

First principles study of the structure, electronic state and stability of Si_nC_m^- anions

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Abstract

Structure, electronic state and energy of Si_nC^- and Si_nC_2^- ($n = 1-7$) anions have been investigated using the density functional theory. Structural optimization and frequency analysis are performed at the level B3LYP/6-311G(d). The charged-induced structural changes in these anions have been discussed. The strong C–C bond is also favored over C–Si bonds in the Si_nC_m^- anions in comparison with corresponding neutral cluster. Among different Si_nC^- and Si_nC_2^- ($n = 1-7$) anions, Si_3C^- , Si_5C^- and Si_2C_2^- are most stable. Their stability has a decreasing tendency with the increase in the size of these clusters.

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1. Introduction

Silicon carbide (SiC) has become one of the most promising semiconductors for high-power, high-frequency and high-temperature applications [1,2]. It has aroused keen attention from physicists, material scientists as well as chemists. In an

ultrahigh vacuum environment, SiC films [3,4] can be obtained by neutral silicon–carbon cluster depositions. Since the cluster-assembled materials may have uncommon properties, information about the geometric structure and electronic ground state of the clusters is of primary importance. Up to the present the structure and electronic state of neutral Si_nC_m ($n + m < 9$) clusters have been well theoretically understood [5–8]. However, experiments by time-of-flight mass spectroscopy [9,10] have found the evidence for the existence of negatively charged clusters. The

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electronic state and relative stability of these Si_nC_m anions remain unclear. Nakajima et al. [11] explained the structure of Si_nC_m^- ($n + m = 3-6$) utilizing the second-order Moller–Plesset (MP2) theory. Hunsicker et al. [12] performed a combination of MD and DF calculations on the geometric structures of Si_nC_m ($n + m < 9$) anions. Nevertheless more accurate theoretical calculation, frequency analyses and a stability check are required to confirm this explanation. In the present study, with standard B3LYP/6-311G(d) method we extend density functional calculations to Si_nC^- and Si_nC_2^- ($n = 1-7$) anions in order to determine their ground state geometry and their relative stabilities. The charged-induced structural changes in these anions will be discussed.

The rest of the paper is organized as follows. In Section 2, we give a brief description of the computational method used in this work. Results, discussion and stability will be presented in Section 3 for silicon–carbon isomers. Finally, we will summarize our conclusions in Section 4.

2. Computational methods

The B3LYP/6-311G(d) method has been employed to optimize the geometry of Si_nC^- and Si_nC_2^- ($n = 1-7$) clusters. The geometrical optimization of the Si_nC_m^- anion considered here was achieved by searching over a symmetry constrained multidimensional potential energy surface. Frequency analysis are also performed at the same theoretical level to check whether the optimized structures are transition states or true minima on the potential energy surfaces of corresponding clusters. The first electron affinity of various Si_nC_m clusters was calculated with adiabatic approximation. All calculations were carried out using the GAUSSIAN 98 program.

3. Results and discussion

3.1. Geometry

The ground state and metastable state geometric sketch figures of Si_nC_m^- ($n = 1-7$, $m = 1, 2$) are

shown in Figs. 1–6, respectively. Geometric parameters are listed in Table 1. In Figs. 1–6, the “bonds” are shown for internuclear separations less than 0.28 nm (Si–Si), 0.24 nm (Si–C) and 0.20 nm (C–C), respectively. The bigger and smaller spheres denote Si and C atoms, respectively.

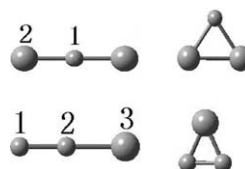


Fig. 1. Structures of (a), (b) Si_2C^- and (c), (d) SiC_2^- clusters.

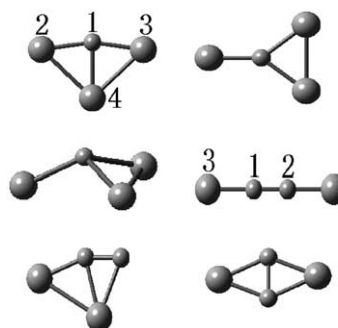


Fig. 2. Structures of (a)–(c) Si_3C^- and (d)–(f) Si_2C_2^- clusters.

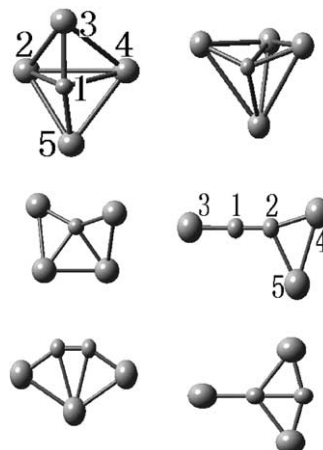
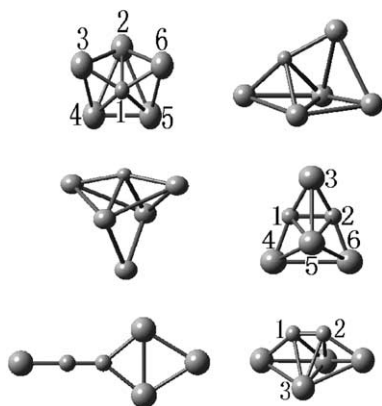
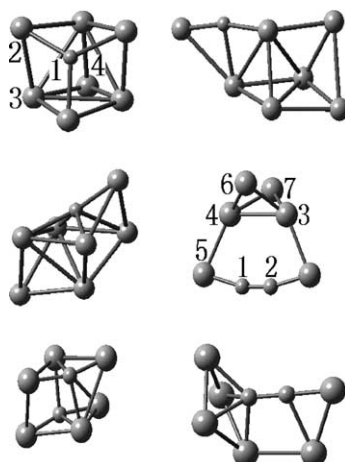
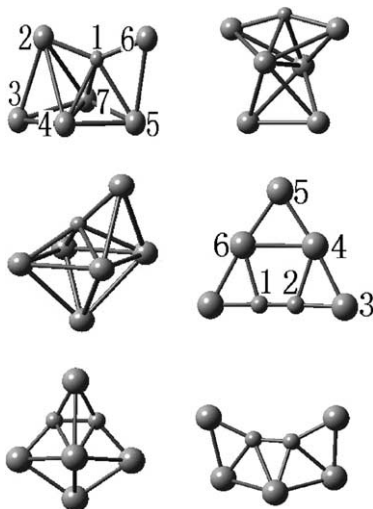


Fig. 3. Structures of (a)–(c) Si_4C^- and (d)–(f) Si_3C_2^- clusters.

Fig. 4. Structures of (a)–(c) Si_5C^- and (d)–(f) Si_4C_2^- clusters.Fig. 6. Structures of (a)–(c) Si_7C^- and (d)–(f) Si_6C_2^- clusters.Fig. 5. Structures of (a)–(c) Si_6C^- and (d)–(f) Si_5C_2^- clusters.

3.1.1. Si_nC^- clusters

The photoelectron spectra [11] of Si_nC^- ($2 < n < 8$) clusters are similar to those of pure Si_{n+1}^- clusters in the peak positions and their envelopes. This similarity indicates that the substitution of a Si atom by a C atom in Si_n^- clusters does not change both the geometrical and electronic structure substantially. This is attributed to the fact that both C and Si atoms take a similar valence structure due to the same family in the periodic table. The structures of Si_4^- , Si_5^- , Si_6^- , Si_7^- and Si_8^- are known to be a rhombus, a trigonal bipyramid, a tetragonal bipyramid, pentagonal

bipyramid, bicapped octahedral structure, respectively [13–16]. Thus the calculated geometrical and electronic structures of Si_nC^- ($2 < n < 8$) clusters should be analogous to those of pure Si_{n+1}^- clusters.

Si_2C^- . The neutral Si_2C can adopt C_{2v} and $\text{D}_{\infty h}$ structures with comparable energy, the linear being $220.28 \text{ kJ mol}^{-1}$ more stable than the C_{2v} isomer. Their energy difference and ordering differ from previous calculations [12] on neutral molecule. This results from two types of different theoretical methods (MP2 and B3LYP). The energy ordering of two structures is preserved in the anion. The linear 1(a) is also predicted to be more stable than that C_{2v} isomer 1(b) by $51.72 \text{ mkJ mol}^{-1}$. The energy difference in two anions is much greater than that in the reference [12].

Addition of an electron to the C_{2v} isomer results in an increase in bond angle α_{CSiC} and stabilizes the linear with respect to the C_{2v} structure. One obtains the linear of the anion 1(a) by starting from either of two neutral species. A comparison of the linear shows that the Si–C bond length in Si_2C anion is longer than that in the neutral molecule by about 1.5%. Additional electron occupies the antibonding lowest unoccupied orbital (LUMO) which is localized between Si and Si atoms and transforms the LUMO in neutral molecule into the highest occupied orbital (HOMO) in anion. The antibonding character of HOMO in anion accounts for the increase of Si–C bond length.

Table 1
Distances between two atoms (L/nm) in Si_nC^- and Si_nC_2^- clusters

Anions	Type	L
Si_2C^-	1–2	0.1721
	1–2	0.1790
	1–4	0.1911
	2–4	0.2430
Si_4C^-	1–2	0.2049
	1–3	0.1806
	2–4	0.2646
	3–5	0.3520
Si_5C^-	1–2	0.2155
	1–3	0.1869
	1–4	0.2057
	2–3	0.2547
	3–4	0.2411
	3–6	0.3330
Si_6C^-	4–5	0.2348
	1–2	0.1896
	1–3	0.3320
	1–4	0.2123
	1–5	0.2127
	1–6	0.1864
	2–3	0.2517
	3–4	0.2385
	3–5	0.4046
	4–7	0.2554
Si_7C^-	5–6	0.2403
	1–2	0.1895
	2–3	0.2483
Si_7C_2^-	3–4	0.2388
	1–2	0.1275
Si_2C_2^-	2–3	0.1756
	1–2	0.1304
Si_3C_2^-	1–3	0.1718
	1–2	0.1318
	1–3	0.1715
	2–4	0.1815
	2–5	0.1955
Si_4C_2^-	4–5	0.2286
	1–2	0.1508
	1–3	0.1870
	1–4	0.1826
	1–5	0.2121
	3–5	0.2551
Si_5C_2^-	4–5	0.2515
	4–6	0.2686
	1–2	0.1329
	2–3	0.1795
Si_5C_2^-	1–6	0.2011

Table 1 (continued)

Anions	Type	L
Si_6C_2^-	4–6	0.2885
	3–4	0.2305
	4–5	0.2288
	1–2	0.1267
	3–4	0.2522
	1–4	0.2729
	1–5	0.1785
	4–5	0.2476
	3–6	0.2318
	6–7	0.3294

Si_3C^- . Rittby [17] has investigated six different neutral isomers using Hartree–Fock (HF) calculation. We support their predictions that the most stable configuration is a rhomboidal C_{2v} structure 2(a). This geometrical structure can be obtained by substitution of a Si atom by a C atom in the Si_4^- anion. The next structure in the energetic ordering is the spatial C_s isomer 2(c), which is an out-of-plane distortion in the planar C_{2v} form 2(b). It is a new isomer with an imaginary bending mode frequency, which locates at $84.80 \text{ kJ mol}^{-1}$ above the rhombus 2(a). The planar 2(b) also with an imaginary bending mode frequency lies $87.95 \text{ kJ mol}^{-1}$ higher in energy. The energy ordering of the anion is partially changed. Two transition states 2(b) ($^2\text{B}_1$) and 2(c) ($^2\text{A}''$) lie 54.35 and $116.05 \text{ kJ mol}^{-1}$ which are less stable than that C_{2v} ($^2\text{A}_2$) isomer 2(a), respectively. The bending mode frequency shows a tendency to want to fold the three silicon atoms into a cyclic 2(a) in both neutral and anionic species.

Addition of an electron to neutral molecule 2(a) yields an increase in Si–Si–Si (2, 4, 3) bond angle by about 3.1%. This results from antibonding nature of the HOMO, which localizes between Si2 and Si3 atoms due to additional electron.

Si_4C^- . Calculations [6] on the Si_4C cluster indicate that the most stable neutral isomer is a trigonal (C_{3v}) bipyramid with the C atom at the apex. The present calculation leads to a different conclusion. This results from two types of different theoretical methods. The trigonal C_{3v} bipyramid [quite similar to the C_s structure 3(b)] lies only 5.78 kJ mol^{-1} higher in energy than the distorted pentagonal ring 3(c) with C_2 symmetry, and

14.18 kJ mol⁻¹ below the C_s isomer [similar to the C_{2v} structure 3(a)]. The energy ordering is significant difference in the anion. As in the previous calculation [12], the energetically most stable structure is the trigonal (C_{2v}, ²A₁) bipyramid 3(a). This is followed by the distorted trigonal C_s bipyramid 3(b) that lies 31.24 kJ mol⁻¹ above the 3(a). Both of them can be obtained by substitution of a Si atom by a C atom in the Si₅⁻ anion. The next low-lying isomer is predicted to be the C₂ (²A) form 3(c) located at 51.46 kJ mol⁻¹ higher in energy. The HOMO–LUMO gap of anion 3(a) is 226.2 kJ mol⁻¹, which is greater than that of any others. This may explain why the trigonal bipyramid 3(a) is stabilized, which is in agreement with the PE spectra [11].

Addition of an electron to the low-lying C_s isomer results in a decrease of separation between atoms (2–4) by about 13.7% in the anionic isomer 3(a). Additional electron occupies the LUMO localized between atom 2 and atom 4, and transforms the LUMO in neutral molecule into the HOMO in the anion. The bonding character of HOMO in anion interprets the decrease of separation between atoms (2–4).

Si₅C⁻. Nakajima et al. [11] and Hunsicker et al. [12] predicted that the lowest-energy Si₅C structure is a C_{2v} octahedron. The present calculation also concludes the same result, which obtained by substitution of a Si atom by a C atom in the Si₆⁻ cluster. Next Si₅C isomer in the energy ordering (only 0.79 kJ mol⁻¹ above the ground state) possesses C_{4v} octahedron geometry with an imaginary axial mode frequency, which corresponds to a relative vibration of four Si atoms in axial direction that ultimately leads to forming the C_{2v} structure. A C_s isomer [quite similar to the 4(b)] lies 34.39 kJ mol⁻¹ above the ground state, which is built by capping a Si atom between atoms (2–4) in the anion 3(a). The energy ordering differs significantly in the anion. The C_{2v} octahedron in the anionic isomers is considerable higher in energy than those discussed as follows and is a transition state. The mode of imaginary frequency shows a tendency for C atom to vibrate in radial direction and leads to a new C_s (²A'') structure 4(a), which is stabilized. This geometrical structure can be viewed as substitution of a Si atom by a C atom in the Si₆⁻ anion. However,

there exists symmetry lowering (C_{2v} → C_s) as the ground state of neutral cluster obtains an electron. The C₁ (²A) structure 4(b) is 8.40 kJ mol⁻¹ higher in energy than 4(a) and 8.14 kJ mol⁻¹ below C_{2v} (²B₁) isomer 4(c). The HOMO–LUMO gap of anion 4(a) is 242.1 kJ mol⁻¹, which is greater than that of any others. This may interpret why the structure 4(a) is stabilized.

Si₆C⁻. Hunsicker et al. [12] gave three lower isomers and found the C_{2v} structure 5(b) to be the most stable both for the anionic and neutral species. We performed geometric optimization with their C_{2v} structure as initial geometry for comparison. The energy of optimized isomer with an imaginary frequency is 63.80 kJ mol⁻¹ less stable than that of C_{5v} (¹A₁) structure we reported [8]. The C_{5v} structure can be obtained by replacing a Si atom with a C atom in structure of Si₇ (a pentagonal D_{5h} bipyramid [18]). A C_s structure lies 15.75 kJ mol⁻¹ higher in energy, which can also be derived from the optimal structure of Si₅C⁻ [4(a)] by capping a Si atom between atoms (2, 4, 5). It is followed at 30.19 kJ mol⁻¹ by another C_s isomer 5(a), which obtained by capping a Si atom between atoms (1,2,3,4) and atoms (1,2,5,4) in the anion 3(a), respectively. The energy ordering of the anionic isomers again differs from that of the neutral structures. The C_{2v} (²B₁) isomer 5(b) and C_s (²A'') isomer 5(c) lie 11.55 and 28.88 kJ mol⁻¹ above the (C_s, ²A'') structure 5(a), respectively. Present calculations indicate that the isomer 5(a) is the most stable form. Nevertheless this assignment must be viewed with caution.

Si₇C⁻. Hunsicker et al. [12] performed a calculation on the three geometric structures of Si₇C and obtained the lowest-energy isomer to be C_s structure 6(c). However, Our present results predict another C_s structure [analogous to 6(a)] as the ground state of Si₇C molecule, which is built from substitution of a Si atom by a C atom in cage-like Si₈ structure [19]. The next structures in the energy ordering are the C₁ isomer 6(b), lying at 3.68 kJ mol⁻¹, and the C_s isomer 6(c) derived from capping the low-energy isomer 5(c) with a Si atom, lying 6.83 kJ mol⁻¹ above the ground state. The energy ordering holds the same trend in the anion. The (C_{3v}, ²A₂) structure 6(a) also is the most favorable form in the anionic isomers. There exists

symmetry increasing ($C_s \rightarrow C_{3v}$) when the ground state of neutral cluster obtains an electron. This results from rearrangement of cluster to minimize its electrostatic energy. The C_1 (2A) isomer 6(b) is 25.20 kJ mol $^{-1}$ higher in energy than the 6(a) and 19.17 kJ mol $^{-1}$ below the C_s ($^2A''$) form 6(c). The HOMO–LUMO gap of anion 6(a) is 230.3 kJ mol $^{-1}$, which is greater than that of any others. This may account for stabilization of the structure 6(a).

3.1.2. $Si_nC_2^-$ clusters

SiC_2^- . The present calculations predict a $C_{\infty v}$ ground state for SiC_2 molecule. A C_{2v} structure 1(d) with bond angle $\alpha_{CSiC} = 40^\circ$ is 6.04 kJ mol $^{-1}$ less stable. Our calculated bond angle compares well with measured value 40–41° [20]. Addition of an electron stabilizes the linear with respect to the C_{2v} form, which is now 34.13 kJ mol $^{-1}$ more stable than the C_{2v} isomer. A comparison of the linear shows that the C–Si bond length in the anion is longer than that in the neutral isomer by about 3.6%. This may be linked to the reduction of electrostatic force between C and Si atoms since an additional electron makes net charge of Si atom to be zero in the anion.

The calculated values of the VDE are 1.44 eV ($C_{\infty v}$) and 1.15 eV (C_{2v}), respectively. While the PE spectrum [11] shows a rather broad peak at 1.54 ± 0.06 eV, which provides further support for the chain 1(c).

$Si_2C_2^-$. Trucks et al. [21] studied rhombic and linear structures of Si_2C_2 molecule. Hunsicker et al. [12] studied six isomers and predicted that the ground state has D_{2h} (1A_g) rhombus 2(f). However, our calculation is that the energy of the rhombus D_{2h} structure is 6.04 kJ mol $^{-1}$ above $D_{\infty h}$ linear and 28.09 kJ mol $^{-1}$ below C_s isomer 2(e). The energy ordering of the structures differs from that of the neutral cluster. Additional electron makes the linear 2(d) stabilized. A noticeable point of this anion is that the charge is equally distributed along the linear (0.4e on per silicon and –0.5e on per carbon) in neutral molecule whereas none of Si atoms bears net charge in the anion. Two low-lying isomers are C_s ($^2A''$) form 2(e) and rhombus D_{2h} ($^2B_{2g}$) isomer 2(f), which locate at 44.63 and 56.71 kJ mol $^{-1}$ above the linear, respectively.

The PE spectrum gives a VDE of 1.93 ± 0.08 eV [11], in satisfactory agreement with the calculated value for the linear. Hence state of $S_2C_2^-$ anion is linear structure, which is different from the calculations [12].

$Si_3C_2^-$. Froudakis et al. [22] investigated five different isomers of neutral Si_3C_2 cluster. We have considered these and other structures and support their results that the most stable configuration is a planar C_{2v} form 3(e). Next in the energy ordering, located at 105.28 kJ mol $^{-1}$ above the 3(e), is a C_{2v} isomer 3(f). There exists an imaginary bending-mode frequency, which shows a tendency to form the bent chain 3(e). The third is two nearly degenerate isomers. One is a D_{3h} bipyramid and another is the C_{2v} isomer quasi-analogous to 3(d). They locate at 107.38 and 107.91 kJ mol $^{-1}$ above the ground state, respectively. The energy ordering of the structures differs significantly in the anion. Addition of an electron stabilizes the C_s ($^2A'$) isomer 3(d) with respect to the other forms. Especially when it obtains an electron, the symmetry of the neutral structure (C_{2v}) is broken into C_s symmetry. Another change is that none of Si atoms bears net charge in the anion whereas all Si atoms bear 0.7e charge in the neutral isomer. The planar C_{2v} (2B_1) pentagon 3(e) is 2.63 kJ mol $^{-1}$ above the ground state, and 89.27 kJ mol $^{-1}$ below the C_{2v} (2A_2) structure 3(f).

Our calculations predict the VDE for the isomers 3(d), (e) and (f) are 2.60 eV (3B_2 state), 1.45 eV (1A_1 state) and 1.62 eV (1A_1 state), respectively. No photoelectron measurements have yet been performed for this cluster, but the pronounced differences between the VDE should facilitate the analysis of future data.

$Si_4C_2^-$. Of the four different isomers of Si_4C_2 investigated by Froudakis et al. [5] and the C_{2v} structure 4(f) has been found to be a stable minimum. We support their conclusions. It can be derived from the minimum structure of Si_3C_2 [3(e)] by capping a Si atom between two C atoms. An octahedron D_{2d} isomer is a stationary point 17.59 kJ mol $^{-1}$ higher in energy. There are several less stable structures, including a C_s structure [similar to 4(d)] 34.39 kJ mol $^{-1}$ above the minimum. The energy ordering differs in the anion. The lowest energy state is found to be the three dimensional C_s

($^2A'$) structure 4(d). Two C_{2v} (2B_1) isomers 4(e) and 4(f) lie 11.29 and 24.68 kJ mol $^{-1}$ less stable relative to 4(d), respectively. The HOMO–LUMO gap of anion 4(d) is 286.9 kJ mol $^{-1}$, and is greater than that of any others. Hence the stabilization of the structure 4(d) may be account for.

The VDE determined from the PE spectrum [2.10 ± 0.08 eV, 11] agrees with our results for 4(d) [2.01 eV] and 4(e) [2.05 eV]. The availability of PE spectra of higher resolution would be particularly valuable if vibrational fine structure could be measured for comparison with the calculated vibrational frequencies. We note, in particular, the pronounced differences between the highest frequencies calculated for the 4(d) and (e) (1064 and 1516 cm $^{-1}$, respectively).

$Si_5C_2^-$. The lowest energy Si_5C_2 isomer is the planar trigonal C_{2v} structure [quite similar to 5(d)]. Strong C–C bond is favored over C–Si bonds in Si_5C_2 which agrees best with Froudakis et al. [5] prediction. Next in the energy ordering is C_s isomer 5(e), which can be derived from the minimum structure of Si_4C_2 [4(f)] by capping an additional Si atom between atoms(1,2,3). This isomer is located at 59.34 kJ mol $^{-1}$ above the ground state. Another C_s structure by replacing two Si atoms with two C atoms in structure of Si_7 (a pentagonal D_{5h} bipyramid [18]) has an energy 65.38 kJ mol $^{-1}$ less stable. The energy ordering of the structures differs in the anion. Additional electron makes the C_2 isomer 5(d) stabilized. The planar trigonal C_{2v} anion corresponding to ground state in neutral cluster lies 5.25 kJ mol $^{-1}$ above the isomer 5(d), which has an imaginary out-of-plane frequency that has a tendency to drive lower-energy structure 5(d). There exists a symmetry lowering ($C_{2v} \rightarrow C_2$) for this isomer. The C_s ($^2A'$) isomer 5(e) and C_1 (2A) isomer 5(f) are 6.56 and 52.77 kJ mol $^{-1}$ less stable above the ground state, respectively.

Our calculations predict the VDE for the isomers 5(d), (e) and (f) are 1.43 eV (1A_1 state), 1.97 eV ($^1A'$ state) and 1.98 eV ($^1A'$ state), respectively. Although no photoelectron measurements are available for this cluster at present, the pronounced differences between the VDE should be useful for future experimental investigations.

$Si_6C_2^-$. The ground state of Si_6C_2 molecule is found to be the C_s structure 6(f). We can very

roughly decompose this structure into two interacting entities: structure 3(a) and 1(b) are bridged with C–C bond. A C_2 isomer is located at 25.47 kJ mol $^{-1}$ higher in energy, which is derived from corner-linked structure 2(a). A C_{3v} isomer locates at 36.76 kJ mol $^{-1}$ above the ground state, which is built from substitution of two Si atoms by two C atoms in cage-like Si_8 structure [19]. Two isomers of the other low-lying species should be pointed out. One is the C_{2v} structure 6(d) and another is the structure quasi similar to 6(e). They are nearly degenerate and lie 42.80 and 45.42 kJ mol $^{-1}$ less stable, respectively. The energy ordering is changed in the anion. The C_{2v} (2A_2) structure 6(d) is energetically favored in the anion. It can be viewed as capping a Si atom in the anion 5(d). Next in energy ordering is the C_{2h} (2A_u) isomer 6(e), which is built from two parallel structures 2(a). This form is located at 42.80 kJ mol $^{-1}$ above the ground state. Structure 6(f) [C_s ($^2A''$)] lies 53.82 kJ mol $^{-1}$ higher in energy. The HOMO–LUMO gap of anion 6(d) is greater than that of any others, so this may explain the stabilization of the structure 6(d).

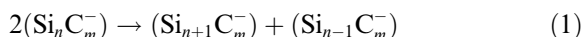
Our calculations predict the VDE for the isomers 6(d), (e) and (f) are 2.76 eV (1A_1 state), 2.34 eV (1A state) and 1.76 eV ($^1A'$ state), respectively. Experimental data on the VDE of this cluster is not available at present.

3.2. Vibrational frequency analysis

A vibrational frequency calculation is important to predict anionic stability. To determine the ground state of clusters, we calculated vibrational frequencies for these clusters. All ground states reported are actually equilibrium states without imaginary frequencies. They are not reported here due to the page limitation.

3.3. Stability

To test the stability of $Si_nC_m^-$ cluster further, The following energy variation of reaction is considered:



We define the energy variation in formula (1) as $D_2(E_n) = E_{n+1} + E_{n-1} - 2E_n$, the second difference in energy for the $Si_nC_m^-$ anions. Hence, we obtain

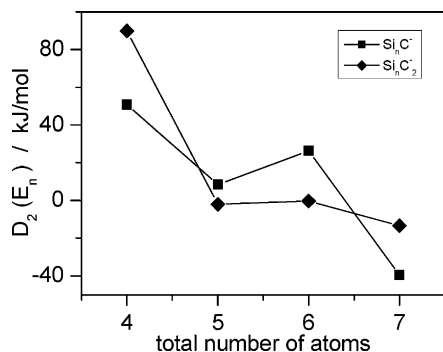


Fig. 7. $D_2(E_n)$ against the number of total atoms.

the curves shown in Fig. 7 corresponding to the energy variation in formulae (1) as the number of total atoms. The larger the $D_2(E_n)$ is, the more stable the cluster corresponding to the number of total atoms is. Thereafter it is clear that the Si_3C^- , Si_5C^- and Si_2C_2^- are more stable in the Si_nC_m^- clusters. The $D_2(E_n)$ values have a decreasing tendency with the increase in the size of these clusters, so the stability of the anionic clusters holds the same trend.

The adiabatic electron affinities (EAs) of Si_nC and Si_nC_2 ($n = 1-7$) are shown in Fig. 8. The trend of EAs values calculated for Si_nC clusters agree reasonably with the measured EAs [11]. The EAs values that the number of total atoms equals to 3 and 6 are smaller values, which correspond to relatively stable state. EAs values have an increasing trend with the increase in the size of these clusters. These results show their stability appears an opposite trend, so this may be the reason that

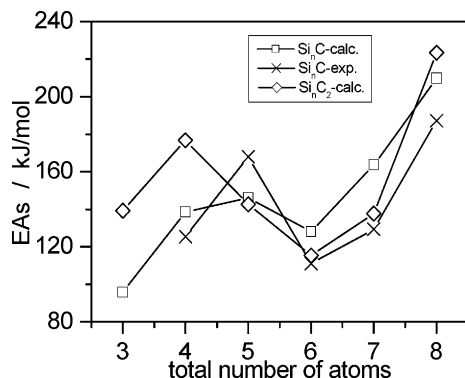


Fig. 8. EAs of Si_nC_m^- cluster against the number of total atoms.

the larger Si_nC and Si_nC_2 clusters have not been observed until now.

4. Conclusions

Geometry, electronic states and energies of Si_nC^- and Si_nC_2^- ($n = 1-7$) have been investigated using the density functional theory. Structural optimization and frequency analysis are performed at the level 6-311G(d). The calculations predict the existence of a number of previously unknown isomers. The strong C–C bond is also favored over C–Si bonds in the Si_nC_m^- anions in comparison with corresponding neutral cluster. The Si_3C^- , Si_5C^- and Si_2C_2^- anions are more stable in the Si_nC^- and Si_nC_2^- ($n = 1-7$) negatively charged clusters. The stability of Si_nC^- and Si_nC_2^- ($n = 1-7$) clusters has a decreasing tendency with the increase in the size of these clusters.

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References

- [1] M. Bhatnagar, B.J. Baliga, IEE Trans. Electron. Devices 40 (1993) 645.
- [2] W.J. Cho, R. Kosugi, J. Senzaki, K. FuKuda, K. Arai, Appl. Phys. Lett. 77 (2000) 2054.
- [3] P. Mélinon, P. Kéghélian, A. Perez, C. Ray, J. Lermé, M. Pellarin, M. Broyer, M. Boudeulle, B. Champagnon, J.L. Rousset, Phys. Rev. B 58 (1998) 16481.
- [4] P. Kéghélian, P. Mélinon, A. Perez, J. Lermé, C. Ray, M. Pellarin, M. Broyer, J.L. Rousset, F.J. Cadete Santos Aires, Eur. Phys. J. D 9 (1999) 639.
- [5] G. Froudakis, A. Zdetsis, M. Mühlhäuser, B. Engels, S.D. Peyerimhoff, J. Chem. Phys. 101 (1994) 6790.
- [6] A.D. Zdetsis, G. Froudakis, M. Mühlhäuser, H. Thümmel, J. Chem. Phys. 104 (1996) 2566.
- [7] S. Erkoc, L. Türker, Phys. E 8 (2000) 50.
- [8] Z.Y. Jiang, X.H. Xu, H.S. Wu, F.Q. Zhang, Z.H. Jin, J. Mol. Struct. (Theochem.) 621 (2003) 279.
- [9] M. Pellarin, C. Ray, P. Mélinon, J. Lermé, J.L. Vialle, P. Kéghélian, A. Perez, M. Broyer, Chem. Phys. Lett. 277 (1997) 96.

- [10] H. Yamamoto, H. Asaoka, *Appl. Surf. Sci.* 169–170 (2001) 305.
- [11] A. Nakajima, T. Taguwa, K. Nakao, M. Gomei, R. Kishi, S. Iwata, K. Kaya, *J. Chem. Phys.* 103 (1995) 2050.
- [12] S. Hunsicker, R.O. Jones, *J. Chem. Phys.* 105 (1996) 5048.
- [13] K. Raghavachari, C.M. Rohlfiing, *J. Chem. Phys.* 89 (1988) 2219.
- [14] K. Raghavachari, C.M. Rohlfiing, *J. Chem. Phys.* 94 (1991) 3670.
- [15] C.M. Rohlfiing, K. Raghavachari, *J. Chem. Phys.* 96 (1992) 2114.
- [16] C.C. Arnold, D.M. Neumark, *J. Chem. Phys.* 99 (1993) 3353.
- [17] C.M.L. Rittby, *J. Chem. Phys.* 96 (1992) 6768.
- [18] S. Li, R.J. Van Zee, W. Weltner Jr., K. Raghavachari, *Chem. Phys. Lett.* 243 (1995) 275.
- [19] F. Hagelberg, J. Leszczynski, V. Murashov, *J. Mol. Struct. (Theochem.)* 454 (1998) 209.
- [20] R.A. Shepherd, W.R.M. Graham, *J. Chem. Phys.* 82 (1985) 4788.
- [21] G.W. Trucks, R.J. Bartlett, *J. Mol. Struct. (Theochem.)* 135 (1986) 423.
- [22] G. Froudakis, M. Mühlhäuser, A. Zdetsis, *Chem. Phys. Lett.* 233 (1995) 619.