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o-, *m*-, and *p*-Carboranes and Their Anions: Ab Initio Calculations of Structures, Electron Affinities, and Acidities[†]

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Ab initio geometry optimizations have been performed for *o*-, *m*-, and *p*-$C_2B_{10}H_{12}$ carborane cages and their mono- and dianions at the Hartree−Fock 3-21G*, 6-31G*, and 6-31G** levels. The *para*-compound is the most stable with a calculated ΔH(*para*−*meta*) value of −10 kJ/mol and a calculated ΔG^{975K}(*para*−*meta*) value of −3 kJ/mol. These small calculated energy differences disagree with the experimental heats of formation, which suggest ΔH to be ca. −65 kJ/mol, but they agree with equilibrium gas mixture measurements at 975 K, which suggest a ΔG value of ca. −1 kJ/mol. Electron distributions, electron affinities, and acidic properties of the carboranes are presented. The structures of the mono- and dianions were determined by optimization, starting from the three neutral carborane cages; we find three energy minima for the $C_2B_{10}H_{12}^{2-}$ ion. The lowest-energy dianion is a *nido*-structure topped by a six-membered ring with the two C atoms in the *meta* position. The captured electrons become distributed over all the H atoms.

1. Introduction

The chemistry of the carborane superaromatics is still to a large extent unexplored, and a number of intriguing experimental findings await elucidation. Scheme 1 summarizes some of the current experimental knowledge concerning the three isomeric icosahedral $C_2B_{10}H_{12}$ carboranes and their anion chemistry. The scheme was adopted from Dunks[1] and updated by us with (our interpretation of) more recent experimental observations from the literature and will be discussed in some detail in the following. We have used quantum-chemical ab initio calculations to investigate a number of quantities related to Scheme 1, such as cage structures, electron densities, electron affinities, and acidities of the unsubstituted carboranes, and the hitherto unsolved structures of their anions. The results are presented in this paper.

Although the existence of $C_2B_{10}H_{12}^{2-}$ ions derived from the *o*-, *m*-, and *p*-carboranes were reported already during the 1960's,[2−7] their structures and number have remained largely unknown. The chemistry of the dianions has been extensively explored, but they have not yet been isolated as salts. In the present study we discuss the uptake of one and two electrons by each of the three carboranes. We present the resulting optimized structures and discuss the charge distributions.

The unsubstituted carboranes are weak Brønsted acids, and the C atoms can be made to let go of their protons in contact with very strong bases such as butyllithium; the resulting carborane anions are much used in synthetic carborane chemistry. Experiments have shown that *p*-carborane is a weaker acid than *m*-carborane, which is a weaker acid than the *o*-compound. In this paper we have computed the energy differences between the protonated and deprotonated cages, and we relate our results to the observed pK_a values.

Many noteworthy theoretical studies of neutral carboranes, unsubstituted and substituted, have appeared in the literature, beginning with Hoffmann's and Lipscomb's[8] population analysis of molecular orbitals in a number of trigonal, tetragonal, pentagonal bipyramidal, and icosahedal carboranes from 1962. Much later Ott et al.[9] optimized the *o*-, *m*-, and *p*-carboranes at the STO-3G level. The rearrangement mechanisms and transition states for the transformation between the isomeric $C_2B_{10}H_{12}$ carboranes have been calculated by Wales[10] at the Hartree−Fock/minimal basis-set level. McKee[11−13] and Bausch and Tebben[14] have studied transition states, rearrangement mechanisms, and reactions of many small- and medium-sized carborane molecules at the Hartree−Fock and MP2 levels. Recently, Diaz et al.[15] computed ^{13}C chemical shifts for some 40

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[†] Dedicated to Professor Göran Bergson on the occasion of his 65th birthday.

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(1) Dunks, G. B.; Wiersma, R. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1973**, *95*, 3174.
(2) Fein, M.; Bobinski, J.; Mayes, N.; Schwartz, N.; Cohen, M. S. *Inorg. Chem.* **1963**, *2*, 1111−1115.
(3) Grafstein, D.; Dvorak, J. *Inorg. Chem.* **1963**, *2*, 1128−1135.
(4) Zakharkin, L.; Kalinin, V.; Podvisotskaya, L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, 2310.
(5) Zakharkin, L.; Kalinin, V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1969**, 194.
(6) Stanko, V.; Gol'tyapin, Yu. V.; Brattsev, V. *Zh. Obsch. Khim.* **1969**, *39*, 1175.
(7) Stanko, V.; Brattsev, V.; Gol'tyapin, Yu. V. *Zh. Obsch. Khim.* **1969**, *39*, 2686.
(8) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 3489−3493.
(9) Ott, J. J.; Gimarc, B. M. *J. Comput. Chem.* **1986**, *7*, 673−692.
(10) Wales, D. J. *J. Am. Chem. Soc.* **1993**, *115*, 1557−1567.
(11) McKee, M. L. *J. Am. Chem. Soc.* **1992**, *114*, 5856−5858.
(12) McKee, M. L. *J. Am. Chem. Soc.* **1992**, *114*, 879.
(13) McKee, M. L. In *The Borane, Carborane, Carbocation Continuum*; Casanova, J., Ed.; Wiley: New York, 1998; Chapter 11 and references quoted therein.
(14) Bausch, J. W.; Tebben, A. J. In *The Borane, Carborane, Carbocation Continuum*; Casanova, J., Ed.; Wiley: New York, 1998; Chapter 9 and references quoted therein.

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Scheme 1

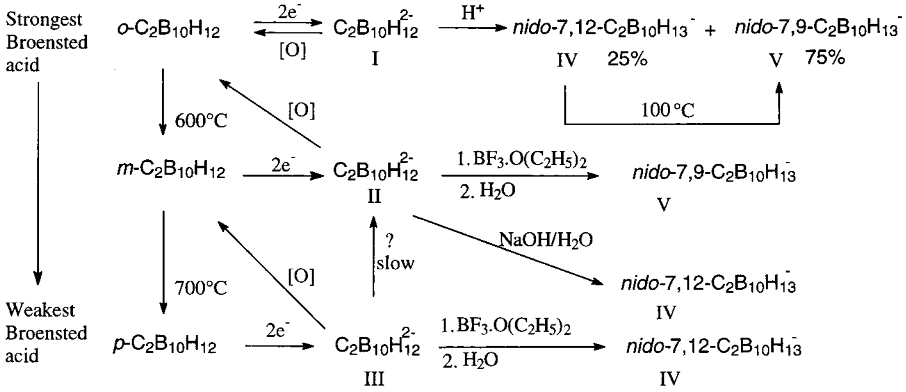

Table 1. Total Molecular Energies (Absolute and Relative Values) at the Optimized Geometries for the Carboranes and Their Singly and Doubly Charged Anions Using Different Basis Sets at the Hartree−Fock Level

	3-21g*		6-31g*		6-31g**	
	E (au)	E_{rel} (kJ/mol)	E (au)	E_{rel} (kJ/mol)	E (au)	E_{rel} (kJ/mol)
o-$C_2B_{10}H_{12}$	−327.744 662	+87.9	−329.620843	+84.4	−329.634463	+85.1
m-$C_2B_{10}H_{12}$	−327.775 528	+7.0	−329.649380	+9.9	−329.663147	+9.8
p-$C_2B_{10}H_{12}$	−327.778 192	0	−329.653142	0	−329.666889	0
o-$C_2B_{10}H_{12}^-$	−327.679 400	+29.2	−329.539682	+30.4	−329.553153	+30.5
m-$C_2B_{10}H_{12}^-$	−327.725 945	0	−329.588186	0	−329.601712	0
p-$C_2B_{10}H_{12}^-$	−327.701 027	+15.6	−329.564516	+14.8	−329.578100	+14.8
o-$C_2B_{10}H_{12}^{2-}$	−327.520 073	+76.2	−329.358432	+86.4		
m-$C_2B_{10}H_{12}^{2-}$	−327.641 507	0	−329.496075	0		
p-$C_2B_{10}H_{12}^{2-}$	−327.501 687	+87.7	−329.337652	−99.4		

unsubstituted and methyl- and Cl-substituted carborane compounds, including the normal *o*-, *m*-, and *p*-carboranes, optimized at the HF/3-21G and 6-31G* levels. The *o*-$C_2B_{10}H_{12}$ and *o*-$Si_2B_{10}H_{12}$ compounds were also recently optimized and compared at the HF/6-31G* and B3LYP/6-31G* levels by Jemmis and Kiran.[16] A number of semiempirical (see, for example, refs 17 and 18) and molecular mechanics calculations (see, for example, refs 19 and 21) for the carboranes have appeared in the literature over the years; these will not be further discussed in this paper.

As for ab initio calculations on carborane anions, McKee[11] and McKee et al.[22] studied different symmetries of the $C_2B_{10}H_{12}^{2-}$ dianion; they considered three *nido*-isomers with open six-membered faces and with the two carbons substituted into the open face in 2,4 and 2,5 positions, respectively. McKee et al. performed geometry optimizations at the HF/3-21G level followed by single-point energy calculations at the HF/6-31G* and MP2/6-31G* levels and found that the relative energies were essentially the same with and without the single-point MP2 correlation corrections. $[B_{12}H_{11}-C_2B_{10}H_{11}]^{2-}$ clusters, consisting of a *closo*-$B_{12}H_{12}^{2-}$ and a *closo*-$C_2B_{10}H_{12}$ molecule (*o*, *m*, and *p*), were recently studied at the HF/6-31G** level by Abe et al.[23]

The paper is arranged as follows. After the Methods section we will discuss the neutral carborane isomers: their structural, electronic, and acidic properties. We then discuss the structures and stabilities of the anions, and particularly the dianions, and relate our results to the existing experimental evidence.

2. Methods

Geometry optimizations at the Hartree−Fock 3-21G*, 6-31G*, and 6-31G** levels were carried out using the programs Spartan 4.1[24] and Gaussian 94/DFT.[25] We will mainly discuss four different quantities, all of which depend on the electronic properties of the carborane cages: (a) electron distribution maps; (b) atomic charges; (c) electron affinities $E_{A,1}$ and $E_{A,2}$, i.e. $-\Delta E$ for the reactions $e^- + [C_2B_{10}H_{12}] \rightarrow [C_2B_{10}H_{12}]^-$ and $e^- + [C_2B_{10}H_{12}]^- \rightarrow [C_2B_{10}H_{12}]^{2-}$; (d) deprotonation enthalpies, i.e. ΔE for the reaction $[C_2B_{10}H_{12}] \rightarrow [C_2B_{10}H_{11}]^- + H^+$.

3. Results and Discussion

3.1. Carboranes

Relative Stabilities of the *o*-, *m*-, and *p*-Compounds. The total energies of the carboranes are listed in Table 1. It is well-known (Grafstein[3]) that, on heating, *o*-carborane is converted to *p*-carborane via the *m*-compound (see Scheme 1). The experimental heats of formation for the three carboranes in the solid state confirm this stability trend: −176, −246, and −315, for *o*-, *m*-, and *p*-carborane, respectively (average values from Gmelin[26]). Our calculated total energies at the 6-31G* and

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(15) Diaz, M.; Jaballas, J.; Arias, J.; Lee, H.; Onak, T. *J. Am. Chem. Soc.* **1996**, *118*, 4405−4410.

(16) Jemmis E. D.; Kiran, B. *J. Am. Chem. Soc.* **1997**, *119*, 4076.

(17) Cheung, C.-C. S.; Beaudet, R. A.; Segal, G. A. *J. Am. Chem. Soc.* **1970**, *92*, 4158.

(18) Siegbahn, H.; Medeiros, R.; Goscinski, O. *J. Electron. Spectrosc. Relat. Phenom.* **1976**, *8*, 149.

(19) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1976**, *99*, 4907−4917.

(20) Dewar, M. J. S.; Dieter, K. M. *J. Am. Chem. Soc.* **1986**, *108*, 8075−8086.

(21) Timofeeva, T. V.; Suponitsky, K. Y.; Yanovsky, A. I.; Allinger, N. L. *J. Organomet. Chem.* **1997**, *536−537*, 481−488.

(22) McKee, M. L.; Bühl, M.; Schleyer, P. v. R. *Inorg. Chem.* **1993**, *32*, 1712−1715.

(23) Abe, J.; Nemoto, M.; Nagase, Yu; Shirai, Y.; Iyoda, T. *Inorg. Chem.* **1998**, *37*, 172−173.

(24) *SPARTAN 4.0*; Wavefunction, Inc.: 18401 Von Karman, Suite 370, Irvine, CA 92715.

(25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts,; R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92/DFT, Revision G.4.* Gaussian, Inc.: Pittsburgh, PA, 1993.

(26) *Gmelin Handbuch Der Organische Chemie*, Ergenzungswerek zur 8. Auflage, Band Berlin-Heidelberg, 1977; Seite 15.

6-31G** levels indicate that the *m*-carborane is ~75 kJ/mol more stable than the *o*-carborane, in reasonable agreement with experiment. However, the calculations show *p*-carborane to be only ~10 kJ/mol more stable than the *m*-carborane; i.e., we get a much smaller stability difference than given by the experimental heats of formation. Moreover, the experimental molar sublimation enthalpies are 70.3, 65.3, and 66.3 for the *o*-, *m*-, and *p*-carboranes,[26] respectively, which suggests that the crystal packing enthalpies do not vary greatly for the carborane crystals, and we are therefore inclined to conclude that there exists a real discrepancy between the experimental and computed stabilization energies for the *m*- and *p*-molecules. Our total energies and our stabilization energies are (of course) in total agreement with the earlier 3-21G* and 6-31G* calculations by Diaz et al.[15] on the neutral, unsubstituted carboranes. Also the minimal-basis calculations by Ott et al.[9] and by Wales[10] resulted in a large energy difference between the optimized *o*- and *m*-carboranes and a small difference between the *m*- and *p*-carboranes. It should be mentioned that another series of experiments do support our calculated stability results: Zakharkin et al.[27−29] established that the rearrangement of *m*- to *p*-carborane at 925−975 K in the gaseous phase is a reversible process with an equilibrium mixture containing 53% of *m*-carborane and 47% of *p*-carborane. Zakharkin's numbers indicate a $\Delta G(p-m)$ difference of +1.0 kJ/mol, i.e. a close similarity in thermodynamic stability between these two species, contrary to the conclusions from the experimental heats of formation. We have made a normal-mode and thermochemical analysis using the Gaussian program, for the *meta* and *para* compounds at 975 K, and find that the *meta* compound has a slightly higher entropy than the *para* compound, giving rise to a $T\Delta S$ term of 6.5 kJ/mol at 975 K with the 6-31G* basis set. Our computed approximation to $\Delta G(p-m) = \Delta E(p-m) - T\Delta S(p-m)$ is thus equal to $(-9.9 + 6.5) = -3.4$ kJ/mol, i.e. very small, in agreement with Zakharkin's experiments.[27−29]

Cage Geometries. The relaxed molecular structures of the unsubstituted *o*-, *m*-, and *p*-carboranes display considerable departure from the "ideal geometry" of the symmetrical $[B_{12}H_{12}]^{2-}$ cage, which has B−B bond lengths of 1.795 Å at the Hartree−Fock/6-31G* level. The distortion of the cage geometry is especially evident for the *o*-carborane (see Table 2), where the C−C bond length is only 1.61 Å, and the C−B bonds lie in the range 1.70−1.72 Å, while the B−B bonds lie in the range 1.77−1.79 Å, i.e. only moderately distorted by the carbons compared to the $[B_{12}H_{12}]^{2-}$ anion. The large distortion of certain distances represents a strain on the rest of the boron cage. The most symmetric molecule, the *p*-carborane, has presumably the lowest strain and, as noted above, is more stable than the *o*-carborane by 84 kJ/mol (Table 1). As a point of comparison, we mention that the C−C bond length in *o*-carborane (1.608 Å with the 6-31G* and 6-31G** bases) is 0.08 Å longer than the C−C bond in the ethane molecule calculated with the same basis sets.

The optimized *o*-, *m*-, and *p*-carborane geometries at the 6-31G* level are shown as **1**, **4**, and **7**, respectively, in Figures 1 and 2, which also show our atom numbering scheme. In this paper we will denote all our computed structures by Arabic numerals or normal capital letters and experimental compounds/structures by Roman numerals.

The B−B and C−B bond lengths display no significant differences between the *o*-, *m*-, and *p*-compounds. Moreover, no obvious trends in the correlation between bond distance and local environment can be discerned. The local surroundings of each B−B bond has been classified in Table 2 in terms of the number of C atoms neighboring the B−B pair. We find no correlations.

Although specific distances can differ by up to some 0.05 Å between the 3-21G* and 6-31G* bases, it must be emphasized that the resulting molecular geometries are very similar indeed with all three basis sets used here. The same conclusion was reached by Diaz et al.,[15] who optimized the neutral *o*-, *m*-, and *p*-carboranes for the purpose of computing ^{13}C chemical shifts, as mentioned in the Introduction. Also for the heavily distorted negatively charged species discussed below we find that the 3-21G* and 6-31G* bases give virtually the same geometries. High-level calculations on negative ions generally require extended basis sets containing diffuse functions; geometry optimizations with such large basis sets are too costly for the current investigation. The basis set improvement between 3 and 21G* and 6-31G* generally changes the distances by between 0.01 and 0.03 Å. Between the 6-31G* and 6-31G** basis sets, all distances in Table 2 change by 0.001 Å or less; the latter results are therefore not included in the table. The trends in crystal stability is well preserved between the three basis sets: the *p*-$C_2B_{10}H_{12}$ carborane is clearly more stable than the *o*- and *m*-compounds, and the relative differences are very similar.

The inclusion of electron correlation corrections appears to have a small but significant effect on the interatomic distances. Jemmis et al.[16] obtained a value of 1.622 Å for the optimized C−C distance in *o*-carborane at the B3LYP/6-31G* level.

Comparisons between our calculated cage geometries and experimental data show that an early electron diffraction study[30] of the carborane cages in the gas phase gave distances in only fair agreement with our 6-31G* and 6-31G** results. With the 6-31G* and 6-31G** basis sets, our C−C bond in the *o*-carborane is 1.61 Å, the C−B bonds lie in the range 1.69−1.72, and the B−B bonds lie in the range 1.77−1.80 Å. The C−C and C−B distances from electron diffraction were 1.65(5) and 1.71(1) Å, respectively, and the B−B distances were found to lie in the range from 1.71(1) to 1.83(5) Å. Experimental B−B distances from X-ray crystallographic investigations of the *o*-, *m*-, and *p*-compounds of hexamethylphosphoramide dicarbadodecaborane[31] and of bis(cyclotriveratrylene)-*o*-dicarbadodecaborane clathrate[32] lie in the range 1.76−1.78 Å, and C−B distances, in the range 1.69−1.71 Å. The crystallographic C−C distances in the *o*-cages are all close to 1.625 Å. The agreement between X-ray data and calculations is quite satisfactory. In all comparisons of this kind it should be borne in mind that electron diffraction, X-ray diffraction, and ab initio calculations do not refer to exactly the same kind of distances. Moreover, systematic errors of course come into play. That systematic errors are present in ab initio calculations is evident not least from our comparison of the optimized distances with the three different basis sets, but also the X-ray diffraction-determined distances can be affected by serious systematic errors. One such source of error is the presence of intermolecular interactions in the crystals but not in our calculated isolated cages. Here we have compared our theoretical results with a

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(27) Zakharkin, L. I.; Kalinin, V. N.; Podvisotskaya, L. S. *Izv. Akad. Nauk SSSR, Ser. Khim*. **1969**, 1197.

(28) Zakharkin, L. I.; Kalinin, V. N.; Podvisotskaya, L. S. *Izv. Akad. Nauk SSSR, Ser. Khim*. **1970**, 1297.

(29) Zakharkin, L. I. *Pure Appl. Chem*. **1972**, *29*, 513−526.

(30) Bohn, R. K.; Bohn, M. D. *Inorg. Chem*. **1971**, *10*, 350−355.

(31) Davidson, M. G.; Hibbert, T. G.; Howard, J. A. K.; Mackinnon, A.; Wade, K. *J. Chem. Soc., Chem. Commun*. **1996**, 2285.

(32) Blanch, R. J.; Williams, M.; Fallon, G. D.; Gardiner, M.G.; Kaddour, R.; Raston, C. L. *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 504.

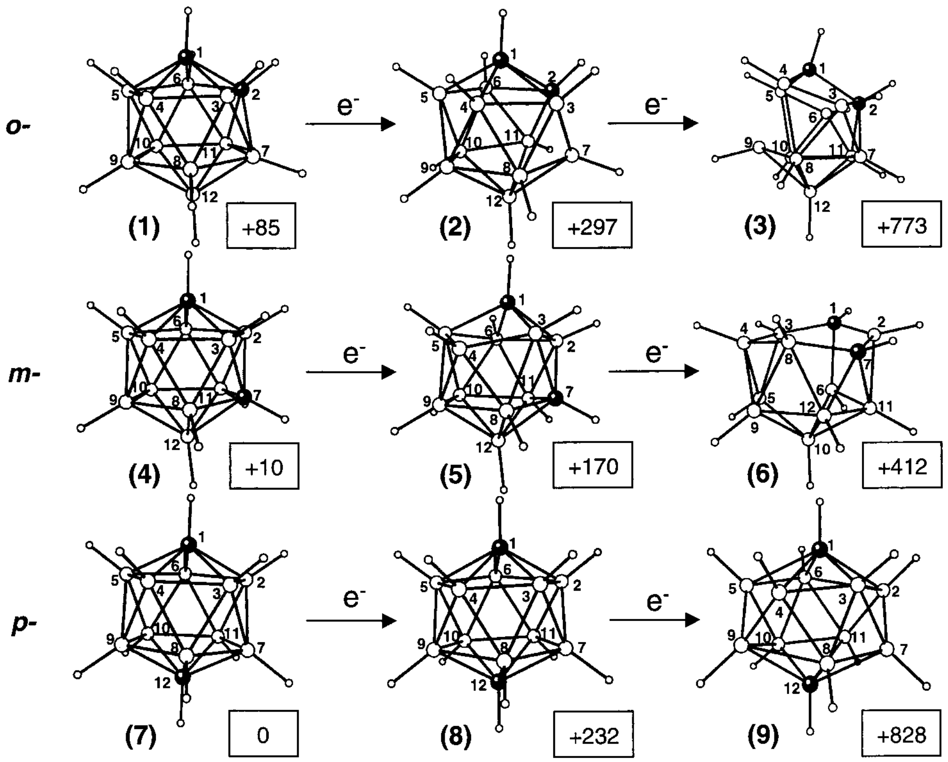

Figure 1. Optimized HF/6-31G* structures of the *o*-, *m*-, and *p*-carboranes and their monoanions and dianions. The cages are generally shown from "as similar a direction as possible", although small rotations have been made to make certain atoms and bonds more visible. The framed numbers are the relative energies in kJ/mol of each structure with respect to the most stable structure of them all: the neutral *p*-carborane. The optimized distances are given in Table 2. Note that in structure **3** the B9−B10 bond is hidden exactly behind the B8−B9 bond.

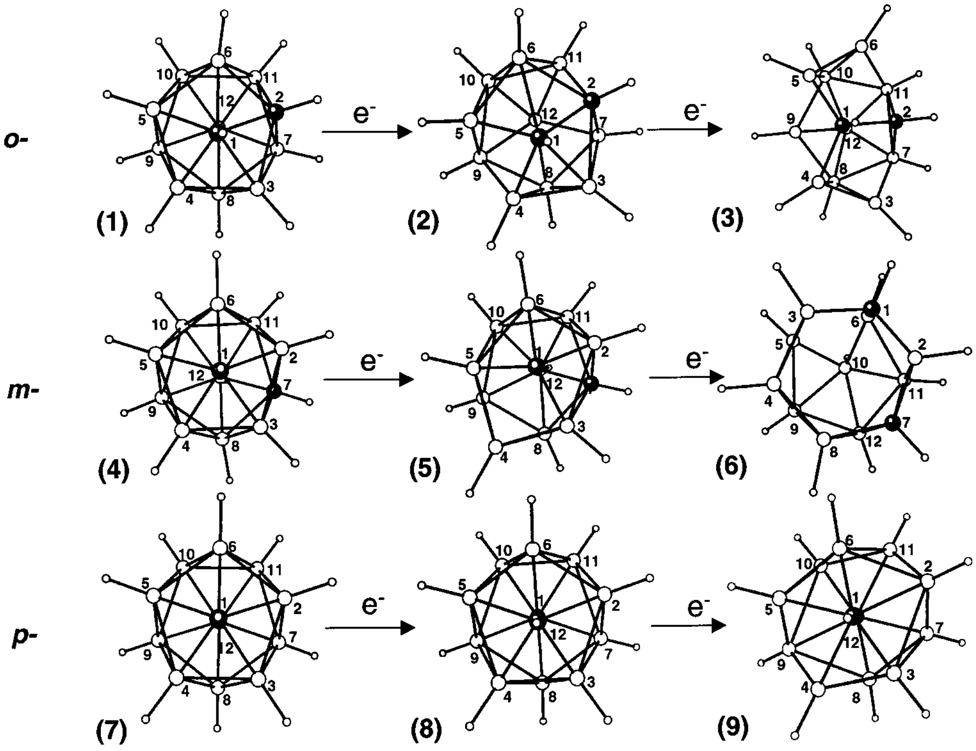

Figure 2. Same optimized cages as in Figure 1, except each cage in Figure 1 has been rotated counterclockwise around "the *x*-axis of the paper coordinate system". The rotation is approximately 90° in each case.

few different crystalline cages, however, representing some different crystalline surroundings; this should lend some more credibility to the comparison. Diffraction-determined distances can also be affected by systematic errors in the refinement procedure (for example the assumption of recilinear harmonic motion usually imposed in the vibrational fitting model) or in the data reduction handling (for example the treatment of absorption and extinction effects); such errors can easily give rise to systematic errors in the diffraction-determined distances of the order of 0.01 Å or more.

Table 2. Interatomic Distances at the Resulting Optimized Geometries for the *o*-, *m*-, and *p*-Carboranes[a]

	1,2-$C_2B_{10}H_{12}$			1,7-$C_2B_{10}H_{12}$			1,7-$C_2B_{10}H_{12}$		
	3-21g*	6-31g*	type	3-21g*	6-31g*	type	3-21g*	6-31g*	type
Top to Upper Ring[b]									
C1−B2				1.712	1.691		1.730	1.708	
C1−B3	1.751	1.716		1.712	1.691		1.730	1.708	
C1−B4	1.719	1.699		1.739	1.716		1.730	1.708	
C1−B5	1.718	1.699		1.736	1.714		1.730	1.708	
C1−B6	1.751	1.716		1.739	1.716		1.730	1.708	
C1−C2	1.639	1.608							
Within Upper Ring									
B2−B3				1.831	1.794	4B	1.815	1.793	2B
B3−B4	1.807	1.785	3	1.786	1.768	3	1.815	1.793	2B
B4−B5	1.810	1.789	2B	1.811	1.789	2B	1.815	1.793	2B
B5−B6	1.807	1.785	3	1.811	1.789	2B	1.815	1.793	2B
B6−B2				1.786	1.768	3	1.815	1.793	2B
C2−B3	1.751	1.716							
C2−B6	1.751	1.716							
Between Rings									
B2−B11				1.786	1.768	3	1.780	1.772	2B
B2−B7							1.780	1.772	2B
B3−B7	1.807	1.785	3				1.780	1.772	2B
B3−B8	1.778	1.770	2A	1.786	1.768	3	1.780	1.772	2B
B4−B8	1.800	1.790	0	1.785	1.776	2B	1.780	1.772	2B
B4−B9	1.797	1.786	0	1.801	1.791	1	1.780	1.772	2B
B5−B9	1.797	1.786	0	1.795	1.784	1	1.780	1.772	2B
B5−B10	1.800	1.790	0	1.795	1.784	1	1.780	1.772	2B
B6−B10	1.778	1.770	2A	1.801	1.791	1	1.780	1.772	2B
B6−B11	1.807	1.785	3	1.785	1.776	2B	1.780	1.772	2B
C2−B11	1.719	1.699							
C2−B7	1.719	1.699							
C7−B2				1.712	1.691				
C7−B3				1.712	1.691				
Within Lower Ring									
B7−B8	1.800	1.790	1				1.815	1.793	2B
B8−B9	1.816	1.805	0	1.801	1.791	1	1.815	1.793	2B
B9−B10	1.816	1.805	0	1.815	1.805	0	1.815	1.793	2B
B10−B11	1.800	1.790	0	1.801	1.791	1	1.815	1.793	2B
B11−B7	1.810	1.789	2B				1.815	1.793	2B
C7−B8				1.739	1.716				
C7−B11				1.739	1.716				
Lower Ring to Bottom									
B12−B7	1.797	1.786	1						
B12−B8	1.816	1.805	0	1.811	1.789	2B			
B12−B9	1.804	1.793	0	1.795	1.784	1			
B12−B10	1.816	1.805	0	1.795	1.791	1			
B12−B11	1.797	1.786	1	1.811	1.789	2B			
C7−B12				1.736	1.714				
C12−B7							1.730	1.708	
C12−B8							1.730	1.708	
C12−B9							1.730	1.708	
C12−B10							1.730	1.708	
C12−B11							1.730	1.708	

[a] In the columns labeled "type", a B−B distance has been classified by the pair's total number of nearest-neighbor C atoms. In type 2A, one boron atom of the pair has two C neighbors and the other has zero; in type 2B each has one C neighbor. "Upper ring" refers to the C2−B3−B4−B5−B6 ring, and other geometry elements of the cage are named correspondingly (cf. leftmost columns in Figures 1 and 2). The C−H distances are all 1.07 Å, and the B−H distances, 1.17−1.18 Å. [b] cf. Figure 1.

A detailed inspection of the experimental X-ray-diffraction-determined B−B distances reveals no correlation between *r*(B−B) and the number of and distance to the nearest-carbon neighbors, in agreement with our theoretical result.

Atomic Charges. We have analyzed the charge distribution in the carborane cages using different tools: electron densities, atomic Mulliken charges, and charges derived from a natural atomic orbitals scheme. The two atomic charge schemes give rise to similar trends and conclusions. In the following, only the Mulliken charges will be discussed, and these are listed in Table 3 for the neutral carboranes. It is well-known that the Mulliken charges are strongly basis-set dependent; nevertheless the trends displayed by the three basis sets used here are roughly the same.

We find that the carbon atoms (electronegativity = 2.6) carry negative charge relative to their nearest boron neighbors (electronegativity = 2.0). The C atoms in the *m*- and *p*-carboranes have only B atoms as neighbors and are more negative than in the *o*-compound. Also for boron, the Mulliken charges reflect well the immediate environment. With the 6-31G* basis, boron atoms with no C neighbors have Mulliken charges in the range −0.09 to −0.11, those with one C neighbor are in the range −0.02 to −0.03, and for those with two C neighbors the Mulliken charges lie between 0.05 and 0.07. The

Table 3. Resulting Mulliken Charges for the *o*-, *m*-, and *p*-Carboranes[a]

	$1,2\text{-}C_2B_{10}H_{12}$				$1,7\text{-}C_2B_{10}H_{12}$				$1,12\text{-}C_2B_{10}H_{12}$			
	3-21g*	6-31g*	6-31g**	type	3-21g*	6-31g*	6-31g**	type	3-21g*	6-31g*	6-31g**	type
C1	−0.92	−0.51	−0.45		−1.07	−0.62	−0.55		−1.05	−0.63	−0.56	
C2	−0.92	−0.51	−0.45									
C7					−1.07	−0.62	−0.55					
C12									−1.05	−0.63	−0.56	
B2					0.27	0.07	0.12	2	0.12	−0.02	0.04	1
B3	0.27	0.05	0.10	2	0.27	0.07	0.12	2	0.12	−0.02	0.04	1
B4	0.10	−0.03	0.03	1	0.12	−0.02	0.04	1	0.12	−0.02	0.04	1
B5	0.10	−0.03	0.03	1	0.13	−0.03	0. 03	1	0.12	−0.02	0.04	1
B6	0.27	0.05	0.10	2	0.12	−0.02	0.04	1	0.12	−0.02	0.04	1
B7	0.10	−0.03	0.03	1					0.12	−0.02	0.04	1
B8	−0.01	−0.09	−0.03	0	0.12	−0.02	0.04	1	0.12	−0.02	0.04	1
B9	0.01	−0.11	−0.05	0	−0.01	−0.09	−0.03	0	0.12	−0.02	0.04	1
B10	−0.01	−0.09	−0.03	0	−0.01	−0.09	−0.03	0	0.12	−0.02	0.04	1
B11	0.10	−0.03	0.03	1	0.12	−0.02	0.04	1	0.12	−0.02	0.04	1
B12	0.01	−0.11	−0.05	0	0.13	−0.03	0.03	1				
H on C	0.33	0.30	0.24		0.32	0.29	0.23		0.32	0.28	0.23	
H on B	0.02−0.03	0.07−0.09	0.01−0.03		0.03−0.06	0.08−0.10	0.02−0.04		0.02	0.09	0.03	

[a] The charges refer to the optimized geometries with the different basis sets. In this table “type” refers to the number of C neighbors of each boron atom.

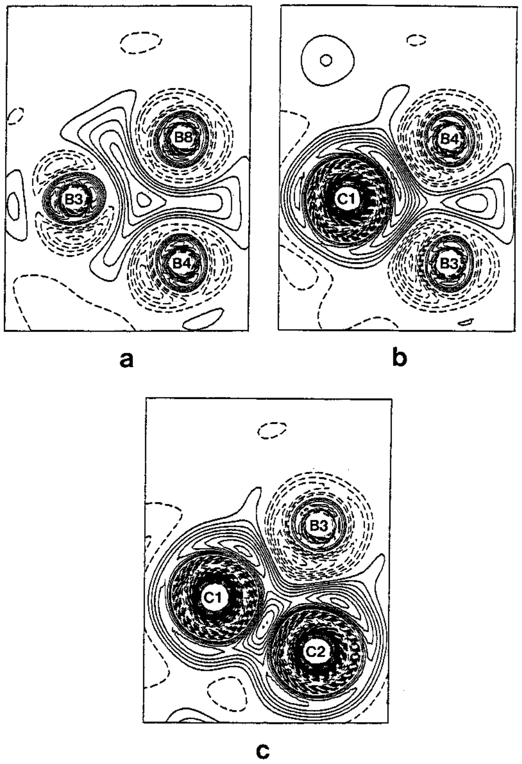

Figure 3. Difference electron density maps ($\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \sum\rho_{\text{atoms}}(\mathbf{r})$) in three sections through the *o*-carborane cage: (a) through B3, B4, and B8; (b) through C1, B3, and B4; (c) through C1, C2, and B3. Solid lines denote electron excess, and dashed lines electron loss. The zero contour has been omitted. Contour levels: ±0.05 e/Å^3.

C atoms induce an electron flow such that the boron atoms on the opposite side of the molecule (furthest away from the C atoms) attain relatively more electronic charge than the other boron atoms. This is clearly shown in colored pictures of the electrostatic potential outside *o*-carborane (not shown here).

It is well-known that nucleophilic attacks on the unsubstituted carborane cages and the subsequent onset of cage breakage to form *nido* structures occur at the B atoms with the maximum numbers of neighboring the C atoms. Table 3 shows that these are the B atoms which carry the highest Mulliken charges.

Electron Density Distribution. Figure 3 shows difference electron density maps through three different sections in the *o*-carborane structure: the triangles through the B3B4B8 atoms (Figure 3a), through the C1B3B4 atoms (Figure 3b), and through C1C2B3 (Figure 3c). The maps show the total electron density minus the electron density of the spherical isolated atoms and thus display the electron redistribution occurring when the molecule is created from its constituent atoms. Both the C and the B atoms lose electron density close to the nuclei in order to form the covalent bonds. The B atom gives up more electron density, however, as evidenced by both the Mulliken charges and the electron density maps. Moreover, the electron density peak in the C−B bond is located closer to C than to B. Figure 3b shows the difference electron density in a plane through C1 and two different types of boron atoms: B3 has two carbon neighbors, while B4 has only one. B3 has a Mulliken charge of +0.05, and B4, −0.03. A count of the dashed contours (electron loss) around B3 and B4 in the electron density map shows seven contours for B3 and five for B4 in the direction toward C1. This is consistent with the Mulliken trend, but more importantly, the maps give a much more complete picture of the very complicated electron redistributions that occur upon bond formation. Because of this complexity, however, it is generally difficult to deduce quantitative information from these maps using pure visual inspection, as is evidenced by Figure 3a, which is a map through three boron atoms of types 0, 1, and 2, respectively. While their Mulliken charges are rather different, the electron density features, at first inspection, look rather similar. Numerical charges and electron density maps thus complement each other in a useful manner.

Electron Affinities. The *m*-carborane is the molecule which most readily takes up electrons, as seen from the electron affinity values in Table 4 and the relative energies in Figure 1. The E_A values (defined as *minus* ΔE for the reactions “cage + e$^-$ → cage$^-$”, and “cage$^-$ + e$^-$ → cage^{2-}”), change in the order *p*-carborane < *o*-carborane < *m*-carborane. The order is the same for the first and second electrons. Our results appear to be partly contradictory to experiment, since Zakharkin[27] performed polarographic reduction experiments on some *o*-, *m*-, and *p*-carboranes and concluded that the *o*-carboranes are reduced the most easily and that the correct order is *p*-carborane < *m*-carborane < *o*-carborane. Zakharkin[27] also cites experiments on the relative rates of alkali metal addition to *o*-, and *m*-, and *p*-carboranes in liquid ammonia; these data support the quoted Zakharkin order.

Table 4. Acid−Base Properties and Electron Affinities Computed for the Optimized Geometries at the 6-31g* Level

quantity	1,2-$C_2B_{10}H_{12}$	1,7-$C_2B_{10}H_{12}$	1,12-$C_2B_{10}H_{12}$
	Protons		
exptl pK_a	23.3[c]	27.9[c]	30.0[c]
ΔE (deprotonation)[a]	+1533	+1584	+1602
q(H on C)	+0.30	+0.29	+0.28
q(C) in $C_2B_{10}H_{12}$	−0.51	−0.62	−0.63
q(C) in in $C_2B_{10}H_{11}^-$	−0.31	−0.40	−0.42
	Electrons		
$E_{A,1}$ (cage + e^- → cage$^-$)[b]	−212	−161	−232
$E_{A,2}$ (cage$^-$ + e → cage^{2-})[b]	−476	−241	−595
largest q(B) in $C_2B_{10}H_{12}$	+0.05 (B3, B6)	+0.07 (B2, B3)	−0.02 (all)

[a] Prototype acid−base reaction (ΔE in kJ/mol): 1,2-$C_2B_{10}H_{12}$ ↔ 1,2-$C_2B_{10}H_{11}^-$ + H^+. [b] Prototype electron capture reactions: 1,2-$C_2B_{10}H_{12}$ + e^- → 1,2-$C_2B_{10}H_{12}^-$ (E_A is $-\Delta E$; in kJ/mol); 1,2-$C_2B_{10}H_{12}^-$ + e^- → 1,2-$C_2B_{10}H_{12}$ (E_A is $-\Delta E$; in kJ/mol). [c] Reference 32.

The electron affinities in Table 4 thus do not follow Zakharkin's trend nor do they follow the trend observed by experimental reaction rates for nucleophilic attack, viz., that the attack proceeds much faster for *o*-carborane compared to the *m*- and *p*-carboranes. There could be many reasons for this discrepancy. The most obvious one concerns the usual problems of comparing kinetic and thermodynamic observations; i.e., it may be necessary to consider activated complexes in order to explain the experimental findings. Finally we want to point out that our computed electron affinities follow the same trend as the charges on the B atoms bonded to the C atoms; this is seen on the last line in Table 4.

Brønsted Acid−Base Properties. Equilibrium acidity constants, pK_a, have been measured experimentally and were found to be 23.3, 27.9, and 30.0 (Streitwieser's scale) and 19, 24, and 26 (polarographic scale) for the *o*-, *m*-, and *p*-carboranes, respectively.[33] The acidity increments, Δ(pK_a), show good agreement between the two data series. Kinetic acidity measurements[33] show the same acidity trend, as exemplified by the deuterium exchange rates in liquid ammonia, which gave k_{obs} values of 6×10^{-2} (at 300 K), 3.1×10^{-6} (at 300 K), and 8.5×10^{-7} s^{-1} (at 325 K) for *o*-, *m*-, and *p*-carboranes, respectively.

The unsubstituted carboranes are thus all very weak Brønsted acids, with *o*-carborane the least weak. We have calculated the energy for deprotonation of the carboranes, by removing the proton bound to a C atom and optimizing the geometry of the resulting negative cage. We also find very high deprotonation energies (Table 4), which follow the same general trend as predicted by the experimentally observed acidities. Our computed ΔE(deprotonation) values in Table 4 are 51 kJ/mol larger for *para* than for *meta* and 18 kJ/mol larger for *meta* than for *ortho*. Using the Boltzmann distribution law, these energy differences result in a pK_a difference of 8.9 between *ortho* and *meta* and 3.2 between *meta* and *para*. The corresponding experimental pK_a differences (Streitwieser's scale) are 4.6 and 2.1, respectively, and, on the polarograpraphic scale, 5 and 2, respectively.[33]

A quantity with a less obvious connection to deprotonation enthalphies and pK_a values is the Mulliken charge on the H to be removed from the neutral compound. These charges are also given in the table and are seen to vary only very little between the *o*-, *m*-, and *p*-carboranes, but the trend suggests a higher acidity for the *o*-compound. On the other hand, one might argue that the bond polarity changes in the opposite direction, since *o*-carborane has both the lowest pK_a value and the lowest C−H bond polarity. We conclude that the most straightforward quantities to discuss in this connection are the energies.

3.2. Anions

3.2.1. Previous Work

Monoanions. On the experimental side, we know of only two cases where it has been possible to isolate and determine the crystal structure of a salt containing the singly charged anions, namely the $[(15\text{-crown-5})_3Na_2]^{2+}[(C_2B_{10}H_{11})_2]^{2-}$ and $[(P(C_6H_5)_3CH_3]_2^{2+}[(C_2B_{10}H_{11})_2]^{2-}$ salts. These structures do not contain the normal, simple monoanions but the biscarborane [1,1′(-*closo*-1′,2′-$C_2B_{10}H_{11}$)-*closo*-1,2-$C_2B_{10}H_{11}]^{2-}$ ion, which is a double cage with one negative charge on each carborane cage.[34,35] The structure of the anion in the latter crystal is centrosymmetric. The observed asymmetries in the two long [C(12)−B(8) and C(12)−B(11)] and the two short [C(12)−B(9) and C(12)−B(10)] C−B distances were explained as being due to crystal packing forces.

Transition Metal−Dianion Complexes in the Solid State. If one turns now to experimental evidence for the existence and structures of the dianions, the three isomeric neutral carboranes have been reduced with sodium to form the $C_2B_{10}H_{12}^{2-}$ ions (**I**, **II**, and **III** in Scheme 1); this was reported already in the 1960'ies.[2−7,36] The chemistry of the dianions has by now been extensively explored, even though the ions have not yet been isolated as salts and their structures are still largely unknown. Some related information may be inferred from the experimental studies of 13-vertex complexes formed by a reaction between the [*o*-carborane]$^{2-}$ dianion (**I**) and a transition metal ion; numerous such studies have been reported, starting with the early observation by Dunks, McKown, and Hawthorne.[37] These structures all consist of the transition metal ion sitting as the 13th vertex on top of a six-membered "rim" of a $C_2B_{10}H_{12}^{2-}$ *nido* basket. The bonding between the transition metal ion and the carborane is believed to involve significant covalent contributions, and it is thus not straightforward to assign a net ionic charge to the carborane ions in these compounds.

Monoprotonated Dianions. Several studies have shown that the dianions obtained from the carboranes can be protonated to $C_2B_{10}H_{13}^-$ ions.[4−6,38−39] The *o*-$C_2B_{10}H_{12}$ compound was found

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(33) Reutov, O. A.; Beletskaya I. P.; Butkin, K. P. *CH−Acids*; Pergamon Press: Oxford, U.K., 1978; pp 13−14, 29, 34−34, 123−124 and references quoted therein.

(34) Getman, T. D.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1990**, *112*, 4593−4594.

(35) Getman, T. D.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem*. **1992**, *31*, 101.

(36) Plešek, J.; Štíbr, B.; Fontaine, X. L. R.; Kennedy, J. D.; Hemánek, S. *Collect. Czech. Chem. Commun.* **1991**, *56*, 1618−1635.

(37) Dunks, G. B.; McKown, M. M.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1971**, *93*, 2541.

(38) Dunks, G. B.; Wiersma, R. J.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1972**, 899−900.

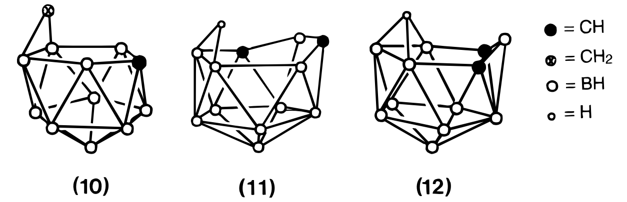

Figure 4. The Three optimized structures of $C_2B_{10}H_{13}^-$ calculated by McKee et al.[22]

to give two products: one thermodynamically favored “stable” isomer and one kinetically favored “unstable” isomer. While no structure determinations of salts of these two unsubstituted $C_2B_{10}H_{13}^-$ ions have been reported, X-ray crystallographic studies of the $[(CH_3)_2C_2B_{10}H_{11}]^-$ anions have been published, both for the thermodynamically stable[40] (**A**) and the kinetically favored[38,39] (**B**) ions; both ions were obtained by protonation of the dianion obtained from the dimethylated *o*-carborane $[(CH_3)_2C_2B_{10}H_{10}]$. X-ray data for the thermodynamic form of the $[Ph_2C_2B_{10}H_{11}^-]$ anion (**A′**) have also been reported.[41,42] The **A** and **A′** structures are both characterized by an open pentagonal face containing one C atom and a bridging RCH group (R = Me or Ph) on the opposite side and have essentially C_s symmetry. The **B** structure has two open faces, a puckered hexagon which forms the “top” of the nido cage with the two carbon atoms in the 7 and 9 positions, and a quadrilateral face.

These findings led to the proposition that the corresponding two unsubstituted $C_2B_{10}H_{13}^-$ anions have analogous structures; i.e., the thermodynamically stable anion has a five-membered ring containing one C atom in the ring and a bridging CH_2 group on the opposite side, and the kinetically preferred anion ring contains two C atoms in the *meta*-position. ^1H and ^{11}B NMR results[40−42] support the existence of two $C_2B_{10}H_{13}^-$ anions in solution with such structures, viz. *nido*-7,12-$C_2B_{10}H_{13}^-$ (**IV**) and *nido*-7,9-$C_2B_{10}H_{13}^-$ (**V**) (Scheme 1). It was not possible, however, to decide from the NMR spectra if **V** in solution is best described as having a static C_s structure or if it represents a mixture of two rapidly interconverting enantiomers with C_1 symmetry.[36] This issue was later studied by McKee et al.,[22] who performed ab initio calculations to try to establish the minimum-energy structures of both **IV** and **V**. They considered geometries as in Figure 4a for **IV** and as in Figures 4b,c for V. It was found that the optimized energies increase in the order **10** < **11** < **12**. **10** was more stable than **11** by 6.7 kcal/mol and **11** more stable than **12** by 17.2 kcal/mol. Moreover, the calculated IGLO ^{11}B NMR shifts for **10** and **11** agreed well with experiment but not for **12**.

Dunks et al.[1,38] found that, after treatment of the dianions derived from *o*- and *m*-$C_2B_{10}H_{12}$ with boron trifluoride etherate followed by water, the tetramethylammonium salt of **V** could be isolated, while treatment of the same anions with aqueous sodium hydroxide after workup gave the tetramethylammonium salt of **IV**. The dianion derived from *p*-$C_2B_{10}H_{12}$ gave the tetramethylammonium salt of **V** when treated with boron trifluoride etherate followed by water. It has later been claimed that the dianion of *o*-$C_2B_{10}H_{12}$ gives **IV** and **V** in the proportions 3/1 regardless of the way of protonation.[36] Whether this is true also for the dianion formed from *m*-$C_2B_{10}H_{12}$ remains to be examined.

Dianions. McKee[11] and McKee et al.[22] also studied the $C_2B_{10}H_{12}^{2-}$ dianion using ab initio calculations, starting their optimizations from a few plausible model *nido*-structures. They thus considered three *nido*-isomers, each with an open six-membered face with two carbons either in the 2,4 or in the 2,5 positions. Just as in the case of their calculations on the $C_2B_{10}H_{13}^-$ ion, two different symmetries were used in the case of the 2,4 isomer: C_s and C_1. Geometry optimizations at the HF/3-21G level followed by single-point energy calculations at the MP2/6-31G* level and ZPE corrections gave that the unsymmetrical (C_1) 2,4-isomer was about 10 kcal/mol more stable than the symmetrical (C_s) 2,4-isomer, which was 3 kcal/mol more stable than the 2,5-molecule (C_s) cage. These large energy differences (10 and 13 kcal/mol) suggest that the unsymmetrical 2,4-isomer would be the only species present in solution at room temperature, unless kinetic aspects play a significant role.

3.2.2. Our ab Initio Results. Starting from the geometries of the neutral carborane cages, we have optimized the structures of the monovalent and divalent *o*-, *m*-, and *p*-carborane anions with the three basis sets discussed in this paper. Figures 1 and 2 show the resulting optimized geometries at the 6-31G* level. The addition of the electrons has a striking effect on the molecular geometries. Already the singly charged molecules show large distortions. In $[o\text{-carborane}]^-$ the spherical cage has started to open up: the B4−B5 and B7−B11 distances are 0.16 Å longer than in the neutral cage. The $[o\text{-carborane}]^{2-}$ dianion (**3**) is heavily distorted, and the B4−B5 distance is now 0.87 Å longer than in the neutral cage. The C1−B3 and C1−B6 distances are also among those which change the most due to electron uptake and increase from 1.72 to 1.88 to 2.38 Å, as we go from the cage with charge 0 to −1 to −2. The B4−B9 (and B5−B9) distance increase is also substantial, from 1.79 to 1.82 to 2.16 Å, and these two bonds are therefore “missing” in structure **3**. Table 5 lists all the relevant C−C, C−B, and B−B distances in the optimized ions. The distance limit for drawing bonds in Figures 1 and 2 has somewhat arbitrarily been set to 1.95 Å, in accordance with the convention in the papers by Getman, Knobler, and Hawthorne;[34,35] the only exception is the $[p\text{-carborane}]^{2-}$ dianion (see below).

It is the *m*-compound which becomes the most distorted on electron capture; the singly charged structure (**5**) still looks like a cage, although distorted, with a quadilateral face formed by C1−B3−B4−B5, and then the cage opens up to a *nido* structure (**6**). The cage thus becomes a basket with the opening formed by a “rather planar” six-membered ring consisting of the C1−B2−C7−B8−B4−B3 atoms. One face is quadrilateral, consisting of the C1−B2−B11−C6 atoms. McKee et al.[22] also found a 4-membered ring in their optimized unsymmetrical (C_1) 2,4-isomer. The transformation from “neutral → monoanion → dianion” for *m*-carborane is more clearly seen in Figure 5, where the first two structures have been rotated to emphasize the similarity between the three structures.

In the papers by McKee[11] and by McKee et al.[22] only schematic pictures, and no distances, were reported for their optimized dianion structures so we cannot make a detailed comparison between their optimized *nido*-cage and our structure **6**. Some structural features (like the quadilateral face) seem to be common to both structures, and it is not unlikely that their unsymmetrical (C_1) 2,4-isomer is equivalent to **6**. We base this conclusion on the fact that we performed an additional optimization, at the 3-21G level like McKee,[11] but starting from our 6-31G*-optimized structure **6**. Our 3-21G-optimized struc-

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(39) Getman, T. D.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1990**, *29*, 158−160.

(40) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1973**, *12*, 2674−2682.

(41) Tolpin, E. I.; Lipscomb, W. N. *J. Chem. Soc., Chem. Commun.* **1972**, 899.

(42) Tolpin, E. I.; Lipscomb, W. N. *Inorg. Chem.* **1973**, *12*, 2257−2262.

Table 5. Interatomic Distances (Å) (Involving Non-Hydrogen Atoms) at the Resulting Optimized Geometries for the Single and Doubly Charged *o*-, *m*-, and *p*-Carborane Ions (Cf. Figures 1 and 2) at the HF/6-31G* Level

	o-$C_2B_{10}H_{12}^{-}$	*m*-$C_2B_{10}H_{12}^{-}$	*p*-$C_2B_{10}H_{12}^{-}$	*o*-$C_2B_{10}H_{12}^{2-}$	*m*-$C_2B_{10}H_{12}^{2-}$	*p*-$C_2B_{10}H_{12}^{2-}$
C1−C2	1.630			1.645		
C1−B2		1.632	1.770		1.517	1.978
C1−B3	1.876	1.667	1.681	2.385	1.503	1.633
C1−B4	1.689	2.419	1.809	1.604	2.869	1.980
C1−B5	1.689	1.702	1.809	1.604	2.869	1.980
C1−B6	1.876	1.652	1.681	2.385	1.774	1.633
C2−B3	1.875			2.150		
C2−B6	1.875			2.150		
C2−B7	1.690			1.705		
C2−B11	1.690			1.705		
B2−B3		1.948	1.871		2.689	2.074
B2−B6		1.760	1.871		2.050	2.074
B2−B7			1.731			1.675
B2−C7		1.677			1.628	
B2−B11		1.756	1.731		1.879	1.675
B3−B4	1.723	1.803	1.745	1.669	1.830	1.739
B3−B5	3.046	2.507	2.941	3.679	1.859	3.027
B3−B6	3.232	2.866	2.908	4.037	2.064	2.891
B3−B7	1.723		1.777	1.759		1.806
B3−C7		1.822			3.268	
B3−B8	1.729	1.861	1.769	1.778	2.926	1.754
B4−B5	1.953	1.904	1.928	2.662	1.751	2.123
B4−B8	1.782	1.719	1.777	1.901	1.718	1.806
B4−B9	1.816	1.744	1.731	2.159	1.773	1.675
B5−B6	1.723	1.907	1.745	1.669	2.003	1.739
B5−B9	1.816	1.834	1.731	2.159	1.746	1.675
B5−B10	1.782	1.863	1.777	1.901	1.762	1.806
B6−B10	1.729	1.777	1.769	1.778	1.835	1.754
B6−B11	1.723	1.758	1.777	1.759	1.876	1.806
B7−B8	1.782		1.745	1.876		1.739
B7−B11	1.952		1.928	1.871		2.123
B7−B12	1.816			1.819		
B7−C12			1.809			1.980
C7−B8		1.714			1.670	
C7−B11		1.737			1.688	
C7−B12		1.730			1.680	
B8−B9	1.800	1.795	1.871	1.748	1.872	2.074
B8−B12	1.801	1.775		1.763	1.854	
B8−C12			1.681			1.633
B9−B10	1.800	1.800	1.871	1.748	1.820	2.074
B9−B12	1.863	1.778		1.835	1.760	
B9−C12			1.770			1.978
B10−B11	1.782	1.798	1.745	1.786	1.741	1.739
B10−B12	1.801	1.797		1.763	1.814	
B10−C12			1.681			1.633
B11−B12	1.816	1.777		1.819	1.750	
B11−C12			1.809			1.980

Table 6. Resulting Mulliken Charges for the Singly and Doubly Charged *o*-, *m*-, *p*-Carborane Anions at Their Optimized HF/6-31G* Geometries[a]

	o-$C_2B_{10}H_{12}^{-}$	*m*-$C_2B_{10}H_{12}^{-}$	*p*-$C_2B_{10}H_{12}^{-}$	*o*-$C_2B_{10}H_{12}^{2-}$	*m*-$C_2B_{10}H_{12}^{2-}$	*p*-$C_2B_{10}H_{12}^{2-}$
C1	−0.57	−0.63	−0.70	−0.35	−0.44	−0.66
C2	−0.57			−0.59		
C7		−0.68			−0.59	
C12			−0.70			−0.66
B2		0.15	0.02		0.24	0.14
B3	0.08	0.14	0.06	0.04	0.14	0.16
B4	0.02	−0.05	−0.04	0.09	−0.06	−0.11
B5	0.02	0.00	−0.04	0.09	−0.05	−0.11
B6	0.08	0.04	0.06	0.04	−0.05	0.16
B7	0.02		−0.04	0.03		−0.11
B8	−0.02	0.02	0.06	−0.10	0.10	0.16
B9	−0.12	−0.06	0.02	−0.02	−0.02	0.14
B10	−0.02	−0.10	0.06	−0.10	0.00	0.16
B11	0.02	0.01	−0.04	0.03	0.02	−0.11
B12	−0.12	0.00		−0.01	0.01	
H on C	0.19, 0.19	0.19, 0.21	0.20, 0.20	0.05, 0.11	0.07, 0.11	0.09, 0.99
H on B	−0.04 to −0.01	−0.03 to −0.01	−0.02 to −0.01	−0.17 to −0.11	−0.20 to −0.11	−0.15 to −0.12

[a] On the line denoted “H and C”, the first value for each entry refers to the charge on H bonded to C1 and the second to H bonded to C7 or C12.

ture is the same as **6** within 0.04 Å for all nearest-neighbor distances. The HF/3-21G//HF/3-21G energy of this dianion lies 9.2 kcal/mol lower than the published HF/3-21G//HF/3-21G energy of the symmetrical (C_s) 2,4-isomer of McKee[11] (Table

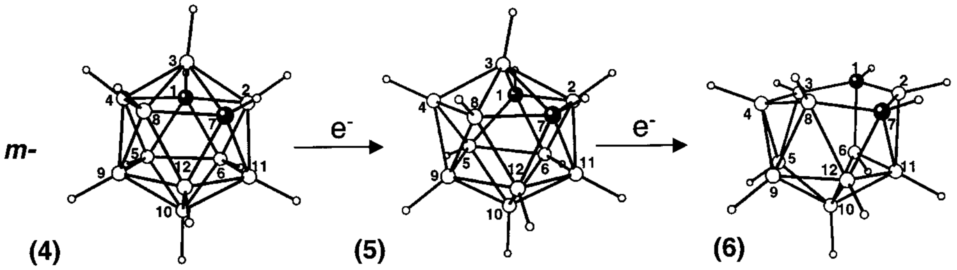

Figure 5. Cage deformation as the *m*-carborane takes up two electrons consecutively. The cages have here been rotated to better display the relation between the three structures.

1 in ref 11); i.e. it should be very close in energy to their unsymmetrical 2,4-isomer.

For *p*-carborane, the cage shape is not quite as drastically affected by the electron uptake, but the interatomic distances still do change drastically. Many of the B−B distances lie around 2.10 Å in this dianion, and here the distance limit in Figures 1 and 2 has been set to 2.10 Å, since it gives a more representative impression of the new shape of the molecule.

For all three compounds, the captured electron(s) become distributed over all the H atoms (see Table 6), which each takes up about 0.1 electrons in the singly charged molecules and 0.2 electrons in the doubly charged molecules (Mulliken values). This systematic uptake of electrons occurs for all H atoms in all the isomers and is little dependent on the local environment around the H atom. It is interesting to note that the B−H and C−H distances are not drastically affected by the electron uptake; they increase by between 0.01 and 0.03 Å. There is also an electron rearrangement occurring within the non-H parts of the cages upon electron uptake. Some atoms gain as much as ∼0.1 electrons, while others lose up to ∼0.1 electrons.

4. Concluding Remarks

Previous experiments on the protonated $C_2B_{10}H_{12}^{2-}$ ions discussed in the section titled *Previous Work* suggest that there are (at least) two different such ions of importance, and accompanying calculations suggested that both are *nido*-cages, one with a B−C−B−B−B five-membered ring on top, the other with a C−B−C−B−B−B six-membered ring. The many transition metal−$C_2B_{10}H_{12}^{2-}$ compounds studied crystallographically all contain a *nido*-cage with a six-membered ring. No experimental structural information exists for the pure $C_2B_{10}H_{12}^{2-}$ ions. Previous ab initio calculations by McKee et al.[22] on isolated dianions found one isomer which lies substantially below other minima; this isomer is a *nido* structure with a six-membered ring on top and the C atoms in the *meta* position. Our own Hartree−Fock calculations at the 6-31G* and 6-31G** levels give three local minima for the $C_2B_{10}H_{12}^{2-}$ ion, namely structures **3**, **6**, and **9** in Figures 1 and 2. None of these has a five-membered ring. Instead, one (the most stable structure, similar to McKee's lowest-energy structure) has a six-membered ring with the C atoms in the *meta* position, another has a heavily distorted cage structure (starting from *o*-carborane), and the third has a fairly symmetric structure akin to the neutral *p*-carborane (although many bond distances are elongated by large amounts). The relative energies of these three isomers are vastly different, and on the basis of energetic arguments, only the *nido*-cage would be found in solution. As always, it is of course possible that kinetic arguments can change that situation. Is there any further experimental evidence which can help shed light on this unclear situation?

Yes. Dunks et al.[1] performed ^{11}B NMR measurements for the dianions derived from *o*-, *m*-, and *p*-$C_2B_{10}H_{12}$ and report that the NMR spectrum of the anions formed from *o*- and *m*-$C_2B_{10}H_{12}$ are virtually identical. They both consist of three broad resonances centered at −3, +5, and +25 ppm and exhibit no defined B−H doublets. The spectrum from the ion formed from *p*-$C_2B_{10}H_{12}$ is different but slowly rearranges to give the first spectrum. Stanko et al.[43] observed that the dianion spectrum from *p*-$C_2B_{10}H_{12}$ showed practically no changes after 1 month and consisted of three lines with a 4/5/1 intensity, while the spectra of the dianions from *o*- and *m*-$C_2B_{10}H_{12}$ changed during the first hours but were then stable for 30 days. The spectra resembled each other except for the intensity of several lines in the 30−33 ppm region,[43] but no definite structural conclusions could be drawn because of the broad spectral lines. Whether or not the dianions **I** and **II** have the same structure thus needs to be more closely examined experimentally. We find such a possibility quite likely and believe that the dianion structure observed should be close to our *nido*-structure **6**.

Other experimental studies have shown that the dianion(s?) **I** and **II** derived from *o*- and *m*-$C_2B_{10}H_{12}$, respectively, both give *o*-$C_2B_{10}H_{12}$ on oxidation. The fact that they do give the same product on oxidation is easy to understand if the dianions are one and the same. At this point, we do not have any arguments for why **6** would choose to oxidize back to **1** instead of **4** (see the relative energies in Figure 1). The anion **III** derived from *p*-$C_2B_{10}H_{12}$ gives *m*-$C_2B_{10}H_{12}$ upon oxidation.[5−7] We would need to examine rearrangement paths and transition states in order to shed further light upon these questions. This is a worthwhile undertaking for the future and ought to be accompanied by newer and more accurate low-temperature NMR experiments.

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[43] Stanko, V. I.; Babushkina, T. A.; Brattsev, V. A.; Klimova, T. P.; Alymov, A. M.; Vassilyev, A. M.; Knyazev, S. P. *J. Organomet. Chem.* **1974**, *78*, 313−322.