Organosilicon Cations: Potential Energy Surfaces for $SiC_2H_n^+$ (n = 1, 3, and 5)

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Ab initio molecular orbital calculations are reported for closed-shell organosilicon cationic species $SiC_2H_n^+$ (n = 1, 3, 5). Gradient optimizations have been performed on all minima and on all transition structures with the standard Gaussian split-valence 6-31G(d,p) basis set, both at the SCF level of theory and with inclusion of electron correlation to second-order Møller–Plesset (MP2) perturbation theory. Several critical points, including those which correspond to the global minimum on each surface, also have been optimized at MP2(full)/6-311G(d,p); all other critical points have been calculated at MP2(full)/6-311G(d,p)//MP2(full)/6-31G(d,p). Each critical point has been characterized by harmonic frequency calculations at the SCF/6-31G(d,p) level of theory, from which, also, zero-point vibrational energies (ZPE) were obtained for each species. Furthermore, the structure at the global minimum on each surface at MP2(full)/6-31G(d,p) was characterized by a harmonic frequency calculation. Vibrational frequencies, as well as zero-point vibrational energies, also are reported at this level for these compounds. In general, for ions $SiC_2H_n^+$, structures having all the hydrogen atoms attached to carbon have the lowest energies; the only exception is for the $SiC_2H_5^+$ surface on which the 1-silaallyl cation, $H_2SiCH{=}CH_2^+$, is at the global minimum, 3.9 kcal mol^{-1} below $CH_3CH_2Si^+$. Large isomerization barriers have been calculated for the interconversions of some low-energy ions. The existence of such barriers suggests the presence of more than one stable isomer on each surface in the gas-phase.

Introduction

The gas-phase formation of organosilicon cations $SiC_2H_n^+$ (where n = 1–5) was first reported in the reaction of ions SiH_m^+ (m = 0–3) with acetylene in a tandem mass spectrometer.[1] A similar study using the same SiH_m^+ ions with ethylene resulted in ions $SiC_2H_n^+$ (n = 4, 5–7).[2]

More recently, considerable experimental work on gas-phase ion–molecule reactions involving silicon-containing species using the SIFT (selected ion flow tube) has been performed. This experimental interest was stimulated in part by the discovery of strong blue-green spectral lines in N-type stars, emissions which were assigned in 1956 to the presence of SiC_2. Subsequently SiC_2, as well as SiC and SiC_4, were observed in the circumstellar envelope of the carbon star IRC+10216. These molecules and their cations have been the subject of subsequent spectroscopic and computational studies. In particular, one of us has reported experimental results for gas-phase ion–molecule reactions involving the addition of Si^+ (^2P) to acetylene, ethylene, and ethane. In each of these reactions, adduct formation was observed to occur. Another major channel, except in the $Si^+–C_2H_6$ system, was the loss of a hydrogen atom from the adduct to give the ions SiC_2H^+ and $SiC_2H_3^+$, respectively.[3] Furthermore, the metastable decomposition of $(CH_3)_4Si^+$ has been reported to produce the ion $(CH_3)_2Si^+$ and the collisional activation spectrum of this latter ion results in loss of all possible numbers of hydrogen atoms to give the ions $SiC_2H_n^+$ (where n = 0–5) with ion $SiC_2H_4^+$ being produced in the largest amount.[4]

Various structural isomers of SiC_2H^+ have been the subject of recent experimental studies using neutralization–reionization mass spectrometry (NRMS),[5] as well as *ab initio* theoretical investigations at post-SCF levels of theory.[6] The most stable isomer for this formula is a linear species in which the hydrogen atom is bonded to the terminal carbon atom.

Recently *ab initio* molecular orbital calculations for the addition of Si^+ (^2P) to acetylene[7] and to ethylene[7b] have been reported. These works involved the optimization and characterization of numerous minima and transition structures on the $SiC_2H_2^+$ and $SiC_2H_4^+$ energy hypersurfaces. We now report similar studies of the potential energy hypersurfaces for the closed-shell molecules $SiC_2H_n^+$ (where n = 1, 3, and 5). All critical points on the SCF-generated surfaces have been characterized by harmonic vibrational frequency calculations, and the most stable isomer on each surface has also been characterized at MP2.

Computational Methods

Ab initio molecular orbital calculations were performed using the GAUSSIAN suite of programs.[8] All structures were optimized at both the SCF/6-31G(d,p)[9] and MP2(full)/6-31G(d,p) levels of theory[9,10] using gradient techniques.[11] Most of the smaller ions and the global minimum on each surface were also optimized at MP2(full)/6-311G(d,p).[9e,12] Transition structures were obtained initially by crude point-by-point profiles, followed by refinement, with either the eigenvector-following (EF) method[13] or the CALCALL algorithm.[8] All critical points were characterized by harmonic frequency calculations and the intrinsic reaction coordinate (IRC) method was used to establish which two minima were associated with each transition structure.[14] Structural features (bond lengths involving two heavy atoms and bond angles involving three heavy atoms) are reported in Figure 1. In addition, C–H and Si–H bond lengths which involve bridging hydrogens also are reported. Computed electronic energies and zero-point vibrational energies are given in Table 1.

Results and Discussion

SiC_2H^+ Potential Energy Surface. We have located four minima structures (**1–4**) on the SiC_2H^+ surface at the RHF/6-31G(d,p) level of theory. Inclusion of electron correlation, however, has a profound effect on this potential energy surface. We were able to locate a minimum for structure **2** at MP2-

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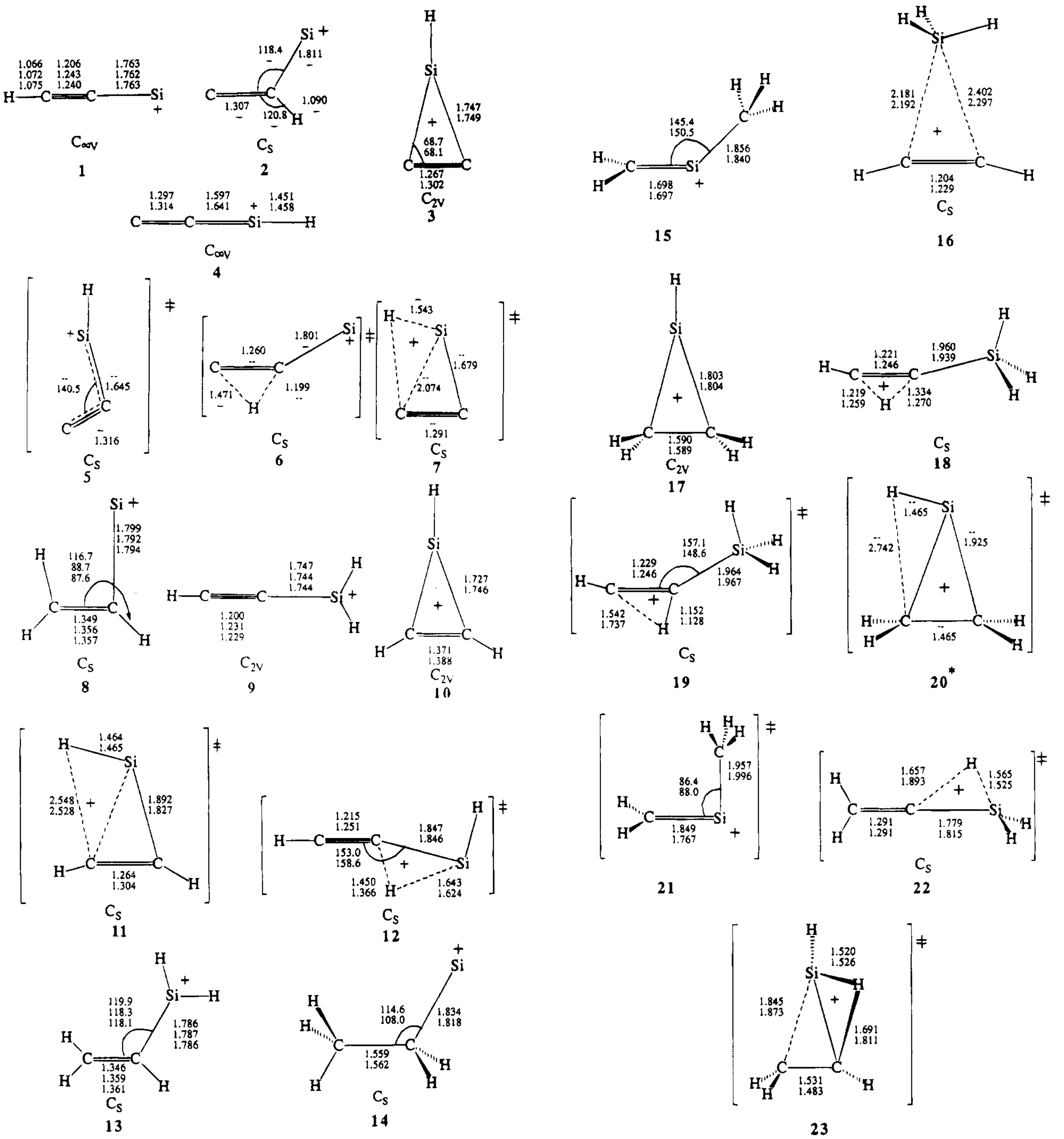
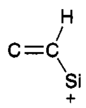


Figure 1. Optimized structural parameters. Bond lengths are in angstroms, and bond angles are in degrees. Where two sets of structural parameters are listed, the upper values are at SCF/6-31G(d,p) and the lower values are at MP2(full)/6-31G(d,p). Where three sets of structural parameters are listed, the top values are at SCF/6-31G(d,p), the middle values are at MP2(full)/6-31G(d,p), and the bottom values are at MP2(full)/6-311G(d,p). Structure **20** did not exist at the SCF level.

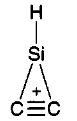
(full)/3-21G(d) and also at MP2(full)/6-31G, but extension of the basis set to include polarization functions at both MP2(full)/6-31G(d) and at MP2(full)/6-31G(d,p) resulted in ion **2** collapsing to ion **1**. We, therefore, conclude that structure **2** exists only on surfaces calculated with SCF and low-level correlated wave functions.

$H{-}C{\equiv}C{-}Si^{+}$

1



2



3

$C{=}C{=}\dot{S}i{-}H$

4

We located transition structure **6**, for the conversion of **2** into **1**, and found it to be 20.6 kcal mol^{-1} above **2** at the SCF level. However, as structure **2** collapses into **1** at the MP2(full)/6-31G(d,p) level of theory, **6** is an artifact of the lower level calculations and will not be discussed further.

At all levels of theory, structure **1** has the lowest energy of the three stable isomers, in agreement with a previous theoretical study.[6] It is linear with the C−C distance (1.243 Å) slightly longer than the C≡C triple bond in acetylene (1.203 Å)[15] and the C−Si distance (1.762 Å) intermediate between a single and double C−Si bond.

Structure **3** is a cyclic species lying 82.7 kcal mol^{-1} above **1** at RHF/6-31G(d,p), an energy difference which is reduced only slightly (to 73.0 kcal mol^{-1}) on inclusion of electron correlation at MP2. The presence of a hydrogen atom bonded to silicon, rather than to carbon, in **3**, is a further illustration of the trend, described elsewhere,[7b] that, on a given organosilicon cationic

TABLE 1: Total Energies (hartrees) for $SiC_2H_n^+$ (n = 1, 3, 5) Isomers and Transition Structures[d]

ion	RHF/6-31G(d,p)	ZPE[a]	MP2(full)/6-31G(d,p)	MP2(full)/6-311G(d,p)
1	−364.863 07 (0)	11.0	−365.190 03 (0)	−365.375 66[c] (0)
2	−364.792 76 (42.4)	9.3		
3	−364.727 55 (82.7)	8.7	−365.070 01 (73.0)	−365.258 04 (71.5)
4	−364.717 48 (88.8)	8.5	−365.039 39 (92.0)	−365.226 06[c] (91.4)
5		8.0[b]	−365.038 09 (92.3)	−365.225 84 (91.0)
6	−364.756 70 (63.0)	7.3		
7		7.5[b]	−364.968 10 (135.8)	−365.157 99 (133.1)
8	−366.070 50 (0)	24.6	−366.414 73 (0)	−366.601 88[c] (0)
9	−366.043 03 (13.6)	21.0	−366.389 06 (12.5)	−366.578 86[c] (10.8)
10	−366.039 98 (17.7)	23.1	−366.389 02 (14.6)	−366.577 39[c] (13.9)
11	−365.996 20 (42.9)	20.9	−366.357 50 (32.2)	−366.545 79 (31.5)
12	−365.905 89 (96.4)	17.7	−366.274 64 (81.0)	−366.467 14 (77.7)
13	−367.262 69 (0)	35.1	−367.624 85 (0)	−367.814 85[c] (0)
14	−367.255 14 (8.2)	38.6	−367.624 27 (3.9)	−367.813 37 (4.4)
15	−367.210 23 (33.3)	35.5	−367.590 57 (21.9)	−367.779 89 (22.3)
16	−367.215 34 (26.5)	31.9	−367.584 07 (22.4)	−367.777 55 (20.2)
17	−367.211 41 (33.0)	35.9	−367.586 89 (24.6)	−367.778 01 (23.9)
18	−367.203 54 (32.1)	30.1	−367.567 99 (30.7)	−367.760 17 (29.3)
19	−367.201 09 (33.6)	30.0	−367.558 80 (36.3)	−367.751 28 (34.8)
20		35.6[b]	−367.568 40 (35.9)	−367.758 30 (40.0)
21	−367.197 00 (41.3)	35.2	−367.562 80 (39.0)	−367.750 70 (40.4)
22	−367.198 57 (36.7)	31.6	−367.556 14 (39.6)	−367.747 29 (38.9)
23	−367.148 68 (69.8)	33.4	−367.515 69 (66.8)	−367.708 14 (65.3)

[a] Zero-point energy from RHF/6-31G(d,p) in kcal mol^{-1}, scaled by a factor of 0.89, except where specified otherwise. [b] Zero-point energy from MP2(full)/6-31G(d,p) in kcal mol^{-1}, scaled by a factor of 0.93. [c] Optimized at MP2(full)/6-311G(d,p). [d] Relative energies in kcal mol^{-1} using scaled zero-point energies from SCF level calculations (except where zero-point energy has been obtained from MP2 level calculations) are listed in parentheses.

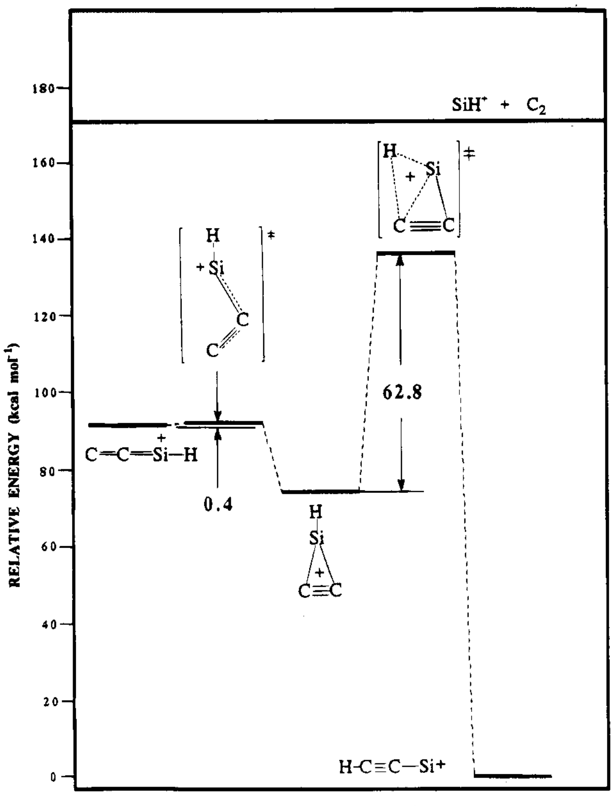


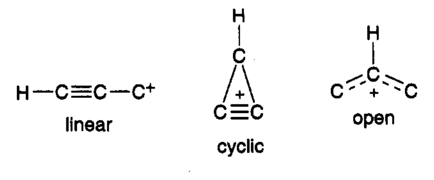
Figure 2. Potential energy surface for SiC_2H^+ as optimized at MP2-(full)/6-31G(d,p).

surface, lower energy isomers tend to have their hydrogen atoms bonded to carbon wherever possible. Ion **3** has the additional destabilizing feature of a multiple bond in a three-membered ring; consequently, **3** is at a very high minimum on the surface. The Si−C bond lengths in **3** (1.749 Å at MP2(full)/6-31G(d,p)) are short when compared to a normal Si−C single bond, as in silaethane (1.867 Å),[15] and the relatively long carbon−carbon distance (1.302 Å), is intermediate between a triple and a double carbon−carbon bond indicating that the formal C≡C triple bond in **3** is elongated by ring strain.

Ion **4**, a linear ion, is the highest energy isomer on the SiC_2H^+ surface,[6] 91.3 kcal mol^{-1} above the global minimum, ion **1**. The structural parameters for **4** show both the C−C and C−Si distances to be slightly shorter than double bonds, and the high energy of this ion can be attributed in part to the instability of the C−Si double bond. Rearrangement of **4** to **3** occurs through bending of the CCSi angle, and the transition structure, **5**, for this process is only 0.36 kcal mol^{-1} above **4** at MP2(full)/6-311G(d,p) (Figure 2), and, when zero-point energy is included, it does not exist at MP2(full)/6-311G(d,p).

The barrier to the isomerization process **3** → **1** via transition structure **7**, is very high (61.6 kcal mol^{-1} at MP2(full)/6-31G-(d,p)). Such a large barrier is unusual for what appears, on initial inspection, to be a simple 1,2-H atom shift accompanied by ring opening. However, on examination of the transition structure (**7**), it is apparent that the three-membered ring, present in **3**, is still fairly intact. Nevertheless, the structure of **7** deviates significantly from that of the original C_{2v} symmetry present in **3**. In **7**, formation of the C−H bond, required to create **1**, has not begun extensively; the migrating H atom still is attached to the Si atom. Although the bond lengths in **7** display relatively small deviations from those of **3**, the C−Si−H angle is distorted considerably from that which exists in **3**.

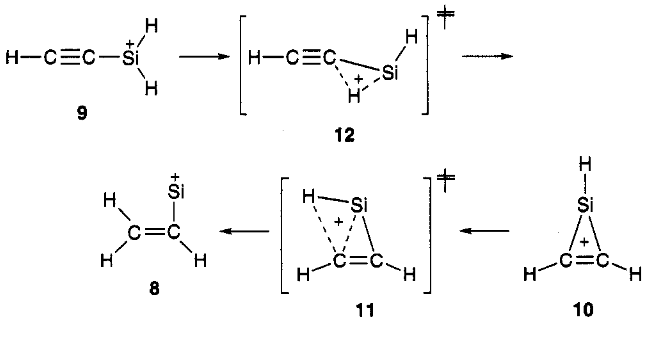
The SiC_2H^+ potential energy surface is considerably different from that of the carbon analogue, C_3H^+. Baker *et al.*[16] have investigated the latter surface and have found three minima at MP2/6-31G(d):



Clearly, the linear structure, the species at the global minimum on the C_3H^+ surface, corresponds to structure **1** on the SiC_2H^+ surface. The cyclic isomer, a structure analogous to **3**, is next lowest in energy. However, the open structure was found to be 48.3 kcal mol^{-1} higher in energy than the cyclic species and to be 64.8 kcal mol^{-1} above that of the global minimum (ZPE not included). The barrier between the cyclic isomer and the linear species was found to be negligible (the transition structure for this process, corresponding to **7** on the SiC_2H^+ surface was found to be lower in energy than the higher energy minimum on inclusion of zero-point vibrational energy), whereas the barrier for interconversion of the open isomer and the linear ion was found to be 20.8 kcal mol^{-1}.

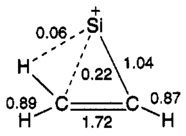
On considering the open C_3H^+ isomer, one can envisage two possible monosilicon analogues: one, in which a terminal carbon atom is replaced by Si; the other, in which the central carbon atom is replaced by Si. The former substitution results in the creation of structure **2** on the SiC_2H^+ surface, a species which exists at the SCF level of theory but which collapses to the structure of species **1** at MP2(full)/6-31G(d,p). The latter substitution results in the formation of an ion $C(SiH)C^+$ with C_{2v} symmetry. An attempt was made to optimize this second structure at HF/6-31G(d,p) and, although such a structure was located and was characterized as existing at a local minimum on the surface, it was found to be 212 kcal mol^{-1} above the global minimum **1** and to be 0.7 kcal mol^{-1} above the products of dissociation, $SiH^+ + C_2$. Such a species, therefore, is extremely unlikely to exist as a stable ion in the gas-phase and, as a result, has not been investigated further in this study.

$SiC_2H_3^+$ Potential Energy Surface. The $SiC_2H_3^+$ ion has been detected in the reactions of ethylene and of acetylene with silane and with silane fragments under tandem mass-spectrometric conditions and under high-pressure MS conditions.[1,2] Also this ion is formed as a primary product in the reaction of $Si^+(^2P)$ with ethylene in the SIFT.[17] However, no *ab initio* studies have been published to date. In the present paper, we report the occurrence of a dramatic topological change on the $SiC_2H_3^+$ potential energy hypersurface on proceeding from SCF-level calculations to those with inclusion of electron correlation. In our initial survey of the $SiC_2H_3^+$ surface at RHF/6-31G(d,p) we located eight critical points, six minima and two transition structures. When electron correlation was included, three of these minima did not exist and the surface was reduced to only three minima, structures **8**–**10**, interconnected through two transition structures, **11** and **12**.



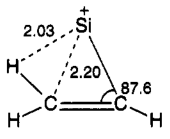
Ion **8** has the lowest energy at all levels of theory. The structure of **8** is similar to that of ethylene with one of the hydrogen atoms replaced by Si^+ (in this respect, the structure is reminiscent of ion **1**, which resembles acetylene with Si^+ replacing one hydrogen atom). The most unusual feature of **8** is angle CCSi, which optimized to 116.7° at HF/6-31G(d,p) but which decreased to 88.7° when electron correlation was included. At the highest level of theory, MP2/6-311G(d,p), the distances between the silicon atom and the carbon and hydrogen (cis) of the CH_2 group are 2.20 and 2.03 Å, respectively, indicating considerable through-space interaction, as is depicted in structure **8b**.

A Mayer bond order analysis[18] at HF/6-31G(d,p) on **8** (shown in structure **8a**) revealed the existence of significant interaction between the Si atom and the terminal carbon atom (Mayer bond order = 0.22), and of a small interaction between the Si atom and the cis-hydrogen atom (0.06). The two carbon atoms, joined formally by a double bond, are shown by this analysis to have a significantly weaker interaction (bond order 1.72) than a double bond (bond order 2). This diminution can be attributed to conjugative π-delocalization and, mainly, to the through-space interaction with Si^+.

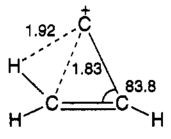


8a

Such an unusual structure is not without precedent. Li and Riggs,[19] in an investigation of the $C_3H_3^+$ potential energy hypersurface, located an isomer (**24**) in which the C–C–C bond angle is 83.8° at MP2/6-31G(d).



8b



24

Ion **9** is 10.8 kcal mol^{-1} above **8** at MP2/6-311G(d,p). Structure **9** has a C–C distance (1.229 Å) slightly longer than a characteristic triple bond and a C–Si distance (1.744 Å) intermediate between a single and a double bond. These distances are consistent with a small amount of π-donation from the triple bond to Si^+, but the structure is best represented as a silyl cation containing an ethynyl substituent. Previous calculations have shown the interaction between the ethynyl group and an α-silyl cation to be stabilizing but it is much smaller than in the $C_3H_3^+$ equivalent, the propargyl cation[20] ($H{-}C{\equiv}C{-}CH_2^+$).

The higher energy of **10** with respect to **8** undoubtedly is associated with the existence of a strained three-membered ring system. However, it is, also, worth noting that the relative energy of **10** with respect to **8** (+13.9 kcal mol^{-1}) is much smaller than the calculated strain energy of silacyclopropane,[21] a topic about which more will be said later.

The silacyclopropenyl cation, **10**, is 13.9 kcal mol^{-1} above **8**. This contrasts sharply with the $C_3H_3^+$ potential energy surface where the cyclopropenyl cation is the global minimum, 24 kcal mol^{-1} below the propargyl cation.[22]

Structure **11** was established by IRC calculations[14] to be the transition structure for ring opening of ion **10** to the global minimum, **8**. Transition structure **11** has considerably longer C–Si distances than in both minima, and the C–C distance is much shorter. These structural differences are much more pronounced at the SCF level and inclusion of electron correlation is clearly essential for an adequate description of this transition structure. The barrier to conversion of **10** into **8** at 0 K from SCF level calculations is 25.2 kcal mol^{-1} but is reduced to 17.6 kcal mol^{-1} when electron correlation is included (Figure 3).

The other transition structure, **12**, is much higher on the surface and IRC calculations established it to be the transition structure for interconversion of **9** and **8**. This rearrangement requires a simultaneous 1,2-H shift from Si to the central carbon of **9** and a 1,3-H shift from Si to the terminal carbon. The

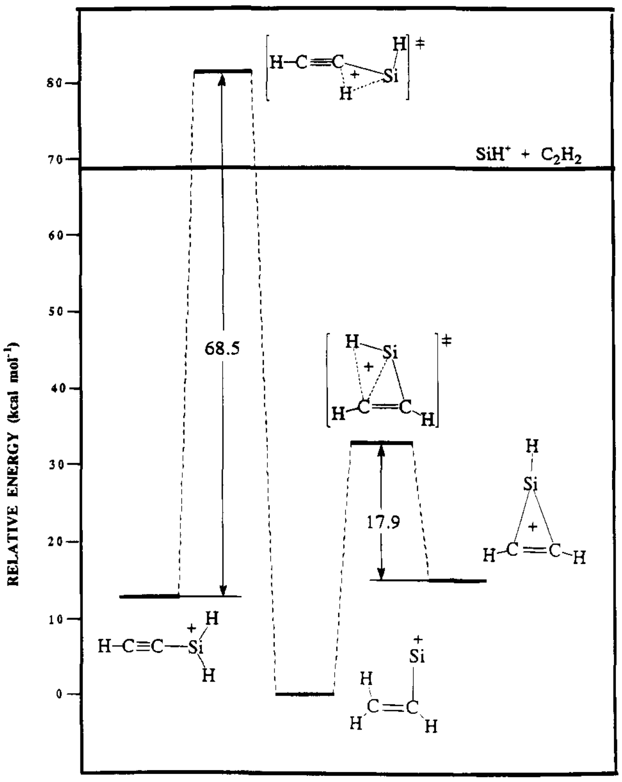


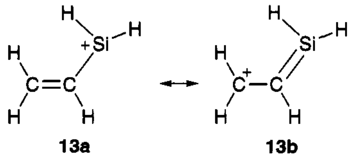
Figure 3. Potential energy surface for $SiC_2H_3^+$ as optimized at MP2-(full)/6-31G(d,p).

structural parameters given for transition structure **12** in Figure 1 show the 1,2-shift to be relatively advanced while the 1,3-shift is at an early stage.

We were unable to locate a transition structure for interconversion of ions **9** and **10**. The absence of such a pathway, coupled with the high barrier for direct interconversion of **9** and **8** indicate that ion **9**, if formed in a gas-phase reaction, should be long-lived and would be expected to have considerably different chemistry than the global minimum, ion **8**.

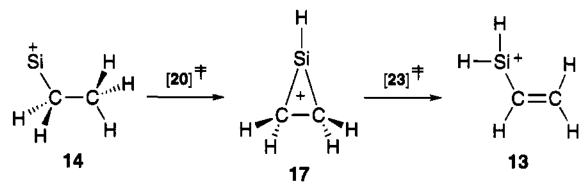
$SiC_2H_5^+$ Potential Energy Surface. The $SiC_2H_5^+$ ion has been detected in tandem MS studies and under high-pressure MS conditions by Lampe and co-workers[1,2] as a product of reactions of silane and of silane fragment ions with ethylene and with acetylene; however, no hypotheses of the structural isomer(s) formed were made and no computational studies of this potential energy hypersurface have been published to date. The results of our *ab initio* studies provide the first insight into possible structures of the $SiC_2H_5^+$ ions formed by Lampe's group.

The 1-silaallyl cation, **13**, is at the global minimum on the $SiC_2H_5^+$ potential energy surface. The carbon–carbon distance (1.361 Å) in this ion is slightly longer than a normal carbon–carbon double bond and the carbon–silicon distance (1.786 Å) is intermediate between a single and a double bond. Most of the charge in this ion is on silicon (+0.9625 at SCF/6-31G-(d,p)). These factors indicate that valence bond structure **13a** is the dominant contributor to this structure.



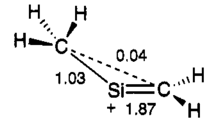
13a **13b**

For other $SiC_2H_n^+$ surfaces, where n = 1–4, the lowest energy isomers all contain Si^+ attached to carbon, with all the hydrogen atoms also attached to carbon. In this respect then, the $SiC_2H_5^+$ potential energy surface is unusual, but ion **14**, an ethane-like structure in which Si^+ replaces H, is close in energy to the global minimum (higher by 4.4 kcal mol^{-1} at MP2/6-311G(d,p)).



Interconversion of **14** and **13** requires the intermediacy of ion **17**. The barrier to the step **17** → **13**, which involves a 1,2-H shift from carbon to silicon and is accompanied by ring opening, is 42.2 kcal mol^{-1} above **17** (using MP2/6-31G(d,p) optimized structures (Figure 4)).

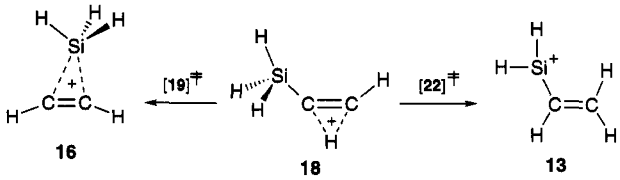
Ions **13**, **14**, and **15** on the $SiC_2H_5^+$ surface are analogous to ions **9**, **8**, and **10**, respectively, on the $SiC_2H_3^+$ surface. The $SiC_2H_5^+$ surface is more complicated than the $SiC_2H_3^+$ surface and contains at least three additional structures, all of which are minima at MP2/6-31G(d,p). These include ion **15**, a structure containing the unusual features of a very short C–Si bond (1.697 Å), shorter than a normal C–Si double bond, and a nonlinear arrangement at the two-coordinate silicon (the angle CSiC is 150.5°) with the carbon of the methyl group in a plane bisecting the CH_2 group. A Mayer bond order analysis[18] of **15** reveals only a small interaction between the two carbon atoms (structure **15a**). Ion **15** rearranges via methyl migration through transition structure **21** to form **14** with a barrier of 17.1 kcal mol^{-1}.



15a

Ion **16** has extremely long C–Si distances (2.192 and 2.297 Å at MP2/6-31G(d,p)) and a short C–C distance (1.229 Å), characteristic of a triple bond, and, from the computed structural parameters, is best described as SiH_3^+ solvated by an acetylene molecule. Despite these small structural changes relative to the separated ion and molecule, the binding energy of SiH_3^+ to acetylene is quite large ($\Delta H_{diss}(0)$ = 39.7 kcal mol^{-1} at MP2/6-31G(d,p).

Ion **18** is at the highest minimum we have located on the $SiC_2H_5^+$ surface. This ion contains a hydrogen atom bridging the two carbons, in a structure reminiscent of that found for the parent vinyl cation.[23] Ion **18** rearranges to cyclic ion **16** by displacing the bridging H atom sideways to the central carbon and having the SiH_3 group, already only weakly attached to carbon in **18** (C–Si is 1.967 Å) become less tightly bound and moving to the center of the C–C triple bond. The barrier (via **19**) to this rearrangement (5.6 kcal mol^{-1}) is slightly lower than that for formation of **13** from **18** via transition structure **22** in



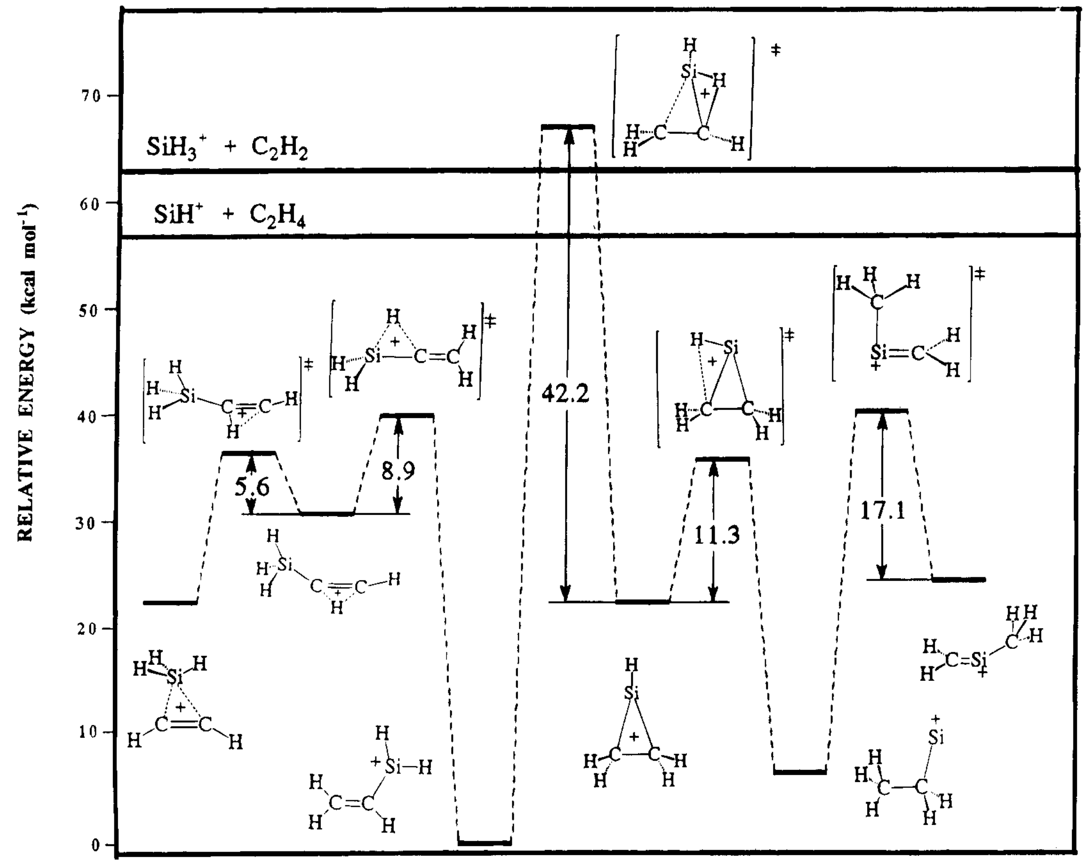


Figure 4. Potential energy surface for $SiC_2H_5^+$ as optimized at MP2(full)/6-31G(d,p).

which a hydrogen atom migrates from silicon to the central carbon atom (barrier 8.9 kcal mol^{-1}).

Formation of **16** from SiH_3^+ and acetylene in the gas phase is symmetry-allowed, but the exothermicity of this addition is higher than the energy required to convert **16** into **13** via structure **18** (Figure 4). It seems probable then that ion **13** was formed from SiH_3^+ + acetylene under the high-pressure MS conditions in Lampe's experiments.[2]

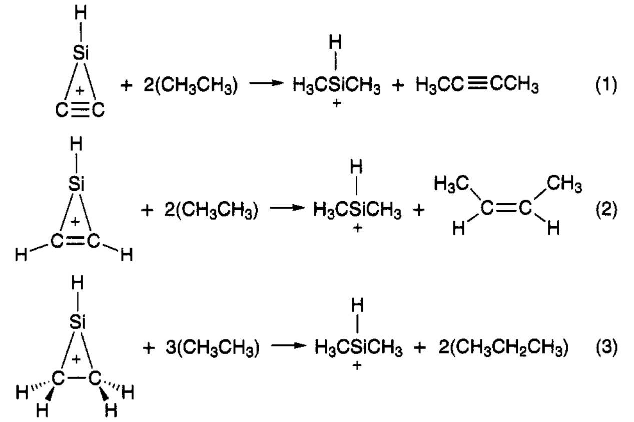
An interesting feature of the $SiC_2H_5^+$ surface is the lack of a π-delocalized isomer associated with a silicon-substituted analogue of the allyl cation, the most stable isomer on the $C_3H_5^+$ surface.[24] The 1-silaallyl cation, **13**, is best described as a vinyl-substituted silyl cation. The 2-silaallyl cation has been studied previously at relatively modest levels of theory,[25] but we have optimized a structure for this ion at MP2(full)/6-31G(d,p); a subsequent frequency calculation has shown it to exist at a local minimum, 40.5 kcal mol^{-1} above that of **13**. However, we also have found this isomer to collapse to cyclic structure **17** with a barrier of only 1.5 kcal mol^{-1}. Thus, the 2-silaallyl cation will not exist in significant amounts as a stable species in the gas phase at room temperature.

Ring Strain. On each potential energy surface, there is one three-membered ring structure in which the SiH^+ group is formally bonded to two carbon atoms by single bonds. These ions may be regarded, formally, as adducts of the gas-phase reactions of SiH^+ to C_2 (ion **3**), to acetylene (ion **10**), and to ethylene (ion **17**), respectively. None of these three ions are at the global minimum on their respective surfaces, and their relative thermodynamic instabilities may be attributable, in part, to the existence of ring-strain. To investigate this situation more closely, we have used isodesmic reactions in eq 1−3 to calculate the strain energies of each of the three cyclic ions. These values, in turn, are compared to those obtained for the neutral organosilicon species in which the SiH^+ of structures **3**, **10**, and **17** are replaced by an SiH_2 group (Table 2).

TABLE 2: Strain Energies[a] for Ring-Opening Reactions of $SiC_2H_n^+$ Ions (Eqs 1−3)

cation	ΔE_{strain} of $SiC_2H_n^+$	ΔE_{strain} of SiC_2H_{n+1}
3 ($n = 1$)	110.3	81.0[b]
10 ($n = 3$)	51.1	46.6,[b] 49.0[c]
17 ($n = 5$)	64.8	43.5,[b] 45.3[c]

[a] Strain energies are in kcal mol^{-1}. [b] This work, optimized at MP2(full)/6-31G(d,p). [c] Reference 21, at HF/6-31G(d)//HF/3-21G.



The ring-strain energies of the cyclic ions are **3** ≫ **17** > **10**. Both ions **3** and **10** have 2π electrons in their valence shells, thereby conforming to the Hückel ($4n + 2$) rule, and from the Si−C bond lengths there appears to be similar amounts of π-delocalization from the carbon−carbon multiple bond to SiH^+ in each ion. However, ion **3** has more multiple bonding between the carbon atoms, and this results in a much larger ring-strain

TABLE 3: Harmonic Vibrational Frequencies (cm^{-1}) and Intensities (km/mol) for Global Minima $SiC_2H_n^+$ (n = 1, 3, 5) from MP2/6-31G(d,p) Calculations[a]

1			8			13		
freq	intensity	sym	freq	intensity	sym	freq	intensity	sym
3445.4	106.4	σ	3354.3	0.1	a′	3340.3	4.8	a′
2011.0	452.1	σ	3268.9	50.1	a′	3285.5	14.7	a′
753.1	21.4	π	2946.4	50.5	a′	3231.6	1.6	a′
753.1	21.4	π	1623.3	22.0	a′	2476.2	16.0	a′
736.4	118.9	σ	1422.3	30.7	a′	2425.5	14.0	a′
166.2	16.8	π	1247.7	29.2	a′	1651.5	57.9	a′
166.2	16.8	π	1046.5	57.5	a″	1473.3	117.5	a′
			990.3	6.6	a″	1318.2	0.1	a′
			924.6	13.3	a′	1102.0	38.3	a″
			765.3	59.8	a′	1070.5	15.7	a′
			426.3	33.3	a″	1029.2	9.9	a″
			261.8	28.6	a′	994.0	105.8	a′
						810.0	23.5	a′
						734.0	90.3	a″
						642.8	37.9	a′
						480.4	3.4	a″
						264.8	0.7	a′
						235.4	3.7	a″
ZPE 10.7,[a] 11.0[b]			24.3,[a] 24.6[b]			35.3,[a] 35.1[b]		

[a] ZPE from HF/6-31G(d,p) optimization in kcal mol^{-1}, scaled by 0.89. [b] ZPE from MP2(full)/6-31G(d,p) optimization in kcal mol^{-1}, scaled by 0.93.

energy. It is interesting to note that the trend in the magnitudes of the cationic strain energies with increasing saturation differs from that of the neutral analogues. Structure **10**, an unsaturated ion, is calculated to have a smaller strain energy than saturated compound **17**, whereas the converse is true for the neutral analogues (see Table 1). This apparent contradiction can be explained in terms of the presence of stabilization of the positive charge due to delocalization through the π-system of **10**. While no positive charge exists in the neutral analogue, it should be noted that the C=C double bond of the neutral species is localized, in contrast to the situation which exists in **10**. Thus, the strain energy of **10** exceeds that of the neutral analogue by only 4.5 kcal mol^{-1}. By contrast, in the case of saturated species **17**, no π-delocalization is present to stabilize the positive charge; thus the strain energy of **17** is greater than that of c-SiC_2H_6 by 21.3 kcal mol^{-1}.

A similar argument can be invoked to explain the larger strain energy of **10** compared to that of c-SiC_2H_4 and of **17** compared to that of c-SiC_2H_6. The C−Si−C bond angles of **8** and **17** are 46.7° and 52.3°; those of the neutral analogues are slightly smaller, 43.4° and 49.5°, respectively. All these angles are compressed by the ring structure, but the distortion in the cations from an ideal angle of 120° is larger than in the neutral compounds where the ideal angle is tetrahedral. Thus, despite the slightly larger angle associated with the structure of the cations, they are, nevertheless, distorted more severely from their preferred bonding arrangements than the neutral molecules.

Vibrational Frequencies. The global minimum on each of the $SiC_2H_n^+$ (n = 1, 3, 5) surfaces (species **1**, **8**, and **13**, respectively) has been subjected to an analytic frequency calculation at the MP2(full)/6-31G(d,p) level of theory. The computed fundamental frequencies and intensities, as well as the assignments to symmetry types, are summarized in Table 3, in the hope that they may be useful in identifying these ions experimentally.

The frequency calculations also yielded zero-point vibrational energies for each of these ions. On scaling the computed values by a factor of 0.93,[26] we obtained ZPE values for the three global minima of 10.7, 24.3, and 35.3 kcal mol^{-1}, respectively. These values compare favorably with those obtained at the HF/6-31G(d,p) level of theory; on scaling those computed values by 0.89,[27] we obtained ZPE values of 11.0, 24.6, and 35.1 kcal mol^{-1}, respectively. Clearly, as the differences between the SCF-level and MP2-level ZPEs, in all cases, are less than 0.3 kcal mol^{-1}, our results justify the use of SCF-level ZPE values in calculating the relative energies used in constructing Figures 2−4.

Conclusions

The critical points of the potential energy hypersurfaces which correspond to organosilicon compounds SiC_2H^+, $SiC_2H_3^+$, and $SiC_2H_5^+$ have been investigated. Isomers which contain Si atoms to which no hydrogen atoms are bonded are the most stable, or are among the most stable, species on each surface. However, it can also be seen that, on each surface, there exist large barriers to the interconversion of stable isomers. Such large barriers suggest the possible existence in the gas phase of isomers of each of these formulas other than the global minimum. This statement has possible important ramifications in the context of experimental research, in which it can be expected that given the appropriate experimental conditions, it should be possible to produce, to verify, and to perform chemical analyses on more than one isomer of a given chemical formula. Furthermore, these results have significance in an interstellar context; where such organosilicon species are identified in interstellar or circumstellar envelopes, the high barriers to isomerization on each surface should result in the presence of more than one structural isomer.

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