

SUPPLEMENTARY INFORMATION

Chemical bonding and dynamic structural fluxionality of a boron-based Al_2B_8 binary cluster: The robustness of a doubly $6\pi/6\sigma$ aromatic $[\text{B}_8]^{2-}$ molecular wheel

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Supplementary Information – Part I

- Table S1.** Cartesian coordinates for optimized global-minimum (GM) and transition-state (TS) structures of Al_2B_8 cluster at the PBE0/6-311+G(d) level.
- Table S2.** Orbital composition analysis for occupied canonical molecular orbitals (CMOs) of GM C_{2v} (1A_1) Al_2B_8 cluster. Main components are highlighted in **bold**.
- Table S3.** Orbital composition analysis for occupied CMOs of TS Al_2B_8 cluster. Main components are highlighted in **bold**.
- Figure S1.** Alternative optimized structures for Al_2B_8 cluster at the PBE0/6-311+G(d) level including zero-point energy (ZPE) corrections, along with their relative energies

(in parentheses). Relative energies are also presented for top 5 lowest-energy isomers at the single-point CCSD(T)/6-311+G(d)//PBE0/6-311+G(d), B3LYP/6-311+G(d) (in square brackets, with ZPE corrections), and single-point CCSD(T)/6-311+G(d)//B3LYP/6-311+G(d) (in curly brackets) levels of theory. All energies are shown in kcal mol⁻¹.

- Figure S2.** Displacement vectors of the vibrational modes of (a) GM and (b) TS structures of the Al₂B₈ cluster.
- Figure S3.** Canonical molecular orbitals (CMOs) of the TS structure of Al₂B₈ cluster. (a) Two CMOs for lone pairs of two Al atoms. (b) Seven CMOs for Lewis-type B–B σ single bonds along peripheral B ring. (c) Three delocalized π CMOs. (d) Three delocalized σ CMOs.
- Figure S4.** AdNDP bonding scheme for TS C_{2v} (¹A₁) Al₂B₈ cluster. Occupation numbers (ONs) are shown.

Supplementary Information – Part II

A short movie extracted from the BOMD simulation for Al₂B₈ cluster. The simulation has been performed at near room temperature (300 K) for 50 ps. The movie roughly covers a time span of 10 ps.

Table S1. Cartesian coordinates for optimized global-minimum (GM) and transition-state (TS) structures of Al₂B₈ cluster at the PBE0/6-311+G(d) level.

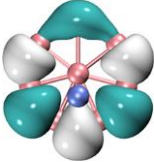
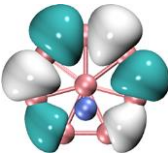
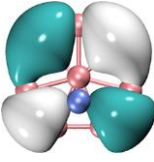
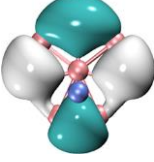
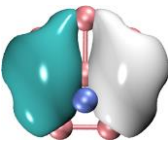
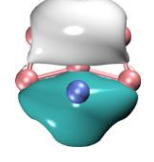
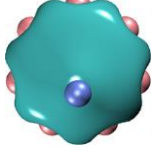
GM (C_{2v}, ¹A₁)

B	0.00000000	0.77365900	-1.3115190
B	0.00000000	-0.7736590	-1.3115190
B	0.00000000	-1.7351360	-0.1015070
B	0.00000000	-1.3984640	1.41124100
B	0.00000000	0.00000000	2.09071600
B	0.00000000	1.39846400	1.41124100
B	0.00000000	1.73513600	-0.1015070
B	0.00000000	0.00000000	0.35217600
Al	2.27614600	0.00000000	-0.4691000
Al	-2.2761460	0.00000000	-0.4691000

TS (C_{2v}, ¹A₁)

B	0.00000000	1.39054600	0.81527500
B	0.00000000	0.00000000	1.49187400
B	0.00000000	-1.3905460	0.81527500
B	0.00000000	-1.7393120	-0.6917170
B	0.00000000	-0.7779250	-1.9107880
B	0.00000000	0.77792500	-1.9107880
B	0.00000000	1.73931200	-0.6917170
B	0.00000000	0.00000000	-0.3515560
Al	-2.2763240	0.00000000	0.46810400
Al	2.27632400	0.00000000	0.46810400

Table S2. Orbital composition analysis for occupied canonical molecular orbitals (CMOs) of GM C_{2v} (1A_1) Al_2B_8 cluster. Main components are highlighted in **bold**.

Subsystem	CMO	B_8 (%)		Al_2 (%)	
		s	p	s	p
B–B 2c-2e σ	 HOMO-6	7.5	91.3	0.0	0.0
	 HOMO-7	7.7	90.7	0.0	0.0
	 HOMO-9	34.6	63.3	0.0	0.2
	 HOMO-10	34.3	63.3	0.3	0.2
	 HOMO-12	33.8	62.9	0.0	0.1
	 HOMO-13	33.8	61.9	0.4	0.2
	 HOMO-14	60.5	31.9	0.8	0.9

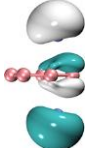
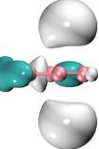
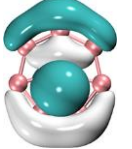
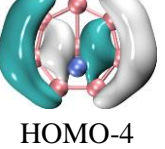
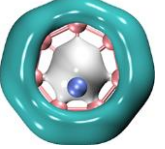
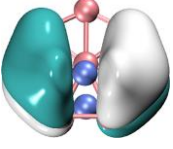
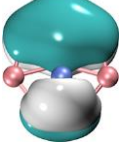
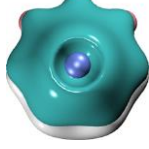
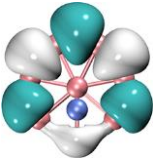
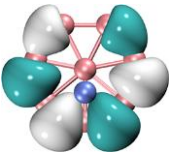
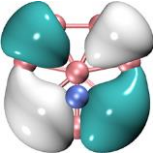
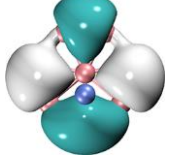
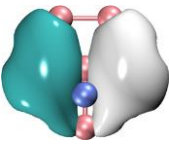
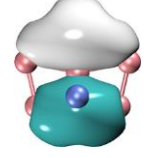
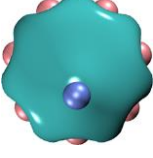
two lone pairs	 HOMO	0.0	20.2	63.8	13.8
	 HOMO-5	9.4	25.7	61.7	1.0
6σ aromaticity	 HOMO-2	17.5	46.0	30.5	2.9
	 HOMO-4	23.5	71.7	0.0	1.7
	 HOMO-8	53.4	42.3	2.2	0.6
6π aromaticity	 HOMO-1	0.0	90.2	0.0	7.5
	 HOMO-3	0.0	83.4	11.3	3.7
	 HOMO-11	0.0	81.9	14.4	0.4

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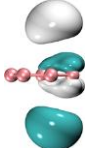
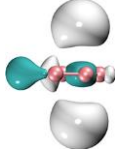
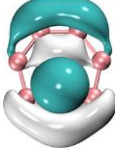

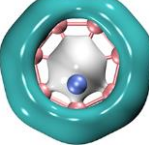
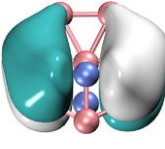
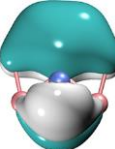

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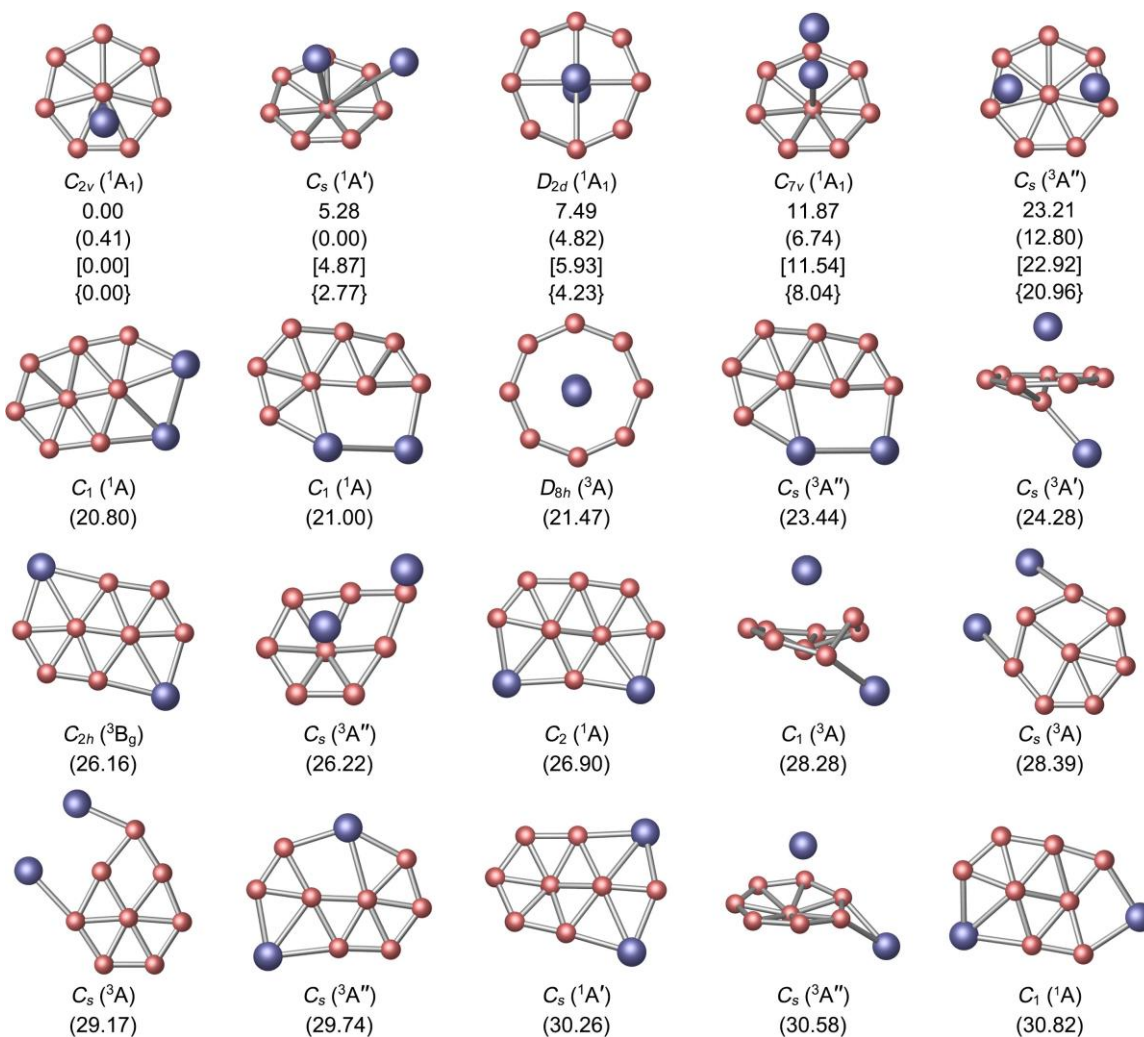


Figure S2. Displacement vectors of the vibrational modes of (a) GM and (b) TS structures of the Al_2B_8 cluster.

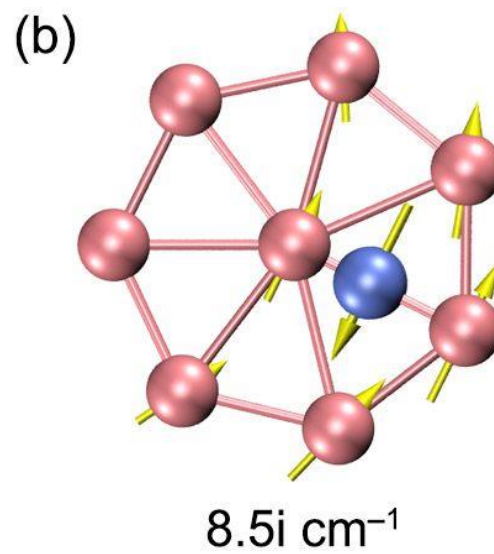
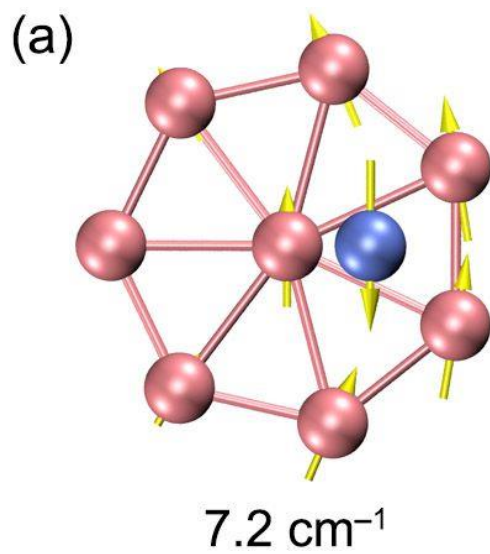


Figure S3. Canonical molecular orbitals (CMOs) of the TS structure of Al_2B_8 cluster. (a) Two CMOs for lone pairs of two Al atoms. (b) Seven CMOs for Lewis-type B–B σ single bonds along peripheral B ring. (c) Three delocalized π CMOs. (d) Three delocalized σ CMOs.

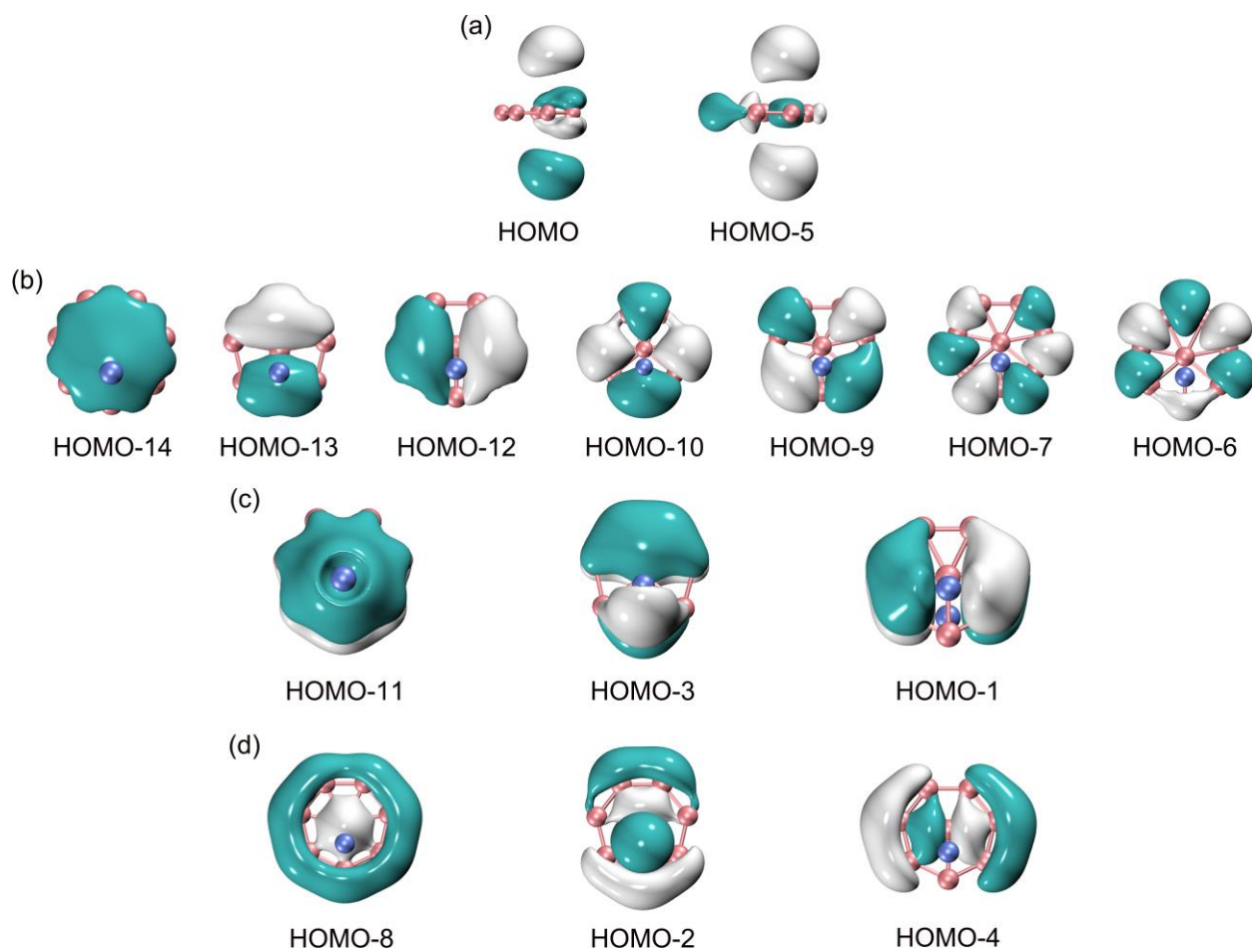


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