



ELSEVIER

Journal of Molecular Structure (Theochem) 313 (1994) 91–109

THEO
CHEM

Calculation of ^{29}Si chemical shifts as a probe for molecular and electronic structure

Dieter Cremer*, Lars Olsson, Henrik Ottosson

Department of Theoretical Chemistry, University of Göteborg, Kemigården 3, S-41296 Göteborg, Sweden

Received 10 November 1993; accepted 19 January 1994

Abstract

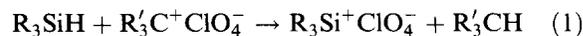
A variety of silylium cations SiR_3^+ (SiH_3^+ , SiMe_3^+ , SiEt_3^+ and SiH_2Ph^+), silylperchlorates ($\text{SiH}_3\text{OCIO}_3$, $\text{SiMe}_3\text{OCIO}_3$ and $\text{SiH}_3\text{OCIO}_3(\text{NH}_3)$), and solvated silylium cations $\text{SiR}_3(\text{S})_n^+$, ($\text{SiH}_3(\text{NH}_3)^+$, $\text{SiH}_3(\text{NCH})^+$, $\text{SiH}_3(\text{NCCH}_3)^+$, $\text{SiH}_3(\text{NH}_3)_2^+$, $\text{SiH}_3(\text{NCH})_2^+$, $\text{SiMe}_3(\text{NH}_3)^+$, $\text{SiMe}_3(\text{NCH})^+$ and $\text{SiMe}_3(\text{NCCH}_3)^+$) were investigated at the Hartree–Fock level using the 6-31G(d) basis set. IGLO and GIAO-MP2 NMR chemical shift calculations with a [7s6p2d/5s4p1d/3s1p] basis were carried out at optimized HF/6-31G(d) geometries to determine the $\delta^{29}\text{Si}$ and $\delta^{13}\text{C}$ chemical shift values. Solvent effects on the calculated chemical shifts were determined using the PISA continuum model. In addition, the nature of Si–S interactions was investigated on the basis of the calculated electron density and energy density distributions. In the gas phase, R_3Si^+ ions (R = H, Me or Et) possess $\delta^{29}\text{Si}$ values between 300 and 400 ppm. In weak or normal nucleophilic solvents, silylium cations react with one or more solvent molecules to tetra- or penta-coordinated covalently bonded silicon compounds with complexation energies that can be as high as $100 \text{ kcal mol}^{-1}$ and $\delta^{29}\text{Si}$ values between -30 and 90 ppm ($\text{SiR}_3(\text{S})^+$) or -130 and 50 ppm ($\text{SiR}_3(\text{S})_2^+$). Silylium cation character is lost in these compounds. Dissociation of silylperchlorates in solution leads directly to tetra- and penta-coordinated silyl cations rather than to tricoordinated silylium cations. The various steps of the dissociation process can be monitored by NMR.

1. Introduction

There is a continuing controversy regarding the question of whether free triorganosilylium cations (R_3Si^+) [1] can be generated in solution [2–16]. Actually, silylium cations are known to be more stable in the gas phase than are their carbon analogues, which is due to the fact that silicon is more electropositive than carbon [17]. Accordingly, silylium cations are easily observable by mass spectrometry or ion cyclotron resonance

spectroscopy of triorganysilyl compounds [18,19]. However, their existence in solvent phases is difficult to prove and, therefore, all recent claims concerning the observation of free trivalent silylium cations must be considered with care.

Lambert and co-workers have reported a number of experiments, which indicated that free silylium ions R_3Si^+ (1) may exist in solution [4–8]. The alleged silylium ions were prepared by hydride abstraction from an alkylsilane with triphenyl-carbenium perchlorate [9]:



The experiments involved compounds such as Me-

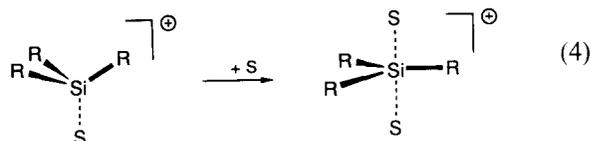
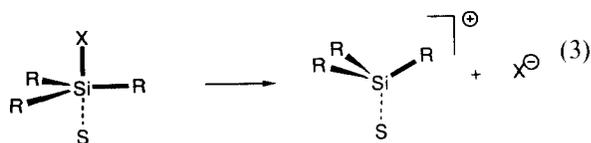
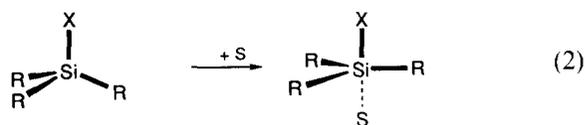
* Corresponding author.

[6–8], Ph- [5,6,8], MeS- [7], EtS- [7] and *i*-PrS-substituted silylperchlorates [4,7] in solvents ranging from sulfolane, dichloromethane and 1,2-dichloroethane to acetonitrile. The evidence for the existence of free silylium cations came from conductance measurements and $^{35}\text{Cl}/^{37}\text{Cl}$ NMR spectroscopy. According to conductance measurements, R_3Si^+ ($\text{R} = \text{Me}$ or Ph) exists as free ion in dilute solutions of sulfolane (below 0.05 M), and as covalent R_3SiClO_4 or $\text{R}_3\text{Si}^+\text{ClO}_4^-$ ion pairs in equilibrium with the free ionic form in concentrated sulfolane solutions and in weakly ionizing solvents such as dichloromethane or 1,2-dichloroethane. $^{35}\text{Cl}/^{37}\text{Cl}$ NMR measurements support these results by giving a measure for the amount of free ionic perchlorate [6].

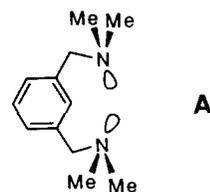
Olah and co-workers have argued that the results of conductance measurements and NMR may best be accounted for by assuming hydrolysis of R_3SiX by residual water in the solvents used [6,7]. Comparing calculated ^{29}Si , ^{13}C and ^1H NMR chemical shifts for the silylium cations SiH_3^+ (1) and $\text{Si}(\text{CH}_3)_3^+$ (2) with observed chemical shifts, Olah and coworkers [7] concluded that no long-lived silylium ion exists in solution. In recent publications, Lambert and coworkers have rejected this interpretation [8] and have suggested new procedures [14,15] which involve weakly coordinating counter ions and weakly nucleophilic solvents to generate silylium cations in solution. These procedures have been investigated critically by Olsson and Cremer [20] and independently by Schleyer et al. [21] with the help of *ab initio* calculations, comparing experimentally determined geometries and $\delta^{29}\text{Si}$ NMR chemical shifts of the alleged silylium cations with calculated values. The cations generated by Lambert and coworkers have been identified as silyl-substituted benzenium ions [20,21], but Olsson and Cremer [20] have also pointed out that the experimental procedures used by Lambert and coworkers should under certain circumstances lead to nearly free silylium cations in solution [20].

Research is presently focusing on the question of the fate of a silylium cation from the moment it is set free in solution. In solvents (S) with considerable donicity (sulfolane, acetonitrile, etc.) there must be an involvement of solvent already in the

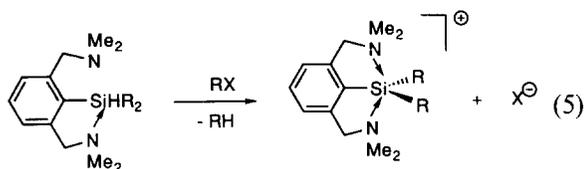
ionization process according to the reactions:



According to reactions (2)–(4), free silylium cations without any solvent interactions will only exist in the case of non-coordinating solvents and counter ions. Probably, there is a continuum of solvent–ion and ion–ion interactions, which ranges from strongly covalent to weakly electrostatic interactions and it is the question of whether the ideal case of a silylium cation together with a non-coordinating counterion in a non-coordinating solvent can be approximated at all. Several experimental investigations have provided the first data in this connection. For example, the binding energies between silyl cations and various bases have been measured by mass spectrometry in the gas phase [22,23]. Systematic NMR measurements have been carried out for perchlorates in solvents ranging from weakly to strongly nucleophilic character [24]. In addition, several successful attempts have been made to crystallize silylium salts from solutions in order to investigate the degree of association between solvent, counter ion, and silylium cations by direct structure analysis [25,26].



In this context, a recent publication by Chuit et al. [27] deserves special mentioning. These authors synthesized silylium cations that can be stabilized by intramolecular solvation. They used the potential bidentated ligand A to generate pentacoordinated siliconium ions according to reaction (5):



As the number and type of intramolecularly associated “solvent” molecules is defined in reaction (5), investigation of the complex formed leads to direct information of silylium cations in solution.

Although the siliconium ions generated in reaction (5) might provide reasonable models of silylium cations in solution, it is difficult to predict from the available experimental results whether they reflect correctly the degree of coordination of a silylium cation in solution. Not enough experimental data have been collected to draw a connection between intramolecularly and intermolecularly solvated silylium cations. Furthermore, it is not clear whether the silyl ions of reaction (5) correspond to weakly coordinated silylium ions or covalently bonded (strongly coordinated) siliconium ions. This question is also unsolved for silyl cations in various solvents.

In this situation, theoretical data are urgently needed to obtain a better understanding of the properties of silylium cations in solution. In this paper we report on silylium cations both in the gas phase and solution phases. For this purpose, we calculated the energy, geometry, charge distribution, bonding properties and NMR chemical shifts of SiH_3^+ (1), $\text{Si}(\text{CH}_3)_3^+$ (2), $\text{Si}(\text{CH}_2\text{CH}_3)_3^+$ (3), planar $\text{SiH}_2\text{C}_6\text{H}_5^+$ (4a), and orthogonal $\text{SiH}_2\text{C}_6\text{H}_5^+$ (4b) in the gas phase and compared their properties with those of perchlorates $\text{SiH}_3\text{OClO}_3$ (5), $\text{Si}(\text{CH}_3)_3\text{OClO}_3$ (6), and $\text{SiH}_3\text{OClO}_3(\text{NH}_3)$ (7) as well as solvated silylium cations (8–15) (Scheme 1). As suitable model solvents we chose NH_3 , HCN , and CH_3CN ; NH_3 was chosen to compare intermolecular and intramolecular

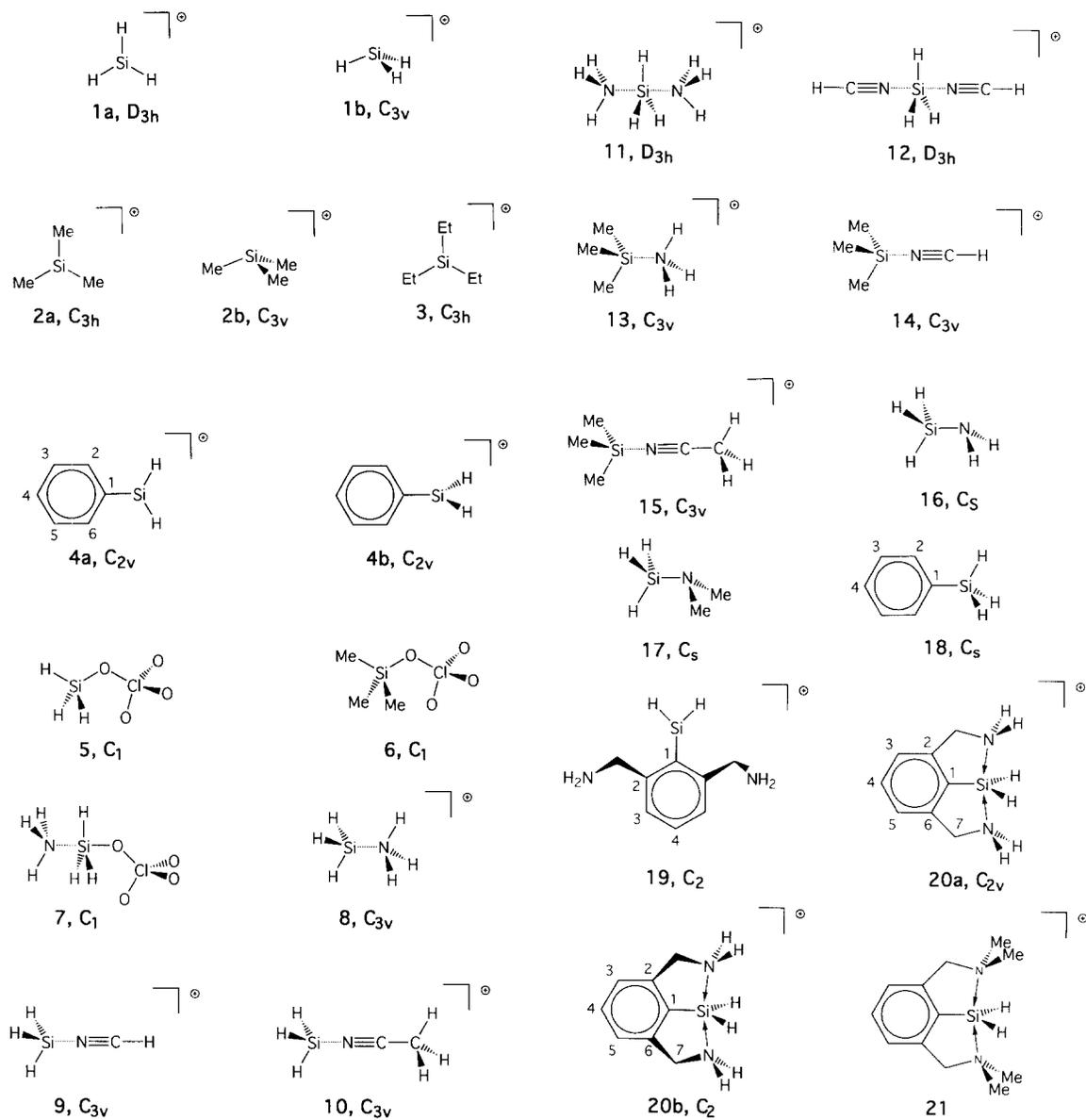
solvation of silylium cations (reaction (5)), while HCN and CH_3CN are interesting because acetonitrile has actually been used as a solvent in experimental investigations of silylium cations. In addition to 1–15, we investigated neutral silicon compounds (16–18) in order to obtain reference data for the analysis of the properties of silylium cations (19–21) (Scheme 1).

In the following, we discuss the structure, stability, charge distribution and NMR chemical shifts of silylium cations in the gas phase and compare their properties with those of solvated silylium cations. In particular, we investigate the various steps that may lead from a neutral silicon compound to a cation and finally to a solvated silylium cation (reactions (2)–(4)). We concentrate on answering the following questions. (1) How strong is the association of the solvent molecules with silicon compounds in the neutral and the ionic state? (2) To what extent does the association with a solvent molecule change the properties of a silylium cation and at what point is it no longer appropriate to speak of a silylium cation? (3) Can NMR spectroscopy be used to follow the various steps of silylium cation formation and solvation? Investigation of these questions is of direct importance for the on-going research on trivalent silylium cations in solution.

2. Computational methods

The geometries of compounds 1–19 (Scheme 1) were optimized at the Hartree–Fock (HF) level using the 6-31G(d) basis set, which is of DZ + P quality in the valence shell [28]. The character of the stationary points thus obtained was tested by means of frequency calculations in order to make sure that the calculated geometries corresponded to the equilibrium geometries.

NMR chemical shift calculations were done using the IGLO (individual gauge for localized orbitals) method of Kutzelnigg and coworkers [29,30] in a version [31] designed for routine calculations using the programs COLOGNE [32] and GAUSSIAN 92 [33]. The (11s7p2d/9s5p1d/5s1p)/[7s6p2d/5s4p1d/3s1p] basis set recommended by Kutzelnigg et al. [30] (called by those authors



Scheme 1.

“basis II”) for ^{29}Si and ^{13}C NMR chemical shift calculations was employed, but in some cases IGLO calculations had to be performed with the 6-31G(d) basis set because of computational limitations. IGLO ^{29}Si shifts for **1** were also checked with the GIAO-MP2 method, which contains correlation corrections and, therefore, leads to very reliable results [34].

We simulated the influence of the medium by using the PISA solvent model [35] where the wavefunction of the solute is recalculated in a solvent cage under the influence of a polarizable continuum that is characterized by the dielectricity constant (ϵ) of the solvent. IGLO NMR chemical shifts were then obtained for a solvent-dependent SCF wavefunction. Such an approach may be denoted as PISA-IGLO/basis B//HF/basis A if it is carried out at HF/basis A geometries [36].

The electronic structure of the silylium cations and the nature of the interactions between the silicon cation and the solvents was investigated

using the calculated electron density distribution $\rho(\mathbf{r})$, its associated Laplace concentration $-\nabla^2\rho(\mathbf{r})$, and the energy density distribution $H(\mathbf{r})$. For this purpose, the virial partitioning method [37] was applied, together with the bonding criteria suggested by Cremer and Kraka [38]. The latter authors have given conditions to distinguish between covalent bonding and electrostatic or non-bonding interactions [38,39]. The existence of a covalent bond between two atoms A and B is given provided that: (1) atoms A and B are connected by a path of maximum electron density (MED path) — the existence of such a MED path implies a (3,−1) saddle point \mathbf{r}_b of the electron density distribution $\rho(\mathbf{r})$ as well as a zero-flux surface between A and B (necessary condition); and (2) the local energy density $H(\mathbf{r}_b)$ is stabilizing, i.e. it must be smaller than zero (sufficient condition).

These two criteria were applied in this work to determine the number of bonding interactions

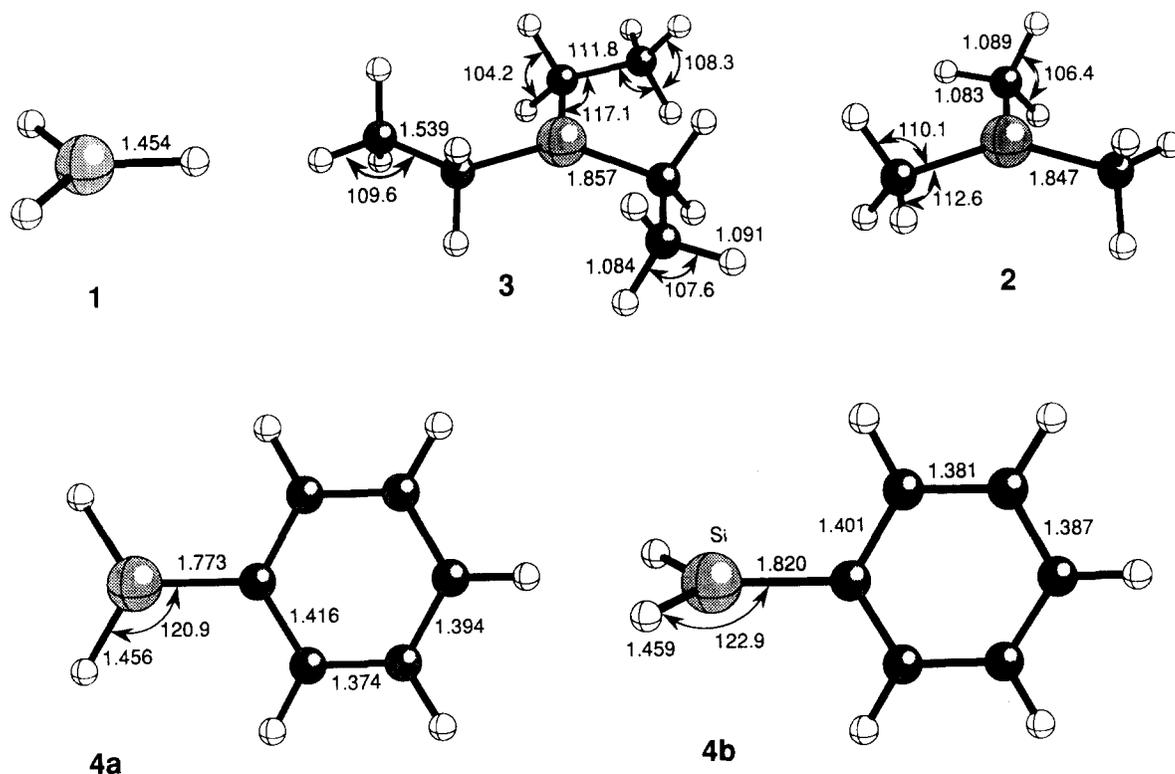
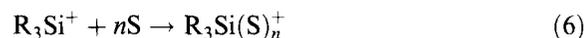


Fig. 1. HF/6-31G(d) geometries of the silylium cations: SiH_3^+ (**1**), $\text{Si}(\text{CH}_3)_3^+$ (**2**), $\text{Si}(\text{CH}_2\text{CH}_3)_3^+$ (**3**), and $\text{SiH}_2\text{C}_5\text{H}_6^+$ (**4**). The calculated bond lengths and angles are given in angstroms and degrees, respectively.

between silicon and its surrounding atoms in a silylium ion and to assess their stability. All calculations were performed on a CRAY XMP-416 computer using the COLOGNE [32], GAUSSIAN 92 [33] and ACES [40] ab initio packages.

3. Results and discussion

The calculated geometries of the silylium cations 1–4 are shown in Fig. 1, the perchlorates 5–7 in Fig. 2, the solvated silylium cations 8–15 in Fig. 3, the silicon compounds 16–19 in Fig. 4, and the cation 20 in Fig. 5. Table 1 lists the calculated HF/6-31G(d) energies together with the complexation and methyl stabilization energies obtained from the reactions:



In Table 2, IGLO/[7s6p2d/5s4p1d/3s1p] values of the $\delta^{29}Si$ and $\delta^{13}C$ NMR chemical shifts (relative to TMS) are given. Tables 3 and 4 contain the calculated silicon charges, charge transfer data, and relevant results of the bond density analysis.

3.1. Silylium cations

Cations 1–3 and 4a all possess a planar equilibrium geometry at the silicon atom. Three alkyl groups stabilize silylium cations by hyperconjugation. In the case of 2, hyperconjugative stabilisation is 36 kcal mol⁻¹ at the HF/6-31G(d) level of theory, which is significantly larger than methyl stabilization for SiH₃X compounds (normally < 10 kcal mol⁻¹ [41]), but only half as large as the corresponding value for CH₃⁺ (65 kcal mol⁻¹, HF/6-31G(d) [42]; 85 kcal mol⁻¹, experimental estimate [43]). The stabilization effect of one phenyl group (31.5 kcal mol⁻¹, HF/6-31G(d)) is almost as large as that of three methyl groups. However, it is reduced to 16.2 kcal mol⁻¹ if the phenyl group is forced to adopt the orthogonal configuration 4b. This suggests a π -delocalization energy of 15.3 kcal mol⁻¹ between phenyl ring and SiH₂⁺ group. Although we have not calculated the stabilizing effect of three phenyl groups, this can be predicted to be at least 50 kcal mol⁻¹.

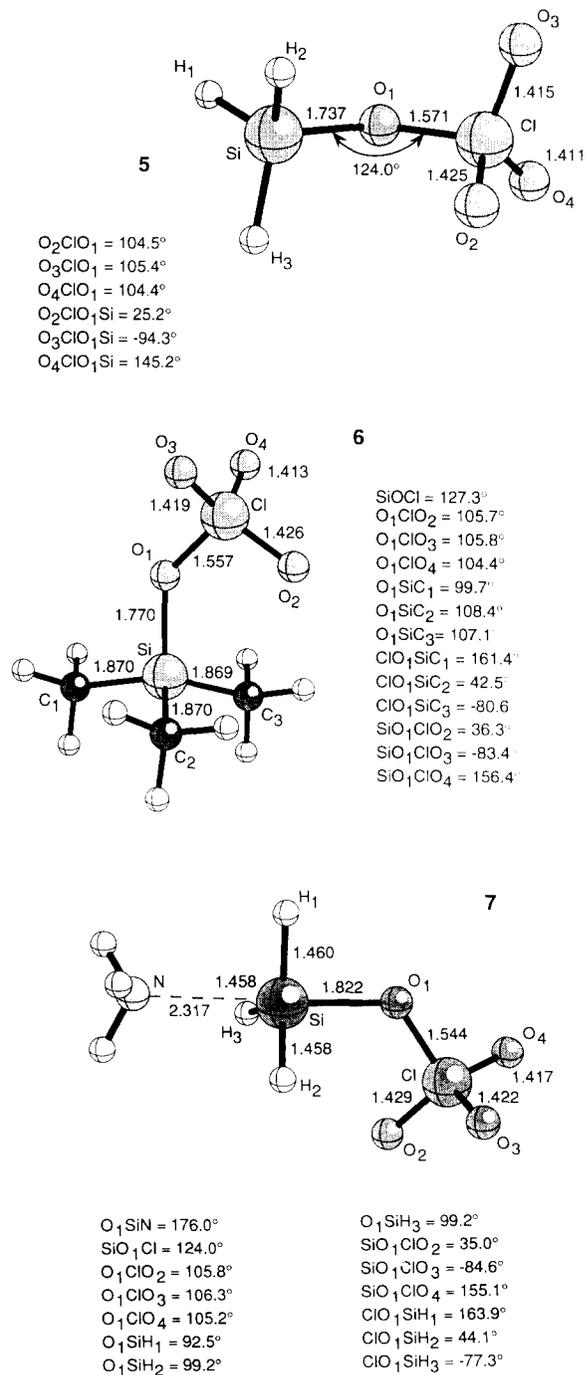


Fig. 2. HF/6-31G(d) geometries of the silyl perchlorates: SiH₃OClO₃ (5), Si(CH₃)₃OClO₃ (6), and Si(CH₃)₃OClO₃(NH₃) (7). The calculated bond lengths and angles are given in angstroms and degrees, respectively.

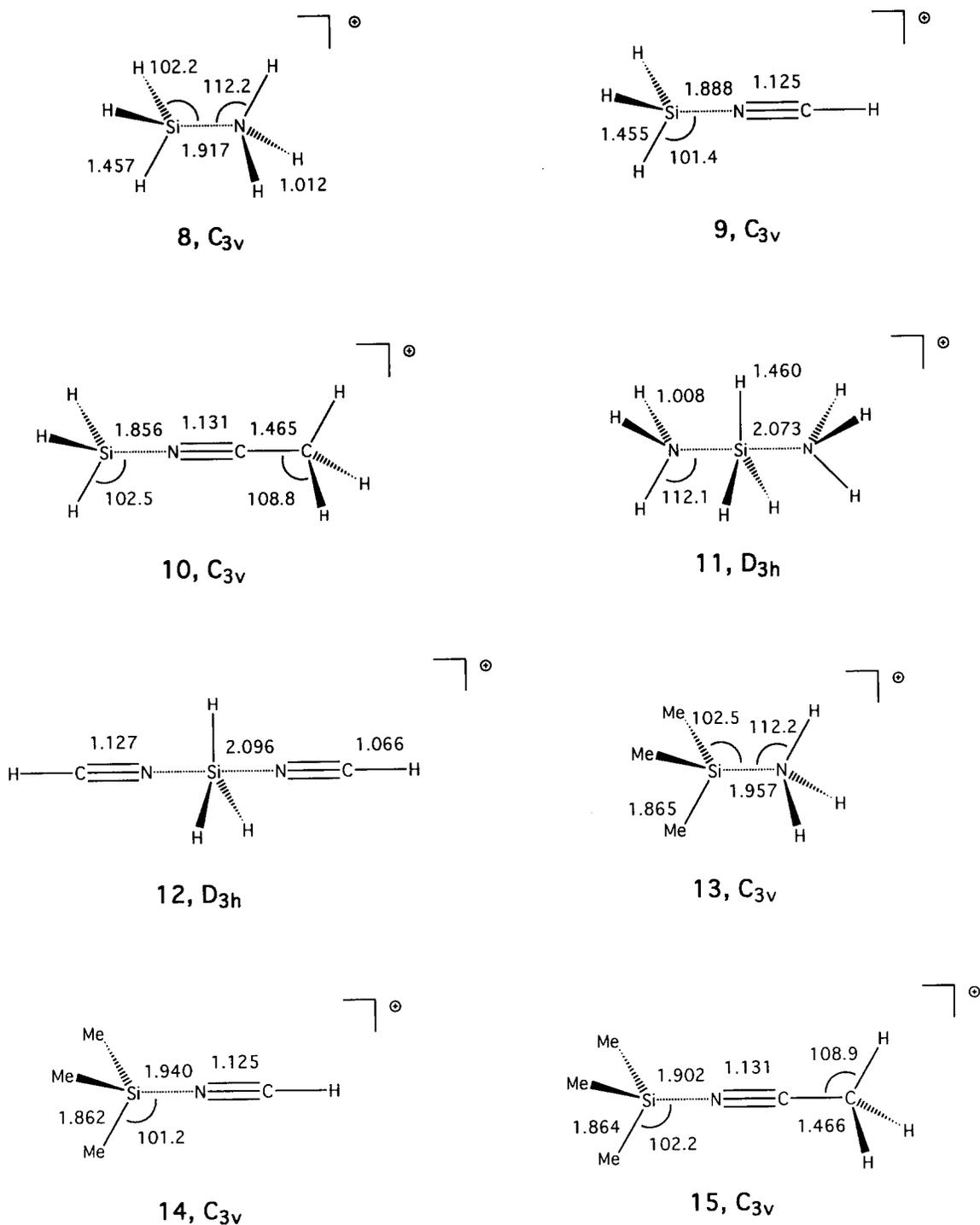


Fig. 3. HF/6-31G(d) geometries of the cations: $\text{SiH}_3(\text{NH}_3)^+$ (8), $\text{SiH}_3(\text{NCH})^+$ (9), $\text{SiH}_3(\text{NCCH}_3)^+$ (10), $\text{SiH}_3(\text{NH}_3)_2^+$ (11), $\text{SiH}_3(\text{NCH})_2^+$ (12), $\text{Si}(\text{CH}_3)_3(\text{NH}_3)^+$ (13), $\text{Si}(\text{CH}_3)_3(\text{NCH})^+$ (14), and $\text{Si}(\text{CH}_3)_3(\text{NCCH}_3)^+$ (15). The calculated bond lengths and angles are given in angstroms and degrees, respectively.

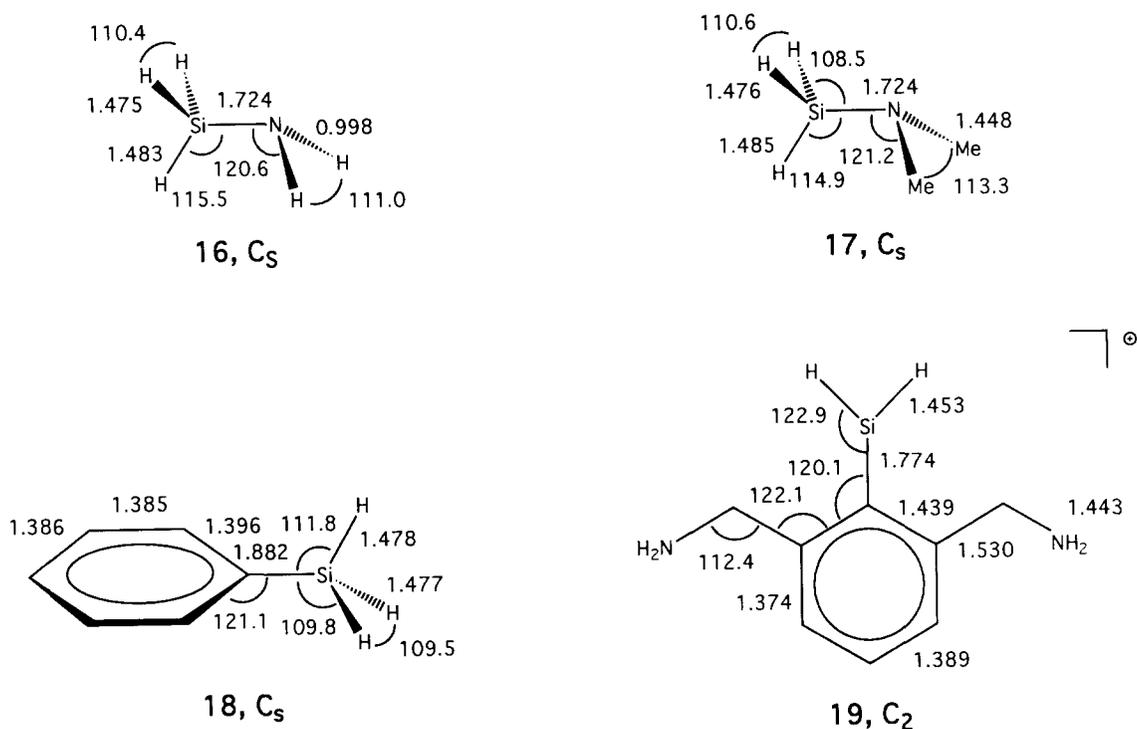


Fig. 4. HF-6-31G(d) geometries of the silicon compounds: SiH_3NH_2 (**16**), $\text{SiH}_3\text{N}(\text{CH}_3)_2$ (**17**), $\text{SiH}_3\text{C}_6\text{H}_5$ (**18**), and $\text{SiH}_2\text{C}_6\text{H}_3(\text{CH}_2\text{NH}_2)_2^+$ (**19**). The calculated bond lengths and angles are given in angstroms and degrees, respectively.

The magnitude of the hyperconjugative stabilization effects depends on the overlap between $2p\pi(\text{C})$ and $3p\pi(\text{Si})$ orbitals, which in general is considerably smaller than $2p\pi(\text{C})-2p\pi(\text{C})$ overlap and, therefore, leads to a reduction in the hyperconjugative stabilization of SiH_3X by methyl groups as compared with the corresponding stabilization of CH_3X compounds. However, a large positive charge at the silicon atom, as in a silylium cation, leads to contraction of the $3p\pi(\text{Si})$ orbital so that $3p\pi(\text{Si})-2p\pi(\text{C})$ overlap is enlarged and, accordingly, hyperconjugative stabilization and π -delocalization are improved.

For **1** and **2**, $\delta^{29}\text{Si}$ shifts of 270 and 356 ppm, respectively, were obtained at the IGLO/[7s6p2d/5s4p1d/3s1p] level of theory (Table 2), which is in line with similar values found by Kutzelnigg et al. [30] and by Olah et al. [12]. When calculations were performed with GIAO-SCF/[7s6p2d/5s4p1d/3s1p], the value obtained for **1** was 271 ppm, thus confirming the IGLO value. However, GIAO-MP2/[7s6p2d/5s4p1d/3s1p] leads to $\delta^{29}\text{Si} = 311$ ppm,

which indicates a correlation correction of 40 ppm. Recently, Gauss and Stanton [44] have shown that GIAO-MP2 slightly exaggerates correlation effects in the case of simple carbocations. Therefore, we can estimate that the true $\delta^{29}\text{Si}$ shift of **1** in the gas phase is 300 ppm and the corresponding value for **2** is 385 ppm.

In a non-coordinating solvent with a dielectricity constant $\epsilon = 80$, the shift values for **1** and **2** are reduced to 260 and 339 ppm according to PISA-IGLO calculations. As most experimental studies on potential silylium cations are carried out in solvents with much smaller dielectricity constants (e.g. sulfolane, $\epsilon = 43.3$), we can predict that $\delta^{29}\text{Si}$ changes in solvents by less than 10 ppm, provided the solvent does not coordinate with the silylium cation. For free **1** and **2** in a non-coordinating or just weakly coordinating solvent, $\delta^{29}\text{Si}$ should be 290–300 ppm and 375–385 ppm, respectively.

For **3**, another down-field shift of 30 ppm ($\delta^{29}\text{Si} = 377$ ppm, IGLO/6-31G(d)) is obtained. This suggests a gas-phase value of about 400 ppm

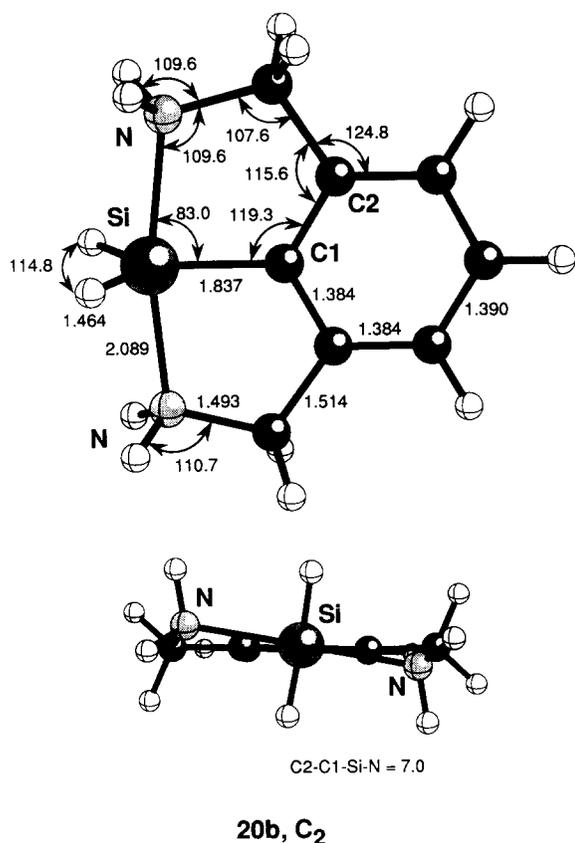


Fig. 5. HF/6-31G(d) geometry of the silylium cation $\text{SiH}_2\text{C}_6\text{H}_3(\text{CH}_2\text{NH}_2)_2^+$ (**20**). The calculated bond lengths and angles are given in angstroms and degrees, respectively.

and a solution value of 390–400 ppm in a non-coordinating solvent. As changes in $\delta^{29}\text{Si}$ become smaller on going to larger alkyl groups, we can expect that R_3Si^+ ions possess $\delta^{29}\text{Si}$ shift values of 400 ± 20 ppm in the gas phase and 380 ± 20 ppm in non-coordinating solvents.

If one hydrogen atom is replaced in **1** by a phenyl group, $\delta^{29}\text{Si}$ is shifted up-field by 70 ppm (**4a**, 200.3 ppm; Table 2). π -Delocalization including the empty $3p\pi(\text{Si})$ orbital redistributes some negative charge to the silicon atom (0.214 electron (e), Table 3), thus shielding the silicon nucleus and leading to a less positive $\delta^{29}\text{Si}$ value than in the case of alkyl substituted silylium ions. This, of course, is a somewhat simplified interpretation of the trends in the calculated shift values, because the latter depend on both the charge distribution, local anisotropies, and other effects. However, in many

cases charge effects dominate changes in shift values. Such a case is **4**, as is confirmed by the fact that rotation of the phenyl ring into a perpendicular position decreases charge transfer from the phenyl ring to silicon to 0.085 e and causes the $\delta^{29}\text{Si}$ value to increase to 266 ppm (Table 2), just 4 ppm below the IGLO value obtained for **1**.

It has been speculated that silylium cations can adopt pyramidal geometries at the silicon atom under the influence of steric or environmental forces [15]. A change from planar to pyramidal geometry has been considered as leading to large up-field shifts of $\delta^{29}\text{Si}$ values [15]. As such effects are important for understanding the experimentally observed $\delta^{29}\text{Si}$ values of potential silylium cations in solution, we calculated energy and shift changes for the case where **1** and **2** adopt pyramidal geometries with all RSiR bond angles decreasing slowly from 120° to 109.5° (**1b** and **2b**, Scheme 1). The calculated energies of **1b** and **2b** reveal that even slight distortions from planar geometry lead to a considerable destabilization of silylium cations. For a tetrahedral arrangement of SiR bonds, destabilization is as large as 24 ($\text{R} = \text{H}$) and 21 kcal mol^{-1} ($\text{R} = \text{CH}_3$), respectively (Table 1). If these calculations are repeated for a non-coordinating solvent with a dielectricity constant of $\epsilon = 80$, a similarly large energy increase (22.3 and 20.2 kcal mol^{-1}) is obtained, thus indicating that only an increase in coordination can distort silylium cations from planarity.

Pyramidalization at the silicon atom leads to a down-field shift of as much as 90 (**1b**) and 40 ppm (**2b**), indicating strong deshielding rather than shielding of the silicon nucleus. IGLO-PISA/[7s6p2d/5s4p1d/3s1p] calculations lead to similar shift changes in non-coordinating solvents (78 and 33 ppm for $\epsilon = 80$). It is interesting to note that, according to calculated charge distributions, silicon is less positive in the pyramidal forms **1b** and **2b**. Therefore, calculated down-field shifts must be dominated by changes in local anisotropies connected with the three Si-H bonds rather than changes in the charge distribution. We conclude that neither geometrical changes nor environmental effects (in non-coordinating solvents) lead to the up-field shifts of $\delta^{29}\text{Si}$ expected by experimentalists [15].

Table 1
HF/6-31G(d) energies^a

Molecule	Symmetry	Absolute energy (hartree)	Relative energy ^a (kcal mol ⁻¹)
1a SiH ₃ ⁺	D _{3h}	-290.32891	
1b SiH ₃ ⁺	C _{3v}	-290.29087	23.9 ^b
2a Si(CH ₃) ₃ ⁺	C _{3h}	-407.52782	36.0
2b Si(CH ₃) ₃ ⁺	C _{3v}	-407.49418	21.1 ^b 38.8
3 Si(CH ₂ CH ₃) ₃ ⁺	C _{3h}	-524.62670	
4a SiH ₂ C ₆ H ₅ ⁺	C _{2v}	-519.93436	
4b SiH ₂ C ₆ H ₅ ⁺	C _{2v}	-519.91034	15.1 ^c
5 SiH ₃ OCIO ₃	C ₁	-1049.18018	
6 Si(CH ₃) ₃ OCIO ₃	C ₁	-1166.33607	9.0
7 SiH ₃ OCIO ₃ (NH ₃)	C ₁	-1105.38407	12.3
8 SiH ₃ (NH ₃) ⁺	C _{3v}	-346.63727	77.8
9 SiH ₃ (NCH) ⁺	C _{3v}	-383.29905	59.6
10 SiH ₃ (NCCH ₃) ⁺	C _{3v}	-422.37113	72.0
11 SiH ₃ (NH ₃) ₂ ⁺	D _{3h}	-402.87153	109.1
12 SiH ₃ (NCH) ₂ ⁺	D _{3h}	-476.20658	79.9
13 Si(CH ₃) ₃ (NH ₃) ⁺	C _{3v}	-463.80230	56.6 14.7
14 Si(CH ₃) ₃ (NCH) ⁺	C _{3v}	-500.46694	40.1 16.5
15 Si(CH ₃) ₃ (NCCH ₃) ⁺	C _{3v}	-539.53583	50.5 14.4
16 SiH ₃ NH ₂	C _s	-346.28394	
17 SiH ₃ (CH ₃) ₂	C _s	-424.33479	
18 SiH ₃ C ₆ H ₅	C _s	-520.78034	
19 SiH ₂ C ₆ H ₅ (CH ₂ NH ₂) ₂ ⁺	C ₂	-708.04216	0
20a SiH ₂ C ₆ H ₅ (CH ₂ NH ₂) ₂ ⁺	C _{2v}	-708.17893	85.8 ^d
20b SiH ₂ C ₆ H ₅ (CH ₂ NH ₂) ₂ ⁺	C ₂	-708.17994	86.5 ^d

^a The complexation energy (first entry) and methyl stabilization energy (second entry) according to reactions (6) and (7).

^b Pyramidalization energy.

^c Rotational barrier.

^d Energy relative to **19**.

3.2. Silylperchlorates

The HF/6-31G(d) geometry of perchlorate **6** obtained in this work differs considerably from that reported by Olah et al. [12]. It seems that differences result from the fact that these authors assumed C_s symmetry for **6**, while a full geometry optimization without any symmetry constraints leads to a C₁ form of somewhat lower energy and different geometry. The same is true for SiH₃OCIO₃ (**5**), which may be best characterized by 25° and 10° rotations of the ClO₃ and SiH₃ groups out of the C_s symmetrical form (Fig. 2). The corresponding angles for **6** are 36° and 19° (Fig. 2). Parallel to these deviations from C_s symmetry is a shortening of the three Cl–O bonds, which probably results from anomeric delocalization of oxygen electron

lone pairs and hyperconjugative effects of the methyl groups. This is in line with the fact that both the Si–O and the O1–Cl bond in **6** are longer for the C₁ form than the C_s form calculated by Olah et al. [12].

Compared with a typical Si–O bond with a length of about 1.65 Å, the bond between silicon and perchlorate group is rather long (1.74 and 1.77 Å, Fig. 2). This has to do with the large group electronegativity of OClO₃ (comparison of the group electronegativities χ(OH) = 3.58, χ(Cl) = 2.94, χ(CN) = 3.78 suggests a χ value larger than 5 [45]), which leads to a relatively large positive charge at silicon in both **5** and **6** (0.913 and 1.268 e, Table 3) and a strongly polar Si–O bond as reflected by the electron density analysis (Table 4). Dissociation into SiR₃⁺ and OClO₃⁻, in particular when assisted by a polar

Table 2
IGLO/[7s6p2d/5s4p1d/3s1p] NMR chemical shifts (ppm) relative to TMS

Molecule	Symmetry	$\delta^{29}\text{Si}$	$\delta^{13}\text{C}$
1a SiH_3^+	D_{3h}	270.2	
1b SiH_3^-	C_{3v}	363.1	
2a $\text{Si}(\text{CH}_3)_3^+$	C_{3h}	355.9	9.0
2b $\text{Si}(\text{CH}_3)_3^+$	C_{3v}	397.1	23.5
3 $\text{Si}(\text{CH}_2\text{CH}_3)_3^+ \text{a}$	C_{3h}	376.9	16.5 (C_α)
4a $\text{SiH}_2\text{C}_6\text{H}_5^+$	C_{2v}	200.3	132.6 (C1), 155.7 (C2), 134.5 (C3), 164.6 (C4)
4b $\text{SiH}_2\text{C}_6\text{H}_5^+$	C_{2v}	265.6	113.5 (C1), 140.6 (C2), 138.0 (C3), 151.1 (C4)
5 $\text{SiH}_3\text{OCIO}_3$	C_1	-27.7	
6 $\text{Si}(\text{CH}_3)_3\text{OCIO}_3$	C_1	58.6 ^b	0.6 ^b
7 $\text{SiH}_3\text{OCIO}_3(\text{NH}_3)$	C_1	-93.8	
8 $\text{SiH}_3(\text{NH}_3)^+$	C_{3v}	-28.7	
9 $\text{SiH}_3(\text{NCH})^+$	C_{3v}	-26.2	123.3
10 $\text{SiH}_3(\text{NCCH}_3)^+$	C_{3v}	-35.3	140.3 (-CN), 5.6
11 $\text{SiH}_3(\text{NH}_3)_2^+$	D_{3h}	-127.7	
12 $\text{SiH}_3(\text{NCH})_2^+$	D_{3h}	-102.8	116.4
13 $\text{Si}(\text{CH}_3)_3(\text{NH}_3)^+$	C_{3v}	52.8	-1.3
14 $\text{Si}(\text{CH}_3)_3(\text{NCH})^+$	C_{3v}	67.0	-1.0, 121.2 (CN)
15 $\text{Si}(\text{CH}_3)_3(\text{NCCH}_3)^+$	C_{3v}	52.2	-0.9 (Si), 136.4 (CN), 5.0 (C)
16 SiH_3NH_2	C_s	-56.6	
17 $\text{SiH}_3\text{N}(\text{CH}_3)_2$	C_s	-68.1	149.1
18 $\text{SiH}_3\text{C}_6\text{H}_5$	C_s	-60.8	135.6 (C1), 144.3 (C2), 134.6 (C3), 138.2 (C4)
19 $\text{SiH}_2\text{C}_6\text{H}_3(\text{CH}_2\text{NH}_2)_2^+ \text{b}$	C_2	179.4	141.6 (C1), 166.0 (C2), 130.6 (C3), 168.4 (C4), 37.9 (C7)
20a $\text{SiH}_2\text{C}_6\text{H}_3(\text{CH}_2\text{NH}_2)_2^+ \text{b}$	C_{2v}	-77.4	122.6 (C1), 147.6 (C2), 129.4 (C3), 142.5 (C4), 40.3 (C7)
20b $\text{SiH}_2\text{C}_6\text{H}_3(\text{CH}_2\text{NH}_2)_2^+ \text{b}$	C_2	-80.5	123.7 (C1), 147.3 (C2), 130.2 (C3), 142.1 (C4), 40.6 (C7)

^a No polarization functions used for hydrogen atoms.

^b Calculated with the 6-31G(d) basis set.

medium, should be facilitated. Association with solvent molecules accompanied by charge transfer to the positively charged silicon atom will already have occurred in the undissociated state (see below) and, therefore, the properties of perchlorates **5** and **6** in solution will deviate from those in the gas phase.

The IGLO $\delta^{29}\text{Si}$ chemical shifts for **5** and **6** are -27.7 and 58.6 ppm, respectively (Table 2). In the latter case the 6-31G(d) basis had to be used because of computational limitations. Experimental measurements led to $\delta^{29}\text{Si}$ values between 27 and 47 ppm, depending on the solvent used [12,24]. Olah et al. [12] obtained from IGLO/[7s6p2d/5s4p1d/3s] calculations a $\delta^{29}\text{Si}$ value of 40.2 ppm for **6**, which is seemingly in better agreement with experimental $\delta^{29}\text{Si}$ values. However, in view of the fact that these authors used a non-equilibrium geometry for their IGLO calculations, agreement can only be accidental, prob-

ably disguising the fact that free perchlorate (**6**) has a much higher $\delta^{29}\text{Si}$ value.

This seems to be confirmed by the investigation of the solvent complex between **5** and NH_3 , namely complex **7**. According to HF/6-31G(d), **7** has a relatively large dissociation energy of 12.5 kcal mol⁻¹ (Table 1) because of charge transfer from NH_3 to **5** (Table 3) and electrostatic interactions between the two molecules. The Si-N distance for complex **7** (2.32 Å, Fig. 2) is close to that found for silatranes (2.2–2.3 Å) [46], while the Si-O bond (1.82 Å) is 0.1 Å longer than in gaseous **5**. The density analysis (Table 4) reveals a weak (polar) covalent bond between silicon and NH_3 that would develop further if the interaction distance became shorter. Complexation with NH_3 leads to substantial planarization of the SiH_3 group, but the geometry of the ClO_3 group is largely unaffected by this.

Obviously, silicon has a strong tendency to

Table 3
Calculated charges^a

Molecule	Symmetry	$q(\text{Si})$ (e)	$q(\text{SiH}_n)$ (e)	Charge transfer from solvent
1a SiH_3^+	D_{3h}	0.932	1.000	
1b SiH_3^+	C_{3v}	0.902	1.000	
2a $\text{Si}(\text{CH}_3)_3^+$	C_{3h}	1.161	1.161	
2b $\text{Si}(\text{CH}_3)_3^+$	C_{3v}	1.079	1.079	
3 $\text{Si}(\text{CH}_2\text{CH}_3)_3^+$	C_{3h}	1.162	1.162	
4a $\text{SiH}_2\text{C}_6\text{H}_5^+$	C_{2v}	0.826	0.785	
4b $\text{SiH}_2\text{C}_6\text{H}_5^+$	C_{2v}	0.945	0.915	
5 $\text{SiH}_3\text{OCIO}_3$	C_1	0.913	0.581	
6 $\text{Si}(\text{CH}_3)_3\text{OCIO}_3$	C_1	1.270	1.270	
7 $\text{Si}(\text{CH}_3)_3\text{OCIO}_3(\text{NH}_3)$	C_1	0.942	0.551	0.121
8 $\text{SiH}_3(\text{NH}_3)^+$	C_{3v}	0.817	0.655	0.345
9 $\text{SiH}_3(\text{NCH})^+$	C_{3v}	0.844	0.700	0.300
10 $\text{SiH}_3(\text{NCCH}_3)^+$	C_{3v}	0.827	0.651	0.349
11 $\text{SiH}_3(\text{NH}_3)_2^+$	D_{3h}	0.883	0.555	0.445
12 $\text{SiH}_3(\text{NCH})_2^+$	D_{3h}	0.935	0.701	0.299
13 $\text{Si}(\text{CH}_3)_3(\text{NH}_3)^+$	C_{3v}	1.184	0.732	0.268
14 $\text{Si}(\text{CH}_3)_3(\text{NCH})^+$	C_{3v}	1.183	0.779	0.221
15 $\text{Si}(\text{CH}_3)_3(\text{NCCH}_3)^-$	C_{3v}	1.171	0.728	0.272
16 SiH_3NH_2	C_s	0.811	0.315	
17 $\text{SiH}_3\text{N}(\text{CH}_3)_2$	C_s	0.821	0.323	
18 $\text{SiH}_3\text{C}_6\text{H}_5$	C_s	0.652	0.207	
19 $\text{SiH}_2\text{C}_6\text{H}_5(\text{CH}_2\text{NH}_2)_2^+$	C_2	0.781	0.710	
20a $\text{SiH}_2\text{C}_6\text{H}_5(\text{CH}_2\text{NH}_2)_2^+$	C_{2v}	0.951	0.695	0.305
20b $\text{SiH}_2\text{C}_6\text{H}_5(\text{CH}_2\text{NH}_2)_2^+$	C_2	0.948	0.701	0.305

^a Calculated at the HF/6-31G(d) level.

coordinate with a solvent molecule of sufficiently large donicity such as NH_3 and to approach a pentacoordinated state with trigonal bipyramidal geometry [46]. IGLO $\delta^{29}\text{Si}$ chemical shifts reveal that the degree of coordination is reflected by an up-field shift of 66 ppm (Table 2) relative to the uncomplexed parent compound **5**. One could expect that the change in $\delta^{29}\text{Si}$ is caused by a transfer of negative charge from NH_3 to **5**. Although this charge transfer really occurs (0.121 e , Table 3), the charge transferred remains only in smaller part at the SiH_3 group while the larger part is passed on to the OCIO_3 substituent. Obviously, OCIO_3 has already been prepared in the complexation process to leave **7** as an anion. Our calculations suggest that the up-field shift of $\delta^{29}\text{Si}$ is more a consequence of changes in the geometry at the silicon atom rather than the charge transfer from NH_3 . Complexation by the solvent molecule enforces planarization of the SiH_3 group, which leads to an up-field shift of

$\delta^{29}\text{Si}$, as discussed above (pyramidalization of SiH_3 leads to a down-field shift).

We conclude that in solution, silylperchlorates such as **5** and **6** will associate with solvent molecules (S) to form pentacoordinated silicon compounds with almost planar silyl groups and relatively short Si–S interaction distances. Solvation of perchlorates can be detected by large up-field shifts, particularly, if strong nucleophilic solvents (DMPU, HMPA, pyridine, etc.) are used.

3.3. Solvated silylium cations

All the molecular data calculated for complexes $\text{SiR}_3(\text{S})_n^+$ with $\text{S} = \text{NH}_3$, HCN or CH_3CN (**8–15**) suggest that these ions are covalently bonded silicon compounds with tetra- or penta-coordinated silicon.

All the calculated complexation energies (Table 1) are rather large and are typical of

Table 4
Bond density analysis^a

Molecule	Symmetry	Atoms involved	Distance A–B (Å)	Type of critical point ^a	$\rho(r_b)$ ($e \text{ \AA}^{-3}$)	$H(r_b)$ (hartree \AA^{-3})	Character of bond ^c
3	$\text{Si}(\text{CH}_2\text{CH}_3)_3^+$	Si, C	1.857	(3, –1)	0.89	–0.57	Covalent
4a	$\text{SiH}_2\text{C}_6\text{H}_5^+$	Si, C	1.773	(3, –1)	0.96	–0.57	Covalent
4b	$\text{SiH}_2\text{C}_6\text{H}_5^+$	Si, C	1.820	(3, –1)	0.94	–0.61	Covalent
5	$\text{SiH}_3\text{OCIO}_3$	Si, O	1.737	(3, –1)	0.64	–0.05	(Covalent)
6	$\text{Si}(\text{CH}_3)_3\text{OCIO}_3$	Si, O	1.770	(3, –1) ^b	0.58	–0.05	(Covalent)
		Si, Cl1	1.870	(3, –1) ^b	0.84	–0.49	Covalent
		Si, Cl2	1.870	(3, –1) ^b	0.84	–0.49	Covalent
		Si, Cl3	1.870	(3, –1)	0.84	–0.49	Covalent
7	$\text{Si}(\text{CH}_3)_3\text{OCIO}_3(\text{NH}_3)$	Si, O	1.822	(3, –1)	0.51	–0.05	(Covalent)
		Si, N	2.317	(3, –1) ^b	0.23	–0.05	(Covalent)
8	$\text{SiH}_3(\text{NH}_3)^+$	Si, N	1.917	(3, –1)	0.53	–0.13	Covalent
9	$\text{SiH}_3(\text{NCH})^+$	Si, N	1.888	(3, –1)	0.49	–0.06	(Covalent)
10	$\text{SiH}_3(\text{NCCH}_3)^+$	Si, N	1.856	(3, –1)	0.53	–0.07	(Covalent)
11	$\text{SiH}_3(\text{NH}_3)_2^+$	Si, N	2.073	(3, –1)	0.37	–0.09	(Covalent)
12	$\text{SiH}_3(\text{NCH})_2^+$	Si, N	2.096	(3, –1)	0.30	–0.05	(Covalent)
13	$\text{Si}(\text{CH}_3)_3(\text{NH}_3)^+$	Si, N	1.957	(3, –1)	0.49	–0.12	Covalent
14	$\text{Si}(\text{CH}_3)_3(\text{NCH})^+$	Si, N	1.940	(3, –1)	0.43	–0.06	(Covalent)
15	$\text{Si}(\text{CH}_3)_3(\text{NCCH}_3)^+$	Si, N	1.902	(3, –1)	0.47	–0.07	(Covalent)
16	SiH_3NH_2	Si, N	1.724	(3, –1)	0.83	–0.25	Covalent
17	$\text{SiH}_3\text{N}(\text{CH}_3)_2$	Si, N	1.724	(3, –1)	0.85	–0.27	Covalent
18	$\text{SiH}_3\text{C}_6\text{H}_5$	Si, C	1.882	(3, –1)	0.83	–0.47	Covalent
20b	$\text{SiH}_2\text{C}_6\text{H}_3(\text{CH}_2\text{NH}_2)_2^+$	Si, N	2.089	(3, –1)	0.38	–0.11	Covalent

^a Each point r_b is characterized by (rank, signature).

^b Another critical point is located in the vicinity indicating an insufficient description of the electron density by the basis set used.

^c The character of the bond is given according to the criteria of Cremer and Kraka [38]. The notation “(covalent)” indicates a strongly polar, covalent bond.

covalent Si–N bonds. For $R = \text{H}$, they are between 60 and 80 kcal mol^{–1}, while for $R = \text{CH}_3$ the corresponding values are 20 kcal mol^{–1} smaller. When a second solvent molecule is associated, the total complexation energy can be as large as 80–110 kcal mol^{–1}, which means that complexation energies are not additive. The first solvent molecule seems to hinder somewhat the association of the second one.

HF/6-31G(d) geometries (Fig. 3) are characterized by Si–N interaction distances that are only 0.2–0.3 Å longer than the Si–N bond lengths (1.72 Å) obtained for SiH_3NH_2 (**16**) or $\text{SiH}_3\text{N}(\text{CH}_3)_2$ (**17**) (see Fig. 4).

For complexes with tetracoordinated silicon, the SiH_3 and SiMe_3 groups are pyramidal with HSiS or CSiS angles of about 101°. Trigonal bipyramidal configurations are found for pentacoordinated silicon (**11** and **12**).

There is a charge transfer of about 0.22 e (to a maximum of 0.44 e) from the associated solvent molecules to the SiR_3 group (Table 3). The charge at the silicon atom is smaller than for a silylium cation, but similar to that found for neutral covalent compounds (SiR_3X), which means that the positive charge is shared between S and the R substituents. The latter are less negatively charged, as in covalent compounds SiR_3X [41].

For all the complexes investigated, the properties of electron density and energy density indicate covalent Si–N bonding (Table 4).

IGLO NMR $\delta^{29}\text{Si}$ values are indicative of strong shielding of the silicon nucleus, similar to that found for covalent compounds.

According to the calculated properties, the silylium cation character has been totally lost in complexes **8–15**. A better characterization of these ions might be given if one speaks of pro-

Table 5
Calculated and estimated $\delta^{29}\text{Si}$ NMR chemical shifts (ppm) relative to TMS^a

Solvent, S	$\text{H}_3\text{SiOCIO}_3^{\text{b}}$	$\text{H}_3\text{SiOCIO}_3(\text{S})$	$\text{H}_3\text{Si}(\text{S})^+$	$\text{H}_3\text{Si}(\text{S})_2^{\ddagger}$
NH_3	-27.7	-93.8	-28.7	-127.7
NCH		(-94)	-26.2	-102.8
NCCH ₃		(-94)	-35.3	(-120)
Solvent, S	$\text{Me}_3\text{SiOCIO}_3^{\text{b}}$	$\text{Me}_3\text{SiOCIO}_3(\text{S})$	$\text{Me}_3\text{Si}(\text{S})^+$	$\text{Me}_3\text{Si}(\text{S})_2^{\ddagger}$
NH_3	58.6	(-7)	52.8	(4)
NCH		(-7)	67.0	(29)
NCCH ₃		(-7)	52.2	(10)
Solvent, S	$\text{Et}_3\text{SiOCIO}_3^{\text{b}}$	$\text{Et}_3\text{SiOCIO}_3(\text{S})$	$\text{Et}_3\text{Si}(\text{S})^+$	$\text{Et}_3\text{Si}(\text{S})_2^{\ddagger}$
NH_3	(79)	(13)	(72)	(23)
NCH		(13)	(86)	(48)
NCCH ₃		(13)	(71)	(30)

^a Estimated shifts (in parentheses) were obtained by using appropriate increments (see text).

^b Gas-phase values.

tonated (**8**, **9**, **11–14**) or CH_3^+ substituted (**10** and **15**) covalent SiR_3X compounds. However, the large positive charge at silicon might justify speaking of tetra- and penta-coordinated silyl cations, where in the later case the term "siliconium ions" might also be justified. This, however, would ignore the fact that the positive charge at silicon is actually similar to that of covalent compounds, which means that it is smaller than in the case of silylium cations.

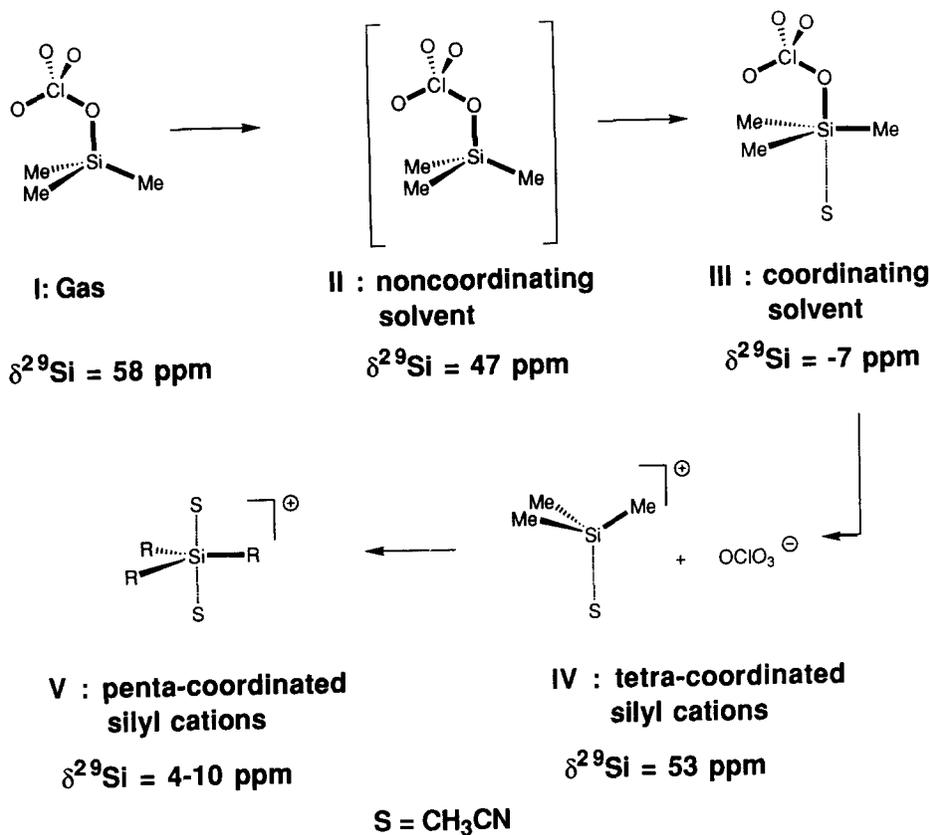
Some trends in the calculated properties deserve further discussion. As mentioned above, three methyl groups stabilize a silylium cation by hyperconjugative interactions. σ -Electrons are withdrawn from the silicon atom by the methyl groups, but some of this charge is back-donated via the pseudo- π -orbitals of CH_3 . Back-donation is facilitated by the fact that the total charge of +1 leads to a contraction of the $3p\pi(\text{Si})$ orbital and an enlargement of the $2p\pi(\text{C})-3p\pi(\text{Si})$ overlap. As there is more electronic charge in the $3p\pi(\text{Si})$ orbital in an alkyl substituted silylium cation than in **1**, the charge transfer from a solvent molecule to the $3p\pi(\text{Si})$ orbital (Table 3) and, accordingly, Si-S interactions are reduced, thus leading to smaller complexation energies (Table 1). Population of the $3p\pi(\text{Si})$ orbital is also the reason why a second solvent molecule has a

smaller effect with regard to charge transfer and complexation energy.

The IGLO $\delta^{29}\text{Si}$ shifts reveal that complexation of a silylium cation by a solvent molecule leads to an up-field shift of about 300 ppm. The $\delta^{29}\text{Si}$ value for **8–10** is about -30 ppm, which is not greatly different from the $\delta^{29}\text{Si}$ shift of SiH_3NH_2 (**16**, -56.6 ppm; Table 2), while the corresponding values for **13–15** are 80–90 ppm at lower field (Table 2). The addition of a second solvent molecule leads to an up-field shift of 99 (**11**) and 77 ppm (**12**, Table 2), respectively, where these shift changes are mainly caused by planarization at the silicon atom, but less by additional charge transfer to silicon.

Both the experimental and the calculated $\delta^{29}\text{Si}$ shifts suggest that one can predict unknown values by using appropriate shift increments for substituents. The shift data shown in Table 5 are based on this assumption. They suggest that the generation of silylium cations and their fate in solutions can be monitored by $\delta^{29}\text{Si}$ measurements (see Scheme 2).

In weakly nucleophilic solvents such as CH_2Cl_2 , the gas phase value (**I**) of $\text{Me}_3\text{SiOCIO}_3$ (**6**) is reduced from 58 to about 47 ppm (**II**). If a stronger solvent such as acetonitrile is used, a complex with pentacoordinated silicon will be formed and $\delta^{29}\text{Si}$



Scheme 2.

is reduced to -7 ppm (**III**). In such a solvent, ionization may already be possible. But this would lead to tetracoordinated silicon cations with $\delta^{29}\text{Si} = 53$ ppm (**IV**) rather than free tricoordinated silylium cations with a much more positive $\delta^{29}\text{Si}$ value. It is likely that a tetracoordinated silicon cation is attacked by another solvent molecule of sufficiently large donicity. The resulting pentacoordinated silicon cation (**V**) would possess a $\delta^{29}\text{Si}$ value of about 10 ppm if $\text{S} = \text{CH}_3\text{CN}$.

Hence, the problem is that both structures **II** and **IV** possess similar $\delta^{29}\text{Si}$ shift values and the same is true for **III** and **V**. Therefore, without additional information resulting, for example, from conductivity measurements or from quantum chemical shift calculations, it is rather difficult to associate a given $\delta^{29}\text{Si}$ value of a silyl perchlorate with one of the structures **II**–**V**. For

example, $\delta^{29}\text{Si}$ values of about 45 ppm have been reported for **6** in CH_2Cl_2 which, according to the discussion given above, should result from weak association between **6** and a solvent molecule (**II**). Lambert and Zhang [14] have found for $\text{Et}_3\text{SiB}(\text{C}_6\text{F}_5)_4$ in CD_3CN a shift value of 36.7 ppm. According to Table 5, this $\delta^{29}\text{Si}$ value can only correspond to structure **V** with penta-coordinated silicon (30 ppm, estimated from ethyl group increments; Table 2), but not to structures **III** or **IV** (estimated $\delta^{29}\text{Si}$ values, 13 and 73 ppm). In other words, $\text{Et}_3\text{SiB}(\text{C}_6\text{F}_5)_4$ in CD_3CN forms a pentacoordinated siliconium ion rather than a tricoordinated silylium cation.

Xie et al. [25] have measured $\delta^{29}\text{Si} = 33.8$ ppm for $(i\text{-Pr})_3\text{Si}^+(\text{Br}_5\text{CB}_9\text{H}_5)^-$ in CD_3CN and have assigned this value to a structure **IV** complex between $(i\text{-Pr})_3\text{Si}^+$ and acetonitrile because such a complex was found in the solid state [25]. As ethyl

and iso-propyl substituents should lead to similar $\delta^{29}\text{Si}$ values (Et_3SiH , 2.5 ppm; $(i\text{-Pr})_3\text{SiH}$, 12.1 ppm [25]) and as structure **IV** with tetracoordinated silicon would imply a shift value of 70–80 ppm, it is more likely that Xie et al. observed a structure **V** complex (30–40 ppm), which they included as a possibility in their discussion of experimental results [25].

These examples clearly show that further experiments with varying solvents and counter ions are needed to describe silylperchlorate dissociation and the fate of silylium cations in solution. These investigations have to be supported by ab initio studies in order to verify and analyse experimental observations.

4. Intramolecular complexation as a model for silylium cation solvation

When going from cation **4** to the C_2 symmetrical cation **19**, which possesses a disubstituted phenyl ring, $\delta^{29}\text{Si}$ decreases from 200 to 179 ppm (Table 2). This is in line with an increase in the π -electron density in the phenyl ring caused by the two CH_2NH_2 substituents and stronger π -electron donation by the phenyl ring to the silicon atom. Cation **19** should have a somewhat higher rotational barrier than **4a**, but its orthogonal form should possess a similar electronic structure at the silicon atom and, hence, a similar $\delta^{29}\text{Si}$ shift value as for **4b**.

Rotation of the SiH_2 group of **19** is most probably coupled with rotations of the two CH_2NH_2 groups, thus leading to **20** (see Scheme 1). Similar to **19**, the CH_2NH_2 groups of **20** are slightly distorted out of the plane of the phenyl ring so that bond eclipsing is reduced and the molecule adopts C_2 symmetry. The C_2 form **20b** is just $0.7 \text{ kcal mol}^{-1}$ more stable than the C_{2v} symmetrical form **20a**, which means that at room temperature **20a** and **20b** are related by a large amplitude vibration and that the cation has, on average, C_{2v} symmetry. In **20**, the two amino groups can donate negative charge to the $3p\pi$ -orbital of silicon, thus stabilizing the silylium cation by intramolecular complexation. At HF/6-31G(d), **20** is more stable

than **19** by about 86 kcal mol^{-1} (Table 1) which, in view of the rotational barrier of the SiH_2 group in **19** of at least 15 kcal mol^{-1} (compare with **4a** and **4b**), suggests that the two NH_2 groups stabilize the SiH_2 group by at least $101 \text{ kcal mol}^{-1}$. As the complexation energy of **11** is $109.5 \text{ kcal mol}^{-1}$ (Table 1), it seems that **20** loses only 8 kcal mol^{-1} of the complexation energy of an intermolecularly solvated silylium cation.

However, a $-\text{CH}_2\text{NH}_2$ group should have a larger donicity than a NH_3 molecule. Comparison of **9** and **10** or **14** and **15** suggests a $10\text{--}12 \text{ kcal mol}^{-1}$ increase in the complexation energy caused by a methyl group [46]. Hence, we can expect that two $-\text{CH}_2\text{NH}_2$ substituents will increase the complexation energy by $20\text{--}25 \text{ kcal mol}^{-1}$. Coordination of the two NH_2 groups at silicon forces the Si-H , N-H and C-H bonds of **20** into eclipsed positions, leading to about 8 kcal mol^{-1} eclipsing strain. In addition, the NH_2 groups cannot orient their lone-pair orbitals in such a way that maximum overlap with the $3p\pi(\text{Si})$ orbital is guaranteed. The calculated geometry of **20** shown in Fig. 5 reveals that the NSiC angle is 83° , thus deviating from the ideal value of 90° by 7° . As a consequence, the Si-N interaction distance (2.089 \AA , Fig. 5) is somewhat longer, as in **11** (2.073 \AA , Fig. 3).

Intramolecular solvation leads to an up-field shift of $\delta^{29}\text{Si}$ from 179.4 to 80.5 ppm (Table 2) where again charge transfer ($0.305 e$; Table 3) accompanied by covalent Si-N bonding (Table 4) is the reason for the shift change. In order to compare the reliability of $\delta^{29}\text{Si}$ IGLO values, we compared the calculated $\delta^{29}\text{Si}$ values with the experimental $\delta^{29}\text{Si}$ of -46.4 ppm determined for ion **21**, which was synthesized by Chuit et al. [27]. As **21** could not be calculated because of computational limitations, we estimated its $\delta^{29}\text{Si}$ shift value by using appropriate model compounds to establish a dimethyl increment. Compounds **16** and **17** turned out not to be useful in this respect because they possess tetrahedral rather than trigonal bipyramidal geometry at the silicon atom and, therefore, the corresponding shift increment is negative (-11.5 ppm ; Table 2) rather than positive. A more reasonable shift increment of 36.6 ppm was obtained by using cation **11** and the corresponding tetramethyl derivative, where in

both cations the Si–N distances, were fixed at 2.09 Å (see Fig. 5). Adding the calculated increment to the shift value of **20b**, we predict $\delta^{29}\text{Si} = -43.9$ ppm for **21** in good agreement with the experimental value (-46.4 ppm [27]). This we consider as convincing proof for the similarity of the electronic structure at the silicon atom in both **20** and **21**. We conclude that both cations contain a pentacoordinated silicon atom with two covalent Si–N bonds (Table 4). The silylium cation character has been lost in **20** and **21**, but in view of the calculated charge distribution it is also not justifiable to speak of siliconium ions. The positive charge at silicon is similar to that in $\text{SiH}_3\text{C}_6\text{H}_5$ (**18**), while the positive charge of +1 is spread over H(Si) atoms, $-\text{CH}_2\text{NH}_2$ groups, and the phenyl ring.

Ions **20** and **21** are suitable models for intramolecular complexation of silylium cations in solution. By replacing the CH_2NR_2 groups by CH_2OR , CH_2SR , CH_2SOR , $\text{CH}_2\text{SO}_2\text{R}$, $\text{CH}_2\text{C}(=\text{O})\text{R}$, etc., complexation of a SiR_3^+ ion can be studied, and by parallel ab initio studies the electronic nature of the coordination complex can be determined.

5. Conclusions

The following conclusions can be drawn from the calculations presented in this paper.

(1) Silylium cations SiR_3^+ (R = alkyl) in the gas phase have $\delta^{29}\text{Si}$ shift values between 300 (R = H, estimated from IGLO and GIAO-MP2) and 400 ppm (R = Et). Phenyl groups lead to a considerable up-field shift of $\delta^{29}\text{Si}$ due to π -donation by the phenyl ring to the empty $3p\pi$ orbital of silicon. The value calculated for **4a** is 200 ppm.

(2) In non-coordinating solvents, the $\delta^{29}\text{Si}$ value is shifted slightly up-field, but the effect is rather small. Enforced pyramidalization leads to a 40–90 ppm down-field shift. The pyramidal forms of silylium cations are more than 20 kcal mol⁻¹ less stable.

(3) Silylium cations form with nucleophilic solvent molecules (S) strong coordination complexes with tetra- and penta-coordinated silicon. Bonding

between silicon and solvent is covalent for the cases investigated in this work (S = NH_3 , HCN or CH_3CN), as revealed by complexation energies, Si–S bond distances, gross atomic charges, and the properties of electron and energy density distributions in the bonding region.

(4) The situation is similar in the intramolecularly solvated cations **20** and **21**, although the complexation energy for **20** indicates that coordination is somewhat weaker than in intermolecularly solvated silylium cations. Complexes such as **20** are suitable models for investigating silylium cation–solvent interactions.

(5) In coordinating solvents with nucleophilic character, silylium cations are probably not generated in their free form. Investigation of silylperchlorates reveals that in solution the silicon atom of a silyl perchlorate is already pentacoordinated. Charge transfer from the solvent molecule facilitates dissociation to a perchlorate anion and a tetracoordinated silyl cation. The life-time of the latter may be rather short, because coordination with another solvent molecule leads to more stable pentacoordinated silyl cations.

(6) Analysis of the available experimental $\delta^{29}\text{Si}$ NMR chemical shifts for SiR_3 cations (R = Me, Et or *i*-Pr) in acetonitrile suggests the existence of pentacoordinated, rather than tri- or tetra-coordinated, silyl cations [14,24,25].

Work is in progress to extend the investigations presented in this work to other solvents and to establish ranges of $\delta^{29}\text{Si}$ values in order to identify forms **I** to **V** shown in Scheme 2.

Acknowledgement

This work was supported by the Swedish Natural Science Research Council (NFR). All calculations were done on the CRAY XMP/416 computer of the Nationellt Superdatorcentrum (NSC), Linköping, Sweden. The authors thank the NSC for a generous allotment of computer time. Technical assistance in some of the calculations by Dr. Elfi Cremer is acknowledged. We thank Professor Peter Pulay for providing a copy of his GIAO-SCF program.

References

- [1] We use the term "silylium cation" for R_3Si^+ rather than silicenium ion, silylenium ion or silyl cation, thus following recent IUPAC recommendations. See: G.J. Leigh (Ed.), *Nomenclature of Inorganic Chemistry*, Blackwell, Oxford, 1990, p. 106.
- [2] For a recent review of the work on silylium cations, see: P.D. Lickiss, *J. Chem. Soc., Dalton Trans.*, (1992) 1333, and references therein.
- [3] (a) R.J.P. Corriu and M. Henner, *J. Organomet. Chem.*, 74 (1974) 1.
(b) D.H. O'Brien and T. Hairston, *J. Organomet. Chem. Rev. A*, 7 (1971) 95.
- [4] J.B. Lambert and W.J.J. Schulz, *J. Am. Chem. Soc.*, 105 (1983) 1671.
- [5] J.B. Lambert, J.A. McConnell and W.J.J. Schulz, *J. Am. Chem. Soc.*, 108 (1986) 2482.
- [6] J.B. Lambert and W. Schilif, *J. Am. Chem. Soc.*, 110 (1988) 6364.
- [7] J.B. Lambert, W.J.J. Schulz, J.A. McConnell and W. Schilif, *J. Am. Chem. Soc.*, 110 (1988) 2201.
- [8] J.B. Lambert, L. Kania, W. Schilf and J.A. McConnell, *Organometallics*, 10 (1991) 2578.
- [9] A.H. Cowley, M.C. Cushner and P.E. Riley, *J. Am. Chem. Soc.*, 102 (1980) 624.
- [10] G.A. Olah, L. Heiliger, X.Y. Li and G.K.S. Prakash, *J. Am. Chem. Soc.*, 112 (1990) 5991.
- [11] G.K.S. Prakash, S. Keyaniyan, R. Aniszfeld, L. Heiliger, G.A. Olah, R.C. Stevens, H.K. Choi and R. Bau, *J. Am. Chem. Soc.*, 109 (1987) 5123.
- [12] G.A. Olah, G. Rasul, L. Heiliger, J. Bausch and G.K.S. Prakash, *J. Am. Chem. Soc.*, 114 (1992) 7737.
- [13] C. Eaborn, *J. Organomet. Chem.*, 405 (1991) 173.
- [14] J.B. Lambert and S. Zhang, *J. Chem. Soc., Chem. Commun.*, (1993) 383.
- [15] J.B. Lambert, S. Zhang, C.L. Stern and J.C. Huffman, *Science*, 260 (1993) 1917.
- [16] Z. Xie, D.J. Liston, T. Jelinek, V. Mitro, R. Bau and C.A. Reed, *J. Chem. Soc., Chem. Commun.*, (1993) 384.
- [17] (a) Y. Apeloig and P.v.R. Schleyer, *Tetrahedron Lett.*, (1977) 4647.
(b) Y. Apeloig, S.A. Godleski and D.J. Heacock, *Tetrahedron Lett.*, 22 (1981) 3297.
(c) T. Truong, M.S. Gordon and P. Boudjouk, *Organometallics*, 3 (1984) 484.
- [18] (a) W.P. Weber, R.A. Felix and A.K. Willare, *Tetrahedron Lett.*, (1970) 907.
(b) M.R. Litzow and T.R. Spaulding, in M.F. Lappert (Ed.), *Mass Spectrometry of Inorganic and Organometallic Compounds*, Physical Inorganic Chemistry Monograph 2, Elsevier, New York, 1973, Chap. 7, and references therein.
- [19] (a) M.K. Murphy and J.L. Beauchamp, *J. Am. Chem. Soc.*, 98 (1976) 5781.
(b) M.K. Murphy and J.L. Beauchamp, *J. Am. Chem. Soc.*, 99 (1977) 2085.
- [20] L. Olsson and D. Cremer, *Chem. Phys. Lett.*, 215 (1993) 433.
- [21] P.v.R. Schleyer, P. Buzek, T. Müller, Y. Apeloig and H.U. Siehl, *Angew. Chem.*, 105 (1993) 1558.
- [22] (a) J.M. Stone and J.A. Stone, *Int. J. Mass Spectrom. Ion Process.*, 109 (1991) 247.
(b) A.C.M. Woytyniak and J.A. Stone, *Int. J. Mass Spectrom. Ion Process.*, 74 (1986) 59.
- [23] G. Cacace, M.E. Crestoni, S. Fornarini and R. Gabrielli, *Int. J. Mass Spectrom. Ion Process.*, 84 (1988) 17.
- [24] U. Edlund, private communication.
- [25] Z. Xie, D.J. Liston, T. Jelinek, V. Mitro, R. Bau and C.A. Reed, *J. Chem. Soc., Chem. Commun.*, (1993) 384.
- [26] K. Hensen, T. Zengerly, P. Pickel and G. Klebe, *Angew. Chem.*, 95 (1983) 739.
- [27] C. Chuit, R.J.P. Corriu, A. Mehdi and C. Reye, *Angew. Chem.*, 105 (1993) 1372.
- [28] P.C. Hariharan and J.A. Pople, *Theor. Chim. Acta*, 28 (1973) 213.
- [29] (a) W. Kutzelnigg, *Isr. J. Chem.*, 19 (1980) 193.
(b) M. Schindler and W. Kutzelnigg, *J. Chem. Phys.*, 76 (1982) 1919.
- [30] W. Kutzelnigg, M. Schindler and U. Fleischer, *NMR, Basic Principles and Progress*, Springer-Verlag, Berlin, Vol. 23, 1989.
- [31] F. Reichel, Ph.D. Dissertation, University of Köln, 1991.
- [32] J. Gauss, E. Kraka, F. Reichel, L. Olsson and D. Cremer, *COLOGNE 93*, University of Göteborg, 1993.
- [33] M.J. Frisch, M. Head-Gordon, G.W. Trucks, J.B. Foresman, H.B. Schlegel, K. Raghavachari, M.A. Robb, J.S. Binkley, C. Gonzalez, D.J. Defrees, D.J. Fox, R.A. Whiteside, R. Seeger, C.F. Melius, J. Baker, R.L. Martin, L.R. Kahn, J.J.P. Stewart, S. Topiol and J.A. Pople, *GAUSSIAN-92*, Gaussian, Inc., Pittsburgh, PA, 1992.
- [34] (a) J. Gauss, *Chem. Phys. Lett.*, 191 (1992) 614.
(b) J. Gauss, *J. Chem. Phys.*, 99 (1993) 3629.
- [35] (a) S. Miertus, E. Scrocco and J. Tomasi, *J. Chem. Phys.*, 55 (1981) 117.
(b) R. Bonaccorsi, R. Cimraglia and J. Tomasi, *J. Comput. Chem.*, 4 (1983) 567.
(c) R. Bonaccorsi, P. Pala and J. Tomasi, *J. Am. Chem. Soc.*, 106 (1984) 1945.
(d) J.L. Pascual-Ahuir, E. Silla, J. Tomasi and R. Bonaccorsi, *J. Comput. Chem.*, 8 (1987) 778.
- [36] F. Reichel and D. Cremer, to be published.
- [37] (a) R.F.W. Bader, T.T. Nguyen-Dang and Y. Tal, *Rep. Prog. Phys.*, 44 (1981) 893.
(b) R.F.W. Bader and T.T. Nguyen-Dang, *Adv. Quantum Chem.*, 14 (1981) 63.
- [38] (a) D. Cremer and E. Kraka, *Croat. Chim. Acta*, 57 (1984) 1259.
(b) D. Cremer and E. Kraka, *Angew. Chem. Int. Ed. Engl.*, 23 (1984) 62.
- [39] (a) E. Kraka and D. Cremer, in Z.B. Maksic (Ed.), *Theoretical Models of the Chemical Bond, Part 2: The Concept of the Chemical Bond*, Springer-Verlag, Berlin, 1990, p. 453.

- (b) D. Cremer, in Z.B. Maksic (Ed.), *Modelling of Structure and Properties of Molecules*, Ellis Horwood, Chichester, 1988, p. 125.
- (c) D. Cremer and E. Kraka, in J.F. Liebman and A. Greenberg (Eds.), *Molecular Structure and Energetics, Structure and Reactivity*, VCH Publishers, Deerfield Beach, FL, 1988, Vol. 7, p. 65.
- (d) D. Cremer, *Tetrahedron*, 44 (1988) 7427.
- [40] J.F. Stanton, J. Gauss, J.D. Watts, W.J. Lauderdale and R.J. Bartlett, ACES II, Quantum Theory Project, University of Florida, 1992.
- [41] L. Olsson, H. Ottosson and D. Cremer, *J. Am. Chem. Soc.*, to be published.
- [42] (a) M.R. Ibrahim and W.L. Jorgensen, *J. Am. Chem. Soc.*, 111 (1989) 819.
(b) K.B. Wiberg and M.A. Murcko, *J. Am. Chem. Soc.*, 110 (1988) 8029.
- [43] F.A. Houle and J.L. Beauchamp, *J. Am. Chem. Soc.*, 101 (1979) 4067.
- [44] J. Gauss and J. Stanton, *J. Chem. Phys.*, to be published.
- [45] D. Bergmann and J.T. Hinze, *Struct. Bond.*, 66 (1987) 145.
- [46] See, e.g., C. Chult, R.J.P. Corriu, C. Reye and J.C. Young, *Chem. Rev.*, 93 (1993) 1371.
- [47] On going from HCl to CH₃Cl and from H₂O to (CH₃)₂O, complexation energies increased by 10 kcal mol⁻¹ [41].