0 (q t, $^1J_{CH} = 126.1$ Hz, $^3J_{CCH} = 2.9$ Hz, CH_3), 53.8 (t q t, $^1J_{CH} = 134.0$ Hz, $^3J_{CCH} = 4.1$ Hz, $^3J_{CNCH} = 4.1$ Hz, CH_2). $^{15}N\{^1H\}$ NMR: δ −225.7 (s). $^{17}O\{^1H\}$ NMR: δ 130.1 (s). ^{29}Si NMR: δ −52.4 (d, $^1J_{SiH} = 324.3$ Hz, SiH). IR (film): 2249 m (ν(SiH)). MS (CI): *m/z* = 294 ($M^+ - 2$), 205 ($M^+ - H - ONEt_2$).

Isopropoxysilane, $H_3SiOCHMe_2$. *n*-Butyllithium (16.3 mL, 1.6 M solution in hexane, 26 mmol) was added dropwise to a solution of absolute isopropanol (2.0 mL, 26 mmol) in pentane (25 mL). After removal of the solvents in vacuo, the residue was dissolved in dimethyl ether (13 mL, bp −24 °C!). Bromosilane (2.9 g, 26 mmol) was condensed onto the solution at −196 °C, which was stirred at −95 °C for 1 h and warmed slowly to −30 °C. All volatiles were separated

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by condensation and isopropoxysilane was isolated as a colorless air-sensitive liquid (mp −116 °C) by repeated fractional condensation. Yield: 0.5 g (21%). ^{1}H NMR: δ 0.79 (d, $^3J_{HCCH} = 6.2$ Hz, 6H, H_3C), 4.03 (sep, $^1J_{HCCH} = 6.2$, ^{1}H, HC). ^{13}C NMR: δ 24.6 (q q d, $^1J_{CH} =$ 125.6 Hz, $^2J_{CCH} = 1.0$ Hz, $^3J_{CCH} = 4.7$ Hz, CH_3), 69.0 (d m, $^1J_{CH} =$ 140.9 Hz, CH). ^{17}O{^{1}H} NMR: δ 9.6 (s). ^{29}Si NMR: δ −36.9 (q d, $^1J_{SiH} = 215.6$ Hz, $^3J_{SiOCH} = 3.4$ Hz, SiH_3). IR (gas): 2156 s (ν(SiH)).

Crystal Structure Determination of 3a, 1b, and $H_3SiOCHMe_2$. General. Diffractometer: Enraf-Nonius CAD4, Mo-K$_a$-radiation, graphite monochromator. Solution: direct methods (SHELXTL, Siemens Analytical X-Ray Instrumentation Inc., Madison, WI, 1995). Refinement: SHELXL93 (Sheldrick, G. M. Universität Göttingen, Germany, 1993). No absorption correction applied. Non-hydrogen-atoms were refined with anisotropic thermal displacement parameters, and hydrogen atoms were located in difference Fourier maps and refined isotropically. The details for the structure determination of **1a** and **2a** are found elsewhere.[1] Single crystals were obtained by the following procedure: a solid/liquid equilibrium of the compound was established in a sealed thin-walled glass capillary within the cryo-stream of the diffractometer; parts of the capillary were repeatedly cooled and heated until a single seed crystal of suitable quality was obtained; the temperature was lowered very slowly until the single crystal occupied the whole capillary diameter. Finally the system was cooled to the temperature of the diffraction experiment.

Data for 3a. Crystal system monoclinic, space group C2/*c*, $Z =$ 16, $a = 26.205(2)$ Å, $b = 7.580(1)$ Å, $c = 26.144(2)$ Å, $\beta = 112.54(1)°$, $V = 4796.4(8)$ Å^3 at 145(2) K, cell from 96 reflections (θ range 18−23°). $2\theta_{max} = 52°$, $\omega/2\theta$ scan, 4790 indep reflections [$R_{int} =$ 0.1154]. Weight $= 1/[\sigma^2(F_o^2) + (0.1373P)^2 + 4.87P]$ where $P =$ (Max $(F_o^2,0) + 2F_c^2)/3$.387 parameters, $R_1 = 0.0658$ for 3099 reflections with $F_o > 4\sigma(F_o)$ and w$R_2 = 0.2182$ for all data.

Data for 1b. Crystal system orthorhombic, space group *Pnma*, Z $= 4$, $a = 7.741(4)$ Å, $b = 12.199(4)$ Å, $c = 7.694(2)$ Å, $V = 726.6(5)$ Å^3 at 133(2) K, cell from 96 reflections (θ range 18−23°). $2\theta_{max} =$ 54°, $\omega/2\theta$ scan, 821 indep reflections. Weight $= 1/[\sigma^2(F_o^2) +$ $(0.0673P)^2 + 0.07P]$ where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$. 64 parameters, $R_1 = 0.0329$ for 757 reflections with $F_o > 4\sigma(F_o)$ and w$R_2 = 0.0910$ for all data.

Data for $H_3SiOCHMe_2$. Crystal system orthorhombic, space group *Pnma*, $Z = 4$, $a = 8.112(1)$ Å, $b = 9.805(1)$, $c = 7.392(1)$ Å, $V =$ 587.95(12) Å^3 at 107(2) K, cell from 92 reflections (θ range 18−23°). $2\theta_{max} = 54°$, $\omega/2\theta$ scan, 675 indep reflections ($R_{int} = 0.020$). Weight $= 1/[\sigma^2(F_o^2) + (0.0974P)^2 + 0.02P]$ where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/$ 3. 50 parameters, $R_1 = 0.0388$ for 600 reflections with $F_o > 4\sigma(F_o)$ and w$R_2 = 0.1208$ for all data.

Synthesis of the Compounds. Most of the *O*-silylhydroxylamines known so far have been prepared by condensation reactions of OH-functional hydroxylamines with either halogenosilanes or aminosilanes with liberation of hydrogen halogenide and amines, respectively.[17,18] We have applied this type of reaction to the synthesis of bis- and tris(hydroxylamino)silanes but faced many problems with separation from the salts of the auxiliary amine bases and the low selectivity of the reactions, probably caused by base-mediated disproportionation of hydridohalogenosilanes. When dichlorosilane is treated with *N*,*N*-dimethylhydroxylamine in the presence of 2, 6-lutidine (lu; eq 1), a complex mixture which contains $HSi(ONMe_2)_3$, $H_2Si(ONMe_2)_2$, and $ClH_2SiONMe_2$ is formed.

$$H_2SiCl_2 + 2HONMe_2 + lu \rightarrow HSi(ONMe_2)_3;\ H_2Si(ONMe_2)_2;\ ClH_2Si(ONMe_2) + lu{\cdot}HC1 \quad (1)$$

$H_2Si(ONMe_2)_2$ can be separated from $HSi(ONMe_2)_3$ and $ClH_2SiONMe_2$ by distillation but always contains unreacted 2,6-lutidine. However, for other systems a complete purification of the products could be achieved, and $HSi(ONEt_2)_3$ and $H_2Si(ONEt_2)_2$ could be prepared in this way (eq 2).

$$H_2SiCl_2 + 2HONEt_2 + lu \rightarrow H_2Si(ONEt_2)_2;\ HSi(ONEt_2)_3 + lu{\cdot}HCl \quad (2)$$

A more selective way to obtain the desired products was found in the reactions of the *O*-lithiated hydroxylamines with the corresponding halogenosilanes (eqs 3−6). In this way $H_3SiONMe_2$, $H_3SiONEt_2$, $H_2Si(ONMe_2)_2$, and $HSi(ONMe_2)_3$ could be prepared in pure form.

$$LiONMe_2 + H_3SiBr \rightarrow H_3Si(ONMe_2) + LiBr \quad (3)$$

$$LiONEt_2 + H_3SiBr \rightarrow H_3Si(ONEt_2) + LiBr \quad (4)$$

$$2LiONMe_2 + H_2SiCl_2 \rightarrow H_2Si(ONMe_2)_2 + 2LiCI \quad (5)$$

$$3LiONMe_2 + HSiCl_3 \rightarrow HSi(ONMe_2)_3 + 3LiCl \quad (6)$$

All the compounds are air-sensitive but not pyrophoric. They are liquids at ambient temperature with low melting points. The *N*,*N*-dimethyl compounds crystallize upon cooling, whereas the *N*,*N*-diethyl compounds (with the exception of $H_3SiONEt_2$) form glassy solids.

The compounds do not decompose when heated up to about 100 °C. This is not self-evident, if the thermodynamics of the systems is considered. The rearrangement of an hydridohydroxylamino−silane into an aminosilanol (eq 7) would liberate about 300 kJ mol^{-1}, as can be calculated from standard bond enthalpies.[19]

$$H_3SiONR_2 \rightarrow (HO)H_2SiNR_2 \quad (7)$$

For $H_2Si(ONMe_2)_2$ the corresponding rearrangement [$H_2Si(ONR_2)_2 \rightarrow (HO)_2Si(NR_2)_2$] is expected to liberate ca. 600 kJ mol^{-1}, which is more than the decomposition energy of 1 mol of hydrogen azide (530 kJ mol^{-1}).[20] In the light of this thermodynamic instability, the preparations have been carried out on small scale for safety reasons. However, as even distillations at elevated temperatures never appeared to cause problems of decomposition in the way depicted above, a large kinetic stability is evident for these compounds. The high inherent energy, however, is of interest for a potential application of these substances as precursors for the low-temperature CVD (chemical vapor deposition) of silicon oxide or oxynitride films,[21] which will be attempted shortly.

Spectroscopic Characterization. Most of the compounds, with their purity checked by other methods, did not give satisfactory mass spectra. Besides problems with the high volatility we often detected masses far higher than the molecular weights, but we could not assign them to likely decomposition products. Moreover, the substances turned out to be too unstable to survive passing over a gas chromatography column coupled to a mass spectrometer. The few mass spectrometry data obtained were those for **2a**, **2b**, and **3b**, but even these compounds showed signs of decomposition during the experiments.

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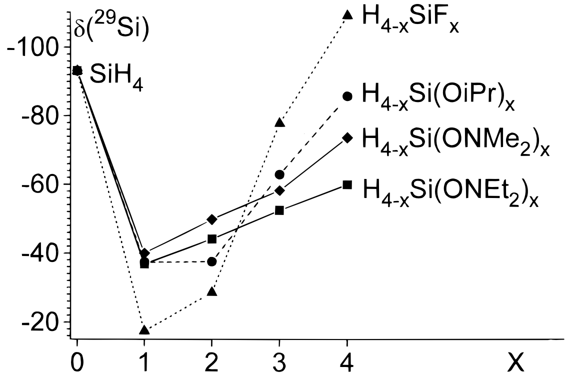

Figure 1. ^{29}Si NMR chemical shifts of the series of compounds $H_xSi(ONMe)_{4-x}$, $H_xSi(ONEt)_{4-x}$, $H_xSi(OCHMe_2)_{4-x}$ and H_xSiF_{4-x} in comparison.

NMR Spectroscopy. All compounds described in this paper comprise elements containing at least one isotope suitable for high resolution NMR spectroscopy. An unequivocal identification is possible by means of this method.

In the ^{1}H NMR spectrum the *N*,*N*-dimethylhydroxylaminosilanes give one sharp singlet for the methyl protons and one for the silicon bound protons, whereas the *N*,*N*-diethylhydroxylaminosilanes show a broad, temperature-dependent feature for the methylene units. The topomerization of the nitrogen centers gives rise to this dynamic behavior. The topomerization barriers can be estimated from the coalescence temperatures, which are 34, 32.5, and 35 °C for $H_3SiONEt_2$, $H_2Si(ONEt_2)_2$, and $HSi(ONEt_2)_3$ at 400.05 MHz proton frequency. The corresponding barriers to topomerization are then 62.8, 63.2, and 61.5 kJ mol^{-1}, which are consistent with the value of 59 kJ mol^{-1} found for $Si(ONEt_2)_4$[2] but are about 20% larger than in trialkylhydroxylamines $R^1ONR^2CH_2Ph$ which were found to be in the range between 51 and 54 kJ mol^{-1}.[22,23] The difference of about 10 kJ mol^{-1} could be attributed to the formation of a weak secondary bond between Si and N atoms; however, care is suggested with such an interpretation of these energy barriers, because other electronic effects exerted from the Si substituents rather than secondary β-donor bonds might be responsible for them.

Another probe for the partial enlargement of the coordination sphere of the silicon atom is the ^{29}Si NMR chemical shift of the compounds. The formation of β-donor bonds in the compounds should result in a low-frequency shift of the signals, but there is no suitable reference material for comparison. As the isoelectronic silicon isopropoxides are probably the most similar compounds for comparison, we prepared the whole series of hydridosilylisopropoxides, $H_xSi(O^iPr)_{4-x}$. The results are shown in Figure 1, which also contains the ^{29}Si NMR chemical shifts of the series H_xSiF_{4-x}. All four series of compounds show a maximum of chemical shift for the compounds H_3SiX. This nonlinear relationship between extent of substitution and chemical shift has been termed “sagging” behavioral[24] and attributed to $\pi-\sigma^*$ interactions[25] (a linear relation is observed for the ^{13}C chemical shifts of analogous carbon compounds H_3CX).[26] The series $H_xSi(ONMe)_{4-x}$ and $H_xSi(ONEt)_{4-x}$ show similar behavior with increasing *x*: the resonance of $H_3SiONMe_2$ is shifted to much higher frequencies than that of SiH_4, while the shifts of the following members of the series decrease almost linearly. However, so far we cannot draw conclusions regarding molecular structure from the ^{29}Si NMR chemical shifts of these compounds.

Table 1. NMR Data of the *N*,*N*-Dialkylhydroxylaminosilanes Isopropoxysilanes and *N*,*N*-Dialkylhydroxylamines in Comparison

no.	compound	^{15}N	^{17}O	^{29}Si	$^1J_{SiH}$
1a	$H_3SiONMe_2$	−249.2	137	−40.0	218.7
2a	$H_2Si(ONMe_2)_2$	−249.2	141	−49.8	256.2
3a	$HSi(ONMe_2)_3$	−248.1	141	−58.2	318.2
4a	$Si(ONMe_2)_4$	−249.2	135	−73.7	
1b	$H_3SiONEt_2$	−210.0	95	−36.8	218.7
2b	$H_2Si(ONEt_2)_2$	−225.6	123	−44.1	257.9
3b	$HSi(ONEt_2)_3$	−225.7	130	−52.4	324.3
4b	$Si(ONEt_2)_4$	−221.8	133	−59.9	
	$H_3SiOCHMe_2$		56	−37.3	215.9
	$H_2Si(OCHMe_2)_2$		55	−37.5	242.7
	$HSi(OCHMe_2)_3$		55	−62.9	282.2
	$Si(OCHMe_2)_4$		43	−85.7	
	$HONMe_2$	−259.4	139		
	$HONEt_2$	−235.3	122		

The ^{15}N and ^{17}O chemical shifts are listed in Table 1. The only compound that deviates significantly from the ranges established by the other compounds $H_xSi(ONR)_{4-x}$ is $H_3SiONEt2$, which is about 10 ppm higher in frequency than those of the other compounds $H_xSi(ONEt)_{4-x}$, in the ^{15}N NMR and about 30 ppm to lower frequency in the ^{17}O NMR spectrum. A possible explanation can be seen in the formation of weak intermolecular Si···N contacts, as have also been observed in the solid state (see below), however, this interpretation is not unequivocal.

Vibrational Spectroscopy. Normal modes of vibration of $H_3SiONMe_2$, the simplest hydroxylaminosilane, were deduced from *ab initio* frequency calculations at the MP2/6-31G* level of theory[28] and the corresponding molecular motions were visualized by using the program Hyperchem 4.0. The results with assignments and the gas-phase IR data of $H_3SiONMe_2$ are listed in Table 2. Theoretical IR frequencies are scaled by a factor of 0.9 to correct for the harmonic oscillator model assumed in the computations.

The results are in reasonable agreement with the experimental frequencies. The ν(NO) band is found at a relatively low wavenumber (724 cm^{-1}) as compared with other assigned ν(NO) bands of hydroxylamines, *e.g.* Me_2NOH with a skeletal stretching mode ν(NO) at 956 cm^{-1}.[27] This relates to a slightly elongated N−O bond in $H_3SiONMe_2$ as compared to $HONMe_2$ (see below). The skeletal deformation mode δ(SiON) was predicted to be 135 cm^{-1} but could not be measured with the IR instrumentation in our hands. The low magnitude of this mode, however, suggests a shallow potential for the deformation of the Si−O−N skeleton.

Structural Chemistry. Single crystals of the low-melting compounds **1a**, **2a**, **3a**, and **1b** could be grown by *in situ* methods on the diffractometer. $HSi(ONMe_2)_3$, **3a**, crystallizes in the monoclinic space group C2/*c* with two independent molecules in the asymmetric unit, which are similar in geometry. There is no crystallographic symmetry imposed on the molecules, but the geometry of both is close to propeller-like C_3 symmetry (see Table 3 and Figure 2).

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Table 2. Vibrational Frequencies of $H_3SiONMe_2$ and Assignments According to the Calculations[a]

measured	calculated	assignment	
	89	A″	τ NO
	135	A′	δ SiON
	221	A″	τ SiO
	242	A″	τ_{as} NC + τ SiO
	269	A′	τ_s NC
	361	A′	δ_s ONC
	414	A″	δ_{as} ONC
	420	A′	γ N
	636	A′	ρ_s SiH_3
682	665	A″	ρ_{as} SiH_3
724	725	A′	ν NO
	803	A′	ν SiO + ν NO
880	898	A′	$(\delta_{as}\ SiH_3)_s$
882	899	A″	$(\delta_{as}\ SiH_3)_{as}$
	905	A′	δ_s SiH_3
958	927	A′	δ_s SiH_3
977	942	A″	$(\rho\ CH_3)_{as}$
1085	1027	A″	$(\rho\ CH_3)_{as}$
	1105	A′	$(\rho\ CH_3)_s$
1213	1148	A′	$(\rho\ CH_3)_s$
	1156	A″	ν_{as} CNC
	1329	A″	$(\delta_s\ CH_3)_{as}$
	1351	A′	$(\delta_s\ CH_3)_s$
	1378	A″	$(\delta_{as}\ CH_3)_{as}$
1442	1391	A′	$(\delta_{as}\ CH_3)_s$
	1395	A″	$(\delta_{as}\ CH_3)_{as}$
1475	1413	A′	$(\delta_{as}\ CH_3)_s$
2171	2085	A′	$(\nu_s\ SiH_3)_s$
2177	2091	A′	$(\nu_{as}\ SiH_3)_s$
	2093	A″	$(\nu_{as}\ SiH_3)_{as}$
2781	2771	A″	$(\nu_s\ CH_3)_{as}$
2784	2774	A′	$(\nu_s\ CH_3)_s$
2826	2862	A″	$(\nu_{as}\ CH_3)_{as}$
2830	2866	A′	$(\nu_{as}\ CH_3)_s$
2903	2902	A″	$(\nu_{as}\ CH_2)_{as}$
	2903	A′	$(\nu_{as}\ CH_3)_s$

[a] The first indices denote the motions relative to the group symmetry, the ones outside the parentheses refer to molecular symmetry.

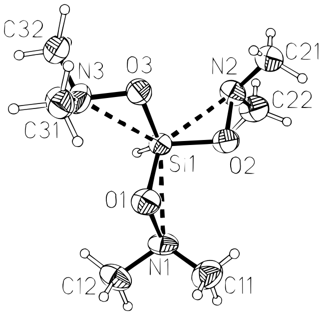

Figure 2. Molecular structure of $HSi(ONMe_2)_3$ (**3a**) as determined by low-temperature X-ray crystallography. One of the two independent molecules is shown only.

The Si−O−N angles are found in the range between 101.7(2) and 105.3(3)°, which is smaller than in $Si(ONMe_2)_4$ (109.1° on averages. The Si···N distances are 244.2 pm on average. The basic tetrahedral coordination at the silicon atom is markedly distorted and leads to compressed O−Si−O angles. The overall geometry at silicon is therefore 4+3, hence the compound has to be compared with other 4+3 coordinate compounds, which have been prepared in the last few years. An example is $FSi(o\text{-}C_6H_4CH_2NMe_2)_3$[28] with Si···N distances of about 327 pm, which is only slightly smaller than the sum of the van der Waals radii of Si and N. Smaller Si···N distances of about 290 pm occur in $HSi(naphNMe_2)_3$ (naph = 1,8-naphtyl).[29]

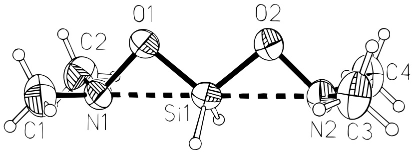

Figure 3. Molecular structure of $H_2Si(ONMe_2)_2$ (**2a**) as determined by low-temperature X-ray crystallography. The Si−O−N angles in this compound are 94.2(1) and 96.2(1)°.

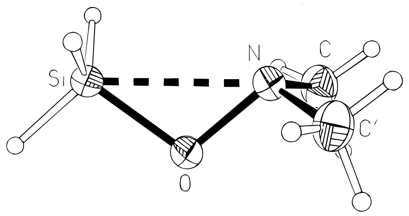

Figure 4. Molecular structure of $H_3SiONMe_2$ (**1a**) as determined by low-temperature X-ray crystallography.

All secondary bonds in $HSi(ONMe_2)_3$ are in the plane perpendicular to the Si−H bond. One of the two independent molecules has slightly shorter N−O bonds than the other, which, however, has little effect on other structural parameters.

The most striking result from X-ray crystallography is the molecular structure of $H_2Si(ONMe_2)_2$ (Figure 3), which strongly supports the picture of β-donor bond formation. The Si−O−N angles in this compound are as small as 94.2(1) and 96.2(1)° with corresponding Si···N distances of only 230.0(1) and 233.6(1) pm. These parameter values compare so well to the predictions of *ab initio* calculations (MP2/6-31G*, Table 4), 94.2° for the Si−O−N angle and 2.333 Å for the Si···N distance, that the presence of any major distorting packing effects within the crystal structure can be excluded with certainty. The Si−O−N angles in $H_2Si(ONMe_2)_2$ are as much as 30° smaller than the Si−O−C angle in $Si(OCHMe_2)_4$,[2] which can be taken as a reference because the $SiONMe_2$ and the $SiOCHMe_2$ units are isoelectronic. The overall coordination geometry of the silicon center is thus 4+2.

The molecules in the crystal lattice adopt geometries which deviate only slightly from C_{2v} symmetry, as is predicted to be the ground state in the *ab initio* calculations. The tetrahedral geometry of the silicon atom is substantially distorted, *i.e.* the O−Si−O angle is compressed to only 101.0(1)°, while the H−Si−H angle is widened to 115.6(10)°. The N−O bond lengths are slightly larger in $H_2Si(ONMe_2)_2$ (147.9 pm on average) than in the free hydroxylamine (145.2 pm on average).[29] The crystal packing of $H_2Si(ONMe_2)_2$ does not show any important intermolecular interactions.

As the Si−O−N angles and the Si···N distances decrease in the series of compounds $Si(ONMe_2)_4$, $HSi(ONMe_2)_3$, and $H_2Si(ONMe_2)_2$, one could expect the values in the simplest representative of this class of compounds to be the most extreme. However, we have already carried out *ab initio* calculations up to the MP2/6-311G** level of theory for $H_3SiONMe_2$, which predicted it to adopt a Si−O−N angle of 102.5°.[2] The analysis of the single-crystal X-ray diffraction data provided a geometry (Figure 4, Table 5) which closely fits the *ab initio* predictions: the experimentally determined Si−O−N angle is 102.6(1)°, corresponding to a Si···N distance of 245.3(1) pm, which matches nicely with the theoretical value of 245.4 pm. Again the Si−O−N angle in this compound appears to be very much

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Table 3. Selected Bond Lengths and Angles for the Two Independent Molecules of $HSi(ONMe_2)_3$ (**3a**) in the Crystal As Determined by X-ray Diffraction (XRD)

bond length (pm)	molecule 1	molecule 2	bond angles (deg)	molecule 1	molecule2
Si−O(1)	165.6(3)	164.7(3)	O(2)−Si−O(1)	106.3(2)	107.1(1)
Si−O(2)	163.8(3)	164.6(3)	O(3)−Si−O(1)	106.26(14)	106.5(1)
Si−O(3)	164.2(3)	164.9(3)	O(2)−Si−O(3)	108.44(14)	107.1(1)
Si−N(1)	246.8(3)	242.8(3)	Si−O(1)−N(1)	105.3(2)	101.7(2)
Si−N(2)	243.2(3)	243.7(3)	Si−O(2)−N(2)	103.3(2)	102.5(2)
Si−N(3)	243.4(3)	244.9(3)	Si−O(3)−N(3)	103.7(2)	103.2(2)
O(1)−N(1)	144.5(4)	148.0(4)	O−N−C (range)	104.9(3)−106 9(3)	
O(2)−N(2)	145.9(4)	147.5(4)			
O(3)−N(3)	144.9(4)	147.4(4)			
N−C (range)	142.9(6)−146.1(6)				

Table 4. Selected Bond Lengths and Angles for $H_2Si(ONMe_2)_2$ (**2a**) As Determined by X-ray Diffraction (XRD) and *ab Initio* Calculations

bond length (pm)	XRD	MP2/6-31G*	bond angles (deg)	XRD	MP2/6-31G*
Si(1)−O(1)	165.6(1)	169.9	O(1)−Si(1)−O(2)	100.95(5)	101.5
Si(1)−O(2)	165.7(1)		Si(1)−O(1)−N(1)	94.16(7)	94.2
Si(1)−N(1)	230.0(1)	233.3	Si(1)−O(2)−N(2)	96.19(7)	
Si(1)−N(2)	233.6(1)		N(1)−Si(1)−N(2)	179.71(4)	179.8
O(1)−N(1)	148.1(1)	147.7	H(1)−Si(1)−H(2)	115.6(10)	113.9
O(2)−N(2)	147.7(1)				

Table 5. Selected Bond Lengths and Angles for $H_3SiONMe_2$ (**1a**) As Determined by X-ray Diffraction (XRD) and *ab Initio* Calculations

bond length (pm)	XRD	MP2/6-311G**	bond angles (deg)	XRD	MP2/6-311G**
Si−O	166.8(1)	168.2	Si−O−N	102.63(5)	102.5
Si−N	245.3(1)	245.4	O−Si−H(1)	110.4(6)	111.5
O−N	147.1(1)	145.9	O−Si−H(2)	101.7(8)	104.4
C−N	145.5(1)	145.8	O−N−C	105.5(1)	105.3

Table 6. Selected Bond Lengths and Angles for $H_3SiONEt_2$ (**1b**) As Determined by X-ray Diffraction (XRD) and *ab Initio* Calculations

bond length (pm)	XRD	MP2/6-311 G**	bond angles	XRD	MP2/6-311G**
Si−O	166.1(1)	168.3	Si−O−N	108.2(1)	106.7
Si−N	253.9(1)	252.5	O−N−C(1)	105.0(1)	105.4
O−N	147.0(2)	146.0	N−C(1)−C(2)	113.4(1)	112.8
C−N	147.4(1)	146.7	C(1)−N−C(1a)	109.4(1)	109.5

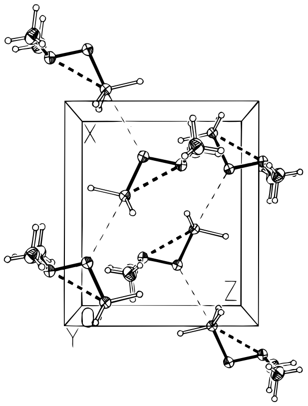

Figure 5. Packing of the molecules of $H_3SiONMe_2$ (**1a**) in the crystal showing intermolecular contacts between oxygen and silicon atoms.

smaller than comparable isoelectronic Si−O−C angles in H_3SiOMe (120.1°) or $H_3SiOCHMe_2$ [118.4(1)°, see below].

As far as crystallographic data allow the location of hydrogen positions, the data show the geometry of the SiH_3 group to be slightly distorted with the O−Si−H angle trans to the nitrogen atom being slightly compressed to 101.7(8)°, whereas the other two O−Si−H angles are slightly widened to 110.4(6)°. The molecules of $H_3SiONMe_2$ have a crystallographic mirror plane which coincides with the SiON plane.

In the crystal lattice the molecules form endless zigzag chain aggregates (Figure 5) through relatively short Si···O contacts of 294 pm, which is much shorter than the sum of the van der Waals radii of Si and O (362 pm).[19] It appears that these intermolecular interactions have little effect on the molecular geometry as the crystal data compares so well with the calculations on the free molecule. Surprisingly, this type of intermolecular secondary bonding makes use of the oxygen center as donor atoms rather than the nitrogen centers, which could be expected to show higher basicity. This can be interpreted in terms of a lone pair of electrons at the nitrogen atom being already involved in the β-donor bonding and thus being not available to other types of secondary bonding. It should be mentioned that the total coordination geometry at the oxygen atom (including the intermolecular contacts) is planar, as has also been found in the crystal structure of $(H_3Si)_2NOMe$.[30] For an sp^3 type oxygen atom the lone pairs should have a preference for an out of plane orientation, as in the crystal structure of the adduct $H_3SiCl{\cdot}OMe_2$.[31] On the other hand an sp^2 hybridized oxygen is an inappropriate description as well because of the narrow Si−O−N angle. None of these simple hybridization models is thus well suited to describe the electronic status of the oxygen atom in this compound.

In order to gauge the effect of different substituents at the nitrogen atom on the structure of the SiON core, we performed a crystal structure analysis on $H_3SiONEt_2$ (**1b**, Figure 6, Table 6). As in the methyl derivative, the ethyl analogue crystallizes with a crystallographic mirror plane passing through the HSiON unit. The Si−O−N angle in this compound is 108.2(1)° and thus significantly larger than that in **1a**. *Ab initio* calculations

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Table 7. Selected Bond Lengths and Angles for $H_3SiOCHMe_2$ As Determined by X-ray Diffraction (XRD) and *ab Initio* Calculations

bond length (pm)	XRD	MP2/-6-311G**	bond and torsion angles (deg)	XRD	MP2/-6-311G**
Si−O	164.9(1)	165.8	Si−O−C(1)	118.4(1)	122.0
O−C	144.0(2)	143.3	O−C(1)−C(2)	108.5(1)	107.3
C−C	151.1(2)	151.9/152.3	C(2)−C(1)−C(2a)	113.1(2)	112.4
			Si−O−C(1)−C(2)	118.4	145.6/−92.1

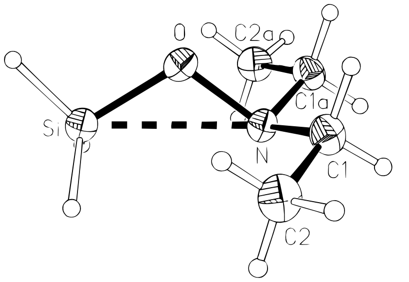

Figure 6. Molecular structure of $H_3SiONEt_2$ (**1b**) as determined by low-temperature X-ray crystallography.

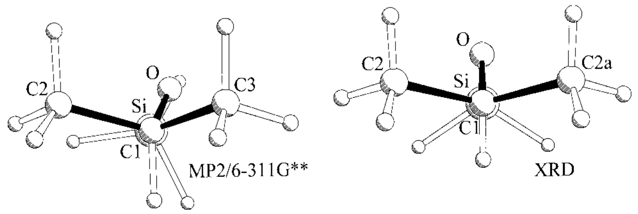

Figure 7. View along the C(1)−Si vector in $H_3SiOCHMe_2$ in the calculated ground state (C_1, MP2/6-311G**) and the crystal (C_s).

at the MP2/6-311G** level of theory predict a slightly smaller Si−O−N angle of 106.7°. As in the other crystal structures discussed in this paper, the N−O bond length is slightly larger than in Me_2NOH.[29] In contrast to the crystal structure of **1a**, intermolecular Si···N contacts occur in the crystal lattice of **1b**, which are 334 pm and thus much weaker than the Si···O contacts of 294 pm in **1a**. This might contribute to the difference in the Si−O−N angles, *i.e.* the strength of the β-donor interaction, between **1a** and **1b** and between the crystal structure geometry of **1b** and that calculated by *ab initio* methods. When the lone pair at the nitrogen atom is involved in a weak intermolecular contact, it is not completely available to a β-donor interaction, which therefore becomes weaker.

For a further comparison of the molecular structure of $H_3SiONMe_2$ with those of silyl ethers, which are not capable of forming β-donor bonds, we determined the crystal structure of the isoelectronic isopropoxysilane, $H_3SiOCHMe_2$, a low-melting compound (mp −116 °C). A crystallographic mirror plane passes through the HSiOC unit of molecules of $H_3SiOCHMe_2$, which are associated into chains by weak Si···O contacts (303.2 pm). The angle Si−O−C is 118.4(1)° and thus substantially wider than the Si−O−N angle in the isoelectronic $H_3SiONMe_2$. It is, however, smaller than that in $Si(OCHMe_2)_4$ [124.7(1)°],[2] and even that of H_3SiOCH_3 (120°).[11] Whereas the difference to $Si(OCHMe_2)_4$ can be rationalized by steric arguments they do not apply for the difference to H_3SiOCH_3. *Ab initio* calculations at the MP2/6-311G** level of theory predict the Si−O−C angle in $H_3SiOCHMe_2$ to be 122.0° for the free molecule and the difference to the value determined for the solid state is probably due to weak packing forces, in particular the Si···O contacts. Surprisingly, the calculations predict the molecules to deviate markedly from mirror symmetry, whereas the C_s symmetric structure is characterized as a transition state on the potential energy hypersurface (Figure7 and Table 7). The energy difference between the calculated ground structure and the calculated transition state (C_s symmetry) is only 0.4 kJ mol^{-1} at the MP2/6311G** level of theory, which indicates the presence of two very shallow minima separated by a very small barrier only. In this way it seems not too surprising that nature decides to pack the molecules into the crystal lattice close to their transition state geometry, while gaining some energy by the formation of weak Si···O contacts.

Theoretical Estimation of the Strength and Description of β-Donor Bonds. In order to get an idea of the strength of SiON β-donor bonds, we performed a series of geometrical optimizations on the structure of $H_3SiONMe_2$ at the MP2/6-31G* level of theory, whereby the Si−O−N angles were kept fixed and were successively varied. In essence, the result is an almost parabolic curve which can be fitted by a function

$$E = 730.6 - 18.18a - 0.1437a^2 - 3.505 \times 10^{-4}a^3 \quad (8)$$

with a being the Si−O−N angle in deg and E being the relative energy in kJ mol^{-1}. This curve shows the energy necessary to achieve a certain deformation of the SiON core. If compared with the Si−O−C angles of isoelectronic SiOCH systems, which are not capable of SiN β-donor-bond formation, the Si−O−N angle can be estimated to be 120° in the hypothetical absence of β-donor interactions. The same magnitude for this angle is predicted from the two bond radii model of Bartell,[32,33] if standard Si−O and N−O bond lengths are assumed. An estimate of 15 kJ mol^{-1} for the β-donor-bond energy can thus be derived from eq 8, by comparing the energy at 120° with that at the minimum structure.

A natural bond orbital (NBO) analysis[34] has been performed based on the molecular MP2/6-31G* geometries of **1a** and **2a**. Second-order perturbation theory analysis of the Fock matrix in the NBO basis provides us with a description of intramolecular donor-acceptor interactions. Both compounds, **1a** and **2a**, show $lp_O \rightarrow \sigma^*_{Si-H}$ (lp = lone pair) interactions of comparable strength (66 and 58 kJ mol^{-1}), which are also similar to those in typical silyl ethers like $H_3SiOCH(CH_3)_2$ also described in this paper (71 kJ mol^{-1}). This description is in accordance with the observation of similar Si−O bond lengths in **1a** and **2a** and $H_3SiOCH(CH_3)_2$. The contribution of $lp_O \rightarrow \sigma^*_{Si-H}$ interactions seems thus not to be dependent on the Si−O−X angle as is suggested by earlier theoretical contributions.

The NBO picture is also suitable to rationalize the nature of β-donor bonding in Si−O−N systems. In **1a** there is a remote NBO donor−acceptor interaction of the $lp_N \rightarrow \sigma^*_{Si-H}$ type (to the in-plane Si−H bond), yielding 18 kJ mol^{-1} of stabilization energy, which explains the compression of the Si−O−N angle. In **2a** there are three significant contributions for delocalization of electron density from the two equivalent nitrogen lone pairs into two σ^*_{Si-H} NBO's, into the σ^*_{Si-O} NBO of the O atom attached to the nitrogen center under consideration and into the $\sigma^*_{Si-O'}$ NBO of the symmetry equivalent Si−O bond, yielding 13, 22, and 27 kJ mol^{-1} of stabilization energy. The total stabilization of 62 kJ mol^{-1} per nitrogen center in **2a** is thus as

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(32) Bartell, L. S. *J. Chem. Phys.* **1960**, *32*, 827.

(33) Glidewell, C. *Inorg. Chim. Acta* **1975**, *12*, 219.

(34) (a) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (b) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

large as the contribution of the $lp_O \rightarrow \sigma^*_{Si-H}$ interaction and much stronger than in **1a** which is reflected in the smaller Si−O−N angle of **2a**.

Conclusions

Simple *O*-hydroxylaminosilanes can be prepared by a selective reaction between *O*-lithiated hydroxylamines and halogenosilanes. Despite the thermodynamic instability of the H−Si−O−N moiety toward the rearrangements into aminosilanols H−O−Si−N these compounds have been found to be reasonably stable and save in handling. We have proved that hydroxylaminosilanes show unique structural features, the most striking being the extremely small Si−O−N angles, which lead to contacts between the silicon and nitrogen atoms and result in partial enlargement of the coordination sphere of both. The strongest Si−N−*β*-donor bond has been found in the compound $H_2Si(ONMe_2)_2$ which has Si−O−N angles of only 95°. The nature of the Si−N−*β*-donor bond can be described in terms of the NBO picture as delocalization of electron density of the nitrogen lone pairs of electrons into empty antibonding orbitals at silicon, in particular the σ^*_{Si-X} NBO of the bond in antiposition relative to the nitrogen atom.

The wide angles in Si−O−C (and Si−O−Si) compounds have been rationalized by $lp_O \rightarrow \sigma^*_{Si-X}$ interactions in the literature.[35] According to this description, significantly elongated Si−O bonds had to be expected for compounds with small Si−O−X angles, as this would diminish the multiple bond character of the Si−O bond or the electron delocalization in the picture of hyperconjugation between *π*-type orbitals of the oxygen with *σ** orbitals localized at silicon. However, the NBO analysis of $H_3SiONMe_2$ (**1a**) and $H_2Si(ONMe_2)_2$ (**2a**) gives roughly the same magnitude of stabilization by $lp_O \rightarrow \sigma^*_{Si-H}$ interactions as in compounds with widened Si−O−X angles like $H_3SiOCHMe_2$ and the Si−O bond length are of similar length. Thus this model has to be checked by means of theoretical methods for its general applicability.

It is also evident that classical qualitative models for structure prediction cannot fully explain our experimental findings. Neither the VSEPR model[36] nor its extension by the two-bond radii model of Bartell,[32,33] which accounts for the repulsion between two atoms in *β*-position to one another (not covered by VSEPR) explain the structures in this paper without taking attractive forces between geminal atoms (Si and N) into consideration.

Marked structural deviations of a class of compounds from other constitutionally similar ones must have some consequences for chemical behavior, reactivity, and physical properties. The partially enlarged coordination sphere of silicon in hydroxylaminosilanes should lead to high reactivity toward substitution reactions at the Si center, which may explain the high reactivity toward hydrolysis and the proposed use of this class of compounds as cold curing catalysts in silicone polymer synthesis, as widely suggested in the patent literature.[12] The catalytic action of OH-functional hydroxylamines in the alcoholysis of Si−H functions can also be rationalized in terms of the formation of *β*-donor bonds in these compounds.

Acknowledgment. This work has been supported by the Bayerischer Staatsminister für Unterricht, Kultus, Wissenschaft und Kunst (Bayerischer Habilitationsförderpreis 1996 for N.W.M.), by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Leonhard-Lorenz-Stiftung, and through chemical donations by Bayer AG, Leverkusen. We are indebted to Mr. J. Riede for carefully establishing the crystallographic data sets, and we are grateful to Prof. H. Schmidbaur for helpful discussions and generous support.

Supporting Information Available: Four figures showing the crystal packing of **2a**, **1b**, and $H_3SiOCHMe_2$ and a plot of relative energies of **1a** calculated at different fixed Si−O−N angles (4 pages). Ordering information is given on any current masthead page.

IC971508E

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