Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information of

Boron-Boron Quadruple Bond in $Li_3B_2^-$ and Li_4B_2 Clusters

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Table S1. Natural valence orbitals of two lowest energy isomers of $Li_3B_2^-$ and their connecting transition state from CASSCF(12e,12o), their occupation numbers (NOON), coefficient c^2 of the ground state wave function and effective bond order (EBO).

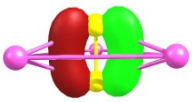
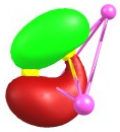
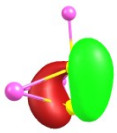
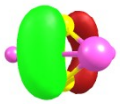
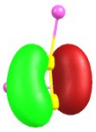
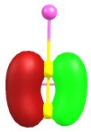
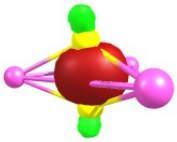
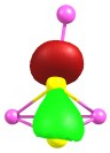
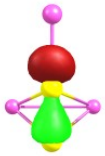
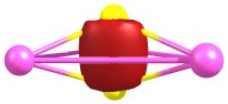
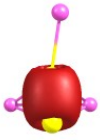
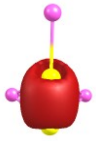
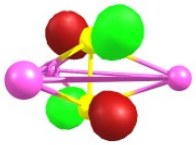
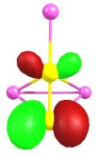
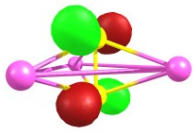
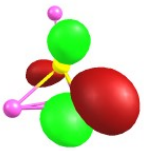
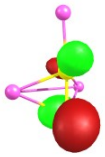
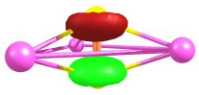
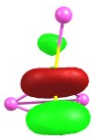
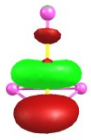
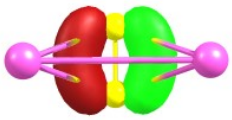
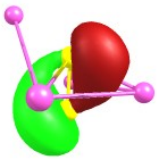
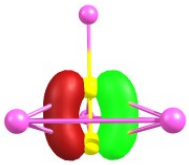
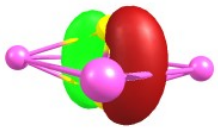
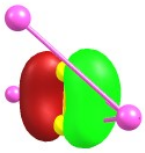
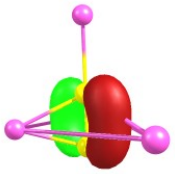
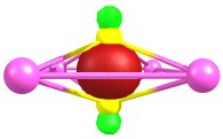
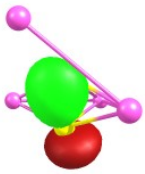
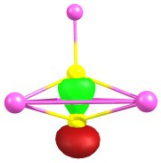
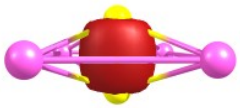
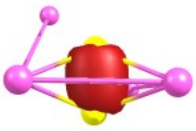
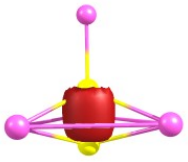
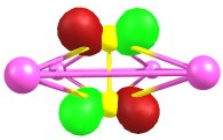
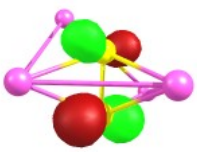
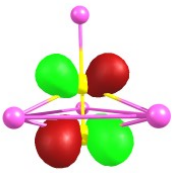
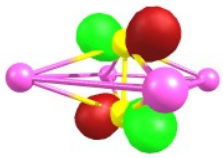
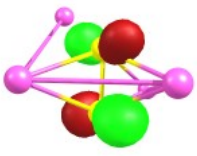
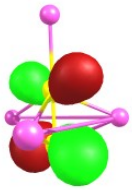
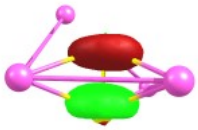
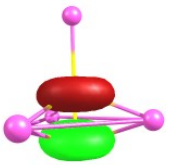
Type	$B_2Li_3^-$ **(1A)**	**TS_{1A-1B}**	**1B**
B-B π-bonding	 NOON (1.90)	 NOON (1.89)	 NOON (1.89)
B-B π-bonding	 NOON (1.91)	 NOON (1.89)	 NOON (1.89)
B-B σ-bonding	 NOON (1.92)	 NOON (1.92)	 NOON (1.92)
B-B σ-bonding	 NOON (1.98)	 NOON (1.98)	 NOON (1.98)
B-B π*-anti-bonding	 NOON (0.07)	 NOON (0.08)	 NOON (0.08)
B-B π*-anti-bonding	 NOON (0.07)	 NOON (0.07)	 NOON (0.08)
B-B σ*-bonding	 NOON (0.02)	 NOON (0.02)	 NOON (0.02)
Coefficient, c^2	0.953	0.941	0.944
EBO	3.77	3.75	3.75

Table S2. Natural valence orbitals of two lowest energy isomers of Li_4B_2 and their connecting transition state from CASSCF(12e,12o), their occupation numbers (NOON), coefficient c^2 of the ground state wave function and effective bond order (EBO).

Type	B_2Li_4 (**2A**)	$\mathbf{TS_{2A\text{-}2B}}$	**2B**
B-B π-bonding	 NOON (1.91)	 NOON (1.92)	 NOON (1.92)
B-B π-bonding	 NOON (1.91)	 NOON (1.92)	 NOON (1.92)
B-B σ-bonding	 NOON (1.93)	 NOON (1.92)	 NOON (1.92)
B-B σ-bonding	 NOON (1.99)	 NOON (1.98)	 NOON (1.99)
B-B π*-anti-bonding	 NOON (0.07)	 NOON (0.07)	 NOON (0.07)
B-B π*-anti-bonding	 NOON (0.07)	 NOON (0.07)	 NOON (0.07)

B-B σ*-bonding	[a]	 NOON (0.02)	 NOON (0.02)
Coefficient, c^2	0.953	0.941	0.944
EBO	3.80	3.79	3.79

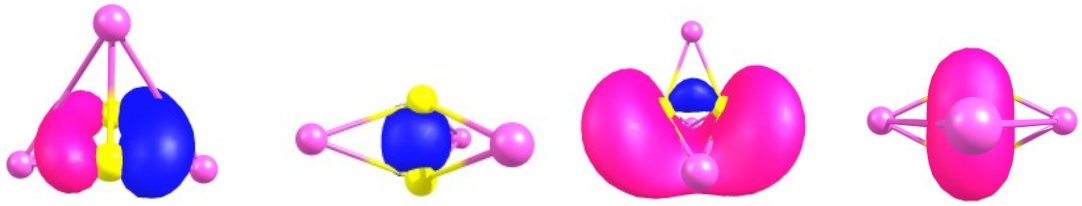
[a] Not located.

Table S3. B-B distance in Å, Wiberg bond index (WBI) and natural charges at B and Li.

Molecules	$\mathbf{r_{B-B}}$	**WBI**	***qB***	***qLi***	**Natural electronic configuration at boron**
1A	1.531	3.17	-1.3	0.5	[core]2S(1.25)2p(3.02)
$\mathbf{TS_{1A-1B}}$	1.532	2.98	-1.8/-0.8	0.5	[core]2S(1.22)2p(2.55) [core]2S(1.26)2p(3.50)
1B	1.533	2.99	-1.7/-0.8	0.5	[core]2S(1.26)2p(3.47) [core]2S(1.22)2p(2.54)
2A	1.517	3.07	-1.7/-1.4	0.7	[core]2S(1.27)2p(3.07)
$\mathbf{TS_{2A-2B}}$	1.518	2.97	-1.7/-1.1	0.7	[core]2S(1.27)2p(2.82) [core]2S(1.27)2p(3.46)
2B	1.517	2.95	-1.9/-1.1	0.7	[core]2S(1.27)2p(2.82) [core]2S(1.26)2p(3.63)

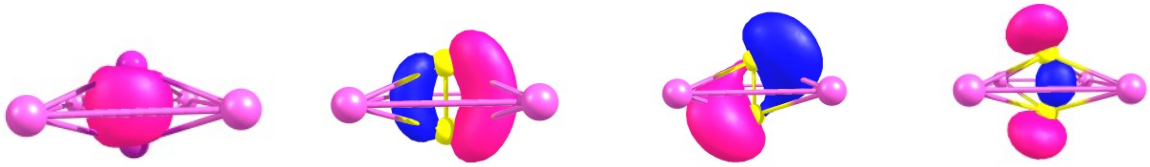
Table S4. Electron density, ρ, at the bond critical point (bcp), ellipticity, ε, laplacian of electron density, $\nabla^2\rho$, local electronic energy density, H(r) and electron localization function, ELF values. All values are in a. u.

Molecule	**bcp**	**ρ**	**$\nabla^2\rho$**	**H(r)**	**ELF**	**ε**
$B_2Li_3^-$	B-B	0.17	-0.33	-0.14	0.87	0.028
B_2Li_4	B-B	0.18	-0.37	-0.16	0.85	0.012



ON = 2.00 ON = 1.96 ON = 1.92 ON = 1.90

Fig S1. AdNDP orbitals of $B_2Li_3^-$ with their corresponding occupation number (O.N).



ON = 1.98 ON = 1.96 ON = 1.92 ON = 1.96

Fig S2. AdNDP orbitals of B_2Li_4 with their corresponding occupation number (O.N).

$$\mathbf{Li_3^- + B_2 \rightarrow Li_3B_2^-,\ \Delta G = -125.6\ kcal/mol}$$

$$\mathbf{Li_4 + B_2 \rightarrow Li_4B_2,\ \Delta G = -141.1\ kcal/mol}$$

Fig S3. M06-2X/def2-TZVP calculated ΔG values at 298.15 K and 1 atm for the formation of $Li_3B_2^-$ and Li_4B_2 clusters.

Cartesian coordinates of the optimized geometries at CCSD(T)/def2-TZVP//M06-2X/def2-TZVP level with the total energy in a.u.

1A , D_{3h} (Singlet)

E = -71.89476

5	-0.000024000	-0.070492000	-0.765972000
5	-0.000016000	-0.070490000	0.765974000
3	0.000273000	1.908447000	-0.000002000
3	1.825715000	-0.836930000	-0.000004000
3	-1.825921000	-0.836547000	0.000002000

TS_{1A-1B}, C_1, (Singlet)

E = -71.87236

5	-0.996383000	0.118895000	-0.719459000
5	0.404616000	-0.115939000	-0.144318000
3	2.483415000	-0.163376000	-0.006075000
3	-1.011625000	-1.441294000	0.723130000
3	-0.485511000	1.599743000	0.722573000

1B, C_S, (Singlet)

E = -71.87333

5	0.497102000	-0.210448000	0.000000000
5	-0.814332000	-1.004731000	0.000000000
3	2.157380000	1.065243000	0.000000000
3	-0.814332000	0.480027000	1.521914000
3	-0.814332000	0.480027000	-1.521914000

$1A_{Na}$, D_{3h} (Singlet)

E = -535.09052

5	-0.000407000	-0.003341000	-0.772997000
5	0.000299000	-0.002285000	0.776803000
11	0.023317000	2.335238000	-0.000682000
11	2.015237000	-1.186468000	-0.000585000
11	-2.038505000	-1.146213000	-0.000464000

2A, D_{4h} (Singlet)

E = -79.35062

5	-0.672167000	0.351954000	-0.000114000

5	0.672167000	-0.351954000	-0.000114000
3	-0.672167000	-1.283805000	1.449270000
3	0.672440000	1.284126000	-1.449080000
3	0.672167000	1.283805000	1.449270000
3	-0.672440000	-1.284126000	-1.449080000

TS_{2A-2B}, C_1 (Singlet)

E = -79.34197

5	0.605806000	-0.004814000	-0.767458000
5	-0.298673000	0.003278000	0.451906000
3	0.040481000	2.002714000	-0.395707000
3	1.826691000	-0.014949000	0.987637000
3	-2.382830000	0.016672000	0.330178000
3	0.003769000	-2.001877000	-0.396188000

2B, C_{3v} (Singlet)

E = -79.37448

5	1.105540000	0.001163000	-0.002834000
5	-0.411659000	0.000270000	-0.000134000
3	0.451663000	-1.515221000	-1.297726000
3	0.451177000	1.884328000	-0.658236000
3	-2.516616000	-0.000718000	0.002857000
3	0.457309000	-0.370777000	1.958051000

$2A_{Na}$, D_{4h} (Singlet)

E = -696.97538

5	-0.017766000	0.768027000	-0.000025000
5	0.017766000	-0.768027000	-0.000025000

11	-1.701372000	-0.036467000	1.701771000
11	1.701372000	0.039796000	-1.701760000
11	1.701372000	0.036467000	1.701771000
11	-1.701372000	-0.039796000	-1.701760000