Ab Initio Studies on the Structures, Vertical Electron Detachment Energies, and Fragmentation Energies of C_nB^- Clusters

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Recently, Wang, Huang, Liu, and Zhang reported experimental and theoretical studies on C_nB^- ($n = 1-13$) as well as the C_nN^- clusters ($n = 1-13$). They claimed that both clusters ($n = 1-13$) should be linear chains based on *ab initio* HF/3-21G geometry optimizations. In the present paper, we report the new results obtained from *ab initio* calculations at higher levels on the ground states of the C_nB^- cluster anions. It can be concluded from our calculated results that for the ground states, the linear structures of C_nB^- up to $n =$ 4 are stable and that those of other C_nB^- clusters ($n = 5-7$) are not linear and are very floppy. The vertical electron detachment and fragmentation energies of C_nB^- ($n = 1-7$) in their ground states are evaluated with the MP4SDTQ method at the MP2 geometry using 6-31G(d) augmented with a set of diffuse sp functions. The fragmentation energies are also evaluated with the QCISD(T) method using the same basis to verify the convergence of the perturbational results. The calculated fragmentation energies show that the C_nB^- clusters with even n's are more stable than those with odd n's, which is consistent with the observed odd−even alternation of the TOF signal intensities.

1. Introduction

The small cluster anions, C_nX^-, formed by adding a heteroatom, X, to the corresponding carbon cluster anions, C_n^-, have attracted much attention[1−6] in recent years. It has been known that low-mass carbon clusters and the corresponding linear C_nX^- clusters exhibit an odd−even intensity pattern in the time-of-flight (TOF) mass spectra, independent of the method of production of the cluster.[7] In a reported TOF mass spectrometry study on C_nN^- clusters, Wang *et al*. observed stronger signal intensities for the C_nN^- clusters with odd n than those with even n.[4] Because their observed signal intensities could be well fitted by a log-normal distribution curve, according to their statistical distribution model,[8] all the C_nN^- clusters should have an analogous structure, and they concluded that the structure of C_nN^- should be a linear chain and that the heteroatom N should be located on one end of the carbon chain.[4] In order to interpret their experimental observations, in the report,[4] the authors also presented the theoretical values of the vertical electron detachment energies (VDEs) and fragmentation energies of C_nN^- obtained from their *ab initio* quantum chemical computations at the RHF/3-21G level. It seems that the calculated results reported by Wang *et al*.[4] are reasonable because they are apparently consistent with the observed odd−even alternation. However, according to our previous experience, the RHF/3-21G level of approximation is too low to give reasonable results at least for VDEs of many small cluster anions.[9]

Recently, we have carried out a detailed *ab initio* study on the C_nN^- clusters.[10] The results obtained from the computations at various levels show that both the d polarization functions and the electron correlation are necessary to determine the geometries. Without the polarization functions or ignoring the electron correlation effect in the calculations, the optimized geometries of C_nN^- could be qualitatively incorrect. The calculated results indicate also that the diffuse sp functions (+) are important in the energy calculations, though they are not important in the geometry optimizations. The calculated vertical electron detachment energy (VDE) without the diffuse functions is substantially smaller than the VDE evaluated with the diffuse functions. In order to obtain the convergent results for the geometries, vibrational frequencies, and VDEs of C_nN^-, both the diffuse and polarization functions have to be included in the basis sets. The results calculated at the reliable levels reveal that the linear structures are stable only for C_2N^-, C_3N^-, and C_5N^- anions. For the singlet states of the other anions considered in the study, the linear geometries are all saddle points on the potential energy surfaces, and their geometries of the ground states are bent.[10] After we finished the theoretical investigation on the C_nN^- clusters and submitted the report for publication, another paper[11] was published presenting the experimental and theoretical results for studying C_nB^- clusters ($n = 1-13$). The experimental results reported are interesting because the observed odd−even alternancy in the TOF signal of C_nB^- is completely opposite to that of C_nN^-, but the conclusions for the linear geometries and the corresponding properties are somewhat doubtful because the authors still optimized the geometries at the poor HF/3-21 level and did not include electron correlation in the calculations. Because the observed TOF signal intensities of C_nX^- can be well fitted by a log-normal distribution curve,[4] according to their statistical distribution model,[8] it is reasonable to conclude that the C_nX^- clusters ($n = 1-13$) appearing in their observed TOF mass spectra should have analogous geometries. From this, they could suggest that their studied C_nX^- clusters are all the chain structures terminated by atom X. However, there is no reason to further assume that all the chains should be linear. Hence, the examination of the results reported by Wang *et al*. for C_nB^- is also necessary. Are the geometries of the C_nB^- clusters in their ground states all really linear chains? If there are bent structures, are the bent structures of C_nB^- similar to those of C_nN^-? How are the changes of the geometries, VDEs, and

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fragmentation energies of C_nB^- with *n*? Really satisfactory answers to these questions should be found only from a series of *ab initio* calculations at reliable levels. In the present study, the higher levels of *ab initio* calculations applied to the investigations of C_nN^- anions have been also employed the study of the structures and properties of the C_nB^- anions. The geomerties of the smaller C_nB^- clusters have been optimized and the harmonic vibrational frequencies, VDEs, and fragmentation energies have been evaluated at various levels of approximations.

2. Calculation Methods

The investigation of C_nN^- anions[10] reveals that to obtain reliable results for both the geometry optimizations and the energy calculations, the calculation level used for studying these kinds of anions cannot be lower than the second-order Møller−Plesset (MP2) method using the 6-31G(d)[END+] basis set. The notation "6-31G(d)[END+]" used here means the 6-31G(d) basis set augmented with diffuse sp functions only on the two end atoms. For the CB^- anion, 6-31G(d)[END+] is identical to 6-31+G(d). But it is not for others. There are two reasons for choosing the 6-31G(d)[END+] basis set instead of 6-31+G(d). One is that if the diffuse functions are placed on every atom, the basis set for the anions C_nN^- and C_nB^- (*n* large) becomes overcomplete because of the large overlap between the diffuse functions. Another reason is that the results calculated with the 6-31G(d)[END+] basis set are very close to those with the 6-31+G(d) basis set. This means that the basis set augmented with diffuse functions only on the end atoms is sufficient to describe the anionic state because the highest occupied orbital of the C_nN^- anion is mostly localized on the end atoms. In this work, we also use the 6-31G(d)[END+] basis set to carry out the *ab initio* calculations on C_nB^- anions. Hence, the geomerties are optimized at the MP2/6-31G(d)[END+] level, and after the geometry optimizations, the harmonic vibrational frequencies are evaluated at the same level to examine the true stability. The MP4SDTQ and QCISD(T) energies are evaluated at the optimized geometries with the same basis set. For all the MP2, MP4SDTQ, and QCISD(T) computations, all the electrons are included in the correlation energy calculations. Besides, to further examine the reliability of the results calculated with the 6-31G(d)[END+] basis set, we also carry out computations with other kinds of extended basis sets on the smaller C_nB^- clusters.

The programs used for the calculations are GAUSSIAN 92[12] and GAUSSIAN 94.[13] Most of the computations were carried out on a NEC-SX3 supercomputer at the computer center of the Institute for Molecular Science, and those for smaller systems were carried out on an IBM-RS6000 workstation.

3. Results and Discussion

3.1. Structures. To examine whether the linear structure of C_nB^- anions are stable or not, the geometry optimizations and the corresponding harmonic vibrational frequency calculations on the linear structures of C_nB^- ($n = 1-7$) have been carried out at the MP2/6-31G(d)[END+] level. The calculated harmonic vibrational frequencies indicate that the linear geometries of C_nB^- up to $n = 4$ are indeed associated with the local minima on the potential energy surfaces and that the linear geometries of C_nB^- ($n = 5-7$) (closed shell) are all of the saddle points on the potential energy surfaces. It turns out that the stable geometries of C_nB^- ($n = 5-7$) in the ground states are slightly bent, which is contrary to the results reported by Wang *et al.*[11] Comparing the calculated energies of the singlet states with those of the corresponding triplet states, we can see that for C_3B^-, the energy of the triplet state is 1.385 eV more stable than the singlet state, and for the other C_nB^-, anions the calculated energies of the lowest triplet states are all higher than the corresponding lowest singlet states. The singlet−triplet separations for C_4B^-, C_5B^-, and C_7B^- are 1.959, 0.094, 3.683, and 1.089 eV, respectively. These conclusions for C_nB^- are different from those for C_nN^- ($n = 1-7$), where the ground state of C_2N^- is a triplet state and the ground states of all the other C_nN^- anions are singlet states; the stable geomerty of C_4N^- is bent and that of C_5N^- is linear.

Furthermore, it is also interesting to compare the results calculated for C_nB^- with those reported previously for C_{n+1}, because they are isoelectronic. In the neutral C_{n+1} molecules, the C−C bond lengths are equal to each other within 0.025 Å, in accord with the cumulenic depiction.[14] In C_nB^- anions, the differences among the C−C bond lengths slightly increase up to 0.069 Å. The maximum difference between the C−C lengths in C_nB^- is much smaller than that in C_nN^-, in $C_{n+1}{}^-$ and in $C_{n+1}{}^{2-}$. It follows that the structures of C_nB^- are much closer to the cumulenic structures than to the acetylenic structures. It was reported that the neutral molecules C_{n+1} ($n = 1-9$) have linear structures and that the ground states of the linear clusters C_{n+1} (n = 3, 5, 7, and 9) are all triplet, while those of C_2 and other C_{n+1} clusters of even *n* are singlet.[14] Why are the ground states of C_5B^- and C_7B^- the singlet states which are different from C_6 and C_8? It is helpful for understanding this difference to qualitatively analyze their molecular orbital levels. For $n = 2m$, the ground electron configuration of C_{n+1} and C_nB^- is $(m\pi)^4[(4m + 3)\sigma]^2$ associated with a singlet state. For $n = 2m - 1$, the ground electron configuration of C_{n+1} and C_nB^- can be either $(m\pi)^4[(4m + 1)\sigma]^0$ or $(m\pi)^2[(4m + 1)\sigma]^2$, depending on the relative energies of the two configurations. The mth π MO is bonding, and the $(4m + 1)$th σ MO is nonbonding. When the energy gap between the mth π and $(4m + 1)$th σ MO is larger, the singlet state with the first configuration is the ground state. When the gap is very small, the triplet state formed by the second configuration becomes the ground state. From C_{n+1} to C_nB^-, the energies of the mth π MO and the $(4m + 1)$th σ MO become slightly higher because the orbital levels of atom B are slightly higher than atom C. The amount of increase of the MO energy should be related to the character of the atomic orbitals of atom B involved in the MO. The calculated MO coefficients indicate that the $(4m + 1)$th σ MO in C_nB^- is mainly located at atom B. The $(4m + 1)$th σ MO contains much more character of the orbitals of atom B than the mth π MO. Hence, the energy difference between the $(4m + 1)$th σ and mth π MO's in C_nB^- are slightly larger than that in C_{n+1} so that the ground states of C_nB^- (n = 5 and 7) are singlet states, while those of C_{n+1} (n = 5 and 7) are triplet states.

In order to examine the reliability of the conclusion for the linear geometry of C_4B^-, the geometry optimization and harmonic vibrational frequency calculation of C_4B^- have also been carried out by using larger extended basis sets, 6-311G(df) and 6-311G(df)[END+]. Similar to 6-31G(d)[END+], the notation "6-311G(df)[END+]" used here indicates the 6-311G(df) basis set augmented with diffuse sp functions only on the two end atoms, C1 and B. The results calculated with the larger extended basis sets, shown in Table 1, confirm the existence of the linear geometry of the C_4B^- anion.

The optimized geometrical parameters and calculated harmonic vibrational frequencies for the ground states of the C_nB^- anions ($n = 1-7$) are listed in Table 1 and displayed in Figure 1 together with the calculated net atomic charges. Listed also in Table 1 are the geometrical parameters and harmonic vibrational frequencies calculated with several other choices of

TABLE 1: Geometrical Parameters (Å and deg) and Harmonic Vibrational Frequencies (cm^{-1}) of C_nB^- (n = 1−7) Optimized by the MP2(Full) Method with Various Basis Sets

C_nB^-	basis set[a]	geometry		frequencies					
CB^- ($C_{\infty v}$, $^1\Sigma$)	6-31G(d)	C−B	1.379			1635.7			
	6-31+G(d)	C−B	1.391			1587.7			
	6-311G(d)	C−B	1.384			1600.4			
	6-311+G(d)	C−B	1.391			1579.5			
	6-311G(df)	C−B	1.377			1612.7			
	6-311+G(df)	C−B	1.383			1592.5			
C_2B^- ($C_{\infty v}$, $^1\Sigma$)	6-31G(d)	C1−C2	1.281	200.3	Π	200.3	Π	1054.3	Σ
		C2−B	1.458	1989.0	Σ				
	6-31G(d)[END+]	C1−C2	1.281	218.4	Π	218.4	Π	1050.5	Σ
		C2−B	1.452	1974.2	Σ				
	6-31G(d)[C1+C2+]	C1−C2	1.280	286.2	Π	286.2	Π	1050.9	Σ
		C2−B	1.452	1978.0	Σ				
	6-31+G(d)	C1−C2	1.280	231.6	Π	231.6	Π	1048.7	Σ
		C2−B	1.452	1975.3	Σ				
C_3B^- ($C_{\infty v}$, $^1\Sigma$)	6-31G(d)	C1−C2	1.273	258.1	Π	258.1	Π	552.1	Π
		C2−C3	1.375	552.1	Π	865.9	Σ	1727.6	Σ
		C3−B	1.335	1985.5	Σ				
	6-31G(d)[END+]	C1−C2	1.272	243.7	Π	243.7	Π	540.6	Π
		C2−C3	1.374	540.6	Π	868.8	Σ	1723.9	Σ
		C3−B	1.336	1978.4	Σ				
	6-31+G(d)	C1−C2	1.273	232.2	Π	232.2	Π	498.5	Π
		C2−C3	1.373	498.5	Π	868.2	Σ	1721.3	Σ
		C3−B	1.335	1972.9	Σ				
C_3B^- ($C_{\infty v}$, $^3\Sigma$)	6-31G(d)[END+]	C1−C2	1.290	312.1	Π	312.1	Π	892.1	Σ
		C2−C3	1.300	1524.2	Σ	1894.9	Σ	1902.4	Π
		C3−B	1.452	1902.4	Π				
C_4B^- ($C_{\infty v}$, $^3\Sigma$)	6-31G(d)	C1−C2	1.279	132.2	Π	132.2	Π	285.2	Π
		C2−C3	1.336	285.2	Π	590.6	Π	590.6	Π
		C3−C4	1.267	730.3	Σ	1262.1	Σ	1928.3	Σ
		C4−B	1.468	2146.4	Σ				
	6-31G(d)[END+]	C1−C2	1.277	124.3	Π	124.3	Π	267.8	Π
		C2−C3	1.336	267.8	Π	514.2	Π	514.2	Π
		C3−C4	1.267	732.8	Σ	1272.0	Σ	1927.0	Σ
		C4−B	1.455	2130.4	Σ				
	6-31G(d)[C1+C4+]	C1−C2	1.277	147.4	Π	147.4	Π	282.8	Π
		C2−C3	1.336	282.8	Π	520.3	Π	520.3	Π
		C3−C4	1.268	730.3	Σ	1265.9	Σ	1927.8	Σ
		C4−B	1.456	2129.2	Σ				
	6-311G(df)	C1−C2	1.274	117.9	Π	117.9	Π	219.0	Π
		C2−C3	1.331	219.0	Π	452.7	Π	452.7	Π
		C3−C4	1.263	726.4	Σ	1258.2	Σ	1918.5	Σ
		C4−B	1.457	2131.6	Σ				
	6-311G(df)[END+]	C1−C2	1.272	107.4	Π	107.4	Π	207.1	Π
		C2−C3	1.332	207.1	Π	390.1	Π	390.1	Π
		C3−C4	1.263	725.8	Σ	1258.2	Σ	1919.3	Σ
		C4−B	1.456	2121.1	Σ				
C_5B^- (C_s, ^{3}A′)	6-31G(d)[END+]	C1−C2	1.289	103.0	A′	198.4	A″	205.5	A′
		C2−C3	1.315	363.4	A′	393.6	A″	495.0	A″
		C3−C4	1.289	610.1	A′	661.3	A′	1105.0	A′
		C4−C5	1.288	1626.0	A′	2030.7	A′	2096.2	A′
		C5−B	1.462						
		∠C1C2C3	177.6						
		∠C2C3C4	172.4						
		∠C3C4C5	176.2						
		∠C4C5B	177.8						
C_5B^- (C_s, ^{3}A′)	6-31G(d)[END+]	C1−C2	1.280	80.9	A′	162.6	A″	168.6	A′
		C2−C3	1.332	185.9	A″	282.4	A′	304.6	A″
		C3−C4	1.260	501.1	A′	504.2	A″	554.3	A′
		C4−C5	1.323	584.8	A′	999.6	A′	1387.2	A′
		C5−C6	1.269	1893.1	A′	2099.2	A′	2140.9	A′
		C6−B	1.465						
		∠C1C2C3	178.4						
		∠C2C3C4	177.8						
		∠C3C4C5	176.4						
		∠C4C5C6	178.9						
		∠C5C6B	178.9						
C_7B^- (C_s, ^{1}A′)	6-31G(d)[END+]	C1−C2	1.286	59.6	A′	142.2	A″	147.3	A′
		C2−C3	1.319	175.0	A″	202.0	A′	304.4	A″
		C3−C4	1.276	327.7	A′	388.3	A″	155.1	A′
		C4−C5	1.288	482.0	A′	514.3	A′	576.7	A″
		C5−C6	1.304	914.5	A′	1262.1	A′	1692.9	A′
		C6−C7	1.276	1996.2	A′	2036.0	A′	2184.8	A′
		C7−B	1.464						

TABLE 1 (Continued)

C_nB^-	basis set[a]	geometry		frequencies
		∠C1C2C3	178.4	
		∠C2C3C4	176.6	
		∠C3C4C5	176.1	
		∠C4C5C6	172.6	
		∠C5C6C7	177.3	
		∠C6C7B	178.6	

[a] See text for 6-31G(d)[END+] and for 6-31G(d)[C1+C*n*+].

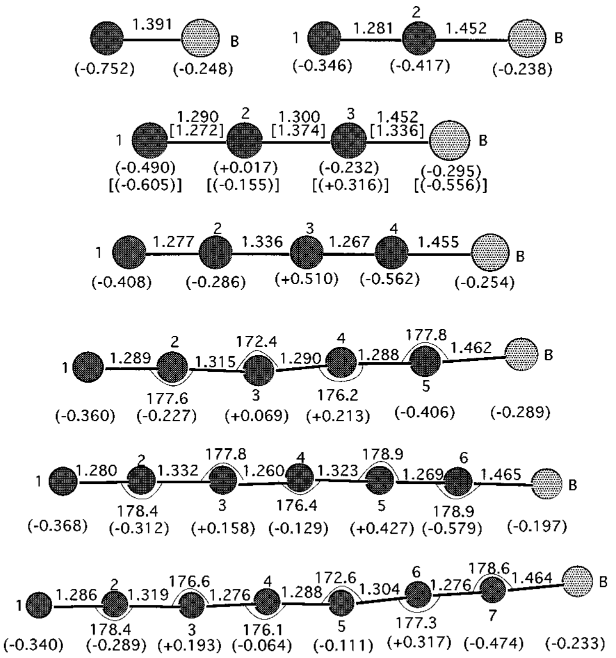

Figure 1. Geometries of C_nB^- cluster anions ($n = 1-7$) in their ground states optimized with the MP2(full) method. The basis set used is the 6-31G(d)[END+] basis set described in the text. The values in parentheses are the net atomic charges obtained from the Mulliken population analysis. The values in brackets are the results calculated for C_3B^- in its lowest singlet state.

the basis set for the smaller C_nB^- anions ($n = 1-4$). The results for the lowest singlet state of C_3B^- are also given in Table 1 and Figure 1. Comparing the calculated results among various basis sets, one can see that the diffuse sp functions and f orbitals are all not very important for the geometry optimizations. There is no substantial difference between the results calculated with 6-31G(df)[END+] and those with 6-31G(d)[END+] (or 6-31G-(d)). For the singlet states of C_2B^- and C_3B^-, we may compare the geometries optimized at the MP2/6-31G(d)[END+] level with those at the MP2/6-31+G(d) level. The two kinds of results are very close to each other. The largest difference for the bond lengths is only 0.001 Å. Besides comparing the calculated net atomic charges for C_nB^- displayed in Figure 1 with those for C_nN^-,[10] we can see some slight differences between them. The two end atoms, C1 and N, in C_nN^- always have much more negative net charges than the other C atoms. But in C_nB^-, the C atom attached to the B atom, denoted by C*n*, usually has more negative charge than the B atom except for $n = 3$. From this, it seems that one of the two sets of diffuse sp functions should be placed on C1 and C*n* atoms instead of C1 and B atoms. We still use the 6-31G(d)[END+] basis set in the calculations of C_nB^- due to the following reasons: (1) We hope to use some kind of basis set as used for C_nN^-. (2) The practical distribution of the electron charge centered at B atom is expected to be more diffuse even if its negative net charge is slightly less than the atom C*n* because the electronegativity of the B atom is smaller than the C atom and its atomic radius is larger than the C atom. (3) Actually, the diffuse sp functions centered at the B atom are diffuse enough to effectively cover the region of the atom C*n*. That means it does not matter whether the two sets of diffuse sp functions are placed on atoms C1 and B (*i.e.*, [END+]) or on atoms C1 and C*n* (*i.e.*, [C1+C*n*+]). To confirm this idea, we have examined both basis sets in the calculations of C_2B^- and C_4B^-. As listed in Table 1, the geometries optimized with the two kinds of basis sets are almost identical. The largest difference for the optimized bond lengths is only 0.001 Å. So the basis set 6-31G-(d)[END+] used for the calculations of C_nN^- is indeed feasible also for the calculations of C_nB^-. This conclusion can be confirmed further from comparison of the calculated VDEs displayed in Table 2 and discussed in the subsequent subsection.

3.2. Electron Detachment Energies. The calculated VDEs listed in Table 2 indicate that the diffuse functions are much more important to the energy calculations. The calculated VDEs without the diffuse functions (+) are obviously smaller than the VDEs evaluated with the diffuse functions (+). The results calculated with the 6-31G(d) basis set augmented with the diffuse functions are closer to those calculated with 6-31+G-(df) than the results with the 6-311G(df) basis set. We can also see from Table 2 that the VDEs calculated with the 6-31G(d)-[END+] basis set are very close to the results calculated with the 6-31G(d)[C1+C*n*+] and 6-31+G(d) basis sets for the smaller C_nB^- anions. These results further confirm the reliability of the 6-31G(d)[END+] basis set to the calculations of C_nB^- anions.

Comparison of the results calculated by using different methods with a basis set reveals the importance of the electron correlation effect. The HF energy calculations give obviously inconsistent results with the MP4SDTQ and MP2 methods. The MP2 VDEs are very close to the MP4SDTQ VDEs in the present case. It follows that the higher-order electron correlation energy effects on the vertical electron detachment energies of the C_nB^- anions are not important. The MP2 VDEs are good enough.

Comparing the VDEs of various anions calculated at the same level, we can see that the VDE for C_3B^- is exceptionally larger than that for the other anions. This is because the ground state of C_3B^- is the triplet state, while the ground states of all others are the singlet state. The VDE values calculated for the singlet state of C_3B^- are 1.083 (HF), 3.968 (MP2), and 3.728 eV (MP4SDTQ). Except for C_3B^-, there are two trends for the changes of VDEs with *n*. One is that no matter whether *n* is even or odd, the VDE of C_nB^- increases with *n*. Another is that the VDE of C_nB^- for $n = 2m$ is always larger than the VDE for $n = 2m - 1$ and even larger than the VDE for $n = 2m + 1$ when $m = 3$.

3.3. Fragmentation Energies and Stabilities. As concluded by other researchers, the odd−even alternations in the TOF signal intensities of the ions of low-mass pure carbon clusters (within 10 carbon atoms) are determined by the alternations in electron affinity or by ionization energies rather than the relative stability of the neutral species.[7] This means that the cluster

TABLE 2: Vertical Electron Detachment Energies (eV) of C_nB^- ($n = 1-7$) Calculated at Different Levels[a]

basis set[b]	method	CB^-	C_2B^-	C_3B^-	C_4B^-	C_5B^-	C_6B^-	C_7B^-
6-31G(d)	HF	−2.419	1.250		1.901			
	MP2	1.962	2.411		3.630			
	MP4SDTQ	2.229	2.435		3.600			
6-31G(d)[END+]	HF	−1.616	1.935	6.213	2.382	1.902	2.531	2.237
	MP2	2.850	3.187	7.331	4.218	3.474	5.368	4.175
	MP4SDTQ	3.100	3.212	7.265	4.175	3.543	5.167	4.158
6-31G(d)[C1+C*n*+]	HF		1.961		2.399			
	MP2		3.187		4.202			
	MP4SDTQ		3.216		4.161			
6-31+G(d)	HF	−1.616	1.973					
	MP2	2.850	3.206					
	MP4SDTQ	3.100	3.238					
6-311G(df)	HF	−1.880						
	MP2	2.783						
	MP4SDTQ	3.012						
6-311+G(df)	HF	−1.597						
	MP2	3.102						
	MP4SDTQ	3.329						

[a] The geometries used for the energy calculations are those optimized by the MP2(full) method with the same basis sets. [b] See text for 6-31G(d)[END+] and for 6-31G(d)[C1+C*n*+].

TABLE 3: Fragmentation Energies (eV) of C_nB^- ($n = 1-7$) Calculated by the MP2(Full), MP4SDTQ(Full), and QCISD(T)(Full) Methods[a]

	$\rightarrow C_{n-1}B^- + C$			$\rightarrow C_{n-2}B^- + C_2$			$\rightarrow C_{n-3}B^- + C_3$		
C_nB^-	MP2	MP4	QCISD(T)	MP2	MP4	QCISD(T)	MP2	MP4	QCISD(T)
CB^-	6.179	5.816							
C_2B^-	8.856	8.562	8.671	8.831	8.453	8.569			
C_3B^-	4.497	4.467	4.716	7.050	6.634	7.358	6.129	5.583	6.208
C_4B^-	8.448	8.083	7.537	6.642	6.154	6.224	8.300	7.649	7.819
C_5B^-	4.266	4.279	4.365	6.411	5.966	5.873	3.710	3.365	3.512
C_6B^-	8.489	8.062	7.712	6.453	5.945	5.986	7.702	6.960	6.446
C_7B^-	4.434	4.484	4.630	6.620	6.151	6.251	3.688	3.362	3.540

[a] The basis functions used are 6-31+G(d) for atoms at the end points of the C_nB^- chain and 6-31G(d) for the other C atoms.

ion with a larger electron affinity or with a larger ionization energy (or VDE) should be more stable. Our calculated VDE of C_nB^- for $n = 2m$ is always larger than the VDEs for $n = 2m - 1$ and $2m + 1$ except for C_3B^-, whose ground state is a triplet state. From this trend in VDEs, we may expect that the electron affinity of the corresponding neutral system for $n = 2m$ may also be larger than those for $n = 2m - 1$ and $2m + 1$ except for C_3B. These can explain the observed odd−even alternation in the TOF signal intensities of C_nB^- except for C_3B^-. The relative stability of the clusters can also be analyzed in terms of the fragmentation reaction energy, because the relative stability of the clusters is correlated with the energy difference of the energies of the neighboring size of the clusters. Such an energy difference is just related to the reaction energy of

$$C_nB^- \rightarrow C_{n-1}B^- + C \tag{1}$$

The reaction energies calculated by using the MP2, MP4SDTQ, and QCISD(T) methods with the 6-31G(d)[END+] basis set are summarized in Table 3. Also listed in the table are the reaction energies to produce the C_2 and C_3 molecules:

$$C_nB^- \rightarrow C_{n-2}B^- + C_2 \tag{2}$$

$$C_nB^- \rightarrow C_{n-3}B^- + C_3 \tag{3}$$

One can see from Table 3 that the fragmentation energies calculated by using the three methods are close to each other, which confirms the convergence of the results obtained from the MP2 and MP4SDTQ perturbational calculations. The strong odd−even alternation in the fragmentation energies for reactions 1 and 3 reveals the odd−even alternation for the stability of C_nB^-. The C_nB^- anions of even *n* should be more stable than the C_nB^- anions of odd *n*, and therefore in the mass spectra, C_nB^- anions of even *n* are dominant.[11] Because C_{n+1} and C_nB^- are isoelectronic, the odd−even alternation for the stability of C_nB^- is the same as that found for C_{n+1} and $C_{n+1}{}^+$.[15] Comparing with the odd−even alternation for the stability of C_nN^-,[10] one can see that the odd−even alternation found for C_nB^- is opposite to the odd−even alternation for C_nN^-. This is because the C_nN^- anion has two additional π electrons than the corresponding C_nB^- anion, and each C atom contributes just two π electrons to the anion. So the total number of π electrons in $C_{n+1}B^-$ is equal to that in C_nN^-. The calculated odd−even alternation in (1) and (3) is consistent with the experimental finding. Under the complicated hot reaction conditions, less stable odd C_nB^- collapses to more stable even C_nB^-.

For examining the contributions of the bending of the structures of C_nB^- ($n = 5-7$) to the stabilities, the MP4SDTQ/6-31G(d)[END+] energy calculations are also carried out by use of the linear geometries corresponding to the saddle points on the MP2/6-31G(d)[END+] energy surfaces. The calculated total energies of the linear structures of the C_5B^-, C_6B^-, and C_7B^- clusters are only 0.551, 0.002, and 0.016 eV higher than the corresponding stable bent structures, respectively. So the contributions of the bending of the structures of C_nB^- ($n = 5-7$) to the stability are very small such that these clusters could appear pseudolinear in experiment. This floppiness in bending motions is also seen in the lowest harmonic frequencies listed in Table 1. By use of the total energies of the linear structures instead of the bent structures for all C_nN^- isomers, the calculated fragmentation energies do not change any trends about the relative stabilities of C_nB^- clusters that we get with the bent isomers. A similar conclusion was also obtained for the C_nN^- anions.[10]

4. Conclusions

A series of *ab initio* calculations have been carried out on the structures, vertical electron detachment energies, and fragmentation energies of the C_nB^- anions ($n = 1-7$). Comparison of the results calculated at various levels reveals that the MP2/6-31G(d)[END+] geometry optimization followed by MP4SDTQ energy evaluation which is reliable for the calculations of C_nN^- is also reliable for C_nB^-. The convergence of the perturbational results can be found from that the fragmentation energies calculated at the QCISD(T)/6-31G(d)[END+] level and are also close to those at the MP2/6-31G(d)[END+] and MP4SDTQ/6-31G(d)[END+] levels.

The geometries optimized and harmonic vibrational frequencies calculated at this uniform level indicate that the linear structures are stable only for C_nB^- anion up to $n = 4$. The C_nB^- anion of larger *n* in the ground state is slightly bent and very floppy for bending motions. These conclusions are different from those reported by Wang *et al.*, who claimed "C_nB^- cluster anions would adopt a linear structure as the C_n^- and C_nN^- anions do", based on the HF/3-21G calculations.[11]

The calculated fragmentation energies to produce C or C_3 have an obvious odd−even alternation, which shows that C_nB^- of even *n* is more stable than odd *n*. The calculated odd−even alternation for C_nB^- is opposite to that for C_nN^-, which is consistent with the odd−even alternation of the TOF signal intensities observed by Wang *et al.*[11]

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