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Family of low-energy elongated Si_n ($n \leq 50$) clusters

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A family of stable elongated silicon clusters built from a simple stacking scheme has been discovered through local density approximation (LDA) molecular cluster calculations. These surprisingly well-bound structures were constructed by layering triangles of atoms with a common axis and adding one or two caps. For small clusters, one cap is significantly more stable than two, and for a few cases we have replaced the caps with other atoms (Be,B,N), which further increased the stability by closing the electronic shells. These clusters show distinct structural features for odd and even numbers of triangles, with a transition to greater stability for an odd number of triangles at n=29. For n=20 we used the quantum Monte Carlo method in order to assess the accuracy of LDA for the energy ordering of various isomers.

Small silicon clusters have recently been the source of numerous experimental and theoretical studies.[1–11] Several interesting experimental results,[5,6] such as reactivity data and the observation of a structural transition, have also sparked much recent activity. In addition, silicon is of great importance in the microelectronics industry, where it is estimated that the minimum structure size will approach the scale of these small clusters within a decade or two. Elongated structures are of particular interest for their role in the fabrication of nanoscale wires, a possibility which is already being intensely explored for carbon tubules.

We present here a class of "stacked" Si clusters that are more stable than elongated clusters previously proposed, which may provide insight into some of the important questions regarding reactivities and structural transitions. Our structures are calculated for the size range n=10–50 atoms (see Fig. 1) and are built from the following simple rules: triangles (1) are equilateral, (2) are always in the x-y plane, (3) have a common z axis, and

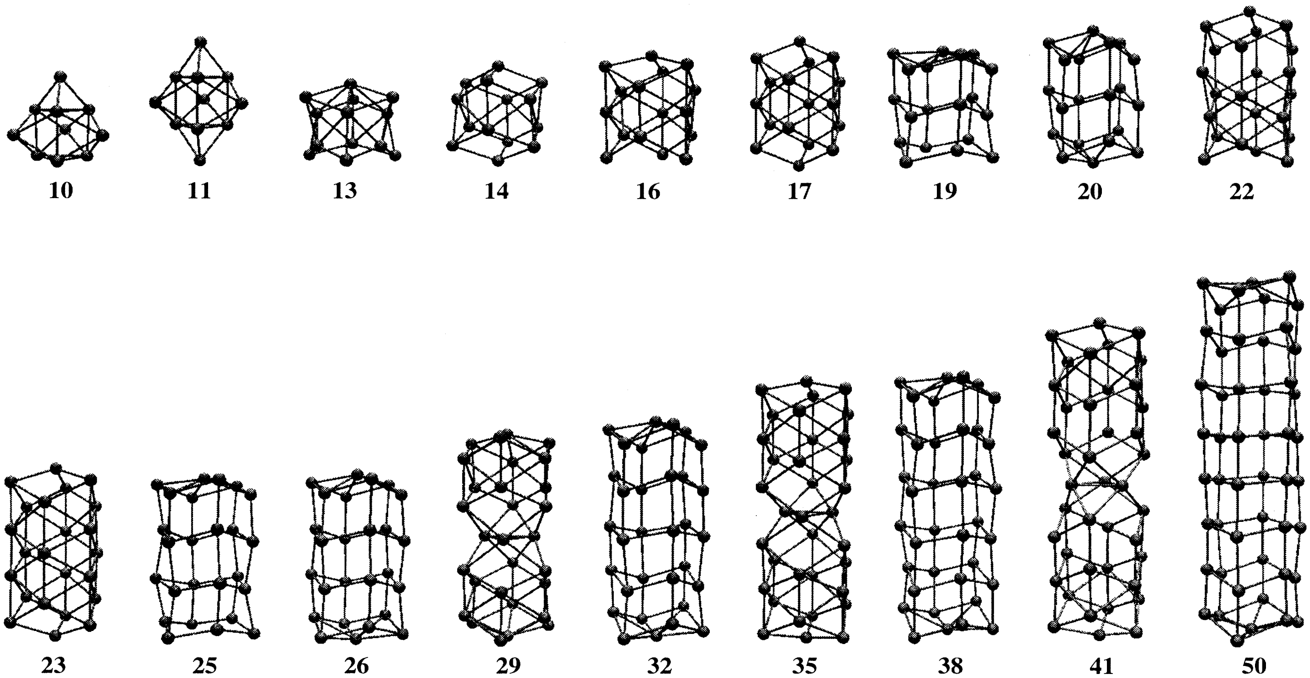

FIG. 1. Class of elongated structures calculated for n=10–50 formed by stacking threefold triangles about a common axis and adding one or two caps.

(4) are rotated by 60° with respect to neighboring triangles. Also, (5) one or two caps are added along the z axis. The n=27 cube and the n=28 fullerene were calculated for comparison, as well as the n=20,26 ring structures proposed previously[8] (see Fig. 2).

Clusters with one cap have closed electronic shells and are found to be more stable than those with two caps, although this effect diminishes rapidly as n increases. We distinguish between an odd and an even number of total triangles in the cluster, and we show that there is a fundamental difference in bonding character between these two cases. In particular, the even case stacks sixfold puckered rings, whereas the odd case has no repeating pattern and undergoes a structural transition from n=23 to n=29 atoms. Furthermore, we were able to enhance the stability for several cases by doping the caps in order to saturate dangling bonds and close the shell.

As has been shown in previous work,[12] the local density approximation (LDA) provides an accurate picture of the energetic ordering of silicon clusters. We therefore use LDA to calculate binding energies of all the clusters studied, and geometries have been optimized in LDA, which is known to predict bond lengths and angles for silicon systems to within a few percent of experiment.[13] Both total energy and atomic force calculations were performed using the DMOL molecular cluster package.[14] A detailed investigation of Si_n ($n \leq 20$) clusters within the quantum Monte Carlo (QMC), LDA, and Hartree-Fock (HF) methods can be found in Ref. 12. In the present work, we apply the QMC approach to several cases in order to ensure an accurate description. The quantum Monte Carlo approach, namely the variational and diffusion Monte Carlo (VMC and DMC) methods, are described in detail elsewhere.[15–17]

The minimum-energy structures for Si_{10} and Si_{13} are typically referred to as tetracapped trigonal prism and capped trigonal antiprism, respectively. From a more basic perspective, however, they can also be described as stacked triangles with a common axis and one cap. In order to illustrate this point, Fig. 3(a) shows a typical view of the ground-state structure for Si_{13}, discovered by Röthlisberger and co-workers;[2] Fig. 3(b) shows the same molecule, but in such a way as to emphasize its three-fold symmetry. We use the labels A and B to denote the two possible orientations for the triangles (each a 60° rotation of the other). Using this description, one can build a new class of larger clusters by adding successive layers of triangles while following the rule that the orientations of the triangles must alternate.

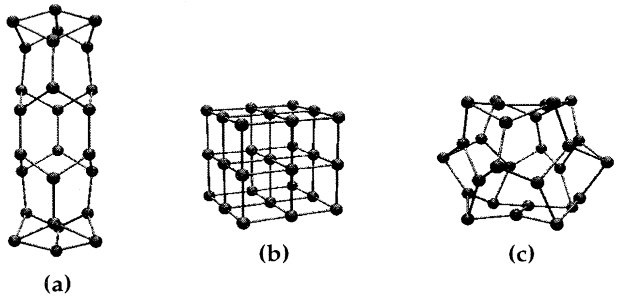

FIG. 2. Structures calculated for comparison. (a) The 26-atom structure of Kaxiras and Jackson Ref. [8]; (b) the 27-atom cube; (c) the 28-atom distorted fullerene.

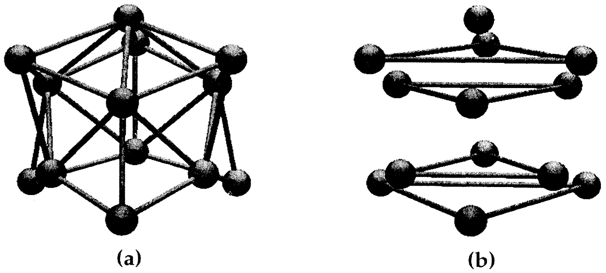

FIG. 3. Two different views of the ground-state structure of Si_{13}, (a) showing the bonding character, and (b) emphasizing the stacked triangles.

As an example of the procedure employed to build these clusters, in order to make Si_{26} we begin with the configuration $A_1 B_1 A_2 B_2 A_3 B_3$ and put one atom at each end as caps. In this case we would have 13 parameters to optimize: the sizes of the triangles (6), the triangle-triangle distances (5), and the triangle-cap distances (2). It is clear from symmetry, however, that six of these parameters are duplicates (i.e., the size of A_1 is equal to that of B_3, etc.), and so we are left with seven independent quantities.

Optimization within the symmetry constraints was performed using several minimization methods as well as experience from the small cases. We tried several different starting configurations for each cluster, usually building on the geometry of well-converged smaller clusters. One trend of the clusters is that they have alternating triangle sizes, so that, for example, if A_1 is smaller than B_1 then *all A* are smaller than *all B*. The triangles next to caps are generally the largest in the cluster since they must accomodate a central-axis atom. In most cases, about 10–15 optimization iterations were sufficient in order to find the equilibrium structures, in which all forces are less than 0.003 a.u. LDA binding energies and gaps for all of these clusters are listed in Table I.

Clusters where the total number of triangles m_Δ is even differ from those with m_Δ=odd in several fundamental ways. The most important difference lies in the fact that when there is an even number of total triangles $|m_A - m_B|$=0, and for an odd number of triangles $|m_A - m_B|$=1. Therefore, in the odd case there is always one "extra" triangle of a given orientation that can naturally be considered to be the central triangle.

A. Even number of triangles

For clusters with m_Δ=even (i.e., for n=14, 20, 26, 32, 38, and 50), there is a pronounced trend toward sixfold puckered rings, as can be seen in Fig. 1. All of these clusters have similar physical features; in particular, the sixfold ring[9] is a stable unit of atoms which can be repeatedly stacked along an axis without changing the

TABLE I. Calculated LDA binding energies (eV/atom), m_Δ/number of caps and HOMO-LUMO (where LUMO is lowest unoccupied molecular orbital) gaps (eV) for elongated Si_n clusters for n=10–50, as well as other structures for comparison.

n	m_Δ/number of caps	Binding energy	Gap
10	odd/1	4.232	2.13
11	odd/2	4.136	
13	even/1	4.187	1.65
14	even/2	4.166	
16	odd/1	4.192	1.76
17	odd/2	4.130	
19	even/1	4.192	1.13
20	even/2	4.194	
22	odd/1	4.126	0.98
23	odd/2	4.147	
25	even/1	4.207	0.84
26	even/2	4.219	
29	odd/2	4.236	
32	even/2	4.229	0.35
35	odd/2	4.225	0.69
38	even/2	4.248	0.53
41	odd/2	4.214	
50	even/2	4.262	0.34
20[a]		4.015	
20[b]	even/2	4.093	0.345
26[b]	even/2	4.096	0.023
27[c]		4.1446	
28[d]		4.278	0.140

[a] Dodecahedron.
[b] Reference 8.
[c] Cube.
[d] Distorted fullerene.

bonding character. The ring structures of Kaxiras and Jackson[8] are also based on sixfold units, but they are rotated by 30° with respect to each other when compared with ours, resulting in overall threefold coordination. By contrast, our m_Δ=even clusters have all fourfold coordinated atoms except for the caps which are usually sixfold coordinated. This is consistent with the Si surface and bulk tendencies toward fourfold coordination, and with recent theoretical work on Si_{45} by Röthlisberger and coworkers.[18]

Another interesting fact is also that, aside from small variations due to shell-filling effects, the binding energy (BE)/atom exhibits a general slowly decreasing function with increasing number of atoms. Evidently larger clusters have more structural degrees of freedom that can be relaxed with resulting small energy gains. This contrasts with previously proposed sequences of elongated structures that have essentially constant BE/atom. For n=20, our stacking scheme forms a cluster which is 2 eV lower in total energy than the stacked ring structure of Kaxiras and Jackson, and 4 eV lower in energy than the dodecahedron. In Table II we show energy differences between these three Si_{20} clusters, and for this case we have used QMC in order to check the accuracy of LDA. These QMC calculations confirm our previous observation for smaller clusters[12] that LDA is able to predict very accurately the energy differences between various isomers and we expect that this will also hold for larger cases. This is in contrast to our recent calculations on carbon clusters where LDA and its variant are much less predictive.[19]

TABLE II. Energy differences (eV) between Si_{20} isomers as calculated by the HF, LDA, and DMC methods.

	HF	LDA	DMC
Si_{20} (new structure)	0.00	0.00	0.00
Si_{20} (Kaxiras+Jackson)	−4.43	1.9	1.4(4)
Si_{20} (dodecahedron)	−1.07	3.6	4.0(6)

B. Odd number of triangles

Although there is a similar trend toward larger BE/atom as n increases, clusters with m_Δ=odd (i.e., for n=11, 17, 23, 29, 35, and 41) differ considerably from their even counterparts. In these clusters the triangles no longer pair together; thus there is no tendency to form six-fold rings. Furthermore, the bonding and coordination vary greatly as a function of cluster size (in contrast to the even case).

We note that there is a sharp increase in stability from n=23 to n=29, which can be understood from the significant difference in the geometry of these two clusters, namely, that the central triangle for n=29 is $\approx$ 40% smaller than that of the n=23 cluster. In both Si_{23} and Si_{29}, the atoms of the central triangle are sixfold coordinated; in the latter case, however, these atoms bond to each other. This has the effect of pushing the second triangle from the center on each side further away in order to avoid eightfold coordination. The n=29 bonding is more favorable, as it allows for a more even distribution of valence charge across the molecule. Clearly these clusters do not have the same stable repetition of bonding characteristics as in the even case, but for $n \geq 29$ the structures with an odd number of triangles have a significantly larger BE/atom.

C. Open-shell character

For $n \leq 29$, all of the clusters with two caps have a doubly degenerate highest occupied molecular orbital (HOMO). We have therefore investigated possible Jahn-Teller distortions by reducing symmetry constraints and further relaxing the atoms. In all these cases we found that the triangles rotate slightly about the x or y axis, leading to a C_{2v} symmetric structure and a closed shell. The geometric as well as energetic changes in these relaxed structures are minimal ($\sim$ 0.10 eV).

In addition to symmetry lowering, each of the open shell C_{3v} structures can be made closed shell by removing one of the caps, effectively reducing the valency of the molecule by 4. Removal of a cap eliminates a sixfold coordinated atom (unfavorable for silicon) from the

TABLE III. Total binding energy (eV) and HOMO-LUMO gaps (eV) for doped clusters

Cluster	Binding energy	Gap
Si_{20} (new structure)	83.88	
$Si_{18}Be_2$	83.18	0.933
$Si_{18}B_2$	86.05	0.644
$Si_{18}N_2$	84.65	0.389

cluster, leaving the last triangle with threefold coordinated atoms. In the case of an even number of triangles, this appears to compensate for the two "extra" bonds at the other end of the cluster. As can be seen in Table I, the resulting molecules are all closed shell with rather large LDA gaps. For the smaller clusters ($n \leq 20$) the effect of removing a cap also significantly increases the BE/atom, furthering the notion that the saturation of dangling bonds and closed shell character of the clusters are key features that lead to stability.

D. Doped caps

The second way in which one can repair possible overcoordination is by doping the caps. There are two extra bonds at each cap, so we replaced the Si atoms with ones which have fewer electrons in the valence. For $n=20$ the HOMO is a degenerate spin triplet, and the next highest molecular orbital is a singlet. Therefore, removing either two or four total valence electrons will result in a closed shell molecule. Thus, good first choices for substitute cap atoms are boron and beryllium. Total binding energies and gaps for these doped clusters (see Table III) show that they are rather stable when compared to the undoped case. The presence of a gap is clearly important for stability, and in light of this we also attempted to dope with N, which provides the molecule with two additional valence electrons, the amount needed to close the outer shell. In Table III we can see that $Si_{18}N_2$ is indeed closed shell and the BE is comparable with that of the other cases.

As one would expect, the position of the doped atom depends largely on its size. Beryllium "feels" almost no energy barrier when passing through the top triangle, and actually prefers to stay between the last two triangles rather than outside. Boron and nitrogen are most stable when they are essentially exactly inside the last triangle.

In conclusion, we have discovered a class of elongated clusters that can be created by following simple rules of stacking triangles of atoms on a common threefold axis and adding one or two caps. The main difference from previous work, which presented prolate clusters with predominantly threefold coordination,[8] is a strong tendency toward fourfold coordination, which results in a significant energy gain in most cases. Many of these structures appear to be excellent candidates for ground state geometries in the size range $n=10$–29, below the experimentally observed structural transition from elongated to more spherical clusters by Jarrold and co-workers.[6] We used the LDA DMOL method to calculate binding energies and find local energy minima by structural relaxation. For Si_{20} isomers we have checked, by the highly accurate quantum Monte Carlo method, that LDA appears to be predictive for energy differences for these systems. The clusters proved to be well bounded up to at least 50 atoms, and for $n=20$ further stabilization was obtained by replacing the Si caps with other atoms such as B, Be, and N.

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