SUPPORTING INFORMATION

Exploring the potential energy surface of B4H4²⁻: An exception of the Wade–Mingos

rules

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Figure S1. Frontier molecular orbitals diagram of a) the tetrahedral (T_d) B₄H₄, b) the hypothetical T_d structure (2 imaginary frequencies) of the B₄H₄²⁻ dianion, and of c) isomer **2** (D_{2d} B₄H₄²⁻).



Figure S2. Bond lengths (in Å) of the global minimum (isomer 1) of $B_4H_4^{2-}$ at the PBE0/def2-TZVP level.



Figure S3. Bond lengths (in Å) of isomer **2** of $B_4H_4^{2-}$ at the PBE0/def2-TZVP level.



Figure S4. Geometric structures, symmetry point group, electronic state and relative energies (in kcal·mol⁻¹) at the DLPNO–CCSD(T)/CBS//PBE0/def2–TZVP and PBE0/def2–TZVP (in brackets) levels for the second and third most stable isomers with triplet multiplicity.



Figure S5. Gibbs Free Energy profile for the topomerization of the global minimum structure of the $B_4H_4^{2-}$ cluster at the PBE0/def2-TZVP level.



Figure S6. Gibbs Free Energy profile for the topomerization of the first local minimum structure of the $B_4H_4^{2-}$ cluster at the PBE0/def2-TZVP level.



Isomer	T ₁ Diagnostic				
1	0.013 0.014 0.023 0.017 0.025				
2					
3					
4					
5					
6	0.019 0.024				
7					
8	0.019				
9	0.027				

 $\label{eq:table_state} \textbf{Table S1.}\ T_1\ Diagnostic\ values\ at\ the\ DLPNO-CCSD(T)/CBS//PBE0/def2-TZVP\ level.$

CARTESIAN COORDINATES

		(1)				(2)	
Н	-2.669525492	0.392888601	0.000000000	Н	0.000000000	2.111087811	0.967761681
Н	2.109837153	-0.123930560	1.022955451	Н	0.000000000	-2.111087811	0.967761681
В	-1.461562902	0.273863355	0.000000000	Н	-2.111087811	0.000000000	-0.967761681
Н	2.109837153	-0.123930560	-1.022955451	Н	2.111087811	0.000000000	-0.967761681
Н	-0.128728981	-2.012010325	0.000000000	В	0.000000000	1.059439999	0.323202890
В	1.430274292	0.063437398	0.000000000	В	0.000000000	-1.059439999	0.323202890
В	-0.252995356	-0.803678475	0.000000000	В	-1.059439999	0.000000000	-0.323202890
В	0.000000000	0.839774290	0.000000000	В	1.059439999	0.000000000	-0.323202890
(3)			(4)				
Н	-3.042252546	-0.725435263	-0.724426128	В	1.364308950	-0.866540012	-0.000009962
Н	3.042493904	0.725751383	-0.723756448	Н	-2.345625872	-0.345071518	-1.003725917
В	-2.361374150	0.000025623	-0.000227767	В	-0.093274365	-0.352964612	0.000047678
В	2.361374319	-0.000163569	-0.000247246	Н	-1.894990497	1.338400221	-0.000030612
Н	-3.042959813	0.724473346	0.724314921	В	1.476549255	0.625789547	-0.000027738
Н	3.042713258	-0.725317034	0.723827385	В	-1.747630688	0.098211298	-0.000009390
В	0.782998222	-0.000049742	0.000245283	Н	1.586537793	1.829234509	0.000071558
В	-0.782997349	0.000293203	0.000237784	Н	-2.345687198	-0.345044302	1.003682032
		(5)				(6)	
Н	-2.582506427	-0.198180172	-0.000144549	Н	0.000000000	1.023212000	3.078710000
Н	2.582507088	-0.198162794	0.000045005	Н	0.000000000	-1.023212000	-3.078710000
Н	0.000025967	1.660710722	-1.024384610	Н	0.000000000	1.023212000	-3.078710000
В	1.372831794	-0.274223710	-0.000085115	Н	0.000000000	-1.023212000	3.078710000
Н	-0.000030940	1.660698053	1.024502405	В	0.000000000	0.000000000	2.392369000
В	-0.000003090	0.930995028	0.000054035	В	0.000000000	0.000000000	-2.392369000
В	0.000001921	-0.967562229	0.000211970	В	0.000000000	0.000000000	0.784404000
В	-1.372829762	-0.274222251	-0.000184540	В	0.000000000	0.000000000	-0.784404000
		(7)				(8)	
Н	0.000000000	1.945739000	-1.507939000	Н	0.860258000	-1.774114000	0.000000000
Н	0.000000000	-1.028263000	2.592269000	Н	1.813369000	3.095783000	0.000000000
В	0.000000000	0.754082000	-1.292608000	Н	-1.926575000	-2.565717000	0.000000000
В	0.000000000	0.000000000	1.904668000	В	1.306098000	2.006782000	0.000000000
Н	0.000000000	1.028263000	2.592269000	В	0.000000000	-0.876840000	0.000000000
Н	0.000000000	-1.945739000	-1.507939000	В	0.637154000	0.616942000	0.000000000
В	0.000000000	-0.754082000	-1.292608000	В	-1.580899000	-1.373963000	0.000000000
1			0.04/01/0000		2 550010000	0.00000000	