The Structures and Energies of SiH_n^{2+} Dications (n = 1—5)

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The structures and energies of SiH_n^{2+} dications (n = 1—5) are reported and compared with the corresponding monocations and the CH_n^{2+} series; in contrast to $CH^{2+\cdot}$, $SiH^{2+\cdot}$ is predicted to be a strongly bound species; also SiH_2^{2+} is predicted to be a kinetically stable species, whereas $SiH_3^{2+\cdot}$, SiH_4^{2+}, and $SiH_5^{2+\cdot}$ are weakly bound complexes of SiH_2^{2+} with atomic and/or molecular hydrogen.

We report for the first time results of an *ab initio* molecular orbital investigation of the siliconhydride dications SiH_n^{2+} (n = 1—5) in comparison with the corresponding monocations as well as the CH_n^{2+} series, which have been studied earlier.[1,2] The full set of total energies, calculated at the MP4(SDTQ)/6–31G**//6–31G* level of theory[3] for SiH_n^{2+} is listed in Table 1, together with the harmonic zero-point corrections (6–31G*, contributions of imaginary frequencies being omitted). The

Table 1. Total energies (in Hartrees) and harmonic zero-point corrections (in kcal/mol)[a] for the SiH_n^{2+} dications.

Molecule	Symmetry	6–31G*[b]	MP4(SDTQ)/ 6–31G**[b]	Zero-point energy
$SiH^{2+\cdot}$ (**1**)	$C_{\infty v}$	−288.49877	−288.54470	1.8
Singlet SiH_2^{2+} (**2**)	$D_{\infty h}$	−289.10958	−289.18258	8.6
Triplet SiH_2^{2+} (**3**)	C_{2v}	−289.02064	−289.07595	3.6
$SiH_3^{2+\cdot}$ (**4**)	C_{2v}	−289.63204	−289.71263	10.7
$SiH_3^{2+\cdot}$ (**5**)	C_{2v}	−289.62362	−289.70795	9.5
SiH_4^{2+} (**6**)	C_{2v}	−290.27086	−290.39300	19.4
SiH_4^{2+} (**7**)	C_{2v}	−290.26900	−290.38412	18.7
$SiH_5^{2+\cdot}$ (**8**)	C_1	−290.78976	−290.91950	21.8
$SiH_5^{2+\cdot}$ (**9**)	C_s	−290.78733	−290.90982	21.1

[a] 1 kcal = 4.184 kJ. [b] At 6–31G* geometries.

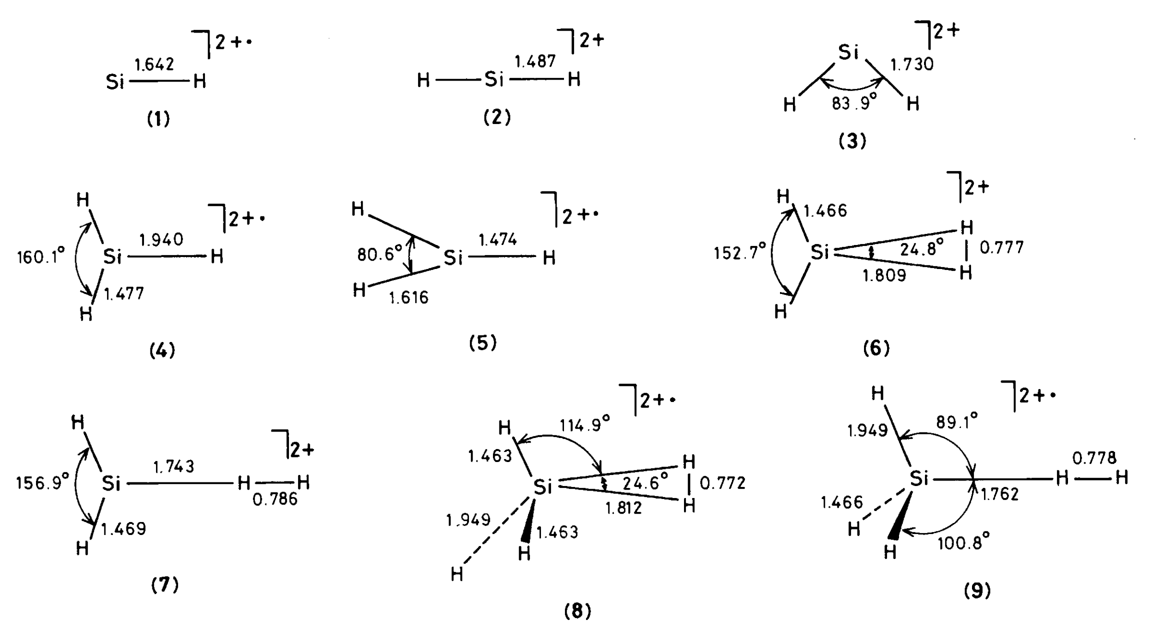

Figure 1. 6–31G* optimized geometries of the SiH_n^{2+} dications (bond lengths in Å, angles in degrees).

optimized minimum structures (6–31G*) are displayed in Figure 1. All calculations were carried out using the CRAY-version of the GAUSSIAN 82 series of programs.[4]

In strong contrast to $CH^{2+\bullet}$ which has a purely repulsive ground state potential,[1b] or at most a very shallow energy dip,[1c] the $^2\Sigma^+$ ground state of $SiH^{2+\bullet}$ (**1**) was found to be clearly a minimum. While the bond length for $SiH^{2+\bullet}$ was calculated to be longer (1.642 Å) compared with the monocationic (1.486 Å) and neutral (1.515 Å) SiH species, the calculated harmonic frequency of 1246 cm^{-1} is rather high. Moreover, preliminary computations indicate a substantial barrier for the charge separation reaction. Whereas calculations at the Hartree–Fock level lead to incorrect dissociation products (Si^{2+} + $H^\bullet$), the results of a CASSCF study predict an activation barrier of more than 10 kcal/mol.[5]

For SiH_2^{2+} we located two minima, a linear singlet structure (**2**) and a C_{2v} triplet species (**3**), the former being 62.4 kcal/mol more stable than the latter. The singlet has a remarkably short Si–H bond of only 1.487 Å, even shorter than in neutral SiH_2 (1.510, 6–31G*). Also SiH_2^{2+} should be prevented from spontaneous deprotonation. The short bond and the high frequency of the Si–H stretching mode (2246 cm^{-1}) indicate an even higher barrier than for $SiH^{2+\bullet}$. We predict that $SiH^{2+\bullet}$ and SiH_2^{2+} are experimentally observable under appropriate gas phase conditions. Like $CH_3^{2+\bullet}$,[1b] the open shell dication $SiH_3^{2+\bullet}$ is expected to be Jahn–Teller distorted from the planar D_{3h} symmetry. Geometry optimizations at 6–31G* lead to two distinct C_{2v} symmetric structures of different electronic states (**4**) ($^2A_1$) and (**5**) ($^2B_2$), (**4**) being more stable by 2.1 kcal/mol. The inspection of the force constant matrix shows one negative eigenvalue for (**5**), thus indicating this structure is not a minimum on the potential energy surface. Species (**4**) can be understood as a loosely bound complex of SiH_2^{2+} and $H^\bullet$ which is supported by a rather long (r = 1.940 Å) and weak ($\tilde{v}$, Si–H stretch = 865 cm^{-1}) one-electron bond and the high spin density of 0.60 (6–31G**) at this hydrogen. Furthermore, the geometry of the SiH_2 unit in (**4**) is quite similar to the isolated SiH_2^{2+} dication (**2**) and 86% of the positive charge is located on this moiety.

Table 2. Deprotonation energies (in kcal/mol)[a] for SiH_n^{2+} and CH_n^{2+} dications.

Molecule	Deprotonation energy[b,c]
$SiH_5^{2+\bullet}$	−13.4
SiH_4^{2+}	−26.1
$SiH_3^{2+\bullet}$	−48.0
SiH_2^{2+}	−20.0
$SiH^{2+\bullet}$	−35.4
CH_4^{2+}	−105.7
$CH_3^{2+\bullet}$	−108.5
CH_2^{2+}	−71.4
$CH^{2+\bullet}$	−147.5

[a] 1 kcal = 4.184 kJ. [b] Values for CH_n^{2+} taken from ref. 1b, calculated at MP4(SDTQ)/6–311G**//6–31G*. [c] Values for SiH_n^{+} taken from 'The Carnegie-Mellon Quantum Chemistry Archive,' 3rd edn., eds. R. A. Whiteside, M. J. Frisch, and J. A. Pople, Carnegie-Mellon University, Pittsburgh, PA, 1983.

While the only minimum found for CH_4^{2+} has a planar, D_{4h} geometry,[1a,b] the situation for SiH_4^{2+} is completely different. The corresponding D_{4h} SiH_4^{2+} has two negative eigenvalues of the hessian matrix. However, for SiH_4^{2+} two different structures (**6**) and (**7**) are calculated as true minima, being 65.0 and 60.8 kcal/mol more stable than the quadratic structure, respectively. Both geometries can be interpreted as weakly bound complexes between H_2 and SiH_2^{2+}: (**6**) arises from the edge-on interaction of a hydrogen molecule with SiH_2^{2+}, whereas (**7**) is the end-on adduct. The donor–acceptor bonds connecting H_2 and SiH_2^{2+} are weak, which is revealed by the relatively long H_2–SiH_2 distances of 1.809 Å and 1.743 Å in (**6**) and (**7**), respectively.

The minimum structures found earlier for the SiH_5^+ monocation are complexes of the relatively stable SiH_3^+ cation and a hydrogen molecule, either in the edge-on or in the end-on arrangement.[2b,c] The loss of a further electron from

SiH_5^+ is accompanied with only slight changes of these geometries. Our optimizations lead to the dications (**8**) and (**9**), which are adducts of H_2 and the $SiH_3^{2+\cdot}$ dication (**4**). Among these two, (**8**) is 5.4 kcal/mol more stable than (**9**). Since the $SiH_3^{2+\cdot}$ dication, as mentioned above, is an adduct of a hydrogen atom and SiH_2^{2+}, the $SiH_5^{2+\cdot}$ species have to be interpreted as weak complexes consisting of $H^\cdot$, H_2, and SiH_2^{2+}. Therefore, $SiH_3^{2+\cdot}$, SiH_4^{2+}, and $SiH_5^{2+\cdot}$ should decompose very fast and they are unlikely to be observed in the gas-phase experimentally. The SiH_n^{2+} dications are shown to be thermodynamically more stable than their carbon counterparts, which is in line with the results for SiH_5^+.[2b] This is reflected by the heats of reaction of the deprotonation reactions $SiH_n^{2+} \rightarrow SiH_{n-1}^+ + H^+$ which are much lower than those found for carbon[1b] (Table 2). The better capability of silicon to accommodate the positive charge is due to its lower electronegativity and its higher polarizability which are general features of second row atoms compared with first row elements.

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