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Synthesis and Molecular Structures in the Gas Phase of *N,N*-Dimethylaminoxy-trimethylsilane and -trimethylgermane

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The compounds $Me_3SiONMe_2$ and $Me_3GeONMe_2$ have been prepared by reacting Me_3SiCl and Me_3GeBr with $LiONMe_2$. Their identity was proven by gas-phase IR and solution NMR spectroscopy of the nuclei ^1H, ^{13}C, ^{15}N, ^{17}O, ^{29}Si, and ^{73}Ge and by mass spectrometry and elemental analyses. Their molecular structures in the gas phase have been determined by analysis of electron diffraction data augmented by restraints derived from ab initio calculations. The molecules adopt C_s symmetry. Important geometry parameter values for $Me_3SiONMe_2$ are: Si−O 1.688(2), $Si-C_{in\text{-}plane}$ 1.870(4), $Si-C_{out\text{-}of\text{-}plane}$ 1.872(2), O−N 1.481(6) Å, Si−O−N 107.9(6), $O-Si-C_{in\text{-}plane}$ 102.1(6), $O-Si-C_{out\text{-}of\text{-}plane}$ 110.9(7)°, for $Me_3GeONMe_2$: Ge−O 1.812(2), $Ge-C_{in\text{-}plane}$ 1.949(3), $Ge-C_{out\text{-}of\text{-}plane}$ 1.950(2), O−N 1.475(6) Å, Ge−O−N 108.9(7), $O-Ge-C_{in\text{-}plane}$ 101.7(6), $O-Ge-C_{out\text{-}of\text{-}plane}$ 110.3(14)°. The structure data are interpreted in terms of weak attractive interactions between the nitrogen donor and the silicon/germanium acceptor atoms. The results are discussed in comparison with other structure data from the literature: the strength of a donor−acceptor interaction in $Me_3SiONMe_2$ is weaker than in $H_3SiONMe_2$ or $ClH_2SiONMe_2$, but stronger than in $Me_3SiON(CF_3)_2$.

Introduction

The reasons for attractive interactions between geminal acceptor and donor atoms have been the subject of intensive studies for various combinations of elements. They have been postulated for E−C−N linkages (E = Si, Ge, Sn; e.g., in $Me_3SnCH_2NMe_2$), to rationalize the unusually low basicities of such amines (also named the α-effect),[1] and explained in terms of a "closed type" three-center bond caused by transitions of σ-electrons of the N atom participating in the N−C bond into the empty d-orbitals of the group 14 element.[2] Typical examples for three-membered ring systems with one Lewis-donor−acceptor bond include the compounds $(F_3C)_2BCPh_2NMe_2$, $RN{=}C\{Al[CH(SiMe_3)_2]\}_2$ and $(Me_3Si)_2C{=}N-N\{Al[CH(SiMe_3)_2]\}_2$ with B−C−N,[3] Al−C═N,[4] and Al−N−N[5] linkages forming three-membered ring systems in the solid state.

The most intensely studied systems in this context are SiON[6] and SiNN[7] linkages. The most intriguing example so far is $ClH_2SiONMe_2$,[8] which adopts a Si−O−N angle of only 79.7(1)° in the crystal, but does not undergo even weak intermolecular interactions. A theoretical treatment of this example showed negative hyperconjugation to be one suitable model to describe the attraction as $lp(N) \rightarrow \sigma^*(Si-Cl)$ interaction.

A recent study of the gas-phase structure of $Me_3SiON(CF_3)_2$[9] sheds more light on the nature of the Si···N attraction. In this molecule the acceptor ability of the Si atom is reduced by methylation and the donor ability of the nitrogen center is reduced because of the two CF_3 substituents. Nevertheless, the Si−O−N angle is still much less than expected on the basis of Bartell's one-angle radii[10] for Si and N. Only if the N basicity is even more reduced by silylation, as verified $MesF_2SiON(SiMe_3)_2$,[11] the Si···N distance (2.692 Å) is consistent with the sum of Bartell's one-angle radii (2.69 Å), indicating the absence of a significant attraction between Si and N atoms.

Determination of the molecular structure of $Me_3SiONMe_2$ seemed desirable to prove the consistency of our present knowledge on those systems. Furthermore, we wanted to extend our studies to the heavier elements of group 14 acceptors and report here about the synthesis and gas-phase molecular structure of $Me_3GeONMe_2$. A structural investigation of $Me_3SiONMe_2$ should also improve our knowledge on trialkylsilicon systems with hydoxylamine and oxime groups, which are used as cold-curing catalysts in silicone polymer production.[12]

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Table 1. Geometry Parameters, Their Values (in r_a and r_α), and Parameter Restraints for the GED Refinements of $Me_3SiONMe_2$ and $Me_3GeONMe_2$[a]

			$Me_3SiONMe_2$				$Me_3GeONMe_2$			
		restraint definition	value				value			
no.	param		r_a	r_α	restraint	MP2/6-31G*	r_a	r_α	restraint	MP2/6-31G*
p1	E−O		1.688(2)	1.684(1)		1.707	1.812(2)	1.808(2)		1.833
p2	E−C7		1.872(2)	1.863(2)		1.877	1.950(2)	1.940(2)		1.938
p3	E−C6	p3 − p2	1.870(4)	1.860(4)	0.001(5)	1.878	1.949(3)	1.938(3)	−0.001(5)	1.937
p4	O−N		1.481(6)	1.461(6)		1.471	1.475(6)	1.459(6)		1.473
p5	N−C	p5 − p4	1.452(4)	1.438(4)	−0.011(10)	1.460	1.460(4)	1.442(4)	−0.014(10)	1.459
p6	C−H(N)		1.108(4)	1.057(3)		1.090	1.107(3)	1.050(3)		1.091
p7	C−H(E)	p7 − p6	1.117(2)	1.067(2)	0.005(5)	1.095	1.111(3)	1.053(3)	0.003(5)	1.094
p8	∠OEC(7)		110.9(7)	110.7(7)		111.0	110.3(14)	110.0(12)		109.9
p9	∠OEC(6)		102.1(6)	103.4(6)		103.1	101.7(6)	101.9(7)		102.7
p10	∠E−O−N		107.9(6)	108.9(5)		106.0	108.9(7)	109.8(7)		102.9
p11	∠O−N−C		104.8(4)	105.0(4)		104.6	105.4(4)	106.1(5)		104.3
p12	∠C−N−C		112.7(12)	110.3(10)		111.0	111.2(10)	110.0(11)		111.0
p13	∠C−E-C		108.1(23)	107.8(23)		110.0	107.1(42)	107.5(33)		109.1
p14	∠ECH(7)	p14	111.3(10)	112.4(9)	111.2(10)	111.2	111.5(6)	112.2(6)	111.8(10)	111.8
p15	∠ECH(6)	p15 − p14	110.6(14)	112.3(13)	−0.2(10)	111.0	109.6(7)	110.3(7)	−1.9(10)	109.9
p16	∠NCH	p16	106.1(6)	106.5(5)	108.8(10)	108.8	107.7(8)	108.4(8)	108.6(10)	108.6
p17	τCECH	p17	−169.1(34)	−173.9(39)	−177.0(50)	−177.0	179.5(44)	177.4(46)	178.3(50)	178.3
p18	τCNCH	p18	−160.3(31)	−168.8(30)	−176.9(50)	−176.9	−181.0(29)	−181.1(29)	−176.6(50)	−176.6

[a] The geometrical parameter values of the ab initio calculations (MP2/6-31G*) are listed for comparison. Distances are given in angstroms, angles and torsion angles in degrees.

Results and Discussion

Synthesis and Characterization of $Me_3SiONMe_2$ and $Me_3GeONMe_2$. $Me_3SiONMe_2$ and $Me_3GeONMe_2$ were prepared from lithiated *N*,*N*-dimethylhydroxylamine and trimethylchlorosilane and trimethylbromogermane, respectively. They were isolated as colorless liquids by fractionation through a series of cold traps in vacuo. Their identity was proven by their gas-phase IR and solution (C_6D_6) NMR spectra (^1H, ^{13}C, ^{15}N, ^{17}O, ^{29}Si, ^{73}Ge) and by mass spectrometry and elemental analyses. $Me_3SiONMe_2$ was previously prepared by West and Boudjouk by a different method.[13]

The ^{29}Si NMR chemical shift of $Me_3SiONMe_2$ (−17.18 ppm) is shifted to lower frequencies relative to the isoelectronic $Me_3SiOCHMe_2$ (12.1 ppm).[14] This is compatible with a shielding by increased electron density at the silicon center, as could be expected if the Me_2NO substituent donated electrons via its NMe_2 group.

In a ^{73}Ge NMR experiment $Me_3GeONMe_2$ gave a signal at 522 ppm vs $GeMe_4$, which is noteworthy, because we have never observed ^{73}Ge NMR signals for other aminoxygermanes even after prolonged periods and varied conditions of NMR experiments, not even for the symmetrically substituted $Ge(ONMe_2)_4$ or $Ge(ONEt_2)_4$. So far, because of the lack of data, a comparison with other ^{73}Ge NMR chemical shifts has been impossible.

More telling are the ^{15}N NMR resonances of $Me_3SiONMe_2$ and $Me_3GeONMe_2$ at −247.8 and −250.6 ppm, which are shifted more than 16 ppm to lower frequencies, i.e. shielded with respect to the simplest aminoxysilane $H_3SiONMe_2$ (−234.0 ppm),[6] but slightly to higher frequencies, i.e. deshielded, compared with $HONMe_2$ (−259.4 ppm).[15] These data are consistent with a less pronounced interaction between the N and the Si or Ge atoms in $Me_3SiONMe_2$ and $Me_3GeONMe_2$ than in $H_3SiONMe_2$, which should result in wider Si−O−N and Ge−O−N angles. However, care is suggested with such interpretations, because chemical shifts of many similar and related compounds fall over a range of 10 ppm. The similarity between the chemical shifts of $Me_3SiONMe_2$ and $Me_3GeONMe_2$ also indicates the similar electronic nature of the nitrogen atoms.

At −13 and 146 ppm the ^{17}O chemical shifts of $Me_3SiONMe_2$ and $Me_3GeONMe_2$ are markedly different. Although one of the bonding partners of oxygen is different (Si and Ge), we cannot provide a more detailed explanation for this fact.

Molecular Structures of $Me_3SiONMe_2$ and $Me_3GeONMe_2$. All attempts to grow single crystalline material for X-ray diffraction experiments from samples of $Me_3SiONMe_2$ and $Me_3GeONMe_2$ were unsuccessful, because the compounds solidify as glass upon cooling. However, the high volatility allowed us to determine their molecular structures in the gas phase by means of electron diffraction. The limitations of structural analyses on electron diffraction data can be overcome to some extent by augmenting the data by restraints taken from ab initio calculations of the molecular geometries in an extended method called SARACEN,[16] a procedure combining and extending Bartell's approach of predicate values[17] and Schäfer's MOCED method.[18] The definition of the models for both compounds was identical and is described in the Experimental Section. The ab initio geometries were calculated at the MP2/6-31G* level of theory, under imposed C_s symmetry. The nature of the stationary points was tested by frequency calculations at the same level. This yielded a force field used for the calculation of vibrational amplitudes (after scaling the force constants by a common factor of 0.93), which were included as further restraints in the GED (Gas-Phase Electron Diffraction) refinements (see Experimental Section for details). Perpendicular amplitude corrections were calculated from the same force field to allow for a refinement of the structures in r_α space.

The parameter values and the applied restraints for both refinements, each in r_a and r_α space, and for the ab initio values are listed in Table 1. Several low calculated frequencies (for a list see the Supporting Information) led to an overestimation of the corrections for some bond lengths in the r_α refinements (e.g.,

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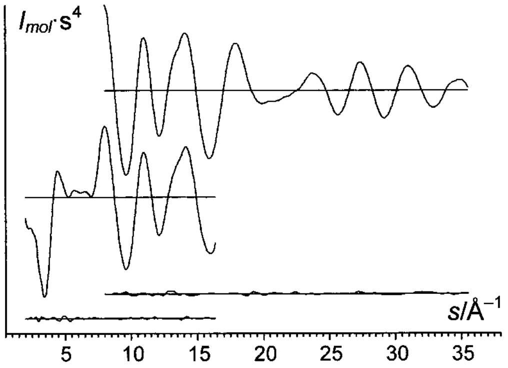

Figure 1. Molecular scattering intensity and final difference curves (vs model) as obtained by electron diffraction of gaseous $Me_3SiONMe_2$.

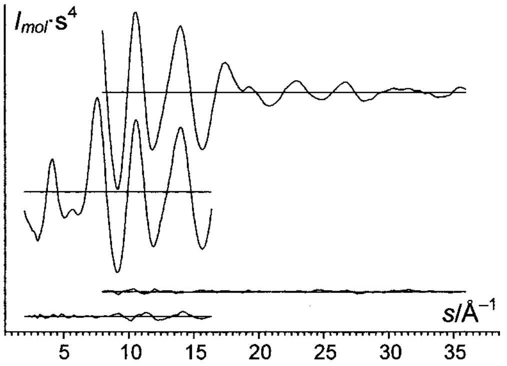

Figure 2. Molecular scattering intensity and final difference curves (vs model) as obtained by electron diffraction of gaseous $Me_3GeONMe_2$.

the N−C distances) if established standard values for such lengths were considered, which led us to prefer the uncorrected, but in this way more realistic r_a values. However, the structural information from both types of refinement is very similar, and the most important geometry parameters, the E−O−N angles, are the same within the standard deviations. This is why the r_a values are used for comparison and structure discussion throughout the rest of this paper.

Although eight restraints had been used, most of the important parameters defining the geometry of the skeleton were freely refined. The satisfactory agreement between theory and experiment in these parameters justified the application of supporting restraints derived from calculations for differences between similar parameters, parameters describing hydrogen positions and vibrational amplitudes. The experimental structures presented correspond to r_a geometries. The success of the refinements of the molecular geometries of $Me_3SiONMe_2$ and $Me_3GeONMe_2$ may be assessed from the small residuals in the electron-scattering intensity curves and radial distribution curves, which are presented in Figures 1−4. The final R factors were 0.0314 and 0.0581 for the refinements on $Me_3SiONMe_2$ and $Me_3GeONMe_2$.

At 1.688(2) Å the Si−O bond length in $Me_3SiONMe_2$ is longer than in Me_3SiOCH_3 [1.639(4) Å],[19] which is the best comparable siloxane studied in the gas phase. It is also longer than in $ClH_2SiONMe_2$ [1.641(3) Å in the gauche conformer], but is still shorter than the ab initio estimate of 1.707 Å. The Si−C distances in $Me_3SiONMe_2$ are similar to those in $SiMe_4$ [1.875(2) Å].[20] Similar comparisons for $Me_3GeONMe_2$ include the Ge−O distance [1.812(2) Å], which is longer than that of $Me_3GeOGeMe_3$ [1.770(10) Å][21] and the Ge−C bond lengths [1.949(3) and 1.950(2) Å], which are almost identical with those of $GeMe_4$ [1.945(3) Å].[22]

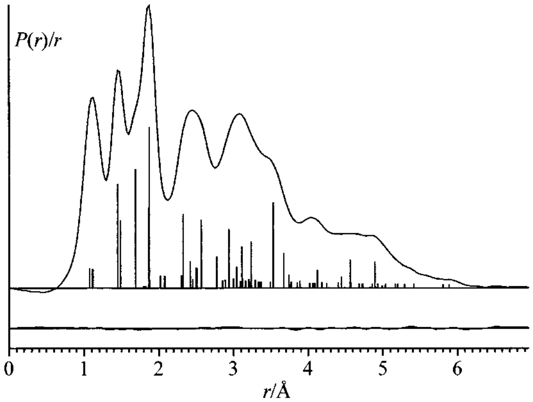

Figure 3. Radial distribution and difference curve for the electron diffraction refinement of $Me_3SiONMe_2$. Vertical lines indicate atom pairs with their height being proportional to their scattering contribution.

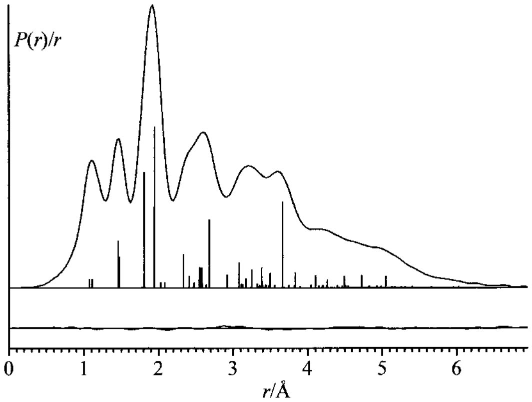

Figure 4. Radial distribution and difference curve for the electron diffraction refinement of $Me_3GeONMe_2$. Vertical lines indicate atom pairs with their height being proportional to their scattering contribution.

The N−O distances in both compounds, $Me_3SiONMe_2$ [1.481(6) Å] and $Me_3GeONMe_2$ [1.475(6) Å], are longer than in the nonsilylated $HONMe_2$ [1.448(11) Å].[23] The angles about the nitrogen centers are very close to that in $HONMe_2$, as is indicated by their sum of 322.3° ($Me_3SiONMe_2$) and 322.0° ($Me_3GeONMe_2$) vs 323.8° in $HONMe_2$.

The most interesting part in these structures is the geometry of the SiON and GeON skeletons. The occurrence of an attractive force between the nitrogen donor center and the acceptor atoms Si and Ge should lead to a shortening of the Si···N and Ge···N distances, which is better described by a contraction of the angles Si−O−N and Ge−O−N, which are 107.9(6)° and 108.9(7)°. On the one hand, this is substantially smaller than typical Si−O−C and Ge−O−C angles [compare Me_3SiOCH_3 $\angle$Si−O−C 122.5(6)°][19] or the even wider angles Si−O−Si and Ge−O−Ge in $Me_3SiOSiMe_3$ [148(3)°][24] and $Me_3GeOGeMe_3$ [141(1)°].[25] On the other hand, the Si−O−N and

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Ge−O−N angles are much wider than in $ClH_2SiONMe_2$ [anti conformer 79.7(1)° in the crystal, 87.1(9)° in the gas phase][8] and in $H_3SiONMe_2$ [102.6(1)° in the crystal],[6] but is smaller than in $Me_3SiON(CF_3)_2$ [113.4(19)° in the gas phase].[9] This can be interpreted as a weak attractive interaction (β-donor−acceptor interaction) between Si and N atoms. It is weaker than in $H_3SiONMe_2$ because of the reduced ability of a $SiMe_3$ group to act as an acceptor compared with a SiH_3 group, but stronger than in $Me_3SiON(CF_3)_2$, because an $N(CF_3)_2$ group is a weaker donor than a Me_2N group.

A comparison of the E−O−N angles of $Me_3SiONMe_2$ and $Me_3GeONMe_2$ with that of the homologous compound $Me_3SnONMe_2$ [102.7(8)°][26] documents the better acceptor ability of tin than its lighter homologues, which also allows this compound to form additional intermolecular Sn···O contacts in the solid state.

Resulting from the weak E···N interactions, the geometries of the Me_3EO groups are distorted, i.e., a slight widening of the two symmetry equivalent out-of-plane angles O−E−C to 110.9(7)° and 110.3(14)° and a compression of the angles O−E−C in the plane of symmetry to 102.1(6)° and 101.7(6)° for $Me_3SiONMe_2$ and $Me_3GeONMe_2$. This deformation is slightly less than in the tin compound $Me_3SnONMe_2$, which has an in-plane angle of 99.6(10)°.[26]

The similarity between the Si−O−N and Ge−O−N angles and the distortions of the Me_3EO group in $Me_3SiONMe_2$ and $Me_3GeONMe_2$ substantiates the electronic similarity of Me_3Si and Me_3Ge groups in their behavior as acceptors. By comparing the experimental data with the ab initio predictions it becomes obvious how inadequately the MP2/6-31G* level describes the situation. Although the geometry of $Me_3SiONMe_2$ is generally well reproduced by the calculations at this level, the predicted Ge−O−N angle is substantially less [102.9°] than the experimentally observed one [108.9(7)°]. Our earlier work documented that the strength of β-donor interactions is slightly overestimated at MP2/6-31G* and a better description is achieved with larger basis sets (in particular MP2/6-311G**). Because of the problem size our present computing resources did not allow us to improve on the applied degree of theoretical sophistication. Apart from this GeON fragment the geometry of $Me_3GeONMe_2$ is reproduced satisfactorily by the calculations.

Oberhammer et al. have already pointed out the advantage of assessing the strength of a possible E···N interaction between geminal atoms by comparing the E−N distance with Bartell's one-angle radii,[9] describing the repulsion between the spheres of two atoms A and B bound to the same center Y. The angle A−Y−B can be calculated with known distances A−Y and B−Y. A selection of compounds containing E−O−N fragments with their angles E−O−N, the distance E···N, and the sum of the corresponding Bartell's radii are listed in Table 2 for comparison.

None of the Si···N distances of the SiON compounds in Table 2 significantly exceeds the sum of Bartell's radii at 2.69 Å. Klingebiel's compound $MesF_2SiON(SiMe_3)_2$ has the widest angle Si−O−N [117.66(11)°] and a distance Si···N of 2.692 Å. This indicates the absence of a significant attraction between N and Si atoms, probably because of the low basicity of the silylated nitrogen atom and despite the two electronegative F substituents at silicon. At 2.566(8) Å the Si···N distance of $Me_3SiONMe_2$ indicates the presence of an attraction weaker than in $H_3SiONMe_2$ [2.453(1) Å] or *trans*-$ClH_2SiONMe_2$ [2.160(7) Å], which is consistent with a less electrophilic Me_3Si group compared with H_3Si or ClH_2Si units.

Table 2. Important Geometry Parameter Values (Å/deg) for $Me_3SiONMe_2$, $Me_3GeONMe_2$, and Reference Compounds in Comparison[a]

compound/method	∠E−O−N	E···N	sum of Bartell's radii
$Me_3SiONMe_2$/GED	107.9(6)	2.566(8)	2.69
$Me_3GeONMe_2$/GED	108.9(7)	2.682(11)	2.72
$Me_3SnONMe_2$/GED	102.5(8)	2.731(14)	3.02
$Me_3SiON(CF_3)_2$/GED	113.4(19)	2.66	2.69
$MesF_2SiON(SiMe_3)_2$/XRD	117.66(11)	2.692	2.69
$ClH_2SiONMe_2$ (anti)/XRD	79.7(1)	2.028(1)	2.69
$ClH_2SiONMe_2$ (anti)/GED	87.1(9)	2.160(7)	2.69
$ClH_2SiONMe_2$ (gauche)/GED	104.7(11)	2.468(25)	2.69
$H_3SiONMe_2$/XRD	102.6(1)	2.453(1)	2.69
$H_2Si(ONMe_2)_2$/XRD	95.2(av)	2.318(av)	2.69

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

The experimental Ge···N distance in $Me_3GeONMe_2$ is only 1.4% shorter than the sum of Bartell's radii of Ge and N (4.6% in $Me_3SiONMe_2$). On this basis we can conclude only a weak attraction between Ge and N atoms if any. The ab initio predicted Ge···N distance is 2.595 Å, which is 4.6% shorter than the sum of Bartell's radii, the same value as for the silicon analogue. In the tin analogue the Sn···N distance is 9.6% shorter than the sum of the one-angle radii, which means that germanium seems to have exceptionally low electrophilicity in this series of compounds, a fact that is not reproduced satisfactorily by theory at the MP2/6-31G* level.

We used our calculated geometries at the MP2/6-31G* level of theory to perform a natural bond orbital analysis (NBO), which provided us with a coarse description of electron delocalization by second-order perturbation theory analysis of the Fock matrix in the NBO basis. In both compounds, $Me_3SiONMe_2$ and $Me_3GeONMe_2$, the largest contributions for orbital interactions through electron delocalization stem from electron density in the lone pair of electrons at nitrogen and oxygen. There are interactions between the oxygen lone pairs and the σ^*(E−C) orbitals belonging to the methyl groups in gauche position relative to the E−O−N plane. Such interactions are established contributions in E−O compounds and this type of negative hyperconjugation has been claimed to be responsible for the low basicity of silylated oxygen atoms and the wide bond angles of silylated oxygen. Concerning the interaction between the nitrogen donor and silicon or germanium acceptor atoms, the NBO calculations reveal a lp(N)$\rightarrow\sigma^*$(E−C) interaction with the σ^*(E−C) orbital of the methyl group in the E−O−N plane. The NBO analysis provides us with stabilization energies gained through electron delocalization, which are neither physically observable nor very meaningful in their absolute values, but give an estimate of the relative strength of such interactions. The lp(N)$\rightarrow\sigma^*$(E−C) interaction energy in $Me_3SiONMe_2$ is about as large as in $H_3SiONMe_2$ [lp(N)$\rightarrow\sigma^*$(Si−H), ∠SiON 102.6(1)° in the crystal], but only 32% of the lp(N)$\rightarrow\sigma^*$(Si−Cl) interaction in the anti conformer of $ClH_2SiONMe_2$, which results in a much smaller SiON angle in the latter [87.1(9)° in the gas phase]. According to the ab initio prediction that the GeON angle in $Me_3GeONMe_2$ is smaller than the SiON angle in $Me_3SiONMe_2$, the lp(N)$\rightarrow\sigma^*$(Ge−C) interaction in $Me_3GeONMe_2$ has been predicted to be stronger by 40% than the lp(N)$\rightarrow\sigma^*$(Si−C) interaction in $Me_3SiONMe_2$.

The E···N donor−acceptor interactions can thus be described as weak type of remote negative hyperconjugation, although other alternative interpretations are possible. In particular the Coulomb attraction between electropositive silicon and germa-

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Table 3. Experimental Conditions (Camera Distances [mm], Electron Wavelengths [Å], Nozzle and Sample Temperatures [°C]), Data Ranges and Weighting Functions [$Å^{-1}$], Correlation Parameters, Scale Factors, and Final *R* Factors for the GED Experiments and Refinements of the Compounds $Me_3SiONMe_2$ and $Me_3GeONMe_2$

compd/data set	camera dist	wavelength	*T* nozz	*T* samp	Δs	s_{min}	s_1	s_2	s_{max}	correlation param	scale factor	R_1	R_g
$Me_3SiONMe_2$/1	746.37	0.04894	25	13	0.2	2.0	4.0	14.0	16.4	−0.0211	0.958(4)	0.0269	0.0314
$Me_3SiONMe_2$/2	300.84	0.04894	24	13	0.4	8.0	10.0	30.4	35.6	0.1485	0.880(10)	0.0446	
$Me_3GeONMe_2$/1	746.37	0.04894	25	4	0.2	2.0	4.0	14.0	16.4	0.4779	1.007(8)	0.0712	0.0581
$Me_3GeONMe_2$/2	299.76	0.04894	23	17	0.4	8.0	10.0	30.8	36.0	0.1220	0.937(14)	0.0458	

nium and electronegative nitrogen centers contributes a great deal to this kind of secondary bonding.

Conclusion

With the determination of the gas-phase structures of $Me_3SiONMe_2$ and $Me_3GeONMe_2$ we have established structural data of a series of compounds, which allow us to assess the acceptor ability of Me_3E groups (E = Si, Ge, Sn) toward donor atoms in the β-position. Tin is clearly the best acceptor, followed by silicon, whereas almost no interaction is detectable for germanium. The high ability of oxygen centers to adopt a wide range of different angles if bound to silicon substituents is documented once more. As expected $Me_3SiONMe_2$ shows a β-donor−acceptor interaction, which is intermediate in strength between $H_3SiONMe_2$ (higher electrophilicity at Si) and $Me_3SiON(CF_3)_2$ (lower nucleophilicity at N). The NBO analyses show that the interaction of the lone pair at nitrogen with the E substituent (E = Si or Ge) in the E−O−N plane is the most important contribution of electron delocalization concerning the secondary bonding in the E−O−N unit. The strength of the interaction increases with the nature of this E substituent in the series Me $<$ H $\ll$ Cl $<$ F.

In an earlier contribution we discussed a mechanism for the catalytic action of hydroxylamines on the alcoholysis of Si−H functions involving β-donor−acceptor interactions between Si and N atoms in Si−O−N systems,[27] leading to partially hypercoordinate silicon centers and thus accelerating S_N2 reactions. This postulate was based on structure determinations of $Si(ONR_2)_4$ and Si-hydrogenated compounds. With the present example we provide evidence that such interactions may also be important even for trialkylsilylhydroxylamines or for reactions involving highly alkylated silicon groups, which are systems more similar to those actually applied in praxis.

Experimental Section

General. The experiments were carried out using a standard Schlenk line or a vacuum line with greaseless PTFE stopcocks, which is attached directly to the gas cell in an FTIR spectrometer (Midac Prospect FTIR). 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)trimethylsilane. At −50 °C, 1.8 g of *n*-butyllithium (28 mmol, 1.6 M in hexane) was added dropwise to a solution of 2.0 mL of *N*,*N*-dimethylhydroxylamine (1.7 g, 28 mmol) in 25 mL of pentane. The mixture was stirred for 1 h at ambient temperature, and solvents were removed in vacuo. At −196 °C ca. 25 mL of dimethyl ether and 3.8 mL of trimethylchlorosilane (3.1 g, 28 mmol) were condensed onto the remaining salt. The mixture was stirred at −96 °C for 1 h, then slowly warmed to −30 °C, and stirred for another 1.5 h. All volatile products were condensed into a trap (−196 °C), and (*N*,*N*-dimethylhydroxylamino)trimethylsilane (2.6 g, 19.5 mmol, 69%) was isolated as a colorless liquid by fractionation through a series of cooled traps (−20, −78, −96, −196 °C) with the product retained in the −78 °C trap. ^1H NMR $\delta = 0.2$ (s, 9H, H_3C), 2.38 (s, 6H, H_3C). ^{13}C NMR $\delta = -1.1$ (q, $^1J_{CH} = 118.3$ Hz $(CH_3)_3Si$), 50.4 (qq, $^1J_{CH} = 135.4$ Hz, $^3J_{CNCH} = 6.0$ Hz, $(CH_3)_2N$), $^{15}N\{^1H\}$ NMR $\delta = -247.8$ (s), $^{17}O\{^1H\}$ NMR $\delta = -13.1$ (s), ^{29}Si NMR $\delta = -17.18$ (dec, $^2J_{SiCH} = 6.5$ Hz). IR (gas): 2967 cm^{-1} s (νCH_3). MS(Cl): $m/z = 133.0$ (M^+), 118.0 ($M^+ - CH_3$), 75.0 ($M^+ - ONME_2$). Anal. $H_{15}C_5NOSi$ (133.27 g/mol). Calcd: C, 45.1; H, 11.3; N, 10.5. Found: C, 44.9; H, 11.3; N, 10.7.

(*N*,*N*-Dimethylhydroxylamino)trimethylgermane. At −50 °C, 0.9 g of *n*-butyllithium (14 mmol, 1.6 M in hexane) was added dropwise to a solution of 1.0 mL of *N*,*N*-dimethylhydroxylamine (0.9 g, 14 mmol) in 20 mL of pentane. The mixture was stirred for 1 h at ambient temperature, and solvents were removed in vacuo. At −196 °C ca. 20 mL of dimethyl ether and 1.0 g of trimethylchlorogermane (6.5 mmol) were condensed onto the remaining salt. The mixture was stirred at −96 °C for 1 h, then slowly warmed to −30 °C and stirred for another 1.5 h. All volatile products were condensed into a trap (−196 °C) and (*N*,*N*-dimethylhydroxylamino)trimethylgermane (1.0 g, 5.9 mmol, 90%) was isolated as a colorless liquid by fractionation through a series of cooled traps (−20, −78, −96, −196 °C) with the product retained in the −78 °C trap. ^1H NMR $\delta = 0.32$ (s, 9H, H_3C), 2.47 (s, 6H, H_3C). ^{13}C NMR $\delta = -0.44$ (q, $^1J_{CH} = 125.9$ Hz, CH_3), 50.8 (q q, $^1J_{CH} = 134.0$ Hz, $^3J_{CNCH} = 5.8$ Hz, CH_3). $^{15}N\{^1H\}$ NMR $\delta = -250.6$ (s). $^{17}O\{^1H\}$ NMR $\delta = 146.4$ (s). $^{73}Ge\{^1H\}$ NMR $\delta = 522$ (s). IR (gas): 2992 cm^{-1} s (νCH_3). MS(Cl): $m/z = 178.7$ ($M^+ - 1$, ^{74}Ge), 118.7 ($M^+ - 1 - ONMe_2$, ^{74}Ge). Anal. $H_{15}C_5GeNO$ (177.79 g/mol). Calcd: C, 33.8; H, 8.40; N, 7.90. Found: C, 34.0; H, 8.49; N, 7.58.

Electron Diffraction Experiments. GED Data. Electron-scattering intensity data for $Me_3SiONMe_2$ and $Me_3GeONMe_2$ were recorded on Kodak Electron Image film using the Oregon State University diffraction apparatus operating at 60 kV acceleration voltage. Two data sets at different camera distances were recorded for each compound from three exposures. Diffraction patterns of CO_2 were recorded concurrently for wavelength calibration. Further experimental conditions and general parameters concerning the refinements are listed in Table 3. The least-squares refinements were carried out using the program ED96[28] with the scattering factors established by Fink and co-workers.[29] The refined molecular parameters, their definition, and the applied restraints, a list with selected interatomic distances including vibrational amplitudes and applied restraints, are listed in Table 4.

GED Model. The geometrical models for $Me_3SiONMe_2$ and $Me_3GeONMe_2$ were defined in C_s symmetry. The atom numbering scheme is provided in Figures 5 and 6. While fixing the differences between the parameters defining hydrogen atom positions (C−H distances, angles, and torsion angles) to calculated values and treating the silicon/

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Table 4. Distances, Amplitudes, and Restraints for the GED Refinements of the Compounds $Me_3SiONMe_2$ and $Me_3GeONMe_2$[a]

		$Me_3SiONMe_2$			$Me_3GeONMe_2$		
no.	atom pair	dist	amplitude	restraint	dist	amplitude	restraint
d1	E1−O2	1.688(2)	0.048(1)		1.812(2)	0.047(3)	
d2	E1−C6	1.870(4)	0.049(4)	1.18(12)[a]	1.949(3)	0.048(6)	1.18(12)[a]
d3	E1−C7	1.872(2)	0.047(2)	1.00(10)[b]	1.950(2)	0.054(3)	1.00(10)[b]
d4	O2−N3	1.481(6)	0.059(5)		1.475(6)	0.047(3)	
d5	N3−C4	1.452(4)	0.047(3)	1.03(10)[c]	1.460(4)	0.047(2)	1.03(10)[c]
d6	C4−H9	1.108(4)	0.074(1)		1.107(3)	0.075(2)	
d7	E1···N3	2.566(8)	0.077(6)	0.082(16)	2.682(11)	0.090(7)	0.082(16)
d8	O2···C6	2.769(12)	0.094(16)	0.093(19)	2.918(13)	0.078(12)	0.093(19)
d9	O2···C7	2.935(11)	0.085(13)	0.088(18)	3.088(26)	0.076(11)	0.088(18)
d10	O2···C4	2.324(6)	0.084(6)	0.064(13)	2.335(6)	0.068(6)	0.064(13)
d11	C6···C7	3.110(13)	0.075(12)	0.102(20)	3.264(16)	0.075(11)	0.102(20)
d12	C7···C8	3.030(45)	0.076(16)	0.101(20)	3.136(85)	0.092(20)	0.101(20)
d13	C4···C5	2.418(18)	0.069(12)	0.067(13)	2.410(16)	0.066(12)	0.067(13)
d14	E1···C4	3.531(6)	0.115(4)	0.112(22)	3.664(6)	0.122(4)	0.112(22)
d15	N3···C6	4.112(10)	0.090(9)	0.089(18)	4.258(13)	0.100(14)	0.089(18)
d16	N3···C7	3.240(14)	0.106(13)	0.172(34)	3.386(22)	0.184(25)	0.172(34)
d17	C6···C4	4.888(11)	0.172(11)	0.149(30)	5.050(13)	0.180(20)	0.149(30)
d18	C7···C4	4.569(12)	0.225(21)	0.184(37)	4.725(15)	0.182(25)	0.184(37)
d19	C7···C5	3.681(21)	0.326(39)	0.233(47)	3.843(36)	0.268(40)	0.233(47)
d20	E1···H15	2.493(19)	0.137(22)	0.120(24)	2.546(8)	0.099(9)	0.120(24)
d21	N3···H9	2.056(7)	0.067(18)	0.101(20)	2.083(11)	0.091(17)	0.101(20)
d22	N3···H10	2.005(7)	0.067(20)	0.100(20)	2.029(11)	0.091	tied u32
d23	N3···H11	2.071(7)	0.071(18)	0.102(20)	2.084(11)	0.091	tied u32
d24	E1···H9	3.495(26)	0.248(46)	0.208(42)	3.495(22)	0.219(42)	0.209(43)
d25	E1···H10	4.426(10)	0.115(13)	0.178(36)	4.485(17)	0.130(22)	0.178(36)
d26	E1···H11	3.731(30)	0.182(32)	0.150(30)	4.104(30)	0.173(24)	0.150(30)

[a] Restraints defined by ratios are marked: [a]u2/u1, [b]u3/u2, [c]u5/u4. Distances and amplitudes are given in Å.

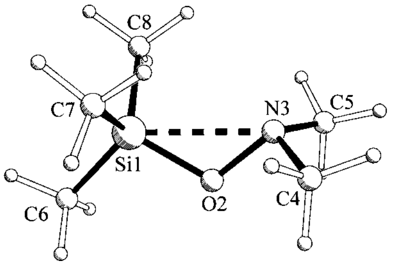

Figure 5. Molecular structure of $Me_3SiONMe_2$ in the gas phase as determined by electron diffraction.

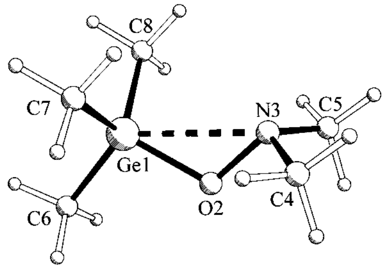

Figure 6. Molecular structure of $Me_3GeONMe_2$ in the gas phase as determined by electron diffraction.

germanium- and nitrogen-bound methyl groups independently, a total of 18 parameters was used to refine the structures. The parameter definitions are listed in Table 1. Eight geometrical restraints based on the ab initio calculated values (MP2/6-31G*) were used to reduce correlation between parameters of similar nature (differences) or those describing hydrogen positions (absolute restraints). Their definition and values with assigned uncertainties based on an educated guess (experience with related structures) are also given in Table 1.

All vibrational amplitudes were refined, which belong to a pair of scatterers contributing more than 5% of the most important pair (Si−O, Ge−O). Restraints for these amplitudes were calculated from harmonic force fields obtained at the MP2/6-31G* level of theory, which were transformed into amplitudes by means of the program ASYM40.[28] Ratios between amplitudes were assigned an uncertainty of 10%, absolute restraints 20% of the calculated value. These amplitudes and restraints are given in Table 3.

Ab Initio Calculations. Ab initio molecular orbital calculations were carried out using the Gaussian 94 program.[30] 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*[31−33] and 6-31G*[34−36] basis sets, whereas the larger basis set was used for calculations at the MP2 level of theory. Vibrational amplitudes for GED restraints were calculated from MP2/6-31G* force fields by means of the program ASYM40.[37]

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Supporting Information Available: Correlation matrix elements and calculated vibrational frequencies for $Me_3SiONMe_2$ and $Me_3GeONMe_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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