Computational Evidence for a Free Silylium Ion

Thomas Müller*

Fachinstitut für Anorganische und Allgemeine Chemie der Humboldt Universität Berlin,
Hessische Strasse 1-2, 10115 Berlin, Federal Republic of Germany

Yan Zhao and Joseph B. Lambert

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

*Summary: Computed structures and properties of tri-arylsilylium ions suggest that trimesitylsilylium (**1**) is the first free silylium ion prepared in the condensed phase.*

In a recent experimental achievement, Lambert and Zhao[1] reported the formation of trimesitylsilylium (**1**). In the absence of any supporting structural data other than ^{29}Si NMR chemical shifts, *ab initio* calculations are the only tool that can provide information about the geometry and the stability of **1**. We will give computational evidence that **1** is a free silylium ion, lacking any coordination to the solvent or counterion.[2,3]

Ab initio calculations[4] on **1** and triphenylsilylium (**2**) optimized at the B3LYP/6-31G* level,[5,6] yield propeller-shaped minimum structures with the positively charged silicon in a planar environment (Scheme 1). Due to steric crowding, the aryl rings in **1** and **2** are twisted out of the silicon plane by 29° (**2**) and 48° (**1**), respectively. The equilibrium structures of **1** and **2** show marked dactylic (long, short, short) bond length patterns for the aryl substituents, typical for conjugating ions (Table 1). The energy difference of 26.2 kcal mol^{-1} between the all-perpendicular D_{3h} conformation **2** (90°) and the equilibrium structure **2** serves as an estimate

Scheme 1
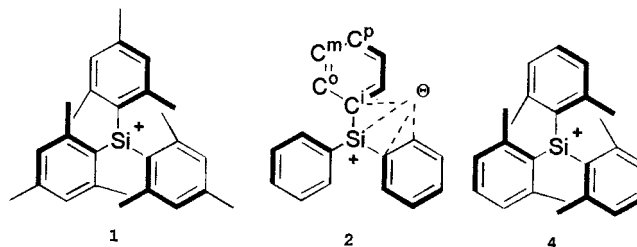
for the stabilization of **2** by π-conjugation (at B3LYP/6-31G*//B3LYP/6-31G*). The net stabilization of **2** by the phenyl groups, computed by using the isodesmic eq 1 for R = Ph, is 24.3 kcal mol^{-1} compared to Me$_3$Si$^+$ (**3**). This is roughly 60% of the stabilization energy

$$R_3Si-H + Me_3Si^+ \rightarrow R_3Si^+ + Me_3SiH \qquad (1)$$

calculated for the tritylcation compared to the *tert*-butyl cation (40.8 kcal mol^{-1}). Despite the increased twist angle Θ ($\Theta = 49°$ at HF/6-31G*), the 2,6-dimethylphenyl group (dmph) in tris(2,6-dimethylphenyl)silylium (**4**), which is used here as close model for **1**, affords an even larger stabilization due to its enhanced π-donating ability. **4** is lower in energy by 3.7 kcal mol^{-1} than **2** (all values at B3LYP/6-311G*/HF/6-31G*). Benzene coordination to cation **3**,[7] computed in **5** has distinct structural consequences (Scheme 2).[8] The pyramidalization at silicon (the total bond angle sum, $\Sigma° = 342°$), the Si−C$^\alpha$ separation of 2.221 Å, and the significant bond length alternations in the coordinated benzene (1.427, 1.388, and 1.402 Å) are indicative of a σ-type complex (B3LYP/6-31G*, Table 1). In contrast, benzene coordination to **1**, calculated for **6**, has virtually no impact on the cationic geometry. In **6**, the benzene approaches the trigonal planar silylium ion ($\Sigma° = 360.0°$ (**6**)) with a Si−C$^\alpha$ distance of 5.375 Å. The C−C bond lengths in the benzene subunit (1.397−1.398 Å (**6**)) are almost identical to the calculated value for free benzene

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Table 1. Selected Calculated Bond Lengths (Å) and Angles (deg) of Silylium Ions (at B3LYP/6-31G*)

compd	Θ	SiC^i	C^{i}C^o	C^{o}C^m	C^{m}C^p	SiC$^\alpha$	PG
1^a	48−49	1.839	1.425−1.428	1.386−1.395	1.387−1.402		C_1
2	28	1.821	1.417	1.391	1.399		D_3
	50^b	1.825	1.415	1.391	1.398		D_3
	90^b	1.839	1.410	1.394	1.396		D_{3h}
3		1.844^c					C_{3h}
5^a		1.867−1.871^c				2.213	C_s
6^a	46−48	1.839−1.841	1.426−1.428	1.393−1.395	1.399−1.401	5.376	C_1

^{a} The respective shortest and longest bond and the smallest and largest angle is given. ^{b} Partially optimized geometry with fixed twist angle Θ. [c] Si−CH$_3$ bond length.

Scheme 2

R = Methyl: **5**
R = Mesityl: **6**

7
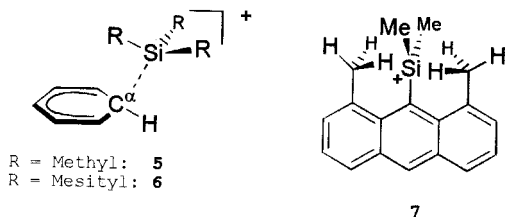
Table 2. Calculated δ^{29}Si of Silylium Ions (versus TMS)^a

compd	method	δ^{29}Si	δ^{29}Si (exp)
1	HF/GIAO/A^{b,c}	230.1	225.5
	B3LYP/GIAO/A^{b,c}	243.9	
2	HF/GIAO/A^{b,c}	198.8	
	B3LYP/GIAO/A^{b,c}	205.0	
	B3LYP/GIAO/B^{b,d}	210.8	
	B3LYP/GIAO/C^{b,e}	207.9	
2 (50°)^f	B3LYP/GIAO/A^{b,c}	234.2	
2 (90°)^f	B3LYP/GIAO/A^{b,c}	290.2	
3	HF/GIAO/A^{b,c}	361.6	
	B3LYP/GIAO/A^{b,c}	413.0	
	B3LYP/GIAO/C^{b,c}	418.0	
	MP2/GIAO/D^{b,g}	386.2	
5	HF/GIAO/A^{b,c}	80.4	83.6
	B3LYP/GIAO/A^{b,c}	106.5	
6	B3LYP/GIAO/A^{b,c}	242.7	
	HF/GIAO/A^{b,c}	228.6	

^{a} $\sigma(^{29}$Si)(TMS): 332.1 (B3LYP/GIAO/A^{b,c}); 339.9 (B3LYP/GIAO/B^{b,d}); 338.9 (B3LYP/GIAO/C^{b,e}); 388.6 (HF/GIAO/A^{b,c}); 371.1 (MP2/GIAO/D^{b,g}). ^{b} B3LYP/6-31G* optimized geometry used. ^{c} Basis A: 6-311+G(2df,p) (Si), 6-31G* (C,H). ^{d} Basis B: 6-311G**. ^{e} Basis C: 6-311+G**. ^{f} Partially optimized structure with fixed Θ. ^{g} Basis D: tz2p (Si), dzp (C,H); see ref 12.

(1.397 Å at B3LYP/6-31G*). The benzene association energy A_E of **3** is quite substantial (−26.3 kcal mol^{-1}, B3LYP/6-31G*//B3LYP/6-31G*), but it becomes very small for **1** (−2.6 kcal mol^{-1}).[9] A weakly bonded complex like **6** will be hardly observable in solution at room temperature.

NMR chemical shift calculations afford even more compelling evidence for a free silylium ion. While GIAO[9] calculations for **3** predict a highly deshielded silicon (δ^{29}Si 361.6 (HF/GIAO), 413.0 (B3LYP/GIAO), 386.2 (MP2/GIAO)), substitution by aryl groups leads to a significant high-field shift. For **2**, δ^{29}Si near 200 ppm is calculated, depending on the applied method and basis set (see Table 2). GIAO/HF and GIAO/DFT calculations predict $\delta(^{29}$Si) = 230.1 and $\delta(^{29}$Si) = 243.9 for the equilibrium structure of **1**, respectively, both values are near to the experimental δ^{29}Si for **1** ($\delta(^{29}$Si

= 225.5). $\delta(^{29}$Si) in **2** depends strongly on the phenyl twist angle Θ. Thus, it varies from 205.0 for the equilibrium geometry of **2** (Θ = 29°) to 234.2 at Θ = 50°, and for the perpendicular conformation **2** (90°), it reaches 290.2 (GIAO/B3LYP/A/B3LYP/6-31G*). The deshielding of the silicon in **1** compared to **2** is only partially due to the larger twist angle Θ. Also the longer Si−C^i distance in **1** (1.839 Å) compared to **2** (1.821, 1.825 Å in **2** (50°) at B3LYP/6-31G*) contributes significantly to the calculated low-field shift. The $\delta(^{29}$Si) (243.9 and 230.1 at GIAO/DFT and GIAO/HF, respectively) computed for **1** remains nearly unchanged for the benzene solvate **6** ($\delta(^{29}$Si) = 242.7 and 228.6 at GIAO/DFT and GIAO/HF, respectively), indicating neglible interactions between the cation and the solvent molecule. This is in sharp contrast to NMR chemical shift calculations for **5**[8] which give $\delta(^{29}$Si) = 106.5 and 80.4 (at GIAO/DFT and GIAO/HF, respectively; experimental 83.6[7b]), at nearly 300 ppm higher field than that predicted for **3**.

Schleyer et al. have shown that trialkylsilylium ions can interact with C−H bonds of alkanes.[10] Furthermore, Olsson, and Cremer suggested that these interactions can be used to stabilize a silylium ion by intramolecular solvation, for example, in **7**.[11] This interaction results in elongation of the C−H bonds and in a marked shielding of the silicon.[11,12] The C−H bonds of the *o*-methyl groups in **1**, however, are too far away from the positively charged silicon to interact with the formally empty 3p(Si) orbital (Si, H distance = 2.990−2.995 Å at B3LYP/6-31G*). All three CH bond lengths of the methyl groups are very similar (1.093−1.097 Å), and $\delta(^{29}$Si) is larger for **1** ($\delta(^{29}$Si) = 243.9) than for **2** at nearly the same twist angle ($\delta(^{29}$Si) = 234.2 for **2** (50°), all values at GIAO/B3LYP/A//B3LYP/6-31G* see Table 2). From this we conclude that no internal solvation by C−H bonds of the *o*-methyl groups contributes to the stabilization of **1**.

This computational study strongly corroborates the experimental finding[1] that **1** is the first free trigonal silyl cation lacking any coordination to solvent or counterion. π-Conjugation between the aryl substituents and the 3p(Si) orbital is smaller than in carbenium ions but is sufficient enough to lower the inherently high nucleophilicity of the positively charged silicon in **1**. While the steric protection by the bulky mesityl substituents is essential to prevent nucleophilic attack by

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solvent molecules, internal solvation[11] of the positively charged silicon by the *o*-methyl groups is not operative in **1**.

After the completion of this work we became aware of a computational study by Kraka et al. reporting similiar results.[13]

Supporting Information Available: Tables of absolute energies and calculated structures of **1**, **2**, **5**, and **6** (8 pages). Ordering information is given on any current masthead page.

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