

## Trisilaallene and the Relative Stability of Si<sub>3</sub>H<sub>4</sub> Isomers

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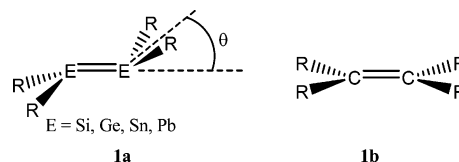
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**Abstract:** A theoretical quantum-mechanical study of trisilaallene, H<sub>2</sub>Si=Si=SiH<sub>2</sub>, and of 15 other Si<sub>3</sub>H<sub>4</sub> isomers was carried out using ab initio and DFT methods with a variety of basis sets. Values given below are at B3LYP/6-31G(d,p). Unlike H<sub>2</sub>C=C=CH<sub>2</sub> which is linear, H<sub>2</sub>Si=Si=SiH<sub>2</sub> is highly bent at the central silicon atom, with a SiSiSi bending angle of 69.4°. The Si=Si bond length is 2.269 Å, longer than a regular Si=Si double bond (2.179 Å) but shorter than a Si–Si single bond (2.351 Å). The distance between the terminal silicon atoms is 2.583 Å, significantly longer than a Si–Si single bond. The geometry and electronic properties of H<sub>2</sub>Si=Si=SiH<sub>2</sub> are similar to those of the corresponding trisilacyclopropylidene, which is only 2.7 kcal/mol higher in energy. A barrier of only 0.1 kcal/mol separates trisilacyclopropylidene and trisilaallene which can be described as bond-stretch isomers. Sixteen minima were located on the Si<sub>3</sub>H<sub>4</sub> PES, most of them within a narrow energy range of ca. 10 kcal/mol. Six of the Si<sub>3</sub>H<sub>4</sub> isomers are analogous to the classic C<sub>3</sub>H<sub>4</sub> minima structures; however, the other Si<sub>3</sub>H<sub>4</sub> isomers do not have carbon analogues, and they are characterized by hydrogen-bridged structures.

### Introduction

The chemistry of compounds containing multiple bonds to silicon developed rapidly since the isolation of the first stable silene and disilene in 1981.<sup>1</sup> A variety of compounds with C=E and E=E (E = Si, Ge, Sn, Pb) bonds were isolated and characterized, and these developments were accompanied by numerous theoretical studies.<sup>1f</sup> These studies revealed that silicon compounds as well as other heavier group 14 analogues can form stable multiply bonded compounds provided that the double bonds are protected by bulky substituents. One of the most interesting conclusions which developed from this new chemistry is the realization that multiply bonded silicon compounds usually adopt structures that are very different from those of the analogous carbon species.<sup>1,2</sup> For example, heavier group 14 doubly bonded compounds usually have a trans-bent geometry as shown in **1a**, in contrast to olefins which are generally planar (**1b**). For H<sub>2</sub>E=EH<sub>2</sub>, E = Si, Ge, Sn, and Pb the calculated bending angle  $\theta$  is 36.1°, 47.3°, 51.0°, and 53.6°, respectively.<sup>1f</sup>

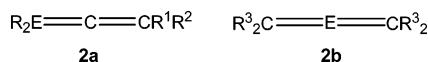


The origin of the trans-bent geometry of heavier group 14 doubly bonded compounds was discussed extensively by us<sup>3</sup> and by others.<sup>4</sup> It was suggested that the degree of trans-bending of R<sub>2</sub>E=E'R'<sub>2</sub> is a function of the sum of the singlet–triplet energy separation ( $\Sigma\Delta E_{st}$ ) of its constituent divalent species, R<sub>2</sub>E and R'<sub>2</sub>E', and the double bond energy,  $E_{\sigma+\pi}$ . According to this model, the double bond adopts a trans-bent structure when  $\Sigma\Delta E_{st}$  is larger than half of  $E_{\sigma+\pi}$ .<sup>4c</sup> A complementary explanation suggests that trans-bending results from effective  $\pi-\sigma^*$  mixing for the heavier group 14 elements.<sup>4c,d</sup> It was also demonstrated that the degree of trans-bending is strongly dependent on the substituents, R.<sup>3</sup>

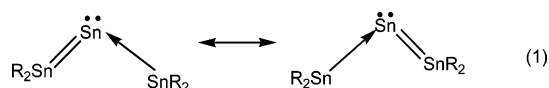
The experimental and theoretical knowledge on compounds containing an extended skeleton of heavier group 14 multiple bonds, e.g., E=E=C, E=C=E, or E=E=E is quite limited.<sup>5–10</sup> The first such compounds, R<sub>2</sub>E=C=CR<sup>1</sup>R<sup>2</sup>, E = Si, Ge, R = 2,4,6-triisopropylphenyl, R<sup>1</sup> = *t*-Bu, R<sup>2</sup> =

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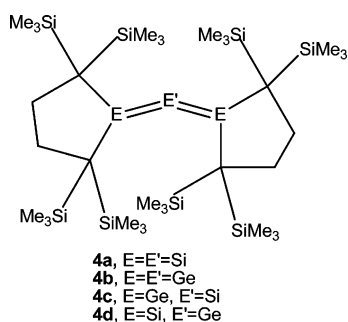
phenyl (**2a**), were synthesized and characterized by X-ray crystallography only recently,<sup>6</sup> revealing that the heavy atom skeletons of **2a** are slightly bent ( $173.5^\circ$ <sup>6a</sup> for E = Si and  $159.2^\circ$ <sup>6c</sup> for E = Ge). An additional 1-germaallene with R = Tbt, Mes, CR<sup>1</sup>R<sup>2</sup> = fluorenyl, was reported by Tokitoh et al.<sup>7</sup> A theoretical study has shown that 1- and 2-silaallenes, **2a** and **2b**, E = Si, with R = H, CH<sub>3</sub>, SiH<sub>3</sub>, R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = H, all have a linear central skeleton and in **2a**, E = Si the terminal R<sub>2</sub>Si and R<sub>2</sub>C fragments are planar and perpendicular to each other, similarly to allene. With R = F, the central skeleton of **2a** is bent with a SiCC bond angle of  $148.7^\circ$ . For E = Ge, R = H, CH<sub>3</sub>, SiH<sub>3</sub>, R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = H, both **2a** and **2b** are bent.<sup>8</sup>



The isolation of the first heavier group 14 allenic compound, (*t*-Bu<sub>3</sub>Si)<sub>2</sub>Sn=Sn=Sn(Si *t*-Bu<sub>3</sub>)<sub>2</sub> (**3**), was reported by Wiberg in 1999.<sup>9a</sup> The X-ray structure of **3** showed significant bending at the central Sn atom with a SnSnSn bond angle of  $155.9^\circ$  and an average Sn=Sn bond length of 2.683 Å—which is shorter than other reported Sn=Sn double bond lengths (2.77–2.91<sup>9b</sup>). However, the authors argued that **3** is not a real analogue of allene and that it is better described by the donor–acceptor resonance structures shown in eq 1.<sup>9a</sup>



A recent spectacular achievement by Kira et al. is the isolation and characterization by X-ray crystallography of the first trisilaallene **4a**.<sup>10a</sup> The X-ray structure of **4a** showed that the central SiSiSi skeleton is strongly bent with a bond angle of  $136.5^\circ$ . The Si=Si bond lengths of 2.177 Å and 2.187 Å are in the range of other known Si=Si double bond lengths. Most recently, Kira has synthesized the analogous trigermaallene, **4b**, and 1,3-digermasilaallene, **4c**,<sup>10b</sup> and 2-germadisilaallene, **4d**,<sup>10c</sup> and they are all strongly bent at E' (EE'E bond angle of  $122.6^\circ$ ,  $125.7^\circ$ , and  $132.4^\circ$ , respectively).



Kira's impressive achievements demonstrate that these interesting compounds are experimentally accessible, and this prompted us to try to understand their basic properties, their bonding characteristics, and their relationship to other isomers. In this study we report a detailed computational quantum-mechanical study, using both traditional *ab initio*<sup>11</sup> and density functional (DFT) methods,<sup>12</sup> of the molecular

structure and the electronic properties of the parent H<sub>2</sub>Si=Si=SiH<sub>2</sub> as well as of its relationship to other Si<sub>3</sub>H<sub>4</sub> isomers. This study reveals an unexpected complex Si<sub>3</sub>H<sub>4</sub> potential energy surface, much more complex than that of C<sub>3</sub>H<sub>4</sub>, with many interesting novel structures, including a bond-stretch isomer<sup>13</sup> of trisilaallene.

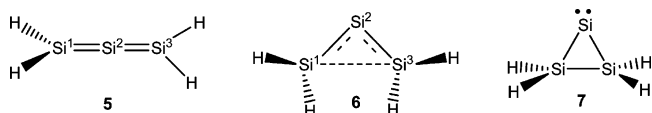
## Computational Methods

Calculations were performed using both *ab initio*<sup>11</sup> and density functional theory (DFT)<sup>12</sup> techniques, as implemented in the Gaussian 98 series of programs.<sup>14</sup> The geometries of all molecules were fully optimized, and vibrational frequencies were computed at the same level of theory in order to characterize the stationary points as minima (no imaginary eigenvalues), transition states (one imaginary eigenvalue), or saddle points of second order (two imaginary eigenvalues). For the DFT calculations we have used mostly the hybrid B3LYP density functional<sup>12</sup> with the doubly polarized 6-31G-(d,p) basis set. The *ab initio* calculations were performed mostly at the MP2/6-31G(d,p)//MP2/6-31G(d,p)<sup>11</sup> level of theory. The geometries of trisilaallene and of several of its isomers were also optimized at the correlated CCSD/6-311+G(2df,p) and CAS(6,6)/6-31G(d,p) levels of theory.<sup>11</sup>

The discussion below is based mainly on the B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p) results (unless otherwise specified), and the values given in parentheses are at MP2/6-31G(d,p)//MP2/6-31G(d,p). The energies reported include zero-point energy (ZPE) corrections at either the B3LYP or MP2 level (unless otherwise specified). The calculated geometries, total energies, and ZPEs of all calculated species are given in the Supporting Information.

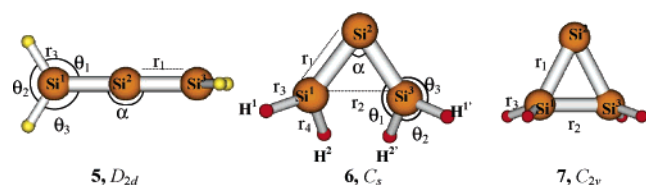
## Results and Discussion

**1. Trisilaallene.** The linear (*D*<sub>2d</sub> symmetry) trisilaallene **5** is *not* a minimum on the Si<sub>3</sub>H<sub>4</sub> potential energy surface (PES). Rather, **5** is a second-order saddle point with two degenerate imaginary frequencies. Full geometry optimization of **5** leads to **6** having an unusual highly bent structure of *C<sub>s</sub>* symmetry, which is a minimum on the Si<sub>3</sub>H<sub>4</sub> PES. The linear *D*<sub>2d</sub> structure **5** lies 20.6 (22.7) kcal/mol above **6**. Another minimum which has quite a similar geometry to that of **6** is the *C*<sub>2v</sub> trisilacyclopropyldiene **7**. Other Si<sub>3</sub>H<sub>4</sub> isomers are discussed below.



**a. Geometry.** The optimized structures of trisilaallene **6** as well as those of the hypothetical linear **5** and of cyclic **7** calculated using several theoretical methods are given in Table 1. The notations for the geometrical parameters are shown in Figure 1.

The structure of trisilaallene **6**<sup>15</sup> is dramatically different from those of the carbon analogue, H<sub>2</sub>C=C=CH<sub>2</sub>, and from 1-silaallenes.<sup>8</sup> The most unusual geometrical feature of trisilaallene is its very acute SiSiSi bond angle of only  $67.1^\circ$ – $70.4^\circ$  (depending on the computation level). In contrast, 1-silaallene, H<sub>2</sub>Si=C=CH<sub>2</sub> is linear<sup>8</sup> and in 1,2-disilaallene,



**Figure 1.** Geometry parameters of linear (**5**) and bent (**6**) trisilaallene and of cyclic silylene **7**. The notation of the geometrical parameters in **6** apply also to **7**.

$\text{H}_2\text{Si}=\text{Si}=\text{CH}_2$ , the SiSiC bending angle is  $140.9^\circ$  (B3LYP/6-31G(d,p)). The structural contrast between trisilaallene and allene demonstrates that carbon chemistry is a poor guide for predicting the geometry of low-coordination silicon compounds.<sup>2a</sup> The calculated bending angle in **6** is much smaller than the angle  $\alpha$  determined experimentally for **4a** ( $136.5^\circ$ ), but it is similar to  $\alpha$  of  $74.2^\circ$  calculated for  $\text{Me}_2\text{-Si}=\text{Si}=\text{SiMe}_2$ .<sup>16</sup>

The two  $\text{H}_2\text{Si}$  fragments in **6** are essentially planar ( $\Sigma\theta = 359.95^\circ$  ( $359.85^\circ$ )), but the hydrogens adopt unusual orientations. Thus, the planes defined by the  $\text{H}_2\text{Si}$  atoms are not mutually perpendicular, as in allene (or in **5**). Instead, the  $\text{H}^1\text{Si}^1\text{Si}^3\text{H}^1$  and  $\text{H}^1\text{Si}^1\text{Si}^3\text{H}^2$  dihedral angles are  $0^\circ$  and  $115.5^\circ$ , respectively (Table 1, these angles are  $90^\circ$  and  $-90^\circ$  in allene).

The distance between the central silicon atom ( $\text{Si}^2$ ) and the two terminal silicon atoms ( $\text{Si}^1$ ,  $\text{Si}^3$ ) is  $2.269 \text{ \AA}$  ( $2.246 \text{ \AA}$ ), by  $0.090 \text{ \AA}$  ( $0.078 \text{ \AA}$ ) longer than the  $\text{Si}=\text{Si}$  double bond in  $\text{H}_2\text{Si}=\text{SiH}_2$  of  $2.179 \text{ \AA}$  ( $2.168 \text{ \AA}$ ), but it is much shorter than a typical Si–Si single bond, e.g.,  $2.351 \text{ \AA}$  ( $2.338 \text{ \AA}$ ) in  $\text{H}_3\text{Si}-\text{SiH}_3$ . This indicates that these bonds have only a partial  $\text{Si}=\text{Si}$  double bond character. The distance between the terminal  $\text{Si}^1$  and  $\text{Si}^3$  atoms is  $2.583 \text{ \AA}$  ( $2.583 \text{ \AA}$ ),  $0.232 \text{ \AA}$  longer than a typical Si–Si single bond. However, this distance is short enough to allow significant bonding interaction between these atoms as demonstrated by the existence of stable molecules with even longer Si–Si bonds, e.g.,  $2.697 \text{ \AA}$  in  $(t\text{-Bu})_3\text{Si}-\text{Si}(t\text{-Bu})_3$ .<sup>17</sup> The nature of the bonding interactions between the terminal silicon atoms in **6** is further discussed below.

**b. Ring Opening of Trisilacyclopopylidene **7** to Trisilaallene **6**.** The geometry of trisilacyclopopylidene, **7**, is quite similar to that of trisilaallene **6**. The SiSiSi bending angle of  $55.8^\circ$  in **7** is smaller than that in **6** (of  $69.4^\circ$ ), but both are in the range of that of a trisilacyclopopyl ring ( $60^\circ$ ). The  $\text{Si}^1-\text{Si}^3$  bond distance of  $2.291 \text{ \AA}$  in **7** is shorter than in **6** ( $2.583 \text{ \AA}$ ), and the  $\text{Si}^1-\text{Si}^2$  and  $\text{Si}^2-\text{Si}^3$  bonds of  $2.446 \text{ \AA}$  in **7** are longer than in **6** ( $2.291 \text{ \AA}$ ), and they are also longer than a regular Si–Si single bond of  $2.345 \text{ \AA}$  in a trisilacyclopopyl ring.<sup>18</sup>

Trisilacyclosilylidene **7** is by only  $2.7 \text{ kcal/mol}$  ( $3.66 \text{ kcal/mol}$  without ZPE correction) higher in energy than **6**, which is expected as their geometries are quite similar (Figure 1, Table 1). The transition state connecting **7** and **6**,  $\text{TS}_{6-7}$ , lies only  $0.1 \text{ kcal/mol}$  above **7** and  $2.8 \text{ kcal/mol}$  above **6** ( $0.02$  and  $3.7 \text{ kcal/mol}$  without ZPE correction respectively,  $0.1$  and  $6.2 \text{ kcal/mol}$ , respectively, at MP2/6-31G(d,p)//MP2/6-31G(d,p)+ZPE). At CCSD/6-311+G(2df,p)//CCSD/6-311+G(2df,p) the relative stability of **6** and **7** is reversed with trisilaallene **6** lying by  $2.5 \text{ kcal/mol}$  above **7** and the  $\text{6} \rightarrow \text{7}$  and  $\text{7} \rightarrow \text{6}$  barriers being of  $3.0$  and  $5.5 \text{ kcal/mol}$ , respectively.<sup>19</sup> The very small energy barriers calculated at several theoretical levels imply that in practice silylidene (**7**) and trisilaallene (**6**), which are very close in energy, undergo rapid rearrangement even at low temperatures, with **6** being the dominant molecule. The energy profile at three theoretical levels for the ring opening of **7** to **6** is shown in Figure 2.

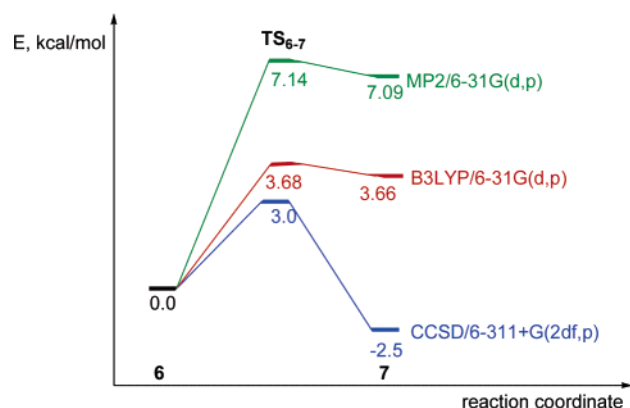
A comparison of the ring opening of **7** to **6** with that of the all-carbon analogue, cyclopropylidene to allene is of interest. The ring opening of **7** to **6** follows a simple disrotatory motion of the  $\text{H}_2\text{Si}$  groups. The ring opening of cyclopropylidene to allene also starts with a disrotatory motion of the methylene groups, but additional geometry changes are required to reach the final linear geometry of allene.<sup>20</sup> The overall barrier for ring opening of cyclopropylidene to allene is also low,  $4.8 \text{ kcal/mol}$ , but in this case the reaction is highly exothermic, by  $69.3 \text{ kcal/mol}$  (B3LYP/TZP//B3LYP/TZP).<sup>20</sup>

The similar geometries and electronic structures (see below) of **6** and **7** indicate that they can be regarded as one

**Table 1.** Calculated Bond Lengths ( $\text{\AA}$ ) and Bond Angles (deg) of **5–7** and of  $\text{TS}_{6-7}$  at Several Theoretical Levels<sup>a</sup>

level of theory	species	$\alpha$	$r_1$	$r_2$	$r_3$	$r_4$	$\Sigma\theta^b$	$\angle(\text{H}^1\text{Si}^1\text{Si}^3\text{H}^1)^c$	$\angle(\text{H}^1\text{Si}^1\text{Si}^3\text{H}^2)^c$
B3LYP/6-31G(d,p),	<b>5</b>	180.0	2.125		1.477		360.0	90.0	–90.0
MP2/6-31G(d,p),		180.0	2.127		1.467		360.0	90.0	–90.0
CCSD/6-311+G(2df,p)		180.0	2.126		1.472		360.0	90.0	–90.0
B3LYP/6-31G(d,p),	<b>6</b>	69.4	2.269	2.583	1.491	1.489	359.9	0.0	115.5
B3LYP/6-311G(2d,p)		70.4	2.262	2.607	1.487	1.485	359.9	0.0	115.0
MP2/6-31G(d,p)		70.2	2.246	2.583	1.479	1.479	359.8	0.0	114.4
MP2/6-311G(2d,p)		71.2	2.260	2.631	1.478	1.478	359.9	0.0	113.9
CCSD/6-311+G(2df,p)		68.6	2.260	2.548	1.484	1.483	360.0	0.0	117.5
CAS(6,6)/6-31G(d,p)		67.1	2.283	2.523	1.477	1.476	359.8	0.0	119.7
B3LYP/6-31G(d,p)		55.8	2.446	2.291	1.486	-	351.8	0.0	146.3
MP2/6-31G(d,p)	<b>7</b>	56.0	2.424	2.277	1.475	-	352.1	0.0	147.3
CCSD/6-311+G(2df,p)		56.0	2.442	2.295	1.481	-	352.2	0.0	147.2
CAS(6,6)/6-31G(d,p)		57.0	2.432	2.322	1.475	-	346.5	0.0	147.8
B3LYP/6-31G(d,p)		56.5	2.431	2.301	1.487	1.486	350.7	0.0	143.8
MP2/6-31G(d,p)		56.8	2.405	2.290	1.476	1.474	350.8	0.0	144.1
CCSD/6-311+G(2df,p) <sup>d</sup>		55.9	2.440	2.290	1.480	1.480	352.3	0.0	147.4
	$\text{TS}_{6-7}$								

<sup>a</sup> Notation of the geometrical parameters and atom numbering is given in Figure 1. <sup>b</sup>  $\Sigma\theta_i = \theta_1 + \theta_2 + \theta_3$ . <sup>c</sup> Dihedral angle. <sup>d</sup> Reference 19.



**Figure 2.** Reaction profile for ring opening of **7** to **6** (the energies are without ZPE corrections).

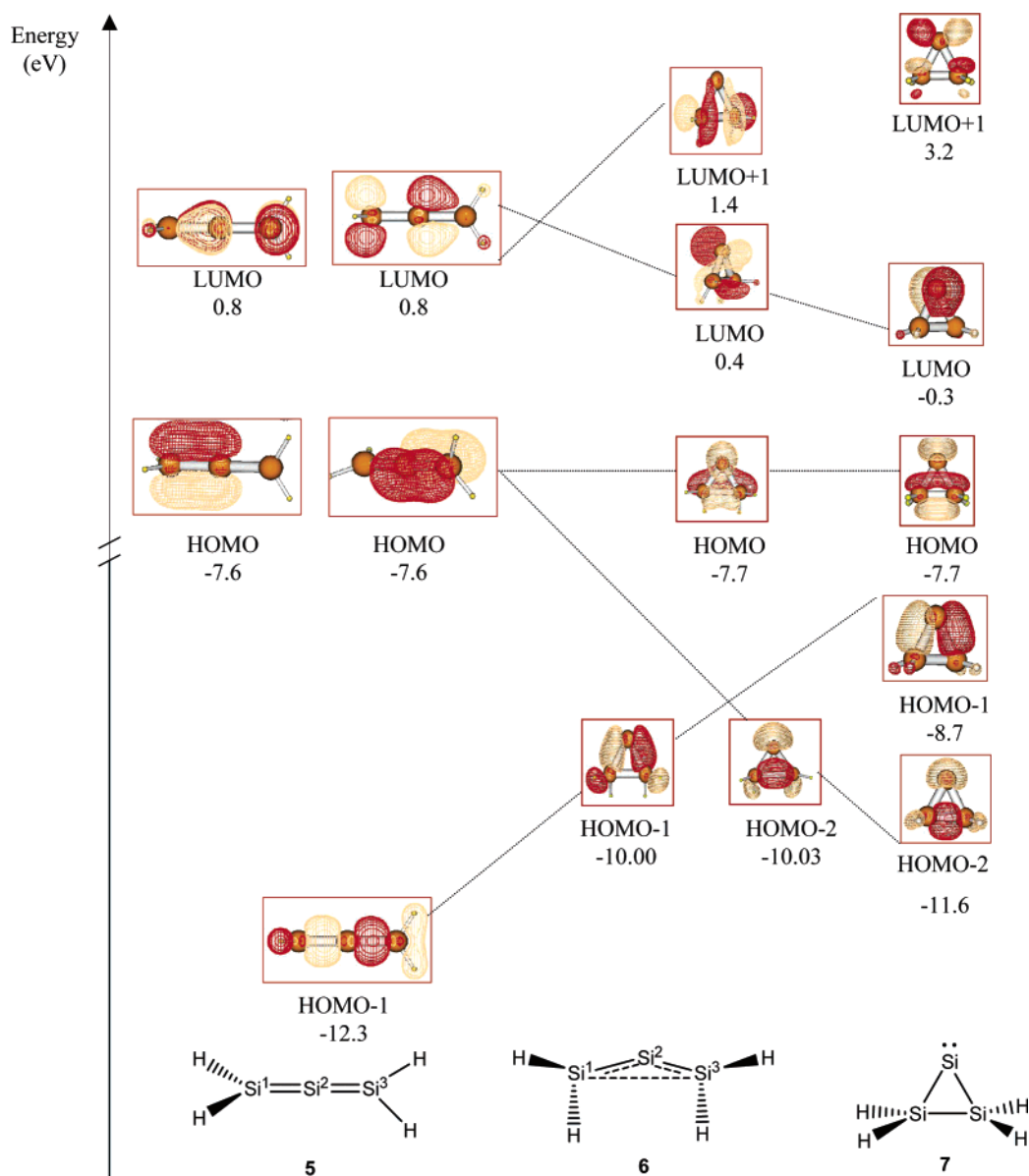
of a few known examples of “bond-stretch” isomers.<sup>12</sup> Bond-stretch isomerism is defined as the phenomenon whereby molecules of the same spin state, on the same potential energy surface, differ only in the length of one or several

bonds. This is indeed the case for **6** and **7**. However, unlike in ideal “bond-stretch” isomers, the terminal  $\text{H}_2\text{Si}$  groups rotate and the  $\text{HSiSiH}$  dihedral angle is changed upon stretching the  $\text{Si}^1\text{—Si}^3$  bond and converting **7** to **6** (Figure 1, Table 1).

**c. Electronic Structure.** To describe the electronic structure and the chemical bonding in trisilaallene **6**, we find it convenient to compare it with those of the hypothetical linear trisilaallene **5** on one hand and with the cyclic trisilacyclopropylidene **7** on the other.

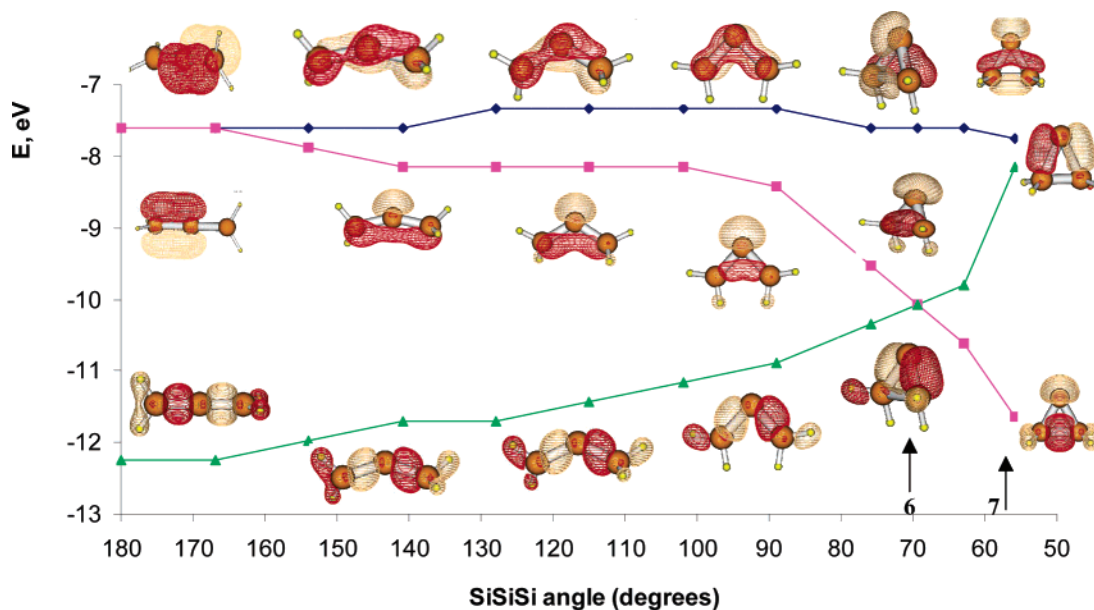
*i. Frontier Molecular Orbitals of 5–7.* The Frontier Molecular Orbitals (FMOs) of **5–7** calculated at the HF/6-31G(d,p)//B3LYP/6-31G(d,p) level are shown in Figure 3.<sup>21</sup>

The shapes of the FMOs of the hypothetical linear trisilaallene **5** are similar to those of allene. The HOMO and LUMO are both degenerate (as in allene), and they have the classic shape of  $\pi$  and  $\pi^*$  orbitals. The HOMO-1 of **5**, which is 4.7 eV lower in energy than the HOMO, is a  $\sigma$ -type orbital with a node at the central silicon atom, again, similar in



**Figure 3.** Frontier molecular orbitals (FMOs) of **5–7**. Orbital energies (HF/6-31G(d,p)//B3LYP/6-31G(d,p)) are given in eV.





**Figure 4.** Walsh diagram (calculated at HF/6-31G(d,p)//B3LYP/6-31G(d,p)) for the **5**  $\rightarrow$  **6**  $\rightarrow$  **7** transformation. The SiSiSi angle was fixed at the indicated values, while all other geometry parameters were optimized.

character to HOMO-1 of allene. The HOMO and the HOMO-1 of **5** are however much higher in energy than those of allene which are at  $-10.1$  eV and  $-16.9$  eV, respectively (at the same level of theory).

Upon bending of **5** to trisilaallene **6** the degenerate HOMO orbitals split: the HOMO of **6** has essentially the same energy as the HOMO of **5**. However, the second orbital (HOMO-2) drops strongly by  $2.4$  eV becoming almost degenerate in energy with the HOMO-1 orbital ( $\sigma$ -type) at  $-10.00$  eV. The HOMO-2 of **6** is further stabilized to  $-11.6$  eV upon ring closure to **7**. On the other hand, the energy of the HOMO-1  $\sigma$ -orbital of **5** rises in energy by  $2.3$  eV upon bending to **6** and by an additional  $1.3$  eV upon ring closure to **7**. The LUMO of **6** is not degenerate (unlike in **5**) with LUMO+1 lying  $1.0$  eV above the LUMO. The HOMO–LUMO gap in **6** is  $8.1$  eV ( $8.4$  eV in **5**), much smaller than in allene ( $15.0$  eV).

The shapes of the FMOs of **6** and of **7** are similar. The HOMO of **6** (and of **7**) have a pronounced lone pair character at the central silicon atom, and they have the same energy. The shapes of the HOMO-1 and HOMO-2 of **6** and of **7** are also very similar, but in **6** these orbitals are almost degenerate, while in **7** the HOMO-1 lies  $2.9$  eV above HOMO-2. The LUMO of **6** and of **7** are similar. In **7** the LUMO is the empty  $3p$  orbital on  $\text{Si}^2$ , while in **6** the LUMO is a mixture of the  $3p$  orbital of  $\text{Si}^2$  and  $\sigma(\text{Si}^1\text{--Si}^3)$ .

A Walsh-type diagram<sup>22</sup> showing the transformation of the degenerate HOMO  $\pi$ -orbitals and the HOMO-1  $\sigma$ -orbital of linear **5** upon bending to **6** and to **7** is shown in Figure 4. Upon bending of **5** to **7** through **6**, the degeneracy of the HOMO orbital is lifted. The energy of one of the HOMO orbitals remains essentially unchanged along the bending process. The energy of the second HOMO is lowered from  $-7.6$  eV in **5** to  $-11.0$  eV in **7**, reflecting the build-up of the  $\text{Si}^1\text{--Si}^3$   $\sigma$ -bond which is evident in the orbital shape. On the other hand, the energy of the HOMO-1 ( $\sigma$ -orbital) is raised upon bending due to increased antibonding interactions

between the molecule's ends. The Walsh curves of the descending HOMO-1 and ascending HOMO-2 cross at a SiSiSi bond angle of  $70^\circ$ , i.e., practically at the bond angle of **6** ( $69.4^\circ$ ), where the HOMO-1 and HOMO-2 orbitals become degenerate. An additional small bending of the SiSiSi angle to  $58^\circ$  (reaching **7**) causes a significant decrease in the energy of the original (i.e. in **5**)  $\pi$ -orbital and a considerable increase in the energy of the original  $\sigma$ -orbital, resulting in a  $2.9$  eV energy difference between the HOMO-1 and HOMO-2 in **7**.

We note that the Walsh diagram in Figure 4 does not explain quantitatively the significantly lower energy of **6** and **7** relative to **5** since the sum of the FMOs energies of **5** ( $-27.5$  eV) is almost identical to that of **6** ( $-27.7$  eV) and **7** ( $-28.0$  eV).

In summary, the FMOs of bent trisilaallene **6** are very similar in shape but are significantly different in energy compared to those of cyclic silylene **7**. However, both sets of FMOs are very different from those of hypothetical linear trisilaallene **5** or of allene.

*ii. Charge Distribution.* The atomic charges, bond orders, and orbital occupancies were calculated at the MP2/6-31G(d,p)//B3LYP/6-31G(d,p) level using Natural Bond Orbital (NBO) analysis.<sup>23a</sup> The main results are given in Table 2.

The charge on the central silicon atom ( $\text{Si}^2$ ) changes gradually upon bending the  $\text{Si}^1\text{Si}^2\text{Si}^3$  bond angle, from a negative charge of  $-0.23$  electrons in the linear trisilaallene **5** to neutral in **6** and to a positive charge of  $+0.27$  electrons in trisilacyclopropylidene **7**. So,  $\text{Si}^2$  is nucleophilic in linear **5** and electrophilic in silylene **7**. The charge on  $\text{Si}^2$  in **7** is very similar to that in the disilylsilylene ( $\text{H}_3\text{Si}$ )<sub>2</sub> $\text{Si}$ : (**8**), in line with its silylenic character. The positive charge on the terminal silicon atoms  $\text{Si}^1$  and  $\text{Si}^3$  decreases gradually from  $+0.38$  el. in **5** to  $+0.32$  el. in **6** to  $+0.11$  el. in **7**. The hydrogens are negatively charged in all molecules,  $-0.13$  el. in **5** and **7** and  $-0.16$  el. in **6**.

**d. The Nature of the Bonding in Trisilaallene 6.** What is the nature of the bonding in trisilaallene and how is it

**Table 2.** Calculated (MP2/6-31G(d,p)//B3LYP/6-31G(d,p)) Charge Distributions, Orbital Occupancies, and Bond Orders in **5**–**7** and in (H<sub>3</sub>Si)<sub>2</sub>Si (**8**)<sup>a</sup>

property		<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>
NPA charge	Si <sup>2</sup>	−0.23	0.00	0.27	0.25
	Si <sup>1</sup> , Si <sup>3</sup>	0.38	0.32	0.11	0.37
	H	−0.13	−0.16	−0.13	−0.16
Wiberg bond index	Si <sup>1</sup> –Si <sup>2</sup>	1.81	1.25	0.90	0.93
	Si <sup>2</sup> –Si <sup>3</sup>	1.81	1.25	0.90	0.93
	Si <sup>1</sup> –Si <sup>3</sup>		0.58	0.98	
NBO occupancy <sup>b</sup>	Si <sup>2</sup> –Si <sup>3</sup>	3.85 <sup>c</sup>	1.89	1.92	1.93
	Si <sup>2</sup> –Si <sup>1</sup>	3.85 <sup>c</sup>	1.89	1.92	1.93
	Si <sup>1</sup> –Si <sup>3</sup>		1.47	1.94	
	Si <sup>2</sup> (LP <sup>1</sup> ) <sup>d</sup>		1.87	1.96	1.94
	Si <sup>2</sup> (LP <sup>2</sup> ) <sup>e</sup>		0.52	0.03	0.05

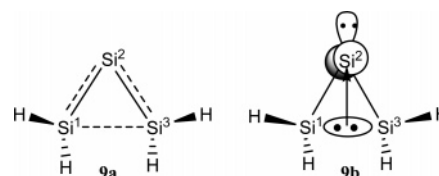
<sup>a</sup> Atom numbering is given in Figure 2. <sup>b</sup> Occupancy in the indicated natural bond orbital. <sup>c</sup> In the  $\sigma$  and  $\pi$  bonds. <sup>d</sup> LP = lone pair; occupancy in the (SiSiSi) plane. <sup>e</sup> LP = lone pair; occupancy in the p orbital perpendicular to the (SiSiSi) plane.

different from the classic familiar bonding in allene? In particular, the strongly bent structure of trisilaallene **6** raises the question if there is a chemical bond between its terminal silicon atoms. To answer this question we used several criteria: The Wiberg Bond Index (WBI),<sup>23b</sup> the electron occupancy of the Si<sup>1</sup>–Si<sup>3</sup> orbital space, and an analysis of the Si<sup>1</sup>–Si<sup>3</sup> orbital interactions. The calculated WBI of the Si<sup>1</sup>–Si<sup>3</sup> bond in **6** is 0.58. This WBI value indicates significant bonding, although weaker than in silylene **7** where the WBI is 0.98. For comparison, in cyclic Si<sub>3</sub>H<sub>6</sub> and in Si<sub>2</sub>H<sub>6</sub> the WBI of the Si–Si bond is 0.94 and 0.95, respectively (MP2/6-31G(d,p)//B3LYP/6-31G(d,p)). According to NBO analysis, 1.47 electrons occupy the Si<sup>1</sup>–Si<sup>3</sup> bond space in **6** compared with 1.94 in **7** and 1.93 and 1.95 el. in trisilacyclopropane and Si<sub>2</sub>H<sub>6</sub>, respectively (MP2/6-31G(d,p)//B3LYP/6-31G(d,p)). This analysis strongly supports the existence of a fairly strong partial Si–Si bond between the terminal silicon atoms of trisilaallene.<sup>24</sup>

The WBI of the allenic Si<sup>1</sup>–Si<sup>2</sup> (or Si<sup>2</sup>–Si<sup>3</sup>) bonds of only 1.25 in **6** as well as their calculated electron occupancy of only 1.89 el. indicate a significant reduction in the double bond character in **6** compared to linear **5** where the occupancy of each of the Si<sup>1</sup>–Si<sup>2</sup> (Si<sup>3</sup>–Si<sup>2</sup>) bonds is 3.85 and the WBI of 1.81 is close to the classic value of 2. The reduced bond order of the Si<sup>1</sup>–Si<sup>2</sup> (Si<sup>2</sup>–Si<sup>3</sup>) bonds in **6** is consistent with the fact that these bonds are longer in **6** (2.269 Å) relative to those in **5** (2.125 Å) or in H<sub>2</sub>Si=SiH<sub>2</sub> (2.179 Å). It is interesting to note how the eight valence electrons connecting the three silicon atoms of **6** are distributed; 1.89 el. are assigned to each of the Si<sup>1</sup>–Si<sup>2</sup> and Si<sup>2</sup>–Si<sup>3</sup> bonds, 1.47 el. to the Si<sup>1</sup>–Si<sup>3</sup> bond, 1.87 el. to the in-plane lone pair at Si<sup>2</sup>, and 0.52 el. to the formally empty out-of-plane orbital at Si<sup>2</sup>.

In conclusion, according to the calculated geometry parameters and the above analysis of the electronic structure and charge distribution, the bonding in **6** is best described as consisting of two partial double bonds between Si<sup>2</sup> atom and the Si<sup>1</sup> and Si<sup>3</sup> atoms and a partial bond between the terminal silicon atoms, as shown schematically in **9a**.

NBO analysis reveals that in **6** there is a substantial stabilizing interaction<sup>25</sup> between the Si<sup>1</sup>–Si<sup>3</sup> bonding elec-



trons and the formally empty 3p orbital on Si<sup>2</sup> which is manifested by charge transfer between these orbitals,<sup>26</sup> as schematically shown in **9b**. In contrast, in **7** this stabilizing interaction cannot occur, because the empty 3p orbital is strictly perpendicular to the Si<sup>1</sup>–Si<sup>3</sup> bond.

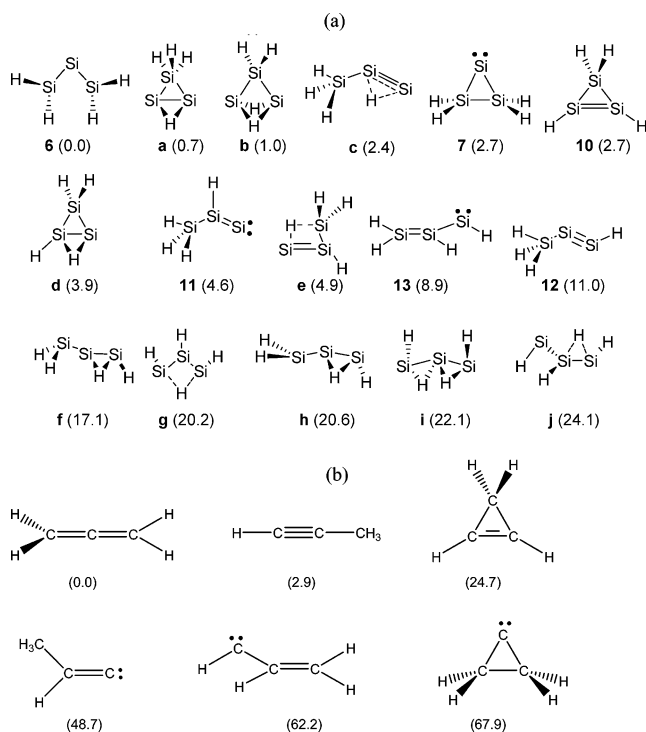
We conclude, based on the molecular geometry as well as on the WBI and NPA analysis, that in trisilaallene **6** a partial bond exists between the terminal Si<sup>1</sup> and Si<sup>3</sup> atoms. Although formally being an allene, trisilaallene **6** has a very different electronic structure from that of allene, including a strong silylenic character at the central silicon atom. Trisilaallene is yet an additional example of low-valent silicon compounds, where traditional valence-bond Lewis structures cannot describe properly the bonding situation.<sup>2a</sup>

**2. Relative Energies of Si<sub>3</sub>H<sub>4</sub> Isomers.** The singlet potential energy surface (PES) is the lowest PES of Si<sub>3</sub>H<sub>4</sub>. The triplets of **6** and **7** lie 22.4 and 6.3 kcal/mol above the corresponding singlets, respectively.<sup>27,28</sup> The quintet state of **6**, which involves unpairing of all four  $\pi$  electrons of trisilaallene, lies 53.7 kcal/mol above the singlet state. We therefore discuss below only the singlet Si<sub>3</sub>H<sub>4</sub> PES.

The Si<sub>3</sub>H<sub>4</sub> PES is much more complex than that of C<sub>3</sub>H<sub>4</sub>. As many as 16 minimum structures, i.e., Si<sub>3</sub>H<sub>4</sub> isomers, were located on the Si<sub>3</sub>H<sub>4</sub> singlet PES, and their relative energies (at B3LYP/6-31G(d,p)) are shown in Chart 1a.<sup>29</sup> Furthermore, all these Si<sub>3</sub>H<sub>4</sub> isomers are within a relatively narrow energy range of only ~25 kcal/mol, and the energies of the nine lowest energy isomers are clustered within a range of only 5 kcal/mol. It is interesting to contrast the complex Si<sub>3</sub>H<sub>4</sub> PES with the PES of C<sub>3</sub>H<sub>4</sub><sup>30a</sup> where only 6 minima exist and where the energy differences between the isomers are much larger, reaching 68 kcal/mol (Chart 1b).<sup>30a</sup> The PESs of C<sub>2</sub>SiH<sub>4</sub>,<sup>30b</sup> Si<sub>4</sub>H<sub>6</sub>, and Si<sub>4</sub>R<sub>6</sub><sup>31</sup> are also simpler than that of Si<sub>3</sub>H<sub>4</sub>.

The Si<sub>3</sub>H<sub>4</sub> isomers include six structures which are analogous to the six C<sub>3</sub>H<sub>4</sub> isomers (Chart 1b). The global minimum on the C<sub>3</sub>H<sub>4</sub> PES is allene with propyne and cyclopropene lying 2.9 and 24.7 kcal/mol higher in energy, respectively. The other minima are the three carbenes, propenylidene, vinylmethylene, and cyclopropenylidene, lying by 48.7, 62.2, and 67.9 kcal/mol above allene, respectively.<sup>30a</sup> The relative energies of the analogous silicon isomers are very different. The global Si<sub>3</sub>H<sub>4</sub> minimum is the bent trisilaallene, **6**, with trisilacyclopropylidene, **7**, lying very close in energy. As the energy barrier separating **6** and **7** is very small (Figure 2), **7** will collapse to **6** even at very low temperatures. Trisilacyclopropene, **10**, lies only 2.7 kcal/mol above **6**. Silyldisilyne (**12**), the silicon analogue of propyne, is only 11–13 kcal/mol higher in energy than either **6** or **7**. **12** is trans-bent at the SiSi triple bond, as expected from previous theoretical<sup>1c</sup> and consistent with recent experimental<sup>32</sup> studies. **11** and **13**, two other silylene-type species, are by 4.6 and 8.9 kcal/mol higher in energy than **6**, respectively.

**Chart 1.** Relative Energies (kcal/mol) of Singlet  $M_3H_4$  Isomers: (a)  $M = Si$  (at B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p)), All Structures Are Minima and (b)  $M = C$  (at B3LYP/6-31G(d)//B3LYP/6-31G(d))<sup>30a</sup>



An unusual feature of the  $Si_3H_4$  PES is the existence of several hydrogen-bridged  $Si_3H_4$  isomers (structures a–j in Chart 1a). This contrasts the  $C_3H_4$  or the  $C_2SiH_4$  PESs where hydrogen-bridged minima structures were not located. For example, **e** is a minimum on the  $Si_3H_4$  PES, but the analogous  $C_3H_4$  structure is a transition state that connects the carbon analogues of **10** and **11**.<sup>30a</sup> The existence of hydrogen-bridged structures for heavier group 14 elements has been noted in other systems and was attributed to the larger size and higher polarizability of these atoms compared to those of carbon.<sup>1f</sup> Interestingly, there are two hydrogen bridged structures, **b** (having two bridging hydrogens) and **d** (having one bridging hydrogen), which are very close in energy to the classic trisilacyclopentene (**10**). Another interesting hydrogen bridged structure is **i**, which can be thought of as originating from a linear trisilaallene and in which a hydrogen bridges each of the two allenic double bonds.<sup>33</sup>

## Conclusions

Trisilaallene, the silicon analogue of allene has an unusual geometry, electronic structure, and bonding. It is strongly bent at the central silicon atom with a SiSiSi bond angle of only  $69.4^\circ$  (B3LYP/6-31G(d,p)) and has planar terminal  $H_2Si$  groups which adopt an unusual mutual orientation. A partial bond exists between the terminal silicon atoms and the two formal  $\pi$ -bonds have only partial occupancy. The formal trisilaallene is close in its geometry and energy to trisilacyclopentylidene, and these two molecules which are connected by a very low barrier can be regarded as bond-stretch isomers.<sup>34</sup>

The singlet PES surface of the  $Si_3H_4$  isomers is very complex and includes at least 16 isomers, many having

nonclassical hydrogen-bridged structures. These isomers lie in a narrow energy range of less than 25 kcal/mol (11 isomers are in the range of 11 kcal/mol) suggesting the possible existence of a very complex mixture of isomers even at moderate temperatures. Many interesting questions are open for future studies, such as the effect of substituents on the structure and energetics of  $Si_3R_4$  isomers. For example, in a recent paper<sup>16</sup> we have demonstrated computationally that boryl-substituted trisilaallenes (and trigermaallenes) have linear classical allenic-type structures. We are continuing our studies of this intriguing group of compounds.

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**Supporting Information Available:** Cartesian coordinates, total energies, and ZPE of all calculated species. This material is available free of charge via Internet at <http://pubs.acs.org>.

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- (26) The sum of the electron density residing between Si<sup>1</sup> and Si<sup>3</sup> and in the formally empty Si<sup>2</sup> 3p orbital (which is not strictly perpendicular to the Si<sup>1</sup>Si<sup>2</sup>Si<sup>3</sup> plane and which becomes partially occupied due to this interaction) is close to 2 (1.47 (Si<sup>1</sup>–Si<sup>3</sup>) + 0.52 (3p(Si<sup>2</sup>)) = 1.99 el., Table 2).
- (27) Fully optimized at UB3LYP/6-31G(d,p). The geometries are given in the Supporting Information.
- (28) The lowest triplet state of **6** (calculated by TDDFT/6-31G-(d,p)) corresponds to the biradical structure of **6** where a radical center is located on each of the terminal silicon atoms and the partial Si<sup>1</sup>–Si<sup>3</sup> bond is broken. The lowest triplet state of silylene **7** (vertical transition) has one electron in the in-plane orbital and one electron in the out-of-plane Si<sup>2</sup>-(3p) orbital. The different electronic structures of the triplet states of **6** and **7** point to the different electronic structures of the singlet ground states of **6** and **7**.
- (29) The most important Si<sub>3</sub>H<sub>4</sub> isomers were optimized also using the larger B3LYP/6-311G(2d,p) basis set. It was found that this does not change significantly their relative energies. There is a relatively good agreement between the relative energy of **12** with respect to **6**, calculated at B3LYP/6-31G(d,p) (11.0 kcal/mol), MP2/6-31G(d,p) (8.5 kcal/mol), and CCSD/6-311+G(2df,p) (12.8 kcal/mol).
- (30) (a) Kakkar, R. *Int. J. Quantum Chem.* **2003**, 94, 93–104, and references therein. (b) (i) Barthelat, J. C.; Trinquier, G.; Bertrand, G. *J. Am. Chem. Soc.* **1979**, 101, 3785. (ii) Gordon, M. S.; Koob, R. D. *J. Am. Chem. Soc.* **1981**, 103, 2939. (iii) Lien, M. H.; Hopkins, A. C. *Chem. Phys. Lett.* **1981**, 80, 114.
- (31) (a) Most Si<sub>3</sub>H<sub>4</sub> isomers lie in a relatively narrow energy range of ca. 10 kcal/mol, while the Si<sub>4</sub>H<sub>6</sub><sup>31b</sup> isomers lie in an energy range of ca. 35 kcal/mol. The Si<sub>4</sub>Me<sub>6</sub> isomers (example of Si<sub>4</sub>R<sub>6</sub><sup>31c</sup>) lie in an energy range of ca. 145 kcal/mol. No hydrogen bridged structures were located on the Si<sub>4</sub>H<sub>6</sub> PES. (b) Müller, T. In *Organosilicon Chemistry IV: From Molecules to Materials* **2000**, 110. (c) Koch, R.; Bruhn, T.; Weidenbruch, M. *Theochem.* **2004**, 680, 91.



- (32) Sekiguchi, A.; Kinjo, R.; Ichinohe, M. *Science* **2004**, 305, 1755.
- (33) We suspect that additional stable structures may exist on the  $\text{Si}_3\text{H}_4$  singlet surface.
- (34) While our paper was in press another paper that discusses the bonding in trisilaallene was published: Veszprémi, T.; Petrov, K.; Nguyen, C. T. *Organometallics* **2006**, 25, 1480.

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