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Structures of Si_7H_{2m} ($m=1-7$) clusters by global optimization

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Structures of Si_7H_{2m} ($m=1-7$) clusters are studied by a global search strategy using a genetic algorithm in combination with tight-binding potentials to describe the interatomic interactions. The low-energy structures obtained from the global search are further studied by *ab initio* calculations. Almost all the lowest-energy structures (except Si_7H_{12}) obtained from our present study are energetically more stable than those structures previously proposed. Using the lower-energy isomers from our calculations, the relationship between the geometric structures and energetic stabilities of the hydrogenated silicon clusters is also discussed.

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I. INTRODUCTION

Hydrogenated silicon clusters have attracted considerable interests because of their important role in chemical vapor deposition (CVD) and plasma enhanced chemical vapor deposition (PECVD) processes and their potential applications in optoelectronic devices. Studies of hydrogenated silicon clusters may also provide useful information for a better understanding the interaction of hydrogen with bulk silicon surfaces and nanostructured silicon surfaces.

There have been a lot of experimental and theoretical studies to investigate the structures of the hydrogenated silicon clusters.[1–40] Experimentally, mass spectrometry has been widely used to probe the hydrogen-to-silicon ratios in hydrogenated silicon clusters generated using a variety of methods.[4–10] Such informations are used to infer the structures of the clusters. Although the experimental data are very useful, it is clear that such information alone is not adequate for determining the structures of the clusters. On the theoretical side, the structures and stabilities of the clusters have also been studied by a wide variety of theoretical methods.[1–3,10–37] However, most of the theoretical studies are limited to small clusters. Structures of hydrogenated silicon clusters with more than six silicon atoms are still largely unknown.

In this paper, we aim at determining the lowest-energy structures for Si_7H_{2m} ($m=1-7$) clusters using a global search strategy. It is well known that the pentagonal bipyramid structure of Si_7 is one of the "magic" silicon clusters.[41,42] It is the most stable structure among the silicon clusters that have bipyramid motif [e.g., trigonal bipyramid for Si_5 and quadrilateral bipyramid for Si_6 (Refs. 41–43)]. Therefore, it is also of interest to see how the stability of such a pentagonal bipyramid silicon skeleton will be affected upon adsorption of hydrogen atoms. We note that some clusters of this size range have been studied previously by Meleshko and co-workers[1] and by Swihart and Girshick.[2] Nevertheless, the success of these studies in hunting for the ground-state structures of the clusters are limited either by the accuracy of the calculation method[1] or by the power of the search algorithm.[2] We will show in this paper that most of the structures obtained from our present global search strategy are more favorable than those previously proposed.

II. COMPUTATIONAL METHODS

Our global structure optimization is divided into two stages. In the first stage, the candidate structures are searched utilizing an efficient and accurate tight-binding (TB) potential model developed by us[44] coupled with the biologically inspired algorithm, genetic algorithm (GA), for the structure optimization. Starting with a population of candidate structures (which can be generated either randomly or by smart guess using our knowledges of bonding properties of Si-H system), we relax these candidates to the nearest local energy minimum using the tight-binding molecular dynamics for quenching. Using the energies of relaxed candidates as the criteria of fitness, a fraction of the population (usually ten different structures) is selected to be kept in the candidate pool. The next generation of candidates is then generated by a "cut-and-paste" mating operation[45] on the parent structures selected from the candidate pool. When the structures of this new generation have been relaxed, the candidate pool is updated according to the fitness criteria discussed above. This optimization procedure is repeated until the candidate pool is "converged," i.e., no more low-energy structure can be found within a reasonable computational time. In the second stage, the candidates that remain in the pool are evaluated by *ab initio* calculations in order to determine the ground-state structure. In the present work, the *ab initio* calculations are performed at the level of DFT-B3LYP with basis set of 6-31G(d) using the GAMESS code.[46] The large basis set of 6-311G(d,p) and different exchange correlation energy functional of B3PW91 are also used to double check the relative stability of the isomers. The DFT-B3PW91 calculations are performed using GAUSSIAN 98.[47]

In order to understand the stability of the clusters, we have also calculated the strain energies of the clusters using the homodesmotic reaction method.[27,48] The strain energy of a Si_7H_{2m} cluster is defined as the energy change of the homodesmotic reaction that converts the cyclic structure into acyclic molecules. In the homodesmotic reaction, the numbers of Si-Si and Si-H bonds are the same on both sides of the equation. Therefore, the average bond energies can be regarded to be the same on both sides of the reaction equation and the strain energy is the difference between the total energies of the reactants and products. Moreover, the ho-

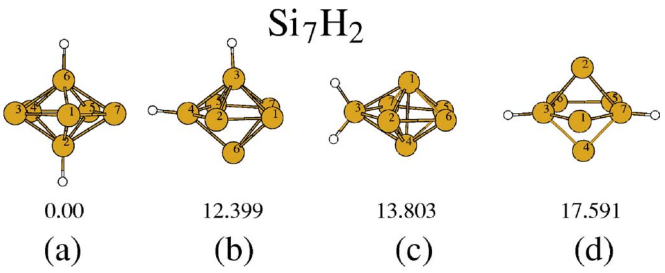


FIG. 1. (Color online) Low-energy isomers of Si_7H_2 clusters. The numbers under the structures are the relative energies in the unit of kcal/mol.

modesmotic reaction preserves the bonding environment around each atom in reactants and products, i.e., a balance is held on both sides of the reaction equation for the number of silicon atoms connected to two hydrogens and two other silicons as well as for the numbers of silicons bonded to one hydrogen and other three silicons. Because of these two features, basis set and electron correlation errors inherent in the calculation of cluster electronic structures might largely cancel when differences are taken between total energies of products and reactants to obtain energy changes for the reactions. The total energy calculations were performed at the level of DFT-B3LYP with basis set of 6-31G(d) using the GAMESS code.[46] The details of the homodesmotic reaction equations for different clusters can be found in Table III. Note that the homodesmotic reaction method is not applicable when the coordination number of any Si atom in the cluster is larger than 4. Therefore, we can calculate the strain energies only for the isomers of the Si_7H_8, Si_7H_{10}, Si_7H_{12}, and Si_7H_{14} clusters.

III. LOWER-ENERGY STRUCTURES

We have systematically studied the structures of Si_7H_{2m} clusters with $m=1-7$. Low-energy isomers of the clusters obtained from our global search strategy are plotted in Figs. 1 and 2, and Figs. 4–8, respectively. In the following subsections, we will discuss the energies and structural features of these isomers in the order of their size. The structures and energies discussed in the subsections Si_7H_2 to Si_7H_{14} are optimized using DFT calculations at the level of B3LYP/6-31G(d). Calculations with larger basis set and different exchange-correlation energy functional will be discussed at the end of this section. For a given m, the isomers are plotted in the order according to their relative energies where (a) is the most stable isomer. Some of the isomers have been proposed by previous studies. But most structures reported here have not been discussed in the literature. The isomers that has been proposed in the literature will be pointed out.

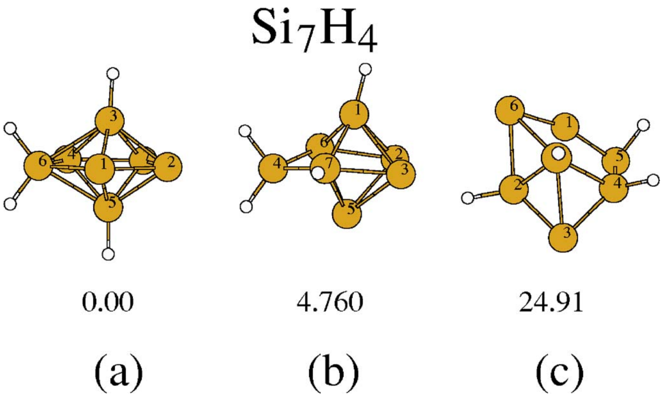


FIG. 2. (Color online) Low-energy isomers of Si_7H_4 clusters. The numbers under the structures are the relative energies in the unit of kcal/mol.

A. Si_7H_2

Figure 1 shows four isomers for Si_7H_2. To our knowledge, only isomer (c) has been discussed in Ref. 1; the other three isomers have not been reported in the literature. Our calculation results show that the energies of isomers (b), (c), and (d) are higher than that of isomer (a) by 12.40, 13.80, and 17.59 kcal/mol, respectively.

Isomer (a) has D_{5h} symmetry and isomers (b), (c), and (d) have C_s, C_{2v}, and C_{2v} symmetries, respectively. All of the four isomers preserve the basic silicon skeleton structure of the pure Si_7 cluster, i.e., the pentagonal bipyramid structure. It can be seen from Fig. 1 that when two hydrogen atoms are added to the Si_7 cluster, the most favorable adsorption sites are the two Si atoms at the top positions of the pyramid [see isomer (a)]. The next favorable structure is isomer (b) where one hydrogen atom is attached to one of the top Si atom while another hydrogen atom is bonded to a Si atom in the pentagon. If both two hydrogen atoms are attached to a Si atom at the top of the pyramid [isomer (c)], the energy is higher. Finally, two hydrogen atoms attached to two silicon atoms in the pentagon results in a structure [isomer (d)] which is highest in energy among the four isomers.

The Si-Si bond lengths in isomer (a) are 2.495 Å among the silicon atoms in the pentagon and 2.667 Å between the two top silicon atoms. The corresponding bond lengths in the pure Si_7 cluster are 2.511 and 2.586 Å, respectively. The effect of hydrogenation in isomer (a) is to stretch the top of the pyramids in the direction perpendicular to the pentagon and at the same time the area of the pentagon is shrunken. The structure nevertheless retains the D_{5h} symmetry of the pure Si_7 cluster.

The symmetry of isomer (b) is reduced to C_s symmetry because one of the hydrogen atoms is switched from the top silicon atom to a Si atom of the pentagon. In contrast to isomer (a), the asymmetric hydrogenation of isomer (b) imposes strong influence on the structure of the silicon skeleton. The distance between the hydrogenated top silicon atom and the pentagonal plane is 1.436 Å and that between the unhydrogenated top silicon atom and the pentagonal plane is 1.676 Å. These distances are longer than the corresponding distances in the pure Si_7 cluster which are both 1.293 Å. Due to the effect of the hydrogenation on the pentagon, the bond lengths among the Si atoms in the pentagon are split into three different bond lengths $R_{17}=2.555$ Å, $R_{12}=2.411$ Å, and $R_{24}=2.362$ Å, respectively.

In isomer (c), the two hydrogen atoms are connected to the same silicon atom in the pentagon, resulting in a structure

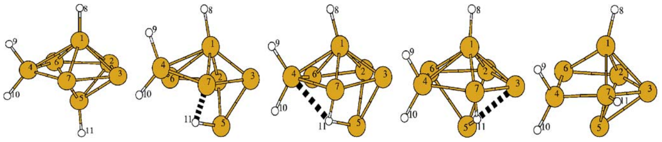


FIG. 3. (Color online) Transition pathway for the isomerization between isomers (a) and (b) of Si_7H_4. The numbers in the brackets are the relative energies (in kcal/mol) with respect to that of isomer (a). The energies are calculated at the level of B3LYP/6-311G(d,p)//B3LYP/6-31G(d).

of C_{2v} symmetry. The bond lengths among the silicon atoms in the pentagon are R_{56}=2.552 Å, R_{26}=2.515 Å, and R_{23}=2.471 Å, respectively. The distance between the two pyramid-top silicon atom is 2.673 Å which is slightly longer than that of the pure Si_7 cluster which is 2.586 Å. Similar to the structure of isomer (b), the bond length between the hydrogenated silicon atom and other Si atom is shorter than that between two pure Si atoms in the same isomer.

B. Si_7H_4

Three isomers of Si_7H_4 are plotted in Fig. 2. The structure of isomer (c) is copied from Ref. 1 and relaxed by present DFT calculation. Isomers (a) and (b) are new structures obtained from our GA/TBMD global search. The energies of isomers (b) and (c) are 4.76 and 24.91 kcal/mol, respectively, higher than that of isomer (a). The lowest-energy isomer [isomer (a)] exhibits C_{2v} symmetry. The structure of this isomer preserves the basic Si_7 pentagonal bipyramidal silicon skeleton. However, the adsorption of hydrogen atoms destroys the D_{5h} symmetry of the pentagon. The bond length of the pentagon is split into three: R_{16}=2.441 Å, R_{12}=2.473 Å, and R_{27}=2.609 Å. Note that the Si-Si bond length between the di-hydride silicon atom (atom 6) and its neighbors is 2.441 Å, which is smaller than other Si-Si bond lengths in the pentagon. The distance between the two pyramid-top silicon atoms is 2.742 Å which is larger than the corresponding distance in isomer (a) of Si_7H_2 (by 0.075 Å) and Si_7 (by 0.156 Å). There are no symmetries for the structures of isomers (b) and (c) due to the asymmetric adsorption of the hydrogen atoms to the Si_7 cluster. Detail comparison between isomers (a) and (b) shows that isomer (a) can be transformed from isomer (b) when the hydrogen atom that bonded to Si atom 7 in isomer (b) is moved to the bonding position with atom 5.

We have calculated the energy barrier for the transformation between isomers (a) and (b). The pathway for the isomerization reaction is shown in Fig. 3. This is a two-step reaction characterized by two transition states TS1, TS2, and an intermediate IM. The forward reaction barriers are 28.0 and 4.8 kcal/mol, respectively, while the reverse reaction barriers are 28.3 and 0.7 kcal/mol, respectively. Therefore, there will be a isomerization barrier of about 30 kcal/mol for the transitions between (a) to (b). Since the energy difference between the two isomers is only about 4 kcal/mol, these two isomers would be coexisted for Si_7H_4. Other isomers have energies much higher than those of two isomers and should be much less abundance for Si_7H_4.

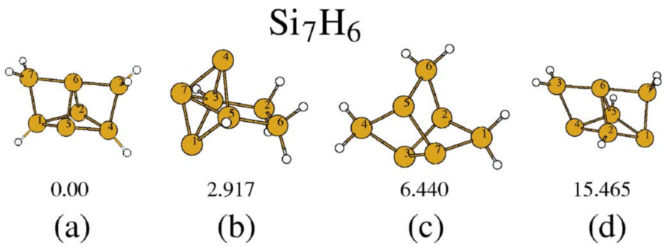


FIG. 4. (Color online) Low-energy isomers of Si_7H_6 clusters. The numbers under the structures are the relative energies in the unit of kcal/mol.

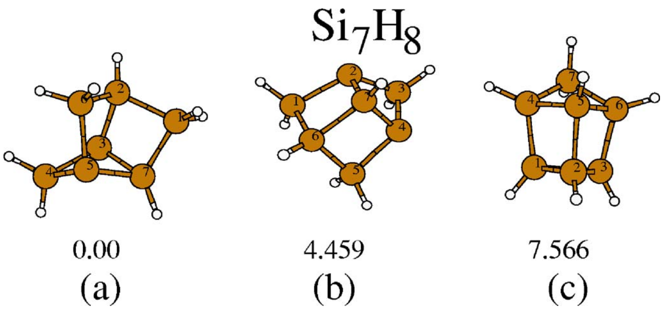
C. Si_7H_6

Figure 4 shows four isomers of Si_7H_6. Isomer (d) was proposed in Ref. 1. However, our calculation results show that the energy of this isomer is higher than other three isomers obtained from our GA/TBMD search. The energies of isomers (b), (c), and (d) are 2.92, 6.44, and 15.47 kcal/mol higher than that of isomer (a), respectively.

The lowest-energy isomer (a) exhibits a C_{2v} symmetry. This cluster has a diradical structure. The radical centers are located on the short diagonal of the four-membered ring {1542}, i.e., on atoms 2 and 4. All Si atoms other than the radical center atoms are fourfold coordinated. All Si-Si bond lengths are close to that of Si-Si single bond: R_{15}=2.357 Å, R_{17}=2.396 Å, R_{76}=2.359 Å, and R_{56}=2.368 Å. The distance between the two radical center is 2.712 Å. There is an interesting difference between isomer (a) and (d) on the adsorption positions of two hydrogen atoms on the four-membered ring {1542}. In isomer (a) the two hydrogen atoms are connected to the Si atoms located on the long diagonal of the four-membered ring. While in isomer (d), the hydrogenated Si atoms are located on the short diagonal of the ring. The stability of the isomers can be attributed to the location of the radical centers as we will discuss in the next section.

Isomers (b) and (c) have different silicon skeleton from that of isomers (a) and (b). Isomer (b) has C_s symmetry. All hydrogen atoms are bonded to the Si atoms in the five-membered ring. The isomer preserves the five-membered ring structure of the Si_7 cluster. However, the two Si atoms at the top positions of the bipyramid have already deviated substantially from the central axis of the pentagon. The six hydrogen atoms in isomer (c) form three dihydrides at the three corners of the isomer. This isomer is more open than the other three isomers.

It is interesting to note that although isomers (a) and (b) have very similar energy, their Si skeletons are very different. Careful examination of these isomers shows that the skeleton of the Si atoms in isomer (a) is very different from that of the Si_7 cluster, while in isomer (b) the shape of the Si_7 cluster can still be recognized. These structure features suggest that the Si_7H_{2m} clusters can keep the skeleton of the Si_7 cluster when m is less than 3. As we will see in the following, the Si_7 skeleton will be destroyed when m is larger than 3. The Si skeleton of isomer (a) is similar to that of the lowest-energy isomers of Si_7H_8 and Si_7H_{10}, while isomer (b) belongs to the same class as Si_7H_2 and Si_7H_4. Therefore m=3 seems to be a transition point for the structure motif of



0.00 (a) 4.459 (b) 7.566 (c)

FIG. 5. (Color online) Low-energy isomers of Si_7H_8 clusters. The numbers under the structures are the relative energies in the unit of kcal/mol.

the Si_7H_{2m} clusters. This interesting point will be further discussed in the next section.

D. Si_7H_8

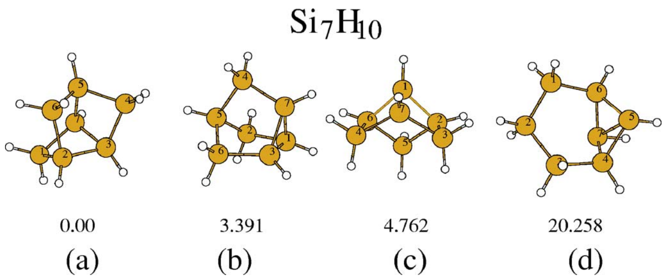
Three isomers of Si_7H_8 are plotted in Fig. 5. Isomers (b) and (c) were proposed for Si_7H_8 by Refs. 1 and 2, respectively. The new structure [isomer (a)] obtained from our GA/TB search is found to has energy lower than those of isomer (b) and (c) by 4.46 and 7.57 kcal/mol, respectively. Isomer (a) has two four-membered rings {4573}, {1237} and a five-membered ring {12657} as well as a diradical structure with the radical centers located on Si atoms 3 and 5. Isomer (b) is composed of three four-membered rings {5476}, {4327}, {6721} and a diradical structure located on Si atoms 2 and 4. Isomer (c) consists of one three-membered ring {123} and three four-membered rings {1254}, {2365}, and {5674}. In Table I we list the structure parameters for the lowest-energy isomer of Si_7H_8. These structure parameter will be compared to those of Si_7H_{10} that will be discussed below.

E. Si_7H_{10}

Four isomers of Si_7H_{10} are shown in Fig. 6. Isomers (c) and (d) are copied from Refs. 2 and 1 and are optimized by the *ab initio* calculations. Isomers (a) and (b) are new structures obtained by our GA/TB search. Isomer (a) has the lowest energy at the level of DFT-B3LYP. Isomers (b) and (c) have energies very close to that of isomer (a), i.e., only about 3.39 and 4.76 kcal/mol, respectively, higher than that of isomer (a). In comparison, the energy of isomer (d) is much higher than that of isomer (a) (by 20.26 kcal/mol). The structure of isomer (a) can be obtained by adding two more hydrogen atoms to the diradical centers of isomer (a) of Si_7H_8 [see Fig. 5(a)]. The structure parameters of isomer (a) of Si_7H_{10} are also listed in Table I. Comparison between the structure parameters of the two isomers show that when two hydrogen atoms are added to two Si atoms at the diradical centers in Si_7H_8, the distance between these two silicon atoms increases from 2.810 to 3.317 Å. This distance increase indicates that the adsorption of the two hydrogen atoms breaks the weak Si-Si bond in the original Si_7H_8 structure. At the same time, the bond angle variation in the four-membered ring {4357} is reduced from 23.5° to 7.3° upon adsorption of the two hydrogen atoms so that the four-membered ring becomes more squarelike. On the other hand, the Si-Si bond length between the Si atoms in the four-membered ring and the torsion angle $\tau(7354)$ change very little upon adsorption of the hydrogen atoms.

TABLE I. Structure parameters of the lowest-energy isomers [isomer (a)] of Si_7H_8 and Si_7H_{10} clusters. Torsion angle $\tau(7354)$ denotes the angle between the plane spanned by atoms 7, 3, 5 and the plane spanned by atoms 3,5,4. It measures the deviation of a four-membered ring from the planner structure. $\tau=180$ means that the four-membered ring is planner.

Cluster	Bond length (Å)	Bond angle (deg.)	Torsion angle (deg.)
Si_7H_8	$R_{45}=2.340$	$\angle 345=73.5$	$\tau(7354)=138.0$
	$R_{43}=2.357$	$\angle 375=73.3$	
	$R_{75}=2.365$	$\angle 457=96.8$	
	$R_{73}=2.347$	$\angle 437=96.8$	
	$R_{35}=2.810$		
Si_7H_{10}	$R_{45}=2.374$	$\angle 345=83.8$	$\tau(7354)=137.0$
	$R_{43}=2.367$	$\angle 375=81.8$	
	$R_{75}=2.397$	$\angle 457=88.7$	
	$R_{73}=2.392$	$\angle 437=89.1$	
	$R_{35}=3.137$		



0.00 (a) 3.391 (b) 4.762 (c) 20.258 (d)

FIG. 6. (Color online) Low-energy isomers of Si_7H_{10} clusters. The numbers under the structures are the relative energies in the unit of kcal/mol.

F. Si_7H_{12}

We report here two isomers for Si_7H_{12} as shown in Fig. 7. Isomer (a) obtained from our search is the same as the one reported in Ref. 1. Both isomers (a) and (b) have C_{2v} symmetry. The bond angles of isomer (a) are $\angle 213=103.5°$, $\angle 127=108.2°$, $\angle 125=100.2°$, and $\angle 256=95.12°$. The bond angles of isomer (b) are $\angle 315=87.1°$, $\angle 345=86.9°$, $\angle 267=113.7°$, $\angle 134=87.0°$, and $\angle 154=87.1°$. By comparing the bond angles of the two isomers we find that in isomer (a) only one of the angles is less than 100° ($\angle 256=95.12°$), while as many as four angles in isomer (b) are less than 100°.

G. Si_7H_{14}

Our GA/TBMD optimization gives five low-energy isomers for Si_7H_{14} as shown in Fig. 8. It can be seen from the figure that each isomer has only one ring. Our calculation results show that the energy of the six-membered ring is the lowest, followed by one of the five-membered, then the seven-membered, and finally four-membered rings. Isomer

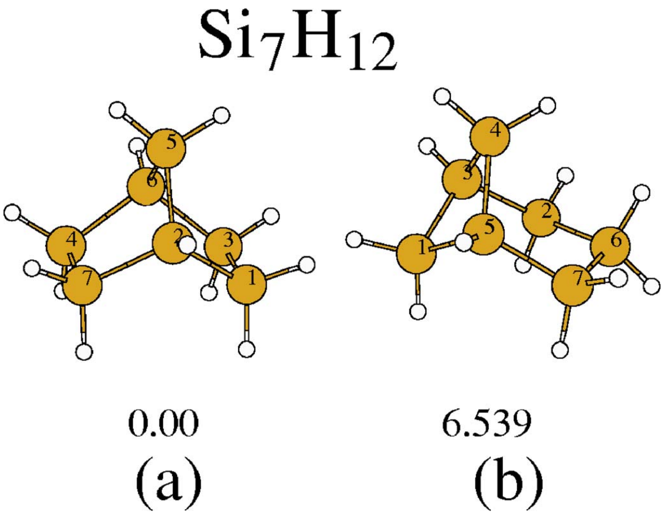


FIG. 7. (Color online) Low-energy isomers of Si_7H_{12} clusters. The numbers under the structures are the relative energies in the unit of kcal/mol.

(a), (b), and (c) all have C_s symmetry. The six-membered ring structure of isomer (a) is an arm-chair structure. There are two five-membered ring isomers, i.e., isomers (b) and (d). In isomer (b) two SiH_3 units are bonded to the same Si atom (atom 3) of the five-membered ring. While in isomer (d) the Si atom 3 is bonded by a Si_2H_5 unit and a hydrogen atom. The six-, five-, and seven-membered ring structures of Si_7H_{14} have bond angles of 112±1°, 105±2°, and 113±2°, respectively which are close to the standard tetrahedral bond angle of 109.48°. These structure features suggest that the strain energies of these rings should be very small. The strain energies obtained from our calculations also confirm this conjecture as we will see the results in next section.

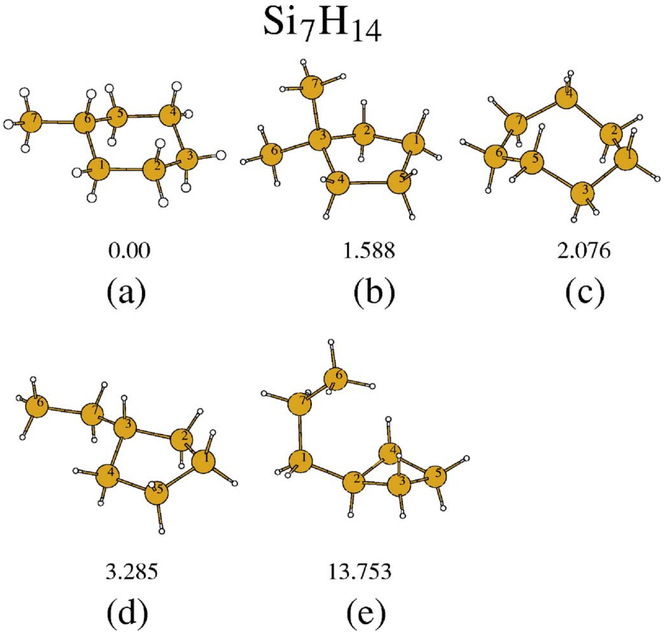


FIG. 8. (Color online) Low-energy isomers of Si_7H_{14} clusters. The numbers under the structures are the relative energies in the unit of kcal/mol.

TABLE II. Relative energies [in the unit of kcal/mol, relative to the energies of isomers (a) at the same level of calculation] from *ab initio* DFT calculations using different basis set and different exchange-correlation energy functionals. All calculations use the structures optimized at the B3LYP/6-31G(d) level.

Cluster	B3LYP/6-31G(d)	B3LYP/6-311G(d,p)	B3PW91/6-311G(d,p)
Si_7H_2-(a)	0.00	0.00	0.00
Si_7H_2-(b)	12.40	11.64	14.90
Si_7H_2-(c)	13.80	14.41	16.57
Si_7H_2-(d)	17.59	16.63	22.59
Si_7H_4-(a)	0.00	0.00	0.00
Si_7H_4-(b)	4.76	3.83	8.25
Si_7H_4-(c)	24.91	23.76	30.76
Si_7H_6-(a)	0.00	0.00	0.00
Si_7H_6-(b)	2.92	3.43	6.82
Si_7H_6-(c)	6.44	6.48	10.91
Si_7H_6-(d)	15.47	16.11	15.98
Si_7H_8-(a)	0.00	0.00	0.00
Si_7H_8-(b)	4.46	4.59	5.31
Si_7H_8-(c)	7.57	7.74	4.44
Si_7H_{10}-(a)	0.00	0.00	0.00
Si_7H_{10}-(b)	3.39	3.24	4.54
Si_7H_{10}-(c)	4.76	4.94	6.94
Si_7H_{10}-(d)	20.26	20.57	27.35
Si_7H_{12}-(a)	0.00	0.00	0.00
Si_7H_{12}-(b)	6.54	6.71	7.26
Si_7H_{14}-(a)	0.00	0.00	0.00
Si_7H_{14}-(b)	1.59	1.79	1.16
Si_7H_{14}-(c)	2.08	2.48	3.06
Si_7H_{14}-(d)	3.29	3.26	2.83

IV. CALCULATIONS WITH LARGER BASIS SET

In order to test the sensitivity of our results to the choice of basis set in our *ab initio* calculations, we have performed calculations using a larger basis set of 6-311G(d,p). The total energy calculations with the larger basis set are based on the geometries from the optimizations at the level of B3LYP/6-31G(d). The relative stability of the isomers have also been examined using a different exchange-correlation energy functional of B3PW91. The relative energies from the different basis set and different exchange-correlation functional are compared in Table II. Comparison between the energies from different basis set indicates that our results discussed in the above subsections are convergent with respect to the choice of basis set [6-31G(d) vs 6-311G(d,p)]. The B3PW91 functional gives slightly larger energy separation among the isomers as compared to those from the B3LYP functional. However, the energy ordering among the isomers are the same as that from the B3LYP functional except for isomers of (b) and (c) of Si_7H_8 and isomers (c) and (d) of Si_7H_{14}. These results suggest that the lowest-energy isomers obtained from our global optimization are not sensitive to the choice of basis set and exchange-correlation functional in our *ab initio* calculations. We also used a larger basis set of 6-311G(d,p) to perform the structure optimization for some of the clusters (i.e., the isomers of Si_7H_2 and Si_7H_4). The structures obtained from the larger basis 6-311G(d,p) optimizations are similar to those from the optimizations using the 6-31G(d) basis. The energies of the same isomers from the B3LYP/6-311G(d,p) optimizations and from the single-point B3LYP/6-311G(d,p) calculations with the B3LYP/6-31G(d) optimized structures [i.e, B3LYP/6-311G(d,p)//B3LYP/6-31G(d)] are also very similar to each other (within 1 kcal/mol). We have also compared the stability of isomers (a) and (c) of Si_7H_{14} including the effects of the vibrational entropy using the option in the GAMESS code. The calculation result at the level of B3LYP/6-31(d,p) shows that the free energy of isomer (a) is lower than that of isomer (c) by 4.0 kcal/mol at room temperature. Since the energy difference of the two isomers at zero temperature is 2.08 kcal/mol at the same level of calculation, isomer (a) should be more stable than isomer (c) even at higher temperatures.

V. STRUCTURE TREND AND STABILITIES

As we mentioned in the Introduction, how the stability of the pentagonal bipyramid skeleton of Si_7 is affected by the adsorption of the hydrogen atoms is a subject of interest. There are two major factors governing the stability of a cluster. One is the energy gain by forming chemical bonds among the atoms, another is the energy loss due to strain. The pentagonal bipyramid structure of Si_7 is highly strained because the Si-Si bonds are far from the tetrahedral bonding configuration. This structure is stable because the large strain energy can be overcome by the chemical bonding energy. We may expect that upon the adsorption of the hydrogen the structure can be transformed to a less strained structure by breaking the strained bonds in the skeleton of Si_7. The dangling bonds created by such bond breaking can be healed by the adsorption of hydrogen atoms. The interesting question is how many hydrogen atoms are needed in order to make such a transformation energetically favorable. Our calculation results as plotted in Figs. 1, 2, and 4 show that the Si_7H_{2m} clusters can keep the skeleton of the Si_7 cluster when m is less than 3, i.e., when the number of hydrogen atoms is less than 6. Otherwise there are not enough hydrogen atoms to heal the Si dangling bonds when the Si_7 skeleton is broken. As shown in Fig. 4, when the number of the adsorbed hydrogen atoms reaches six, a new structural motif [isomer (a) of Si_7H_6] appears in which all Si atoms except two (atoms 2 and 5) are fourfold coordinated. This motif is found to be energetically more favorable. Nevertheless, in isomer (a) of Si_7H_6, the bonding configuration of atom 6 is still far away from the tetrahedral bonding configuration of Si although it is fourfold coordinated. Therefore, the energy of this new motif is only slightly lower than that of the old motif of pentagonal bipyramid skeleton as shown in Fig. 4(b). Although their energies are very close to each other, the structure of isomer (a) is similar to that of Si_7H_8 and Si_7H_{10}, while isomer (b) belongs to the same class as Si_7H_2 and Si_7H_4. These results suggest that $m=3$ is a critical value for the transformation of the Si_7H_{2m} clusters from the pentagonal bipyramid structure to a more open new motif as shown in Fig. 4(a). As the number of hydrogen atoms increases, this new motif becomes more and more stable as can be seen in the ground state structures for Si_7H_8 and Si_7H_{10} (see Figs. 5 and 6).

Another interesting feature of the lowest-energy structures of Si_7H_6 and Si_7H_8 is that they can be classified as a diradical structure. In Si_7H_6, the radical centers are located on the atoms 2 and 4, i.e., the short diagonal of the four-membered ring {1542}. In the case of Si_7H_8, the radical centers also lie on the short diagonal of a four-membered ring ({4375}), i.e., on atoms 3 and 5. All Si atoms other than the radical center atoms are fourfold coordinated and Si-Si bond lengths are close to that of the Si-Si single bond. The distance between the two radical center is 2.712 Å in Si_7H_6 and 2.810 Å in Si_7H_8. This suggests that a weak Si-Si bond can be formed between the two radical centers so that the stability of the isomers can be enhanced. The strength of chemical bonding between two atoms can be measured by the bond order between the two atoms. The bond order value of 0 means that there is no chemical bonding between the two atoms, while the value of 1 represents a full single bond between the two atoms. Our conjecture of weak bonding between the two radical centers is confirmed by bond order analysis which shows that the bond order between the two radical center Si atoms is 0.473 for Si_7H_6 and 0.507 in Si_7H_8. It is interesting to note that the difference between isomers (a) and (d) of Si_7H_6 is the adsorption positions of two hydrogen atoms on the four-membered ring {1542}. In isomer (a) the two hydrogen atoms are connected to the Si atoms located on the long diagonal of the four-membered ring. While in isomer (d), the hydrogenated Si atoms are located on the short diagonal of the ring. Since the radical centers at the short diagonal can form about a half of bond while those at the long diagonal (distance of 3.699 Å) cannot, this may explain why isomer (a) is much stable than isomer (d) (by an energy of 15.465 kcal/mol). The role of diradical structures for the stability of hydrogenated silicon clusters has been discussed by Swihart and Girshik[3] for Si_4H_6 and Si_6H_6. They suggested that diradical species with the radical centers at the opposite corners of a four-membered ring would be energetically favorable. Our present calculation results support this suggestion. Isomer (a) of Si_7H_6 and isomer (a) of Si_7H_8 discussed above belong to this class of structures. More precisely, the diradical structure should be the structure that has the diradical centers located at the short diagonal corners of a four-membered ring. As discussed above, diradical centers that are located on the short diagonal corners (distance about 2.7 to 2.9 Å) can form a weak bond while those located at the long diagonal corners (distance of 3.6–3.9 Å) can not form any chemical bond. The location of diradical center at the short diagonal corners therefore make the structure more stable. Note that isomers (a) and (b) of Si_7H_8 are both diradical structures. Their energies are the best among many isomers of Si_7H_8 in our global search. When two more hydro-

TABLE III. Strain energies (kcal/mol) calculated from homodesmotic reactions.

Cluster	Strain energy	Homodesmotic reaction
Si_7H_8-(a)	6.87	Si_7H_8-(a)$+9SiH_3-SiH_3$ $\Rightarrow 3SiH_3-SiH_2-SiH_3+2(SiH3)_3SiH+2(SiH_3)_3Si$
Si_7H_8-(b)	11.32	Si_7H_8-(b)$+9SiH_3-SiH_3$ $\Rightarrow 3SiH_3-SiH_2-SiH_3+2(SiH_3)_3SiH+2(SiH_3)_3Si$
Si_7H_8-(c)	73.22	Si_7H_8-(c)$+10SiH_3-SiH_3$ $\Rightarrow 3SiH_3-SiH_2-SiH_3+6(SiH_3)_3SiH$
Si_7H_{10}-(a)	34.38	Si_7H_{10}-(a)$+9SiH_3-SiH_3$ $\Rightarrow 3SiH_3-SiH_2-SiH_3+4(SiH_3)_3SiH$
Si_7H_{10}-(b)	37.77	Si_7H_{10}-(b)$+9SiH_3-SiH_3$ $\Rightarrow 3SiH_3-SiH_2-SiH_3+4(SiH_3)_3SiH$
Si_7H_{10}-(c)	39.14	Si_7H_{10}-(c)$+9SiH_3-SiH_3$ $\Rightarrow 3SiH_3-SiH_2-SiH_3+4(SiH_3)_3SiH$
Si_7H_{10}-(d)	54.64	Si_7H_{10}-(d)$+9SiH_3-SiH_3$ $\Rightarrow 3SiH_3-SiH_2-SiH_3+4(SiH_3)_3SiH$
Si_7H_{12}-(a)	8.13	Si_7H_{12}-(a)$+8SiH_3-SiH_3$ $\Rightarrow 5SiH_3-SiH_2-SiH_3+2(SiH_3)_3SiH$
Si_7H_{12}-(b)	14.67	Si_7H_{12}-(b)$+8SiH_3-SiH_3$ $\Rightarrow 5SiH_3-SiH_2-SiH_3+2(SiH_3)_3SiH$
Si_7H_{14}-(a)	−0.20	Si_7H_{14}-(a)$+6SiH_3-SiH_3$ $\Rightarrow 5SiH_3-SiH_2-SiH_3+(SiH_3)_3SiH$
Si_7H_{14}-(b)	2.73	Si_7H_{14}-(b)$+5SiH_3-SiH_3$ $\Rightarrow 4SiH_3-SiH_2-SiH_3+(SiH_3)_4Si$
Si_7H_{14}-(c)	1.10	Si_7H_{14}-(c)$+7SiH_3-SiH_3$ $\Rightarrow 7SiH_3-SiH_2-SiH_3$
Si_7H_{14}-(d)	3.51	Si_7H_{14}-(d)$+5SiH_3-SiH_3$ $\Rightarrow 4SiH_3-SiH_2-SiH_3+SiH_3-SiH_2-SiH(SiH_3)_2$
Si_7H_{14}-(e)	14.31	Si_7H_{14}-(e)$+4SiH_3-SiH_3$ $\Rightarrow 3SiH_3-SiH_2-SiH_3+SiH_3-SiH_2-SiH_2-SiH(SiH_3)_2$

gen atoms are added to isomer (a) of Si_7H_8, the hydrogens simply saturate the radical centers and result in the most stable isomer of Si_7H_{10}.

As the number of hydrogen atom increases and more and more silicon atoms become fourfold coordinated, the strain energies of the clusters play a more important role in determining the stability of the clusters. The strain energies of the clusters calculated by the homodesmotic reaction methods as discussed in Sec. II are shown in Table III along with their homodesmotic reaction paths. In Si_7H_8, Si_7H_{10}, and Si_7H_{12}, the ordering of the strain energies is consistent with that of the total energies. The lower-energy isomers of the Si_7H_{14} clusters are less compact and all have a single ring. This suggests that the strain energies of these structures should be very small as indeed confirmed by the results shown in Table III. The six-membered ring has the smallest strain energy, followed by seven-, five-, and finally four-membered rings. In the four-membered ring structure, the bond angles are only $87\pm2°$, much smaller than the tetrahedral bond angle. Therefore, the four-membered ring structure has large strain energy which makes the isomer less stable than the others. The total energies of the isomers of Si_7H_{14} basically follow the ordering of the strain energies except for isomers (b) and (c). The fact that isomer (b) has one Si atom (atom 3) bonded to another four Si atoms in a almost perfect tetrahedral configuration may have more favorable bonding contribution to the total energy, although its strain energy is slightly higher than that of isomer (c). Another reason of the energy ordering discrepancy may be due to the accuracy of the computational methods since the energy differences are very small in this case.

In order to have a more quantitative measure of what $[H]/[Si]$ ratio is favorable by the Si_7H_{2m} clusters, we have calculated the binding energy (ΔE) for each adsorbed hydrogen atom in the Si_7H_{2m} clusters which is defined by

$$\Delta E = [E(Si_7H_{2m}) - E(Si_7) - mE(H_2)]/2m, \qquad (1)$$

where $E(Si_7H_{2m})$, $E(Si_7)$, and $E(H_2)$ are the total energies of Si_7H_{2m}, Si_7 clusters and that of the H_2 molecule, respec-

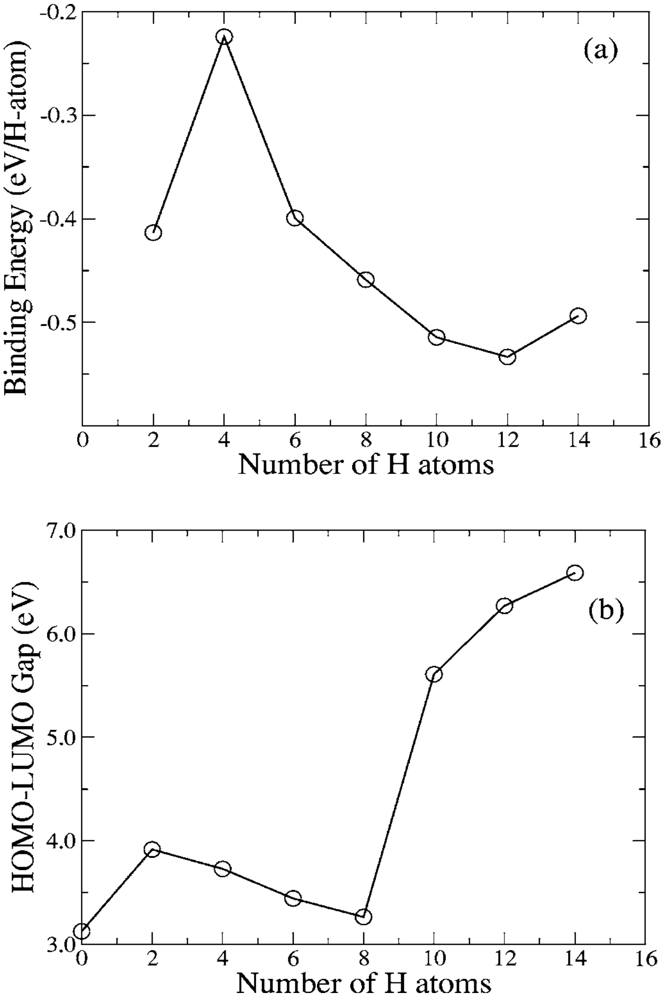


FIG. 9. (a) Binding energy per hydrogen atom and (b) the HOMO-LUMO gaps of the Si_7H_{2m} clusters as the function of number of hydrogen atoms.

tively. The lower (more negative) the ΔE, the more stable is the Si_7H_{2m} upon the adsorption of hydrogen atoms. In Fig. 9(a), the binding energy ΔE as a function of the number of hydrogen atoms in the Si_7H_{2m} clusters is plotted. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gaps of the the Si_7H_{2m} clusters are also plotted as a function of the number of hydrogen atoms in the cluster [Fig. 9(b)]. As one sees from Fig. 9(a), adsorption of four hydrogen atoms to the Si_7 cluster is energetically the worst case among the Si_7H_{2m} studied in this paper. This may explain why the structure transformation occurs in the silicon skeleton of the Si_7H_{2m} cluster as the number of hydrogen atoms increases from four to six as we discussed in the beginning of this section. Figure 9(a) also shows that when the number hydrogen atoms $2m \geqslant 10$, the binding energies are lower because all Si atoms in these clusters are fourfold coordinated with bonding configurations close to tetrahedral bonding. The HOMO-LUMO gaps of the clusters also open up sharply when the Si atoms are fully saturated as shown in Fig. 9(b). It is interesting to note that Si_7H_{12} has the lowest binding energy according to our definition of Eq. (1). This cluster is the largest one among the Si_7H_{2m} clusters that has multi-ring structures. Further increase of the number of hydrogen atoms will change the motif of the clusters from multiple- to single-ring structures as one sees from Fig. 8 for Si_7H_{14}. Consequently, the binding energy of the single-ring Si_7H_{2m} clusters increases again.

The hydrogen-to-silicon ratios [H]/[Si] in hydrogen-terminated silicon clusters have been studied by a number of experiments using mass spectrometry.[4–10] A wide range of [H]/[Si] ratios from zero to about 2 have been observed depending on the number of Si atoms in the clusters, the experimental temperatures, and the methods used to generate the clusters. For small clusters with number of Si atoms n less than 10, most experiments found that the most abundant clusters have the [H]/[Si] ratio between 1.5 and 2. For example, it has been observed by Haller that the mean [H]/[Si] ratio is about 1.5 for $n=3-7$ in the growth of $Si_nH_x^+$ using an rf glow discharge in silane.[7] Murakami and Kanayama found that $Si_5H_{10}^+$ and $Si_6H_{12}^+$ are abundant in the growth of $Si_nH_x^+$ ($n=2-10$) cation in a quadrupole ion trap.[5] Hollenstein *et al.* show that the [H]/[Si] ratio is sensitive to the number of Si atoms in the cluster and the ratio is slightly smaller than 2 when $n=7$.[9] These experimental results are consistent with our present results for $n=7$. Further theoretical studies with increasing number of Si atoms will be useful for understanding the size dependence of [H]/[Si] ratio observed in experiments.

VI. CONCLUSIONS

Using genetic algorithm in combination with tight-binding potentials for Si-Si and Si-H interatomic interactions, we have performed a global structure optimization to study the geometric structures of Si_7H_{2m} ($m=1-7$) clusters. The low-energy cluster structures obtained from our GA/TB search are further studied by ab initio calculations at the level of DFT-B3LYP using the 6-31G(d) basis set. Many structures obtained from our search are found to be energetically more stable than those structures proposed in the literature. We have also investigated the effects of hydrogenation on the Si skeleton structure of Si_7 clusters and discussed the relationship between the geometric structures and stabilities of the clusters. Our studies show that as long as there are no more than four hydrogen atoms in the cluster (i.e., Si_7H_2 and Si_7H_4), the silicon skeleton of the cluster is still similar to the pentagonal bipyramid structure of the Si_7 cluster. The most favorable adsorption sites for these hydrogen-poor clusters are the silicon atoms at the top of the pyramid. Our studies also show that cluster structure with two radical centers located at the short diagonal of a four-membered ring [e.g., isomer (a) of Si_7H_6 and Si_7H_8] are energetically more favorable, consistent with the results for Si_4H_6 and Si_6H_6 reported by Swihart and Girshik.[3] For hydrogen-rich clusters (e.g., Si_7H_{12} and Si_7H_{14}) where chemical bonds are saturated, the stabilities of the clusters are mainly determined by the strain energies of the clusters. It should be noted that while the knowledge obtained from our present study could provide useful insights into chemical vapor deposition process which can be used to growth nanostructures, the cluster size in this paper is still too small to address any properties of nanostructures of current interest. Further studies with increasing system size will be useful for understanding the physics and chemistry of hydrogen-terminated silicon clusters at the nanoscale.

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