

Computational studies of the properties of 1,3-bis(borane)imidazolidine adduct for chemical hydrogen storage systems

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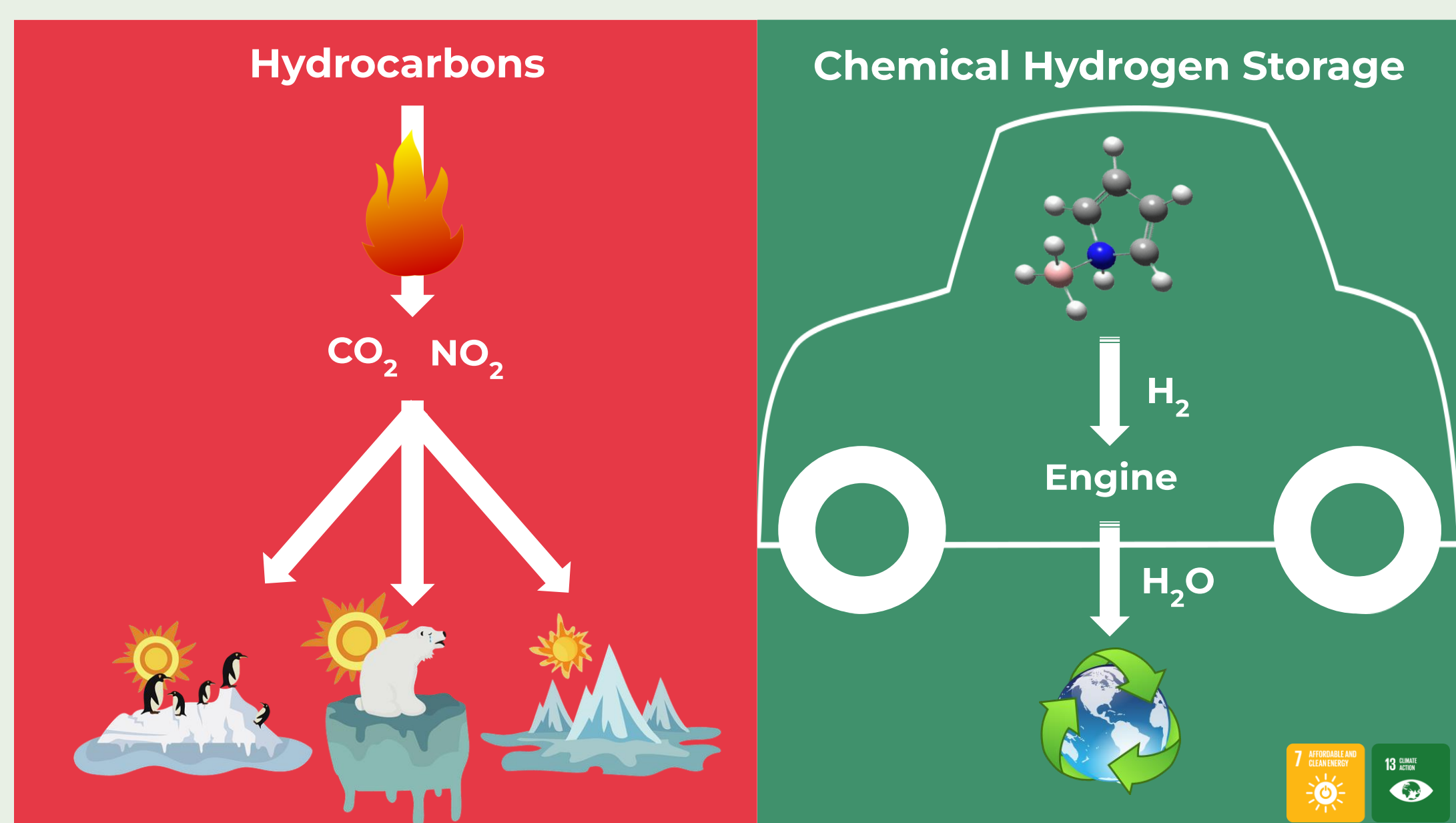
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INTRODUCTION

- Given the environmental impact of burning fossil fuels, hydrogen is a potential replacement.
- Hydrogen is a green fuel for future generations whilst meeting UN Sustainable Development Goals #7 and #13 (Figure 1).
- Amine boranes can act as hydrogen storage materials due to their high hydrogen content.¹
- Hydrazine bisborane can release 16.8 wt.% hydrogen.²
- Ethylene diamine bisborane releases approximately 10wt.% hydrogen at temperatures ranging from 373 K to 473 K.³
- This project is investigating the structural parameters of the various conformers of 1,3-bis(borane)imidazolidine (**IMBB**), as well as the thermochemistry and thermodynamics for the dehydrogenation of the most stable conformer.

Figure1: Fossil fuels for vehicular use and its environmental impacts and solution for the issue.



COMPUTATIONAL METHODS

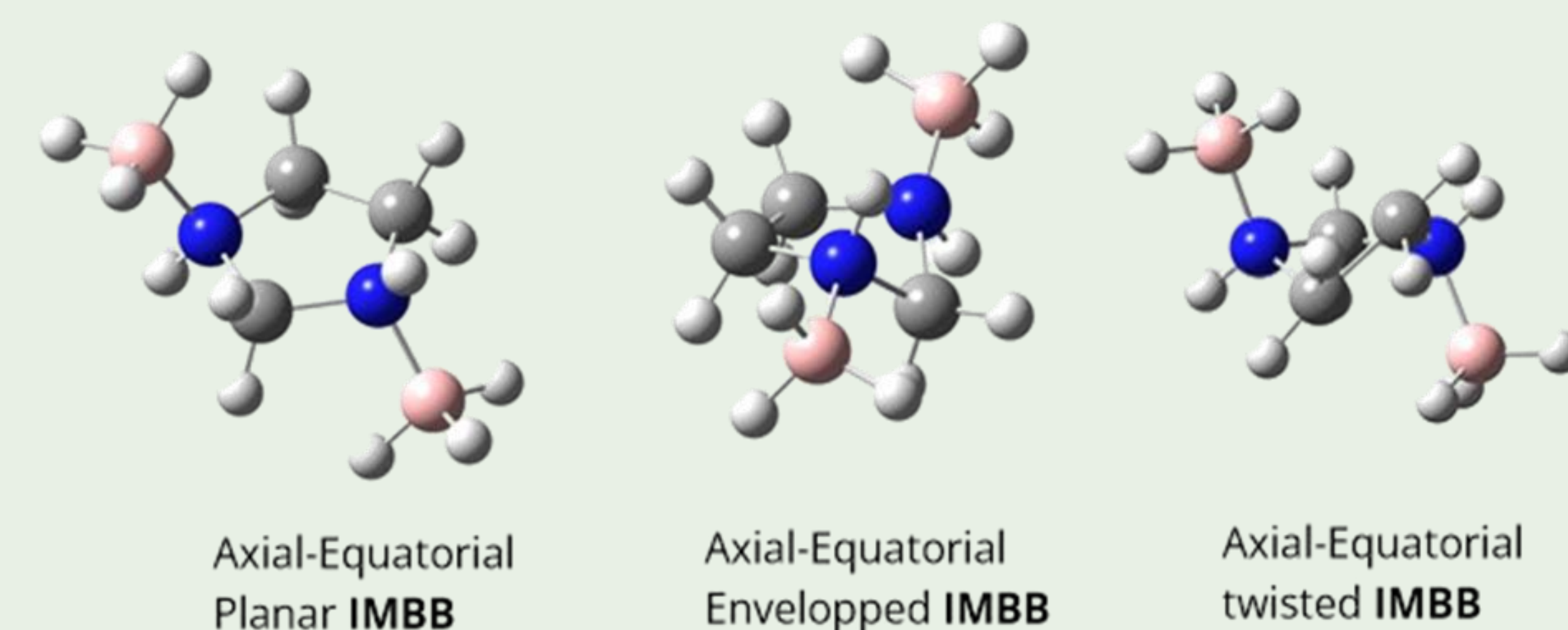
- Thermochemical parameters and bond dissociation energies for the H₂ elimination of **IMBB** were predicted at CBS-QB3
- Transition state structures of the hydrogen evolution reaction of **IMBB** were identified at CBS-QB3.

RESULTS

Conformational Analysis:

Three minima were identified and the Axial-Equatorial planar conformer is used for further studies.

Figure 2: Structures of the three stable conformers of **IMBB**



- rB-N is similar in **IMBB** cf. 1,4-bis(borane)piperazine (PPZBB).⁴
- The energy needed to break the first B-N bond to form imidazolidine borane (B-N_{BDE}1) is lower than for the second B-N bond to form the free imidazolidine (B-N_{BDE}2). (Table 1)
- All the B-N_{BDEs} are lower than the respective energy barriers along the dehydrogenation reaction. (Table1/Figure 3)
- The B-N_{BDEs} are lower in **IMBB** than PPZBB (Table 1).

Table 1: Optimized B-N distance (pm) and B-N bond dissociation energies (kJ/mol) for **IMBB** and PZBB at CBS-QB3 level.

	IMBB	PPZBB
rB-N	164.7	163.3
B-N _{BDE} 1	102.7	151.7
B-N _{BDE} 2	117.0	165.5

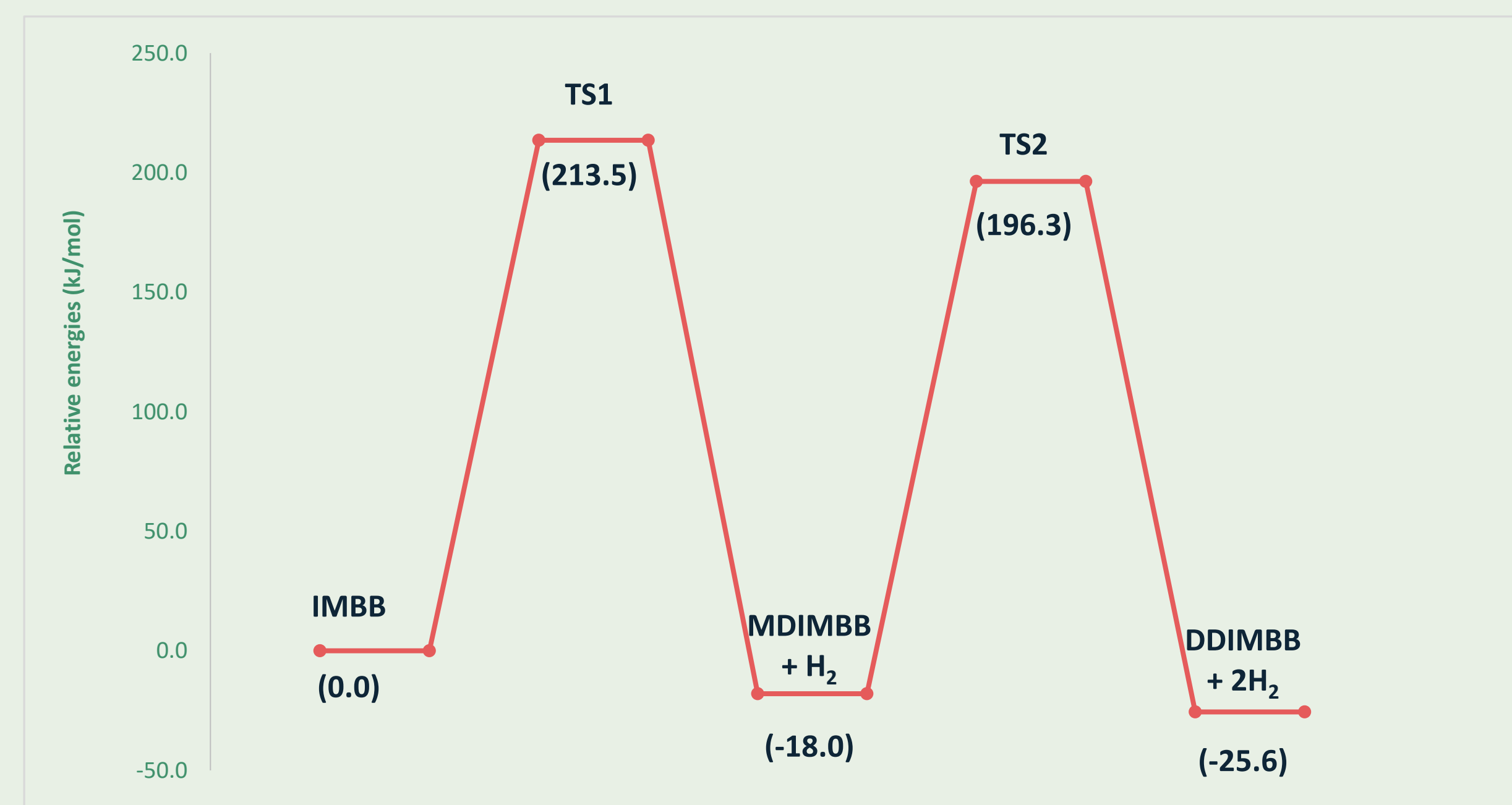
- Reaction energies for the release of both H₂ molecules are similar.
- This indicates a spontaneous, exothermic, reaction and simultaneous hydrogen release near thermoneutral process of the two H₂ molecules rather than releasing one followed by another.
- ΔH_r and ΔG_r are larger in **IMBB** than PPZBB (Table 2).

Table 2: Thermochemical parameters predicted at CBS-QB3 level of theory at 298.15 K.

Property	IMBB		PPZBB ⁴	
	1 st	2 nd	1 st	2 nd
ΔH_r	-56.9	-49.8	-44.9	-41.5
ΔG_r	-93.8	-86.8	-82.1	-75.6
ΔS_r	+123.8	+124.0	+125.5	+114.6

Units in kJ/mol except ΔS_r which is in J/K/mol
1st and 2nd implies the reaction to release the first and second H₂ molecule

Figure 3: Energy profile for the dehydrogenation of **IMBB** at 298.15K at CBS-QB3 level. Relative energies are in kJ/mol



CONCLUSIONS

- Predicted enthalpy of dehydrogenation shows the H₂ release reaction of **IMBB** is a thermoneutral process.
- ΔG_r is negative and ΔS_r is positive and with a free energy change of the products less than that of the reactants (Figure 3) suggesting a fast exergonic and favourable dehydrogenation reaction.
- IMBB** is predicted to dissociate across the B-N bond rather than evolve H₂ due to the lower B-N_{BDEs}
- Transition-state structures for the dehydrogenation reaction pathways also reinforce that dissociation of **IMBB** will be favoured over dehydrogenation.

FUTURE PLANS

- Thermochemical investigation of **IMBB** will be extended at CCSD(T) level to obtain accurate thermochemistry results.
- BH₃ catalysed dehydrogenation for the **IMBB** will be investigated to determine if this makes the hydrogen elimination reaction more favourable.
- This will allow better evaluation of the suitability of **IMBB** for on-board vehicular applications with the aim of meeting the UN sustainable Development Goals.

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REFERENCES

- G. W. Crabtree, M. S. Dresselhaus and M. V. Buchanan, Phys. Today, 2004, 57, 39–44.
- L. Li, Y. Tan, Z. Tang, G. Xia, F. Yuan, Q. Li and X. Yu, Mater. Chem. Phys., 2014, 143, 1055–1060.
- D. Neiner, A. Karkamkar, M. Bowden, Y. Joon Choi, A. Luedtke, J. Holladay, A. Fisher, N. Szymczak and T. Autrey, Energy Environ. Sci., 2011, 4, 4187–4193.
- A. M. Ja'o, 2019. Experimental and theoretical study of new compounds for hydrogen storage. Thesis (PhD). University of Canterbury.