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Additives in protic–hydridic hydrogen storage compounds: a molecular study†

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Here we have studied the dehydrogenation energetics of protic–hydridic based hydrogen storage compounds. Various set of compounds are studied having different ratio of protic and hydridic hydrogens. Moreover, protic–hydridic based chemical additives (NH_3, BH_3 and NH_3BH_3) are added to protic–hydridic based hydrogen storage compounds to increase their hydrogen gravimetric density. Our study shows such chemical additives not only increase their hydrogen gravimetric density but also improve their dehydrogenation properties. Such practice turned out to be excellent as we not only generated some model compounds [$LiBH_2NH_3$ ($\Delta E_{avg} = 3.47$ eV), $LiNH_2BH_3\cdot BH_3$ ($\Delta E_{avg} = 3.75$ eV), $LiBH_2NH_3\cdot BH_3$ ($\Delta E_{avg} = 3.95$ eV] but also compounds like $LiNH_2BH_3{:}NH_3BH_3$ ($\Delta E_{avg} = 3.85$ eV), which has already been reported to be a promising hydrogen storage material. We find the dehydrogenation properties of the reported compounds are best when they have close to equal numbers of protic and hydridic hydrogens.

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1. Introduction

The serious environmental problems associated with fossil fuel burning are the foremost concern of this century. Therefore finding an alternative and sustainable energy source is very important which can replace the fossil fuel based energy.[1–3] The desirable energy source must be green, sustainable and renewable[4] and have the least adverse effect on the environment. Hydrogen instead of carbon-based (fossil fuel) energy has enormous potential to be used as an uninterrupted and secure energy carrier which can fulfil the demand of global energy.[5–8] Moreover, it produces H_2O as a by-product after electrochemical or combustion processes which is suitable for mankind.[9] But the biggest problem with hydrogen is its storage. To utilize H_2 as a globally acceptable fuel in vehicles and portable electronics, we require a solid on-board hydrogen storage material which can store a high gravimetric density of hydrogen and can deliver large amounts of hydrogen at moderate conditions.[10] For this purpose several potential storage media have been developed such as carbon materials,[11–13] metal organic frameworks (MOFs),[14–17] metal hydrides,[18] and complex hydrides.[19] But these materials are not suitable for practical use in the sense that either these materials bind with hydrogen in the surface by weak dispersive interactions (physisorption) or through stronger chemical associations (chemisorption). The goal is therefore to develop some low-cost, light-weight solid chemical hydrides (*i.e.* the chemical storage of hydrogen) which have high hydrogen energy density with faster dehydrogenation kinetics. Recently, ammonia borane[20–22] (NH_3BH_3, AB for short) received unique attention as a promising hydrogen storage material due to its exceptionally high hydrogen density (19.6 wt%) with releasing the first equivalent of H_2 (*i.e.* 6.5 wt% of H_2) under moderate thermal condition (below 100 °C) having significant air stability. The better desorption properties of AB might be due to the equal combination of protic and hydridic hydrogens present in the system. However, for the maximum use of H_2 coming from AB needs higher temperature which release undesirable borazine as side product.[23] Similarly, there are many other examples of protic–hydridic based light weighted hydrogen storage materials such as (1) lithium borohydride ammoniate [$Li(NH_3)_{4/3}BH_4$],[24] (3) lithium borohydride ammonia borane [$LiBH_4\cdot NH_3BH_3$],[25] (4) borohydride hydrazinates [$LiBH_4\cdot NH_2NH_2$],[26] (5) $Mg(BH_4)_2\cdot NH_3$,[27] (6) $Mg(BH_4)_2\cdot(NH_3BH_3)_2$,[28] (7) $Mg(BH_4)_2\cdot(NH_3)_2\cdot(NH_3BH_3)$,[28] (8) $Al(BH_4)_3\cdot 6NH_3$-4AB,[29] (9) $Li_2Al(BH_4)_5(NH_3BH_3)_3\cdot 6NH_3$ (ref. 29) and many more.[27,28] These materials drew great attention as a promising hydrogen storage material for their light weight, high gravimetric density and faster dehydrogenation. This opens up a new direction for hydrogen storage materials where the combination of protic and hydridic hydrogens is very important. Though the hydrogen dehydrogenation kinetics is very promising but still they are very far from the practical usages. Therefore the biggest challenge is to release the maximum number of hydrogen molecules at moderate thermal condition. For this several approaches have been adopted such as

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† Electronic supplementary information (ESI) available: We have tabulated the energetic for all the probable dehydrogenation steps for all compounds in Table S6. Table S7 lists NBO charge distributions for all the compounds. Full list of authors of Gaussian 09 reference (ref. 50) is given. See DOI: 10.1039/c4ra09778e

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transition metals catalysis,[23] nano-scaffolding,[29,30] ionic liquids[31] and additives.[24–28] Among all these, chemical additives having protic and hydridic hydrogens can be very promising because it not only increases their gravimetric density but can also improve their dehydrogenation properties.[32,33] Therefore, we have adopted chemical additives approach to lower the decomposition temperature and improve the dehydrogenation properties. As we all know light alkali metal doping[34,35] such as Li does not reduce the gravimetric density much but can improve the dehydrogenation kinetics significantly. Moreover, mixing light metal hydrides are reported to be very effective to improve their dehydrogenation properties.[36] So here we would like to study whether alkali metal doping with different additives can play a major role in increasing their gravimetric density as well as their dehydrogenation properties. For this, such a combination of ligands are chosen where the ratio of protic and hydridic hydrogen changes. So we have considered those set of ligands which has either protic, hydridic or both type of hydrogens. There are many possible compounds with such kind of hydrogens but initially we chose to study those set of compounds which are experimental characterized.[23] Then we have proposed some model compounds which can be very promising for future applications. Considering all these, the following series of compounds are chosen to see how mixing of certain additives could improve their dehydrogenation properties.

(I) NH_3, BH_3, NH_3BH_3.[20–22,38–40]

(II) $LiNH_2$,[41,42] $LiBH_2$,[43,44] $LiNH_2BH_3$,[45–47] $LiBH_2NH_3$.[48]

(III) $LiNH_2$:NH_3, $LiBH_2$:NH_3 $LiNH_2BH_3$:NH_3,[49] $LiBH_2NH_3$:NH_3.

(IV) $LiNH_2$:BH_3 $LiBH_2$:BH_3, $LiNH_2BH_3$:BH_3, $LiBH_2NH_3$:BH_3.

(V) $LiNH_2$:NH_3BH_3, $LiBH_2$:NH_3BH_3, $LiNH_2BH_3$:NH_3BH_3,[35,37] $LiBH_2NH_3$:NH_3BH_3.

In our work, we prefer the gas phase approach for the calculations of atomic and molecular dehydrogenation energy because it gives us the freedom to model any molecular structure which can be restricted for the bulk calculations. As we try to model some light weighted hydrogen storage material by introducing different kind of protic–hydridic based additives to improve their dehydrogenation properties, so the molecular approach is the most suitable one.

2. Computational details

The geometries of all the structures are fully optimized at B3LYP/6-311++G(d,p) using Gaussian 09 suit of programs.[50] This uses well known three parameter functional of Becke's including Hartree–Fock exchange contribution with a nonlocal correction for the exchange potential proposed by Becke,[51] with nonlocal corrections for the correlation energy suggested by Lee, Young and Parr.[52] The presence of stationary point is characterized by vibrational frequency calculation computing analytical Hessian matrix. Here we have calculated the atomic and molecular hydrogen liberation energy in each step of every compound. By this calculation we try to set a trend that how the atomic hydrogen desorption energy improves with the presence of dopant and additives. This type of calculation gives an idea that what type of dopant and additives are important for better dehydrogenation and encourage us to model some compounds which can be useful as a hydrogen storage materials. The atomic (ΔE_H) and molecular hydrogen (ΔE_{H_2}) liberation energy is calculated using the following eqn (1) and (2).

$$\Delta E_{\mathrm{H}} = (E_{\mathrm{SP}} + E_{\text{atomic hydrogen}}) - E_{\mathrm{GS}} \tag{1}$$

$$\Delta E_{\mathrm{H_2}} = (E_{\mathrm{SP}} + E_{\text{molecular hydrogen}}) - E_{\mathrm{GS}} \tag{2}$$

Here E_{SP} denotes the single point energy of the optimized molecule after hydrogen removal and E_{GS} is the ground state energy of the optimized structure. The natural-bond orbital (NBO)[53] charge also calculated for all the molecules to understand their charge distributions during the de-hydrogenation process.

3. Results and discussion

The results and discussion part is divided into three sections. In our first section, we discuss the standard hydrogen storage compounds having protic (NH_3), hydridic (BH_3) and protic–hydridic (NH_3–BH_3) hydrogens. In our next section, the Li substituted protic ($LiNH_2$), hydridic ($LiBH_2$), and protic–hydridic compounds ($LiNH_2BH_3$ and $LiBH_2NH_3$) are discussed. In our last section, we have used protic, hydridic and protic–hydridic based chemical additives (NH_3, BH_3, and NH_2BH_3) on the Li-substituted protic ($LiNH_2$), hydridic ($LiBH_2$), and protic–hydridic compounds ($LiNH_2BH_3$ and $LiBH_2NH_3$) for increasing their hydrogen gravimetric density. The last section has been divided into three parts based on the three different type of chemical additives (NH_3, BH_3, and NH_2BH_3) used on the Li-substituted protic ($LiNH_2$), hydridic ($LiBH_2$), and protic–hydridic compounds ($LiNH_2BH_3$ and $LiBH_2NH_3$).

Therefore, we try to understand whether such combination of hydrogens could facilitate the hydrogen desorption or not? The successive hydrogen desorption energy is calculated to understand whether stability of the intermediate compounds play an important role to their dehydrogenation or not?

3.1. NH_3, BH_3, NH_3BH_3

We begin our analysis by calculating atomic hydrogen desorption energies of the first series of compounds having protic, hydridic and protic–hydridic hydrogens. The calculated hydrogen removal energies are listed in Table 1. Their optimized structures are shown in Schemes 1–3.

3.1.1. Ammonia [NH_3, 21.42 wt%]. We have calculated the H removal energy of NH_3 and we find the successive N–H bond energies (Scheme 1) are 4.92, 6.46 and 4.34 eV respectively. Therefore first hydrogen removal energy is lower than the second one where as third one is the lowest. Interestingly, the molecular hydrogen liberation energy is very high (6.61 eV) for ammonia.

3.1.2. Borane [BH_3, 27.75 wt%]. Similarly, It is considered that BH_3 is the simplest compound of hydridic hydrogens. Here the atomic hydrogen liberation energy shows (Scheme 2) that the second hydrogen (3.94 eV) removal energy is lower than the first one (4.80 eV). It is interesting because in case of NH_3 (protic

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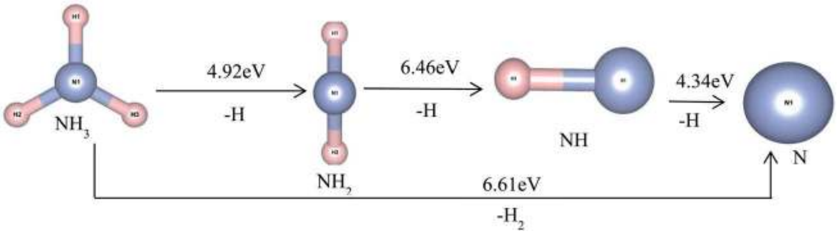
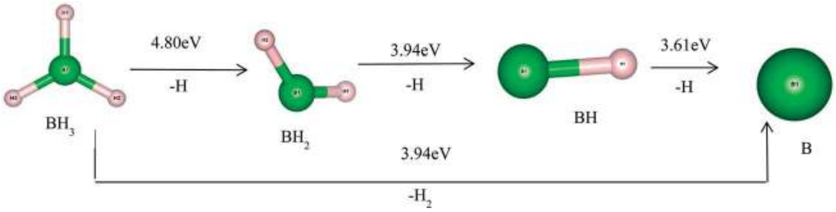
Table 1 The calculated atomic and molecular hydrogen removal energies (eV) are presented. Here ΔE_{avg} is the average hydrogen removal energy for the complete dehydrogenation

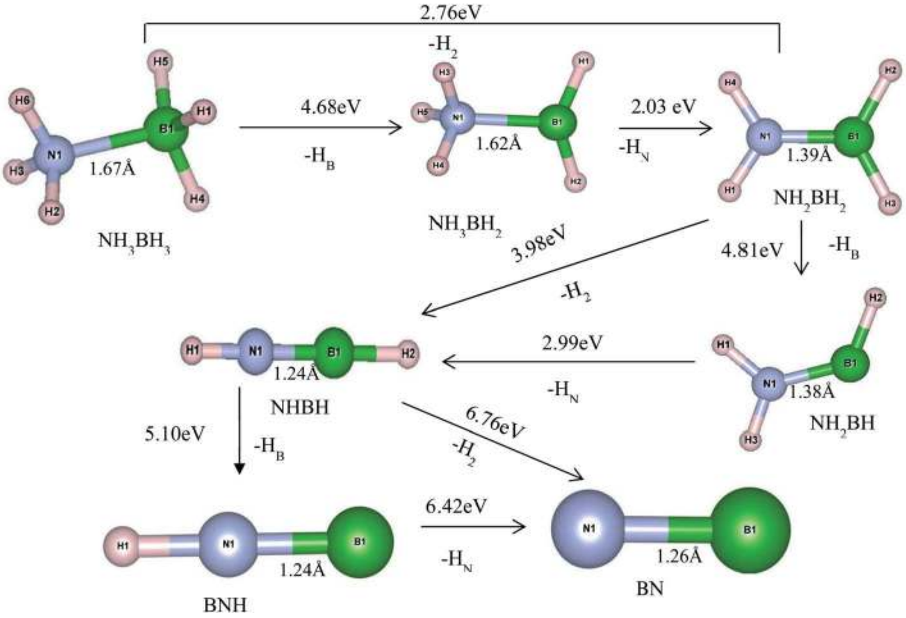
	H liberation steps (energy in eV)							H_2 liberation steps (energy in eV)			
Compounds	1st	2nd	3rd	4th	5th	6th	ΔE_{avg}	1st	2nd	3rd	ΔE_{avg}
NH_3	4.92	6.46	4.34				5.24	6.61			6.61
BH_3	4.80	3.94	3.61				4.12	3.94			3.94
NH_3BH_3	4.68	2.03	4.81	2.99	5.10	6.42	4.33	2.76	3.98	6.76	4.50



Scheme 1 Successive dehydrogenation energetics for NH_3.



Scheme 2 Successive dehydrogenation energetics for BH_3.



Scheme 3 Successive dehydrogenation energetics for NH_3BH_3, (here, H_N and H_B means hydrogen attached to nitrogen and boron atom respectively).

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hydrogens) the second N–H bond energies were higher than the first one where as in case of hydridic hydrogens the second hydrogen removal is easier than the first one. Interestingly, in BH_3, the successive dehydrogenation energies are lessening for each steps. Even, the molecular hydrogen liberation energy (3.94 eV) of BH_3 is far lower than in NH_3 (6.61 eV).

3.1.3. Ammonia borane [NH_3BH_3, 19.44 wt%]. In ammonia borane (AB), it has both types of hydrogen: protic and hydridic. First the atomic hydrogen liberation energy is calculated in NH_3BH_3 and the calculated N–H and B–H bond energies (Table 1) are 4.92 and 4.68 eV respectively.

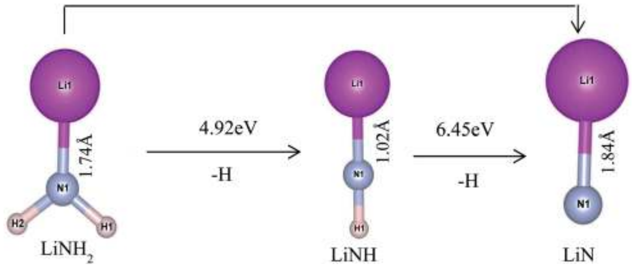
Therefore, the B–H bond energy is lower than the N–H bond energy. Interestingly, B–H bond energies in NH_3BH_3, are lower than in BH_3 (4.80 eV). The reason of lower H removal energy can be explained from their atomic charge distributions. The NBO charges on N atom of NH_3BH_3 and NH_3 are −0.837 and −1.049 respectively. Hence, N is less electronegative in NH_3BH_3 than in NH_3.

This might be due to the electron deficient nature of the B atom of BH_3 group. Similarly B is more electron negative (−0.151) in NH_3BH_3 than in (0.335) BH_3. Hence, in NH_3BH_3 the N is more electropositive than in NH_3 and B (−0.151) is more electro negative than in BH_3. The NBO charge differences (−0.685) between the N and B bond also decreases in AB.

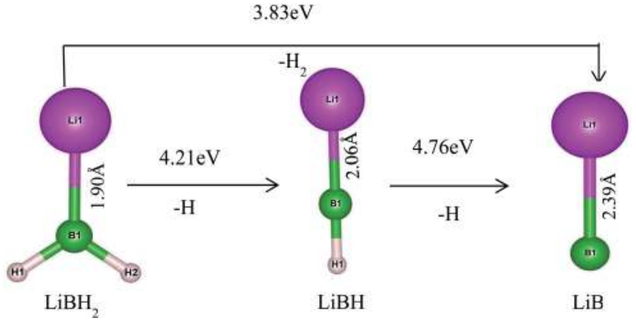
The second hydrogen removal energy of AB is lower for the N–H (2.03 eV) bond than the B–H (4.68 eV) bond. Such a lower removal energy (2.03 eV) can be related to the combination of protic and hydridic hydrogens. The NBO charge analysis shows B is more electronegative (−0.176) in NH_2BH_3 than in NH_3BH_3. We find, if the protic hydrogen liberates first then it might be facilitating the hydridic hydrogen elimination so that the electro neutrality is maintained. This can be seen from their atomic charge distribution also. Moreover, after atomic hydrogen removal, the charge difference in N–B bond decreases to −0.516. In AB, the calculated H_2 molecular desorption energy is of 2.76 eV. Such dehydrogenation, gives a stable planner geometry of NH_2BH_2 with high negative charge on N (−0.996) and positive charge on B (0.422). This compound has been experimentally characterized and found to be an important intermediate for borazine formation.[23] So, for NH_2BH_2 (Scheme 3) the boron hydrogen removal energy (4.81 eV) is very high. This might be due to the extra stability gained by the planner NH_2BH_2 intermediate. But interestingly the next hydrogen is calculated to be released easily (2.99 eV) from the N centre. As in the previous step hydridic hydrogen was released, so to maintain the electron neutrality protic hydrogen can be released easily. We find the removal energy is quite high (5.10 and 6.42 eV) for the next two steps. This might be due to the fact that the negative charges on N and positive charges on B increases in the NHBH and NHB compounds. Therefore, the N–H and B–H bond energies can be lowered if we can induce more positive charges on the N centre and negative charges on the B centre respectively. Moreover, lower the charge differences in the N–B bond, facilitates the atomic hydrogen liberation process.

3.2. $LiNH_2$, $LiBH_2$, $LiNH_2BH_3$, $LiBH_2NH_3$

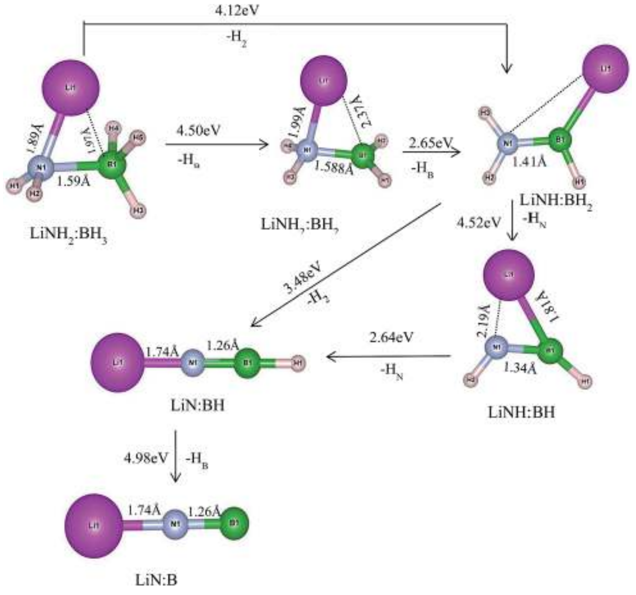
In our second series, we wanted to study the effect of alkali metal doping on the dehydrogenation properties of protic–hydridic compounds. Here we consider Li doping as Li is a very light weight metal and promising for improving their dehydrogenation properties. Therefore, Li substitution is done on the protic or hydridic hydrogens of NH_3, BH_3 and NH_3BH_3,



Scheme 4 Successive dehydrogenation energetics for $LiNH_2$.



Scheme 5 Successive dehydrogenation energetics for $LiBH_2$.



Scheme 6 Successive dehydrogenation energetics for $LiNH_2BH_3$ (here, H_N and H_B means hydrogen attached to nitrogen and boron atom respectively).

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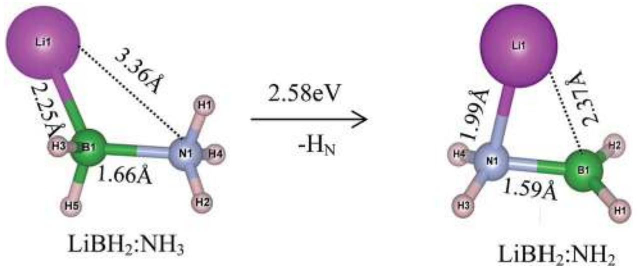

Scheme 7 Successive dehydrogenation energetics for $LiBH_2NH_3$ (here, H_N and H_B means hydrogen attached to nitrogen and boron atom respectively).

respectively. All the optimized structures are shown in Schemes 4–7.

3.2.1. $LiNH_2$ (8.78 wt%). The first compound in this set is $LiNH_2$ having two protic hydrogens. This compound can be synthesized using various methods. The very first method used to synthesize was the gas phase method. Here, the reaction between lithium vapour and ammonia is carried out in the argon environment (Ar acting as a carrier gas).[42] The most popular method for the preparation of $LiNH_2$ is the ball milling method by taking Li_3N as a starting material.[43]

We also calculate the atomic hydrogen liberation energy of $LiNH_2$. The first and second hydrogen liberation energy (Scheme 4) of $LiNH_2$ is exactly same with the first and second liberation energy of NH_3 (4.92 eV). As Li is substituting one of the hydrogen of NH_3, so comparison can be made with the first hydrogen removal energy of $LiNH_2$ with the second hydrogen removal energies of NH_3. We find the second hydrogen removal energy (6.45 eV) of NH_3 is higher than the first one (4.92 eV) of $LiNH_2$. Therefore, Li is improving the dehydrogenation properties of NH_3. So our plan is to mix such kind of chemical compounds (like $LiNH_2$:NH_3) so that we not only increase their gravimetric density but also improves their dehydrogenation properties.

3.2.2. $LiBH_2$ (5.92 wt%). $LiBH_2$ can be synthesized by decomposing $LiBH_4$ at 320 °C–380 °C under 10 atm H_2 pressure.[44] The B–H bond energy (4.21 eV) of $LiBH_2$ is surprisingly lower than the N–H bond energy (4.92 eV) of $LiNH_2$ and B–H bond energy (4.80 eV) of BH_3. This might be due to the presence of Li atom in the vicinity of boron centre which weakens the B–H bond strength.

3.2.3. $LiNH_2$:BH_3 (13.58 wt%). The third compound in this series is $LiNH_2BH_3$ (LiAB). LiAB can be synthesized from the commercially available compounds like LiH and NH_3BH_3 (AB).[45]

The structure of LiAB (Scheme 6) was optimized where we find Li is bridged between the N and B atoms. Our NBO charge calculation shows Li (0.837) is positively charged and bonded to negatively charged B (−0.189) and N (−1.139) atoms. The Li–N and Li–B bond distances are 1.89 Å and 1.98 Å respectively. So, Li is more closely bonded to N atom. Now, comparing the NBO charges on N (−0.837) and B (−0.151) in AB with N (−1.139) and B (−0.189) in LiAB, we find N is more electro-negative in LiAB.

We have calculated the N–H and B–H bond energy in the Li-doped ammonia borane (LiAB). The Li doping effect is clearly shown in the first atomic hydrogen liberation energy *i.e.* B–H bond breaking energy (4.50 eV) is lower than B–H bond energy (4.68 eV) in AB. Interestingly, the N–H bond energy (4.89 eV) of AB is not much changed compare to the N–H bond energy (4.92 eV) in NH_3BH_3. This might be due to the presence of positively charged Li (0.837), which induces more negative charges on N (−1.139) than in B (−0.189). Therefore, the first atomic hydrogen liberation is favourable from the B centre. The Li doping effect is visible for the second atomic hydrogen liberation also. We find N–H bond energy (2.65 eV) is very lower than the N–H bond energy (5.47 eV) in the NH_2BH_2. Similarly, the B–H bond energy is lower (4.59 eV) than the B–H bond energy (4.81 eV) in NH_2BH_2. So the atomic hydrogen liberation is more favourable from the N centre. The successive hydrogen removal energy (Scheme 6) for the third, fourth and fifth steps are 4.52, 2.64 and 4.98 eV respectively. Interestingly, in $LiNH_2BH_3$, the average hydrogen removal energy (Table 2) is 3.86 eV, which is much lower than the average hydrogen removal energy of NH_3BH_3 (4.33 eV).

3.2.4. $LiBH_2$:NH_3 (13.58 wt%). The last compound of this series is $LiBH_2NH_3$. Here, Li doping was considered on the boron hydrogen of ammonia borane (AB). The optimized structure of $LiBH_2NH_3$ is presented in Scheme 7. In $LiBH_2NH_3$, the distance between the Li–B and Li–N are 2.25 Å and 3.36 Å respectively. Therefore here Li is directly bonded to the B atom. The NBO charge distribution shows Li (0.416) is positively charged and inducing more negative charges on B (−0.569) whereas N (−0.862) has similar charges as in AB. Therefore, in $LiNH_2BH_3$, the first atomic hydrogen liberation is easier from the N–H bond (2.58 eV). The calculated N–H bond energy (2.58 eV) is quite lower than the N–H bond energy in (4.92 eV) NH_3BH_3 and (4.89 eV) $LiNH_2BH_3$. In case of $LiBH_2NH_3$, after the

Table 2 The calculated atomic and molecular hydrogen removal energies (eV) are presented. Here ΔE_{avg} is the average hydrogen removal energy for the complete dehydrogenation

	H liberation steps (energy in eV)						H_2 liberation steps (energy in eV)			
Compounds	1st	2nd	3rd	4th	5th	ΔE_{avg}	1st	2nd	3rd	ΔE_{avg}
$LiNH_2$	4.92	6.45				5.69	6.42			6.42
$LiBH_2$	4.21	4.76				4.49	3.83			3.83
$LiNH_2$:BH_3	4.50	2.65	4.52	2.64	4.98	3.86	4.12	3.48		3.80
$LiBH_2$:NH_3	2.58	2.65	4.52	2.64	4.98	3.47	2.25	3.48		2.86

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first hydrogen removal, the energetic steps are similar as reported for $LiNH_2BH_3$. But here the average hydrogen removal energy is 3.47 eV which is quite lower than in (3.86 eV) $LiNH_2BH_3$. This is because the first hydrogen removal energy (2.58 eV) of $LiBH_2NH_3$ was lower than in the $LiNH_2BH_3$ (4.50 eV).

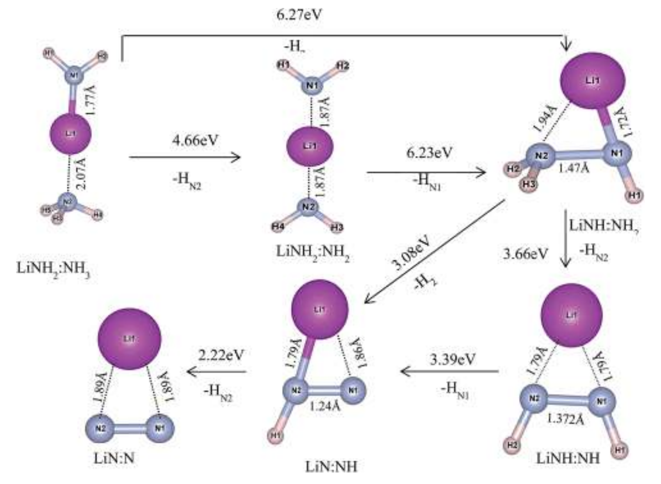
Therefore, Li doping highly influences the hydrogen removal energies of the protic and hydridic hydrogens and more importantly, the average hydrogen removal energies are lower for the compounds having more hydridic hydrogens.

3.3. $LiNH_2$:NH_3, $LiBH_2$:NH_3, $LiNH_2BH_3$:NH_3, $LiBH_2NH_3$:NH_3

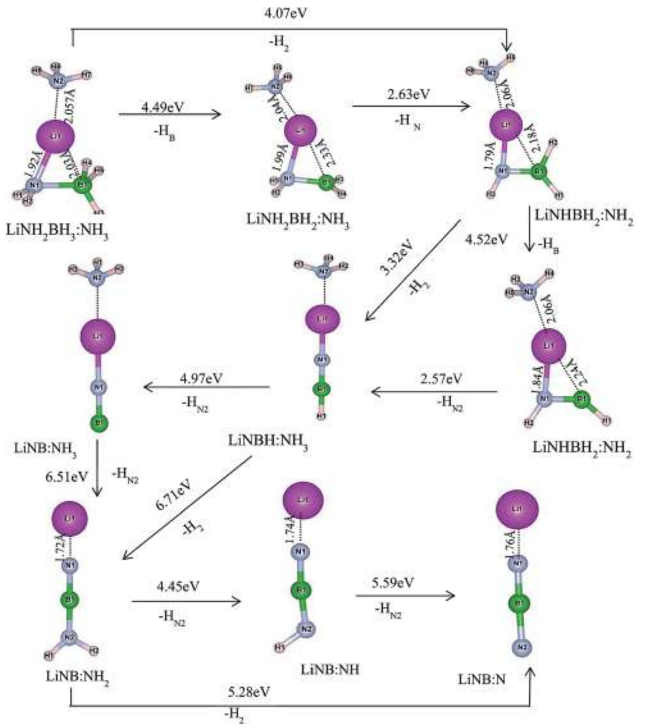
So, from our first set of calculations, we realised mixing of protic and hydridic hydrogens could improve their dehydrogenation properties. Hence, we decided to study the following set of compounds $LiNH_2$:NH_3, $LiBH_2$:NH_3, $LiNH_2BH_3$:NH_3, $LiBH_2NH_3$:NH_3 where NH_3 used as an additive having protic hydrogens. So, that the ratio of protic and hydridic hydrogens are changed from one compound to other. All the optimized structures are presented in Schemes 8–10.

3.3.1. $LiNH_2$:NH_3 (12.50 wt%). $LiNH_2$:NH_3 is a model compound having protic hydrogens where NH_3 used as a chemical additive on $LiNH_2$. The first hydrogen liberation energy (4.66 eV) of $LiNH_2$:NH_3 is lower compare to the liberation energy of (4.92 eV) $LiNH_2$ and (4.92 eV) NH_3. If we compare the NBO charges on N1 and N2 (Scheme 8) in $LiNH_2$:NH_3, we find N2 is more positively charged than in N1 (−1.507). Therefore the H from the N2 (−1.085) (ammonia) is easier to release. Here also it shows higher the positive charges on N, easier to remove the hydrogen.

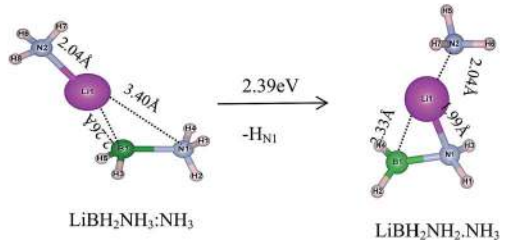
The second hydrogen can be liberated from any of the four equivalent hydrogens. The second hydrogen removal energy is higher 6.23 eV than the first one. On the other hand, the third (3.66 eV), fourth (3.39 eV) and fifth (2.22 eV) hydrogen desorption energy is quite low compare to the first two. Therefore, the trend of atomic H liberation is mainly depending on their charge distribution and structural rearrangements. The average energy needs to remove one H from $LiNH_2$:NH_3 is about 4.03 eV which is quite lower than in NH_3 (5.24 eV) and (5.69 eV) $LiNH_2$. Therefore, mixing of Li and NH_3 certainly improving their dehydrogenation properties.



Scheme 8 Successive dehydrogenation energetics for $LiNH_2$:NH_3 (here, H_N and H_B means hydrogen attached to nitrogen and boron atom respectively).



Scheme 9 Successive dehydrogenation energetics for $LiNH_2BH_3$:NH_3 (here, H_N and H_B means hydrogen attached to nitrogen and boron atom respectively).



Scheme 10 Successive dehydrogenation energetics for $LiBH_2NH_3$:NH_3 (here, H_N and H_B means hydrogen attached to nitrogen and boron atom respectively).

3.3.2. $LiBH_2$:NH_3 (13.58 wt%). The NH_3 addition to $LiBH_2$ will give the structure of $LiBH_2$:NH_3 which is basically Li substituted hydrazine borane. Therefore, this compound has already been studied and discussed in the previous section.

3.3.3. $LiNH_2BH_3$:NH_3 (14.86 wt%). Here $LiNH_2BH_3$:NH_3 is studied as a model compound where NH_3 used as a chemical additive. In this compound the number of protic hydrogens are more than hydridic hydrogens. We have calculated the first atomic hydrogen liberation energy and we find the B–H bond energy is 4.49 eV same with the B–H bond energy (4.50 eV) of $LiNH_2BH_3$. Therefore, NH_3 addition does not change the B–H

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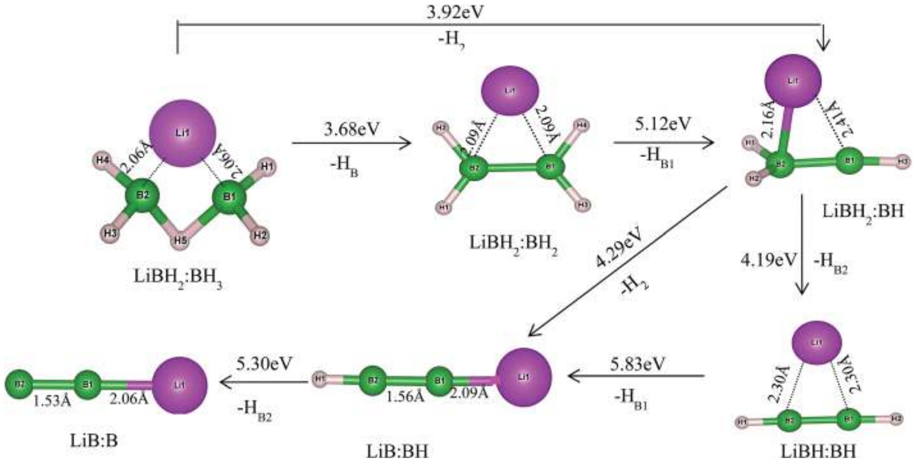
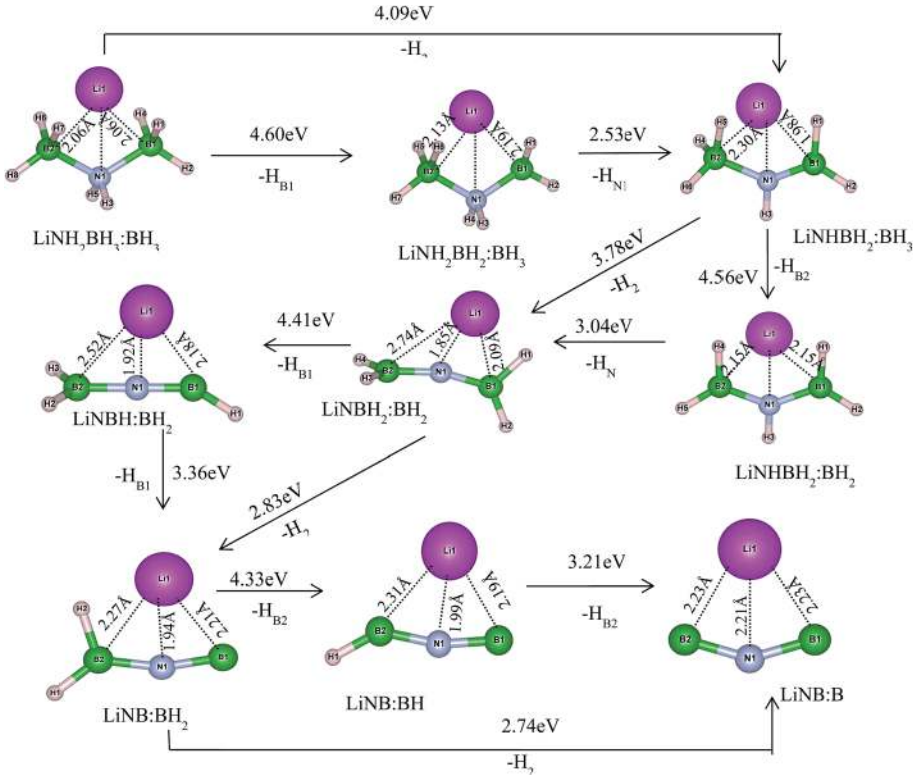
Table 3 The calculated atomic and molecular hydrogen removal energies (eV) are presented. Here ΔE_{avg} is the average hydrogen removal energy for the complete dehydrogenation

	H liberation steps (energy in eV)									H_2 liberation steps (energy in eV)				
Compounds	1st	2nd	3rd	4th	5th	6th	7th	8th	ΔE_{avg}	1st	2nd	3rd	4th	ΔE_{avg}
$LiNH_2:NH_3$	4.66	6.23	3.66	3.39	2.22				4.03	6.27	3.08			4.67
$LiNH_2BH_3:NH_3$	4.49	2.63	4.52	2.57	4.97	6.51	4.45	5.59	4.46	4.07	3.32	6.71	5.28	4.84
$LiBH_2NH_3:NH_3$	2.39	2.63	4.52	2.57	4.97	6.51	4.45	5.59	4.20	1.97	3.32	6.71	5.28	4.32



Scheme 11 Successive dehydrogenation energetics for $LiBH_2:BH_3$ (here, H_N and H_B means hydrogen attached to nitrogen and boron atom respectively).



Scheme 12 Successive dehydrogenation energetics for $LiNH_2BH_3:BH_3$ (here, H_N and H_B means hydrogen attached to nitrogen and boron atom respectively).

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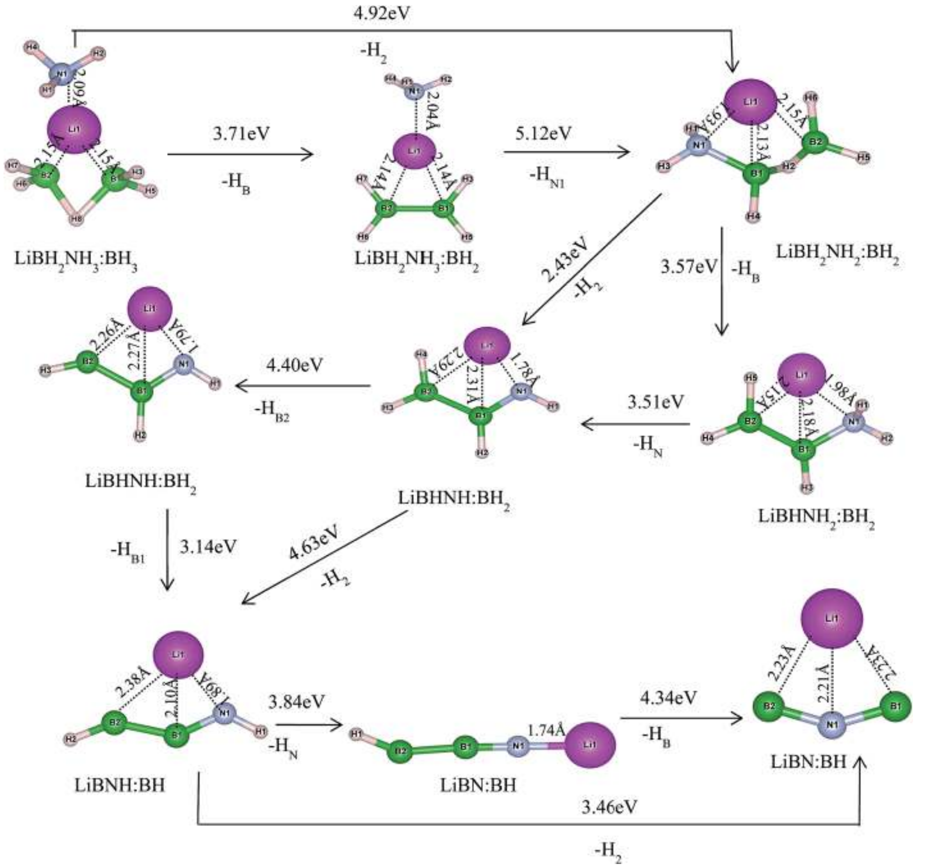
bond energy. The second hydrogen liberation is favourable from the N1–H (Scheme 9) side with removal energy of 2.63 eV. This might be due to the positive charge increases on the N1 (1.14) centre. The successive dehydrogenation energies from third to eight steps (Scheme 9) are 4.52, 2.57, 4.97, 6.51, 4.45, and 5.59 eV respectively. The average dehydrogenation energy is of 4.21 eV which is quite higher than in (3.86 eV) $LiNH_2BH_3$. Therefore, in this case, adding chemical additives such as NH_3 only increase the gravimetric density but not their dehydrogenation properties.

3.3.4. $LiBH_2NH_3$:NH_3 (14.86 wt%). In $LiBH_2NH_3$:NH_3, the ratio of protic and hydridic hydrogens is 3 : 1. The first hydrogen liberation energy (2.39 eV, Table 3) value is slightly lower than the (2.58 eV, Table 2) $LiBH_2NH_3$. But, from there on, the energetic will be same as in $LiNH_2BH_3 \cdot NH_3$. But as the first hydrogen removal energy is lower, the average hydrogen removal energy (4.20 eV) is better than in (4.46 eV) $LiNH_2BH_3 \cdot NH_3$. Therefore in this case chemical additive such as NH_3 is less helpful for improving their dehydrogenation properties (Table 3).

3.4. $LiNH_2$:BH_3, $LiBH_2$:BH_3, $LiNH_2BH_3$:BH_3, $LiBH_2NH_3$:BH_3

Here we discuss another set of compounds where BH_3 used as chemical additive. Therefore, the ratio of hydridic hydrogens are more than the protic hydrogens.

3.4.1. $LiNH_2$:BH_3 (13.58 wt%). The BH_3 addition to $LiNH_2$ will give the structure of $LiNH_2BH_3$ which is basically Li



Scheme 13 Successive dehydrogenation energetics for $LiBH_2NH_3$:BH_3 (here, H_N and H_B means hydrogen attached to nitrogen and boron atom respectively).

Table 4 The calculated atomic and molecular hydrogen removal energies (eV) are presented. Here ΔE_{avg} is the average hydrogen removal energy for the complete dehydrogenation

	H liberation steps (energy in eV)									H_2 liberation steps (energy in eV)				
Compounds	1st	2nd	3rd	4th	5th	6th	7th	8th	ΔE_{avg}	1st	2nd	3rd	4th	ΔE_{avg}
$LiBH_2$:BH_3	3.68	5.24	4.19	5.83	5.30				4.85	3.92	4.29			4.10
$LiNH_2BH_3$:BH_3	4.60	2.53	4.56	3.04	4.41	3.36	4.33	3.21	3.75	4.09	3.78	2.83	2.74	3.36
$LiBH_2NH_3$:BH_3	3.71	5.12	3.57	3.51	4.40	3.14	3.84	4.34	3.95	4.92	2.43	4.63	3.46	3.69

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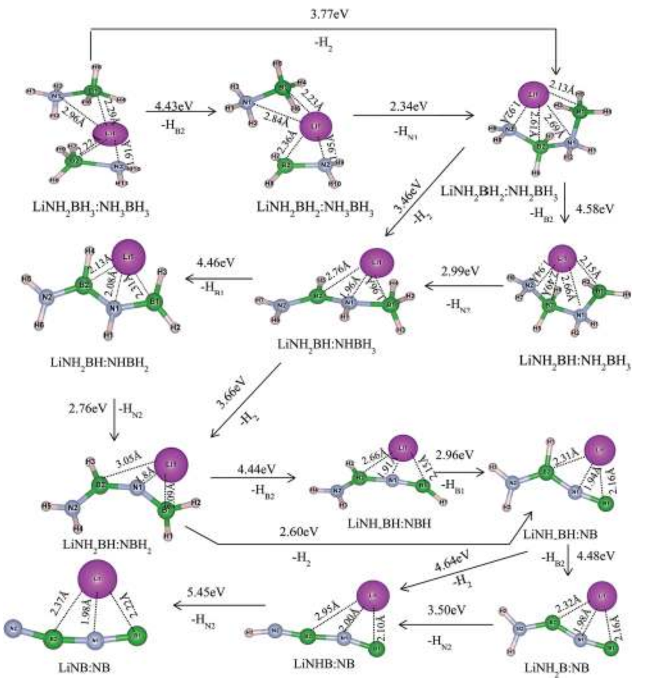
substituted hydrazine borane. Therefore, this compound has already been studied and discussed in the previous section.

3.4.2. $LiBH_2$:BH_3 (14.88 wt%). The first compound of this set is $LiBH_2$:BH_3 having hydridic hydrogens only. The optimized structure of $LiBH_2$:BH_3 has B_2H_6 geometry where Li is taking one of the bridging hydrogen's positions. The successive dehydrogenation energies for the second to fifth steps are (Scheme 11) 5.12, 4.19, 5.83 and 5.30 eV respectively. The average atomic hydrogen removal energy is 4.85 eV which is higher than in (4.49 eV) $LiBH_2$ and (4.12 eV) BH_3. Therefore, chemical additive BH_3 could not improve the dehydrogenation properties of $LiBH_2$.

3.4.3. $LiNH_2BH_3$:BH_3 (15.79 wt%). Therefore, the average hydrogen removal energy is 3.75 eV which is low in comparison to (3.86 eV) $LiNH_2BH_3$ and (4.12 eV) BH_3. Therefore BH_3 could be a very promising chemical additive for compounds having both protic and hydridic hydrogens.



Scheme 14 Successive dehydrogen energetics for $LiNH_2BH_3$:NH_3BH_3 (here, H_N and H_B means hydrogen attached to nitrogen and boron atom respectively).

3.4.4. $LiBH_2NH_3$:BH_3 (15.79 wt%). In case of $LiBH_2NH_3$:BH_3, we have more hydridic hydrogens than protic. Similarly, we have studied $LiNH_2BH_3$:BH_3 where hydridic and protic hydrogen ratio is 2 : 1. The successive hydrogen removal steps are presented in Scheme 12. Here, we find N–H hydrogens are easier to remove than the B–H hydrogens.

This can be concluded by NBO charge calculation as the positive charge on N (−0.882) is more than in $LiNH_2BH_3$ as well as the negative charge on B1 (−0.172) is more than AB and LiAB.

The calculated dehydrogenation steps are presented in Scheme 13. The average hydrogen removal energy calculated to be 3.95 eV which is high in comparison to (3.47 eV, Table 2) $LiBH_2NH_3$ but low in compare to (4.12 eV, Table 1) BH_3.

In these set of calculations we find $LiNH_2BH_3$:BH_3 having best dehydrogenation properties (Table 4).

3.5. $LiNH_2$:NH_3BH_3, $LiBH_2$:NH_3BH_3, $LiNH_2BH_3$:NH_3BH_3, $LiBH_2NH_3$:NH_3BH_3

Here in this series, NH_3BH_3 used as a chemical additive having equal number of protic and hydridic hydrogens.

3.5.1. $LiNH_2$:NH_3BH_3 (14.86 wt%). After structural relaxation, the structure of $LiNH_2$:NH_3BH_3 is converted into the geometry of $LiNH_2BH_3$:NH_3 which has been studied and discussed in the previous section.

3.5.2. $LiBH_2$:NH_3BH_3 (15.79 wt%). Similarly we could not optimize the geometry of $LiBH_2$:NH_3BH_3. After optimization the structure turned out to be $LiBH_2NH_3$:BH_3, already discussed in the previous section.

3.5.3. $LiNH_2BH_3$:NH_3BH_3 (16.25 wt%). In this series, the very first compound we have studied is $LiNH_2BH_3$:NH_3BH_3. This compound can be synthesized[35] by ball milling method. The reactant mixture (LiH and AB) are taken in 1 : 2 ratio into the milling machine.

Here we have almost equal number of protic and hydridic hydrogens but the hydrogen gravimetric density is as high as 16.2 wt%. The first atomic hydrogen is easy to remove from B2–H and the value is calculated to be 4.43 eV (Table 5). Similarly all the successive dehydrogenation steps are calculated and presented in Scheme 14. The average hydrogen removal energy is of 3.85 eV which is quite low in compare to NH_3BH_3 (4.33 eV, Table 1) but very much similar with $LiNH_2BH_3$ (3.86 eV, Table 2) which is already reported to be very promising material for hydrogen storage. This kind of low dehydrogenation value can also be explain by the low NBO charge difference between the N

Table 5 The calculated atomic and molecular hydrogen removal energies (eV) are presented. Here ΔE_{avg} is the average hydrogen removal energy for the complete dehydrogenation

Compounds	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	11th	ΔE_{avg}
H liberation steps												
$LiNH_2BH_3$:NH_3BH_3	4.43	2.34	4.58	2.99	4.46	2.76	4.44	2.96	4.48	3.50	5.45	3.85
H_2 liberation steps												
$LiNH_2BH_3$:NH_3BH_3	3.77	3.46	3.66	2.60	4.64							3.63

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and B centre as discussed earlier. Therefore, addition of such kind of chemical additives (NH_3BH_3) is very much helpful and promising for the hydrogen storage application. It looks the dehydrogenation thermodynamics depend lot of the ratio of protic and hydridic hydrogens. In this particular case we found the protic and hydridic hydrogen ratio is almost equal and the dehydrogenation properties are very promising.

3.5.4. $LiBH_2NH_3$:NH_3BH_3 (16.25 wt%). The next material we tried to model in this series is $LiBH_2NH_3$:NH_3BH_3. Similarly, here NH_3BH_3 is added as a substituent in the vicinity of $LiBH_2NH_3$. Here also the protic and hydridic hydrogen ratio is almost equal as in $LiNH_2BH_3$:NH_3BH_3. But when we try to relax then it takes the geometry of $LiNH_2BH_3$:NH_3BH_3 (Table 5).

4. Conclusions

In the present work, molecular level calculations are performed to understand the dehydrogenation properties of protic–hydridic (NH_3, BH_3 and NH_3BH_3) based hydrogen storage compounds. Li-substitution is done to improve their dehydrogenation properties. Protic–hydridic based chemical additives were added to improve their hydrogen storage density as well as their dehydrogenation properties. We find, the dehydrogenation properties of these compounds depend lot on their charge distribution. We find the hydrogen removal is easier if we could induce more positive charge on N and negative charge on B. Chemical additives, such as NH_3, BH_3 and NH_3BH_3, certainly increase their gravimetric density as well as improve their dehydrogenation properties. The dehydrogenation properties of the compound are best when they have close to equal numbers of the protic and hydridic hydrogens. The protic and hydridic hydrogens are easier to remove if more positive and negative charges could be induced on N and B-centre. Therefore, such mixing, led us to get some model compounds $LiBH_2NH_3$ ($\Delta E_{avg} = 3.47$ eV), $LiNH_2BH_3 \cdot BH_3$ ($\Delta E_{avg} = 3.75$ eV), $LiBH_2NH_3 \cdot BH_3$ ($\Delta E_{avg} = 3.95$ eV) which not only improves their gravimetric density but also their dehydrogenation properties. Moreover, such practise turned out to be excellent as we could even model compounds like $LiNH_2BH_3$:NH_3BH_3 ($\Delta E_{avg} = 3.85$ eV) which has already been experimentally characterized and reported to be a very promising hydrogen storage material. Therefore, the results we get through mixing of chemical additives are expected to develop a new generation of light-weighted hydrogen storage materials.

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