The Silaguanidinium Cation and the Search for a Stable Silylium Cation in Condensed Phases

Ulrich Pidun, Martin Stahl, and Gernot Frenking*

Abstract: Quantum mechanical calculations at the MP2/6-31 G(d) level are reported for the silaguanidinium cation $Si(NH_2)_3^+$ (**1**) and derivatives thereof. The equilibrium structure **1a** has D_3 symmetry with planar amino groups rotated out of the SiN_3 plane by 19.6°. The Si–N bond length of **1a** (1.658 Å) is intermediate between a single and a double bond. Isodesmic reactions show that the stabilization of the silylium cation **1a** by the amino groups (63.5 kcal mol^{-1}) is about 40% of the resonance stabilization of the guanidinium cation (159.3 kcal mol^{-1}), but **1a** is clearly better stabilized than alkyl-substituted silylium cations. The electronic stabilization of **1a** by the amino groups is also made obvious by the calculated complexation energy with one molecule of water. The calculated stabilization through complexation of water at HF/6-31 G(d) is markedly lower for $Si(NH_2)_3(H_2O)^+$ (**6**) (28.8 kcal mol^{-1}) than for $SiMe_3(H_2O)^+$ (40.6 kcal mol^{-1}). The tris(dimethylamino) silylium cation $Si(NMe_2)_3^+$ (**8**) is even more stable than **1a**. The complexation energy of $Si(NMe_2)_3(H_2O)^+$ (**10**) is only 17.3 kcal mol^{-1}. IGLO calculations of the ^{29}Si NMR chemical shifts predict that **1a** and **8** should not show the same extremely low shielding that is calculated for alkyl-substituted silylium ions. The calculated ^{29}Si resonances for **8** are in reasonable agreement with the experimental NMR spectrum of $(Me_2N)_3SiB(C_6F_5)_4$. AM1 calculations predict that the substituted tripyrrolidino silylium cation **12** would be an even better candidate for a stable tricoordinate silylium cation in condensed phases. One of the pyrrolidine rings of **12** has *tert*-butyl groups in the 2 and 5 positions, which serve as a steric fence around the silicon atom.

Keywords
ab initio calculations · silaguanidinium cations · silylium cations

Introduction

The search for a silylium cation with the general formula SiR_3^+ that is stable in solution is a hotly debated topic in experimental and theoretical research.[1–7] While silylium cations are well-characterized species in the gas phase,[8] the identification of an isolated SiR_3^+ cation in a condensed phase remains an elusive goal for synthetic chemistry. A very recent review by Lambert et al.[1a] summarizes the progress made in the last 20 years. Because the most important aspects of the chemistry of silylium cations in condensed phases are presented in the review, we give only the current state of research in this area without discussing the details of previous studies, unless they are significant for the present work.

The closest approach to tricoordinate, positively charged silicon in the solid state involves transition-metal-substituted species, which have been isolated and structurally characterized by Tilley et al.[4] These compounds may rather be formulated as transition-metal-substituted silylene complexes as suggested by the authors. The attempted preparation of metal-free species SiR_3^+ using ethyl or isopropyl groups as substituents R and weakly coordinating anions as counterions led to structures that had considerable silylium ion character.[2j, 5c] However, X-ray structure analysis showed that the fourth coordination site around silicon was still occupied by either a solvent molecule or a counterion.[2j, 5c] After discussing the physical properties of the compounds, Lambert comes to the conclusion that these systems "...probably are about a third of the way from full covalent bonding to a free silylium cation".[1a]

The lower stability of silylium cations SiR_3^+ relative to carbenium ions CR_3^+ can be explained by less conjugative or hyperconjugative stabilization of Si^+ by the ligands R, by the lower electronegativity of silicon, by the much greater tendency of Si to form stable five-, six- or even eight-coordinate compounds, and by the longer bond lengths Si–R as compared to C–R, which make steric shielding of the ion center of silylium cations more difficult than that of carbenium ions. The stability difference between $SiMe_3^+$ and CMe_3^+ can be estimated from the recent ab initio study of Olsson et al.,[7c] who calculated the properties of a large number of silylium and carbenium ions. The complexation energy of $SiMe_3^+$ stabilized by a water molecule in the complex $SiMe_3(H_2O)^+$ calculated at HF/6-31 G(d) was 40.6 kcal mol^{-1}. The stabilization by two water molecules in the complex $SiMe_3(H_2O)_2^+$ is 52.5 kcal mol^{-1}. For comparison, the stabilization of CMe_3^+ in the complex $CMe_3(H_2O)_2^+$ is only 25.7 kcal mol^{-1}.[7c] The methyl stabilization energy of the isodesmic reaction $XH_3^+ + HXMe_3 \rightarrow XMe_3^+ + XH_4$ for X = Si is 36.0 kcal mol^{-1}, while for X = C it amounts to 67.7 kcal mol^{-1}.[7c] The calculated values demonstrate that the silicon atom of SiR_3^+ interacts much more strongly with an

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electron-donor solvent than the carbon atom of the corresponding CR_3^+, and that the methyl groups stabilize the central carbon atom in CMe_3^+ much more than the silicon in $SiMe_3^+$.

Most research on stable silylium ions SiR_3^+ has focused on species where R is an organic substituent, but some work has been carried out in which R is an amino[2f] or thiol[2d] group. The experimental results suggest that the latter substituents are probably better suited to stabilize Si^+ than alkyl or aryl groups. The measurement of the conductive properties of silylium perchlorates in weakly coordinating solvents showed that aminosilylium and thiosilylium perchlorates exhibit high molar conductance in sulfolane, while the trialkyl- and triarylsilylium perchlorates are virtually nonconducting.[1a] The cryoscopic results clearly indicated that unhydrolyzed, free ions exist in sulfolane. However, the ^{29}Si NMR signals of the compounds did not show extremely low shielding as expected for silylium ions.[1a] Therefore, the authors concluded that the silicon atoms of the observed species have a close association with a fourth coordination site. We want to point out that the conclusion was drawn by comparing the observed ^{29}Si resonances with the calculated ^{29}Si NMR of $SiMe_3^+$, for which a value of $\delta = 355.7$ was predicted using the IGLO method.[3e] We will show that the calculated ^{29}Si resonance of $Si(NH_2)_3^+$ has a much higher shielding than $SiMe_3^+$.

In this paper we report quantum mechanical ab initio studies of the structure and properties of the silaguanidinium cation $Si(NH_2)_3^+$ (**1**) and several analogues of **1**. The work is a continuation of our previous study of the Y-conjugated compounds guanidine, guanidinium cation, urea, and 1,1-diaminoethylene.[9a] While guanidine and the guanidinium cation have been subject of many theoretical studies,[9] the silicon analogues have not been investigated before, except for a semiempirical study of **1**.[10] Thus, the present work is the first quantum mechanical *ab initio* study of **1**[11]. Besides the cation **1**, we also present theoretical results for the neutral silaguanidine $Si(NH_2)_2NH$ (**2**) and the methyl-substituted derivative $Si(NMe_2)_3^+$ (**8**). We calculated the stabilizing effect of the amino groups and the complexation energy of the Si cations with one water molecule. The bonding situation in the molecules was investigated with the natural bond orbital method (NBO) of Weinhold and coworkers[12] and with the topological analysis of the electron density distribution and its associated Laplacian developed by Bader.[13] In order to facilitate the experimental identification of the molecules we report the theoretically predicted ^{29}Si NMR chemical shifts of the compounds using the IGLO method.[14] We also present semiempirical (AM 1)[15] calculations of sterically more hindered derivatives of **1**, where the amino groups are substituted by pyrrolidine. With the latter studies we intended to predict silicon compounds that could possibly be isolated and characterized in a condensed phase with a higher silylium ion character than found in previous compounds.[1-6]

Methods

The geometries of the molecules have been fully optimized at the Hartree-Fock (HF) and MP2 (Møller-Plesset perturbation theory terminated at second order) [16] levels of theory using a 6-31 G(d) basis set [17]. The nature of the stationary points was investigated by calculating the second analytical derivatives at HF/6-31 G(d) and MP2/6-31 G(d). Improved energies have been obtained for some molecules at MP4(SDTQ) using a 6-311G(d,p) basis set [18]. Unless otherwise noted, results are discussed at MP4(SDTQ)/6-311G(d,p)//MP2/6-31 G(d). The energies and vibrational frequencies were calculated using Gaussian 92 [19]. The pyrrolidine derivatives of **1** were only optimized with the semiempirical method AM1 [15].

NMR chemical shift calculations were carried out with the IGLO (individual gauge for localized orbitals) method of Kutzelnigg and Schindler [14], using the direct version of the program [20]. The basis set for the IGLO calculations is the original basis set II + sp of the authors, which has about TZ + P quality [14c]. The NBO calculations were performed with the subroutines available in Gaussian 92 [19]. For the calculation of the electron density distribution $\rho(\mathbf{r})$, the gradient vector field $\nabla\rho(\mathbf{r})$, and its associated Laplacian $\nabla^2\rho(\mathbf{r})$, the programs PROAIM, SADDLE, GRID, and GRDVEC were used [21].

Results and Disussion

1. Structure and bonding: The optimized geometries of the molecules are shown in Figures 1 and 2. Table 1 shows the calculated energies. The results of the IGLO calculations and the NBO population analysis are listed in Table 2.

The theoretically predicted equilibrium structure of the silaguanidinium cation (**1a**) has D_3 symmetry. **1a** has planar amino groups which are rotated about the Si-N bonds by 19.6° (12.9° at HF/6-31 G(d), Fig. 1). It should be noted that the energy minimum structure of the guanidinium cation calculated at MP2/6-31 G(d) has also D_3 symmetry and amino groups rotated by 15°.[9a] The planar (D_{3h}) form **1b** is a transition state for the in-plane rotation about the Si-N bond. Structure **1b** is only 0.7 kcal mol^{-1} higher in energy than **1a** (Table 1). The Si-N bond length of **1a** (1.658 Å) is intermediate between that reported for a Si-N double bond (1.568 Å)[22] and the average Si-N single bond distance (1.748 Å).[23] The silicon atom carries a high positive charge (+2.24) while the nitrogen atoms are negatively charged (−1.35). This indicates a large ionic contribution to the Si-N bonding interactions and a very polar Si-N bond. The coefficients for the Si-N bond orbitals show that more than 80% of the bond is located at the nitrogen end (Table 2), yet there is considerable π back-donation from the nitrogen lone pair into the formally empty p(π) orbital at Si. The NBO analysis gives an occupation of 0.45 e for this orbital (Table 2). This is an important quantity for the interactions between the silicon atom and solvent donor molecules, which are discussed below.

The polarity of the Si-N bond and the large ionic contribution is also revealed by the results of the topological analysis of **1a**. Figure 3 shows the contour line diagram of the Laplacian of **1a** in the SiN_3 plane. The nitrogen end of the Si-N bond has an area of relative charge concentration ($\nabla^2\rho(\mathbf{r})<0$, solid lines), while at the silicon end there is relative charge depletion ($\nabla^2\rho(\mathbf{r})>0$, dashed lines). The weakly negative value for the energy density at the Si-N bond critical point $H_b = -0.348$ hartree Å^{-3} indicates a moderate covalent character.[24]

We calculated the barrier for the out-of-plane rotation about the Si-N bond of **1a** at MP2/6-31 G(d). Figure 1 shows that the Si-N bond of the rotated amino group in the transition state **1c** is only slightly longer (1.668 Å) than the Si-N bond of **1b**. The rotational barrier is rather low, only 5.5 kcal mol^{-1} (Table 1). The calculations show that the guanidinium cation has a somewhat higher energy barrier for rotation of one amino group (12.1 kcal mol^{-1}) than **1a**.[9a] This indicates more π contribution to the C-N bonds of the guanidinium ion as compared to the π bonding of the Si-N bonds of **1a**. It is interesting to note that the rotated amino group of **1c** is planar while the rotated amino group of the guanidinium cation is strongly pyramidal.[9a]

We also performed calculations for the neutral parent compound silaguanidine (**2**). Figure 1 shows that the equilibrium structure **2a** has C_1 symmetry. The amino groups are not planar, but slightly pyramidal. The planar C_s form **2b**, which is a transition state, is calculated as 0.6 kcal mol^{-1} higher in energy than **2a** (Table 1). The calculated sila-imino bond of **2a** (1.599 Å) is slightly longer than the experimentally observed

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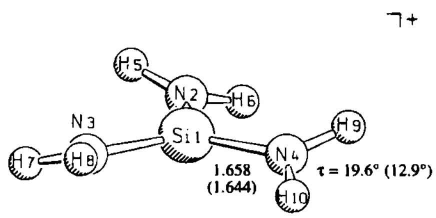
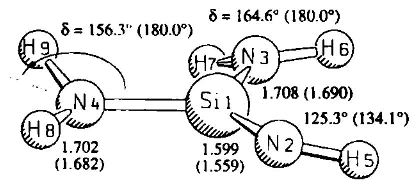
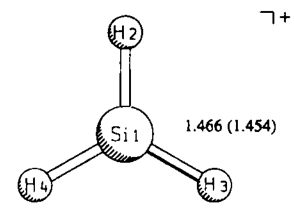


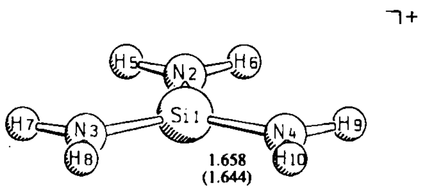
1a (D_3)



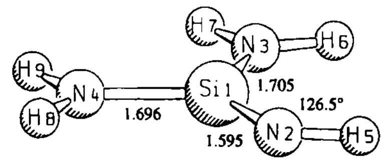
2a (C_1)



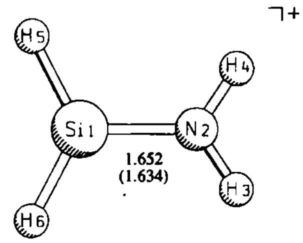
3 (D_{3h})



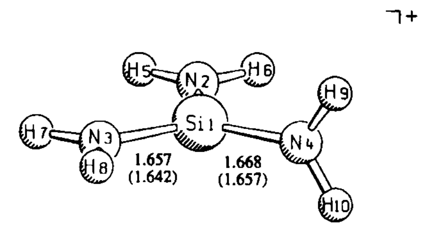
1b (D_{3h})



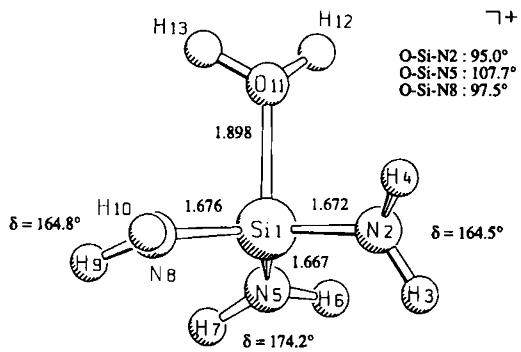
2b (C_S)



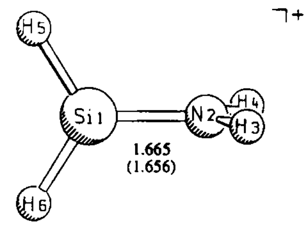
4a (C_{2v})



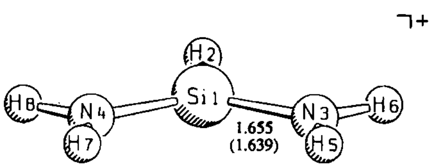
1c (C_{2v})



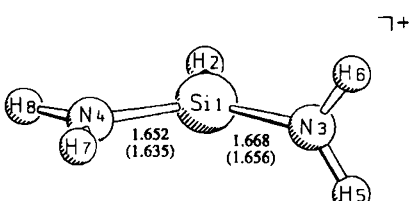
6 (HF, C_1)



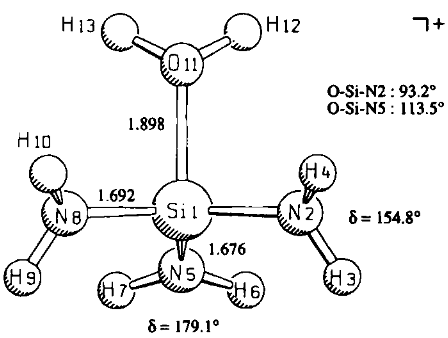
4b (C_{2v})



5a (C_{2v})



5b (C_S)



6 (MP2, C_S)

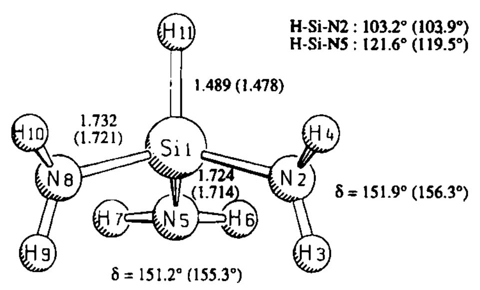
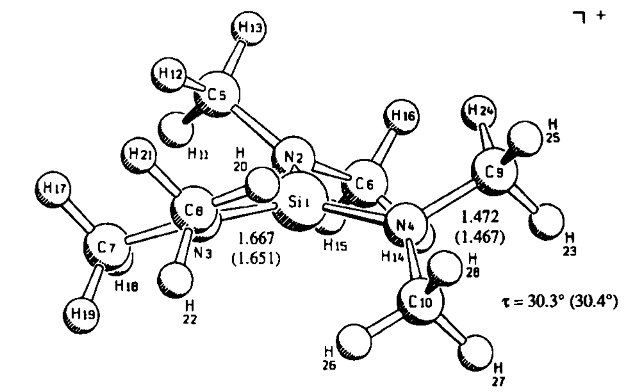
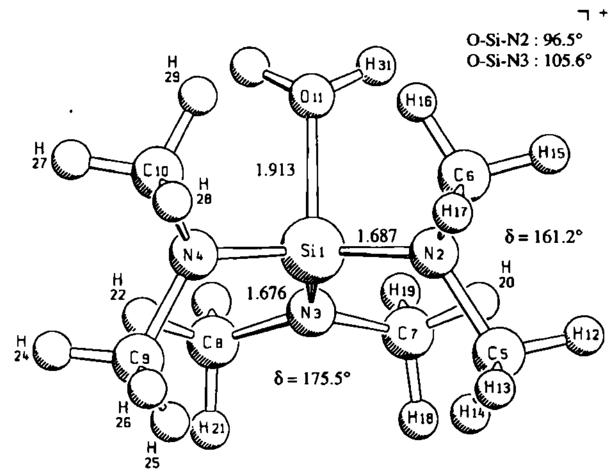


Fig. 1. Calculated geometries of **1**–**7** at MP2/6-31 G(d). Values at HF/6-31 G(d) are given in parentheses. Bond lengths are given in Å, angles in °. The torsion angle τ is defined as the dihedral angle H^{10}-N^4-Si^1-N^2 (**1a**). For the definition of the puckering angle δ see structure **2a**.

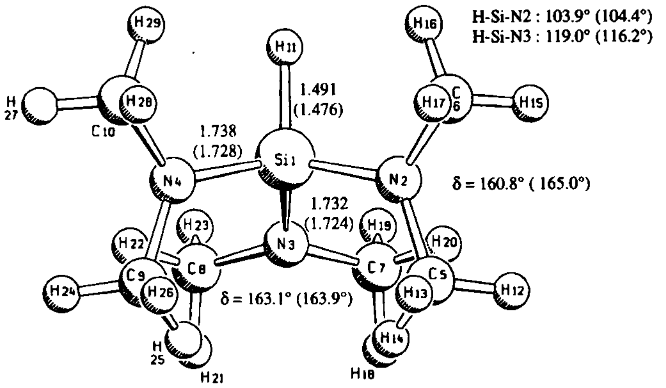
7 (C_S)



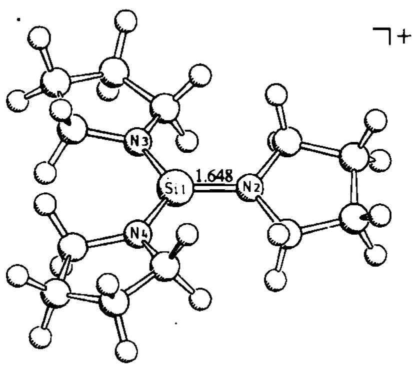
8 (D_3)



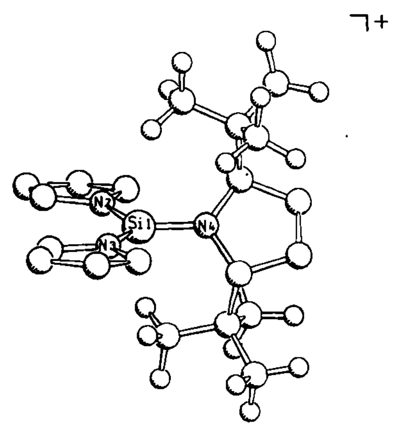
10 (C_s)



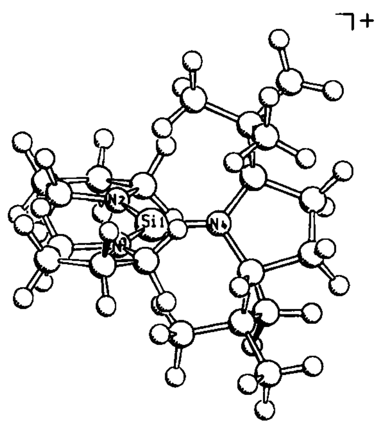
9 (C_s)



11 (D_3)



12 (C_1)



12 (C_1)

Si–N double bond length in $(tBu)_2Si{=}NSi(tBu)_3$ (1.568 Å).[22] The sila-amino bonds of **2a** (1.702 and 1.708 Å) are longer than in **1a** and a little shorter than the standard Si–N single bond (1.748 Å).[23]

The energy difference between **1a** and **2a** gives the theoretically predicted proton affinity of silaguanidine. At MP4(SDTQ)/6-311G(d,p)//MP2/6-31G(d), the proton affinity of **1** is calculated to be 258.1 $kcal\,mol^{-1}$. ZPE correction lowers this to 249.2 $kcal\,mol^{-1}$ (Table 1). The proton affinity of guanidine calculated at the same level of theory is 240.9 $kcal\,mol^{-1}$.[9a] It follows that *the intrinsic basicity of silaguanidine is higher than that of guanidine.* This may seem surprising, because the high basicity of guanidine, which is one of the strongest organic bases known in chemistry ($pK_a = 13.6$),[25] is frequently ascribed to the favorable π conjugation of the guanidinium cation. There is theoretical evidence, however, that the very high basicity of guanidine in solution is partly caused by other effects such as strong hydrogen bonding.[9a, 26] The higher proton affinity of **1** as compared to that of guanidine can be explained by i) the higher negative charge at the nitrogen atoms of **1** and ii) the unstable Si–N double bond of **2**, which adopts single bond character upon protonation.

We calculated the stabilization energies when the hydrogen atoms of the parent silylium ion SiH_3^+ (**3**) are successively substituted by amino groups as given by the isodesmic reactions (1–3) in Scheme 1. For comparison, we also calculated the respective stabilization energies for CH_3^+:

Fig. 2. Calculated geometries of **8–11** at MP2/6-31G(d). Values at HF/6-31G(d) are given in parentheses. Bond lengths are given in Å, angles in °. The torsion angle τ is defined as the dihedral angle C^{10}-N^4-Si^1-N^2 (**8**). Structure **12** was optimized using AM1. The optimized geometry of **12** is shown with and without the hydrogen atoms of the pyrrolidine rings. For the definition of the puckering angle δ see structure **2a** (Fig. 1).

Table 1. Calculated total energies E_{tot} (hartree), relative energies E_{rel} (kcal mol^{-1}), zero-point energies ZPE (kcal mol^{-1}), and number of imaginary frequencies *i* of the molecules **1**-**10**.

molecule	HF/6-31 G(d) // HF/6-31 G(d) E_{tot}	E_{rel}	ZPE	*i*	MP2/6-31 G(d) //MP2/6-31 G(d) E_{tot}	E_{rel}	ZPE	*i*	MP4/6-311G(d,p)//MP2/6-31 G(d) E_{tot}	E_{rel}
1a	-455.61995	0.0	54.0	0	-456.17964	0.0	51.4	0	-456.37783	0.0
1b	-455.61978	+0.1	53.7	1	-456.17873	+0.6	50.8	1	-456.37665	+0.7
1c	-455.61000	+6.2	53.7	1	-456.17049	+5.7	50.9	1	-456.36907	+5.5
2a	-455.19901	-	44.6	0	-455.77155	0.0	42.5	0	-455.96646	0.0
2b	-	-	-	-	-455.77107	+0.3	41.9	1	-455.96543	+0.6
3	-290.32891	-	15.1	0	-290.39137	-	14.5	0	-	-
4a	-345.43914	0.0	29.1	0	-345.67268	0.0	27.7	0	-345.78700	0.0
4b	-345.40512	+21.3	27.4	1	-345.63195	+25.6	26.1	1	-345.74733	+24.9
5a	-400.53378	0.0	41.8	0	-400.93135	0.0	39.6	0	-401.08731	0.0
5b	-400.51644	+10.9	41.0	1	-400.91371	+11.1	38.9	1	-401.07044	+10.6
6	-531.67668	-	70.9	0	-532.42839	-	-	-	-	-
7	-456.42049	-	59.0	0	-456.99427	-	56.5	0	-	-
8	-689.78361	-	169.9	0	-691.13431	-	-	-	-	-
9	-690.56796	-	174.0	0	-691.93149	-	-	-	-	-
10	-765.82188	-	187.0	0	-	-	-	-	-	-
H_2O	-76.01075	-	14.4	0	-76.19685	-	-	-	-	-
SiH_4	-291.22513	-	21.0	0	-291.30712	-	-	-	-	-

Table 2. ^{29}Si NMR chemical shifts at IGLO/II + sp // MP2/6-31 G(d) and results of the NBO analysis at MP2/6-31 G(d) [a].

Molecule		δ ^{29}Si	%Si(Si-N)	P(Si-N)	p(π) Si	q(Si)	q(N)
1a		+40.0	19.3	0.85	0.45	+2.24	-1.35
1b			19.4	0.84	0.46	+2.25	-1.35
1c					0.40	+2.25	
	N1/4		18.9	0.87			-1.33
	N3		19.8	0.78			-1.40
2a		+26.6			0.55	+2.00	
	N2		24.0 (σ) 19.4 (π)	1.36			-1.38
	N3		17.8	0.69			-1.36
	N4		18.2	0.71			-1.36
3		+270.2	-	-	0.00	+1.42	-
4a		+122.2	18.9 (σ) 15.2 (π)	1.07	0.30	+1.57	-1.26
4b		-	19.6	0.75	0.03	+1.83	-1.45
5a		+65.8	19.5	0.92	0.41	+1.90	-1.32
5b		-			0.30	+1.95	
	N3		18.4 (σ) 14.3 (π)	1.00			-1.28
	N6		20.1	0.79			-1.40
6		-21.0			-	+2.27	
	N2/8		15.2	0.73			-1.39
	N5		16.5	0.77			-1.37
7		-37.1			-	+1.90	
	N2/8		17.8	0.67			-1.36
	N5		18.2	0.67			-1.36
8		+42.1	17.3	0.78	0.51	+2.23	-0.94
9		-20.8			-	+1.96	
	N2/4		16.1	0.59			-0.94
	N3		16.6	0.60			-0.94
10		-20.5			-	+2.37	
	N2/4		12.6	0.64			-1.00
	N3		14.8	0.69			-0.98

[a] %Si(Si-N) gives the polarity of the Si-N bond, P(Si-N) gives the Wiberg bond index, p(π) Si gives the occupation of the p_π orbital at silicon, and q(Si) and q(N) give the partial charges at silicon and nitrogen, respectively.

$XH_3^+ + H_3XNH_2 \longrightarrow XH_2NH_2^+ + XH_4$	-37.5	-103.4	(1)
$XH_2NH_2^+ + H_3XNH_2 \longrightarrow XH(NH_2)_2^+ + XH_4$	-23.3	-44.3	(2)
$XH(NH_2)_2^+ + H_3XNH_2 \longrightarrow X(NH_2)_3^+ + XH_4$	-16.8	-27.1	(3)
$\Sigma(1)-(3)$	-77.6	-174.8	
$XH_3^+ + HX(NH_2)_3 \longrightarrow X(NH_2)_3^+ + XH_4$	-63.5	-159.3	(4)
$XH_3^+ + HX(Me)_3 \longrightarrow X(Me)_3^+ + XH_4$	-36.0	-67.7	(5)[27]

Scheme 1. ΔE (kcal mol^{-1}) is given for X = Si (left) and X = C (right).

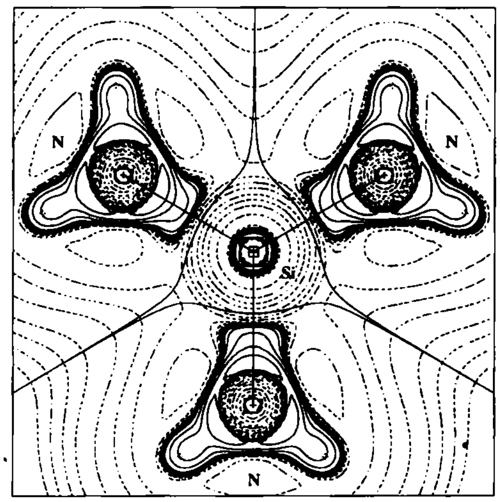


Fig. 3. Contour line diagrams of the Laplacian distribution $\nabla^2\rho(\mathbf{r})$ at MP2/6-31 G(d) of **1a** in the SiN_3 plane. Dashed lines indicate charge depletion ($\nabla^2\rho(\mathbf{r})>0$), solid lines indicate charge concentration ($\nabla^2\rho(\mathbf{r})<0$). The solid lines connecting the atomic nuclei are the bond paths; the solid lines separating the atomic nuclei indicate the zero-flux surfaces in the plane. The crossing points of the bond paths and zero-flux surfaces are the bond critical points $\mathbf{r}_b$.

The stabilization by the amino groups is clearly higher for the carbenium ions than for the corresponding silylium ions. The reaction energies become less exothermic with each additional amino group, but the decrease from reaction (1) to (3) is less sharp for the silylium ions than for the carbenium ions. The three amino groups of the silaguanidinium ion have a stabilizing effect upon the cation that is 44% of the carbon analogue. A similar ratio between the resonance stabilization of **1a** and the guanidinium cation is given by the related isodesmic reaction (4) (40%). The stabilization by the amino groups is substantially higher than that by the methyl groups for both carbenium and silylium ions. This becomes obvious from a comparison of the total stabilization energy of the amino groups and the methyl groups [reactions (4) and (5)]. It follows that amino-substituted silylium ions should be better candidates for the search of a stable silylium cation in solution than alkyl-substituted species.

Figure 1 shows that the calculated Si-N bond lengths of the energy minimum structures of $H_2SiNH_2^+$ (**4a**) (1.652 Å), $HSi(NH_2)_2^+$ (**5a**) (1.655 Å), and $Si(NH_2)_3^+$ (**1a**) (1.658 Å) increase only marginally upon further substitution by amino groups. Herein they differ from the carbenium ions, whose C–N bond lengths show a clear increase from $H_2CNH_2^+$ (1.282 Å) to $HC(NH_2)_2^+$ (1.313 Å) and $C(NH_2)_3^+$ (1.334 Å).[9a] The differences in bond lengthening can be explained by the more ionic and less π-covalent character of the Si–N bond compared to the C–N bond. The silicon atoms of $(NH_2)_nSiH_{3-n}^+$ carry positive charges between +1.57 in **4a** and +2.24 in **1a** (Table 2), while the carbon atoms of the corresponding carbenium ions $(NH_2)_nCH_{3-n}^+$ have positive charges of between +0.231 and +0.737.[9a] In both systems the π bonding becomes more delocalized and, therefore, weaker when the number of amino groups increases. The opposite trend holds for the charge attraction between the central silicon or carbon atom and nitrogen. Here, the carbon and silicon atoms become more positively charged when more amino groups are attached, resulting in an increase of the ionic contribution to the bond. The two opposing effects upon the bond lengths roughly cancel each other out in the case of the silylium ions, while the effect of the covalent contribution dominates in the case of the carbenium ions. In spite of the similar bond lengths, the rotational barriers of the Si–N bonds decrease by a factor of two from $H_2SiNH_2^+$ (25.6 kcal mol^{-1}) to $HSi(NH_2)_2^+$ (11.1 kcal mol^{-1}) to $Si(NH_2)_3^+$ (5.5 kcal mol^{-1}) (see Table 1). The Si–N bonds of the perpendicular amino groups of the transition states **4b** and **5b** are only slightly longer than the Si–N bonds of **4a** and **5a**, respectively (Fig. 1). This is another proof that the Si–N bonds of aminosilylium ions are more ionic and have less π character than the C–N bonds of aminocarbenium ions.

2. Towards a stable silylium cation in solution: Is the silaguanidinium cation **1** a possible candidate for a stable silylium cation in solution? We calculated the structure and complexation energy of **1a** with one molecule of water, which was taken as a model for a solvent. Figure 1 shows the optimized geometry of the complex $Si(NH_2)_3(H_2O)^+$ (**6**). The calculated structure **6** at HF/6-31 G(d) has C_1 symmetry with slightly twisted pyramidal amino groups and a Si–O distance of 1.898 Å. The MP2/6-31 G(d) optimized geometry has the same Si–O interatomic distance as calculated at HF/6-31 G(d). However, the optimization at the correlated level yields a C_s structure as energy minimum. There are two pyramidal amino groups with a longer (1.692 Å) Si–N bond and a nearly planar amino group with a shorter (1.676 Å) Si–N bond (Fig. 1). The water–silaguanidinium complex **6** has slightly longer Si–N bonds than **1a** (1.658 Å). The O-Si-N angles (93.2 and 113.5°) indicate that the silaguanidinium moiety is distorted from a planar form towards a pyramidal structure. The calculated complexation energy of **6** is 32.6 kcal mol^{-1} at MP2/6-31 G(d) and 28.8 kcal mol^{-1} at HF/6-31 G(d) (Table 3). The calculated complexation energies for $SiH_3(H_2O)^+$ and $SiMe_3(H_2O)^+$ at HF/6-31 G(d) are 57.7 and 40.6 kcal mol^{-1}, respectively.[7c] It follows that the silaguanidinium cation should be more weakly coordinate and retain a higher degree of silylium ion character in solution than alkyl-substituted silylium cations.

Table 3. Calculated complexation energies for different silylium cations (kcal mol^{-1}).

Molecule	HF/6-31 G(d)	MP2/6-31 G(d)
$SiH_3(H_2O)^+$	57.7 [a]	
$SiMe_3(H_2O)^+$	40.6 [a]	
$Si(NH_2)_3(H_2O)^+$ (**6**)	28.8 [b]	32.6 [b]
$Si(NMe_2)_3(H_2O)^+$ (**10**)	17.3 [b]	

[a] Values are taken from ref. [7c]. [b] This work.

A crucial measure to distinguish between a genuine tricoordinate silylium cation SiR_3^+ and a higher-coordinate species is the ^{29}Si NMR chemical shift. It has been shown computationally that the ^{29}Si resonances of $SiMe_3^+$ and SiH_3^+ are shifted by more than 350 ppm downfield relative to the signals for the neutral compounds $SiMe_4$ and SiH_4, respectively.[3e, 7c, 28] The lack of extremely low shielding expected by analogy with carbenium ions and by comparison with the theoretically predicted ^{29}Si NMR chemical shifts was the most important criterion that led to the conclusion that the observed candidates for silylium ions are tetracoordinate rather than tricoordinate silicon compounds.[1a, 3e]

We calculated the ^{29}Si NMR chemical shifts of **1a** and the neutral compound $HSi(NH_2)_3$ (**7**) in order to see if amino-substituted silylium cations exhibit the same downfield shift as the alkyl-substituted species. Figure 1 shows the optimized geometry of **7**, which has C_s symmetry. The calculated Si–N bond lengths (1.724 and 1.732 Å) are in the range of normal single bonds. Table 2 shows the calculated NMR chemical shifts at IGLO/II + sp//MP2/6-31 G(d). The ^{29}Si resonances of **7** and **1a** are predicted to be $\delta = -37.1$ (**7**) and $\delta = 40.0$ (**1a**). The calculations show that *the silaguanidinium cation does not have the same extremely low shielding of the silicon atom as calculated for $SiMe_3^+$ and SiH_3^+*.[29] This is an important result for experimental studies of amino-substituted silylium cations. It should be noted that the carbon atom of the guanidinium ion $C(NH_2)_3^+$ is also much less deshielded than the central carbon atoms of CH_3^+ and CMe_3^+. The IGLO/II value for the ^{13}C signal of the guanidinium ion is $\delta = 159.4$ (experimental value 158.3[30]), while the calculated ^{13}C resonances for CH_3^+ ($\delta = 367.4$) and CMe_3^+ ($\delta = 347.7$) are at much lower field.[28]

Table 4 shows a comparison of the ^{13}C and ^{29}Si NMR chemical shifts for XH_3^+, XMe_3^+, and $X(NH_2)_3^+$. The effect of the amino groups upon the NMR chemical shifts of carbon and silicon relative to XH_3^+ is very similar, while the effect of the methyl groups is quite different. The amino groups lead to upfield shifts of 230.2 ppm for the carbenium ion and 208.2 ppm for the silylium ion. The methyl groups lead to a downfield shift of 85.5 ppm for the silylium ion, while the carbenium ion becomes slightly more shielded by 19.7 ppm. The different effect of the methyl groups can be explained by the electronegativities of carbon and silicon.

Table 4. IGLO/II values for the NMR chemical shifts (δ) of silylium and carbenium cations.

Molecule	δ ^{29}Si	δ ^{13}C [a]
XH_3^+	270.2 [b]	367.4
$X(CH_3)_3^+$	355.9 [b]	347.7
$X(NH_2)_3^+$	40.0 [c]	159.4

[a] Values are taken from ref. [28]. [b] Values are taken from ref. [7c]. [c] This work (IGLO/II + sp).

The effect of the amino groups upon the NMR chemical shifts can be explained by the π donation of electronic charge from the nitrogen lone pairs into the formally empty p(π) orbital of the central atom. It is important to recognize that the upfield shift of the NMR resonances of X in $X(NH_2)_3^+$ relative to XH_3^+ and XMe_3^+ is caused by the p(π) occupancy of X,[28] and that the resonances are *not* related to the *total* atomic charge of X! It was recently reported by Olsson et al.[7c] that the ^{29}Si NMR chemical shifts of H_nSiMe_{4-n} are correlated with the charge at Si. This is possible, because the nature of the substituents remains the same in the whole series of molecules. In general, however, there is no simple relationship between chemical shifts and atomic charges. The partial charge of Si in $Si(NH_2)_3^+$ (+2.24 e) is clearly higher than in SiH_3^+ (+1.42 e, Table 2), but the silicon atom of SiH_3^+ is much more deshielded than that of the silaguanidinium cation (Table 2). The effect of π donation upon the NMR resonances can also vary strongly for different atoms. It has been shown in a combined experimental/theoretical study that the effect of π back-donation upon the chemical shifts of the atom X in the compounds Me_nXCl_{4-n} (X = C, Si, Ti) leads to qualitatively different trends in the NMR spectra.[31] Table 2 also shows the calculated ^{29}Si NMR signal for the silaguanidinium water complex **6**. The theoretically predicted NMR resonance ($\delta = -21.0$) is shifted by only 15.9 ppm towards lower field relative to the neutral compound **7** ($\delta = -37.1$).

We also carried out calculations for the hexamethyl derivatives of **1a**, **6**, and **7**. Figures 1 and 2 show the optimized geometries. The hexamethyl silaguanidinium cation **8** is more strongly twisted ($\tau = 30.3°$) than the silaguanidinium cation **1a** ($\tau = 19.6°$) because of the steric interactions between the methyl groups. The NMe_2 groups stabilize the silylium cation more than the NH_2 groups. This is revealed by the calculated stabilization energy for the isodesmic reaction 6 at MP2/6-31G(d):

$$SiH_3^+ + HSi(NMe_2)_3 \longrightarrow Si(NMe_2)_3^+ + SiH_4 - 74.4\ \mathrm{kcal\,mol^{-1}} \quad (6)$$

The calculated stabilization energy by the NMe_2 groups is 74.4 kcal mol^{-1}, while the stabilization of the silylium ion by the NH_2 groups amounts to only 63.5 kcal mol^{-1} [reaction (4)]. The calculated geometries of the neutral compounds **9** and **7** are very similar (Figs. 1, 2). The Si–O distance of the complex **10**, which could only be calculated at HF/6-31G(d), is longer (1.913 Å) than that of **6** (1.898 Å). As expected, the complexation energy of **10** is lower (17.3 kcal mol^{-1}) than that of **6** (28.8 kcal mol^{-1}, Table 3). It is interesting to note that the difference between the stabilization energies of the water complexes **6** and **10** (11.5 kcal mol^{-1}) is nearly the same as the difference in stabilization of the silylium ions by the NH_2 and NMe_2 groups [11.1 kcal mol^{-1}, reactions (4) and (6)].

Table 5. IGLO/II values for the ^{29}Si NMR chemical shifts (δ) of silicon compounds.

Molecule	R = Me [a]	R = NH_2 [b]	R = NMe_2 [b]
R_3Si^+	355.9	40.0	42.1
$R_3Si(H_2O)^+$	99.0	−21.0	−20.5
R_3SiH	−16.6	−37.1	−20.8

[a] Values are taken from ref. [7c]. [b] This work (IGLO/II + sp).

We calculated the ^{29}Si NMR chemical shifts of **8**–**10** (Table 2). The signal of the ^{29}Si resonance for the neutral compound **9** ($\delta = -20.8$) is shifted downfield for the cation **8** ($\delta = 42.1$) by 62.9 ppm. This is less than the calculated ^{29}Si NMR shift from **7** to **1a** (77.1 ppm). More important is the chemical shift of the water complex **10**. The calculations predict that the ^{29}Si resonance of **10** ($\delta = -20.5$) is virtually the same as for the neutral compound **9** ($\delta = -20.8$). The measured ^{29}Si NMR shifts of $(Me_2N)_3SiB(C_6F_5)_4$ are $\delta = -30.8$ in C_6D_6 and $\delta = -39.3$ in CH_2Cl_2.[32] This is in reasonable agreement with the calculated values for **10**. The cryoscopic measurements of aminosilylium perchlorates clearly indicated unhydrolyzed, free ions in sulfolane, and the conductivity measurements revealed intermediate conductivity for these species.[1a] The calculated NMR chemical shifts of **9** and **10** explain why the investigated aminosilylium compounds exhibit ionic properties, although the observed ^{29}Si resonances apparently did not indicate siliylium ion character.[1a] There may be little or no difference in the ^{29}Si signals between a counterion- or a solvent-stabilized silylium cation. Table 5 shows a comparison of the ^{29}Si NMR chemical shifts of R_3Si^+, R_3SiH and $R_3Si(H_2O)^+$ for R = Me, NH_2, and NMe_2. It is obvious that the effect of the amino group upon the chemical shift is very different from that of the methyl group, and that the NMe_2 substituent is even more shielding than the NH_2 group.

Although the calculations indicate that $Si(NMe_2)_3^+$ (**8**) is a strongly stabilized silylium cation, the theoretically predicted complexation energy for **10** makes it unlikely that **8** can be isolated as a truly tricoordinate silylium cation. In order to sterically prevent interaction between Si and a donor molecule in an aminosilylium cation, we considered derivatives of **8** which have some steric protection. To this end we calculated first the structure of the tripyrrolidino silylium cation **11**. Figure 2 shows the AM1 optimized geometry of **11**. It is obvious that **11** has little steric shielding of the silicon center. As the next candidate we calculated a substituted derivative of **11**, where one pyrrolidine ring has *tert*-butyl groups at the 2 and 5 position of the ring (structure **12**). The optimized geometry of **12** is shown in Figure 2. It is obvious that the steric interactions between the *tert*-butyl groups and the two other amino substituents of **12** lead to a rotation of the substituted pyrrolidine ring. This places the *tert*-butyl groups in such a position that one methyl group is above, and one methyl group is below the silicon center. The position of the methyl groups indicates a nearly perfect steric shielding of the Si atom against donor molecules from above and below the SiN_3 plane. The rotation of one amino group would mean a loss of electronic stabilization of the silylium cation. However, the calculated barrier for rotation about the Si–N bond of **1a** (5.5 kcal mol^{-1}, Table 1) suggests that the loss of stabilization is not very severe. It follows that the silicon atom in **12** is electronically stabilized nearly as well as **8**. Since the binding energy between the silicon atom of **8** and the strong donor molecule H_2O is not very high, it is conceivable that the steric protection of the silylium center in **12** could be strong enough to prevent a significant interaction between the silicon atom and a (weaker) donor molecule.

The final question concerns the intramolecular stabilization of the silicon atom of **12** by the methyl groups. Are there any agostic interactions in **12**, which would suggest that the compound is rather a pentacoordinate silyl cation? Intramolecularly stabilized pentacoordinate silyl cations are well known.[33] However, the reported compounds have strong donor substituents as stabilizing groups, and the silicon atom is covalently bonded to carbon or hydrogen rather than to an amino group.[33] Our calculations show that the closest distance between silicon and a hydrogen atom of the methyl groups in **12** is 2.487 Å. It can be argued that weak agostic interactions may not be accurately predicted at the AM1 level. However, the stabilization of the silicon atom of **12** by the methyl groups should not be very strong, since the complexation energy of the water complex **10** is only 17.3 kcal mol^{-1}. The calculations suggest that the triaminosilylium cation **12** should be a promising candidate to get significantly closer to the desired goal of a stable silylium cation in a condensed phase than previous systems.[2j, 5c] The combination of strong electronic stabilization by the amino groups and the steric shielding by the *tert*-butyl groups in **12** could help to overcome the obstacles to isolate a true silylium cation.

Conclusion

The silaguanidinium cation **1a** has an equilibrium geometry with planar amino groups twisted out of the SiN_3 plane by 19.6°. The Si–N bond length of **1a** is 1.658 Å, which is intermediate between a single and a double bond. Isodesmic reactions show that the stabilization of the amino groups in the silaguanidinium cation is 63.5 kcal mol^{-1}, while the guanidinium ion is stabilized by 159.3 kcal mol^{-1}. The amino groups are much better stabilizers for silylium cations than alkyl groups. The calculated stabilization energy of $SiMe_3^+$ is only 36.0 kcal mol^{-1}. The dimethylamino substituents stabilize the silylium cation in $Si(NMe_2)_3^+$ (**8**) even more than the amino groups in **1a**. The electronic stabilization of silylium cations by amino groups is further supported by the calculated complexation energies with one water molecule. IGLO calculations of the ^{29}Si NMR chemical shifts predict that the silaguanidinium cation should not show the same extremely low shielding of the silicon atom as calculated for $SiMe_3^+$ and SiH_3^+. The ^{29}Si signals of the water complexed cations $Si(NH_2)_3(H_2O)^+$ (**6**) and $Si(NMe_2)_3(H_2O)^+$ (**10**) are not very different from the calculated resonances of the respective neutral compounds $HSi(NH_2)_3$ (**7**) and $HSi(NMe_2)_3$ (**9**). The theoretically predicted ^{29}Si resonance of $Si(NMe_2)_3(H_2O)^+$ is in reasonable agreement with the experimental NMR spectrum of $(Me_2N)_3SiB(C_6F_5)_4$. Although the calculated complexation energy for **10** is rather low (17.3 kcal mol^{-1}), it still indicates that it will be very difficult to observe $Si(NMe_2)_3^+$ as an isolated species in a condensed phase. A much better candidate would be the related pyrrolidino silylium cation **12**. The silicon atom of **12** is stabilized by electronic effects of the amino groups. In addition, it is also sterically protected by the *tert*-butyl substituents of one pyrrolidine ring. We suggest compound **12** as a promising candidate for a truly tricoordinate silylium cation.

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