SUPPLEMENTARY INFORMATION

The structure and chemical bonding in the inverse sandwich B_6Ca_2 and B_8Ca_2 clusters: conflicting aromaticity vs. double aromaticity†

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Supplementary Information

Table S1. Cartesian coordinates for global-minimum (GM) structures of (a) (D_{2h}, ^1A_g) B_6Ca_2 and (b) (D_{8h}, $^1A_{1g}$) B_8Ca_2 clusters at the PBE0/6-311+G* level.

Figure S1. Alternative optimized structures of B_6Ca_2 cluster at the PBE0/6-311+G* level. Relative energies are shown in eV at PBE0 level with corrections for zero-point energy (ZPE), as well as for top two isomers (in square bracket) at the single-point CCSD(T)/6-311+G*//PBE0/6-311+G* level.

Figure S2. Alternative optimized structures of B_8Ca_2 cluster at the PBE0/6-311+G* level. Relative energies are shown in eV at PBE0 level with corrections for zero-point energy (ZPE), as well as for top four isomers (in square bracket) at the single-point CCSD(T)/6-311+G*//PBE0/6-311+G* level.

Figure S3. Canonical molecular orbitals (CMOs) of B_8Ca_2 (D_{8h}, $^1A_{1g}$). The CMOs are sorted into three subsets: (a) eight σ CMOs for eight two-center two-electron (2c-2e)

Lewis B–B σ single bonds in B_8 ring; (b) three globally delocalized CMOs for the σ framework in B_8 ring; and (c) three globally delocalized CMOs for π framework in B_8 ring.

Figure S4. Canonical molecular orbitals (CMOs) of the competitor (C_s, ^{1}A') of B_8Ca_2. The CMOs are sorted into four subsets: (a) seven σ CMOs for seven two-center two-electron (2c-2e) Lewis B–B σ single bonds in the periphery of B_8 wheel; (b) two globally delocalized CMOs for σ framework in B_8 wheel; (c) three globally delocalized CMOs for π framework in B_8 wheel; and (d) one σ CMOs in Ca_2 dimer, as well as the LUMO.

Figure S5. Chemical bonding pattern for the competitor (C_s, ^{1}A') of B_8Ca_2 cluster on the basis of AdNDP analysis. Occupation numbers (ONs) are indicated.

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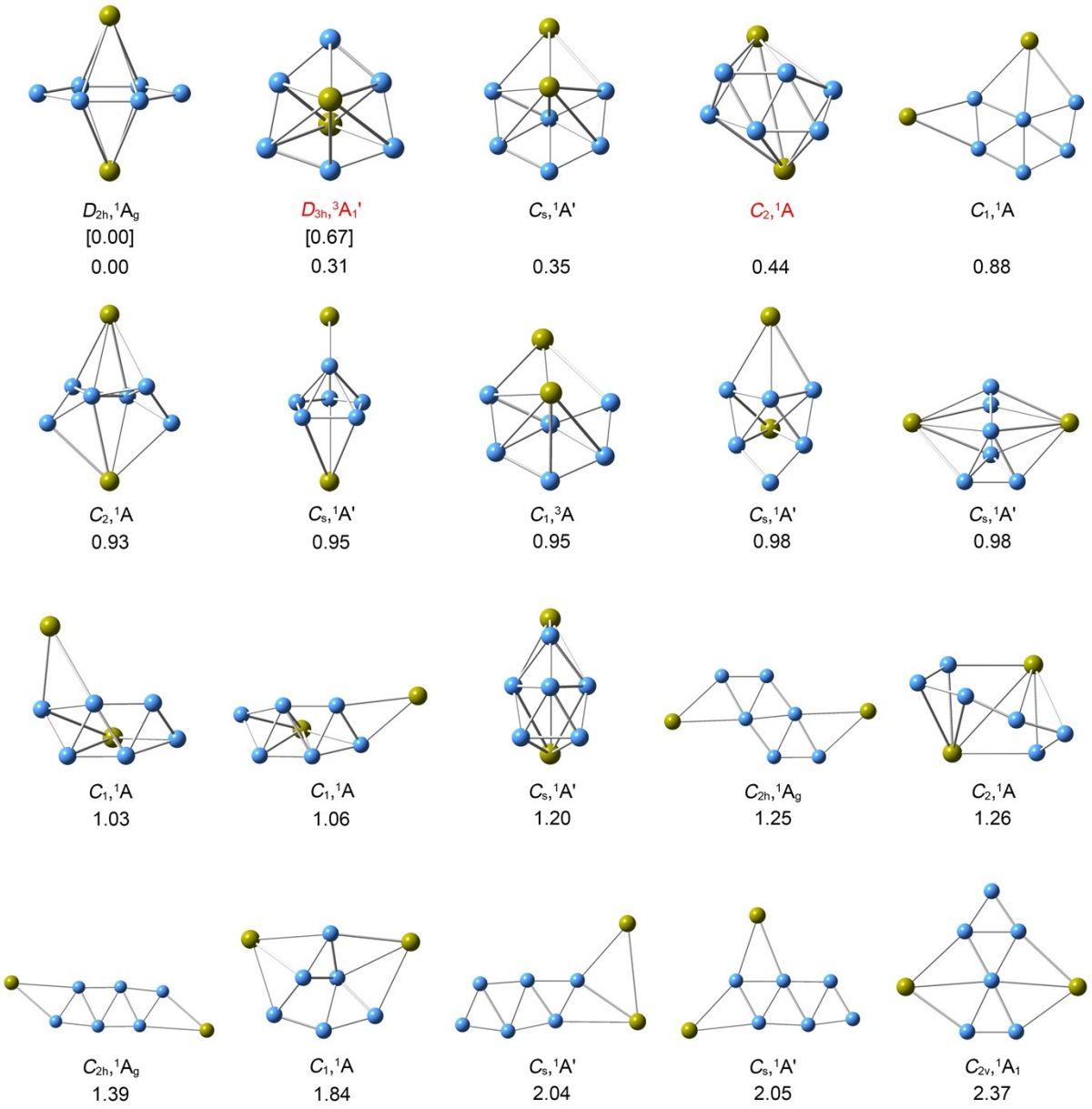

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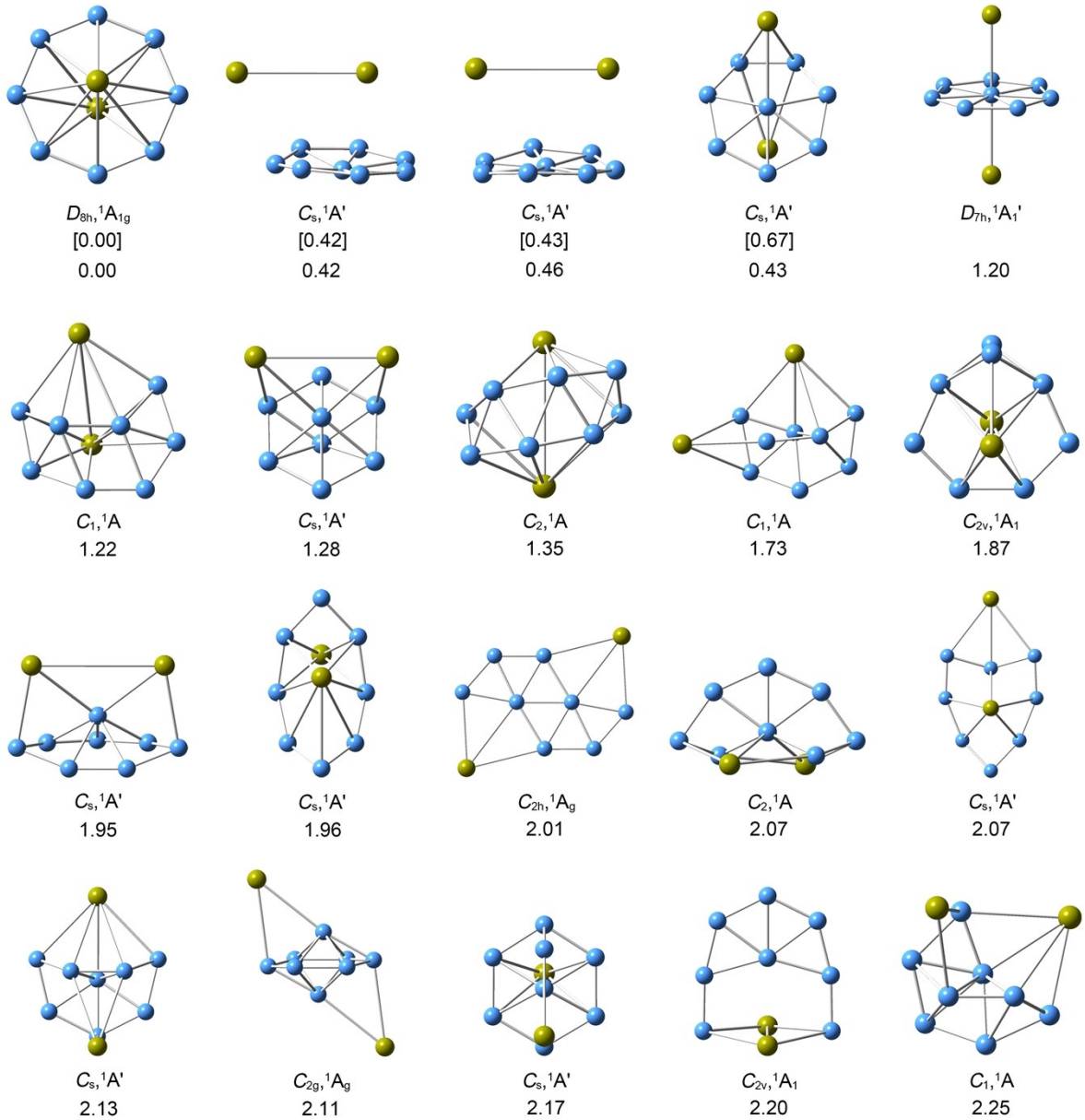

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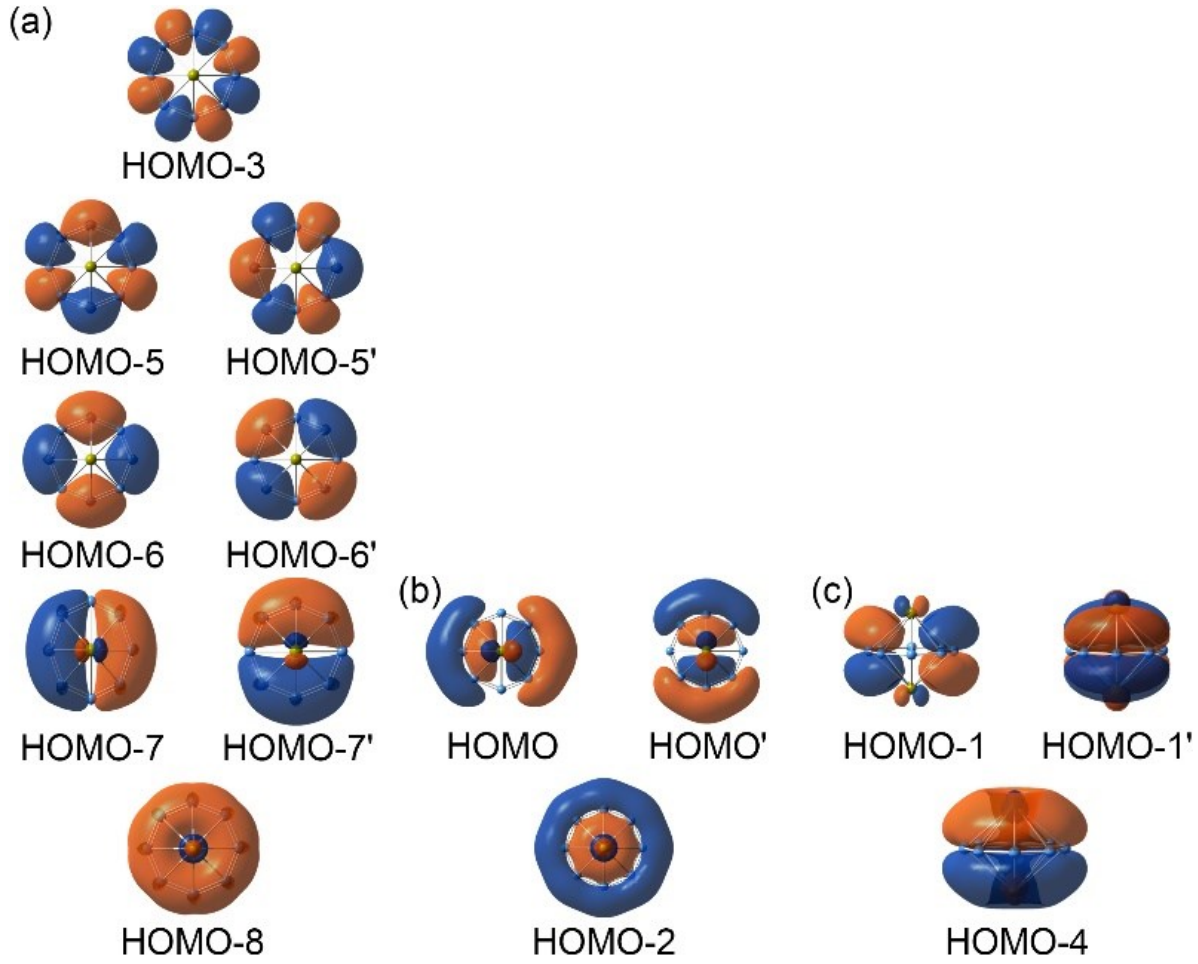

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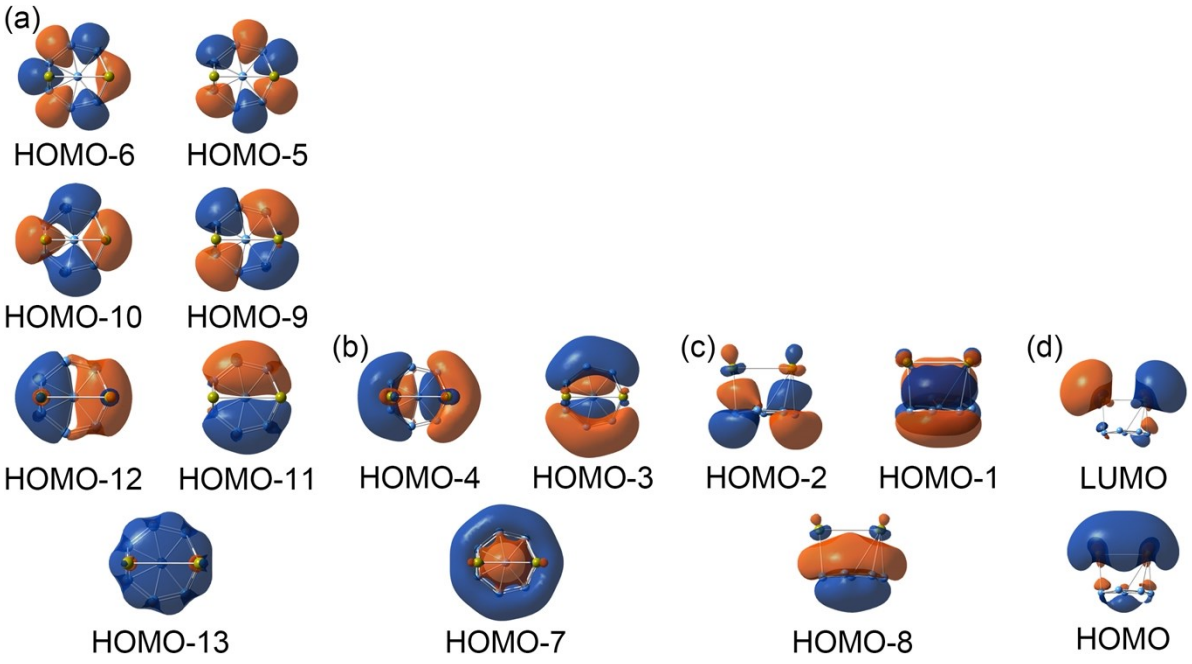
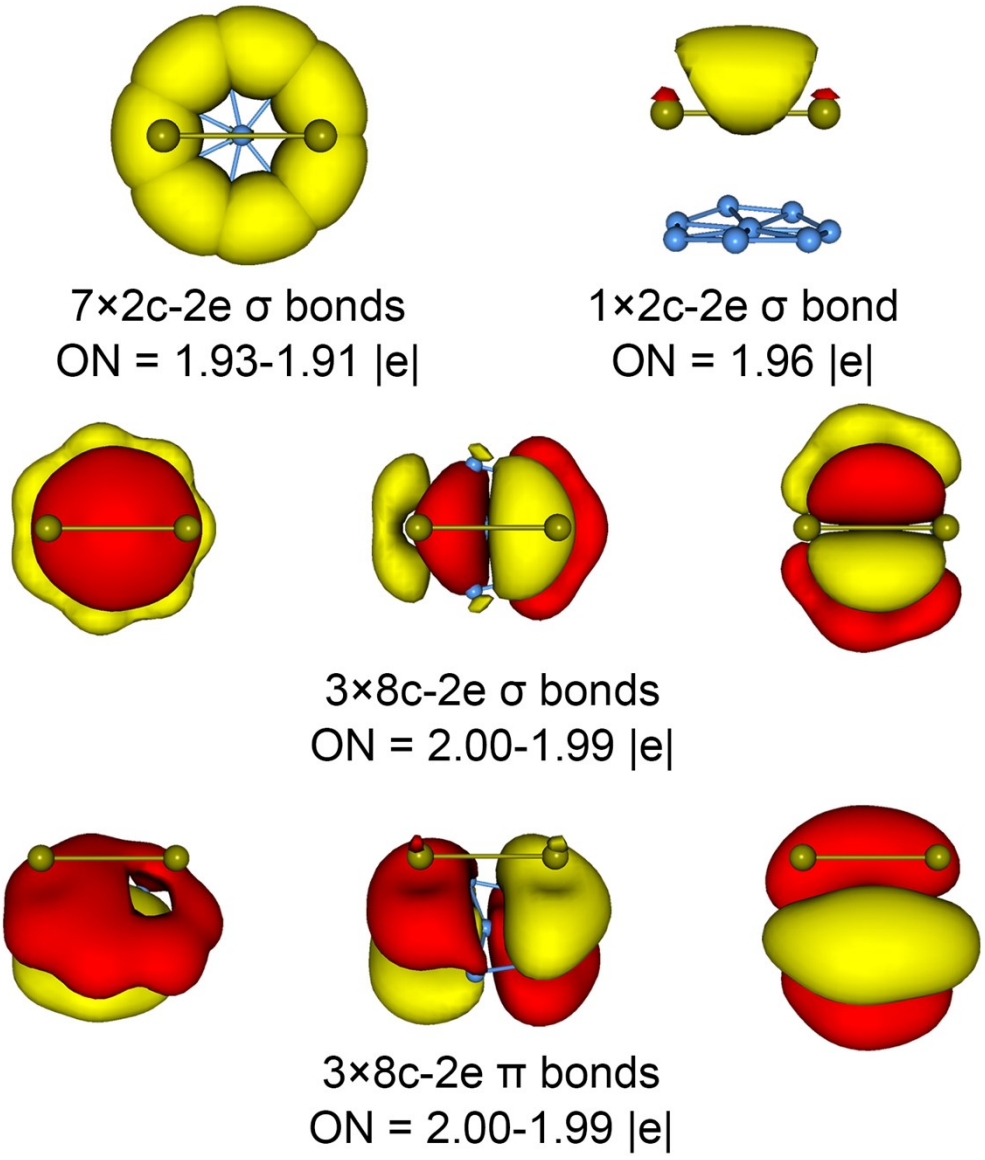


Figure S5. Chemical bonding pattern for the third isomer (C_s, ^{1}A') of B_8Ca_2 cluster on the basis of AdNDP analysis. ONs are indicated.



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(a) B_6Ca_2 GM (D_{2h}, ^1A_g)

B	0.00000000	1.93579800	0.00000000
B	0.00000000	-0.80223400	1.05404300
B	-0.00000000	0.80223400	1.05404300
B	0.00000000	0.80223400	-1.05404300
B	-0.00000000	-0.80223400	-1.05404300
B	0.00000000	-1.93579800	0.00000000
Ca	-2.12915100	0.00000000	-0.00000000
Ca	2.12915100	0.00000000	-0.00000000

(b) B_8Ca_2 GM (D_{8h}, $^1A_{1g}$)

B	0.00000000	2.02311700	0.00000000
B	1.43056000	1.43056000	0.00000000
B	0.00000000	-2.02311700	0.00000000
B	-1.43056000	1.43056000	0.00000000
B	-1.43056000	-1.43056000	0.00000000
B	1.43056000	-1.43056000	0.00000000
B	-2.02311700	0.00000000	0.00000000
B	2.02311700	0.00000000	0.00000000
Ca	0.00000000	0.00000000	1.78402600
Ca	0.00000000	0.00000000	-1.78402600