Comparative ab Initio Study of the Structures and Stabilities of the Ethane Dication $C_2H_6^{2+}$ and Its Silicon Analogues $Si_2H_6^{2+}$ and $CSiH_6^{2+}$

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Ab initio MP2/6-311G** and QCISD(T)/6-311G** levels as well as Gaussian-2 theory were used to perform a comparative study of the structures and stabilities of the ethane dication $C_2H_6^{2+}$ and its silicon analogues $Si_2H_6^{2+}$ and $CSiH_6^{2+}$. Similar to previous HF/6-31G* results, our present calculations also indicate that the two-electron three-center (2e−3c) bonded carbonium−carbenium structure **1** is more stable than the doubly hydrogen bridged diborane-type structure **2** by about 12 kcal/mol. For the silicon analogue $Si_2H_6^{2+}$ the calculations, however, indicate that the 2e−3c bonded siliconium−silicenium structure **8** is about 9 kcal/mol less stable than doubly hydrogen bridged structure **9**. Similar results were also computed for carbon−silicon mixed $CSiH_6^{2+}$ dication structures. These studies are in agreement with the more electropositive character of silicon compared to carbon. Possible dissociation paths of the minimum structures were also calculated.

Introduction

The methane dication CH_4^{2+} is the parent alkane dication. The planar C_{2v} symmetrical structure with a two-electron three-center (2e−3c) bond (Chart 1) is preferred for the dication.[1] Earlier calculations, however, predicted a square planar D_{4h} symmetrical structure for the dication.[2] The dication was observed experimentally by charge stripping of the $CH_4^{\bullet+}$ radical cation in a mass spectrometer.[3]

Unlike the structure of methane dication, DFT study, however, indicates that the global minimum structure of SiH_4^{2+} is not the one with a 2e−3c bond but one with two 2e−3c bonds (Chart 2).[4] The two-2e−3c bonded structure is 3.1 kcal/mol more stable than the single 2e−3c bonded structure.

The ethane dication $C_2H_6^{2+}$ was first investigated theoretically by Olah and Simonetta, who found that a doubly bridged, diborane-type D_{2d} symmetric structure (Chart 3) is a minimum.[5] Later, Schleyer and Pople showed that the C_{2v} symmetrical carbonium−carbenium ion isomer is energetically favored over the diborane-like structure by 9.0 kcal/mol at the MP4SDQ/6-31G**//HF/6-31G* level.[6] Subsequently, Olah et al.[7] showed that the global minimum of this dication is a C_s symmetrical structure with a 2e−3c bond. This carbonium−carbenium dication structure can be considered either as a complex between H_2 and the ethylene dication $C_2H_4^{2+}$ or as the protonated ethyl cation. The C_s symmetrical structure is 3.5 kcal/mol more stable than the C_{2v} symmetrical structure. The $C_2H_6^{2+}$ dication has also been observed experimentally by charge-stripping mass spectrometery.[8]

The related dimer of the ethyl cation ($C_4H_{10}^{2+}$ dication) was recently investigated by Olah, Prakash, and Rasul at the ab initio MP2/6-31G** level.[9] Several doubly hydrogen bridged structures including the dimethyl analogue of $C_2H_6^{2+}$ (D_{2d} symmetric structure, Chart 3) were found to be minima. Previously, we were able to show by hydrogen/deuterium exchange experiments and by theoretical calculations that long-lived stable *tert*-butyl[10] as well as isopropyl[11] cations undergo C−H protonation in superacids to form highly electron deficient protio-*tert*-butyl ($C_4H_{10}^{2+}$) and protioisopropyl ($C_3H_8^{2+}$) dications, respectively.

CHART 1

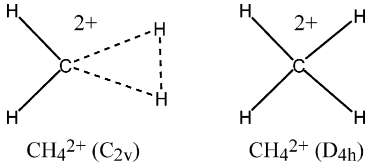
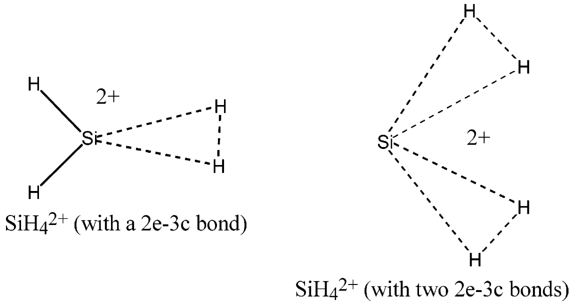


CHART 2



No such study of silicon analogues, however, has been reported. Silicon-containing ions are also intriguing. Silicon-containing molecules and ions were found as constituents of the gas associated with late-type stars and star-forming regions. It has been found that about 10% of the molecules of the regions contain a silicon atom.[12] We herein report ab initio calculations to establish the structures and stabilities of $Si_2H_6^{2+}$ and $CSiH_6^{2+}$ and compare them with those of $C_2H_6^{2+}$.

Calculations

All calculations were carried out with the Gaussian 98 program.[13] The geometry optimizations were performed at the MP2/6-311G** level. Vibrational frequencies at the MP2/6-311G** level were used to characterize stationary points as

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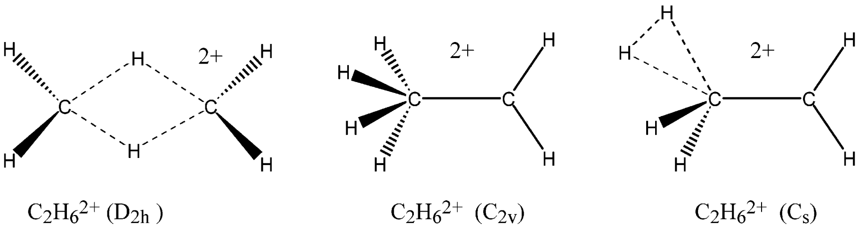
CHART 3



$C_2H_6^{2+}$ (D_{2h}) $C_2H_6^{2+}$ (C_{2v}) $C_2H_6^{2+}$ (C_s)

TABLE 1: Total Energies (−au) and ZPEs[a] and Relative Energies[b] (kcal/mol)

compd no.	MP2/ 6-311G**	ZPE	NIMAG[c]	QCISD(T)/ 6-311G**	G2	rel energy
1	78.56282	40.4	0	78.60712	78.61721	35.4
2	78.54608	41.2	0	78.58986	78.59747	47.8
3	78.61344	38.8	0	78.65494	78.67360	0.0
4	78.47257	35.7	1	78.51644	78.53497	87.0
5	77.31557	28.1	0	77.35849	77.37874	
6	39.35619	19.3	0	39.38115	39.38559	
7	78.50474	40.1	1	78.55648	78.56441	68.5
8	580.72929	29.4	0	580.77963	580.80646	8.7
9	580.74925	31.3	0	580.80004	580.82024	0.0
10	580.66109	25.0	0	580.71015	580.74746	45.7
11	580.65907	26.3	0	580.70858	580.74704	45.9
12	580.57087	24.9	1	580.62003	580.65620	102.9
13	579.53836	20.2	0	579.58090	579.61274	
14	290.44148	13.9	0	290.46623	290.47765	
15	580.73518	29.3	1	580.80869	580.78566	21.7
16	329.68034	34.6	1	329.72308	329.74067	4.0
17	329.62361	35.2	0	329.67470	329.69314	33.8
18	329.68838	36.5	0	329.73220	329.74698	0.0
19	329.67185	32.9	0	329.71378	329.74116	3.7
20	329.58154	30.4	1	329.63275	329.66118	53.9
21	329.48299	29.1	1	329.53362	329.56103	116.7
22	328.42810	24.5	0	328.47111	328.49527	
23	329.66160	34.9	1	329.71062	329.72448	14.1
$\mathbf{B_2H_6}$	53.05651	38.7	0	53.10412	53.10750	
$\mathbf{Al_2H_6}$	487.49108	27.5	0	487.53878	487.56039	

[a] Zero point vibrational energies at the MP2/6-311G**//MP2/6-311G** level scaled by a factor of 0.96. [b] Using G2. [c] Number of imaginary frequencies.

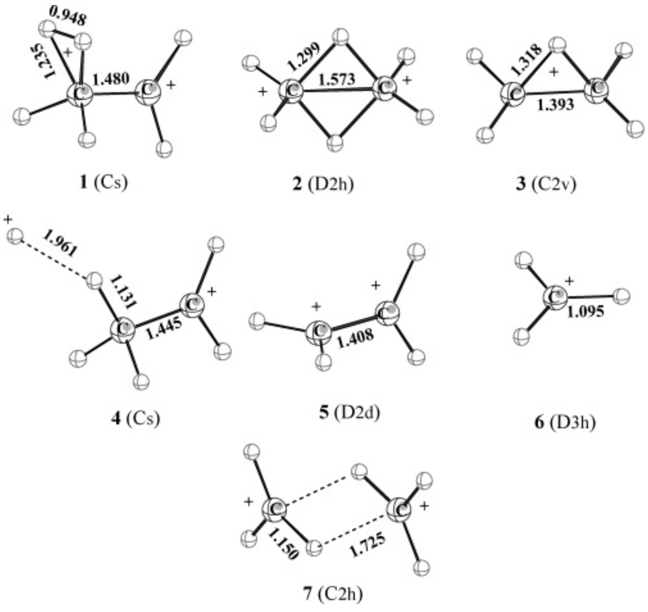


Figure 1. QCISD(T)/6-311G**-optimized structures of **1**−**7**.

TABLE 2: Dissociation Energy (ΔE_0) and Respective Kinetic Barrier at 298 K for the Selected Processes[a]

process	ΔE_0[a] (kcal/mol)	barrier (kcal/mol)
$C_2H_6^{2+}$ **1** → $C_2H_5^+$ **3** + H^+	−35.4	51.6
$Si_2H_6^{2+}$ **8** → $Si_2H_5^+$ **10** + H^+	+37.0	94.2
$CSiH_6^{2+}$ **17** → $CSiH_5^+$ **20** + H^+	+20.1	82.9
$C_2H_6^{2+}$ **2** → $2CH_3^+$ **6**	−109.9	20.7
$Si_2H_6^{2+}$ **9** → $2SiH_3^+$ **14**	−84.8	21.7
$CSiH_6^{2+}$ **18** → CH_3^+ **6** + SiH_3^+ **14**	−73.0	14.1
$C_2H_6^{2+}$ **1** → $C_2H_4^{2+}$ **5** + H_2	−45.3	
$Si_2H_6^{2+}$ **8** → $Si_2H_4^{2+}$ **13** + H_2	−17.1	
$CSiH_6^{2+}$ **17** → $CSiH_4^{2+}$ **22** + H_2	−70.6	

[a] Using G2 theory.

minima (number of imaginary frequencies (NIMAG) = 0) and to evaluate zero-point vibrational energies (ZPEs), which were scaled by a factor of 0.96.[14] The transition states were also checked by IRC (intrinsic reaction coordinate) calculations.[13] For MP2/6-311G** structures, further geometry optimizations were carried out at the QCISD(T)/6-311G** level. For improved energy, the Gaussian-2 (G2) energies[15] were computed. Atomic charges at the QCISD(T)/6-311G**//QCISD(T)/6-311G** level were obtained using the natural bond orbital (NBO) analysis method.[16] Calculated energies are given in Table 1. QCISD(T)/6-311G** geometrical parameters and G2-calculated energies will be discussed throughout, unless stated otherwise.

Results and Discussion

Structures. Structures of $C_2H_6^{2+}$ dication were previously calculated at the HF/6-31G* level by Lammertsma et al.[7] Similar to previous calculations, our present calculations at the MP2/6-311G** level also show that both the C_s symmetric structure **1** and D_{2h} symmetric structure **2** are minima on the potential energy surface (PES) of $C_2H_6^{2+}$ as indicated by frequency calculations at the same level (Figure 1). The structures were further optimized at the higher QCISD(T)/6-311G** level. Structure **1** with a C−C bond length of 1.480 Å contains a pentacoordinate carbon with a 2e−3c bond and a tricoordinate carbon and can be considered as a carbonium−carbenium dication. We also calculated the NBO charges of ion **1** (Figure 1). Charges of the carbonium (CH_4) and carbenium (CH_3) groups of **1** were found to be evenly distributed (+0.96 and +1.04, respectively). On the other hand, structure **2** with a C−C bond length of 1.573 Å is a doubly hydrogen bridged diborane-type structure which contains two pentacoordinate carbons and can be considered as a carbonium−carbonium dication. Structure **2** can also be considered as a dimer of the methyl cation CH_3^+. G2 energy calculations indicate that structure **1** is 12.4 kcal/mol more stable than **2**. This is in good agreement with the previously reported value[8] of 12.0 kcal/mol at the lower level of calculations (MP3/6-31G**//HF/6-31G*).

Possible dissociation paths of **1** and **2** were also calculated. Deprotonation of **1** into ethyl cation **3** is exothermic by 35.4 kcal/mol (Table 2). Transition structure **4** for deprotonation was located (Figure 1). Structure **4** lies 51.6 kcal/mol above **1**. Thus, **1** has a substantial kinetic barrier for deprotonation, although the deprotonation process is exothermic by 35.4 kcal/mol. Dissociation of **2** into two methyl cations CH_3^+ was computed to be even more exothermic by 109.9 kcal/mol. Transition state

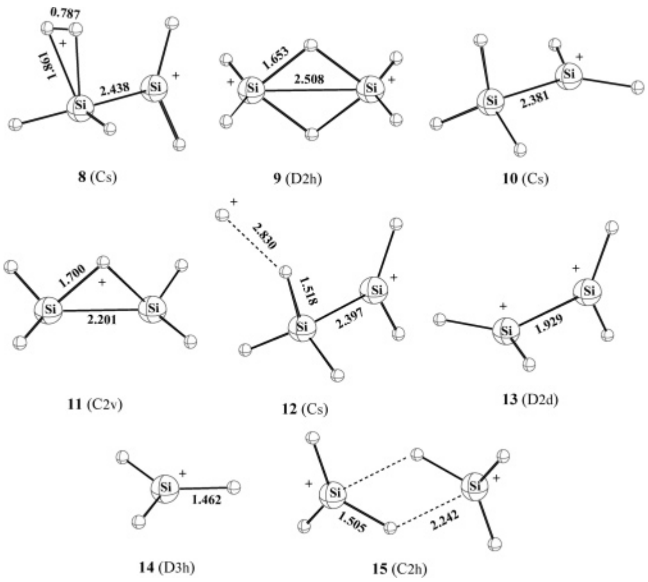


Figure 2. QCISD(T)/6-311G**-optimized structures of **8**−**15**.

7 for the dissociation was located. Structure **7** lies 20.7 kcal/mol above **2**. Dissociation of **1** into ethylene dication **5** and H_2 was also calculated and found to be endothermic by 45.3 kcal/mol (Table 2).

Neutral diborane, B_2H_6, is isoelectronic with the $C_2H_6^{2+}$ dication. For comparison we also calculated the structure of B_2H_6 at the same QCISD(T)/6-311G** level, which is given in Figure 1. The D_{2h} symmetric structure is the only minimum located on the PES of B_2H_6. A structure similar to **1** was found to be not a minimum on the PES of B_2H_6. The B−B bond length of B_2H_6 (1.778 Å) is 0.205 Å longer than the C−C bond length of $C_2H_6^{2+}$ structure **2** (1.573 Å). This indicates that despite charge−charge repulsion the bonding interaction between two electron-deficient CH_3^+ groups is more than that between two (neutral but relatively less electron deficient) BH_3 groups.

Like the $C_2H_6^{2+}$ dication, two similar $Si_2H_6^{2+}$ (disilane dication) structures, C_s symmetric **8** and D_{2h} symmetric **9**, were found to be the stable minima at the MP2/6-311G** level (Figure 2). The calculated structures show that they are in fact isostructural with the corresponding carbon analogues **1** and **2**, respectively. However, unlike the carbon analogues, the relative stability of the silyl dication structures is opposite. At the MP2/6-311G** level **8** is 12.5 kcal/mol less stable than **9**. The MP2/6-311G** structures were further optimized at the higher QCISD(T)/6-311G** level. At this level **8** is also 12.8 kcal/mol less stable than **9**. At our highest level (i.e., using G2 theory) **8** is still 8.7 kcal/mol less stable than **9**. This difference in relative stabilities of **1** and **2** vs **8** and **9** is probably due to charge−charge repulsion. This can be rationalized by the high electropositive character of silicon compared to carbon (Pauling electronegativity scale: C, 2.5; Si, 1.8).[17] The penta- and tricoordinate silicon atoms of **8** bear relatively more positive charges (+0.79 and +1.21, respectively) compared to penta- and tricoordinate carbon atoms of **1** (−0.80 and +0.52, respectively). Thus, overall charge−charge repulsion in **1** compared to **2** is less than that in **8** compared to **9**. Significantly different C−C and Si−Si bond distances might also play an important role in their relative stabilities. Similar to those of **1**, charges of the siliconium (SiH_4) and silicenium (SiH_3) groups of **8** were found to be evenly distributed (+0.97 and +1.03, respectively).

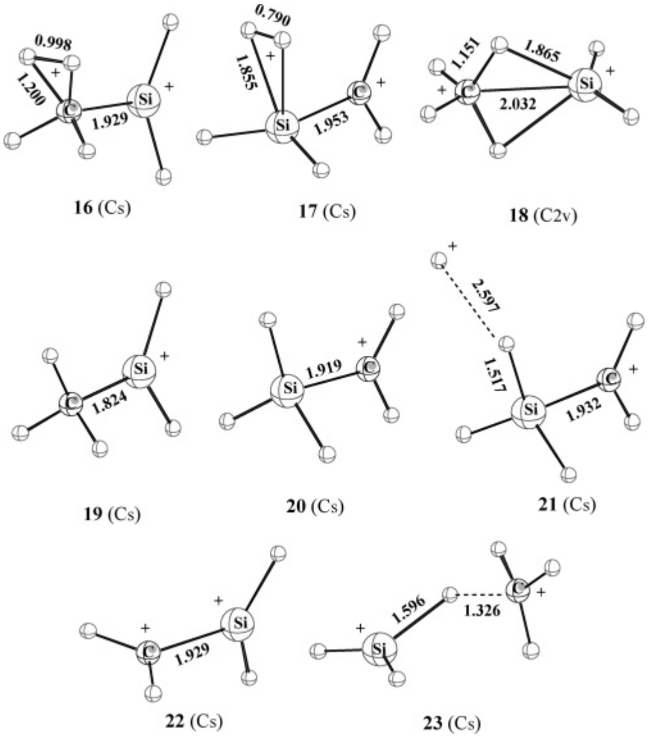
Doubly hydrogen bridged **9** is therefore the most favorable structure on the PES of $Si_2H_6^{2+}$ and can be viewed as a dimer of the parent silicenium ion (SiH_3^+). Dication **9** with a Si−Si bond length of 2.508 Å contains two pentacoordinate silicon atoms and can be considered as a siliconium−siliconium dication. The nature of the hydrogen bridge in structure **9** was previously analyzed theoretically by Trinquier and Malrieu.[18] On the other hand, structure **8** with a Si−Si bond length of 2.438 Å contains a pentacoordinate silicon and a trivalent silicon, making it a siliconium−silicenium dication.

We have also calculated the energy changes and barriers for possible dissociation paths of **8** and **9**. Deprotonation of **8** into disilyl cation **10** is endothermic by 37.0 kcal/mol. Hydrogen-bridged disilyl cation **11**, although a minimum on the PES of $Si_2H_5^+$, is slightly (0.2 kcal/mol) less stable than the open structure **10**. Structure **8** has a very high kinetic barrier for deprotonation as the transition structure **12** for deprotonation lies 94.2 kcal/mol above **8** (Figure 2 and Table 2). Dissociation of **8** into disilene dication **13** and H_2 is slightly endothermic by 17.1 kcal/mol. Dissociation of **9** into two silyl cations SiH_3^+ was calculated to be exothermic by 84.8 kcal/mol. Transition state **15** for the dissociation lies 21.7 kcal/mol higher in energy than structure **9** (Table 2).

Neutral Al_2H_6 is isoelectronic with the $Si_2H_6^{2+}$ dication. For comparison we also calculated the structure of Al_2H_6, which is given in Figure 2. The D_{2h} symmetric structure is the only minimum located on the PES of Al_2H_6. A structure similar to **8** was found to be not a minimum on the PES of Al_2H_6. The Al−Al bond length of Al_2H_6 (2.608 Å) is also longer than the Si−Si bond length of the $Si_2H_6^{2+}$ structure **9** (2.508 Å) only by 0.100 Å. This indicates that despite charge−charge repulsion the bonding interaction between two electron-deficient SiH_3^+ units is more than that between two (neutral but relatively less electron deficient) AlH_3 units.

For comparison, carbon−silicon mixed $CSiH_6^{2+}$ dication structures were also calculated. In this case there are two types of 2e−3c-bonded structures, i.e., **16** and **17**, as well as a doubly hydrogen bridged **18** (Figure 3). Structure **16** contains a pentacoordinate carbon and a tricoordinate silicon, and structure **17** contains a pentacoordinate silicon and tricoordinate carbon. At the MP2/6-311G** level C_s symmetric **16** was found to be not a minimum as indicated by frequency calculations at the same level. Without symmetry constraints (i.e., at C_1 symmetry) the structure converted into the more stable C_{2v} structure **18** upon optimization without any activation barrier. Structure **17** was found to be a minimum on the PES of $CSiH_6^{2+}$ and can be considered as a siliconium−carbenium dication. However, **17** is significantly less stable than the dihydrogen-bridged structure **18** by 33.8 kcal/mol (Table 1). Again, the higher electropositive character of silicon supports the stability of **18**. Structure **18** can be considered as a complex between groups CH_4 and SiH_2^{2+} as the calculated charges of the groups were found to be +0.40 and +1.60, respectively (Figure 3).

Dissociation of $CSiH_6^{2+}$ dication into $CSiH_5^+$ monocation was also calculated and is given in Table 2. For the $CSiH_5^+$ monocation two possible isomers, **19** and **20**, were calculated. At the MP2/6-311G** level C_s symmetric structure **20** was found not to be a minimum as indicated by frequency calculations at the same level. Energy comparison also indicates that structure **19** is substantially more stable than **20** by 50.2 kcal/mol. This is also in agreement with the electropositive character of silicon. Possible dissociation of **17** into **20** through transition state **21** and the dissociation of **18** into CH_3^+ and SiH_3^+ through transition state **23** were calculated and are given in Table 2.



16 (Cs) **17** (Cs) **18** (C2v)

19 (Cs) **20** (Cs) **21** (Cs)

22 (Cs) **23** (Cs)

Figure 3. QCISD(T)/6-311G**-optimized structures of **16**−**33**.

Dissociation energy of **17** into **22** and H_2 was also calculated and is given in Table 2.

Ethyl cation **3** and protonated ethyl dications **1** and **2** and their silicon analogues are structurally intriguing. For example, structure **3** is stabilized not only by external solvation but also intramoleculary by C−H hyperconjugations. The hyperconjugative interactions with the carbocationic center contribute to the overall stability of the ion. With further protonation of ethyl cation **3**, C−H hyperconjugative stabilization decreases. This would lead to an enhanced electron deficiency and reactivity of the carbocationic center.

Conclusion

A comparative study of the structures and stabilities of the ethane dication $C_2H_6^{2+}$ and its silicon analogues $Si_2H_6^{2+}$ and $CSiH_6^{2+}$ was carried out at the ab initio MP2/6-311G** and QCISD(T)/6-311G** levels and also by using G2 theory. In good agreement with the previously reported calculations at the HF/6-31G* level our present calculations also indicate that the 2e−3c bonded carbonium−carbenium structure **1** is more stable than the doubly hydrogen bridged diborane-type structure **2** by 12.4 kcal/mol. For the silicon analogue $Si_2H_6^{2+}$ the calculations, however, indicate that the 2e−3c bonded siliconium−silicenium structure **8** is 8.7 kcal/mol less stable than doubly hydrogen bridged structure **9**. A similar result was also obtained for mixed carbon−silicon $CSiH_6^{2+}$ dication structures. These studies are in agreement with the more electropositive character of silicon compared to carbon. Possible dissociation paths of the minimum structures were also calculated.

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Supporting Information Available: Cartesian coordinates and total energies (hartrees) of the optimized geometries (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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