Electronic Supporting Information

Heats of Formation of Boron Hydride Anions and Dianions and their Ammonium Salts $[\text{B}_n\text{H}_m^y][\text{NH}_4^+]_y$ with $y = 1 - 2$

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Supporting Information: Calculated and experimental geometry parameters for B_3H_8^- , $\text{B}_{10}\text{H}_{14}$, and $\text{B}_{11}\text{H}_{14}^-$ bonds; CCSD(T) total energies, unscaled MP2 zero point energies and thermal corrections for B_5H_9 , B_3H_8^- (both isomers), $\text{B}_5\text{H}_5^{2-}$ and $\text{B}_6\text{H}_6^{2-}$; G3 and G3B3 energies and enthalpies for all species considered; heats of reaction (10) at 0 K for the H_2 release from the salts; and optimized geometries (Cartesian coordinates) at different levels of calculation.

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Table S1. Comparison between the calculated and experimental values for the bond distances (Å) and angles (degrees) for the B₃H₈⁻ isomers.

B _n H _m ^{y-}	Parameter	Calculated	Experimental
B ₃ H ₈ ^{-a}	B _{bl} -H _b	1.469	1.50
	B _{b2} -H _b	1.192	1.20
	B _{bl} -H _{r1}	1.206	1.05 - 1.20
	B _{b2} -H _{r2}	1.205	1.05 - 1.20
	B _{bl} -B _{b2}	1.787	1.77
	B _{b2} -B _{b2}	1.831	1.80
	∠(B _{bl} -H _b -B _{b2})	81.3	-
B ₃ H ₈ ⁻ (b)	B _b -H _b	1.331	
	B _b -B _b	1.723	
	B-B _b	1.858	
	B-H _{r1}	1.209	
	B-H _{r2}	1.217	
	B _b -H _{r3}	1.201	
	B _b -H _{r4}	1.203	
	∠(B _b -H _b -B _b)	80.7	

^a Experimental values from Peters, C. R.; Nordman, C. E. *J. Am. Chem. Soc.* **1960**, 82, 5758.

Table S2. Comparison between the calculated and experimental values for the bond distances (Å) and angles (degrees) for B₁₀H₁₄.

Geometry parameters	MP2(full)/6-31G(<i>d</i>)	Average from
	This work	experiment ^a
B1–B2	1.780	1.786 (0.005)
B1–B3	1.776	1.775 (0.005)
B1–B5'	1.744	1.756 (0.004)
B2–B3	1.717	1.715 (0.004)
B2–B5	1.773	1.778 (0.005)
B5–B5'	1.770	1.772 (0.006)
B4'–B1	1.978	1.973 (0.004)
B1–H1	1.189	1.183 (0.005)
B2–H2	1.188	1.177 (0.006)
B3–H3	1.188	1.182 (0.007)
B5–H5	1.191	1.192 (0.004)
B1–H6	1.317	1.298 (0.005)
B3–H6	1.332	1.337 (0.007)
B2–B1–B5'	60.4	60.3 (0.2)
B2–B1–H1	126.6	125.3 (0.3)
B3–B1–B2	57.7	57.6 (0.2)
B3–B1–B4'	116.6	116.6 (0.2)
B3–B1–H1	119.2	120.3 (0.3)
B3–B1–H6	48.3	49.1 (0.3)
B3–B1–B5'	109.2	108.8 (0.2)
B4'–B1–H1	117.1	116.9 (0.3)
B4'–B1–B5'	55.5	55.7 (0.2)
B5'–B1–H1	123.7	121.4 (0.2)
H1–B1–H6	105.3	107.1 (0.3)
B1–B2–B3	61.0	60.9 (0.2)
B1–B2–B5'	58.8	59.0 (0.2)
B1–B2–H2	124.4	124.7 (0.4)

B3–B2–H2	120.4	120.7 (0.4)
B5–B2–B5'	59.9	59.8 (0.2)
B5–B2–H2	120.3	119.9 (0.4)
B1–B3–B2	61.3	61.5 (0.3)
B1–B3–H3	126.5	126.7 (0.5)
B1–B3–B4	105.2	105.3 (0.2)
B1–B3–H6	47.6	46.7 (0.3)
B2–B3–H3	130.6	132.0 (0.4)
H3–B3–H6	107.7	107.1 (0.5)
B1'–B4–H7	91.0	90.6 (0.3)
B2–B4–H7	103.3	104.0 (0.3)
B1'–B5–B4	69.0	68.4 (0.2)
B1'–B5–H5	114.6	115.7 (0.3)
B2–B5–B4	60.8	60.6 (0.2)
B2–B5–B5'	60.1	59.9 (0.2)
B2–B5–H5	118.3	118.8 (0.3)
B5'–B5–H5	128.2	127.2 (0.2)

^a Schwoch, D.; Burg, A. B.; Beaudet, R. A. *Inorg. Chem.* **1977**, *16*, 3219. The standard deviation is shown in parenthesis.

Table S3. Comparison between the calculated and experimental values for the bond distances (Å) for B₁₁H₁₄⁺.

Geometry parameters	MP2(full)/6-31G(<i>d</i>)		Experiment ^a	
B–B distances within the cage				
B1–B8	1.777	Range	1.747 – 1.775	
B1–B10	1.740			
B2–B3	1.747			
B2–B5	1.770			
B2–B7	1.761			
B3–B8	1.762			
B5–B6	1.769			
B5–B7	1.775			
B6–B7	1.763			
B6–B9	1.772			
B6–B10	1.794			
Average	1.765			
B–B distances about the open face				
B1–B3	1.838	Range	1.875 -1.895	
B1–B9	1.946			
B3–B4	1.926			
Average	1.899			1.886 (8)
B–H distances for exo H ^b				
B1–H12	1.196	Range	0.99 – 1.16	
B2–H14	1.197			
B3–H15	1.197			
B5–H18	1.196			
B6–H19	1.196			
B7–H20	1.196			
B9–H23	1.200			
Average	1.197			1.08 (5)
B–H distances for endo H				

B9–H22	1.210		1.13
B–H distances for the bridge ^c			
B1–H13	1.349	Range	1.19 – 1.38
B3–H13	1.279		
Average	1.314		1.30 (9)

^a Getman, T. D.; Krause, J. A.; Shore, S. G. *Inorg. Chem.* **1988**, 27, 2399; McGrath, T. D.; McGrathand, A. J. *Acta Cryst. C* **1997**, 53, 229.

^b Some values seem to be the same but the difference is in the fourth digit after the point.

^c The bond angle of the bridge, B1–H13–B3, is 88.7°.

Table S4. CCSD(T) total energies, unscaled MP2 zero point energies (ZPE) and thermal corrections (TC) for B₅H₉, B₃H₈[−] (both isomers), B₅H₅^{2−} and B₆H₆^{2−}.

Dianion	Basis set				Unscaled ZPE	TC
	aVDZ	aVTZ	aVQZ	CBS		
B ₅ H ₉	-129.204525	-129.333564	-129.365283	-129.382249	67.61 ^b	3.60 ^b
B ₃ H ₈ [−]	-79.103442	-79.188597	-79.209153	-79.220096	52.48 ^c	3.57 ^c
B ₃ H ₈ [−] (1b)	-79.100930	-79.185579	-79.206041	-79.216937	52.08 ^c	3.25 ^c
B ₅ H ₅ ^{2−}	-126.696878	-126.815421	-126.845184	-126.861193	36.28 ^d	4.12 ^d
B ₆ H ₆ ^{2−}	-152.165861	-152.307616	-152.343438	-152.362738	46.67 ^d	4.04 ^d

^a Total energy values are given in Hartrees. ZPE and TC values are given in kcal/mol. ^b Harmonic vibrational frequencies and TC calculated with MP2/cc-pVTZ. ^c Harmonic vibrational frequencies and TC calculated with MP2/aVTZ. ^d Harmonic vibrational frequencies and TC calculated with MP2/aVDZ.

Table S5. Calculated G3 and G3B3 energies for $B_nH_m^{y-}$ species and related compounds and atoms.

Species	G3: E(0 K)	G3: H(298 K)	G3B3: E(0 K)	G3B3: H(298 K)
$B_5H_5^{2-}$	-127.020244	-127.013566	-127.022473	-127.016003
$B_6H_6^{2-}$	-152.547662	-152.541019	-152.551201	-152.544662
$B_7H_7^{2-}$	-178.005785	-177.998428	-178.009408	-177.002213
$B_8H_8^{2-}$	-203.456094	-203.447745	-203.459792	-203.451668
$B_9H_9^{2-}$	-228.931513	-228.922418	-228.935743	-228.926933
$B_{10}H_{10}^{2-}$	-254.430250	-254.421242	-254.434850	-254.426125
$B_{11}H_{11}^{2-}$	-279.870484	-279.860337	-279.875899	-279.865982
$B_{12}H_{12}^{2-}$	-305.428755	-305.419200	-305.434521	-305.425228
$B_3H_8^-$	-79.273505	-79.273936	-79.267700	-79.267916
$B_3H_8^-$ (1b)	-79.269477	-79.27127	-79.263387	-79.265912
$B_{11}H_{14}^-$	-281.689426	-281.694554	-281.679001	-281.684339
B_3H_7	-78.599909	-78.601285	-78.594435	-78.595836
B_5H_9	-129.493063	-129.494791	-129.486867	-129.48877
$B_{10}H_{14}$	-256.709672	-256.714653	-256.699759	-256.704865
BH_3	-26.567524	-26.567898	-26.563683	-26.564059
BH_4^-	-27.211922	-27.212258	-27.208030	-27.208365
H_2	-1.167379	-1.167471	-1.164074	-1.164166
B	-24.642568	-24.640208	-24.643219	-24.640859
H	-0.501003	-0.498642	-0.501087	-0.498726

Table S6. Calculated heats of reaction (10) at 0 K for the H₂ release from the salts.^a

Reaction	G3(0 K)	G3B3(0 K)
$[\text{B}_3\text{H}_8^-][\text{NH}_4^+](\text{s}) \rightarrow 6\text{H}_2 + \text{BN}(\text{s}) + 2\text{B}(\text{s})$ ^b	-60.0b	-60.4
$[\text{B}_{11}\text{H}_{14}^-][\text{NH}_4^+](\text{s}) \rightarrow 8\text{H}_2 + \text{BN}(\text{s}) + 10\text{B}(\text{s})$	-52.9	-51.7
$[\text{B}_5\text{H}_5^{2-}][\text{NH}_4^+]_2(\text{s}) \rightarrow {}^{13}/_2\text{H}_2 + 2\text{BN}(\text{s}) + 3\text{B}(\text{s})$ ^c	-173.7d	-173.1
$[\text{B}_6\text{H}_6^{2-}][\text{NH}_4^+]_2(\text{s}) \rightarrow 7\text{H}_2 + 2\text{BN}(\text{s}) + 4\text{B}(\text{s})$ ^d	-124.6e	-123.3
$[\text{B}_7\text{H}_7^{2-}][\text{NH}_4^+]_2(\text{s}) \rightarrow {}^{15}/_2\text{H}_2 + 2\text{BN}(\text{s}) + 5\text{B}(\text{s})$	-127.8	-126.7
$[\text{B}_8\text{H}_8^{2-}][\text{NH}_4^+]_2(\text{s}) \rightarrow 8\text{H}_2 + 2\text{BN}(\text{s}) + 6\text{B}(\text{s})$	-133.3	-132.3
$[\text{B}_9\text{H}_9^{2-}][\text{NH}_4^+]_2(\text{s}) \rightarrow {}^{17}/_2\text{H}_2 + 2\text{BN}(\text{s}) + 7\text{B}(\text{s})$	-118.9	-117.7
$[\text{B}_{10}\text{H}_{10}^{2-}][\text{NH}_4^+]_2(\text{s}) \rightarrow 9\text{H}_2 + 2\text{BN}(\text{s}) + 8\text{B}(\text{s})$	-91.4	-90.2
$[\text{B}_{11}\text{H}_{11}^{2-}][\text{NH}_4^+]_2(\text{s}) \rightarrow {}^{19}/_2\text{H}_2 + 2\text{BN}(\text{s}) + 9\text{B}(\text{s})$	-99.5	-98.0
$[\text{B}_{12}\text{H}_{12}^{2-}][\text{NH}_4^+]_2(\text{s}) \rightarrow 10\text{H}_2 + 2\text{BN}(\text{s}) + 10\text{B}(\text{s})$	-29.7	-28.1

^a The heats of formation of H₂ and B are 0 kcal/mol as they are the form of the element. The heat of formation of BN (crystal) was taken from Chase, M. W. Jr. *NIST-JANAF Tables*, 4th ed., *J. Phys. Chem. Ref. Data* **1998**, Monograph 9 (Suppl. 1): -59.27 ± 0.4 kcal/mol at 0 K. ^b CCSD(T)/CBS -60.1 at 0 K. ^c CCSD(T)/CBS -175.7 at 0 K. ^d CCSD(T)/CBS -126.1 at 0 K.

Table S7. Optimized geometries of $B_nH_m^{y-}$ species given in Cartesian coordinates (Å).

B₅H₉, MP2/cc-pVTZ, C_{4v} symmetry

B	0.000000	1.265945	-0.143216
B	-1.265945	0.000000	-0.143216
B	0.000000	-1.265945	-0.143216
B	0.000000	0.000000	0.985159
B	1.265945	0.000000	-0.143216
H	0.000000	2.438848	-0.014049
H	0.000000	-2.438848	-0.014049
H	-2.438848	0.000000	-0.014049
H	2.438848	0.000000	-0.014049
H	0.940665	0.940665	-1.041889
H	0.940665	-0.940665	-1.041889
H	-0.940665	-0.940665	-1.041889
H	-0.940665	0.940665	-1.041889
H	0.000000	0.000000	2.162273

B₁₀H₁₄, MP2(full)/6-31G(d), C_{2v} symmetry

B	0.000000	1.784406	-0.977210
B	0.000000	1.490292	0.714212
B	1.410726	0.988944	-0.249074
B	-1.410726	0.988944	-0.249074
B	0.884859	0.000000	1.088239
B	-0.884859	0.000000	1.088239
B	0.000000	-1.490292	0.714212
B	1.410726	-0.988944	-0.249074
B	-1.410726	-0.988944	-0.249074
B	0.000000	-1.784406	-0.977210
H	0.000000	2.804833	-1.584596
H	0.957796	1.011558	-1.485927
H	-0.957796	1.011558	-1.485927
H	2.467757	1.530921	-0.292625
H	-2.467757	1.530921	-0.292625
H	0.000000	2.396122	1.482136
H	0.000000	-2.804833	-1.584596
H	0.000000	-2.396122	1.482136
H	0.957796	-1.011558	-1.485927
H	-2.467757	-1.530921	-0.292625
H	-1.621628	0.000000	2.024100
H	1.621628	0.000000	2.024100
H	-0.957796	-1.011558	-1.485927
H	2.467757	-1.530921	-0.292625

B₃H₈⁻, MP2/aug-cc-pVTZ, C_{2v} symmetry

H	1.027973	1.316778	-1.023324
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H	-1.027973	1.316778	-1.023324
H	1.027973	-1.316778	-1.023324
H	-1.027973	-1.316778	-1.023324
H	-1.019001	0.000000	1.640158
H	1.019001	0.000000	1.640158
H	0.000000	-1.419817	0.617339
H	0.000000	1.419817	0.617339
B	0.000000	0.000000	0.994762
B	0.000000	-0.915679	-0.539551
B	0.000000	0.915679	-0.539551

B₃H₈⁻ (1b), MP2/aug-cc-pVTZ, *C_s* symmetry

H	1.026647	-0.903283	1.377298
H	1.026647	-0.903283	-1.377298
H	-1.102188	1.595542	0.000000
H	0.660594	1.408584	0.971522
H	0.660594	1.408584	-0.971522
H	-0.292241	-1.522177	0.000000
B	-0.001540	-0.550758	0.861448
B	-0.001540	-0.550758	-0.861448
B	-0.001540	1.095664	0.000000
H	-0.978477	-0.527354	1.560473
H	-0.978477	-0.527354	-1.560473

B₁₁H₁₄⁻, MP2(full)/6-31G(*d*), *C_s* symmetry

B	-0.784740	-0.533406	1.535177
B	1.612269	-0.115380	0.000000
B	0.779068	-1.311421	0.962865
B	0.779068	-1.311421	-0.962865
B	0.737530	0.379028	-1.457733
B	-0.784740	1.085474	-0.897176
B	0.701675	1.391418	0.000000
B	0.737530	0.379028	1.457733
B	-1.856986	-0.002848	0.000000
B	-0.784740	1.085474	0.897176
B	-0.784740	-0.533406	-1.535177
H	-1.334071	-0.856145	2.547143
H	-0.437116	-1.706843	0.967486
H	2.805853	-0.206937	0.000000
H	1.366054	-2.143593	1.591507
H	1.366054	-2.143593	-1.591507
H	-0.437116	-1.706843	-0.967486
H	1.296192	0.763321	-2.442543
H	-1.335102	1.952623	-1.510439
H	1.215289	2.471604	0.000000
H	1.296192	0.763321	2.442543

H	-1.890331	-1.212294	0.000000
H	-2.998703	0.366207	0.000000
H	-1.335102	1.952623	1.510439
H	-1.334071	-0.856145	-2.547143

B₅H₅²⁻, MP2/aug-cc-pVTZ, *D*_{3h} symmetry

B	0.000000	1.046786	0.000000
B	0.000000	0.000000	1.326893
B	0.000000	0.000000	-1.326893
B	0.906544	-0.523393	0.000000
B	-0.906544	-0.523393	0.000000
H	0.000000	2.258181	0.000000
H	0.000000	0.000000	2.529649
H	0.000000	0.000000	-2.529649
H	1.955642	-1.129091	0.000000
H	-1.955642	-1.129091	0.000000

B₆H₆²⁻, MP2/aug-cc-pVTZ, *O*_h symmetry

B	0.000000	0.000000	1.233228
B	0.000000	1.233228	0.000000
B	1.233228	0.000000	0.000000
B	0.000000	-1.233228	0.000000
B	-1.233228	0.000000	0.000000
B	0.000000	0.000000	-1.233228
H	0.000000	0.000000	2.443994
H	0.000000	2.443994	0.000000
H	2.443994	0.000000	0.000000
H	0.000000	-2.443994	0.000000
H	-2.443994	0.000000	0.000000
H	0.000000	0.000000	-2.443994

B₇H₇²⁻, MP2(full)/6-31G(*d*), *D*_{5h} symmetry

B	0.000000	0.000000	1.153093
B	1.404721	0.000000	0.000000
B	0.434083	-1.335969	0.000000
B	-1.136443	-0.825674	0.000000
B	-1.136443	0.825674	0.000000
B	0.434083	1.335969	0.000000
B	0.000000	0.000000	-1.153093
H	0.000000	0.000000	2.373373
H	2.620840	0.000000	0.000000
H	0.809884	-2.492567	0.000000
H	-2.120304	-1.540491	0.000000
H	-2.120304	1.540491	0.000000
H	0.809884	2.492567	0.000000
H	0.000000	0.000000	-2.373373

B₈H₈²⁻, MP2(full)/6-31G(d), *D*_{2d} symmetry

B	0.000000	1.258285	0.316462
B	0.000000	-1.258285	0.316462
B	1.258285	0.000000	-0.316462
B	-1.258285	0.000000	-0.316462
B	0.000000	0.805282	-1.331894
B	0.000000	-0.805282	-1.331894
B	0.805282	0.000000	1.331894
B	-0.805282	0.000000	1.331894
H	0.000000	1.601377	-2.246220
H	0.000000	-1.601377	-2.246220
H	1.601377	0.000000	2.246220
H	-1.601377	0.000000	2.246220
H	0.000000	2.439065	0.614714
H	0.000000	-2.439065	0.614714
H	2.439065	0.000000	-0.614714
H	-2.439065	0.000000	-0.614714

B₉H₉²⁻, MP2(full)/6-31G(d), *D*_{3h} symmetry

B	-0.981065	0.566418	0.892762
B	-0.981065	0.566418	-0.892762
B	0.000000	1.637875	0.000000
B	-1.418442	-0.818938	0.000000
B	0.981065	0.566418	-0.892762
B	0.000000	-1.132836	-0.892762
B	0.000000	-1.132836	0.892762
B	0.981065	0.566418	0.892762
B	1.418442	-0.818938	0.000000
H	-1.713759	0.989439	1.761456
H	-1.713759	0.989439	-1.761456
H	0.000000	2.845237	0.000000
H	-2.464048	-1.422619	0.000000
H	1.713759	0.989439	-1.761456
H	0.000000	-1.978878	-1.761456
H	0.000000	-1.978878	1.761456
H	1.713759	0.989439	1.761456
H	2.464048	-1.422619	0.000000

B₁₀H₁₀²⁻, MP2(full)/6-31G(d), *D*_{4d} symmetry

B	0.000000	0.000000	1.859687
B	0.000000	1.291637	0.757708
B	1.291637	0.000000	0.757708
B	0.000000	-1.291637	0.757708
B	-1.291637	0.000000	0.757708
B	0.913326	0.913326	-0.757708

B	0.913326	-0.913326	-0.757708
B	-0.913326	-0.913326	-0.757708
B	-0.913326	0.913326	-0.757708
B	0.000000	0.000000	-1.859687
H	0.000000	0.000000	3.064535
H	0.000000	0.000000	-3.064535
H	0.000000	2.433285	1.157368
H	2.433285	0.000000	1.157368
H	0.000000	-2.433285	1.157368
H	-2.433285	0.000000	1.157368
H	1.720592	1.720592	-1.157368
H	1.720592	-1.720592	-1.157368
H	-1.720592	-1.720592	-1.157368
H	-1.720592	1.720592	-1.157368

B₁₁H₁₁²⁻, MP2(full)/6-31G(d), C_{2v} symmetry

B	0.000000	0.000000	1.402801
B	0.000000	1.481165	-0.829066
B	0.000000	-1.481165	-0.829066
B	0.904419	0.000000	-1.225693
B	-0.904419	0.000000	-1.225693
B	0.000000	1.669462	0.909184
B	0.000000	-1.669462	0.909184
B	1.326560	0.924729	0.230360
B	-1.326560	0.924729	0.230360
B	-1.326560	-0.924729	0.230360
B	1.326560	-0.924729	0.230360
H	0.000000	2.427115	-1.581632
H	0.000000	-2.427115	-1.581632
H	1.622879	0.000000	-2.196412
H	-1.622879	0.000000	-2.196412
H	0.000000	2.640722	1.622303
H	0.000000	-2.640722	1.622303
H	2.445337	1.356755	0.383561
H	-2.445337	1.356755	0.383561
H	-2.445337	-1.356755	0.383561
H	2.445337	-1.356755	0.383561
H	0.000000	0.000000	2.611781

B₁₂H₁₂²⁻, MP2(full)/6-31G(d), I_h (C_{2h}) symmetry

B	0.000000	0.000000	1.690434
B	0.000000	0.000000	-1.690434
B	0.888714	-1.223210	0.755985
B	-0.888714	-1.223210	0.755985
B	-1.437969	0.467225	0.755985
B	0.000000	1.511970	0.755985

B	1.437969	0.467225	0.755985
B	1.437969	-0.467225	-0.755985
B	0.888714	1.223210	-0.755985
B	-0.888714	1.223210	-0.755985
B	-1.437969	-0.467225	-0.755985
B	0.000000	-1.511970	-0.755985
H	0.000000	0.000000	2.897367
H	0.000000	0.000000	-2.897367
H	1.523236	-2.096554	1.295742
H	-1.523236	-2.096554	1.295742
H	-2.464647	0.800812	1.295742
H	0.000000	2.591484	1.295742
H	2.464647	0.800812	1.295742
H	2.464647	-0.800812	-1.295742
H	1.523236	2.096554	-1.295742
H	-1.523236	2.096554	-1.295742
H	-2.464647	-0.800812	-1.295742
H	0.000000	-2.591484	-1.295742