Ab Initio Study of Nine- and Ten-Vertex Nido and Arachno Boranes and Heteroboranes

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A series of nine- and ten-vertex nido and arachno boranes and heteroboranes have been studied by ab initio methods. At the highest level of optimization (HF/6-31G*), bond distances are in good agreement with X-ray data. The heat of formation of $B_{10}H_{14}$ is estimated to be −8.6 kcal/mol from a consideration of the reaction $10BH_3 - 8H_2 \rightarrow B_{10}H_{14}$. With this value, heats of formation of other cages are calculated through near-isodesmic reactions.

Introduction

Theory has played an important role in advancing the field of boron hydride and carborane chemistry.[1] However, to date, the bulk of work has been devoted to clusters of six or fewer vertices or to cages with a closo structure. While experimental work has proceeded on larger nido and arachno clusters, few calculations on the larger nido and arachno heteroboranes, except for calculations on B_9H_{15} and $B_{10}H_{14}$,[2] have been reported.

Method

All geometries were optimized at the HF/3-21G and HF/6-31G* levels.[3] Vibrational frequencies were determined at both levels to determine the nature of the potential energy surface and to make zero-point corrections (frequencies weighted by a 0.9 factor). Single-point calculations are made at the MP2/6-31G* level. The geometries are consistently better at the HF/6-31G* level as judged from MP2/6-31G* energies which decreased from 0.8 to 7.1 kcal/mol for the various structures (Table 1). Dipole moments calculated with the HF/6-31G* electron density are also reported in Table 1. Molecular plots of all structures based upon HF/6-31G* geometries are given in Figure 1. Z-matrices (HF/6-31G*) of the structures are provided as supplementary material.

A boldface number has been assigned to each nine-vertex (**1**−**6**) and ten-vertex cage (**7**−**12**). When more than one isomer or conformation of a cage has been studied, a boldface letter is added. Total energies (hartrees) and zero-point energies (kcal/mol) of all nine and ten-vertex systems are presented in Table 1.

NMR chemical shift data is widely available for these compounds.[4,5] It is now possible to calculate ^{11}B chemical shifts with surprising accuracy provided that geometries at a sufficiently high level of theory are available.[6−8] These calculations are now in progress (in collaboration with P. v. R. Schleyer) and will be reported in due course.

Results and Discussion

Except for **3a**, all nine- and ten-vertex cages have been reported in the literature either as the object of investigation or as a reactant in formation of new cages.[4,5,9−24] In addition, MNDO calculations[25] have been reported for **4** and **5a** as well as STO-3G calculations[26] for **5a** and **6**. While larger heteroborane cages are known in the literature,[27] the present work will focus on nine and ten-vertex non-closo cages.

I. Structures. For **1**,[28] **3b**,[29] **5a**,[30] **6a**,[31] **7**,[32] **9a**,[33] and **11**[34] X-ray (neutron diffraction for $B_{10}H_{14}$) structures of either the parent cage or a closely related derivative are available.

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Table 1. Absolute Energies (hartrees) of Various Nine- and Ten-Vertex Heteroboranes Calculated at HF/3-21G and HF/6-31G* Optimized Geometries

		//3-21G			//6-31G*				
	sym	HF/3-21G	ZPE (NEV)[a]	MP2/6-31G*	HF/6-31G*	ZPE (NEV)[a]	MP2/6-31G*	DM[b]	ΔE[c]
B_9H_{15} (**1**)	C_s	−229.42633	120.54 (0)	−231.63191	−230.76687	121.14 (0)	−231.63331	2.73	0.9
1-CB_8H_{12} (**2**)	C_s	−240.87648	104.11 (0)	−243.15491	−242.26985	104.71 (0)	−243.15795	1.85	1.9
2,5-$C_2B_7H_{11}$ (**3a**)	C_s	−253.40333	99.60 (0)	−255.77732	−254.85778	100.07 (0)	−255.78167	2.80	2.7
1,2-$C_2B_7H_{11}$ (**3b**)	C_1	−253.39836	99.02 (0)	−255.77291	−254.85721	99.85 (0)	−255.78145	2.57	5.4
4-CB_8H_{14} (**4a**)	C_s	−242.00064	116.25 (1)	−244.29257	−243.39646	116.77 (1)	−244.30046	3.13	5.0
4-CB_8H_{14} (**4b**)	C_1	−242.00473	117.46 (0)	−244.29863	−243.40110	118.06 (0)	−244.30083	3.18	1.4
4,6-$C_2B_7H_{13}$ (**5a**)	C_s	−254.57567	113.40 (0)	−256.95742	−256.02943	113.91 (0)	−256.96097	3.20	2.2
4,5-$C_2B_7H_{13}$ (**5b**)	C_1	−254.54626	113.23 (0)	−256.92835	−256.00663	114.08 (0)	−256.93549	3.22	4.5
4-NB_8H_{13} (**6a**)	C_s	−257.98202	109.47 (1)	−260.37666	−259.45895	110.39 (0)	−260.38801	3.44	7.1
4-NB_8H_{13} (**6b**)	C_1	−257.98602	110.61 (0)	−260.38132	−259.46172	111.39 (0)	−260.38477	3.45	2.1
$B_{10}H_{14}$ (**7**)	C_{2v}	−253.44727	118.38 (0)	−255.87738	−254.92214	118.92 (0)	−255.87875	3.30	0.8
6-CB_9H_{13} (**8**)	C_s	−265.99004	112.07 (1)	−268.50397	−267.52073	112.69 (1)	−268.50675	3.38	1.7
5,6-$C_2B_8H_{12}$ (**9a**)	C_1	−278.55000	109.56 (0)	−281.16688	−280.15046	110.03 (0)	−281.16990	3.25	1.9
6,9-$C_2B_8H_{12}$ (**9b**)	C_{2v}	−278.48336	105.38 (0)	−281.11122	−280.06966	105.34 (0)	−281.11559	2.66	2.7
6,9-$C_2B_8H_{12}$ (**9c**)	C_{2v}	−278.51280	105.73 (3)	−281.11698	−280.10052	106.27 (2)	−281.12077	3.22	2.4
6-NB_9H_{12} (**10**)	C_s	−281.99764	107.40 (0)	−284.61578	−283.60736	108.03 (0)	−284.61808	3.87	1.4
$B_{10}H_{14}^{2-}$ (**11**)	C_{2v}	−253.41001	114.23 (0)	−255.84684	−254.85979	114.14 (0)	−255.84816		0.8
6,9-$N_2B_8H_{12}$ (**12**)	C_{2v}	−311.67450	110.45 (0)	−314.49425	−313.42519	111.05 (0)	−314.49925	3.83	3.1

[a] Zero-point energy in kcal/mol and number of imaginary frequencies. [b] Dipole moment (debye) calculated with the HF/6-31G* density. [c] Energy lowering in kcal/mol at the MP2/6-31G* level when HF/6-31G* geometries are used rather than HF/3-21G geometries.

Comparisons between the HF/6-31G* geometries and X-ray or neutron diffraction results are made in Table 2. In general, the differences between calculated and experimental bond lengths are only a few hundredths of an Å. An exception is $C_2B_7H_{11}$ (**3b**) where the C_2B_3 distance is calculated too long by 0.1 Å and the C_2B_5 distance is calculated too short by 0.1 Å.[29] Given the good agreement for the other distances (Table 2), it is suggested that the labels for these two distances were reversed in the figure caption.[29] With the exception of the two errors discussed above, the largest errors are associated with long B−B bonds. Of the five B−B bonds calculated to be over 1.9 Å, three have errors between 0.040 and 0.055 Å. The boron atoms are probably bound by a fractional multicenter bond which is characterized by a small force constant.

Nitrogen is incorporated into three cages, 4-NB_8H_{13} (**6a**), 6-NB_9H_{12} (**10**), and 6,9-$N_2B_8H_{12}$ (**12**). In all three cages, nitrogen is tetracoordinate and the average calculated N−B distances are very similar: 1.537 Å (**6a**), 1.536 Å (**10**), and 1.532 Å (**12**). In contrast, the C−C distances vary more in the four cages (**3a**, **3b**, **5b**, **9a**) where there are directly bonded C−C distances. The C−C distance in **9a** is distinctly shorter (1.459 Å) than in **3a** (1.550 Å), **3b** (1.581 Å) or **5b** (1.552 Å). The probable reason is that the C−C bond in **9a** has more 2c−2e character as the coordination around the two carbons is four and five. On the other hand, the coordination around both carbons is five in **3a**, **3b**, and **5b**.

In **4a/4b** and **6a/6b** two closely related stationary points were found. In **4a** and **6a**, the heteroborane has a plane of symmetry and four bridging hydrogens. In **4b** and **6b**, the plane of symmetry is lost and one bridging hydrogen is converted into a terminal B−H hydrogen. At the HF/3-21G level, **4a** and **6a** are characterized by one imaginary frequency. A reduction in symmetry led to a minimum 2.6 kcal/mol lower for **4a** → **4b** and 2.5 kcal/mol lower for **6a** → **6b** at the HF/3-21G level (computed from absolute energies in Table 1). At the HF/6-31G* level, C_1 minima were also found, 2.9 kcal/mol more stable than **4a** and 1.7 kcal/mol more stable than **6a** (computed from absolute energies in Table 1). However, the preference nearly disappears at the MP2/6-31G*//6-31G* level and when zero-point corrections are included, the symmetrical C_s structures **4a** and **6a** become more stable than the unsymmetrical structures **4b** and **6b** (Table 4). In an NMR study of **6a/6b**, Wallbridge and co-workers[14] reported that the two bridging hydrogens in question ($B_6H_bB_7$, $B_8H_bB_7$) were more closely associated with borons B_6 and B_8 than to B_7. However, in a recent review of carboranes, Williams[12] indicated a rapid interconversion of C_1 minima (**6b** → **6a**(TS) → **6b**). While the energy difference is small, ab initio calculations favor a static C_s minimum (C_s structure is 2.9 kcal/mol lower in energy than C_1 minimum; Table 4). A similar situation arose with the $C_2B_{10}H_{13}^-$ anion in solution where the nmr data could be interpreted as either a static C_s structure or as a pair of rapidly interconverting C_1 structures.[35] The question was unambiguously resolved[35] by calculating the ^{11}B NMR chemical shifts. Averaging the calculated chemical shifts of the C_1 structure over the symmetry-related boron positions reproduced the experimental shifts to within about 3 ppm. On the other hand, the calculated ^{11}B chemical shifts of the C_s structure were up to 30 ppm different from experiment. Similar chemical shift calculations are underway for the molecules studied presently, which will unambiguously establish the structural nature of **4a/4b** and **6a/6b** in solution.

II. Energetics. Heats of formation are useful in making predictions about which species will be favored by pyrolysis.

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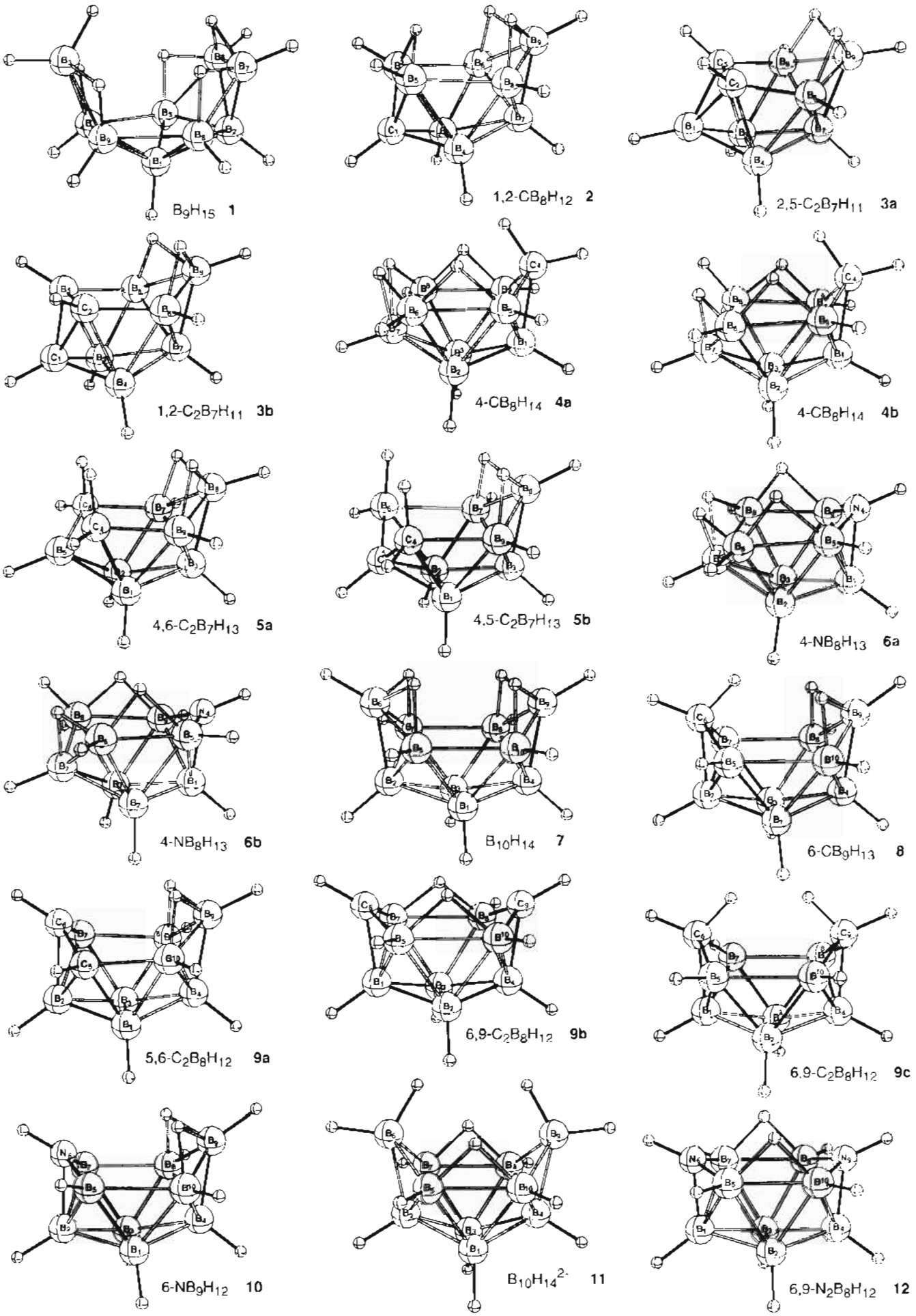

Figure 1. Molecular geometries of nine- and ten-vertex cages calculated at the HF/6-31G* level. See Tables 2 and 3 for interatomic distances.

Table 2. Comparison of HF/6-31G* Geometries with X-ray or Neutron Diffraction Structures

B_9H_{15} (**1**)			$1,2\text{-}C_2B_7H_{11}$ (**3b**)			$4,6\text{-}C_2B_7H_{13}$ (**5a**)			$5,6\text{-}C_2B_8H_{12}$ (**9a**)			$B_{10}H_{14}$ (**7**)		
dist	6-31G*	X-ray[a]	dist	6-31G*	X-ray[b]	dist	6-31G*	X-ray[c]	dist	6-31G*	X-ray[f]	dist	6-31G*	neut[e]
B_1B_2	1.793	1.77	C_1C_2	1.550	1.55	B_1B_2	1.708	1.714	B_1B_2	1.751	1.752	B_1B_2	1.798	1.778
B_1B_4	1.768	1.76	C_1C_3	1.565	1.60	B_1B_3	1.796	1.776	B_1B_3	1.806	1.789	B_1B_3	1.791	1.772
B_1B_5	1.743	1.75	C_1B_4	1.587	1.60	B_1C_4	1.698	1.672	B_1B_4	1.787	1.782	B_1B_5	1.759	1.756
B_2B_5	1.829	1.82	C_1B_5	1.599	1.60	B_1B_5	1.745	1.732	B_1C_5	1.664	1.657	B_2B_5	1.800	1.786
B_2B_6	1.749	1.78	C_2B_3	1.776	1.67	B_1B_9	1.806	1.784	B_1B_{10}	1.826	1.805	B_2B_6	1.737	1.715
B_3B_4	1.886	1.86	C_2B_5	1.654	1.75	B_3B_7	1.837	1.821	B_2B_3	1.784	1.758	B_5B_6	1.803	1.775
B_4B_5	1.969	1.95	C_2B_6	1.662	1.65	B_3B_8	1.727	1.719	B_2C_5	1.714	1.709	B_5B_{10}	2.020	1.973
B_4B_9	1.790	1.80	B_3B_4	1.852		C_4B_5	1.707	1.703	B_2C_6	1.695	1.691	B_5H_b	1.320	1.298
B_5B_6	1.816	1.84	B_3B_6	1.861		C_4B_9	1.717	1.710	B_2B_7	1.831	1.813	B_6H_b	1.328	1.347
B_6B_7	1.781	1.78	B_3B_7	1.814		B_7B_8	1.853	1.824	B_3B_4	1.836	1.815			
B_3H_b	1.432		B_4B_5	1.828		B_7H_b	1.395	1.34	B_3B_7	1.805	1.777	$B_{10}H_{14}^{2-}$ (**11**)		
B_4H_b	1.244		B_4B_7	1.838		B_8H_b	1.276	1.18	B_3B_8	1.760	1.774	dist	6-31G*	X-ray[g]
B_5H_b	1.339		B_4B_8	1.784	1.75				B_4B_8	1.788	1.788	B_1B_2	1.787	1.781
B_6H_b	1.304		B_5B_8	1.863		$4\text{-}NB_8H_{13}$ (**6a**)			B_4B_9	1.739	1.727	B_1B_3	1.836	1.807
B_6H_b	1.335		B_6B_7	1.836		dist	6-31G*	X-ray[d]	B_4B_{10}	1.818	1.814	B_1B_5	1.789	1.784
			B_6B_9	1.792		B_1B_2	1.754	1.746	C_5C_6	1.459	1.457	B_2B_5	1.754	1.748
			B_7B_8	1.840		B_1N_4	1.585	1.584	C_5B_{10}	1.747	1.751	B_2B_6	1.768	1.748
			B_7B_9	1.737	1.69	B_1B_5	1.864	1.860	C_6B_7	1.504	1.508	B_5B_6	1.921	1.881
			B_8B_9	1.800		B_2B_3	1.841	1.807	B_7B_8	1.992	1.937	B_5H_{10}	1.915	1.887
			B_6H_b	1.365		B_2B_5	1.815	1.815	B_8B_9	1.775	1.782	B_5H_b	1.324	
			B_9H_b	1.278		B_2B_6	1.762	1.746	B_9B_{10}	1.800	1.783			
			B_9H_b	1.314		B_2B_7	1.835	1.829	B_8H_b	1.330				
			B_8H_b	1.317		N_4B_5	1.513	1.518	B_9H_b	1.312				
						B_5B_6	1.844	1.826	B_9H_b	1.313				
						B_6B_7	1.879	1.860	$B_{10}H_b$	1.317				
						B_5H_b	1.446							
						B_6H_b	1.259							
						B_6H_b	1.238							
						B_7H_b	1.500							

[a] Reference 28. [b] Reference 29. [c] Reference 30. [d] Reference 31. [e] Reference 32. [f] Reference 33. [g] Reference 34.

Table 3. Calculated (HF/6-31G*) Geometries of Nido and Arachno Heteroboranes

$1\text{-}CB_8H_{12}$ (**2**)		$4\text{-}CB_8H_{14}$ (**4a**)		$4\text{-}CB_8H_{14}$ (**4b**)		$4,5\text{-}C_2B_7H_{13}$ (**5b**)		$4\text{-}NB_8H_{13}$ (**6b**)		$6\text{-}CB_9H_{13}$ (**8**)		$6,9\text{-}C_2B_8H_{12}$ (**9b**)		$6\text{-}NB_9H_{12}$ (**10**)	
C_1B_2	1.593	B_1B_2	1.743	B_1B_2	1.744	B_1B_2	1.763	B_1B_2	1.775	B_1B_2	1.768	B_1B_2	1.751	B_1B_2	1.770
C_1B_3	1.608	B_1C_4	1.688	B_1B_3	1.757	B_1B_3	1.765	B_1B_3	1.762	B_1B_3	1.876	B_1B_5	1.823	B_1B_3	1.861
B_2B_5	1.912	B_1B_5	1.774	B_1C_4	1.676	B_1C_4	1.718	B_1B_4	1.560	B_1B_4	1.821	B_1C_6	1.691	B_1B_4	1.827
B_2B_6	1.973	B_2B_3	1.825	B_1B_5	1.759	B_1C_5	1.660	B_1B_5	1.900	B_1B_5	1.740	B_2B_3	1.876	B_1B_5	1.746
B_3B_4	1.832	B_2B_5	1.833	B_1B_9	1.788	B_1B_9	1.792	B_1B_9	1.848	B_1B_{10}	1.766	B_2B_5	1.872	B_1B_{10}	1.780
B_3B_7	1.823	B_2B_6	1.755	B_2B_3	1.822	B_2B_3	1.827	B_2B_3	1.830	B_2B_5	1.752	B_5C_6	1.548	B_2B_5	1.812
B_6B_{10}	1.796	B_2B_7	1.795	B_2B_5	1.862	B_2C_5	1.709	B_2B_5	1.837	B_2B_6	1.690	B_5B_{10}	2.039	B_2N_6	1.639
B_7B_{10}	1.713	C_4B_5	1.723	B_2B_6	1.830	B_2B_6	1.825	B_2B_6	1.759	B_4B_8	1.791	B_5H_b	1.363	B_4B_8	1.786
B_5H_b	1.337	B_5B_6	1.885	B_2B_7	1.736	B_2B_7	1.701	B_2B_7	1.789	B_4B_9	1.728			B_4B_9	1.732
B_6H_b	1.312	B_5H_b	1.342	B_3B_7	1.788	B_3B_7	1.828	B_3B_7	1.732	B_5B_{10}	2.034	(**9c**)		B_5N_6	1.484
B_6H_b	1.333	B_6H_b	1.298	B_3B_8	1.738	B_3B_8	1.728	B_3B_8	1.840	B_5B_6	1.664	B_1B_2	1.792	B_5B_{10}	1.961
				B_3B_9	1.834	B_3B_9	1.807	B_3B_9	1.874	B_8B_9	1.783	B_1B_5	1.753	B_8B_9	1.767
$2,5\text{-}C_2B_7H_{11}$ (**3a**)				B_4B_5	1.726	C_4C_5	1.552	N_4B_5	1.513	B_8H_b	1.291	B_1C_6	1.685	B_8H_b	1.291
B_1C_2	1.617			C_4B_9	1.730	C_4B_9	1.823	N_4B_9	1.529	B_9H_b	1.378	B_2B_3	1.983	B_8H_b	1.374
B_1B_3	1.687			B_5B_6	1.957	C_5B_6	1.644	B_5B_6	1.826			B_2B_5	1.747		
C_2B_4	1.762			B_6B_7	2.035	B_6B_7	2.126	B_6B_7	1.825			B_5C_6	1.647	$6,9\text{-}N_2B_8H_{12}$ (**12**)	
C_2C_5	1.581			B_7B_8	1.808	B_7B_8	1.807	B_7B_8	2.020			B_5B_{10}	2.056	B_1B_2	1.777
C_2B_6	1.638			B_8B_9	1.856	B_8B_9	1.829	B_8B_9	1.919					B_1B_5	1.935
B_3B_4	1.780			B_6H_b	1.342	B_7H_b	1.345	B_5H_b	1.414					B_1B_6	1.540
B_3B_7	1.816			B_7H_b	1.391	B_8H_b	1.297	B_6H_b	1.267					B_2B_3	1.854
B_3B_8	1.871					B_8H_b	1.313	B_7H_b	1.387					B_2B_5	1.840
B_6B_7	1.846					B_9H_b	1.331	B_8H_b	1.317					B_5N_6	1.528
B_6B_9	1.804							B_9H_b	1.316					B_5B_{10}	1.837
B_7B_9	1.751													B_5H_b	1.324
B_6H_b	1.370														
B_9H_b	1.272														

In an earlier study,[2] estimates were made of heats of formation of the boron hydrides up to $B_{10}H_{14}$ using HF/3-21G geometries. The exothermicity of the reaction $xBH_3 + yH_2 \rightarrow$ boron hydride was calculated at the MP2/6-31G* level (or an approximation of that level through additivity). By adjusting the heat of formation of BH_3 and using the calculated enthalpy of reaction, estimates were made of the boron hydride heats of formation.[36]

Full MP2/6-31G* calculations on B_9H_{15} and $B_{10}H_{14}$ (which were not carried out in the earlier study) lead to lower heats of formation than reported previously.[2] The new values are 8.8 and −8.6 kcal/mol (at 298K), for B_9H_{15} and $B_{10}H_{14}$, respectively. The value for $B_{10}H_{14}$ (−8.6 kcal/mol) is particularly noteworthy, since previously reported experimental values (at 298 K) are much higher, 11.3 ± 4.5,[37] 7.5[38] and 7.1[39] kcal/mol. A redetermination of the experimental ΔH_f for $B_{10}H_{14}$ would be highly desirable.

(36) The estimated heat of formation of B_9H_{15} using the additivity approximation was incorrect in ref 2. It should have been 15.7 kcal/mol rather than the reported value of 26.5 kcal/mol.

Table 4. Calculated Reaction Energies (kcal/mol) and Heats of Formation (kcal/mol) at 0 K for Various Nine- and Ten-Vertex Nido and Arachno Boranes and Heteroboranes

	MP2/6-31G*+ZPC		
	//3-21G	//6-31G*	heat of formation[a]
1 [B_9H_{15}] + BH_3 → **7** [$B_{10}H_{14}$] + $2H_2$	−49.1	−49.2	14.2
B_9H_{15} + CH_4 → **2** [1-CB_8H_{12}] + BH_3 + $2H_2$	21.4	20.6	−7.6
B_9H_{15} + $2CH_4$ → **3a** [2,5-$C_2B_7H_{11}$] + $2BH_3$ + $3H_2$	75.5	74.0	3.4
B_9H_{15} + $2CH_4$ → **3b** [1,2-$C_2B_7H_{11}$] + $2BH_3$ + $3H_2$	77.8	74.0	3.4
B_9H_{15} + CH_4 → **4a** [4-CB_8H_{14}] + BH_3 + H_2	30.4	26.4	−1.8
B_9H_{15} + CH_4 → **4b** [4-CB_8H_{14}] + BH_3 + H_2	27.7	27.4	−0.8
B_9H_{15} + $2CH_4$ → **5a** [4,6-$C_2B_7H_{13}$] + $2BH_3$ + $2H_2$	59.4	58.4	−12.2
B_9H_{15} + $2CH_4$ → **5b** [4,5-$C_2B_7H_{13}$] + $2BH_3$ + $2H_2$	77.5	74.6	4.0
B_9H_{15} + NH_3 → **6a** [4-NB_8H_{13}] + BH_3 + H_2	−9.5	−14.8	−39.7
B_9H_{15} + NH_3 → **6b** [4-NB_8H_{13}] + BH_3 + H_2	−11.4	−11.9	−36.8
$B_{10}H_{14}$ + CH_4 → **8** [6-CB_9H_{13}] + BH_3 + H_2	49.9	49.3	−1.7
$B_{10}H_{14}$ + $2CH_4$ → **9a** [5,6-$C_2B_8H_{12}$] + $2BH_3$ + $2H_2$	80.5	79.8	−13.6
$B_{10}H_{14}$ + $2CH_4$ → **9b** [6,9-$C_2B_8H_{12}$] + $2BH_3$ + $2H_2$	111.6	109.7	16.3
$B_{10}H_{14}$ + $2CH_4$ → **9c** [6,9-$C_2B_8H_{12}$] + $2BH_3$ + $2H_2$	108.4	107.2	13.8
$B_{10}H_{14}$ + NH_3 → **10** [6-NB_9H_{12}] + BH_3 + H_2	−5.4	−5.3	−49.6
$B_{10}H_{14}$ → **11** [$B_{10}H_{14}^{2-}$]	15.4	14.9	6.3
$B_{10}H_{14}$ + $2NH_3$ → **12** [6,9-$N_2B_8H_{12}$] + $2BH_3$ + H_2	−1.7	−2.6	−82.6
	MP2/6-31G*+ZPC		
	//3-21G	//6-31G*	energy of reacn[b]
4a [4-CB_8H_{14}] + BH_3 → **8** [6-CB_9H_{13}] + $2H_2$	−29.6	−26.4	−26.3
5a [4,6-$C_2B_7H_{13}$] + BH_3 → **9a** [5,6-$C_2B_9H_{12}$] + $2H_2$	−28.1	−27.8	−27.8
6a [4-NB_8H_{13}] + BH_3 → **10** [6-NB_9H_{12}] + $2H_2$	−45.1	−39.7	−39.7
4a [4-CB_8H_{14}] → **2** [1-CB_8H_{12}] + H_2	−9.0	−5.9	−5.8
5a [4,6-$C_2B_7H_{13}$] → **3a** [2,5-$C_2B_7H_{11}$] + H_2	16.1	15.6	15.6
5b [4,5-$C_2B_7H_{13}$] → **3b** [1,2-$C_2B_7H_{11}$] + H_2	0.3	−0.6	−0.6

[a] Heats of formation at 0 K are calculated for the species in brackets from the reaction energy (MP2/6-31G*//6-31G*) and the experimental heats of formation of BH_3 (26.4 kcal/mol), NH_3 (−9.3 kcal/mol), and CH_4 (−16.0 kcal/mol).[37] The heat of formation of $B_{10}H_{14}$ (**7**) is taken to be −8.6 kcal/mol which is obtained from the adjusted heat of formation of BH_3 and the enthalpy of reaction of $10BH_3 - 8H_2 \rightarrow B_{10}H_{14}$ calculated at the MP2/6-31G*//3-21G+ZPC level. See ref 2. The heat of formation of B_9H_{15} (**1**) (14.2 kcal/mol) is determined from the first reaction. [b] The energies of reaction are computed from the heats of formation reported above.

In the present study, heats of formation at 0 K (heat capacity corrections are not included) have been estimated by constructing various reactions where the heats of reaction can be combined with experimental heats of formation[37] to calculated the heat of formation of the unknown cage. Care was taken to ensure that the reactant and product cage were as similar as possible to maximize cancellation of error in the calculation of reaction energies.

For this work, the heat of formation of $B_{10}H_{14}$ was taken to be −8.6 kcal/mol. From that value and the heat of reaction of the first reaction in Table 4, a heat of formation of 14.2 kcal/mol can be derived for B_9H_{15}. All other heats of formation are relative to B_9H_{15} and $B_{10}H_{14}$.[40] A comparison is made with energies of reaction computed at the MP2/6-31G*//3-21G level with values at the MP2/6-31G*//6-31G* level. The differences (which would also show up in estimated heats of formation) are as large as 5 kcal/mol.

The structure of **5b**, *arachno*-4,5-$C_2B_7H_{13}$, originally assigned to *nido*-2,6-$C_2B_7H_{11}$,[41] is unusual in that one carbon resides in a "less favorable" position of higher coordination.[11] The present calculations indicate that **5b** is indeed higher in energy. In the more symmetrical isomer, **5a**, where the carbons are apart and in positions of lower coordination, the energy is lower by 16.2 kcal/mol. Since both **5a** and **5b** can be isolated,[25,2642-44] they must be separated by a high rearrangement barrier. It is probable that **5b**, formed in the reaction of B_8H_{12} with acetylene, is a kinetic product. The known[11] $C_2B_7H_{11}$ cage, **5b**, may be formed in a similar reaction with the additional step of dehydrogenation (**5b** → H_2 + **3b**). The **3b** cage, like the **5b** cage, has carbons in nonsymmetrical positions and can be formed exothermically from **5b** (0.6 kcal/mol exothermic, Table 4). To investigate whether **3b** is also a kinetic product, a cage structure with a plane of symmetry was calculated for $C_2B_7H_{11}$ (**3a**). In contrast to **5a**, **3a** still has directly bonded carbon atoms. While both **5a** and **5b** have been experimental observed, only **3b** has been reported, which may be because the reaction **3b** → **3a** is less exothermic than **5b** → **5a** (0.0 and −16.2 kcal/mol, respectively) (Table 4) or because the activation barrier **3b** → **3a** is too large.

An interesting thermal disproportionation reaction of the anion of **9a** is shown in eq 1

$$2\,\mathbf{9a}^{-} \xrightarrow{\Delta} H_2 + \textit{closo}\text{-}1,2\text{-}C_2B_8H_{10} + \mathbf{9b}^{2-} \qquad (1)$$

where the driving force may be the stability of the closo

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carborane.[45] The carbons, which are adjacent in **9a**, move apart in the dianion (**9b**$^{2-}$). This rearrangement is opposite to the stability order of the neutral cages where **9a** is 29.9 kcal/mol more stable than **9b** (and 27.4 kcal/mol more stable than **9c**).

Conclusions

A systemic study has been undertaken of known nine- and ten-vertex nido and arachno heteroboranes. Structures calculated at the HF/6-31G* level are in good agreement with available X-ray data. Heats of formation of the cages have been calculated by taking the heat of formation of $B_{10}H_{14}$ as −8.6 kcal/mol and constructing near-isodesmic reactions.

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Supplementary Material Available: Tables of computer-generated coordinates (Z-matrix) are available for all species optimized at the HF/6-31G* level (22 pages). Ordering information is given on any current masthead page.

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