

β -Donor Bonds in SiON Units: An Inherent Structure-Determining Property Leading to (4 + 4)-Coordination in Tetrakis-(*N,N*-dimethylhydroxylamido)silane

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Abstract: Tetrakis(*N,N*-dimethylhydroxylamido)silane, Si(ONMe₂)₄ (**1**), and the analogous ethyl compound, Si(ONEt₂)₄ (**2**), have been prepared by the reaction of silicon tetrachloride with 4 equiv of the corresponding lithium *N,N*-dialkylhydroxylamide. The compounds have been characterized by elemental analysis, IR spectroscopy, NMR spectroscopy of the nuclei ¹H, ¹³C, ¹⁵N [including the determination of ¹J(²⁹Si¹⁵N) coupling constants], ¹⁷O, and ²⁹Si, and nominal and high-resolution mass spectrometry. A crystal structure determination on **1** showed the molecule to be (4 + 4)-coordinate with short Si···N contacts [2.514(3)–2.555(3) Å] and narrow SiON angles [109.1° on average]. For comparison, the crystal structure of the isoelectronic Si(OCHMe₂)₄ (*in situ* grown crystal) was determined, showing the absence of β -donor interactions and an SiOC angle of 124.7(1)°. *Ab initio* calculations have been performed on the model compounds Si(OH)₂ and H₃SiONMe₂ as well as the electronegatively substituted fluoro derivatives FH₂SiONMe₂ and F₃SiONMe₂ up to the MP2/6-311G** level of theory. Si(OH)₂ is predicted to adopt C₂ symmetry and to have an SiON angle of only 109.5°, while the interactions in the other model compounds are predicted to be much stronger, as indicated by their SiON angles: H₃SiONMe₂ 102.5°, FH₂SiONMe₂ 90.0°, and F₃SiONMe₂ 93.8°. The results are discussed with respect to the consequences of enlargement of the coordination sphere at the silicon atom, the unique chemical behavior of *O*-silylhydroxylamines (in particular their fast nucleophilic substitutions reactions), and the resulting use of this class of compounds in the silicone rubber industry.

Introduction

Organosilicon ethers of hydroxylamine and oximes have been widely used as cross-linking agents for low-molecular-weight silicone rubbers used for example in electrical and transport engineering, construction, and medicine.^{1,2} Their advantages are their stability under anhydrous conditions but ready hydrolysis by exposure to air moisture. Not only are they acting as polyfunctional reagents which form the basis for the cross-links but also as catalysts which accelerate the cross-linking process.² Recently, an increased reactivity and sensitivity of Si–H functions in poly(phenylsilane) toward hydrolysis or alcoholysis in the presence of catalytic amounts of OH functional hydroxylamines was reported, induced by the high reactivity of initially formed *O*-hydroxylamidossilanes³ (Scheme 1). These facts raised the question whether the nitrogen atoms of those hydroxylamines exert a purely electronic effect on the oxygen atoms or whether they can act as donor centers toward silicon in such compounds and reactions. The verification of the latter case would help to explain the increased reactivity of both,

–ONR₂ groups that are already bound to a silicon center and HONR₂ reagents which could be bound intermediately to a silicon atom, which would become hypercoordinate in this way. The enhanced reactivity of hypercoordinate silicon compounds has been subject of many investigations and has been discussed in detail in recent reviews by Holmes⁴ and Chuit *et al.*⁵ The interaction of four-coordinate silicon with weak nucleophiles is also well established, *e.g.*, from the work of Martin *et al.*⁶

We have now investigated the synthesis of tetrakis(*N,N*-dialkylhydroxylamido)silanes, Si(ONR₂)₄, and report here the hypercoordination of the octamethyl derivative, including comparisons with the isoelectronic but donor-free alkoxides and theoretical studies on simpler related model compounds. Rapid progress in the chemistry of hypercoordinated silicon compounds in the last few years has included the description of some “seven-coordinated” species^{7,8} and has recently found its high point in establishing a (4 + 4)-coordinated molecule, bis-1-[2,6-bis(dimethylaminomethyl)phenyl]silane.⁹ The coordination geometry of silicon in this compound was described as a SiC₂H₂ tetrahedron, tetracapped by four nitrogen donor centers having distances of 2.895 and 3.117 Å. Another silicon compound, [C₆H₂(CF₃)₃]₂SiF₂, was also reported to have a tetracapped tetrahedral geometry about the silicon atom, with the four donor bonds made up from Si···F contacts in the range 2.715–3.056 Å.¹¹

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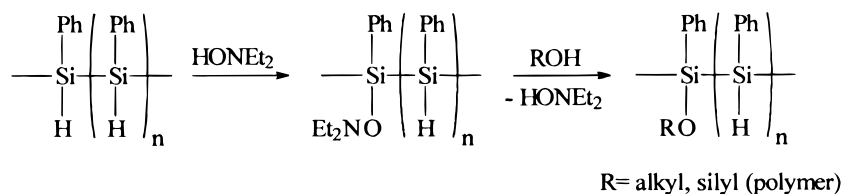
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Scheme 1



Based on the knowledge of the existence of eight-coordinate transition metal hydroxylamides such as $\text{Ti}(\text{ONMe}_2)_4$,^{12,13} our recent observation of β -donor bonding by hydrazide ligands toward silicon centers in the compound $\text{Cl}_2\text{Si}(\text{NMeNMe}_2)_2$ ¹⁴ has stimulated us to attempt the synthesis and structure elucidation of homoleptic *O*-hydroxylamides of p-block elements. *O*-Hydroxylamides also contain β -donor functionalities, but bound to α -oxygen atoms, which are more electron-withdrawing than the α -nitrogen atoms in the hydrazides.

Because of the backbonding exerted from the most electronegative elements (F, N, O), the electrophilic properties of silicon do not increase as much as might be expected from the electronegativity of such substituents. The limit of hypercoordination of homoleptic silicon species has been seen in the six-coordinate SiF_6^{2-} and tris(catechol)silicates.⁵ It has also been postulated that an enlargement of the coordination sphere of silicon in homoleptic compounds is unlikely because of the increase of the energy of such systems with decreasing molecular and crystal symmetry, which cannot be compensated for by the formation of weak $\text{Si}\cdots\text{N}$ donor bonds.⁸

Experimental Section

Standard inert gas techniques were applied [¹³C NMR: Bruker AM250, ²⁹Si NMR: Bruker WP200, ¹H, ¹⁵N, and ¹⁷O NMR Jeol JNM-GX 400 spectrometer, MS/HRMS: Kratos MS50TC, IR: Perkin Elmer FTIR 1650].

Si(ONMe₂)₄ (1). A 2.5 M solution (50.0 mL) of *n*-butyllithium (0.125 mol) was added dropwise to a solution of 7.8 g of Me₂NOH in 150 mL of hexane at 0 °C. Silicon tetrachloride (3.57 mL) was added, and the resulting suspension was allowed to warm to ambient temperature and refluxed for 1 h. The mixture was filtered, and the volume of the solution was reduced to ca. 30 mL by distillation under reduced pressure. Large crystals (6.23 g, 74%) were obtained upon slowly cooling the solution to -30 °C: mp 42 °C. ¹H-NMR (250.13 MHz, C₆D₆): δ = 2.61 [s, ¹J(CH) = 137.8 Hz]. ¹³C{¹H}-NMR (62.90 MHz, C₆D₆): δ = 20.6 [s]. ¹⁵N{¹H}-NMR (40.51 MHz, C₆D₆): δ = -249.2 [s, ^J(²⁹Si;¹⁵N) = 1.8 Hz]. ¹⁷O-NMR (54.21 MHz, C₆D₆): δ = 135. ²⁹Si-NMR (39.76 MHz, C₆D₆): δ = -73.7 [s]. IR: (solid film): ν = 2998 s, 2951 s, 2860 s, 2812 s, 2774 m, 2765 s, 1471 s, 1465 s, 1442 s, 1427 m, 1414 s, 1392 vw, 1215 m, 1208 s, 1177 w, 1148 w, 1088 m, 997 s, 964 vs, 910 vs, 767 s, 688 m cm⁻¹. MS (EI, 70 eV): m/z (%) = 268, 208 [69, Si(ONMe₂)₃⁺], 183, 165, 138, 122, 106, 44 (100). HRMS: C₈H₂₄N₄O₄Si, Calcd. 268.15668, Found 268.15748. Elemental analysis (calcd/found in %): H, 9.02/8.93; C, 35.80/35.52; N, 20.89/21.07.

Crystal Structure Determinations. 1: Crystal data: C₈H₂₄N₄O₄Si: M = 268.40, monoclinic, space group $P2_1/n$ (Alt. $P2_1/c$, no. 14), a = 8.094(3), b = 19.200(8), c = 10.138(4) Å, β = 107.88(4)°, U = 1499.4(10) Å³ [from setting angles of 13 reflections, $30 \leq 2\theta \leq 32^\circ$, λ = 0.71073 Å, T = 150.0(2) K], Z = 4, D_{calcd} = 1.189 Mg m⁻³,

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$\mu(\text{Mo-K}\alpha) = 0.167 \text{ mm}^{-1}$. A colorless plate of dimensions 0.65 × 0.65 × 0.10 mm³ was mounted on a Stoe Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems open-flow cryostat¹⁵ and graphite-monochromated Mo-K α X-radiation. A total of 2637 unique reflections was collected to $2\theta_{\text{max}} = 50^\circ$ using $\omega/2\theta$ scans. Of these 1804 had $F_o \geq 4\sigma(F_o)$, and 2582 were used in all calculations. The structure was solved by direct methods and refined on F_o^2 using *SHELXTL/PC*,¹⁶ with H and non-H atoms allowed isotropic and anisotropic thermal motion, respectively. After their location in a Fourier difference synthesis the H atoms could be refined without geometrical restraints. With the weighting scheme $w^{-1} = \sigma^2(F_o^2) + (0.05P)^2 + 1.35P$, $P = 1/3[\text{MAX}(F_o^2, 0) + 2F_c^2]$, final convergence gave conventional $R_1[F_o \geq 4\sigma(F_o)] = 0.0457$ and $wR_2[F_o^2, \text{all data}] = 0.273$ for 251 refined parameters, $S[F^2] = 1.06$. A secondary extinction correction¹⁶ refined to 0.0042(13) and the final Fourier difference synthesis had no feature outside the range +0.36 → -0.31 e Å⁻³.

3: Crystal data: C₁₂H₂₈O₄Si: M = 264.43, tetragonal, space group $I4_1/a$, a = 8.0422(5), c = 24.653(2) Å, U = 1594.4(3) Å³ [from 88 reflections, $30 \leq 2\theta \leq 32^\circ$, λ = 1.54184 Å, T = 150.0(2) K], Z = 4, D_{calcd} = 1.102 Mg m⁻³, $\mu(\text{Cu-K}\alpha) = 1.325 \text{ mm}^{-1}$. A colorless cylindrical crystal was grown by cooling the sample sealed in a glass capillary from 148.3 to 145.0 K (after growing a suitable seed crystal) on a Stoe Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems open-flow cryostat¹⁵ and graphite-monochromated Cu-K α X-radiation. Empirical absorption correction by Ψ -scans was applied ($T_{\text{min/max}}$: 0.245 and 0.330). A total of 2226 reflections were collected to $2\theta_{\text{max}} = 120^\circ$ as ω - θ scans of which 593 were independent. Of these 555 had $F_o \geq 4\sigma(F_o)$. The structure was solved by direct methods *SHELXTL/PC*¹⁶ and refined on F_o^2 using *SHELXL93*¹⁷ with H and non-H atoms allowed isotropic and anisotropic thermal motion respectively. After their location in a Fourier difference synthesis the H atoms could be refined without geometrical restraints. With the weighting scheme $w^{-1} = \sigma^2(F_o^2) + (0.0335P)^2 + 0.77P$, $P = 1/3[\text{MAX}(F_o^2, 0) + 2F_c^2]$ final convergence gave conventional $R_1[F_o \geq 4\sigma(F_o)] = 0.0314$ and $wR_2[F_o^2, \text{all data}] = 0.0827$ for 68 refined parameters, $S[F^2] = 1.10$. A secondary extinction correction¹⁷ was refined to 0.0179(11), and the final Fourier difference synthesis had no feature outside the range +0.10 → -0.18 e Å⁻³.

Ab initio Calculations. *Ab initio* molecular orbital calculations were carried out for the systems Si(OH)₂, H₃SiONMe₂, FH₂SiONMe₂, and F₃SiONMe₂ using the Gaussian 94 program.¹⁸ Geometry optimization calculations on model compounds were undertaken at the SCF level using the standard 3-21G*,^{19–21} 6-31G*,^{22–24} and 6-311G**^{25,26} basis sets, while the larger two basis sets and one to probe the effects of

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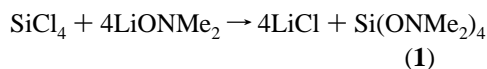
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diffuse functions (6-31+G*) were used for calculations at the MP2 level of theory. A single additional geometry optimization was performed for H₃SiONMe₂ at the MP4SDQ/6-31G* level to test the effects of a more complete description of electron correlation. Vibrational frequency calculations were performed from analytic second derivatives at the SCF level of theory (MP2 for H₃SiONMe₂). Molecular geometries and absolute energies are reported in the tables and the Supporting Information.

Results and Discussion

Synthesis. The reaction of silicon tetrachloride with lithium *N,N*-dimethylhydroxylamide in *n*-hexane affords Si(ONMe₂)₄ (**1**) in 74% yield as a crystalline and sublimable material.



The identity of **1** was proved by elemental analysis, IR spectroscopy, nominal and high resolution mass spectrometry, and by NMR studies of the nuclei ¹H, ¹³C, ¹⁵N, ¹⁷O, and ²⁹Si. The ethyl analogue of **1**, Si(ONe₂)₄ (**2**), was also prepared by a similar route, although a different synthetic pathway to this compound has been described before.²⁷ At ambient temperature it is a liquid, which solidifies as a glass upon cooling and is difficult to purify by distillation due the occurrence of some decomposition at the boiling temperature (78 °C, 0.1 mbar).

NMR Spectroscopy. In the ²⁹Si NMR spectrum of **2** a resonance is found at -59.9 ppm, whereas that of **1** appears at a much lower frequency of -73.7 ppm, indicating a higher coordination number of the silicon center in **1** as compared to **2**. The difference can be attributed to the larger space required by the ethyl groups in **2** as compared to the methyl groups in **1**, thereby reducing the interaction between the nitrogen atoms and the silicon center in **2**. However, the ²⁹Si chemical shifts of **1** and **2** are not very different from those of the tetraalkoxides of silicon [Si(OMe)₄ -79.2, Si(OEt)₄ -82.4 ppm] and so do not provide definitive evidence for hypercoordination in solution.

The proton NMR spectrum of **1** shows only one sharp resonance, which remains unchanged upon cooling. This indicates that either the coordination of the NMe₂ group to the silicon atom is weak (< 30 kJ mol⁻¹) or the molecule adopts the maximum possible time averaged S₄ symmetry in solution. In contrast, the ¹H NMR spectrum of **2** shows a significantly broadened resonance for the methylene group at ambient temperature. By cooling a toluene solution of **2**, this resonance splits into two well-resolved doublets of quartets, whereas upon heating a single sharp quartet can be recorded. The coalescence temperature is ca. 20 °C (at 400 MHz proton frequency), providing us with an estimate of an equilibration barrier of ca. 59 kJ mol⁻¹. The diastereotopism of the methylene units is caused by the chirality of the helicoidally coordinated silicon atom, and the equilibration is equivalent to inversion of the chirality at silicon, which involves partial rotation of the ONe₂ groups about the Si-O and N-O bonds. Comparable systems have been discussed previously.²⁸ The magnitude of this

inversion activation energy is in the range observed for inversion of the nitrogen pyramids in comparable alkyhydroxylamines.²⁹

The ¹⁵N NMR spectra of **1** and **2** show resonances at -249.2 and -221.8 ppm, respectively, which are shifted toward higher frequencies as compared to the free hydroxylamines HONMe₂ and HONe₂ (-267.6 and -244.1 ppm respectively),³⁰ which are probably aggregated by H-bridges in solution, as has been shown for solid state OH-functional hydroxylamines by X-ray crystallography.^{31,32} In light of this comparison, the deshielding of the nitrogen nuclei in **1** and **2** is consistent with involvement of the nitrogen atoms in donor Si...N bonds, which should be stronger than the hydrogen bonds in the corresponding OH functional hydroxylamines.

Under high resolution conditions, the ¹⁵N NMR resonances of **1** and **2** are flanked by pairs of ²⁹Si satellites corresponding to *J*(²⁹Si¹⁵N) coupling constants of 1.8 and 2.7 Hz, respectively. Values for ²*J*(²⁹Si¹⁵N) are rarely found in the literature, and one example is a value of 5.0 Hz for (Me₃Si)(Cl₃Si)NSN(SiMe₃)-(SiCl₂SiCl₃).³³ However, the occurring of such a coupling has never been observed before in SiON systems, even not in an ultrahigh-resolution study of *N,O*-bis-(trimethylsilyl)hydroxylamine.³⁴ The observation of these couplings in **1** and **2** is therefore indicative of an unusual Si...N interaction, and the magnitude of these couplings is consistent with the range of values of ¹*J*(²⁹Si¹⁵N) for Si...N donor bonds in silatranes (0.1–3.4 Hz).³⁵

In contrast to the observed differences in the ¹⁵N chemical shifts of **1** and **2** as compared to those of the OH functional hydroxylamines, the ¹⁷O chemical shifts of both pairs of compounds are rather similar and nearly indistinguishable, considering the experimental uncertainties caused by the broadness of the resonances: **1** and **2** have resonances at 135 and 133 ppm, while HONMe₂ and HONe₂ resonate at 139 and 122 ppm, respectively (uncertainties ca. 3 ppm).³⁰

X-ray Crystallographic Analysis of **1 and the Isoelectronic Si(OⁱPr)₄.** Structural studies on compound **2** have not proved possible, because it is a liquid, which is difficult to purify and solidifies as a glass. However, we were fortunate to be able to crystallize compound **1** and successfully carry out the analysis of single crystal X-ray diffraction data. The crystals comprise monomers of **1** with no crystallographically imposed symmetry. However, the molecular geometry of **1** is close to C₂ symmetry (see Figure 1 and Table 1). The basic tetrahedral structure of the SiO₄ core is retained, but it is markedly distorted (four O-Si-O angles are ca. 106°, two are ca. 116°). The N-O bond lengths in **1** are 1.474 Å on average, which is about 0.02 Å longer than in the hydroxylamine HONMe₂ [1.452(2) Å].³²

Most intriguingly, the β -nitrogen atoms come close to the silicon center, leading to overall (4 + 4)-coordination. The conformations of the NMe₂ groups are such that the nitrogen lone pairs are oriented toward the silicon centers to maximize the interaction. The angles at the nitrogen atoms in **1** [ONC 104.1(3)–105.9(3)°, CNC 110.3(3)–111.1(3)°] are very similar to those of HONMe₂ in the solid state where the latter molecule is aggregated by hydrogen bonds in infinite chains [HONMe₂: ONC 104.8(2)–106.6(2)°, CNC 110.5(2)–110.6(2)°].³²

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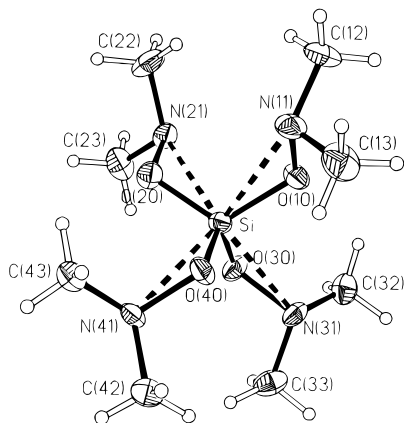
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Table 1. Selected Geometrical Parameter Values [Å/deg] of Si(ONMe₂)₄ (**1**) and Si(OⁱPr)₄ (**3**) as Determined by X-ray Crystallography

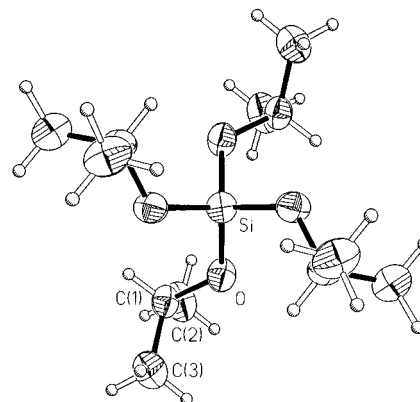
	Si(ONMe ₂) ₄ (1)	Si(O ⁱ Pr) ₄ (3)	
Si—O(10,20,30,40)	1.646(2), 1.637(2), 1.636(2), 1.636(2)	Si—O	1.615(1)
O(10,20,30,40)—N	1.471(3), 1.478(3), 1.474(3), 1.474(3)	O—C(1)	1.445(2)
N—C (range)	1.452(4)—1.460(4)	C(1)—C(2,3)	1.499(2), 1.507(2)
O(10)—Si—O(20,30,40)	116.4(1), 106.1(1), 105.7(1)	O—Si—O'	106.82(4)
O(20)—Si—O(30,40)	106.5(1), 106.1(1)	O'—Si—O''	114.91(8)
O(30)—Si—O(40)	116.4(1)		
Si—O—N(11,21,31,41)	110.0(2), 108.1(2), 107.7(2), 110.4(2)	Si—O—C(1)	124.7(1)
O—N—C (range)	104.1(3)—105.9(2)	O—C—C(2,3)	108.3(1), 108.4(1)
C—N—C (range)	110.3(3)—111.1(3)	C(2)—C(1)—C(3)	113.1(2)

**Figure 1.** Structure of **1** in the crystal. The thermal ellipsoids represent the 50% probability level, and hydrogen atoms are drawn as spheres of arbitrary size.

The average Si \cdots N distance is 2.537 Å, which is much shorter than the sum of the van der Waals radii of silicon and nitrogen (3.54 Å).³⁶ However, because the Si and N atoms are separated by only two bonds, the maximum distance between them is necessarily restricted to *ca.* 3.1 Å (if \angle SiON is 180°). A better parameter to describe the strength of an Si \cdots N interaction and to elucidate the bonding in this kind of compound is the SiON angle, the average of which is 109.1° for **1**. This is much more acute than in comparable compounds with Si—O linkages such as H₃SiOCH₃, where it is as large as 120.1(2)°.³⁷

It should be mentioned that in the related compound tetrakis(acetoximato)silane, Si(ON=CMe₂)₄, an angle of 111.9° has been found by crystallography.³⁸ In the compound bis(acetoximato)methylchlorosilane,³⁹ SiClMe(ON=CMe₂)₂, the SiON angles are even narrower than in Si(ON=CMe₂)₄ and comparable to those in **1**. Recent crystallographic studies of two *N,N*-bis(trimethylsilyl)-*O*-(organofluorosilyl)hydroxylamines showed these compound to have much wider SiON angles (117.6 and 120.5°) than **1**, probably because of steric repulsion and the reduced basicity of the silylated nitrogen atom.⁴⁰

In order to elucidate the nature of bonding in SiON linkages we wished to compare the structure of **1** with that of the isoelectronic tetraisopropoxysilane, Si(OⁱPr)₄ (**3**). We therefore also investigated the structure of **3**, which does not contain donor centers like the nitrogen atoms in **1**. As **3** is a liquid at ambient temperature, a crystal had to be grown by *in situ* techniques on the diffractometer. Molecules of **3** have crystallographic S₄

**Figure 2.** Structure of **3** in the crystal. The thermal ellipsoids represent the 50% probability level, and hydrogen atoms are drawn as spheres of arbitrary size.

symmetry and are present as monomers in the crystal. Only a few other related acyclic compounds containing the Si(OC)₄ core have been structurally elucidated: silicon(IV) acetate⁴¹ (**4**) and tetrakis(*N,N*-diisopropylcarbamato-*O*)silicon⁴² (**5**) and one organometallic compound containing a R₃COSi(OMe)₃ (**6**) unit.⁴³ In all of these compounds including **3** there is a similar distortion of the tetrahedral coordination sphere of silicon, with two OSiO angles being markedly compressed (107°) while four OSiO angles are widened (115°). A similar pattern is found for **1** (four of 106, two of 116°), indicating that this part of the structure is not markedly affected by the short Si \cdots N contacts. The Si—O bond length in **3** is 1.615(1) Å, which is in a well established range for this parameter (compare **4**: 1.624; **5**: 1.621 and 1.623 Å).

A comparison of the SiON angle in **1** with the corresponding SiOC angle in **3** enabled us to show that it is compressed by not less than 15.6° relative to the latter, which is as wide as 124.7(1)° and seems to be typical for such a structural unit. Compare the average angles in **4**: 125.7, **5**: 124.4, and **6**: 130.3°. According to the predictions of VSEPR theory⁴⁴ substitution of a CHMe₂ group by a more electronegative NMe₂ group might be expected to compress this angle slightly but by very much less than the observed difference of 15.6°.

Three major contributions to the magnitude of the SiON angle in **1** have to be considered: contraction caused by the attractive interaction of Si and N atoms (either by donor bond formation or electrostatic attraction); widening caused by negative hyperconjugation between p-type orbitals at oxygen and low-lying antibonding orbitals at the silicon center;⁴⁵ and widening caused

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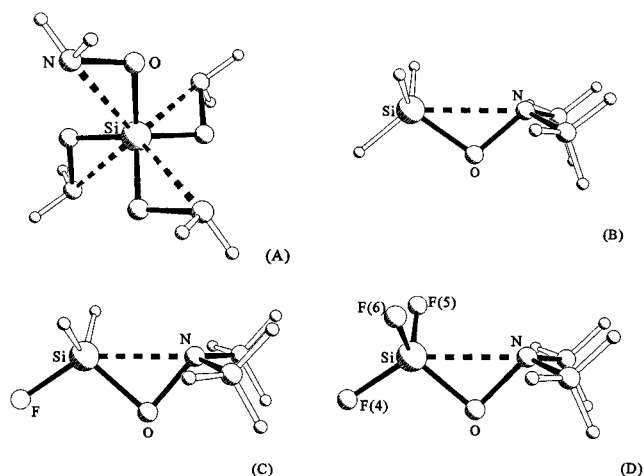


Figure 3. Calculated molecular structures of $\text{Si}(\text{ONH}_2)_4$ (A), $\text{H}_3\text{SiONMe}_2$ (B), $\text{FH}_2\text{SiONMe}_2$ (C), and $\text{F}_3\text{SiONMe}_2$ (D) at the MP2/6-311G** level of theory. See Table 2 for a comparison of relevant geometrical parameter values.

Table 2. Selected Geometrical Parameter Values for $\text{Si}(\text{ONH}_2)_4$, $\text{H}_3\text{SiONMe}_2$, $\text{FH}_2\text{SiONMe}_2$, and $\text{F}_3\text{SiONMe}_2$ Deduced from *ab Initio* Calculations at the MP2/6-311G** Level of Theory

	$\text{Si}(\text{ONH}_2)_4$	$\text{H}_3\text{SiONMe}_2$	$\text{FH}_2\text{SiONMe}_2$	$\text{F}_3\text{SiONMe}_2$
Si—O	1.656	1.682	1.679	1.642
O—N	1.448	1.459	1.465	1.478
Si—O—N	109.5	102.5	90.0	93.8
Si \cdots N	2.538	2.454	2.229	2.281
O—Si—O'	114.1			
O—Si—O''	114.2			
N—C	1.461		1.458	1.458
Si—H/F(4)	1.490		1.616	1.590
Si—H/F(6/5)	1.489		1.466	1.589
O—N—C	104.9		106.2	105.7
O—Si—H/F(4)	104.6		104.9	106.0
O—Si—H/F(4)	111.6		112.1	114.0

by the steric repulsion between the four NMe_2 groups at the SiO_4 core.

***Ab Initio* Calculations on Model Systems.** In order to distinguish between the contributions outlined above we performed a carefully graded series of *ab initio* calculations on the model system $\text{Si}(\text{ONH}_2)_4$ as well as on the simpler $\text{H}_3\text{SiONMe}_2$ and its electronegatively substituted fluoro derivatives $\text{FH}_2\text{SiONMe}_2$ and $\text{F}_3\text{SiONMe}_2$. Their calculated geometries are shown in Figure 3. Table 2 shows some important geometrical parameter values. In general, the quantum chemical results for systems containing Si—O—N linkages are sensitive to the theoretical method adopted, and high level calculations are necessary for a correct description. Simple SCF calculations tend to underestimate grossly the strength of the Si \cdots N interaction, giving angles which are much too large.

For the model compound $\text{Si}(\text{ONH}_2)_4$, which is the analogue of **1** without methyl groups, the introduction of polarization functions and electron correlation was crucial to obtaining realistic estimates for the SiON angles, in the range defined by the crystal structure of **1**. Our best estimate for this angle is 109.5° at the MP2/6-311G** level of theory, which is close to the magnitude found experimentally for **1** (109.1° on average), and indicates the absence of strong repulsive forces between the methyl groups and of significant distortions due to packing forces in the crystal. The strength of the Si \cdots N donor interaction in **1** is therefore not overestimated by the crystallographic results.

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The calculations on the model system $\text{Si}(\text{ONH}_2)_4$ also reproduce the C_2 symmetry, which was also found (approximately) for the skeleton of the parent compound **1**. Calculations with symmetry restrictions to D_{2d} and S_4 symmetry do not correspond to local minima on the potential energy hypersurface, as was shown by frequency calculations.

Markedly lower values for the SiON angle are predicted for $\text{H}_3\text{SiONMe}_2$, with our best estimate being 102.5° at the MP2/6-311G** level of theory (similar to that calculated for $\text{MeH}_2\text{SiONMe}_2$ at the MP2/6-31G* level³⁴). In comparison to this, the wider angle in $\text{Si}(\text{ONH}_2)_4$ can be explained by the competition of the four nitrogen donors for the silicon acceptor atom, which leads to a weaker coordination of each of the nitrogen donor centers. The coordination sphere of $\text{H}_3\text{SiONMe}_2$ can be described as (4+1)-coordinated, as also indicated by the different angles OSiH: those two hydrogen atoms which are close to the NMe_2 group have OSiH angles widened to 111.6° , whereas the position of the third hydrogen atom is defined by an angle of only 104.6° .

To gauge the effects of electron-withdrawing substitution at the silicon atom we calculated the structure for the fluoro-substituted compound $\text{FH}_2\text{SiONMe}_2$. The prediction for the SiON angle in this compound is as low as 90.0° at the MP2/6-311G** level of theory. This value is comparable to the TiON angles in $\text{Ti}(\text{ONMe}_2)_4$ which are $82.1(1)$ and $74.1(1)^\circ$ according to a crystal structure determination.¹² The OSiH angles in $\text{FH}_2\text{SiONMe}_2$ become as wide as 112.1° , whereas the OSiF angle is compressed to only 104.9° .

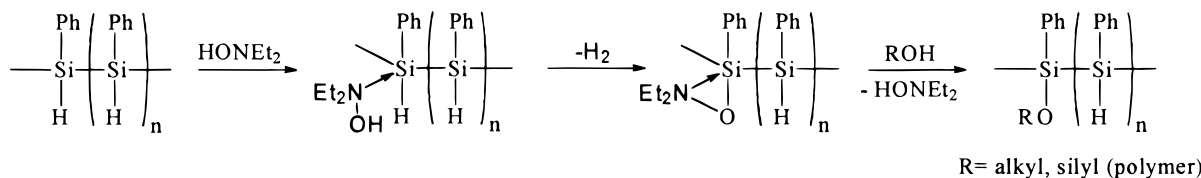
Going one step further, we calculated the structure of $\text{F}_3\text{SiONMe}_2$. Despite the presence of three electron withdrawing fluorine substituents at the silicon atom, the SiON angle is predicted to be slightly wider (93.8°) than in $\text{FH}_2\text{SiONMe}_2$. This can be rationalized by a subtle balance between the electron withdrawing effect, which should lead to a further compression of the SiON angle with more fluorine substituents at the silicon atom, and the increasing back-bonding exerted by more fluorine lone pairs of electrons, leading to a widening of the SiON angle by decreasing the electrophilicity of the silicon center. An alternative explanation is the greater steric demand of the F_3Si group as compared with the FH_2Si group.

Conclusions

By comparing the crystal structures of $\text{Si}(\text{ONMe}_2)_4$ and of the isoelectronic $\text{Si}(\text{OCHMe}_2)_4$ we have shown that the silicon atom in $\text{Si}(\text{ONMe}_2)_4$ is a (4 + 4) coordinate due to the β -donor interactions exerted from the nitrogen atoms of the NMe_2 groups. *Ab initio* calculations on the model compound $\text{Si}(\text{ONH}_2)_4$ support this finding. Calculations (up to MP2/6-311G**) on the simple model compound $\text{H}_3\text{SiONMe}_2$ show that the occurrence of Si—N— β -donor interactions is an inherent property of compounds containing the SiON unit. These interactions are stronger if electronegative substituents are bound to the silicon atom and amongst all the model compounds $\text{FH}_2\text{SiONMe}_2$ was predicted to that with the maximum strength of the Si—N— β -donor interaction.

The occurrence of Si—N— β -donor interactions is probably one of the reasons for the unique behavior of the class of *O*-hydroxylamidossilanes, $\equiv\text{Si—ONR}_2$: the partial five-coordination [or better (4+1)-coordination] can be expected to lead to a dramatic acceleration of nucleophilic substitution reactions at the silicon centers, as has been shown experimentally for a few systems before¹² and which has already found wide application in the silicone rubber industry.^{1,2} According to our experimental and theoretical findings, the "cold curing catalysts"

Scheme 2



used in the cross-linking step for silicone rubber production could be made more active if strongly electronegative elements are bound to their silicon atoms. However, the influence of different substituents R in the $\equiv\text{Si}-\text{ONR}_2$ unit have not yet been studied in great detail but can be expected to be an important contribution to the electronic properties of the nitrogen atom and thus for the strength of the $\text{Si}-\text{N}-\beta$ -donor interaction. Such investigations have to follow.

The β -donor bonding in SiON systems can also be seen as one contribution to the observed 1,2-dyotropic rearrangements of *N,O*-disilyl- and -germylhydroxylamines, which have been the subject of many investigations on the mechanisms involved.^{47,48}

The catalytic action of OH-functional hydroxylamines in the derivation of $\text{Si}-\text{H}$ functional polymers by hydrolysis and alcoholysis reactions, which was found recently,³ can be rationalized in terms of intermediate hypercoordination of silicon: As a first step, the hydroxylamine replaces the $\text{Si}-\text{H}$ hydrogen atom probably mediated by the donor bond formation of the hydroxylamine nitrogen atom toward the polymers silicon atom followed by the nucleophilic attack of the oxygen atom and the loss of hydrogen (Scheme 2). The replacement of the ONMe_2 groups by OR groups is then facilitated by the hypercoordination of silicon due to the presence of $\text{Si}-\text{N}-\beta$ -donor interactions. However, more experimental and theoretical work is needed in order to prove this mechanism and to understand the details more fully.

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Further studies on model systems involving β -donor bonding with a systematic variation of the electronic properties of the silicon and nitrogen centers will provide us with estimates about the facilitation of $\text{S}_{\text{N}}2$ reactions in these systems, with the promise of a broader application in synthesis. Numerous attempts to prepare the basic model system $\text{H}_3\text{SiONMe}_2$, which was discussed above have so far been unsuccessful, but further investigations are in progress. We have also started a study of the structure of **1** in the gas phase by electron diffraction in order to exclude the omnipresent effects of packing forces in crystals.

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Supporting Information Available: Tables of crystal data, atomic coordinates, equivalent isotropic thermal parameters and anisotropic thermal parameters for **1** and **3** and a complete data set of *ab initio* calculated parameters at different levels of theory for **6–9** (11 pages). See any current masthead page for ordering and Internet access instructions.

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