SiONB Unit as Reference for Blocked Si···N Interactions in SiON Compounds

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Introduction

Attractive secondary interactions between donor and acceptor atoms in geminal positions relative to one another have been shown to be structure-determining in certain classes of p-block compounds containing SiON,[1] GeON,[2] SnON,[3] AlON,[4] SiNN,[5] BCN,[6] BNN,[7] AlCN,[8] and AlNN[9] linkages. We have systematically studied SiON compounds (i.e., oximatosilanes[10] and aminoxysilanes) and found a broad range of different strengths for such β-donor interactions, from predictably weak ones in $Me_3SiONMe_2$ [11] to medium ones in $H_2SiONMe_2$ [11] to really strong ones in anti-$ClH_2SiONMe_2$.[12] These interactions are indicated by short Si···N distances leading to a three-membered ring with one weakly bound edge and are advantageously characterized by the contraction of their SiON angles. The corresponding alkoxysilanes containing SiOC units served as reference systems because they are not capable of secondary interaction formation. Their respective SiOC angles are much wider than the SiON angles in aminoxysilanes and oximatosilanes. The generally observed widening of oxygen valence angles in SiO compounds has been the subject of much debate,[13] and a detailed understanding of the factors that determine the small angles in SiON compounds seemed desirable in order to provide suitable contrasting reference data. Because it might be argued that SiON and SiOC linkages are too different in their electronic nature to allow direct comparison, we aimed to find a new reference system that contains a SiON unit in which the nitrogen donor ability is blocked. This could be realized by binding it to a Lewis acid, which should be as small as possible

to minimize steric effects, and BH_3 is ideal in this respect. We report here the synthesis of the compound $MeHSi[ON(BH_3)-Me_2]_2$ and results of theoretical studies of $H_3SiON(BH_3)Me_2$ and $FH_2SiON(BH_3)Me_2$, two borane adducts of aminoxysilanes that adopt very different structures in their SiON cores compared to the corresponding aminoxysilanes.

Results

We have tried to synthesize $H_3SiON(BH_3)Me_2$ and $H_2Si[ON-(BH_3)Me_2]_2$ by reacting $H_3SiONMe_2$ and $H_2Si(ONMe_2)_2$ with $BH_3·THF$ in THF solution. A reaction took place in both cases, but hydrogen gas was liberated and a complex product mixture resulted, which was not further separated into its components. However, $MeHSi(ONMe_2)_2$, prepared from MeH_2SiCl_2 and $LiONMe_2$, reacted smoothly with $BH_3·THF$ to give $MeHSi-[ON(BH_3)Me_2]_2$, which crystallizes from THF solution upon concentration and cooling.

$$MeHSiCl_2 + 2LiONMe_2 \rightarrow MeHSi(ONMe_2)_2 + 2LiCl$$

$$MeHSi(ONMe_2)_2 + 2BH_3·THF \rightarrow$$
$$MeHSi[ON(BH_3)Me_2]_2 + 2\ THF$$
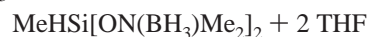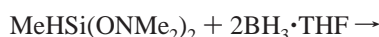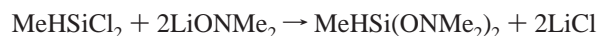
This compound has been identified by NMR spectroscopy and elemental analysis.

We were able to obtain a crystal suitable for X-ray crystallography and thus determined the structure of $MeHSi[ON(BH_3)-Me_2]_2$ (Figure 1, Table 1). The molecules are monomeric in the crystal. The two $ON(BH_3)Me_2$ groups are bound to a relatively asymmetric silicon atom, as is evident from the C−Si−O angles, which are as different as 113.6(1) and 101.4-(1)°. However, the geometries of both $ON(BH_3)Me_2$ groups are almost the same. They adopt similar Si−O−N angles of 124.0-(1) and 124.6(1)° and O−N−B angles of 112.8(2) and 113.2-(2)° and have remarkably similar torsion angles Si−O−N−B of 29.8(2) and −30.5(2)° (i.e., these groups behave almost like mirror images of each other). However, it remains unclear why the conformation is not such that a Si−O−N−C torsional angle of approximately 180° is realized, and it might be speculated that this is due to a hybridization at oxygen, which leads to two different lone pairs, one p-type and one that is in the SiON plane and causes this conformation by minimizing the repulsion. The Si−O−N angles are rather large if compared to those of nonborylated aminoxysilanes such as $MesF_2SiON(SiMe_3)_2$ [117.7(1)° in the crystal],[11] $Me_3SiONMe_2$ [107.9(6)° in the gas phase],[12] $H_2Si(ONMe_2)_2$ [95.6° (ave) in the crystal][13] or $ClH_2-SiONMe_2$ [79.1(1)° in the crystal],[14] which shows that an attractive force between silicon and nitrogen atoms is absent in the borane adduct $MeHSi[ON(BH_3)Me_2]_2$ but definitely operative in the aminoxysilanes. Moreover, a credible argument may be advanced that in the borane adducts the lone pair of electrons at the nitrogen is completely involved in the B−N adduct formation and thus is not accessible for an intramolecular interaction with the silicon center. Therefore, it seems obvious that the $ONMe_2$ group does not adopt local C_s symmetry, as is found in all aminoxysilanes and as is necessary to maximize the interaction between N and Si atoms.

It is appropriate at this point to compare our structure to values predicted from Bartell's one-angle-radii model,[16,17] which takes in addition to the valence-shell electron-pair repulsion

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Table 1. Bond Lengths (Å) and Angles (deg) of MeHSi[ON(BH$_3$)Me$_2$]$_2$ as Determined by Low-Temperature X-ray Crystallography

Me$_2$NO group 1		Me$_2$NO group 2	
Si−O1	1.669(1)	Si−O2	1.672(1)
Si−C5	1.838(2)		
O1−N	1.443(2)	O2−N2	1.451(2)
N1−C1	1.477(2)	N2−C3	1.480(2)
N1−C2	1.482(2)	N2−C4	1.477(3)
N1−B1	1.610(3)	N2−B2	1.613(3)
C5−Si−O1	113.6(1)	C5−Si−O2	101.4(1)
O1−Si−O2	101.0(1)		
Si−O1−N1	124.0(1)	Si−O2−N2	124.6(1)
O1−N1−B1	112.8(2)	O2−N2−B2	113.2(2)
O1−N1−C1	106.0(2)	O2−N2−C3	103.3(1)
O1−N1−C2	103.4(2)	O2−N2−C4	106.5(1)
τSiO1N1B1	29.8(2)	τSiO2N2B2	−30.5(2)
τSiO1N1C1	−93.1(2)	τSiO2N2C3	−150.4(2)
τSiO1N1C2	149.8(2)	τSiO2N2C4	93.8(2)

Table 2. Bond Lengths (Å) and Angles (deg) of H$_3$SiON(BH$_3$)Me$_2$, FH$_2$SiON(BH$_3$)Me$_2$, and H$_3$SiOC(CH$_3$)Me$_2$ Calculated ab Initio at the MP2/6-311G** Level of Theory

	H$_3$SiON(BH$_3$)Me$_2$ X = N	FH$_2$SiON(BH$_3$)Me$_2$ X = N	H$_3$SiOC(CH$_3$)Me$_2$ X = C
Si−O	1.707	1.700	1.657
O−X	1.433	1.428	1.437
X−C(1)	1.480	1.480	1.524
X−C(2)	1.478	1.477	1.527
X−(B/C′)	1.618	1.616	1.528
Si−F		1.613	
Si−O−N	121.4	119.7	127.9
O−X−(B/C′)	112.6	110.8	110.5
O−X−C(1)	106.2	106.4	105.3
O−X−C(2)	103.9	104.6	108.9
O−Si−F		97.9	
τSiOX(B/C)	−30.0	−29.0	45.4
τSiOXC(1)	92.7	93.1	−76.6
τSiOXC(2)	−150.9	−150.0	164.7

Figure 1. Molecular structure of MeHSi[ON(BH$_3$)Me$_2$]$_2$ as determined by low-temperature X-ray crystallography.
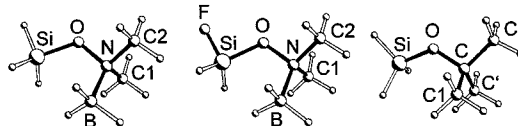
Figure 2. Molecular structures of H$_3$SiON(BH$_3$)Me$_2$, FH$_2$SiON-(BH$_3$)Me$_2$, and H$_3$SiOC(CH$_3$)Me$_2$ calculated at the MP2/6-311G** level of theory.

(VSEPR) model the repulsion between geminal atoms into account. The sum of these one-angle radii for Si and N atoms is 2.69 Å, and the Si···N distances in MeHSi[ON(BH$_3$)Me$_2$]$_2$ are somewhat longer at 2.750(2) and 2.768(2) Å. This indicates that some steric repulsion is operative in MeHSi[ON(BH$_3$)Me$_2$]$_2$.

To provide more detailed insight into the structural chemistry of our reference compounds with the SiONB skeleton, we have calculated (MP2/6-311G**) the structures of two representatives (Figure 2), H$_3$SiON(BH$_3$)Me$_2$ and FH$_2$SiON(BH$_3$)Me$_2$, which are the borane adducts of two aminoxysilanes with very different Si−O−N angles. (H$_3$SiONMe$_2$ was prepared and its crystal structure studied: Si−O−N 102.6(1)° and 102.5 at MP2/6-311G**. The geometry of FH$_2$SiONMe$_2$ was calculated at the MP2/6-311G** level: Si−O−N 90.0°.) The geometries of these borane adducts are listed in Table 2.

The Si−O−N angles in H$_3$SiON(BH$_3$)Me$_2$ (121.4°) and FH$_2$SiON(BH$_3$)Me$_2$ (119.7°) are slightly smaller than in MeHSi-[ON(BH$_3$)Me$_2$]$_2$ but substantially larger than in the parent aminoxysilanes. Particularly impressing is the difference of almost 30° between FH$_2$SiON(BH$_3$)Me$_2$ and FH$_2$SiONMe$_2$. The angle in FH$_2$SiON(BH$_3$)Me$_2$ is slightly smaller than that in H$_3$-SiON(BH$_3$)Me$_2$. In comparison to the aminoxysilanes, their borane adducts also have longer Si−O bonds [H$_3$SiON(BH$_3$)-Me$_2$, 1.707 vs 1.682 Å; FH$_2$SiON(BH$_3$)Me$_2$, 1.700 vs 1.679 Å] and shorter N−O bonds [H$_3$SiON(BH$_3$)Me$_2$, 1.433 vs 1.459 Å;

FH$_2$SiON(BH$_3$)Me$_2$, 1.428 vs 1.465 Å]. This could indicate an elongation of the N−O bond due to ring strain in three-membered SiON rings with a Si−N donor acceptor bond. The conformations of H$_3$SiON(BH$_3$)Me$_2$ and FH$_2$SiON(BH$_3$)Me$_2$ are surprisingly similar to that of MeHSi[ON(BH$_3$)Me$_2$]$_2$ in the crystal, as is best described by the torsion angles Si−O−N−B, which fall over a range of less than 2° for all compounds under consideration. The difference between the crystal structure value for the Si−O−N angle and those of the calculations is probably best attributed to the greater steric bulk of the silyl group in MeHSi[ON(BH$_3$)Me$_2$]$_2$.

For a further assessment of the influence of steric repulsion between the silyl group and the N(BH$_3$)Me$_2$ groups, we have calculated the structure of the alkoxysilane H$_3$SiOCMe$_3$, which is isoelectronic to H$_3$SiON(BH$_3$)Me$_2$. The corresponding Si−O−C angle in H$_3$SiOCMe$_3$ is 127.9°, which gives some indication of the steric repulsion between the H$_3$Si group and the Me$_3$C unit because the Si−O−C angle in H$_3$SiOCHMe$_2$ (isoelectronic to H$_3$SiONMe$_2$) was calculated to be 122.0°.[1c] This means that steric repulsion might be responsible for an angle widening of about 5−6°, which would provide us with an estimate of 116° for a Si−O−N angle in a compound without Si···N interaction, a value that is close to the value of 118° predicted from Bartell's one-angle radii and standard Si−O and N−O bond lengths. We therefore propose this value of 116° as a standard reference for assessment of Si···N interactions in SiON compounds.

Experimental Section

Bis(*N,N*-dimethylhydroxylamino)methylsilane. *n*-Butyllithium (1.6 M in 17.6 mL of hexane, 28 mmol) was added dropwise to a solution of *N,N*-dimethylhydroxylamine (2.0 mL, 28 mmol) in 50 mL of pentane at −40 °C. The mixture was stirred overnight while being slowly warmed to ambient temperature. The solvents were removed under reduced pressure. The white residue was suspended in 50 mL of diethyl ether and cooled to −196 °C, and methylchlorosilane (1.6 g, 1.4 mL, 28 mmol) was condensed onto the mixture. The reaction mixture was warmed to ambient temperature overnight and was fractionated through a series of cold traps (−40, −60, −196 °C). An amount of 2.34 g of bis(*N,N*-dimethylhydroxylamino)methylsilane (14 mmol, 51%) was retained in the −40 °C trap as a colorless liquid. ^{1}H NMR: δ 0.34 (d, $^3J_{HCSiH}$ = 1.5 Hz, Si−CH$_3$), 2.45 (s, N−CH$_3$), 2.49 (s, N−CH$_3$), 4.94 (q, $^3J_{HSiCH}$ = 1.5 Hz, Si−H). ^{13}C NMR: δ −3.5 (qd, $^1J_{CH}$ = 119.9 Hz, $^2J_{CSiH}$ = 18.2 Hz, Si−CH$_3$), 50.0 (qq, $^1J_{CH}$ = 133 Hz, $^3J_{CNCH}$ = 6.0 Hz, N−CH$_3$), 50.3 (qq, $^1J_{CH}$ = 133 Hz, $^3J_{CNCH}$ = 6.0 Hz, N−CH$_3$).

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^{29}Si NMR: δ −21.8 (dq, $^1J_{SiH}$ = 250 Hz, $^2J_{SiCH}$ = 7.7 Hz). IR (gas): ν(Si−H) = 2180 (s). MS (GC-coupled, EI, 70 eV): m/z = 164 (M$^+$).

Bis(*N*-boranato-*N,N*-dimethylaminoxy)methylsilane. MeHSi-(ONMe$_2$)$_2$ (0.30 g, 1.6 mmol) was dissolved in THF (20 mL), treated with a BH$_3$·THF solution (1.0 M in hexane, 1.8 mmol) at −78 °C, and warmed to ambient temperature. After concentration to a volume of about 5 mL, the clear solution was slowly cooled to −30 °C while crystals of MeHSi[ON(BH$_3$)Me$_2$]$_2$ grew over a period of 3 weeks. Yield: 0.22 g, 63%. Anal. Calcd for C$_5$H$_{22}$N$_2$O$_2$B$_2$Si: H, 11.55; C, 31.29; N, 14.59. Found: H, 11.51; C, 30.88; N, 14.31. ^{1}H NMR: δ 0.57 (s, 3H, H$_3$CSi), 2.53 (s, 6H, H$_3$CN), 2.6 (q, broad, 6H, H$_3$B), 2.73 (s, 6H, H$_3$CN), 5.96 (s, 1H, HSi). ^{11}B NMR: δ −27.4 (q, $^1J_{BH}$ = 99.8 Hz). ^{13}C NMR: δ 1.1 (qd, $^1J_{CH}$ = 122.2 Hz, $^2J_{CSiH}$ = 17.6 Hz, CSi), 57.3 (q quint, $^1J_{CH}$ = 141.5 Hz, $^3J_{CNCH}$ = 3.8 Hz, CN), 58.21 (qd, $^1J_{CH}$ = 141.5 Hz, $^3J_{CNCH}$ = 3.8 Hz, CN). ^{29}Si NMR: δ = −18.3 (dq, $^1J_{SiH}$ = 277.0 Hz, $^2J_{SiCH}$ = 7.6 Hz).

Crystal Structure Determination of MeHSi[ON(BH$_3$)Me$_2$]$_2$. A single crystal of MeHSi[ON(BH$_3$)Me$_2$]$_2$ was mounted on a glass fiber under inert perfluoropolyether. C$_5$H$_{22}$B$_2$N$_2$O$_2$Si, M_r = 191.96, crystal system orthorhombic, space group $Pna2_1$, Z = 4, a = 9.478(3) Å, b = 10.919(3) Å, c = 11.914(3) Å, V = 1233.0(7) Å^3 at 148(2) K, μ = 0.162 mm^{-1}, $2\theta_{max}$ = 54°, ω-scan, 2670 independent reflections, 197 parameters, R_1 = 0.0363 for 2469 reflections with $F_o > 4\sigma(F_o)$ and wR2 = 0.1050 for all 2665 data. Structure solution and refinement were undertaken with the program SHELXTL, version 5.01.[17]

Ab Initio Calculations. Ab initio molecular orbital calculations were carried out using the Gaussian 94 program.[18] 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 standard 3-21G*[19−21] and 6-31G*[22−24] basis sets, while the larger basis set was used for calculations at the MP2 level of theory.

Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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