Density Functional Theory Study of the Isomers of C_nB and C_nB_2

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C_nB and C_nB_2 clusters, $n = 4-10$, were studied at the B3LYP/6-311G** level of theory. When $n = 5$, the linear and cyclic structures are comparable in energy. For $n \geq 6$, the minimal-energy structures were found to be cyclic. Moreover, in contrast to all other reported heteroatom−carbon clusters, the lowest-energy linear structures were not those terminated by the boron atoms. These observations result from the electron-deficient nature of boron. The calculations predict that linear and cyclic forms will coexist for smaller cluster sizes, but that monocyclic forms will be the exclusive product as n increases. In their structural tendencies, the boron−carbon clusters are similar to pure carbon clusters.

Introduction

Small carbon chains have been studied extensively.[1] Above a size threshold, C_n clusters may exist in both linear and cyclic forms, and at a later stage the fullerene cages will dominate.[1] The ground electronic states of linear C_n clusters[2] depend on the parity of the carbon chain and alternate with each new added carbon atom. Clusters of carbon with one or two heteroatoms have become the focus of recent research interest[3−9] after the discovery of these species in the interstellar medium and in the atmosphere of some planets.[10−14] Such particles have been synthesized successfully[15] and some are stable under normal conditions.[16]

Most of the currently available data for heteroatom−carbon clusters are for linear, doubly terminated XC_nX clusters in which the heteroatoms are from Groups IVB−VIIB[16] or the transition metals.[17] Detailed computational results for carbon clusters containing N, P, O, S, and Se have indicated that these atoms participate in the π-electron system of the clusters and that linear structures with terminal heteroatoms are lowest in energy.[18−20] The heteroatom in the current work is boron, typically used as a *p*-type dopant in semiconductor studies. The valence shell of boron has one less electron than the carbon atoms in the cluster. This is a significant difference in comparison to the other, electron-rich heteroatoms that have been attached to carbon clusters. Chemically, boron atoms are known to form electron-deficient bonds of order less than one. Moreover, boron has a lower electron negativity (Pauling)[21] than C, N, P, O, S, and Se. These facts combine to make boron-containing carbon clusters interesting for computational study and for comparison with those of pure carbon and carbon clusters containing N, P, O, S, and Se.

Aside from studies of networked C_3B and C_4B, there are few published results for compounds of carbon and boron. The matrix isolation synthesis and spectroscopy of small BC_nB clusters have been reported.[22] Boron-containing fullerenes have been synthesized[23] and computationally studied.[24] Computational data for boron-doped carbon nanotubes are also available.[25] Finally, geometry/energy calculations for boron-terminated linear C_nB^- clusters have been reported.[26] The focus of the current work is to determine the preferred cluster geometries for C_nB and C_nB_2 clusters and to compare the results with those for pure carbon and N-, P-, or S-terminated carbon chains. In particular, we wish to explore the relationship between electronic structure and the cyclic or acyclic geometry preference, the relationship of electronic structure to the position of the heteroatoms in linear clusters, and the mechanism, in relation to that of carbon clusters, for cyclic isomer formation.

Computational Details

All of the clusters were studied with the Gaussian98 program package[27] at the B3LYP/6-311G** level of theory. A significant number of the possible positional isomers for the linear C_nB and C_nB_2 geometries were examined. For cyclic clusters, rings of 3 to 8 atoms were studied. Since the C_nB_2 clusters have an even number of electrons, two optimizations were performed for each structure: one each for the lowest singlet and triplet electronic states. The clusters were treated without any symmetry constraints. For each optimized structure, harmonic frequencies and force constants were obtained at the same level of theory. In each group of isomers, the reference energy is taken as that of the lowest-lying linear geometry. All reported structures were local minima and the relative energies have been corrected for the zero-point energies.

Previous calculations for carbon−heteroatom systems have shown that there is no significant difference in the results from a DFT treatment with the 6-311G** and aug-cc-PVTZ basis sets.[28] The latter gives slightly lower absolute energies, but the energy differences between different cluster geometries remain unchanged. Relative DFT energy differences of the order of 0.03 eV are not significant, due to uncertainties in the absolute energies of the clusters. While DFT geometry optimizations are generally regarded as reliable, some energies may be overestimated. In a study such as this, in which the lowest-energy isomer is sought, it is necessary to confirm that the relative energy ordering, not necessarily the magnitude of the differences, is correct. Therefore, the geometries of some of the isomers that are close in energy were also treated by the CASSCF formalism, using five π-electrons and five orbitals as the active space. These results are included in the discussion.

Results

Linear C_nB Clusters. Computational studies have shown that carbon clusters containing N, P, S, or O, energetically prefer to exist as linear clusters terminated by the heteroatom(s).[16−20] However, all of these clusters are electron-rich in comparison

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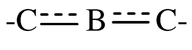
TABLE 1: B3LYP/6-311G Energies (zero-point-corrected) and Bond Lengths for Linear C_nB Clusters**

Geometry	**E, eV**
C — C — C — C — B 1.2796 1.2927 1.2702 1.3641	**0**
C — C — C — B — C 1.2997 1.2762 1.4005 1.3649	1.96
C — C — B — C — C 1.2156 1.4577 1.3689 1.2769	0.35
C — C — C — C — C — B 1.2983 1.2890 1.2774 1.2822 1.3677	0.53
C — C — C — C — B — C 1.2877 1.2935 1.2685 1.3849 1.4792	1.31
C — C — C — B — C — C 1.3231 1.2606 1.4367 1.3738 1.2839	**0**
C — C — C — C — C — C — B 1.2810 1.2937 1.2644 1.2834 1.2734 1.3658	0.08
C — C — C — C — B — C — C 1.2911 1.3082 1.2500 1.4259 1.3819 1.2836	**0**
C — C — C — B — C — C — C 1.3028 1.2788 1.3956 1.3919 1.2794 1.3030	0.75
C — C — C — C — C — C — C — B 1.2932 1.2911 1.2728 1.2792 1.2780 1.2811 1.3659	0.77
C — C — C — C — C — B — C — C 1.3072 1.2706 1.3054 1.2450 1.4374 1.3738 1.2813	**0**
C — C — C — C — B — C — C — C 1.2843 1.2937 1.2681 1.3731 1.4235 1.2656 1.3174	0.30
C — C — C — C — C — C — C — C — B 1.2816 1.2945 1.2646 1.2838 1.2675 1.2820 1.2748 1.3669	0.34
C — C — C — C — C — C — B — C — C 1.2906 1.3029 1.2527 1.3134 1.2411 1.4354 1.3761 1.2809	**0**
C — C — C — C — B — C — C — C — C 1.2867 1.3013 1.2582 1.3984 1.3982 1.2580 1.3013 1.2867	0.05
C — C — C — C — C — C — C — B — C — C 1.3005 1.2770 1.2931 1.2526 1.3149 1.2393 1.4392 1.3740 1.2798	**0**
C — C — C — C — C — C — B — C — C — C 1.2850 1.2928 1.2654 1.2857 1.2685 1.3773 1.4165 1.2690 1.3139	0.48
C — C — C — C — C — B — C — C — C — C 1.3041 1.2738 1.3001 1.2502 1.4257 1.3728 1.2661 1.2949 1.2822	0.17
C — C — C — C — C — C — C — C — C — C — B 1.2819 1.2951 1.2647 1.2843 1.2676 1.2821 1.2693 1.2816 1.2758 1.3670	0.48
C — C — C — C — C — C — C — C — B — C — C 1.2897 1.3005 1.2561 1.3051 1.2450 1.3205 1.2365 1.4397 1.3745 1.2794	**0**
C — C — C — C — C — C — B — C — C — C — C 1.2884 1.2998 1.2564 1.3046 1.2490 1.4153 1.3833 1.2624 1.2980 1.2833	0.07

to those containing boron. Moreover, boron atoms are restricted in the range of hybrid orbital configurations typically exhibited in bonding. Therefore, there is no a priori reason to assume that carbon−boron clusters will follow any of the trends observed for the other heteroatom−carbon clusters. We begin with the mono-boron clusters in the linear geometry. The optimized structures for the three lowest-energy linear configurations for each cluster, beginning with $n = 4$, are shown in Table 1. In general, the carbon−boron bond lengths in these structures indicate that the two elements are multiply bonded. The lengths of the carbon−boron bonds fall into two classes. The first, in a range around 1.36 Å, is indicative of a substantial doubly bonded contribution to the mix of resonance structures. The other bond lengths, near 1.42 Å, are characteristic of doubly bonded structures with a less significant contribution.[29] Although there are exceptions, the general rule is that the lowest-energy linear isomer is that with the boron atom in position 3, that is, a C_iBCC conformer. As discussed in a later section, in these structures the boron−carbon bonds are best described in global terms as a mixture of doubly and singly bonded resonance forms.



The effect of the boron atom position in the linear chain is evident if the first three C_nB clusters in Table 1 are considered. For $n = 4$, the lowest-energy cluster is that terminated by the boron atom. It lies 0.35 eV below the cluster with boron as the central atom and almost 2 eV below the cluster in which the boron is displaced by one position from the terminus. However, increasing the number of carbon atoms by one, the C_5B cluster, the lowest-energy positional isomer is C_3BCC, which lies 0.53 eV below the boron-terminated structure. At $n = 6$, the energy of the C_4BCC structure is nearly identical to that of the boron-terminated cluster. Finally, for $7 \leq n \leq 10$, the most stable linear cluster is that with the boron atom in the third position. For the ground-state structures terminated by boron, C_4B and

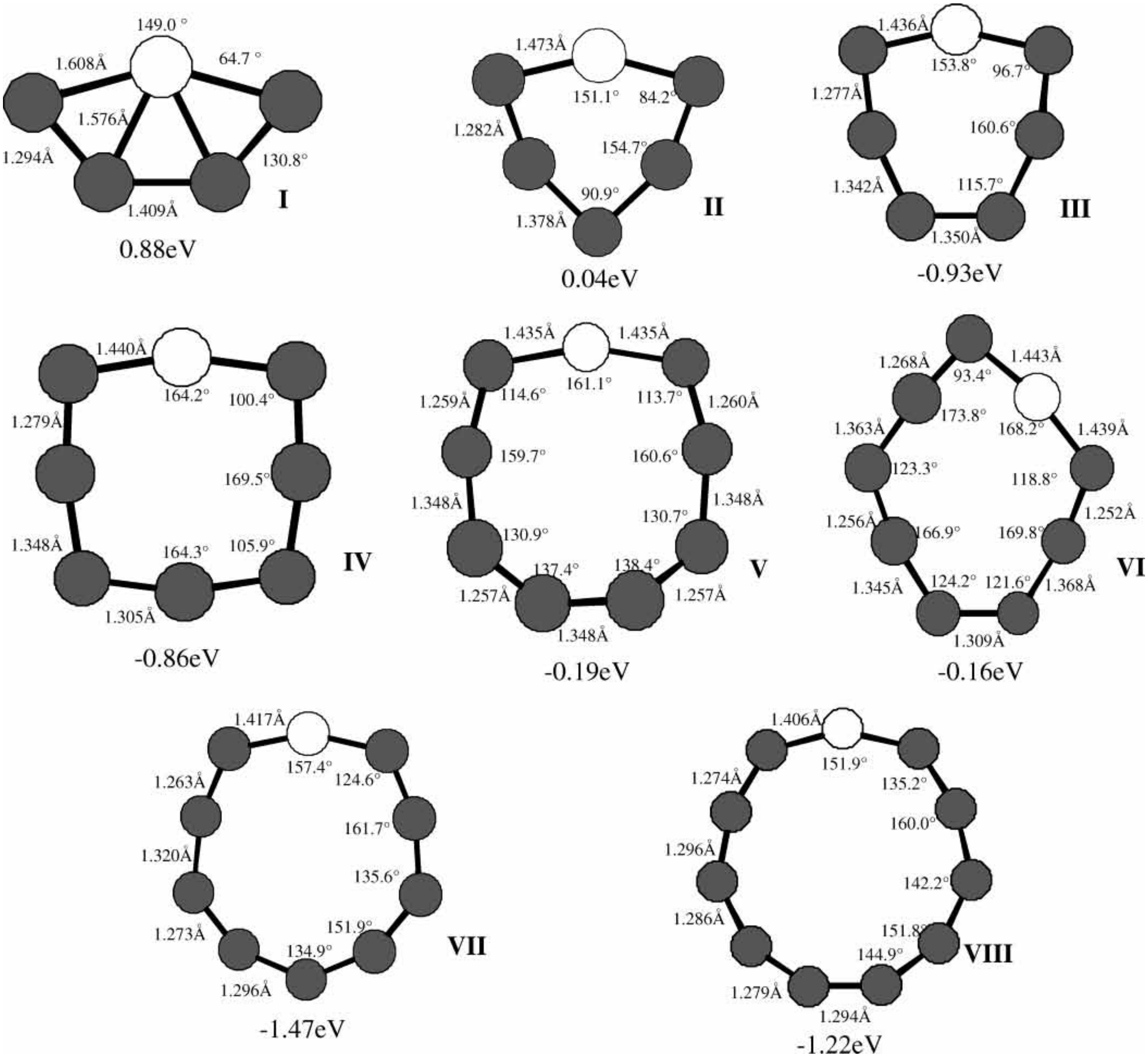


Figure 1. Geometries and energies of the lowest-energy cyclic structures for the C_nB clusters at the B3LYP/6-311G** level of theory. Energies are relative to the lowest-energy linear structure in Table 1.

C_6B, the unpaired electron is *localized* on the boron atom. For the remaining ground-state clusters, in which the boron atom is found at position three, the unpaired electron is *delocalized*, primarily over the longer section of carbon atoms. Terminal boron atoms have a Mulliken charge of approximately 0.33*e*, while boron atoms in the third position have much greater charges, typically 0.70*e*. All of the minimum-energy structures with terminal boron atoms represent a $^2\Sigma_g$ electronic state and are essentially spin uncontaminated with $\langle S^2 \rangle$ values within 5% of the expected 0.75 (before annihilation of the contaminants). The $C_nB{-}C{-}C$ structures have a $^2\Pi_u$ ground state, with similar results for the eigenvalue of the spin operator. The higher-energy positional isomer structures for each n show more spin contamination. The minimum-energy structures are confirmed stationary points on the respective potential surfaces as indicated by harmonic frequency calculations.

Cyclic C_nB Clusters. For $n \leq 8$, all possible cyclic structures were optimized. This includes all clusters from three-membered rings up to $(n + 1)$-membered rings. In general, the most stable structures correspond to the latter. With two exceptions, these cyclic forms were the global minima for the mono-boron clusters. The optimized structures, including bond lengths, angles, and energies, are presented in Figure 1. Only one stable cyclic C_4B isomer, **I**, could be identified. The energy of this isomer is 0.88 eV greater than that of the linear structure. C_4B is expected to exist only as a boron-terminated linear chain. Among the C_5B species, the most stable cyclic form, the six-membered ring, **II**, lies 0.04 eV above the lowest-energy linear cluster. From these results, we may conclude that the probability of forming the linear C_3BCC and the six-membered ring shown in Figure 1 are essentially equivalent. For C_6B, the lowest-energy structure is the seven-membered ring, **III**, which lies 0.93 eV below the most stable linear C_6B. Its shape follows analogously from C_5B. At this stage in the size progression of C_nB clusters, we have reached the point at which the clusters are expected to exist exclusively in the cyclic form. In C_7B, the eight-membered ring, **IV**, lies 0.86 eV below the most stable linear form. In terms of structure it is a continuation of the monocyclic C_5B

TABLE 2: B3LYP/6-311G Energies (zero-point-corrected) and Bond Lengths for Linear C_nB_2 Clusters**

Geometry	E, eV
B — C — C — C — C — C — C — B (s)1.5334 1.2274 1.3434 1.2224 1.3434 1.2274 1.5334	1.91
C — B — C — C — C — C — C — B (s)1.4414 1.3582 1.3111 1.2411 1.3287 1.2346 1.5286	3.42
C — B — C — C — C — C — B — C (s) 1.4458 1.3727 1.2868 1.2680 1.2680 1.3727 1.4458	4.68
C — C — B — C — C — C — B — C (s) 1.2802 1.3736 1.4392 1.2397 1.3167 1.3553 1.4447	2.48
C — C — B — C — C — B — C — C (s) 1.2810 1.3664 1.4585 1.2224 1.4585 1.3364 1.2810	**0**
C — C — C — B — C — B — C — C (s) 1.3011 1.2707 1.4156 1.3490 1.4319 1.3821 1.2804	1.65
C — C — C — B — B — C — C — C (s) 1.2995 1.2788 1.4047 1.4937 1.4047 1.2788 1.2995	2.67
B — C — C — C — C — C — C — C — B (t) 1.3607 1.2816 1.2764 1.2756 1.2756 1.2764 1.2816 1.3607	0.91
C — C — B — C — C — C — C — B — C (t) 1.2776 1.3730 1.4450 1.2276 1.3379 1.2294 1.4435 1.3651	1.42
C — C — B — C — C — C — B — C — C (t) 1.2836 1.3788 1.4245 1.2743 1.2740 1.4245 1.3794 1.2837	**0**
B — C — C — C — C — C — C — C — C — B (s)1.5301 1.2286 1.3412 1.2249 1.3366 1.2249 1.3412 1.2286 1.5301	2.08
C — C — B — C — C — C — C — C — B — C (s)1.2789 1.3734 1.4414 1.2331 1.3240 1.2428 1.3091 1.3591 1.4431	2.48
C — C — B — C — C — C — C — B — C — C (s) 1.2797 1.3691 1.4511 1.2238 1.3434 1.2238 1.4501 1.3691 1.2798	**0**
B — C — C — C — C — C — C — C — C — C — B (t) 1.3616 1.2814 1.2768 1.2756 1.2759 1.2759 1.2756 1.2766 1.2815 1.3615	1.33
C — C — B — C — C — C — C — C — C — B — C (t)1.2772 1.3738 1.4434 1.2286 1.3348 1.2288 1.3329 1.2317 1.4405 1.3655	1.67
C — C — B — C — C — C — C — C — B — C — C (t) 1.2813 1.3771 1.4308 1.2571 1.2904 1.2904 1.2571 1.4309 1.3769 1.2814	**0**
C — C — B — C — C — C — C — C — C — B — C — C (s)1.2789 1.3709 1.4475 1.2259 1.3386 1.2247 1.3387 1.2259 1.4474 1.3707 1.2789	**0**
C — C — C — B — C — C — C — C — C — B — C — C (s)1.2988 1.2755 1.4049 1.3563 1.3050 1.2460 1.3212 1.2353 1.4389 1.3749 1.2783	1.30
C — C — C — C — B — C — C — B — C — C — C — C (s)1.2812 1.2928 1.2685 1.3641 1.4496 1.2268 1.4488 1.3642 1.2685 1.2928 1.2811	0.33

and C_6B structural trend. Small-sized C_8B rings are unstable relative to the chain structures, but two nine-membered rings have energies below that of that of the lowest chain structure. These are shown in Figure 1. The first, **V**, is similar in structure to the minimum-energy isomers reported for the lower homologues. The energy of this structure is 0.19 eV less than that of the most stable linear cluster. A second monocyclic structure, **VI**, with an energy only 0.03 eV higher, has a more rhomboid appearance. In agreement with the smaller clusters, the energies of monocyclic C_9B, **VII**, and $C_{10}B$, **VIII**, lie 1.47 and 1.22 eV below the lowest-energy linear forms.

The boron atom in all of these monocyclic molecules carries a positive Mulliken charge of approximately 0.4*e* and the compensating negative charge is typically distributed between its two nearest-neighbor carbon atoms. The unpaired electron is equally distributed over either the carbon atoms opposite to boron (C_5, C_6, C_8, C_9) or with alternating carbon atoms (C_7, C_{10}). The −C−B−C− bond angle is always greater than 150°. In all monocyclic clusters there is a slight shortening of the carbon−boron bond lengths with increasing ring size—from 1.47 Å in C_5B, through 1.44 Å in the intermediate-sized rings, to 1.41 Å in the last two monocycles. With increasing number of carbon atoms, the bond alternation decreases as a result of delocalization that affects the carbon−boron as well as the carbon−carbon bonds and makes the former become more carbon−carbon-like in its bond characteristics.

Linear C_nB_2 Isomers. Carbon clusters containing two heteroatoms from the nitrogen, phosphorus, and sulfur set were predicted to be most stable when the carbon chain was doubly terminated. Some of these species have been observed experimentally.[15,30] The computational data for linear C_nB indicate that because of the electron-deficient (relative to carbon) nature of boron, these observations might not be valid for the doubly terminated carbon−boron chains. Again, we report both linear chain geometries and monocyclic forms. The optimized structures for three different structural permutations of each cluster are shown in Table 2, along with the relative energies. On the basis of extensive calculations for the first two clusters, $n = 6$ and $n = 7$, calculations were completed for all C_nB_2 clusters, $6 \leq n \leq 10$, with the boron atom only in the terminal or the adjacent two positions at each end of the carbon chain. This requires calculations for three such structures per cluster. Without exception, the general rule is that the lowest-energy linear isomer is that with both boron atoms in position 3, that is, the $C_2BC_iBC_2$ conformers. Unlike the mono-boron clusters, however, the energy difference between this geometry and any other possible linear geometry was usually substantial. As was described for the linear C_nB clusters, the lengths of the carbon−boron bonds fall into two categories—one has bond lengths in a range around 1.37 Å, indicative of a substantial doubly bonded contribution to the mix of resonance structures, and the other involves bond lengths near 1.42 Å, characteristic of structures with less significant doubly bonded contributions.[29] The ground state of linear C_n clusters alternates: even carbon clusters have a $^3\Sigma$ ground state, while the odd clusters have the $^1\Sigma$ electronic state. This electronic state trend was also observed in studies of doubly terminated C_nX_2 clusters (X = O, S, or Se),[19,20] where the preferred position of the heteroatoms was found to be at the ends of the chain. For doubly terminated nitrogen and phosphorus carbon clusters, the odd carbon clusters have the triplet ground state and the even carbon clusters are singlets. It seems clear that the ground electronic state of linear heteroatom-terminated carbon clusters depends on the parity of the carbon chain and the number of heteroatom valence electrons, so that odd carbons + an odd number of valence electrons and even carbons + an even number of valence electrons result in a $^3\Sigma$ ground state and mixed combinations yield the $^1\Sigma$ ground state. This arises from the fact that all MOs with π-symmetry are doubly degenerate. Addition of an extra carbon atom adds two electrons to the π−system. These electrons are accommodated in a new π-orbital leading to a triplet state. Anticipating (correctly) that this trend would continue in the boron clusters, two optimizations were carried out for each structure: one each for the singlet and triplet states. The even-carbon clusters were indeed found to have singlet ground states, $^1\Sigma_g$ and the odd-carbon clusters, the triplet multiplicity, $^3\Sigma_g$.

For the C_6B_2 group of structures, all possible linear positional isomers are included in Table 2 to illustrate the importance of the boron position. All energy comparisons are relative to that of the lowest-energy linear $C_2BC_2BC_2$ singlet electronic state conformer. The data in the table show that if either boron atom is moved closer to the center, the energy rises substantially. The highest-energy conformer is that with both boron atoms moved in one position from the respective terminus. The linear C_7B_2 clusters are the first in the current study to have a triplet ground electronic state. For the linear C_8B_2 structure, the most stable form is again a singlet with the boron atoms two positions from the ends of the chain. The predicted ground state for the C_9B_2 linear cluster is the triplet. $C_{10}B_2$ clusters are the largest studied in this work. The results for the linear forms are similar to those for the other even carbon C_nB_2 clusters.

The boron atoms in these symmetric geometries have Mulliken charges of approximately 0.70*e*. The adjacent carbon atoms located toward the end of the chain have a negative charge of approximately one-half that value. The interior carbon atoms, except for the central atom(s), carry the remainder of the compensating negative charge. Based upon the values of $\langle S^2 \rangle$, spin contamination for the triplet states was not an issue. For all linear C_nB_2 isomers in the $CCBC_{n-4}BCC$ form, the unpaired electrons of the clusters with triplet ground states (i.e., the ones with an odd number of carbon atoms) are delocalized throughout the entire chain with maxima at the odd positions in the inner carbon bridge and at the terminating carbon atoms. In general, the even carbon species are more acetylenic than the odd. The bond alternation of the even carbon di-boron species is also greater than that of the C_nB analogues.

Cyclic C_nB_2 Isomers. The C_nB calculations for $n \geq 6$ found that the monocyclic structures were lower in energy than the linear isomers. All possible monocyclic structures, including those of smaller ring size with attached linear chains, were studied. Invariably, the maximum size monocycles were also the lowest in energy. Using these results as the basis for selecting potential C_nB_2 structural candidates, only the positional isomers of the largest possible monocycles were optimized. The minimum-energy structures are shown in Figure 2, along with their respective bond lengths, bond angles, and energies relative to the lowest-energy linear cluster. The minimum-energy cyclic C_6B_2 isomer, **IX**, 0.16 eV below the linear form, is the most symmetric monocycle and is in the triplet electronic state. Note that the linear geometry ground electronic state was the singlet. The relatively small energy difference indicates that cluster synthesis may result in concurrent production of both singlet linear and triplet cyclic forms. The energy difference between monocyclic rings and linear chains increases for C_7B_2, and the expectation is that all of the remaining clusters prefer the cyclic geometry over the linear structures. Two structures, differing in the arrangement of the boron atoms, lie 1.27 (**X**) and 1.22 eV (**XI**) below the linear chain. The preferred electronic state of the monocycles is the singlet, but that of the linear form is the triplet. Two of the four possible C_8B_2 rings lie lower in energy than the linear form. The global energy minimum is **XII**, which lies 0.47 eV below the linear minimum. It is in a singlet electronic state, as was true of the linear form. The most stable monocyclic C_9B_2 clusters are all singlets and lie more than 2.6 eV below the lowest linear chain. These three isomers **XIII**, **XIV**, and **XV** are separated by approximately 0.1 eV and may appear in similar proportions in any synthetic procedure. The triplet state is the preferred electronic state for the lowest-lying cyclic $C_{10}B_2$ isomers. Again, three isomers lie below the linear minimum. The lowest-energy structures, **XVI** and **XVII**, are stabilized by more than 1 eV with respect to the linear chains.

The Mulliken charge on the two boron atoms is identical in these cyclic isomers and lies in the range 0.35−0.45*e*. The corresponding negative charge is primarily distributed over the two adjacent carbon atoms. For structures with a triplet ground state, the unpaired electrons are delocalized over those same carbon atoms. In general, the bonding around the boron atoms reflects a compromise between the tendency for boron to form linear structures and the energetic effects of cyclization. The −C−B−C− bond angles are generally greater than 150°, and bond lengths are similar to those reported for the linear geometries.

Discussion

Several sets of mono-boron clusters have nearly isoenergetic isomers. In two instances, C_6B and C_8B, the isoenergetic isomers are both linear. However, one important case, the C_5B isomers, is more challenging, since the nearly isoenergetic species include a linear and a cyclic isomer. All of the C_5B isomers were optimized using the CASSCF theoretical method to test the relative accuracy of the DFT energy ordering of the linear isomers. The active space included five π-electrons and five π-orbitals, totaling 75 electron configurations. The results are shown in Figure 3. The bond lengths and angles for the cyclic isomer are essentially unchanged (within 0.5%) from those in Figure 2. For the linear C_5B clusters, the bond length variation between the two theoretical methods is between 1 and 5%. However, the terminal-boron cluster becomes considerably more acetylenic than in the DFT results, with a concomitant increase in its

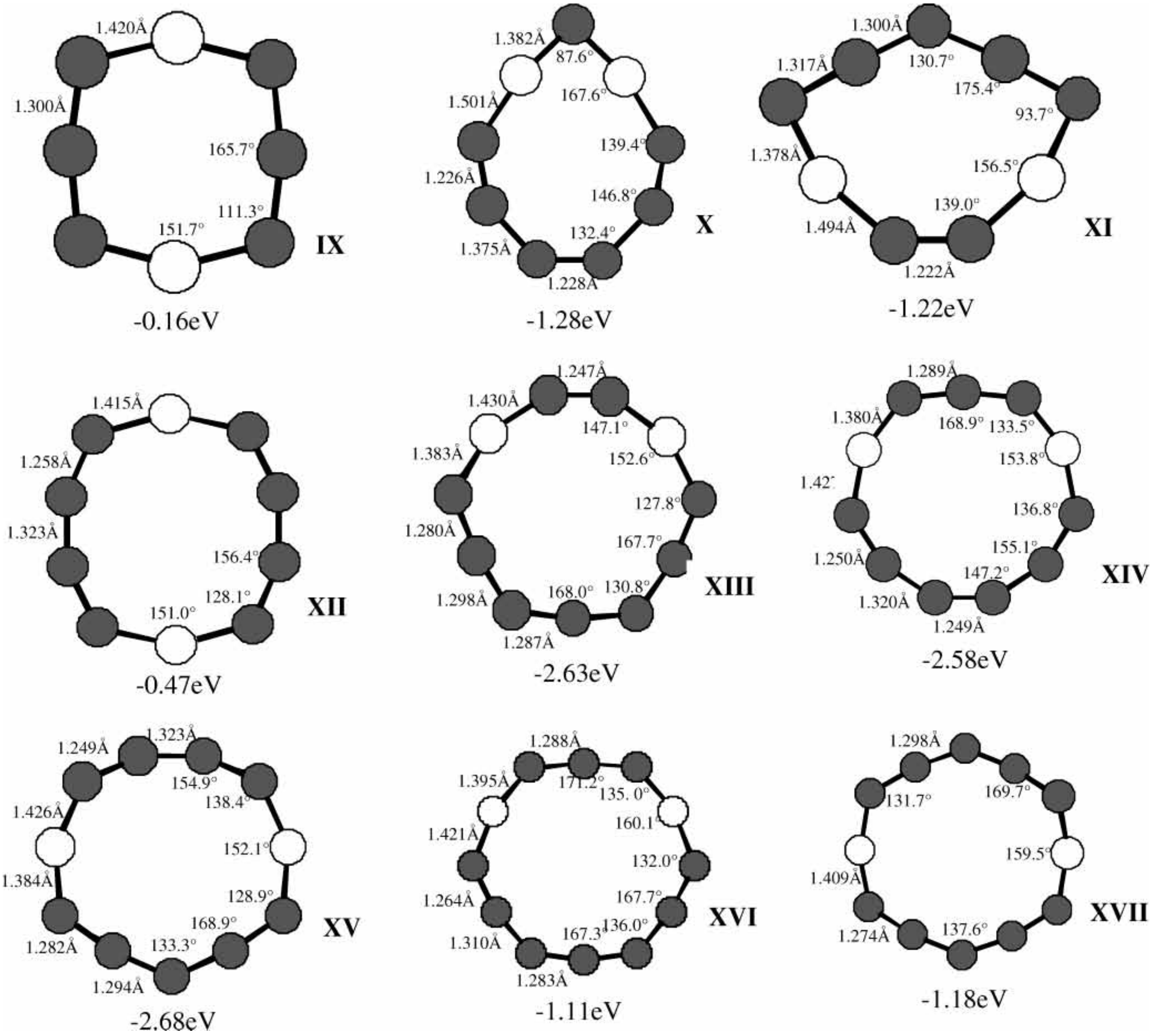


Figure 2. Geometries and energies of the lowest-energy cyclic structures for the C_nB_2 clusters at the B3LYP/6-311G** level of theory. Energies are relative to the lowest-energy linear structure in Table 2.

relative energy. The two lowest-energy isomers from the DFT study remain the lowest-energy structures in the CASSCF results as well. In the case of the C_6B clusters, the boron-terminated and the C_4BC_2 clusters were optimized. The CASSCF bond lengths varied from those found by DFT in the same range, 1−5%, reported above. However, the energy difference between these two isomers was nearly identical to that from the DFT results, confirming that these two isomers are essentially isoenergetic. Two C_8B clusters, C_6BC_2 and C_4BC_4, were optimized using an active space of the same size. Again, the bond length deviations from the DFT values were in the range of 1−5%. Although the magnitude of the energy difference is greater for the CASSCF results, the relative energy ordering was unchanged. These CASSCF studies involving the isomers with the smallest energy differences provide confirmation of the minimum-energy structures assigned from the DFT results.

There are three previous reports involving only *anionic* C_nB clusters. In an experimental study,[33] it was reported that only the *even carbon* cluster anions, C_nB^- could be observed in a time-of-flight mass spectrometer. The observed spectrum was assigned to anions terminated by boron and having a linear geometry. This geometry assignment was assumed for the ab initio calculations and followed logically from the statistical analysis of the experimental data. A later C_nB^- computational study,[26] at a higher level of theory, assigned the structures for $n > 3$ as loosely floppy chains assumed, from the same experimental data, to be terminated by boron atoms. In neither instance did the authors have reason to examine chains, linear or floppy, in which the boron atoms were in other than terminal positions or cyclic structures. A later mass spectrometric study[34] of the cationic clusters led to the conclusion that the C_nB^+ structures, where $10 \leq n \leq 30$, were monocyclic rings, as one might observe for the C_n^+ series in the same size range.

Boron is similar to carbon in its physical properties.[31] In particular, the difference in atomic radius is only 0.1 Å, and the electronegativity difference is 0.5. However, in contrast to carbon, boron atoms typically exhibit three-coordinate bonding. One expects then, a priori, that boron may be substituted into a carbon structure with minimal physical or chemical disruption. This suggestion has been confirmed in several studies of, for example, hetero-fullerenes.[32] Additional evidence to bolster the hypothesis that it is the chemical similarity plus the bonding

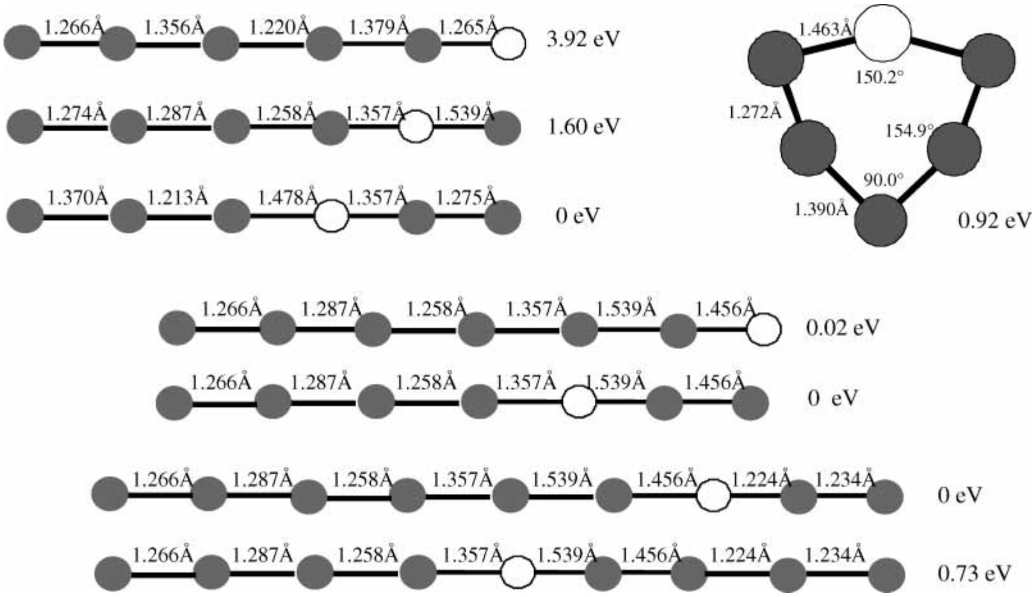


Figure 3. Geometries and relative energies of selected structures for the C_nB clusters at the CASSCF(5,5)/6-311G** level of theory.

differences that lead to the observed geometries for the clusters was obtained by metal atom substitution in the clusters. DFT calculations, at the same level of theory used for the carbon−boron clusters, were completed for the analogous aluminum molecules using C_7Al as the example molecule. Aluminum is in the same period as boron, but it is significantly larger (nearly double the radius of a carbon atom) and significantly less electronegative (Pauling values of 1.6 as compared with carbon at 2.6).[21] The linear C_7Al isomer with a terminal aluminum atom is the most stable geometry. It is 2.5 eV more stable than the C_5AlC_2 isomer and 1.7 eV more stable than the monocyclic ring. The aluminum cluster has physical properties analogous to carbon clusters containing phosphorus, oxygen, or nitrogen.

Our predicted bond lengths for the boron−carbon bonds are significantly shorter than those typically encountered, but are in the range of multiply bonded species reported in a recent literature survey.[29] The presence of multiply bonded boron atoms in a molecule is generally accepted, but still rather rare. To explore this observation more fully, we have examined, at the same level of theory, smaller boron−carbon clusters in which chemical reasoning suggests that the bond lengths might also be in the observed length range. For example, in the symmetric BCCB molecule, the bonding appears to be a central carbon−carbon triple bond ($r = 1.2263$ Å) with terminal boron−carbon single bonds of length 1.5526 Å. In the CBBC isomer, we find a structure best described by a $-B{=}B-$ central bond ($r = 1.4593$ Å) and terminal $-B-C$ bonds, where $r = 1.4588$ Å. These results provide more evidence that the cluster bond lengths in our larger systems reflect what would be described in general terms as a mixture of resonance structures with singly and doubly bonded boron atoms.

Our neutral C_nB clusters are isoelectronic with the C^+_{n+1} clusters. For the latter, chains and monocyclic rings are expected to coexist[1] for n near 7 or 8 and the structures become exclusively rings at $n = 10$. The greater stability of chains with boron in the interior of the chain leaves carbon atoms at the terminal positions and, essentially, leads to a situation in which the hetero-chains may chemically behave as carbon chains. We should expect, then, that at some point in the growth of larger boron−carbon chains, there would be a switch from chains to rings, just as was observed in the case of the pure carbon clusters. Our calculations indicate that at $n = 5$ or 6 (ring size of six or seven atoms), the two forms will coexist and that for the larger C_nB clusters in this study, the preferred form will be that of the monocyclic ring. This is in agreement with the C_nB^+ experimental results.[34] In those spectra, the relative intensities of the various clusters in the mass spectrum did not present a regular pattern as would be expected for a series of linear chains. Our data cannot differentiate a formation mechanism for the ring, only relative thermodynamic stability. However, one would expect that the mechanism postulated as functioning for pure clusters,[1] initial growth of chains that become sufficient in length to form monocyclic rings and eventually fullerenes, would be appropriate here as well. The experimental study included mass spectra[34] with peaks assigned to the di-boron clusters. The carbon chains in these clusters were of a size for which monocyclic ring structures would be appropriate and, indeed, our calculations indicate that for all of the structures we studied, the monocyclic rings would be the preferred form, confirming the generally accepted postulate that boron is easily substituted into a carbon molecule with little disruption of the structure.

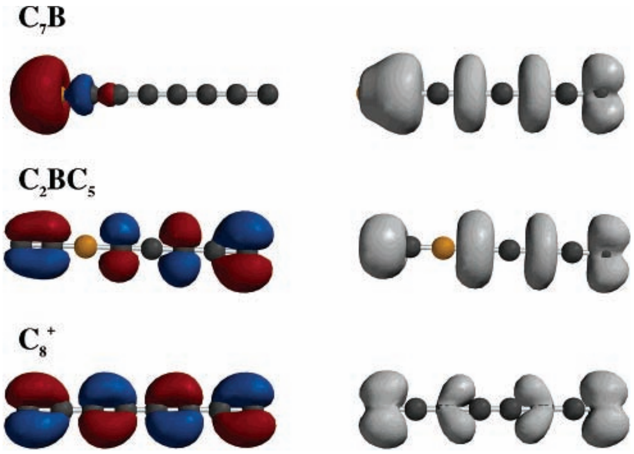


Figure 4. Comparison of the (left) HOMO and (right) spin density for C_7B, C_2BC_5, and C_8^+.

The analogy with pure carbon clusters is also present in a comparison of the molecular orbitals for the two types of molecules. Figure 4 presents the HOMOs and the spin densities for two different C_7B isomers as well as C_8^+. The HOMO of the latter is a π-bonding orbital. The HOMO of the boron-terminated structure is primarily a nonbonding orbital located

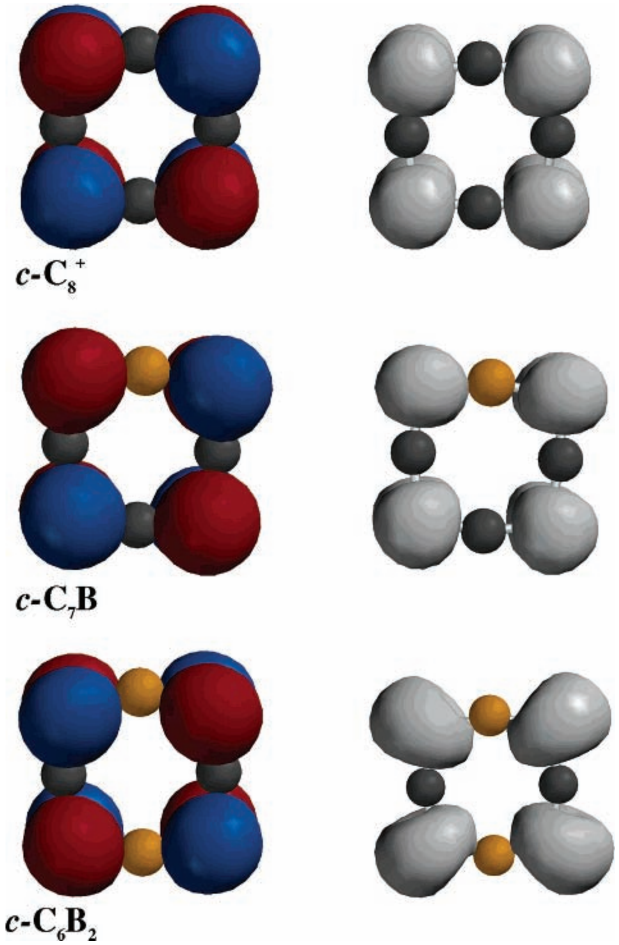


Figure 5. Comparison of the (left) HOMO and (right) spin density for c-C_8^+, c-C_7B and c-C_6B_2.

on the boron atom. This is reflected in the spin density map. This form of the cluster would be very reactive at the boron atom and would readily add additional carbon atoms at that site. This should be contrasted with the HOMO and spin density map for the structure having boron internally accommodated in the carbon chain. Here, the electron density is on the more electronegative carbon atoms and the general appearance of the electronic structure is similar to that of the pure carbon cluster. These two factors drive the minimal-energy geometry toward that reported in Table 1. Figure 5 presents similar data for the analogous cyclic structures, c-C_7B, c-C_6B_2, and c-C_8^+. The similarities in the three molecular orbitals and spin density maps are clear. Both of the boron−carbon clusters have the same electronic structure as the pure carbon molecule, which has been reported to coexist with the linear form of C_8^+. The total number of atoms in the monocyclic ring is the important factor for boron−carbon cluster stability. This reflects the fact that boron is readily substituted into carbon structures because of the relatively close match in both size and electronegativity. We should expect, therefore, that the structural properties of the heteroatom-containing clusters will follow that of the pure carbon clusters as reported here.

Summary

We have shown that, for C_nB and C_nB_2 clusters, both linear and cyclic forms will coexist for smaller cluster sizes, but that the monocyclic forms will be the exclusive product as n increases. The boron−carbon clusters are most similar to pure carbon clusters in their structural tendencies, and this is reflected also in the electronic properties of the clusters. Moreover, in contrast to all other reported heteroatom−carbon clusters, the lowest-energy linear structures were not those terminated by the boron atoms. These observations are indicative of the electron-deficient nature of boron.

Supporting Information Available: Additional optimized structures obtained at the B3LYP/6-311G** level of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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