J. Phys. Chem. A **2004,** *108,* 5704−5709

Theoretical Study of Arsenic-Doped Carbon Clusters C_nAs^- ($n = 1-11$)

J. W. Liu, M. D. Chen,* L. S. Zheng, and Q. E. Zhang

State Key Laboratory of Physical Chemistry of Solid Surface, Department of Chemistry,
Center for Theoretical Chemistry, Xiamen University, Xiamen 361005, People's Republic of China

C. T. Au

Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong,
People's Republic of China

Received: February 26, 2004; In Final Form: April 16, 2004

Structures of C_nAs^- ($n = 1-11$) clusters have been determined by means of B3LYP density functional method. A comparison of structure stability shows that the lowest-lying structures are linear, with the arsenic atom located at one end of the carbon chain. Also, the linear C_nAs^- ($n = 1-11$) anions with an odd number of carbon atoms are more stable than those with an even number, in good agreement with the peak pattern of time-of-flight investigation. The trend of such odd/even alternation is explained on the basis of concepts of electronic configurations, incremental binding energies, vertical electron detachment energies, and dissociation channels.

1. Introduction

In the past decades, carbon clusters have been studied both experimentally and theoretically for better understanding of a large variety of chemical systems.[1,2] Even before the development of fullerene chemistry, small carbon clusters were studied with great interest because they are intermediates in chemical vapor deposition of carbon clusters. In astrochemistry, they also have a role to play; due to the interstellar quasicollisionless condition, small carbon clusters take the highly stable (albeit highly reactive) form of linear chains.

Heteroatom-doped carbon clusters have also attracted much attention in recent years, and these ions are considered to have structures analogous to C_n. By means of secondary ionic emission or laser ionization, a series of heterocarbon anionic C_nX^- clusters were generated by adding a heteroatom X to the corresponding carbon clusters C_n^-, where X is either a main group element (such as N, F, Cl, H, Al, Si, S, B, Ge) or a transition metal (such as Ti, Zr, V, Cr,W, Fe, Ni).[3−6] Huang et al. produced a series of cluster anions C_nX^- (X = N, P, As, Sb, Bi,) from laser ablation of the appropriate samples.[7] From the observed records of time-of-flight (TOF) mass spectra, C_nN^-, C_nP^-, and C_nAs^- exhibit a dramatic even/odd alternation in signal intensity, and generally the anionic clusters with odd numbers of carbon atoms show relatively higher signal intensities than those with even numbers.

To explore these interesting experimental observations, there have been a lot of theoretical investigations on C_nX^- clusters. Leleyter studied a series of C_nX^- by the Hückel method.[8−10] Zheng et al. studied C_nN^-,[11] C_nB^-,[12] C_nP^-,[13,14] and AlC_n^- [14] ($n = 1-11$) clusters by means of HF/3-21G level. The theoretical studies of C_nSe^- ($1 \leq n \leq 11$) clusters were carried out with B3LYP/6-31G* density functional method by Wang et al.[15] Zhan et al. reinvestigated C_nN^-,[16] C_nB^-,[17] and C_nP^-[18] at different approximations such as MP2, MP4SDTQ, and QCISD(T) methods. Pascoli and Lavendy proposed structures of C_nN^-[19] and C_nP^-[20] ($n = 1-7$) based on data collected in B3LYP/6-311G* density functional calculation. Fisher et al. conducted BLYP density functional calculations on structures of C_nP^-.[21] Besides anionic C_nX^- clusters of Group VB elements, Li et al. carried out a comparative study on the "second-row-atom-doped" linear carbon clusters $C_nX/C_nX^+/C_nX^-$ ($n = 1-10$; X = Na, Mg, Al, Si, P, S or Cl) by means of DFT/B3LYP method.[22] Recently, theoretical studies on AlC_n^- ($n = 1-7$),[23] $Si_nC_m^-$ ($n + m \leq 8$),[24] SiC_n^- ($n = 2-5$),[25] C_nSe^- ($n \leq 11$),[26] RbC_n^-,[27] C_nH^- ($n \leq 10$),[28] and PbC_n^- ($n = 1-10$)[29] were reported by Largo et al., Hunsicker et al., Gomei et al., Wang et al., Vandenbosch et al., Pan et al., and Li et al., respectively. From the calculation results, it seems that the ground-state structures of medium-size heteroatom-doped carbon clusters are linear or near linear and show an even/odd alternation in stability.

Theoretical works on C_nN^- and C_nP^- were reported,[11,16,18−22] but no theoretical report on C_nAs^- clusters has been published, and our understandings of Group VA heteroatom-doped clusters are still limited. Despite the fact that N, P, and As are the same group elements and that their chemical properties are recognizably similar (being more or less governed by the identical valence electron configuration ns^2np^3), there are substantial differences among them.[30] The time-of-flight mass spectra of C_nAs^- clusters showed distinct peaks at odd n (Figure 1).[10] To view the issue theoretically, we designed some structural models of C_nAs^- ($n = 1-11$) and performed geometry optimization and calculations on vibration frequencies by means of the B3LYP density functional method. Their stabilities, geometry structures, electronic configurations, energy differences, incremental binding energies, vertical electron detachment energies, and dissociation channels have all been investigated. On the basis of the results, we explained why the C_nAs^- ($n = 1-11$) isomers with odd n are more stable than those with even n. The outcome can serve as helpful guidelines for the synthesis of related materials as well as for future theoretical studies of heteroatom-doped carbon clusters.

10.1021/jp049142w CCC: \$27.50

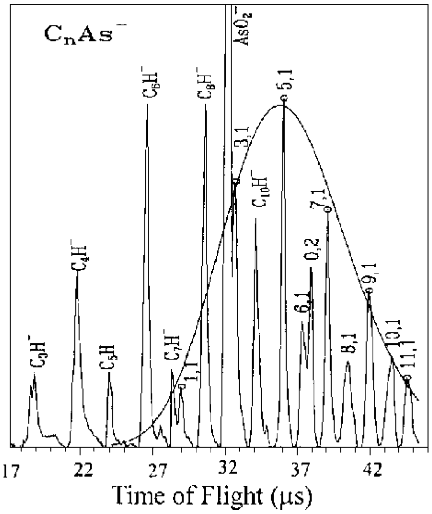

Figure 1. TOF mass spectrum of clusters anions C_nAs^- ($n = 1-11$) generated from laser ablation of the arsenic triphenyl.

2. Computational Details

We performed molecular modeling with HyperChem 5.10 for Windows[31] on a PC/Pentium IV computer. Geometry optimization and calculations of vibration frequencies were conducted using the hybrid density functional theory B3LYP method,[32,33] i.e., Becke's 3-parameter nonlocal exchange functional with the correlation functional of Lee−Yang−Parr, plus the standard 6-311G* basis set. The single point energy calculation following the optimizations was performed using the larger 6-311+G* basis set (i.e., B3LYP/6-311+G*//B3LYP/6-311G*). Note that this hybrid method was previously proved to be agreeable with but yet less computationally demanding than the more rigorous ab initio methods such as CCSD(T) for geometries of carbon clusters and carbon clusters with heteroatoms.[34] Open-shell calculation was done in unrestricted formalism. All calculations were carried out using the Gaussian 98 program suite[35] on a server of PC clusters.

3. Results and Discussion

3.1. Structures. In Figure 2, isomers corresponding to the local minima of C_nAs^- ($n = 1-11$) clusters with real vibration frequencies are shown; dark gray balls represent carbon atoms, and light gray ones denote arsenic atoms. The models are arranged in order of ascending relative total energy. In previous theoretical investigation, a linear carbon chain bonded to a heteroatom is the most favorable structure. Such structure of linearity is verified by the fact that all vibration frequencies of linear geometries are real, and the isomers are local minima on the energy surface. For $n = 2-8$, we gave two different initial guesses of chain structures; one is standard linear, and the other is curved. The energies of the two optimized structures are different only by 0.06−0.3 kcal/mol, suggesting that they belong to the same linear structure. In Figure 2, only the linear and planar or near-planar geometries of the C_nAs^- ($n = 1-11$) are shown. We have performed calculations on the stereostructures; because the resulting energies are much higher than those of the planar ones, they are not included in this paper.

Listed in Table 1 are the symmetries, total energies, electronic states, and relative energies of the C_nAs^- ($n = 1-11$) structures

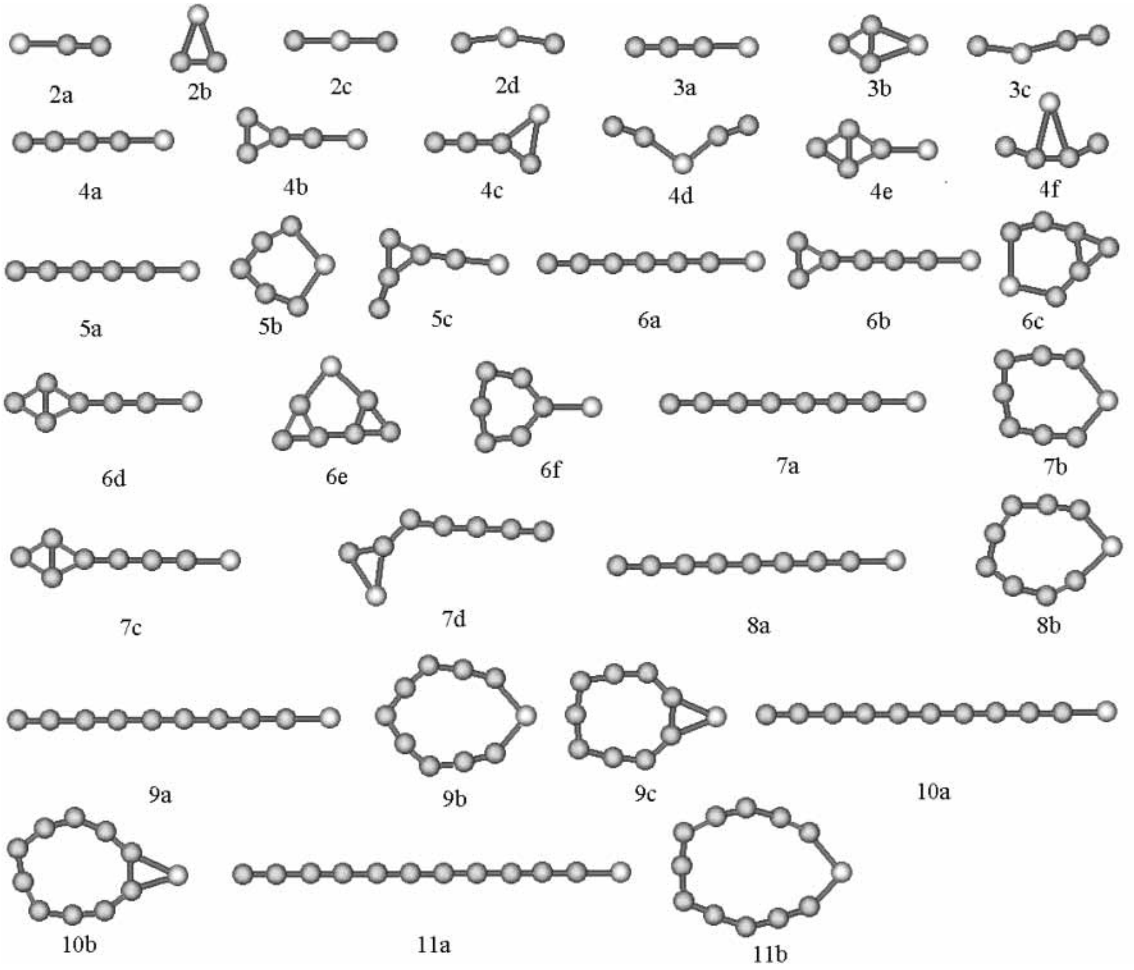

Figure 2. Geometries of C_nAs^- ($n = 1-11$) structures.

TABLE 1: Symmetries, Electronic State, Total Energies (a.u.), and Relative Energies (kcal/mol) of C_nAs^- ($n = 1-11$) Based on B3LYP/6-311G* Geometries and B3LYP/ 6-311+G* Energies

figure	cluster	symmetry	state	total energy	relative energy	figure	cluster	symmetry	state	total energy	relative energy
2a	C_2As^-	$C_{\infty v}$	$^3\Sigma^-$	−2312.019 6	0	6c	C_6As^-	C_s	$^1A'$	−2464.303 6	52.90
2b	C_2As^-	C_{2v}	$^1A_1$	−2311.972 9	29.30	6d	C_6As^-	C_s	$^1A'$	−2464.295 4	58.04
2c	C_2As^-	$C_{\infty h}$	$^3\Sigma_g^-$	-2311.868 3	94.94	6e	C_6As^-	C_s	$^1A'$	−2464.274 1	71.41
2d	C_2As^-	C_{2v}	$^1A_1$	−2311.830 9	118.41	6f	C_6As^-	C_{2v}	$^1A_1$	−2464.246 6	88.67
3a	C_3As^-	$C_{\infty v}$	$^1\Sigma^+$	−2350.132 6	0	7a	C_7As^-	$C_{\infty v}$	$^1\Sigma^+$	−2502.489 1	0
3b	C_3As^-	C_{2v}	$^1A_1$	−2350.048 9	52.52	7b	C_7As^-	C_s	$^1A'$	−2502.389 5	62.50
3c	C_3As^-	C_s	$^1A'$	−2349.997 6	84.71	7c	C_7As^-	C_s	$^1A'$	−2502.389 4	62.56
4a	C_4As^-	$C_{\infty v}$	$^3\Sigma^-$	−2388.207 7	0	7d	C_7As^-	C_s	$^1A'$	−2502.348 7	88.10
4b	C_4As^-	C_s	$^1A'$	−2388.157 0	31.81	8a	C_8As^-	$C_{\infty v}$	$^3\Sigma^-$	−2540.564 3	0
4c	C_4As^-	C_s	$^1A'$	−2388.152 3	34.76	8b	C_8As^-	C_s	$^1A'$	−2540.499 2	40.85
4d	C_4As^-	C_{2v}	$^1A_1$	−2388.135 3	45.43	9a	C_9As^-	C_s	$^1A'$	−2578.666 1	0
4e	C_4As^-	C_s	$^1A'$	−2388.116 0	57.54	9b	C_9As^-	C_s	$^1A'$	−2578.628 6	23.53
4f	C_4As^-	C_s	$^1A'$	−2388.110 5	61.00	9c	C_9As^-	C_s	$^1A'$	−2578.576 3	56.35
5a	C_5As^-	$C_{\infty v}$	$^1\Sigma^+$	−2426.313 4	0	10a	$C_{10}As^-$	C_s	$^1A'$	−2616.721 9	0
5b	C_5As^-	C_{2v}	$^1A_1$	−2426.257 8	34.89	10b	$C_{10}As^-$	C_s	$^1A'$	−2616.673 4	30.43
5c	C_5As^-	C_s	$^1A'$	−2426.211 6	63.88	11a	$C_{11}As^-$	C_s	$^1A'$	−2654.839 8	0
6a	C_6As^-	$C_{\infty v}$	$^3\Sigma^-$	−2464.387 9	0	11b	$C_{11}As^-$	C_s	$^1A'$	−2654.772 4	42.29
6b	C_6As^-	C_s	$^1A'$	−2464.337 7	31.50						

presented in Figure 2. According to the relative energies, the ground-state geometries are linear, with the arsenic atom located at one end of the carbon chains. The linear structures with the arsenic atom bonded to two carbon atoms are much higher in energy. For instance, the energies of 2c and 2d isomers are around 100 kcal/mol higher than that of 2a. Models 3b and 10b are clusters with an arsenic atom bonded to one side of a monocyclic C_n ring. Models 4b and 6b are structures with a C_3 ring connected to a chain of carbon having an arsenic atom at its end. Among the numerous isomers, those with cyclic structures are relatively stable. Models 2b, 5b, 7b, 8b, 9b, and 11b are all cyclic; they are the second most stable structures. There are cases that we started with initial cyclic geometries but ended up with noncyclic structures such as 4f and 6e.

The ordering of energy is often dependent on the theoretical methods adopted for isomers of similar energies. We performed CCSD(T)/6-311+G* computations on C_2As^- and C_3As^-. The CCSD(T) energies for 2a, 2b, 2c, 2d, 3a, 3b, and 3c are −2310.2065, −2310.1689, −2310.0579, −2310.0258, −2348.2227, −2348.1455, and −2348.0977 au, respectively, exhibiting the same ordering of B3LYP/6-311+G* energies. Although temperature change would eventually cause changes in the incremental binding energies, the change should display systemic characters, and the trend of odd/even alternation should show a similar pattern. We performed calculations on the energies of the linear C_nAs^- ($n = 1-11$) clusters at higher temperature (600 K), and the curve of energy differences (that reflects the magnitudes of incremental binding energies) exhibits similar odd/even alternation.

3.2. Electronic Configurations. Shown in Figure 3 are the bond lengths of the most stable C_nAs^- ($n = 1-11$) structures. Parent et al. suggested that the bonding of the linear carbon chain is either cumulene- or polyacetylene-like.[36] According to the bond lengths given in Figure 3, the last C−C bond of the C_n chain is 1.26−1.27 Å long. Along the straight C_n chains, C−C bond lengths for even n clusters tend to average out, showing some sort of cumulene character. For odd n species, there is a weak alternating long-and-short pattern in C−C length (∼1.32 and ∼1.25 Å), reflecting some sort of polyacetylene character. The C−As bond lengths show a short/long alternation with odd/even n: For odd n, the lengths are within 1.70−1.72 Å, and there is a slight decrease with increasing n; for even n, C−As bond lengths are within 1.80−1.85 Å, decreasing from ∼1.80 Å (C_2As^-) to ∼1.75 Å ($C_{10}As^-$) with increasing n.

Shown in Table 2 are the valence orbital configurations of linear C_nAs^- ($n = 1-11$) clusters. The electronic configurations can be summarized as

$$(\mathrm{core})1\sigma^2 \cdots 1\pi^4 \cdots (n+2)\sigma^2\left(\frac{n}{2}+1\right)\pi^4 \qquad \text{odd } n$$

$$(\mathrm{core})1\sigma^2 \cdots 1\pi^4 \cdots (n+2)\sigma^2\left(\frac{n+1}{2}\right)\pi^2 \qquad \text{even } n$$

(except for CAs^-). With the inclusion of a negative charge, the linear C_nAs^- ($n = 1-11$) clusters possess ($4n + 6$) valance electrons, among which are ($2n + 2$) π electrons. The outermost doubly-degenerate π orbitals of linear C_nAs^- clusters with odd n are fully occupied ($^1\Sigma^+$ electronic state); for even n, they are half-filled ($^3\Sigma^-$ electronic state). The HOMO with fully filled π orbitals is always energetically more stable than that with an unfilled electron shell.

The ground-state C_nAs^- ($n = 1-11$) alternates between $^1\Sigma^+$ (odd n) and $^3\Sigma^-$ (even n) electron states. When n is odd, the numbers of α and β electrons in the singlet state are equal, whereas when n is even, the number of α electrons in triplet state is larger (by 2) than that of the β electrons. The effects of different parity suggest that the ground states with odd n are more stable. The general idea is that it requires more energy to remove an electron from a closed-shell configuration (odd n) than from an open-shell configuration (even n).

Both phosphorus and arsenic are VA group elements; each provides five valence electrons for chemical bonding. It is thus expected that small anionic carbon clusters doped with a P or an As atom, respectively, should have some similar structure characteristics. Indeed, the clusters of these two series of binary clusters all show structures with the heteroatom located at one end of the carbon chain, and they show similar odd/even parity. According to theoretical studies on small C_nP^-, the ground-state geometry is predicted to be linear, with the phosphorus atom located at one end of the carbon chain.[13,14,20] The bond lengths of C−P also show a dramatic long/short alternation:[20] For odd n, the bond lengths of C−P are 1.59−1.61 Å (it is 1.70−1.72 Å for C−As), whereas for even n they are 1.63−1.68 Å (it is 1.80−1.85 Å for C−As). The straight C_n chains of C_nP^- also show characters similar to that of C_nAs^-, cumulene-like for even-n, and polyacetylene-like for odd-n.[20] Various theoretical considerations, such as incremental binding energies and fragmentation patterns can explain the trend of odd/even alternation of C_nP^- clusters.

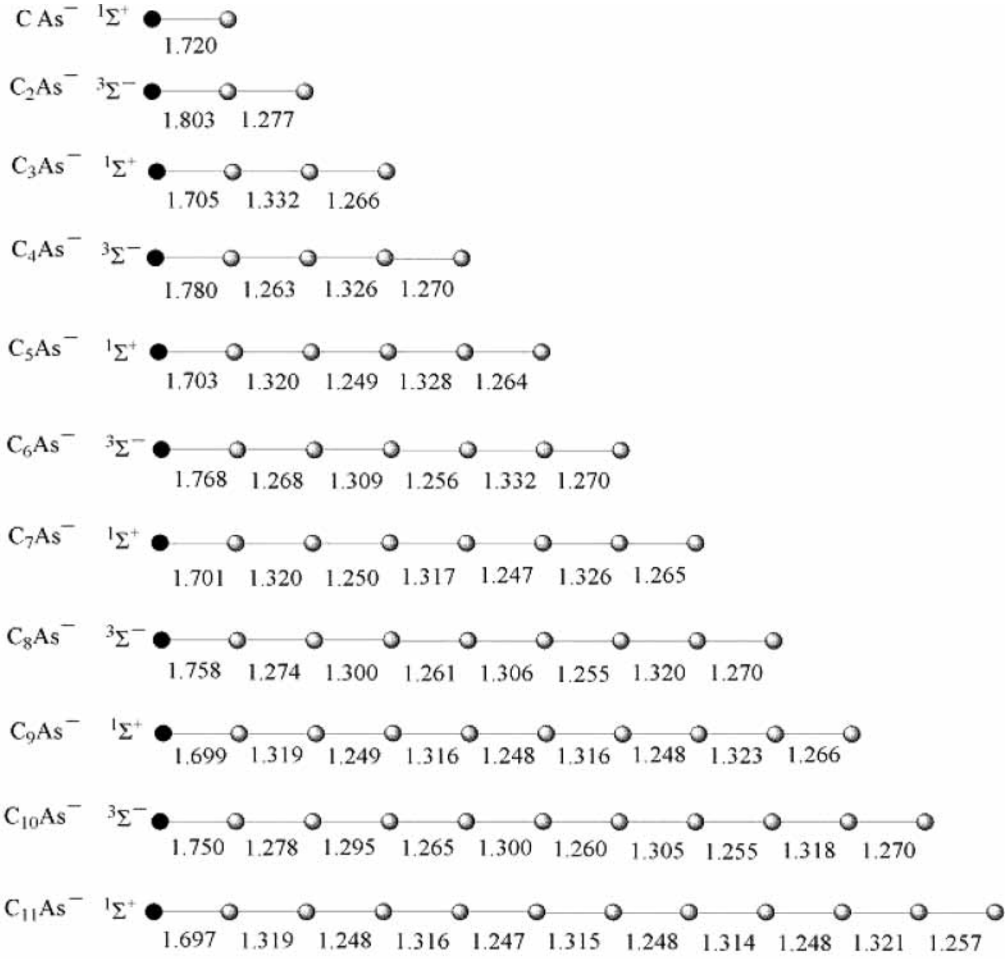

Figure 3. Bond lengths (in Å) of linear C_nAs^- ($n = 1-11$) clusters optimized at the B3LYP/6-311G* level.

TABLE 2: Valence Orbital Configuration for Linear C_nAs^- ($n = 1-11$) Clusters

isomers	configuration
CAs^-	(core) $\sigma^2\sigma^2\pi^4\sigma^2$
C_2As^-	(core) $\sigma^2\sigma^2\sigma^2\pi^4\sigma^2\pi^2$
C_3As^-	(core) $\sigma^2\sigma^2\sigma^2\sigma^2\pi^4\sigma^2\pi^4$
C_4As^-	(core) $\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\pi^4\pi^4\sigma^2\pi^2$
C_5As^-	(core) $\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\pi^4\sigma^2\pi^4\sigma^2\pi^4$
C_6As^-	(core) $\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\pi^4\sigma^2\pi^4\sigma^2\pi^4\pi^2$
C_7As^-	(core) $\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\pi^4\pi^4\sigma^2\pi^4\pi^4$
C_8As^-	(core) $\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\pi^4\sigma^2\pi^4\pi^4\sigma^2\pi^4\pi^2$
C_9As^-	(core) $\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\pi^4\pi^4\pi^4\sigma^2\pi^4\pi^4$
$C_{10}As^-$	(core) $\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\pi^4\sigma^2\pi^4\pi^4\pi^4\sigma^2\pi^4\pi^2$
$C_{11}As^-$	(core) $\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\pi^4\sigma^2\pi^4\pi^4\pi^4\sigma^2\pi^4\pi^4$

Selenium belongs to VIA group and is just next to arsenic in the periodic table; it can provide six valence electrons for chemical bonding. The geometry of the C_nSe^- clusters has been assumed to be in a form of linear chain with the selenium atom locating at one of its terminals. The calculated total energies, vertical electron detachment energies, fragmentation energies, bond lengths, and other structural parameters exhibit the alternation effect, showing that C_nSe^- clusters with even n are more stable than those with odd n, in a reverse odd/even alternation fashion compared to those of C_nP^- and C_nAs^- clusters. When n is even, the straight C_n chains show an alternating long-and-short pattern (between 1.25 and 1.32 Å) in bond length, leaving the terminal C−C bond fixed at a length of about 1.276 Å, similar to that of a polyacetylene-like structure. When n is odd, the C−C bond lengths of the straight chain average out, similar to that of a cumulenic-like structure.[15] As for the C−Se bonds, although there is a long/short pattern with even/ odd n, the difference tends to get smaller with an increase in carbon number n. Wang et al. considered whether the high conjugativity of “even n” carbon chain results in a stable structure, while the “odd n” carbon chain does not adopt a conjugative structure.[15]

TABLE 3: Atomization Energy ΔE_a (kcal/mol), Incremental Binding Energy ΔE^I (kcal/mol), Vertical Electron Detachment Energies VDE (kcal/mol), Spin Contamination $\langle S^2\rangle$, Zero-Point Energy ZPE (kcal/mol), Dipole Moment μ (D), and Rotational Constants B_e (MHz) for Linear C_nAs^- ($n = 1-11$)

n	ΔE_a	ΔE^I	VDE	$\langle S^2\rangle$	ZPE	μ	B_e
1	7.2		67.80	0.00	1.42	3.51	16522.68
2	13.4	6.2	66.05	2.02	4.15	6.04	4275.90
3	20.3	7.0	82.56	0.00	7.76	7.31	1933.32
4	26.2	5.9	76.02	2.05	10.56	9.11	1006.63
5	33.0	6.8	87.99	0.00	14.54	10.30	621.20
6	38.9	5.9	82.60	2.08	17.55	11.60	401.95
7	45.6	6.6	91.79	0.00	22.10	13.02	283.21
8	51.5	5.9	84.85	2.12	25.30	13.88	204.24
9	57.9	6.5	94.75	0.00	30.31	15.60	154.94
10	63.9	5.9	78.01	2.14	33.41	16.02	119.26
11	70.6	6.7	96.87	0.00	33.45	18.11	94.85

3.3. Incremental Binding Energies and Electron Affinities. Listed in Table 3 are the atomization energy, incremental binding energy, vertical electron detachment energies, spin contamination, zero-point energy, dipole moment, and rotational constants for linear C_nAs^- ($n = 1-11$). Taking a closer look at the other structural parameters listed in Table 3, one can see that the rotational constants (B_e) of C_nAs^- clusters decrease with the increasing size (n increasing) of the clusters. The dipole

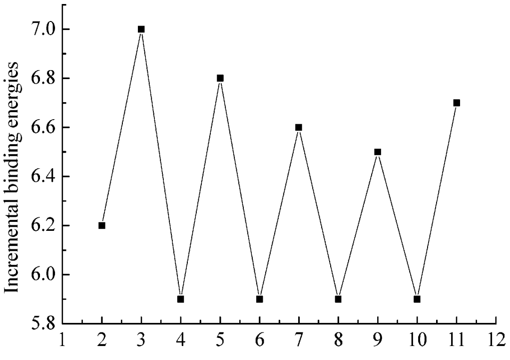

Figure 4. Incremental binding energies ΔE^{I} (kcal/mol) for linear C_nAs^- ($n = 2-11$) clusters (as shown in Table 3) vs the number of carbon atoms.

moment of linear clusters increases with the length of the carbon chain. It is expected since the dipole moment is a monotonic function of carbon atoms. As for spin contamination, the $\langle S^2\rangle$ values of even n triplet clusters rise with increasing number of carbon atoms, but the deviation is small.

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).[37] We have

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

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

$$\Delta E_a = nE(C) + E(As) - E(C_nAs^-)$$

As shown in Figure 4, the values of ΔE^{I} vary according to a pattern of odd/even alternation: When n is odd, the ΔE_n value is large; when n is even, the ΔE_n is small. Because a larger ΔE^{I} value implies a more stable C_nAs^- structure, one can deduce that a C_nAs^- cluster with odd n is more stable than one with even n.

It is known that the anion signal intensity in mass spectrum can be related to the electron affinity energy of a molecule. The anionic cluster with a larger electron affinity is generally more stable. Vertical electron detachment energy (*VDE*), defined as the energy required to remove an electron from an anion but without any geometric change, can be used as another criterion to evaluate the relative stability of anionic clusters with different sizes. VDE is defined as

$$\text{VDE} = E(\text{neutral at optimized anion geometry}) - E(\text{optimized anion})$$

Figure 5 depicts the VDE values versus the number of carbon atoms in C_nAs^- ($n = 1-11$). There is an obvious parity effect on the VDE curve of C_nAs^-: Odd-n clusters having higher VDEs than even-n ones. This behavior is related to the higher stability of C_nAs^- clusters with odd n. It is also obvious in Figure 5 that with rising n, the VDE rises with respect to odd- and even-n C_nAs^-.

3.4. Dissociation Channel. Due to the existence of an arsenic atom at one of the ends of the carbon chain, the possible dissociation channels of C_nAs^- ($n = 1-11$) can be rather complicated. Although we do not attempt to characterize in this work the reaction pathways and transition states for fragmentation, we evaluated the relative stability of the clusters in term of fragmentation energy based on hypothetical reactions. The energies for fragmentation as a function of n are depicted in Figure 6. The six dissociation channels are divided into two categories; those that show the losing of small carbon particles C, C_2, and C_3, and those that show the losing of As, CAs, and C_2As fragments. The corresponding dissociation channels are as follows:

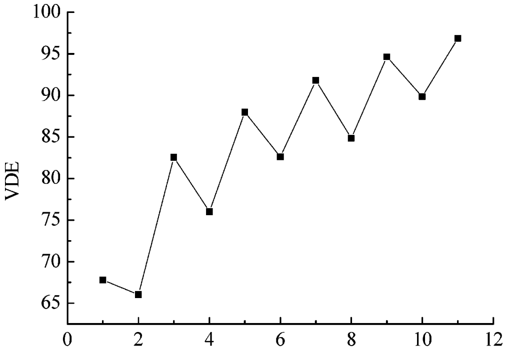

Figure 5. Vertical electron detachment energy (VDE) (kcal/mol) of C_nAs^- ($n = 1-11$) clusters vs the number of carbon atoms.

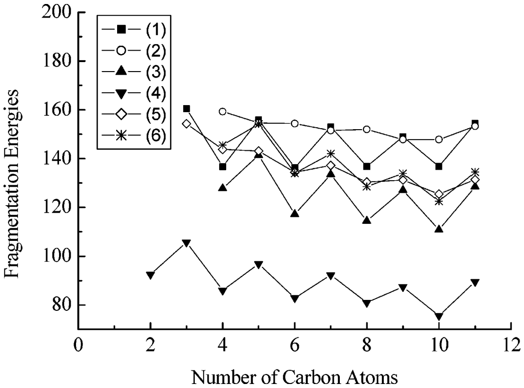

Figure 6. Fragmentation energies (kcal/mol) vs the number of carbon atoms.

$$C_nAs^- \rightarrow C_{n-1}As^- + C \tag{1}$$

$$C_nAs^- \rightarrow C_{n-2}As^- + C_2 \tag{2}$$

$$C_nAs^- \rightarrow C_{n-3}As^- + C_3 \tag{3}$$

$$C_nA^- \rightarrow C_n^- + As \tag{4}$$

$$C_nAs^- \rightarrow C_{n-1}^- + CAs \tag{5}$$

$$C_nAs^- \rightarrow C_{n-2}^- + C_2As \tag{6}$$

Fragmentation energy related to reaction 1 with the release of one carbon atom exhibits distinct odd/even alternation, and the dissociation energies of C_nAs^- with odd n are always larger than those of even n (Figure 6). The results are consistent with the observation that C_nAs^- with odd n are relatively stable; the ejection of a single carbon atom will cause an inverse in parity of the clusters, and the more stable odd-n clusters require more energy for fragmentation than the less stable even-n ones. In the case of losing a C_2 fragment, there will be no change in parity of the parent anionic clusters, and the alternation effect for reaction 2 is much less drastic than those of reactions 1 and 3. The dissociation energies of reaction 3 repeat the alternation tendency of reaction 1. Furthermore, the energy is found to be much smaller than those of reactions 1 and 2. Such difference could be attributed to the special structural stability of the C_3 fragment, as previously pointed out by Rao et al.[38] In the studies of Raghavachari et al.[39] and Geusic et al.,[40] the ejection of C_3 was found to be the major dissociation channel of small carbon clusters.

The dissociation energies of reactions 4 and 6, which involve the loss of the arsenic atom, exhibit the same odd/even alternation as that of reactions 1 and 3. In other words, the energy of C_nAs^- with odd n is always larger than that with even n. According to the bond lengths shown in Figure 3, the C−As bond lengths also show a long/short pattern along with even/odd variation of n. Hence, the dissociation energy of reaction 4 shows the same tendency: The dissociation energies of C−As bonds of "short-bond" nature at odd n are higher than those of "long-bond" nature at even n. In the case of losing a CAs fragment (reaction 5), the change in parity is relatively small. The alternation effect for reaction 6 of losing three atoms (C_2As) is obvious. The results indicate that the channel for lowest energy fragmentation is reaction 4, and the loss of As could be the dominant dissociation pathway.

4. Conclusions

The ground-state structures of C_nAs^- are linear. The clusters with odd-n are more stable than those with even-n. The odd/even alternation trend can be explained according to the variation of electronic configurations, incremental binding energies, vertical electron detachment energies, and dissociation channels. The results of calculation are in good agreement with the experimental phenomena observed in mass spectrometric studies.

Acknowledgment. The authors thank the National Science Foundation (Grant 2957117), and the Fujian Science and Technology Project (Grant 2002F010), P. R. China, for financial support.

References and Notes

(1) Weltner, W., Jr.; Van Zee, R. J. *Chem. Rev.* **1989**, *89*, 1713.

(2) Raghavachari, K.; Binkley, J. S. *J. Chem. Phys.* **1987**, *87*, 2191.

(3) Consalvo, D.; Mele, A.; Stranges, D.; Giardini-Guidoni, A.; Teghil, R. *Int. J. Mass Spectrosc. Ion Proc.* **1989**, *91*, 319.

(4) Leleyter, M.; Joyes, P. *Surf. Sci.* **1985**, *156*, 800.

(5) Orth, R. G.; Jonkmann, H. T.; Michl, J. *Int. J. Mass Spectrosc. Ion Proc.* **1982**, *43*, 41.

(6) Becker, S.; Dietze, H. J. *Int. J. Mass Spectrosc. Ion Proc.* **1988**, *82*, 287.

(7) Huang, R. B.; Wang, C. R.; Liu, Z. Y.; Zheng, L. S.; Qi, F.; Sheng, L. S.; Yu S. Q.; Zhang Y. W. *Z. Phys. D* **1995**, *33*, 49.

(8) Leleyter, M. *Z. Phys. D* **1989**, *12*, 381.

(9) Leleyter, M. *Z. Phys. D* **1991**, *20*, 81.

(10) Leleyter, M. *Z. Phys. D* **1991**, *20*, 85.

(11) Wang, C. R.; Huang, R. B.; Liu, Z. Y.; Zheng, L. S. *Chem. Phys. Lett.* **1995**, *237*, 463.

(12) Wang, C. R.; Huang, R. B.; Liu, Z. Y.; Zheng, L. S. *Chem. Phys. Lett.* **1995**, *242*, 355.

(13) Liu, Z. Y.; Huang, R. B.; Zheng, L. S. *Chem. J. Chin. Univ.* **1997**, *18*, 2019.

(14) Liu, Z. Y.; Huang, R. B.; Tang, Z. C.; Zheng, L. S. *Chem. Phys.* **1998**, *229*, 335.

(15) Wang H. Y.; Huang, R. B.; Chen, H.; Lin, M. H.; Zheng, L. S. *J. Phys. Chem. A* **2001**, *105*, 4653.

(16) Zhan C. G.; Iwata, S. *J. Chem. Phys.* **1996**, *104*, 9058.

(17) Zhan C. G.; Iwata, S. *J. Phys. Chem. A* **1997**, *107*, 591.

(18) Zhan C. G.; Iwata, S. *J. Chem. Phys.* **1997**, *107*, 7323.

(19) Pascoli, G.; Lavendy, H. *Chem. Phys. Lett.* **1999**, *312*, 333.

(20) Pascoli, G.; Lavendy, H. *J. Phys. Chem. A*, **1999**, *103*, 3518.

(21) Fisher, K.; Dance, I.; Willett, G. *Eur. Mass Spectrom.* **1997**, *3* (5), 331.

(22) Li, G. L.; Tang, Z. C. *J. Phys. Chem. A* **2003**, *107*, 5317.

(23) Largo, A.; Redondo, P.; Barrientos, C. *J. Phys. Chem. A* **2002**, *106*, 4217.

(24) Hunsicker, S.; Jones, R. O. *J. Chem. Phys.* **1996**, *105*, 5048.

(25) Gomei, M.; Kishi, r.; Nakajima, A.; Iwata, S.; Kaya, K. *J. Chem. Phys.* **1996**, *107*, 10051.

(26) Wang, H. Y.; Huang, R. B.; Chen, H.; Lin, M. H.; Zheng, L. S. *J. Phys. Chem. A* **2001**, *105*, 4653.

(27) Vandenbosch, R.; Will, D. I. *J. Chem. Phys.* **1996**, *104*, 5600.

(28) Pan, L.; Rao, B. K.; Gupta, A. K.; Das, G. P.; Ayyub, P. *J. Chem. Phys.* **2003**, *119*, 7705.

(29) Li, G. L.; Xing, X. P.; Tang, Z. C. *J. Chem. Phys.* **2003**, *118*, 6884.

(30) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: Oxford, 1984; pp 637.

(31) *Hyerchem Reference Manual*; Hypercube Inc.: Waterloo, Canada, 1996; pp 79−290.

(32) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(33) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(34) Martin, J. M. L.; Taylor, P. R. *J. Phys. Chem.* **1996**, *100*, 6047.

(35) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E., Jr.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98 (Revision A.7)*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(36) Parent, D. C.; Anderson, S. L. *Chem. Rev.* **1992**, *92*, 1541.

(37) Pascoli, G.; Lavendy, H. *Int. J. Mass Spectrom. Ion Processes* **1998**, *173*, 41.

(38) Rao, B. K.; Khanna, S. N.; Jena, P. *Solid State Commun.* **1986**, *58*, 53.

(39) Raghavachari, K.; Birkley, J. S. *J. Chem. Phys.* **1987**, *87*, 2191.

(40) Geusic, M. E.; Mcllrath, T. J.; Jarrold, M. F.; Bloomfied, L. A.; Freeman, R. R.; Brown, W. L. *J. Chem. Phys.* **1986**, *84*, 2421.