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SUPPLEMENTARY INFORMATION

Boron-Based $Be_2B_5^{+/0/-}$ Alloy Clusters: Inverse Sandwiches with a Pentagonal Boron Ring and Reduction-Induced Structural Transformation to Molecular Wheel

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Table S1. Cartesian coordinates for the global-minimum (GM) structures of $Be_2B_5^{+/0/-}$ clusters at the PBE0/6-311+G* level.

Figure S1. Alternative optimized low-lying structures of cationic $Be_2B_5^+$ cluster. Relative energies are shown in square brackets at the PBE0/6-311+G* level with corrections for zero-point energies (ZPEs). Also shown are relative energies for top five isomers at the single-point CCSD(T)/6-311+G*//PBE0/6-311+G* level, including the ZPE corrections at PBE0. All energies are in eV. For the CCSD(T) calculations, all T1 diagnostic values are 0.020–0.028, which are normal relative to the recommended threshold value (~0.02).

Figure S2. Same as Figure S1, except for neutral Be_2B_5 cluster. For the single-point CCSD(T) calculations, the T1 diagnostic values of the 3rd and 4th isomers (marked with an asterisk) are 0.053 and 0.048, respectively, which are abnormal with respect to the recommended threshold value (~0.02). Nevertheless, all CCSD(T) energies appear to be closely consistent with those at PBE0. We consider that the CCSD(T) data are valid for this system.

Figure S3. Same as Figure S1, except for anion $Be_2B_5^-$ cluster. For the single-point CCSD(T) calculations, the T1 diagnostic value of the 5th isomer (marked with an asterisk) amounts to 0.056, which is abnormal relative to the recommended threshold value (~0.02), generating a relative energy that is highly inconsistent with the PBE0 trend. This specific CCSD(T) number should not be trusted. In contrast, the T1 values of the 1st to 4th isomers are normal. Overall, the 1st isomer is tentatively assigned to be the lowest in energy, according to the CCSD(T) calculations.

Figure S4. Calculated Wiberg bond indices (WBIs; in black color) and natural atomic charges (in |e|; red color) from natural bond orbital (NBO) analyses at the PBE0/6-311G* level. (a) Cationic $Be_2B_5^+$ (**1**, D_{5h}, $^1A_1'$) cluster. (b) Neutral Be_2B_5 (**2**, C_{2v}, $^2A_1$) cluster. (c) Anion $Be_2B_5^-$ (**3**, C_s, $^1A'$) cluster.

Figure S5. The pictures for occupied canonical molecular orbitals (CMOs) of neutral Be_2B_5 (**2**, C_{2v}, $^2A_1$) cluster, which differs from cationic $Be_2B_5^+$ (**1**, D_{5h}, $^1A_1'$) cluster by one more electron in the singly occupied molecular orbital (SOMO). (a) Five σ CMOs for peripheral two-center two-electron (2c-2e) B–B σ single bonds. (b) The π sextet. (c) Two delocalized σ CMOs within the B_5 ring.

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(a) $Be_2B_5^+$ (**1**, D_{5h}, $^1A_1'$)

B	0.00000000	1.34052500	0.00000000
B	1.27491500	0.41424500	0.00000000
B	0.78794100	-1.08450700	0.00000000
B	-0.78794100	-1.08450700	0.00000000
B	-1.27491500	0.41424500	0.00000000
Be	0.00000000	0.00000000	1.33493100
Be	0.00000000	0.00000000	-1.33493100

(b) Be_2B_5 (**2**, C_{2v}, $^2A_1$)

B	0.00000000	1.17658600	0.41172700
B	0.00000000	0.00000000	1.52238000
B	0.00000000	-1.17658600	0.41172700
B	0.00000000	-0.77787800	-1.14899000
B	0.00000000	0.77787800	-1.14899000
Be	-1.29067200	0.00000000	-0.02990900
Be	1.29067200	0.00000000	-0.02990900

(c) $Be_2B_5^-$ (**3**, C_s, $^1A'$)

B	-0.24075000	0.04496200	0.00000000
B	0.05706300	-1.58844100	0.00000000

B	0.03584700	-0.85763900	1.41800300
B	0.05463800	1.76913300	0.00000000
B	0.03584700	-0.85763900	-1.41800300
Be	0.03584700	0.93101600	-1.62738100
Be	0.03584700	0.93101600	1.62738100

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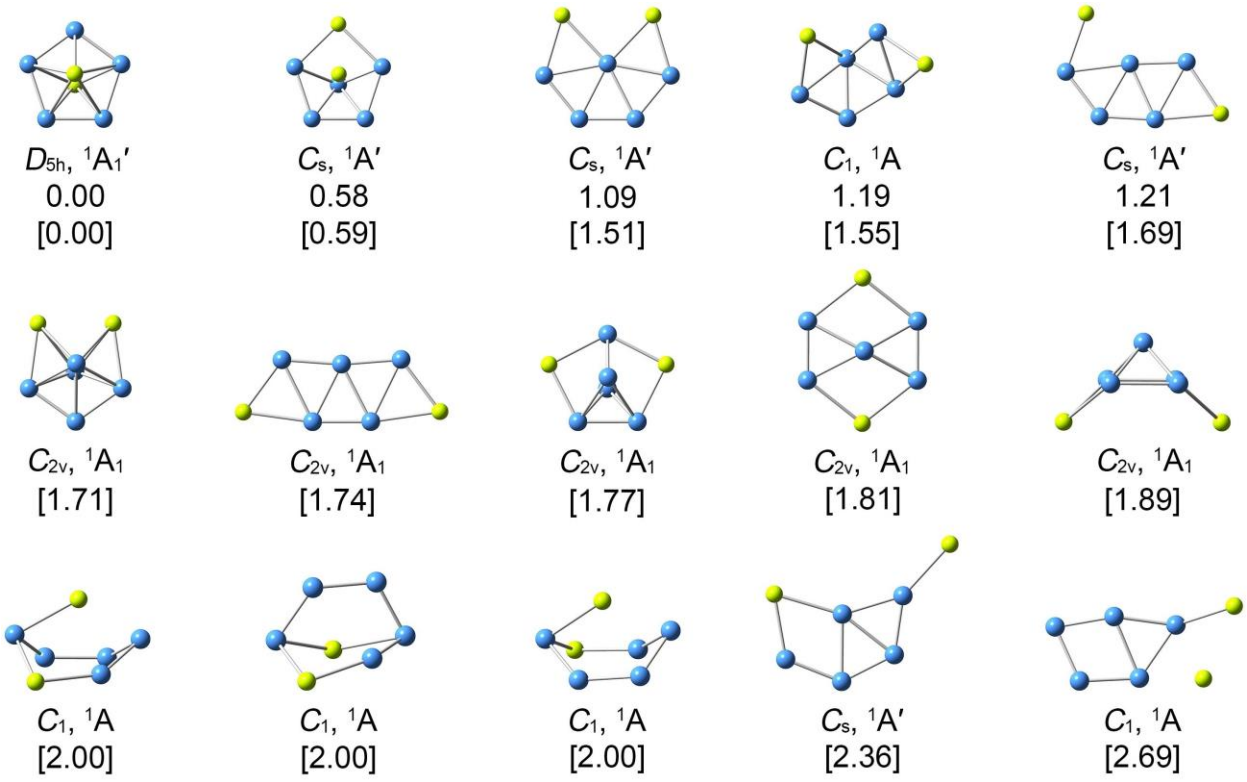

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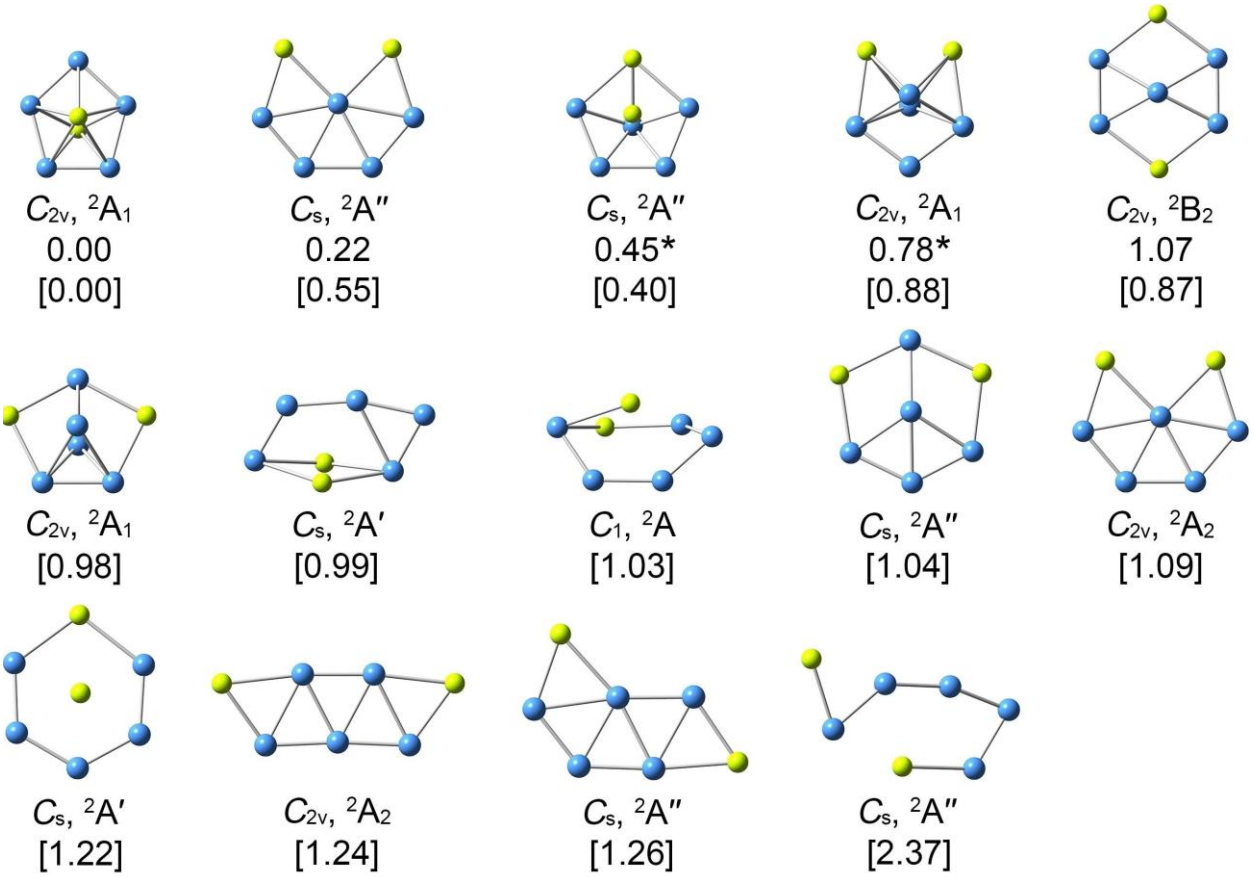

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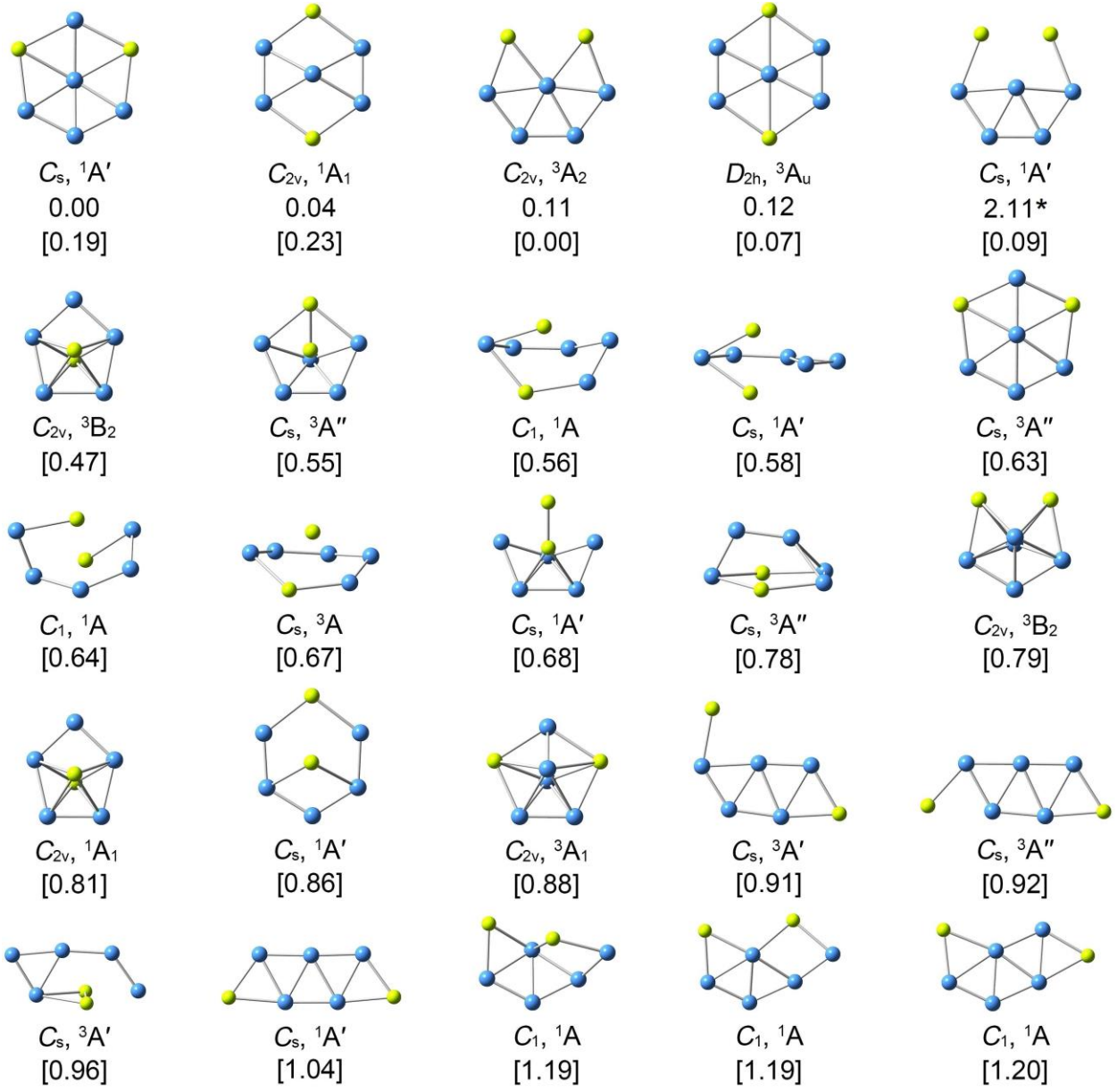

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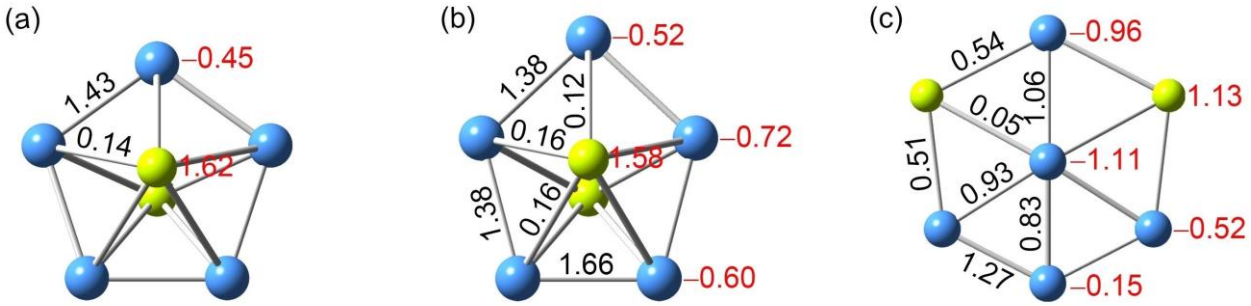

1 $Be_2B_5^+$ (D_{5h}, $^1A_1'$) **2** Be_2B_5 (C_{2v}, $^2A_1$) **3** $Be_2B_5^-$ (C_s, $^1A'$)

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