

# A theoretical investigation of small Si/C clusters by a combination of MM and QM method

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## Abstract

Global minima of clusters  $C_{n-x}Si_x$  ( $n = 9, 10, 11, x = 0-n$ ) were investigated by a combination of molecular mechanics (MM) and quantum mechanics (QM) methods. The results showed that when the number of C atoms is large enough, C atoms prefer to form pentagons, hexagons, or even large carbon rings. The rest C and Si atoms form triangles and quadrangles around the carbon rings. When the number of Si atoms increases, the structures obtained with MM method distort dramatically when they are further optimized with QM method. The reason might be the inaccuracy of Brenner potential in describing Si atoms.

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## 1. Introduction

After the discovery of  $C_{60}$  [1] and its production in macroscopic quantities [2], a lot of investigations have been prompted on the functionalization and doping of fullerenes. By doping, the electronic, optical, and conducting properties of fullerenes can be modified and tailored. One kind of doping is the substitution of a number of C atoms by heteroatoms such as boron and nitrogen [3–5].

Silicon is a very interesting element for doping fullerenes. SiC compounds and alloys exhibit outstanding properties such as polymorphism, extraordinary hardness, and variable band gaps. The hollow-cage structure of fullerenes also offers a unique framework for developing new SiC compounds. Although silicon is in the same main group as carbon, it exhibits quite different physical and chemical properties. For example, it prefers three-dimensional structures instead of the  $sp^2$  networks of carbon element, and Si–C bonds are 30% longer than C–C bonds. These features would make the substitutional incorporation of silicon in fullerenes to be difficult.

However, in recent years, Si-doped fullerenes have been synthesized by several groups [6–10]. The method of laser ablation of Si/C composite rods was first used to produce Si-doped fullerenes [6]. After that, different techniques such as photofragmentation [11] and mixing of the vapor of fullerenes with silicon vapor [9] were developed to produce heterofullerenes. Substitutionally-doped fullerenes can all be produced in these experiments.

The previous theoretical studies of substitutionally-doped fullerenes mainly focused on large fullerenes, such as  $C_{60}$  and  $C_{70}$  [12–15]. In these studies, some C atoms were substituted with Si atoms without changing the whole configuration of the fullerenes. This is reasonable when the ratio of the number of Si atoms to that of C atoms is not very large. However, for small fullerenes, or even smaller carbon clusters such as  $C_{10}$ , the substitution of C atoms with Si atoms may change the original configuration dramatically. Thus, we might obtain quite different structures compared with the original one when the number of substitutional Si atoms increases.

In this work, the most stable structures of clusters  $C_{n-x}Si_x$  ( $n = 9, 10, 11, x = 0-n$ ) were investigated by the adaptive immune optimization algorithm (AIOA) [16], which has been applied to the optimization of

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molecular and atomic clusters. Then, semi-empirical PM3 and DFT B3LYP/6-31G\* method were employed to further optimize the optimized structures and calculate the corresponding energies. It was found that C atoms favor planar conjugate ring-like structures, such as pentagons and hexagons, while Si atoms lead to three-dimensional geometries. The results may help us to understand what transformation Si atoms would bring to fullerenes and different roles of these two elements in Si/C compounds.

## 2. Method

The global minima were located by using AIOA. Then, the obtained minima were optimized again with semi-empirical PM3 method. At last, DFT B3LYP method with basis set 6-31G\* was employed to calculate the energies of these optimized structures. The PM3 and B3LYP calculations employed the GAUSSIAN 98 suite of programs [17].

### 2.1. Potential model

In AIOA, the interaction among C and Si atoms is represented by Brenner potential, which can be written as a sum of pairwise interactions,

$$E_b = \sum_i \sum_{j(>i)} [V_R(r_{ij}) - \bar{B}_{ij} V_A(r_{ij})], \quad (1)$$

where  $V_R$  and  $V_A$  are the repulsive and attractive pair terms,  $\bar{B}_{ij}$  is the many-body coupling correction term which includes the effects of bonding bending, bond order, and bond conjugation. Detailed description of Brenner potential can be found in [18,19].

### 2.2. Adaptive immune optimization algorithm

AIOA is a novel algorithm based on biological immune mechanism. In AIOA, one structure of a cluster is called an individual. The algorithm randomly generates a set of individuals at first and optimizes them by the limited memory quasi-Newton algorithm (L-BFGS) to construct the gene library. The size of the gene library was set to 30 in this work. Then, the algorithm selects some of the individuals from the gene library. This process is called ‘clone’. The individuals that have lower energies and are different in structures compared with others are easily selected. The selected individuals are then mutated. In this process, some of the atoms with the highest energies in an individual will randomly be moved to a new location and the structures will be optimized again. At last, the algorithm compares the newly obtained individuals with those in the gene library based on energies and similarities of structures and updates the gene library. The whole process from

the clone to the gene library updating step will be repeated until the iteration reaches the preset number. Therefore, a set of global minima (30 in this work) can be found by AIOA and three of them with the lowest energies were selected for discussion in this work. AIOA is a little like the genetic algorithm (GA), the difference is that it has no crossover operation of GA but it adds a new kind of similarity check based on structures. Detailed description of AIOA can be found in [16].

## 3. Results and discussion

At first, global minima of  $C_{9-x}Si_x$  (0–6) were obtained with AIOA. Then, these minima were further optimized with PM3 method and the energies of these structures were calculated by employing DFT B3LYP/6-31G\* method. It was found that there is no evident difference between the structures obtained by AIOA and PM3. Fig. 1 shows the optimized structures and the corresponding energies calculated with B3LYP/6-31G\* is listed in Table 1.

In Fig. 1, for each  $x$ , three structures with the lowest energies are listed. It can be seen that the most stable configuration of  $C_9$  is a ring-like structure, which is in keeping with the result obtained by Hobday and Smith [20] by using the genetic algorithm (GA). The main part of the second stable configuration of  $C_9$  is an 8-member carbon ring, and the rest one C atom connects with one of the C atom of the ring through a 0.135-nm C–C bond. The third stable configuration consists of a hexagon and a pentagon.

The configurations of  $C_8Si$  look like those of  $C_9$ . The difference is that, for the second stable configuration, the Si atom connects with two C atoms of the 8-member carbon ring through a 0.175- and a 0.177-nm Si–C bond. And for the third stable configuration, one of the C atoms of the pentagon is substituted with the Si atom. The main parts of the most stable and the third stable configurations of  $C_7Si_2$  both are a 7-member carbon ring. In the former, each Si atom connects with two C atoms of the ring to form a triangle. And in the latter, the Si atoms and two C atoms of the ring form a quadrangle. In the second stable configuration, six C atoms construct a hexagon. The rest one C atom, the two Si atoms, and three C atoms of the hexagon form two adjacent quadrangles. All of these three configurations have  $C_{2v}$  symmetry.

The most stable two configurations of  $C_6Si_3$  have a carbon hexagon and the third stable one has a carbon pentagon. The Si atoms construct some triangles and quadrangles with C atoms around the carbon ring. The most stable and the third stable configurations have symmetry of  $C_{3h}$  and  $C_{2v}$ , respectively. When the number of Si atoms increases to four, the two most stable

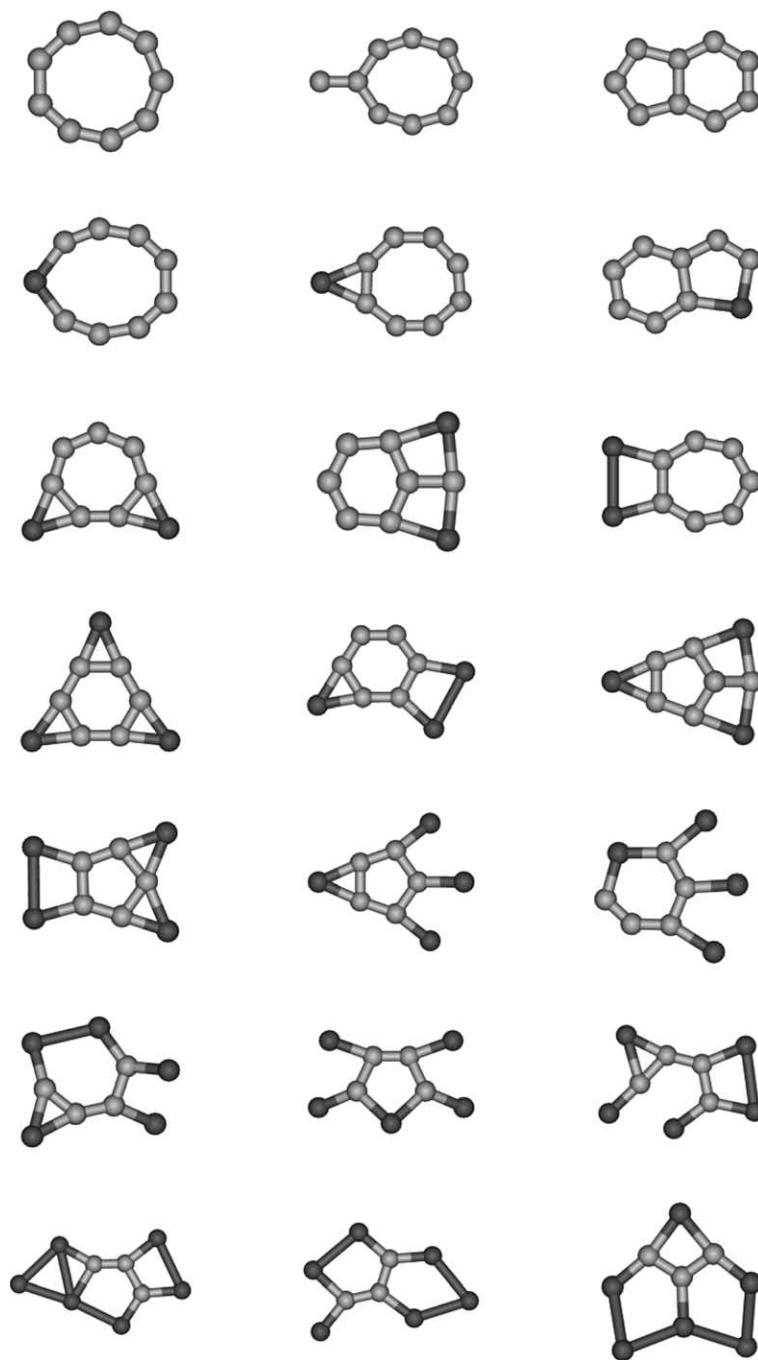


Fig. 1. The optimized configurations of  $C_{9-x}Si_x$  ( $x = 0-6$ ). Three most stable structures are listed with the energy increasing from left to right for each  $x$ . The light and the dark balls represent carbon and silicon, respectively.

configurations have a carbon pentagon while the third one have a carbon hexagon with one C atom replaced with one Si atom.

From above results it can be seen that when the number of C atoms is enough, the C atoms can form 7-, 8-, or even 9-member rings. As the number of C atoms decreases, the C atoms prefer to form pentagons and hexagons, which are very common in fullerenes. As the number of Si atoms further increases, some

pentagons and hexagons constructed by both C atoms and Si atoms appear. Unlike those with relatively less Si atoms, these configurations do not exhibit any apparent symmetry.

When the number of Si atoms is no more than 6, there is only slight difference between the structures optimized with AIOA and those further optimized with PM3 method. However, as the number of Si atoms increases to 7 and 8, this difference becomes apparent, as

Table 1

Energies of the most stable structures of  $C_{9-x}Si_x$  (0–6) calculated with B3LYP/6-31G\*

	$E1$ (kcal/mol)	$E2$ (kcal/mol)	$E3$ (kcal/mol)
$C_9$	0.0	35.8	44.1
$C_8Si$	0.0	5.7	46.8
$C_7Si_2$	0.0	18.0	57.4
$C_6Si_3$	0.0	9.8	19.3
$C_5Si_4$	0.0	10.1	30.1
$C_4Si_5$	0.0	1.2	2.2
$C_3Si_6$	0.0	1.1	4.6

For each  $x$ ,  $E2$  and  $E3$  are the relative energies of the second and the third stable structures compared with  $E1$ , which is the energy of the most stable structure.

shown in Fig. 2. When C atoms are all substituted with Si atoms, structures optimized with the two methods almost have no common features.

Figs. 3 and 4 show some of the optimized structures of  $C_{10-x}Si_x$  ( $x = 0–10$ ) and  $C_{11-x}Si_x$  ( $x = 0–11$ ), which are obtained by AIOA and PM3 optimization. From Fig. 3, it can be found that, as that of  $C_9$ , the most stable configuration of  $C_{10}$  is a ring-like structure, which is also in keeping with the previous result obtained with GA [20]. Furthermore, ring-like structures including pentagons and hexagons exist in all of the most stable configurations from  $C_8Si_2$  to  $C_5Si_5$ . However, the ring-like structure, which is the most stable configuration of  $C_8Si$ , no longer has the lowest energy in  $C_9Si$ . The structure that is similar to the second stable configuration of

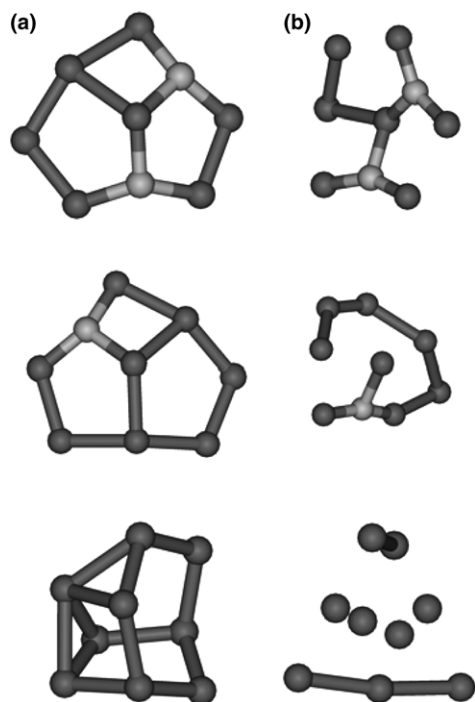


Fig. 2. The most stable configurations of  $C_2Si_7$ ,  $CSi_8$ , and  $Si_9$  optimized with AIOA (a) and the further optimized structures with PM3 (b).

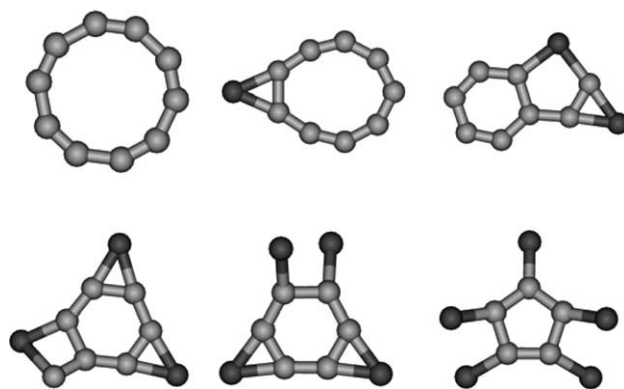


Fig. 3. The most stable configurations of  $C_{10-x}Si_x$  ( $x = 0–5$ ).

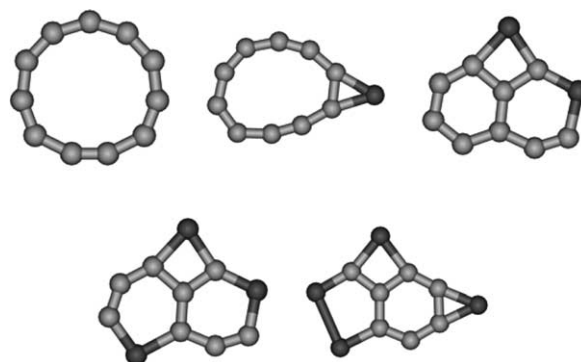


Fig. 4. The most stable configurations of  $C_{11-x}Si_x$  ( $x = 0–4$ ).

$C_8Si$  becomes the most stable structure. From Fig. 4, it can also be found that the most stable configurations of  $C_{11}$  and  $C_{10}Si$  are similar to those of  $C_{10}$  and  $C_9Si$ . Except  $C_8Si_3$ , all the configurations from  $C_9Si_2$  to  $C_7Si_4$  contain carbon hexagons.

However, both for the cases of  $C_{10-x}Si_x$  ( $x = 0–10$ ) and  $C_{11-x}Si_x$  ( $x = 0–11$ ), when the number of Si atoms further increases, there is not enough carbon atom to form pentagon or hexagon, and the structures optimized with the two methods (AIOA and PM3) become to be inconsistent. Clusters containing more Si atoms distort dramatically when further optimized with PM3 method. These structures are not shown in the paper for the sake of the length.

From the results above, it can be found that the more C atoms substituted with Si atoms, the bigger difference between the configurations optimized with AIOA and those further optimized with PM3 method. It is well known that C atoms prefer to  $sp^2$  hybridization, which leads to planar configuration. Si atoms, unlike C atoms, prefer to  $sp^3$  hybridization, which leads to three-dimensional configuration. From the results above, it can be seen that when Brenner potential was applied to clusters that contain relatively more C atoms, the C atoms tend to form planar ring-like structure, which is a conjugate system. For

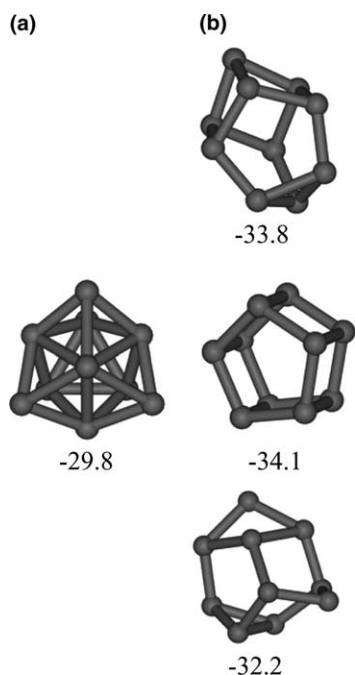


Fig. 5. A comparison of the reported  $C_{3v}$  structure of  $\text{Si}_{10}$  with its energy calculated with Brenner potential (a) and the structures optimized with AIOA with Brenner potential (b).

these clusters, the structures optimized with AIOA are in good keeping with those further optimized with PM3. However, when Brenner potential was applied to clusters that contain relatively more Si atoms, because there are not enough C atoms, carbon rings no longer appear. The optimized structures have apparent three-dimensional features, and dramatic difference appears between the structures optimized with AIOA and those further optimized with PM3. The reason for this may be that Brenner potential is more appropriate in describing clusters that contain planar conjugate system. However, when it is applied to three-dimensional systems such as  $\text{sp}^3$  network of silicon, new amendment need to be induced.

To verify this explanation, a  $C_{3v}$  structure of  $\text{Si}_{10}$ , which was previously found by several groups as the ground state [21,22], was selected and its energy was calculated with Brenner potential. Then, this energy was compared with the energies of the three most stable configurations optimized by AIOA with Brenner potential. The result is shown in Fig. 5. It can be seen from the figure that the energy of the previously reported  $C_{3v}$  configuration is much higher than those obtained with AIOA, which shows the Brenner potential may not be accurate for Si atoms.

#### 4. Conclusion

Structures of clusters  $\text{C}_{n-x}\text{Si}_x$  ( $n = 9, 10, 11$ ,  $x = 0-n$ ) were optimized by using AIOA with Brenner potential.

Then, the three configurations with the lowest energies were further optimized with the semi-empirical PM3 method and the energies of these configurations was calculated by using DFT B3LYP method with 6-31G\* basis set. It was found that the most stable structures of  $\text{C}_9$ ,  $\text{C}_{10}$ , and  $\text{C}_{11}$  are all ring-like structures, which is in keeping with the result obtained by GA. When C atoms are gradually substituted with Si atoms, the remaining C atoms prefer to form pentagons and hexagons, which are very common in fullerenes. As the number of Si atoms further increases, it was found that the structures optimized with AIOA and those further optimized with PM3 method differ greatly. The reason for this might be the inaccuracy of Brenner potential in describing Si atoms.

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