

Computed Properties of the CB_9H_{10} and $\text{CB}_{11}\text{H}_{12}$ Free Radicals

Michael L. McKee

Contribution from the Department of Chemistry, Auburn University, Auburn, Alabama 36849

Received December 17, 1996[⊗]

Abstract: Density functional calculations (B3LYP/6-31G(d)) are presented for the anion and radical of the mono-carbon carboranes, $\text{CB}_n\text{H}_{n+1}$, $n = 4, 9, 11$. The CB_4H_5^- , $\text{CB}_9\text{H}_{10}^-$, and $\text{CB}_{11}\text{H}_{12}^-$ anions, which are isoelectronic with the *closo*-dicarba species $\text{C}_2\text{B}_3\text{H}_5$, $\text{C}_2\text{B}_8\text{H}_{10}$, and $\text{C}_2\text{B}_{10}\text{H}_{12}$, are predicted to have significant ionization potentials (2.88, 4.36, and 5.19 eV). The recently reported synthesis of the permethyl derivative of the $\text{CB}_{11}\text{H}_{12}$ radical is remarkable in view of the large predicted ionization potential of the $\text{CB}_{11}\text{Me}_{12}^-$ anion (4.32 eV). All calculated properties are consistent with the removal of an electron from a cage-bonding orbital with significant unpaired spin density on the boron opposite the carbon vertex.

Introduction

closo-Carborane cages of formula $\text{C}_2\text{B}_n\text{H}_{n+2}$ are known to be stable closed-shell molecules that are fairly resistant to oxidation due to their large HOMO/LUMO gap.¹ In fact, the remarkable stability of the icosahedral $\text{C}_2\text{B}_{10}\text{H}_{12}$ has led to its use in such diverse fields as medicine (neutron capture therapy²), molecular scaffolding (rigid building units³), and material science (precursor of boron carbide thin films⁴). Since a HB^- unit is isoelectronic (and isolobal⁵) with HC, similar stability might be expected with the $\text{CB}_{11}\text{H}_{12}^-$ anion. Indeed, a number of X-ray structures are known of salts with $\text{CB}_{11}\text{H}_{12}^{6-9}$. The $\text{CB}_{11}\text{H}_{12}^-$ anion and similar anions such as $\text{CB}_9\text{H}_{10}^-$ ^{10,11} have become known as anions with very little nucleophilic character.¹² The negative charge in these anions is delocalized over the entire cage, making them ideal counterions that do not distort the structure of the cation.¹²

Recently, Michl and co-workers¹³ have succeeded in synthesizing a completely methyl-substituted analog of $\text{CB}_{11}\text{H}_{12}^-$.¹⁴ They found that $\text{CB}_{11}\text{Me}_{12}^-$ was less stable to electrolytic oxidation

than $\text{CB}_{11}\text{H}_{12}^-$. Most recently, they have reported^{13b} that the free radical $\text{CB}_{11}\text{Me}_{12}$ could be prepared from the anion by either chemical or electrochemical oxidation. The free radical is stable in air for a few days and temperature stable to 150 °C. The IR spectra and X-ray crystallographic study of the free radical $\text{CB}_{11}\text{Me}_{12}$ indicate that it has a similar structure to the anion.^{13b} The stability of $\text{CB}_{11}\text{Me}_{12}$ was attributed to the steric protection afforded by the “sheath of methyl groups”.^{13b} It was predicted that $\text{CB}_{11}\text{Me}_{12}$ was the “first member of a new family of strongly oxidizing neutral radicals”.^{13b}

The object of the present work is to compare and contrast the properties of the anion and radical of $\text{CB}_{11}\text{H}_{12}$ and CB_9H_{10} , as the parents of the first two members of this family.

Method

All calculations were made with the Gaussian program system.¹⁵ Geometries were optimized with use of the B3LYP exchange/correlation functional combination, which has proven to be extremely effective in describing a number of molecular properties.¹⁶ The 6-31G(d) basis set was used for geometry optimization while single-point calculations were made with the 6-31+G(2d,p) basis set. Total energies (hartrees) and zero-point energies (kcal/mol) are given in Table 1, while the calculated and observed structures are presented in Figure 1 for CB_9H_{10} and $\text{CB}_{11}\text{H}_{12}$. Ab initio calculations on $\text{CB}_9\text{H}_{10}^-$ have been reported previously.^{17,18}

(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian94* (Rev. B.1); Gaussian, Inc.: Pittsburgh, PA, 1995.

(16) (a) Bartolotti, L. J.; Flurchick, K. An Introduction to Density Functional Theory. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH: New York, 1996; Vol. 7. (b) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford Press: Oxford, 1989. (c) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651. (d) *Density Functional Methods in Chemistry*; Labanowski, J. K., Andzelm, J. W., Eds.; Springer: Berlin, 1991. (e) Johnson, B. G.; Gill, P. M. W.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 5612. (f) Gill, P. M. W.; Johnson, B. G.; Pople, J. A.; Frisch, M. J. *J. Chem. Phys. Lett.* **1992**, *197*, 499. (g) Raghavachari, K.; Strout, D. L.; Odom, G. K.; Scuseria, G. E.; Pople, J. A.; Johnson, B. G.; Gill, P. M. W. *Chem. Phys. Lett.* **1993**, *214*, 357. (h) Raghavachari, K.; Zhang, B.; Pople, J. A.; Johnson, B. G.; Gill, P. M. W. *Chem. Phys. Lett.* **1994**, *220*, 1994. (i) Johnson, B. G.; Gonzales, C. A.; Gill, P. M. W.; Pople, J. A. *Chem. Phys. Lett.* **1994**, *221*, 100. (j) Baker, J.; Scheiner, A.; Andzelm, J. *Chem. Phys. Lett.* **1993**, *216*, 380. (k) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(17) Zahradník, R.; Balaji, V.; Michl, J. *J. Comput. Chem.* **1991**, *12*, 1147.

(18) Bühl, M.; Schleyer, P. v. R.; Havlas, Z.; Hnyk, D.; Heřmánek, S. *Inorg. Chem.* **1991**, *30*, 3107.

[⊗] Abstract published in *Advance ACS Abstracts*, April 15, 1997.

- (1) Plešek, J. *Chem. Rev.* **1992**, *92*, 269.
- (2) Hawthorne, M. F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 950.
- (3) (a) Grimes, R. N. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1289. (b) Jiang, W.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1996**, *35*, 3056.
- (c) Jiang, W.; Knobler, C. B.; Hawthorne, M. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2536.
- (4) (a) Getman, T. D.; Garrett, P. M.; Knobler, C. B.; Hawthorne, M. F.; Thorne, K.; Mackenzie, J. D. *Organometallics* **1992**, *11*, 2723. (b) Sneddon, L. G.; Mirabelli, M. G.; Lynch, A. T.; Fazen, P. J.; Su, K.; Beck, J. S. *Pure Appl. Chem.* **1991**, *63*, 407.
- (5) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.
- (6) Štíbr, B. *Chem. Rev.* **1992**, *57*, 1262.
- (7) Shelly, K.; Finster, D. C.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 5955.
- (8) Liston, D. J.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 6643.
- (9) Gupta, G. P.; Lang, G.; Lee, Y. J.; Scheidt, W. R.; Skelly, K.; Reed, C. A. *Inorg. Chem.* **1987**, *26*, 3022.
- (10) Xie, Z.; Liston, D. J.; Jelínek, T.; Mitro, V.; Bau, R.; Reed, C. A. *J. Chem. Soc., Chem. Commun.* **1993**, 384.
- (11) Nestor, K.; Štíbr, B.; Kennedy, J. D.; Thornton-Pett, M.; Jelínek, T. *Collect. Czech. Chem. Commun.* **1992**, *57*, 1262.
- (12) Reed, C. A.; Xie, Z.; Bau, R.; Benesi, A. *Science* **1993**, *262*, 402.
- (13) (a) King, B. T.; Janoušek, Z.; Grüner, B.; Trammell, M.; Noll, B. C.; Michl, J. *J. Am. Chem. Soc.* **1996**, *118*, 3313. (b) King, B. T.; Noll, B. C.; McKinley, A. J.; Michl, J. *J. Am. Chem. Soc.* **1996**, *118*, 10902.
- (14) (a) It is interesting to note that several hydrogens of $\text{CB}_9\text{H}_{10}^-$ and $\text{CB}_{11}\text{H}_{12}^-$ can also be replaced by fluorine. See: Ivanov, S. V.; Ivanova, S. M.; Miller, S. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. *Inorg. Chem.* **1996**, *35*, 6914 and references cited therein. (b) For the recent synthesis of $\text{HCB}_{11}\text{I}_{11}^-$ see: Srivastava, R. R.; Hamlin, D. K.; Wilbur, D. S. *J. Org. Chem.* **1996**, *61*, 9041.

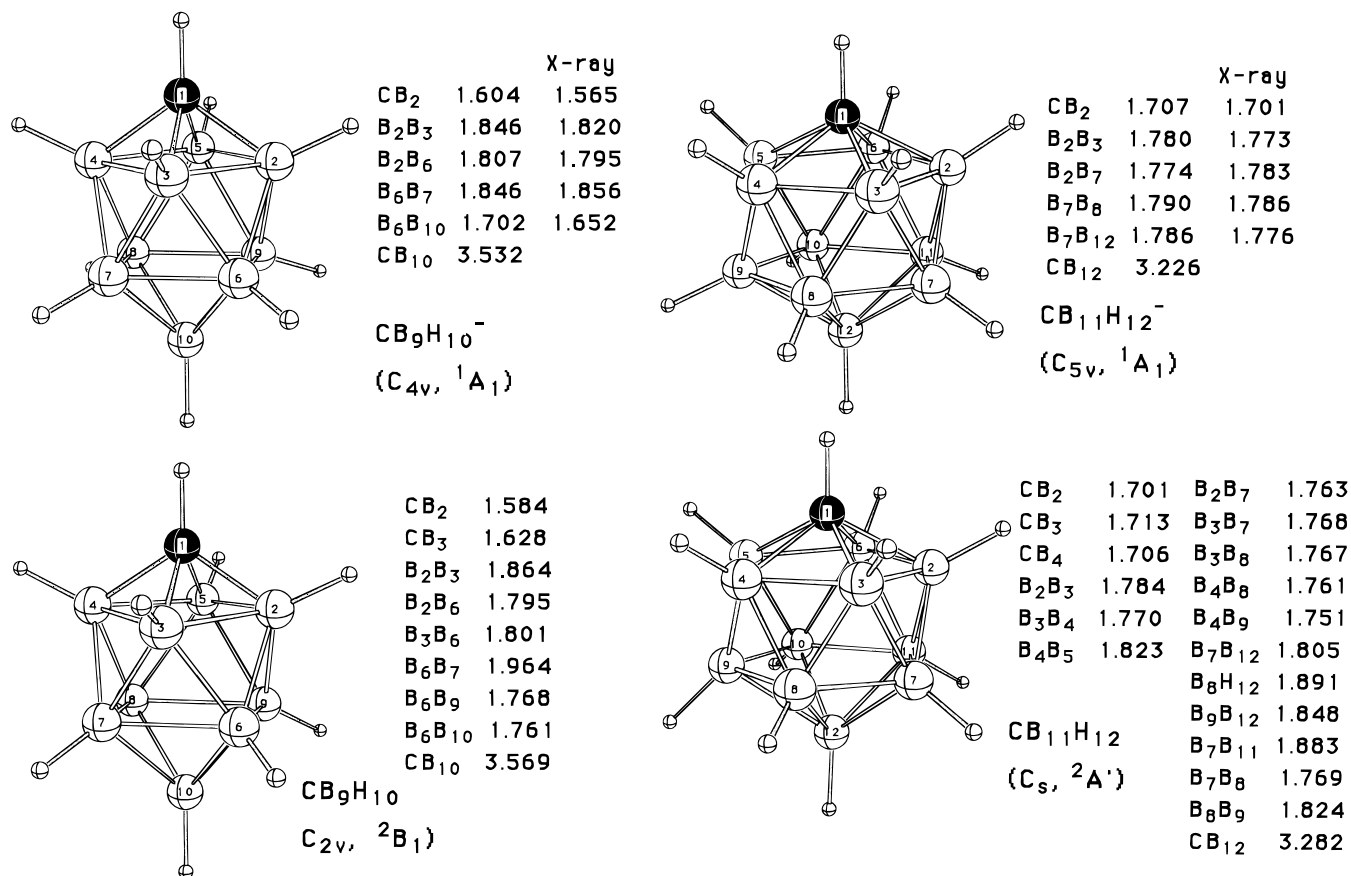


Figure 1. Selected geometric parameters of the anion and radical of CB₉H₁₀ and CB₁₁H₁₂. Comparison is made with X-ray values for CB₉H₁₀⁻ (ref 11) and CB₁₁H₁₂⁻ (ref 7).

Table 1. Absolute Energies (hartrees) and Zero-Point Energies (kcal/mol) for Various Anions and Radicals

	PG	ES	B3LYP/6-31G(d)		B3LYP/6-31G(2d,p)	
			energy	ZPE (NIF) ^a	energy	$\langle S^2 \rangle$
F ⁻	K	¹ S	-99.754 09	0.00	-99.862 04	
F	K	² P	-99.715 53	0.00	-99.733 88	0.75
Cl ⁻	K	¹ S	-460.252 23	0.00	-460.273 55	
Cl	K	² P	-460.136 26	0.00	-460.137 35	0.75
BH ₄ ⁻	T _d	¹ A ₁	-27.247 12	21.46(0)	-27.268 65	
BH ₄	C _{2v}	² B ₂	-27.143 69	20.34(0)	-27.153 73	0.75
B ₃ H ₈ ⁻	C _{2v}	¹ A ₁	-79.386 31	51.85(0)	-79.408 88	
B ₃ H ₈ ⁻	C _s	¹ A ₁	-79.384 54	51.72(1)	-79.406 48	
B ₃ H ₈	C _s	² A ₁	-79.266 55	51.90(0)	-79.281 10	0.75
CB ₄ H ₅ ⁻	C _{3v}	¹ A ₁	-140.538 64	41.32(0)	-140.564 96	
CB ₄ H ₅	C _s	² A ₁	-140.445 42	41.02(0)	-140.458 57 ^b	0.75
CB ₉ H ₁₀ ⁻	C _{4v}	¹ A ₁	-267.999 16	88.98(0)	-268.023 61	
CB ₉ H ₁₀	C _{2v}	² B ₁	-267.843 84	87.11(0)	-267.860 43 ^c	0.75
CB ₁₁ H ₁₂ ⁻	C _{5v}	¹ A ₁	-318.994 25	108.72(0)	-319.018 75	
CB ₁₁ H ₁₂	C _s	² A ₁	-318.804 35	104.79(0)	-319.821 94 ^d	0.75

^a Zero-point energy (kcal/mol) and number of imaginary frequencies.

^b If the C_s-symmetry structure is averaged to C_{3v} symmetry, the total energy becomes -140.44726, an increase of 7.1 kcal/mol over the C_s structure. ^c If the C_{2v}-symmetry structure is averaged to C_{4v} symmetry, the total energy becomes -267.85181, an increase of 5.4 kcal/mol over the C_{2v} structure. ^d If the C_s-symmetry structure is averaged to C_{5v} symmetry, the total energy becomes -318.81434, an increase of 4.8 kcal/mol over the C_s structure.

The ab initio calculations presented here will address the gas-phase stability of the radical. In Table 2, calculated adiabatic ionization energies are presented for several species. The adiabatic ionization potential of the anion has the same numerical value as the adiabatic electron affinity of the neutral (given the common definition of electron affinity).

One can see that while the IPs for F⁻ and Cl⁻ are underestimated at the B3LYP/6-31G(d) level, agreement with experiment¹⁹ is good at

Table 2. Calculated and Experimental Adiabatic Ionization Potentials (eV) for Various Anions^a

	B3LYP/6-31G(d)	B3LYP/6-31+G(2d,p)	exptl ^b
F ⁻	1.05 (1.05)	3.49 (3.49)	3.399
Cl ⁻	3.16 (3.16)	3.71 (3.71)	3.617
BH ₄ ⁻	2.81 (2.76)	3.13 (3.08)	
B ₃ H ₈ ⁻	3.26 (3.26)	3.48 (3.48)	
CB ₄ H ₅ ⁻	2.54 (2.53)	2.89 (2.88)	
CB ₉ H ₁₀ ⁻	4.23 (4.15)	4.44 (4.36)	
CB ₁₁ H ₁₂ ⁻	5.17 (5.00)	5.36 (5.19)	
CB ₁₁ Me ₁₂ ⁻	4.32 ^c	(4.32) ^d	

^a The value including zero-point energy at the B3LYP/6-31G(d) level is given in parentheses. ^b Reference 19. ^c Single-point calculations are made on the anion and radical with all methyl groups optimized at the AM1 level (with C_s symmetry for both anion and radical) and vertex positions frozen to the B3LYP/6-31G(d) optimized positions of CB₁₁H₁₂⁻ and CB₁₁H₁₂. ^d The effect of basis set improvement and zero-point correction taken from CB₁₁H₁₂⁻ → CB₁₁H₁₂.

the B3LYP/6-31+G(2d,p) level. Two well-known boron hydride anions were also computed, BH₄⁻ and B₃H₈⁻. The BH₄ radical is predicted to have C_{2v} symmetry with a ²B₂ electronic state, in agreement with a recent study by Boldyrev and Simons.²⁰ The computed IP of the anion is 3.08 eV, which is very close to a value of 3.12 eV at the QCISD(T)/6-311++G(2df,2pd) level. Two structures of the B₃H₈⁻ anion are known to be very similar in energy.²¹ The 2013 (styx notation²²) dibridged structure is predicted to be 1.6 kcal/mol more stable than the 1104 monobridged structure at the B3LYP/6-31+G(2d,p)//B3LYP/6-31G(d)+ZPC level. Interestingly, the radical prefers

- (19) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. No. 1.
 (20) Boldyrev, A. I.; Simons, J. *J. Phys. Chem.* **1993**, *99*, 4628.
 (21) McKee, M. L.; Lipscomb, W. N. *Inorg. Chem.* **1982**, *21*, 2846.
 (22) For styx notation see: Eberhardt, W. H.; Crawford, B. L., Jr.; Lipscomb, W. N. *J. Chem. Phys.* **1954**, *22*, 989.

Table 3. Effect of Ionization on Geometry for $\text{CB}_{11}\text{H}_{12}^-$ (B3LYP/6-31G(d)) and $\text{CB}_{11}\text{Me}_{12}$ (X-ray)

	$\text{CB}_{11}\text{H}_{12}$ (calc ^a)			$\text{CB}_{11}\text{Me}_{12}$ (X-ray ^b)		
	anion \rightarrow radical	Δ		anion \rightarrow radical	Δ	
av edge distance	1.768	1.780	0.012	1.77	1.797	0.03
av opposite vertex separation	3.363	3.383	0.020	3.38	3.417	0.04

^a Geometries optimized at the B3LYP/6-31G(d) level. ^b For the structure of the anion see ref 13a and for that of the radical see ref 13b.

the monobridged form. The IP of B_3H_8^- (B_3H_8^- (2013-styx) \rightarrow B_3H_8 (1104-styx)) is predicted to be 3.48 eV at the highest level.

Three monocarbon carborane anions were considered, CB_4H_5^- , $\text{CB}_9\text{H}_{10}^-$, and $\text{B}_{11}\text{H}_{12}^-$. The first, CB_4H_5^- , is the smallest anionic *closo*-carborane while the last, $\text{CB}_{11}\text{H}_{12}^-$, is expected to be the most stable (isoelectronic with $\text{C}_2\text{B}_{10}\text{H}_{12}$). In accordance with expectation, the IP of the three anions increase (2.88 to 4.36 to 5.19 eV) as the size of the cage increases (five to ten to twelve vertices).

Since the experimentally observed free radical is $\text{CB}_{11}\text{Me}_{12}$ rather than the parent $\text{CB}_{11}\text{H}_{12}$,¹⁴ an attempt was made to estimate the effect of 12 methyl groups. To do this, the anion and radical of $\text{CB}_{11}\text{Me}_{12}$ were both optimized at the AM1 level in C_s symmetry while freezing the CB_{11} core positions to the B3LYP/6-31G(d) values. Single-point calculations at the B3LYP/6-31G(d) level yield an estimate of 4.32 eV for the energy difference between the anion and radical. If the effect of basis extension (6-31G(d) \rightarrow 6-31G(2d,p)) and zero-point correction are taken from the parent system (the two effects are of equal magnitude but of opposite sign), a best estimate of 4.32 eV is made for the gas-phase IP. The remarkable nature of the $\text{CB}_{11}\text{Me}_{12}$ radical is reinforced by noting that the EA (which is the same as the IP of the anion) is more than 0.8 eV greater than fluorine!

Methyl groups on $\text{CB}_{11}\text{H}_{12}$ have the effect of reducing the EA by 0.87 eV (5.19 to 4.32 eV). Such an effect is not unexpected. For example, the gas-phase EA of the radical of *p*-benzoquinone is reduced 0.32 eV by the substitution of four methyl groups for hydrogens (1.91 \rightarrow 1.59 eV).¹⁹

The calculated structures of $\text{CB}_9\text{H}_{10}^-$ and $\text{CB}_{11}\text{H}_{12}^-$ compare reasonably well with X-ray structures.^{7,11} Also, the effect of ionization on geometry can be considered in Table 3. While the calculations are for the parent and X-ray structures^{13,14} are for the permethyl derivative, there is agreement in the predicted overall increase in size of the cage for the free radical. This would be consistent with removing an electron from a cage-bonding molecular orbital.

Electronic Description of $\text{CB}_n\text{H}_{n+1}$, $n = 4, 9, 11$

The natural population analysis (NPA) charges²³ are given in Table 4 for CB_4H_5 and CB_9H_{10} and in Table 5 for $\text{CB}_{11}\text{H}_{12}$ and $\text{CB}_{11}\text{Me}_{12}$. In each case, the value reported is for the vertex atom plus substituent. The carbon vertex is the most negatively charged position in the anion, carrying 61% of the charge in CB_4H_5^- , 50% in $\text{CB}_9\text{H}_{10}^-$, and 38% in $\text{CB}_{11}\text{H}_{12}^-$. When the anion loses an electron, the charge on the carbon vertex remains almost unchanged. The position most affected is the boron vertex opposite carbon. Ionization removes 0.40 e^- from the boron position opposite carbon in CB_4H_5^- , 0.32 e^- in $\text{CB}_9\text{H}_{10}^-$, and 0.24 e^- in $\text{CB}_{11}\text{H}_{12}^-$. In contrast, the loss of electrons from the carbon positions is 0.10 e^- , 0.08 e^- , and 0.04 e^- for the same three anions. The loss of electron density opposite to carbon in the ionization of $\text{CB}_n\text{H}_{n+1}$ anions is closely related to the "antipodal" effect,^{18,24,25} the downfield $\delta(^{11}\text{B})$ chemical

(23) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

(24) (a) Plešek, J.; Heřmánek, S. *J. Chem. Soc., Chem. Commun.* **1975**, 127. (b) Heřmánek, S.; Gregor, V.; Štíbr, B.; Plešek, J.; Janousek, Z.; Antonovich, V. A. *Collect. Czech. Chem. Commun.* **1976**, *41*, 1492. (c) Heřmánek, S.; Jelínek, T.; Plešek, J.; Štíbr, B.; Fusek, J.; Mareš, F. In *Boron Chemistry, Proceeding of the 6th IMEBORON*; Heřmánek, S., Ed.; World Scientific: Singapore, 1987; pp 26–73.

Table 4. Calculated Natural Population Analysis (NPA) Charges and α -Spin Densities in $\text{CB}_4\text{H}_5^-/\text{CB}_4\text{H}_5$ and $\text{CB}_9\text{H}_{10}^-/\text{CB}_9\text{H}_{10}$ ^a

vertex	NPA charges		α -spin density	
	CB_4H_5^-	CB_4H_5	atom	CB_4H_5
HC ₁	-0.61 (-0.61)	-0.52 (-0.51)	C ₁	0.078 (0.083)
HB ₂	0.00 (0.00)	0.11 (0.11)	B ₂	0.219 (0.183)
HB ₃ /HB ₄	0.00 (0.00)	0.20 (0.20)	B ₃ /B ₄	0.095 (0.106)
HB ₅	-0.39 (-0.39)	0.00 (0.01)	B ₅	0.523 (0.515)

vertex	NPA charges		α -spin density	
	$\text{CB}_9\text{H}_{10}^-$	CB_9H_{10}	atom	CB_9H_{10}
HC ₁	-0.51 (-0.50)	-0.43 (-0.42)	C ₁	0.065 (0.057)
HB ₂ /HB ₄	0.07 (0.06)	0.13 (0.12)	B ₂ /B ₄	0.006 (0.007)
HB ₃ /H ₃	0.07 (0.06)	0.12 (0.11)	B ₃ /B ₅	0.005 (0.026)
HB ₆ /HB ₇ / HB ₈ /HB ₉	-0.15 (-0.15)	-0.05 (-0.05)	B ₆ /B ₇ / B ₈ /B ₉	0.125 (0.116)
HB ₁₀	-0.16 (-0.16)	0.14 (0.16)	B ₁₀	0.376 (0.365)

^a The first value is calculated at the B3LYP/6-31G(d) level. The value in parentheses is calculated at the B3LYP/6-31+G(2d,p) level.

shift observed for the boron nucleus across the cage from X in $\text{B}_9\text{H}_9\text{X}$ and $\text{B}_{11}\text{H}_{11}\text{X}$ systems. The largest coefficient in the highest occupied molecular orbital (HOMO) is on the boron opposite to heteroatom.¹⁸ Thus, removing an electron from the HOMO of $\text{CB}_n\text{H}_{n+1}^-$ would remove electron density at the position opposite carbon.

An inspection of α -spin density for carbon and boron in the $\text{CB}_n\text{H}_{n+1}$ radicals (Tables 4 and 5) reveals the greatest unpaired spin density opposite carbon. In CB_4H_5 , 0.515 α -spin density resides on the antipodal boron, compared to 0.365 in CB_9H_{10} and 0.274 in $\text{CB}_{11}\text{H}_{12}$. In $\text{CB}_{11}\text{H}_{12}$, there was also significant unpaired spin density on B₉ (0.210) as well as on the hydrogen attached to B₉ (0.093). If methyl groups replace hydrogen in $\text{CB}_{11}\text{H}_{12}$, the vertex charges and α -spin densities are very similar.

Since the $\text{CB}_n\text{H}_{n+1}$ ($n = 4, 9, 11$) anions have degenerate HOMOs, the ionized species is subject to the Jahn–Teller effect, which will reduce the symmetry of the radical. Thus, the ground state symmetry of CB_4H_5 and $\text{CB}_{11}\text{H}_{12}$ is only C_s while it is C_{2v} for CB_9H_{10} . However, the radicals are expected to have small barriers for rearranging to give an effective symmetry of C_{3v} for CB_4H_5 , C_{4v} for CB_9H_{10} , and C_{5v} for $\text{CB}_{11}\text{H}_{12}$. To compute an upper limit for this barrier, single-point calculations were made on the radicals with the structure averaged to the higher point group. As expected for these Jahn–Teller systems, the wave function displayed a lower point group than the nuclear positions. The symmetry-averaged structures are higher in energy by 7.1, 5.4, and 4.8 kcal/mol than the minimum-energy structures for CB_4H_5 , CB_9H_{10} , and $\text{CB}_{11}\text{H}_{12}$, respectively.

If these energy differences are similar to the rearrangement barriers, then the radicals will have a higher effective symmetry at room temperature (298 K) but will still have a lower symmetry at liquid nitrogen temperature (77 K). Thus, in the ESR spectrum of the $\text{CB}_{11}\text{Me}_{12}$ radical at 77 K, the unpaired electron should couple to hydrogen and boron characteristic of the C_s -symmetry structure. The predicted isotropic hyperfine coupling constants²⁶ for ^1H (a_{H}) and ^{11}B (a_{B}) in the $\text{CB}_{11}\text{Me}_{12}$ radical are given in the Supporting Information (Table S1). Unfortunately, in the experimental low-temperature solid-state ESR spectrum of $\text{CB}_{11}\text{Me}_{12}$, only a broad signal with a peak-to-peak width of 37 G was reported.^{13b}

Vibrational frequencies and IR intensities have been tabulated for the anion and radical of CB_4H_5 , CB_9H_{10} , and $\text{CB}_{11}\text{H}_{12}$

(25) (a) Todd, L. J.; Siedle, A. R.; Bodner, G. M.; Kahl, S. B.; Hicke, J. P. *J. Magn. Reson.* **1976**, *23*, 301. (b) Leyden, R. N.; Sullivan, B. P.; Baker, R.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1978**, *100*, 3758. (c) Teixidor, F.; Vinas, C.; Rudolph, R. W. *Inorg. Chem.* **1986**, *25*, 3339.

Table 5. Calculated Natural Population Analysis (NPA) Charges and α -Spin Densities in CB₁₁R₁₂⁻ and CB₁₁R₁₂ (R = H, Me)^a

vertex	NPA charges (R = H)		NPA charges (R = Me)		α -spin density (R = H, Me) ^b		
	CB ₁₁ H ₁₂ ⁻	CB ₁₁ H ₁₂	CB ₁₁ Me ₁₂ ⁻	CB ₁₁ Me ₁₂	atom	CB ₁₁ H ₁₂	CB ₁₁ Me ₁₂
RC ₁	-0.39 (-0.38)	-0.35 (-0.34)	-0.44	-0.43	C ₁	0.001 (0.013)	0.013
RB ₂	0.03 (0.02)	0.09 (0.08)	0.04	0.10	B ₂	0.037 (0.007)	0.052
RB ₃ /RB ₆	0.03 (0.02)	0.07 (0.07)	0.05	0.09	B ₃ /B ₆	-0.011 (-0.007)	-0.014
RB ₄ /RB ₅	0.03 (0.02)	0.07 (0.07)	0.05	0.09	B ₄ /B ₅	0.002 (-0.001)	0.014
RB ₇ /RB ₁₁	-0.13 (-0.13)	-0.04 (-0.04)	-0.14	-0.05	B ₇ /B ₁₁	0.099 (0.094)	0.087
RB ₈ /B ₁₀	-0.13 (-0.13)	-0.07 (-0.07)	-0.14	-0.07	B ₈ /B ₁₀	0.024 (0.055)	0.014
RB ₉	-0.13 (-0.13)	0.06 (0.07)	-0.14	0.05	B ₉	0.276 ^c (0.210) ^d	0.247 ^e
RB ₁₂	-0.11 (-0.10)	0.12 (0.14)	-0.10	0.15	B ₁₂	0.271 (0.274)	0.251

^a The first value is calculated at the B3LYP/6-31G(d) level. The value in parentheses is calculated at the B3LYP/6-31+G(2d,p) level. ^b A negative number indicates an excess of β -spin density on that atom. ^c There is 0.082 α -spin density on hydrogen. ^d There is 0.093 α -spin density on hydrogen. ^e There is a total of 0.102 α -spin density on the methyl group.

Table 6. Comparison of Vibrational Frequencies (cm⁻¹) for Corresponding Modes in the Anion and Radical of CB₁₁H₁₂^a

CB ₁₁ H ₁₂ ⁻ (C _{5v})	CB ₁₁ H ₁₂ (C _s)	Δ	description
a ₁	3200	a'	3224 24 CH stretch
a ₁	1004	a'	972 -32 cage deformation
a ₂	951	a''	937 -14 BH bend
a ₁	798	a'	774 -24 C-B ₅ apical stretch
a ₁	762	a'	748 -14 cage expansion/contraction
a ₁	586	a'	563 -23 cage flatten/elongation
a ₂	528	a''	537 9 B ₅ /B ₅ "belt" twist

^a Frequencies calculated at the B3LYP/6-31G(d) level.

(Supporting Information, Tables S2–S4). Although several experimental bands have been reported for the anion and radical of CB₁₁Me₁₂, a comparison with the calculated frequencies of CB₁₁H₁₂ suggests that most (if not all) of the bands are due to methyl groups. In the IR spectrum of AgCB₁₁H₁₂ in the solid state a strong broad band at 2550 cm⁻¹ can be assigned to three intense bands calculated at 2658, 2642, and 2630 cm⁻¹. A comparison of the vibrational frequencies of the anion and radical of CB₁₁H₁₂ is difficult due to the complicated nature of the modes and the change in symmetry. Nevertheless, a correspondence has been found between several of the a₁ and a₂ modes of the C_{5v} anion and a' and a'' modes in the C_s radical. In general, there is a significant decrease in the vibrational

frequencies as one goes from the anion to the radical (Table 6), which is in keeping with removing the electron from a cage-bonding orbital.

Conclusions

Ab initio calculations on the anion and radical forms of CB_nH_{n+1}, $n = 4, 9, 11$, indicate that the ionization potentials increase as the size of the cage increases. A value of 5.19 eV for the IP of CB₁₁H₁₂⁻ indicates that the related radical should have a very large electron affinity (5.19 eV). The replacement of hydrogens with methyl groups is predicted to decrease the EA of the radical to 4.32 eV, still a remarkably large value. In CB₁₁H₁₂⁻, the boron position opposite carbon loses the largest amount of charge (and bears the largest amount of α -spin density) when the anion is ionized. Calculated properties (structure, energetics, and vibrational frequencies) are consistent with loss of an electron from an orbital that is cage bonding with a large contribution from the boron opposite carbon.

Acknowledgment. Computer time for this study was made available by the Alabama Supercomputer Network. I thank Dr. Nico J. R. van Eikema Hommes for making Molecule available, which was used for drawing the structures in Figure 1, and Dr. Vince Cammarata for help with simulating ESR spectra.

Note Added in Proof: A neutral radical with an even larger EA than CB₁₁Me₁₂ has been predicted for ClO₄ (5.2 eV): Van Huis, T. J.; Schaefer, H. F. *J. Chem. Phys.* **1997**, *106*, 4028.

Supporting Information Available: Predicted isotropic hyperfine coupling constants for ¹H (a_H) and ¹¹B (a_B) in the CB₁₁Me₁₂ radical are given in Table S1 while vibrational frequencies and infrared intensities for the anion and radical of CB₄H₅, CB₉H₁₀, and CB₁₁H₁₂ are given in Tables S2–S4 (5 pages). See any current masthead page for ordering and Internet access instructions.

(26) (a) Malkin, V. G.; Malkina, O. L.; Eriksson, L. A.; Salahub, D. R. The Calculation of NMR and ESR Spectroscopy Parameters Using Density Functional Theory In *Modern Density Functional Theory: A Tool for Chemistry*; Theoretical and Computational Chemistry, Seminario, J. M., Politzer, P., Eds.; Elsevier: Amsterdam, 1995; Vol. 2. (b) Austen, M.; Eriksson, L. A.; Boyd, R. J. *Can. J. Chem.* **1994**, *72*, 695. (c) Eriksson, L. A.; Malkina, O. L.; Malkin, V. G.; Salahub, D. R. *J. Chem. Phys.* **1994**, *100*, 5066. (d) Barone, V. *Theor. Chim. Acta* **1995**, *91*, 113. (e) Adamo, C.; Barone, V.; Fortunelli, A. *J. Chem. Phys.* **1995**, *102*, 384. (f) Batra, R.; Giese, B.; Spichy, M.; Gescheidt, G.; Houk, K. N. *J. Phys. Chem.* **1996**, *100*, 18371. (g) Gauld, J. W.; Eriksson, L. A.; Radom, L. *J. Phys. Chem. A* **1997**, *101*, 1352.

JA964328X