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Theoretical Prediction of the Structure and Nonrigidity of $B_7H_8^-$. Application of the ab Initio/IGLO/NMR Method

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Ab initio calculations on $B_7H_8^-$, the protonated form of $B_7H_7^{2-}$, at the MP2/6-31G*//MP2/6-31G* + ZPE(3-21G) level suggest that the "additional" proton (H*) is coordinated unsymmetrically to a face of the boron bipyramid, forming a three-center bridge bond with two equatorial boron atoms (structure **2**). The barrier to oscillation of the H* via an equatorial edge (**2** → **3** → **2′**) is only 2.6 kcal/mol. For H* rotation around the polyhedron 5-fold axis, exchange **2** → **5** → **2′**) and migration (**2** → **4** → **2′**) mechanisms are competitive with barriers of ~15 and ~17 kcal/mol, respectively. IGLO calculations predict the ^{11}B NMR chemical shifts for $B_7H_8^-$: four signals with intensity ratio 1:2:2:2 at low temperatures and only two signals (5:2) at elevated temperatures. The predicted NMR temperature dependence of the monoanion $B_7H_8^-$ also would distinguish it from the behavior of the stable dianion, $B_7H_7^{2-}$. The computed proton affinity (PA) of $B_7H_7^{2-}$ [414.8 kcal/mol, MP2(FC)/6-31+G*//MP2(FU)/6-31G* + ZPE(3-21G)] is less than that of $B_6H_6^{2-}$ but is larger than the PA's of $B_8H_8^{2-}$, $B_9H_9^{2-}$, and $B_{10}H_{10}^{2-}$. As the PA of $B_7H_7^{2-}$ exceeds that of OH^- [381.9 kcal/mol, MP2(FU)/6-31+G*//MP2(FU)/6-31+G* + ZPE(6-31G*)], the dianion might deprotonate water or other proton donors to form $B_7H_8^-$.

Introduction

Protonation of $B_nH_n^{2-}$ *closo*-borane dianions leads to a new class of $B_nH_{n+1}^-$ monoanions.[1] Some examples have been studied experimentally. Vibrational and NMR spectra have been reported for the $B_6H_7^-$,[1a,b] $B_9H_{10}^-$,[2] and $B_{10}H_{11}^-$ [1d] anions. X-ray structures of $B_6H_7^-$ [1c] and $B_{10}H_{11}^-$ [2] are available. $B_{12}H_{12}^{2-}$ is peculiar. Protonation does not give $B_{12}H_{13}^-$; instead, a $B_{24}H_{23}^{3-}$ "dimer" is formed with loss of molecular hydrogen. The $B_nH_{n+1}^-$ anions have temperature-dependent NMR spectra and interesting, flexible structures.[2] *Structural nonrigidity* is well-known in some *closo*-boranes and carboranes,[3-7] but fluxionality of $B_nH_{n+1}^-$ is due to the rapid hydrogen migration which has precedents in many common boron hydrides.[8]

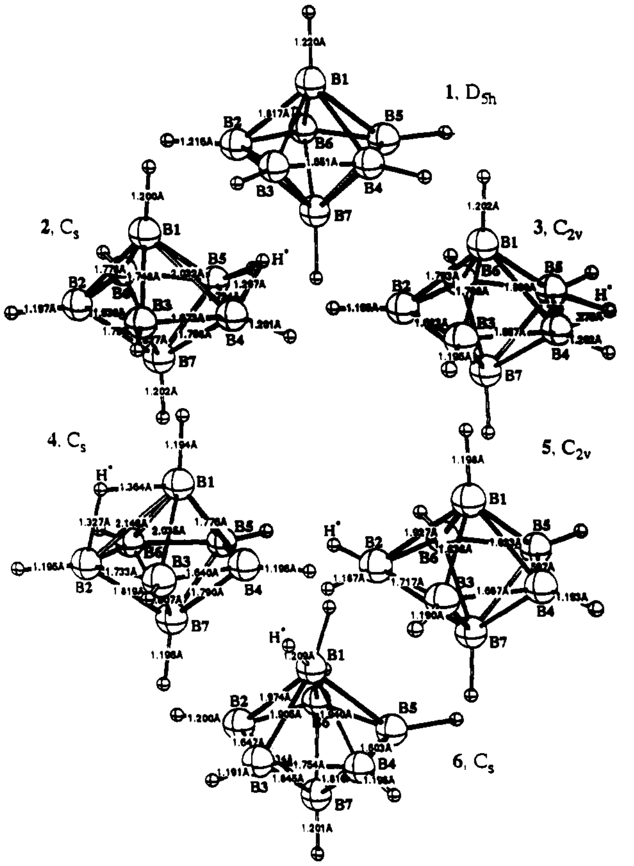

Figure 1. MP2/6-31G*-optimized geometries for $B_7H_7^{2-}$ (**1**) and $B_7H_8^-$ (**2**–**6**). For **4**–**6**, SCF/6-31G* methods were used.

The $B_nH_{n+1}^-$ anion series (n = 6–12) was first studied theoretically at the STO-3G//MNDO and LP-31G//MNDO

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Table I. Absolute (–au) and Relative (kcal/mol, in Brackets) Energies for Different Structures of $B_7H_7^{2-}$ and $B_7H_8^-$

	level of theory				
struct, symm (no.)	HF/3-21G	ZPE[a]	HF/6-31G*	MP2/6-31G*[b]	final[c]
			$B_7H_7^{2-}$		
D_{5h} (**1**)	175.725 12	59.4 (0)	176.722 73	177.380 01 (0.420 91)	
			$B_7H_8^-$		
t445, C_s (**2**)	176.403 64 [0]	67.2 (0)	177.417 96 [0]	178.072 99 [0] (0.114 89 [0])	[0] ([0])
b44, C_{2v} (**3**)	176.391 76 [7.5]	67.2 (1)	177.408 40 [6.0]	178.068 96 [2.5] (0.110 71 [2.6])	[2.5] ([2.6])
b45, C_s (**4**)	176.379 62 [15.1]	65.0 (1)	177.390 77 [17.1]	178.042 19 [19.3]	[17.3]
v4, C_{2v} (**5**)	176.366 94 [23.0]	65.2 (2)	177.378 39 [24.8]	178.046 34 [16.7]	[14.9]
v5, C_s (**6**)	176.347 89 [35.0]	63.6 (2)	177.350 58 [42.3]	178.006 79 [41.5]	[38.3]

[a] 3-21G zero-point energy; in parentheses are the number of imaginary frequencies. [b] MP2(frozen core)/6-31G*//6-31G* energy; in parentheses is the MP2(full)/6-31G*//MP2(full)/6-31G* energy. [c] MP2(FC)/6-31G*//6-31G*+ZPE(3-21G); in parentheses is the MP2(FU)/6-31G*//MP2(FU)/6-31G*+ZPE(3-21G) energy. ZPE's scaled by 0.89 as recommended in ref 16.

Table II. Optimized Geometric Parameters for $B_7H_7^{2-}$ and $B_7H_8^-$ with Bond Distanes in Å[a]

	$B_7H_7^{2-}$	$B_7H_8^-$				
	D_{5h} (**1**)	t445, C_s (**2**)	b44, C_{2v} (**3**)	b45, C_s (**4**)	v4, C_{2v} (**5**)	v5, C_s (**6**)
B1B2	[1.817] 1.839 (1.862)	[1.778] 1.787 (1.806)	[1.793] 1.811 (1.826)	2.146 (2.268)	1.927 (1.923)	1.974 (1.988)
B1B3		[1.748] 1.764 (1.787)	[1.788] 1.799 (1.824)	2.035 (2.108)	1.838 (1.868)	1.905 (1.927)
B1B4		[2.032] 2.135 (2.205)	[1.890] 1.936 (1.961)	1.776 (1.780)	1.823 (1.847)	1.940 (1.957)
B2B3	[1.651] 1.660 (1.676)	[1.638] 1.654 (1.674)	[1.623] 1.630 (1.643)	1.733 (1.749)	1.717 (1.738)	1.647 (1.663)
B3B4		[1.673] 1.691 (1.700)	[1.667] 1.674 (1.687)	1.640 (1.661)	1.667 (1.675)	1.754 (1.768)
B4B5		[1.724] 1.753 (1.789)	[1.706] 1.759 (1.790)	1.707 (1.730)	1.597 (1.610)	1.603 (1.621)
B2B7	[1.817] 1.839 (1.862)	[1.799] 1.804 (1.807)		1.819 (1.854)		1.834 (1.860)
B3B7		[1.827] 1.850 (1.876)		1.807 (1.828)		1.845 (1.876)
B4B7		[1.798] 1.808 (1.822)		1.790 (1.791)		1.816 (1.843)
$B1H_t$	[1.220] 1.217 (1.206)	[1.200] 1.191 (1.185)	[1.202] 1.196 (1.189)	1.194 (1.188)	1.198 (1.190)	1.209 (1.212)
$B2H_t$	[1.216] 1.218 (1.208)	[1.197] 1.195 (1.188)	[1.196] 1.194 (1.187)	1.195 (1.189)	1.187 (1.191)	1.200 (1.193)
$B3H_t$		[1.196] 1.195 (1.189)	[1.195] 1.192 (1.186)	1.194 (1.189)	1.190 (1.184)	1.191 (1.187)
$B4H_t$		[1.201] 1.195 (1.189)	[1.202] 1.197 (1.191)	1.196 (1.189)	1.193 (1.187)	1.196 (1.190)
$B7H_t$	[1.220] 1.217 (1.206)	[1.202] 1.197 (1.190)		1.196 (1.189)		1.201 (1.192)
BH*		[1.297] 1.302 (1.317) [2.146] 2.062 (2.104)	[1.278] 1.263 (1.275)	1.327 (1.351) 1.364 (1.418)	1.187 (1.191)	1.209 (1.212)

[a] HF/6-31G*; in brackets are the MP2(FULL)/6-31G* data; in parentheses are the HF/3-21G data.

levels (i.e., ab initio single points using MNDO geometries).[9,10] More recently, higher level ab initio optimizations were performed for $B_6H_7^-$, $B_8H_9^-$, and $B_{10}H_{11}^-$ taking electron correlation into account.[9a,11] The NMR ^{11}B chemical shifts were computed[11] and the combined ab initio/IGLO[12]/NMR method[13,14] employed for structure differentiation. The nonrigid behavior and experimental chemical shifts for $B_6H_7^-$ and $B_{10}H_{11}^-$ are in agreement with the theoretical results.

The $B_7H_8^-$ anion has not been reported experimentally yet. This may due to the lower chemical stability of the parent $B_7H_7^{2-}$ dianion relative to other members of the $B_nH_n^{2-}$ (n = 6–12) *closo*-borane family.[15] $B_9H_{10}^-$ and $B_{10}H_{11}^-$ are easier to study experimentally. Since the calculated proton affinity of $B_7H_7^{2-}$ is larger than that of $B_9H_9^{2-}$ and $B_{10}H_{10}^{2-}$ (see Table IV), $B_7H_8^-$ should exist as well. Now we continue our systematic theoretical study of the $B_nH_{n+1}^-$ series and report results of ab initio MO calculations for $B_7H_8^-$. Our objectives are (i) to ascertain the best geometry of $B_7H_8^-$ and to determine the degree of deformation of the boron skeleton of $B_7H_7^{2-}$ upon protonation, (ii) to compare the nonrigid behavior of $B_7H_8^-$ with that of other $B_nH_{n+1}^-$ anions, and (iii) to analyze the dianion vs monoanion differences in the vibrational spectra. The ab initio/IGLO[12]/NMR method[13,14] has been applied successfully to the structural elucidation of carbocations,[13] electron-deficient boron compounds,[14] and protonated *closo*-boranes as well.[11] We hope our IGLO chemical shift calculations and other theoretical predictions will stimulate the experimental search for $B_7H_8^-$.

Methods

Geometries were fully optimized by employing standard procedures[16] with the 3-21G and 6-31G* basis sets[17] and the Gaussian 90[18] program. Electron correlation effects were included using Moller–Plesset perturbation theory to second order[19] with the frozen core approximation (notation MP2/6-31G*//6-31G*). In addition, the most stable configurations of $B_7H_7^{2-}$ and $B_7H_8^-$ were reoptimized with inclusion of correlation effects (full MP2) (notation MP2(FU)/6-31G*//MP2(FU)/

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6-31G*). The nature of the stationary points was probed by HF/3-21G frequency calculations; transition structures have one and minima have zero imaginary frequencies.

Chemical shifts were computed using the IGLO (individual gauge for localized orbitals) method[12] and Huzinaga[20] basis sets, contracted as follows: basis DZ, B 7s3p [4111,21], H 3s [21]; basis II′, B 9s5p1d [51111,2111,1], p-exponent 0.5 (H same as DZ).

Results

Five possible structures (**2**–**6**) were calculated for the $B_7H_8^-$ anion. These have the "extra" hydrogen (designated H*) located over a face as well as various edges and vertices of the parent pentagonal bipyramid, $B_7H_7^{2-}$. The optimized geometries of $B_7H_7^{2-}$ (**1**) and of $B_7H_8^-$ (**2**–**6**) are given in Figure 1. The energies of the various structures with the different theoretical approximations are summarized in Table I. We use the structural notation suggested earlier:[9-11] "t" and "b" denote tridentate capping and bidentate bridge positions, respectively, and "v" indicates involvement in a terminal BH_2 group. The "4" and "5" in the notation denote the skeletal coordination numbers of the boron atoms bonded to H*.

As with previous results,[9c,10] only one minimum **2** (t445) is found on the potential energy surfaces (PES) for $B_7H_8^-$ at HF/3-21G (all other structures have one or more imaginary frequencies; see Table I). In **2** (C_s) H* is bound to the B1B4B5 face via a bridge bond with two four-coordinated boron atoms in the polyhedron base (B4H* = B5H* = 1.30 Å at MP2/6-31G*, Table II). The B(H*)B bridge bond is tilted toward B1, but H* interacts only weakly with the five-coordinated apical boron (B1H* = 2.15 Å, and the Wiberg bond index[21] is 0.05; see Table III). H* lies nearly in the B4B5B7 plane, but the dihedral (B2B4B5,H*B4B5) angle between the H*B4B5 plane and the bipyramid ring is 46.7°. The bonding between H* and the boron skeleton in $B_7H_8^-$ differs in character from that in the $B_6H_7^-$ [9a] and in the $B_{10}H_{11}^-$ [11c] anions where H* prefers capping positions and symmetrical ($B_6H_7^-$) or nearly symmetrical ($B_{10}H_{11}^-$) four-center bonds. $B_7H_8^-$ also differs from $B_8H_9^-$ where the three-center bridge bond B(H*)B is located in the basal symmetry plane of the anion.[11b] At HF/6-31G*, the $B_8H_9^-$ structure in C_s symmetry with a tilted BH*B bond is the global minimum. However, at the correlated level (MP2/6-31G*), the C_{2v} form is the most favorable.[11b] For $B_7H_8^-$ the C_s structure **2** is the global minimum both at the HF and MP2/6-31G* levels.

The MP2(FC)/6-31G*//MP2(FU)/6-31G* + ZPE(3-21G) computed value of the proton affinity (PA) for $B_7H_7^{2-}$ is 414.8 kcal/mol (see Table IV). The PA for $B_7H_7^{2-}$, similar to that of $B_8H_8^{2-}$ (413.1 kcal/mol),[11b] is significantly larger than that of OH^- [381.9 kcal/mol at MP2(FU)/6-31+G*//MP2(FU)/6-31+G* + ZPE(6-31G*); the experimental value is 390 kcal/mol[22]]. Thus, the reaction $B_7H_7^{2-} + H_2O \rightarrow B_7H_8^- + OH^-$ is quite exothermic in the gas phase and may be favorable in solution as well. Hence, $B_7H_7^{2-}$ might deprotonate water (or other proton donors) in solution and form the $B_7H_8^-$ monoanion (however, solvatation of OH^- must be considered in a more sophisticated treatment).

Table III. Natural Charges and Wiberg Bond Indexes for the $B_7H_8^-$ Anion (HF/3-21G)

		$B_7H_8^-$				
atoms	$B_7H_7^{2-}$ D_{5h} (**1**)	t455, C_s (**2**)	b44, C_{2v} (**3**)	b45, C_s, (**4**)	v4, C_{2v} (**5**)	v5, C_s (**6**)
			Charges			
B1	–0.091	–0.118	–0.042	–0.033	–0.069	–0.486
B2	–0.272	–0.175	–0.234	–0.254	–0.541	–0.294
B3	–0.272	–0.307	–0.231	–0.061	–0.056	–0.022
B4	–0.272	–0.148	–0.195	–0.281	–0.247	–0.186
B7	–0.091	–0.091	–0.042	–0.060	–0.069	+0.062
H1	–0.072	–0.050	–0.034	–0.019	–0.032	+0.157
H2	–0.062	–0.016	–0.003	–0.005	+0.196	–0.021
H3	–0.062	–0.002	0.000	–0.030	–0.027	–0.033
H4	–0.062	–0.004	+0.020	–0.007	+0.006	–0.025
H7	–0.072	–0.021	–0.034	–0.009	–0.032	–0.045
H*		+0.158	+0.200	+0.141	+0.196	+0.157
			WBI			
1–2	0.645	0.493	0.523	0.275	0.497	0.465
1–3	0.645	0.657	0.564	0.360	0.548	0.392
1–4	0.645	0.305	0.483	0.600	0.521	0.445
2–3	0.856	0.804	0.814	0.739	0.597	0.861
3–4	0.856	0.774	0.729	0.878	0.734	0.682
4–5	0.856	0.591	0.561	0.699	0.894	0.969
2–7	0.645	0.537	0.523	0.481	0.497	0.532
3–7	0.645	0.490	0.564	0.514	0.548	0.454
4–7	0.645	0.559	0.483	0.544	0.521	0.532
$B1H_t$	0.822	0.971	0.972	0.963	0.971	0.796
$B2H_t$	0.814	0.952	0.945	0.955	0.759	0.948
$B3H_t$	0.814	0.946	0.942	0.955	0.960	0.959
$B4H_t$	0.814	0.952	0.931	0.948	0.935	0.953
$B7H_t$	0.822	0.967	0.972	0.958	0.971	0.968
BH*		0.440 0.047	0.447	0.419 0.393	0.759	0.796

Table IV. Calculated Proton Affinities of $B_nH_n^{2-}$ Anions

level of theory	$B_6H_6^{2-}$	$B_7H_7^{2-}$	$B_8H_8^{2-}$	$B_9H_9^{2-}$	$B_{10}H_{10}^{2-}$
3-21G//3-21G+ZPE		418.0	409.4	401.7[c]	382.9[d]
6-31G*//6-31G*+ZPE[a]	445.1[b]	429.3	424.1	408.5[c]	
MP2(FU)/6-31G*// MP2(FU)/ 6-31G*+ZPE[a]		428.5	425.9		
MP2(FC)/6-31+G*// MP2(FU)/ 6-31G*+ZPE[a]		414.8	413.1		

[a] ZPE's were calculated at the HF/3-21G level for $B_7H_7^{2-}$ and $B_9H_9^{2-}$ and at the SCF/6-31G* level for $B_8H_8^{2-}$ (ref 11b) and scaled by 0.89 as recommended at ref 16. [b] Data from ref 11a. [c] Data from ref 11d. [d] Data from ref 11c.

Geometry and Dynamic Behavior. Compared with that of the reference dianion, $B_7H_7^{2-}$, the boron skeleton in $B_7H_8^-$ is distorted significantly. In particular, the B1B4 and B1B5 edges (adjacent with the B4H*B5 bridge bond) are elongated (to 2.03 Å, MP2/6-31G*). [The B1B4 distance is a nonrigid geometric parameter, and its length changes most (by 0.18 Å) from HF/3-21G to MP2/6-31G* (Table II).] The B4B5 bond length also increases significantly, by 0.07 Å (MP2/6-31G*). The distances between B1 and the basal B2, B3, and B6 atoms are reduced by 0.04–0.07 Å. Thus, tilting of the bridge bond plane to the bipyramidal vertex results in shifting of the B1 atom to the opposite part of the base. The other BB bond lengths change to a lesser extent, 0.01–0.02 Å, due to protonation. The BH bonds are shortened by ca. 0.02 Å and bent from the cluster axis (between center of mass and boron atoms) by 5–10°. The same qualitative picture was found in previous calculations.[10] In general, the structural deformation of the $B_7H_8^-$ cage due to the additional proton is similar to that found previously in the $B_6H_7^-$ and the $B_{10}H_{11}^-$ anions.[9,11]

Oscillation of the H* hydrogen from one face to the equivalent adjacent face via a base edge is facile. The activation energy is only 2.6 kcal/mol [MP2(FU)/6-31G*//MP2(FU)/6-31G* + ZPE(3-21G)] via transition structure b44 (**3**), in which H* is

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located in the middle of the base edge (see Figure 1) in C_{2v} symmetry. This part of PES is very flat, and the B(H*)B bridge hydrogen can oscillate between one bipyramidal vertex and another even at low temperatures. This would result in an "effective" C_{2v} symmetry for the $B_7H_8^-$ anion. The geometry of the bridge B4(H*)B5 bond changes only slightly from **2** and **3**, whereas deformation of the boron skeleton is noteworthy. The two elongated (2.03 Å) B1B4 and B1B5 distances and the two "short" (1.80 Å) B7B4 and B7B5 lengths in **2** are transformed into the four intermediate distances (1.89 Å, MP2/6-31G*) in **3**. Thus, the H* oscillations are accompanied by pulsation of the boron cage.

However, face-to-face migration of H* on the same side of the bipyramid via an inclined edge involves a higher barrier, 17.3 kcal/mol [MP2(FC)/6-31G*//6-31G* + ZPE(3-21G)]. The transition structure b45 (**4**), C_s, is characterized by a bridge B1(H*)B2 bond involving apical and equatorial boron atoms. The H* bridging is slightly nonsymmetrical; H* is 0.03 Å closer to the 4-coordinated B2 (SCF/6-31G*) than to 5-coordinated B1. The b45 structure is significantly less stable than b44. Thus, in $B_7H_7^{2-}$, the H* bridging to a pair of bonded four-coordinated B_4 atoms is more favorable than protonation of a B_4B_5 bond between four- and five-coordinated B_4 and B_5 atoms. The same trend was observed earlier for other anions $B_nH_{n+1}^-$.[9,11] Like **2**, **4** also shows significant deformation of the boron polyhedron as compared with the parent $B_7H_7^{2-}$ dianion, e.g. strong elongation of the bridged B1B2 and adjacent B1B3 and B1B6 bonds (see Table II).

The v4 structure (**5**), C_{2v} (with an equatorial BH_2 group), has two imaginary frequencies at HF/3-21G. However, at MP2(FC)/6-31G*//6-31G* + ZPE(3-21G), **5** is 2.4 kcal/mol more favorable than **4**. Hence, the 5-fold axial $B_7H_8^-$ exchange mechanism (**2** → **5** → **2′**) with BH_2 group formation may be preferable to face-face migration (**2** → **4** → **2′**). This higher-energy $B_7H_8^-$ rearrangement would be possible at elevated temperatures and would result in effective D_{5h} symmetry for the anion (e.g. in the NMR). The BH_2 group in **5** is characterized by B2B1 and B2B7 bond length increases of 0.09 Å; B2B3 and B2B6 also increase by 0.06 Å (SCF/6-31G*). Similar structural changes in other $B_nH_{n+1}^-$ anions with BH_2 groups have been found as well.[9]

Structure **6** (v5), C_s with a BH_2 group in the apical position, is very unfavorable. This also is so for other $B_nH_{n+1}^-$ systems.[9] $B_7H_8^-$ (**6**) has two imaginary frequencies and corresponds to a second-order stationary point.

The nonrigid behavior of $B_7H_8^-$ differs from that of other $B_nH_{n+1}^-$ anions, computed previously.[9-11] In $B_7H_8^-$, the additional hydrogen (H*) rotates most easily over the equatorial region of the bipyramid (local nonrigidity), whereas in $B_6H_7^-$ [9a] and in $B_8H_9^-$ [11b] the H* migrates over the whole boron skeleton (global nonrigidity). In $B_8H_9^-$, the H* migration is accompanied by a skeletal DSD rearrangement. In $B_{10}H_{11}^-$, the polyhedron pole region is most favorable for the H* motion.[11c]

Electronic Structures. The natural changes of the atoms and the Wiberg bond indices obtained by the natural population analysis[23] (NPA) of the $B_7H_7^{2-}$ dianion and the various $B_7H_8^-$ structures are summarized in Table III. It was suggested earlier[9] that of the most favorable position of the additional hydrogen atom in $B_nH_{n+1}^-$ anions might be predicted from the atomic charge distribution in corresponding dianions $B_nH_n^{2-}$. This is also the case for $B_7H_8^-$. In the parent $B_7H_7^{2-}$ dianion (**1**), the four-coordinated B2–B6 atoms in the bipyramidal base have larger negative charges (–0.27 e) than the five-coordinated B1 and B7 (–0.09 e) in the apical positions. In accord with such simple *electrostatic considerations*, the t445, b44, and v4 structures are more stable than b45 and v5. The extra H* in $B_7H_8^-$ can migrate in the region where the four-coordinated borons are located.

Table V. Calculatd IR Wavenumbers[a] and Intensities[b] (3-21G Basis Set) for $B_7H_7^{2-}$ and $B_7H_8^-$

	$B_7H_8^-$				
$B_7H_7^{2-}$ D_{5h} (**1**)	t445, C_s (**2**)	b44, C_{2v} (**3**)	b45, C_s (**4**)	v4, C_{2v} (**5**)	v5, C_s (**6**)
429, e_1' [7]	326 [9]	529 [8]	224 [5]	469 [4]	317 [14]
637 [4]	465 [22]	694 [6]	349 [7]	592 [5]	440 [3]
800, e_1' [0.5]	594 [13]	708 [6]	532 [13]	711 [39]	558 [8]
971, e_1' [12]	700 [9]	887 [13]	538 [5]	747 [22]	573 [13]
984 [38]	763 [7]	947 [14]	733 [44]	787 [14]	602 [3]
1150, e_1' [23]	773 [4]	993 [8]	800 [22]	798 [22]	734 [58]
	846 [22]	1007 [15]	815 [5]	819 [3]	743 [6]
	900 [7]	1142 [25]	828 [18]	905 [4]	839 [3]
	917 [8]	2122 [0.4]	839 [15]	960 [15]	901 [35]
	987 [8]	2186 [0.4]	858 [17]	983 [22]	918 [10]
	992 [4]		894 [5]	988 [8]	953 [7]
	1033 [6]		913 [18]	1045 [20]	976 [4]
	1116 [10]		997 [8]	1171 [57]	1011 [7]
	1122 [4]		1127 [8]		1013 [14]
	1849 [59]		1540 [97]		1131 [24]
	2010 [22]		1835 [192]		1169 [4]
2571, e_1' [886]	2723 [103]	2717 [100]	2726 [46]	2715 [4]	2574 [19]
2579 [719]	2725 [7]	2726 [107]	2729 [76]	2730 [10]	2592 [6]
	2725 [21]	2738 [36]	2736 [214]	2732 [419]	2694 [173]
	2736 [479]	2743 [400]	2741 [232]	2743 [34]	2705 [271]
	2740 [423]	2745 [145]	2754 [433]	2748 [17]	2717 [126]
	2755 [157]	2757 [381]	2757 [258]	2758 [183]	2735 [281]
	2789 [107]	2780 [52]	2777 [5]	2772 [478]	2754 [444]
				2788 [10]	2768 [22]

[a] Harmonic frequencies, cm^{-1}. [b] kM/mol.

Upon protonation, over 0.8 e is transferred from the $B_7H_7^{2-}$ dianion to H* (and the negative charges for boron atoms are reduced). Nevertheless, the bridging H* hydrogen in the various $B_7H_8^-$ structures is more positively charged (+0.15 to +0.20 e) than the terminal H's. As in $B_7H_7^{2-}$, in $B_7H_8^-$ the equatorial boron atoms with the largest negative charges are B2 in **3**, as well as B3 and B6, adjacent to the B4H*B5 bridge bond, in **2**. Hence, the nonprotonated equatorial B atoms in the $B_7H_8^-$ anion would be preferred centers for electrophilic attack; the apical B1 and B7 atoms are good sites for nucleophilic attack. The large negative charge of boron of the BH_2 group in v4 and v5 structures is noteworthy. This is a common feature of the $B_nH_{n+1}^-$ series.[9] The WBI values (see Table III) correspond to the geometric deformations (see Table II).

IR Frequencies. A distinctive displacement of the terminal BH bond stretch vibrations to higher wavenumbers was found both theoretically[11] and experimentally[2] for the $B_6H_7^-$, $B_8H_9^-$, and $B_{10}H_{11}^-$ monoanions. The data for $B_7H_8^-$, summarized in Table V, reveal a similar trend. The calculated displacement, 150–200 cm^{-1}, parallels the shortening of the BH bonds (by ca. 0.02 Å; see Table II) from the $B_7H_7^{2-}$ dianion (**1**) to the $B_7H_8^-$ monoanion (**2**). Characteristic IR spectral features are associated with the bridging hydrogen as well.[24] The frequencies at 1849 and 2010 cm^{-1} (SCF/3-21G) for the global minimum **2** are due to B(H*)B bridge bond vibrations (H* parallel and perpendicular to the bridged BB edge, respectively). In the transition structure, **3**, these vibrations have higher frequencies and very small IR intensities. A peculiarity of the IR spectrum of **6** (v5) is a notable decrease (by 200 cm^{-1} with respect to other terminal BH bonds) in the frequencies of the BH stretching vibrations in the BH_2 group.

Chemical Shift Calculations. The IGLO chemical shifts for the $B_7H_7^{2-}$ dianion and for various $B_7H_8^-$ structures are sum-

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Table VI. IGLO ^{11}B Chemical Shifts (ppm) for the $B_7H_7^{2-}$ and $B_7H_8^-$ Anions

level of theory	configuration	
	$B_7H_7^{2-}$	
	1, D_{5h}	
	B(1,7)	B(2-6)
DZ//6-31G*[a]	-19.3	-2.2
DZ//MP2/6-31G*	-20.5	-3.1
II'//MP2/6-31G*	-25.7	-2.6
exp.[b]	-22.5	-0.1

level of theory	$B_7H_8^-$											
	2, C_s							3, C_{2v}				
	B(1)	B(2)	B(3,6)	B(4,5)	B(7)	B(1,7)[c]	B(2-6)[c]	B(1,7)	B(2)	B(3,6)	B(4,5)	B(2-6)[c]
DZ//6-31G*	+14.2	+23.3	+2.9	+4.7	-21.2	(-3.5)	(+7.7)	-16.3	-7.0	+7.2	-6.1	(-1.0)
DZ//MP2/6-31G*	+4.1	+14.6	+3.2	-0.8	-24.7	(-10.3)	(+3.9)	-20.0	-8.5	+5.7	-8.3	(-2.7)
II'//MP2/6-31G*	-0.5	+14.1	+3.6	-1.7	-27.6	(-14.1)	(+3.6)	-23.0	-6.8	+5.6	-10.7	(-3.4)

level of theory	4, C_s					5, C_{2v}			
	B(1)	B(2)	B(3,6)	B(4,5)	B(7)	B(1,7)	B(2)	B(3,6)	B(4,5)
DZ//6-31G*	-13.3	-11.5	+24.7	0.0	+2.2	-21.1	-13.8	+21.0	-4.5

level of theory	6, C_s				
	B(1)	B(2)	B(3,6)	B(4,5)	B(7)
DZ//6-31G*	-30.3	+3.5	+29.5	+12.9	+55.0

[a] Data from ref 25. [b] Data from ref 26. [c] Averaged values.

marized in Table VI. Five signals with a 1:1:2:2:1 intensity ratio are calculated for the global minimum of **2**. However, the face-face oscillations of the bridging hydrogen would scramble the apical B1 and B7 atoms even at low temperatures (the computed barrier is only 2.6 kcal/mol) and would lead to effective C_{2v} symmetry on the NMR time scale. As a result of averaging, only four signals should be observable in the NMR ^{11}B spectrum at ambient temperatures with δ = +14.1 (1B), +3.6 (2B), -1.7 (2B), and -14.1 ppm (2B) (II'//MP2/6-31G*). Our calculated IGLO chemical shifts for $B_7H_7^{2-}$ are in good agreement with experiment.[26] The II'//MP2/6-31G* approximation usually reproduces NMR ^{11}B chemical shifts for boron hydrides with an average accuracy of ±2 ppm.[14] Similar accuracy for the hypothetical $B_7H_8^-$ anion can be expected. The ^{11}B chemical shifts of **2** differ drastically from those for **3**, -6.8 (1B), +5.6 (2B), -10.7 (2B), and -23.0 (2B), although the intensity ratios (after averaging for **2**) are the same. Although **2** and **3** are close in energy, experimental NMR ^{11}B spectra should be effective for the detection and the structure elucidation of $B_7H_8^-$.

At higher temperatures effective migration of the extra H* around the 5-fold axis of the bipyramid (barrier ca. 15 kcal/mol) should render all equatorial borons equivalent on the NMR time scale. Hence, the NMR ^{11}B spectrum for $B_7H_8^-$ should display the characteristic temperature dependence of nonrigid molecules. Three signals should coalesce and merge into a single resonance at higher temperatures. As a result, two signals are expected with a 5:2 intensity ratio: the chemical shifts are predicted to be +3.6 and -14.1 ppm for **2** as well as -3.4 and -23.0 ppm for **3**. Note that the average chemical shifts for **3** are very close to those for $B_7H_7^{2-}$ (**1**), -2.6 and -25.7 ppm, which is a stable species. The different temperature dependence of the NMR spectra of the anions would help in their recognition.

Conclusions

As with earlier calculations,[9c,10] the "extra" hydrogen in the hypothetical $B_7H_8^-$ anion is predicted to prefer coordination to a face of skeleton bipyramid. However, this hydrogen is located nearer an equatorial edge and forms a bridge bond with two boron atoms. This three-center bridge bond can oscillate relative to the base plane with a small potential barrier, 2.6 kcal/mol [MP2(FU)/6-31G*//MP2(FU)/6-31G* + ZPE(3-21G)]. Rotation of H* around the polyhedron 5-fold axis requires higher activation energy. Two mechanisms, exchange (barrier ~15 kcal/mol) and migration (barrier ~17 kcal/mol), are competitive for this rearrangement. The ^{11}B NMR spectrum of $B_7H_8^-$ should display the temperature dependence typical for structurally nonrigid molecules. Four signals with a 1:2:2:2 intensity ratio should be observed in the spectrum at low temperatures, and only two signals (5:2 ratio), at elevated temperatures. At moderately high temperatures, the NMR spectrum of the monoanion $B_7H_8^-$ might be the nearly same as the dianion $B_7H_7^{2-}$, but only the former should be temperature dependent.

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