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Structures and stability of medium-sized silicon clusters. III. Reexamination of motif transition in growth pattern from Si_{15} to Si_{20}

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Structures and stability of medium-sized silicon clusters. III. Reexamination of motif transition in growth pattern from Si_{15} to Si_{20}

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It has been established from experiments that stable medium-sized ionic clusters Si_{15}–Si_{20} are prolate in shape. Density-functional theories (DFTs) also predict that nearly all low-lying neutral clusters in this size range are prolate in shape. Moreover, most of them are built onto two generic structural motifs, either the tricapped-trigonal-prism (TTP) Si_9 motif or the six/six Si_6/Si_6 (sixfold-puckered hexagonal ring Si_6 plus six-atom tetragonal bipyramid Si_6) motif. However, it appears that the exact location of the TTP-to-six/six motif transition is dependent on the functional (e.g., PBE or BLYP) used in the DFT calculations. Here, we present total-energy calculations for two series of clusters (one series containing six/six motif and the other containing the TTP motif) in the size range of Si_{16}–Si_{20}. The calculations were based on all-electron DFT methods with a medium $[6\text{-}311G\ (2d)]$ and a large (cc-pVTZ) basis sets, as well as coupled-cluster single and double substitutions (including triple excitations) $[CCSD(T)]$ method with a modest (cc-pVDZ) basis set. In the DFT calculations, two popular hybrid density functionals, the B3LYP and PBE1PBE, were selected. It is found that the B3LYP total-energy calculations slightly favor the six/six motif, whereas the PBE1PBE calculations slightly favor the TTP motif. The CCSD(T) total-energy calculations, however, show that isomers based on the six/six motif are energetically slightly favorable in the size range of Si_{16}-Si_{20}. Hence, the TTP-to-six/six motif transition is more likely to occur at Si_{16}. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2043127]

I. INTRODUCTION

In the previous two papers of this series (Papers I and II),[1,2] we have presented *ab initio* molecular-orbital calculations of geometric structures, total energies, vibrational frequencies, and ionization potentials of a number of small-sized $(Si_n, n=7\text{-}11)$ and medium-sized clusters $(Si_n, n=12\text{-}20)$. For medium-sized silicon clusters, most selected low-lying isomers were taken from those reported by Ho and co-workers[3] who performed an unbiased search of global-minimum clusters with a combined tight-binding (TB)/genetic algorithm method, as well as those by Rata *et al.*[4] who performed an unbiased search with a density-functional TB method combined with single-parent evolution algorithm. Since publication of Paper II, a few new candidates of the global-minimum clusters in the size range $n=13\text{-}18$ have been reported in the literature, including Si_{13} and Si_{14} by Tekin and Hartke[5] and Si_{16}–Si_{18} in our previous work.[6] In addition, we predicted that a TTP-to-*six/six* motif transition may occur at Si_{16}. This prediction was based on a constrained (or biased) basin-hopping search with the six/six motif as the seeding,[6] for clusters Si_{16}–Si_{22}. The search was coupled with the plane-wave-pseudopotential density-functional theory (PWP-DFT) with the Becke exchange and Lee-Yang-Parr correlation (BLYP) functional, implemented in the CPMD program.[7] That search not only reproduced previously reported global-minimum structures of Si_{19}–Si_{21} by Rata *et al.*,[4] but also resulted in new candidates for the global

minima of Si_{16}–Si_{18}, and Si_{22}. We showed that these new candidates built onto the six/six Si_6/Si_6 motif are lower in energy than the lowest-energy isomers reported previously. For Si_{16}, we also performed an unconstrained basin-hopping search with the Perdew, Burke, and Ernzerhof (PBE) functional and obtained the same lowest-energy structure within limited basin-hopping Monte Carlo steps (<5000).

Recently, Goedecker *et al.*[8] reported a new candidate for the global minimum of Si_{16} as well as for Si_{19}, based on a novel minima-hopping method[9] and total-energy calculation using the PWP-DFT with the PBE functional implemented in the CPMD program. More interestingly, they found that these new structures of Si_{16} and Si_{19} all contain the TTP Si_9 motif rather than the six/six Si_6/Si_6 motif. Because the total-energy differences calculated based on PWP-DFT/PBE method between the new candidates and previously reported ones are less than 0.01 eV/at. (within the accuracy of PWP-DFT), there is a possibility that the obtained global-minimum structures are dependent on the functional selected. The purpose of this paper is to further examine this functional dependence by using all-electron DFT total-energy calculations associated with two popular hybrid functionals (implemented in GAUSSIAN 03 package[10]), which are Becke's three parameter hybrid functional with the Lee-Yang-Parr correlation (B3LYP)[11] functional and the 1997 hybrid PBE (PBE1PBE)[12] functional. We also examined this functional dependence on the predicted lowest-energy structures using two different basis sets: One medium basis set and one large one. Finally, we computed total energies for all candidate

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TABLE I. (A) Calculated total energies (in a. u.) and zero-point energies (ZPES) at various levels of theory for the six/six-motif-based clusters. (B) and (C) are the calculated energy differences (in eV) with respect to the corresponding six/six-motif-based isomers listed in (A). The bold-faced energy differences denote those isomers that have a lower energy than the corresponding isomers containing the six/six motif.

(A)	PBE1PBE/6-311G(2d)		B3LYP/6-311G(2d)	
Clusters	E (a.u.)	ZPE (a.u.)	E (a.u.)	ZPE (a.u.)
16ss-1	−4630.176 250 1	0.0280 41	−4632.231 271 9	0.026 334
17ss-1	−4919.577 232 2	0.030 089	−4921.762 708 0	0.028 248
18ss-1	−5208.968 651 7	0.031 826	−5211.278 479 7	0.029 920
19ss-1	−5498.363 878 1	0.032 894	−5500.796 782 7	0.030 596
20ss-1	−5787.771 568 9	0.035 825	−5790.331 134 3	0.033 463
	PBE1PBE/	B3LYP/	CCSD/cc-pVDZ	CCSD(T)/cc-pVDZ
Clusters	cc-pVTZ (a.u.)	cc-pVTZ (a.u.)	(a.u.)	(a.u.)
16ss-1	−4630.235 285 8	−4632.277 797 2	−4624.301 458 3	−4624.452 846
17ss-1	−4919.640 186 2	−4921.812 544 8	−4913.343 837 6	−4913.500 482 9
18ss-1	−5209.034 967 3	−5211.331 052 8	−5202.363 120	−5202.532 293 9
19ss-1	−5498.433 971 0	−5500.851 678 0	−5491.388 033 4	−5491.574 200 2

(B)	PBE1PBE/6-311(2d)		B3LYP/6-311(2d)	
Clusters	ΔE (eV)	$\Delta E + \Delta ZPE$ (eV)	ΔE (eV)	$\Delta E + \Delta ZPE$ (eV)
16bilayer-1	0.142	0.143	0.025	0.030
16bilayer-1r	0.122	0.107	0.258	0.238
16cage-1	0.179	0.184	0.003	0.010
16ttp-1	0.187	0.152	0.655	0.607
17ttp-1	0.098	0.076	0.391	0.358
18ttp-1	**−0.333**	**−0.338**	0.195	0.174
18ss-2	**−0.124**	**−0.134**	0.042	0.025
19ttp-1	**−0.033**	**−0.030**	0.419	0.412
20ttp-1	0.590	0.546	0.551	0.503

(C) Clusters	PBE1PBE/cc-pVTZ (eV)	B3LYP/cc-pVTZ (eV)	CCSD/cc-pVDZ (eV)	CCSD(T)/cc-pVDZ (eV)
16bilayer-1	0.109	**−0.005**	0.116	0.042
16bilayer-1r	0.119	0.246	0.341	0.013
16cage-1	0.124	**−0.022**	0.116	0.004
16ttp-1	0.179	0.666	0.735	0.085
17ttp-1	0.082	0.393	0.582	0.080
18ttp-1	**−0.337**	0.221	0.358	0.154
18ss-2	**−0.127**	0.055	**−0.90**	**−0.125**
19ttp-1	**−0.024**	0.441	0.522	0.402

clusters in the size range of $Si_{16}-Si_{19}$ using a high-level coupled-cluster theory with a modest basis set.

II. COMPUTATIONAL DETAILS

For all candidate clusters, we first performed geometric optimization using all-electron density-functional theory with both B3LYP and PBE1PBE hybrid functionals and the 6-311G(2d) (triple split for the valence basis functions plus polarization) basis set, compiled in the GAUSSIAN 03 software package.[10] Next, harmonic vibrational frequencies were computed using both DFT methods and the 6-311G (2d) basis set to assure that these clusters are local minima without any imaginary frequency. Zero-point energies (ZPES) were recorded and included in the total energies. Calculation re-

sults are given in Table I. In order to examine the basis-set effects, we also performed geometric optimization using both B3LYP and PBE1PBE functionals and a larger Dunning's correlation consistent polarized valence triple zeta plus polarization (cc-pVTZ) basis set.[13] Finally, single-point energies at the coupled-cluster single and double substitutions (including triple excitations) [CCSD(T)] level of theory with a modest Dunning's correlation consistent polarized valence double zeta plus polarization (cc-pVDZ) basis set were carried out on basis of the PBE1PBE/6−311G(2d) optimized geometries (Table I). CCSD(T) calculations based on B3LYP/6-311G(2d) optimized geometries were also performed, and the same energy orders were obtained as those based on PBE1PBE/6-311G(2d) optimized geometries.
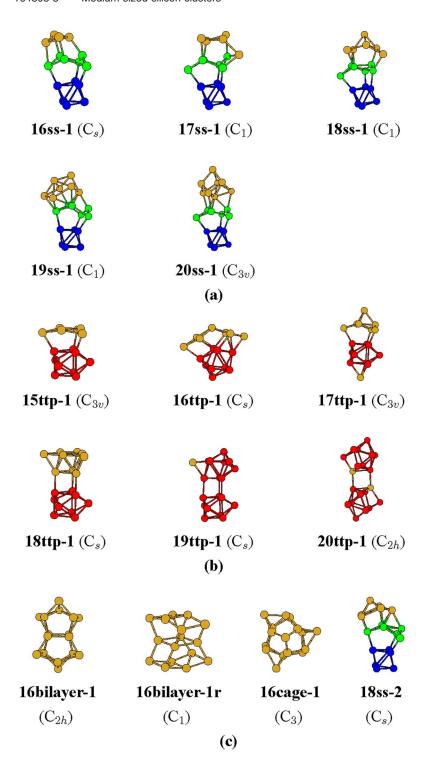
16ss-1 (C_s)   **17ss-1** (C_1)   **18ss-1** (C_1)

19ss-1 (C_1)   **20ss-1** (C_{3v})

(a)

15ttp-1 (C_{3v})   **16ttp-1** (C_s)   **17ttp-1** (C_{3v})

18ttp-1 (C_s)   **19ttp-1** (C_s)   **20ttp-1** (C_{2h})

(b)

16bilayer-1   **16bilayer-1r**   **16cage-1**   **18ss-2**

(C_{2h})   (C_1)   (C_3)   (C_s)

(c)

FIG. 1. (Color online). (a) Geometries of clusters with lowest (BLYP and B3LYP) energies and containing the six/six motif, i.e., the *sixfold-puckered ring* Si_6 (green color) and the *tetragonal bipyramid* Si_6 structural subunits (blue color). The yellow-colored atoms show growth patterns on the basis of the six/six motif. (b) Geometries of clusters with lowest (PBE and PBE1PBE) energies and containing the TTP motif, i.e., the *tricapped-trigonal-prism* Si_9 motif (red color). (c) Geometries of other low-lying clusters of Si_{16} (Refs. 3 and 8) and Si_{18} (Ref. 4) predicted previously.

III. RESULTS AND DISCUSSIONS

As pointed out in Sec. I, our attention will be given primarily to two series of low-lying clusters; one containing the six/six Si_6/Si_6 motif and another containing the TTP Si_9 motif both in the size range of Si_{16}-Si_{20}. Figure 1(a) displays the lowest-energy isomers of the six/six-motif-based family, obtained previously based on the constrained (biased) basin-hopping search coupled with PWP-DFT calculation with the BLYP functional.[6] Hereafter, we name these six/six-motif-based lowest-energy isomers 16ss-1 to 20ss-1. In Fig. 1(a), the *sixfold-puckered ring* Si_6 and the *tetragonal bipyramid*

Si_6 subunits of the six/six motif are highlighted by the green and blue colors, respectively, whereas the yellow-colored atoms show growth patterns of these clusters on top of the six/six motif. Figure 1(b) displays the lowest-energy isomers containing the TTP (*tricapped-trigonal-prism* Si_9) motif[3] (highlighted in red color). Hereafter, we name these TTP-motif-based lowest-energy isomers 15ttp-1 to 20ttp-1. These isomers can be obtained based on a constrained basin-hopping search with the TTP motif as the seeding.[6] We performed this search in conjunction with PWP-DFT/PBE method (implemented in the CPMD program). For Si_{16} and

Si_{19}, we reproduced identical lowest-energy structures (16ttp-1 with C_s symmetry and 19ttp-1 with C_s symmetry) as reported by Goedecker *et al.*,[8] whereas for Si_{17} and Si_{18}, we reproduced identical lowest-energy structures (17ttp-1 with C_{3v} symmetry and 18ttp-1 with C_s symmetry) reported by Ho *et al.*[3] and our previous work,[2] respectively. Interestingly, 19ttp-1 has the same geometric structure as the lowest-energy isomer of Ge_{19} predicted previously.[14]

In Table I(A), the total energies of the first series of isomers which contain the six/six motif are listed. The total-energy differences of other isomers with respect to the corresponding six/six-motif-based isomers are given in Tables I(B) and I(C). These energy differences were calculated with various levels of theory and basis sets. Discussion of these results is given below for each size of clusters.

A. Si_{16}

Goedecker *et al.*[8] showed that 16ttp-1 has the lowest energy whereas 16ss-1 is the second in the energy order on the basis of PWP-DFT calculations with the PBE functional. However, on basis of all-electron DFT calculations with both B3LYP and PBE1PBE hybrid functionals and the 6-311G (2d) basis set, we found that 16ss-1 is always lower in energy than 16ttp-1. The total-energy difference (including ZPE) is 0.607 eV (B3LYP) and 0.152 eV (PBE1PBE), respectively. With the larger basis set (cc-pVTZ), the energy difference becomes slightly larger, i.e. 0.666 and 0.179 eV, respectively. The larger energy difference with the B3LYP functional appears to be consistent with our previous PWP-DFT calculations with the BLYP functional. As such, it seems that both B3LYP and BLYP functionals slightly favor the six/six-motif-based isomers over the TTP-motif-based isomers. The *ab initio* energy calculations at the CCSD and CCSD(T) levels of theory with the cc-pVDZ basis set also show that the 16ss-1 is lower in energy than 16ttp-1, although the energy difference is much smaller (0.085 eV) at the highest-level CCSD(T) theory.

In Fig. 1(c), we display one bilayer like isomer of Si_{16} named 16bilayer-1 and its variant named 16bilayer-1r. The 16bilayer isomer was previously predicted to be the global minimum by Ho *et al.*,[3] and its structure can be viewed as a network of eight parallel silicon dimers. The 16bilayer-1r, which was reported by Goedecker *et al.* as the third lowest-energy isomer,[8] can be constructed by rotating three pairs of silicon dimers of 16bilayer-1 by 90° at the top. In addition, we display a cagelike isomer of Si_{16} named 16cage-1. The 16cage-1 was obtained from a lengthy unconstrained basin-hopping search combined with PWP-DFT with the BLYP functional. Note that when the PBE functional was used we found that 16cage-1 has an appreciably higher energy than both 16ss-1 and 16ttp-1. Here, in the all-electron DFT calculations, when the smaller basis set [6-311G (2d)] is used both B3LYP and PBE1PBE calculations show that 16cage-1 is higher in energy than 16ss-1. However, when the larger basis set (cc-pVTZ) is used, as shown in Table I(C), the B3LYP calculations show that 16cage-1 has the lowest energy (lower than all other four Si_{16} isomers), whereas the PBE1PBE calculations show that

16-ss1 still has the lowest energy. Both DFT calculations with the larger basis set however show that 16ttp-1 has the highest energy among the five Si_{16} isomers, and so do the CCSD/cc-pVDZ and CCSD(T)/cc-pVDZ energy calculations. Finally, the CCSD(T)/cc-pVDZ energy calculations show that the three Si_{16} isomers 16ss-1, 16cage-1, and 16bilayer-1r are very close in total energy (within 0.013 eV). Thus, a large basis set is needed with the CCSD(T) level of theory to determine the true energy order among these three Si_{16} isomers.

B. Si_{17}

As reported previously,[6] both B3LYP/6-311G(2d) and PBE1PBE/6-311G(2d) calculations as well as the CCSD/cc-pVDZ and CCSD(T)/cc-pVDZ single-point energy calculations show that 17ss-1 is lower in energy than 17ttp-1. Even with the larger cc-pVTZ basis set for geometry optimizations, both DFT calculations show little changes in energy differences [see Tables I(B) and I(C)]. Again, the energy difference calculated based on the PBE1PBE/cc-pVTZ theory (0.082 eV) is appreciably less than that based on the B3LYP/cc-pVTZ theory (0.393 eV), indicating again that the PBE1PBE functional slightly favors the TTP-motif-based isomers whereas B3LYP slightly favors six/six-motif-based isomers.

C. Si_{18}

Si_{18} is an interesting case since the total-energy order predicted based on the B3LYP calculations is opposite to that predicted based on the PBE1PBE calculations, regardless of sizes of the basis set considered here. Furthermore, the PBE1PBE total-energy calculations are consistent with the PWP-DFT calculations with the PBE functional. Because the energy order is apparently functional dependent, if one performs unbiased global search combined with DFT, the predicted lowest-energy structure will be dependent on the functional selected. Indeed, we found that this was even the case when we performed constrained (biased) basin-hopping search (for which the six/six motif was used as the seeding[6]) coupled with PWP-DFT and with the PBE functional, instead of the BLYP functional. With the PBE functional, we obtained the 18ss-2 as the lowest-energy isomer [Fig. 1(c)] rather than 18ss-1. Note that 18ss-2 has been previously reported by Rata *et al.*[4] and studied in Paper II. This sensitivity of the predicted lowest-energy structure to the functional selected demonstrates that there exist several low-lying isomers with nearly the same energy for Si_{18}. Hence, in order to determine the true global minimum of Si_{18}, first-principles theories with much higher accuracy in total-energy calculation than DFT are required. Possible choices include quantum Monte Carlo method[15] or CCSD(T) level of theory with a large basis set, e.g., cc-pVTZ or correlation-consistent palarized valence quadruple zeta (cc-pVQZ). The latter calculations are not yet feasible with current computing resources. Here, the CCSD(T)/cc-pVDZ calculations may still offer some guidance in the prediction of energy order, that is, the 18ss-2 structure may have a better chance as the candidate for the global minimum of Si_{18} over 18ss-1 (having the

lowest B3LYP energy) and 18ttp-1 (having the lowest PBE1PBE energy). If so, it still shows that this six/six-motif-based isomer is energetically favorable over the TTP-motif-based isomer for Si_{18}.

D. Si_{19}

The 19ttp-1 contains two TTP motifs and can be constructed by adding one atom on top of 18ttp-1 structure [Fig. 1(b)]. Thus, it is expected that when the PBE functional is selected in search for global minimum of Si_{19} 19ttp-1 will be slightly favored over the six/six-motif-based isomers. We found that this is also the case when the all-electron PBE1PBE/6-311G(2d) and PBE1PBE/cc-pVTZ methods were used (see Table I). However, the total-energy difference between 19ttp-1 and 19ss-1 is less than 0.04 eV with the PBE1PBE calculations whereas the energy difference is an order of magnitude larger (>0.4 eV) than the B3LYP calculations as well as with the CCSD/cc-pVDZ and CCSD(T)/cc−pVDZ calculations. Hence, the chance for the six/six-motif-based isomer 19ss-1 to be the true global minimum is higher than 19ttp-1.

E. Si_{20}

For Si_{20}, the global-minimum structure was predicted to be 20ss-1 by Rata *et al.*[4] for which the total energies were calculated based on all-electron DFT with both PBE and Perdew-Wang-Becke 88 (PWB) functionals. As mentioned above, the PBE functional tends to slightly favor the TTP-motif-based isomers over the six/six-motif-based isomers in total-energy calculations. For Si_{20}, the fact that even the DFT/PBE calculations show that the six/six-motif-based isomer 20ss-1 is energetically favorable over the TTP-motif-based isomer 20ttp-1 (Ref. 15) indicates that the TTP-to-six/six motif transition occurs definitely at a cluster size smaller than Si_{20}. Indeed, as shown in Table I, all-electron DFT calculations with both PBE1PBE and B3LYP functionals also support this indication. Moreover, the calculated total-energy differences amount to more than 0.5 eV with both functionals. These results are consistent with our previous CCSD(T) calculations[2] with a smaller basis set [6-31G(d)], with which the calculated energy difference also amounts to about 0.4 eV. We thus expect that CCSD(T) calculations with larger basis sets may still give the same energy order as the DFT.

On basis of above total-energy results and previous ones, it is tempting to draw a tentative rule of thumb, that is, if both the B3LYP and PBE1PBE total-energy calculations (with a large basis set) give the same energy order and if the energy difference calculated with one of the functionals is greater than typical error bar of DFT for total-energy calculation (~0.2 eV or less),[16] then the CCSD(T) energy order will be most likely the same as predicted by the DFT. Thus far, we have not seen any exception to this simple rule of thumb. If this rule is further tested and proved for other larger clusters, one may no longer needs to perform very expensive (or impractical) CCSD(T) total-energy calculations for large-sized silicon clusters. On the other hand, we note that if the B3LYP energy order is different from the PBE1PBE energy order, as in the cases of Si_{16} and Si_{18}, one has to perform high-level first-principles calculations [e.g., quantum Monte Carlo or CCSD(T) with a large basis set] to determine the true global-minimum structure.

IV. CONCLUSIONS

We have performed total-energy calculations for prolate-shaped low-lying silicon clusters[17] in the size range of Si_{16}–Si_{20} using all-electron DFT with two hybrid functionals B3LYP and PBE1PBE, and *ab initio* theory at the CCSD(T) level. Particular attention is placed on two series of low-lying clusters: one containing the TTP Si_9 structural motif whereas another containing the six/six Si_6/Si_6 structural motif. It is found that the B3LYP total-energy calculations slightly favor the six/six-motif-based isomers whereas the PBE1PBE calculations slightly favor the TTP-motif-based isomers. Consequently, when the total-energy difference between the low-lying isomers is less than typical accuracy of total-energy calculations of DFT, the predicted global minimum can be dependent on the functional selected. This is particularly seen in the cases of Si_{18} and Si_{19}. On the other hand, these DFT results still support that isomers containing either the TTP or the six/six structural motif are energetically very favorable in the size range Si_{16}–Si_{19}. Previous theoretical studies have shown that TTP structural motif is prevailing in the small-sized low-lying clusters of Si_{11}–Si_{15} (Ref. 3), whereas the six/six or six/ten (the ten refers to magic-number cluster Si_{10}) structural motif is energetically more favorable in the medium-sized low-lying clusters Si_{20}–Si_{26} (Refs. 3, 6, and 18). So the TTP-to-six/six motif transition is likely to occur in the range of Si_{16}–Si_{19}.

Although the exact location for the motif transition cannot be determined unambiguously with DFT total-energy calculations, the observation of the two generic structural features is still of fundamental importance towards the understanding of the structural evolution of silicon clusters. It is known that as the size of cluster increases, locating the global minima becomes increasingly difficult because of the much increased complexity of the potential energy surface as well as the rapid increase of the number of low-lying isomers. Therefore, any identification of certain types of generic structural feature (e.g., TTP motif) can dramatically reduce computation cost for the first-principles global search and more importantly it can provide additional physical insight (or guide) into growth patterns of medium-to-large-sized clusters. For example, we have recently used the carbon fullerene as structural motifs[19] to construct "stuffed fullerene-type"[20,21] low-lying medium-sized clusters Si_{40}, Si_{45}, and Si_{50}. The physical insight for this fullerene-cage-based cluster construction was gained through an unbiased global search using genetic algorithm combined with TB method.[22]

Finally, we note that the present *ab initio* total-energy calculations at the CCSD(T) level with a modest basis set (cc-pVDZ) show that the six/six-motif-based isomer series generally has a lower energy than the corresponding TTP-motif-based isomer series for Si_{16}-Si_{19}. More definite determination of the relative energy between these two series

requires much larger basis sets, e.g., cc-pVTZ or cc-pVQZ. Such a calculation is currently beyond our computing capability. Nevertheless, we have recently performed CCSD(T)/cc-pVQZ, CCSD(T)/cc-pVTZ, and CCSD(T)/cc-pVDZ total-energy calculations[23] for two nearly isoenergy isomers of Si_6 with their energy difference on the order of 0.01 eV [based on CCSD(T)/cc-pVQZ calculations]. We found that the CCSD(T)/cc-pVDZ calculations predicted the same energy order as CCSD(T)/cc-pVQZ but underestimates the energy difference (0.002 eV). Assuming the accuracy of total-energy calculations with CCSD(T)/cc-pVDZ is on the order of 0.1 eV for medium-sized silicon clusters, we then expect that the calculated energy differences (0.28 eV) between 18ss-2 and 18ttp-1, and (0.402 eV) between 19ss-1 and 19ttp-1 are fairly reliable. As such, 18ss-2 and 19ss-1 are very likely to be the global minimum compared to 18ttp-1 and 19ttp-1, respectively. In other words, the TTP-to-six/six motif transition is most likely to occur at a cluster size less than Si_{18}.

ACKNOWLEDGMENTS

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