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Are There Structurally Relevant Attractive Interactions between Nitrogen Atoms and Group 14 Elements in Their Aminomethyl Compounds?

Norbert W. Mitzel,*,† Christoph Kiener,† and David W. H. Rankin‡

Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstrasse 4,
85747 Garching, Germany, and Department of Chemistry, University of Edinburgh,
West Mains Road, Edinburgh EH9 3JJ, U.K.

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The three compounds $H_3SiCH_2NMe_2$, $Me_3GeCH_2NMe_2$, and $Me_3SnCH_2NMe_2$ have been prepared for the purpose of the determination of their molecular structures. The gas-phase structure of $H_3SiCH_2NMe_2$ has been established by electron diffraction (GED) and ab initio calculations up to the MP2/6-311G** level of theory. The geometry of $Me_3GeCH_2NMe_2$ could be studied only by theoretical methods, while the structure of $Me_3SnCH_2NMe_2$ has been determined by single-crystal X-ray diffraction (XRD) and computational methods. The E−C−N units (E = Si, Ge, Sn) in all three compounds adopt angles that are larger than the tetrahedral angle ($H_3SiCH_2NMe_2$ GED 114.7(3)°, MP2/6-311G** 111.4°; $Me_3GeCH_2NMe_2$ SCF/6-31G* 116.1°; $Me_3SnCH_2NMe_2$ XRD 113.0(2)°, SCF/dzp 115.4°), and all three compounds adopt gauche conformations; that is, the lone pairs at nitrogen are declined away from the plane E−C−N. These facts are interpreted in terms of the absence of an earlier postulated α-effect, which should lead to an attractive interaction between E and N centers. The structures, energies, and orbital interactions in the natural bond orbital (NBO) model for three possible conformations of the $SiCH_2NC_2$ skeleton (lone pairs at N vs Si atom) of $H_3SiCH_2NMe_2$ have been calculated ab initio and show the gauche conformer to be the ground state and the syn form (+6.6 kJ mol^{-1}) as well as the anti form (+10.2 kJ mol^{-1}) to be transition states to rotation about the N−C(H_2) bond. The NBO calculations do not confirm the earlier postulated lp(N) → d(E), σ(NC) → d(E), or lp(N) → σ^*(EX) interactions as important contributors to electron delocalization. Calculations on the model system $FH_2SiCH_2NMe_2$ predict a tendency of SiCN units to adopt small bond angles if very electronegative groups are bound to silicon. The conformational preferences of the unsubstituted $H_3SiCH_2NMe_2$ are overridden in favor of a conformation bringing the lone pair of electrons closer to the electrophilic Si center. This compound is predicted to have significant lp(N) → σ^*(SiF) interactions.

Introduction

Compounds with heteroatoms in geminal position relative to a group 14 element often show unusual reactivity and exhibit unexpected spectroscopic properties. This has been termed the α-effect since the 1960s.[1] The facts upon which this hypothesis is built include unusual stabilities of halogenomethyl compounds and the surprising decrease of nitrogen basicities in the series of compounds $R_3E{-}CH_2{-}NR'_2$ (with E = C, Si, Ge, Sn; R = Me, Et; R′ = H, Me, Et).[2] Whereas the low basicity of $Me_3C{-}CH_2{-}NR'_2$ compounds has been attributed to the steric shielding of the neopentyl group, the even more reduced N-basicity in $Me_3SiCH_2NMe_2$ has been rationalized by intramolecular interaction between the Si and N atoms or by the formation of a three-center bond between Si, C, and N atoms,[3] and structural motifs have been drawn as shown in structure A,[4] while intermolecular aggregation (B) was excluded on the basis of molecular weight determinations in solution (Scheme 1).The assumption of hypercoordinate silicon, germanium, and tin atoms as well as quaternary nitrogen atoms served to explain the anomalies. Moreover, the basicities of the amines Me_3ECH_2NRR' decrease sharply in the series E = Si, Ge, and Sn, despite the change in the inductive +I effect of the Me_3E group.[5] This interpretation of the bonding situation was further supported by a marked fall in the basicity of the amine $Me_3SiCH_2NH_2$ upon substitution of the methyl groups by electronegative substituents (Ph, EtO, R_3SiO) and

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* Corresponding author. E-mail: N.Mitzel@lrz.tum.de.
† Technische Universität München.
‡ University of Edinburgh.

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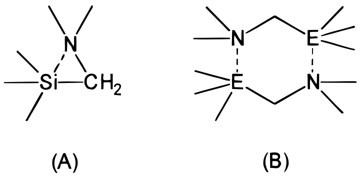
10.1021/om990166c CCC: $18.00

Scheme 1



the absence of absorption characteristics of free NH_2 or NH groups in the IR spectra of such compounds.[6]

The nature of the α-effect has been described with various models of orbital interactions, and the most plausible were the following: the $\sigma \rightarrow$ d conjugation[7] between the filled σ-orbitals of the N−C bond and empty d-orbitals of the group 14 element, and lp(N) → d interaction between the lone pair of electrons at nitrogen and an empty d-orbital of the group 14 element.

Recently we have systematically studied isoelectronic compounds containing E−N−N[8] and E−O−N[9] fragments and found attractive interactions between the nitrogen and group 14 centers. In addition to these hydrazinosilanes and aminoxysilanes our studies included also aminoxygermanes[10] and -stannanes.[11] Determinations of the solid-state and gas-phase structures of the compound $ClH_2SiONMe_2$ were the key experiments in this respect, as they showed this system to have a very strong intramolecular secondary Si···N bond, which turns the SiON unit into a three-membered ring with a very small SiON angle (79.7(1)° in the crystal).[12] However, the gas-phase study showed the attractive forces to be strongly dependent upon the adoption of certain conformations: the anti conformation of the ClSiON fragment is the optimum, whereas the gauche conformation leads to a much weaker Si···N interaction. We interpreted these observations as β-donor−acceptor interactions and rationalized them by means of a natural bond orbital analysis in terms of negative hyperconjugation of the type lp(N) → σ^*(Si−Cl), i.e. without involving any d-orbital participation. Alternatively, intermolecular interactions between local dipoles could be seen as an important contribution, whereas a simple attraction between a positively charged silicon center and a negatively charged nitrogen atom can be excluded on the basis of a series of experiments and calculations on this and related compounds.

Having studied EON and ENN compounds, we wanted to extend our investigations to the organometallic ECN systems. In a very recent crystal structure determination of $[(Me_3Si)_3Si]_2CHNMe_2$ Oehme et al. reported the NMe_2 group being bent toward one silicon atom leading to two very different Si−C−N angles in the same molecule [114.2(4)° and 102.9(4)°],[13] which could be interpreted as an attractive effect between Si and N atoms. We aimed to evaluate the importance of such effects on the structures of these molecules and possibly to rationalize the "α-effect" on the basis of experimental structure determination accompanied by theoretical studies of likely orbital interactions. Therefore we report here the syntheses and structure elucidation of three model compounds, $H_3SiCH_2NMe_2$, $Me_3GeCH_2NMe_2$, and $Me_3SnCH_2NMe_2$.

Experimental Section

General. All experiments were carried out in standard Schlenck lines or a vacuum line with greaseless PTFE stopcocks (Young's taps), directly connected 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.

***N,N*-Dimethylaminomethylsilane (1): (A) Preparation from *N,N*-Dimethylaminomethyllithium[14] and Bromosilane.[15]** A 10 mL sample of dry (CaH_2) dimethyl ether was condensed onto 15.5 mmol (1.01 g) of *N,N*-dimethylaminomethyllithium at −196 °C followed by 15.5 mmol of bromosilane. The mixture was allowed to warm slowly to −40 °C and was kept at this temperature for 1 h. The volatile products were fractionated through a series of cold traps held at −53, −78, −106, and −196 °C, whereby the desired product was retained in the −78 and −106 °C traps and was further purified by repeated distillation. However, a purity greater than 95% (NMR) was never achieved in this way.

(B) From Chloromethyltriethoxysilane. A 46 g (207 mmol) sample of (*N,N*-dimethylaminomethyl)triethoxysilane was almost quantitatively obtained by reacting 211 mmol (41.9 g) of chloromethyltriethoxysilane with liquid dimethylamine (ca. 150 mL) under reflux (+7 °C) for 15 h, followed by evaporation of the excess dimethylamine, extraction with pentane, filtration from the dimethylammonium chloride, and evaporation of the pentane in vacuo. The 33.7 mmol (7.47 g) of the obtained (*N,N*-dimethylaminomethyl)triethoxysilane was added dropwise at −20 °C to a stirred suspension of 10.1 mmol (384 mg, 1.2 equiv) of lithium alanate in 75 mL of di-*n*-butyl ether, warmed to 10 °C, and stirred for 1 h. The solvent and the volatile reaction products were evaporated in vacuo and condensed at −196 °C. This solution was fractionated through a series of cold traps held at −10, −35, −50, −76, and −196 °C, with the desired product retained in the −50 °C trap. Further purification was achieved by repeating this fractional condensation. Yield: 76%. ^{1}H NMR: $\delta = 1.86$ (q, 2H, CH_2), 2.06 (s, 6H, H_3C), 3.63 (t, 3H, SiH_3, $^1J_{SiH} = 195.7$ Hz). ^{13}C NMR: $\delta = 42.3$ (t m, CH_2, $^1J_{CH} = 127.8$ Hz, $^2J_{CSiH} = 5.5$ Hz, $^3J_{CNCH} = 5.5$ Hz), 48.6 (q q t, CH_3 $^1J_{CH} = 132.3$ Hz, $^2J_{CH3} = 5.5$ Hz, $^4J_{CNCH} = 5.5$ Hz). ^{14}N NMR: $\delta = -361$ (s). ^{15}N NMR: $\delta = -363.8$ (s). ^{29}Si NMR: $\delta = -66.2$ (q t, SiH_3, $^1J_{SiH} = 195.6$ Hz, $^3J_{SiCH} = 5.4$ Hz). IR: see Table 1.

Gas-Phase Electron Diffraction. Electron scattering intensity data for $H_3SiCH_2NMe_2$ were recorded on Kodak Electron Image plates using the Edinburgh electron diffraction apparatus. The sample was held at −40 °C and the inlet nozzle at 20 °C during the experiments. Scattering data for benzene were recorded concurrently and used to calibrate the electron wavelength: 285.47 mm camera distance, 3 plates, wavelength 0.06016 Å, data range $s_{\min} = 2.0$ to $s_{\max} = 13.0$, weighting points (trapezoidal weighting function) $s_1 = 4.0$ and $s_2 = 11.0$, scale factor 0.626(12), correlation parameter −0.4496; 128.08 mm camera distance, 3 plates, wavelength 0.06016 Å, data range $s_{\min} = 6.0$ to $s_{\max} = 32.8$, weighting points $s_1 = 8.0$ and $s_2 = 28.8$, scale factor 0.731(17), correlation parameter −0.0857. Data were obtained in digital form using the microdensitometer at the Royal Greenwich Observatory at Cambridge. The data analysis followed standard procedures, using established

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Table 1. Assignment of the Vibrational Frequencies [cm^{-1}] of $H_3SiCH_2NMe_2$ by Comparison of Experimental and Theoretical Data[a]

no.	exptl		calcd		assignment
1			60	vw	$\tau(NC(2))$
2			144	vw	$\tau(CSi)$
3			191	vw	$\delta(SiCN)$
4			254	vw	$\tau_{as}(NCH_3)$
5			271	vw	$\tau_s(NCH_3)$
6			359	w	$\gamma(C_3N)$
7			378	vw	$\delta_s(CNC)$
8			413	vw	$\delta_{as}(CNC)$
9	531	w	521	w	$\rho(SiH_3)$
10	592	w	571	m	$\rho(SiH_3) + \rho(CH_2)$
11			739	m	$\nu(SiC)$
12	760	w	823	m	$\nu_s(NC_3)$
13	843	m	852	m	$\rho(CH_2)$
14	928	vs	914	vs	$\delta_{as}(SiH_3)$
15	934	s	932	m	$\delta_s(SiH_3)$
16			934	m	$\rho(SiH_3)$
17	1039	w	1018	w	$\rho(CH_3)$
18	1044	w	1026	w	$\rho(CH_3)$
19	1059	w	1082	w	$\rho(CH_3)$
20	1141	w	1114	m	$\rho(CH_2)$
21	1160	w	1141	m	$\rho(CH_3)$
22			1236	m	$\tau(CH_2)$
23	1248	w	1245	m	$\nu(NC)$
24	1255	w	1287	m	$\delta(CH_2)$
25			1401	vw	$\delta_{as}(CH_3)+ \delta(CH_2)$
26			1420	vw	$\delta(CH_2)$
27			1440	vw	$\delta_{as}(CH_3)$
28	1437	w	1453	m	$\delta_{as}(CH_3)$
29			1465	m	$\delta_{as}(CH_3)$
30			1467	m	$\delta_{as}(CH_3)$
31	1454	w	1477	m	$\delta_{as}(CH_3)$
32			2158	s	$\nu(SiH)$
33	2161	s	2177	s	$\nu_{as}(SiH)$
34	2167	s	2184	s	$\nu_{as}(SiH)$
35	2771	s	2813	m	$\nu(CH_2)$
36	2825	s	2826	m	$\nu(CH_3)$
37	2873	m	2834	m	$\nu_s(CH_3)$
38	2910	w	2934	w	$\nu_{as}(CH_2)$
39	2954	m	2959	s	$\nu_{as}(CH_3)$
40	2975	m	2969	m	$\nu_{as}(CH_3)$
41	2989	m	3007	m	$\nu_{as}(CH_3)$
42			3023	m	$\nu_{as}(CH_3)$

[a] Calculated frequencies scaled by a factor of 0.94.

data reduction and least-squares refinement programs[16] and the scattering factors established by Fink and co-workers.[17] The refined molecular parameters, their definition 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 the Supporting Information.

(*N*,*N*-Dimethylaminomethyl)trimethylgermane (2). Trimethylchlorogermane (30 mmol, 5.92 g) was dissolved in hexane (10 mL), and a suspension of (*N*,*N*-dimethylaminomethyl)lithium (30 mmol, 1.95 g) in hexane (10 mL) was added at ambient temperature. After 24 h the insoluble residue was removed by centrifugation and the solvent was removed under reduced pressure from the centrifugate. The product was purified by fractional condensation through a series of traps held at −10, −20, −30, −50, and −76 °C with the product being retained at −30 °C. ^{1}H NMR: $\delta = 0.19$ (s, 9H, CH_3), 1.98 (m, 2H, CH_2), 2.12 (s, 6H, H_3C). ^{13}C NMR: $\delta = -1.86$ (q m, CH_2, $^1J_{CH} = 132$ Hz), 49.23 (q q, N−CH_3, $^1J_{CH} = 132$ Hz, $^2J_{CCH_3} = 5.4$ Hz), 51.23 (t m, CH_2, $^1J_{CH} = 132$ Hz). ^{14}N NMR: $\delta = -355$ (s).

(*N*,*N*-Dimethylaminomethyl)trimethylstannane (3). A suspension of (*N*,*N*-dimethylaminomethyl)lithium (6.9 mmol, 0.45 g) in hexane (5 mL) was added dropwise to a solution of trimethyltin chloride (6.9 mmol, 0.75 g) in hexane (5 mL) and stirred for 24 h. The solid residue was separated by centrifugation and the solvent removed under reduced pressure. The remaining liquid is sufficiently pure (mp −90 °C). ^{1}H NMR: $\delta = 0.12$ (s, 9H, CH_3, $^3J_{^{119}SnCH} = 195.7$ Hz), 2.11 (s, 6H, H_3C), 2.33 (m, 2H, CH_2). ^{13}C NMR: $\delta = -9.15$ (q t, CH_2, $^1J_{CH} = 128$ Hz, $^3J_{CSnCH} = 1.2$ Hz), 49.43 (q q, N−CH_3, $^1J_{CH} = 132$ Hz, $J_{CCH_3} = 7.4$ Hz), 49.76 (t m, CH_2, $^1J_{CH} = 132$ Hz, $^3J_{CSnCH} = 1.2$ Hz). ^{14}N NMR: $\delta = -348$ (s). ^{119}Sn−NMR: $\delta = -24.4$ (dec t sex., $Sn(CH_3)_3$, $^2J_{SnCH} = 52.8$ Hz, $^2J_{SnCH} = 26$ Hz, $^4J_{SnCNCH} = 4.6$ Hz.

Crystal Structure Determination of 3. A single crystal of $Me_3SnCH_2NMe_2$ (**3**) was grown in situ by slowly cooling the melt in a sealed capillary from 184 to 182 K after generation of a suitable seed crystal: crystal system triclinic, space group $P\bar{1}$, $Z = 4$, $a = 6.667(2)$ Å, $b = 12.774(2)$ Å, $c = 12.848(2)$ Å, $\alpha = 66.04(1)°$, $\beta = 75.00(2)°$, $\gamma = 74.88(2)°$, $V = 590.7(3)$ Å^3 at 123(2) K, cell from 100 reflections (θ-range 19−24°). $2\theta_{max.} = 54°$, ω-scan, 4140 indep. reflections [$R_{int.} = 0.017$]. Diffractometer: Enraf-Nonius CAD4, Mo Kα radiation, graphite monochromator, $k = 0.71073$ Å. Solution: direct methods (SHELXTL, Siemens Analytical X-ray Instrumentation Inc., Madison, WI, 1995). Refinement: SHELXL93 (Sheldrick, G. M. Universität Göttingen, Germany, 1993). No absorption correction applied. Non-H atoms were refined with anisotropic thermal displacement parameters; hydrogen atoms were located in difference Fourier maps and refined isotropically. Weight $= 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.44P]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$; 187 parameters, $R_1 = 0.0259$ for 3720 reflections with $F_o > 4\sigma(F_o)$ and $wR_2 = 0.0824$ for all 4140 data.

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] 6-31G*,[20] and 6-311G**[21] basis sets, while the larger two basis sets were used for calculations at the MP2 level of theory. For tin a basis set of dzp quality was employed in the SCF calculations.[22] NBO calculations were undertaken with the NBO 3.0 facilities built into Gaussian 94.

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Results and Discussion

Preparation of the Compounds. The compound $H_3SiCH_2NMe_2$ has already been prepared with moderate yields for the purpose of NMR studies[23] by reacting (chloromethyl)triphenoxysilane with dimethylamine in benzene in a pressure tube at 120 °C followed by LAH reduction. We have chosen an analogous reaction starting with (chloromethyl)triethoxysilane, which is quantitatively aminated in liquid dimethylamine already at its boiling point (+7 °C) to give (dimethylaminomethyl)triethoxysilane. This product can be hydrogenated by lithium aluminum hydride, to give dimethylaminomethylsilane $H_3SiCH_2NMe_2$ in good yield (76%) and high purity.

$$(EtO)_3SiCH_2Cl + 2HNMe_2 \rightarrow [H_2NMe_2]Cl + (EtO)_3SiCH_2NMe_2$$

$$4(EtO)_3SiCH_2NMe_2 + 3LiAlH_4 \rightarrow H_3SiCH_2NMe_2 + 3LiCl + 3AlCl_3$$

$H_3SiCH_2NMe_2$ is unstable at ambient temperature, but can be stored below −40°, preferably at the temperature of liquid nitrogen. We have also tried alternative preparative routes including the reaction of bromosilane with dimethylaminomethyllithium in dimethyl ether or butane as a solvent, but these procedures led to purities always less than 95%, which was too low for the purpose of a structural study by electron diffraction.

$$LiCH_2NMe_2 + BrSiH_3 \rightarrow LiBr + H_3SiCH_2NMe_2$$

However, this synthetic pathway was employed to prepare $Me_3GeCH_2NMe_2$ and $Me_3SnCH_2NMe_2$, which both could be obtained in pure form in this way.

$$LiCH_2NMe_2 + BrGeMe_3 \rightarrow LiBr + Me_3GeCH_2NMe_2$$

$$LiCH_2NMe_2 + ClSnMe_3 \rightarrow LiCl + Me_3SnH_2NMe_2$$

It should be noted that $Me_3SnCH_2NMe_2$ has earlier been prepared using a different synthetic pathway.[24]

IR spectra for the three compounds recorded in the gas phase were compared to those calculated ab initio and were in good agreement with one another. The gas-phase infrared spectrum of $H_3SiCH_2NMe_2$ and the simulation as obtained from the calculated frequencies at the MP2/6-31G* level of theory are in good agreement with the experiment. The assignment provided in Table 1 is based on the modes of vibration visualized by the FREQCHK/Hyperchem combination of programs.

The compounds were further characterized by NMR spectroscopy of the nuclei ^1H, ^{13}C, ^{14}N, ^{15}N as well as ^{29}Si and ^{119}Sn. The ^{119}Sn spectrum of $Me_3SnCH_2NMe_2$ shows an impressive splitting into 21 lines with an intensity pattern of

1:2:10:18:45:72:120:168:210:252:252:252:210:
168:120:72: 45:18:10:2:1

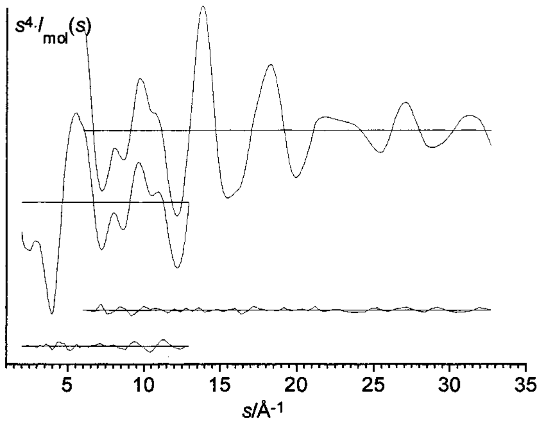

Figure 1. Observed and final weighted difference molecular-scattering intensity curves for the GED study of $H_3SiCH_2NMe_2$.

which is due to a $^2J_{SnCH}$ coupling of 53 Hz (decet) and a $^2J_{SnCH}$ coupling of 26 Hz (triplet). This pattern is further split into septets originating from a $^4J_{SnCNCH}$ coupling of 4.6 Hz.

The nitrogen resonances obtained either as ^{14}N or ^{15}N NMR spectra show increasing chemical shift in the series of compounds $H_3SiCH_2NMe_2$ (^{14}N −361, ^{15}N −363.8 ppm), $Me_3GeCH_2NMe_2$ (^{14}N −355 ppm), and $Me_3SnCH_2NMe_2$ (^{14}N −348 ppm), which would be consistent with increasing deshielding by donation of nitrogen electron density toward the Si, Ge, and Sn centers. The carbon homologue of $H_3\mathit{Si}CH_2NMe_2$, $H_3\mathit{C}CH_2NMe_2$, which was measured for comparison, shows a ^{14}N resonance at −355 ppm and could thus be regarded as electronically similar to the germanium compound. The ^{29}Si NMR chemical shift of $H_3SiCH_2NMe_2$ (−66.2 ppm) is only slightly different from that of H_3SiCH_3(−65.2),[25] which would support the argument for the absence of an α-effect in SiCN units in solution.

Gas-Phase Structure of $H_3SiCH_2NMe_2$. $H_3SiCH_2NMe_2$ forms a glassy solid at temperatures below −130 °C, and even by application of steep temperature gradients we could not observe seed crystal formation. A determination of its crystal structure was thus impossible. However, the high volatility allowed the complete determination of the molecular structure by electron diffraction in the gas phase, which also has the advantage of providing data for the free molecule undistorted by lattice forces. The vapor pressure of $H_3SiCH_2NMe_2$ is large enough to allow data collection at a sample reservoir temperature of −40 °C, at which the compound is stable for many hours. The molecular scattering intensities are shown in Figure 1.

The molecular model used for the least-squares refinement of the molecular geometry was defined by 42 parameters, describing the complete geometry in C_1 with bond lengths, angles, and torsion angles including all hydrogen positions. The C_2NCSi skeleton was defined by a C2−N3 bond length, the differences between this distance and the C8−N3 and C7−N3 length, the Si1−C2 distance, the angles Si1−C2−N3 and C7−N3−C8, and the torsion angles C8−N3−C2−Si1 and C7−N3−C2−Si1. The hydrogen distances (Si−H and C−H) were also defined by one distance and differences to the others, and equivalent schemes were

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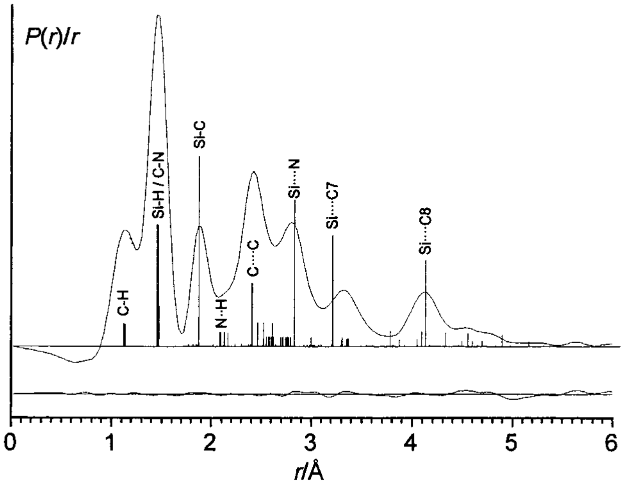

Figure 2. Observed and final weighted difference radial distribution curves for $H_3SiCH_2NMe_2$. Before Fourier inversion the data were multiplied by $s\exp[(-0.002s^2)/(Z_{Si} - f_{Si})/(Z_C - f_C)]$. Contributions of individual interatomic distances are shown as vertical lines.

used to define the angles and torsion angles defining hydrogen positions. The usual limitations of gas-phase electron diffraction were overcome by the SARACEN procedure,[26] i.e. application of restraints to most of the differences between above parameters of similar nature. The restraints were derived from ab initio calculations at the MP2/6-311G** level of theory, with uncertainties assigned to these restraints based on the experience with the reliability of these calculations.

Restraints were also applied to ratios between amplitudes of vibrations, all amplitudes for distances of atom pairs with a relative contribution of more than 5% of the most important pair of scatterers being refined. The amplitude restraints were calculated with the normal coordinate program ASYM40,[27] based on a force field computed at the MP2/6-31G* level of theory. The uncertainties are 5% for ratios between amplitudes and 10% for direct restraints. Although most of the parameters describing hydrogen positions refined to values close to the restraints and with esd's similar to the restraint uncertainties, they were kept refining, as in sum they make up for a significant contribution to scattering and doing so slightly increases the esd's of other correlated parameters, thus leading to a more realistic estimation of errors. The parameter definitions and applied restraints can be found in the Supporting Information of this publication.

The radial distribution curve for $H_3SiCH_2NMe_2$ is shown in Figure 2; selected geometrical parameter values are listed in Table 2 with the theoretical data for comparison. The C−N bond lengths concerning the methyl groups in $H_3SiCH_2NMe_2$ [1.456(5) and 1.463(5) Å] are slightly shorter than the C−N distance to the methylene unit [1.471(3) Å]. All are comparable to the reference compound Me_3N (1.47 Å).[28] The Si−C bond length (1.879(2) Å) is slightly larger than that in $MeSiH_3$ (1.86 Å).[29] As the SiCN angle is 114.7(3)°, which is even larger than the expected tetrahedral angle, the only valid conclusion is that no attractive Si···N interaction is operative in the free molecules of $H_3SiCH_2NMe_2$. The absence of an involvement of the nitrogen lone pair of electrons in a donor interaction toward the silicon atom is also obvious from the conformation of $H_3SiCH_2NMe_2$, as the lone pair is oriented away from the silicon center, with the torsion angle lp-N−C−Si being 55.6°, as was calculated from an idealized lone pair position enclosing equal angles to all nitrogen substituents. In contrast, the isoelectronic compound $H_3SiONMe_2$[9] and the related $H_3SiNMeNMe_2$[8] show Si···N attraction and adopt angles at the O and N centers separating the geminal Si and N atoms of 108.(1)° and 102.6(1)° (both solid state), despite the usual widening of angles at silylated nitrogen or oxygen centers.

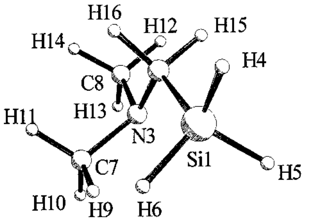

Figure 3. Molecular structure of $H_3SiCH_2NMe_2$, as determined in the gas phase by electron diffraction.

Table 2. Selected Bond Lengths, Angles, and Torsion Angles of $H_3SiCH_2NMe_2$ As Determined by Gas-Phase Electron Diffraction and by ab Initio Calculations (Å, deg)

parameter	GED (r_a)	MP2/6-311G** (r_e)
Si(1)−C(2)	1.879(2)	1.893
C(2)−N(3)	1.471(3)	1.468
N(3)−C(7)	1.463(5)	1.458
N(3)−C(8)	1.456(5)	1.458
Si(1)···N(3)	2.828(7)	2.787
∠Si(1)−C(2)−N(3)	114.7(3)	111.4
∠C(7)−N(3)−C(2)	110.9(4)	110.2
∠C(8)−N(3)−C(2)	110.9(5)	110.5
∠C(7)−N(3)−C(8)	111.1(5)	110.2
τC(7)−N(3)−C(2)−Si(1)	62.4(12)	82.7
τC(8)−N(3)−C(2)−Si(1)	−173.7(14)	−156.5

The calculated geometry of $H_3SiCH_2NMe_2$ is similar to that of the experimental structure (see Table 2). The calculated Si−C bond length is somewhat larger , the Si···N distance is somewhat smaller, and the angle Si−C−N is also smaller than the measured value. The most noteworthy difference is the deviation in the torsion angles SiCNC, which experimentally are closer to the values of an ideally staggered conformation than when predicted by the calculations. The deviation of the idealized nitrogen lone pair position from the NCSi plane expressed by the torsion angle lp-N−C−Si is predicted to be 36.8°, but experimentally determined as 55.6° (denoted "gauche" from here on; that is, the torsion angle lp−N−C−Si is close to 60°). The deviation can, however, be rationalized by the different nature of the geometries of experiment and calculation and by the shallow potential to conformational changes. This is indicated by the small height of the barrier to rotation about the N3−C2 bond expressed by the differences in

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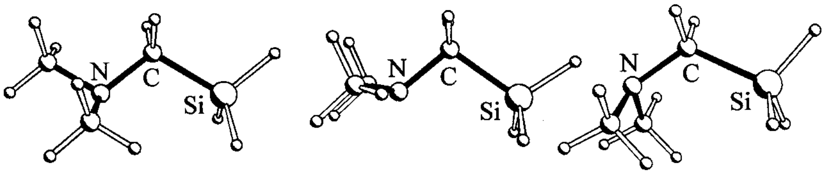

Conformation SiCN vs. lp_N	*gauche*	*syn*	*anti*
<SiCN	111.4°	105.3°	119.5°
τlp_NSiCN	36.8°	0.0°	180.0°
E [kJ/mol]	0.0	6.6	10.2

Figure 4. Energies and SiCN angles of different conformations of $H_3SiCH_2NMe_2$ as calculated at the MP2/6-311G** level of theory.

energy between the gauche and the syn structure (torsion angle lp-N–C–Si: 0°), which is only 6.6 kJ mol^{-1}. This value was derived from the structures and energies of other possible conformers calculated ab initio at the MP2/6-311G** level of theory, as shown in Figure 4. Interestingly the SiCN angle appears to be markedly dependent on the orientation of the NMe_2 group relative to the silicon center. As expected, the syn conformation shows the smallest SiCN angle, as its lone pair of electrons at nitrogen is now oriented toward the silicon atom, as it is also in the hydroxylaminosilanes, e.g., $H_3SiONMe_2$. However, according to natural bond orbital (NBO)[30] analyses, important contributions of orbital interactions of the type $\sigma(NC) \rightarrow d(Si)$, $lp(N) \rightarrow d(Si)$, or $lp(N) \rightarrow \sigma^*(SiH)$ occur in none of these conformers. The relative importance of such contributions is at least 10 times less than those of the type $lp(N) \rightarrow \sigma^*(CH)$, which are always present in the NBO picture of alkylamines, and these are the most pronounced effects of electron delocalization in such molecules. In the most favorable case for a $lp(N) \rightarrow \sigma^*(SiH)$ interaction, the C_s conformer, the contribution of $lp(N) \rightarrow \sigma^*(SiH)$ is only 6% of the sum of all $lp(N) \rightarrow \sigma^*(CH)$ delocalization effects. The contribution of d-orbitals is generally very small.

Calculations on $Me_3GeCH_2NMe_2$. Several attempts to obtain good quality diffraction data from a single crystal of $Me_3GeCH_2NMe_2$ grown in situ failed, so we have no experimental structural data for this compound. However, the results for $H_3SiCH_2NMe_2$ and $Me_3SnCH_2NMe_2$ (vide infra) are so consistent with the calculations that we present here ab initio results at the SCF/6-31G* level of theory for $Me_3GeCH_2NMe_2$. As in $H_3SiCH_2NMe_2$, the molecule is predicted to adopt a gauche conformation (lp-N–C–Ge = 0°) with a relatively wide Ge–C–N angle (116.1°), which is again an argument against a structurally observable α-effect. The other geometrical values are listed in Table 3 and deserve no further comment.

Table 3. Selected Bond Lengths, Angles, and Torsion Angles for $Me_3GeCH_3NMe_2$ As Calculated at the SCF/6-31G* Level of Theory

parameter	value
Ge1–C2	1.967
C2–N3	1.455
N3–C4	1.448
N3–C5	1.446
Ge1–C2–N3	116.1
C2–N3–C4	111.6
C2–N3–C5	112.9
Ge1–C2–N3–C4	−165.5
Ge1–C2–N3–C5	68.8

Crystal Structure of $Me_3SnCH_2NMe_2$. A single crystal of $Me_3SnCH_2NMe_2$ was grown in situ on the diffractometer and allowed the determination of the structure of a SnCN linkage in a simple molecule with most electronic effects of other functional groups absent. Incorporated as monomers into the crystal lattice, the molecules do not form even weak intermolecular Sn···N contacts, which makes us confident in determining the structure of almost undistorted molecules. In both crystallographically independent molecules in the asymmetric unit the SnCN angle is 112.9(2)° and the dihedral angle lp-N–C–Sn between the idealized position of the nitrogen lone pair of electrons and the NCSn plane is 53.4° (compare $H_3SiCH_2NMe_2$: 55.6° in the gas phase), both of which prove again the absence of structurally observable attractive forces between the tin and nitrogen atoms. The coordination geometry at the tin atom is almost perfectly tetrahedral, with the CSnC angles falling between 108.4(1)° and 110.9(1)°, a marginal distortion caused by the steric requirements of the NMe_2 group. In contrast, the isoelectronic compound $Me_3SnONMe_2$ has much smaller an angle at the oxygen atom, i.e. 102.5(8)° in the gas phase, with a substantial distortion of the coordination at tin, with one small [99.6(10)°] and two larger OSnC angles [108.1(6)°]. This originates from the close proximity of the nitrogen and tin centers in the $Me_3SnONMe_2$ molecule.[11] The distortion in this case is even larger in the solid state through additional intermolecular Sn···O contacts. This shows clearly the structural differences between SnON and SnCN linkages and points to two possible electronic prerequisites for the occurrence of *β*-donor–acceptor interactions: an electron-withdrawing element bound to the electrophilic center and greater flexibility of the coordination geometry of the atom separating donor and acceptor centers.

The geometry of $Me_3SnCH_2NMe_2$ optimized by ab initio methods at the SCF/dzp level of theory is so close to the experimental results (Table 4) that only the SnCN angle deserves some comment. It is predicted to be 115.4° and thus slightly overestimated, but this might be due to the fact that electron correlation was not taken into account in these calculations for reasons of the size of the problem. In this light the Ge–C–N angle in $Me_3SnCH_2NMe_2$ seems also to be overestimated by the

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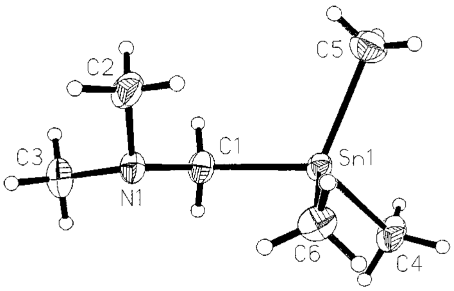

Figure 5. Molecular geometry of $Me_3SnCH_2NMe_2$ as determined by low-temperature single-crystal X-ray diffraction. Only one molecule of two in the asymmetric unit is shown.

Table 4. Selected Bond Lengths, Angles, and Torsion Angles of the Two Independent Molecules in the Crystal Structure of $Me_3SnCH_2NMe_2$ and Geometrical Parameter Values Calculated at the SCF/dzp Level for Comparison

parameter	molecule 1	molecule 2	SCF/dzp
Sn(1)−C(1)	2.160(3)	2.161(3)	2.196
Sn(1)−C(4)	2.145(3)	2.138(3)	2.178
Sn(1)−C(5)	2.148(3)	2.139(3)	2.178
Sn(1)−C(6)	2.140(3)	2.146(3)	2.172
N(1)−C(1)	1.468(3)	1.463(3)	1.459
N(1)−C(2)	1.454(4)	1.456(4)	1.451
N(1)−C(3)	1.457(4)	1.455(4)	1.447
Sn(1)−C(1)−N(1)	112.9(2)	112.9(2)	115.4
C(1)−Sn(1)−C(4)	108.7(1)	109.1(1)	106.7
C(1)−Sn(1)−C(5)	110.9(1)	108.4(1)	112.1
C(1)−Sn(1)−C(6)	109.1(1)	111.1(1)	109.8
C(1)−N(1)−C(2)	110.0(2)	110.2(2)	111.5
C(1)−N(1)−C(3)	110.9(2)	110.8(2)	112.5
C(2)−N(1)−C(3)	109.6(2)	109.8(2)	110.8
Sn(1)−C(1)−N(1)−C(2)	66.3(2)	66.2(2)	68.2
Sn(1)−C(1)−N(1)−C(3)	−172.5(2)	−172.3(2)	−166.7

ab initio predictions, as the magnitudes of Si−O−N angles are also overestimated at the SCF level. Alternatively, the differences between solid-state geometry and calculations can be rationalized by distortions of the structure through lattice forces in the crystal, which seems easily possible in the light of the small differences in energies for the different geometries and conformations, as was shown for the related $H_3SiCH_2NMe_2$ above.

Calculations on $FH_2SiCH_2NMe_2$. To test the prerequisites for the occurrence of Si···N interactions in SiCN units proposed above and to give a future perspective, we have calculated the structures of several possible conformers of $FH_2SiCH_2NMe_2$ (MP2/6-311G**). They are shown in Figure 6 with their relative energies, SiCN angles, and dipole moments. In comparison with the nonfluorinated $H_3SiCH_2NMe_2$ there are some important differences in these structures. The ground state of $FH_2SiCH_2NMe_2$ adopts a C_1-gauche conformation with the NMe_2 group not perfectly staggered with respect to the methylene unit, but with the lone pair of electrons being much closer to the electrophilic silicon center than in $H_3SiCH_2NMe_2$. The values for the dihedral angles lp-N−C−Si between the idealized positions of the nitrogen lone pairs of electrons and the NCSi planes is 21.0° for the ground state of $FH_2SiCH_2NMe_2$, but 55.6° for the gas-phase structure of $H_3SiCH_2NMe_2$.

In this ground-state conformation of $FH_2SiCH_2NMe_2$ the Si−C−N angle is substantially compressed (by nearly 14°) relative to the unsubstituted $H_3SiCH_2NMe_2$. However, complete alignment of the nitrogen lone pair in the SiCN plane, resulting in a C_s structure, does not correspond to a minimum, but is predicted to result in a structure with even further compression of the SiCN unit, i.e., an SiCN angle of only 94.4°. The dipole moment of this structure is the largest for all conformers of $FH_2SiCH_2NMe_2$, which would open up the possibility to observe it in a crystal lattice where the increased dipole lattice forces could compensate for the small barrier of only 0.8 kJ mol^{-1}.[31] As already observed in $ClH_2SiONMe_2$,[11] the orientation of the halogen atom relative to the SiCN or SiON unit is very important for the structure of this three-center body. With the fluorine atom in gauche position relative to the SiCN plane, the SiCN angle opens up and reaches a value (112.8°) close to that of $H_3SiCH_2NMe_2$ and the torsional angle lp-N−C−Si becomes 38.5°.

The energy differences between the different conformers are very small, indicating an enormous flexibility of the geometry at the methylene unit (in particular the Si−C−N angle), which points to a pronounced dynamic behavior of this molecule. This flexibility seem much greater than in methylene units bound to typical organic groups, e.g., alkyl groups. It might be rationalized by two competing effects: energy loss by angle deformation at the CH_2 group and energy gain by electrostatic and donor−acceptor interaction between Si and N centers, the latter being most favored if the FSiCN unit is coplanar. Because of the high flexibility of the system and the shallow potentials, care is suggested with too detailed interpretations of certain geometries of stationary points rather than the dynamic behavior.

Electron delocalization from the lone pair of electrons into the σ^*(SiF) orbital can be analyzed using the NBO formalism. In this picture there is indeed a significant contribution of a lp(N) → σ^*(SiF) interaction, which is 19% of the contribution of all lp(N) → σ^*(CH) interactions in the most favorable case, the C_s conformation of $FH_2SiCH_2NMe_2$. This serves to rationalize the small angle SiCN in this transition state; as in the ground state with the nitrogen lone pair pointing out of the SiCN plane, this contribution is only 8% of the lp(N) → σ^*(CH) interactions, resulting in a wider SiCN angle. In the gauche conformer the lp(N) → σ^*(SiF) interaction becomes even less important, so that an effect on the molecular structure is no longer significant. Attempts to verify these predictions experimentally are in progress.

Conclusion

On the basis of our structural studies on simple representatives of the class of compounds containing E−C−N units (E = Si, Ge, Sn) without electronegatively substituted E atoms we cannot observe structurally significant attractive interaction between E and N centers, which could serve to explain the anomalies in basicities and spectroscopic data and thus confirm the earlier postulated “α-effect” in this way. The angles E−C−N in the compounds $H_3SiCH_2NMe_2$ and $Me_3SnCH_2NMe_2$ are even slightly wider than the ideal tetrahedral angle. However, earlier postulated orbital

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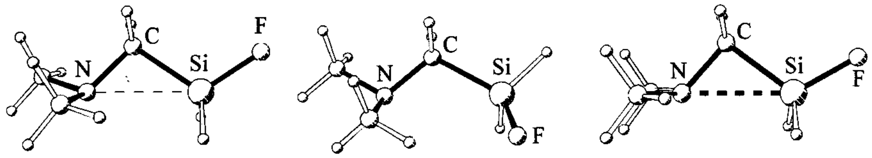
(31) For the differences between gas-phase and solid-state structures caused by dipole moment changes see for example: (a) Leopold, K. R.; Canagaratna, M.; Phillips, J. A. *Acc. Chem. Res.* **1997**, *30*, 57. (b) Mitzel, N. W. *J. Chem. Soc., Dalton Trans.* **1998**, 3239.



Symmetry	C_1	C_1	C_S (transition state)
F position	*anti*	*gauche*	*anti*
<SiCN	101.0°	112.8°	94.4°
τFSiCN	171.5°	62.3°	180.0°
τlp$_N$SiCN	21.0°	38.5°	0.0°
E [kJ/mol]	0.0	0.3	0.8
μ [D]	2.74	2.24	3.16

Figure 6. Energies, SiCN angles, and dipole moments of different conformations of $FH_2SiCH_2NMe_2$, as calculated at the MP2/6-311G** level of theory. The C_1-anti and C_1-gauche conformations are minima on the potential hypersurface.

interactions such as σ(CN) → d(E) conjugation or lp(N) → d interactions would normally lead to an attractive interaction, resulting in compression of the E–C–N angle. Our ab initio calculations are in full agreement with experimental geometry determinations and give no indication of a dominating occurrence of those types of orbital interactions involving d-orbitals on the group 14 elements, but indicate a weak interaction of the centers E and N in E–C–N units, which can be rationalized as lp(N) → σ* hyperconjugation. However, predictably for many cases this interaction is too weak to be observable by means of methods for structure determination, but it might be seen as a contribution to change the reactivity of such systems.

For compounds bearing electronegative substituents at the Si atom we predict attractive forces between Si and N atoms in the model compound $FH_2SiCH_2NMe_2$, which can be rationalized by lp(N) → σ*(SiF) interactions. This behavior can be expected, as a more electrophilic silicon atom should interact more strongly with a donor center. However, the interactions become only strong enough to change the molecular geometry if the electronegative substituent is placed anti relative to the nitrogen lone pair of electrons or close to that geometry. The dependence on the orientation of the electronegative substituents excludes simple electrostatic interactions as the major contribution, as the charges of the silicon and nitrogen atoms are almost the same in the different conformations. The dipole moments are highly dependent on the conformation, which makes it probable that even conformations that are unstable in the gas phase could be important in polar solvents or in the crystal lattice and therefore contribute to the chemical behavior in these phases.

We are presently extending our work on donor–acceptor interactions between geminal centers to M–C–X units with M = group 2 and 13 elements and X = OR, NR_2, and SR.

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Supporting Information Available: Tables of crystal data, atomic coordinates, and equivalent isotropic thermal parameters of $Me_3SnCH_2NMe_2$ and molecular parameter definitions, parameter values and restraints, vibrational amplitudes and amplitude restraints, and a correlation matrix for the GED refinement of $H_3SiCH_2NMe_2$.

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