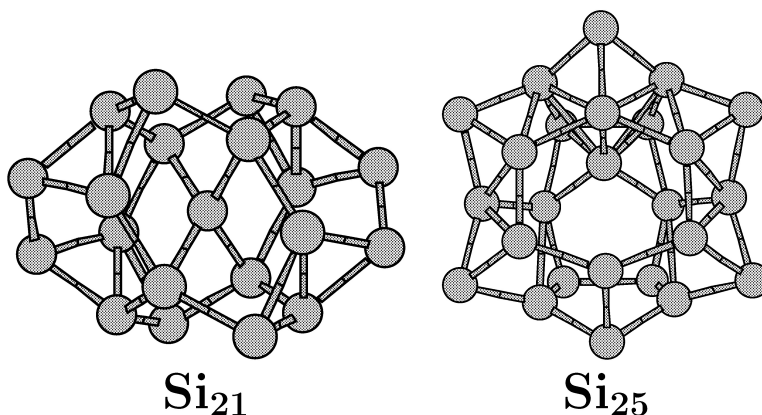Communication

Possible Lowest-Energy Geometry of Silicon Clusters Si and Si

Soohaeng Yoo, Xiao Cheng Zeng, Xiaolei Zhu, and Jaeil Bai

Si_{21} Si_{25}

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 7 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Possible Lowest-Energy Geometry of Silicon Clusters Si₂₁ and Si₂₅

Soohaeng Yoo, Xiao Cheng Zeng,* Xiaolei Zhu, and Jaeil Bai

Department of Chemistry, University of Nebraska-Lincoln, Lincoln, Nebraska 68588
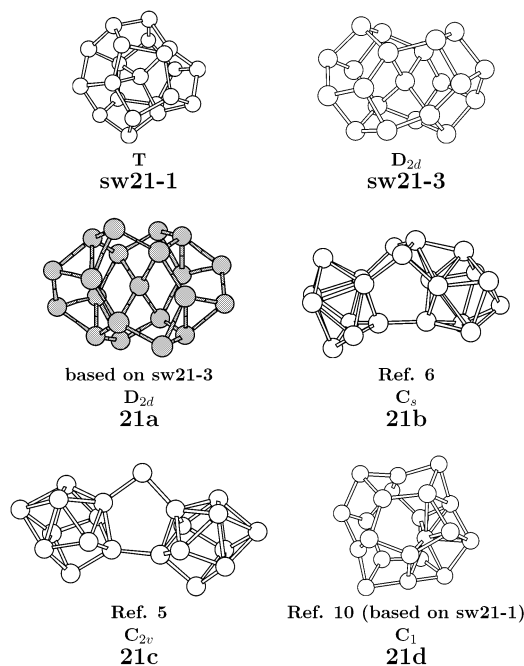
Received June 9, 2003; E-mail: xzeng1@unl.edu

Silicon clusters (Si$_n$) can be considered as "bridging" isolated Si atoms and nanocrystalline quantum dots.[1] Considerable experimental and theoretical efforts have been devoted to determine geometric structures of small to mid-sized silicon clusters. To date, the global (potential-energy) minima of small silicon clusters (Si$_n$) up to $n = 11$ have been well established through all-electron molecular-orbital calculations and ab initio simulated-annealing searches.[2] Measurement of the mobility of mid-sized silicon cation clusters Si$_n^+$ indicates that both prolate and more spherical-like isomers can coexist over the size range of $25 \leq n \leq 33$.[3] Subsequent annealing allows prolate isomer to convert into spherical-like isomer for $n > 30$. Measurement of the ionization potentials (IPs) for neutral clusters Si$_n$ shows a marked change in IP from $n = 21$ to 22 (then the IP levels off for $n \geq 22$).[4] The large IP change may suggest that the "more spherical" clusters become energetically more favorable for $n \geq 22$. Thus far, this measurement has not yet been supported by the lowest-energy structures predicted by theories for $21 \leq n \leq 23$.[5,6] Recently, an unbiased global-minimum search for Si$_n$ ($n \leq 23$) by Rata et al.,[6] who used a novel single-parent evolution algorithm similar to the genetic algorithms used by Ho et al.,[5] suggested that the lowest-energy structures of Si$_n$ ($21 \leq n \leq 23$) all have prolate structure as they are all built upon stacks of Si$_9$ in the tricapped-trigonal-prism motif. However, on the basis of quantum Monte Carlo calculations, Mitas et al.[7] found that the lowest-energy spherical-like isomer is more stable than the lowest-energy prolate isomer for Si$_{25}$. In this Communication, we present an approach that can be very efficient to locate the lowest-energy geometry for certain mid-sized silicon clusters such as Si$_{21}$ and Si$_{25}$. The two newly found Si$_{21}$ and Si$_{25}$ isomers are appreciably lower in energy than any previously reported, and they are more spherical-like.

Our approach takes a combined molecular mechanics/quantum mechanics procedure. First, we employed the basin-hopping global optimization technique[8] with three empirical model potentials for the bulk, amorphous, and small-sized cluster silicon[9] − the Stillinger−Weber (SW) potential, the modified-SW (MSW) potential, and the Gong potential − to locate the global-minimum structures for Si$_n$ ($n = 21-30$).[10] The MSW potential has a slightly stronger three-body interaction than the SW potential, which favors the tetrahedral bonding. We previously reported that if the global-minimum geometries based on the SW and MSW potentials are the same, the resulting global-minimum clusters are typically lower in energy (per atom) than their nearest-neighbor clusters.[10] Some of these nearly identical SW and MSW global-minimum clusters can yield very low-energy isomers after ab initio geometry optimization.[10] However, the Gong clusters generally yield isomers with much higher energy. It is known that the selection of good starting structures can be very important in searching for the global minima, particularly for mid- and large-sized clusters, as the number of possible isomers increases exponentially with the number of atoms. **sw21-1** is the global-minimum structure of SW Si$_{21}$, and **sw21-3** is the third most stable SW Si$_{21}$ isomer; **sw25-1** is the

global-minimum structure of SW Si$_{25}$, and **sw25-19**, a prolate structure, is the 19th most stable isomer.

Next, we performed geometry optimization for the top 20 most stable isomers of SW Si$_{21}$ and Si$_{25}$ using Gaussian 98 quantum chemistry software[11] at the B3LYP/6-31G(d) level of density-functional theory. For symmetric SW isomers, we slightly perturbed their structures to ensure that the ab initio geometry optimization has no symmetry constraint. Harmonic vibrational frequency analysis was also performed to ensure the optimized structures are truly stable. We then calculated the energy at the coupled-cluster single and double substitutions [CCSD/6-31G(d)] level, adding the zero-point energy correction. As a result, we find a new lowest-energy isomer for Si$_{21}$ (**21a**) as well as one for Si$_{25}$ (**25a**). Note that the starting geometric structure for **21a** is **sw21-3**; the starting structure for **25a** is **sw25-1**, and that for **25c** is **sw25-19**. Both lowest-energy isomers show quite high degrees of symmetry.
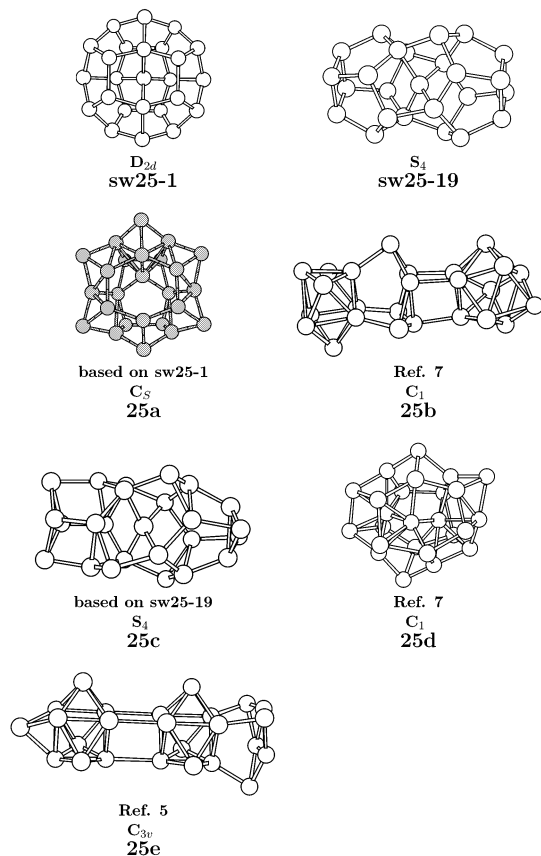

T
sw21-1

D$_{2d}$
sw21-3

based on sw21-3
D$_{2d}$
21a

Ref. 6
C$_s$
21b

Ref. 5
C$_{2v}$
21c

Ref. 10 (based on sw21-1)
C$_1$
21d

We also display the isomers whose structure is optimized at the B3LYP/6-31G(d)level with the starting structures the same as various previously found lowest-energy structures. The prolate structure **21b** is based on the lowest-energy structure obtained by Rata et al;[6] another prolate structure **21c** is based on a low-energy isomer with C_{2v} symmetry suggested by Ho et al.[5] After the geometry optimization at the B3LYP/6-31G(d) level, the final geometry of **21c** is somewhat different from the original one. As reported previously,[10] the spherical-like isomer **21d** can be obtained on the basis of the starting structure **sw21-1**, and it resembles the ground-state isomer reported by Pederson et al.[12] Table 1 shows that the more spherical-like isomer **21a** is lower in energy than the

Table 1. Relative Energy of the Low-Lying Isomers from That of the Lowest-Energy Isomer, and Their Ionization Potentials

isomers	B3LYP/6-31G*[eV]	CCSD/6-31G*[eV]	IP [eV]
21a	0.000	0.000	6.853
21b	0.411	0.586	7.027
21c	0.575	0.817	7.094
21d	0.733	1.127	6.597
25a	0.000	0.000	6.488
25b	0.369	0.527	6.853
25c	0.393	0.635	6.212
25d	0.781	0.690	6.499

prolate isomers **21b** and **21c**. Table 1 also shows the vertical IPs calculated at the B3LYP/6-31G(d) level, which are in good agreement with the experiment (6.80−6.94 eV).[4]

For Si_{25}, the prolate structure **25b** and spherical-like structure **25d** are obtained on the basis of the starting structures reported by Mitas et al.[7] Using all-electron quantum Monte Carlo calculations, Mitas et al. found that **25d** is slightly lower in energy than **25b**. Here, a new low-energy prolate structure **25c** is found that is based on **sw25-19**. We also optimized another low-energy prolate structure **25e**.[5] Yet **25e** gives four imaginary frequencies. The new spherical-like isomer **25a** is lower in energy than isomers **25b** and **25d** (Table 1). Table 1 also shows the calculated IPs which agree reasonably with the experiment (5.90−5.95 eV).[4] A good reason for **25a** to be a leading candidate of the global minimum is that its structure somewhat resembles that of the Si(111) surface, a well-known stable surface structure. Indeed, the high stability of larger clusters Si_{33} and Si_{45}[13] has been previously investigated via the building of clusters with the Si(111) surface-like structure.[14,15]

D$_{2d}$
sw25-1

S$_4$
sw25-19

based on sw25-1
C$_S$
25a

Ref. 7
C$_1$
25b

based on sw25-19
S$_4$
25c

Ref. 7
C$_1$
25d

Ref. 5
C$_{3v}$
25e

To understand the existence of the prolate-to-spherical-like structural transition for mid-size silicon clusters, two theoretical explanations have been put forth.[7,14] Both invoke the idea that endohedral atoms may play a key role to the structural transition. Here, both new lowest-energy isomers **21a** and **25a** entail an endohedral atom. Hence, our results support the notion that the prolate-to-spherical-like structural transition occurs when the Si atoms prefer to be organized into two shells with the inner shell being the endohedral atom.[15]

In summary, the possible lowest-energy geometry of Si_{21} and Si_{25} is found on the basis of the starting structures obtained via the global search for nearly identical low-energy SW and MSW structures. The fact that the SW and MSW potentials (obtained by fitting to bulk silicon properties) can provide good starting structures for certain mid-sized silicon clusters may signify the onset of some bulk-like properties in these clusters. Indeed, the new lowest-energy isomers **21a** and **25a** exhibit Si(111) surface-like structure. Moreover, **25a** and, to some extent, **21a** are spherical-like. This suggests that the prolate-to-spherical-like structural transition is likely to occur in the range of $21 \leq n \leq 25$.

Supporting Information Available: Tables of B3LYP/6-31G(d) and CCSD/6-31G(d) energies, zero-point corrections, and total energies (XLS). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Alivisatos, A. P. *Science* **1996**, *271*, 933.
(2) (a) Raghavachari, K.; Rohlfing, C. M. *J. Chem. Phys.* **1988**, *89*, 2219. (b) Rohlfing, C. M.; Raghavachari, K. *Chem. Phys. Lett.* **1990**, *167*, 559. (c) Honea, E. C.; Ogura, A.; Murray, C. A.; Raghavachari, K.; Spreenger, W. O.; Jarrold, M. F.; Brown, W. L. *Nature* **1993**, *366*, 42. (d) Zhu, X.; Zeng, X. C. *J. Chem. Phys.* **2003**, *118*, 3558. (e) Lu, Z.-Y.; Wang, C.-Z.; Ho, K.-M. *Phys. Rev. B* **2000**, *61*, 2329.
(3) (a) Jarrold, M. F.; Constant, V. A. *Phys. Rev. Lett.* **1991**, *67*, 2994. (b) Jarrold, M. F.; Bower, J. E. *J. Chem. Phys.* **1992**, *96*, 9180.
(4) Fuke, K.; Tsukamoto, K.; Misaizu, F.; Sanekata, M. *J. Chem. Phys.* **1993**, *99*, 7807.
(5) Ho, K.-M.; Shvartsburg, A. A.; Pan, B.; Lu, Z.-Y.; Wang, C.-Z.; Wacker, J. G.; Fye, J. L.; Jarrold, M. F. *Nature* **1998**, *392*, 582.
(6) Rata, I.; Shvartsburg, A. A.; Horoi, M.; Frauenheim, T.; Michael Siu, K. W.; Jackson, K. A. *Phys. Rev. Lett.* **2000**, *85*, 546.
(7) Mitas, L.; Grossman, J. C.; Stich, I.; Tobik, J. *Phys. Rev. Lett.* **2000**, *84*, 1479.
(8) (a) Wales, D. J.; Scheraga, H. A. *Science* **1999**, *285*, 1368. (b) Wales, D. J.; Doye, J. P. K. *J. Phys. Chem. A* **1997**, *101*, 5111.
(9) (a) Stillinger, F. H.; Weber, T. A. *Phys. Rev. B* **1985**, *31*, 5262. (b) Vink, R. L. C.; Barkema, G. T.; van der Weg, W. F.; Mousseau, N. *J. Non-Cryst. Solids* **2001**, *282*, 248. (c) Gong, X. G. *Phys. Rev. B* **1993**, *47*, 2320.
(10) Yoo, S.; Zeng, X. C. *J. Chem. Phys.* **2003**, *119*, 1442.
(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Rega, N.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A. M.; Challacombe, P. M.; Gill, W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11; Gaussian, Inc.: Pittsburgh, PA, 2002.
(12) Pederson, M. R.; Jackson, K.; Porezag, D. V.; Hajnal, Z.; Frauenheim, T. *Phys. Rev. B* **1996**, *54*, 2863.
(13) Elkind, L.; Alford, J. M.; Weiss, F. D.; Laakonen, R. T.; Smalley, R. E. *J. Chem. Phys.* **1987**, *87*, 2397.
(14) Kaxiras, E.; Jackson, K. *Phys. Rev. Lett.* **1993**, *71*, 727.
(15) Röthlisberger, U.; Andreoni, W.; Parrinello, M. *Phys. Rev. Lett.* **1994**, *72*, 66.

JA0365678