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Ab Initio MO Study of Diverse $Si_3H_3^+$ Isomers

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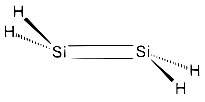
Structures and energies of many $Si_3H_3^+$ isomers were investigated theoretically at the MP2/6-31G* level. The global minimum was the classical aromatic planar D_{3h} structure (**5**). Isodesmic equations indicate the resonance stabilization energy to be half that of the analogous cyclopropenyl cation. The next lowest energy minimum, with a divalent silicon and a bridging hydrogen, also exhibits the 2π aromaticity. Five planar $Si_3H_3^+$ isomers display cyclic three-center−two-electron (3c−2e) delocalization, and eight minima have 3c−2e Si−H−Si bridged bonds. The planar tetracoordinated silicon and five-coordinated silicon also are represented. Eleven other minima were found within a 46 kcal/mol range. An H-bridged C_{3v} structure, derived from $B_3H_6^+$, is 42.1 kcal/mol above the global minimum. However, for Ge, Sn, and Pb these $A_3H_3^+$ forms are more stable than the classical structures (**5**, *J. Am. Chem. Soc.* **1995**, *117*, 11361). In contrast to $Si_3H_3^+$, $C_3H_3^+$ has only four isomers in the 189 kcal/mol range. The silicon analogues of the $C_3H_3^+$ acyclic structures, the prop-2-en-1-yl-3-ylidene cation and the 1-propynyl cation, are not favorable.

Introduction

The large-scale industrial use of silicon in semiconductor technology raises many questions about silanes and their cations.[1] The structure and bonding of Si compounds are inherently complex. The well-established bonding rules of carbon chemistry are of little help in deducing the structure of the compounds of Si and the heavier group 14 analogues.[2] For example, unlike ethylene and acetylene, Si_2H_4, C_{2h} (**1**), is nonplanar and Si_2H_2, C_{2v} (**2**), has a doubly bridged geometry.[3,4] The potential energy surface of Si_6H_6 is equally surprising. For example, hexasilaprismane (**3**), is lower in energy than a benzene-like structure.[5] Indeed, a derivative of hexasilaprismane (Si_6R_6; R = 2,6-diisopropylphenyl) has been characterized experimentally, but no hexasilabenzene has been reported.[6]



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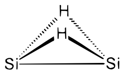

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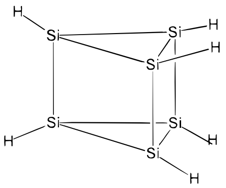

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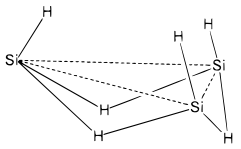

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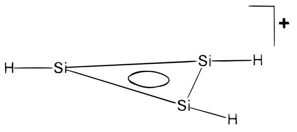

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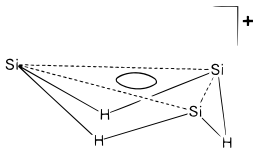

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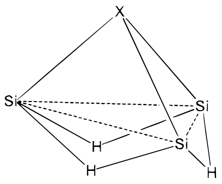

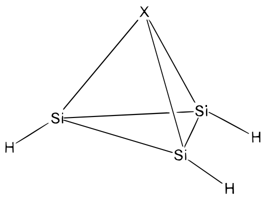

X = CH, SiH

7 **8**

The structural contrast between carbon and silicon chemistry is not restricted to unsaturated compounds. A triply H-bridged structure, C_{3v} (**4**), is a minimum for trisilacyclopropane.[7] The heavier group 14 X_3H_6 bridged structures are even lower in energy than the classical cyclopropane-like alternatives.[7] Since Si and the heavier elements of group 14 are more electropositive, cations involving these elements should be more stable than the corresponding carbocations. $Si_3H_3^+$, produced by ion−molecule reactions of silicon ions with silane, has been detected by ion cyclotron resonance (ICR) spectroscopy.[8] Theoretical studies have shown that the conventional 2π electron structure **5** is lowest in energy even though a triply H-bridged structure (**6**) also is a minimum.[9,10] However, the bridged structures for $Ge_3H_3^+$ and heavier analogues are calculated to be lower in

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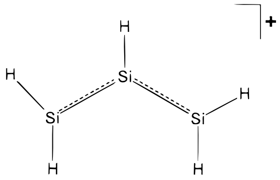
energy than the **5**-like alternatives. Recently, $(^tBu_3Si)_3Ge_3^+$ has been generated experimentally.[11] A single-crystal X-ray diffraction study showed that the $(^tBu)_3Si$ substituents prefer terminal rather than bridged positions.[11] Recently, a derivative of trisilacyclopropene had been synthesized.[12] It is only a question of time before $Si_3H_3^+$ and their derivatives are synthesized and characterized.

Previous experience indicates that alternative lower energy $Si_3H_3^+$ isomers might exist. For example, tetrahedrane derivatives obtained formally by capping $Si_3H_3^+$ rings by groups such as CH^-, SiH^-, etc. are calculated to favor H-bridged (**7**) over the classical structures (**8**).[13] The trisilaallyl cation is not even a $Si_3H_5^+$ (**9**) minimum.[14] A dibridged structure is the lowest energy isomer at the CCSD(T) level of theory (**10**).[14] Similarly, the structure of the $Si_2H_3^+$ cation contrasts dramatically with that of $C_2H_3^+$. $C_2H_3^+$ has two minima, the bridged (**11**) and the classical vinyl cation (**12**),[15] but the lowest energy structure of $Si_2H_3^+$ has three bridging hydrogens (**13**).[16] The lowest energy structure calculated for $Si_5H_5^+$ is also unconventional; the global minimum is the pentasila[1.1.1]propellanyl cation (**14**); in contrast, **15** is the most stable $C_5H_5^+$ isomer.[17,18] The potential energy surface of $Si_3H_3^+$ is rich in possibilities. The cyclopropenyl cation **16** is the global $C_3H_3^+$ minimum and the other minima **17**, **18**, and **19** are higher in energy than **16** by 31.5, 76.5, and 189.2 kcal/mol, respectively.[19] In contrast, we now find several relatively low-energy structures on the $Si_3H_3^+$ potential energy surface. These have three-center and two-electron (3c−2e) bonds, bridging hydrogens and silicons, cyclic π delocalization, and pentacoordinate silicons.



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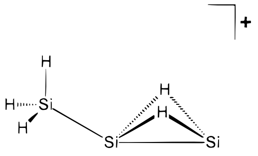

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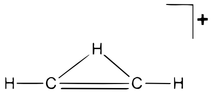

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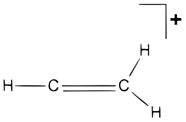

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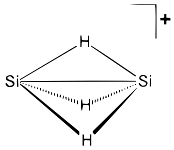

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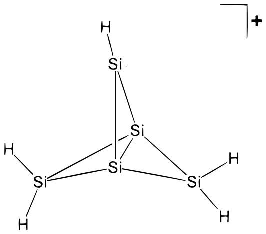

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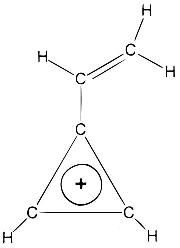

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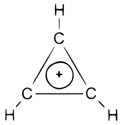

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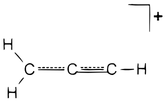

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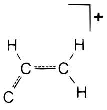

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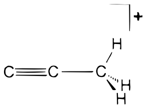

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TABLE 1: Total Energy (hartrees), Unscaled Zero-Point Energy (ZPE, kcal/mol), Relative Energies (kcal/mol, after scaling the ZPE), and Number of Imaginary Frequencies (NIM) at MP2(Full)/6-31G* Level for the $Si_3H_3^+$ and $C_3H_3^+$ Structures and Other Molecules Used in the Equations

structures	total energy	ZPE	relative energy	NIM
5 (D_{3h})	−868.409 70	16.52	0.0	0
20 (C_{2v})	−868.387 19	16.85	14.4	0
21 (C_s)	−868.385 59	16.22	14.9	0
22 (C_s)	−868.382 44	15.66	16.3	1
23 (C_s)	−868.374 05	16.36	22.2	1
24 (C_s)	−868.378 66	15.96	19.0	1
25 (C_1)	−868.380 10	16.88	18.9	0
26 (C_1)	−868.375 49	16.51	21.5	0
27 (C_{2v})	−868.370 33	15.86	24.1	0
29 (C_{3v}, ^3E)	−868.368 58	17.80	27.0	0
30 (C_{3v})	−868.251 57[a]			
31 (C_{2v})	−868.365 28	16.89	28.2	0
32 (C_{2v})	−868.345 21	14.66	38.7	0
6 (C_{3v})	−868.342 26	16.24	42.1	0
34 (D_{3h})	−868.322 97	16.46	54.4	0
35 (C_1)	−868.340 02	14.91	42.2	0
36 (C_s)	−868.340 43	17.80	44.7	0
37 (C_s)	−868.338 46	17.75	45.9	0
38 (C_s,$^3A'$)	−868.332 05	16.44	48.7	0
39 (C_{2v})	−868.324 00	16.55	53.8	2
40 (C_{2v})	−868.295 13	17.84	73.1	2
41 (C_s)	−868.296 61	17.76	72.1	2
42 (C_2)	−868.334 40	13.67	44.6	1
16 (D_{3h})	−115.363 65	28.82	0.0	0
17 (C_{2v})	−115.311 30	27.41	31.5	0
18 (C_s)	−115.238 72	26.77	76.5	0
19 (C_{3v})	−115.061 33	28.24	189.2	0
$\mathbf{Si_3H_6}$ (C_s)	−870.436 66[a]			
$Si_3H_5^+$	−869.577 13[a]			

[a] Frequency analysis not performed.

Computational Methods

The geometries of all the structures were optimized at the Hartree−Fock (HF) and the MP2(Full) levels of theory with the 6-31G* basis set[20,21] using the Gaussian 94 program.[22,23] The unrestricted SCF reference wave function (UHF or UMP2) was used for open-shell species. The nature of the stationary points was determined by analytical evaluation of the harmonic force constants and the vibrational frequencies at the HF as well as at the MP2 level.[24] In addition the five lowest energy structures were studied at G2MP2 and B3LYP/6-311+G** levels.[24] The energy comparisons are at MP2/6-31G*//MP2/6-31G*+ZPE. Zero-point energies were scaled by 0.94 as recommended.[20] The MP2/6-31G* geometries and NBO analysis at the HF level are discussed (Table 1 and Figure 1).[25,26]

Results and Discussions

The trisilacyclopropenyl cation, **5** (Figure 1),[9] the cyclopropenyl cation (**16**) congener, is the $Si_3H_3^+$ global minimum. The SiSi distance of 2.198 Å is slightly longer than the typical SiSi double bond length (2.138 Å in the D_{2h} planar and 2.165 Å in the C_{2h} bent (**1**) structures of disilene)[3] but is much shorter than the normal SiSi single bond value (the SiSi distance in trisilacyclopropane is 2.327 Å and in disilane 2.335 Å).[27] The delocalized π orbital is the HOMO of **5**. According to NBO analysis, positive charge is delocalized on silicon atoms (Si, 0.426; H, −0.093). In contrast, the opposite electronegativity order of C and H results in positive charge buildup on the H's

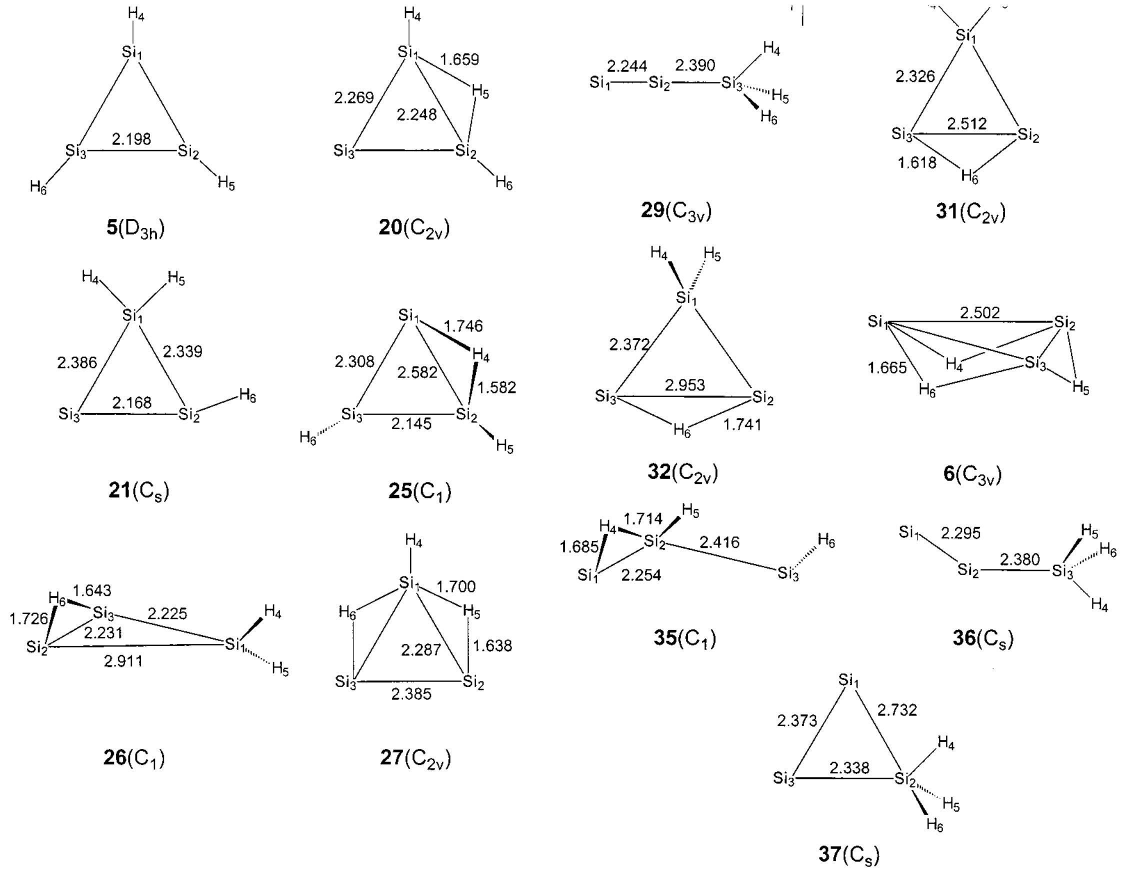
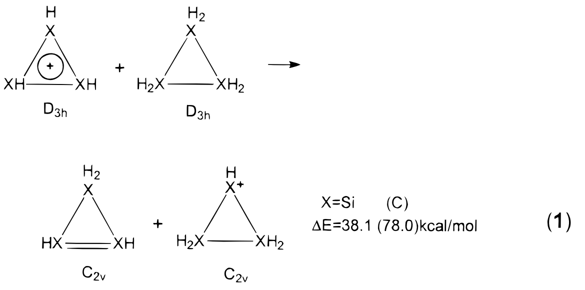
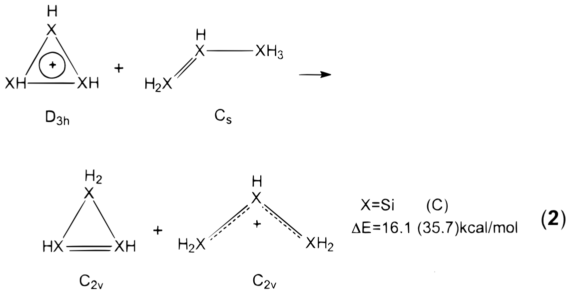


Figure 1. Optimized $Si_3H_3^+$ minima (MP2(Full)/6-31G*). Important bond lengths (in Å) are shown.

in $C_3H_3^+$ (**16**) (C, 0.019; H, 0.314). The isodesmic eqs 1 [21] and



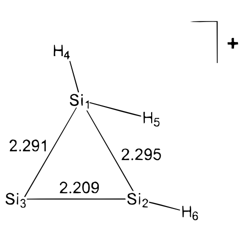
2 provide estimates of the resonance stabilization energy (RSE)



and the aromatic stabilization energy (ASE) in **5** and in the cyclopropenyl cation (**16**, values in parentheses). The RSE's from eq 1 reflect the total 3c−2e delocalization, while the ASE's in eq 2 measure the extra cyclic π delocalization, the aromaticity of the rings over the acyclic 3c−2e π-delocalized species. Both the RSE and the ASE of **5** are only half that of the cyclopropenyl cation (**16**).

The second lowest energy $Si_3H_3^+$ minimum **20** (C_{2v}, Figure 1), with one hydrogen bridging the Si(1)Si(2) bond, is 14.4 kcal/mol higher in energy than **5**. The Si(1)Si(2) bond distance (2.248 Å) is shorter than the SiSi distance (2.370 Å) in the tribridged $Si_2H_3^+$(**13**),[16] but it is longer than that (2.202 Å) in the doubly bridged Si_2H_2 (**2**).[4d] The electronic structure of **20**, with a cyclic π-delocalized MO, a lone pair on the divalent Si and an H-bridged SiSi bond, is quite remarkable. The Si(2)−Si(3) bond length is 2.269 Å and the π-overlap population (0.099) is less than that in **5** (0.110). The most stable geometries of CB_2H_4[28] and of $B_3H_4^-$ [29] are related to **20**. A similar structure with a divalent Si has been characterized experimentally for C_2SiH_2.[30] Another species with two divalent silicons and an H-bridged SiSi bond is calculated to be the global minimum for CSi_2H_2.[31]

The C_s planar minimum, **21** (Figure 1), close in energy to **20** (Table 1) has a terminal rather than a bridging hydrogen. The Si−Si bond lengths in **21** reflect the Si(3)−Si(1)−Si(2) 3c−2e bond in the σ framework, the 3c−2e π bond, and the σ lone pair. The interconversion of **20** and **21** involves transition state **22** (1.4 kcal/mol above **21**).



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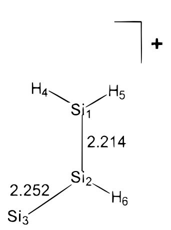
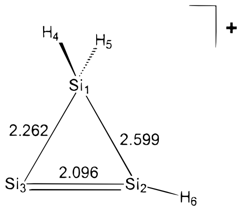


21a

The dramatic effect of electron correlation is seen in the collapse of **21a**, a minimum at HF, into **21** when optimized at

MP2. The localized Si(1)−Si(2) bond in **21a** is transformed into an SiH_2-bridged bond in **21**. However, the carbon analogue (**18**) of **21a** has been detected mass spectrometrically.[32] Rotation of the SiH_2 group in **21** out of the SiSiSi plane leads to the C_s transition structure **23**, which has an Si(2)−Si(3) π bond.



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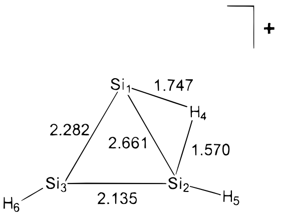

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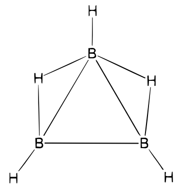
The planar C_s transition structure **24** has an unsymmetrical H bridge; the bonding is similar to that of the C_{2v} minimum **20**, but **24** is 4.6 kcal/mol higher in energy. The related nonplanar minimum, **25** (Figure 1),[9a] is only 0.1 kcal/mol more stable than **24**. The bridging hydrogen in **25** is 0.65 Å above the Si_3 plane.

Structure **26** (C_1, Figure 1)[9a] is 21.5 kcal/mol higher in energy than **5**. MO analysis reveals a 2c−2e bond between Si(1) and Si(3), a 3c−2e hydrogen-bridged bond between Si(2) and Si(3), and lone pair orbitals on Si(2) and on Si(3). The charge is mainly localized on Si(1) ($q_{NBO} = 0.793$) and on Si(3) ($q_{NBO} = 0.635$). The Si(1)−Si(2) separation (2.911 Å) is much longer than the normal Si−Si single bond distance and is even longer (3.268 Å) at HF.

A planar structure with a pentacoordinated silicon, **27**, 24.1 kcal/mol higher in energy, is related to the global B_3H_5 minimum (**28**).[29,33] Both **27** and **28** have the same number of valence electrons, and trivalent boron is isolobal with the divalent Si with a lone pair.[31] Electron correlation favors the 3c−2e delocalization present in the H-bridged structure, since the HF C_s minimum **27a** collapses to the planar C_{2v} (**27**) on reoptimization at MP2.



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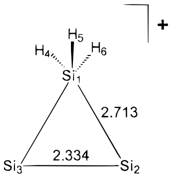
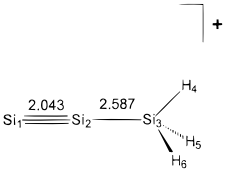


27a



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The most stable acyclic structure obtained in this study, the C_{3v} triplet isomer **29** (^3E, Figure 1), is 27.0 kcal/mol higher in energy than **5**. The π bond in **29** is formed by two equivalent one-electron half-bonds in perpendicular planes. The corresponding triple-bonded singlet structure, **30**, with an empty σ-hybrid orbital on Si(1), is high in energy (99.2 kcal/mol relative to **5**) and shows UHF instability. However, the carbon analogue (**19**) has been detected in collisional activation mass spectra.[32]

The preference for the planar tetracoordinate Si and cyclic 3c−2e π bonding in **31** over the tetrahedral arrangement in **32** is another example of an anti van't Hoff preference.[33] Both **31** and **32** have two H-bridged divalent silicons. Because of the favorable $p_\pi - p_\pi$ overlap, the H-bridged SiSi bond in **31** (2.512 Å) is much shorter than that in **32** (2.953 Å). The nonplanar C_s HF minimum **31a** optimizes to **31** at the MP2 level.

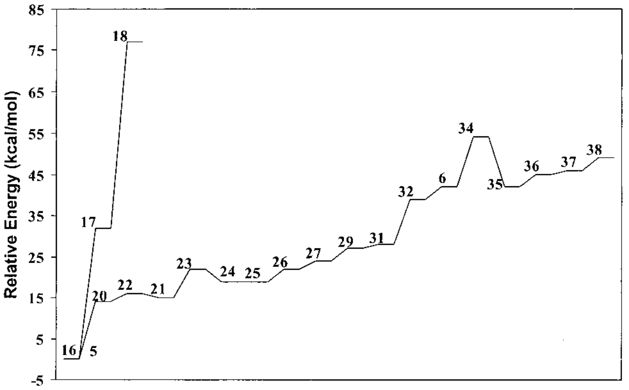
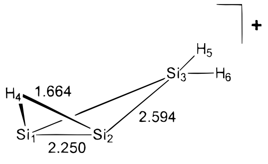


Figure 2. Schematic diagram representing the contrasting relative energies of the isomers of $Si_3H_3^+$ and $C_3H_3^+$. Isomer **19** is not shown in the diagram.



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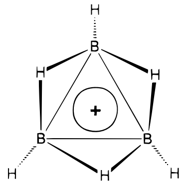

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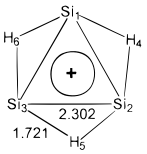

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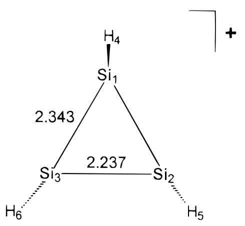
The isolobal analogy between trivalent boron and divalent silicon[31] relates the triply H-bridged nonplanar C_{3v} minimum **6** (Figure 1) (42.1 kcal/mol above **5**) to the C_{3v} global $B_3H_6^+$ minimum **33**.[29,34] The SiSi distance in **6** is close to that of hydrogen-bridged SiSi bond distances in **25** and **31**. Similarly, the SiH_b bond distance is close to that in **20** and **31**. The bridging hydrogens are 0.833 Å below the Si_3 plane in **6**. HOMO, HOMO-1, and HOMO-2 comprise the three lone pair orbitals on Si. HOMO-3 involves the Si_3 p orbitals with substantial contributions from the hydrogen 1s orbitals. This leads to cyclic delocalization similar to that in $B_3H_6^+$ (**33**).[29,34] The planar triply H-bridged D_{3h} structure **34** is 12.3 kcal/mol above **6** but is a minimum at MP2/6-31G*. However, **34** is a higher order saddle point at the Becke3LYP level of theory.[10] The corresponding triply bridged $C_3H_3^+$ structures are not minima.[10]

MO analysis of the acyclic C_1 minimum **35** (Figure 1) reveals a 3c−2e bond involving Si(1)H(4)Si(2). Both Si(1) and Si(3) have lone pairs. The positive charge is localized on Si(1) ($q_{NBO} = 0.846$) and Si(3) ($q_{NBO} = 0.715$).

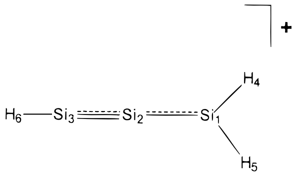
The bent singlet C_s isomer **36** (Figure 1) is related to the linear triplet **29**. The linear C_{3v} singlet with a lone pair on Si(1) is unfavorable, as is linear $SiSiH^+$.[3e] Isomer **37** (Figure 1) with a pentacoordinated silicon is a minimum and 45.9 kcal/mol higher in energy than **5**. Lone pairs are present both on Si(1) and on Si(3). The charge is mostly localized on Si(1). The 2.732 Å bond distance implies a weak bond between Si(1) and Si(2). Similarly, in **27a** Si(1) has a weak interaction with Si(2) and Si(3) (2.713 Å).

A C_s triplet state ($^3A'$, **38**), in which an electron from SiSi σ-bonding orbital (a″) of **5** is transferred to a π* antibonding orbital (a″), also is a minimum 48.7 kcal/mol higher in energy than **5**.

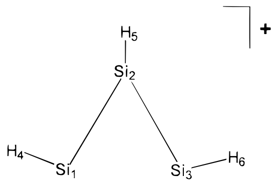
Several other acyclic structures considered here turned out not to be minima. In particular, the trisilapropargyl cation, **39**, is a second-order saddle point 53.8 kcal/mol higher in energy than **5**. The analogous propargyl cation **17** is only 31.5 kcal/mol above the cyclopropenyl cation[19d] and is known experimentally.[35] The open-chain HSiSi(H)SiH structures **40** and **41** have two imaginary frequencies each and are very unfavorable



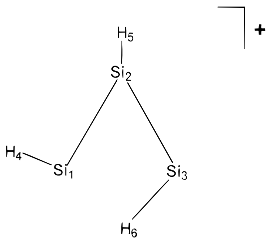
38



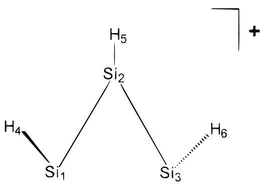
39



40



41



42

energetically. Structure **42** has one imaginary frequency; further optimization with relaxed symmetry constraints led to **35**.

The large number of low-energy structures calculated for the $Si_3H_3^+$ cation is contrasted with the scarce isomer population for $C_3H_3^+$ (Figure 2). While there are 13 isomers for $Si_3H_3^+$ within a range of 46 kcal/mol, the four $C_3H_3^+$ isomers **16**−**19** span a magnitude of 189 kcal/mol. The tendency of multiple valence exhibited by the known compounds of Si and the low Si−Si bond energy are also the major reasons for the large number of isomers seen for the molecular formula $Si_3H_3^+$. The dependence of the relative energies on the level of theory used is also verified by further calculations. Studies at the G2MP2 and B3LYP/6-311+G** levels indicate that the lowest energy structure remains the same (Table 2). The relative energies at these two levels are comparable, but there is a major stabilization of the C_1 structure **25** at these two levels, making it comparable in energy to structures **20**−**22**. However, the magnitude of changes at these higher levels is small.

Conclusions

The potential energy surface of $Si_3H_3^+$ contrasts dramatically with that of $C_3H_3^+$. Although the 2π aromatic D_{3h} structure **5** is the $Si_3H_3^+$ global minimum, its resonance and aromatic stabilization energies are only half that of **16** (eqs 1 and 2). There is only one cyclic $C_3H_3^+$ minimum (the cyclopropenyl cation) within a 189 kcal/mol range. In contrast, $Si_3H_3^+$ has nine cyclic structures with varying number of bridging hydrogens within a range of 46 kcal/mol from the global minimum, the trisilacyclopropenyl cation, **5**. The second lowest energy minimum **20** has a divalent silicon and a H-bridged bond and also benefits from 2π delocalization. Structure **21** with a planar tetracoordinated silicon (the third lowest energy minimum) interconverts into **20** via transition state **22**, with 1.4 kcal/mol barrier. Another structure with a planar tetracoordinate silicon (**31**) is preferred over a tetrahedral arrangement (**32**) by 10.5 kcal/mol. The silicon analogues of the $C_3H_3^+$ acyclic structures, the prop-2en-1-yl-3-ylidene cation (**21a**) and the 1-propynyl (**30**) cation, are not stable. The singlet trisila-1-propynyl cation (**30**) is a minimum but is unstable to UHF; however, the triplet state (**29**) is a minimum. Isomers **27** and **6**, derived from B_3H_5 and $B_3H_6^+$ using the isolobal analogy between trivalent boron and divalent silicon, also are minima. The triply H-bridged C_{3v} structure **6** is 42.1 kcal/mol higher in energy than the global minimum **5**. However, **6** is more stable than **5** for heavier group 14 analogues Ge to Pb.[10] In general, hydrogen-bridged structures with divalent silicon dominate the potential energy surface of $Si_3H_3^+$, even though the global minimum is the familiar aromatic structure. The recent synthesis of $(^tBu_3Si)_3Ge_3^+$ is an important step toward the experimental study of 2π aromatic systems of heavier group 14 elements.[11] It should also be possible to realize derivatives of $Si_3H_3^+$.

TABLE 2: Relative Energies (kcal/mol) of the Five Low-Energy Structures of $Si_3H_3^+$ Isomers at the G2MP2 and B3LYP/6-311+G Levels**

structures	G2MP2	B3LYP/6-311+G**
5 (D_{3h})[a]	0.0	0.0
20 (C_{2v})	8.8	10.8
21 (C_s)	12.4	13.8
22 (C_s)	12.6	14.7
25 (C_1)	13.02	12.41

[a] Total energy (hartrees) is −868.606 33 (G2MP2) and −869.999 65 (B3LYP/6-311+G**).

For additional information, coordinates of the structures discussed in this paper are available from the authors on request.

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