

Novel silicon-carbon fullerene-like cages

A class of sp^3 – sp^2 covalent-ionic hybridized nanosystems

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Abstract. A class of highly symmetric silicon carbide fullerene-like cage nanoclusters with carbon atoms *inside* the Si_{20} cage and with high stability are presented. The Generalized Gradient Approximation of Density Functional Theory (GGA-DFT) is used to study the electronic and geometric structure properties of these structures and full geometry optimizations are performed with an all electron 6-311G^{**} basis set. The stability of the clusters is found to depend on the geometrical arrangements of the carbon atoms inside the clusters and the partly ionic nature of the bonding. Possibilities of extending these structures into a larger class of nanostructures are discussed.

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1 Introduction

In recent years, atomic and molecular clusters have been vigorously investigated by a wide class of scientists [1–4]. Cage-like compact clusters are particularly important for two reasons: they can be used as building blocks of more stable materials and the hollow space inside the cage can be used to dope different atoms yielding a wide variety of atomically engineered materials. For example, well-controlled nanostructures with varying HOMO-LUMO gaps and desired conduction properties can be achieved by controlled doping of atoms in C_{60} [5]. The spin property of the doped atom inside the cage can be used as the smallest memory devices for quantum computers; for instance, tungsten in Si_{12} clusters is quantum mechanically isolated from outside so that it can preserve its spin state [6].

Silicon is one of the more important semiconductors with widespread applications and silicon clusters, preferring sp^3 hybridization, have been studied extensively. Hartree-Fock (HF) and density functional theories (DFT) [7–10] have been used to determine the ground state structures, though still controversial, of Si clusters. There are not, however, enough experimental studies to confirm or predict the energetically favorable structures [11]. Discovery of the magically stable C_{60} fullerene cage have prompted scientists to study fullerene-like silicon structures and Si_{60} was found to have a distorted fullerene-cage-like structure [12]. Attempt also has been made to replace carbon atoms by Si atoms in C_{60} , also

resulting in a distorted structure [13]. In carbon clusters, preferring sp^2 hybridization, fullerene like structures are found in structures as small as C_{20} [14, 15]. In Si_n clusters such structures are unstable for small n values.

It has been pointed out recently, primarily based on DFT studies, that highly stable small silicon cage clusters are possible if transition *metal* atoms are encapsulated in the cage [16–19]. The combinations of silicon and carbon atoms in a cluster have also generated a number of studies on structures *rich in carbon atoms*, in areas from cluster science [20] to astrophysics [21]. Density functional calculations with simulated annealing have been performed by Hunsicker and Jones [22] for neutral and singly charged silicon-carbon cluster anions with up to eight atoms. The calculations identified two classes of anion structures: carbon-rich (chainlike) and silicon-rich (three-dimensional), with pronounced differences in the vertical detachment energies. The largest silicon-rich cluster studied was Si_7C^- . Studies have also been reported of Si_{60} cage with a C_{60} fullerene cage inside it [23, 24]. Ray et al. [25] have reported on the synthesis of $C_{2n-q}Si_q$ clusters with $2n = 32–100$ and $q < 4$. Both experimental and theoretical results indicate that such clusters remain in the fullerene geometry and that the Si atoms are close to each other in the fullerene network. Subsequent experiments by them indicated surprising capability of substituting a large number of silicon atoms, up to 12, into fullerenes without destabilizing the cage structure significantly. Branz et al. [26] have reported photoelectron mass spectra of metal-fullerene clusters with one carbon atom of the fullerene cage replaced by a transition metal atom. Recently, Connetable et al. [27] have reported an ab initio

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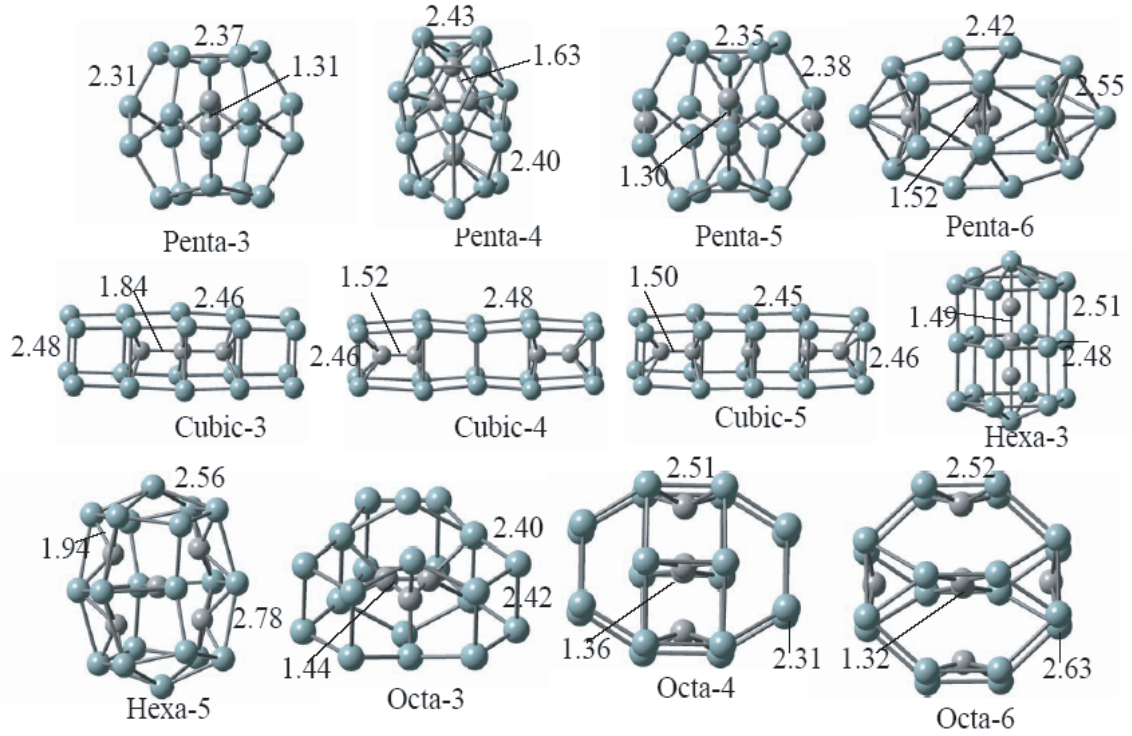


Fig. 1. Optimized structures of Si_{20}C_n clusters. Bond lengths are given in Å.

study of $\text{I}_8@{\text{Si}}\text{-46}$ and related doped clathrates. On the basis of quasi-particle GW calculations, they found that the band gap of such compounds can be as large as ~ 2.25 eV, with possibilities in optoelectronic applications.

However, to the best of our knowledge, *Si rich cage type* silicon carbide clusters have not been studied in detail so far. We have recently shown that *carbon dimers* trapped into medium size silicon clusters produces structures *comparable in stability* to metal encapsulated silicon cage clusters. For this purpose, we carried out ab initio Hartree-Fock based second order Møller Plesset perturbation theory calculations to study the electronic and geometric structures of Si_nC_2 ($n = 8\text{--}14$) clusters and predicted Si_{14}C_2 , with a close fullerene like structure, to be a magic cluster [28]. Given the similarities between carbon and silicon and the fact that C_{20} can make the smallest fullerene system, we report here a novel class of Si_{20}C_n systems. It is well-known that bare silicon clusters do not form closed structures, because of their sp^3 bonding nature. Si_{20} , for example, is a prolate type structure with two Si_{10} units joined by intermediate bonds [29]. We demonstrate here, with gradient corrected density functional theory (DFT) [30] and an all electron 6-311G** set [8], that *multiple carbon atoms inside the Si_{20} do in fact produce highly stable fullerene like structures*. The GAUSSIAN 98 suite of programs [31] has been used.

2 Results and discussions

Figure 1 shows the Si_{20}C_n ($3 \leq n \leq 6$) optimized structures and Table 1 lists the binding energies per atom

Table 1. Binding energy (B.E.) per atom, HOMO-LUMO gap, VIP and VEA (all in eV) for optimized Si_{20}C_n clusters.

Structure	State	B.E./atom	Gap	VIP	VEA
Penta-3	1A_g	4.01	0.56	6.60	3.09
Penta-4	$^1A'$	4.01	0.61	6.89	3.29
Penta-5	1A_g	4.16	0.70	6.52	2.89
Penta-6	1A_g	4.16	0.66	6.10	2.47
Cubic-3	$^1A_{1g}$	3.20	0.16	6.15	3.15
Cubic-4	$^1A_{1g}$	3.98	0.32	6.96	3.13
Cubic-5	$^1A_{1g}$	4.05	0.57	6.27	2.84
Hexa-3	$^1A_{1g}$	3.72	0.32	5.87	2.59
Hexa-5	1A_g	3.94	0.32	6.50	3.18
Octa-3	1A_1	3.83	0.18	6.27	3.13
Octa-4	1A_g	3.90	0.34	6.53	3.18
Octa-6	1A_g	4.12	0.65	6.56	2.98

(BE), highest occupied molecular orbital — lowest unoccupied molecular orbital (HOMO-LUMO) gaps, vertical ionization potentials (VIP) and vertical electron affinities (VEA). The binding energies per atom of the clusters are computed as the relative energies of the clusters in the separated atom limit, with the atoms in their respective ground states. The VIP and the VEA are calculated as the difference in total energies between the neutral clusters and the corresponding positively and negatively charged clusters, respectively, at the neutral optimized geometry. We have considered different numbers of carbon atoms with various possible orientations in the Si cages and the

structures are divided into four different categories. Given the large number of atoms in the cluster, the number of possible structures are quite large and only the most stable structures are reported here. For the first set, the input geometry was a silicon cage with pentagons (Penta- n) and in Table 1 or Figure 1, "Penta-4", for example, means that the input geometry was a pentagonal cage with four carbon atoms inside it. The second category is a cubic (Cube- n) cage, where the cubes are placed on top of another cube to form a chain-like cage with the carbon atoms inside the cage. This is followed by a hexagonal cage (Hexa- n), where the cages are made up of Si hexagons, with carbon atoms inside. The last one is the octagonal cage (Octa- n) where Si octagons are used to form the cages. The minimum number of carbon atoms inside the cage reported here is three and the maximum number is six. As the cage size increased to twenty silicon atoms, we found that at least three carbon atoms were necessary to stabilize the cage.

We have four structures in the Penta-series as shown in Figure 1. Penta-6 is more like a prolate structure with a BE per atom of 4.16 eV. Out of six carbon atoms, four formed a rhombus-shaped structure at the middle, while the other two are near the two rear ends, below the two Si capping atoms. Penta-5 has the same BE per atom as Penta-6, but is more compact. Here three carbon atoms formed a chain in the middle, and the other two carbon atoms are at the boundary of the cage. This cluster is a unique cluster in that the carbon atoms are on the surface of the cage. However, both the VIP and VEA are higher than the Penta-6 cluster, indicating increased stability. The HOMO-LUMO gaps are comparable. In Penta-4, the three carbon atoms make a triangle on one side inside the cage, while the other carbon atom is attached to the other end. Penta-4 also has a lower symmetry than the other structures in this series. In Penta-3 all three carbon atoms formed a linear structure in the middle. Both Penta-4 and Penta-3 has the same binding energy, namely 4.01 eV per atom, though Penta-4 has the highest VIP and VEA in this series. Structures in the Penta- n series are the most stable ones among the other series for a given n (where, $n = 3$ to 6). The vibrational frequencies of these structures are listed in Table 2.

In the cubic series, the structures are cubic chain like structures. For Cubic-5, each of the rectangular layers has one carbon atom each; with each rear end carbon atoms being clearly inside the cage as shown. Binding energy is the highest in the series, 4.05 eV per atom. We believe that longer cubic chains, *similar to carbon nanotubes*, can easily be constructed by extending this structure on both sides. In Cubic-4, carbon atoms are in the two rear end cube, leaving the middle part empty. Among the four-carbon atom clusters, Cubic-4 is the second most stable, with a binding energy of only 0.03 eV per atom lower than the corresponding energy of Penta-4. In Cubic-3, the three carbon atoms formed a linear chain in the middle part of the cage, leaving the two outer cubes empty. Cubic-3 has the lowest binding energy of 3.20 eV per atom among the class of clusters considered in this study, possibly due to the linear arrangement of the carbons. It also has the low-

est HOMO-LUMO gap of 0.16 eV. For this series, HOMO and HOMO-1 are found to be degenerate.

The optimized structures of Hexa-5 are distorted from the straight hexagonal cage, converging to the capping atoms at both ends. Out of five carbon atoms, one is in the center and the other four are like the inside capping of the four walls of the cage. The binding energy of 3.94 eV per atom and a HOMO-LUMO gap of 0.32 eV are lower than the previous two five-carbon atom clusters. Hexa-3 is like a straight hexagonal cage with the three carbon atoms along the axis of the hexagons. The binding energy of 3.72 eV per atom is lower, again possibly due to the linear arrangement of the carbons and the gap is the same as the gap of Hexa-5.

The last set is the octa-series consisting of two octagons capped with two Si atoms on the top and two at the bottom. For this series we have three optimized structures as shown in Figure 2. Octa-6 and Octa-4 has almost the same structures with Octa-6 being slightly more circular. Octa-6 has a binding energy of 4.12 eV per atom and a HOMO-LUMO gap of 0.65 eV, comparable to the Penta-6, though its VIP and VEA are slightly higher. Octa-4 has a binding energy of 3.90 eV per atom, and a lower HOMO-LUMO gap of 0.34 eV. The VEA is one of the highest. Octa-3 has a different structure than the other two in this series. The structure does not appear to be circular and the three carbon atoms sit in the cage as a triangle. The binding energy is 3.83 eV per atom; and the gap is 0.18 eV, comparable to the Cubic-3 gap.

From Table 1, it is evident that, in general, binding energy per atom increases with the number of carbon atoms in each group. Only one exception was found for the pentagonal group where Penta-3 is as stable as Penta-4. The compactness of Penta-3 might contribute to its higher binding energy. Also the two six-carbon atoms structures Penta-6 and Octa-6 have almost similar binding energies. We believe that the coordination of carbon atoms to silicon atoms contributes to the binding energy. Closer the number of silicon atoms to the number of carbon atoms, more bound is the system. Mulliken charge distribution analysis indicates that in most cases, carbon atoms acquired negative charges and the silicon atoms acquired positive charges, as is also expected from electronegativity considerations. Two exceptions are noted: one is in Penta-3 where the middle carbon atom gets positive charge (+0.99e), but the other two carbon atoms got $-1.25e$ charge each. Another is in Penta-5 where in the middle three carbon atoms, the center one acquired $+1.27e$ and the two end atoms got $-1.37e$ each. This means that there is a strong Columbic interaction between the carbon atoms contributing to their high binding energies. Since normally Si atoms participate in sp^3 bonding and carbon atoms prefer sp^2 bonding, we have here a hybrid sp^3 and sp^2 bonding, with more contribution from sp^3 as the number of Si atoms is increased. Distortions in pure silicon clusters are also believed to be due to sp^3 bonding. We believe that the admixture of the two types of bonding, *covalent and ionic*, helps minimize

Table 2. Harmonic vibrational frequencies (in cm^{-1}) for the most stable structures.

Penta-3					
35.1140	53.8279	89.0475	100.0479	103.5490	106.0307
106.4208	108.7800	109.8237	112.8201	113.1134	119.4699
124.9458	127.1016	135.2268	143.6739	152.7315	181.5678
184.5268	210.8142	227.9306	232.6878	255.3398	257.6895
265.2431	272.3758	298.6129	309.3788	315.0936	346.3126
348.8724	365.3211	373.3656	377.3000	378.9661	373.3656
377.3000	378.9661	399.4884	408.9807	413.3980	419.8683
420.9676	431.9771	435.3815	435.7197	437.2260	441.5723
442.7002	451.7733	455.9603	464.6111	475.7040	478.8853
1130.1134	1745.0544				
Penta-4					
42.4708	57.1596	61.2863	82.6625	87.4220	87.7755
101.4196	115.8958	118.0920	123.9148	125.1709	137.0166
152.7887	153.7905	157.4562	167.1414	167.6852	178.1813
179.5810	180.3372	182.3706	190.8606	196.6119	200.6812
206.6529	223.4634	226.8537	234.5397	254.3563	258.9272
264.0900	276.4648	279.9449	294.3384	295.9496	301.9569
307.1680	308.7460	318.7423	321.4568	329.1277	348.7715
356.9333	358.7851	363.6471	368.9444	382.3460	386.9039
392.7324	403.3444	405.0279	414.9373	427.3120	433.8238
440.6952	490.0991	546.0796	564.7137	569.2167	601.0173
644.1130	683.3112	721.8126	1324.7885		
Penta-5					
40.0664	49.9265	67.1873	90.5978	91.0016	95.4523
96.5796	102.8595	102.8989	110.3653	116.9224	123.8610
125.2618	127.6675	128.4062	140.0196	150.6259	157.7977
165.7127	178.6115	182.7941	188.7470	200.2681	215.4324
216.8174	223.0826	243.6100	246.6712	249.8960	251.7762
254.3070	261.3066	284.0470	284.7176	295.6408	307.8489
321.0733	324.1203	338.2031	354.9111	357.6939	361.3469
365.9470	370.2012	376.1968	385.0085	387.9554	390.5559
393.7816	398.3344	400.7942	416.5418	417.3897	421.4783
425.2103	430.4160	433.0441	436.1318	455.0837	478.9167
497.5499	505.5985	516.2651	542.9828	1112.2151	1122.6445
1207.0616	1829.6420				
Penta-6					
20.5348	47.4349	51.2947	59.4691	65.6917	70.6214
81.9828	111.5504	120.7604	128.4334	130.8759	132.1093
138.5859	138.6906	139.2070	161.3086	161.4530	164.7564
167.2410	189.7812	194.1973	197.0345	197.3393	207.9544
209.3868	213.6394	226.2559	232.4419	234.1336	236.1318
237.4645	242.3706	248.8556	262.1858	272.6666	281.6857
282.1966	284.6875	297.1928	297.1935	299.5237	301.7802
311.0144	321.6005	331.2969	338.8640	347.0249	355.9614
357.0717	368.3633	393.3162	394.1103	402.5762	407.2895
411.6804	447.3317	499.1467	550.9866	555.0077	562.4648
581.2674	592.7316	618.4960	698.0665	703.7108	807.4389
841.5490	894.9058	934.2630	1070.1990		

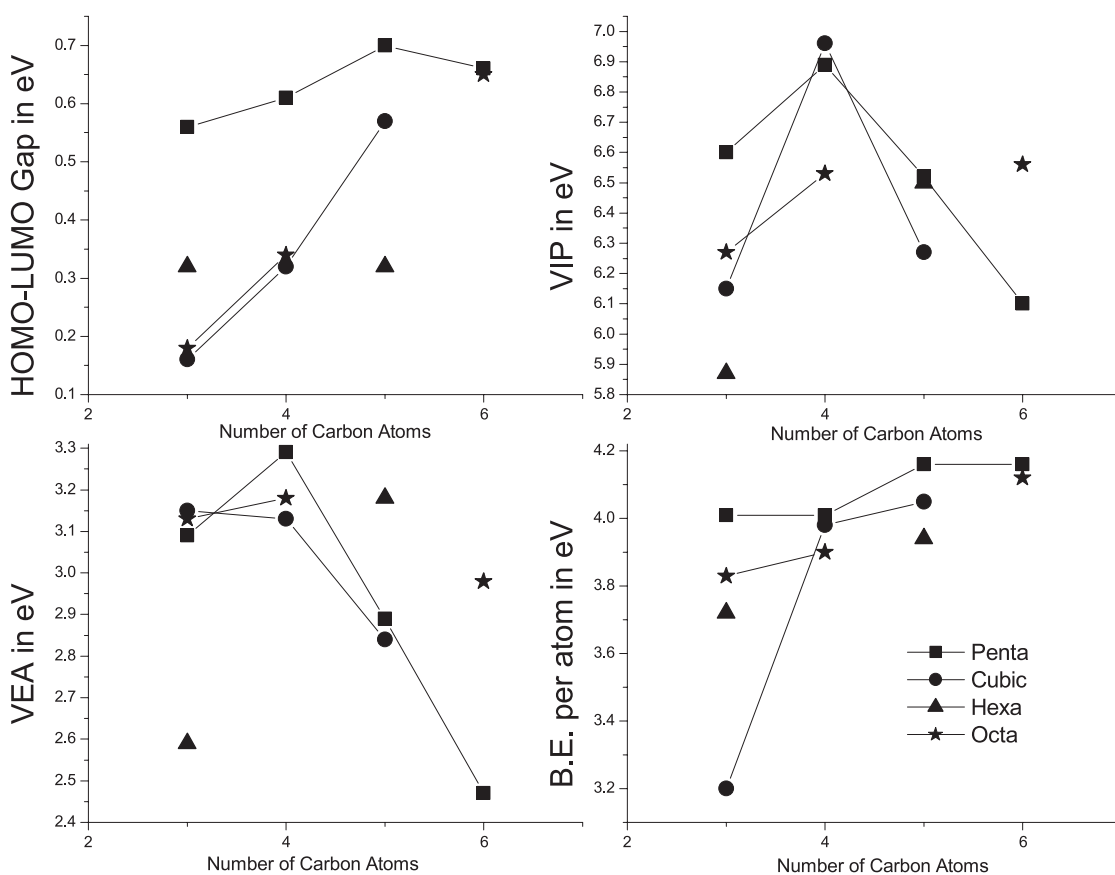


Fig. 2. HOMO-LUMO gap, VIP, VEA and B.E. per atom in eV versus the number of carbon atoms in the Si_{20} nano-structures.

the distortions on the cluster surfaces and contributes to fullerene like structures.

Vertical ionization potentials are considerably higher for all the clusters discussed above. The highest one of 6.96 eV is for Cubic-4, while the lowest one is for Hexa-3 (5.87 eV). No general pattern is however observed in the ionization potentials. They do not depend on the number of carbon atoms in the clusters; the particular structures seem to influence these potentials. Similar comments are found to be true for the vertical electron affinities. These EAs are similar to the DFT study of chromium encapsulated Si_{11} to Si_{14} clusters [18]. Also IPs are of the same order. From Table 1, we can also conclude that, in general, the HOMO-LUMO gaps increase with the carbon atoms. Similar to the study of Connetable et al. [27], one can “tailor” the band gap of such systems for particular applications. Also, except for Penta-4 and Octa-3, all other structures have zero dipole and quadrupole moments. This implies that the overall charge distribution is symmetric contributing to their stability.

As indicated before, we find that putting *at least* three carbon atoms inside the silicon cage helps symmetrize and stabilize the Si cage. In a recent study of Si_{60} with C_{60} fullerene inside the silicon cage, it was observed that the overall structures were highly distorted [24]. Our study along with this fact suggests that the number of carbon atoms in the cage is a variable, which has to be optimized with respect to the number of silicon atoms on the cage

surface to yield highly symmetric and stable cages. If we increase the silicon cage size, the number of carbon atoms inside the cage, their orientations and geometries have to be determined carefully.

In conclusion, we have studied a class of highly symmetric and highly stable Si_{20}C_n clusters. The stability is found to depend on the number of carbon atoms in the Si_{20} cage as also their orientations. The Penta- n structures are found to be more stable, and this fact should be explored further to yield bigger nano-structures. The ionic part of the bonding plays a major role in the electronic and geometric properties of these clusters. Further theoretical and experimental studies are urgently needed to give precise information about hybrid bonding, symmetry and stability of larger cages than considered here.

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