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β-Donor Interactions of Exceptional Strength in *N*,*N*-Dimethylhydroxylaminochlorosilane, $ClH_2SiONMe_2$

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Abstract: The compounds $ClH_2SiONMe_2$ and $ClH_2SiONEt_2$ have been prepared by the reaction of the corresponding *O*-lithiated hydroxylamines and dichlorosilane. Their identity has been proved by gas-phase IR and solution NMR (^1H, ^{13}C, ^{15}N, ^{17}O, and ^{29}Si) spectroscopy. In contrast to $ClH_2SiONMe_2$, $ClH_2SiONEt_2$ is unstable at ambient temperature and decomposes to give H_2SiCl_2 and $H_2Si(ONEt_2)_2$. $ClH_2SiONEt_2$ shows dynamic behavior in the solution as shown by low-temperature NMR. In the crystal $ClH_2SiONMe_2$ (low-temperature crystallography) is present as anti-conformer (torsional angle Cl−Si−O−N 180°) and shows an exceptionally small Si−O−N angle of 79.7(1)° and a Si···N distance of 2.028(1) Å, corresponding to a relatively strong Si−N-β-donor interaction. Ab initio calculations predict a wider Si−O−N angle of 91.6° (MP2/6-311G**). A gas-phase structure determination by electron diffraction shows the presence of two conformers (anti and gauche), which are equal in potential energy. The Si−O−N angle in the anti-conformer is 87.1(9)° and that in the gauche-conformer 104.7(11)° [Cl−Si−O−N torsion angle: 72.9(28)°]. Calculations (MP2/6-31G*) have shown the angle Si−O−N and the energy of the system to be largely dependent on the torsion angle Cl−Si−O−N, with a variation of the angle Si−O−N over a range of 30° during a full rotation of Cl−Si−O−N. Analysis of the calculated charges on the Si and N atoms show the β-donor interaction not to be simply caused by electrostatic interaction. Natural bond orbital analysis describes a lp-N → σ^*_{Si-X} type negative hyperconjugation as an important contribution to β-donor bonding. The silicon substituent in anti position to nitrogen exerts the major effect on the strength of the β-donor bond. Simultaneous analysis of negative hyperconjugation lp-O → σ^*_{Si-X} shows the Si−O−N compounds to have similar contributions to this interaction as H_3SiOCH_3 and questions negative hyperconjugation to be quoted in isolation for the rationalization of the wide bond angles in silyl ethers.

Introduction

Only recently we could show that *O*-silylhydroxylamines are able to form intramolecular donor acceptor bonds between silicon and nitrogen centers, separated by one oxygen atom only.[1] This type of nonclassical secondary bonds between p-block donor and acceptor atoms in β-position to one another was so far unprecedented or neglected. For the prediction of molecular geometries of compounds having electropositive and electronegative atoms in β-position to one another, this interaction turns out to be an important factor and has to be considered in semiquantitative structure prediction in addition to the general VSEPR concept[2] (which accounts mainly for electron repulsion within the coordination sphere of one atom) and Bartell's two bond radii model[3] (which considers internuclear repulsion over two bonds). Besides hydroxylaminosilanes examples for such compounds are the hydrazinosilanes[4] and other classes of p-block compounds which are capable of forming β-donor interactions can be imagined. One example is the silylperoxide $Me_3SiOOSiMe_3$ which has a small Si−O−O angle of 106.6(14)° in the gas phase,[5] although the Me_3Si group in general is a poor acceptor. The scarce examples for β-donor-interactions in main group systems also include a few reports about lithiated hydrazines,[6] with the lithium atoms coordinated to both nitrogen centers of the hydrazine unit. It has also to be mentioned that such interactions are well-known for transition metal acceptor atoms bound to μ^2-coordinating ligands, e.g., in the eight-coordinate $Ti(ONR_2)_4$ complexes,[7] but the 4+4-coordination in the analogous compound $Si(ONMe_2)_4$ was shown only recently.[8]

The finding of small angles in Si−O−N units was completely unexpected, as numerous examples of molecular structures of molecules containing Si−O linkages show them to adopt almost always substantially widened angles at the oxygen atom.[9] After almost half a century of controversial discussion negative hyperconjugation is often quoted—but not generally accepted—for rationalization of the large differences in bonding of the

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[1] Mitzel, N. W.; Losehand, U. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2807.

[2] Gillespie, R. J.; Johnson, E. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 495.

[3] Bartell, L. S., *J. Chem. Phys.* **1960**, *32*, 827.

[4] (a) Mitzel, N. W.; Schmidbaur, H.; Rankin, D. W. H.; Smart, B. A.; Hofmann, M.; Schleyer, P. v. R. *Inorg. Chem.* **1997**, *39*, 44360. (b) Mitzel, N. W. *Chem. Eur. J.*, **1998**, in press.

[5] (a) Oberhammer, H.; Boggs, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 7241. (b) Käss, D, Oberhammer, H.; Brandes, D.; Blaschette, A. *J. Mol. Struct.* **1977**, *40*, 65.

[6] (a) Nöth, H.; Sachdev H.; Schmidt, M.; Schwenk, H. *Chem. Ber.* **1995**, *128*, 105. (b) Drost, C.; Jäger, C.; Freitag, S.; Klingebiel, U.; Noltemeyer, M.; Sheldrick, G. M. *Chem. Ber.* **1994**, *127*, 845. (c) Bode, K.; Klingebiel, U.; Noltemeyer, M.; Witte-Abel, H. *Z. Anorg. Allg. Chem.* **1995**, *621*, 500. (d) Metzler, N.; Nöth, H.; Sachdev H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1746.

[7] (a) Wieghardt, K.; Tolksdorf, I.; Weiss, J.; Swiridoff, W. *Z. Anorg. Allg. Chem.* **1982**, *399*, 182. (b) Mitzel, N. W.; Parsons, S.; Blake, A. J.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1996**, 2089.

[8] Mitzel, N. W.; Blake, A. J.; Rankin, D. W. H. *J. Am. Chem. Soc.* **1997**, *119*, 4143.

[9] Lukevics, E.; Pudova, O.; Strukokovich, R. *Molecular Structure of Organosilicon Compounds*; Ellis Horwood: Chichester, 1989.

first-row-element compounds and the homologues of the second row of the periodic table,[10] e.g., for the large difference between the bond angles at the oxygen atoms in $O(CH_3)_2$ (111.4°)[11] and $O(SiH_3)_2$ (144°).[12] Even in H_3COSiH_3 (120.6°)[13] the angle at oxygen is markedly widened as compared with $O(CH_3)_2$.

Weak β-donor interactions could be the reason for the frequently reported high reactivity of hydroxylaminosilanes. Claims for new cross-linking agents and cold curing catalysts for silicone polymers on the basis of hydroxylaminosilanes are to be found in patent literature,[14] but without providing an explanation for the behavior of these compounds. Recently, the alcoholysis of Si−H functions in poly-phenylsilane has been found to be catalyzed by hydroxylamines.[15] The knowledge about β-donor interactions can provide valuable arguments for the explanation of these reactivity patterns, considering the consequences of a partial enlargement of the coordination sphere of silicon.

Here we report about model compounds ClH_2SiONR_2 with exceptionally strong β-donor bonds. We have studied these species in detail by structural methods in the crystal and in the gas phase, by spectroscopy in solution, and by means of theoretical calculations, which give more detailed insight into the nature of such interactions.

Results and Discussion

Synthesis. The *O*-chlorosilylhydroxylamines can be prepared by a condensation reaction of the appropriate OH-functional hydroxylamine with an excess of dichlorosilane in the presence of a sterically hindered base in order to avoid basically catalyzed disproportionation of dichlorosilane.

$$H_2SiCl_2 + HONR_2 + 2,6\text{-lutidine} \rightarrow ClH_2SiONR_2 + 2,6\text{-lutidine}\cdot HCl \quad (1)$$

$$R = Me, Et$$

However, this side reaction cannot be suppressed completely, and thus considerable amounts of $H_2Si(ONR_2)_2$ and $HSi(ONR_2)_3$ are formed. These products can be separated by careful distillation, but high purities are achieved only with difficulty.

Despite its high reactivity, *O*-lithiated hydroxylamine reacts more selectively with dichlorosilane, as the reaction can be performed at low temperature.

$$HONR_2 + n\text{BuLi} \rightarrow n\text{BuH} + LiONR_2 \quad (2)$$

$$H_2SiCl_2 + LiONR_2 \rightarrow LiCl + ClH_2SiONR_2 \quad (3)$$

$$R = Me, Et$$

The yields achieved in this way are higher than 75%.

The compounds $ClH_2SiONMe_2$ and $ClH_2SiONEt_2$ are extremely air-sensitive and fume enormously, although they are not pyrophoric. Whereas $ClH_2SiONMe_2$ is fairly stable (it can be stored for days at room temperature), its ethyl analogue $ClH_2SiONEt_2$ undergoes decomposition even at temperatures as low as 0 °C. The best way of storage is in sealed containers at liquid nitrogen temperature. The decomposition could be followed to some extent by NMR showing the major decomposition products to be $H_2Si(ONEt)_2$ and dichlorosilane, with traces of $HSi(ONEt_2)_3$ and $H_3SiONEt_2$ also detected.

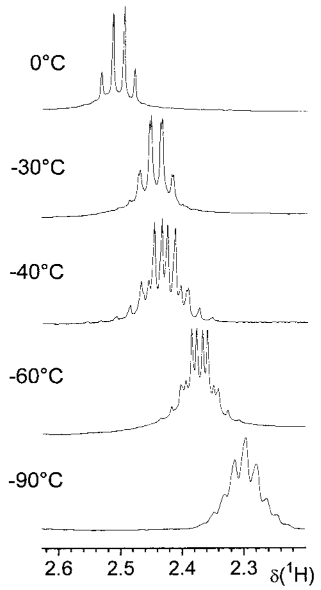

Figure 1. ^1H NMR spectra of the methylene region of $ClH_2SiONEt_2$ in d^8-toluene solution recorded at different temperatures.

Spectroscopy. The identity of these compounds was proved by gas-phase IR spectroscopy, by NMR spectroscopy of the nuclei ^1H, ^{13}C, ^{15}N, ^{17}O, and ^{29}Si, and by mass spectrometry.

The behavior of $ClH_2SiONMe_2$ and $ClH_2SiONEt_2$ in the proton NMR is different due to the presence of diastereotopic CH_2 groups in $ClH_2SiONEt_2$: Whereas the methyl groups in $ClH_2SiONMe_2$ give a singlet, $ClH_2SiONEt_2$ gives rise to a quartet for the methylene units at 20 °C, which begins to split into a more complex coupling pattern at −30 °C and further changes its appearance on cooling to lower temperatures (Figure 1). However, the observed coupling patterns are grossly different from those observed for $H_3SiONEt_2$, $H_2Si(ONEt_2)_2$, $HSi(ONEt_2)_3$,[16] and $Si(ONEt_2)_4$.[8] These compounds show quartets for the methylene groups at temperatures above ca. 40 °C, which coalescence in the range between 20 and 30 °C and split into two quartets of doublets upon cooling. This reflects the topomerization process of simultaneous N inversion and rotation about the N−O bond. The fact that such behavior is not observed for $ClH_2SiONEt_2$ and changes in the spectrum appear at much lower temperatures than in the reference compounds indicates the existence of a different dynamic process in $ClH_2SiONEt_2$. As will be shown in the paragraph describing the gas-phase structure analysis of $ClH_2SiONMe_2$, two conformers of comparable energy exist, describing anti and gauche position of the chlorine atom relative to the Si−O−N plane. A similar behavior can be expected for the analogous ethyl compound. Hence, dynamic processes with considerable barriers to topomerization in $ClH_2SiONEt_2$ combine rotation about the Si−O and N−O bond and inversion of the nitrogen center. However, even though we have some knowledge about the individual processes, we cannot offer a simple explanation for the experimental results shown in Figure 1.

The ^{13}C NMR data deserve no detailed comment. The ^{15}N NMR chemical shifts of $ClH_2SiONMe_2$ and $ClH_2SiONEt_2$ are −249.5 and −228.9 ppm. These values are very similar to those

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(10) Albright, T. H.; Burdett, J. K.; Whangho, M. H. Orbital Interactions in Chemistry; Wiley: New York, 1985.

(11) Tamagava, K.; Takemura, M.; Konaka, S.; Kimura, M. *J. Mol. Struct.* **1984**, *125*, 131.

(12) Almenningen, A.; Bastiansen, O.; Ewing, V.; Hedberg, K.; Traetteberg, M. *Acta Chem. Scand.* **1963**, *17*, 2455.

(13) Glidewell, C.; Rankin, D. W. H.; Robiette, A. G.; Sheldrick, G. M. *J. Mol. Struct.* **1970**, *5*, 417.

(14) A collection of patent literature references can be found in: Voronkov, M. G.; Maletina, E. A.; Roman, V. K. *Heterosiloxanes, Vol. 2*: *Derivates of Nitrogen and Phosphorus*; Harwood Academic Publishers GmbH: Chur, Switzerland, 1991.

(15) Hamada, Y.; Mori, S. *Proceedings of the 29th Organosilicon Symposium*; March 1996, Evanston, IL.

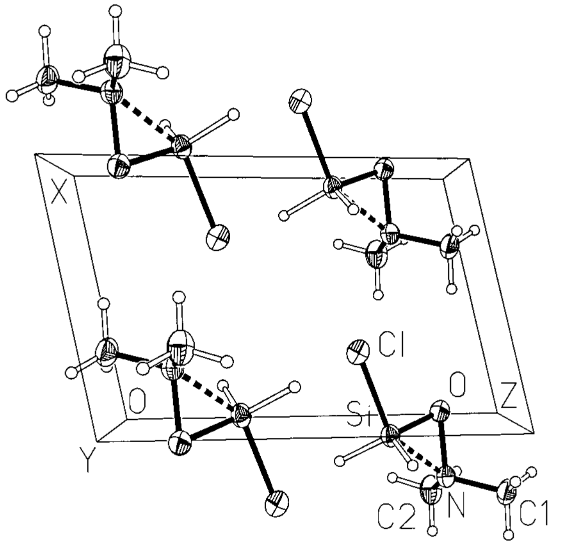

Figure 2. Unit cell of the crystal structure of $ClH_2SiONMe_2$ showing the molecular structure and the absence of important intermolecular interactions.

found in the compounds in $H_3SiONMe_2$, $H_2Si(ONMe_2)_2$, $HSi(ONMe_2)_3$, and $Si(ONMe_2)_4$ and the corresponding ethyl analogues and so are the ^{17}O NMR chemical shifts. The large structural differences as observed in the solid state and in the gas phase (discussed below) are not reflected in according changes of the solution NMR data, thus indicating dissimilarity between the structures in the different phases. This interpretation is also supported by the ^{29}Si NMR spectra for $ClH_2SiONMe_2$ and $ClH_2SiONEt_2$, with triplets occurring at -54.6 and -52.3 ppm, which are in the range of shifts for $H_3SiONMe_2$, $H_2Si(ONMe_2)_2$, and $HSi(ONMe_2)_3$ (-40.0, -49.8, and -58.2 ppm, respectively) and the corresponding ethyl analogues. Extreme changes of the chemical shift values, as could be expected from the enlargement of the coordination sphere of silicon (and nitrogen, see below for structural details) are not observed in solution, which leads to the conclusion that β-donor interactions are broken even by noncoordinating solvents such as benzene or toluene.

Crystal Structure Determination of $ClH_2SiONMe_2$. A single crystal was grown by in situ methods in a sealed capillary on the diffractometer. The molecules crystallize as monomers with no crystallographic symmetry imposed on the molecular structure, which is shown in Figure 2. The chlorine atom is placed in almost perfect anti position, with respect to the Si−O−N unit [torsion angle 178.7(1)°]. Geometry parameters are listed in Table 1.

The most striking structural parameter value is the extraordinarily small Si−O−N angle of 79.7(1)°, which leads to a Si···N distance of only 2.028(1) Å. Hence this is by far the strongest β-donor bond, which has been found so far leaving no doubt about its existence. For comparison: the Si−O−N angles in the compounds $H_3SiONMe_2$ [102.6(1)°] and $H_2Si(ONMe_2)_2$ (95.2°) are much larger.[1] The finding of such a small Si−O−N angle is even more surprising, as silicon oxygen compounds generally have wider angles if the silicon atom bears electronegative substituents, as this strengthens the multiple bond contribution of the Si−O linkage. Examples for this behavior are the relative bond angles in the disiloxanes $(H_3Si)_2O$ [144.1(8)°],[12] $(Cl_3Si)_2O$ [146(4)°],[17] and $(F_3Si)_2O$ [155.7(20)°][18] and those in the methoxysilanes H_3SiOCH_3 [120.6(10)°][13] and F_3SiOCH_3 [131.4(32)°].[17]

The small Si−O−N angle was also unexpected in the light of simultaneously performed ab initio calculations (up to MP2/6-311G**), which predicted it to be 91.6°, and the experience with those calculations showed them generally to agree well with the experimental values from X-ray-crystallography in a number of cases studied so far. The convergence of our calculations with respect to the level of theory is not perfect but satisfactorily. Calculations at lower levels of theory give Si−O−N angles of 99.5° (SCF/3-21G*), 104.7° (SCF/6-31G*), and 88.9° (MP2/6-31G*), which means that increasing the size of the basis set leads to larger angles Si−O−N, whereas taking the effects of electron correlation into account leads to an angle compression.

The closest intermolecular distances between silicon and oxygen atoms is 4.996 Å, between silicon and chlorine atoms 3.775 Å, and between silicon and nitrogen atoms 4.820 Å. Only the Si···Cl distance is in the same range as sum of the van der Waals radii (3.81 Å). The absence of any pronounced intermolecular contacts shows the nitrogen lone pair of electrons to be (completely) involved in secondary bonding and the coordination sphere of silicon to be saturated as well. Intermolecular interactions are otherwise quite common in cases with basic nitrogen centers and chloro-substituted silicon-acceptor centers present in the same system.[19]

The values for the Si−O and Si−Cl bond length are in the established range. The N−O bond, however, is significantly longer (about 0.02 Å) than in other hydroxylamines and even longer than in other *O*-hydroxylaminosilanes.

Gas-Phase Structure Determination of $ClH_2SiONMe_2$. To clarify the discrepancy between ab initio calculated and crystallographically determined molecular geometry of $ClH_2SiONMe_2$ we determined the gas-phase structure of this compound experimentally by means of electron diffraction. This experiment was complicated by the presence of a second conformer, the gauche-conformer with respect to two possible orientations of the Cl−Si vector relative to the Si−O−N plane. Calculations at lower levels of theory always favored the anti-conformer slightly in energy, but with increasing level of theory, the energy difference between the two conformers decreased and at MP2/6-311G** the gauche-conformer is favored by 0.17 kJ mol^{-1}. Thus we had to expect an anti-to-gauche ratio of 1:2 according to the relative degeneracies of each form. The calculations also predicted largely different molecular structures, which did not allow to refine just average parameters for both apart from the torsion angles. However, the recently developed SARACEN method[20] is well suited to tackle with problems of this size and complexity. SARACEN is the natural extension of two earlier approaches: Bartell's "predicate value" method and Schäfer's MOCED method.[21] In essence both structures have been calculated ab initio and parameters which are

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(16) Losehand, U.; Mitzel, N. W. *Inorg. Chem.* In press.

(17) Airey, W.; Glidewell, C.; Robiette, A. G.; Sheldrick, G. M. *J. Mol. Struct.* **1971**, *8*, 413.

(18) Airey, W.; Glidewell, C.; Rankin, D. W. H.; Robiette, A. G.; Sheldrick, G. M. *Trans. Faraday Soc.* **1970**, *66*, 551.

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

(20) (a) Mitzel, N. W.; Smart, B. A.; Blake, A. J.; Robertson, H. E.; Rankin, D. W. H. *J. Chem. Phys.* **1996**, *100*, 9339−9347. (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. Chem. Phys.* **1996**, *100*, 12280−12287.

(21) (a) Bartell, L. S. in Molecular Structure by Diffraction Methods, *Specialist Periodical Reports*; The Chemical Society: 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.

Table 1. Selected Bond Length (Å) and Angles (deg) for $ClH_2SiONMe_2$ as Determined by Low Temperature X-ray Diffraction (XRD), Gas-Phase Electron-Diffraction (GED), and Ab Initio Calculations

	anti conformer			gauche conformer	
parameter	XRD (r)	GED (r_a)	MP2/6-311G** (r_e)	GED (r_a)	MP2/6-311G** (r_e)
Si−O	1.668(1)	1.654(4)	1.678	1.641(3)	1.664
Si−Cl	2.108(1)	2.050(4)	2.063	2.042(2)	2.054
Si···N	2.028(1)	2.160(7)		2.468(25)	2.477
N−O	1.490(1)	1.475(6)	1.468	1.474(8)	1.463
N−C	1.461(1) 1.459(1)	1.460(5)	1.458	1.457(7) 1.460(7)	1.458 1.459
⟨Si−O−N	79.7(1)	87.1(9)	91.6	104.7(11)	104.5
⟨O−Si−Cl	101.1(1)	105.5(17)	105.4	109.4(9)	112.1
⟨O−Si−H	116.4(7) 115.6(6)	112.0(11)	112.3	104.2(12) 111.7(13)	104.7 112.2
⟨O−N−C	107.7(1) 108.4(8)	105.5(4)	106.0	104.5(5) 104.8(5)	105.1 105.3
⟨C−N−C	112.8(1)	109.8(10)	111.5	114.4(15)	111.0

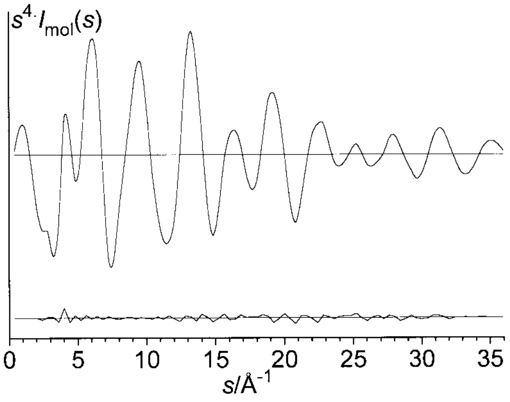

Figure 3. Combined molecular intensity curve from the GED experiment on $ClH_2SiONMe_2$. Theoretical data are shown in the regions 0−1.8 and 35.0−36.0 $Å^{-1}$ for which no experimental data are available.

calculated to have closely similar values were restrained flexibly by the calculated difference with an uncertainty assigned, based on the experience with the reliability of such values. The same principle has been applied to the vibrational amplitudes: Those which relate to interatomic distances with a relative scattering contribution of more than 5% of the maximum became subject to restraints, if they could not be refined on their own. Amplitudes belonging to distances of smaller contribution were fixed at their calculated values. The amplitude calculations were based on force fields obtained at the MP2/6-31G* level of theory and converted by the ASYM40 program.[22]

Figure 3 shows the experimental molecular intensity curve. The radial distribution curve, obtained by Fourier inversion of the latter, is shown in Figure 4. The molecular structures of the anti- and the gauche-conformer obtained by the least squares refinement on the experimental scattering intensities are shown in Figure 5; the geometrical parameter values are listed in Table 1. The molecular composition was determined to comprise 34(5)% anti- and 66(5)% gauche-conformer, which reproduces the predicted ration of 33:67 very well. The contributions of each conformer to the radial distribution curve are presented in Figure 4. This shows that neither of the two models is solely suitable to describe the experimental curve. The major contributions of the anti-conformer are in the region about 3.0, 4.0, and 5.0 Å, while the experimental curve is dominated by the contributions of the gauche-conformer mainly found at 3.3 and 4.7 Å.

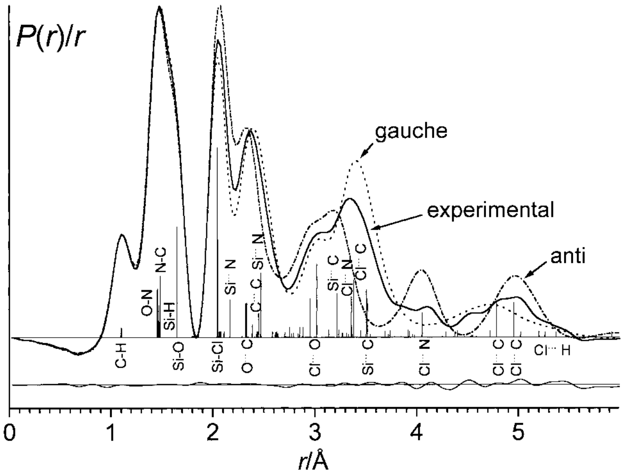

Figure 4. Radial distribution curve for the conformer mixture of $ClH_2SiONMe_2$. The black line shows the experimental curve, obtained by Fourier inversion of the molecular intensities [after multiplication by 0.002 $s^2/(Z_{Si}\text{-}f_{Si})/(Z_{Cl}\text{-}f_{Cl})$]. The contributions of the individual conformers are shown as dotted and dashed lines.

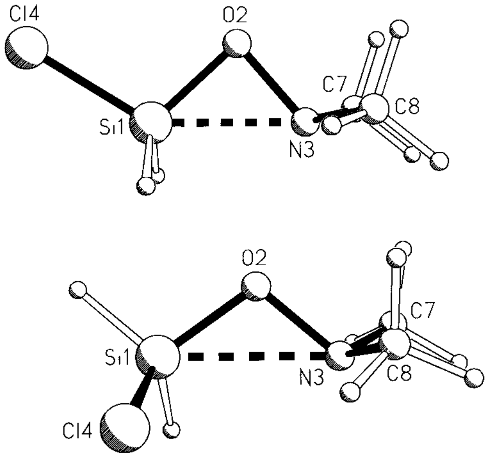

Figure 5. Molecular geometries of the anti and gauche conformers of $ClH_2SiONMe_2$ as determined by gas-phase electron-diffraction augmented by restraints derived from ab initio calculations.

The important core angles Cl−Si−O and Si−O−N, which were not restrained by the ab initio geometries, refined to values which were only slightly different from those predicted ab initio. This justifies the application of calculated restraints. In essence, the gas-phase structure determination verified the ab initio predictions of geometry parameters.

The *anti-conformer* has a relatively small Si−O−N angle of 87.1(9)°. However, this is more than 7° larger than observed in the crystal structure. Apart from the Si−O−N angle, the

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[22] 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.

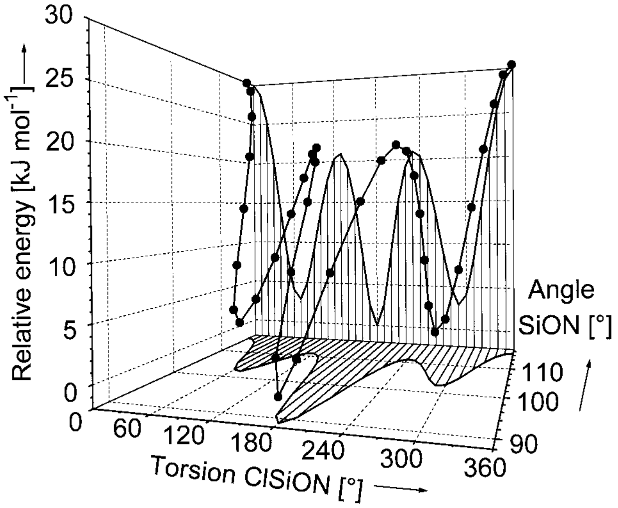

Figure 6. Dependence of the relative energy and the angle Si−O−N on variation of the torsion angle Cl−Si−O−N in $ClH_2SiONMe_2$ as calculated at the MP2/6-31G* level of theory.

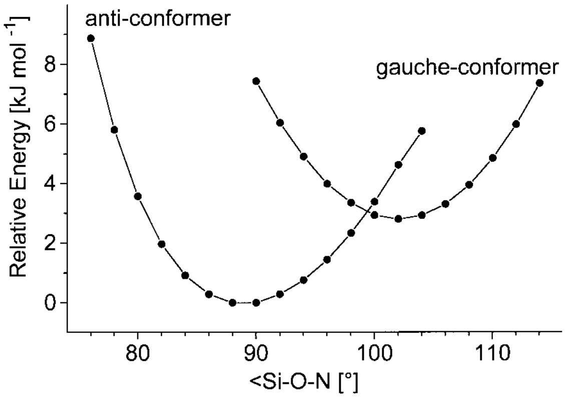

Figure 7. Dependence of the relative energy of $ClH_2SiONMe_2$ on variation of the angle Si−O−N as calculated at the MP2/6-31G* level of theory.

other geometrical parameter values are quite similar between gas-phase and crystal structure. The O−Si−Cl angle refined to 105.5(17)° for the gas-phase anti-conformer and is 101.1(1)° in the crystal. The bond lengths in the gas-phase match with those in the crystal taking the usual differences between the two methods into account. Both the gas-phase and the crystal structure show a significantly elongated N−O bond [1.475(6) and 1.490(1) Å] as compared with the nonsilylated *N*,*N*-dimethylhydroxylamine (gas: 1.448, solid: 1.456 Å).[23]

The structure of the *gauche-conformer* of $ClH_2SiONMe_2$ is again markedly different from that of the anti-conformer, not only in the torsion angle. The Si−O−N angle in the gauche conformer is more than 16° larger than in the anti-conformer. Figure 6 shows the interdependence of the torsion angle Cl−Si−O−N, the bond angle Si−O−N, and the relative energy, as was calculated ab initio (MP2/6-31G*) by fixing the torsion angle to certain values, while allowing the rest of the structure to relax without symmetry constraints. The plot shows that variations of the angle Si−O−N with changing torsion angle Cl−Si−O−N are almost as large as 30° (extrema at torsional angles of 0 and 180°). The two different conformers are separated by barriers of about 20 kJ mol^{-1}, while the conversion of one gauche-form into the other, passing a torsion angle of 0°, requires more than 25 kJ mol^{-1}. Such large structural changes with varying torsion angles are very uncommon.

Figure 7 shows the energy dependence on the variation of the Si−O−N angles in both conformers, which were calculated by fixing these angles to certain values while allowing the rest of the geometry to optimize on the MP2/6-31G* level of theory. During this procedure, the torsional angle Cl−Si−O−N remained at exactly 180° for the anti-conformer, while it varied about 2° to either side of the optimum geometry in the gauche-conformer. The curves indicate a comparatively flat potential function, as only 2−4 kJ mol^{-1} are necessary to achieve angle deformations of about 10°. However, it also indicates the geometry adopted by the molecules in the crystal lattice to lie 4 kJ mol^{-1} above that of the ground state. This is surprising since no pronounced intermolecular contacts have been detected in the crystal structure, which could be responsible for that difference. However, it reflects the ease of deformation of this angle. As the ground state geometry has been proved by the ED experiment, this means that the sum of weak interactions in the lattice must be the reason for this finding. Thus great care is suggested in the interpretation of low energy deformations of molecular systems based solely on crystallographic data.

Comparison with Related Structures. To facilitate classifying the results, we compare the new structural results with known molecular geometries of $H_3SiONMe_2$, $H_2Si(ONMe_2)_2$[1] and $Me_3SiON(CF_3)_2$.[24] Table 2 lists important parameter values for comparison.

The anti conformer of $ClH_2SiONMe_2$ has by far the smallest Si−O−N angle of all the compounds listed, regardless of the phase the compound has been studied in. In the gauche conformer, this angle is markedly widened. It is, however, close to that of $H_3SiONMe_2$ [102.6(1)°][1] and thus indicates that the substituent at the silicon center in anti-position relative to nitrogen is responsible for the strength of the β-donor bond formed between the Si and N atoms. This interpretation is consistent with the observation of a small Si−O−N angle in $H_2Si(ONMe_2)_2$, as there is also an electronegative element (oxygen) in anti-position with respect to the nitrogen donor center. The ability for back-bonding makes oxygen a worse electron-withdrawing substituent as compared to chlorine. In this way, silicon becomes less electrophilic, as was also shown by the relatively wide Si−O−N angles of the 4+3 coordinate $HSi(ONMe_2)_3$ [103.5°][16] and the 4+4 coordinate $Si(ONMe_2)_4$ [109.1°].[8]

The Si−O−N angle in $Me_3SiON(CF_3)_2$ is as much as 25.5° wider than in $ClH_2SiONMe_2$, if the gas-phase values are compared. This can be explained by the reduced electrophilicity of a Me_3Si group as compared to a ClH_2Si group and the decreased nucleophilicity of a $(F_3C)_2N$ group relative to a Me_2N group and is thus consistent with the description of β-donor bonds as Lewis-base-acceptor bonds.

Small angles at oxygen should lead to a weakening and lengthening of the Si−O bond, as the multiple bond character is expected to be more pronounced if the bonds at oxygen enclose wider angles. In contrast to this prediction the GED Si−O distance of $ClH_2SiONMe_2$ (anti-conformer) is shorter than that of $Me_3SiON(CF_3)_2$ by 0.07 Å, while the Si−O−N angle of $Me_3SiON(CF_3)_2$ is 33.7° wider. However, comparison of the solid-state values of $ClH_2SiONMe_2$ and $H_3SiONMe_2$ shows them to have identical Si−O bond length but largely different Si−O−N angles (difference 22.9°).

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(23) Mitzel, N. W.; Smart, B. A.; Parsons, S.; Robertson, H. E.; Rankin, D. W. H. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2727.

(24) Oberhammer, H. Proceedings of the 17th Austin Symposium on Molecular Structure; Austin, TX, 1998.

Table 2. Important Geometry Parameter Values (Å/deg) for $ClH_2SiONMe_2$ and Reference Compounds in Comparison[a]

compound/method	⟨Si−O−N	Si···N	Si−O	N−O
$ClH_2SiONMe_2$ (anti)/XRD	79.7(1)	2.028(1)	1.668(1)	1.490(1)
$ClH_2SiONMe_2$ (anti)/GED	87.1(9)	2.160(7)	1.654(4)	1.475(6)
$ClH_2SiONMe_2$ (gauche)/GED	104.7(11)	2.468(25)	1.641(3)	1.474(8)
$H_3SiONMe_2$/XRD	102.6(1)	2.453(1)	1.668(1)	1.471(1)
$H_2Si(ONMe_2)_2$/XRD	95.2(av)	2.318(av)	1.657(av)	1.479(av)
$Me_3SiON(CF_3)_2$/GED	113.4(19)		1.724(8)	1.450(18)

[a] av = averaged value, GED values all r_a.

The N−O bond length and the Si−O−N angle seem to be correlated: The compounds with the smallest Si−O−N angles have the longest N−O bonds. However, detailed analysis of the scarce available data is complicated by the insufficient compatibility of bond length determined by solid-state XRD and GED, and so a detailed interpretation seems not feasible at present.

Theoretical Description of the Nature of the Si−N-*β*-Donor Bond. An NBO (Natural Bond Orbital) analysis has been performed using the geometry calculated at the MP2/6-311G** level of theory. The results can be used to draw the following picture.

In the *anti-conformer* the σ_{Si-O} NBO is formed by approximately a silicon sp^3 hybrid ($sp^{3.05}d^{0.13}$) and a $sp^{1.70}$ hybrid at oxygen. Hence, the d-contribution is very small. The oxygen−nitrogen σ NBO consists of two orbitals having very large p-character (O $sp^{5.4}$ and N $sp^{5.8}$). The oxygen atom bears two lone pairs described as $sp^{1.1}$ and $sp^{1.0}$. The nitrogen lone pair of electrons is a $sp^{3.25}$ hybrid. The description of the *gauche-conformer* is only slightly different. The Si−O σ bond is formed from a silicon $sp^{3.05}d^{0.11}$ hybrid and an $sp^{1.58}$ hybrid at oxygen. The σ_{O-N} NBO is formed by $sp^{4.32}$ hybrid and an $sp^{6.03}$ hybrid of oxygen.

Second-order perturbation theory analysis of the Fock matrix in the NBO basis provides us with a description of delocalization of electrons into antibonding orbitals, as was used to rationalize for instance the wide Si−O−Si angle of $H_3Si-O-SiH_3$,[25] by $lp_O \rightarrow \sigma^*_{Si-H}$ (lp = lone pair) interaction, termed negative hyperconjugation. Here we describe the nature of such interactions and quote calculated electron delocalization stabilization energies (EDSE), which do not have real physical meaning but are helpful in assessing the relative importance of electron delocalization contributions in terms of the NBO picture.

In the present case of $ClH_2SiONMe_2$, the analysis of the *anti-conformer* shows two marked $lp_O \rightarrow \sigma^*_{Si-H}$ contributions into the antibonding Si−H orbitals (EDSE each 35 kJ mol^{1}). Surprisingly, this interaction seems to be as important as calculated for the two $lp_O \rightarrow \sigma^*_{Si-H}$ contributions in $H_3SiOCH(CH_3)_2$ (EDSE: 40 and 31 kJ mol^{-1}, the molecule symmetry here is C_1). As the sum of these contributions is in both cases of similar importance and the angles at oxygen are extremely different (calculated $ClH_2SiONMe_2$ 91.6° and $H_3SiOCHMe_2$ 122.0°), care is suggested for the uncritical acceptance of the picture of $lp_O \rightarrow \sigma^*_{Si-H}$ interaction, i.e., negative hyperconjugation, as the major contribution for the widening of angles at oxygen centers with silicon substituents attached, as these contributions should be much less important for $ClH_2SiONMe_2$ if dependent on the magnitude of the Si−O−X angle.

Moreover, if a compression of a Si−O−X angle would result in a substantial weakening of the $lp_O \rightarrow \sigma^*_{Si-H}$ interactions, the bond lengths Si−O in compounds with small Si−O−X angles should be significantly longer and more close to the sum of the covalent radii of Si and O (1.83 Å). Nothing like this is observed in compounds with Si−O−N atom sequence (Table 2), and the Si−O bond length are all in the established range between 1.63 and 1.68 Å. Only $Me_3SiON(CF_3)_2$ has a longer Si−O bond [1.724(8) Å], but this compound has a comparatively wide Si−O−N angle.

Table 3. Dipole Moments μ (Debeye) and Atomic Charges q (Mulliken Charges in e) for Selected Compounds, Conformers, and Conformers with Fixed SiON Angles (Calculated at MP2/6-31G*)

compound	μ	q(Si)	q(O)	q(N)
$ClH_2SiONMe_2$ anti (minimum)	4.57	1.06	−0.61	−0.33
$ClH_2SiONMe_2$ anti (⟨SiON = 80°)	5.51	1.08	−0.59	−0.37
$ClH_2SiONMe_2$ anti (⟨SiON = 104°)	3.54	1.05	−0.63	−0.28
$ClH_2SiONMe_2$ gauche (minimum)	2.60	1.04	−0.63	−0.28
$ClH_2SiONMe_2$ gauche (⟨SiON = 90°)	3.04	1.05	−0.62	−0.33
$H_3SiONMe_2$	1.63	0.92	−0.65	−0.29
$H_2Si(ONMe_2)_2$	1.45	1.24	−0.63	−0.31

The lone pair at oxygen in the *gauche-conformer* shows a different stabilization by negative hyperconjugation. The most important contribution here is the $lp_O \rightarrow \sigma^*_{Si-Cl}$ interaction (EDSE: 51 kJ mol^{-1}), while the $lp_O \rightarrow \sigma^*_{Si-H}$ interaction is less important (EDSE: 25 kJ mol^{-1}). It is thus only the antibonding orbitals of the gauche-positioned substituents, which contribute to an interaction with one of the oxygen lone pairs.

The NBO perturbation analysis also provides some rationalization for the small Si−O−N angle in the *anti-conformer* of $ClH_2SiONMe_2$. The lone pair of electrons at nitrogen is delocalized into the σ^*_{Si-Cl}, the σ^*_{Si-O}, and the two σ^*_{Si-H} NBOs (EDSEs: 40, 26, and (2×) 11 kJ mol^{-1}). Electron delocalization of the nitrogen lone pair in the *gauche-conformer* is much less pronounced (EDSEs: 3, 9, 9, and 3 kJ mol^{-1}). However, this kind of electron delocalization is calculated to be of similar importance as in $H_3SiONMe_2$, which has an Si−O−N angle of 102.6° (EDSE: 29 kJ mol^{-1}) which is similar to that in $ClH_2SiONMe_2$. However, the calculations show that the stabilization by negative hyperconjugation $lp_N \rightarrow \sigma^*_{Si-X}$ becomes larger with decreasing angle and with chlorine rather than hydrogen substituents placed into anti-position relative to nitrogen.

We have also tried to rationalize our experimental results of β-donor bonding in terms of simple electrostatic arguments, i.e., by an attractive force between the positively charged silicon and the negatively charged nitrogen atom. Table 3 lists dipole moments and the calculated Mulliken charges for selected systems. Indeed, the anti-conformer of $ClH_2SiONMe_2$ has a higher negative charge at its nitrogen atom than the gauche conformer has, but if the anti-conformer is calculated with the Si−O−N angle fixed at the value of the minimum geometry of the gauche conformer, the charges become the same. The same applies for a comparison between a hypothetical gauche conformer with an Si−O−N angle adopted by the ground state of the anti-conformer. Thus this does not explain the differences between the two structures.

Comparison of the gauche-conformer of $ClH_2SiONMe_2$ with $H_3SiONMe_2$ (both have about the same Si−O−N angles) shows

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[25] Shambayati, S.; Blake, J. F.; Wierschke, S. G.; Jorgensen, W. L.; Schreiber, S. L. *J. Am. Chem. Soc.* **1990**, *112*, 697.

also the charges to be no major determining factor for the strength of β-donor bonds, as the charge on the Si atom in $H_3SiONMe_2$ is much smaller.

On the other hand, a system with anti-conformation having a higher charge on silicon is $H_2Si(ONMe_2)_2$. It has, however, a wider Si−O−N angle than the anti-conformer of $ClH_2SiONMe_2$.

The calculated dipole moments show some interesting trends. For the anti-conformer of $ClH_2SiONMe_2$ the dipole moment becomes larger with decreasing Si−O−N angle, and this can serve as an explanation for the fact that the Si−O−N angle in the solid state is smaller than in the gas phase, because of intermolecular dipole interactions. It is generally observed that crystallization drives (partial) bonds toward completion.[26] The higher dipole moment of the anti-conformer can also be seen as the reason, why this conformer is preferred in the crystallization process.

Conclusion

$ClH_2SiONMe_2$ is a compound with an unusual bonding situation. The attractive interaction between the silicon and nitrogen atoms, a β-donor bond, is stronger than in all compounds of this type studied before. This nonclassical interaction is capable of overriding the natural tendency of oxygen atoms with silicon substituents to adopt wide bond angles and prevents the nitrogen centers from the formation of intermolecular donor interactions. The strength of a β-donor bond is dependent on the nature and relative orientation of the substituents at the silicon atom. Clearly, electron-withdrawing groups attached to silicon will strengthen a β-donor bond, but only if placed in anti-position relative to the nitrogen-donor center, as can be shown by the Si−O−N angle in $ClH_2SiONMe_2$ which is exceptionally small in the anti-conformer but substantially larger in the gauche-conformer. This shows that a β-donor bond cannot simply be described as electrostatic attraction between positively charged Si and negatively charged N atoms and points the analysis of the bonding situation in the direction of an overlap of the lone pair of electrons at the nitrogen atom with acceptor orbitals related to the $Si-X_{anti}$ bond. In the NBO description of bonding, there is an important contribution of electron delocalization stemming from $lp_N \rightarrow \sigma^*_{Si-X(anti)}$ type negative hyperconjugation. This interaction is much stronger for X = Cl than for X = H, thus explaining the different geometries of the anti- and gauche-conformer of $ClH_2SiONMe_2$ as well as the large differences in structure and strength of β-donor interactions in a series of compounds with Si−O−N atom sequence.

The nature of the Si−O bond has often been associated with negative hyperconjugation of the type $lp_O \rightarrow \sigma^*_{Si-X}$ and used to rationalize the wide angles at oxygen, e.g., in $(H_3Si)_2O$ and H_3COSiH_3. Marked contributions to electron delocalization $lp_O \rightarrow \sigma^*_{Si-X}$ have also been found in the NBO description of the Si−O−N compounds with their small angles at oxygen. This questions whether $lp_O \rightarrow \sigma^*_{Si-X}$ negative hyperconjugation should be seen as the only or even major contribution to the observed widening of angles in Si−O−X compounds.

It is obvious that further experiments and calculations are needed to get a better insight into the nature of β-donor interactions. As a next step we intend to perform crystallographic high-resolution electron density determinations on Si−O−N compounds followed by the analysis of their topology in the hope to prove experimentally above hypotheses derived from calculations.

Experimental Section

General. The experiments were carried out using a standard Schlenk line or, when H_2SiCl_2 was involved, in a vacuum line with greaseless stopcocks (Young taps), which is directly attached to the gas cell in an FTIR spectrometer (Midac Prospect FTIR). *N*,*N*-Dimethylhydroxylamine was prepared according to lit. cit.[27] All NMR spectra were recorded at 21 °C on a JEOL JNM-LA400 spectrometer in sealed tubes with C_6D_6 as a solvent directly condensed onto the sample from K/Na alloy.

(*N*,*N*-Dimethylhydroxylamino)chlorosilane. *n*-Butyllithium (35.0 mL of a 1.6 M solution in hexane, 56 mmol) was slowly added to a solution of *N*,*N*-dimethylhydroxylamine (4.0 mL 3.44 g, 56 mmol) in 50 mL of pentane with stirring, which was prolonged for 1 h after complete addition. The solvents were removed under reduced pressure, and the residue was suspended in diethyl ether (40 mL). Dichlorosilane (98 mmol) was condensed onto the frozen suspension at −196 °C. The mixture was allowed to warm to 0 °C, and the volatile contents were condensed into a cooled trap. *N*,*N*-Dimethylhydroxylaminochlorosilane was isolated by fractional condensation from a −78 °C trap. Yield 5.3 g (42 mmol, 75%), colorless, very moisture sensitive liquid (fp = −55 °C).

^{1}H NMR: $\delta = 2.16$ (s, 6H, H_3C), 4.93 (s, 2H, H_2Si). ^{13}C NMR: $\delta = 48.1$ (q t, $^1J_{CH} = 137.0$ Hz, $^3J_{CNCH} = 4.8$ Hz, CH_3). ^{15}N{^{1}H}-NMR: $\delta = -249.5$ (s). ^{17}O{^{1}H}-NMR: $\delta = 136.5$ (s). ^{29}Si NMR: $\delta = -54.6$ (t,$^1J_{SiH} = 287.0$ Hz, SiH_2). IR(gas): ν(SiH) = 2217.

(*N*,*N*-Diethylhydroxylamino)chlorosilane. This compound was prepared in the same way as described above. Yield: 78%.

^{1}H NMR: $\delta = 0.71$ (t, 6H, $^3J_{HCCH} = 7.2$ Hz, H_3C), 2.49 (q, 4H, $^3J_{HCCH} = 7.2$ Hz, H_2C), 5.0 (s, 2H, H_2Si). ^{13}C NMR: $\delta = 9.3$ (q, $^1J_{CH} = 126.9$ Hz, CH_3), 49.2 (t, $^1J_{CH} = 137.4$ Hz, CH_2). ^{15}N{^{1}H}-NMR: $\delta = -228.9$ (s). ^{17}O{^{1}H}-NMR: $\delta = 121.6$ (s). ^{29}Si NMR: $\delta = -52.3$ (t,$^1J_{SiH} = 285.6$ Hz, SiH_2). IR(gas): ν(SiH) = 2218.

Crystal Structure Determination $ClH_2SiONMe_2$. A single crystal was grown in situ by slowly cooling the melt in a sealed capillary from 217 to 213 K after generation of a suitable seed crystal. Crystal system triclinic, space group *P*), $Z = 2$, $a = 5.7284(4)$, $b = 6.5347(5)$, $c = 8.7954(4)$ Å, $\alpha = 101.236(7)$, $\beta = 102.126(8)$, $\gamma = 96.056(7)°$, $V = 312.85(5)$ Å^3 at 134(2) K, cell from 100 reflections (θ-range 20−25°). $2\theta_{max.} = 72°$, $\omega/2\theta$-scan, 3335 independent reflections [$R_{int.} = 0.0353$]. Diffractometer: Enraf-Nonius CAD4, Mo−K_a-radiation, graphite monochromator, Solution: direct methods (SHELXTL, Siemens Analytical X-ray Instrumentation Inc. Madison, WI, 1995); refinement: SHELXL93 (Sheldrick, G. M. Universität Göttingen, Germany, 1993). No absorption correction applied. Non-H-atoms were refined with anisotropic thermal displacement parameters, hydrogen atoms were located in difference Fourier maps and refined isotropically. Weight = $1/[\sigma^2(F_o^2) + (0.0621P)^2 + 0.03 \cdot P]$ where $P = (\max.(F_o^2,0) + 2 \cdot F_c^2)/3.88$ parameters, $R_1 = 0.0356$ for 3323 reflections with $F_o > 4\,\sigma(F_o)$ and $wR_2 = 0.1132$ for all data.

Ab Initio Calculations. Ab initio molecular orbital calculations were carried out using the Gaussian 94 program.[28] Geometry optimizations and vibrational frequency calculations were performed from

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(26) Leopold, K. R.; Canagaratna, M.; Phillips, J. A.; *Acc. Chem. Res.* **1997**, *30*, 57.

(27) Davies, M.; Spiers, N. A. *J. Chem. Soc.* **1959**, 3971.

(28) 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.

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

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

(31) 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.

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

analytic first- and second- derivatives at the SCF and MP2 levels of theory. Calculations were undertaken at the SCF level using the standard 3-21G*,[29−31] 6-31G*,[32−34] and 6-311G** [35,36] basis sets, while the larger two basis sets were used for calculations at the MP2 level of theory. NBO calculations were undertaken with the NBO 3.0 facilities built into Gaussian94.[37,38] Cartesian coordinates of the calculated structures of the anti- and gauche-conformer of $ClH_2SiONMe_2$ can be found in the Supporting Information.

Gas-Phase Electron-Diffraction. Electron scattering intensity data for $ClH_2SiONMe_2$ 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. 500.0 mm camera distance: wavelength 0.048869(10) Å, data range $s_{min.} = 2.0$ to $s_{max.} = 11.0$, weighting points (trapezoidal weighting function) $s_1 = 4.0$ and $s_2 = 11.0$, scale factor 0.984(4); 250.0 mm camera distance: wavelength 0.048868(9) Å, data range $s_{min.} = 8.0$ to $s_{max.} = 34.8$, weighting points (trapezoidal weighting function) $s_1 = 10.0$ and $s_2 = 29.6$, scale factor 0.727(15). 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[39] and the scattering factors established by Fink and co-workers.[40] The refined molecular parameters, their definition and the applied restraints, a list with selected interatomic distances including vibrational amplitudes, and applied restraints and elements of the correlation matrix are given in the Supporting Information.

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Supporting Information Available: Tables of crystal data, atomic coordinates, equivalent isotropic thermal parameters; molecular parameter definition, parameter values, and restraints for the GED refinement of $ClH_2SiONMe_2$; selected distances, vibrational amplitudes, and amplitude restraints for the GED refinement of $ClH_2SiONMe_2$, correlation matrix elements with absolute values > 0.50 (times 100) for the GED refinement of $ClH_2SiONMe_2$; and Cartesian coordinates of the geometry of $ClH_2SiONMe_2$ calculated at MP2/6-311G** (4 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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

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

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

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

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

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

(39) 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.

(40) Ross, A. W.; Fink, M.; Hilderbrandt, R. *International Tables for X-ray Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dodrecht, Boston, 1992; Vol. C, p 245.

(41) Emsley, J. *The Elements*; Clarendon Press: Oxford, 1989.