

## Octa- and nona-hydridosiliconium di- and tri-cations ( $\text{SiH}_8^{2+}$ and $\text{SiH}_9^{3+}$ ) containing eight- and nine-coordinate silicon atoms

Golam Rasul\* and G. K. Surya Prakash

Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California,  
University Park, Los Angeles, CA 90089-1661, USA

E-mail: [rasul@usc.edu](mailto:rasul@usc.edu)

This paper is dedicated to our friend Prof. Kenneth Laali, on the occasion of his 65<sup>th</sup> birthday,  
and in recognition of his lifetime contributions to chemistry

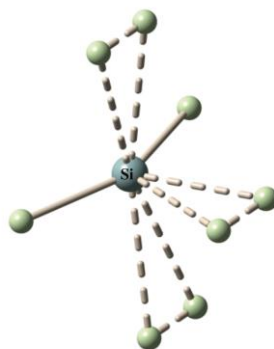
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### Abstract

Structures of octahydrido siliconium dication ( $\text{SiH}_8^{2+}$ ) and nonahydrido siliconium trication ( $\text{SiH}_9^{3+}$ ) were found to be computationally viable minima at the MP2/cc-pVTZ level and CCSD(T)/cc-pVTZ levels. Their structure has three and four two-electron three-center (2e-3c) bonds, respectively. The protonation of  $\text{SiH}_7^+$  to form the dication was found to be slightly endothermic by 4.1 kcal/mol at the CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVTZ + ZPE level. Further protonation to form the trication was found to be highly endothermic by 162.2 kcal/mol. The deprotonation barriers of the ions were also computed.



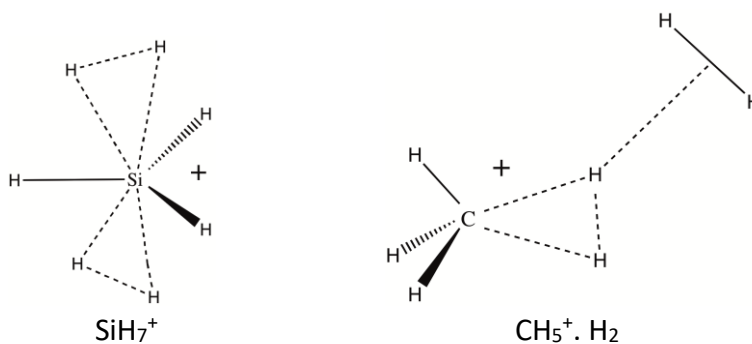
Octacoordinate hydrido siliconium dication

**Keywords:** Siliconium, dication, trication, higher coordinations

## Introduction

Higher coordinate<sup>1</sup> multicharged main group compounds are of substantial interest both theoretically<sup>2-6</sup> and experimentally.<sup>7</sup> Schmidbaur *et al.* have prepared a variety of monopositively charged higher coordinate gold complexes of main group elements.<sup>7</sup> They have also prepared dipositively charged carbon  $\{[(C_6H_5)_3PAu]_6C\}^{2+}$ ,<sup>8</sup> nitrogen  $\{[(C_6H_5)_3PAu]_5N\}^{2+}$ ,<sup>9</sup> phosphorus  $\{[(C_6H_5)_3PAu]_5P\}^{2+}$ ,<sup>10</sup> sulfur  $\{[(C_6H_5)_3PAu]_4S\}^{2+}$ ,<sup>11</sup> and oxygen  $\{[(o-CH_3C_6H_4)_3PAu]_4O\}^{2+}$ ,<sup>12</sup> and determined their X-ray structures. These represent isolobal analogs of  $CH_6^{2+}$ ,  $NH_5^{2+}$ ,  $PH_5^{2+}$ ,  $SH_4^{2+}$  and  $OH_4^{2+}$ , respectively.

Cao *et al.*<sup>13</sup> reported the first spectroscopic observation of  $SiH_7^+$ . Their IR data suggest that  $SiH_7^+$  is a symmetric complex ( $H_2 \cdots SiH_3 \cdots H_2$ ) with two two-electron three-center (2e-3c) bonds and with two two-electron two-center (2e-2c) bonds. This is in contrast to the species  $CH_7^+$ , which has been concluded, from both IR spectrum<sup>14</sup> and calculations,<sup>15</sup> to have a structure consisting of a  $H_2$  subunit weakly bound to one of the hydrogen atoms of the 2e-3c bond ( $CH_5^+ \cdot H_2$ ). Hu *et al.*<sup>16</sup> have also reported the calculated structures and Infrared spectrum of parent heptacoordinate siliconium ion,  $SiH_7^+$ . A similar structure has also been reported for  $GaH_7^+$ .<sup>17</sup>



**Scheme 1.** Structures of  $SiH_7^+$  and  $CH_5^+ \cdot H_2$ .

In continuation of our study of hypercoordinate compounds, we have now extended our theoretical investigations to the next higher homologues of  $SiH_7^+$  *i.e.*  $SiH_8^{2+}$  and  $SiH_9^{3+}$  ions at the MP2/cc-pVTZ and CCSD(T)/cc-pVTZ levels.

## Results and Discussion

Structures of **1** and **2** were optimized in the gas phase at the MP2/cc-pVTZ and CCSD(T)/cc-pVTZ levels. CCSD(T)/cc-pVTZ level structures are discussed throughout unless otherwise stated. Structure **1** was found to be a viable minimum (Figure 1) on the potential energy surface (PES) of  $SiH_8^{2+}$  at the both MP2/cc-pVTZ and CCSD(T)/cc-pVTZ levels. Computed energies are given in Table 1. Structure **1** contains three 2e-3c bonds involving the silicon atom and three hydrogen molecules and two 2e-2c bond involving the silicon atom and a hydrogen molecule. The ion can be considered as a complex between  $SiH_4^{2+}$  (protonated silicium dication)<sup>18</sup> and two hydrogen molecules (Scheme 2). The Si-H bond distance (1.995 Å) of the axial 2e-3c bond units is considerably longer than that of the equatorial unit (1.842 Å). The possible stability of the eight-coordinate  $SiH_8^{2+}$  is due to the fact that the silicon can undergo  $sp^3d$  hybridization. In comparison, the eight-coordinate  $CH_8^{2+}$  ion was found not be a minimum on the PES. The dication dissociated into  $CH_6^{2+}$  and  $H_2$  upon

optimization. This is because, unlike silicon, carbon is unable to undergo  $sp^3d$  hybridization. Computed vibrational frequencies of the structure **1** are given in Table 2.

**Table 1.** Energies (-au), ZPE and relative energies (kcal/mol) of ions **1-4**

Structure no.	MP2/cc-pVTZ	ZPE (kcal/mol)	NIMAG <sup>b</sup>	rel. energy <sup>a</sup> (kcal/mol)	CCSD(T)/cc-pVTZ	rel. energy <sup>b</sup> (kcal/mol)
SiH <sub>7</sub> <sup>+</sup>	-292.82964	32.5	0	-4.8	-292.87141	-4.1
<b>1</b>	-292.82986	37.4	0	0.0	-292.87264	0.0
<b>2</b>	-292.57167	38.9	0	163.5	-292.61650	162.2
<b>3</b> <sub>TS</sub>	-292.71363	34.7	1	68.3		
<b>4</b> <sub>TS</sub>	-292.54590	36.2	1	177.0		

<sup>a</sup> Relative energy at MP2/cc-pVTZ//cc-pVTZ + ZPE level; <sup>b</sup> at the CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVTZ + ZPE level.

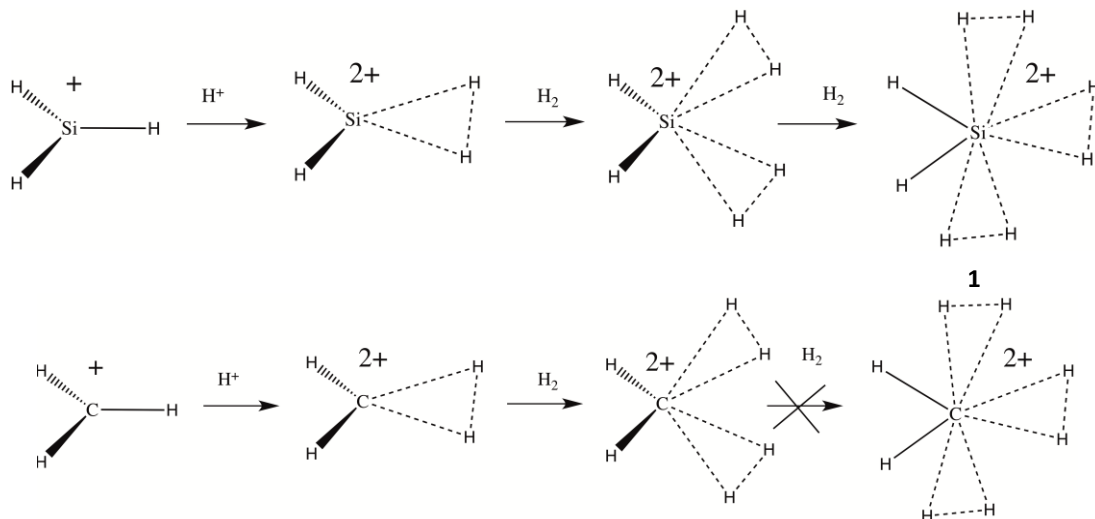
**Table 2.** Calculated frequencies<sup>a</sup> (cm<sup>-1</sup>) and IR intensities (km/mol) of **1**

MP2/cc-pVTZ		CCSD(T)/cc-pVTZ	
frequency	intensity	frequency	intensity
306	0	281	0
335	0	309	0
383	11	366	0
388	0	385	45
437	3	438	19
501	142	504	47
618	0	613	7
639	112	633	68
733	32	695	7
800	28	768	4
850	0	786	0
859	69	790	88
869	0	847	0
902	27	898	22
996	2	975	1
1079	60	1025	68
2307	16	2253	26
2398	142	2345	225
3779	295	3702	280
4005	721	3924	695
4042	6	3959	6

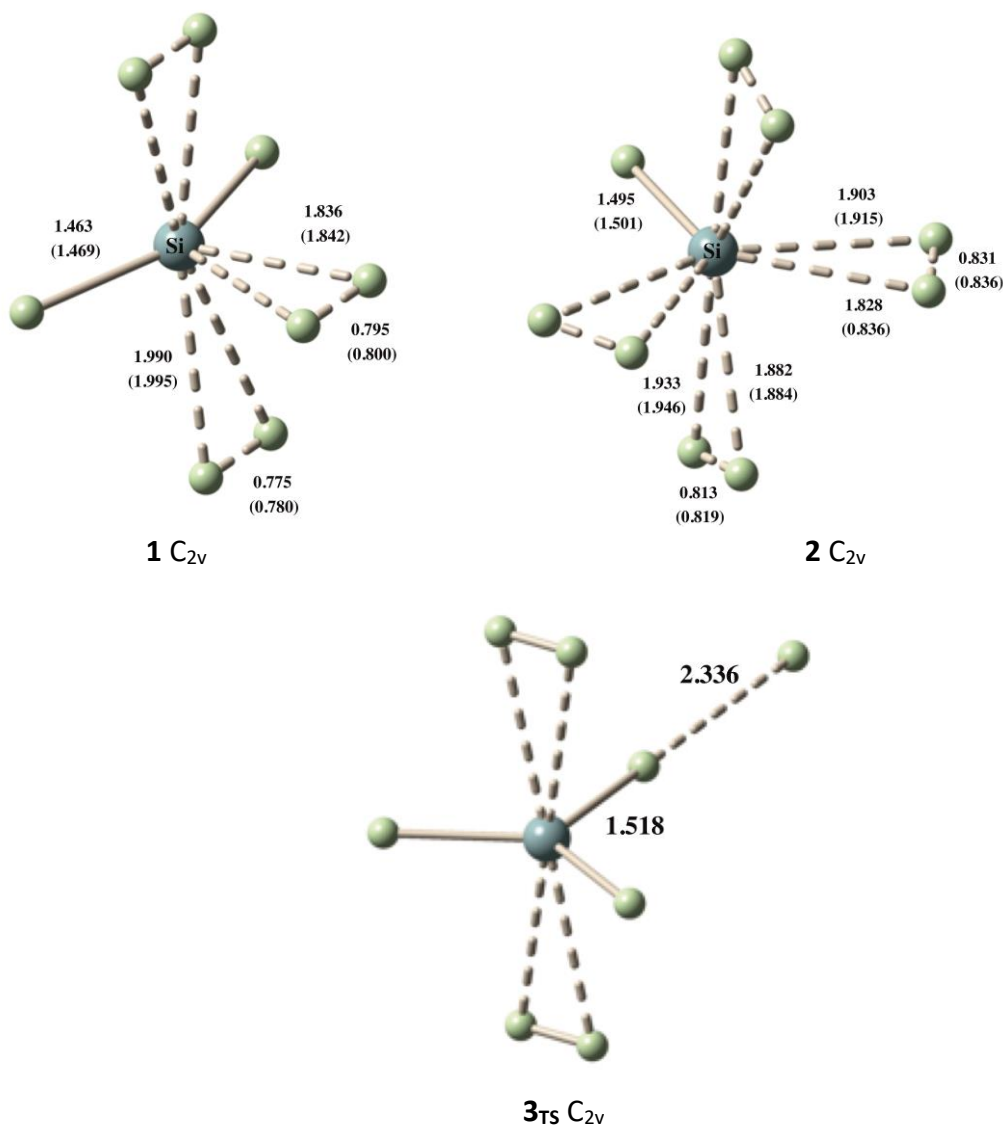
<sup>a</sup> Computed frequencies were not scaled.

Protonation of SiH<sub>7</sub><sup>+</sup> to form **1** was found to be endothermic by 4.8 kcal/mol at the MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level (4.1 kcal/mol at the CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVTZ + ZPE level).

Transition structure,  $3_{TS}$  (Figure 1) for the deprotonation of **1** was also located. The structure  $3_{TS}$  lies 68.3 kcal/mol higher in energy than structure **1**. Thus the trication has also a high barrier for deprotonation.

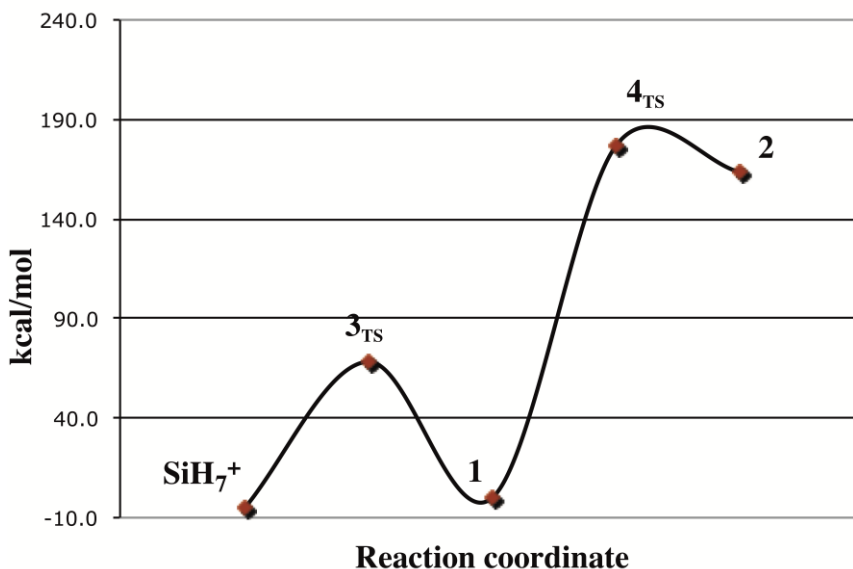


**Scheme 2.** Formation of  $\text{SiH}_8^{2+}$  and  $\text{CH}_6^{2+}$ .



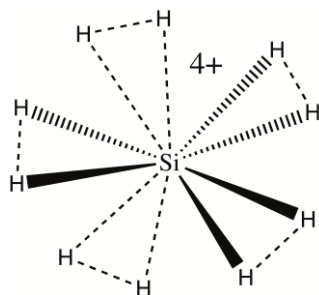
**Figure 1.** MP2/cc-pVTZ (CCSD(T)/cc-pVTZ) optimized structures of **1**, **2** and  $3_{TS}$ .

MP2/cc-pVTZ and CCSD(T)/cc-pVTZ optimizations show that the nine-coordinate siliconium structure **2** is also a minimum on the potential energy surface of  $\text{SiH}_9^{3+}$ . Tricationic structure **2** (Figure 1) contains four 2e-3c bonds involving the silicon atom and four hydrogen molecules and a 2e-2c bond involving the silicon atom and a hydrogen atom. The Si-H bond distances (1.946 and 1.884 Å) of the axial 2e-3c bond units are slightly longer than those of the equatorial units (1.915 and 1.836 Å). Charge-charge repulsions in the trications are substantial. However, the bonding interactions are strong enough to counter charge-charge repulsions rendering them remarkably stable. Dissociation of **2** into **1** and  $\text{H}^+$  was calculated to be very exothermic by 163.5 kcal/mol at the MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level (162.2 kcal/mol at the CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVTZ + ZPE level). The transition structure **4<sub>TS</sub>** for the dissociation lies just 13.5 kcal/mol higher in energy than structure **2**. This shows that the trication **2**, if formed will dissociate spontaneously into **1** and  $\text{H}^+$ . Potential energy surface of **1** and **2** calculated MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level is depicted in Figure 2.



**Figure 2.** Potential energy surface of **1** and **2**.

We also searched for any minimum-energy structures of deca-coordinate siliconium ion,  $\text{SiH}_{10}^{4+}$ . At the MP2/cc-pVTZ level no minimum could be found on the PES of  $\text{SiH}_{10}^{4+}$  (including a structure with five 2e-3c bonds as shown in Scheme 3). Thus in  $\text{SiH}_{10}^{4+}$  charge-charge repulsion may have reached its prohibitive limit.



**Scheme 3.** Possible structure of  $\text{SiH}_{10}^{4+}$ .

## Conclusions

The present calculational study at the MP2/cc-pVTZ and CCSD(T)/cc-pVTZ levels shows that the octahydrido-silconium dication ( $\text{SiH}_8^{2+}$ ) **1** and nonahydridosilconium trication ( $\text{SiH}_9^{3+}$ ) **2** are viable energy minima. Structures **1** and **2** were found to be stabilized by three and four 2e-3c bonds, respectively. The protonation of  $\text{SiH}_7^+$  to form **1** was calculated to be slightly endothermic by about 5 kcal/mol. Charge-charge repulsions in these di- and tri-cations are substantial. However, the bonding interactions are strong enough to counter charge-charge repulsions rendering them remarkably stable.

## Experimental Section

### Calculations

Geometry optimizations and frequency calculations were carried out with the Gaussian 09 program.<sup>19</sup> Vibrational frequencies at the MP2/cc-pVTZ//MP2/cc-pVTZ level were used to characterize stationary points as minima (NIMAG (number of imaginary frequency) = 0 or transition state NIMAG = 1) and to compute zero point vibrational energies (ZPE), which were scaled by a factor of 0.96.<sup>20</sup> CCSD(T)/cc-pVTZ optimizations and frequency calculations have been performed with the CFOUR program.<sup>21,22</sup>

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