Electronic supplementary information

Three-dimensional aromatic B_6Li_8 complex as a high capacity hydrogen storage material

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1. Computational methods

All standard electronic structure calculations are carried out using the Gaussian 03 program.[1] Geometries and harmonic vibrational frequencies of the lower-lying isomers are determined using density functional theory (DFT) with the popular hybrid B3LYP functional which involves the Becke three-parameter exchange[2] and Lee–Yang–Parr correlation[3] functionals. The initial search for all possible low-lying isomers of B_6Li_8 is performed using a stochastic search algorithm that was implemented by us.[4] Firstly, the possible structures of B_6Li_8 are generated by random "kick" method, and then rapidly optimized at the B3LYP/3-21G level.[5] In this search procedure, the minimum and maximum distances between atoms are limited to 1.5 and 10 Å, respectively. Geometries of the lower-lying isomers with relative energy of 2.00 eV and their vibrational frequencies are further refined using the B3LYP functional in conjunction with the 6-311+G(d) basis set.[6] In order to obtain more accurate energetic properties, the optimizations and geometries and calculations of vibrational frequencies of few lowest-lying isomers are further performed at the MP2/6-311+G(d) level of theory.

Nucleus independent chemical shift (NICS) of the global minimum B_6Li_8 (C_i) and $B_6H_6^{2-}(O_h)$, Si_6^{2-} (O_h) is calculated at center positions of the B_6 and Si_6 cages by using GIAO-B3LYP/6-311+G(d) method.[7] Natural charge populations and Wiberg bond indices of compounds are computed at the B3LYP/6-311+G(d) level of theory by using NBO software.[8] Electron localization function (ELF) of the B_6Li_8 is obtained at the B3LYP/6-311+G(d) wavefunction using Dgrid-4.5 software.[9] Total (DOS) and partial (pDOS) densities of states of B_6Li_8 are obtained at the wB97XD/6-31++G(2d,2p) level.

2. Plots of average adsorption energies (E_{ads}, eV) per H_2 molecule of B_6Li_8-nH_2 and reaction enthalpy (ΔH, eV) of processes: B_6Li_8-$nH_2 \rightarrow B_6Li_8 + nH_2$. All values are calculated at wB97XD/6-31++G(2d,2p) level.
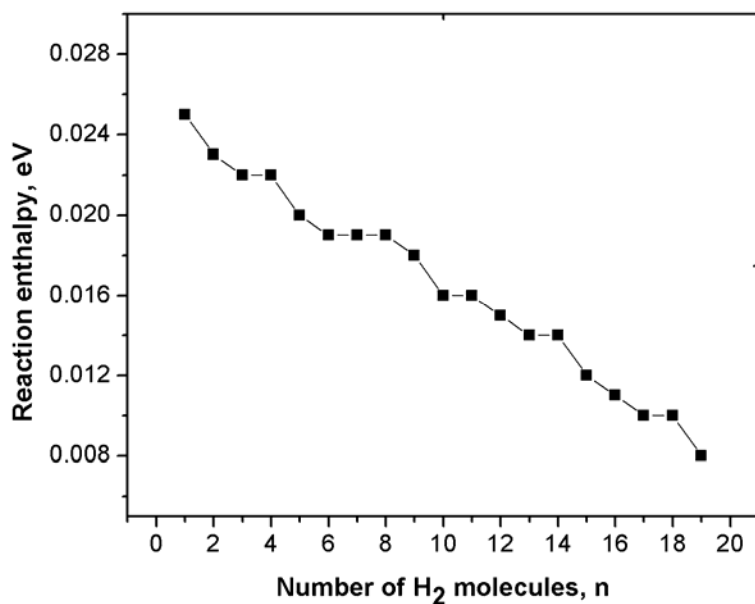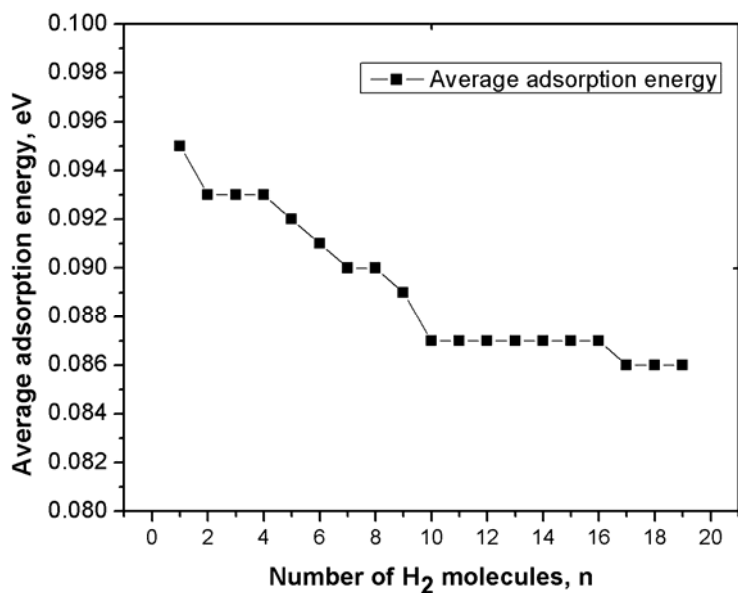
3. Cartesian coordinates of the low-lying isomers B_6Li_8 obtained at the B3LYP/6-311+G(d) level and configurations I, II and III obtained at the wB97XD/6-31++G(2d,2p) levels.
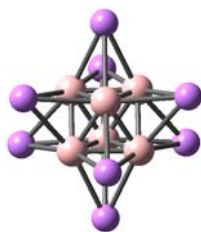
$C_i, {}^1A_g$

5	0.960767000	0.621260000	-0.481108000
5	-0.487552000	1.066989000	0.405472000
5	0.487537000	-1.067625000	-0.405234000
5	-0.960924000	-0.621611000	0.480795000
5	0.616391000	-0.125167000	1.070172000
5	-0.616155000	0.124906000	-1.070386000
3	1.352810000	1.939019000	1.230547000
3	-0.178651000	2.248790000	-1.419753000
3	0.178492000	-2.248579000	1.420732000
3	-1.031088000	0.398633000	2.425562000
3	-2.559559000	0.708107000	-0.227491000
3	2.560336000	-0.705935000	0.227381000
3	1.031833000	-0.399948000	-2.425190000
3	-1.354278000	-1.938005000	-1.231305000
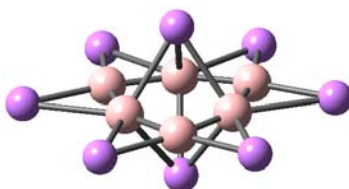
$D_{3d}, {}^1A_{1g}$

5	0.000000000	1.337484000	0.000001000
5	0.000000000	-1.800062000	0.000004000
5	1.558899000	0.900031000	0.000004000
5	1.158295000	-0.668742000	0.000001000
5	-1.158295000	-0.668742000	0.000001000
5	-1.558899000	0.900031000	0.000004000
3	-1.664634000	-2.909149000	-0.000004000
3	-3.351714000	0.012959000	-0.000004000
3	-1.687079000	2.896190000	-0.000004000
3	1.687079000	2.896190000	-0.000004000
3	3.351714000	0.012959000	-0.000004000
3	1.664634000	-2.909149000	-0.000004000
3	0.000000000	0.000000000	-1.731937000
3	0.000000000	0.000000000	1.731939000

5	-0.260844000	-0.129449000	1.194373000
5	1.204610000	-0.339910000	0.264856000
5	-1.119322000	0.311394000	-0.263329000
5	0.346941000	0.098746000	-1.193203000
5	0.332752000	1.170924000	0.187286000
5	-0.247423000	-1.200838000	-0.185765000
3	1.477406000	0.923811000	2.049305000
3	0.755085000	-2.045576000	1.586299000
3	-0.668337000	2.010828000	-1.591209000
3	2.235931000	1.214466000	-0.911726000
3	1.523672000	-1.753961000	-1.385575000
3	-1.430774000	1.717958000	1.400980000
3	-2.147353000	-1.248901000	0.910339000
3	-1.384769000	-0.944940000	-2.056192000
1	1.280872000	-3.740401000	3.008052000
1	0.859247000	-3.303429000	3.446268000
1	-1.318177000	3.902795000	-2.673055000
1	-1.972907000	3.554639000	-2.557435000
1	-2.755185000	3.305349000	2.358363000
1	-3.184109000	3.048860000	1.797020000
1	2.620740000	1.778959000	3.809660000
1	2.470904000	2.403031000	3.427018000
1	2.964856000	-3.234490000	-2.299540000
1	2.425846000	-3.235318000	-2.813118000
1	-2.610206000	-2.040283000	-3.620646000
1	-3.108061000	-1.530618000	-3.387696000
1	3.934307000	2.502085000	-1.692179000
1	4.077285000	1.860066000	-2.052865000
1	-3.858235000	-2.553822000	1.558737000
1	-4.193320000	-1.892807000	1.663665000

Configuration **I**

5	0.936599000	0.637868000	-0.532762000
5	-0.475681000	1.027025000	0.440754000
5	0.504960000	-1.065379000	-0.472646000
5	-0.907469000	-0.676036000	0.500643000
5	0.684140000	-0.154618000	1.009205000
5	-0.654629000	0.116140000	-1.040876000
3	1.409283000	1.893319000	1.245758000
3	-0.295147000	2.277919000	-1.363610000
3	0.320859000	-2.315230000	1.333930000
3	-0.897448000	0.269250000	2.490203000
3	-2.579818000	0.655322000	-0.115736000
3	2.608656000	-0.697443000	0.073686000
3	0.925291000	-0.303368000	-2.523679000
3	-1.377959000	-1.933552000	-1.277891000
1	1.351951000	3.495076000	2.915267000
1	0.449745000	3.551646000	-3.160241000
1	-4.006519000	2.314117000	-0.786168000
1	-1.032446000	1.753586000	4.273690000
1	-1.318201000	-3.528973000	-2.954416000
1	-0.429238000	-3.582392000	3.134167000
1	4.016618000	-2.281773000	0.998955000
1	1.065437000	-1.785416000	-4.307118000
1	-1.213821000	2.108294000	3.639002000
1	3.442897000	2.977149000	1.443349000
1	1.017438000	3.174255000	-2.846839000
1	3.653464000	-1.931010000	1.553058000
1	1.246896000	-2.140408000	-3.672626000
1	-3.404833000	-3.028493000	-1.474383000
1	-0.995153000	-3.204149000	2.818875000
1	-3.760037000	2.012001000	-1.425241000
1	4.752709000	0.184486000	0.304725000
1	0.704974000	3.504180000	2.536264000
1	-1.724917000	4.041869000	-1.831793000
1	-4.715195000	-0.244164000	-0.349428000
1	-1.054508000	-0.845559000	4.523154000
1	1.737617000	-4.085591000	1.818830000
1	-0.671140000	-3.538509000	-2.575573000
1	1.058752000	0.815315000	-4.553569000
1	0.356388000	0.864020000	-4.295950000
1	4.360585000	0.595218000	-0.184347000
1	1.713602000	-3.985767000	1.076377000
1	-3.262989000	-2.898727000	-0.749748000
1	-0.350622000	-0.898262000	4.270973000
1	-4.322363000	-0.650675000	0.142824000
1	-1.694291000	3.938613000	-1.089937000
1	3.300944000	2.847235000	0.718715000

Configuration **II**

5	-0.988068000	-0.142479000	0.785563000
5	-0.889290000	-0.018228000	-0.960690000
5	0.775307000	-0.133774000	0.883854000
5	0.871630000	-0.009836000	-0.864159000
5	-0.040966000	-1.308827000	-0.127804000
5	-0.077440000	1.161283000	0.048961000
3	-2.140934000	-1.737698000	-0.263362000
3	-2.296819000	1.400170000	-0.076506000
3	2.172771000	-1.569354000	-0.000723000
3	0.116220000	-1.458905000	-2.316197000
3	-0.004235000	1.589886000	-2.119318000
3	-0.112187000	-1.750958000	2.039799000
3	-0.229649000	1.313356000	2.233833000
3	2.046619000	1.584981000	0.121382000
1	-3.842104000	-2.255107000	-1.696757000
1	-3.544893000	2.693215000	1.430648000
1	-0.989311000	3.493106000	-2.953294000
1	-1.276596000	-2.476313000	-3.899277000
1	3.490757000	2.273114000	1.801056000
1	3.657846000	-2.626394000	-1.439919000
1	0.673879000	-3.739008000	2.911636000
1	1.042396000	2.055770000	4.052103000
1	-1.579324000	-1.852687000	-3.608609000
1	-3.782194000	-2.667169000	1.061721000
1	-3.249628000	2.084646000	1.758140000
1	0.535949000	-3.837564000	2.180820000
1	1.335030000	1.442207000	3.731272000
1	4.174270000	1.820537000	-0.973205000
1	3.350647000	-2.015128000	-1.752377000
1	-0.866549000	3.584661000	-2.217827000
1	-1.571334000	-2.657355000	3.643353000
1	-3.492526000	-1.617160000	-1.893467000
1	-3.593658000	2.870010000	-1.272908000
1	1.653361000	3.022200000	-3.012313000
1	1.345405000	-3.067259000	-3.404895000
1	3.188807000	-3.254559000	1.206714000
1	3.130810000	1.631424000	1.965158000
1	-1.141889000	3.190371000	3.264657000
1	-0.988647000	3.329049000	2.542618000
1	-1.838946000	-2.029966000	3.326490000
1	2.969065000	-2.723892000	1.688715000
1	3.704086000	1.312306000	-1.271083000
1	1.069445000	-3.380247000	-2.781535000
1	1.919093000	2.335214000	-2.862252000
1	-3.348954000	2.338051000	-1.742025000
1	-3.463736000	-2.060848000	1.376334000
1	4.435926000	-0.748701000	0.409833000
1	3.909135000	-0.516296000	0.893343000
1	-4.093641000	0.151953000	0.410867000
1	-4.590209000	0.415411000	-0.088889000
1	2.009236000	3.766473000	-0.183625000
1	2.747771000	3.860804000	-0.286560000

Configuration III

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