# Synthesis, Decomposition, and Structural Studies in the Gas Phase and Solid State of *N*,*N*-Dimethylaminoxygermane

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*N*,*N*-Dimethylaminoxygermane, $H_3GeONMe_2$, was prepared by the reaction of $H_3GeBr$ with $LiONMe_2$ in dimethyl ether at −96 °C. The identity of $H_3GeONMe_2$ was proven by gas-phase IR and solution NMR spectroscopy ($^1H$, $^{13}C$, $^{15}N$, $^{17}O$). It is an unstable volatile liquid compound. It decomposes by cleavage of a Ge−O and a Ge−H bond giving $HONMe_2$ and an insoluble germanium hydride polymer $(GeH_2)_n$. This decomposition reaction has been modeled at the MP2/6-311G(d,p) level of theory by the homodesmotic reaction $H_3GeONMe_2 + Ge_2H_6 \rightarrow Ge_3H_8 + HONMe_2$, which is predicted slightly exothermic by 14 kJ mol$^{-1}$. The molecular structure of $H_3GeONMe_2$ was determined by gas-phase electron diffraction supported by an ab initio geometry [MP2/6-311G(d,p)] and a force field [MP2/6-31G(d)]. The structure of the compound in the crystal lattice was determined by low-temperature crystallography using a single crystal of $H_3GeONMe_2$ grown in situ [$C_2H_9NOGe$, orthorhombic, *Pnma*, $Z = 4$, $a = 8.1280(12)$ Å, $b = 9.7037(15)$ Å, $c = 7.0722(12)$ Å]. Important bond lengths and angles (gas phase/solid state, Å/deg) are Ge−O 1.785(2)/1.815(1), O−N 1.462(7)/1.460(2), N−C 1.460(4)/1.453(2), Ge−O−N 105.2(5)/104.6(1), O−N−C 105.8(5)/105.8(1), C−N−C 110.8(9)/111.2(2), Ge···N 2.587(6)/2.601(1). In the solid state the compound forms infinite chains by intermolecular Ge···O contacts of 2.808 Å. The question of the attraction between Ge and N atoms is discussed with respect to reference Ge/O and N/O compounds, which have wider angles at oxygen than $H_3GeONMe_2$. For comparison the structures of the compounds $H_3CONMe_2$, $H_3SiONMe_2$, and $H_3SnONMe_2$ were also calculated to reflect the influence of the group 14 atom on the structure and to discuss the occurrence of weak E···N interactions in the compounds $H_3EONMe_2$.

## Introduction

The chemistry of germanium is often viewed as very similar to that of silicon, but is far less well developed, because germanium is much more expensive. The acceptor quality of the carbon group elements is generally seen as increasing from carbon to lead, but a closer look at listed electronegativities of the elements shows germanium to be an exception to a steady decrease of electronegativity, i.e., it is slightly more electronegative than silicon on various scales (Pauling, Mulliken, Allen).[1] However, the atomic and covalent radii of silicon (1.17 Å) and germanium (1.22 Å) are similar.[2]

There are not very many compounds that allow a direct comparison of the acceptor qualities of carbon, silicon, germanium, and tin. For example, the bipyridyl adducts of $SiF_4$, $GeF_4$, and $SnF_4$ have been investigated by crystal structure determinations,[3] but there is no reference material for estimation of the structural changes that occur upon adduct formation, and a direct comparison of element−nitrogen distances is not possible due to the different element radii.

We have recently determined the molecular structures of a series of compounds with intramolecular E···N interactions, i.e., gaseous $Me_3SiONMe_2$, $Me_3GeONMe_2$,[4] and $Me_3SnONMe_2$.[5] The germanium compound turned out to have the widest E−O−N angle in this series, but there was a substantial discrepancy between the experimental values for this parameter [108.9(7)°] and Ge···N distance [2.682(11) Å] and those theoretically predicted at the MP2/6-31G(d) level [102.9°, 2.595 Å]. By contrast, in the molecule $Me_3SnONMe_2$ a Sn···N attraction leads to a small angle of 102.5(8)° in the gas phase and a markedly distorted geometry at the Sn atom, while in the solid state an additional intermolecular Sn···O contact leads to [4 + 2]-coordination at an even more distorted tin center.[5] The interactions between E and N centers in such compounds were recently investigated in considerable detail and were found to be predominantly electrostatic with interactions between group dipole moments playing a major role. This was proven by the gas-phase structure determination of two conformers (gauche and anti) of $ClH_2SiONMe_2$, which reveal drastically different strengths in their Si···N interactions.[6] Even in the electronically extreme case of $F_3SiONMe_2$, with an extremely short Si···N distance [1.963(1) Å in the crystal, ∠SiON 77.1(1)°], there is no covalent contribution to the Si···N secondary bond.[7]

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(1) Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9003.

(2) Emsley, J. *The Elements*; Clarendon Press: Oxford, 1991.

(3) Adley, A. D.; Bird, P. H.; Fraser, A. R.; Onyszchuk, M. *Inorg. Chem.* **1972**, *11*, 1402.

(4) Mitzel, N. W.; Losehand, U.; Richardson, A. D. *Inorg. Chem.* **1999**, *38*, 5323.

(5) Mitzel, N. W.; Losehand, U.; Richardson, A. *Organometallics* **1999**, *18*, 2610.

(6) (a) Mitzel, N. W.; Losehand, U. *J. Am. Chem. Soc.* **1998**, *120*, 7320. (b) Mitzel, N. W.; Losehand, U.; Bauer, B. *Inorg. Chem.* **2000**, *39*, 1998.

(7) Mitzel, N. W.; Losehand, U.; Wu, A.; Cremer, D.; Rankin, D. W. H. *J. Am. Chem. Soc.* **2000**, *122*, 4471.

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**Table 1.** Crystallographic Data for **1**

| | |
|---|---|
| $C_2H_9NOGe$ | fw 135.69 |
| $a = 8.1280(12)$ Å | space group *Pnma* |
| $b = 9.7037(15)$ Å | $T = 153(2)$ K |
| $c = 7.0722(12)$ Å | $\lambda = 0.71073$ Å |
| $V = 557.8(2)$ Å$^3$ | $\rho_{calc} = 1.616$ g cm$^{-3}$ |
| $Z = 4$ | 5.350 mm$^{-1}$ |
| | $R1(F_o) = 0.0249$ |
| | $wR2(F_o^2) = 0.0638$ |

To reduce the steric and electronic influences at the germanium center, we decided to study the simplest possible GeON compound that can be prepared, $H_3GeONMe_2$. The absence of steric repulsion in this compound and its C, Si, and Sn homologues allows comparison of the E···N distances and E−O−N angles and so the assessment of the influence of the group 14 atom on the molecular structure of the E−O−N units.

## Experimental Section

**General.** The experiments were carried out using a standard Schlenk line or a vacuum line with greaseless stopcocks (Young taps), directly attached 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 solvent directly condensed onto the sample from K/Na alloy. Bromogermane was prepared according to a literature procedure from $GeH_4$ and HBr in the presence of $AlBr_3$.[8]

**(*N*,*N*-Dimethylaminoxy)germane (1).** At −50 °C *n*-butyllithium (0.3 g, 5 mmol, 1.8 M in hexane) was added dropwise to a solution of *N*,*N*-dimethylhydroxylamine (0.6 mL, 0.5 g, 8 mmol) in pentane (25 mL). The mixture was slowly warmed to ambient temperature, and all volatiles were pumped off. Dimethyl ether (30 mL) and 0.86 g of bromogermane (5.5 mmol) were condensed onto the remaining $LiONMe_2$ (0.33 g, 4.9 mmol). The mixture was stirred for 10 h at −96 °C while $H_3GeBr$ was carefully washed off the flask wall. (*N*,*N*-Dimethylaminoxy)germane was isolated in low yield as a colorless, air and temperature sensitive liquid (mp −22 °C) by fractionated condensation through a series of cold traps held at −20, −96, −196 °C. The product was retained in the −96 °C trap. $^1H$ NMR: $\delta = 2.41$ (s, 6H, $H_3C$), 5.11 (s, 3H, $H_3Ge$). $^{13}C$ NMR: $\delta = 49.6$ (q q, $^1J_{CH} = 134.4$ Hz, $^3J_{CNCH} = 5.7$ Hz, $CH_3$). $^{15}N\{^1H\}$ NMR: $\delta = -237.9$ (s). $^{17}O\{^1H\}$ NMR: $\delta = 113$ (s). IR (gas): 2101 cm$^{-1}$ (s, $\nu$GeH).

**Crystal Structure Determination of 1.** A single crystal of **1** was grown in situ by slowly cooling the melt in sealed capillaries after generation of a suitable seed crystal. The crystal and refinement data are listed in Table 1.

**Gas-Phase Electron Diffraction of 1.** Electron scattering intensity data for **1** were recorded on Kodak Electron Image plates using the Edinburgh electron diffraction apparatus and a wavelength of 0.06016 Å.[9] Scattering data for benzene were recorded concurrently and used to calibrate the electron wavelength and camera distances. Three exposures were taken at each camera distance. Data were obtained in digital form using the microdensitometer at the Institute of Astronomy at Cambridge.[10] The data analysis followed standard procedures, using established data reduction and least-squares refinement programs[11] and the scattering factors established by Fink and co-workers.[12] The experimental conditions are summarized in Table 2. The refined molecular parameters, their definitions and the applied restraints, a list of selected interatomic distances including vibrational amplitudes and applied restraints, and elements of the correlation matrix are given in Tables 2, 4, and 6.

**Ab Initio Calculations.** Ab initio molecular orbital calculations were carried out using the Gaussian 98 program.[13] Geometry optimizations and vibrational frequency calculations were performed from analytic first and second derivatives at the SCF and MP2 levels of theory. Different basis sets of increasing size were employed, namely, the standard basis sets 3-21G(d), 6-31G(d), and 6-31G(d,p) as well as the more extended 6-311G(d,p) basis set.[14] For calculations involving tin atoms 3-21G(d) and a basis set of double-ζ quality by Dunning were employed.[15]

## Results and Discussion

The stoichiometrically simple *N*,*N*-dimethylaminoxygermane, $H_3GeONMe_2$ (**1**), was prepared from bromogermane and *N*,*N*-dimethylaminoxy lithium (eq 1). Due to the instability of monohalogenogermanes, the preparation of *N*,*N*-dimethylaminoxygermane (**1**) had to be conducted at −96 °C. Dimethyl ether (bp −24 °C) was advantageously applied as a solvent, as its volatility exceeds that of all starting materials and products and thus allows complete separation. $H_3GeONMe_2$ is obtained as a colorless liquid in moderate yield by trap-to-trap distillation. It is highly sensitive to air and unstable at ambient temperature. Decomposition of the compound can be observed even near the melting point of −22 °C by the occurrence of a yellow-brownish color and later by formation of a red-brown precipitate.

$$H_3GeBr + LiONMe_2 \rightarrow LiBr + H_3GeONMe_2 \qquad (1)$$

The compound has been identified by gas-phase IR spectroscopy and NMR spectroscopy of the nuclei $^1H$, $^{13}C$, $^{15}N$, and $^{17}O$. The Ge−H stretching vibrational mode corresponds to an absorption at 2101 cm$^{-1}$ in the IR spectrum, and correct relative intensities of the proton signals and the occurrence of the expected quartet of quartet splitting in the proton-coupled $^{13}C$ NMR proved the identity of $H_3GeONMe_2$. An attempt to record a $^{73}Ge$ NMR spectrum failed as well as attempts to obtain a mass spectrum and a reliable elemental analysis.

Despite having the different elements bound to the $ONMe_2$ unit, the $^{15}N$ and $^{17}O$ NMR chemical shifts of $H_3GeONMe_2$ (−234.0 and 112 ppm) and $H_3SiONMe_2$ (−237.9 and 113 ppm)[16] are surprisingly similar. This indicates that the bonding situations in the two compounds are similar.

The decomposition of $H_3GeONMe_2$ can be monitored by recording proton NMR spectra at suitable time intervals. Figure 1 displays two spectra of a freshly prepared sample in $C_6D_6$

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(8) Dennis, L. M.; Judi, P. R. *J. Am. Chem. Soc.* **1929**, *51*, 2321.

(9) Huntley, C. M.; Laurenson G. S.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1980**, 945.

(10) Lewis, J. R.; Brain P. T.; Rankin, D. W. H. *Spectrum* **1997**, *15*, 7.

(11) 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.

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

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A., *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(14) (a) Binkley, J. S.; Pople, J. A.; Hehre W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (b) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797. (c) 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. (d) 6-31G(d): Hariharan, P. C.; Pople J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (e) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *66*, 217. (f) 6-311G(d): Krishnan, R.; Frisch, M. J.; Pople, J. A. *Chem. Phys.* **1980**, *72*, 4244.

(15) Dunning, T. H. Unpublished work.

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

**Table 2.** Geometric Parameters, Their Values ($r_a$), and Parameter Restraints for the GED Refinements of $H_3GeONMe_2$[a]

| | | GED ($r_a$, $\angle_a$) | | | |
|---|---|---|---|---|---|
| | parameter | value | restraint | MP2/6-311G** | XRD |
| $p_1$ | $r$(Ge−H4) | 1.547(8) | | 1.533 | 1.45(5) |
| $p_2$ | $r$(Ge−H5/6) | 1.548(8) | $p_1 - p_2 = 0.001(5)$ | 1.532 | 1.37(2) |
| $p_3$ | $r$(Ge−O) | 1.785(2) | | 1.816 | 1.815(1) |
| $p_4$ | $r$(O−N) | 1.462(7) | | 1.459 | 1.460(2) |
| $p_5$ | $r$(N−C) | 1.460(4) | $p_4 - p_5 = 0.001(10)$ | 1.458 | 1.453(2) |
| $p_6$ | $r$(C7−H9) | 1.100(7) | | 1.091 | 1.02(3) |
| $p_7$ | $r$(C7−H10) | 1.105(7) | $p_7 - p_6 = 0.003(5)$ | 1.094 | 0.95(3) |
| $p_8$ | $r$(C7−H11) | 1.109(7) | $p_8 - p_6 = 0.009(5)$ | 1.100 | 0.95(2) |
| $p_9$ | ∠(Ge−O−N) | 105.2(5) | | 104.2 | 104.64(8) |
| $p_{10}$ | ∠(O−N−C) | 105.8(5) | | 105.0 | 105.76(9) |
| $p_{11}$ | ∠(C−N−C) | 110.8(9) | | 110.6 | 111.2(2) |
| $p_{12}$ | ∠(O−Ge−H4) | 102.9(14) | $p_{17} = 103.9(15)$ | 103.9 | 107.2(10) |
| $p_{13}$ | ∠(OGeH5/6) | 108.4(15) | $p_{13} - p_{12} = 5.5(5)$ | 109.4 | 101.0(15) |
| $p_{14}$ | ∠(NC7H9) | 109.1(12) | | 109.0 | 107.2(16) |
| $p_{15}$ | ∠(NC7H10) | 108.6(12) | $p_{15} - p_{14} = 0.009(5)$ | 108.3 | 107.3(15) |
| $p_{16}$ | ∠(NC7H11) | 111.4(12) | $p_{16} - p_{14} = 0.009(5)$ | 111.3 | 115(2) |
| $p_{17}$ | $\tau$(C8NC7H9) | −188.9(29) | $p_{17} = -177.4(50)$ | −177.4 | −178.7(25) |
| $p_{18}$ | $\tau$(CNC7H10) | 49.5(30) | $p_{18} - p_{17} = 241.5(30)$ | 64.1 | 67.3(25) |
| $p_{19}$ | $\tau$(CNC7H11) | −67.4(34) | $p_{19} - p_{17} = 120.5(30)$ | −56.9 | −57.1(24) |
| $p_{20}$ | $\tau$(NOGeH5) | 62.2(29) | $p_{20} = 60.9(30)$ | 60.9 | 59.7(23) |
| $p_{21}$[b] | $r$(Ge1···N3) | 2.587(6) | | 2.592 | 2.6013(14) |

[a] The geometrical parameter values determined in the ab initio calculations [MP2/6-311G(d,p)] are listed for comparison. Distances are given in Å, angles and torsion angles in deg. [b] Dependent parameter.

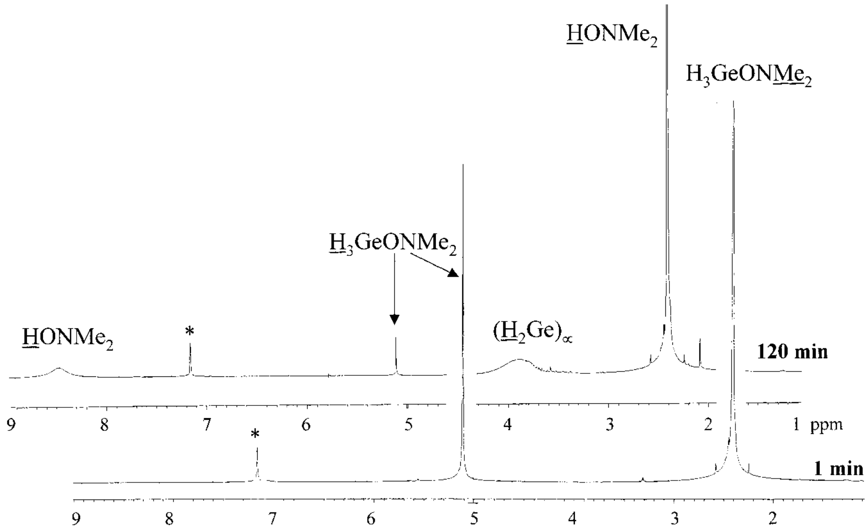

**Figure 1.** $^1H$ NMR spectra of a freshly prepared solution of **1** in $C_6D_6$ (1 min) and of the same sample after 120 min at room temperature.

recorded at 21 °C 1 and 120 min after removing the liquid nitrogen coolant. After 120 min at ambient temperature the decomposition is almost complete and the signals of $H_3GeONMe_2$ at 2.42 (methyl protons) and 5.11 ppm (germyl protons) have disappeared. New signals have appeared at 2.40 and 8.65 ppm and are identified as $HONMe_2$, which is further verified by $^{13}C$, $^{15}N$, and $^{17}O$ NMR experiments, which reproduce the literature data for this compound.[17] A new broad signal at 3.8 ppm is typical of the decomposition products of $GeH_3$ compounds and is usually assigned as $(GeH_2)_n$ polymer, which fulfills the stoichiometry of the proposed decomposition reaction

$$H_3GeONMe_2 \rightarrow HONMe_2 + (1/n)(GeH_2)_n \qquad (2)$$

No hydrogen or other gas evolution is observed, but after a few hours a brown precipitate is formed. Attempts to trap a proposed intermediate germylene $GeH_2$ by decomposition in the presence of reactants such as cyclohexene (germacyclopropane formation) failed, i.e., so far we have no evidence that $H_3GeONMe_2$ could serve as a clean source for the simplest germylene $GeH_2$.

This decomposition reaction seems thermodynamically surprising as a relatively strong Ge−O bond and a Ge−H bond are broken, while a Ge−Ge and an O−H bond are formed. To understand the energetic contributions involved in this reaction we have estimated the energy difference occurring in the homodesmotic reaction in eq 3, which mimics the insertion of the germylene unit of $H_3GeONMe_2$ into the Ge−Ge backbone of the $(GeH_2)_n$ polymer. Fully optimized geometries for all four

$$H_3GeONMe_2 + H_3Ge{-}GeH_3 \rightarrow HONMe_2 + H_3Ge{-}GeH_2{-}GeH_3 \qquad (3)$$

compounds were calculated at the MP2/6-311G(d,p) level of theory (Figure 2). The energies were calculated at the same level and corrected for zero-point vibration estimated from frequency calculations at SCF/6-31G(d) calculations. The result favors the products $HONMe_2$ and $H_3Ge{-}GeH_2{-}GeH_3$ by 14 kJ mol$^{-1}$

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(17) Mitzel, N. W.; Schmidbaur, H. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1087.

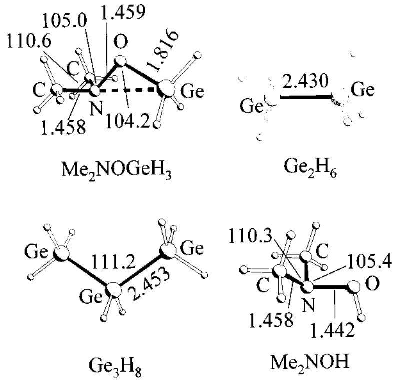

**Figure 2.** Molecular geometries of the reference molecules used in the homodesmotic reaction (eq 3). Distances are in Å, angles in deg.

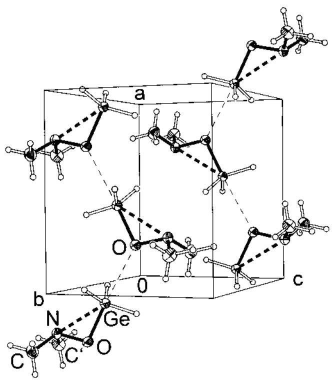

**Figure 3.** Contents of a unit cell of **1** showing the intermolecular Ge···O contacts 2.808(2) Å in length and the geometry of the molecules of **1** in the solid state.

over the starting materials $H_3GeONMe_2$ and $H_3Ge-GeH_3$, which does not represent a great driving force for the decomposition, but proves its thermodynamical feasibility.

**Structure Determination in the Gas Phase and in the Solid State. Crystal Structure.** Utilizing in situ techniques, growth of a single crystal of **1** from the melt at −22 °C was successfully performed. This was despite the fact that decomposition of **1** starts at this temperature, which means that crystal growth had to be achieved within ca. 15 min, before the higher-melting decomposition products caused problems as competitive crystal seeds. The single-crystal specimen allowed successful determination of the solid-state structure of **1** by X-ray diffraction. Geometrical results are included in Table 2, and the contents of the unit cell are presented in Figure 3.

In the crystal lattice (*Pnma*) the molecules form infinite chains of molecules of **1** connected by weak intermolecular Ge···O contacts of 2.808(2) Å distance with the O···Ge−O unit adopting an angle of 177.0(1)° at the germanium atom. These contacts are similar to the intermolecular Si···O contacts in solid $H_3SiONMe_2$,[16] $MeOSiH_3$,[18] $(H_3Si)_2O$,[19] and $(H_3Si)_2NOMe$.[20] The intramolecular structure will be compared with the gas-phase structure.

**Gas-Phase Structure.** The high volatility of **1** allowed a gas-phase electron-diffraction experiment to be performed. The experimental conditions are described in Table 3, and the geometry including the atomic numbering scheme is presented in Figure 4. The model for least-squares refinement had $C_s$ symmetry, with the mirror plane passing through the atoms Ge, O, and N. The geometrical model is thus defined by 20 independent parameters, which are listed in Table 4. Applying the principles of the SARACEN[21] procedure to overcome the usual limitations of the GED technique, the refinement was supported by 12 restraints. These were applied to the O2−Ge1−H4 angle, the torsional angles C8−N3−C7−H9 and N3−O2−Ge1−H5, the differences between the N−O and N−C distances, and various differences between parameters of similar nature (see Table 2). Fifteen vibrational amplitudes were refined simultaneously under the action of 10 restraints. These amplitudes represent all pairs of scatterers with a contribution exceeding 5% of the Ge−O scatterer pair. The restraints were taken from a MP2/6-31G(d) force field and transformed into amplitudes by means of the program ASYM40[22] after scaling it by an overall factor of 0.93 previously used in connection with the SARACEN method.[23] The success of the refinement can be assessed from the molecular scattering intensity curves and the radial distribution curve displayed in panels a and b of Figure 5. The most important geometrical parameter is the Ge−O−N angle, which is 105.2(5)° in the gas phase and 104.6(1)° in the crystal. This is a smaller valence angle than in most Ge−O compounds studied in the gas phase, such as $(H_3Ge)_2O$ [126.5(3)°],[24] slightly smaller than in the methyl derivative $Me_3GeONMe_2$ [gas: 108.9(7)°],[4] and almost identical to that in gaseous $Cl_3GeONMe_2$ [104.0(11)°].[25] There is to the best of our knowledge no suitable Ge−O−C compound which could be used for a comparison of Ge−O−N and Ge−O−C angles. The only crystal structure of an open chain germanium(IV) alkoxide is that of a cage Si/Ge/N compound with a terminal EtO group at the Ge atom,[26] which is surrounded by three additional N atoms. In this case a Ge−O−C angle of 120.0° was observed, which might serve as a coarse value for comparison with the Ge−O−N angle in our simple $H_3GeONMe_2$ compound.

In the crystalline phase of $Cl_2Ge(ONMe_2)_2$[27] smaller Ge−O−N angles [102.0(1)°] were found than in solid **1**. The theoretical prediction of the Ge−O−N angle in **1** is 104.2° at the MP2/6-311G(d,p) level. These calculations thus provide an adequate description of the molecular geometry. The Ge···N distance has been determined in the gas phase to be 2.587(6) Å and in the solid state to be 2.601(1) Å.

The Ge−O distance in **1** is 1.815(1) Å in the solid state and 1.785(2) Å in the gas phase, which is a relatively large difference even considering the fact that two different methods have been applied. The gas-phase value is somewhat larger than in gaseous $(H_3Ge)_2O$ [1.766(4) Å],[24] gaseous $Cl_3GeONMe_2$ [1.759(6) Å],[25] and solid $Cl_2Ge(ONMe_2)_2$ [1.745(2) and 1.753(2) Å],[27] but

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(18) Barrow, M. J.; Ebsworth, E. A. V.; Harding, M. M. *Acta Crystallogr., Sect. B* **1979**, *35*, 2093.

(19) Blake, A. J. Dyrbush, M.; Ebsworth, E. A. V.; Henderson, S. G. D. *Acta Crystallogr., Sect. C* **1988**, *44*, 1.

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

(21) (a) Blake, A. J.; Brain, P. T.; McNab, H.; Miller, J.; Morrison, C. A.; Parsons, S.; Rankin, D. W. H.; Robertson H. E.; Smart, B. A. *J. Phys. Chem.* **1996**, *100*, 12280. (b) Brain, P. T.; Morrison, C. A.; Parsons, S.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1996**, 4589.

(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.

(23) This scaling factor fits well with the generally accepted scaling factor of 0.9496 for MP2-fc/6-311G(d,p): Scott, A. P.; Radom L. *J. Phys. Chem.* **1996**, *100*, 16502.

(24) (a) Glidewell, C.; Rankin, D. W. H.; Robiette, A. G.; Sheldrick, G. M.; Beagley, B.; Cradock, S. *J. Chem. Soc. A* **1970**, 315. (b) Glidewell, C.; Rankin, D. W. H.; Robiette, A. G.; Sheldrick, G. M.; Cradock, S.; Ebsworth, E. A. V.; Beagley, B. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 417.

(25) Losehand, U.; Mitzel, N. W.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1999**, 4291.

(26) Veith, M.; Detempke, A.; Huch, V. *Chem. Ber.* **1991**, *124*, 1135.

(27) Losehand, U.; Mitzel, N. W. *Eur. J. Inorg. Chem.* **1998**, 2023.

**Table 3.** Experimental Conditions (Camera Distances [mm], Electron Wavelengths [Å], Nozzle and Sample Temperatures [°C]), Data Ranges and Trapezoidal Weighting Functions [$Å^{-1}$], Correlation Parameters, Scale Factors, and Final *R* Factors for the GED Experiments and Refinements of $H_3GeONMe_2$

| | | | *T* | | | | | | | correlation | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| data set | camera dist | wavelength | nozz | samp | $\Delta s$ | $s_{min}$ | $s_1$ | $s_2$ | $s_{max}$ | param | scale factor | $R_1$ | $R_g$ |
| 1 | 285.51 | 0.06016 | 20 | −30 | 0.2 | 2.0 | 4.0 | 11.8 | 13.8 | 0.3503 | 0.761(12) | 0.0728 | 0.0967 |
| 2 | 128.21 | 0.06016 | 20 | −16 | 0.4 | 9.2 | 11.2 | 30.0 | 31.2 | 0.2746 | 0.705(64) | 0.1678 | |

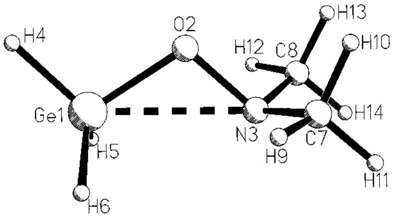

**Figure 4.** Molecular structure of **1** in the gas phase as determined by electron diffraction, with the atom-numbering scheme.

**Table 4.** Distances, Amplitudes, and Restraints for the GED Refinements of $H_3GeONMe_2$

| no. | atom pair | distance[a] | amplitude[a] | restraint |
|---|---|---|---|---|
| $d_1$ | Ge1−H4 | 1.547(8) | 0.102(9) | $u_2/u_1 = 1.000(50)$ |
| $d_2$ | Ge1−H5 | 1.548(8) | 0.102(10) | |
| $d_3$ | Ge1−O2 | 1.785(2) | 0.050(6) | |
| $d_4$ | O2−N3 | 1.462(7) | 0.058(5) | $u_4/u_5 = 1.059(53)$ |
| $d_5$ | N3−C7 | 1.460(4) | 0.055(4) | $u_5/u_1 = 0.538(27)$ |
| $d_6$ | C7−H9 | 1.100(7) | 0.087(7) | $u_6 = 0.077(15)$ |
| $d_7$ | C7−H10 | 1.105(7) | 0.088(8) | $u_7/u_6 = 1.004(50)$ |
| $d_8$ | C7−H11 | 1.109(7) | 0.089(8) | $u_8/u_6 = 1.014(51)$ |
| $d_9$ | Ge1···N3 | 2.587(6) | 0.091(6) | |
| $d_{10}$ | Ge1···C7 | 3.587(5) | 0.156(5) | |
| $d_{11}$ | O2···C7 | 2.331(6) | 0.073(6) | |
| $d_{12}$ | C7···C8 | 2.404(17) | 0.073(7) | $u_{12}/u_{11} = 0.994(50)$ |
| $d_{13}$ | Ge1···H9 | 3.424(25) | 0.254(24) | $u_{13} = 0.257(26)$ |
| $d_{14}$ | Ge1···H10 | 4.175(33) | 0.174(16) | $u_{14} = 0.182(18)$ |
| $d_{15}$ | Ge1···H11 | 4.433(22) | 0.181(17) | $u_{15} = 0.190(19)$ |

[a] Distances and amplitudes are given in Å.

similar to the Ge−O distance in gaseous $(Me_3Ge)_2O$ [1.770(10) Å].[28] The N−O distance in **1** is 1.462(7) Å in the gas phase and 1.460(2) Å in the solid state. This is similar to the value in other E−O−N units with weak E···N interactions [$H_3SiONMe_2$ 147.1(1) Å] and relatively small in comparison to those in systems with electronegative substituents at the E atom, such as $ClH_2SiONMe_2$ [anti conformer, solid state 1.490(1) Å][6] and $F_3SiONMe_2$ [solid state 1.508(1) Å].[7] Other structural parameters require no detailed comments.

**Comparison of the $H_3EONMe_2$ Compounds (E = C, Si, Ge, Sn).** For a comparison of the interactions between the elements E = C, Si, Ge, and Sn and the N atoms in geminal position of an EON unit, we have calculated the structures of the compounds $H_3EONMe_2$ at two levels of theory, MP2/6-311G(d,p) and B3LYP/6-311G(d,p). The results for the angles E−O−N and the E···N distances are listed in Table 5. The values for the E−O−N angles show that the MP2 results are closer to experimental parameters for E = C,[29] Si,[16] and Ge than the DFT results, which give slightly too large E−O−N angles. The deviation between experiment and DFT theory becomes greater with increasing strength of the secondary interaction, as has already been shown for $F_3SiONMe_2$, which has an Si−O−N angle of 94.3(9)° in the gas phase. In this case B3LYP/6-311++G(d,p) calculations predict 105.5°, whereas MP2/6-31G(d,p) predicts correctly 94.1°.[7]

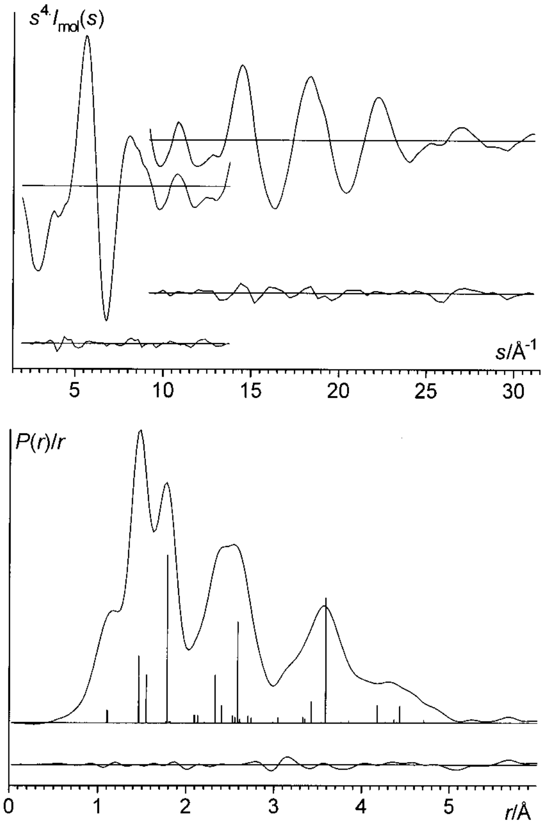

**Figure 5.** (a) Molecular intensity and difference curve and (b) radial distribution and difference curve for the electron diffraction refinement of **1**. Vertical lines in the radial distribution curve indicate atom pairs with their height being proportional to their scattering contribution.

**Table 5.** Molecular Geometry Parameters for $H_3EONMe_2$ with E = C, Si, Ge, and Sn Calculated at Different Levels of Theory[a]

| | ∠(E−O−N) [deg] | | *r*(E···N) [Å] | |
|---|---|---|---|---|
| | MP2 | B3LYP | MP2 | B3LYP |
| $H_3CONMe_2$ | 107.6 | 109.2 | 2.304 | 2.335 |
| $H_3SiONMe_2$ | 102.5 | 106.9 | 2.454 | 2.532 |
| $H_3GeONMe_2$ | 104.2 | 107.5 | 2.592 | 2.650 |
| $H_3SnONMe_2$ | 98.2 | 103.9 | 2.664 | 2.757 |

[a] The basis set 6-311G(d,p) was used for E = C, Si, and Ge, while a basis set of double-ζ quality was used for calculations on the Sn compound.[15]

In the series E = C, Si, Ge, Sn the E−O−N angles become smaller from C to Si, become slightly wider from Si to Ge, and reach a minimum at Sn. This parallels the electronegativities for the elements of the carbon group, which also do not decrease monotonically, but feature Ge as an exception with a higher electronegativity than Si.

To gauge the effect of a $Me_2N$ substituent at an oxygen atom we calculated the molecular structure of $Me_2NONMe_2$ up to the MP2/6-311G(d,p) level of theory. The results of these calculations are shown in Figure 6. Two $Me_2N$ groups lead to a valence angle at oxygen (106.4°), which is slightly smaller

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(28) Vilkov, L. V.; Tarasenko, N. A. *Zh. Strukt. Khim.* **1969**, *10*, 1102.

(29) Riddell, F. G.; Turner, E. S.; Rankin, D. W. H.; Todd, M. R. *J. Chem. Soc., Chem. Commun.* **1979**, 72.

**Table 6.** Elements of the Least-Squares Correlation Matrix (×100) for $H_3GeONMe_2$[a]

| | $p_1$ | $p_4$ | $p_6$ | $p_9$ | $p_{11}$ | $p_{12}$ | $p_{14}$ | $p_{15}$ | $p_{17}$ | $u_1$ | $u_2$ | $u_3$ | $u_4$ | $u_5$ | $u_6$ | $u_{7/8}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $p_2$ | 80 | | | | | | | | | | | | | | | |
| $p_5$ | | −54 | | | | | | | | | | | | | | |
| $p_7$ | | | 73 | | | | | | | | | | | | | |
| $p_8$ | | | 73 | | | | | | | | | | | | | |
| $p_9$ | | −57 | | | 57 | | −57 | | | | | | | | | |
| $p_{13}$ | | | | | | 94 | | | | | | | | | | |
| $p_{15}$ | | | | −58 | | | 90 | | | | | | | | | |
| $p_{16}$ | | | | −53 | | | 91 | 82 | | | | | | | | |
| $p_{18}$ | | | | | | | | | 56 | | | | | | | |
| $p_{19}$ | | | | | | | | | 62 | | | | | | | |
| $u_2$ | | | | | | | | | | 86 | | | | | | |
| $u_3$ | | | | | | | | | | 78 | 73 | | | | | |
| $u_4$ | | | | | | | | | | 67 | 59 | 75 | | | | |
| $u_5$ | | | | | | | | | | 83 | 72 | 82 | 80 | | | |
| $u6$ | | | | | | | | | | | | 58 | 52 | 56 | | |
| $u_{7/8}$ | | | | | | | | | | | | 55 | | 53 | 82 | |
| $u_{20}$ | | | | | −64 | | | | | | | | | | | |
| $u_{21}$ | | | | | −57 | | | | | | | | | | | |
| $k_2$ | | | | | | | | | | 78 | 71 | 91 | 84 | 89 | 62 | 59 |

[a] Only elements with absolute values greater 50 are shown. *p*, *u*, and *k* denote parameters, amplitudes, and scale factors, which can be identified in Tables 1 and 3.

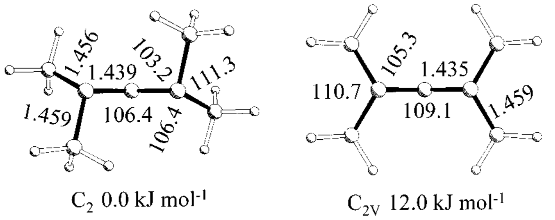

**Figure 6.** Calculated molecular geometries of $Me_2NONMe_2$ (MP2/dzp). Shown are the ground state of $C_2$ symmetry and a transition state of $C_{2v}$ symmetry. Distances are given in Å, angles in deg.

than the tetrahedral angle, but still significantly larger than in $H_3GeONMe_2$ (**1**).

In contrast, germyl substitution at an oxygen center in general leads to a marked widening of its valence angle [e.g., $(H_3Ge)_2O$[24] 126.5(3)°, $(Me_3Ge)_2O$[28] 141(1)°, $((F_3C)_3Ge)_2O$[30] 151.5(15)°], whereas alkyl substitution does not grossly affect the valence angle at oxygen. This and the knowledge about systems with stronger E···N interactions in EON units ($ClH_2SiONMe_2$,[6] $F_3SiONMe_2$,[7] $Me_3SnONMe_2$)[5] leads us to the conclusion that $H_3GeONMe_2$ (**1**) with a mixed germyl and $Me_2N$ substitution at oxygen contains a very weak attractive force between the Ge and N atoms.

Electrostatic forces are of major importance for the E···N interactions.[7] Apart from the more complicated group dipole interactions, the attraction between negatively charged N atoms and positively charged E atoms is an important contribution. In the series E = C, Si, Ge ($H_3EONMe_2$) the charge at the N atom is almost unchanged as is shown by the Mulliken charges calculated at the MP2/6-311G(d,p) level (C −0.27, Si −0.29, Ge −0.28 e), but the charges on the E atoms are very different (C 0.05, Si 1.11, Ge 0.95 e). This reflects again the more electropositive character of Si as compared with Ge and is consistent with the E···N interaction being weaker for the Ge system than for the Si system.

However, much care is needed in a final assessment of the strength of this Ge···N interaction in $H_3GeONMe_2$ (**1**). Other compounds such as $ClH_2GeONMe_2$ or $F_3GeONMe_2$ have to be synthesized and studied to obtain a more detailed insight into the details of bonding in the Ge−O−N system.

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**Supporting Information Available:** An X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(30) Eujen, R.; Laufs, F. E.; Oberhammer, H. *Z. Anorg. Allg. Chem.* **1988**, *561*, 82.