Bonding Properties of Siloxanes: Gas Phase Structures of *N*,*N*-Bis(trifluoromethyl)-*O*-(trimethylsilyl)hydroxylamine, $Me_3SiON(CF_3)_2$, and Trimethylsilyl Nitrate, Me_3SiONO_2

Thomas Hertel,[†] **Jens Jakob,**[†] **Rolf Minkwitz,**[†] **and Heinz Oberhammer***[,‡]

Anorganische Chemie, Universität Dortmund, 44221 Dortmund, Germany, and Institut für Physikalische und Theoretische Chemie, Universität Tübingen, 72076 Tübingen, Germany

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The geometric structures of *N*,*N*-bis(trifluoromethyl)-*O*-(trimethysilyl)hydroxylamine, $Me_3SiON(CF_3)_2$ (**1**), and of trimethylsilyl nitrate, Me_3SiONO_2 (**2**), have been determined by gas electron diffraction and quantum chemical calculations (HF/3-21G*, B3LYP/6-31G*). Both compounds possess C_s symmetry. In **1** the Si−O bond is oriented syn with respect to the nitrogen lone pair (anti with respect to the CNC bisector of the $N(CF_3)_2$ group). In **2** the Si−O bond is coplanar with the nitrate group. The following skeletal parameters (r_a values with 3σ error limits) have been derived: for **1**, Si−O 1.724(8) Å, N−O 1.450(18) Å, Si−O−N 113.4(19)°; for **2**, Si−O 1.715(4) Å, N−O 1.383(5) Å, Si−O−N 120.1(9)°. The unusually long Si−O bonds in both compounds can be rationalized by the electron-withdrawing power of the $N(CF_3)_2$ and NO_2 groups. This leads to a reduction of the polarity of the Si^+-O^- bond and to lengthening of these bonds. The siloxane **2** possesses an extremely short 1,4-nonbonded contact between silicon and the cis-standing oxygen of the nitrate group, Si···O = 2.70 Å, which indicates a strong intramolecular Si···O donor interaction.

Introduction

The unusually short Si−O bonds and large SiOSi bond angles in disiloxanes (e.g., Si−O = 1.634(2) Å and SiOSi = 144.1(9)° in $H_3SiOSiH_3$[1]) have commonly been attributed to $(p\rightarrow d)\pi$ back-bonding between the oxygen lone pairs and the unfilled silicon d orbitals[1−4] or by negative hyperconjugation.[5] Ab initio calculations, however, indicate that the energetically high lying silicon d orbitals are of minor importance in the bonding of disiloxanes.[6,7] The short bond can be rationalized as a consequence of the high ionic character of the Si−O bond ($Si^{+1.27}-O^{-1.12}$ or $Si^{+3.03}-O^{-1.72}$ according to ref 6 or 7, respectively). The large bond angle is due to electrostatic repulsion between the positive net charges of the silicon atoms and due to steric repulsions. This concept provides a straightforward explanation for the structural properties of siloxanes of the type R_3SiOX, where X is a more electronegative substituent than SiH_3. In the peroxide $Me_3SiOOSiMe_3$ (X = $OSiMe_3$) the Si−O bonds are appreciably longer (1.681(3) Å) than in disiloxane and the SiOO angle decreases to 106.6(14)°.[8] An even smaller SiOO angle of 101.2° was predicted by ab initio calculations for $H_3SiOOSiH_3$.[6] Recently, experimental and theoretical structural studies of compounds which contain an Si−O−N skeleton have been reported by Mitzel et al.[9−11] For crystalline and gaseous $ClH_2SiONMe_2$ Si−O bond lengths of 1.668(1) and 1.654(4) Å, respectively, and Si−O−N bond angles of 79.7(1)° (crystal) and 87.1(9)° (gas) were derived.[9] These extremely small oxygen bond angles and the resulting short 1,3-nonbonded Si···N distances of 2.028(1) Å in the crystal and 2.160(7) Å in the gas phase have been explained by intramolecular Si···N β-donor interactions and (4 + 1) coordination of silicon. Similar structural properties have also been observed for $H_3SiONMe_2$, $H_2Si(ONMe_2)_2$, and $Si(ONMe_2)_4$.[10,11]

In the present work we report gas phase structures of two compounds which also contain Si−O−N skeletons, $Me_3SiON(CF_3)_2$ and Me_3SiONO_2. The gas phase electron diffraction analyses (GED) were supplemented by ab initio calculations in the HF/3-21G* approximation. The geometries of the ground state structures were optimized also with the B3LYP/6-31G* method. The calculated geometric parameters are listed together with the experimental results in the respective tables. The theoretical results were used primarily to support the GED analyses (see below). The calculations were performed with the GAUSSIAN 94 program system.[12]

[†] Universität Dortmund.

[‡] Universität Tübingen.

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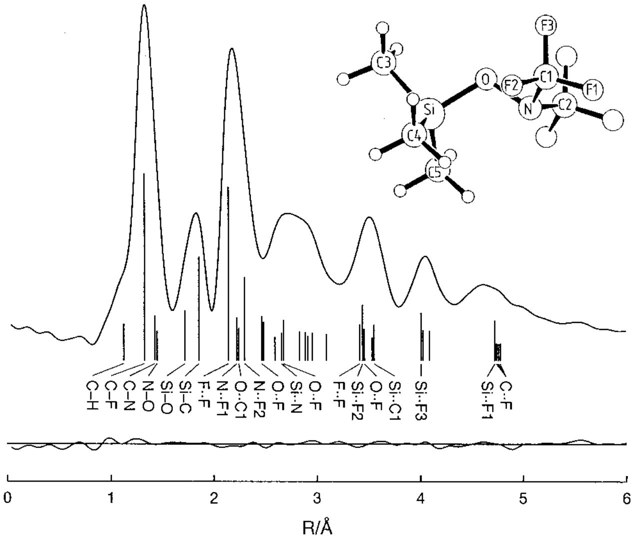

Figure 1. Experimental radial distribution function for $Me_3SiON(CF_3)_2$ and difference curve. The positions of important interatomic distances are given by vertical bars.

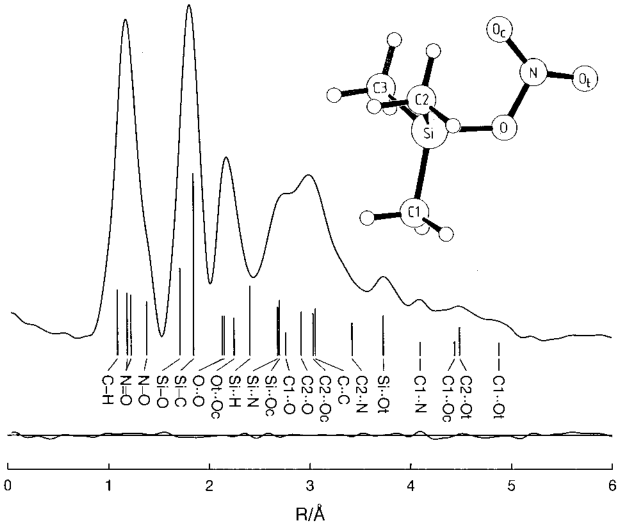

Figure 2. Experimental radial distribution function for Me_3SiONO_2 and difference curve. The positions of important interatomic distances are given by vertical bars.

Structure Analyses

The radial distribution functions (RDF) were derived by Fourier transformation of the molecular intensities which were multiplied with an artificial damping function $\exp(-\gamma s^2)$, $\gamma = 0.0019$ Å^2. The RDF for $Me_3SiON(CF_3)_2$ (Figure 1) is reproduced satisfactorily only with a structure in which the Si−O bond is syn with respect to the nitrogen lone pair. This implies anti orientation of the $SiMe_3$ group relative to the CNC bisector of the $N(CF_3)_2$ group. According to the HF/3-21G* calculations, the anti form (Si−O anti to nitrogen lone pair) does not correspond to a stable structure. Optimization of this conformer leads to inversion at nitrogen. Analysis of the RDF for Me_3SiONO_2 (Figure 2) results in a staggered orientation of $SiMe_3$ relative to the nitrate group. The calculated barrier to internal rotation around the Si−O bond is 6.4 kcal mol^{-1} (HF/3-21G*), which makes a rigid molecular model fully adequate for the GED analysis. Preliminary geometric parameters, which were derived from the RDFs, were refined in least-squares analyses. The molecular intensities were multiplied with a diagonal weight matrix, and known complex scattering amplitudes were used.[13]

Table 1. Experimental and Calculated Geometric Parameters for $(CH_3)_3SiON(CF_3)_2$[a]

	GED		HF/3-21G*[b]	B3LYP/6-31G*[b]
C−H	1.109(15)	p_1	1.087	1.096
C−F	1.328(2)	p_2	1.338	1.340
N−C	1.430[20][c]		1.420	1.449
N−O	1.450(18)	p_3	1.438	1.421
Si−O	1.724(8)	p_4	1.716	1.734
Si−C	1.858(4)	p_5	1.868	1.879
C−Si−C	112.9(13)	p_6	111.9	111.8
Si−O−N	113.4(19)	p_7	116.3	115.2
O−N−C	102.2(12)	p_8	107.7	107.6
C−N−C	116.2(11)	p_9	118.3	115.5
F−C−F	107.7(2)	p_{10}	108.3	108.2
H−C−H	108.0[d]		107.3	107.8
tilt ($SiMe_3$)	6.2(29)	p_{11}	5.8	6.9
tilt (CF_3)	1.6[d]		1.4	1.9
$\tau(CF_3)$[e]	3.7(25)	p_{12}	1.6	2.5

[a] r_a values in angstroms and degrees. Error limits are 3σ values and include possible systematic errors (see text). The molecular model is shown in Figure 1. [b] Mean values are given for parameters which are not unique. [c] Not refined, but varied within the given range. [d] Not refined. [e] Torsional angle of the CF_3 groups around the N−C bonds. For $\tau = 0°$ the CF_3 groups stagger exactly the opposite N−C bond.

For both compounds the CH_3 groups were constrained to C_{3v} symmetry, and tilt angles between the C_3 axis and the Si−C bond direction were set to 0. This constraint is justified by the results of the theoretical calculations, which predict these tilt angles to be less than 1°. C_{3v} symmetry was also assumed for the $SiMe_3$ groups, and the tilt angle between the C_3 axis and the Si−O bond was refined. Vibrational amplitudes were collected in groups according to their distances and according to their dependence on torsional vibrations.

$Me_3SiON(CF_3)_2$. In addition to the assumptions described above, the CF_3 groups were constrained to local C_{3v} symmetry and the tilt angle was set to the calculated value. The N−C bond length could not be derived from the GED data, because of large correlations. This bond length was set to 1.43 Å. Similar values have been determined for $(CF_3)_2NOMe$ (1.429(7) Å)[14] and $(CF_3)_2NONO$ (1.426(10) Å).[15] The uncertainty for this bond length is estimated to be ±0.02 Å, and possible systematic errors due to this constraint are included in the error limits for the refined parameters. The torsional orientation of the CF_3 groups around the N−C bonds was described by the torsional angle τ. For $\tau = 0°$, the CF_3 group staggers exactly the opposite N−C bond (dihedral angle $\phi(CNCF) = 180°$). On the basis of the ab initio calculations, the two CF_3 groups are rotated in opposite directions by the same angle, resulting in C_s overall symmetry for the molecule. With these assumptions, 12 geometric parameters p_i and seven vibrational amplitudes l_k were refined simultaneously. The following correlation coefficients had values larger than $|0.7|$: $p_6/p_{11} = -0.89$, $p_8/p_{12} = -0.89$, and $p_{12}/l_5 = 0.72$. The final results are listed in Tables 1 (geometric parameters) and 2 (vibrational amplitudes).

Me_3SiONO_2. Only a mean value of the two N=O double bonds could be determined in the GED analysis. The difference was constrained to 0.02 Å, and an uncertainty of ±0.02 Å was estimated. Ten geometric parameters p_i and eight vibrational amplitudes l_k were refined simultaneously, and only one

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Table 2. Interatomic Distances and Vibrational Amplitudes for $Me_3SiON(CF_3)_2$ (without Distances Involving Hydrogen)[a]

	distance	amplitude			distance	amplitude	
C−F	1.33	0.041(2)	l_1	N···C4	3.33	0.221(29)	l_6
N−C	1.43	0.045[b]		F···F	3.42	0.221(29)	l_6
N−O	1.45	0.045[b]		Si···F2	3.45	0.221(29)	l_6
Si−O	1.72	0.047(5)	l_2	C···F	3.54	0.221(29)	l_6
Si−C	1.86	0.047(5)	l_2	Si···C1	3.55	0.100[b]	
F···F	2.15	0.054(4)	l_3	Si···F3	4.02	0.120[b]	
N···F	2.23−2.30	0.054(4)	l_3	F···F	4.02−4.09	0.120[b]	
O···Cl	2.24	0.060[b]		N···C3	4.10	0.120[b]	
C1···C2	2.42	0.060[b]		C···F	4.41−4.46	0.175[b]	
X···F[c]	2.47−2.89	0.096(20)	l_4	Si···F1	4.74	0.262(51)	l_7
Si···N	2.66	0.096(20)	l_4	C···C	4.62−4.78	0.262(51)	l_7
O···C	2.73−2.93	0.098(34)	l_5	C···F	4.67−4.76	0.262(51)	l_7
C···F	2.96	0.098(34)	l_5	C···F	5.29−6.08	0.300[b]	
C3···C4	3.10	0.098(34)	l_5				

[a] Distances and amplitudes in angstroms; error limits are 3σ values. For atom numbering see Figure 1. [b] Not refined. [c] X = C, O, or F.

Table 3. Experimental and Calculated Geometric Parameters for $(CH_3)_3SiONO_2$[a]

	GED		HF/3-21G* [b]	B3LYP/6-31G* [b]
C−H	1.095(6)	p_1	1.087	1.096
$(N{=}O)_{mean}$	1.210(2)	p_2	1.229	1.216
$\Delta(N{=}O) = (N{=}O_c) - (N{=}O_t)$	0.020[20][c]		0.039	0.016
$N{=}O_t$	1.200(11)		1.210	1.208
$N{=}O_c$	1.220(11)		1.249	1.224
N−O	1.383(5)	p_3	1.386	1.385
Si−O	1.715(4)	p_4	1.735	1.761
Si−C	1.850(2)	p_5	1.865	1.877
C−Si−C	112.1(6)	p_6	112.4	112.4
Si−O−N	120.1(9)	p_7	119.9	120.1
$(O-N{=}O)_{mean}$	111.5(5)	p_8	116.0	115.9
$\Delta(O-N{=}O) = (O-N{=}O_c) - (O-N{=}O_t)$	−1.6(30)	p_9	0.2	2.6
$O-N{=}O_t$	112.3(16)		115.9	113.6
$O-N{=}O_c$	110.7(16)		116.1	117.2
H−C−H	108.0 [d]		107.8	107.9
tilt ($SiMe_3$)	5.3(12)	p_{10}	5.8	7.0

[a] r_a values in angstroms and degrees. Error limits are 3σ values and include possible systematic errors (see text). The molecular model is shown in Figure 2. [b] Mean values are given for parameters which are not unique. [c] Not refined, but varied within the given range. [d] Not refined.

correlation coefficient, $p_3/p_8 = -0.72$, had a value larger than $|0.7|$. The results of this least-squares refinement are listed in Tables 3 (geometric parameters) and 4 (vibrational amplitudes).

Discussion

Table 5[16,17] compares skeletal geometric parameters of some siloxanes of the type R_3SiOX. The Si−O bond length increases with increasing electronegativity of the substituent X from 1.629(3) Å for X = $SiMe_3$ to 1.724(8) Å for X = $N(CF_3)_2$. This trend can be rationalized with the high ionic character of this bond. Electron-withdrawing substituents X reduce the negative net charge of oxygen and thus lower the polarity of the Si^+-O^- bond, which in turn leads to lengthening. The Si−O bond in $Me_3SiON(CF_3)_2$ is the longest such bond derived for a gaseous siloxane. A still longer Si−O bond (1.741 Å) was observed in the crystal structure of $Me_3SiOSO_2N(SO_2Me)_2$.[18]

Table 4. Interatomic Distances and Vibrational Amplitudes for Me_3SiONO_2 (without Distances Involving Hydrogen)[a]

	distance	amplitude			distance	amplitude	
N=O	1.21	0.039(3)	l_1	$C2\cdots O_c$	3.04	0.250[b]	
N−O	1.38	0.045[b]		C···C	3.06	0.101(25)	l_5
Si−O	1.72	0.051(2)	l_2	N···C2	3.43	0.143(34)	l_6
Si−C	1.85	0.051(2)	l_2	$Si\cdots O_t$	3.74	0.095(14)	l_7
O···O	2.14−2.25	0.053(5)	l_3	N···C1	4.10	0.090[b]	
Si···N	2.69	0.080[b]		$C1\cdots O_c$	4.44	0.110[b]	
$Si\cdots O_c$	2.70	0.149(48)	l_4	$C2\cdots O_t$	4.50	0.273(78)	l_8
O···C	2.77−2.92	0.101(25)	l_5	$C1\cdots O_t$	4.88	0.150[b]	

[a] Distances and amplitudes in angstroms; error limits are 3σ values. For atom numbering see Figure 2. [b] Not refined.

Table 5. Skeletal Structural Parameters of Some Siloxanes R_3SiOX

$R_3Si-O-X$	Si−O	Si−O−X	Si···X (exp)	∑(one-angle radii)
$Me_3Si-O-SiMe_3$[a]	1.629(3)	151.7(30)	3.16	3.10
$H_3Si-O-SiH_3$[b]	1.634(2)	144.1(9)	3.10	3.10
$H_3Si-O-CH_3$[c]	1.640(3)	120.6(10)	2.66	2.72
$ClH_2Si-O-NMe_2$[d]	1.654(4)	87.1(9)	2.16	2.69
$H_3Si-O-NMe_2$[e]	1.668(1)	102.6(1)	2.45	2.69
$Me_3Si-O-OSiMe_3$[f]	1.681(3)	106.6(14)	2.54	2.68
$Me_3Si-O-NO_2$[g]	1.715(4)	120.1(9)	2.69	2.69
$Me_3Si-O-N(CF_3)_2$[g]	1.724(8)	113.4(19)	2.66	2.69

[a] Reference 16. [b] Reference 1. [c] Reference 17. [d] Reference 9. [e] Reference 10. [f] Reference 8. [g] This work.

The oxygen bond angles in these siloxanes show a very large variation from 152° to 87°, and no correlation between bond lengths and angles is observed. Several concepts have been proposed for predicting or rationalizing bond angles. The concept of hybridization or the VSEPR model cannot explain such a large range of oxygen bond angles, and these approaches do not allow quantitative predictions. A rough estimate of such bond angles can be made on the basis of "one-angle" nonbonded radii. Such radii describe the size of atoms A and B which are separated by one angle in an AYB entity. The A···B one-angle nonbonded distance and the AYB angle can be predicted from the sum of these radii for A and B. One-angle radii are about 20−30% smaller than van der Waals radii, and values have been derived from experimental gas phase structures: Si, 1.55 Å; N, 1.14 Å; O, 1.13 Å.[19] For C we propose a value of 1.17 Å, which was derived from the structures of dimethyl ether and trimethylamine. Since one-angle radii depend also on the central

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atom Y and on other substituents,[20] we estimate an uncertainty of ±0.05 Å. Table 5 compares experimental Si⋯X one-angle distances with the sum of one-angle radii. The agreement between experimental and predicted values is good for X = $SiMe_3$, SiH_3, and CH_3. In $ClH_2SiONMe_2$ and $H_3SiONMe_2$, however, the experimental Si⋯N distances are by 0.53 and 0.24 Å shorter than the predicted value. With oxygen bond angles of 87.1(9)° and 102.6(1)°, these differences can certainly not be attributed to steric strain. It rather demonstrates a strong intramolecular Si⋯N β-donor interaction as suggested by Mitzel.[9,10] A somewhat smaller difference of 0.14 Å between experimental and predicted Si⋯O distances occurs in $Me_3SiOOSiMe_3$. Again, this difference and the Si−O−O angle (106.6(14)°), which is smaller than tetrahedral, suggest an Si⋯O β-donor interaction in this peroxide. In the two molecules studied in the present investigation, the experimental Si⋯N distances are very close to the predicted values and the oxygen bond angles are larger than tetrahedral. From these results we conclude that Si⋯N β-donor interactions are absent or play a minor role in these compounds. This is obvious in the case of the nitrate, and it is expected in $Me_3SiON(CF_3)_2$, since the $N(CF_3)_2$ group is a much weaker donor than NMe_2 and because of the reduced electrophilicity of $SiMe_3$.

We have recently observed a strong dependence of N−O single bond lengths in covalent nitrates $XONO_2$ on the electronegativity of X.[21] This bond lengthens steadily with increasing electronegativity of X from 1.402(5) Å in CH_3ONO_2[22] to 1.507(4) Å in $FONO_2$.[21] The N−O bond derived for Me_3SiONO_2 (1.384(5) Å), which is the shortest such bond observed for a gas phase nitrate, is in perfect agreement with this correlation, since $SiMe_3$ is more electropositive than methyl. A surprising structural feature of this nitrate is the short contact between Si and the cis-standing oxygen atom of the nitrate group. This 1,4-nonbonded Si⋯O_c distance of 2.70 Å is much shorter than the corresponding van der Waals distance of 3.44 Å (see Figure 2 for atom numbering). The two O−N═O angles in the silyl nitrate are equal within their experimental error limits, whereas for all other nitrates $XONO_2$ with X = CH_3, F, Cl, Br, the O−N═O_c angle is larger by 6−10° than the O−N═O_t angle. In these compounds the NO_2 group is pushed away from the substituent X, but not in the nitrate with the bulkiest substituent X = $SiMe_3$. Furthermore, the theoretical calculations predict the N═O_c bond to be longer than N═O_t. This small difference could not be determined in the GED analysis. All of these features, short Si⋯O_c distance, equal O−N═O angles, and N═O_c > N═O_t, demonstrate that there is a strongly attractive Si⋯O_c interaction in this compound.

Of course, the short 1,3- and 1,4-nonbonded distances in the siloxanes $ClH_2SiONMe_2$, $H_3SiONMe_2$, $Me_3SiOOSiMe_3$, and Me_3SiONO_2 can also be explained by electrostatic attractions between the high positive net charge of Si and the expected negative net charges of N and O. On the other hand, a Mulliken overlap population analysis for Me_3SiONO_2 at the B3LYP/6-31G* level results in a positive overlap population for the 1,4-Si⋯O_c distance of 0.035 au, which is about 15% of that for the Si−O bond (0.245 au). This result suggests that the donor interaction concept is a more realistic explanation for the short contact than the ionic model. Furthermore, an ionic model cannot explain the difference between the two N═O bond lengths.

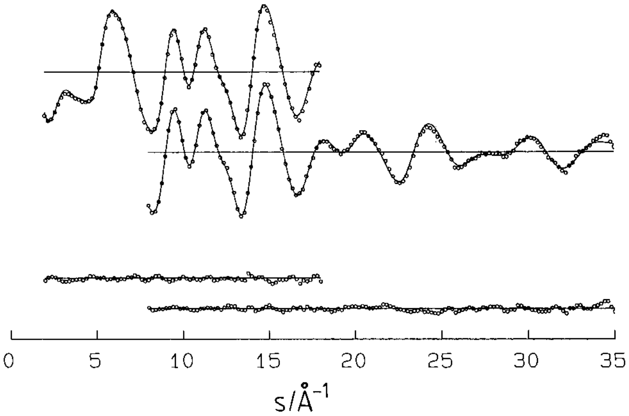

Figure 3. Experimental (dots) and calculated (full line) molecular intensities and differences for $Me_3SiON(CF_3)_2$.

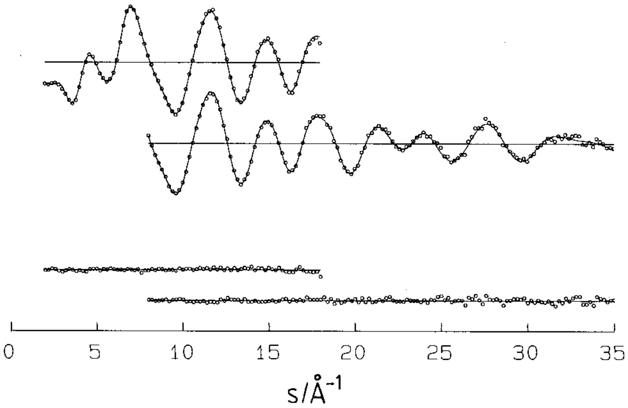

Figure 4. Experimental (dots) and calculated (solid lines) molecular intensities and differences for Me_3SiONO_2.

Both quantum chemical methods reproduce the experimental structures satisfactorily (i.e., to within ±0.03 Å for bond lengths and ±3° for bond angles), except for the nitrogen bond angles. The calculated O−N−C angles in $Me_3SiON(CF_3)_2$ and the O−N═O angles in the nitrate are larger than the experimental values by ca. 4−5°.

Experimental Section

Synthesis of *N*,*N*-Bis(trifluoromethyl)-*O*-(trimethylsilyl)hydroxylamine $Me_3SiON(CF_3)_2$. $(CF_3)_2NOH$ was synthesized by the reaction of trifluoronitrosomethane with ammonia.[23] The sodium salt was prepared by stirring 10 mmol of $(CF_3)_2NOH$, 10 mmol of NaOH, and 5 mmol of THF in a 50-mL reaction vessel for 8 h. After THF was pumped off and the sodium salt was dried for 24 h in vacuo, a colorless, hygroscopic powder was obtained.[24] In a slight modification to ref 23, 10 mmol of Me_3SiCl was added and the reaction mixture was stirred for 24 h at 50 °C. At −30 °C, $Me_3SiON(CF_3)_2$ was condensed into a trap at −196 °C. The yield was 50%, and no further purification was needed. $Me_3SiON(CF_3)_2$ is a colorless liquid with mp −60 °C and bp 78−79 °C.[25] The purity was checked by NMR and vibrational spectroscopy.

Synthesis of Trimethylsilyl Nitrate, Me_3SiONO_2. The compound was prepared by the reaction of trimethylchlorosilane and chlorine nitrate.[26] $ClONO_2$ (2.5 g) was condensed onto 0.44 g of Me_3SiCl at −196 °C. The mixture was slowly warmed to −35 °C and kept at this temperature for several days. At −50 °C the evolved chlorine

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and the surplus chlorine nitrate were removed in vacuo. The yield was about 95%, and no further purification was needed. Me_3SiONO_2 is a colorless liquid with mp −63 °C and bp 70−75 °C (150 Torr).[27] The purity was checked by NMR and vibrational spectroscopy. Other synthetic routes have been described previously. Schmidt and Schmidbauer prepared this compound by reacting Me_3SiCl with $AgNO_3$.[28] Voronkov et al. reacted $(Me_3SiO)_2SO_2$ or $(Me_3SiO)_3PO$ with KNO_3.[27,29] The disadvantages of these methods are a higher temperature during reaction or during the following distillation, which leads to partial decomposition of Me_3SiONO_2 into the disiloxane $Me_3SiOSiMe_3$ and nitric oxides.

The electron diffraction intensities were recorded with a Gasdiffraktograph KG-G2[30] at 25- and 50-cm nozzle-to-plate distances and with an accelerating voltage of ca. 60 kV. The sample reservoirs were kept at −17 °C ($Me_3SiON(CF_3)_2$) and 20 °C (Me_3SiONO_2), and the inlet system and nozzle were at room temperature. The photographic plates were analyzed with the usual methods,[31] and averaged molecular intensities in the s-ranges 2−18 and 8−35 $Å^{-1}$ in steps of $\Delta s = 0.2$ $Å^{-1}$ are shown in Figures 3 and 4 ($s = (4\pi/\lambda)\sin(\theta/2)$, λ = electron wavelength, and θ = scattering angle).

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