A Steeply Pyramidal Silylamine: *N,O*-Dimethyl-*N*-silylhydroxylamine

Norbert W. Mitzel*,[†] and Heinz Oberhammer[‡]

Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstrasse 4,
85747 Garching, Germany, and Institut für Physikalische und Theoretische Chemie,
Universität Tübingen, Auf der Morgenstelle 8, 72076 Tübingen, Germany

Received March 24, 1998

N,O-Dimethyl-*N*-silylhydroxylamine ($H_3SiMeNOMe$) has been prepared by reaction of HMeNOMe with H_3SiBr and 2,6-lutidine as an auxiliary base. Its identity has been proved by gas-phase IR and solution NMR spectroscopy of the nuclei ^1H, ^{13}C, ^{15}N, ^{17}O, and ^{29}Si and by mass spectrometry. The solution NMR data indicate aggregation of the compound in solution. $H_3SiMeNOMe$ decomposes within weeks at ambient temperature, and an extrusion of methylnitrene is probably the mechanistic pathway involved. The final products of this decomposition are an insoluble precipitate and SiH_4. The energy of $H_3SiMeNOMe$ relative to its potential rearrangement isomer MeHN−H_2Si−OMe has been estimated by ab initio calculations to be 289 kJ mol^{-1}. The molecular structure of $H_3SiMeNOMe$ has been determined by gas-phase electron diffraction and by ab initio calculations. The results show $H_3SiMeNOMe$ to possess a steeply pyramidal nitrogen atom and to adopt a trans conformation. It is thus the first silyl nitrogen compound that adopts a typically pyramidal nitrogen coordination for purely electronic reasons. The Si−N bond is found to be only slightly elongated with respect to those of comparable compounds with planar nitrogen coordination. Important bond length and angles are Si−N 1.742(1), N−O 1.449(4), N−C 1.460(3), and O−C 1.425(4) Å and Si−N−C 121.8(5), Si−N−O 104.3(4), C−N−O 106.2(12), and N−O−C 103.2(12)°. Results of an NBO analysis show the silyl group to be bound by a nitrogen sp^2 hybrid, the d-orbital contribution at silicon to be less than 2%, and the N−O bond to comprise mainly p-orbital contribution. The presence of a marked p(lp-N)−σ^*(Si−H) hyperconjugation in the NBO description shows that this effect cannot be solely responsible for the generally observed flattening of the nitrogen coordination in silylamines.

Introduction

In contrast to alkylamines, which almost always have pyramidal nitrogen atoms,[1] it is a generally accepted rule that silylated nitrogen compounds have planar coordination at the nitrogen atoms,[2] and only a few exceptions have been found so far.[3,4] Compounds with slight deviation from planarity include $R_xSi(NH_2)_{4-x}$ (crystal structures for $x = 1-3$, R = bulky aryl group),[5] $H_3CH_2SiNMe_2$,[6] H_3SiNMe_2,[7] and ClH_2SiNMe_2,[8] all studied by gas-phase electron diffraction (GED). Moreover, the nitrogen coordination can be forced to be pyramidal by incorporation into a small ring cycle such as aziridine as a result of ring strain.[9] For acyclic strain-free systems, it was only recently established that the pyramidal nitrogen coordination is an inherent phenomenon in the chemistry of silylhydroxylamine derivatives.[10,11] $(H_3Si)_2NOMe$, the simplest compound of this class prepared so far, has been studied in both the gas phase and the solid state to prove this.[12] However, the examples studied so far were always doubly silylated at nitrogen and showed only slight deviations from planarity: the sum of angles at the nitrogen atoms never fell below 350°, and the corresponding declination of the N−O vector from the NSi_2 plane never exceeded ca. 30°.

It is now agreed that silyl substituents lower the inversion barrier of nitrogen centers, and the more silyl substituents attached to a nitrogen atom, the lower is its barrier to inversion. In most cases known, this leads to a complete vanishing of a barrier and to only one (shallow) minimum in the potential function, which corresponds to a planar nitrogen coordination.

On the other hand, it is well known that organohydroxylamines have high barriers to inversion of the nitrogen pyramids, and organic derivatives of dihydroxy- and trihydroxyamines

---

[†] Technische Universität München.

[‡] Universität Tübingen.

(1) (a) An important example of planar nitrogen coordination in alkylamines is triisopropylamine: Bock, H.; Göbel, J.; Havlas, Z.; Liedle, S.; Oberhammer, H. *Angew. Chem.* **1991**, *103*, 193; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 187 and references therein. (b) Triisopropylamine is pyramidal in the crystal: Boese, R.; Bläser, D.; Antipin, M. Y.; Chaplinski, V.; de Meijere, A. *J. Chem. Soc., Chem. Commun.* **1998**, 781.

(2) (a) Hedberg, K. *J. Am. Chem. Soc.* **1955**, *77*, 6491. (b) Beagley, B.; Conrad, A. R. *J. Chem. Soc., Faraday Trans.* **1970**, 2740. The structure of $N(SiH_3)_3$ was first presented at the International Congress of Crystallography, Stockholm, July 1951, and at the XII International Congress of Pure and Applied Chemistry, New York, Sept 1951.

(3) Ebsworth, E. A. V. *Acc. Chem. Res.* **1987**, *20*, 295.

(4) Bock, H. *Angew. Chem.* **1989**, *101*, 1659; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1627.

(5) Ruhlandt-Senge, K.; Bartlett, R. A.; Olmstead, M. M.; Power, P. P. *Angew. Chem.* **1993**, *105*, 495; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 425.

(6) Gundersen, G.; Mayo, R. A.; Rankin, D. W. H. *Acta Chem. Scand.* **1984**, *38A*, 579.

(7) (a) Rudmann, R.; Hamilton, W. C.; Norvich, S.; Goldfarb, T. D. *J. Am. Chem. Soc.* **1967**, *89*, 5157; b) Blake, A. J.; Ebsworth, E. A. V.; Welch, A. J. *Acta Crystallogr. (C)* **1984**, *40*, 895.

(8) Anderson, D. G.; Blake, A. J.; Cradock, S.; Ebsworth, E. A. V.; Rankin, D. W. H.; Welch, A. J. *Angew. Chem.* **1986**, *98*, 97; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 107.

(9) Huber, G.; Jokisch, A.; Schmidbaur, H. *Eur. J. Inorg. Chem.* **1998**, *1*, 107.

(10) Dressler, U.; Niecke, E.; Pohl, S.; Saak, W.; Schoeller, W. W.; Schäfer, H.-G. *J. Chem. Soc., Chem. Commun.* **1986**, 1086.

(11) Mitzel, N. W.; Angermaier, K.; Schmidbaur, H. *Organometallics* **1994**, *13*, 1762.

(12) Mitzel, N. W.; Breuning, E.; Blake, A. J.; Robertson, H. E.; Smart, B. A.; Rankin, D. W. H. *J. Am. Chem. Soc.* **1996**, *118*, 2664.

S0020-1669(98)00323-1 CCC: $15.00

have been intensively studied, in particular by Rudchenkow,[13] as examples for compounds with isolable chiral nitrogen centers. Substitution of a nitrogen atom with silicon and oxygen ligands means, therefore, to play with competing effects on the inversion barrier of the nitrogen atom.

In this context, it was desirable to get information about the structure of the simplest isolable mono-*N*-silylated hydroxylamine, which is probably $H_3SiMeNOMe$, as NH or OH functions are unstable in compounds with $NSiH_3$ groups because of the tendency for further condensation.

Here we present the synthesis of this compound and the theoretical as well as the experimental determination of its molecular structure accomplished by explanations from theoretical methods. Furthermore, we try to shed light on the decomposition chemistry of this class of high-energy compounds.

Results and Discussion

Synthesis. $H_3SiMeNOMe$ has been prepared by the reaction of bromosilane with *N*,*O*-dimethylhydroxylamine in the presence of 2,6-lutidine as an auxiliary base. The reaction was carried out at low temperature and in the absence of a solvent and yielded 72% of the desired product.

$$\mathrm{HMeNOMe} + \mathrm{H_3SiBr} + \text{2,6-lutidine} \rightarrow \mathrm{H_3SiMeNOMe} + \text{2,6-lutidine}\cdot\mathrm{HBr}$$

The compound can be purified by fractional condensation at low temperature. $H_3SiMeNOMe$ is a colorless liquid which tends to ignite when in contact with air if traces of moisture are involved. The compound decomposes within a few days in liquid form or in solution at ambient temperature to give SiH_4 and an insoluble (benzene, toluene) solid residue.

Decomposition of $H_3SiMeNOMe$. Traces of H_3SiOMe could be detected by NMR (^1H, ^{29}Si) during the decomposition process, which is an indication for the decomposition to proceed via nitrene extrusion, a reaction which is known for *O*-trimethylsilylhydroxylamines and synthetically applicable for nitrene generation.[14] The insertion of a nitrene generated in this way into the Si−H bond (a concerted mechanism could also be considered) would result in the formation of the compound $H_3C(H)NSiH_2OMe$.

$$\mathrm{H_3SiMeNOMe} \rightarrow \mathrm{H_3C\text{-}N|} + \mathrm{H_3SiOMe} \rightarrow \mathrm{H_3C(H)NSiH_2OMe}$$

Although this is a likely product and is consistent with the appearance of a new triplet in the ^{29}Si NMR spectrum at −35.5 ppm [tm, $^1J(SiH) = 233.5$ Hz] and two new singlets in the ^1H NMR at 3.42 and 2.91 ppm, we could not further prove the identity of this decomposition product, which decomposes further to give finally SiH_4 and an insoluble precipitate. To demonstrate the high energy content of $H_3SiMeNOMe$, we calculated the amount of energy liberated by this hypothetical rearrangement, which is mainly due to the cleavage of the weak Si−H and N−O bonds, while strong N−H and Si−O bonds are formed. An ab initio calculation (MP2/6-311G**) on $H_3C(H)NSiH_2OMe$ (the calculated structure is shown in Figure 1) predicted this compound to be 289 kJ mol^{-1} lower in energy than the educt $H_3SiMeNOMe$, which is in the same range as the molar enthalpy of formation for hydrazoic acid, HN_3 ($\Delta H_0 = 269$ kJ mol^{-1}).

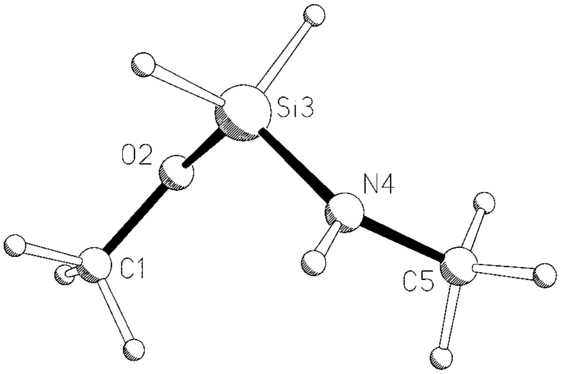

Figure 1. Calculated molecular structure of $H_3C(H)NSiH_2OMe$, an isomer of $H_3SiMeNOMe$, which is 289 kJ mol^{-1} lower in energy than the latter. Selected distances and angles (Å, deg): Si−N 1.714, Si−O 1.662, N−C 1.458, O−C 1.418; O−Si−N 117.0, Si−O−C 121.4, Si−N−C 125.0, Si−N−H 119.0, C−N−H 113.9.

Spectroscopic Characterization of $H_3SiMeNOMe$. The ^1H NMR spectrum of $H_3SiMeNOMe$ dissolved in C_6D_6 contains three resonances: two sharp singlets at 2.65 and 3.32 ppm, corresponding to the nitrogen and oxygen bound methyl groups, and one at 4.19 ppm which is surprisingly broad. Only in concentrations below ca. 5%, this resonance sharpens to give a feature as is expected for such compounds. However, the broadening of this peak is also dependent on temperature, and a 5% solution in toluene-d_8 at −50 °C also shows a markedly broadened signal.

The same effect is observed in the ^{29}Si NMR spectra, which give a quartet with line widths of 110 Hz for a 25% solution in C_6D_6 at ambient temperature. This behavior, which has not been observed in $(H_3Si)_2NOMe$ nor other compounds of this type, is probably due to intermolecular aggregation between silicon centers and nitrogen or oxygen atoms in solution and a first indication for a nitrogen center, which is markedly basic despite the silyl group attached to it. In a 5% solution in toluene-d_8, the ^{29}Si NMR spectrum appears as a sharp quartet of quartets, proving the identity of the H_3SiMeN unit.

The ^{15}N NMR spectrum of $H_3SiMeNOMe$ shows a signal at −249.0 ppm, which is 13 ppm higher in frequency than that of $(H_3Si)_2NOMe$ (−261 ppm). This value is almost identical with that of the methyl derivative $H_3CH_2SiMeNOMe$ at −249.1 ppm. The fact that this chemical shift is not between the resonances of $(H_3Si)_2NOMe$ and MeNOH (−267.6 ppm; a chemical shift for Me_2NOMe, which should be preferred for comparison, is not available) could be an indication for an unusual Si−N bonding situation, which would occur if the nitrogen atom is markedly pyramidal and thus hybridized differently than in most silylamines, including the only slightly pyramidal $(H_3Si)_2NOMe$. The proton-decoupled signal has a line width smaller than 1 Hz, which does not reflect the behavior of the signals caused by the silicon nuclei and silyl protons, and thus a Si⋯O interaction in solution should be favored, as is paralleled by the Si⋯O contacts found in the crystal structure of $(H_3Si)_2NOMe$.[12]

A resonance at 84 ppm appears in the ^{17}O NMR spectrum of $H_3SiMeNOMe$. This value is identical to that of $H_3CH_2SiMeNOMe$ but shifted to higher frequency as compared to that of $(H_3Si)_2NOMe$ at 61 ppm. However, until now, no relationship is established between molecular structure and ^{17}O chemical shifts. As signals in ^{17}O NMR signals are generally broad due to quadrupolar relaxation, no conclusions concerning intermolecular contacts can be drawn.

---

(13) Rudchenko, V. F. *Chem. Rev.* **1993**, *93*, 725.
(14) Chang, Y. H.; Chiu, F.-T.; Zon, G. *J. Org. Chem.* **1981**, *46*, 352.

Table 1. Molecular Parameters for $H_3SiMeNOMe$ (Distances in Å, Angles in deg)

parameter $r_a/\angle_a$	MP2/6-311G**	GED	GED restraint
	Independent Parameters		
$p1$, Si4−N3	1.758	1.742(1)	
$p2$, C5−N3	1.455	1.460(3)	
$p3$, N3−O2	1.444	1.449(4)	$p2 - p3 = 0.011(5)$
$p4$, O2−C1	1.420	1.425(4)	$p2 - p4 = 0.035(5)$
$p5$, Si4−H9	1.472	1.483(8)	
$p6$, Si4−H10	1.477	1.488(9)	$p5 - p6 = -0.005(5)$
$p7$, Si4−H11	1.480	1.490(9)	$p5 - p6 = -0.008(5)$
$p8$, C1−H6	1.092	1.115(2)	
$p9$, C1−H7	1.095	1.117(5)	$p8 - p9 = -0.003(5)$
$p10$, C1−H8	1.095	1.117(5)	$p8 - p10 = -0.003(5)$
$p11$, C5−H12	1.094	1.116(5)	$p8 - p11 = -0.002(5)$
$p12$, C5−H13	1.094	1.117(5)	$p8 - p12 = -0.002(5)$
$p13$, C5−H14	1.099	1.121(5)	$p8 - p13 = -0.007(5)$
$p14$, ∠O2−N3−Si4	105.4	104.3(4)	
$p15$, ∠O2−N3−C5	107.9	106.2(12)	
$p16$, ∠N3−O2−C1	107.8	103.2(12)	
$p17$, ∠N3−Si4−H9	107.5	107.3(13)	$p17 = 107.5(15)$
$p18$, ∠N3−Si4−H10	106.5	106.3(14)	$p17 - p18$, 1.0(5)
$p19$, ∠N3−Si4−H11	113.6	109.8(6)	$p23 = 109.7(15)$
$p20$, ∠O2−C1−H6	105.6	105.7(4)	$p20 = 105.6(15)$
$p21$, ∠O2−C1−H7	111.2	111.3(6)	$p20 - p21 = -5.6(5)$
$p22$, ∠O2−C1−H8	110.9	111.0(6)	$p20 - p22 = -5.3(5)$
$p23$, ∠N3−C5−H12	109.7	109.8(6)	$p23 = 109.7(15)$
$p24$, ∠N3−C5−H12	108.1	108.2(6)	$p23 - p24 = -2.5(5)$
$p25$, ∠N3−C5−H14	112.8	112.9(6)	$p23 - p24 = -7.2(5)$
$p26$, τC1−O2−N3−Si4	120.7	127.9(17)	
$p27$, τC1−O2−N3−C5	−109.1	−102.4(15)	
$p28$, τO2−N3−Si4−H9	−61.5	−31.5(64)	
$p29$, τO2−N3−Si4−H10	179.7	209.5(64)	$p28 - p29 = -241.2(30)$
$p30$, τO2−N3−Si4−H11	59.6	89.8(67)	$p28 - p30 = -121.1(30)$
$p31$, τO2−N3−C5−H12	64.4	73.7(114)	
$p32$, τO2−N3−C5−H13	−177.8	−167.6(111)	$p31 - p32 = -242.0(30)$
$p33$, τO2−N3−C5−H14	−56.8	−47.5(118)	$p31 - p33 = 121.2(30)$
$p34$, τN3−O2−C1−H6	177.6	168.0(83)	
$p35$, τN3−O2−C1−H7	−63.1	−71.4(85)	$p34 - p35 = 121.2(30)$
$p36$, τN3−O2−C1−H8	58.7	49.4(88)	$p34 - p36 = 118.9(30)$
	Dependent Parameter		
$p37$, ∠Si4−N3−C5	120.7	121.8(5)	

The gas-phase IR spectrum of $H_3SiMeNOMe$ shows the ν(SiH) modes in the region between 2180 and 2141 cm^{-1}. $(H_3Si)_2NOMe$ shows a broad absorption centered at 2178 cm^{-1}, which indicates similarity in Si−H bond length.[15]

The mass spectrum of $H_3SiMeNOMe$ confirms its molecular weight and also indicates methylnitrene extrusion, with formation of a methoxysilane cation detected at $m/z = 62$. For organosilicon derivatives of $H_3SiMeNOMe$, such a nitrene extrusion was already postulated on the basis of mass spectrometry data.[16]

Experimental and Theoretical Structure Determination of $H_3SiMeNOMe$. We undertook several attempts to crystallize $H_3SiMeNOMe$ by applying in situ methods but failed each time. Thus, we cannot prove the existence of intermolecular interactions as indicated by solution NMR studies for the solid state. However, we were successful in obtaining a complete gas-phase structure by means of analysis of electron diffraction data supported by ab initio restraints in the sense of the recently described SARACEN method,[17] which is a natural extension of Bartell's "predicate value" method and Schäfer's MOCED method.[18] SARACEN has been successfully applied even in the gas-phase structure determination of relatively large systems of low symmetry.[19] Restraints for geometrical parameters were obtained at the MP2/6-311G** level of theory and are listed in Table 1 with the refined GED parameters and the theoretical values. The chosen restraint uncertainties are based on our experience with the analysis of similar compounds. The applied uncertainties were 0.005 Å for differences in distances, 1.5° for angles, 0.5° for differences between angles (both to H atoms), and 3.0° for differences between torsion angles. Calculated amplitudes of vibration (MP2/6-31G* force field converted into amplitudes by the ASYM40 program[20]) were applied to all distances with relative intensity contributions of less than 5%; otherwise, the amplitudes were refined and the absolute values or ratios restrained by the calculated values in cases where a free refinement was not possible (see Table 2). Restraints on absolute values were 10% of the amplitude and 5% for ratios between amplitudes.

---

(15) McKean, D. C.; Torto, I.; Boggs, J. E.; Fan, K. *J. Mol. Spectrosc.* **1992**, *152*, 389.

(16) Schwarz, H.; Steiner, B.; Zon, G.; Chang, Y. H. *Z. Naturforsch. B* **1978**, *33*, 129.

(17) (a) Mitzel, N. W.; Smart, B. A.; Blake, A. J.; Robertson, H. E.; Rankin, D. W. H. *J. Phys. Chem.* **1996**, *100*, 9339. (b) Blake, A. J.; Brain, P. T.; McNab, H.; Miller, J.; Morrison, C. A.; Parsons, S.; Rankin, D. W. H.; Robertson, H. E.; Smart, B. A. *J. Phys. Chem.* **1996**, *100*, 12280.

(18) (a) Molecular Structure by Diffraction Methods; Specialist Periodical Reports; The Chemical Society: London, 1975; p 72. (b) Klimkowski, V. J.; Ewbank, J. D.; Van Alsenoy, C.; Scarsdale, J. N.; Schäfer, L. *J. Am. Chem. Soc.* **1982**, *104*, 1476−1480.

(19) Mitzel, N. W.; Schmidbaur, H.; Rankin, D. W. H.; Smart, B. A.; Hoffmann, M.; Schleyer, P. v. R. *Inorg. Chem.* **1996**, *35*, 4360.

(20) Hedberg, L.; Mills, I. M. ASYM20, ASYM40, Programs for Force Constants and Normal Coordinate Analysis, Version 3.0, June 1994. See also: Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc.* **1993**, *160*, 117.

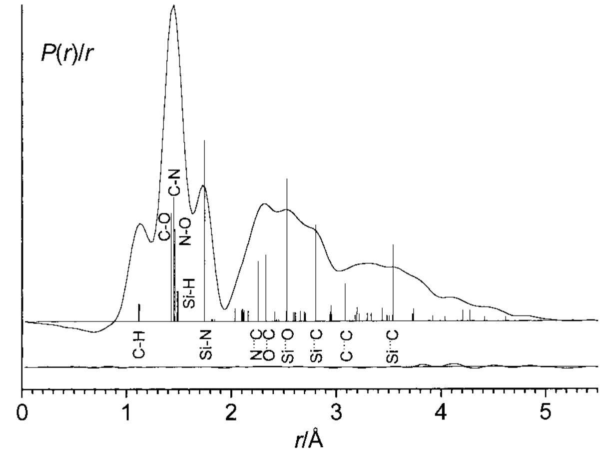

Figure 2. Radial distribution and difference curve as obtained by the refinement of gas-phase electron diffraction data of $H_3SiMeNOMe$.

Table 2. Selected Distances (Å), Vibrational Amplitudes, and Amplitude Restraints

	distances (r_a)	amplitudes	restraints
*d*1, Si4−N3	1.742(1)	0.050(1)	
*d*2, C5−N3	1.460(3)	0.054(2)	
*d*3, O2−C1	1.425(4)	0.054(2)	$u2/u3 = 1.012(50)$
*d*4, N3−O2	1.449(4)	0.056(2)	$u2/u4 = 0.953(45)$
*d*5, H6−C1	1.115(2)	0.064(2)	
*d*6, H7−C1	1.117(5)	0.065(3)	$u5/u7 = 0.995(50)$
*d*7, H8−C1	1.117(5)	0.065(3)	$u5/u8 = 0.994(50$
*d*8, H9−Si4	1.483(8)	0.095(5)	$u8 = 0.088(9)$
*d*9, H10−Si4	1.488(9)	0.097(7)	$u8/u9 = 0.993(50)$
*d*10, H11−Si4	1.490(9)	0.097(7)	$u8/u10 = 0.989(49)$
*d*11, H12−C5	1.116(5)	0.065(3)	$u5/u11 = 0.996(50)$
*d*12, H13−C5	1.117(5)	0.064(3)	$u5/u12 = 0.997(50)$
*d*13, H14−C5	1.121(5)	0.065(3)	$u5/u13 = 0.987(49)$
*d*14, N3···C1	2.253(19)	0.065(14)	
*d*15, C5···O2	2.326(18)	0.068(14)	$u14/u15 = 0.981(49)$
*d*16, C5···Si4	2.800(6)	0.085(4)	
*d*17, Si4···O2	2.526(5)	0.104(6)	
*d*18, H6···O2	2.033(6)	0.084(5)	$u18 = 0.105(11)$
*d*19, H7···O2	2.106(8)	0.081(6)	$u18/u19 = 1.033(52)$
*d*20, H8···O2	2.103(8)	0.081(6)	$u18/u22 = 1.031(52)$
*d*21, H12···N3	2.117(8)	0.083(6)	$u18/u21 = 1.012(51)$
*d*22, H12···Si4	3.731(21)	0.105(9)	
*d*23, H13···N3	2.097(8)	0.084(6)	$u18/u23 = 0.989(49)$
*d*24, H14···N3	2.159(8)	0.083(6)	$u18/u24 = 1.018(51)$
*d*25, H10···N3	2.589(24)	0.104(8)	$u18/u25 = 0.809(40)$
*d*26, H9···N3	2.602(22)	0.100(8)	$u18/u26 = 0.835(42)$
*d*27, H11···N3	2.705(22)	0.100(8)	$u18/u27 = 0.839(42)$
*d*28, C5···C1	3.079(16)	0.143(13)	$u28 = 0.140(14)$
*d*29, Si4···C1	3.537(20)	0.193(18)	
*d*30, H13···Si4	2.945(81)	0.176(17)	$u30 = 0.174(17)$
*d*31, H14···Si4	3.193(89)	0.186(18)	$u31 = 0.184(18)$
*d*32, H6···Si4	4.270(55)	0.189(18)	$u32 = 0.185(19)$
*d*33, H9···O2	2.655(47)	0.196(20)	$u33 = 0.198(20)$
*d*34,H8···Si4	3.433(90)	0.199(20)	$u34 = 0.200(20)$
*d*35, H7···Si4	4.201(80)	0.270(27)	$u35 = 0.276(28)$

Figure 2 shows the radial distribution curve derived by Fourier inversion of the experimental electron diffraction intensities shown in Figure 3. The success of the refinement can be assessed by the good fit of the model to the experimental intensities and the residuals of the radial distribution curve. Although the theoretical values have been used to restrain the refinement, the important core angles were free to refine and are in very good agreement with the theoretical predictions, thus justifying the application of restraints.

For a better description of the bonding situation in $H_3SiMeNOMe$, we carried out an NBO analysis on the calculated minimum structure. The results are discussed in context with the experimental results in the following text.

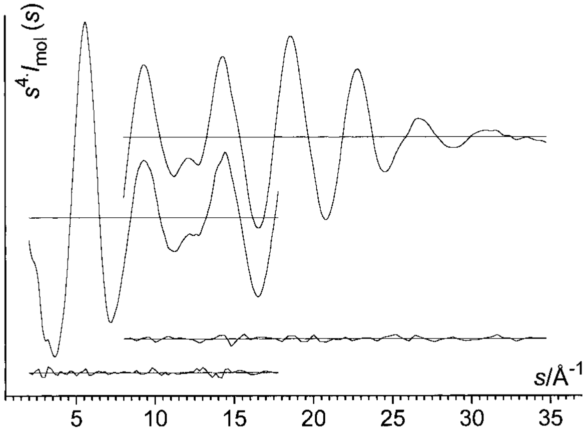

Figure 3. Electron diffraction molecular intensity and difference curves for $H_3SiMeNOMe$.

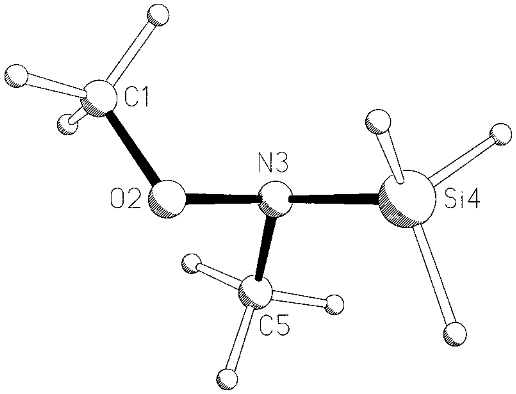

Figure 4. Molecular structure of $H_3SiMeNOMe$ as determined by gas-phase electron diffraction.

The geometry of $H_3SiMeNOMe$ is shown in Figure 4. Most intriguing is the steeply pyramidal coordination of the nitrogen atom. The sum of angles is 332.3(14)°, which is close to the value of 328.2° adopted by a nitrogen atom with all substituents enclosing ideal tetrahedral angles. The nitrogen−oxygen bond vector encloses an angle of 57.2(13)° with the N3/Si4/C5 plane, corresponding to a deviation of the nitrogen atom of 0.476 Å from the O2/Si4/C5 plane. The coordination in $H_3SiMeNOMe$ is thus markedly more pyramidal than that in $(H_3Si)_2NOMe$, with the nitrogen−oxygen bond vector enclosing an angle of 33.2(25)° relative to the NSi_2 plane and the sum of angles at the nitrogen atom being 351.8(12)°.[12]

The NBO results describe the silicon atom as entirely sp^3 hybridized, as was expected. The Si−N bond appears to be made up from an N-$sp^{1.94}$ and an Si-$sp^{3.09}d^{0.08}$ hybrid. This is somewhat surprising, as a pyramidal N atom would normally be expected to be described by sp^3 hybridization. A nitrogen contribution which is almost sp^2 in the NBO description can serve as an explanation for the fact that the Si−N bond length in $H_3SiMeNOMe$ ($r_a = 1.742(1)$ Å) is only slightly longer than that in $(H_3Si)_2NOMe$ ($r_a = 1.736(1)$ Å) and not substantially increased, as was expected for a “real single bond” between tetrahedrally coordinated silicon and pseudotetrahedrally coordinated nitrogen atoms in $H_3SiMeNOMe$. Such a case is unprecedented, as Si/N compounds almost always contain (completely) flattened nitrogen atoms. The sp^2-type hybrids used for bonding of the N atom to Si and C (N−C bond, N-$sp^{2.05}$ and C-$sp^{2.80}$ hybrids) are also responsible for the large Si−N−C angle of 121.8(5)° in the experiment, which is much the same as predicted ab initio (120.7°). It is thus that $H_3SiMeNOMe$

has a steeply pyramidal nitrogen atom, which is, however, markedly distorted from pseudotetrahedral coordination geometry.

In this context, it is worth mentioning that an NBO analysis of H_3SiNH_2 describes the Si−N bond to be formed from an N-$sp^{1.61}$ and a Si-$sp^{2.93}d^{0.09}$ hybrid, which is not very different from that in $H_3SiMeNOMe$, although the differences in the coordination are profound: the sum of angles about the N atom are calculated to be 348.6° in H_3SiNH_2 but 334° in $H_3SiMeNOMe$, showing that an isolated treatment of dependence of nitrogen coordination on the nature and strength of the Si−N bond is not valid.

The angle O−N−Si is only 104.3(4)° in the gas phase (predicted 105.4°), which is significantly smaller than the corresponding one in $(H_3Si)_2NOMe$ [110.6(6)°]. It may be speculated whether the slight angle contraction relative to $(H_3Si)_2NOMe$ is caused by attractive forces between the negatively charged oxygen and the positively charged silicon atom in the sense of the recently found β-donor interactions.[21] These interactions do not compensate another, as in $(H_3Si)_2NOMe$, due to the presence of only one such O/Si pair in $H_3SiMeNOMe$. The angle O−N−C is 106.2(12)° (predicted 107.9°) and thus also relatively small. According to the NBO calculation, the N−O bond is made up from a formal N-$sp^{4.98}$ and an O-$sp^{4.22}$ hybrid, and almost the same high p-contribution is found in the nitrogen lone pair of electrons (N-$sp^{5.02}$).

The C−O−N angle refined to 103.2(12)°, which is somewhat smaller than that predicted ab initio (107.8°) or found in $(H_3Si)_2NOMe$ [109.1(4)°]. According to the NBO analysis, the bonding orbitals at oxygen are $sp^{2.40}$ and $sp^{4.22}$ hybrids in the C−O and N−O bonds, respectively. The two lone pairs consist of one almost pure p-type orbital and one sp hybrid.

In essence, the main difference between the structure of $(H_3Si)_2NOMe$ and $H_3SiMeNOMe$ is the large Si−N−Si angle of 131.8(2)° in the first, which is more than 11° larger than the corresponding C−N−Si angle in the latter and is the major contribution to the larger sum of angles at the nitrogen atom, and thus the reason $(H_3Si)_2NOMe$ is so much flatter than the steeply pyramidal $H_3SiMeNOMe$.

Negative hyperconjugation ($p-\sigma^*$) is widely used to rationalize the differences between the chemical and structural properties of second row and third row elements. The planar structure of $(H_3Si)_3N$ (proved by gas-phase and crystal structures) and the markedly flattened nitrogen coordination in H_3SiNH_2 (calculated only) are assigned to p(lp-N)−σ^*(Si−H) interactions. Hence, we were interested to see whether such effects are absent or markedly reduced in $H_3SiMeNOMe$. For this molecule, a second-order perturbation theory analysis of the Fock matrix in the NBO basis suggests delocalization of electron density from the nitrogen lone pair of electrons into the σ^*(Si−H) orbital, with the corresponding stabilization being 34 kJ mol^{-1}. This is less than that gained by the simultaneous delocalization into the σ^*(C−H) orbital with a corresponding stabilization energy of 38 kJ mol^{-1}.

These values have to be compared with the stabilization energies in H_3SiNH_2 [p(lp-N)−σ^*(Si−H), 54 kJ mol^{-1}] and $(H_3Si)_3N$ [p(lp-N)−σ^*(Si−H), 188 kJ mol^{-1}, which is distributed over three SiH_3 groups], both being substantially larger. In H_3CNH_2, the p(lp-N)−σ^*(C−H) interaction yields 59 kJ mol^{-1}. In essence, the p(lp-N)−σ^*(Si−H) interaction in $H_3SiMeNOMe$ is weaker than that in H_3SiNH_2 and much weaker than that in $(H_3Si)_3N$. However, the difference between $H_3SiMeNOMe$ and H_3SiNH_2 is not as large as the changes in structure might suggest, showing that the flattening of nitrogen coordination pyramids cannot solely be ascribed to p(lp-N)−σ^*(Si−X) interactions. It has to be mentioned that the NBO stabilization energies given here do not have any real physical meaning and are given only to allow comparison between the relative importance of electron delocalization in different systems in the NBO picture.

Conclusion

As shown by gas-phase electron diffraction of the model compound $H_3SiMeNOMe$, a steeply pyramidal nitrogen coordination is an inherent structural property of mono-*N*-silylated hydroxylamines, which thus form a unique group within the class of Si/N compounds. Despite the pyramidal coordination, the hybrid at nitrogen used for bond formation toward silicon is not simply sp^3 and rather is described as an sp^2-type hybrid in the NBO picture. The N−O bond is formed by overlap of two orbitals with very high p-contribution. The widely used picture of negative hyperconjugation [p(lp-N)−σ^*(Si−X)] cannot be solely responsible for the flattening of the nitrogen coordination spheres in silylamines, as $H_3SiMeNOMe$ also donates electron density from its nitrogen lone pair into the antibonding orbitals of the Si−H bonds, with the magnitude of stabilization comparable to that of the clearly flattened H_3SiNH_2. Moreover, a negative hyperconjugation of the type [p(lp-N)−σ^*(C−H)] is also operative in $H_3SiMeNOMe$, but without the consequences of any planarization of the nitrogen coordination.

Experimental Section

General. All experiments were carried out in a vacuum line[22] with greaseless stopcocks (Young taps), which was directly attached to the gas cell in an FTIR spectrometer (Midac Prospect FTIR). Bromosilane was prepared from phenylsilane and liquid HBr.[23] *N,O*-Dimethylhydroxylamine was liberated from its hydrochloride by concentrated NaOH solution, purified by repeated fractional condensation, and dried over NaOH and BaO. 2,6-Lutidine was 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 (or toulene-d_8) as solvent directly condensed onto the sample from K/Na alloy.

$H_3SiMeNOMe$ (1). A 2.78-g portion of *N,O*-dimethylhydroxylamine (46 mmol) and 5.35 mL of 2,6-lutidine were placed into a 500-mL bulb and distributed over the glass surface while cooling the bulb in liquid nitrogen. Next, 46 mmol of bromosilane was condensed onto it, and the bulb was isolated from the vacuum line and warmed to −78 °C while rotating slowly for 30 min. The flask was allowed to stand at 0 °C for a further hour, and then it was cooled to −196 °C and attached to a vacuum line. While the coolant was removed, the volatile contents were passed through two traps held at −78 °C into one at −196 °C. While the first two traps contained only minor amounts of product and barely volatile lutidinium salts and lutidine, the contents of the last trap were fractionated through a series of traps held at −60/−78/−96/−110/−196 °C. The −96 °C trap contained 33 mmol (72%) of **1**. ^1H NMR: δ 2.65 (s, 3H, H_3CN), 3.32 (s, 3H, H_3CO), 4.19 (s, ca. 100 Hz broad, 3H, H_3Si). ^{13}C NMR: δ 38.6 [q, $^1J(CH) = 135.0$ Hz, CN], 60.4 [q, $^1J(CH) = 142.0$ Hz, CO]. ^{15}N NMR: δ −249.0. ^{17}O NMR: δ 84. ^{29}Si NMR: δ −44.5 [qq, $^1J(SiH) = 212.0$, $^3J(CH) = 5.8$ Hz]. MS (EI, 70 eV): m/z = 91, 76, 62, 61, 31.

Ab Initio Calculations. Ab initio molecular orbital calculations were carried out using the Gaussian 94 program.[24] Geometry optimizations and vibrational frequency calculations were performed from analytic first and second derivatives at the SCF and MP2 levels of theory. Calculations were undertaken at the SCF level using the

---

(21) Mitzel, N. W.; Losehand, U. *Angew. Chem.* **1997**, *109*, 2897; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2807.

(22) Shriver, D. F.; Drezdon, M. A. *The manipulation of air-senesitive compounds*, 2nd ed.; Wiley: New York, 1986.

(23) Ward, L. G. L. *Inorg. Synth.* **1968**, *11*, 161.

standard 3-21G*,[25−27] 6-31G*,[28−30] and 6-311G** [31,32] basis sets, while the larger two basis sets were used for calculations at the MP2 level of theory. NBO analyses were carried out with the subprograms built into Gaussian 94.[33,34]

Gas-Phase Electron Diffraction. Electron scattering intensity data for $H_3SiMeNOMe$ were recorded on Kodak electron image plates using the KDG2-Eldigraph at the University of Tübingen. The sample and the inlet nozzle were held at 20 °C during the experiments. Scattering data for ZnO were recorded concurrently and used to calibrate the electron wavelength. Data were obtained in digital form using the microdensitometer at the University of Ulm. The data analysis followed standard procedures, using established data reduction and least-squares refinement programs[35] and the scattering factors established by Fink and co-workers.[36] Further parameters are listed in Table 3, and significant elements of the correlation matrix are given in the Supporting Information.

Table 3. Camera Distances (mm), Weighting Points (Trapezoidal Function), Correlation Parameters (*p*), Scale Factors, and Wavelengths (Å) for the GED Refinement of $H_3SiMeNOMe$

distance	Δs	s_{min}	s_{w1}	s_{w2}	s_{max}	p	scale factor	wavelength
500.0	0.2	2.0	4.0	15.2	17.8	0.2200	0.798(6)	0.048 87
250.0	0.4	8.0	10.0	32.0	34.8	−0.0207	0.963(17)	0.048 87

Acknowledgment. This work was supported by the Bayerischer Staatsminister für Unterricht, Kultus, Wissenschaft und Kunst (Bayerischer Habilitationsförderpreis 1996), by the Deutsche Forschungsgemeinschaft, and by the Fonds der Chemischen Industrie and the Leonhard-Lorenz-Stiftung. The Leibniz-Rechenzentrum-München provided computational resources. We are grateful to Professor H. Schmidbaur for generous support.

Supporting Information Available: Tables 4−7, with correlation matrix elements (×100) with absolute values > 50 and Cartesian atomic coordinates for $H_3SiMeNOMe$ as obtained from the GED refinement and for $H_3SiMeNOMe$ and $H_3C(H)NH_2SiOMe$ as calculated at MP2/6-311G** (2 pages). Ordering information is given on any current masthead page.

IC980323K

---

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

(25) Binkley, J. S.; Pople, J. A.; Hehre W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(26) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797.

(27) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; Defrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.

(28) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

(29) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta*, **1973**, *28*, 213.

(30) Gordon M. S. *Chem. Phys. Lett.* **1980**, *76*, 163.

(31) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(32) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

(33) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(34) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

(35) Mitzel, N. W.; Brain, P. T.; Rankin, D. W. H. *ED96*, Version 2.0, 1998. A program developed on the basis of formerly described ED programs: Boyd, A. S. F.; Laurenson, G. S.; Rankin, D. W. H. *J. Mol. Struct.* **1981**, *71*, 217.

(36) Ross, A. W.; Fink, M.; Hilderbrandt, R. In *International Tables for X-ray Crystallography*; Wilson, A. J. C., Eds.; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C, p 245.