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Octa- and nona-hydridosiliconium di- and tri-cations (SiH_8^{2+} and SiH_9^{3+}) containing eight- and nine-coordinate silicon atoms

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

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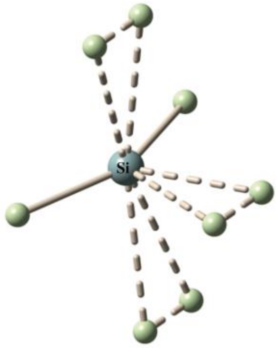
Abstract

Structures of octahydrido silconium dication (SiH_8^{2+}) and nonahydrido silconium trication (SiH_9^{3+}) were found to be calculationally 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 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: Silconium, dication,trication, higher coordinations

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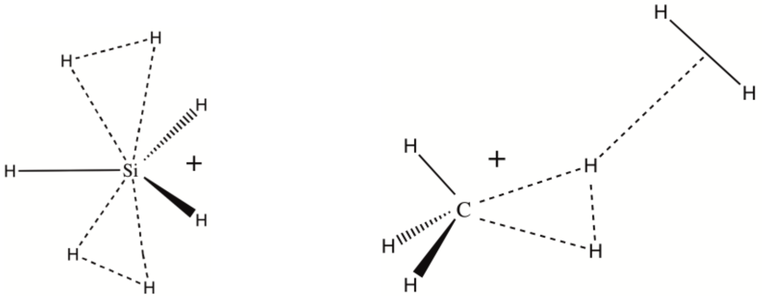
Introduction

Higher coordinate[1] multicharged main group compounds are of substantial interest both theoretically[2-6] and experimentally.[7] Schmidbaur *et al*. have prepared a variety of monopositively charged higher coordinate gold complexes of main group elements.[7] They have also prepared dipositively charged carbon $\{[(C_6H_5)_3PAu]_6C\}^{2+}$,[8] nitrogen $\{[(C_6H_5)_3PAu]_5N\}^{2+}$,[9] phosphorus $\{[(C_6H_5)_3PAu]_5P\}^{2+}$,[10] sulfur $\{[(C_6H_5)_3PAu]_4S\}^{2+}$,[11] and oxygen $\{[(o\text{-}CH_3C_6H_4)_3PAu]_4O\}^{2+}$,[12] 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.*[13] 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[14] and calculations,[15] 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^+. H_2). Hu *et al.*[16] have also reported the calculated structures and Infrared spectrum of parent heptacoordiate siliconium ion, SiH_7^+. A similar structure has also been reported for GaH_7^+.[17]



SiH_7^+ CH_5^+. H_2

Scheme 1. Structures of SiH_7^+ and CH_5^+. 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 thee 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 silicenium dication)[18] 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^{3}d 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^{3}d 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[b]	rel. energy[a] (kcal/mol)	CCSD(T)/cc-pVTZ	rel. energy[b] (kcal/mol)
SiH_7^+	-292.82964	32.5	0	-4.8	-292.87141	-4.1
1	-292.82986	37.4	0	0.0	-292.87264	0.0
2	-292.57167	38.9	0	163.5	-292.61650	162.2
$\mathbf{3}_{\mathbf{TS}}$	-292.71363	34.7	1	68.3		
$\mathbf{4}_{\mathbf{TS}}$	-292.54590	36.2	1	177.0		

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

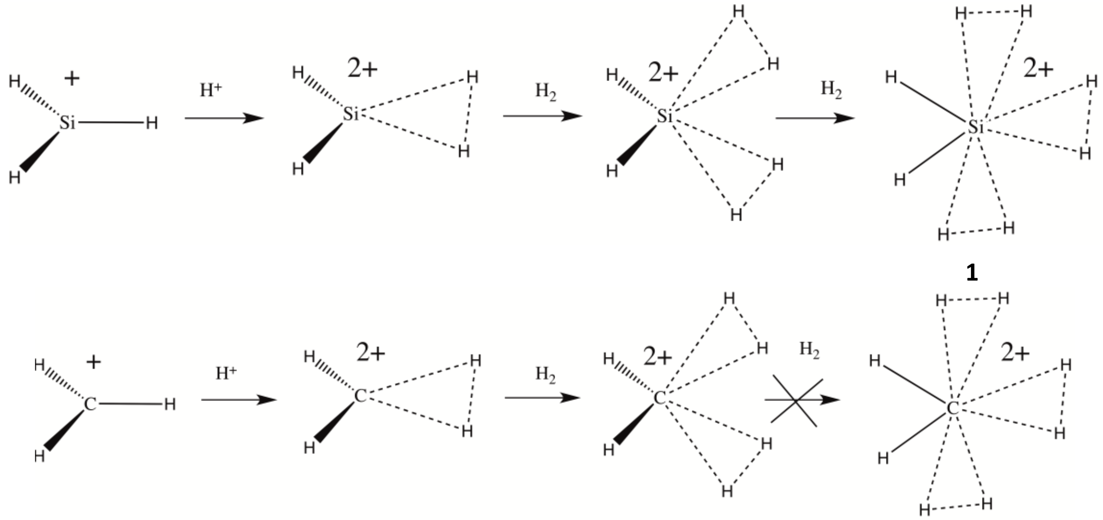
Table 2. Calculated frequencies[*a*] (cm^{-1}) and IR intensities (km/mol) of **1**

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

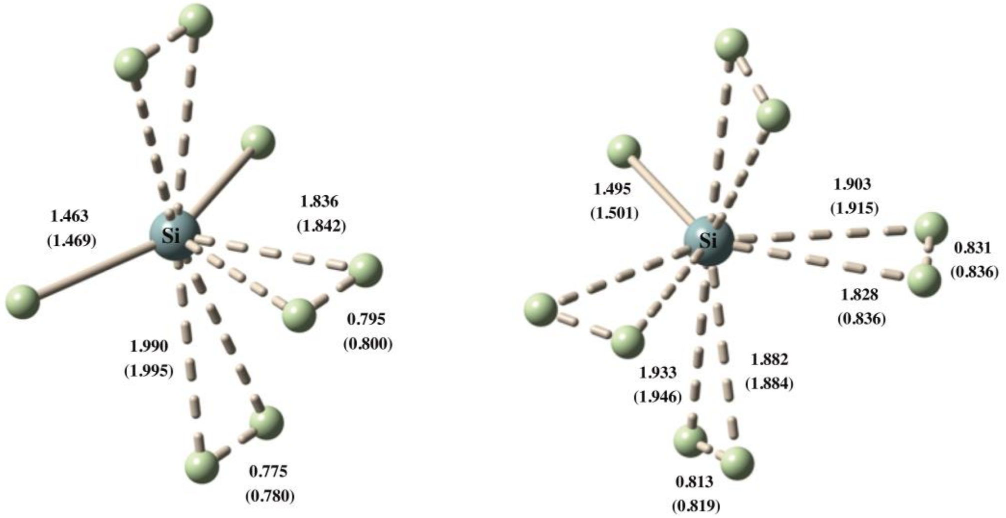
[a] Computed frequencies were not scaled.

Protonation of SiH_7^+ 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).

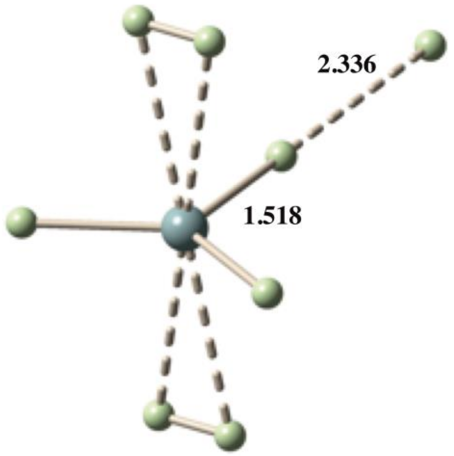
Transition structure, **3_{TS}** (Figure 1) for the deprotonation of **1** was also located. The structure **3_{TS}** lies 68.3 kcal/mol higher in energy than structure **1**. Thus the trication has also a high barrier for deprotonation.



Scheme 2. Formation of SiH_8^{2+} and CH_6^{2+}.



1 C_{2v} **2** C_{2v}



3_{TS} C_{2v}

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 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 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 $\mathbf{4_{TS}}$ 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 H^+. Potential energy surface of **1** and **2** calculated MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level is depicted in Figure 2.

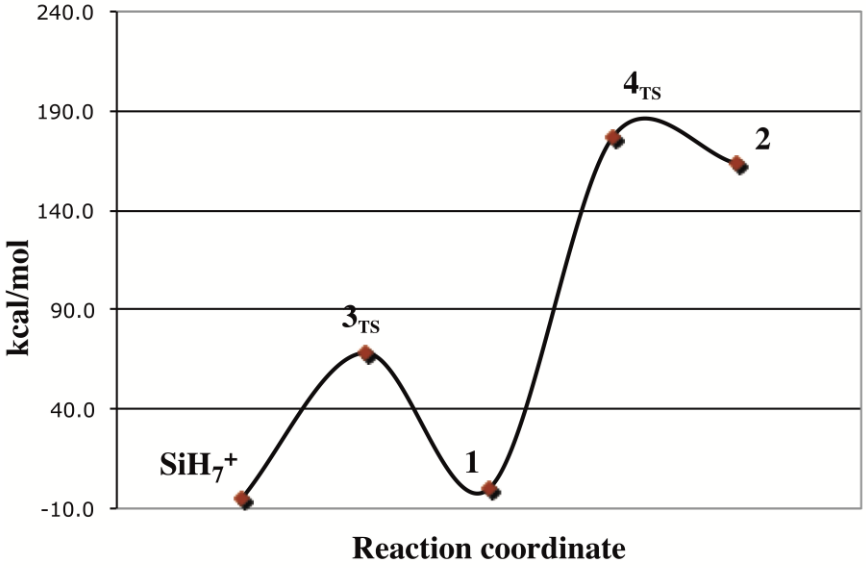
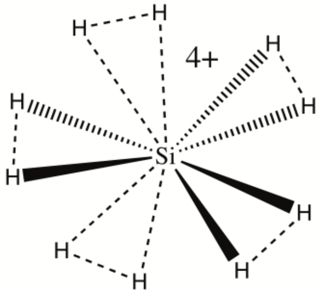


Figure 2. Potential energy surface of **1** and **2.**

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



Scheme 3. Possible structure of SiH_{10}^{4+}.

Conclusions

The present calculational study at the MP2/cc-pVTZ and CCSD(T)/cc-pVTZ levels shows that the octahydridosilconium dication (SiH_8^{2+}) **1** and nonahydridosilconium trication (SiH_9^{3+}) **2** are viable energy minima. Structures **1** and **2** were found to stabilized by three and four 2e-3c bonds, respectively. The protonation of 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.[19] 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.[20] CCSD(T)/cc-pVTZ optimizations and frequency calculations calculations have been performed with the CFOUR program.[21,22]

Acknowledgements

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References

1. Olah, G. A.; Prakash, G. K. S.; Wade, K.; Molnar, A.; Williams, R. E. *Hypercarbon Chemistry,* John Wiley & Sons, New York, 2011. https://doi.org/10.1002/9781118016466
2. Olah, G. A.; Rasul, G. *Acc. Chem. Res.* **1997**, *30*, 245. https://doi.org/10.1021/ar960103f
3. Haberlen, O. D.; Schmidbaur, H.; Rosch, N. *J. Am. Chem. Soc.* **1994**, *115*, 8241. https://doi.org/10.1021/ja00097a034
4. Gorling, A.; Rosch, N.; Ellis, D. E.; Schmidbaur, H. *Inorg. Chem.* **1991**, *30*, 3986. https://doi.org/10.1021/ic00021a005
5. Schreiner, P. R.; Schaefer, H. F.; Schleyer, P. v. R. *Advances in Gas Phase Ion Chemistry ,* JAI Press Inc., 1996, p-125.
6. Schreiner, P. R.; Schaefer, H. F.; Schleyer, P. v. R. *J. Chem. Phys.* **1995**, *103*, 5565. https://doi.org/10.1063/1.470540
7. Schmidbaur, H. *Chem. Soc. Rev.,* **1995**, *24*, 391. https://doi.org/10.1039/cs9952400391
8. Scherbaum, F.; Grohmann, A.; Huber B.; Krüger, C. ; Schmidbaur, H. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1544. https://doi.org/10.1002/anie.198815441
9. Grohmann, A.; Riede, J.; Schmidbaur, H. *Nature* **1990**, *345*, 140.

https://doi.org/10.1038/345140a0

10. Schmidbaur, H.; Beruda, H.; Zeller, E. *Phosphorus, Sulfur Silicon* **1994**, *87*, 245. https://doi.org/10.1080/10426509408037457
11. Zeller, E.; Beruda, H.; Schmidbaur, H. *Inorg. Chem.* **1993**, *32*, 3203. https://doi.org/10.1021/ic00067a002
12. Schmidbaur, H.; Hofreiter, S.; Paul, M. *Nature* **1995**, *377*, 503. https://doi.org/10.1038/377503a0
13. Cao, Y.; Choi, J. H.; Haas, B. M.; Johnson, M. S.; Okumura, M. *J. Phys. Chem.* **1993**, 97, 5215. https://doi.org/10.1021/j100122a008
14. Boo, D. W.; Lee, Y. T. *Chem. Phys. Lett*. **1993**, *211*, 358. https://doi.org/10.1016/0009-2614(93)87073-C
15. Kim, S. J.; Schreiner, P. R.; Schleyer, P. v. R.; Schaefer, H. F. *J. Phys. Chem*. **1993**, *97*, 12232. https://doi.org/10.1021/j100149a023
16. Hu, C.-H.; Schreiner, P. R.; Schleyer, P. v. R.; Schaefer, H. F. *J. Phys. Chem.* **1994**, *98*, 5040-5043. https://doi.org/10.1021/j100070a015
17. So, S. P. *J. Phys. Chem.* **1996**, *100*, 5250. https://doi.org/10.1021/jp953020+
18. Rasul, G.; Prakash, G. K. S.; Olah, G. A. *Inorg. Chem.* **1999**, *38*, 4132. https://doi.org/10.1021/ic9901620
19. Frisch, M. J. *et al. Gaussian 09*, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.
20. Alecu, I. M.; Zheng, J.; Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2010,** *6*, 2872. https://doi.org/10.1021/ct100326h
21. CFOUR, a quantum chemical program package, Stanton, J. F.; Gauss, J.; Harding, M. E.; Szalay, P. G. with contributions from Auer, A. A.; Bartlett, R. J.; Benedikt, U.; Berger, C.; Bernholdt, D. E.; Bomble, Y. J.; Cheng, L.; Christiansen, O.; Heckert, M.; Heun, O.; Huber, C.; Jagau, C.; Jonsson, D.; Jusélius, J.; Klein, K.; Lauderdale, W. J.; Mathews, D. A.; Metzroth, T.; O'Neill, D. P.; Price, D. R.; Prochnow, E.; Ruud, K.; Schiffmann, F.; Schwalbach, W.; Stopkowicz, S.; Tajti, A.; Vµzquez, J.; Wang, F.; Watts, J. D.; and the integral packages MOLE-CULE (Almlçf, J and Taylor, P. R.), PROPS (Taylor, P. R.), ABACUS (Helgaker, T.; Aa, H. J.; Jensen H. J. A.; Jørgensen, P.; Olsen, J.), and ECP routines (Mitin, A. V.; Wüllen, C. van), **2010**.
22. Harding, M. E.; Metzroth, T.; Gauss, J.; Auer, A. A. *J. Chem. Theory Comput.* **2008**, *4*, 64. https://doi.org/10.1021/ct700152c