Theoretical Investigation of Four-Center Two-Electron Bonding Involving Boron Derivatives

Michael L. McKee,* Michael Bühl, Oleg P. Charkin, and Paul von Ragué Schleyer*

Department of Chemistry, Auburn University, Auburn, Alabama 36849, Institut für Organische Chemie der Universität Erlangen-Nürnberg, Henkestrasse 42, D-91054 Erlangen, Germany, and Institute of New Chemical Problems, Chernogolovka, Moscow Region 142432, Russia

Received March 23, 1993®

Factors contributing to the stability of 4c2e bonds have been investigated by means of ab initio calculations on boranes and carboranes. Electron density plots and "deformation energies", the energy required to deform the deprotonated species into a geometry optimal for interacting with the added proton, have been used to help evaluate the propensity of 4c2e vs 3c2e bonding. Two molecules exhibiting 4c2e bonding, CB_5H_7 (**1**) and $B_6H_7^-$ (**2**), have been optimized at MP2/6-31G* with the "extra" hydrogen capping a triangular face or bridging two boron atoms. Face-capping is predicted to be more stable than BHB bridging by 16.8 kcal/mol (CB_5H_7) and by 12.1 kcal/mol ($B_6H_7^-$). Computed chemical shifts (IGLO) are in reasonable agreement with experiment. The "antipodal effect" is manifested by the boron atom opposite carbon in CB_5H_7; the upfield shift relative to $B_6H_7^-$ is calculated to be 20 ppm.

Introduction

Polyhedral boranes, the multicenter bond prototypes, necessitated the development of the three-center–two-electron (3c2e) bond concept.[1] This concept encompasses a large number of boron hydrides and heteroboranes, as well as carbocations[2a] and many other electron-deficient systems.[2b,c] In contrast, examples of four-center–two-electron (4c2e) bonds are much less common.[3] Tetrahedral X_4^{2+} species (where the neutral X components have one unbound electron) are the simplest possible 4c2e systems. Thus, in e.g. H_4^{2+},[4] Li_4^{2+},[5] Na_4^{2+},[5] and $(CH_3)_4^{2+}$,[5] only one bonding MO, formed by the overlap of the four inward-oriented orbitals, is occupied. However, such unsupported T_d complexes, at best, are only high-lying metastable local minima (Li_4^{2+}, Na_4^{2+}); H_4^{2+} and $(CH_3)_4^{2+}$ are not bound.

Recently, a "purely organic" 4c2e T_d representative has been realized,[6] the 1,3-dehydro-5,7-adamantanediyl dication (**1**, Figure 1). In contrast to the X_4^{2+} tetramers, 4c2e bonding in **1** is facilitated by the rigid external framework. The four tetrahedrally-oriented atomic orbitals overlap in the center of the cage. The excellent agreement between the calculated and experimental chemical shifts for the tetrahedral geometry establishes the structure of **1** securely.[6]

The *closo*-carborane CB_5H_7 and the isoelectronic $B_6H_7^-$ anion are inorganic examples of 4c2e bonds involving a triply bridging hydrogen. The intent of this contribution is to explore the factors which lead to stable 4c2e bonds.

Methods

All calculations employed the GAUSSIAN 88 or GAUSSIAN 90 program systems.[7,8] Geometries were fully optimized at the HF/6-31G* and MP2/6-31G* levels, and analytical frequencies were calculated at HF/6-31G*; 0.89 was used as the zero-point correction factor. In addition, for smaller systems, MP2/6-31G* frequencies were computed to check the effect of electron correlation on the nature of the stationary points.

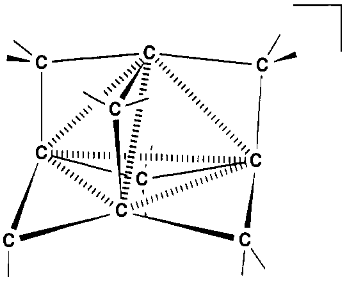


Figure 1. Geometry of 1,3-dehydro-5,7-adamantanediyl(2+). Dashed lines indicate the four carbons bound by a 4c2e bond.

Absolute energies (hartrees), relative energies (kcal/mol), and zero-point energies (kcal/mol) are given in Table I; geometries are plotted in Figure 2. Unless otherwise indicated, the energy data discussed below are at the MP2/6-31G*//MP2/6-31G* + 6-31G*/ZPE level.

The IGLO (individual gauge for localized orbitals) method was used[9] to calculate ^{11}B chemical shifts. Provided geometries of sufficient accuracy are used, the calculated ^{11}B chemical shifts are in remarkable accord with the experimental shifts.[10-12] The IGLO basis set denoted DZ is a 7s,3p basis on boron contracted to (4111,21) while II′ refers to a 9s5p1d basis on boron contracted to (51111,2111,1).[11] Chemical shifts for ^{11}B

---

* To whom correspondence should be addressed at Auburn University (M.L.M.) and Universität Erlangen-Nürnberg (P.v.R.S.).

® Abstract published in *Advance ACS Abstracts,* August 15, 1993.

(1) Lipscomb, W. N. *Boron Hydrides*; Benjamin: New York, 1963.

(2) (a) Buzek, P.; Schleyer, P. v. R.; Sieber, S. *Chem. Unserer Zeit* **1992,** 116. (b) See: *Electron Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; Wiley: New York, 1991. (c) Williams, R. E. *Chem. Rev.* **1992,** *92,* 177.

(3) Harcourt, R. D. *J. Phys. Chem.* **1991,** *95,* 6916.

(4) Glukhovtsev, M. N.; Schleyer, P. v. R.; Hommes, N. J. R. v. E.; Carneiro, J. W. de M.; Koch, W. *J. Comput. Chem.* **1993,** *14,* 285.

(5) Glukhovtsev, M. N.; Schleyer, P. v. R.; Stein, A. *J. Phys. Chem.* **1993,** *97,* 5541.

(6) Bremer, M.; Schleyer, P. v. R.; Schötz, K.; Kausch, M.; Schindler, *Angew. Chem., Int. Ed. Engl.* **1987,** *26,* 761.

(7) (a) GAUSSIAN 88. Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1988. (b) GAUSSIAN 90. Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzales, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1990.

(8) For a description of basis sets see: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(9) (a) Kutzelnigg, W. *Isr. J. Chem.* **1980,** *19,* 193, (b) Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982,** *76,* 1919. Review: (c) Kutzelnigg, W.; Fleischer, U.; Schlindler, M. In *NMR, Basic Principles and Progress*; Springer Verlag: Berlin, 1990; p 165.

(10) (a) Schleyer, P. v. R.; Bühl, M.; Fleischer, U.; Koch, W. *Inorg. Chem.* **1990,** *29,* 153. (b) Schleyer, P. v. R.; Bühl, M. *Angew. Chem., Int. Ed. Engl.* **1990,** *29,* 304. (c) Bühl, M.; Schleyer, P. v. R. *Angew. Chem., Int. Ed Engl.* **1990,** *29,* 886. (d) Bausch, J. W.; Prakash, G. K. S.; Bühl, M.; Schleyer, P. v. R. *Inorg. Chem.* **1992,** *31,* 3060.

(11) Bühl, M.; Schleyer, P. v. R. In *Electron Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K.; Williams, R. E., Eds.; Wiley: New York, 1991, pp 113–142.

(12) Bühl, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992,** *114,* 477.

0020-1669/93/1332-4549$04.00/0

Table I. Absolute Energies (hartrees), Deformation Energies (kcal/mol), and Relative Energies (kcal/mol)

					MP2 (FU)/6-31G*//MP2/6-31G*			
no.	compd	sym	HF/6-31G*	ZPE[a]	energy	DE[b]	E_{rel}[c]	E_{rel}[d]
1a	CB_5H_7	C_s	−165.306 91	61.2 (0)	−165.923 11	9.2	0.0	
1b	CB_5H_7	C_s	−165.271 97	60.6 (1)	−165.895 49	10.3	16.8	
1c	$CB_5H_6^-$	C_{2v}	−164.791 33	54.1 (0)	−165.413 92		313.1	
2a	$B_6H_7^-$	C_{3v}	−152.150 07	57.8 (0)	−152.746 08	8.6	0.0	
2b	$B_6H_7^-$	C_{2v}	−152.130 51	57.2 (1)	−152.725 93	6.6	12.1	
2c	$B_6H_6^{2-}$	O_h	−151.427 64	49.6 (0)	−152.024 72		445.3	
2d	B_6H_8	D_{3h}	−152.660 77	65.6 (0)	−153.251 26	10.6	−310.0	
3a	$B_3H_4^-$	C_{3v}	−76.243 15	25.7 (0,0)	−76.515 84	1.2	0.0	0.0
3b	$B_3H_4^-$	C_{2v}	−76.284 08	29.3 (0,0)	−76.566 45	4.4	−28.5	−26.6
3c	$B_3H_3^{2-}$	D_{3h}	−75.442 76	21.4 (0,0)	−75.725 33		492.1	500.6
3d	B_3H_5	D_{3h}	−76.750 22	33.4 (2)	−77.025 66		−313.1	−319.5
3e	B_3H_5	C_{2v}	−76.865 11	36.4 (0)	−77.148 40		−387.4	−389.6
4a	$B_4H_5^+$	C_{3v}	−101.209 35	36.1 (2,0)	−101.541 02	9.4	0.0	0.0
4b	$B_4H_5^+$	C_{2v}	−101.200 28	38.2 (1,1)	−101.544 51	19.4	−0.3	8.7
4c	B_4H_4	T_d	−100.925 70	32.6 (0,0)	−101.292 18		153.0	168.7

[a] The first number in parentheses gives the number of imaginary frequencies at the HF/6-31G* level, while the second number (if present) gives the same information at the MP2/6-31G* level. The zero-point energy in kcal/mol is calculated at the HF/6-31G* level. [b] Deformation energy (kcal/mol) is defined as the energy required to deform the relaxed deprotonated geometry into the geometry of the protonated form. [c] Relative energies (kcal/mol) calculated at the MP2(FU)/6-31G*//MP2(FU)/6-31G* level. Zero-point corrections (with a 0.89 factor) are included at the HF/6-31G* level. [d] Relative energies (kcal/mol) calculated at the MP4/6-31G(d,2p)//MP2(FU)/6-31G*+ZPC level. If a set of diffuse functions are added (i.e. MP4/6-31+G(d,2p)), the relative energies of **3a**, **3b**, **3c**, **3d**, and **3e** are 0.0, −28.2, 460.9, −311.1, and −381.1 kcal/mol, respectively. Zero-point corrections (with a 0.89 factor) are included at the HF/6-31G* level.

are computed with respect to B_2H_6 and adjusted to the experimental scale using $\delta(B_2H_6) = 16.6$ ppm with respect to the experimental standard of $BF_3{\cdot}OEt_2$.[13]

Results and Discussion

CB_5H_7. As discussed previously,[12,14,15] the location of the face-bridging hydrogen in CB_5H_7 (**1a**) is very sensitive to the ab initio level used for optimization. The small HF/3-21G basis set gives a very unsymmetrical arrangement with respect to the triangular face, two normal BH_bB distances of 1.353 Å and one very long BH_b distance of 1.847 Å. As the level of theory is improved, the third distance is shortened considerably (to 1.591 Å at HF/6-31G* and 1.475 Å at MP2/6-31G*). The nature of this bridge changes from an essentially three-center bond at the HF/3-21G level to a nearly pure four-center bond at the MP2/6-31G* level. The experimental gas-phase electron diffraction study[16] of CB_5H_7 revealed a face-bridging structure with BH_b distances of 1.329(16), 1.329(16), and 1.397(19) Å, but there is considerable uncertainly in these locations.

Which of these geometries is best? One test is provided by single-point MP4SDTQ/6-31G* calculations for all the candidates. While the experimental geometry performed poorly[12] (the energy with the experimental geometry is 7.8 kcal/mol higher than that of MP2 optimized geometry), both the Hartree–Fock and the MP2 optimized geometries gave energies within ca. 3 kcal/mol (Table II). Hence, the energy differences between the near double-bridging and triple-bridging hydrogen arrangements is small.

IGLO chemical shift calculations provide excellent monitors of the quality of calculated or experimental geometries. In recent extensive comparisons of experimental with calculated ^{11}B chemical shifts,[11,12] the standard deviation was less than 3 ppm, provided MP2/6-31G* optimized geometries were used. At both the DZ(IGLO)//MP2/6-31G* and II′(IGLO)//MP2/6-31G* levels, the average deviation of the calculated ^{11}B chemical shifts of CB_5H_7 was only ca. 1.5 ppm from the experimental values.[12] The HF/3-21G, HF/6-61G*, and experimental geometries did not perform as well. It can be concluded that the MP2/6-31G* geometries are likely to be the most accurate.

The earlier calculations of the transition structure and the barrier for hydrogen scrambling in CB_5H_7[14,15] have now been refined. The transition structure (**1b**, C_s symmetry) possesses a nearly symmetric three-center BHB bond. The MP2/6-31G*//3-21G + ZPE(3-21G) barrier, 14.8 kcal/mol, already agreed well with the experimental value (14 kcal/mol).[17] Our refinement at MP2/6-31G*//MP2/6-31G* + ZPE(6-31G*), i.e. essentially using the MP2 rather than the 3-21G geometries, increases the theoretical value slightly (to 16.8 kcal/mol).

$B_nH_{n+1}^-$ Species. The structures of numerous protonated closo boron hydride dianions have been studied recently: $B_6H_7^-$,[18] $B_7H_8^-$,[19] $B_8H_9^-$,[20] $B_9H_{10}^-$,[21] and $B_{10}H_{11}^-$.[22] In general, the "extra" hydrogen can move over the surface of the boron cage with barriers of 15 kcal/mol or less. The face-centered structures are generally relatively low in energy but are not always best. For example, the ground state of $B_8H_9^-$ favors a double bridging hydrogen; the triply bridged isomer is about 10 kcal/mol higher in energy. In $B_9H_{10}^-$, the triply bridged form (C_{3v} symmetry) is about 14 kcal/mol less favorable than a structure with a BH_2 group. In contrast, $B_{10}H_{11}^-$ does favor a face-bridged ground state, about 2 kcal/mol lower than an edge-bridged alternative. We endeavor to understand such differences in behavior.

$B_6H_7^-$. In the X-ray structure of $B_6H_7^-$ (**2a**), the critical hydrogen caps a triangular BBB-face in C_{3v} symmetry.[18g] Unfortunately, its position could not be located securely exper-

---

(13) Onak, T. P.; Landesman, H. L.; Williams, R. E.; Shapiro, I. *J. Phys. Chem.* **1959**, *63*, 1533.

(14) McKee, M. L. *J. Am. Chem. Soc.* **1988**, *110*, 5317.

(15) Onak, T.; Tseng, J.; Tran, D.; Correa, M.; Herrera, S.; Arias, J. *Inorg. Chem.* **1992**, *31*, 2161.

(16) McNeill, E. A.; Scholer, F. R. *Inorg. Chem.* **1975**, *14*, 1081.

(17) Groszek, E.; Leach, J. B.; Wong, G. T. F.; Ungermann, C.; Onak, T. *Inorg. Chem.* **1971**, *10*, 2770.

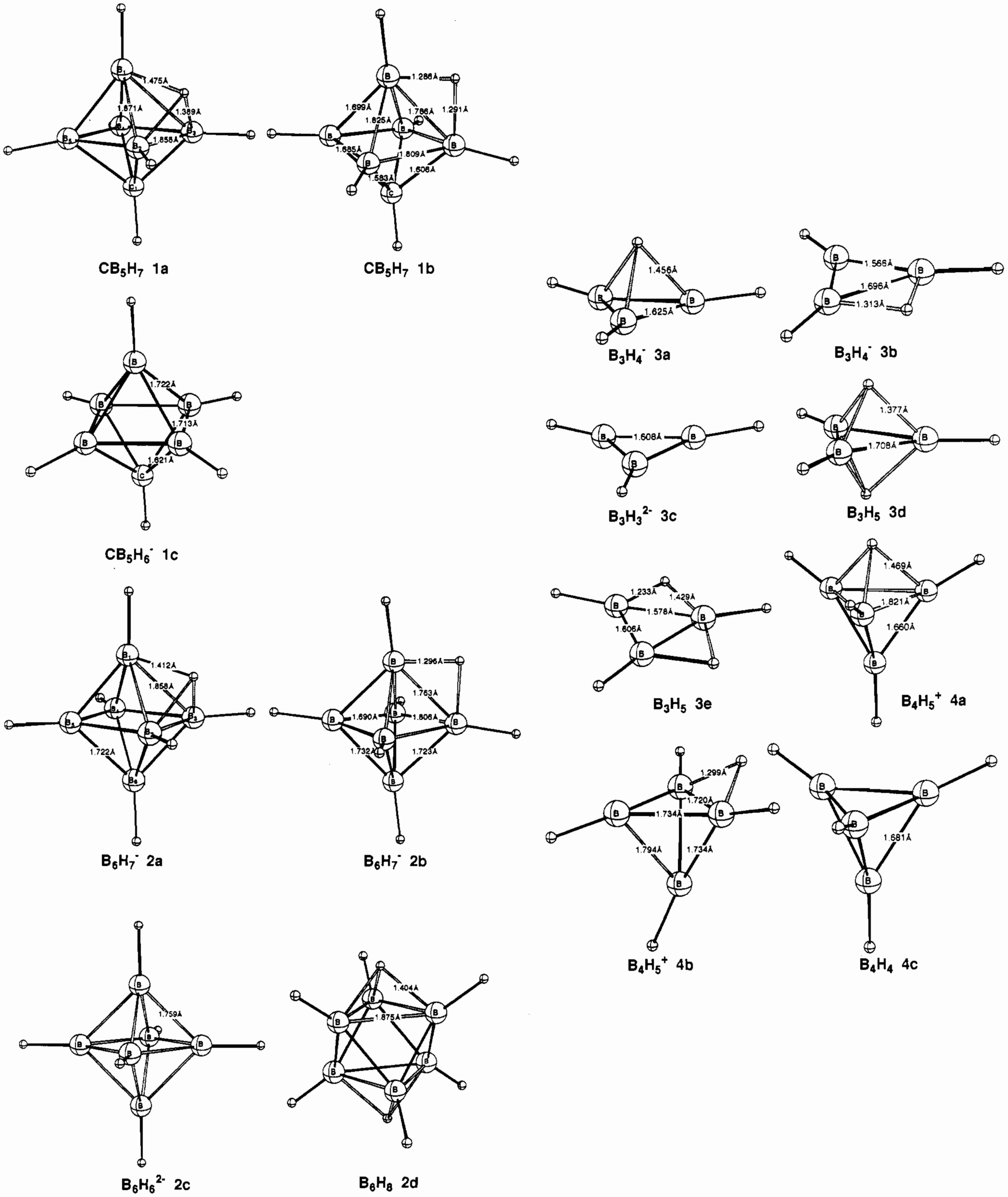
(18) (a) Mebel, A. M.; Charkin, O. P.; Kuznetsov, I. Yu.; Solntsev, K. A.; Kuznetsov, N. T. *Russ. J. Inorg. Chem.* **1988**, *33*, 958. (b) Mebel, A. M.; Charkin, O. P.; Solntsev, K. A.; Kuznetsov, N. T. *Russ. J. Inorg. Chem.* **1988**, *33*, 1292. (c) Mebel, A. M.; Charkin, O. P.; Solntsev, K. A.; Kuznetsov, N. T. *Russ. J. Inorg. Chem.* **1989**, *34*, 808. (d) Mebel, A. M.; Charkin, O. P. In *Chemistry of Inorganic Hydrides*; Nauka Publ.: Moscow, 1990; p 43 (in Russian). (e) Mebel, A. M.; Charkin, O. P. *J. Struct. Chem.* **1989**, *33*, 173. (f) Privalov, V. I.; Tarasov, V. P.; Meladze, M. A.; Vinitskii, D. M.; Solntsev, K. A.; Buslaev, Y. A.; Kuznetsov, N. T. *Russ. J. Inorg. Chem.* **1986**, *31*, 5. (g) Kuznetsov, N. T.; Solntsev, K. A. In *Chemistry of Inorganic Hydrides*; Nauka Publ.: Moscow, 1990; p 5 (in Russian).

(19) Mebel, A. M.; Charkin, O. P.; Schleyer, P. v. R. *Inorg. Chem.* **1993**, *32*, 469.

(20) Bühl, M.; Mebel, A. M.; Charkin, O. P.; Schleyer, P. v. R. *Inorg. Chem.* **1992**, *31*, 3769.

(21) Mebel, A. M.; Charkin, O. P.; Bühl, M.; Schleyer, P. v. R. *Inorg. Chem.*, manuscript in preparation.

(22) Mebel, A. M.; Charkin, O. P.; Bühl, M.; Schleyer, P. v. R. *Inorg. Chem.* **1993**, *32*, 463.


CB_5H_7 1a

CB_5H_7 1b

$B_3H_4^-$ 3a

$B_3H_4^-$ 3b

$CB_5H_6^-$ 1c

$B_3H_3^{2-}$ 3c

B_3H_5 3d

B_3H_5 3e

$B_4H_5^+$ 4a

$B_6H_7^-$ 2a

$B_6H_7^-$ 2b

$B_4H_5^+$ 4b

B_4H_4 4c

$B_6H_6^{2-}$ 2c

B_6H_8 2d

Figure 2. Geometries of species **1**–**4** with relevant distances in Å indicated.

imentally. The $(Ph_4P)B_6H_7$ crystal was disordered, and only an average B–B distance (1.733 Å) could be determined.[18g] However, the dimensions of the capped BBB face were larger than that of the opposite face.

The MP2/6-31G* geometry provides confirmation; the B–B distances in the capped face are extended by 0.136 Å (**2a**, Figure 2). $B_6H_7^-$ is fluxional at higher temperatures, as the two NMR signals coalesce into one single line; a barrier of 10–11.5 kcal/mol was estimated roughly.[18f] The computed barriers agree well and are insensitive to the level of theory employed (10.9 kcal/mol, HF/4-31G,[18e] 12.1 kcal/mol, MP2/6-31G*//MP2/6-31G* + ZPE, Table I). In the transition structure (**2b**, C_{2v}), the migrating hydrogen bridges a BB-edge (Figure 2 (**2b**), BH_bB, 1.296 Å). Both the 4c2e (**2a**) and the 3c2e (**2b**) bonds in $B_6H_7^-$ are symmetrical.

The IGLO $\delta(^{11}B)$ values for **2a** (Table III) show the usual dependence on the geometry employed.[10–12] At the highest level, II′//MP2/6-31G*, the deviations (up to 3–4 ppm) from the experimental chemical shifts are small but still are somewhat larger that those for other borane anions.[18–22]

Table II. Single-Point Calculations at the MP4SDTQ(FC)/6-31G* Level for Various Structures of 1a

geometry	absolute energy (hartrees)	rel energy (kcal/mol)
exptl[a]	−165.944 21	7.8
HF/3-21G	−165.951 57	3.2
HF/6-31G*	−165.956 11	0.4
MP2(FU)/6-31G*	−165.956 68	0.0

[a] Reference 16.

A comparison of the ^{11}B chemical shifts of the isoelectronic **1a** and **2a** is revealing. The boron atoms in **1a** directly attached to the carbon have δ values very similar to those of their "counterparts" in **2a** (−19.0 and −9.8 vs −17.8 and −9.9 ppm, respectively; see ref 12 and Table III). In contrast, B_1 in **1a** (2.7 ppm) is shifted ca. 20 ppm upfield with respect to the analogous boron (B_1) in **2a** (−17.8 ppm). Therefore, this system affords another example of the "antipodal" effect of heteroatoms incorporated in borane cages.[23] However, the magnitude of this effect is considerably smaller than that found in the ten-vertex cages.[24]

Four-Center–Two-Electron Bonding. General Considerations. Why is the preference for a four-center over a three-center bridge in **1** and **2** so strong? The *nido*- and *arachno*-boranes and carboranes typically exhibit three-center B–H–B bonds at the "open edges" of the cage. Although triply bridging hydrogens might occur in some cases (e.g. in B_5H_{11}[10a] and B_8H_{12}[12]), such arrangements correspond to transition structures; the ground states prefer "normal" B–H–B bonds. In B_5H_{11}, the C_s symmetry (4c2e) structure is only about 1 kcal/mol higher in energy than the equivalent 3c2e bonding arrangements (C_1 point group). Likewise, the C_{2v} symmetry B_8H_{12} structure with two 4c2e bonds is about 3 kcal/mol less stable than the C_s form with two 3c2e bonds. Thus, the energy differences between 4c2e bonding and 3c2e bonding alternatives are often small.

What factors favor 4c2e bonding? A 4c2e bond should result when an unstrained geometric arrangement of four atoms provides four atomic orbitals which overlap well (Figure 3). The in-phase interaction produces one strongly bonding molecule 4c orbital which binds the two electrons. However, in the situations we are discussing, an H^+ s-orbital must overlap with three boron orbitals already present in the cage structures. However, the deformation or "strain" energy required to bring these four atomic orbital into good overlap may be greater than the additional stabilization the 4c2e bonding provides. In such cases, the system may prefer a 3c2e bond instead. Likewise, if the strain to bring these three orbitals together is greater than the gain in stabilization, a 2c2e bond may be the best arrangement.

When can a 4c2e bond formed between three borons and one hydrogen be expected to be favorable? One condition is fulfilled if the related deprotonated species has a BBB 3c2e bond, formed from the overlap of three hybridized boron orbitals directed toward the center of the triangle. In localization nomenclature,[1] this is called a BBB closed 3c2e bond (Figure 4a; as opposed to the BBB open 3c2e bond, Figure 4b). The overlap of the three orbitals should result in an increased electron density in or near the center of the triangle. The fourth orbital, an empty 1s orbital on hydrogen, should be able to interact favorably with the three orbitals on boron with very little reorganization of the geometry.

We used two simple probes to help determine if 4c2e bonding might be favorable or not. First, we analyzed the total electron density plots (HF/6-31G*) in the BBB faces of the *deprotonated* species. Proton attachment to form a 4c2e bond should be favorable when the BBB triangle provides a negative charge concentration. Our probe has an obvious weakness. The electron density maximum due to the overlap of the three boron orbitals might be elsewhere along the 3-fold axis rather than in the BBB plane. As a matter of fact, the extra protons we are considering lie above, rather than in, the BBB faces. Nonetheless, such in-plane electron density plots are easy to calculate and should provide qualitative information.

Our second probe is the "deformation (strain) energy". This is the energy required to deform a deprotonated species to the optimum geometry adopted by the protonated species. This deformation energy also is easy to assess. The single-point energy, obtained by a calculation employing the geometry of the fixed fragment remaining after removing the proton, is compared with the energy of the fully relaxed, unprotonated species. The smaller deformation energy is expected to correspond to the more favorable binding (e.g., for 4c2e vs 3c2e situations).

Applications

$B_3H_4^-$ (3a). Face-protonated $B_3H_4^-$ (**3a**),[25] isoelectronic with $C_3H_4^{2+}$ (the face protonated cyclopropenium ion),[26] is the simplest model for a 4c2e hydrogen bridge involving three borons. Indeed, triply-bridged (C_{3v}) **3a** is a minimum both at HF/6-31G* and at MP2/6-31G*. However, like the carbon analogue, **3a** is not the most stable form; the edge-protonated C_{2v} minimum **3b** is 28.5 kcal/mol lower in energy (MP2/6-31G*//MP2/6-31G* + ZPE). (The corresponding energy difference between the $C_3H_4^{2+}$ isomers is nearly the same, 25.8 kcal/mol at the last level of theory and 24.4 kcal/mol at MP4/6-31G*//MP2/6-31G*.)[26]

The bonding in the $B_3H_3^{2-}$ ring involves three B–B σ bonds and one delocalized π bond. Despite the possibility of central Walsh-type overlap and the fact that the face-centered protonation corresponds to an minimum, the electron density lies around the perimeter of the $B_3H_3^{2-}$ ring, not in the center (Figure 5a). Indeed, the most stable site of protonation is in the plane of the ring where a B–B 2c2e σ bond is converted into a BH_bB 3c2e bond. If a localized π bond in $B_3H_3^{2-}$ were protonated instead, the proton would have been located off-center above the ring.

In this case, our second probe does not give the correct qualitative result. The deformation energy for face-binding is somewhat smaller than for edge-binding (1.2 vs 4.4 kcal/mol), yet 4c2e bonding in **3a** is strongly disfavored. However, **3b** benefits from additional stabilization due to relief of σ-strain in the three-membered ring which may not be accounted for by our simple probes.

B_3H_5. If both faces of $B_3H_3^{2-}$ (**3c**) are capped, a neutral B_3H_5 species results (**3d**) having, in a formal sense, a 5c2e bond. The BH_b distances in **3d** are shorter compared to **3a**, and the B–B distances are longer. However, the trigonal bipyramid **3d** is very much higher in energy (Table I, 74.3 kcal/mol) than the dibridged species, **3e**, which is the global minimum at the MP2/6-31G* level.

$B_4H_5^+$ (4a). Another 4c2e bond occurs when the tetrahedral B_4H_4 is face protonated to give $B_4H_5^+$ (**4a**, C_{3v} symmetry). This structure, which is a minimum at MP2/6-31G* (but has two imaginary frequencies at 6-31G*), is comparable in stability to the edge-protonated form **4b**. The situation concerning **4a** and **4b** is complicated. While **4b** is slightly more stable than **4a** at MP2/6-31G*, one imaginary frequency is calculated for **4b** at

---

(23) (a) Plešek, J.; Heřmánek, S. *J. Chem. Soc., Chem. Commun.* **1975**, 127. (b) Heřmánek, S.; Gregor, V.; Štibr, B.; Plešek, J.; Janousek, Z.; Antonovich, V. A. *Collect. Czech. Chem. Commun.* **1976**, *41*, 1492. (c) Heřmánek, S.; Jelinek, T.; Plešek, J.; Štibr, B.; Fusek, J.; Mares, F. In *Boron Chemistry, Proceeding of the 6th IMEBORON*; Heřmánek, S., Ed.; World Scientific: Singapore, 1986; pp 26–73. (d) Todd, L. J.; Siedle, A. R.; Bodner, G. M.; Kahl, S. B.; Hicke, J. P. *J. Magn. Reson.* **1976**, *23*, 301. (e) Leyden, R. N.; Sullivan, B. P.; Baker, R. T.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1978**, *100*, 3758. (f) Teixidor, F.; Vinas, C.; Rudolph, R. W. *Inorg. Chem.* **1986**, *25*, 3339. (g) Heřmánek, S.; Hnyk, D.; Havlas, Z. *J. Chem. Soc., Chem. Commun.* **1989**, 1895. (h) Fehlner, T. P.; Czech, P. T.; Fenske, R. F. *Inorg. Chem.* **1990**, *29*, 3103.

(24) (a) Plešek, J.; Štibr, B.; Fontaine, X. L. R.; Kennedy, J. D.; Heřmánek, S.; Jelinek, T. *Collect. Czech. Chem. Commun.* **1991**, *56*, 1618. (b) Bühl, M.; Schleyer, P. v. R.; Havlas, Z.; Hnyk, D.; Heřmánek, S. *Inorg. Chem.* **1991**, *30*, 3107.

(25) Bigot, B.; Lequan, R. M.; Devaquet, A. *Nouv. J. Chim.* **1978**, *2*, 449.

(26) Lammertsma, K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 7935.

Table III. Geometric Parameters (Å) and IGLO ^{11}B Chemical Shifts (ppm) for $B_6H_7^-$ (**2a**)

geometry params					IGLO chem shifts (ppm)		
level of theory	B_1B_2	B_1B_4	B_4B_5	B_1H_b	level of theory	$B_1/B_2/B_3$	$B_4/B_5/B_6$
HF/6-31G*	1.888	1.713	1.731	1.419	DZ//6-31G*	−17.8	−10.7
MP2/6-31G*	1.858	1.701	1.722	1.412	DZ//MP2/6-31G*	−18.3	−10.8
					II′//MP2/6-31G*	−21.8	−13.2
					exptl[a]	−18.6	−10.5
					exptl[b]	−17.8	−9.9

[a] $(PPh_4)B_6H_7$ in acetone.[18g] [b] $(Bu_4N)B_6H_7$ in acetone.[18f]

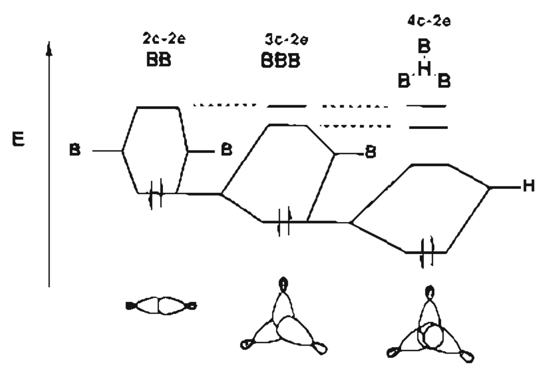
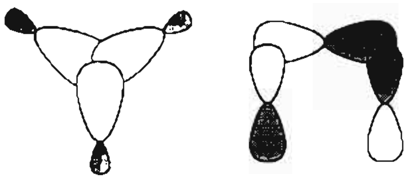


Figure 3. Qualitative scheme indicating the progression from 2c2e to 3c2e to 4c2e as an addition center is allowed to interact. The stability of the 4c2e bond results because only the inphase bonding orbital is occupied.



BBB closed bond BBB open bond

Figure 4. (a) Left: Closed center BBB bond. (b) Right: Open center BBB bond.

the same level! However, at higher levels of theory [MP4/6-31G(d,2p)] there is a clear indication that **4a** is more stable than **4b** (see Table I).

On the other hand, the deformation energy for face-protonation is also considerably *smaller* than for edge-protonation (9.4 vs 19.4 kcal/mol). This would suggest that the "intrinsic" 4c2e bond has about the same strength as the "intrinsic" 3c2e bond. A cut through one of the B_4H_4 faces (Figure 5b) does *not* show an electron density maximum in the center of the ring.

CB_5H_7. Returning to CB_5H_7, the electron density in the BBB face of $CB_5H_6^-$ (**1c**) does show a maximum near the center of the ring (Figure 5c). If the geometry of CB_5H_7 (**1a**) is frozen and the triple-bridging proton removed, a very similar plot is obtained (Figure 5d). In contrast, if the electron density in the CBB face of **1c** is plotted, no central maximum is found (Figure 5e). The deformation energy for face-protonation is slightly less than for edge-protonation (9.2 vs 10.3 kcal/mol). The combination of the accumulation of negative charge in the center of the ring with the relatively small deformation energy leads to the favorable 4c2e bonding in CB_5H_7.

$B_6H_7^-$ (2c). The electron density map of one of the eight equivalent BBB faces of $B_6H_6^{2-}$ (**2c**) reveals no maximum in electron density (Figure 5f). However, if the $B_6H_7^-$ geometry is frozen with the capping proton removed, an electron density maximum is found in the center of the ring (Figure 5g). Thus, expanding the ring distances in the BBB face increases the electron density in the center. The deformation energy for face protonation is slightly greater than for edge protonation (Table I, 8.6 kcal/mol vs 6.6 kcal/mol) in $B_6H_6^{2-}$.

B_6H_8. An electron density plot of the opposite $B_6H_7^-$ face also shows an electron density maximum (Figure 5h). This suggests that the neutral boron hydride, B_6H_8, might tolerate *two* face-capping hydrogens. The geometry of B_6H_8 was calculated in D_{3d} symmetry, and the structure proved to be a minimum at the HF/6-31G* level. The deformation energy[27] of B_6H_8 (10.6 kcal/mol) is very similar to the deformation energies of CB_5H_7 and $B_6H_7^-$. At the MP2 level, the BH_b distances in B_6H_8 (1.404 Å) are shorter than the BH_b distances in CB_5H_7 (1.418 Å, averaged) and $B_6H_7^-$ (1.412 Å).

The reaction energies of eqs 1 and 2, compared at MP2/6-31G*//MP2/6-31G* + ZPE, point to the stability of the unknown

$$B_6H_{10}{}^{12} \rightarrow \underset{\textbf{2d}}{B_6H_8} + H_2 \qquad \Delta H_{rxn} = 23.1\ \text{kcal/mol} \qquad (1)$$

$$B_4H_{10} \rightarrow B_4H_8 + H_2 \qquad \Delta H_{rxn} = 22.1\ \text{kcal/mol}^{28} \qquad (2)$$

boron hydride B_6H_8 relative to B_4H_8. Another indicator is the protonation energy of $B_6H_7^- + H^+ \rightarrow B_6H_8$ (−310.0 kcal/mol) relative to $CB_5H_6^- + H^+ \rightarrow CB_5H_7$ (−313.1 kcal/mol). Since the protonation energy of OH^- is 381.9 kcal/mol (MP2/6-31+G*//MP2/6-31+G*+ZPC),[20] it appears that B_6H_8 might be a reasonable synthetic target.

B_5H_{11}. As a final qualitative example of an unfavorable 4c2e bond, B_5H_{11} will be considered. The structure of B_5H_{11} is rather interesting in that one of the terminal hydrogens on the apical boron can either be described as a 4c2e bond if it is interacting with three borons in a C_s symmetry structure or as a 3c2e bond if it is interacting with two borons in a C_1 symmetry structure.[10a] The 4c2e bond is disfavored because the energy required to bring the two basal borons closer together is not sufficiently compensated for by the interaction of the unique hydrogen with the additional boron center. The electron density for $B_5H_{10}^-$, which is missing the unique proton while fixed in the B_5H_{11} optimized geometry (MP2/6-31G*), has been calculated for a slice through the BBB plane (Figure 5i). In contrast to $CB_5H_6^-$ (Figure 5d), there is no electron density maximum in the center of the triangle. Rather the density maximum lies between the two bonded borons. This is also the position that the unique hydrogen adopts in the lowest energy B_5H_{11} structure.

Conclusions

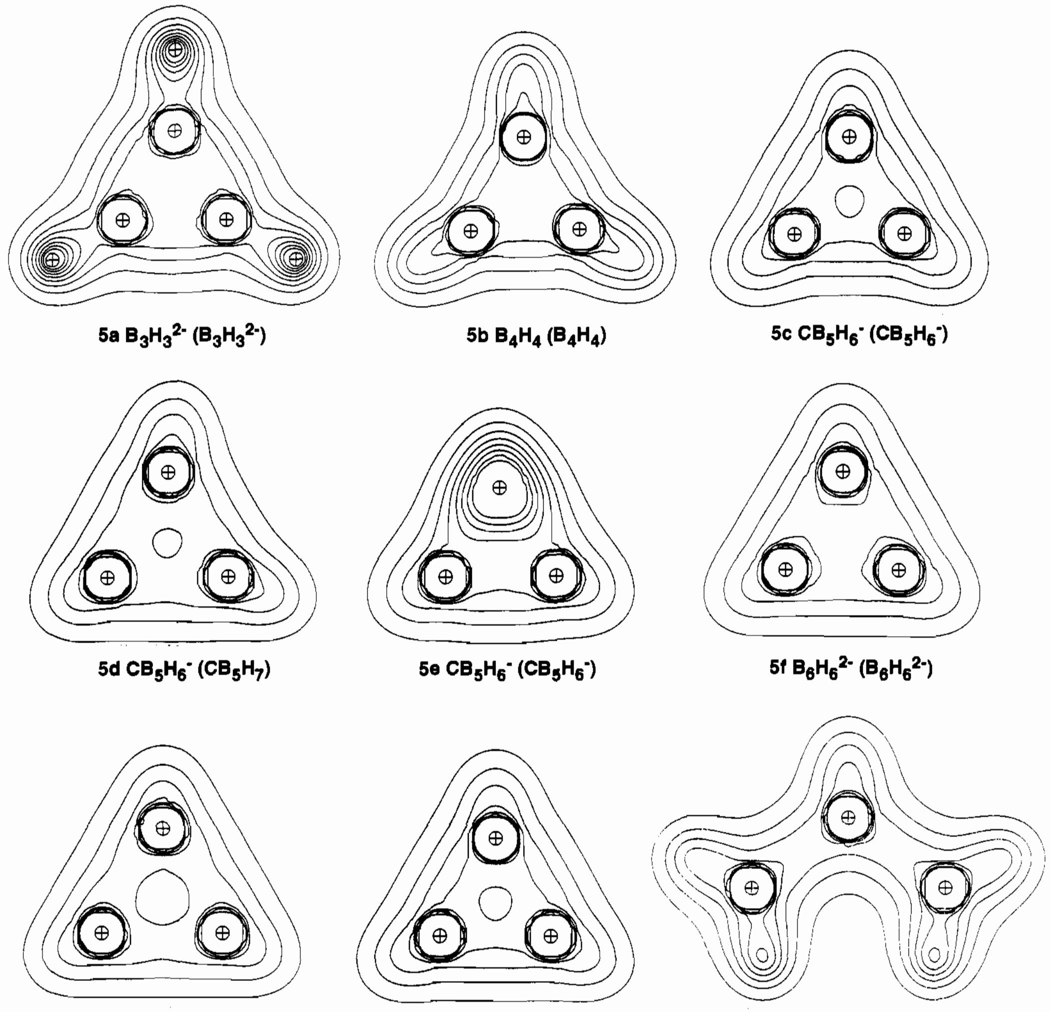
A stable 4c2e bond can exist when only the bonding molecular orbital is occupied, which arises from the unstrained overlap of four atomic orbitals. In the case of borane and carborane cages, a 4c2e capping proton is predicted when the "deformation" energy is small, i.e. the energy required to "rearrange" the deprotonated geometry into the optimal face-protonated geometry, and when a BBB face has a maximum of electron density in the center of the face due to the presence of a closed three-center BBB bond.

The most stable CB_5H_7 and $B_6H_7^-$ structures have capping 4c2e hydrogens. Both molecules are fluxional; the computed barriers, 16.8 and 12.1 kcal/mol, respectively, agree with experiment. A new boron hydride B_6H_8 is calculated to prefer a D_{3d} structure; its stability should be comparable to that of B_4H_8.

---

(27) The deformation energy for B_6H_8 is computed by freezing the B_6H_8 geometry, removing one proton, and comparing the MP2/6-31G* energy with that of $B_6H_7^-$.

(28) McKee, M. L. *J. Am. Chem. Soc.* **1990**, *112*, 6753.



5a $B_3H_3^{2-}$ ($B_3H_3^{2-}$) 5b B_4H_4 (B_4H_4) 5c $CB_5H_6^-$ ($CB_5H_6^-$)

5d $CB_5H_6^-$ (CB_5H_7) 5e $CB_5H_6^-$ ($CB_5H_6^-$) 5f $B_6H_6^{2-}$ ($B_6H_6^{2-}$)

5g $B_6H_6^{2-}$ ($B_6H_7^-$) 5h $B_6H_7^-$ ($B_6H_7^-$) 5i $B_5H_{10}^-$ (B_5H_{11})

Figure 5. Total electron density plots (HF/6-31G*) through a BBB face. The molecular species plotted is frozen in the geometry given in parentheses below the figure. Key: (a) BBB face in $B_3H_3^{2-}$; (b) BBB face in B_4H_4; (c) BBB face in $CB_5H_6^-$; (d) deprotonated BBB face in $CB_5H_6^-$ frozen in CB_5H_7 geometry; (e) CBB face in $CB_5H_6^-$; (f) BBB face in $B_6H_6^{2-}$; (g) deprotonated BBB face in $B_6H_6^{2-}$ frozen in $B_6H_7^-$ geometry; (h) BBB face opposite protonated face in $B_6H_7^-$; (i) BBB face in $B_5H_{10}^-$ frozen in B_5H_{11} geometry (in C_s symmetry).

The calculated IGLO chemical shifts for $B_6H_7^-$ are in reasonable agreement with experiment. The "antipodal" boron opposite carbon in CB_5H_7 has an upfield shift of 20 ppm with respect to $B_6H_7^-$.

Acknowledgment. M.L.M. thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support and the Deutscher Akademischer Austauschdienst (DAAD) for a Study Visit Award. Computer time was made available by the Alabama Supercomputer Network and the NSF-supported Pittsburgh Supercomputer Center. Calculations were also carried out on a Cray Y-MP4 of the Leibniz Rechenzentrum Munich and on a Convex C-220 of the Institut für Organische Chemie. This work was supported in Germany by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Professor W. Kutzelnigg and Dr. M. Schindler for the Convex version of the IGLO program and Dr. N. J. R. van Hommes for providing access to the graphical display program Molecule.