

# Computational Evidence for a Free Silylium Ion

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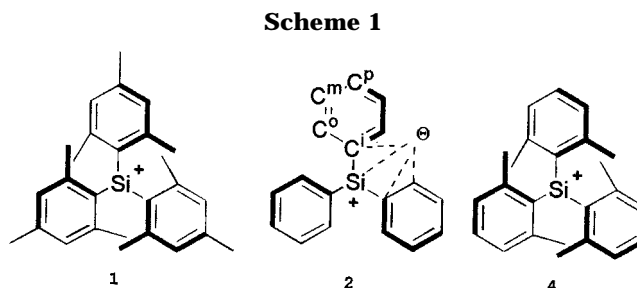
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Received November 14, 1997

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

In a recent experimental achievement, Lambert and Zhao<sup>1</sup> reported the formation of trimesitylsilylium (**1**). In the absence of any supporting structural data other than <sup>29</sup>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.<sup>2,3</sup>

*Ab initio* calculations<sup>4</sup> on **1** and triphenylsilylium (**2**) optimized at the B3LYP/6-31G\* level,<sup>5,6</sup> 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<sup>-1</sup> between the all-perpendicular *D*<sub>3h</sub> conformation **2** (90°) and the equilibrium structure **2** serves as an estimate



for the stabilization of **2** by  $\pi$ -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<sup>-1</sup> compared to Me<sub>3</sub>Si<sup>+</sup> (**3**). This is roughly 60% of the stabilization energy



calculated for the tritylcation compared to the *tert*-butyl cation (40.8 kcal mol<sup>-1</sup>). Despite the increased twist angle  $\Theta$  ( $\Theta = 49^\circ$  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  $\pi$ -donating ability. **4** is lower in energy by 3.7 kcal mol<sup>-1</sup> than **2** (all values at B3LYP/6-311G\*/HF/6-31G\*). Benzene coordination to cation **3**,<sup>7</sup> computed in **5** has distinct structural consequences (Scheme 2).<sup>8</sup> The pyramidalization at silicon (the total bond angle sum,  $\Sigma^\circ = 342^\circ$ ), the Si-C <sup>$\alpha$</sup>  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  $\sigma$ -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 ( $\Sigma^\circ = 360.0^\circ$  (**6**)) with a Si-C <sup>$\alpha$</sup>  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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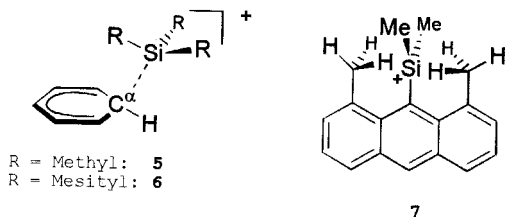
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**Table 1. Selected Calculated Bond Lengths (Å) and Angles (deg) of Silylium Ions (at B3LYP/6-31G\*)**

compd	$\Theta$	SiC <sup>i</sup>	C <sup>i</sup> C <sup>o</sup>	C <sup>o</sup> C <sup>m</sup>	C <sup>m</sup> C <sup>p</sup>	SiC <sup>a</sup>	PG
<b>1</b> <sup>a</sup>	48–49	1.839	1.425–1.428	1.386–1.395	1.387–1.402		C <sub>1</sub>
<b>2</b>	28	1.821	1.417	1.391	1.399		D <sub>3</sub>
	50 <sup>b</sup>	1.825	1.415	1.391	1.398		D <sub>3</sub>
	90 <sup>b</sup>	1.839	1.410	1.394	1.396		D <sub>3h</sub>
<b>3</b>		1.844 <sup>c</sup>					C <sub>3h</sub>
<b>5</b> <sup>a</sup>		1.867–1.871 <sup>c</sup>				2.213	C <sub>s</sub>
<b>6</b> <sup>a</sup>	46–48	1.839–1.841	1.426–1.428	1.393–1.395	1.399–1.401	5.376	C <sub>1</sub>

<sup>a</sup> The respective shortest and longest bond and the smallest and largest angle is given. <sup>b</sup> Partially optimized geometry with fixed twist angle  $\Theta$ . [c] Si–CH<sub>3</sub> bond length.

**Scheme 2****Table 2. Calculated  $\delta^{29}\text{Si}$  of Silylium Ions (versus TMS)<sup>a</sup>**

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

<sup>a</sup>  $\sigma^{29}\text{Si}(\text{TMS})$ : 332.1 (B3LYP/GIAO/A<sup>b,c</sup>); 339.9 (B3LYP/GIAO/B<sup>b,d</sup>); 338.9 (B3LYP/GIAO/C<sup>b,e</sup>); 388.6 (HF/GIAO/A<sup>b,c</sup>); 371.1 (MP2/GIAO/D<sup>b,g</sup>). <sup>b</sup> B3LYP/6-31G\* optimized geometry used. <sup>c</sup> Basis A: 6-311+G(2df,p) (Si), 6-31G\* (C,H). <sup>d</sup> Basis B: 6-311G\*\*. <sup>e</sup> Basis C: 6-311+G\*\*. <sup>f</sup> Partially optimized structure with fixed  $\Theta$ . <sup>g</sup> 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<sup>−1</sup>, B3LYP/6-31G\*/B3LYP/6-31G\*), but it becomes very small for **1** (−2.6 kcal mol<sup>−1</sup>).<sup>9</sup> 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<sup>9</sup> calculations for **3** predict a highly deshielded silicon ( $\delta^{29}\text{Si}$  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**,  $\delta^{29}\text{Si}$  near 200 ppm is calculated, depending on the applied method and basis set (see Table 2). GIAO/HF and GIAO/DFT calculations predict  $\delta^{29}\text{Si}$  = 230.1 and  $\delta^{29}\text{Si}$  = 243.9 for the equilibrium structure of **1**, respectively, both values are near to the experimental  $\delta^{29}\text{Si}$  for **1** ( $\delta^{29}\text{Si}$

= 225.5).  $\delta^{29}\text{Si}$  in **2** depends strongly on the phenyl twist angle  $\Theta$ . Thus, it varies from 205.0 for the equilibrium geometry of **2** ( $\Theta$  = 29°) to 234.2 at  $\Theta$  = 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  $\Theta$ . Also the longer Si–C<sup>i</sup> 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  $\delta^{29}\text{Si}$  (243.9 and 230.1 at GIAO/DFT and GIAO/HF, respectively) computed for **1** remains nearly unchanged for the benzene solvate **6** ( $\delta^{29}\text{Si}$  = 242.7 and 228.6 at GIAO/DFT and GIAO/HF, respectively), indicating negligible interactions between the cation and the solvent molecule. This is in sharp contrast to NMR chemical shift calculations for **5**<sup>8</sup> which give  $\delta^{29}\text{Si}$  = 106.5 and 80.4 (at GIAO/DFT and GIAO/HF, respectively; experimental 83.6<sup>7b</sup>), 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.<sup>10</sup> Furthermore, Olsson, and Cremer suggested that these interactions can be used to stabilize a silylium ion by intramolecular solvation, for example, in **7**.<sup>11</sup> This interaction results in elongation of the C–H bonds and in a marked shielding of the silicon.<sup>11,12</sup> 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  $\delta^{29}\text{Si}$  is larger for **1** ( $\delta^{29}\text{Si}$  = 243.9) than for **2** at nearly the same twist angle ( $\delta^{29}\text{Si}$  = 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<sup>1</sup> that **1** is the first free trigonal silyl cation lacking any coordination to solvent or counterion.  $\pi$ -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<sup>11</sup> 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 similar results.<sup>13</sup>

**Acknowledgment.** This work was supported by the Fonds der Chemischen Industrie (Liebig Scholarship for T.M.) and by the National Science Foundation (North Western University). We are indebted to Profs. Y. Apeloig and P. v. R. Schleyer for very fruitful discus-

sions. Large amounts of computational time provided by the computer centers of the Technion, Haifa, the Humboldt University, Berlin, and the Israelian High Performance Computing Unit made this work possible. T.M. thanks Prof. N. Auner for support and interest during the work.

**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.

OM971003W