

Parity alternation in the linear ground-state beryllium-doped carbon clusters BeC_n^- ($n = 1-8$)

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Abstract

Making use of molecular graphics software, we designed numerous models of BeC_n^- ($n = 1-8$). Geometry optimization and calculation on vibration frequency were carried out by the B3LYP density functional method. After comparison of structure stability, we found that the ground-state isomers of BeC_n^- ($n = 1-8$) are linear with the beryllium atom located at one end of the C_n chain, except that the linear BeC_5^- isomer is slightly higher in energy than the planar cyclic BeC_5^- isomer. When n is even, the C_n chain of BeC_n^- ($n = 1-8$) is polyacetylene-like whereas when at odd n , the carbon chain is cumulene-like. The BeC_n^- ($n = 1-8$) with even n are found to be more stable than those with odd n , and the result is in good accord with the relative intensities of BeC_n^- ($n = 1-8$) observed in mass spectrometric studies. In this paper, we provide satisfactory explanation for such trend of even/odd alternation based on concepts of bonding nature, electronic configuration, electron affinity, incremental binding energy, and dissociation channels.

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1. Introduction

In the past decades, carbon clusters have been studied experimentally and theoretically for better understanding of a large variety of chemical systems [1]. Even before the development of fullerene chemistry, small carbon clusters were studied with considerable interest in astrophysics for the identification of species in interstellar and circumstellar media. Under quasi-collisionless conditions, reactivity is forfeited in the interstellar medium, carbon takes the highly stable, albeit highly reactive, form of linear chains; some of the chains may be terminated by heteroatom(s) [2].

In recent years, carbon clusters doped with heteroatom(s) have received much attention because the addition of heteroatom(s) provides a means to stabilize the carbon chain. By means of secondary ionic emission or laser ionization, a series of hetero-carbon anionic C_nX^- clusters were generated by adding

a heteroatom X to the corresponding carbon clusters C_n^- , where X can be an atom of main group, transition or non-metal element [3–7]. As for beryllium carbon clusters, BeC_n^- ($n = 2-7$) species were detected experimentally by Klein et al. in accelerator mass spectrometry (AMS) investigation [8].

Due to the said interest in astrochemistry and being the basic structural units of new materials with potential applications, the heteroatom-doped carbon clusters have been subject to extensive theoretical investigations. Zheng and coworkers studied C_nN^- ($n = 1-13$) [9], C_nB^- ($n < 13$) [10], C_nP^- ($n = 1-13$) [11], AlC_n^- ($n = 1-11$) [12], and C_nSe^- ($1 \leq n \leq 11$) [13] clusters by means of HF/3-21G level or B3LYP/6-31G* density functional method. Zhan and Iwata reinvestigated C_nN^- ($n = 1-13$) [14], C_nB^- ($n = 1-7$) [15] and C_nP^- ($n = 1-7$) [16] using methods of different approximations such as ab initio. Pascoli and Lavendy proposed structures of C_nN^- ($n = 1-7$) [17] and C_nP^- ($n = 1-7$) [18] based on data collected in B3LYP/6-311G* density functional calculation. Fisher et al. conducted BLYP density functional calculations on structures of C_nP^- ($n = 3-9$) [19]. Tang and coworkers carried out a comparative study on the linear ground-state carbon clusters C_nX^- ($n = 1-10$, X = Na, Mg, Al,

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Si, P, S or Cl) [20], PbC_n^- ($n = 1-10$) [21], and GeC_n^- ($n = 1-9$) [22] by means of DFT/B3LYP method. Vandenbosch and Will analyzed RbC_n^- ($n = 1-10$) clusters theoretically by ab initio method [23]. Hunsicker and Jones performed density functional calculations with annealing simulation on Si_nC_m^- ($n + m \leq 8$) [24]. Gomei et al. investigated various SiC_n^- ($n = 2-5$) anions by ab initio molecular orbital approach [25]. Pan et al. carried out calculations on C_nH^- ($n \leq 10$) using density functional calculations [26]. Using density functional method, Largo et al. carried out studies on AlC_n^- ($n = 1-7$) [27,28], NaC_n^- ($n = 1-8$) [29], MgC_n^- ($n = 1-7$) [30,31], CaC_n^- ($n = 1-8$) [32], and C_nCl^- ($n = 1-7$) [33]. Zhai and Wang performed theoretical study on CrC_n^- ($n = 2-8$) by density functional method [34]. We carried out density functional study on the structures and energies of C_nAs^- ($n = 1-11$) anions [35].

Until now, no theoretical result on BeC_n^- has been published, while in the figure of relative intensity in AMS study, BeC_n^- ($n = 2-7$) show a distinct even/odd pattern of intensity variation: the signals of even n anions are more intense than those of odd n anions by more than an order of magnitude [8]. To explore the experimental observation theoretically, we designed a large number of structural models for BeC_n^- ($n = 1-8$), and performed geometry optimization and calculations on vibration frequencies by means of the B3LYP density functional method. The geometry structure, stability, electronic configuration, bonding character, electron affinity, incremental binding energy, and dissociation channels of the anionic clusters were investigated. Based on the results, we provide explanation on why the BeC_n^- ($n = 1-8$) isomers with even n are more stable than those with odd n . The outcome can serve as helpful guideline for the synthesis of related materials as well as for future theoretical studies of carbon/beryllium binary clusters.

2. Computational method

During the investigation, devices for molecular graphics, molecular mechanics, and quantum chemistry examination were used. First, a three-dimensional model of a cluster was designed using HyperChem for Windows on a PC/Pentium IV computer [36]. Then, the model was optimized by MM+ molecular mechanics and semi-empirical PM3 quantum chemistry. At the final stage, geometry optimization and calculations of

vibration frequencies were conducted using the B3LYP density functional method of Gaussian 98 package [37] with 6-31G* basis sets, i.e., Becke's 3-parameter non-local exchange functional with the correlation functional of Lee–Yang–Parr [38,39]. The single point energy calculations following the optimizations were performed using the larger 6-311+G* basis set, including diffuse functions (i.e., B3LYP/6-311+G*/B3LYP/6-31G*) [40]. All energies were calculated with zero point energy (ZPE) correction. It has been pointed out that geometries computed with more expensive basis sets do not necessarily lead to more accurate final results [41]. The optimized models were again displayed using HyperChem for Windows. The data of partial charges and bond orders were analyzed with Gaussian Natural Bond Orbital (NBO). All of the calculations were carried out on the servers of SGI.

3. Results and discussion

3.1. Geometry and energy

At the beginning of the study, nothing was known other than the BeC_n^- ($n = 1-8$) formula. The “guessing” of a reasonable geometrical structure was the initial step for the optimization process. We examined many isomers, among which are linear, cyclic and bicyclic as well as three-dimensional in structure. In this paper, those with imaginary frequency, high energy, and large spin contamination are excluded. Shown in Figs. 1 and 2 are the BeC_n^- ($n = 1-8$) isomers corresponding to local minima with real vibration frequencies. In the figures, light gray (bigger) balls represent carbon atoms and dark gray (smaller) ones denote beryllium atoms; also for the models of a particular n , they are arranged in the order of ascending total energy. The 23 isomers of BeC_n^- ($n = 1-5$) acquired are shown in Fig. 1: one for BeC^- (Model 1a), three for BeC_2^- (Models 1b–1d), four for BeC_3^- (Models 1e–1h), six for BeC_4^- (Models 1i–1n), and nine for BeC_5^- (Models 1o–1w). Depicted in Fig. 2 are 23 isomers of BeC_n^- ($n = 6-8$): 7 for BeC_6^- (Models 2a–2g), 11 for BeC_7^- (Models 2h–2r), and 5 for BeC_8^- (Models 2s–2w). As far as we know, none of these models have been reported before.

Listed in Table 1 are the symmetry, electronic state, spin contamination (before annihilation), total energy, and relative energy of the BeC_n^- ($n = 1-8$) structures displayed in

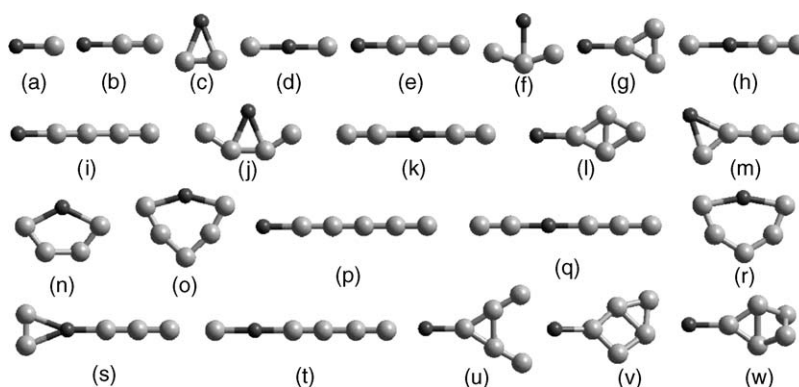
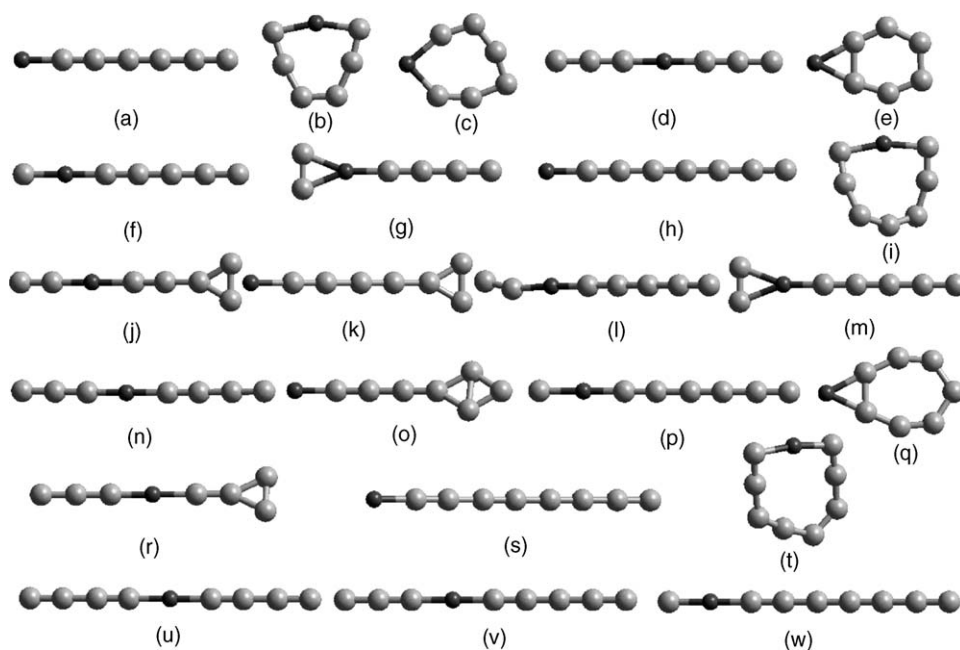


Fig. 1. Twenty-three isomers of C_nBe^- ($n = 1-5$).

Fig. 2. Twenty-three isomers of $C_n\text{Be}^-$ ($n=6-8$).

Figs. 1 and 2. According to the relative energies and with BeC_5^- being the only exception, the ground-state geometries of BeC_n^- ($n=1-8$) are linear in configuration with the beryllium atom located at the end of C_n chain. As for BeC_5^- , the linear structure with the beryllium atom located at the end of C_5 (Model 1p) is the second most stable isomer, it is beaten by the planar cyclic structure (Model 1o) by 3.8 kcal/mol. In view of such a small difference in relative energy, we consider that Model 1p is also

a candidate for ground-state BeC_5^- and in the later discussion Model 1p is considered as the ground-state of BeC_5^- . In some cases of NaC_n^- and MgC_n^- clusters, the ground-state isomers are cyclic rather than linear in configuration [29–31]. In the planar ring of Model 1o, the p_z orbital of the six atoms overlap and the six π electrons delocalize to form a cyclic π bond, causing a reduction in total energy. The six outward orbitals form pseudo cyclic π orbitals, and other 5 carbon valence electrons

Table 1
Symmetry, electronic state, spin contamination ($\langle S^2 \rangle$) (before annihilation), total energy (a.u.), and relative energy (kcal/mol) of BeC_n^- ($n=1-8$) based on B3LYP/6-31G* geometries and B3LYP/6-311+G* energies

Model	Anion	Symmetry	State	$\langle S^2 \rangle$	Total energy	Relative energy	Model	Anion	Symmetry	State	$\langle S^2 \rangle$	Total energy	Relative energy
1a	BeC^-	$C_{\infty v}$	$4\Sigma^-$	3.7650	-52.6396	0.00	2a	BeC_6^-	$C_{\infty v}$	$2\Sigma^+$	0.7540	-243.2297	0.00
1b	BeC_2^-	$C_{\infty v}$	$2\Sigma^+$	0.7527	-90.8650	0.00	2b	BeC_6^-	C_s	$2A'$	0.7634	-243.2236	3.86
1c	BeC_2^-	C_s	$4A'$	3.7565	-90.7598	60.00	2c	BeC_6^-	C_s	$2A'$	0.7597	-243.1661	39.92
1d	BeC_2^-	$D_{\infty h}$	$4\Pi_g^-$	3.8005	-90.4160	157.49	2d	BeC_6^-	$D_{\infty h}$	$2\Pi_u$	0.7582	-243.1352	59.30
1e	BeC_3^-	$C_{\infty v}$	$4\Sigma^-$	3.7801	-128.9147	0.00	2e	BeC_6^-	C_s	$4A'$	3.7886	-243.1226	67.22
1f	BeC_3^-	C_{2v}	$4B_1$	3.7881	-128.8869	17.41	2f	BeC_6^-	C_s	$4A'$	3.7642	-243.1046	78.51
1g	BeC_3^-	C_{2v}	$2A_1$	0.7557	-128.8788	22.53	2g	BeC_6^-	$C_{\infty v}$	$4\Sigma^-$	3.7930	-243.0855	90.49
1h	BeC_3^-	$C_{\infty v}$	$4\Sigma^-$	3.7590	-128.8577	35.73	2h	BeC_7^-	$C_{\infty v}$	$4\Sigma^-$	3.8308	-281.2907	0.00
1i	BeC_4^-	$C_{\infty v}$	$2\Sigma^+$	0.7538	-167.0520	0.00	2i	BeC_7^-	C_2	$2B$	0.7978	-281.2718	11.90
1j	BeC_4^-	C_2	$2A$	0.7553	-167.0254	16.72	2j	BeC_7^-	C_{2v}	$2B_2$	0.7643	-281.2540	23.06
1k	BeC_4^-	$D_{\infty h}$	$2\Sigma_u$	0.7681	-167.0084	27.37	2k	BeC_7^-	C_{2v}	$2A_1$	0.7553	-281.2532	23.52
1l	BeC_4^-	C_s	$2A'$	0.7577	-166.9434	68.14	2l	BeC_7^-	C_s	$4A''$	3.8074	-281.2407	31.39
1m	BeC_4^-	C_s	$4A'$	3.7587	-166.9360	72.82	2m	BeC_7^-	C_s	$4A''$	3.8116	-281.2376	33.34
1n	BeC_4^-	C_2	$4A$	3.7663	-166.9124	87.65	2n	BeC_7^-	C_s	$4A''$	3.7858	-281.2365	34.01
1o	BeC_5^-	C_{2v}	$2B_1$	0.7650	-205.1135	0.00	2o	BeC_7^-	$C_{\infty v}$	$4\Sigma^-$	3.7631	-281.2219	43.20
1p	BeC_5^-	$C_{\infty v}$	$4\Sigma^-$	3.8051	-205.1074	3.80	2p	BeC_7^-	C_{2v}	$2A_1$	0.7547	-281.2058	53.28
1q	BeC_5^-	$C_{\infty v}$	2Π	0.7762	-205.0933	12.68	2q	BeC_7^-	C_s	$4A''$	3.7726	-281.1999	57.01
1r	BeC_5^-	C_s	$4B_1$	3.7866	-205.0544	37.10	2r	BeC_7^-	C_{2v}	$4B_2$	3.7820	-281.1844	66.70
1s	BeC_5^-	C_s	$4A''$	3.8003	-205.0464	42.08	2s	BeC_8^-	$C_{\infty v}$	$2\Sigma^+$	0.7540	-319.4044	0.00
1t	BeC_5^-	$C_{\infty v}$	$4\Sigma^-$	3.7618	-205.0445	43.32	2t	BeC_8^-	C_s	$2A'$	0.7665	-319.3931	7.08
1u	BeC_5^-	C_{2v}	$2A_1$	0.7563	-204.9699	90.10	2u	BeC_8^-	$D_{\infty h}$	$2\Pi_g$	0.7664	-319.3871	10.88
1v	BeC_5^-	C_s	$4A''$	3.7711	-204.9597	96.52	2v	BeC_8^-	$C_{\infty v}$	4Π	3.8086	-319.3368	42.45
1w	BeC_5^-	C_2	$4B$	3.7581	-204.9049	130.91	2w	BeC_8^-	$C_{\infty v}$	4Π	3.7890	-319.2649	87.54

stay in the three bonding orbitals. This monocyclic structure with $4m + 2$ ($m = 1$) π electrons show aromatic character and is a stable structure.

With n bigger than 4, there are quite a number of monocyclic BeC_n^- ($n = 4-8$) structures (Models 1n, 1o, 1r, 2b, 2c, 2i, and 2t). The distance from beryllium atom to the terminus carbon atoms in Models 1f and 1j are 1.838 and 1.996 Å, respectively, exhibiting some characters of weak bonding between the Be atom and the terminus carbon atoms. Models 2e and 2q are clusters with a beryllium atom bonded to one side of a C_n ($n = 6, 7$) cyclic ring. Models 2j, 2k, and 2r are structures with a C_3 ring connected to a carbon chain with the beryllium atom located either inside or at the other end of the carbon chain. Models 1s, 2g, and 2m are structures with a C_2Be ring connected to a carbon chain via the beryllium atom. We find that linear structures with the beryllium atom located inside the chain configuration are not uncommon among the BeC_n^- ($n = 2-8$) isomers, for example, Models 1d, 1h, 1k, 1q, 1t, 2d, 2f, 2n, 2p, 2u, 2v, and 2w.

For isomers close in energy, a difference in calculation method might result in difference in energy ordering. In order to test the authenticity of the obtained DFT energies, CCSD(T)/6-311+G* and QCISD(T)/6-311+G* calculations were also applied on BeC_2^- and BeC_3^- isomers. The CCSD(T) energies for Models 1b, 1c, 1d, 1e, 1f, 1g, and 1h are -90.5902, -90.4911, -90.3845, -128.5334, -128.5168, -128.5074, and -128.4928 a.u., respectively. The QCISD(T) energies are

-90.5910, -90.4921, -90.3842, -128.5350, -128.5184, -128.5083, and -128.4937 a.u., respectively. In both cases, the energy ordering is the same as that of B3LYP/6-311+G*.

3.2. Bonding character

Depicted in Fig. 3 are the bond lengths, NBO charges and bond orders of the linear ground-state BeC_n^- ($n = 1-8$) structures (Models 1a, 1b, 1e, 1i, 1p, 2a, 2h, and 2s). It is apparent that the deviation of bond lengths (Å) at the B3LYP/6-311G* level (shown in parentheses in Fig. 3) have little effect on the geometries of the linear ground-state BeC_n^- ($n = 1-8$). According to the calculated bond lengths, the Be–C bond lengths are in the 1.554–1.600 Å range, and Be–C bond length increases with a rise in n , exhibiting essentially the characteristic of single bond. The bonding of small linear carbon chains could be either cumulene- or polyacetylene-like [42]. Along the straight carbon chains of the linear ground-state BeC_n^- ($n = 2-8$) isomers, there is an alternate short-and-long pattern in C–C length (1.246–1.254 and 1.328–1.345 Å, respectively) when n is even, displaying a typical polyacetylene-like character; when n is odd, the C–C bond lengths tend to average out (1.270–1.315 Å), exhibiting some sort of cumulenic character. As an illustration, depicted in Fig. 4 are the bond lengths of the linear ground-state BeC_7^- and BeC_8^- clusters versus the number of bond (as counted from the left side of chains in Fig. 3, e.g., the Be–C

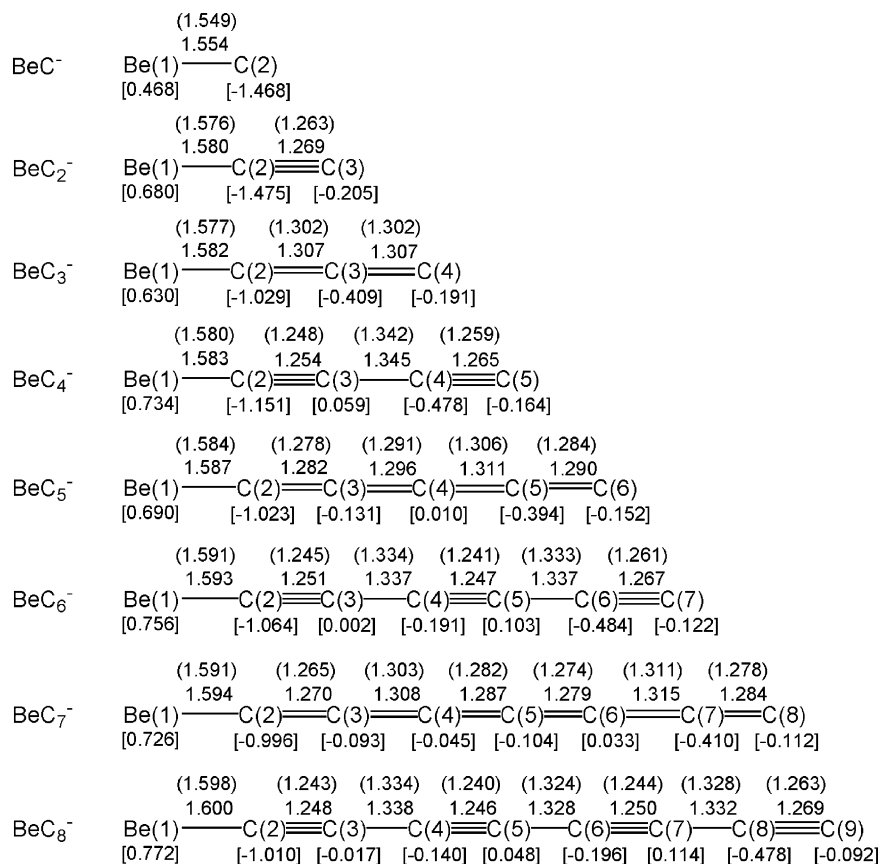


Fig. 3. Bond lengths (Å) at B3LYP/6-31G* level, bond lengths (Å) at B3LYP/6-311G* level (in parentheses), NBO charges (in square parentheses), and bond orders (line number between two atoms) of the linear ground-state BeC_n^- ($n = 1-8$) clusters.

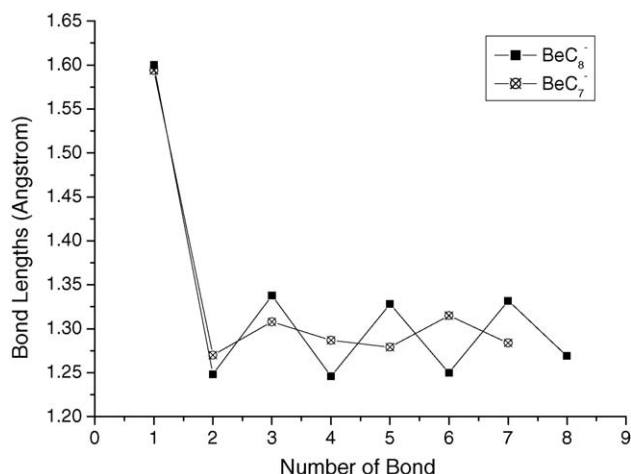


Fig. 4. Bond lengths (in Å) of the linear ground-state BeC₇⁻ and BeC₈⁻ clusters based on B3LYP/6-31G* geometries vs. the number of bond (as counted from the left side of chains in Fig. 3).

bond length is plotted against “1” and so on), the curve of BeC₈⁻ with polyacetylene-like carbon chain displays obvious short/long alternation, whereas that of BeC₇⁻ with cumulene-like carbon chain exhibits sign of averaging out. Shown in Fig. 5 is the length of the last C–C bonds (at the right side of the BeC_n⁻ ($n=2-8$) isomers as shown in Fig. 3) versus the number of carbon atoms; there is an obvious trend of odd/even alternation: for odd n , the C–C lengths at the end of chain are within 1.284–1.307 Å; for even n , the C–C lengths at the terminus of the chain are within 1.265–1.269 Å.

According to the NBO charges shown in Fig. 3, the majority of positive charge is located on the beryllium atom (in the range of 0.466–0.772). There is also a sort of small/big alternation with odd/even n : the positive charge at the beryllium atom of an even n isomer is bigger than that of neighboring odd n isomers, and the level of the positive charge increases with a rise in n (Fig. 6). The negative charge is distributed among the carbon atoms, and the carbon atom bonded to the beryllium atom shows the highest level of negative charge.

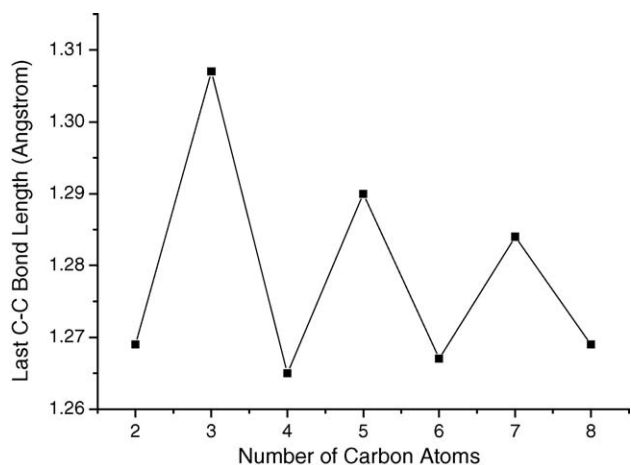


Fig. 5. Length (Å) of the last C–C bond of the linear ground-state BeC_n⁻ ($n=2-8$) clusters (at the right side of chains in Fig. 3) based on B3LYP/6-31G* geometries vs. n .

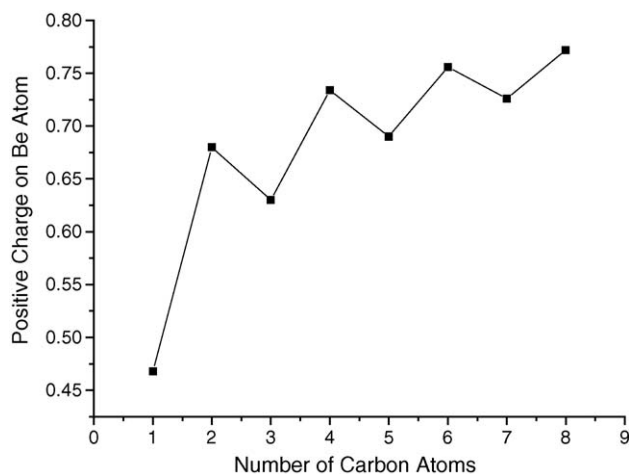


Fig. 6. Positive charge on beryllium atom of the linear ground-state BeC_n⁻ ($n=1-8$) clusters vs. n .

Also, according to the results of NBO bond order analysis shown in Fig. 3, when n is even, the carbon chains are clearly characterized by a series of alternate single and triple bond, and the anions adopt a Be(–C≡C)_x ($x=1-4$) structure that shows characteristics of polyacetylene-like clusters. For odd n , the carbon chains show character of double bond and the cumulene-like isomers adopt a Be–C(=C=C)_y ($y=0-3$) structures.

3.3. Electronic configuration

Shown in Table 2 are the configuration of valence orbital for the linear ground-state BeC_n⁻ ($n=1-8$) clusters.

The electronic configurations can be depicted as (except for BeC⁻):

$$(\text{core})1\sigma^2 \dots 1\pi^4 \dots (n+2)\sigma^1 \left(\frac{n+1}{2}\right)\pi^2, \quad n = \text{odd}$$

$$(\text{core})1\sigma^2 \dots 1\pi^4 \dots (n+2)\sigma^1 \left(\frac{n}{2}\right)\pi^4, \quad n = \text{even}$$

The linear ground-state BeC_n⁻ ($n=1-8$) clusters possess $(4n+3)$ valence electrons, among which are $2n$ π electrons, and $2n+3$ σ electrons. Thus for even n , the highest occupied molecular orbital (HOMO) with doubly degenerate π orbital is fully occupied. Such a situation (i.e., with fully filled π orbital) is energetically more favorable than that with a half-filled electron shell. The linear ground-state BeC_n⁻ ($n=1-8$) alternates between $^2\Sigma^+$ (even n) and $^4\Sigma^-$ (odd n) electronic states. This

Table 2

Valence orbital configuration of the linear ground-state BeC_n⁻ ($n=1-8$) clusters

Isomers	Configuration
BeC ⁻	(core) $\sigma^2\sigma^2\sigma^1\pi^2$
BeC ₂ ⁻	(core) $\sigma^2\sigma^2\sigma^2\sigma^1\pi^4$
BeC ₃ ⁻	(core) $\sigma^2\sigma^2\sigma^2\pi^4\sigma^2\sigma^1\pi^2$
BeC ₄ ⁻	(core) $\sigma^2\sigma^2\sigma^2\sigma^2\pi^4\sigma^2\sigma^1\pi^4$
BeC ₅ ⁻	(core) $\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\pi^4\pi^4\sigma^2\sigma^1\pi^2$
BeC ₆ ⁻	(core) $\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\pi^4\pi^4\sigma^2\sigma^1\pi^4$
BeC ₇ ⁻	(core) $\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\pi^4\pi^4\pi^4\sigma^2\sigma^1\pi^2$
BeC ₈ ⁻	(core) $\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\pi^4\pi^4\pi^4\pi^4\sigma^2\sigma^1\pi^4$

Table 3

Electron affinity EA (kcal/mol), atomization energy ΔE_a (a.u.), incremental binding energy ΔE^I (a.u.) of the linear ground-state BeC_n^- ($n=1-8$) based on B3LYP/6-31G* geometries and B3LYP/6-311+G* energies

Clusters	EA	ΔE_a	ΔE^I
BeC^-	16.77	0.1111	
BeC_2^-	72.09	0.4793	0.3682
BeC_3^-	61.89	0.6718	0.1925
BeC_4^-	90.21	0.9519	0.2802
BeC_5^-	74.54	1.1501	0.1982
BeC_6^-	99.69	1.4152	0.2651
BeC_7^-	76.19	1.6190	0.2038
BeC_8^-	106.56	1.8755	0.2565

arises from the fact that all MOs with π -symmetry are doubly degenerate. When n is odd, the addition of an extra carbon atom would result in having two more electrons included in the π -system, and the accommodation of these two electrons in a π orbital would lead to a quartet state. When n is even, the addition of an extra carbon atom would lead to a doublet state.

3.4. Electron affinity

Electron affinity (EA, adiabatic) is computed as the energy difference between the optimized neutral and anionic (i.e., $E_{\text{neutral}} - E_{\text{anion}}$) clusters. A higher electron affinity means that more energy is released when an electron is added to the neutral molecule, and the production of the corresponding anion is more readily done. The anionic cluster with a larger electron affinity is generally more stable. Hence, electron affinity can be used as another criterion to evaluate the relative stability of anionic clusters with different sizes.

Listed in Table 3 are the electron affinity, atomization energy (ΔE_a), and incremental binding energy (ΔE^I) of the linear ground-state BeC_n^- ($n=1-8$) whereas Fig. 7 depicts the electron affinity values versus the number of carbon atoms in the linear ground-state BeC_n^- ($n=1-8$) clusters. There is a parity effect on the EA curve of BeC_n^- : the EA of even n clusters

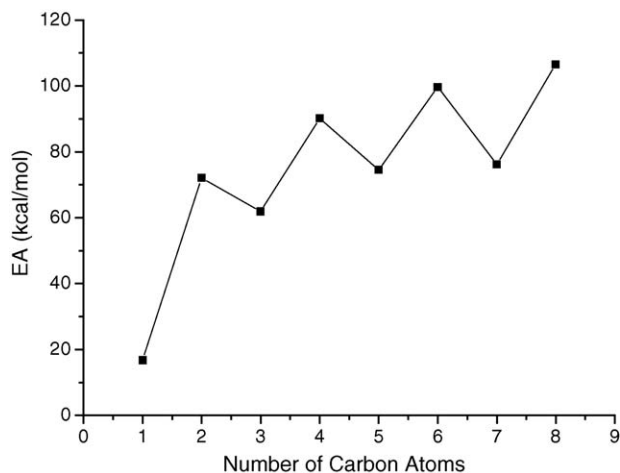


Fig. 7. Electron affinity EA (kcal/mol) of the linear ground-state BeC_n^- ($n=1-8$) clusters (as shown in Table 3) based on B3LYP/6-31G* geometries and B3LYP/6-311+G* energies vs. n .

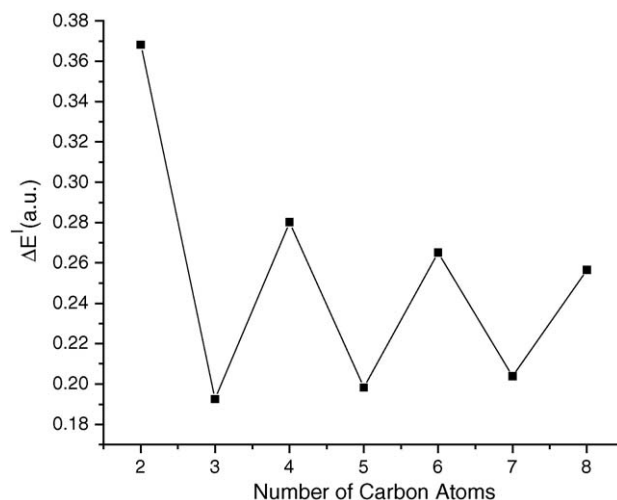


Fig. 8. Incremental binding energies ΔE^I (kcal/mol) of the linear ground-state BeC_n^- ($n=2-8$) clusters (as shown in Table 3) based on B3LYP/6-31G* geometries and B3LYP/6-311+G* energies vs. n .

are higher than those of adjacent odd n cluster(s). This behavior reflects the higher stability of the even n BeC_n^- ($n=1-8$) clusters.

3.5. Incremental binding energy

The incremental binding energy (ΔE^I) which is the atomization energy (ΔE_a) difference of adjacent clusters can also reflect the relative stability of the anionic clusters (Table 3) [43]. It is expressed as:

$$\Delta E^I = \Delta E_a(\text{BeC}_n^-) - \Delta E_a(\text{BeC}_{n-1}^-);$$

where ΔE_a is defined as the energy difference between a molecule and its component atoms:

$$\Delta E_a = n E(\text{C}) + E(\text{Be}) - E(\text{BeC}_n^-).$$

As showed in Fig. 8, the values of ΔE^I vary according to a pattern of odd/even alternation: when n is even, the ΔE_n value is big; when n is odd, the ΔE_n is small. Because a larger ΔE^I value implies a more stable BeC_n^- structure, one can deduce that a BeC_n^- cluster with even n is more stable than one with odd n . Such odd/even alternate pattern of electron affinity and incremental binding energy is in consistency with the experimental observation of Klein and Middleton by means of accelerator mass spectrometry (AMS) of BeC_n^- ($n=2-7$) [8].

3.6. Dissociation channels

Due to the existence of a beryllium atom at one end of the carbon chains, the possible dissociation channels of BeC_n^- ($n=1-8$) could be rather complicated. Although we do not attempt to characterize the reaction pathways and transition states for fragmentation in this work, we evaluated the relative stability of the clusters in term of fragmentation energy based on hypothetical reactions. The energies for fragmentation versus n are depicted in Fig. 9. The six dissociation channels are divided into two categories: reactions (1)–(3) with C, C_2 , and

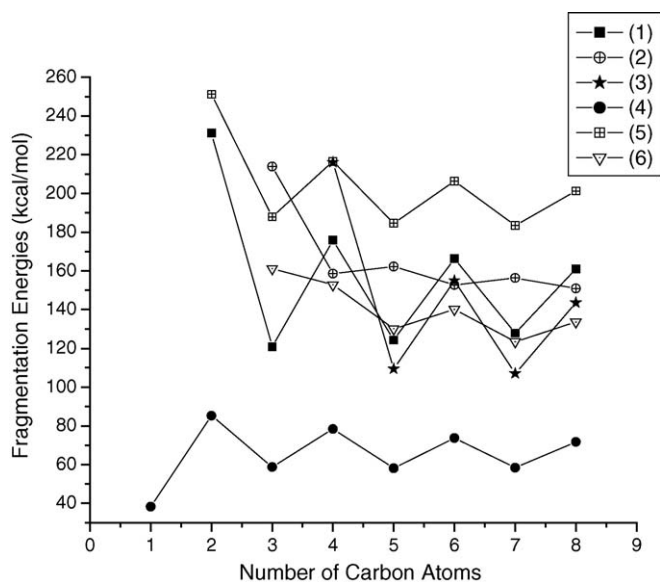
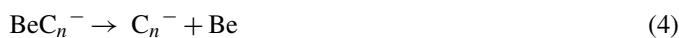


Fig. 9. Fragmentation energy (kcal/mol) based on B3LYP/6-31G* geometries and B3LYP/6-311+G* energies vs. n .

C_3 generation and reactions (4)–(6) with Be, BeC, and BeC₂ generation.



Fragmentation energy related to reaction (1) with the release of one carbon atom exhibits distinct odd/even alternation, and the dissociation energies of BeC_{*n*}[−] with even *n* are always larger than those with odd *n* (Fig. 9). The results are consistent with the observation that BeC_{*n*}[−] anions with even *n* are relatively more stable; the ejection of a single carbon atom will cause an inverse in parity of the clusters and the more stable “even *n*” clusters requires more energy for fragmentation than the less stable “odd *n*” clusters. According to the curve of the last C–C bond lengths shown in Fig. 5, the bond lengths show a long/short pattern along with odd/even variation of *n*, whereas in Fig. 9, the energy curve of reaction (1) shows the inverse tendency. It is understandable because the energy needed for the breaking of a triple bond (*n*-even cases) is bigger than that of a double bond (*n*-odd cases). In reaction 2, the losing of a C₂ fragment does not cause significant change in parity of the parent anionic clusters, and the alternation effect is less apparent than that of reaction (1). The dissociation energy needed for reaction (3) repeats the alternation tendency of reaction (1). In reaction (3), the energy needed for dissociation is smaller than that required for reactions (1) and (2) due to the special structural stability of the C₃ fragment as previously pointed out by Rao et al. [44]. The dissociation energy of reactions (4) and (5) which involve

the loss of Be and BeC, respectively, exhibit similar odd/even alternation. Relatively speaking, reaction (6) with the loss of a BeC₂ fragment does not cause a significant change in parity. In other words, the energy needed for BeC_{*n*}[−] anions dissociation in reactions (1), (3), (4), and (5) is bigger in the cases of even *n* as compared to those of odd *n*. The results also indicate that the fragmentation channel of lowest energy is reaction (4) and the loss of a beryllium atom could be the dominant dissociation pathway for BeC_{*n*}[−] (*n* = 1–8).

4. Conclusion

The ground-state isomers of BeC_{*n*}[−] (*n* = 1–8) are linear in structure with the beryllium atom located at one end of the C_{*n*} (*n* = 1–8) units, except for BeC₅[−]. For the chain with even number of carbon atoms, the bond lengths and bond orders suggest a polyacetylene-like structure, whereas for those with odd number of carbon atoms, the data suggest a cumulene-like arrangement. The anionic clusters with “even *n*” are more stable than those with “odd *n*”. The trend of odd/even alternation can be observed from the variation of bonding length, positive charge of beryllium atom, electron affinity, incremental binding energy, and dissociation channels. The results of calculation are in good agreement with the relative intensity of the BeC_{*n*}[−] species observed in AMS studies.

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