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The geometric dependence of acidity: hexamethyldisilazide anion

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Abstract

Experimental data, and molecular orbital calculations at a variety of levels, provide support for the existence of hexamethyldisilazide anion with an sp-hybridized nitrogen when free of the counterion, but a more conventional sp^2 nitrogen when lithium is present. The cyclic compound 1,1,3,3-tetramethyl-1,3-disila-2-azacyclopentane is experimentally 10.5 kcal/mol weaker as an acid in the gas phase than the open chain equivalent, 1,1,1,3,3,3-hexamethyldisilazane, by ion cyclotron resonance spectrometry. The calculated energetics for each case agrees well with gas-phase and solution-phase experimental data. (Int J Mass Spectrom 210/211 (2001) 231–240) © 2001 Elsevier Science B.V.

Keywords: Gas-phase; Acidity; Rehybridization; Amine

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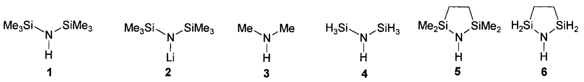
1. Introduction



Scheme 1

We have reported [1] that the gas-phase acidity of hexamethyldisilazane **1**, $(Me_3Si)_2NH$, is on the order of 15 kcal/mol stronger than expected, based on its solution phase acidity relative to other amines or to functional groups such as ketones and esters. For example, lithium hexamethyldisilazide **2** readily deprotonates ketones, nitriles, and even dichloromethane in solution to yield lithium enolates [2] and the corresponding other carbanions [3], but in the gas phase with no counterion present, proton transfer reaction from acetone to hexamethyldisilazide anion is endergonic by 13 kcal/mol [1]. Likewise, **1** is 10 kcal/mol more acidic than the structurally analogous di-isopropylamine in tetrahydrofuran (THF) solution [2], but 33.4 kcal/mol more acidic in the gas phase [1]. In the gas phase, **1** is more strongly acidic than CF_3CH_2OH and comparable in acidity to ethanethiol [1].

We rationalized this behavior in terms of a major geometrical change in **1** on proton removal: the nitrogen atom becomes sp hybridized, with a resultant

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180° angle for the Si–N–Si structure. Such a change in geometry allows orbitals on both silicon atoms to mix with both p orbitals on nitrogen, to achieve maximum stabilization. In the condensed phase, the presence of the lithium counterion constrains the nitrogen to remain sp^2 hybridized, presumably providing more stabilization than would be obtained by rehybridization [4]. Dialkylamines such as di-isopropylamine do not undergo this rehybridization upon deprotonation. These rationalizations were based [1] on molecular orbital calculations, first at the modified neglect of differential overlap (MNDO) semi-empirical level [5], followed up by ab initio calculations. We report these calculations in full here. In addition, we have devised an experimental test of our hypothesis that rehybridization of the nitranion is the reason for the strengthening of acidity. By constraining the disilylamine to a bent geometry, in a five-membered ring, an appreciable weakening of acidity should occur.

2. Experimental

Acidities were determined using a previously described ion cyclotron resonance (ICR) spectrometer [6], with a capacitance bridge detector operated in rapid scan mode [7]. Neutral gas pressures were measured using a Bayard–Alpert style ionization gauge, calibrated against a capacitance manometer to obtain true pressures. Care was taken that the rapid scan method did not perturb the measured equilibria by translational excitation of an endothermic reaction [8].

1,1,3,3-Hexamethyl-1,3-disila-2-aza-cyclopentane **5** was synthesized by the method of Baney and Haberland [9] from 1,2-bis(chlorodimethylsilyl) ethane (Aldrich) and ammonia. Other standard acids were obtained commercially or synthesized as previously indicated [10]. Purities were checked by gas chromatography and by the ICR mass spectra. Anions were formed by dissociative attachment (thermal electrons) of isoamyl nitrite at 1×10^{-7} torr partial pressure.

Ab initio calculations were performed with the GAUSSIAN 98 program [11], implemented on a Gateway PIII-600 PC, at both the MP2/6-31+G*//MP2/6-31+G* level and at the G2 level [12]. Complete geometry optimizations were done on all structures, including examination for no imaginary frequencies. For the radical species, the unrestricted Hartree–Fock (UHF) level was used.

The semiempirical calculations were carried out with two different programs. MNDO calculations [5] were carried out on Gateway PII-166 computer, utilizing a locally modified version of QCMP004. The AM1 method, and MNDO for radicals, was carried out with MOPAC 6.0 on a SunSparc workstation. Except where noted, all geometric variables were optimized. For the radicals, the calculations were done at the UHF level.

3. Results

Using the usual gas-phase equilibrium techniques [10], the acidity of **5** was found to be 0.4 kcal/mol stronger than meta-methylaniline at $\Delta G_{acid} = 359.9$ kcal/mol, and 0.4 kcal/mol weaker than acetoxime at $\Delta G_{acid} = 359.1$ kcal/mol [13], yielding $\Delta G_{acid} = 359.5 \pm 2.0$ kcal/mol and $\Delta H_{acid} = 367.4 \pm 2.1$ kcal/mol. A ΔS_{acid} of 26.0 cal/mol-K is predicted by the usual statistical mechanistic methods involving negligible loss of rotation and no change in symmetry number on simple deprotonation [10]. This places the cyclic disilazane **5** at 10.5±0.2 kcal/mol weaker in acidity than the acyclic structure **1** [1]. The uncertainty in this comparison of acidities represents the relative uncertainty of ±0.1 kcal/mol for the equilibrium of each disilizane with its reference acid. This is much smaller than that for the absolute values (±2.0 kcal/mol) due to the anchoring of the scale [10].

Ab initio calculations at the G2 [12] level were carried out for two series of molecules, based on dimethylamine **3** and disilylamine **4**. For both parent series, the geometry and energies were calculated for (a) the neutral acid $(H_3X)_2NH$ where X = C or Si, (b) the anionic conjugate base $(H_3X)_2N^-$, (c) the species where the hydrogen on nitrogen has been replaced by lithium, $(H_3X)_2NLi$, and (d) the radical produced by removal of the hydrogen on nitrogen, $(H_3X)_2N^{\cdot}$. The first two are necessary for evaluation of the energetics of the acidity reaction, the lithiated species is a model for the form of the anion/counterion species present in solvents such as THF, and the radical is part of the thermochemical cycle [14] in Scheme 2 which is used to evaluate gas-phase acidities. The cyclic disilazane **6** and its conjugate base were likewise calculated at the G2 level. These structures were also examined at the MP2/6-31+G*//MP2/6-31+G* level, along with various methylated analogs too large for calculation at the G2 level. The obtained acidities, bond strengths and electron affinities are given in Table 1.

$$\begin{tikzcd} R_2NH \arrow[r, "\Delta H_{acid}"] \arrow[d, "DH^\circ(R_2N\text{-}H)"'] & R_2N^- + H^+ \\ R_2N^\cdot + H^\cdot \arrow[r, "IE(H^\cdot)"] & R_2N^\cdot + H^+ \arrow[u, "-EA(R_2N^\cdot)"'] \end{tikzcd}$$

Scheme 2

An experimental gas-phase acidity is available for Me_2NH [13], which agrees with the G2 value to 0.6 kcal/mol. Similarly, the experimental and G2 acidities of silanol and methanol [15] agree within “chemical accuracy” [12]. It would thus be useful to have such a calculational value for **1**, or an experimental acidity for **4**. Lacking these, we estimate the acidities in two ways. From Table 2, it is seen that the MP2/6-31+G* method yields ΔH_{acid} values for silylamines -1.3 ± 0.3 kcal/mol stronger than the G2 method. These are also consistently 7 to 8 kcal/mol more strongly acidic than the energies of acidity obtained with no thermal or zero-point energy correction at the MP2 level. Applying this correction to the energies of acidity of **1** and **5** at the MP2 level, we obtain ΔH_{acid} values of 358 and 364, respectively, in reasonable agreement with the experimental values.

We also approach this using the effect of methyl groups on silylamine acidities. Methylation of alkylamines and alcohols strengthen the acidity by ~2 kcal/mol per α-methyl [13]. In contrast, it has been shown that methyl-for-hydrogen replacement in H_3SiOH has little effect on the acidity [16]. It thus may be assumed that **4** will be a reasonable approximation for **1**, at least to within several kcal/mol. This can be rationalized, in that methyl versus hydrogen substitution on sp^3 carbon results in a considerable increase in acidity for a variety of gas-phase acids, due to polarizability effects [17]. The corresponding replacement on silicon, however, results in both the expected polarizability effect (anion stabilizing), plus a offsetting polar effect (carbon more electronegative than silicon) not present in the alkyl case. Thus, methyl-for-hydrogen replacement in silanols and silylamines should have a much smaller negative ion stabilizing effect than in alcohols and alkylamines. As seen in Table 2, at the MP2/6-31+G* level, for **4**, silylamine H_3SiNH_2, and **6**, replacement of the Si–H bonds with Si–Me consistently weakens ΔE_{acid} by 0.7 kcal/mol per methyl. We can thus estimate the G2 acidity of **1** as 6×0.7 kcal/mol weaker than the calculated 354.9 ΔH_{acid} value for **4**, or 359 kcal/mol, and that of **6** as 4×0.7 kcal/mol weaker than that of **5** at 361.7 kcal/mol, or 364.5, compared to the experimental value of 367.4.

The calculated geometries of the species involved are given in Table 2. The “G2” geometries are actually at the MP2(full)/6-31G* level, in contrast to the MP2/6-31+G* ones. At both levels of calculation, the neutral dialkylamine **3a** is appreciably pyramidal at nitrogen. This is in contrast to the disilylamine **4a**, which is calculated to be planar and near trigonal, consistent with its experimental geometry from electron diffraction studies [18]. Bonds lengths are likewise reasonable, compared to experimental values. For example, the Si–N bond length in **4a** is calculated at the MP2(full)/6-31G* level to be 1.742Å; the electron diffraction structure [18] for **4a** reveals a bond length of 1.724Å ± 0.002Å. The Si–N–Si angle in **4a** is 127.7° ± 2.0° experimentally [18], and calculated here at MP2(full)/6-31G* to be 128.9°. The finding that **4a** is near planar (SiNHSi) at all levels of calculations carried out gives further support to the idea that (d-p)π bonding is of minor importance in

Table 1
Energetics of calculated reactions[a]

	G2					MP2/6–31+G*//MP2/6–31+G*			
	ΔH_{acid}	ΔG_{acid}	ΔS_{acid}	DH°	EA[b]	ΔE_{acid}[c]	ΔH_{acid}	DH°	EA[b]
$(H_3Si)_2NH$ 4	354.9	348.7	20.7	112.1	70.8	360.8	353.3	102.4	62.7
Me_2NH 3	395.9	388.6	24.6	95.3	12.8	402.4	392.3	84.4	5.4
expt:[d]	396.4	389.2	24.3	91.5					
$(Me_3Si)_2$ NH 1						364.9			
expt:[d]	356.1	349.0	23.8	>106.3					
H_3SiNH_2	376.7	369.5	24.3	110.9	47.8	383.3	375.6	101.1	39.0
expt:[e]	375.4	368.0	25.0						
Me_3SiNH						385.6	377.4	100.7	36.8
expt:[f]	378.5	371.0	25.1						
$c(CH_2SiH_2)_2NH$ 6	361.7	354.4	24.5	115.6	67.4	368.2	360.6	106.2	59.3
$c(CH_2SiMe_2)_2NH$ 5						371.1			
expt:[d]	367.4	359.5	26.0						
H_3SiOH	357.2	351.0	20.6	120.5	46.8	357.1	350.3	108.3	71.6
expt:[g]	358.4	352.0	21.5						
MeOH	382.6	376.1	21.8	105.5	36.6	404.4	395.1	92.8	11.4
expt:[d]	380.6	374.0	22.0	104.4	36.2				
Me_3SiOH						360.8	354.0	108.2	67.7
expt:[g]	362.5	356.0	21.8						

[a] kcal/mol, save ΔS in cal/mol-K. 298 K unless otherwise noted.
[b] 0 K.
[c] ΔE_{acid}, not zero-point corrected.
[d] Experimental data from [13]. ±2.0 kcal/mol on ΔH and ΔG, save as noted. ΔS_{acid} estimated from statistical mechanics.
[e] As [d], but ±3.0 kcal/mol for ΔH and ΔG.
[f] As [d], but ±5.0 kcal/mol for ΔH and ΔG.
[g] As [d], but ±4.0 kcal/mol for ΔH and ΔG.

determining the geometry of organosilicon compounds [19]. The geometries of H_3SiNH_2 and H_3SiOH calculated at the 3-21G* basis level [20] are essentially the same as found at both levels here.

On anion formation by proton loss, both levels of calculations indicate that for all species, the Si–N and C–N bonds (or equivalent ones to oxygen) shorten appreciably [21]. The C–N bond in **3a** shortens by 0.042Å (0.037Å for MP2/6- 31+G*), while the Si–N bond in **4a** changes considerably more, shortening by 0.105Å at MP2(full)/6-31G* and by 0.086Å at MP2/6-31+G*. At both levels of calculation employed, the C–N–C angle in **3a** on proton loss contracts by 5°. In contrast, the Si–N–Si angles in **1** and **4** open up to essentially 180°, on proton loss. Based on the geometry optimization, this is a broad, flat minimum, with a bend of up to 10° only raising the energy by ~1.5 kcal/mol. The calculated vibrational frequency (doubly degenerate) for the Si–N–Si bend in **4b** is only 85 cm^{-1} at the HF/6-31G* level employed in the G2 calculations.

Silylamine and trimethylsilylamine, at both levels of calculation, on proton loss do not undergo a similar linearization of the Si–N–H group; in fact, that angle becomes somewhat smaller on ionization. The cyclic disilylamines **5** and **6** at both levels of calculation also shrink at the Si–N–Si angle. This is probably due to the concomitant shortening of the Si–N bond, and the resulting strain that that causes in the five-membered ring.

On lithiation, the C–N bond in **3c** shortens by 0.010Å, and the Si–N in **4c** shortens by 0.047Å. The C–N–C angle in **3c** narrows 3°, and the Si–N–Si angle in **4c** widens by 4°. Thus, the changes in geometry on lithiation of the dialkyl species are comparable in direction, but at a fraction of the magnitude, to those found for simple proton removal. For the disilyl species, however, lithiation has a much smaller effect

Table 2
Geometries of calculated species[a]

Compound	X–N[b]	X–N–X[c]	H–X[d]	XXNH[e]	N–H[f]	δX–N–X[g]	δX–N[h]
$(H_3Si)_2NH$	1.748	127.9	1.486	172.	1.017		
	1.748	*127.7*	*1.485*	*178.*	*1.017*		
$(H_3Si)_2N^-$	1.637	180.0	1.519			+52.1	−0.105
	1.662	*180.0*	*1.517*			*+52.3*	*−0.086*
$(H_3Si)_2N^{\cdot}$	1.743	140.4	1.483			+12.5	−0.005
	1.748	*141.7*	*1.485*			*+14.0*	*0.000*
$(H_3Si)_2NLi$	1.701	132.0	1.502	180.		+4.1	−0.047
Me_2NH	1.456	111.7	1.096	122.	1.018		
	1.459	*112.1*	*1.097*	*121.9*	*1.019*		
Me_2N^-	1.412	106.6	1.126			−5.1	−0.044
	1.422	*107.3*	*1.122*			*−4.8*	*−0.037*
$Me_2N^{\cdot}$	1.444	110.7	1.096			−1.0	−0.012
	1.445	*111.0*	*1.098*			*−1.1*	*−0.014*
Me_2NLi	1.446	108.5	1.104	180.		−3.2	−0.010
$(Me_3Si)_2NH$	*1.756*	*134.0*	*1.882*	*180.0*	*1.021*		
$(Me_3Si)_2N^-$	*1.650*	*178.9*	*1.916*			*+44.9*	*−0.106*
H_3SiNH_2	1.723	122.0	1.484		1.009		
	1.742	*120.4*	*1.486*		*1.014*		
H_3SiNH^-	1.668	113.8	1.513		1.024	−8.2	−0.055
	1.682	*116.5*	*1.527*		*1.024*	*−3.9*	*−0.060*
$H_3SiNH^{\cdot}$	1.775	112.5	1.488		1.026	−9.5	+0.052
	1.780	*114.1*	*1.484*		*1.026*	*−6.3*	*+0.042*
Me_3SiNH_2	*1.753*	*109.0*	*1.889*	*142.*	*1.016*		
Me_3SiNH	1.680	118.1	1.924		1.024	+9.1	−0.073
$Me_3SiNH^{\cdot}$	*1.789*	*108.4*	*1.874*		*1.028*	*−0.6*	*+0.036*
$c(CH_2SiH_2)_2NH$	1.745	114.7	1.888		1.014		
	1.752	*115.0*	*1.892*		*1.019*		
$c(CH_2SiH_2)_2N^-$	1.683	108.5	1.927			−6.2	−0.062
	1.692	*108.9*	*1.932*			*−6.1*	*−0.060*
$c(CH_2SiH_2)_2N^{\cdot}$	1.777	107.4	1.897			−7.3	+0.032
	1.782	*107.7*	*1.902*			*−7.3*	*+0.030*
$c(CH_2SiMe_2)_2NH$	*1.756*	*115.6*	*1.895*	*180.0*	*1.017*		
$c(CH_2SiMe_2)_2N^-$	*1.694*	*109.3*	*1.933*			*−6.3*	*−0.062*
H_3SiOH	1.670		1.477		0.969		
	1.682		*1.475*		*0.970*		
H_3SiO^-	1.579		1.535				−0.098
	1.597		*1.528*				*−0.085*
$H_3SiO^{\cdot}$	1.677		1.480				+0.007
	1.708		*1.481*				*+0.026*
MeOH	1.423		1.090		0.970		
	1.425		*1.093*		*0.970*		
MeO^-	1.323		1.149				−0.100
	1.325		*1.149*				*−0.100*
$MeO^{\cdot}$	1.388		1.098				−0.035
	1.388		*1.099*				−0.037
MeOLi	1.384		1.103				*−0.039*
Me_3SiOH	*1.694*		*1.870*		*0.971*		
Me_3SiO^-	*1.599*		*1.925*				*−0.095*
$Me_3SiO^{\cdot}$	*1.719*		*1.877*				*+0.025*

[a] MP2 (full)/6–31G*; MP2/6–31+G* geometries are in *italics*.

[b] Or X–O, as pertinent, Angstroms.

[c] Or X–N–H, as pertinent, Angstroms.

[d] Or C–X, as pertinent, average value, in Angstroms.

[e] Dihedral angle, X–N–X(H), in degrees.

[f] Angstroms.

[g] Relative to neutral acid, degrees.

[h] Relative to neutral acid, Angstroms.

Table 3
AM1 energetics for R_2NY species[a]

AH:	Me_2NH	iPr_2NH	$(H_3Si)_2NH$	$(Me_3Si)_2NH$	5
$\Delta_fH(AH)$	−5.6	−25.6	−27.4	−117.2	−110.1
expt:[a]	(−4.4)	(−34.4)		(−122.8)	
$\Delta_fH(A^-)$	22.4	(1.8)	−30.2	−118.4	−91.7
expt:[a]	(26.4)	(−9.9)		(−113.9)	
$\Delta_fH(A\cdot)$	26.4	8.7	19.6	−69.2	−47.2
$\Delta_{acid}H(AH)$	393.7	393.1	362.9	364.5	384.1
expt:[b]	(396.5)	(390.2)		(356.8)	(367.3)
DH° (A–H)	84.1	86.4	99.1	100.1	115.0
expt:[c]	(91.5)			(>106)	
EA_{ad} (eV)	0.17	0.30	2.16	2.13	1.93
Δ (X–N)[d]	−0.047	−0.048	−0.114	−0.123	−0.084
Δ (X–N–X)[e]	1.3	0.3	48.5[f]	41.1[f]	3.6

[a] See [27].
[b] See [13].
[c] See [28].
[d] Change in C–N or Si–N bond length on proton removal, A.
[e] Change in C–N–C or Si–N–Si bond angle on proton removal, degrees.
[f] Anion Si–N–Si geometry linear to within 0.5°.

than removal of the proton does; the lithiated species can be described as still essentially sp^2 hybridized.

On loss of a hydrogen atom to yield a nitrogen centered radical, there is very little change in the geometry of **3d**: the C–N bond shortens 0.012Å, and the C–N–C angle narrows by 1°. For **4d**, formation of the radical results in negligible change in the length of the Si–N bond, but the Si–N–Si angle widens to 140°. At the G2 level, the linear form of **4d** is a saddle point, with one imaginary frequency, but only 1.2 kcal/mol higher in energy than the minimum at 140°. Like anion **4b**, this is a broad, flat minimum, but with a low central barrier.

We have also performed semiempirical calculations (MNDO and AM1) on all species discussed here, as per Table 3. Although the AM1 method in general appears to be more accurate for calculating acidities than MNDO, especially for nominally localized ions like these nitranions [22,23], we carried out MNDO calculations as well. This was to check some contradictory results in the literature [24,25]. The geometries generally are comparable to those obtained by ab initio methods, especially in regard to the Si–N–Si group being linear in the anions **1b** and **4b**, and bent by 130° in the radical **1d** and **4d**. On proton removal, the cyclic disilazane **5** has a very small (1 to 4 degree) bond angle increase, and about half the Si–N bond length decrease seen for the acyclic compounds. For the energetics, the heats of formation of Me_2NH and $(Me_3Si)_2NH$ are comparable to the experimental enthalpies of formation [26].

4. Discussion

The experimentally measured weakening of acidity of **5**, compared to **1**, of 10.5 kcal/mol must be due solely to geometric factors, because these acids differ only by removal of two hydrogens and formation of a carbon–carbon bond, well distant from the acidic site. This should have negligible effect on any polar or polarizability effect exerted by the substituents on the stability of the nitranion. The G2 calculations indicate that the Si–N–Si bond angle in the conjugate base of **6** is 108°, narrowed from the 115° in the acid form. The change in geometry due to rehybridization at nitrogen must be the source of the considerable strengthening of acidity of **1** over **5**. The cyclic disilylamine anion is a strong enough base to deprotonate aldehydes exothermically in the gas phase, and is comparable in acidity to most aliphatic ketones

[13], thus making it comparable to the relative acidities expected from solution phase data.

Why does the silyl substituent alter the geometry and stability of nitranions, compared to an alkyl substituent? When **3** and **4** are compared in isodesmic

$$Me_2N^- + (H_3Si)_2NH \rightarrow Me_2NH + (H_3Si)_2N^- \qquad (1)$$

equilibrium (1), the disilyl species is found to be 40 kcal/mol stronger as an acid than the dialkyl, at the G2 level; experimentally, **1** is 39.3±2.6 kcal/mol stronger than **3**, in good agreement. At the MP2/6-31+G* level, **1** is a stronger acid than **3** by 39.9 kcal/mol. Similarly an isodesmic comparison as in

$$Me_2NLi + (H_3Si)_2NH \rightarrow Me_2NH + (H_3Si)_2NLi \qquad (2)$$

equation (2) of the lithiated species and their respective conjugate acids indicates that the lithiated disilyl species **4** is 20.0 kcal/mol stronger as an acid (ΔH) than the dialkylamine **3**, while Arnett and Moe find **1** to be 17 kcal/mol stronger calorimetrically than **3** when lithiated, in 90% hexane/10% ether solvent [2]. Finally, as in equation (3),

$$Me_2N^{\cdot} + (H_3Si)_2NH \rightarrow Me_2NH + (H_3Si)_2N^{\cdot} \qquad (3)$$

the N–H homolytic bond strength in **3** is calculated to be 16.8 kcal/mol weaker than that in **4**. There is an experimental value known for DH°(Me_2N–H) of 91.5±2.0 kcal/mol,[27] but only a lower limit of >106.3 kcal/mol for the corresponding bond in **1**[28], giving a experimental bond strength difference of >14.8 kcal/mol, consistent with the calculations.

These values are in line with trimethylsilyl effects on other acidic atoms: Me_3Si– strengthens the acidity of ethane by 29 and by 16 kcal/mol, on successive trimethylsilane-for-methyl substitution (i.e. Me_3SiCH_3 and $(Me_3Si)_2CH_2$) [29,30], of methanol by 22 kcal/mol [31], and of methylamine by 25 and 22 kcal/mol [1].

The shortening of the Si–N bonds and lengthening of the Si–H bonds on deprotonation of **1** implies that electron density from the nitrogen anion might be mixing into silicon-based orbitals, corresponding to "negative hyperconjugation" [21]. This is supported by the calculations (Table 3), which show a lengthening of the Si–H or Si–C bonds on proton loss, in every case. A rationale for this can be found in the orbital energies. For **1**, experimentally, the energy of the highest occupied molecular orbital (HOMO) is raised from 8.55 eV bound [13] in the acid form, to about 2.8 eV bound in the anion. The latter value is the electron affinity obtained from Scheme 1, using the experimental anion proton affinity [1] plus the lower bound on the homolytic bond strength mentioned above. The corresponding value for **4b** from G2 calculations is 3.1 eV. The HOMO in the anion is much closer in energy to the empty π^* orbitals on silicon, so can mix with them much more strongly in the anion, than in the neutral acid form. Such mixing has been invoked as being important for the shorter than expected Si–O bond length in siloxanes [32].

The rehybridization allows both lone pairs on the nitrogen to have maximal overlap with the adjacent silicons. When only one silicon is present, however, as in silylamine, the Si–N–H bond stays bent, comparable in angle to the acid form. The stability offered by such rehybridization is not that seen in the usual acidity series of $CH_3CH_3 < CH_2{=}CH_2 < HC{\equiv}CH$ and rationalized as due to the increasing electronegativity of the charge-bearing orbital. Rehybridization in the disilylamine anions results in the electron residing in a less electronegative orbital, p vs. sp^2 [33].

Although the Mulliken charges reported by GAUSSIAN 98 can only be taken as approximate measures of the electron density, they are instructive in these cases. Of the full additional charge created upon proton loss, in the conjugate base of **3**, −0.44 remains on the nitrogen, while −0.28 appears on each methyl. For the conjugate base of **4**, −0.35 remains on nitrogen, and −0.33 is distributed to each silyl group, indicating more extensive delocalization of charge than for the alkylamine.

The shortening of the Si–N bond on proton loss, however, may also be attributed to the shorter sp bonds from the nitrogen in the anion, due to the change in hybridization state, with no recourse to (d-p)π bonding. The lower electronegativity of silicon, relative to carbon, has been invoked to favor an increase in s character at nitrogen [20]; this effect might be even greater in the anion.

We previously found [1] that Et_3SiOH and Me_3SiOH are appreciably more acidic in the gas phase than predicted by the master equation of Taft and coworkers[34] for correlation of XOH acidities. This was attributed to the parameters for the R_3Si groups being derived from cationic species, but it may also be due to an actual strengthening of acidity beyond what would normally be expected, due to factors not present in other XOH acids. For the silanols, there is no simple geometric parameter equivalent to the Si–N–Si bond angle in the disilylamines to make this evident, however. We have performed ab initio calculations on MeO^-, H_3SiO^- and their conjugate acids to examine this point. The results given in Table 2 indicate that the silanol is calculated at the G2 level to be 25.1 kcal/mol more acidic than methanol, compared to the experimental difference of 22.2 ± 5.0 kcal/mol found for MeOH versus H_3SiOH [13].

The geometry changes seen for both silanol and methanol, of shortening X–O bonds and lengthening H–X bonds, have previously been noted [21] as a measure of anionic hyperconjugation: the mixing of the lone pair electrons on oxygen into the π^* orbital of the H_3X- group. The shortening of the C–O bond (0.100Å) on proton removal is more than calculated for the C–N change in **3b** (0.042Å), while the Si–O shortening (0.098Å) is comparable to the Si–N change (0.105Å) in **4b**.

There have been several previous sets of calculations done on the species involved here. Glidewell and Thomson [35] stated that the Si–N–Si angle was 120.00° in the anion **4b** at the 3-21G//3-21G level, but that the isoelectronic species $(H_3Si)_2O$ and $(H_3Si)_2C^{-2}$ were linear. They also stated that for **4b**, "the calculated skeletal angle is rather sensitive to the basis set employed", and promised further elaboration in a subsequent publication. This has not appeared, to our knowledge. The geometry for the acid **4a** was comparable to that obtained here at the G2 level.

There are two studies using the MNDO method of the species here. Cuthbertson and coworkers [24] found the anion **4b** to be bent (Si–N–Si = 122°) with relative long Si–N bonds, at 1.712Å. The linear form was 2.4 kcal/mol higher in energy than the bent minimum. Brand et al. [25] likewise found a bent geometry (120°) for Si–N–Si in **4b**. These results are contradictory to our calculations, at all levels from MNDO to G2. These conflicting results are probably due to the fact that MNDO has had three different sets of parameters for silicon over time [5,36]. Even now, the current set of parameters predicts $H_3SiOSiH_3$ to be linear in Si–O–Si, in agreement with the older parameters [24], although experimentally the bond angle is 144° [37].

Curtiss et al.[38] have calculated a ΔH_{acid}(0 K) for H_3SiOH at the G2 level of 356.2 kcal/mol. We obtain the same result, in good agreement with the experimental value of 358.4±4.0 kcal/mol.

There is a strengthening of the N–H bond on going from ammonia, with a DH° of 108.5[13] experimentally, and 107.9 by our G2 calculations, to 110.9 (G2) for H_3SiNH_2, to 112.1 (G2) for **4**. In contrast, successive methylation weakens the DH°: $MeNH_2$ is 100, and Me_2NH is 91.5 kcal/mol [13]. A possible rationale for this is found in the work of Leroy and coworkers [39]. Their molecular orbital calculations indicate that the bond dissociation energy of the N–H bond for substituted amines is strengthened by electron accepting substituents like nitro and cyano, and weakened by electron donors like methoxy and amino. This is due to a complex mixture of effects on both the amine and the aminyl radical. This would imply that the trimethylsilyl group is acting as an electron acceptor here, in spite of its usual behavior as a polar electron donor [40]. Considering the stabilization afforded the anion, this must be true.

5. Conclusions

The strengthening of acidity of gaseous hexamethyldisilazane **1** over that expected from solution phase data, has been shown to be due to a rehybridization at nitrogen to a linear Si–N–Si geometry in the free anion. The strengthening is least 10 kcal/mol based on the acidity of the analogous five-membered ring disilazane **5**. Molecular orbital calculations for the lithiated species do not show this acidity change. This implies that the acidity of **1** might be variable in solution, based on how strongly complexed the counterion is with the nitranion. Variation of the cation, and of the solvent, may allow the tuning of the anion's basicity over a considerable range, without change in the nominal structure of the anion.

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