# An automatically generated reaction network for the synthesis of hBN using the Molecular High-Index Saddle Dynamics Search method

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## 1. Introduction

The construction of reliable datasets for chemical reactivity is often bottlenecked by "chemical intuition" - the requirement that researchers manually hypothesize reaction coordinates. This introduces bias and limits the discovery of complex, non-intuitive mechanisms. In this work, we present a generated dataset of reaction pathways for the synthesis of hexagonal boron nitride (hBN) from ammonia borane ($BNH_6$ - leftmost molecule in Fig 1, a) to borazine ($B_3N_3H_6$ - rightmost molecule in Fig 1, b) produced via the k-index Molecular High-Index Saddle Dynamic Method (k-MHiSD).

## 2. Methods

The k-MHiSD method is based on previous High-index Saddle Dynamics (HiSD) methods that targeted other physical systems.[1, 2] This approach is intended to start from a local energy minimum of the potential energy surface (PES) and searching along the paths of slightest gradient ascent to find the closest neighbouring stationary states. By repeating this process iteratively, and including down-ward searches from higher index stationary states, full reaction networks can be generated. A key feature of this method is its ability to locate high-index ($k$) saddle points and perform bidirectional searches - stepping up to index $k + 1$ or down to index $k - 1$. This branching capability allows us to map a dense connectivity graph of the PES, potentially identifying $2^k$ reaction channels from a single high-order state.

The k-MHiSD method requires energies, gradients, and hessian values which can be output from any electronic structure method. We are currently using the psi4[3] computational package to generate these values using density functional theory (DFT) methods, and we are exploring low cost computational methods, such as xTB,[4] to accelerate reaction network discovery. We are also exploring the combination of low and high cost methods in a multi-fidelity approach that can accelerate saddle-point searching, which retain high accuracy final data points.

## 3. Results

We apply this workflow to the growth of hBN. Experimental mass spectrometry suggests a mechanism involving borazine intermediates, and reaction pathways for the initial reactions of ammonia-borane have been proposed,[5] but a definitive reaction mechanism is not yet established. Our automated search reveals a minimum energy path starting at ammonia borane and ending with borazine (Fig. 1), a proposed pathway previously undocumented in theoretical literature, in addition to multiple other side reactions.

We are currently extending the search algorithm to map the subsequent growth from borazine to the hBN monolayer. The final contribution will be a comprehensive "Reaction Route Map" - a graph connecting stable minima via transition states (Fig. 2). This presentation will discuss new results and future directions.

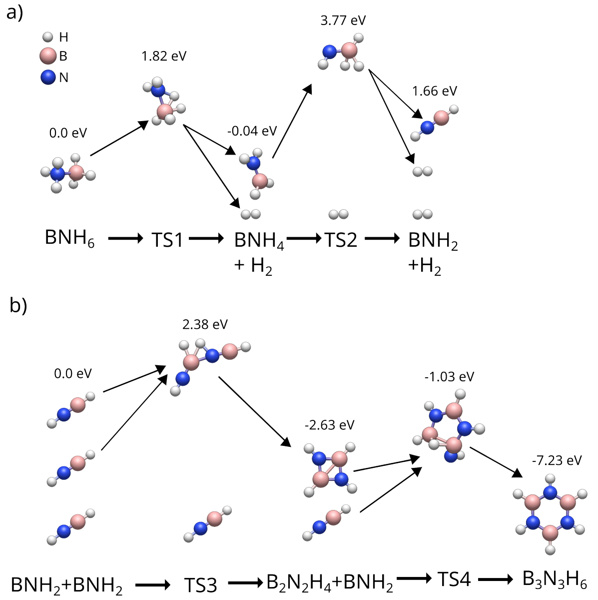

Fig. 1: Schematic of the ammonia borane to borazine pathway with key intermediates. **(a)** The stepwise dehydrogenation of ammonia borane ($BNH_6$). The pathway proceeds through transition state TS1 to form aminoborane ($BNH_4$) and release one $H_2$ molecule. A second dehydrogenation step via TS2 yields iminoborane ($BNH_2$) and a second $H_2$ molecule. **(b)** Three iminoborane ($BNH_2$) molecules react sequentially via transition states TS3 and TS4 to form borazine ($B_3N_3H_6$).

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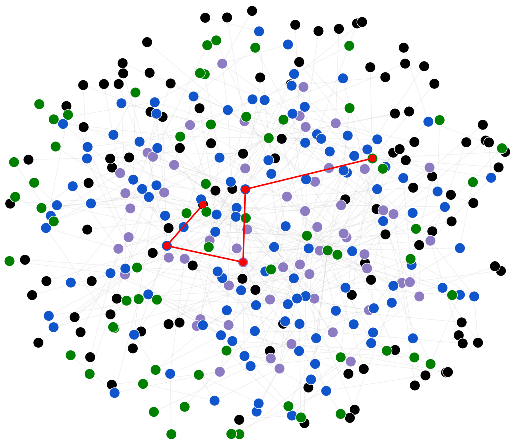

Fig. 2: Graph visualization of the stationary points found on the $B_2N_2H_4$ potential energy surface. Nodes are colored according to their saddle point order: green (order 0, minima), blue (order 1), and lavender (order 2). Black nodes represent fragmented molecular states. Edges indicate connected pathways discovered by the search algorithm. The path highlighted in red corresponds to the specific formation pathway of $B_2N_2H_4$ from $2(BNH_2)$ via transition state TS3, as detailed in Figure 1.

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## References

[1] Jianyuan Yin, Lei Zhang, and Pingwen Zhang. High-index optimization-based shrinking dimer method for finding high-index saddle points. *SIAM J. Sci. Comput.*, 41(6):A3576–A3595, 2019.

[2] Jianyuan Yin, Zhen Huang, and Lei Zhang. Constrained high-index saddle dynamics for the solution landscape with equality constraints. *J. Sci. Comput.*, 91(2):62, 2022.

[3] Daniel G. A. Smith, Lori A. Burns, Andrew C. Simmonett, Robert M. Parrish, Matthew C. Schieber, Raimondas Galvelis, Peter Kraus, Holger Kruse, Roberto Di Remigio, Asem Alenaizan, Andrew M. James, Susi Lehtola, Jonathon P. Misiewicz, Maximilian Scheurer, Robert A. Shaw, Jeffrey B. Schriber, Yi Xie, Zachary L. Glick, Dominic A. Sirianni, Joseph Senan O'Brien, Jonathan M. Waldrop, Ashutosh Kumar, Edward G. Hohenstein, Benjamin P. Pritchard, Bernard R. Brooks, III Schaefer, Henry F., Alexander Yu. Sokolov, Konrad Patkowski, III DePrince, A. Eugene, Uğur Bozkaya, Rollin A. King, Francesco A. Evangelista, Justin M. Turney, T. Daniel Crawford, and C. David Sherrill. Psi4 1.4: Open-source software for high-throughput quantum chemistry. *The Journal of Chemical Physics*, 152(18):184108, 05 2020.

[4] Marvin Friede, Christian Hölzer, Sebastian Ehlert, and Stefan Grimme. dxtb – an efficient and fully differentiable framework for extended tight-binding. *The Journal of Chemical Physics*, 161(6):062501, 08 2024.

[5] Ting Cheng, Ksenia V. Bets, and Boris I. Yakobson. Synthesis landscapes for ammonia borane chemical vapor deposition of h-bn and bnnt: Unraveling reactions and intermediates from first-principles. *Journal of the American Chemical Society*, 146(13):9318–9325, 2024. PMID: 38517068.