Stable *O,O′*-Bis(hydroxylamino)silanes $R_2Si(ONH_2)_2$ and Isomeric *N,N′*- and *O,O′*-Bis(silylhydroxylamino)silanes $R_2Si(NHOSiR_3)_2$ and $R_2Si(ONHSiR_3)_2$

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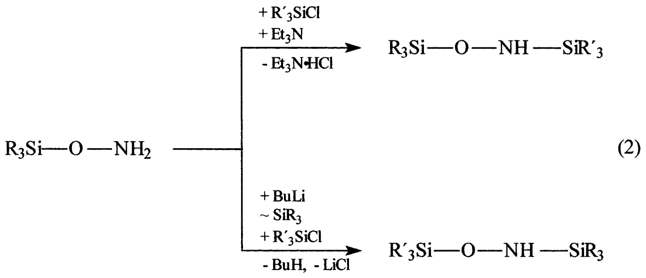
The first bis(hydroxylamino)silanes, $Me_3C(R)Si(ONH_2)_2$, R = Me (**1**), CMe_3 (**2**), are isolated from a two-phase reaction. They crystallize as dimers via NH···N bridges. In the reaction of the monosilylhydroxylamine Me_3SiONH_2 and the dichlorosilane $Me(Me_3C)SiCl_2$ the *N,N′*-bis(−*O*-trimethylsilyl-hydroxylamino)silane $Me(Me_3C)Si(NHOSiMe_3)_2$ (**4**) is obtained. Starting from **1**, it is now possible to synthesize the isomeric *O,O′*-bis(−*N*-trimethylsilyl-hydroxylamino)silane $Me(Me_3C)Si(ONHSiMe_3)_2$ (**5**). The results of the crystal structure analyses of **2** and **4** are reported. Quantum chemical calculations of the bis(hydroxylamino)silanes $Me_2Si(ONH_2)_2$ and $(Me_3C)_2Si(ONH_2)_2$ are reported and discussed with particular emphasis on conformational structure.

Introduction

Pioneering work on (organosilyl)hydroxylamines was performed by Wannagat[1] and West.[2] It was found that substitution by the first silyl group occurs at the oxygen atom, whereas in organyl hydroxylamines the organyl group is bonded to the nitrogen atom (eq 1).

$$2\,H_2NOH + R_3SiCl \longrightarrow H_2N{-}O{-}SiR_3 + HONH_2{\cdot}HCl \qquad (1)$$

Whether the second silyl group is again attached to the oxygen atom or to the nitrogen atom depends on the reaction pathway;[2−4] for example, the reaction of a *O*-silyl-hydroxylamine with a chlorotriorganylsilane leads—in the presence of Et_3N—to the bonding of the second silyl group to the nitrogen. However, starting with the lithium salt of the *O*-silylhydroxylamine, the new silyl group is bonded to the oxygen atom. This includes a silyl group migration from the oxygen to the nitrogen atom. Isomeric *N,O*-bis(silyl)hydroxylamines are preparable (eq 2).



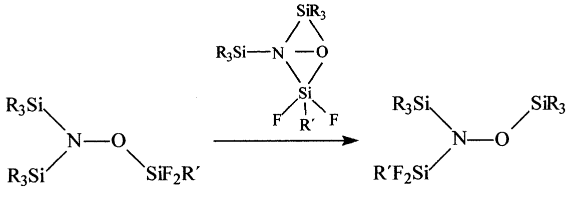
(2)

N,N,O-Tris(organylsilyl)hydroxylamines can be obtained from the *N,O*-bis(organylsilyl)hydroxylamines, butyllithium, and organohalosilanes.[2] In every case, the new silyl group is attached to the oxygen atom.[2,5] This again implies a 1,2-anionic silyl group migration from the oxygen to the nitrogen atom[3] and means that isomeric *N,O*- and *O,N*-bis(silyl)hydroxylamines form the same *N,N,O*-tris(silyl)hydroxylamine (eq 3). Although lithium(silyl)hydroxylamides have been successfully used in these reactions since the end of the 1960s, crystal structures of these compounds were described only recently.[6] Depending on the bulkiness of the substituents the lithium salts crystallize as four-, six-, or eight-membered Li−O rings (eq 3).

$$R_3Si{-}O{-}NH{-}SiR_3 \xrightarrow[-\,BuH]{+\,BuLi,\ \sim R_3Si} \tfrac{1}{n}\,[(R_3Si)_2NO{-}Li]_n \xrightarrow[-\,LiHal]{+\,HalSiR'_3} (R_3Si)_2N{-}O{-}SiR'_3 \qquad (3)$$

$$n = 2,3,4$$

O-Fluorosilyl-*N,N*-bis(organosilyl)hydroxylamines undergo an irreversible rearrangement with formation of the isomeric *N*-(fluorosilyl)-*N′,O*-bis(organosilyl)hydroxylamines[5,7] (eq 4).



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In summary, mono-, bis-, and tris(silyl)hydroxylamines and several structural isomers of bis- and tris-

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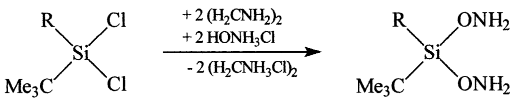
(silyl)hydroxylamines are known. It was found that no other class of compounds is comparably rich in isomerization reactions as silylhydroxylamines. Anionic, radicalic, and neutral silyl group migrations and silyl group insertions into the N−O bond have been described.[3,6−9] However, bis(hydroxylamino)silanes have not been isolated so far. Knowing that in contrast to carbon chemistry it is possible to stabilize compounds with two or three electronegative groups such as OH,[10] NH_2,[10] and PH_2[11] bonded to one silicon atom, we tried to prepare bis(hydroxylamino)silanes and report our recent results.

Results and Discussion

Experiments. Analogous to a method used by Bottaro,[12] 2 equiv of ethylenediamine is added to a suspension of 2 equiv of hydroxylamine hydrochloride in CH_2Cl_2 (eq 5). The principle of this reaction is the in situ release of $HO-NH_2$, which together with the HCl-acceptor base ethylenediamine forms a second phase above the heavier dichloromethane. The dialkyldichlorosilane is added dropwise to this phase at −30 °C and reacts with the hydroxylamine.



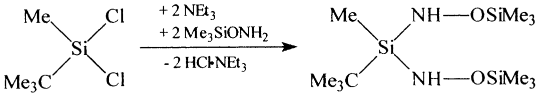
(5)

	1	2
R	Me	CMe_3

The chlorine atoms are substituted by ONH_2 groups. The bis(hydroxylamino)silane moves through the phase boundary and is protected against further reactions in the upper, basic phase.

Reaction temperatures above 0 °C promote side reactions. Above room temperature $(Me_3C)_2Si(OH)_2$ (**3**) emerges as a byproduct of the synthesis of **2**. $(Me_3C)_2Si(OH)_2$ is the longest known silanediol. Its synthesis was published by Sommer and Tyler in 1954,[10] and its crystal structure, space group *C*2/*c*, by Eaborn et al. in 1985.[13] Compound **3**, however, crystallizes in the orthorhombic space group *Ccca*.

***N,N*′- and *O,O*′-Bis(trimethylsilyl-hydroxylamino)silanes ($Me(Me_3C)Si(NHOSiMe_3)_2$ (4), $Me(Me_3C)Si(ONHSiMe_3)_2$ (5)).** Starting with hydroxylamine, the first silyl group attacks the oxygen atom. For that reason until now it was possible to prepare only *N,N*′-bis(−O-silylhydroxylamino)silanes, e.g., **4**, in the reaction of $Me(Me_3C)SiCl_2$ and Me_3SiONH_2 (eq 6). The synthesis of *O,O*′-bis(hydroxylamino)silanes now allows the preparation of isomeric *O,O*′-bis(−N-silyl-hydroxylamino)silanes, e.g., **5** (eq 7).



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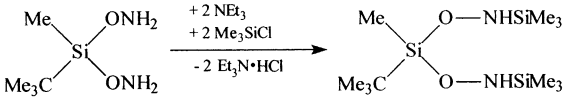

(7)

5

X-ray Structure Analysis of 2. Compound **2** forms a dimer via NH···N hydrogen bridges in the crystal (Figure 1). At 296.9° the nitrogen atoms show a remarkably small sum of angles. They exhibit a pyramidal environment. The Si−O−N angles amount to 112.3°. The nonbinding N···Si distances are found to be 260 pm, which is noticeable longer than those found and calculated in silylhydroxylamines methylated at the nitrogen atom.[14,15]

X-ray Structure Analysis of 5. Compound **5** crystallizes in the monoclinic space group $P2_1/n$ (Figure 2). In the solid state it forms a dimer via NH···O bridges. The nitrogen atoms show a tetrahedral environment. The sum of angles at N(1) is 327.9° and at N(2) 329.4°. The hydrogen atoms of the NH groups are in *trans* position to each other. The N−O bond lengths (147.9 and 146.8 pm) are shorter than the N−O bond length that was measured in a tris(silyl)hydroxylamine (150.5 pm).[16] The nonbinding distances Si(3)···N(1) and Si(1)···O(1) are measured at 262.3 and 259.4 pm. The orientation of the monomeric units to each other is found to be about 90°.

Quantum Chemical Study on the Conformation of $R_2Si(ONR'_2)_2$ Systems. In a recent interesting work, Mitzel and Losehand reported the existence of Si−N *β*-donor bonds in $H_3SiONMe_2$ and of even stronger *β*-donor interactions in $H_2Si(ONMe_2)_2$, where two such bonds are present.[17] In a subsequent paper,[15] the same authors gave an interpretation of the structure and the *β*-donor bonding in terms of a natural bond orbital (NBO) analysis. In particular, small Si−O−N angles have been found indicating the strong influence of *β*-donor interactions on molecular structure.

Obviously, the $Si-O-NH_2$ units reported in the present work should show similar effects. Since the *β*-donor bonding is interpreted in terms of delocalization of the lone electron pair at the nitrogen atom into an antibonding σ^* orbital of the polar Si−O bond, the *trans* conformation of the lone pair with respect to the SiO_2 unit is anticipated according to the results of ref 17. Surprisingly, in our study, the lone pairs at nitrogen are not in *anti* position to the Si−O bond. With respect to the planar N−O−Si−O−N structure[17] the amino groups are tilted out of the plane in the opposite direction.

To elucidate the structures of the $R_2Si(ONH_2)_2$ (R = Me, CMe_3) species, quantum chemical (density functional, DFT) calculations have been carried out. The structures of the stationary points on the potential energy hypersurface (PES) were fully optimized using

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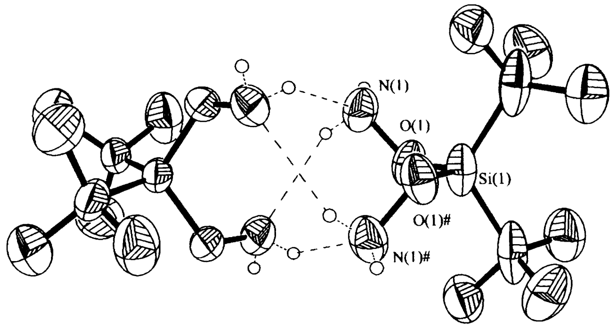

Figure 1. Crystal structure of **2**. Selected bond lengths [pm] and angles [deg]: Si(1)−O(1) 165.7(3), Si(1)−C(4) 199.4(8), O(1)−N(1) 147.0(6), O(1)#1−Si(1)−O(1) 112.3(2), H(1)−N(1)−O(1) 95.6, H(2)−N(1)−H(1) 94.3, H(2)−N(1)−O(1) 107.0, O(1)−Si(1)−C(4)#1 100.7(2), O(1)−Si(1)−C(4) 112.4(2), N(1)−O(1)−Si(1) 112.3(3).

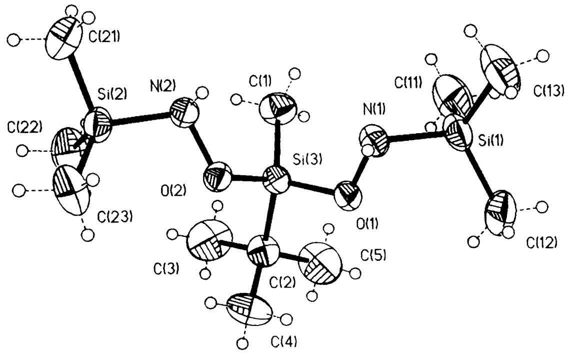

Figure 2. Crystal structure of **5**. Selected bond lengths [pm] and angles [deg]: Si(1)−N(1) 175.7(2), Si(3)−C(1) 184.6(3), Si(3)−O(1) 166.0(2), O(1)−N(1) 147.9(2), Si(3)−C(2) 187.9(3), Si(1)−O(1) 259.4(3), Si(3)−N(1) 262.3(2), N(1)−H(1) 81.6(5), N(1)−O(1)−Si(3) 113.3(1), O(1)−N(1)−Si(1) 106.2(1), H(1)−N(1)−Si(1) 115.9(3), H(1)−N(1)−O(1) 105.8(2).

Becke's three-parameter hybrid method with Becke's exchange functional[18] and the Lee, Yang, and Parr correlation functional[19] (B3LYP) as implemented in GAUSSIAN98.[20] It should be pointed out that Mitzel et al. have reported MP2/6-311G** calculations on the model compound $Si(ONH_2)_4$.[21]

First, the experimental dimer structure of $Me_2Si(ONH_2)_2$ was optimized employing B3LYP in conjunction with the 6-31+G(d) basis set, which includes a set of diffuse functions to properly account for the intermolecular interactions. The pertinent potential energy surface exhibits a large number of local minima. Here, we report only the obviously global minimum of the dimer which shows S_4 symmetry, in good agreement with the crystallographic result (data given in parentheses). The two amino groups in the monomers are in *trans* conformation with Si−O−N angles of 112.6° (112.3°). The O−Si−O angles are calculated to be 111.6° (112.3°). The four Si−O bond distances are 168.9 pm (165.7 pm), and the four O−N bonds amount to 145.8 pm (147.0 pm). The highly symmetric structure has four intermolecular N···H bridges with distances of 225 pm. In the dimer structures pertinent to other local minima, intermolecular O···H bonds are possible as well. However, the total number of intermolecular interactions is smaller than in the S_4 structure, with four intermolecular N···H bonds. For the planar N−O−Si−O−N monomer structure the formation of four N···H bonds upon dimerization is not possible.

Table 1. Energies of the Three Conformers 6a, 6b and 6c of $Me_2Si(ONH_2)_2$[a]

	E(**6a**)/E_h	E(**6b**) − E(**6a**)/ kcal mol^{-1}	E(**6c**) − E(**6a**)/ kcal mol^{-1}
B3LYP/6-31G(d)	−631.657443	−1.09	−1.49
B3LYP/6-311G(d,p)	−631.795602	−1.28	−1.74
B3LYP/6-311+G(2d,p)	−631.821690	−1.29	−1.68
MP2/6-31G(d)	−630.104279	−0.56	−0.84
MP2/6-311G(d,p)	−630.360195	−0.62	−0.94
MP2/6-311+G(2d,p)	−630.468625	−0.88	−1.12
ZPE correction B3LYP/6-31G(d)		0.04	0.10
ZPE correction MP2/6-31G(d)		−0.01	−0.02

[a] For details see the text. Absolute energies are given for **6a**, whereas relative energies are reported for **6b** and **6c**. Zero-point energy (ZPE) corrections (harmonic level) are given separately.

It is surprising that the structure of the $Me_2Si(ONH_2)_2$ monomers differs from the crystal structure and the MP2 results for $H_2Si(ONMe_2)_2$.[17] To answer the question whether the *trans* structure of the monomer is a consequence of the dimerization with the favorable situation of four N···H bonds, three possible conformations of each of the monomers $Me_2Si(ONH_2)_2$ (**6**), $(Me_3C)_2Si(ONH_2)_2$ (**2**), and $Me_2Si(ONMe_2)_2$ (**7**) have been investigated in detail: The planar N−O−Si−O−N structure (**a**), one O−N bond bent (**b**), and both nitrogen atoms tilted out of the O−Si−O plane (**c**).

The structures were calculated employing B3LYP and MP2 in conjunction with three different basis sets: 6-31G(d) (129, 243, and 205 contracted Gaussian-type orbitals (cGTOs) for **6**, **2**, and **7**, respectively), 6-311G(d,p) (194, 374, and 314 cGTOs), and 6-311+G(2d,p) (257, 491, and 413 cGTOs). To confirm that true minima on the PES were found, the Hessian matrices at the stationary points obtained at the B3LYP/6-31G(d) and, in addition, at the MP2/6-31G(d) level of theory were calculated. Results are given in Tables 1−3. B3LYP results for selected bond angles and torsional angles are reported in Table 4.

The structure with the two nitrogen atoms, the two oxygen atoms, and the silicon atom in one plane is a minimum on the PES for $Me_2Si(ONH_2)$ (Table 1). The two hydrogen atoms of the amino groups point away from the silicon center so that the lone electron pair is in *anti* position with the bond between the silicon and γ-oxygen atoms and in *syn* position with the bond between the silicon and the α-oxygen atoms.

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Table 2. Energies of the Three Conformers 2a, 2b, and 2c of $(Me_3C)_2Si(ONH_2)_2$[a]

	E(**2a**)/E_h	E(**2b**) − E(**2a**)/ kcal mol^{-1}	E(**2c**) − E(**2a**)/ kcal mol^{-1}
B3LYP/6-31G(d)	−867.515219	−2.30	−2.75
B3LYP/6-311G(d,p)	−867.714215	−2.63	−3.30
B3LYP/6-311+G(2d,p)	−867.742577	−2.53	−3.13
MP2/6-31G(d)	−865.089464	−2.30	−2.37
MP2/6-311G(d,p)	−865.524031	−2.37	−2.48
ZPE correction B3LYP/6-31G(d)		−0.01	−0.01

[a] For details see the text. Absolute energies are given for **2a**, whereas relative energies are reported for **2b** and **2c**. Zero-point energy (ZPE) corrections (harmonic level) are given separately.

Table 3. Energies of the Three Conformers 7a, 7b, and 7c of $Me_2Si(ONMe_2)_2$[a]

	E(**7a**)/E_h	E(**7b**) − E(**7a**)/ kcal mol^{-1}	E(**7c**) − E(**7a**)/ kcal mol^{-1}
B3LYP/6-31G(d)	−788.912832	−1.60	−0.64
B3LYP/6-311G(d,p)	−789.081188	−1.99	−0.93
B3LYP/6-311+G(2d,p)	−789.108441	−1.60	−0.65
MP2/6-31G(d)	−786.766710	−0.99	0.52
MP2/6-311G(d,p)	−787.128542	−1.18	0.002
MP2/6-311+G(2d,p)	−787.269404	−1.06	0.25
ZPE correction B3LYP/6-31G(d)		0.02	−0.03

[a] For details see the text. Absolute energies are given for **7a**, whereas relative energies are reported for **7b** and **7c**. Zero-point energy (ZPE) corrections (harmonic level) are given separately.

Table 4. Bond Angles (α(N−O−Si) and α(Si−O−N)) and Torsional Angles θ(N−O−Si−O) and θ(O−Si−O−N)) (in deg) of the Three Conformers of 6, 2, and 7[a]

	α(N−O−Si)	α(Si−O−N)	θ(N−O−Si−O)	θ(O−Si−O−N)
1a	108.5 (106.6)	108.5 (106.6)	180.0 (180.0)	180.0 (180.0)
1b	109.2 (107.3)	112.2 (111.3)	67.6 (68.8)	179.6 (178.3)
1c	112.3 (111.1)	112.3 (111.1)	62.5 (62.7)	62.5 (62.7)
2a	114.6 (113.0)	114.6 (113.0)	160.2 (161.2)	160.2 (161.2)
2b	112.9 (110.9)	114.4 (113.5)	63.9 (65.9)	172.8 (175.0)
2c	115.4 (114.4)	115.4 (114.4)	57.7 (61.6)	57.7 (61.6)
3a	109.0 (107.7)	109.0 (107.7)	180.0 (180.0)	180.0 (180.0)
3b	109.7 (108.7)	112.5 (111.6)	67.2 (65.9)	178.9 (175.0)
3c	114.1 (113.3)	114.1 (113.3)	72.3 (61.6)	72.3 (61.6)

[a] B3LYP/6-311+G(2d,p) results (values in parentheses: B3LYP/6-31G(d)). Note that for the sterically hindered system **2a** an exactly planar configuration of the N−O−Si−O−N skeleton is not possible ($\theta = 160°$)!

However, when one of the amino groups is tilted out of the N−O−Si−O plane, the energy is slightly lowered by 1.3 kcal mol^{-1} (B3LYP/6-311+G(2d,p)). MP2/6-311+G(2d,p) decreases this difference to 0.9 kcal mol^{-1}.

The energetic stabilization becomes even more pronounced when both amino groups are tilted out of the O−Si−O plane in opposite direction (**6c**). The energy with respect to the "planar" conformation is lowered by −1.7 kcal mol^{-1} (B3LYP/6-311+G(2d,p)) and −1.1 kcal mol^{-1} (MP2/6-311+G(2d,p)), respectively.

With regard to the small energetic differences we point out that all structures are fully optimized; that is, the results obtained with larger basis sets do not stem from single-point calculations. To gain further insight into the energetics, the zero-point energies have been calculated at the harmonic level. Conformers **6b** and **6c** are less stabilized by 0.04 and 0.10 kcal mol^{-1}, respectively. MP2 on the other hand, increases the differences by 0.005 and 0.02 kcal mol^{-1}. These vanishingly small differences are on the order of a few cm^{-1} and only quantitatively change the results. The zero-point energies of the three conformers are very similar since the structures do not markedly change.

When the methyl groups at the central silicon atom are substituted by *tert*-butyl groups (Table 2), the differences between the three structures **2a**−**c** show a trend in the same direction, that is even more pronounced. With one or two amino groups tilted out of plane, the conformers are stabilized by 2.5 and 3.3 kcal mol^{-1} according to the B3LYP/6-311+G(2d,p) calculations. The respective MP2/6-311+G(2d,p) results amount to 2.4 and 2.5 kcal mol^{-1}. Thus, MP2 predicts that the two structures with one or two amino groups tilted out of plane are almost isoenergetic. Here, the B3LYP zero-point energies increase the differences very slightly (0.008 and 0.006 kcal mol^{-1}). Note that an exactly planar N−O−Si−O−N structure is not possible for **2** due to sterical hindrance of the two *tert*-butyl groups.

In conclusion, the planar situation N−O−Si−O−N is the least stable conformation. Since this finding is surprising in view of previous data,[17] for completeness we performed calculations for species **6** with NMe_2 groups instead of NH_2 groups (Table 3). Compared to $Me_2Si(ONH_2)$ the stabilization by tilting out of plane of the dimethylamino group in $Me_2Si(ONMe_2)_2$ is even stronger (−1.6 kcal mol^{-1} at the B3LYP/6-311+G(2d,p) level, −1.1 kcal mol^{-1} at MP2/6-311+G(2d,p)). On the other hand, tilting of *both* dimethylamino groups out of the SiO_2 plane results in a lower stabilization energy at B3LYP (−0.7 kcal mol^{-1}) or even in destabilization (+0.25 kcal mol^{-1}) at the MP2 level of theory. Taking zero-point energy differences into account, both absolute energetic differences are slightly decreased. Mitzel and Losehand could give experimental evidence for a tilted conformation in $Cl_2Si(ONMe_2)_2$[22] but not for the systems reported in ref 17.

To rationalize the β-donor contribution, we have calculated second-order perturbative estimates of donor−acceptor interactions in the natural bond orbital (NBO) basis.[15] The stabilization energy associated with delocaliztion from donor NBO i into acceptor NBO j is given by $\Delta E_{ij} = q_i F_{ij}^2/(\epsilon_j - \epsilon_i)$, where q_i is the donor orbital occupancy, $\epsilon_{i,j}$ are the diagonal elements (orbital energies), and F_{ij} are the off-diagonal elements of the NBO Fock matrix.[23,24]

In the case of $Me_2Si(ONH_2)$, the lone pairs of the nitrogen atoms are delocalized in both Si−O σ^* orbitals with stabilization energies of 4.6 (Si−O(γ)) and 3.8 kcal mol^{-1} (Si−O(α)). In **6b**, the nitrogen lone pair that is in the SiO_2 plane is delocalized in the two Si−O σ^* orbitals (4.9 (Si−O(γ)) and 3.0 (Si−O(α)) kcal mol^{-1}), whereas the other nitrogen lone pair is delocalized in the Si−O(α) σ^* orbital ((2.6 kcal mol^{-1}) and in the Si−C σ^* orbital (3.0 kcal mol^{-1}). Obviously, the delocalization energy is smaller. In the case of **6c**, both nitrogen lone pairs are delocalized into the Si−C σ^* and Si−O(α) σ^* orbitals with stabilization energies of 2.9 and 2.5 kcal mol^{-1}, respectively.

The conclusion of the reported calculations is that β-donor bonding definitely plays a nonnegligible role,

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Table 5. Crystallographic Data for Compounds 2 and 5

	2	**5**
empirical formula	$C_{32}H_{88}N_8O_8Si_4$	$C_8H_{22}N_2O_2Si$
fw	825.46	308.66
cryst color	colorless	colorless
temp (K)	200(2)	203(2)
cryst size (mm)	0.9 × 0.8 × 0.8	0.8 × 0.6 × 0.4
cryst syst	tetragonal	monoclinic
space group	I4(1)/a	P2(1)/n
a (Å)	11.8677(17)	11.470(2)
b (Å)	11.8677(17)	32.857(5)
c (Å)	18.278(4)	11.517(2)
α (deg)	90	90
β (deg)	90	113.799(15)
γ (deg)	90	90
cell vol (Å^3)	25742(7)	3971.4(12)
Z	2	8
ρ_c (mg mm^{-3})	1.065	1.032
μ (mm^{-1})	0.162	0.238
F(000)	912	1360
2θ range (deg)	3.76−22.47	3.61−22.63
no. of data measd	3677, 841	9898, 5158
unique	($R_{\text{int}} = 0.1965$)	($R_{\text{int}} = 0.356$)
R,[a] wR2[b] ($I > 2\sigma(I)$)	0.0941, 0.2615	0.0372, 0.0910
R, wR2 (all data)	0.1021, 0.2724	0.0442, 0.1073
goodness of fit, S[c]	1.129	1.054
no. of refined params	71	358
largest diff peak/hole (e Å^{-3})	0.711/−0.281	0.253/−0.235

[a] $R = \Sigma||F_0| - |F_c|\Sigma|F_o|^{1/2}$. [b] $\text{wR2} = \{[\Sigma w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$. [c] $S = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma n - p)]\}^{1/2}$.

but it appears to be unlikely that it *completely* determines the structure of silylhydroxylamines. Rather, other electronic and steric effects considerably contribute to the overall conformation adopted by the molecule. In particular, the NBO theory cannot explain the energetic order of the conformers. For the systems studied in this work, the Si−O−N angles are almost tetrahedral (see Table 4) and not as small as found in refs 14 and 17. For the tilted O−N bonds, the angle is larger than the tetrahedral angle by about 4°. However, the structures of $H_2Si(ONMe_2)_2$, $ClH_2SiONMe_2$, and $F_3SiONMe_2$ are, as reported by Mitzel et al., clearly dominated by β-donor bonding with considerably smaller Si−O−N angles.

Conclusion

Starting from dichlorosilanes and hydroxylamine hydrochloride, bis(hydroxylamino)silanes were prepared in a two-phase reaction. They crystallize as dimers via NH···N hydrogen bridges. Short nonbinding N···Si distances (260 pm) were found in these compounds, which are in a good agreement with the distances calculated by quantum chemical methods. The monomers show interesting conformational behavior that has been discussed in detail.

Experimental Section

All reactions were conducted under an argon or nitrogen atmosphere. Mass spectra were taken on either a Varian CH5-spectrometer, a Finnigan MAT 8200-spectrometer, or a Finnigan MAT 95 spectrometer. NMR spectra were recorded in $CDCl_3$ (TMS) on either a Bruker AM 250, an MSL-400, or an AVANCE 500 DRX-spectrometer.

Synthesis of *tert*-Butylmethyl- and Di-*tert*-butyl-*O,O′*-bis(hydroxylamino)silanes (1, 2). A solution of 6.0 g of ethylenediamine (0.1 mol) and 6.9 g of hydroxylamine hydrochloride (0.1 mol) in 100 mL of CH_2Cl_2 was stirred for 6 h. The resulting two phases were treated with 9.2 g of *tert*-butylmethyldichlorosilane (0.05 mol) (**1**) or 10.7 g of di-*tert*-butyldichlorosilane (0.05 mol) (**2**) at −30 °C. Overnight the mixture was stirred and warmed to room temperature. $(H_2CNH_2{\cdot}HCl)_2$ was removed by filtration. Compounds **1** (6.2 g, 38 mmol, 76% yield) and **2** (6.2 g, 30 mmol, 60% yield) were isolated as crystals (mp 36 °C (**1**), 66 °C (**2**)) at room temperature.

$Me(Me_3C)Si(ONH_2)_2$ (1): ^1H NMR ($CDCl_3$) δ 0.28 [s, $SiCH_3$], 1.07 [s, $SiC(CH_3)_3$], 5.04 [s, ONH_2]; ^{13}C NMR ($CDCl_3$) δ −8.62 [s, $SiCH_3$], 18.56 [s, $Si\mathit{C}C_3$], 26.85 [s, $SiC\mathit{C}_3$]; ^{29}Si NMR ($CDCl_3$) δ 3.66; ^{15}N NMR ($CDCl_3$; $MeNO_2$, ext) δ −264.62. Anal. Calcd for $C_5H_{16}N_2O_2Si$ (164.1 g/mol): C, 36.60; H, 9.83. Found: C, 36.86; H, 10.02.

$(Me_3C)_2Si(ONH_2)_2$ (2): ^1H NMR (C_6D_6) δ 1.23 [s, CH_3], 4.81 [s, ONH_2]; ^{13}C NMR (C_6D_6) δ [s, 20.99 $\mathit{C}(CH_3)_3$], 28.57 [s, $C(\mathit{C}H_3)_3$]; ^{29}Si NMR (C_6D_6) δ [s, −4.09]; ^{15}N NMR (C_6D_6) δ [s, −263.51]; MS (EI) *m/z* [%]: 207 (8) [M^+,H], 149 (100) [M − C_4H_9]; IR (cm^{-1}) 3243.8, 3303 NH_2. Anal. Calcd for $C_8H_{22}N_2O_2Si$ (206.4 g/mol): C, 46.55; H, 10.74. Found: C, 46.68; H, 10.98.

Synthesis of *tert*-Butylmethyl-*N,N′*-bis(−O-trimethylsilyl-hydroxylamino)silane (4). To a solution of 8.2 g of **1** (0.05 mol) and 10.1 g of Et_3N (0.1 mol) in 50 mL of Et_2O is added 10.9 g of Me_3SiCl (0.1 mol) dropwise. $Et_3N{\cdot}HCl$ is removed by filtration. Crystals (mp 45 °C) of **4** (13.3 g, 43 mmol, 86% yield) were obtained by crystallization: ^1H NMR ($CDCl_3$) δ 0.16 [s, $Si(CH_3)_3$], 0.21 [s, $SiCH_3$], 0.97 [s, $SiC(CH_3)_3$], 4.97 [s, ONH]; ^{13}C NMR ($CDCl_3$) δ −8.85 [s, $Si\mathit{C}H_3$], 1.91 [s, $Si(\mathit{C}H_3)_3$], 18.42 [s, $Si\mathit{C}(CH_3)_3$], 26.49 [s, $SiC(\mathit{C}H_3)_3$]; ^{15}N NMR ($CDCl_3$) δ −265.0; MS (EI) *m/z* [%] 308 (10) [M^+], 251 (46) [M^+ − CMe_3]. Anal. Calcd for $C_{11}H_{32}N_2O_2Si_3$ (308.2 g/mol): C, 42.87; H, 10.46. Found: C, 43.03; H, 10.62.

Synthesis of *tert*-Butylmethyl-*O,O′*-bis(−*N*-trimethylsilyl-hydroxylamino)silane (5). To a solution of 10.5 g of Me_3SiONH_2 (0.1 mol) and 10.1 g of Et_3N (0.1 mol) in 50 mL of Et_2O is added 9.2 g of $Me_3C(Me)SiCl_2$ (0.05 mol) dropwise. $Et_3N{\cdot}HCl$ is removed by filtration. Compound **5** (8.6 g, 28 mmol, 56% yield) is purified by distillation (bp 48 °C (5 × 10^{-3} mbar)) in vacuo. $C_{11}H_{32}N_2O_2Si_3$: molecular weight = 308.2 g/mol, yield = 56%; ^1H NMR δ 0.11 [s, $Si(CH_3)_3$], 0.12 [s, $SiCH_3$], 0.94 [s, $SiC(CH_3)_3$], 5.02 [s, ONH]; ^{13}C NMR ($CDCl_3$) δ −9.53 [s, $Si\mathit{C}H_3$], −1.01 [s, $Si(\mathit{C}H_3)_3$], 17.95 [s, $Si\mathit{C}(CH_3)_3$], 26.83 [s, $SiC(\mathit{C}H_3)_3$]; ^{29}Si NMR ($CDCl_3$) δ 6.26 [s, SiN_2], 23.12 [s, SiO]; ^{15}N NMR ($CDCl_3$) δ −261.14. MS (70 eV) *m/z* (%) 308 (4) [M^+]; Anal. Calcd for $C_{11}H_{32}N_2O_2Si_3$ (308.2 g/mol): C, 42.87; H, 10.46. Found: C, 42.99; H, 10.53.

Crystal Structure Solution and Refinement for 2 and 5 (Table 5). Data for structures **2** and **5** were collected on a Stoe AED4II four-circle diffractometer by use of φ and ω scans. A semiempirical absorption correction was applied. All structures were solved by direct methods (SHELXTL[25]) and refined against F^2 using SHELXL-97. All non-hydrogen atoms were refined anisotropically. For the hydrogen atoms a riding model was employed.

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Supporting Information Available: Tables of crystal data, complete fractional coordinates, bond lengths and angles, and anisotropic displacement parameters of the structures **2** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030025H

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