4132 *Inorg. Chem.* **1999,** *38,* 4132−4134

Theoretical Study of SiH_{2n}^{2+} ($n = 1-3$) Dications[1]

Golam Rasul, G. K. Surya Prakash, and George A. Olah*

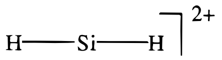
Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry,
University of Southern California, University Park, Los Angeles, California 90089-1661

Received February 8, 1999

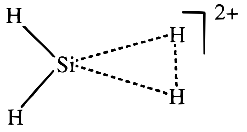
Structures and energies of SiH_{2n}^{2+} ($n = 1-3$) dications were calculated at the density functional theory (DFT) B3LYP/6-311+G(d,p) and B3LYP/6-311++G(3df,2pd) levels. Contrary to the previously reported theoretical studies at the HF/6-31G* level, the singlet SiH_2^{2+} is not of linear $D_{\infty h}$ symmetric **1** but a C_{2v} symmetrical **2** with a two electron three center (3c-2e) bond. The structure **2** is significantly more stable than **1** by 14.7 kcal/mol. For calibration, structures **1** and **2** were also calculated at the ab initio CCSD(T)/cc-pVTZ level and found results which are in good agreement with the DFT results. DFT calculations also indicate that the singlet SiH_4^{2+} is not of C_{2v} symmetric **4** with a 3c-2e bond but a C_{2v} symmetric **5** with two 3c-2e bonds. The C_{2v} symmetric **7** with two 3c-2e bonds and two 2c-2e bonds was found to be the global minimum for SiH_6^{2+} dications.

Introduction

Koch, Frenking, and Schwarz[2] reported the ab initio HF/6-31G* calculated structures of SiH_2^{2+} and SiH_4^{2+}.[3] The linear $D_{\infty h}$ symmetrical structure was preferred for the singlet SiH_2^{2+}.[2] Linear $D_{\infty h}$ symmetrical structure is also preferred for the carbon analogue CH_2^{2+} as shown by Pople, Tidor, and Schleyer.[4] The planar C_{2v} symmetrical structure was found to be the global minimum for the singlet SiH_4^{2+} which can be considered as SiH_2^{2+} dication complexed with a hydrogen molecule.[2] The sp^2-hybridized silicon atom of SiH_4^{2+} contains a two electron three center (3c-2e) bond and an empty p-orbital perpendicular to the plane of the molecule. Similar planar C_{2v} symmetrical structure is preferred for the carbon analogue CH_4^{2+} as shown by Wong and Radom.[5] The structure of hexacoordinated SiH_6^{2+} dication has never been reported. On the other hand, the calculated parent six coordinate carbocation, diprotonated methane (CH_6^{2+}) has been reported by Lammertsma et al.[6] and has two 3c-2e bonding interactions in its minimum-energy structure (C_{2v}).



SiH_2^{2+} ($D_{\infty h}$)



SiH_4^{2+} (C_{2v})

We report now based on density functional theory (DFT) calculations that the global minimum structure of SiH_2^{2+} is not of linear $D_{\infty h}$ symmetry but of C_{2v} symmetry with a 3c-2e bond. The $D_{\infty h}$ structure although a minimum on the potential energy surface (PES), is significantly less stable than the C_{2v} structure. Similarly, the global minimum structure of SiH_4^{2+} is not one with a 3c-2e bond but one with two 3c-2e bonds. In addition, we also report the structures of SiH_6^{2+} dication which can be derived by reacting SiH_4^{2+} and H_2.

Results and Discussion

Calculations were carried out with the Gaussian 98 program system.[7] The geometry optimizations and frequency calculations were performed at the DFT[8] B3LYP[9]/6-311+G(d,p)[10] and B3LYP/6-311++G(3df,2pd)[10] levels. From calculated frequencies, the optimized structures were characterized as minima (number of imaginary frequency (NIMAG) = 0) or transition structure (NIMAG = 1). Final energies were calculated at the B3LYP/6-311++G(3df,2pd)//B3LYP/6-311++G(3df,2pd) + ZPE (B3LYP/6-311++G(3df,2pd)//B3LYP/6-311++G(3df, 2pd)) level. For SiH_2^{2+} geometry optimizations and energy

---

(1) Chemistry in Superacids 44. Part 43, Olah, G. A.; Prakash, G. K. S.; Rasul, G. *J. Mol. Struct. (THEOCHEM),* in press.

(2) Koch, W.; Frenking, G.; Schwarz, H.; *J. Chem. Soc., Chem. Commun.,* **1985**, 1119. Koch, W.; Frenking, G.; Schwarz, H.; Maquin, F.; Stahl, D.; *J. Chem. Soc., Perkin Trans. 2*, **1986**, 757.

(3) For a review on gas-phase chemistry of silicon-containing ions, see Goldberg, N.; Schwarz, H. *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons Ltd.: New York, 1998. Koch, W.; Schwarz, H. *Structure/Reactivity and Thermochemistry of Ions*; Ausloos, P., Lias, S. G., Eds.; Reidel: Dordrecht, 1987. Lammertsma, K.; Schleyer, P. v. R.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1321. Koch, W.; Maquin, F.; Stahl, D.; Schwarz, H. *Chimica* **1985**, *39*, 376.

(4) Pople, J. A.; Tidor, B.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1982**, *88*, 439.

(5) Wong, M. W.; Radom, L. *J. Am. Chem. Soc.* **1989**, *111*, 1155.

(6) Lammertsma, K.; Olah. G. A.; Barzaghi, M.; Simonetta, M. *J. Am. Chem. Soc.* **1982**, *104*, 6851. Lammertsma, K.; Barzaghi, M.; Olah, G. A.; Pople, J. A.; Schleyer, P. v. R.; Simonetta, M. *J. Am. Chem. Soc.* **1983**, *105*, 5258.

(7) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, R. E.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; M. Head-Gordon, M.; Pople, J. A. *Gaussian 98*, Revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

(8) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.

(9) Becke's three-parameter hybrid method using the LYP correlation functional: Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

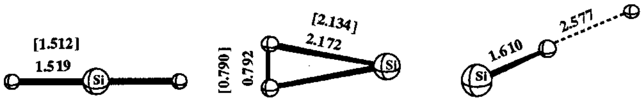
(10) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

10.1021/ic9901620 CCC: \$18.00

Table 1. Total Energies (-au), ZPE[a] (kcal/mol)

	B3LYP/ 6-311+G(d,p)	B3LYP/ 6-311++G(3df,2pd)	rel. energy[b]
SiH_2^{2+} **1**	289.69024 [289.22684][c]	289.69166 (7.2)	14.7
SiH_2^{2+} **2**	289.71080 [289.24610][c]	289.71432 (6.7)	0.0
SiH_2^{2+} **3**	289.62003	289.62141 (3.3)	54.9
SiH_4^{2+} **4**	290.92387	290.92801 (16.6)	3.1
SiH_4^{2+} **5**	290.92288	290.92929 (14.3)	0.0
SiH_4^{2+} **6**	290.82318	290.82701 (11.6)	61.5
SiH_6^{2+} **7**	292.15287	292.15920 (26.6)	0.00
SiH_6^{2+} **8**	292.13130	292.14024 (22.7)	8.0
SiH_6^{2+} **9**	292.05450	292.06003 (22.5)	58.1

[a] *Zero point vibrational energies (ZPE) at B3LYP/6-311++G(3df,2pd)//B3LYP/6-311++G(3df,2pd) scaled by a factor of 0.96 are given in parentheses.* [b] *Relative energy based on B3LYP/6-311++G(3df,2pd)//B3LYP/6-311++G(3df,2pd) + ZPE.* [c] *CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVTZ energies are given in square brackets.*



SiH_2^{2+} **1** ($D_{\infty h}$) SiH_2^{2+} **2** (C_{2v}) SiH_2^{2+} **3** TS ($C_{\infty v}$)

Figure 1. B3LYP/6-311++G(3df,2pd) [CCSD(T)/cc-pVTZ] optimized structures of **1**−**3**.

calculations were also carried out with the ab initio coupled cluster method[10] at the CCSD(T)/cc-pVTZ[11] level. Calculated energies are given in Table 1.

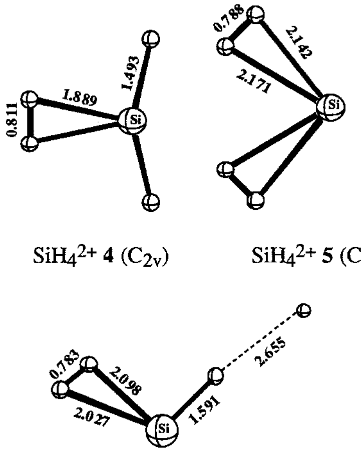
SiH_2^{2+}. Linear $D_{\infty h}$ structure **1** and C_{2v} structure **2** (Figure 1) were found to be minima on the potential energy surface (PES) of singlet SiH_2^{2+} at the DFT B3LYP/6-311+G(d,p) and B3LYP/6-311++G(3df,2pd) levels as indicated by frequency calculations. The structure **2** is 12.9 kcal/mol more stable than **1** at the B3LYP/6-311+G(d,p) level (Table 1). The difference becomes 14.2 kcal/mol at the higher B3LYP/6-311++G(3df,2pd) level. At our highest level i.e., at the B3LYP/6-311++G(3df,2pd)//B3LYP/6-311++G(3df,2pd) + ZPE level the structure **2** is significantly more stable than **1** by 14.7 kcal/mol. Thus, the structure **2** is the global minimum on the PES of SiH_2^{2+}. For calibration, structures **1** and **2** were also calculated at the ab initio CCSD(T)/cc-pVTZ level and found results which are in good agreement with the DFT results. Thus, at the CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVTZ level the structure **2** is also 12.1 kcal/mol more stable than **1**. Previously Koch et al.[2] calculated singlet SiH_2^{2+} at the ab initio HF/6-31G* level. They concluded,[2] in contrast to our present results, that the global minimum for singlet SiH_2^{2+} is the structure **1**. Calculated linear $D_{\infty h}$ symmetrical structure for carbon analogue CH_2^{2+} was also reported.[4]

Structure **2** is characterized with a 3c-2e bond and can be considered as a complex between Si^{2+} and a hydrogen molecule. It is interesting to note that the interaction between silicon and hydrogens can also be considered as three center four electron (3c-4e) bonding as there are four electrons involved including the silicon lone pair. However, such bonding involving two hydrogen atoms and silicon is highly unlikely.[12a] The sp-hybridized silicon atom of **2** possesses two formal vacant p-orbitals and a sp-orbital (formally containing a pair of electrons) perpendicular to the p-orbitals. The 3c-2e Si−H bond distance of **2** is 2.172 Å. This is expectedly longer than that of 2c-2e Si−H bond of **1** (1.519 Å).

Table 2. Kinetic Barrier of Deprotonation and ΔH_0 of Dehydrogenation (in kcal/mol)[a]

reaction	ΔH_0	kinetic barrier
SiH_2^{2+} **2** → SiH^+ + H^+	−63.3	54.9
SiH_2^{2+} **2** → Si^{2+} + H_2	+25.4	
SiH_4^{2+} **5** → SiH_3^+ + H^+	−23.2	61.5
SiH_4^{2+} **5** → SiH_2^{2+} **2** + H_2	+20.6	
SiH_6^{2+} **7** → SiH_5^+ + H^+	−9.6	58.1
SiH_6^{2+} **7** → SiH_4^{2+} **5** + H_2	+25.3	

[a] *Based on B3LYP/6-311++G(3df,2pd)//B3LYP/6-311++G(3df,2pd) + ZPE.*



SiH_4^{2+} **4** (C_{2v}) SiH_4^{2+} **5** (C_{2v})

SiH_4^{2+} **6** TS (C_s)

Figure 2. B3LYP/6-311++G(3df,2pd) optimized structures of **4**−**6**.

In a related study Kapp, Schreiner, and Schleyer reported[12b] ab initio and DFT study on XH_3^+ cations (X = C, Si, Ge, Sn, Pb). The highly symmetric D_{3h} structure as well as C_s symmetric structure with a 3c-2e bond were found to be the minima on the potential energy surfaces of XH_3^+. The D_{3h} forms were found to be favorable energetically for X = C, Si and Ge. On the other hand, C_s form were found to be energetically favorable for X = Sn and Pb. Recently Rasul, Prakash, and Olah also reported[13] an ab initio study which indicates that the global minimum structure of XH_3^{2+} (X = Si, Ge) as well as XH_3^+ (X = Al, Ga) are not of C_{2v} symmetry but of C_s symmetry with 3c-2e bonds.

We also have located transition structure, **3** (Figure 1), for the deprotonation process in **2**. Structure **3** lies 54.9 kcal/mol higher in energy than **2** (Table 2). Thus **2** has considerable kinetic barrier for deprotonation, although the deprotonation process is exothermic by 63.3 kcal/mol.

SiH_4^{2+}. Two C_{2v} symmetrical structures, **4** and **5**, were found to be minima on the PES of singlet SiH_4^{2+} at the B3LYP/6-311+G(d,p) level (Figure 2) as indicated by frequency calculations at the same level. The structure **5** is only 0.6 kcal/mol less stable than **4** at this level of calculations (Table 1). At the higher level of B3LYP/6-311++G(3df,2pd), both **4** and **5** were also found to be minima. But at this level the structure **5** is 0.8 kcal/mol more stable than than **4**. At our highest level the structure **5** is more stable than **4** by 3.1 kcal/mol. Thus, the structure **5** is the global minimum for the singlet SiH_4^{2+}.

---

(11) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(12) (a) Akiba, K. *Chemistry of Hypervalent Compounds;* Wiley-VCH: New York, 1999. (b) Kapp, J.; Schreiner, P. R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1996**, *118*, 12154.

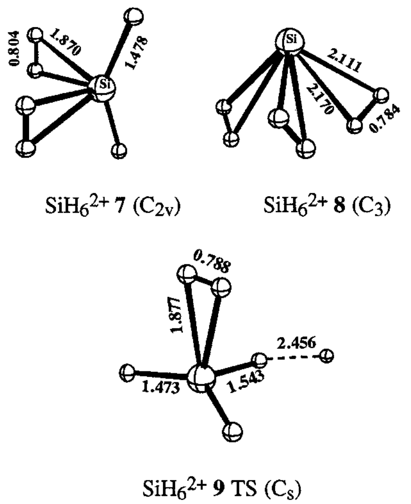
(13) Rasul, G.; Prakash, G. K. S.; Olah, G. A. *J. Mol. Struct. (THEOCHEM)* **1998**, *455*, 101.

Structure **5** resembles a complex between Si^{2+} with two hydrogen molecules resulting in formation of two 3c-2e bonds with an empty p-orbital orthogonal to the plane of the molecule. The 3c-2e Si−H bond distances of **5** are 2.142 and 2.171 Å.

Previously Koch et al.[2] calculated SiH_4^{2+} at the ab initio HF/6-31G* level and concluded, in contrast to our present results, that the global minimum for SiH_4^{2+} is the structure **4**. The reported[2] structure of **4** at the HF/6-31G* level agrees very well with our B3LYP/6-311++G(3df,2pd) calculated structure (Figure 2). Transition state **6** for deprotonation of **5** was also located. Structure **6** lies 61.5 kcal/mol higher in energy than structure **5** (Table 2).

SiH_6^{2+}. At the B3LYP/6-311+G(d,p) and B3LYP/6-311++G-(3df,2pd) levels the C_{3v} symmetric form **7** and C_3 symmetric form **8** were found to be the stable minima for singlet SiH_6^{2+} (diprotonated silane). Structure **7** is isostructural with CH_6^{2+}.[6] Six coordinated SiH_6^{2+} **7** contains two 3c-2e bonds and two 2c-2e bonds (Figure 3). The Si−H bond distance of 3c-2e interactions is 1.870 Å. On the other hand, the six hydrogens in structure **8** are bonded to the silicon by three 3c-2e bonds (Figure 3). However, the structure **8** is less stable than **7** by 8.0 kcal/mol. Transition state **9** for deprotonation of **7** was also located. Structure **9** lies 58.1 kcal/mol higher in energy than structure **7** (Table 2).

Hydrogenations of Si^{2+}, SiH_2^{2+} (**2**), and SiH_4^{2+} (**5**) to form SiH_2^{2+} (**2**), SiH_4^{2+} (**5**), and SiH_6^{2+} (**7**), respectively, were also calculated and listed in Table 2.



SiH_6^{2+} **7** (C_{2v})

SiH_6^{2+} **8** (C_3)

SiH_6^{2+} **9** TS (C_s)

Figure 3. B3LYP/6-311++G(3df,2pd) optimized structures of **7**−**9**.

Conclusions

The structure of SiH_{2n}^{2+} ($n = 1-3$) dications were calculated by using DFT theory. Contrary to previous theoretical studies at the HF/6-31G* level,[2] present DFT study at the B3LYP/6-311+G(d,p) and B3LYP/6-311++G(3df,2pd) levels indicates that the global minimum structure of singlet the SiH_2^{2+} is not of linear $D_{\infty h}$ symmetric **1** but a C_{2v} symmetrical **2** with a 3c-2e bond. The $D_{\infty h}$ symmetric **1**, although a minimum on the PES, is 14.7 kcal/mol less stable than **2**. Similar study also indicates that the global minimum structure of the singlet SiH_4^{2+} is not of C_{2v} symmetric **4** with a 3c-2e bond but a C_{2v} symmetrical **5** with two 3c-2e bonds. The structure **4** is 3.1 kcal/mol less stable than **5**. The C_{2v} symmetrical structure **7** with two 3c-2e bonds and two 2c-2e bonds was found to be the global minimum for the singlet SiH_6^{2+} dication.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

IC9901620