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A density functional study of the structures and energies of $C_nP_5^-$ ($n = 1$–7) clusters

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Abstract

Using molecular graphics software, we have designed numerous models of $C_nP_5^-$ ($n = 1$–7). We carried out geometry optimization and calculation on vibrational frequency by means of the B3LYP density functional method. After comparing the total energies of the isomers, we found that the ground state structures are straight carbon chains with a P_4C ring connected at one end and a phosphorus atom at the other. The alternate behaviours in electron affinity, bond length, and incremental binding energy with odd and even "n" match the peak pattern observed in the laser-induced mass spectra of $C_nP_5^-$ ($n = 1$–7) and the results of experimental reactions. When n is even, the electron state is $^1A_1$, whereas it is $^3A_2$ with odd n. The bond lengths of straight C_n chains show a polyacetylene-like structure. As for the C–P bonds within the straight chains, there is an alternate pattern in length, i.e., compared to the C–P bonds at even n, those at odd n show a bigger bond length.

Keywords: Binary cluster anions; $C_nP_5^-$; Phosphorus-doped carbon clusters; Density functional study

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1. Introduction

Studies of carbon clusters and compounds have opened up research fields of new dimensions. Recently, experimental and theoretical research on binary clusters has prompted much interest. Compared to the other elements, carbon and phosphorus clusters are more likely to show close-cage structures. Binary clusters of carbon and a non-metal element (e.g., O, N, and S) have been discovered in celestial bodies [1,2]. The existence of organo-phosphorus species in circumstellar and interstellar media is possible [3]. It is known that stable C/P binary anions can be prepared by reacting small anionic carbon clusters with gaseous P_4 [4]. It has also been reported that C/P binary clusters could be generated by means of unconventional methods such as laser ablation and high-energy electron bombardment [5–7].

Recently, there have been reports on the theoretical investigations of C/P binary clusters. Zhan and Iwata optimized the geometric structures of C_nP^- ($n = 1$–7) using ab initio calculation [8]. Pascoli and Lavendy proposed structures of C_nP, C_nP^-, C_nP^+ ($n = 1$–7) and $C_nP_p^+$ ($n + p = 3$–6) based on data collected in density functional calculations [9–11]. Using the HF method, Liu et al. carried out calculations on linear C_nP^- ($n = 1$–11) [12,13]. Fisher et al. conducted BLYP density functional calculations on structures of C_nP^- and $C_nP_2^-$ ($n = 3$–9), some $C_4P_4^-$, two $C_4P_5^-$ and one $C_6P_5^-$ structures [4]. Zeng et al. analysed C_nP_2 ($n = 3$–9) clusters theoretically by adopting the density functional method [7]. del Río et al. investigated various geometries of C_3P and C_3P^+ by ab initio calculation [14]. Largo et al. carried out an ab initio molecular orbital study of C_2P entities and cations [15]. Despite the work that has already been reported, our understandings of these materials are still limited. Until now, few theoretical report on $C_nP_5^-$ binary clusters has been published, while the time-of-flight mass spectra of C/P binary clusters showed distinct peaks of $C_nP_5^-$ at even n [5–7]. The $C_nP_5^-$ anions were observed only for $n = 4, 6, 8$ by the reactions of small carbon anions with gaseous P_4 [4]. To view the issue theoretically, we designed tens of structural models of $C_nP_5^-$ ($n = 1$–7), and performed geometry optimization and calculations on vibrational frequencies on the basis of the B3LYP density functional method. After comparing the stability of all of the models, we summarized the general patterns and proposed

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structural rules for $C_nP_5^-$. We explained why the $C_nP_5^-$ ($n = 1$–7) isomers with even n are more stable than those with odd n. The outcome can serve as helpful guidelines for the synthesis of related materials as well as for future theoretical studies of binary clusters.

2. Computational method

During the investigation, devices for molecular graphics, molecular mechanics, and quantum chemistry were used. First, a three-dimensional model of a cluster was designed using HyperChem 5.0 for Windows [16] and Desktop Molecular Modeler 3.0 for Windows [17]. Then, the model was optimized in an orderly manner by MM+ molecular mechanics and semi-empirical PM3 quantum chemistry. Last, geometry optimization and calculations of vibrational frequencies were conducted using the B3LYP density functional method of Gaussian 98 package [18] with 6-31G* basis sets. The single point energy calculations following the optimizations were performed using the larger 6-311+G* basis set (i.e., B3LYP/6-311+G*//B3LYP/6-31G*); geometries computed with more expensive basis sets do not necessarily lead to more accurate final results [19]. The optimized model was displayed using molecular graphic software. All of the calculations were carried out on a server of PC clusters.

3. Model structures

In Figs. 1–7, isomers corresponding to local minima of $C_nP_5^-$ ($n = 1$–7) with real vibrational frequencies are shown. In each figure, the models are arranged in the order of ascending total energy; large balls represent carbon atoms and small ones denote phosphorus atoms. Most of the models depicted here have never been reported before. After a great deal of calculations on $C_nP_5^-$, we found that except for several structures, the isomers with interconnecting carbon and phosphorus are either unstable (with high total energy) or imaginary in frequency with no local minima. The C_n entity can be considered as a submolecular unit whereas the phosphorus atoms appear in P, P_2, P_3, P_4 and P_5 submolecular units. The seven isomers for CP_5^- acquired are shown in Fig. 1. Fig. 2 shows the 13 isomers of $C_2P_5^-$. The seven isomers of $C_3P_5^-$ are shown in Fig. 3. Fig. 4 shows the eight isomers of $C_4P_5^-$. The seven isomers of $C_5P_5^-$ are shown in Fig. 5. Fig. 6 shows the 10 isomers of $C_6P_5^-$. Ten isomers of $C_7P_5^-$ are shown in Fig. 7.

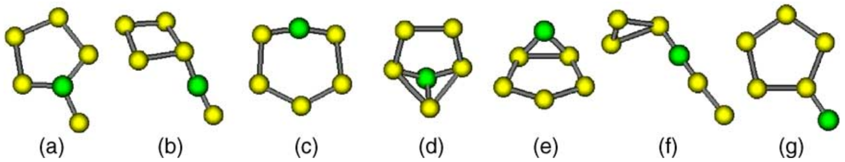

Fig. 1. Seven isomers of CP_5^-.

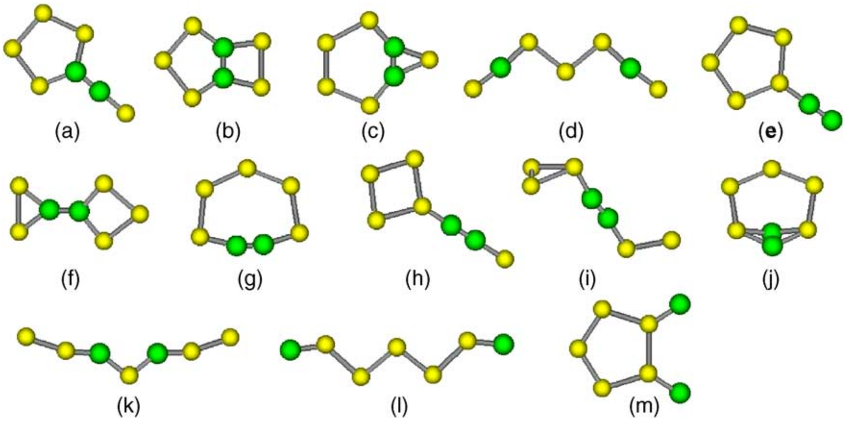

Fig. 2. Thirteen isomers of $C_2P_5^-$.

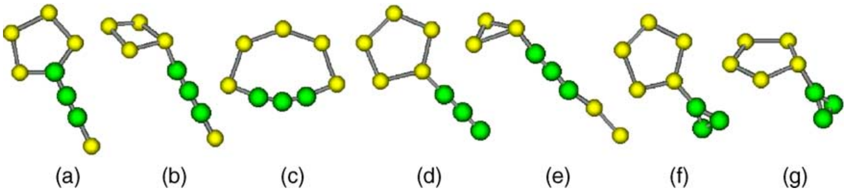

Fig. 3. Seven isomers of $C_3P_5^-$.

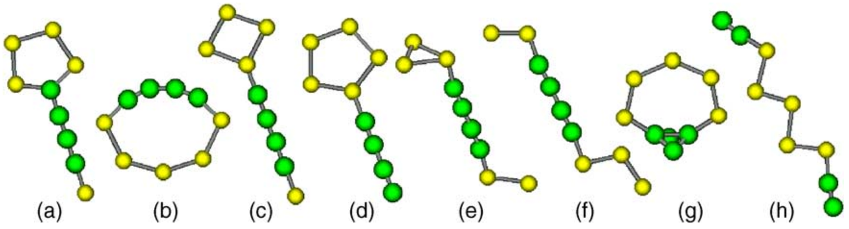

Fig. 4. Eight isomers of $C_4P_5^-$.

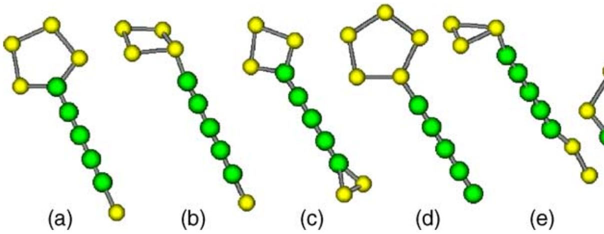

Fig. 5. Seven isomers of $C_5P_5^-$.

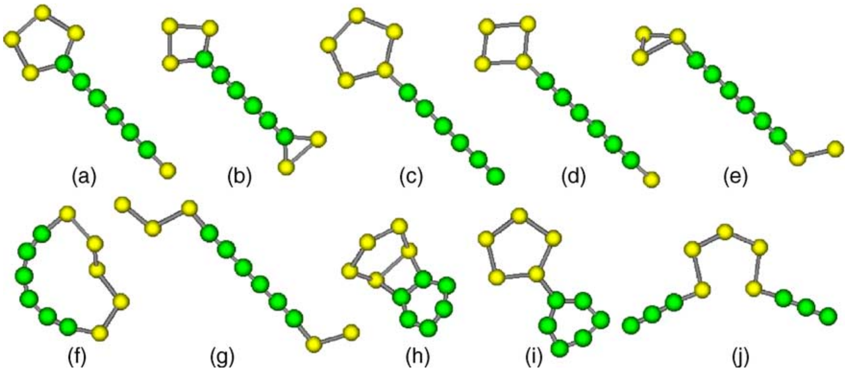

Fig. 6. Ten isomers of $C_6P_5^-$.

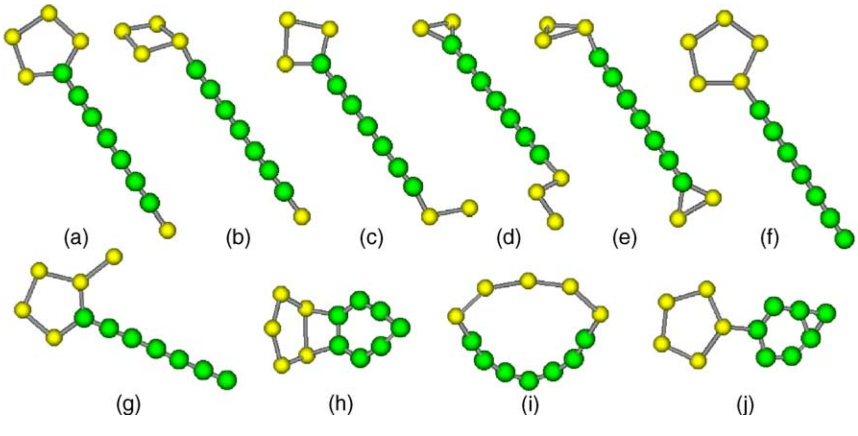

Fig. 7. Ten isomers of $C_7P_5^-$.

4. Results and discussion

Displayed in Fig. 8 are five categories of $C_nP_5^-$ ($n = 1$–7) structures. Category 8a denotes the most stable ground-state structures. Category 8b are those with a P_4 ring connected to a C_nP chain of even n; the structures are C_{2v} in symmetry (models 2h, 4c, 6d). No such configuration is found when n is odd; the structures for odd n (models 1b, 3b, 5b, 7b) are non-planar with C_s symmetry. Category 8c are C_{2v} structures with a P_5 ring connected to a C_n chain (models 1g, 2e, 3d, 4d, 5d, 6c and 7f). Category 8d are C_{2v} structures of P_5C_n rings (models 1c, 2g, 3c, 4b, 5f and 7i). Category 8e are C_s

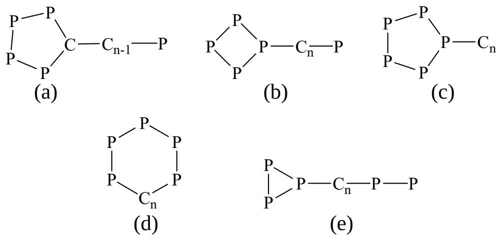

Fig. 8. Five main categories of $C_nP_5^-$ (n = 1–7).

structures with a P_3 ring connected to a C_nP_2 chain (models 1f, 2i, 3e, 4e, 5e and 6e).

Because of the fact that there are numerous isomers in the structures of clusters, the identification of the ground state is important. For a particular family of molecules, the basic structure with the lowest energy affects the “building up” of larger molecules, and this is an important area in biochemical research. The structures of C_n and C_n^- ($n < 14$) clusters are usually linear or cyclic in structure [20]. The most stable structures of C_nP^- are linear [8,9,12,13], with the phosphorus atom located at one end of the chain. The most stable structures of C_nP_2 and $C_nP_2^-$ are also linear [4,7], with one phosphorus atom located at each end of the carbon chain.

According to the relative total energies listed in Table 1, model 1a is the CP_5^- structure with the lowest energy. The most stable structures of $C_nP_5^-$ (n = 2–7) can be regarded as the outcomes of increasing the carbon chain of model 1a, with one phosphorus atom locating at one end and a P_4C ring at the other. Fisher et al. compared six structures of $C_4P_5^-$ and model 6a, and considered model 4a to be most stable [4].

Shown in Fig. 9 are the bond lengths of the most stable $C_nP_5^-$ (n = 1–7) structures optimized with B3LYP/6-31G* method. Within the five-membered rings, the P–P bond lengths are either about 2.14 or 2.11 Å, and the C–P bond length is about 1.79 Å. The first C–C bond length of the C_n chain is about 1.39 Å. The straight C_n chains show an alternate long and short pattern in bond lengths, that is similar to that of polyacetylene. As for the C–P bonds within the straight chains, the length is about 1.58 Å when n is even; when n is odd (i.e., in the cases of $C_3P_5^-$, $C_5P_5^-$, and $C_7P_5^-$), the length is about 1.64 Å, slightly shorter than those of even anions. When n is odd, the anions are indicative of $[P_4C(–C{\equiv}C)_n–P]$ (n = 0–3) in structures, and when n is even, the anions show a $[P_4C(–C{\equiv}C)_n–C{\equiv}P]$ (n = 0–2) structure with character of triple bonding at the end of chain. Such characteristic of $C_nP_5^-$ (n = 1–7)

Table 1
Symmetries, electronic state and total energies (a.u.) of $C_nP_5^-$ (n = 1–7) isomers using B3LYP/6-31G* geometries and B3LYP/6-311+G* energies

Figure	Cluster	Symmetry	Electronic state	Total energy	Figure	Cluster	Symmetry	Electronic state	Total energy
1a	CP_5^-	C_{2v}	$^3A_2$	−1745.054277	4e	$C_4P_5^-$	C_s	$^3A''$	−1859.275022
1b	CP_5^-	C_s	$^1A'$	−1745.033924	4f	$C_4P_5^-$	C_s	$^3A''$	−1859.266477
1c	CP_5^-	C_{2v}	$^3A_2$	−1745.010534	4g	$C_4P_5^-$	C_{2v}	$^1A_1$	−1859.182990
1d	CP_5^-	C_s	$^3A''$	−1745.002431	4h	$C_4P_5^-$	C_{2v}	$^1A_1$	−1859.173654
1e	CP_5^-	C_s	$^1A'$	−1744.976288	5a	$C_5P_5^-$	C_{2v}	$^3A_2$	−1897.442894
1f	CP_5^-	C_s	$^1A'$	−1744.966885	5b	$C_5P_5^-$	C_s	$^1A'$	−1897.407690
1g	CP_5^-	C_{2v}	$^3A_2$	−1744.959406	5c	$C_5P_5^-$	C_{2v}	$^3A_1$	−1897.376659
2a	$C_2P_5^-$	C_{2v}	$^1A_1$	−1783.186846	5d	$C_5P_5^-$	C_{2v}	$^3A_2$	−1897.353895
2b	$C_2P_5^-$	C_{2v}	$^1A_1$	−1783.161609	5e	$C_5P_5^-$	C_s	$^1A'$	−1897.345364
2c	$C_2P_5^-$	C_{2v}	$^1A_1$	−1783.135094	5f	$C_5P_5^-$	C_{2v}	$^3A_2$	−1897.330460
2d	$C_2P_5^-$	C_{2v}	$^1A_1$	−1783.122307	5g	$C_5P_5^-$	C_{2v}	$^3B_2$	−1897.248918
2e	$C_2P_5^-$	C_{2v}	$^1A_1$	−1783.114543	6a	$C_6P_5^-$	C_{2v}	$^1A_1$	−1935.559738
2f	$C_2P_5^-$	C_{2v}	$^3A_1$	−1783.113771	6b	$C_6P_5^-$	C_{2v}	$^3A_1$	−1935.481736
2g	$C_2P_5^-$	C_{2v}	$^3B_2$	−1783.109444	6c	$C_6P_5^-$	C_{2v}	$^1A_1$	−1935.478812
2h	$C_2P_5^-$	C_{2v}	$^1A_1$	−1783.103199	6d	$C_6P_5^-$	C_{2v}	$^1A_1$	−1935.478796
2i	$C_2P_5^-$	C_s	$^3A''$	−1783.087832	6e	$C_6P_5^-$	C_s	$^3A''$	−1935.460666
2j	$C_2P_5^-$	C_{2v}	$^3B_1$	−1783.008706	6f	$C_6P_5^-$	C_1		−1935.452862
2k	$C_2P_5^-$	C_{2v}	$^1A_1$	−1782.994859	6g	$C_6P_5^-$	C_s	$^3A'$	−1935.450394
2l	$C_2P_5^-$	C_{2v}	$^1A_1$	−1782.928432	6h	$C_6P_5^-$	C_1		−1935.404369
2m	$C_2P_5^-$	C_{2v}	$^3B_2$	−1782.910559	6i	$C_6P_5^-$	C_{2v}	$^1A_1$	−1935.384234
3a	$C_3P_5^-$	C_{2v}	$^3A_2$	−1821.252612	6j	$C_6P_5^-$	C_1		−1935.324501
3b	$C_3P_5^-$	C_s	$^1A'$	−1821.222715	7a	$C_7P_5^-$	C_{2v}	$^3A_2$	−1973.629804
3c	$C_3P_5^-$	C_{2v}	$^1A_1$	−1821.183105	7b	$C_7P_5^-$	C_s	$^1A'$	−1973.590539
3d	$C_3P_5^-$	C_{2v}	$^3A_2$	−1821.159908	7c	$C_7P_5^-$	C_s	$^3A''$	−1973.558251
3e	$C_3P_5^-$	C_s	$^1A'$	−1821.156066	7d	$C_7P_5^-$	C_s	$^3A''$	−1973.557372
3f	$C_3P_5^-$	C_1		−1821.138696	7e	$C_7P_5^-$	C_s	$^1A'$	−1973.545613
3g	$C_3P_5^-$	C_s	$^3A''$	−1821.118457	7f	$C_7P_5^-$	C_{2v}	$^3A_2$	−1973.543004
4a	$C_4P_5^-$	C_{2v}	$^1A_1$	−1859.375226	7g	$C_7P_5^-$	C_s	$^3A''$	−1973.523770
4b	$C_4P_5^-$	C_{2v}	$^1A_1$	−1859.295680	7h	$C_7P_5^-$	C_s	$^1A'$	−1973.515157
4c	$C_4P_5^-$	C_{2v}	$^1A_1$	−1859.292143	7i	$C_7P_5^-$	C_{2v}	$^1A_1$	−1973.489717
4d	$C_4P_5^-$	C_{2v}	$^1A_1$	−1859.296239	7j	$C_7P_5^-$	C_s	$^1A'$	−1973.467684

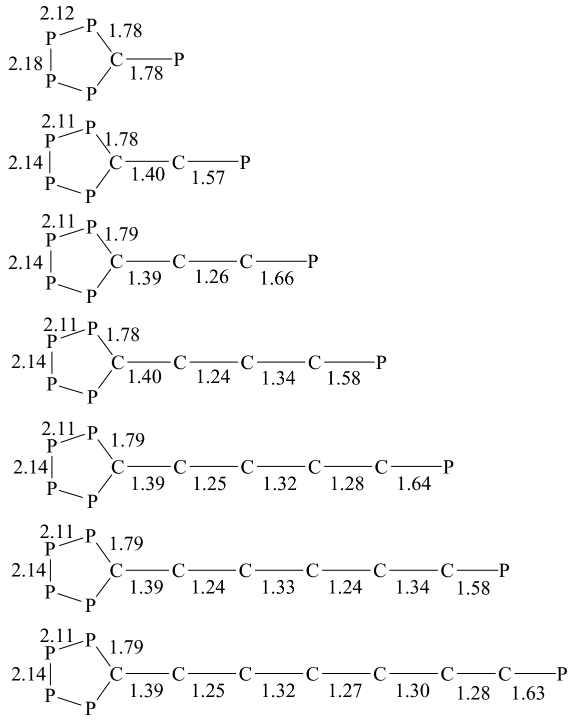

Fig. 9. Bond length of ground state $C_nP_5^-$ (n = 1–7) optimized with B3LYP/6-31G* method.

bond length is similar to that of C_nP^- [8,9,12,13]. In the collision-induced dissociation (CID) experiments, Fisher et al. observed the decomposition of $C_4P_5^-$ and $C_6P_5^-$ anions to C_4P^- and C_5P^-, respectively, and a P_4 unit [4].

The isomers listed in Table 1 are with both the singlet and triplet forms optimized; we only include the stable ones with real vibrational frequencies. For example, the singlet of model 1a is not included because of its imaginary frequency. We found that the singlet energies ($^1A_1$) of models 3a, 5a, and 7a are higher than those of the triplet forms ($^3A_2$) by 0.019656, 0.016010, 0.013512 (a.u.), respectively. The triplet energies ($^3A_1$) of models 2a, 4a, and 6a are higher than those of the corresponding singlet forms ($^1A_1$) by 0.069316, 0.062882, 0.055655 (a.u.), respectively.

The most stable structures are planar and subject to C_{2v} symmetry. The p orbitals of carbon atoms within the chain overlap to form delocalized π bonding. Within the CP_4 planar ring and the straight chain, the p orbitals of all of the carbons and four phosphorus atoms overlap and the delocalized cyclic π bond causes a reduction in the total energy. In Fig. 10 , π molecular orbital of 3D isosurface for ground state $C_2P_5^-$ and $C_3P_5^-$ is depicted schematically. The other ground state models of $C_nP_5^-$ exhibit π orbitals of similar nature, the rest of the models show no such delocalized π bonds. The most stable C_nP and C_nP^- are linear in structures [8,9,12,13], with the phosphorus atom located at one end of the chain. The most stable CP_4^- structure is in the form of planar aromatic ring. The most stable $C_nP_5^-$ structure can be considered as a combination of CP_4^- ring and linear $C_{n-1}P$ submolecular units.

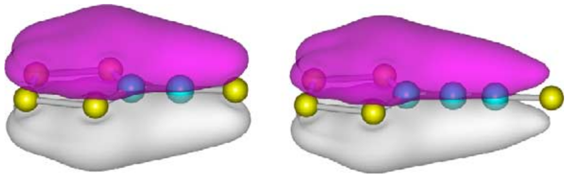

Fig. 10. Schematic diagram of π molecular orbital of 3D isosurface for ground state $C_2P_5^-$ and $C_3P_5^-$.

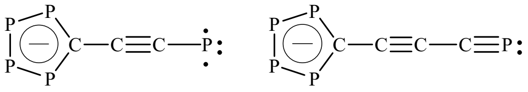

Fig. 11. Valence-bond structures of the most stable $C_3P_5^-$ and $C_4P_5^-$.

It has been pointed out that the electron states of ground state $C_nP_5^-$ with odd and even number of carbon atoms are different. For $C_nP_5^-$, the electron state is $^1A_1$ for even n, and is $^3A_2$ with odd n. When n is odd, the number of alpha electrons in the ground triplet state is larger than that of the beta electrons by 2, whereas when n is even, the numbers of alpha and beta electrons in the singlet state are equal. The effects of different parity suggests that the ground states with even n are more stable. The general idea is that it requires more energy to remove an electron from a closed-shell configuration ("n-even" $C_nP_5^-$) than from an open-shell configuration ("n-odd" $C_nP_5^-$).

Fig. 11 shows the valence-bond structures of the most stable $C_3P_5^-$ and $C_4P_5^-$. For $C_3P_5^-$, the phosphorus atom at the end has two unpaired electrons and triplet structures are favorable. For $C_4P_5^-$, due to the very character of triple bonding at the end of chain, singlet is preferred. This explains why when n is odd, the $C_nP_5^-$ (n = 1–7) ground state is triplet whereas when n is even it is singlet.

Electron affinity (EA) is computed as the energy difference between the neutral and anionic ($E_{\text{neutral}} - E_{\text{anion}}$) 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 accomplished. Listed in Table 2 are the electron affinities of the most stable $C_nP_5^-$ (n = 1–7) structures using B3LYP/6-31G* geometries and zero point energy

Table 2
Electron affinities (EA) with zero point energy correction, atomization energies (ΔE_a) and incremental binding energy (ΔE^I) for ground state $C_nP_5^-$ (n = 1–7) (a.u.) using B3LYP/6-31G* geometries and ZPE and B3LYP/6-311+G* energies

Figure	Cluster	EA	ΔE_a	ΔE^I
1a	CP_5^-	0.110456	0.776879	
2a	$C_2P_5^-$	0.137490	1.046480	0.269601
3a	$C_3P_5^-$	0.120099	1.251049	0.204569
4a	$C_4P_5^-$	0.142636	1.510244	0.259195
5a	$C_5P_5^-$	0.128398	1.71679	0.206546
6a	$C_6P_5^-$	0.146419	1.969583	0.252793
7a	$C_7P_5^-$	0.134509	2.178811	0.209228

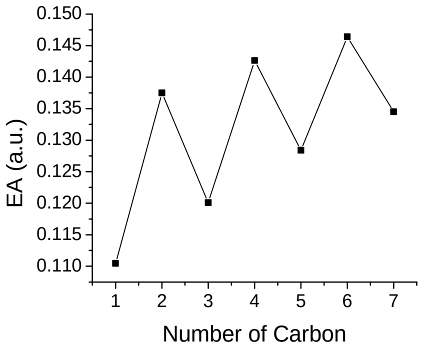

Fig. 12. Curve of electron affinity (EA) (shown in Table 2) in $C_nP_5^-$ against n (the number of carbon atoms).

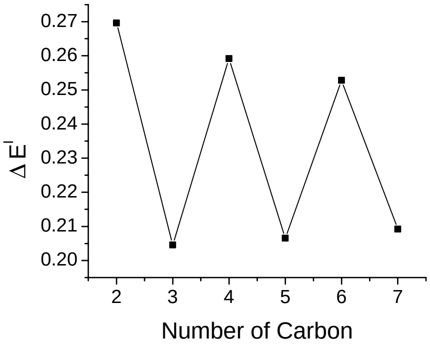

Fig. 13. Curve of ΔE^I of $C_nP_5^-$ ($n = 2$–7) shown in Table 2 against n.

correction and B3LYP/6-311+G* energies. The optimized neutral structures exhibit configurations similar to those of ground state anions, respectively, but the geometry parameters are different. Shown in Fig. 12 is the variation curve of election affinity as related to the number of carbon atoms, n, within the clusters. One can see that the EA values of $C_nP_5^-$ ($n = 1$–7) with even n are higher than those with odd n, reflecting an alternate pattern of high and low. This implies that compared to the cases of odd n, it is easier to add an electron to C_nP_5 with even n (i.e., forming $C_2P_5^-$, $C_4P_5^-$, $C_6P_5^-$, and $C_8P_5^-$). Such an odd–even alternate pattern of electron affinity matches well with the peak profiles of the mass spectra [5–7] and production patterns [4] of carbon phosphide anions.

The incremental binding energy (ΔE^I) [9,21] which is the atomization energies (ΔE_a) difference of adjacent clusters can also reflect the relative stability of the anionic clusters (Table 2). We have

$$\Delta E^I = \Delta E_a(C_nP_5^-) - \Delta E(C_{n-1}P_5^-)$$

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

$$\Delta E_a = nE(C) + 5E(P) - E(C_nP_5^-)$$

Fig. 13 shows that, according to n, the values of ΔE^I vary alternately: when n is even, the ΔE_n value is larger; when n is odd, the ΔE_n is smaller. Because a larger ΔE^I value implies a more stable $C_nP_5^-$ structure, one can deduce that a $C_nP_5^-$ cluster with even n is more stable than one with odd n. Such odd–even alternate pattern of incremental binding energy is also consistent with the observations of Liu et al. [5,6], Zeng et al. [7] and Fisher et al. [4]. In conclusion, the missing of “n-odd” peaks or products can be explained by a combined consideration of electron affinities for the neutral, and incremental binding energies for the anionic clusters. Since the electron affinities of the neutral clusters and the incremental binding energies of the anionic clusters are smaller when n is odd, it implies that compared to the “n-even” $C_nP_5^-$ ($n = 1$–7) clusters, the “n-odd” ones are less stable and decompose more readily.

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