

Lithium Decorated Borane Clusters ($B_nH_nLi_6$, $n=5-7$) as Promising Materials for Hydrogen Storage: A Computational Study

Shakti S Ray

Indian Institute of Technology (Indian School of Mines): Indian Institute of Technology

Sridhar Sahu (✉ sridharsahu@iitism.ac.in)

Indian Institute of Technology (Indian School of Mines): Indian Institute of Technology

Research Article

Keywords: DFT, Borane clusters, adsorption, AIMALL, Molecular Dynamics Simulations

Posted Date: September 20th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-671186/v1>

License:  This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

In this study, we have investigated the hydrogen adsorption potential of lithium decorated borane clusters ($B_nH_nLi_6$, $n = 5-7$) using density functional theory calculations. The principle of maximum hardness and minimum electrophilicity confirmed the stability of the hydrogen adsorbed complexes. The outcomes of the study reveals that, the hydrogen molecules are adsorbed in a quasi-molecular fashion via Niu-Rao-Jena type of interaction with average adsorption energy falling in the range of 0.10-0.11 eV/ H_2 and average Li- H_2 bond length is in the range of 2.436–2.550 Å. It was found that the hydrogen molecules are physisorbed at the host clusters at low temperature range 0K- 77K with gravimetric density up to 26.4 wt% which was well above target set by U.S. Department of Energy (US-DOE). ADMP-MD simulations showed that almost all the H_2 molecules are desorbed at higher temperature from 373K-473K without distorting the host clusters which indicates the studied clusters can be promoted as promising reversible hydrogen storage

1. Introduction

Rapid consumption of fossil fuel and their restricted supply have not only depleted the natural source of energy to a shocking amount but also engendered many environmental problems such as global warming, greenhouse issues, and air-pollution etc [1–4]. Hence, during the past couple of decades tremendous effort has been devoted to explore clean, efficient and cost-effective alternative energy sources that should be non-polluting and non-hazardous in nature. In this regard, hydrogen being the most abundant element in the earth can be considered as one of the prominent energy carriers that can be projected as the future fuel [5, 6]. In addition, the combustion of the hydrogen fuel yields water and non-toxic by-products which insure it to be one of the most environment friendly gas available [7–9]. However, the major bottleneck of utilizing it is to find an efficient storage system that can trap hydrogen in a large specific area and with high gravimetric and volumetric densities (4.5 wt% and > 30 g H_2 /L by 2020) as proposed by US Department of Energy (US-DOE) [10, 11]. In addition, to achieve cost-effective reversible hydrogen storage and to release hydrogen at ambient conditions, hydrogen binding energy should be in the intermediate range of physisorption and chemisorption process [12, 13]. Moreover, fast adsorption and desorption kinetics of hydrogen at ambient conditions are also taken into account while considering the storage materials. Therefore, for the practical onboard application, tremendous research efforts have been put for designing materials for effective hydrogen storage.

Nanostructured clusters are of particular interest in hydrogen storage due to their riveting reaction kinetics, thermodynamics and catalytic behavior and which possess high diffusivity and surface to volume ratio as compared to their bulk counterparts [14, 15]. Since last few years hydrogen storage in carbonaceous nano-clusters have been widely reported in literature. Alongside of carbon based compounds, boron nanostructured clusters, having numerous structural analogies with carbonaceous clusters, were also investigated by different researchers. For example, hydrogen storage capacity of lithium decorated B_{60} was theoretically investigated by Wang *et al.* who reported that the hollow cage

could trap maximum up to 28 H₂ through van der Waals interactions with an average binding energy of 0.33 eV/H₂ leading to a gravimetric density of 8.19 wt% [16]. Zhang *et al.* performed molecular dynamics simulations to study the hydrogen storage in the Ca doped B₄₀ and found that the clusters could store up to 30 H₂ molecules with an average adsorption energy of 0.17 eV/H₂ via orbital hybridisation and charge polarisation mechanism that leads to 8.11 wt% of gravimetric density. Molecular dynamic simulation reveals that the adsorbed hydrogen molecules could be release very quickly at room temperature. [17]. Scandium decorated B₃₈ clusters was theoretically explored by Liu *et al.* who reported that Dewar-Kubas mechanism between Sc atom and adsorbed H₂ molecules was responsible for adsorption of 6H₂ on each Sc atom with a moderate adsorption energy of 0.22 eV/H₂ resulting a gravimetric density of 7.57wt% [18]. Juan *et al.* theoretically predicted the hydrogen storage efficiency of Ca doped hexagonal B₃₆ clusters with van der Waals corrections and found that this cluster could adsorb 4.97 wt% of hydrogen with an average binding energy of 0.36 eV/H₂ that could easily desorbed at near ambient temperatures [19]. Similar kind of observations were also reported by Ye *et al.* and Leu *et al.* [20, 21]. Tang *et al.* have shown that maximum of 16 number of H₂ molecules were captured by alkali, alkaline-earth and transition metal doped smallest boron cage (B₂₈) via strong Dewar-Kubas with a moderate average adsorption energy (0.2–0.6 eV/H₂) resulting in 7.99 wt% gravimetric density [22]. Wang *et al.* studied the H₂ interaction with Li decorated B₂₄ cluster and who reported that through charge polarization mechanism the cluster could capture 9.24 wt% hydrogen molecules with 0.10 eV/H₂ of average adsorption energy [23]. Recently, our investigation on Sc doped small boron clusters for hydrogen storage capacity using molecular dynamics simulations revealed that these clusters could accommodate maximum of 9.43 wt% with average adsorption energy in the range 0.08–0.10 eV/H₂ and which are desorbable at ambient conditions [24]. Besides, a lot of boron based materials have also been investigated for hydrogen storage by many other authors [25–27].

Besides, hydrogen storage in boranes (B_mH_n) which are synthetic class of boron hydrides possessing non classical 3-centre-2-electron bonding, were also reported by many authors. For instance, Using first principle calculation Ghosh *et al.* studied the hydrogen uptake in lithium doped closo borane and found that the designed material could bind molecular hydrogen through charge-dipole interaction with average binding energy of 2.2 Kcal/mol giving rise to gravimetric density up to 7.3 wt% [28]. The hydrogen adsorption capacity of lithium decorated diborene and diboryne was also explored by Ghosh *et al.* who reported that these clusters could capture H₂ molecules through ion quadruple and ion induced dipole interaction resulting in a gravimetric density up to 23% and 24% respectively [29]. Chaudhuri *et al.* investigated the hydrogen capturing ability of Li, Sc, and Be decorated B₆H₆ using first principle calculation and found that these complexes could be considered as a promising candidate for hydrogen storage at low temperatures with a gravimetric density up to 12.5 wt% [30]. Similarly, Ali *et al.* explored the interaction of hydrogen molecules with B₆H₆²⁻ complex and reported the adsorption energy close to 3.5 Kcal/mol per H₂ which was the optimal adsorption energy required for reversible hydrogen storage at

ambient temperature [31]. A similar study was also reported by Wan and co-workers. [32]. In addition, hydrogen storage in other borane and carborane based clusters are reported by many others [33–36].

In the present study we have investigated hydrogen storage in inorgano-metallic complexes, ($B_nH_nLi_6$, $n = 5-7$).

2. Computational Details

The geometry optimization of the structures with and without H_2 molecules has been carried out using Minnesota 06 (M06) hybrid functional implemented with 6-311++G(d,p) basis set within the framework of Density Functional Theory (DFT). M06 functional has been considered to be an efficient method to successfully investigate the non-covalent interactions. Therefore, it has proven to perform well in hydrogen storage investigations because the process of hydrogen storage involves many kind of non-covalent interactions [37]. No optimizations were accomplished with any imaginary harmonic frequencies. All the calculations were performed using computational chemistry program Gaussian 09 and Chemcraft was used to create 3D molecular complexes [38]. To investigate the stability as well as the reversibility of adsorbed hydrogen molecules on the lithium decorated borane clusters, the optimized structures were subjected to Atom-centered Density Matrix Propagation (ADMP) molecular dynamics simulations at different temperatures. The time step for the ADMP-MD simulations was set at 1 fs with maximum 1000 steps were specified for each trajectory. Furthermore, to explore the nature of interaction between the hydrogen molecules and sorption centers of the host cluster we have employed the Bader's Quantum Theory of Atoms in Molecules (QTAIM) [39]. The partial density of states (PDOS) were calculated and analyzed using GaussSum program [40].

The stability and reactivity of the lithium decorated borane clusters and their H_2 trapped analogues were examined by calculating their, global reactivity descriptors, e.g hardness (η), electrophilicity (ω) and electronegativity (χ) [41–44].

Now, hardness (η) is computed by the ionization potential (I) and electron affinity (A) using Koopman's Theorem [45].

$$\eta = \frac{I-A}{2} \quad (1)$$

Similarly, the electrophilicity index can be defined as 1

$$\omega = \frac{\chi^2}{2\eta} \quad (2)$$

where

$$\chi = \frac{I+A}{2}$$

The kinetic stabilities of the complexes were determined by calculating the energy gap (E_g) between their highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs).

The average hydrogen adsorption energy without zero point energy correction (E_{ads}), are obtained using the following equation:

$$E_{ads} = \left[\{E_{Host} - nE_{H_2}\} - E_{Complex} \right] \quad (3)$$

Here $E_{Complex}$, E_{H_2} and E_{Host} is the total electronic energies without zero point energy correction of hydrogenated complex and hydrogen molecule and host cluster respectively.

The hydrogen storage gravimetric density was determined using following equation:

$$H_2(\text{wt}\%) = \frac{M_{H_2}}{M_{H_2} + M_{Host}} \times 100 \quad (4)$$

Where M_{H_2} indicates the mass of total number of adsorbed H_2 molecules and M_{Host} indicates the mass of lithium doped borane cluster

3. Results And Discussion

We optimized the geometries of bare $B_nH_nLi_6$, $n = 5-7$ clusters employing M06/6-311++G(d,p) level of theory and the structural parameters computed are found in good agreement with earlier reported data by Boldyrev et al. [46]. Figures 1 and 2 show the optimized ground state geometries of bare $B_nH_nLi_6$ and H_2 adsorbed compounds respectively. Hydrogen molecules were added sub sequentially till no further hydrogen molecules could be adsorbed in an allowed range of Li- H_2 distance as per the standard of US-DOE. A maximum of eighteen number of hydrogen molecules get adsorbed by the studied $B_nH_nLi_6$ i.e $B_5H_5Li_6$, $B_6H_6Li_6$ and $B_7H_7Li_6$ clusters. As expected the adsorption centers mostly lie on Li atoms leading to small elongation in Li-Li bond length in the range of 0.01Å -0.03Å. However, from the table, it can be observed that, there is almost no change in B-B bond lengths after the H_2 adsorption. Hence, the insignificant geometrical changes in host clusters after the H_2 adsorption signifies the process to be physisorption kind. The average distance between the sorption center (Li) and hydrogen molecule was found to be in the range of 2.042Å -3.637Å. Hydrogen molecules are found to bind with the lithium adsorbents in a quasi-molecular fashion leading to H-H bond elongation in the range of 0.75–0.77 Å. Because Li has large second ionization energy, therefore H_2 -Li interaction occurs due charge polarization giving rise to Niu-Rao-Jena kind of bonding [47–49].

Stability of the hydrogenated clusters is an important aspect to focus on while studying hydrogen storage mechanism. We have calculated the global reactivity descriptors such as; hardness (η) and electrophilicity index (ω) which provide a quantitative measure of the stability of the clusters. According to the principle of *maximum hardness and minimum electrophilicity index* proposed by Parr *et al.*, molecules with a high value of hardness (η) and low value of electrophilicity (ω) gives rise to stable configuration [50, 51]. We computed the reactivity parameters at M06/6-311++G(d,p) level of theory and the values are provided in Table 2. It has been observed that, the η value increases while ω value decreases with sequential adsorption of H_2 molecules in all studied complexes indicating the stability of the systems. For example, in the case $B_7H_7Li_6-18H_2$ the hardness is found to increase by 7% being maximum for $B_7H_7Li_6-18H_2$ whereas ω value decreases by 18% being minimum for the same cluster. Similar observation is also observed in other studied compounds. Therefore all the hydrogen decorated complexes considered here are considered stable. The above fact can be reassured by analysing their HOMO-LUMO energy gaps (E_g) which is found to consistently increases with the number of hydrogen molecules for all the clusters (Fig. 3). So the kinetic stabilities of the clusters increase up to the adsorption of 18 number of H_2 molecules imparting the whole systems a non-reacting atmosphere for further addition of H_2 .

To study the hydrogen adsorption mechanism of lithium decorated borane clusters, the average adsorption energies (E_{ads}) are calculated using the Eq. 2 \uparrow and the values are plotted in the Fig. 4. It can be observed from plot that the H_2 decorated clusters display an decreasing E_{ads} with increasing H_2 molecule at a adsorption site (Li) which is obvious due to steric repulsion among the H_2 molecules. However, if we look into the H_2 adsorption on the cluster as a whole, an almost odd-even effect is observed. This might be due to a non local effect of H_2 interaction on one site on the H_2 binding on the other. The calculated adsorption energy found in the ideal range of 0.10 eV/ H_2 to 0.16 eV/ H_2 which is the required range of physisorption mechanism.

Table 1

Average bond lengths between Boron atoms (B-B), Boron Hydrogen (B-H), Center of the complex and central Lithium (C-M), Center of the complex and peripheral Lithium (C-P), Lithium Hydrogen (Li-H) and Hydrogen Hydrogen (H-H) in Å.

| Complexes | B-B (Å) | B-H (Å) | C-M (Å) | C-P (Å) | Li-H (Å) | H-H (Å) |
|---|------------|------------|------------|------------|-------------|------------|
| B ₅ H ₅ Li ₆ | 1.692 | 1.255 | 3.367 | 3.024 | | |
| B ₅ H ₅ Li ₆ -18H ₂ | 1.692 | 1.252 | 3.367 | 3.044 | 2.436 | 0.75 |
| B ₆ H ₆ Li ₆ | 1.675 | 1.258 | 2.990 | 3.341 | | |
| B ₆ H ₆ Li ₆ -18H ₂ | 1.674 | 1.254 | 2.962 | 3.331 | 2.552 | 0.75 |
| B ₇ H ₇ Li ₆ | 1.666 | 1.256 | 2.635 | 3.619 | | |
| B ₇ H ₇ Li ₆ -18H ₂ | 1.666 | 1.253 | 2.608 | 3.622 | 2.550 | 0.75 |

Table 2

Calculated Hardness (η) Electrophilicity Index (ω), and HOMO - LUMO Energy Gap (E_g) of lithium doped boranes as well as hydrogen trapped complexes.

| Complexes | η | ω | E_g | wt% |
|---|--------|----------|-------|-------|
| B ₅ H ₅ Li ₆ | 1.692 | 1.255 | 3.367 | 3.024 |
| B ₅ H ₅ Li ₆ -18H ₂ | 1.692 | 1.252 | 3.367 | 3.044 |
| B ₆ H ₆ Li ₆ | 1.675 | 1.258 | 2.990 | 3.341 |
| B ₆ H ₆ Li ₆ -18H ₂ | 1.674 | 1.254 | 2.962 | 3.331 |
| B ₇ H ₇ Li ₆ | 1.666 | 1.256 | 2.635 | 3.619 |
| B ₇ H ₇ Li ₆ -18H ₂ | 1.666 | 1.253 | 2.608 | 3.622 |

Hirshfeld charge analysis has been carried out to study the charge distribution mechanism during the hydrogen adsorption in lithium decorated borane clusters. The variation of average Hirshfeld charges on B, Li and H atoms with the number of H₂ per clusters are presented in the Fig. 5. It is observed that the average Hirshfeld charge on lithium atom increases with increase in hydrogen content indicating that the Li atom gets more positively ionic in comparison to H₂ molecules due to induced polarization. However,

increase of H₂ molecules about the Li center slightly decreases its positive charge distribution. Because there is no noticeable change in average charge distribution over H₂ and B atoms, the superposition of charge distribution of all H₂ molecules tends to induce negative charge on Li, thereby decreasing the degree of its positive charge distribution. This confirms a Niu-Rao-Jena type of interaction among Li and H₂ molecules.

In order to reveal the bonding characteristic and frontier molecular orbital, partial density of state (PDOS) of the host clusters as well as hydrogen adsorbed system has been investigated. We set the value of full width half maxima value at 0.3 eV. The PDOS of B and Li atoms in host and hydrogen adsorbed clusters are shown in Fig. 6. For every studied cluster, a very weak overlap between B and Li atom observed which suggests ionic-like bonding between B and Li which is in good agreement with the QTAIM results. It can be observed that, as compared to the host clusters there exist some new peaks in hydrogenated clusters and near Fermi level, LUMO of H₂ has comparatively less contribution than Li LUMO which suggests that prominent charge transfer between them is unlikely to happen. Therefore the H₂-Li bonding is most probably due to polarization (Niu-Rao-Jena kind of interaction).

Table 3

Electron density in (ρ) a.u., $\nabla^2\rho$, Total energy density (H_{BCP}) in a.u at BCP of (Li,H) and (Li,B).

| Complexes | ρ_{Li-H} | $\nabla^2\rho_{Li-H}$ | ρ_{Li-B} | $\nabla^2\rho_{Li-B}$ | $\mathcal{H}_{BCP_{Li-H}}$ | $\mathcal{H}_{BCP_{Li-B}}$ |
|---|---------------|-----------------------|---------------|-----------------------|----------------------------|----------------------------|
| B ₅ H ₅ Li ₆ -18H ₂ | 0.0065 | 0.0377 | 0.0305 | 0.1345 | 0.0018 | 0.0006 |
| B ₆ H ₆ Li ₆ -18H ₂ | 0.0066 | 0.0444 | 0.0274 | 0.1238 | 0.0023 | 0.0012 |
| B ₇ H ₇ Li ₆ -18H ₂ | 0.0161 | 0.0844 | 0.0204 | 0.0878 | 0.0022 | 0.0014 |

The nature of the interaction between the adsorbed H₂ molecule and the Li decorated borane clusters have been investigated by performing topological analysis using Bader's Quantum Theory of Atoms in Molecules (QTAIM) [52]. In order to describe the relative decrease or increase of charge accumulation at the bonding sites, we computed topological parameters such as electron density (ρ), and its Laplacian $\nabla^2\rho$ at the BCPs along with total energy density (H_{BCP}) that can give a qualitative knowledge about nature of bonding interaction[53, 54]. The negative H_{BCP} is an indicator of shared-kind bonding. In Table 3 we provide the computed topological parameters, which were calculated using QTAIM. From Table 3, it is found that for the Li doped borane clusters, $\rho < 0.20$ a.u. and positive $\nabla^2\rho$ with positive H_{BCP} at bond critical points (BCPs) of (Li, H) inferring that H₂ molecule is more likely to have somewhat closed-shell type interaction with Li atoms corresponding to van der Waals type of bonds. Moreover, the positive value of H_{BCP} (in the ranges of 0.0012 a.u. - 0.0031 a.u. for Li-H) also suggest that, in all studied clusters, kinetic energy density dominates over the potential energy density [53, 54].

In order to explore the thermodynamic stability and desorption of H₂ molecules at different temperatures, hydrogen adsorbed complexes are subjected to ADMP molecular dynamics simulations. The relaxed geometries obtained at M06/6-311++G(d,p) level of theory have been used for initial structures for the

ADMP simulations. The thermostatic simulations were carried out at 1 atm pressure and at seven different temperatures viz: 0, 77, 100, 200, 300, 373 and 473 K for 1ps time-scale. The potential energies trajectories during the simulations were presented in Fig. 7↑ and the corresponding snapshots at different time steps are provided in the Supplementary Information. From Fig. 7 it can be observed at 0K and 77K hydrogen adsorbed systems are stable enough and almost all hydrogen molecules remain adsorbed on Li sites resulting in gravimetric density in the range of 22.5 wt% – 26.4 wt% which fairly good as per the standard of US-DOE. Upon increasing the temperature to 100K, first H₂ molecule starts desorbing from the host cluster starts around 200fs. Further increasing the temperatures it is found that, at 373K and 473K only two hydrogen molecules are weakly attached to the host clusters. The ADMP simulation reveals that, the systems are stable at lower temperature and releases maximum of hydrogen molecules at the higher temperatures for all the systems. Moreover, it is noteworthy to say that, during the simulations insignificant deformation in the host clusters makes them potential reversible storage medium for future application.

3. Conclusion

Lithium decorated borane clusters (B_nH_nLi₆, n = 5–7) have been investigated for hydrogen storage medium using first principle calculation. On full saturation, the clusters can adsorb maximum up to 18 H₂ molecules in quasi molecular form through Niu-Rao-Jena type of bonding with average adsorption energy range of 0.10–0.11 eV/H₂ and average Li-H₂ distance 2.436–2.550 Å. The hydrogen adsorbed compounds followed the maximum hardness and minimum electrophilicity principle signifying their better stabilization. The calculated HOMO-LUMO energy gap increased with the increasing number of H₂ molecules also reconfirming their kinetic stability. The analysis of the QTAIM results revealed the the nature of the interaction between Li-H to be weak van der Waals type. The MD simulations shows that the H₂ molecules are physisorbed at 0K and 77K, giving rise to gravimetric density up to 26.2 wt% which was well above the target set by US-DOE. At higher temperature such as 373K and 473K the host clusters almost all hydrogen molecules without any structural distortion. The above discussion supports the fact that the studied clusters could be promoted as a potential hydrogen storage medium.

Declarations

Acknowledgements:

We acknowledge the financial support from Science & Engineering Research Board (SERB), DST, India under grant no. EMR/2014/000141. Authors also acknowledge Indian Institute of Technology (Indian School of Mines), Dhanbad for providing support and other research facilities.

Ethical Approval:

We hereby declare that all the authors are aware of and approve of the submission.

Consent to Participate:

We hereby declare that they have consent to participate

Consent to Publish:

We hereby declare that we are agree to publish the manuscript

Authors' Contributions:

Shakti S Ray: Conceptualization, Software, Formal analysis, Investigation, Writing-Original Draft, Sridhar Sahu: Supervision, Review & Editing, Project administration, Funding acquisition.

Funding Information:

Engineering Research Board (SERB), Govt. of India under Extramural Research grant (No. EMR/2014/00014)

Competing Interests:

We hereby declare that we have no competing interest.

Conflict of interest:

We hereby declare that we have no conflicts of interest.

Availability of data and material:

All data generated or analysed during this study are included in this published article and its supplementary information files.

Code availability:

Not applicable.

References

1. Jena P (2011) Materials for Hydrogen Storage: Past, Present, and Future. *J Phys Chem Lett* 2(3):206–211
2. Raupach MR, Marland G, Ciais P, Quere CL, Canadell JG, Klepper G, Field CB (2007) Global and regional drivers of accelerating CO₂ emissions. *PNAS* 104:10288–10293
3. Niaz S, Manzoor T, Pandith AH (2015) Hydrogen storage: Materials, methods and perspectives. *Renewable Sustainable Energy Rev* 50:457–469
4. Niemann MU, Srinivasan SS, Phani AR, Kumar A, Goswami DY, Stefanakos EK. Nanomaterials for Hydrogen Storage Applications: A Review. *J Nanomaterials* 2008; 950967
5. Edwards PP, Kuznetsov VL, David WIF, Brandon NP (2008) Hydrogen and fuel cells: Towards a sustainable energy future. *Energy Policy* 36:4356–4362
6. Bououdina M, Grant D, Walker G (2006) Review on hydrogen absorbing materials—structure, microstructure, and thermodynamic properties. *Int J Hydrogen Energy* 31:177–182
7. Sakintuna B, Lamari-Darkrim F, Hirscher M (2007) Metal hydride materials for solid hydrogen storage: A review. *Int J Hydrogen Energy* 32(9):1121–1140
8. Crabtree GW, Dresselhaus MS, Buchanan MV (2004) The hydrogen economy. *Phys Today* 57(12):39–44
9. Jain IP (2009) Hydrogen the fuel for 21st century. *Int J Hydrogen Energy* 34:7368–7378
10. <https://www.energy.gov/eere/fuelcells/hydrogen-storage>
11. Mahdizadeha SJ, Goharshadi EK (2019) Hydrogen storage on graphitic carbon nitride and its palladium nanocomposites: A multiscale computational approach. *Int J Hydrogen Energy* 44:8325–8340
12. Du J, Sun X, Jiang G, Zhang C (2019) Hydrogen capability of bimetallic boron cycles: A DFT and ab initio MD study. *Int J Hydrogen Energy* 44:6763–6772
13. Du J, Sun X, Jiang G, Zhang C (2019) Hydrogen capability of bimetallic boron cycles: A DFT and ab initio MD study. *Int J Hydrogen Energy* 44:6763–6772
14. Lang SM, Bernhardt TM (2012) Gas phase metal cluster model systems for heterogeneous catalysis. *Phys Chem Chem Phys* 14:9255–9269
15. Schwarz H (2015) Doping Effects in Cluster-Mediated Bond Activation. *Angew Chem Int Ed* 54:10090–10100
16. Wang J, Wei ZJ, Zhao HY, Liu Y (2016) Hollow Li₂₀B₆₀ Cage: Stability and Hydrogen Storage. *Scientific Reports* 6:24500
17. Zhang Y, Cheng X (2018) A novel hydrogen storage medium of Ca-coated B₄₀: First principles study. *Int J Hydrogen Energy* 43:15338–15347
18. Liu P, Liu F, Wang Q, Ma Q (2018) DFT simulation on hydrogen storage property over Sc decorated B₃₈ fullerene. *International J of Hydrogen Energy* 43:19540–19546

19. Liu P, Liu F, Peng Y, Wang Q, Juan R (2019) A DFT study of hydrogen adsorption on Ca decorated hexagonal B₃₆ with van der Waals corrections. *Physica E* 28:113576
20. Ye XJ, Teng ZW, Yang XL, Liu CS (2018) Na-Coated hexagonal B₃₆ as Superior Hydrogen Storage Materials. *J Saudi Chem Soc* 22:84–89
21. Liu CS, Wang X, Ye XJ, Yan X, Zeng Z (2014) Curvature and ionization-induced reversible hydrogen storage in metalized hexagonal B₃₆. *J Chem Phys* 141:194306
22. Si L, Tang C (2017) The reversible hydrogen storage abilities of metal Na (Li, K, Ca, Mg, Sc, Ti, Y) decorated all-boron cage B₂₈. *Int J Hydrogen Energy* 42:16611–16619
23. Song N, Lv J, Wang Y (2013) B₂₄ cluster as promising material for lithium storage and hydrogen storage applications. *Comput Mater Sci* 77:31–34
24. Ray SS, Sahoo SR, Sahu S (2019) Hydrogen storage in scandium doped small boron clusters (B_nSc₂, n = 3–10): A density functional study. *International J of Hydrogen Energy* 44:6019–6030
25. Bai H, Bai B, Zhang L, Huang W, Mu YW, Zhai HZ, Li SD (2016) Lithium-Decorated Borospherene B₄₀: A Promising Hydrogen Storage Medium. *Scientific Reports* 6:35518
26. Wang YS, Wang F, Li M, Xu B, Sun Q, Jia Y (2012) Theoretical prediction of hydrogen storage on Li decorated planar boron sheets. *Appl Surf Sci* 258:8874–8879
27. Li L, Zhang H, Cheng X (2017) The high hydrogen storage capacities of Li-decorated borophene. *Comput Mater Sci* 137:119–124
28. Srinivasu K, Ghosh SK (2010) An ab initio investigation of hydrogen adsorption in Li-doped closo-boranes. *J Phy Chem C* 115:1450–1456
29. Srinivasu K, Ghosh SK (2011) Theoretical studies on hydrogen adsorption properties of lithium decorated diborane (B₂H₄Li) and diboryne(B₂H₂Li₂). *Int J Hydrogen Energy* 36:15681–15688
30. Konda R, Deshmukh A, Titus E, Chaudhari A Alkali, alkaline earth and transition metal doped B₆H₆ complexes for hydrogen storage. *Int J Hydrogen Energy* 2017; 1–8
31. Rahamani A, Zabardasti A, Kakanejadifard (2019) Intermolecular complexes of [B₆H₆]²⁻ with nH₂ (n = 1–8) molecules: a theoretical study. *Struct Chem* 30:669–680
32. Lu Q, M JW, Song JW, Wan GJ (2013) High capacity hydrogen storage in closo-hexaborate dianion B₆H₆²⁻. *Int J Hydrogen Energy* 38:13328–13334
33. Adsorption of molecular hydrogen (2018) on inorganometallic complexes B₂H₄M (M = Be, Sc, Ti, V). *Struct Chem* 29:1593–1599
34. Pathak B, Pradhan K, Hussain T, Ahuja R, Jena P (2012) Functionalized boranes for hydrogen storage. *Chem Phys Chem* 13:300–304
35. Chen L, Chen X, Duan C, Huang Y, Zhang Q, Xiao B (2018) Reversible hydrogen storage in pristine and Li decorated 2D boron hydride. *Phys Chem Chem Phys* 20:30304–30301
36. Bora PL, Singh A (2013) New insight in to designing metallocarborane based room temperature hydrogen storage media. *J of Chem Phys* 139:164319

37. Zhao Y, Truhlar DG (2008) The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Non-covalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals. *Theor Chem Acc* 120:215–241
38. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR et al. Gaussian 09, Revision E.01, Gaussian, Inc, Wallingford CT; 2013
39. Keith TA. AIMALL (Version 11.02.27, Standard). 2011. TK Gristmill Software. Overland Park, KS, USA
40. O'Boyle NM (2008) tenderholt AI, Langner KM. cclib: a library for package-independent computational chemistry algorithm. *J Comput Chem* 29:839–845
41. Parr RG (1983) Absolute Hardness: Companion Parameter to Absolute Electronegativity. *J Am Chem Soc* 105:7512–7516
42. Sen KD, Jorgenson CK. *Electronegativity; Structure and Bonding*. 66; Springer: Berlin, 1987
43. Parr RG, Szentpaly LV, Liu S (1999) Electrophilicity Index. *J Am Chem Soc* 121:1922–1924
44. Chatraji PK (2009) *Chemical Reactivity Theory: A Density Functional View*. Taylor and Francis. CRC Press: Boca Raton, FL
45. Koopmans TA (1934) Über die Zuordnung von Wellenfunktionen und Eigenwerten zu den Einzelnen Elektronen eines Atoms. *Physica* 1:104–113
46. Alexandrova AN, Birch KA, Boldyrev AI (2003) Flattening the $B_6H_6^{2-}$ Octahedron. Ab Initio Prediction of a New Family of Planar All-Boron Aromatic Molecules. *J Am Chem Soc* 125:10786–10787
47. Niu J, Rao BK, Jena P (1995) Interaction of H_2 and He with metal atom, clusters and ions. *Phys Rev Lett* 75:4475–4484
48. Niu J, Rao BK, Jena P (1992) Binding of hydrogen molecules by a transition-metal ion. *Phys Rev Lett* 68:2277–2280
49. Kumar S, Kumar TJD (2017) Electronic structure calculation on hydrogen storage in lithium-decorated metal-graphyne framework. *Appl Mater Interface* 9:28659–28666
50. Chamorro E, Chattaraj PK, Fuentealba P (2003) Variation of the Electrophilicity Index along the Reaction Path. *J Phys Chem A* 107:7068–7072
51. Parr RG, Chattaraj PK (1991) Principle of maximum hardness. *J Am Chem Soc* 113:1854–1855
52. Bader RFW (1990) *Atoms in Molecules. A Quantum Theory*. Clarendon press, Oxford
53. Cremer D, Kraka E (1984) Chemical Bonds without Bonding Electron Density – Does the Difference Electron-Density Analysis Suffice for a Description of the Chemical Bond? *Int Ed Engl* 23:627
54. Espinosa E, Alkorta I, Elguero J, Molins E (2002) From weak to strong interactions: A comprehensive analysis of the topological and energetic properties of the electron density distribution involving $X-H\cdots F-Y$ systems. *J Chem Phys* 117:5529–1320

Figures

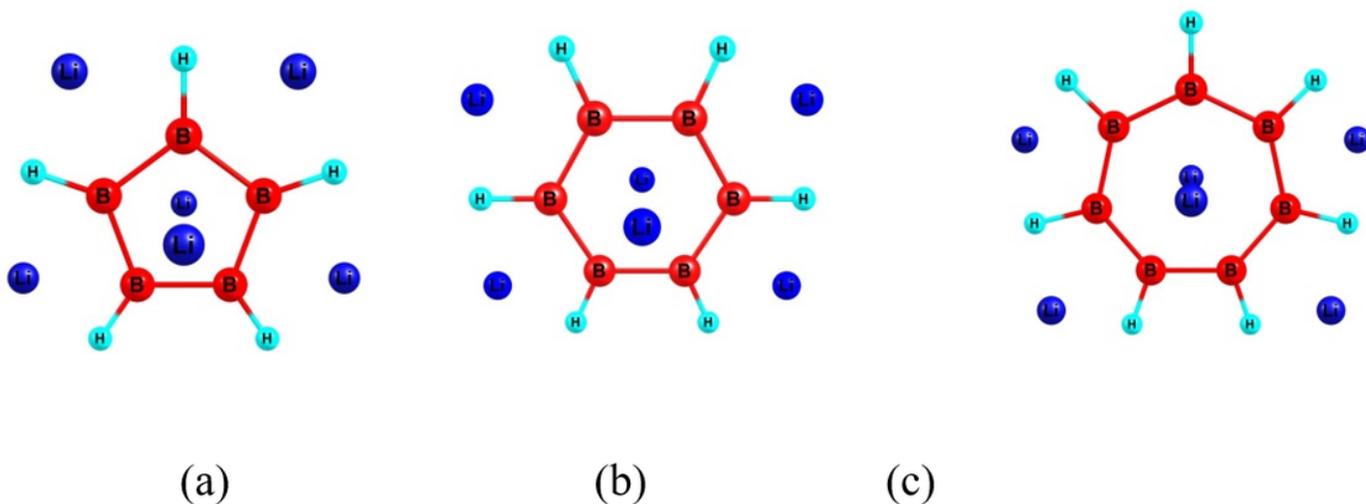


Figure 1

Optimized geometry of Lithium doped Boranes at M06/6-311++G(d,p) level of theory. Stability of the hydrogenated clusters is an important aspect to focus on while studying

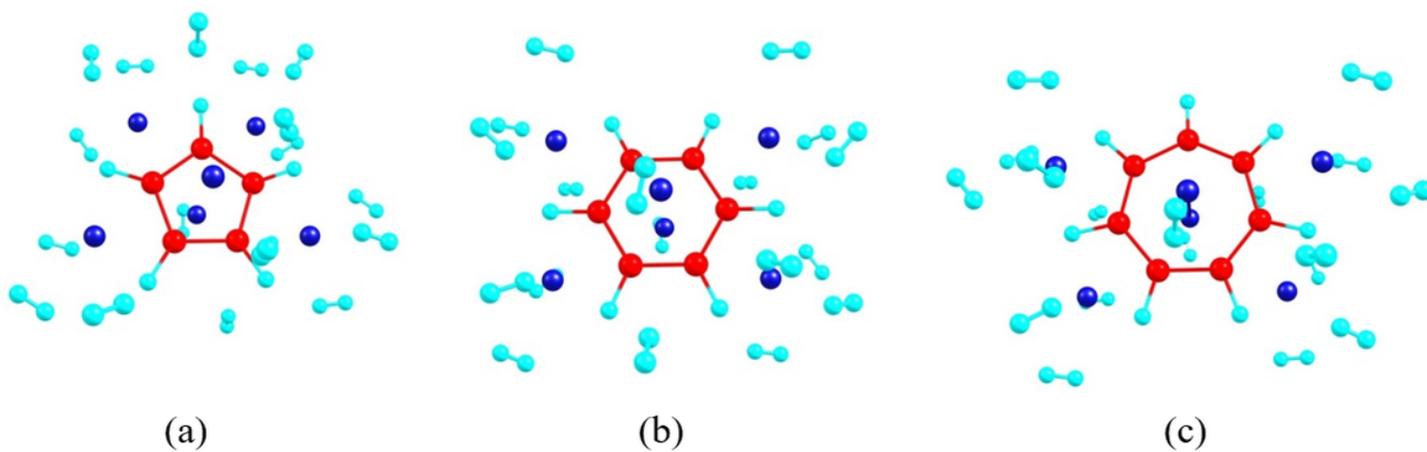


Figure 2

Optimized geometry of Hydrogen trapped lithium doped boranes at M06/6-311++G(d,p) level of theory.

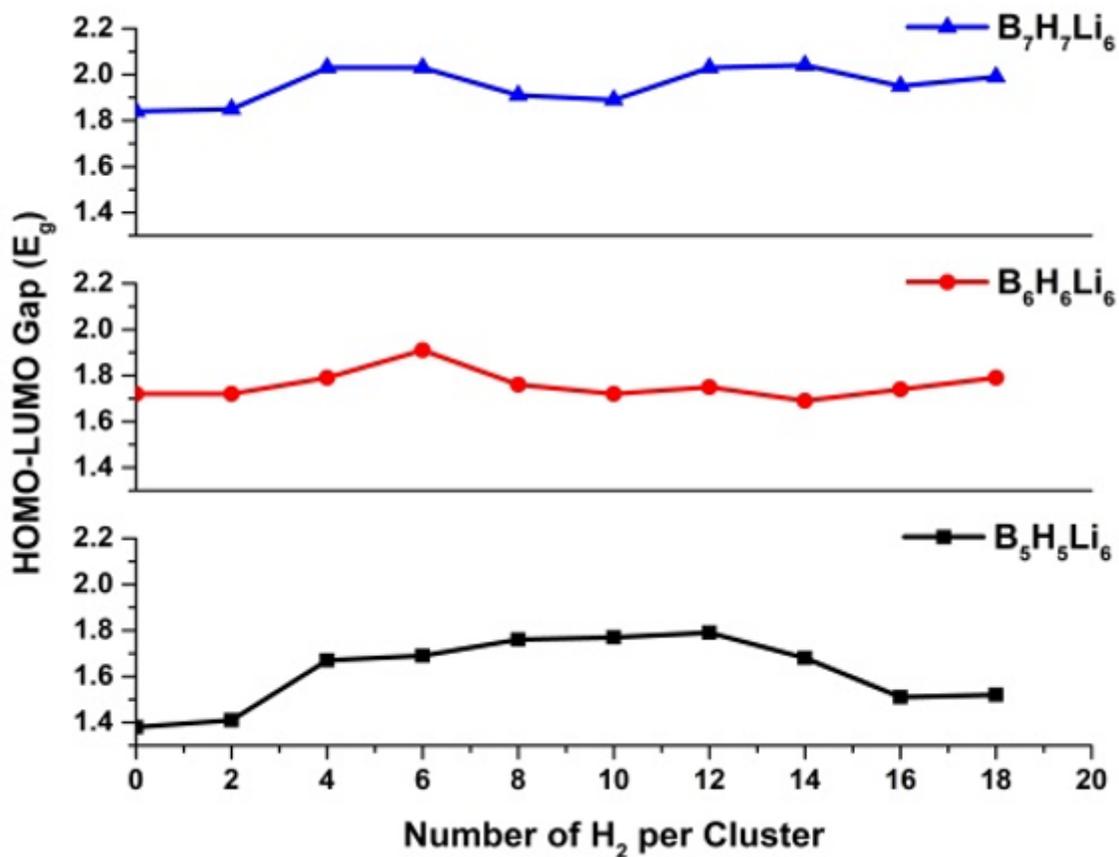


Figure 3

Variation of HOMO-LUMO gap with number of H_2 molecules per cluster of hydrogen trapped lithium decorated borane clusters.

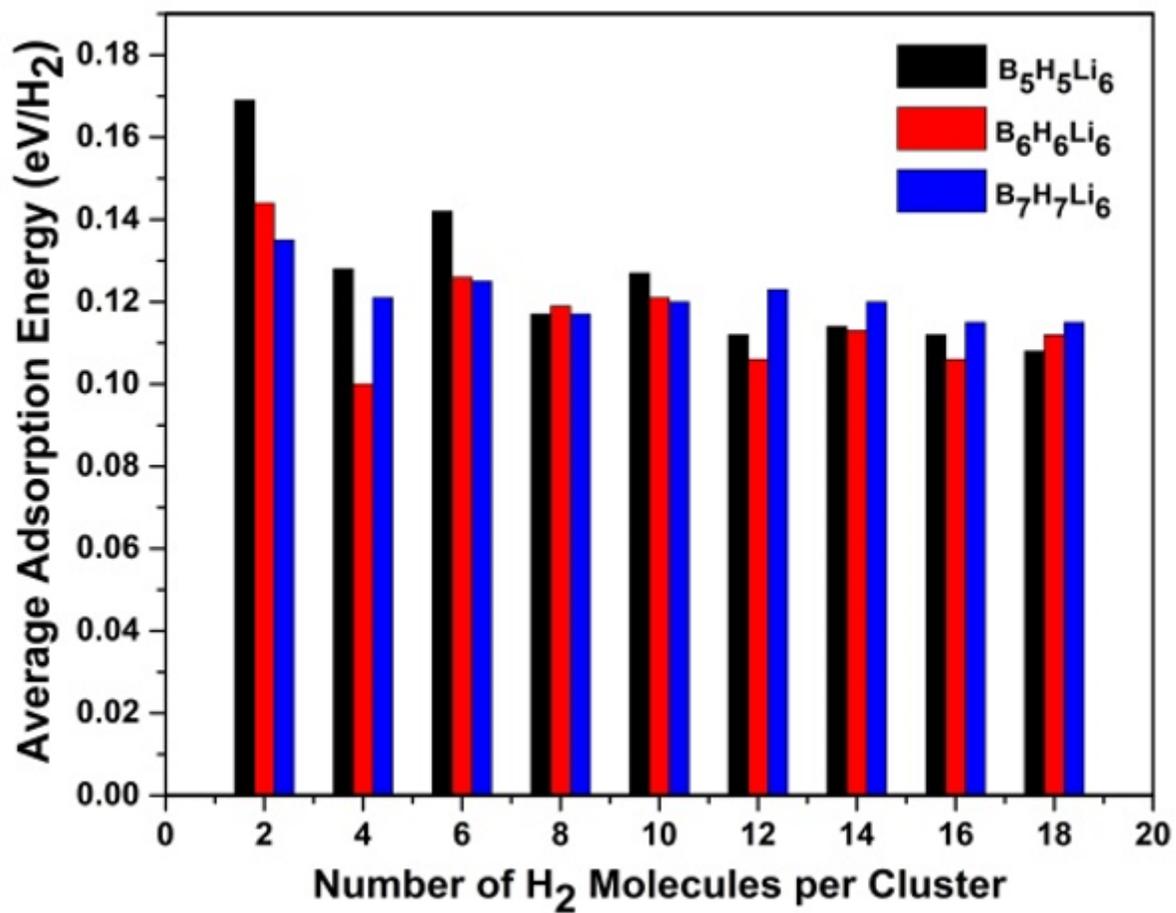


Figure 4

Variation of average adsorption energy with number of adsorbed H₂ molecules per cluster.

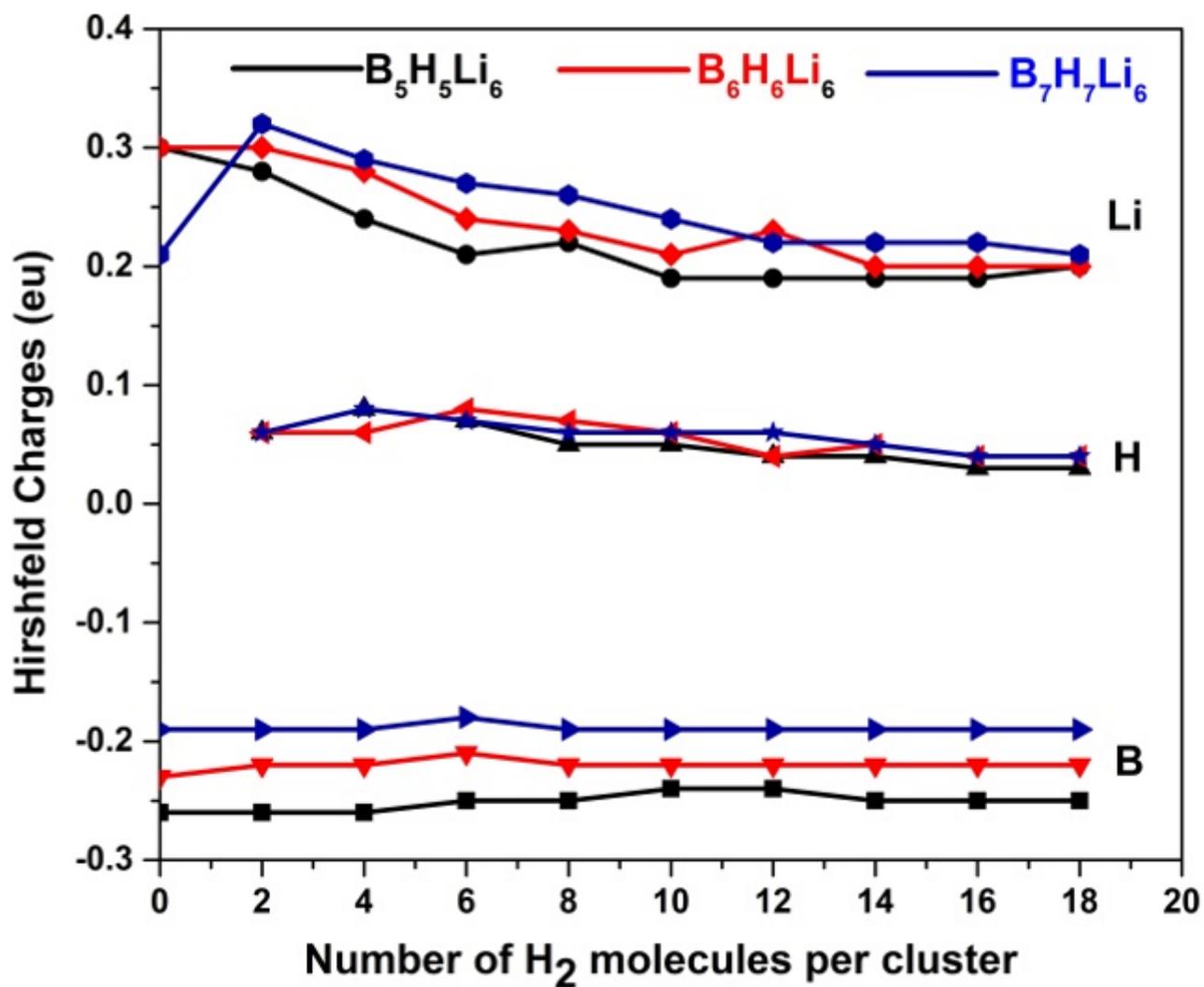


Figure 5

Hirshfeld charges of B, Li and H of B_nH_nLi₆, n=5-7 clusters at M06/6-311++G(d,p) level of theory

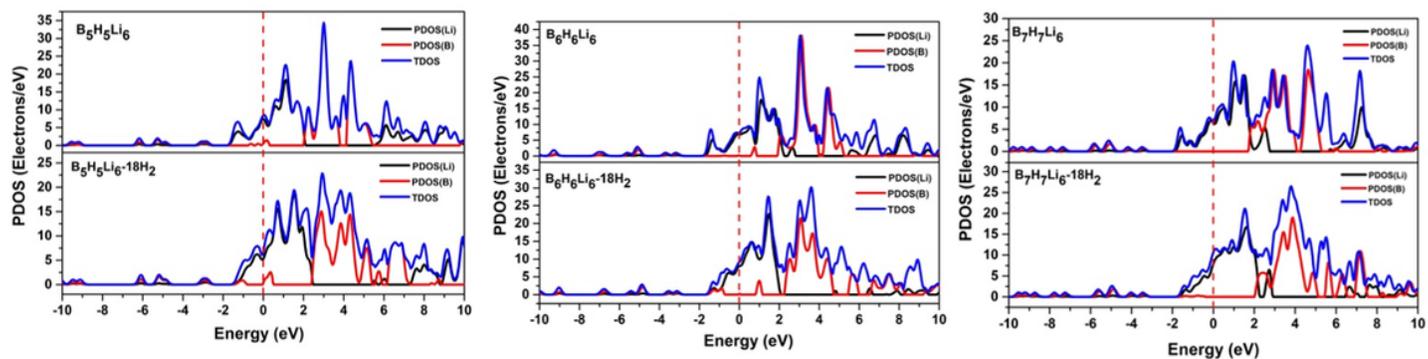


Figure 6

Partial density of states (PDOS) of host as well as hydrogen trapped complexes. A Fermi energy is set to zero and indicated by red dashed line.

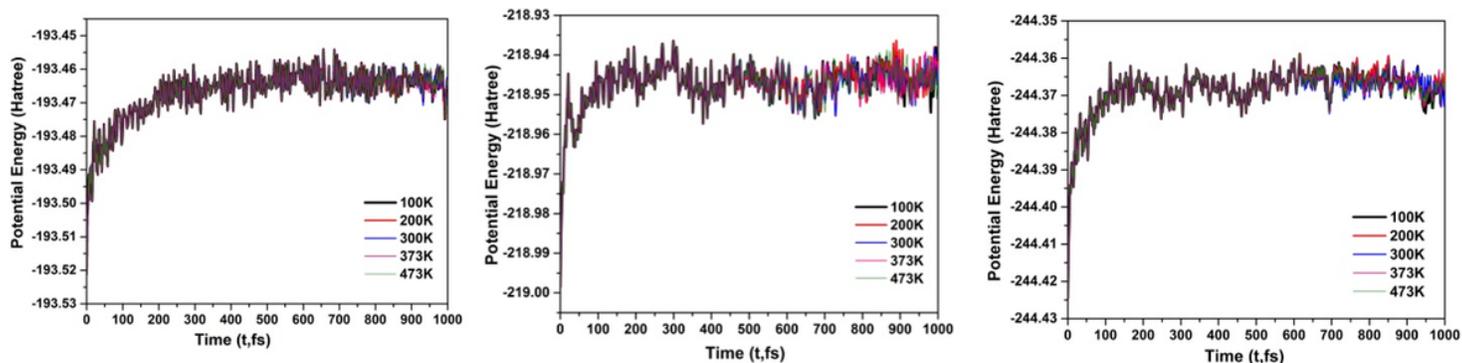


Figure 7

Potential energy trajectories of hydrogen loaded lithium doped boranes at 0K, 77K, 100K, 200K, 300K, 373K and 473K temperatures.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SupplymenraryInformation.pdf](#)