A Theoretical Study of the Stability of the Fullerene-Like Cage Structures of Silicon Clusters#

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In order to provide theoretical insight into the structures of silicon clusters of current interest, several representative structural models proposed up to now for the medium size clusters are investigated by means of semi-empirical and *ab initio* molecular orbital calculations. Unlike general expectation based on the hitherto proposed structural models, it is suggested that silicon clusters also prefer spherical cage (fullerene-like) frameworks with the increase in the size, as do carbon clusters.

Silicon clusters are currently of growing interest as new materials with interesting properties, as in recent reviews.[1—3] In spite of numerous experimental and theoretical investigations, however, the structural determination remains elusive except for very small clusters. Since there is not yet direct experimental information, several attempts have been made to speculate the possible structures indirectly from the experimental data (obtained with ions rather than neutral clusters) about the reactivities toward small molecules[4] or the fragmentation pattern.[5] However, the reactivity pattern may be a little related to the stability of clusters since the former is a kinetic issue while the latter is thermodynamic. In addition, it should be noted that the reactivities observed for singly charged ions with open-shell electronic states have little to do with those of the closed-shell species. In this sense, the fragmentation data may be more helpful for the structural speculation.

For the silicon cluster ions containing up to 80 atoms, it has been experimentally established that six or ten atom units are predominantly ejected upon fragmentation.[5] In order to explain this fragmentation pattern, successive stackings of benzene-like Si_6 or naphthalene-like Si_{10} plates in a quasigraphic cylindrical way have been proposed for the probable structures of silicon clusters (for the Si_{60} case, see Fig. 1).[6—8] These cylindrically stacked structures were expected to be considerably stabilized by electron delocalization within each plate, most silicon atoms being tetracoordinated through inter-plate bonding to minimize dangling bonds. On the basis of the calculations of Si_{30}, Si_{50}, and Si_{60}, however, we have recently suggested that hollow spherical cage (fullerene-like) structures are much more stable than the stacked structures and the fragmentation data of cations do not provide much information on the stable structures of neutral clusters.[9—11]

There is currently great progress in the fullerene chemistry of carbon clusters.[12] Since, however, fullerene-like structures have not been generally accepted for silicon clusters,[13] it is of crucial importance to provide further insight into the stability. Therefore, we have undertaken the molecular orbital calculations of the representative structural models proposed up to now for medium size silicon clusters in an attempt to confirm the stability of the fullerene-like cage structures of silicon clusters.

Computation

Complete geometry optimizations were carried out with the semi-empirical AM1 method.[14] In order to obtain improved energies, single point calculations were carried out on the AM1 optimized geometries at the Hartree–Fock (HF) level with the double-zeta (DZ) basis set using the *ab initio* effective-core potentials on Si.[15] The energies of important geometries were also calculated by the DZ(d) basis set augmented by a set of six d polarization functions (exponent 0.45) on Si. All calculations were carried out using the Gaussian 92 program[16] on the IBM RS6000 workstations.

Results and Discussion

Among the medium size silicon clusters, Si_{45} has attracted special attention as a size of particular unreactivity (the so called "magic number") and several structural models have been proposed. By analogy with the

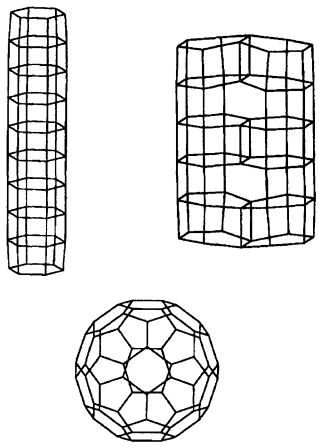


Fig. 1. The stacked benzene (upper-left), stacked naphthalene (upper-right), and fullerene structures of the Si_{60} cluster.

#In Memory of Professor Hiroshi Kato.

fragments of bulk silicon, most models begin with tetrahedrally bonded silicon atoms as a core. The structural model presented by Kaxiras[17] is perhaps the most ingenious and representative which incorporates the knowledge about the surface reconstructions of bulk silicon. In this model, the structure of Si_{45} contains five tetracoordinated silicon atoms as a core, as in the diamond-like structure of bulk silicon, which are surrounded by a surface similar to the (2×1) reconstruction of the Si(111) surface (the lowest energy surface of silicon). This tetrahedral structure in T_d symmetry is calculated to be stable under a variety of classical force field potentials (non-state-specific potentials).[17]

As Fig. 2 shows, however, the full geometry optimization based on molecular orbital calculations leads to a structure (**1**) of lower C_2 symmetry. This may not be surprising since the highly symmetrical structure proposed by Kaxiras has a degenerate electronic state and should undergo Jahn–Teller distortion. As in the original T_d structure, however, the core atoms (a central atom and four neighboring atoms bonded to the central atom) in **1** are in almost tetrahedral arrangement, as in bulk silicon, and the remaining atoms are responsible for a surface similar to the reconstruction of the Si(111) surface. Thus, we consider the relaxed C_2 structure (**1**) as a more reasonable model which fulfills Kaxiras' idea.

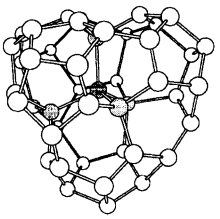
During the optimization, we have also located another energy minimum (**2**) of C_1 symmetry which resembles **1** in the structural features. As is apparent from Fig. 2, there are hexagonal and pentagonal rings on the surface. A key structural difference between **1** and **2** is that each of the four atoms bonded to the central atom constitutes the junction of three hexagonal rings in **1**, while it is responsible for the junction of three pentagonal rings in **2**. In another view, the central atom is bonded to the atoms at the common vertexes of three hexagons in **1** while it is bonded to the atoms at the common vertexes of three pentagons in **2**. The optimized structure of **2** shows that the angles around the core atoms are significantly deviated from the tetrahedral angle. Reflecting this angle-strain, **2** was calculated to be 83 kcal mol^{-1} (1 cal=4.184 J) less stable than **1** at the HF/DZ level, confirming the stability of **1**, as shown in Table 1.

As Fig. 3 shows, however, it is interesting to note that a fullerene structure of Si_{44} is obtained from **1** (or **2**) if one removes the central core atom and smooths out the remaining shell to a spherical shape.[4b] The binding energy per atom of Si_{44} is 5.4 and 4.2 kcal mol^{-1}

Table 1. The Total Energies (au) and Relative Energies (kcal mol^{-1}) of the Isomers of the Si_{45} Cluster[a]

	HF/DZ	HF/DZ(d)
1(C_2)	−167.78153(0)	−168.94698(0)
2(C_1)	−167.64956(83)	
3(C_2)	−168.14089(−226)	−169.22949(−177)
4(C_1)	−167.40819(234)	−168.82075(79)
5(C_s)	−168.18866(−256)	−169.28083(−209)
6(C_s)	−168.25798(−299)	−169.31158(−229)

a) Values in parentheses are relative energies.



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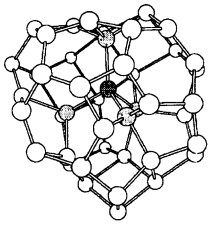

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Fig. 2. The tetrahedral-like structures of the Si_{45} cluster with C_2 (**1**) and C_1 (**2**) symmetry. Core atoms are denoted by shaded spheres.

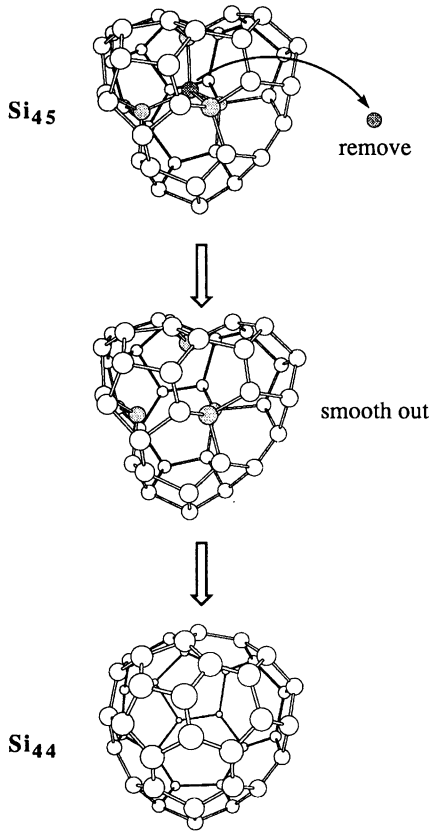

Fig. 3. The generation of an Si_{44} fullerene of C_2 symmetry upon removal of the central atom of the Si_{45} cluster (**1**).

larger than that of **1** at the HF/DZ and HF/DZ(d) levels, respectively, suggesting that Si_{44} is more strongly bound and thermodynamically stable. This is noteworthy since it conflicts with Kaxiras' demonstration that the binding energy per atom of **1** is the largest in the size range from Si_{40} to Si_{50}, **1** being stable to removal or addition of atoms. Our result is rather close to the recent local density function calculations based on empirical potentials by Brenner et al.[18] which show that Si_{44} is almost as stable as Si_{45}, though the stability of Si_{44} seems somewhat underestimated in the local density function calculations. It appears that the stability of Si_{44} is due to its less strained and more round structure. This is clearly rationalized by the fact that the energy required to transform the spherical cage of Si_{44} into the structure of **1** is as large as 295 kcal mol^{-1} at the HF/DZ level; this energy loss is too large to be compensated just by the energy gain due to bonding to the central atom in **1**.

It is rather instructive to view **1** as a sort of highly deformed "endohedral complex" with a single silicon atom at the center of the hollow spherical Si_{44} cage. As demonstrated in our recent calculations of endohedral metalofullerenes ($M@C_{82}$, M=Sc, Y, La),[19] the central position is not always the most stable inside the fullerene cage. Therefore, we have moved the central atom in **1** toward the Si_{44} cage. The resultant optimized structure (**3**) is shown in Fig. 4.[20] This side-attached C_2 structure with a more spherical shape was calculated to be 226 and 177 kcal mol^{-1} more stable at the HF/DZ and HF/DZ(d) levels, respectively, than the central-packed structure (**1**) based on the core model. With what structure silicon clusters are actually produced in experiments (especially before annealing) may be strongly dependent on the growth mechanism as well as preparation conditions. However, the huge energy difference favoring **3** over **1** does suggest that even if **1** is produced for any reason, it will isomerize rapidly to fullerene-like structures such as **3**.

One may consider that the Si_{44} cage is too large to be connected to just a single internal atom without excessive strain. For this purpose, we have calculated the smaller silicon clusters, Si_{21} and Si_{29}, as shown in Fig. 5.[21] As expected, the energy differences between the side-attached and central-packed structures become smaller with the decrease in cage size. However, the side-attached structures with a more round cage were calculated to be still more stable by 46 and 31 kcal mol^{-1} for Si_{21} and 88 and 95 kcal mol^{-1} for Si_{29} than the strained central-packed structures at the HF/DZ and HF/DZ(d) levels, respectively.

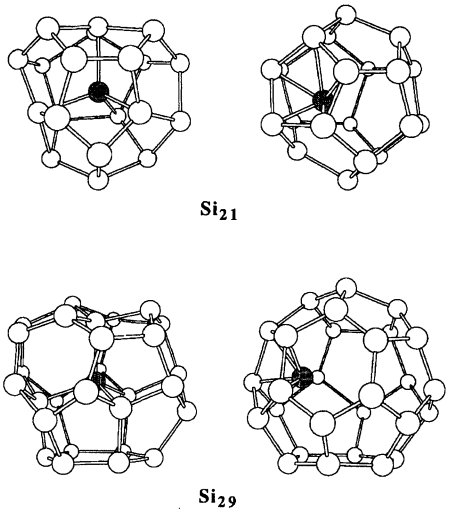

Fig. 5. The central-packed (left) and side-attached (right) structures of Si_{21} and Si_{29}.

Patterson and Messmer have recently proposed an O_h structure of Si_{45} containing seventeen bulk-like atoms as a stable core (a central atom and first and second shells of tetrahedrally bonded atoms).[22] More recently, Jelski et al. have compared several structural models which include the structure proposed by Patterson and Messmer as well as Kaxiras' structure and cylindrically stacked structures by means of tight binding calculations and proposed a new tetrahedral-like structure.[23] It is concluded that the new structure (**4**) as shown in Fig. 6 is the most probable candidate for the structure of the Si_{45} cluster among the structures examined. According to our calculations in Table 1, however, the compact structure was 460 (HF/DZ) and 256 (HF/DZ(d)) kcal mol^{-1} less stable than the side-attached structure (**3**) with a fullerene cage, though inclusion of d polarization functions tends to stabilize the compact structure. It is interesting to note that an Si_{40} fullerene structure is obtained upon the removal of the central atom and four cap atoms (denoted by shaded spheres in Fig. 6) from the compact structure (**4**).

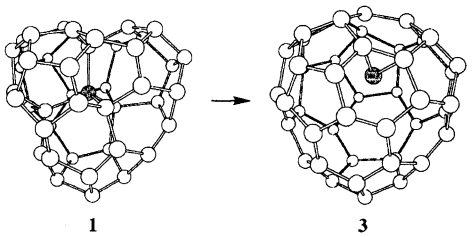

Fig. 4. Transformation of Si_{45} from the central-packed (**1**) to the side-attached (**3**) structure.

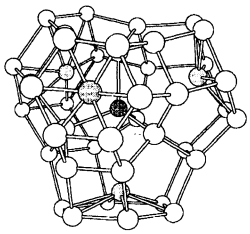

Fig. 6. A compact structure proposed for the Si_{45} cluster.

Fullerene cages are always composed of twelve pentagonal rings with any number of hexagonal rings to make a closed cage. However, it is well-known as the isolated pentagon rule for carbon clusters that the fusion of pentagons leads to destabilization as a result of increased strain and induced antiaromaticity.[24] Therefore, we have calculated an Si_{44} fullerene of D_{3h} symmetry which has fewer adjacent pentagons on the cage, as show in Fig. 7. This D_{3h} fullerne was calculated to be 61 kcal mol^{-1} more stable at the HF/DZ level than the C_2 isomer in Fig. 3. Accordingly, the side-attached structure (**5**) of the Si_{45} cluster with this Si_{44} cage was 30 and 32 kcal mol^{-1} more stable than **3** at the HF/DZ and HF/DZ(d) levels, respectively. We next placed the attaching silicon outside the cage, as also shown in Fig. 7. The resultant exohedral structure (**6**) of Si_{45} was calculated to be 73 (HF/DZ) and 52(HF/DZ(d)) kcal mol^{-1} more stable than **3**, as shown in Table 1. To our knowledge, **6** is probably the most stable. However, a more important point to be emphasized is that fullerene-like cages are stable even in silicon clusters. In this context, it is interesting to note a recent theoretical study which shows that hollow cage-like structures (though not fullerene cages in this case because of the size) are generated as a stable form even from the crystalline (fcc and hcp) and noncrystalline (icosahedral) structures of the small clusters such as Si_{13} upon removal of an inner or an outer atom.[25]

We can learn more about the stability of fullerene-like cage structures also from other proposed strucural models. Through the molecular dynamics simulations based on empirical potential functions, Wales and Waterworth have recently located a structure for the Si_{34} cluster from the fragment of the diamond lattice.[26] However, the located structure of T_d symmetry undergoes Jahn–Teller distortion. As the more stable structure optimized by us with C_1 symmetry in Fig. 8 shows, it is regarded as an exohedral complex of an Si_{28} fullerene with six atoms on the outside to make Si_{34}. A similar view is also applicable to the structure proposed for the Si_{33} cluster (a magic number).[17,22] As Fig. 9 shows, the proposed structure of Si_{33} is regarded this time as an endohedral complex of Si_{28} with five tetrahedrally bonded atoms inside the cage. In this context, we could suggest a more stable isomer for the Si_{33} cluster by attaching a single atom to an Si_{32} fullerene cage, as shown in Fig. 9. This side-attached structure closer to the hollow fullerene structure was calculated to be 236 kcal mol^{-1} more stable at the HF/DZ level. In addition, the HOMO and LUMO levels of -6.2 and -1.9 eV calculated for the side-attached structure are significantly lower and higher than those of -5.5 and -2.3 eV for the proposed structure, respectively, suggesting the kinetic stability, too.

Despite the strong support for fullerene-like cage structures, there is not yet direct experimental evidence. However, it is interesting to note the recent measurement of the mobilities of size selected silicon clusters (Si_n^+, $n=10$—60).[27] According to this mobility measurement, silicon clusters follow a prolate growth sequence to have sausage-shaped structures. As the cluster size increases, however, more spherical structures

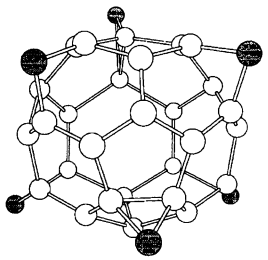

Fig. 8. A structure of the Si_{34} cluster.

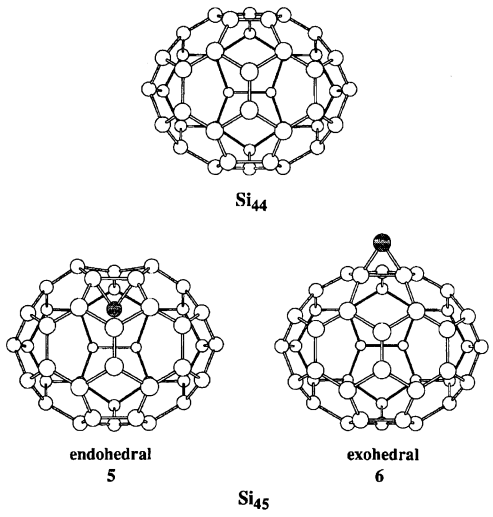

Fig. 7. An Si_{44} fullerene of D_{3h} symmetry and its endohedral and exohedral complexes (Si_{45}) of C_s symmetry.

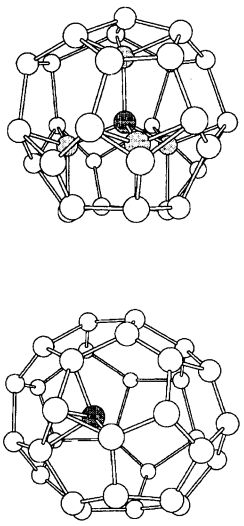

Fig. 9. A proposed structure (upper) of the Si_{33} cluster and a more stable isomer (lower) with an Si_{32} fullerene cage.

appear with $n>23$ and completely dominate for clusters with $n>30$. In addition, recent saturation studies suggest that nearly all the silicon atoms in Si_{40}^{+} and Si_{60}^{+} are surface atoms.[3,4c] These may be all consistent with our view that silicon clusters prefer (hollow) spherical cage structures to reduce their surface energy whereas smaller clusters favor compact structures.[28]

Conclusion

The present calculations suggest that silicon clusters also have a strong tendency to take on fullerene-like spherical cage structures as the cluster size increases, as do carbon clusters. It is expected that silicon-based fullerenes are subjected to experimental tests and open a new field in silicon chemistry. Most proposed structures have been based on the bulk-like cores which are surrounded by surfaces resembling those found in reconstructed silicon surfaces. However, it will be more fruitful to consider clusters as clusters (i. e., rather as a new chemical entry not by analogy with fragments of bulk silicon).

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