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The Pyramidal Si_2N−O Skeleton of *O*-Methyl-*N*,*N*-disilylhydroxylamine: An Inherent Phenomenon As Confirmed by Structural Studies in Different Phases

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Abstract: *O*-Methyl-*N*,*N*-disilylhydroxylamine, $(H_3Si)_2NOCH_3$ (**1**), has been prepared by the reaction of bromosilane with O-methylhydroxylamine in the presence of 2,6-lutidine. The compound has been found to be reasonably stable at ambient temperature, but explodes if heated to 200 °C. **1** has been completely characterized by MS, HRMS, IR in the solid state and gas phase, and NMR spectra of the nuclei ^{1}H, ^{13}C, $^{14/15}$N, ^{17}O, and ^{29}Si. The NMR chemical shifts are compared with those of Si-methylated derivatives and with values obtained in high-level *ab initio* calculations. It has been concluded that there is close similarity between the structure in solution and the calculated one. A single crystal of **1** grown *in situ* and studied by X-ray diffraction is orthorhombic, space group $P2_12_12_1$, $a = 6.3664(11)$ Å, $b = 8.488(2)$ Å, $c = 11.783(4)$ Å, $\rho_{\text{calc}} = 1.119$ g cm^{-1}, $Z = 4$. Intermolecular Si···O interactions (2.92 Å) are found in the solid state structure leading to a zigzag type aggregation of the molecules. The gas phase structure of **1** has been determined by electron diffraction showing the molecule to have C_s symmetry. In both phases, the crystalline and the gas phase, the nitrogen atom configuration of **1** is pyramidal [$\sum$<(N) GED 351.8(12)°, XRD 352.8(3)°], showing this to be an inherent feature of *N*-silylated hydroxylamines and not caused by packing forces. Most of the geometrical parameters are consistent for both phases showing that the intermolecular Si···O interactions cause only minor structure distortions. The structural results are discussed in comparison with *ab initio* calculated geometries, and it is concluded that the exceptional nitrogen configuration is caused by repulsion between the nitrogen and oxygen lone pairs of electrons.

Introduction

The structural chemistry of group 14/nitrogen compounds is unique in several respects. The ZSi_3 cores in all compounds of the type $Z(R_3Si)_3$ (R = alkyl, aryl, H) are steep pyramids for Z = P, As, Sb, and Bi[1] but are completely planar for Z = N. Almost all NR_3 species (R = H, alkyl) exhibit a pyramidal configuration,[2] but silylated amines are generally planar.[3] This was originally established by Hedberg in 1951 [gas-phase electron-diffraction (GED) of $N(SiH_3)_3$],[5] and since then many investigations followed in order to explore the limitations of such general rules.[6]

In the course of these studies, some singly silylated nitrogen compounds with slightly pyramidal nitrogen coordination have been found. These include the systems $R_xSi(NH_2)_{4-x}$ (crystal structures for $x = 1-3$, R = bulky aryl group[7]) and $(CH_3)H_2SiN(CH_3)_2$,[8] $H_3SiN(CH_3)_2$,[9] and $ClH_2SiN(CH_3)_2$,[10] all studied by GED. Expansion of the coordination sphere of both the silicon and the nitrogen atoms has been observed in the crystal structures[9,10] of the last two of these.

The structures of numerous nitrogen compounds with *two Si substituents* have been elucidated, but only two examples of nonplanar nitrogen coordination have been found to date: a (bis(trimethylsilyl)amino)diazaphosphene[11] and *O*-methylbis(*p*-tolylsilyl)hydroxylamine.[12] In both cases, nitrogen is bound to an atom with high effective nuclear charge. The question therefore arises of whether the nonplanarity in those systems is induced by the high effective nuclear charge of the bonding partner, caused by lone pair repulsions or simply the result of packing forces in the crystal. The latter seems not unlikely, as some silylated nitrogen atoms have been shown to have low inversion barriers.[13]

In essence, nitrogen configuration in silylated nitrogen compounds has to be treated in terms of the potential function for nitrogen inversion. Si_3N cores have one distinct minimum, Si_2NX species show a more shallow potential, $SiNX_2$ com-

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pounds have a very shallow potential or even two minima separated by a low inversion barrier, whereas NX_3 skeletons generally show a high barrier to inversion. Therefore, the molecules Si_2NX, but particularly $SiNX_2$, are floppy. They can be distorted by weak forces, which may be electronic or steric in nature or arise from packing forces in the solid state.

In this paper we try to answer the question: Why is the Si_2NO skeleton pyramidal? We chose *O*-methyl-*N*,*N*-disilylhydroxylamine (**1**), $(H_3Si)_2NOCH_3$, one of the simplest molecules containing this fragment, and studied its structure in the gas phase, in the solid state, and in solution and compare these findings with the results of previous studies by *ab initio* methods.[14]

Experimental Section

General Methods and Equipment. All reactions were carried out in a grease-free vacuum line.[15] 2,6-Lutidine was dried over CaH_2 and distilled prior to use. O-Methylhydroxylamine was liberated from its hydrochloride by concentrated NaOH solution, distilled, dried over NaOH then over BaO, and distilled from 3 Å molecular sieves prior to use. Bromosilane was prepared according to a literature procedure,[15] carefully distilled, and stored at −196 °C. MS: Hiden HAL quadrupole MS. HRMS: KRATOS MS50TC. NMR: Bruker AM360 (^{14}N, ^{15}N, ^{17}O) and Bruker AC250 (^1H, ^{13}C); samples were dissolved in C_6D_6 (dried over K/Na and distilled), references: solvent for ^1H and ^{13}C NMR, external references for ^{14}N, ^{15}N ($MeNO_2$), and ^{17}O (H_2O). IR: Perkin Elmer 1650 FT-IR.

***O*-Methyl-*N*,*N*-disilylhydroxylamine (1):** *O*-Methylhydroxylamine (0.71 g (15 mmol) and 3.25 g (30 mmol) of 2,6-lutidine were placed in a reaction flask, which was then evacuated and cooled in liquid nitrogen. Bromosilane (30 mmol) was condensed onto the mixture which was then warmed to −60 °C for 1 h. Ater warming to −30 °C all volatile material was condensed into a trap and then purified by repeated trap-to-trap distillation. The product stopped at −95 °C. ^1H-NMR: δ 3.24 (s, 3H, ^1J(C,H) 142 Hz, H_3C), 4.4 (s, 6H, ^1J(Si,H) 215 Hz). $^{13}C\{^1H\}$-NMR: δ 62.1. $^{14}N\{^1H\}$-NMR: δ −262. $^{15}N\{^1H\}$-NMR: δ -261. $^{17}O\{^1H\}$-NMR: δ 61. ^{29}Si-NMR: δ −50.9 (qq, ^1J(Si,H) 215 Hz, ^3J(Si,H) 2 Hz). MS (EI, 40 eV): 107, 92, 76, 74, 46, 31. HRMS (EI, 70 eV): m/z = 107.02238; calcd for CH_9OSi_2 107.02227. IR: (solid state, liquid N_2 temperature) ν [cm^{-1}] 2960 (w), 2933 (w), 2215 (m), 2162 (vs), 1460 (w), 1431 (w), 1085 (m), 1048 (m), 1025 (w), 997 (w), 979 (m), 946 (s), 906 (vs), 762 (m), 749 (m), 709 (m); (gas phase, ambient temperature) ν [cm^{-1}] 2998(w, νCH), 2948 (w, νCH), 2904 (w, νCH), 2178 (vs, νSiH), 2073 (vw), 1470 (w, δH_3C), 1441 (w, δH_3C), 1182 (w), 1140 (w), 1039 (m, νNO, ν_{as}SiNSi), 964 (s, δH_3Si), 935 (vs, δH_3Si), 713 (m), 562 (w), 432(w). Calculated IR frequencies (MP2/6−31G*, scaled by a factor of 0.9): 2982 A′, 2959 A″, 2897 A′, 2165 A′, 2158 A′, 2154 A″, 2149 A″, 2143 A′, 2138 A″, 1493 A′, 1471 A″, 1456 A′, 1206 A′, 1170 A″, 1123 A′, 1000 A″, 988 A′, 959 A′, 956 A″, 948 A′, 931 A″, 931 A′, 921 A″, 726 A′, 713 A′, 672 A″, 626 A″, 540 A′, 396 A′, 280 A″, 184 A′, 171 A″, 166 A′, 139 A″, 123 A″, 119 A′.

Electron Diffraction Experiments. Electron scattering intensity data for **1** were recorded on Kodak Electron Image plates using the Edinburgh gas diffraction apparatus.[17] The sample of **1** was maintained at −25 °C and the inlet nozzle was held at ambient temperature (293 K) during the experiments. Scattering data for benzene were recorded concurrently and used to calibrate the camera distance and electron wavelength, which were 285.90 mm and 0.05677 Å for the long camera distance and 128.24 mm and 0.05669 Å for the short camera distance, respectively. Three plates were taken at each camera distance. Data were obtained in digital form using the Joyce Loebl MDM6 microdensitometer[18] at the EPSRC Daresbury Laboratory. The data analysis followed standard procedures, using established data reduction[18] and least-squares refinement programs[19] and the scattering factors established by Fink and co-workers.[20] The following data range, interval, and weighting points (trapezoidal weighting function) were used in the refinement: s_{min} = 2.0 $Å^{-1}$, s_{max} = 14.4 $Å^{-1}$, Δs = 0.2 $Å^{-1}$, sw_1 = 4.0 $Å^{-1}$, sw_2 = 12.2 $Å^{-1}$ for the long camera data; s_{min} = 10.0 $Å^{-1}$, s_{max} = 32.0 $Å^{-1}$, Δs = 0.4 $Å^{-1}$, sw_1 = 14.0 $Å^{-1}$, sw_2 = 26.8 $Å^{-1}$ for the short camera data. The scale factors refined to 0.756(5) and 0.680(30) for long and short camera data, respectively.

Crystal Structure Determination. A cylindrical crystal (>0.8 mm long, 0.5 mm diameter) was grown from the melt in a capillary mounted on a Stoe Stadi-4 diffractometer with an Oxford Cryosystems low-temperature device.[21] CH_9NOSi_2: orthorhombic, space group $P2_12_12_1$, a = 6.3664(11) Å, b = 8.488(2) Å, c = 11.783(4) Å, V = 636.7(3) $Å^3$, Z = 4, ρ_{calc} = 1.119 Mg m^{-3}, $2\Theta_{max}$ = 55.0°; MoKα, λ = 0.71073 Å, T = 110.0 K; 2018 reflections, 874 independent, R_{int} = 0.104; no absorption correction; solution by Direct Methods (G. M. Sheldrick, Universität Göttingen, SHELXS 86), refinement of 83 parameters on F^2 (G. M. Sheldrick, Universität Göttingen, SHELXL-93), all H atoms located and refined isotropically, R = 0.0332, R_w = 0.0673 for 871 reflections with $I > 2\sigma(I)$, Goodness-of-fit (on F^2): 1.037, residual electron density 0.46 and −0.41 e $Å^{-3}$.

Results and Discussion

Compound **1** has been prepared by the reaction of bromosilane with *O*-methylhydroxylamine in the presence of a base. The choice of the right auxiliary base is crucial: using tetramethylethylenediamine, successfully employed in the syntheses of similar compounds,[22] or an excess of O-methylhydroxylamine led to almost complete decomposition of the bromosilane, probably induced by adduct formation. These problems could be overcome by using 2,6-lutidine as a base, giving excellent yields.

$$2H_3SiBr + H_2NOCH_3 \xrightarrow[-2HBr]{(2,6\text{-lutidine})} (H_3Si)_2NOCH_3$$

Compound **1** is highly air-sensitive. Although not pyrophoric in dry air, it ignites in air upon contact with traces of moisture. It seems to be stable for a few days at ambient temperature, but decomposes explosively upon heating to about 200 °C.

The absence of peaks higher than m/z = 107 in the mass spectra of **1** showed it to be monomeric in the gas phase. Higher aggregation in the solid state could be ruled out, as the vibrational spectrum of **1** in the gas phase is very similar to that in the annealed solid state. Generally, the bands in the gas-phase spectrum are about 10 to 30 cm^{-1} higher in wavenumbers than the corresponding ones in the solid state spectrum. The ν(CH) stretching modes of **1** are of surprisingly weak intensity as compared with the ν(SiH) modes.

The proton NMR spectrum of **1** shows two resonances: one at 3.24 ppm corresponding to the methyl protons with ^{13}C satellites 142 Hz apart from another, and the other one at 4.40 ppm corresponding to the silyl protons, which shows satellites arising from the coupling to the ^{29}Si nucleus. The ^1H-coupled ^{29}Si spectrum confirms the presence of a $(H_3Si)_2N$ group by the coupling pattern, which is a quartet of quartets (^1J(SiH) = 215 Hz, ^3J(SiNSiH) = 2 Hz). The chemical shifts of all

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Table 1. Experimental NMR Parameters of **1** and Chemical Shifts Calculated[15] at Different Levels of Theory (the Calculations Are Based on a MP2/6-31+G* Geometry)

	exptl	GIAO/MP2/tzp/dz	GIAO-SCF/tzp/dz	IGLO(II')
$\delta(^{13}C)$	62.1	66.4	59.0	61.2
$\delta(^{14}N)$	−262			
$\delta(^{15}N)$	−261	−267	−279	−292
$\delta(^{17}O)$	61	54	13	−8
$\delta(^{29}Si)$	−50.9	−56.6	−48.8	−48.9

Table 2. Structural Parameters of **1** Obtained by Gas-Phase Electron Diffraction (ED), Single-Crystal X-ray Diffraction (XRD), and *ab Initio* Calculations (Distances in Å, Angles in deg, Estimated Standard Deviations In Parentheses)

	GED $r_\alpha/\angle_\alpha$	XRD r	MP2/6-31+G* r_e
Si−N	1.728(1)	1.735(2) 1.734(2)	1.763
N−O	1.449(13)	1.458(2)	1.474
C−O	1.414(13)	1.415(3)	1.436
Si−H	1.439(6)	1.39[a]	1.484[a]
C−H	1.097(8)	0.94[a]	1.094[a]
∠Si−N−Si′	131.8(2)	132.6(1)	130.3
∠Si−N−O	110.0(6)	110.6(1) 109.6(1)	107.0
∠N−O−C	109.1(4)	109.0(2)	107.7
$\angle NOC/Si_2N$	90[b]	89.7(1)	90
Σ∠(N)	351.8(12)	352.8(3)	344.3
$\angle NO/Si_2N$	33.2(25)	31.3(2)	37.7

[a] Average values. [b] Fixed.

heteronuclei, ^{13}C, ^{14}N, ^{15}N, ^{17}O, and ^{29}Si (Table 1), fit well in the established ranges of resonances for such compounds.[22]

There is a common trend of the chemical shifts of the ^{29}Si, ^{15}N, $^{13}C(CO)$, and both ^{1}H nuclei in the series of compounds $(H_3Si)_2NOMe$ (**1**), $(MeH_2Si)_2NOMe$,[14] and $(Me_2HSi)_2NOMe$.[22] The values for the chemical shifts are as follows: $\delta(^{29}Si)$ −50.9, −29.4, −10.9; $\delta(^{15}N)$ −261, −248, −234; $\delta(^{13}C)$ 62.1, 63.0, 64.2; $\delta(^{1}H, HSi)$ 4.40, 4.46, 4.58; $\delta(^{1}H, OMe)$ 3.24, 3.39, 3.44 ppm, respectively. This corresponds to a high-frequency shift depending on the degree of methylation at the silicon atoms. The reverse trend is observed for the atom with the highest effective nuclear charge in these compounds, oxygen, and for $\delta(^{17}O)$ the corresponding series of values has been found to be 61, 58, and 51 ppm, respectively.

As shown in Table 1, the chemical shifts $\delta(^{13}C)$, $\delta(^{15}N)$, $\delta(^{17}O)$, and $\delta(^{29}Si)$ of **1** obtained in C_6D_6 solution are in excellent agreement with values calculated by various *ab initio* methods.[14] This indicates a close similarity between the molecular structure in solution and the calculated MP2(fc)/6-31+G* geometry (see Table 2). The data show that the IGLO-(II′) and GIAO-SCF/tzp-dz methods give reliable values for the chemical shifts of ^{13}C and ^{29}Si, but the highest level of theory applied here (GIAO-MP2/tzp-dz) is necessary to reproduce the $\delta(^{15}N)$ and $\delta(^{17}O)$ values.

Crystal Structure Analysis of 1. An X-ray diffraction analysis has been performed at 110 K with a single crystal (mp 189 K), which was grown *in situ* on the diffractometer. The bond lengths and angles are listed in Table 2 and a plot of the molecular geometry is given in Figure 1. This shows the Si_2-NO skeleton to be nonplanar, as has already been observed for the *p*-tolyl derivative of **1** in the solid state.[12]

A crystal packing plot of **1** is shown in Figure 2. It is mainly the intermolecular Si···O interaction (see also Figure 1) that dominates the arrangement of the molecules. The distance Si···O of 2.92 Å is very much shorter than the sum of the van der Waals radii of Si and O (3.62 Å). The Si···O vector is very close to the bisector of the N−O−C angle of **1** and almost parallel to the Si−N bond. The total *inter-intra*molecular coordination of the oxygen atom is completely planar. Similar findings of a planar coordination environment of oxygen and a zigzag-chain-like aggregation have been reported for $(H_3Si)_2O$[23] [r(Si···O) = 3.115(5) Å] and H_3SiOCH_3[24] [r(Si···O) = 2.847(2) Å]. As in these cases, the direction of the donor bond in **1** implies that the donating lone pair at the oxygen atom has sp^2-character (see also below and Figure 5). This has also been concluded for the systems $(H_3Si)_2O$ and H_3SiOCH_3 and rationalized in terms of a $p \rightarrow \sigma^*$ interaction between the oxygen lone pair and Si−H antibonding orbitals.[6,14] However, this argument cannot be used to explain the situation in **1**, as there are only first-row elements directly bound to oxygen and at present we cannot offer a simple explanation for this type of interaction. In a related case, the adduct of dimethyl ether to

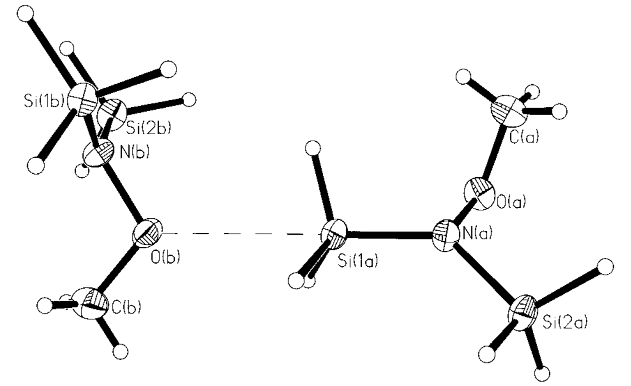

Figure 1. Two molecules of **1** in the crystal showing the intermolecular Si···O interaction. The atoms N(b), O(b), and C(b) lie in the plane of the paper, the atom Si(1a) 0.060 Å above it. Nonhydrogen atoms are plotted as thermal ellpsoids at the 50% probability level and the hydrogen atoms are shown as circles of arbitrary size.

Table 3. Selected Distances (r_a/Å) and Vibrational Amplitudes (u/Å) from the GED Refinement of **1**

	r_a	u
r_1(N−Si)	1.736(1)	0.045(2)
r_2(O−N)	1.454(13)	0.055(4)
r_3(O−C)	1.429(13)	0.052 (tied to u_2)
r_4(Si···Si)	3.154(2)	0.088(3)
r_5(O···Si)	2.607(2)	0.095(2)
r_6(N···C)	2.342(4)	0.056(5)
r_7(Si···C)	3.421(3)	0.125(4)
r_8(Si−H)	1.486(6)	0.077[a]
r_9(C−H)	1.137(8)	0.083(7)
r_{10}(O···H)	2.078(10)	0.110[a]
r_{11}(N···H)	2.629(5)	0.130[a]
r_{12}(Si−H)	3.786(5)	0.256[a]
r_{13}(Si−H)	4.269(6)	0.118[a]
r_{14}(Si−H)	3.489(5)	0.223[a]

[a] Fixed.

Table 4. Correlation Matrix (×100) for the GED Refinement of **1** (Only Elements with Absolute Values Greater Than 50 Are Listed)

	r(Si−H)	r(Si−N)	r(CO/NO)	Δr(CO/NO)	u_1	u_4	u_5
r(Si−H)	100		−88				
<(ONSi)				−97			
<(SiNSi)		−61					
<(NOC)	66		−71				
u_2				−51			
u_5					54		100
u_8						57	
k_2					89		59

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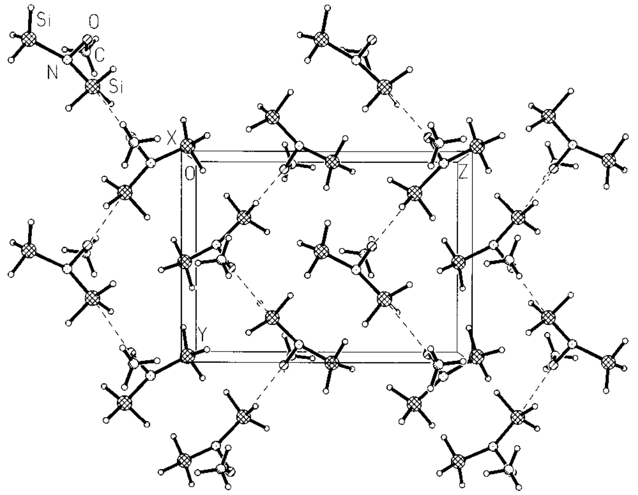

Figure 2. The packing of molecules of **1** in the crystal, viewed along (100) and showing the intermolecular O···Si contacts.

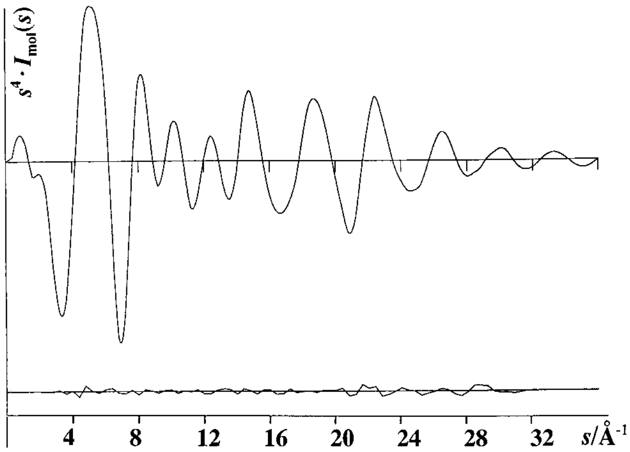

Figure 3. Observed and final weighted difference combined molecular-scattering intensity curves for the GED study of **1**. Theoretical data are shown for the regions 0−2 and 32−36 Å^{-1}, for which no experimental data are available.

silyl chloride,[25] the oxygen atom adopts a pyramidal configuration, clearly indicating sp^3 hybridization.

It is interesting that, despite the pyramidal configuration of the nitrogen atom in **1**, it seems to be less basic than the oxygen atom, resulting in the formation of Si···O rather than Si···N contacts. The intermolecular Si···O contact leads to a slight distortion of the Si_2NO skeleton indicated by the two different Si−N−O angles of 110.6(1) and 109.6 (1)°. Other structural details are discussed in comparison below.

Gas-Phase Electron-Diffraction Analysis of 1. A gas-phase electron-diffraction study of **1** has been performed in order to see whether the nitrogen atom configuration is truly pyramidal, *i.e.* without the potentially distorting crystal packing forces, which have been shown (see above) to play a significant role in crystals of compound **1**.

The radial distribution curve (RDC) derived by Fourier inversion of the experimental gas-phase electron diffraction intensities (Figure 3) is shown in Figure 4. It exhibits four resolved peaks, one corresponding to the three similar bond distances r(C−O), r(N−O), and r(Si−H), and the three others corresonding to the bond distance r(Si−N), the nonbonded distance r(Si···O), and the distance r(Si···Si). Various structural models have been tested to fit the experimental intensities. The best one includes a pyramidal nitrogen configuration and a *trans* conformation of the OC bond *vs* the bisector of the SiNSi angle. Models which deviate from C_s symmetry are less satisfactory. The following constraints were applied in the least-squares refinement: overall C_s symmetry, local C_{3v} symmetry for CH_3 and SiH_3 groups. In order to get a realistic estimate of errors for the similar N−O and C−O distances, the usual procedure of refining a mean value with a fixed difference d(NO)−d(CO) was not followed. Instead, this difference was included in the GED analysis as a flexible constraint (0.043(12) Å) derived from the crystal structure and both the effective C−O and N−O distances could then be refined. This procedure gives more realistic estimates of uncertainties in the distances. Vibrational amplitudes (u) which could not be refined and perpendicular amplitude corrections (K) were set at values calculated from an *ab initio* force field (MP2/6-31+G*) using the program ASYM40.[26] The structure was then refined as an r_α geometry to account for the effects of perpendicular motions (shrinkage effect). In the late stages of the refinements, the conformations of the H_3Si groups were also shown to agree with C_s symmetry, rather than local C_2 symmetry of the $(H_3Si)_2N$ group, which would lead to C_1 symmetry for the whole molecule. The geometry of the structure obtained in the final refinement, which converged with $R_G = 5.21\%$ ($R_G = 3.7$ and 10.0% for the long and short camera distance data, respectively), is in excellent agreement with that obtained by crystal structure analysis (Figure 1). Bond lengths and angles are listed in Table 2 together with those obtained from the crystal structure and previously published theoretical data.

The *trans* conformation of the hydroxylamine skeleton is confirmed by theory and by the experiments relating to different phases. Even in the gas phase at ambient temperature, there is no evidence from the GED data for a second conformer.

The sum of bond angles describing the coordination geometry of nitrogen is 351.8(12)° in the gas phase and 352.8(3)° in the crystal, corresponding to declinations of the N−O vectors from the Si_2N planes of 33.2(25) and 31.3(2)°, respectively. The extremely wide Si−N−Si angle and the Si−N−O angle are both underestimated by theoretical methods which give the sum of angles at nitrogen as 344.3°.

A comparison of the gas-phase structural data for Si−N−Si angles in the series of compounds $(H_3Si)_2N-CH_3$[27] [125.4(4)°], $(H_3Si)_2N-H$[28] [127.7(1)°], $(H_3Si)_2N-N(SiH_3)_2$[29] [129.5(7)°], and $(H_3Si)_2N-OCH_3$ (**1**) [131.8(2)°] gives some information about the influence of the electron-withdrawing properties of the nitrogen substituents X on this parameter. The observed values can be explained by VSEPR theory in the context of the maximum electron density along the N−X bond, which is shifted from N to X in the series discussed. Surprisingly, the Si−N−Si angle in **1** is the widest of these angles, despite the pyramidal nitrogen configuration (the other compounds have planar nitrogen environments), and the Si−N−O angle has thus to be as small as 110.0(6)° (ED). One might expect the Si−N bond length in **1** to be shorter than those in the other members of the above series, because of the formally different hybridization of the nitrogen atom (between sp^2 and sp^3), but the Si−N bond lengths are all the same within the limits of error [values: 1.726(3), 1.725(3), 1.731(4), and 1.728(1) Å].

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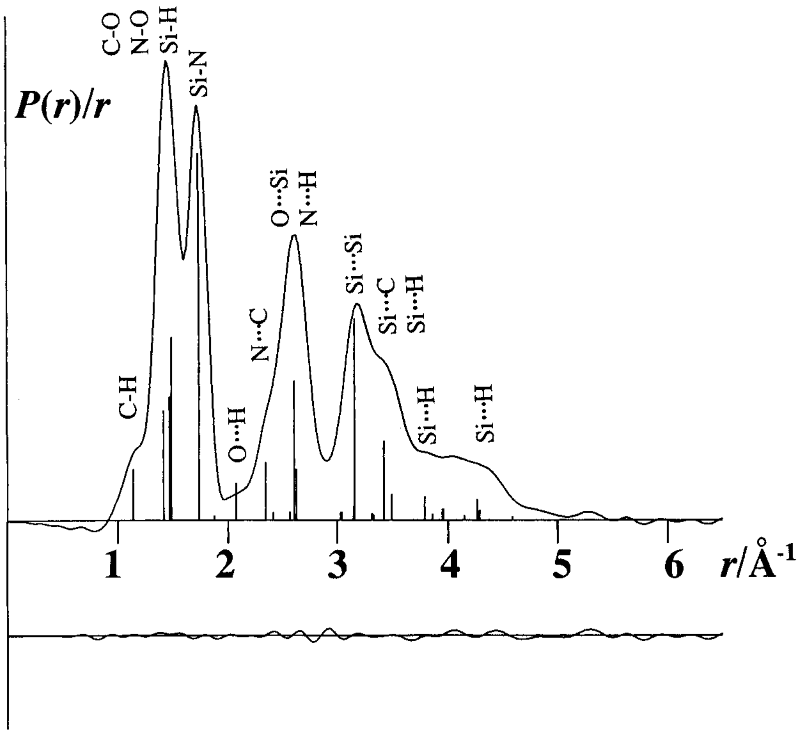

Figure 4. Observed and final weighted difference radial distribution curves for **1**. Before Fourier inversion the data were multiplied by $s\ \exp[(-0.002s^2)/(Z_N - f_N)/(Z_{Si} - f_{Si})]$.

All the other main structural parameters (bond lengths N−O and C−O and angle N−O−C) are very consistent between the gas phase and the solid state and are also well predicted by theory. This is particularly remarkable, as N−O distances are often difficult to calculate to a high degree of accuracy.[30] However, comparison with the N−O distances in other hydroxylamines [$(CH_3)_2NOH$ 1.448(11) Å[31] and H_2NOCH_3 1.463(3) Å[32]] studied in the gas phase adds support to the reliability of the N−O distance determined for **1** [1.449(13) Å].

The close similarity of the crystal and gas-phase structures indicates the absence of geometrical distortion due to packing forces in the crystal (the intermolecular Si···O interactions are clearly too weak to cause distortions) and therefore shows the pyramidal Si_2NO core to be an inherent feature of this class of compounds. The obvious reason for this is the repulsion between the nitrogen and oxygen lone pairs, which is minimized by mixing s-character into the nitrogen lone pair. This leads to the observed deformation to a nonplanar structure, the distortion being facilitated by the generally shallow nitrogen inversion potential of Si_2NX systems. This is demonstrated in Figure 5, which shows a contour plot of the natural localized molecular orbitals of the lone pairs in the C_s mirror plane. Recent *ab initio* calculations for the related system $(H_3Si)_2NOH$ showed the energy difference between planar and pyramidal nitrogen configuration to be about 2 kcal mol^{-1},[33] which is about 25% of the amount for the whole inversion process involving rotation of the hydrogen atom (or CH_3 in **1**) about the NO bond.[15] Further support for this theory is the extremely shallow potential for the nitrogen inversion of $(H_3Si)_2NF$, the structure of which has recently been calculated by Engels and Mühlhäuser.[33] In contrast to the asymmetric OCH_3 group, the more symmetric F substituent causes no distortion of the planar Si_2NX core. Consequently, $(H_3Si)_2NF$ has been predicted to be planar and the high effective nuclear charge of the group X can be ruled out as an explanation for the nonplanarity of the Si_2NO skeleton.

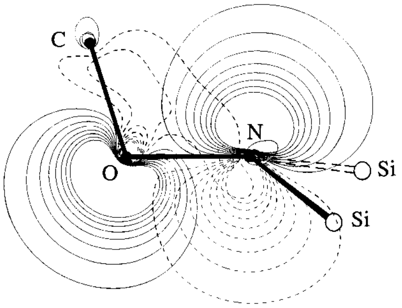

Figure 5. Plot of the natural localized molecular orbitals of the lone pairs at the nitrogen and oxygen atoms of **1** showing the repulsive interaction which leads to the nonplanarity of the nitrogen configuration.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates and thermal parameters, hydrogen atom parameters, bond distances and angles (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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