

IV.B.1h Hydrogen Storage by Novel CBN Heterocycle Materials

Shih-Yuan Liu

University of Oregon
Department of Chemistry
1253 University of Oregon
Eugene, OR 97403-1253
Phone: (541) 346-5573; Fax: (541) 346-0487
E-mail: lsy@uoregon.edu

DOE Technology Development Manager:
Grace Ordaz

Phone: (202) 586-8350; Fax: (202) 586-9811
E-mail: Grace.Ordaz@ee.doe.gov

DOE Project Officer: Jim Alkire

Phone: (303) 275-4795; Fax: (303) 275-4753
E-mail: James.Alkire@go.doe.gov

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Technical Targets

This project is developing new liquid phase materials for hydrogen storage that can be readily regenerated. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- System Gravimetric Density = 4.5 wt%
- System Volumetric Density = 28 g/L

Accomplishments

- Identified three materials with favorable thermodynamics and down-selected four potential materials with the help of computation.
- Synthesized a complete set of model heterocycle materials with different degree of hydrogen content. This will allow the determination of the thermodynamics of hydrogen desorption and absorption via experimental measurement and thus provide a feedback loop to the calculated values.
- Demonstrated that the spent fuel readily absorbs two equivalents of H₂ under mild conditions.



Objectives

The objective of this project is to develop novel boron-nitrogen heterocycles as liquid-phase hydrogen storage materials with storage capacities and thermodynamic properties that have the potential to lead to rechargeable systems capable of meeting DOE targets. We seek to:

- Develop new materials that:
 - (a) exhibit appropriate enthalpy of H₂ desorption
 - (b) are liquids at operating temperatures
 - (c) possess high H₂ storage capacities
- Identify catalysts that will release hydrogen from these materials at temperatures <200°C.
- Develop conditions that will readily recharge the spent fuel.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (C) Efficiency
- (R) Regeneration Process

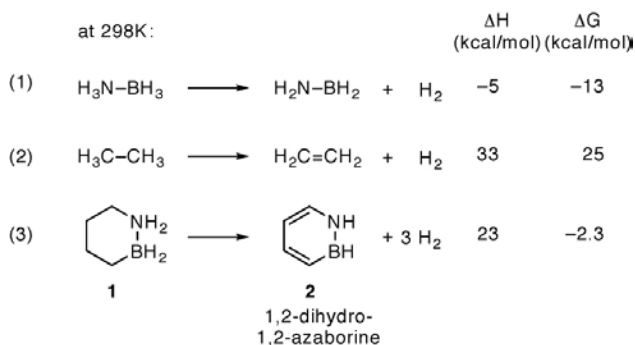
Introduction

Hydrogen storage is a vital component in the development of a hydrogen-based energy infrastructure. Boron nitrogen containing compounds, e.g., ammonia-borane (H₃N-BH₃ or AB), have attracted much attention as chemical H₂ storage materials because of their high gravimetric hydrogen densities and fast kinetics of H₂ release [1]. This project is developing CBN hydrogen storage materials (i.e., heterocycles containing carbon, boron, and nitrogen) that are liquid-phase and have the potential to be reversibly regenerated using molecular hydrogen. A liquid phase, hydrogen storage system that can be regenerated using molecular hydrogen is highly desired for many reasons, including versatility, lower cost and improved efficiency, and durability. Such a storage material will allow on-board hydrogen storage. It can also be applied as an off-board energy carrier for vehicle and stationary applications that takes advantage of the existing liquid fuels infrastructure.

Approach

In order to accomplish reversibility, neutrality in free energy of the hydrogen release process (i.e., $\Delta G \sim 0$ kcal/mol) at the operating temperature is

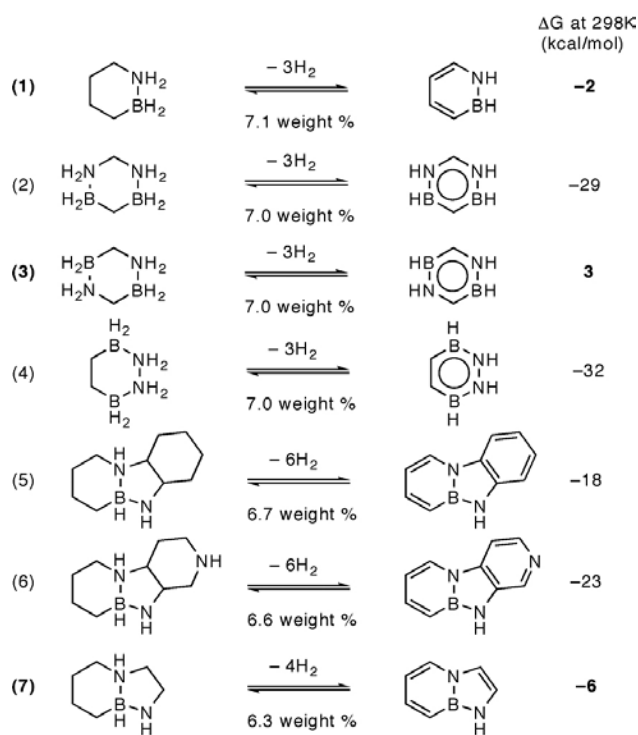
pivotal. The dehydrogenation of AB is exergonic by -13 kcal/mol at 298 K (Eq. 1). In contrast to AB, the dehydrogenation of its isoelectronic organic counterpart, ethane ($\text{CH}_3\text{-CH}_3$), is endergonic by $+25$ kcal/mol (Eq. 2). The coupling of endothermic dehydrogenation from carbon-carbon with exothermic dehydrogenation from BN in a cyclic six-membered framework could lead to a reversible H_2 storage system. Indeed, high-level computational analysis indicates that the release of H_2 from CBN heterocycles (denoted as “1” in Eqs. 1-3) has favorable overall thermodynamics conducive to reversibility, (e.g., see Eq. 3) [2]. The potential for reversible hydrogen release/uptake and the relatively high gravimetric hydrogen density of CBN heterocycle materials (e.g. 7.1 wt% for 1) render their preparation and development an important goal. In a collaborative effort with the Chemical Hydrogen Storage Center of Excellence (CHSCoE), this project is investigating several CBN heterocycle materials for H_2 storage applications using a synergistic theoretical and experimental approach. Synthesis will be a crucial component of this project given the relatively unexplored nature of these CBN heterocycles.



Results

Thermodynamic Analysis of CBN Heterocycle Materials

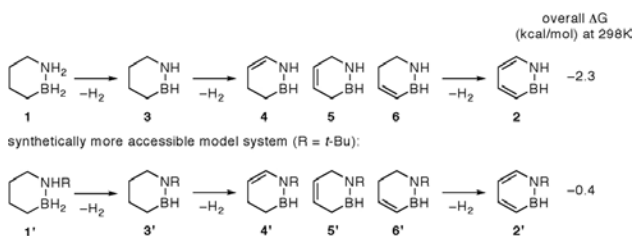
We used theory to guide our initial target selection for synthesis. Scheme 1 illustrates the calculated thermodynamic data for H_2 desorption for the seven proposed CBN materials. Theory predicts that Materials (1), (3), and (7) have the potential for reversibility ($\Delta\text{G} \sim 0$ kcal/mol) [2]. Detailed thermodynamic analyses, including consideration of multiple pathways for H_2 release have been calculated for Materials (1)-(3). Current efforts are geared toward completing the detailed pathway analysis for all the proposed materials. With the help of theory we conclude that our synthetic efforts should be initially directed toward Materials (1), (3), and (7).



SCHEME 1. Calculated Thermodynamic Properties of CBN Heterocycles

Synthesis of Model CBN Heterocycle Materials

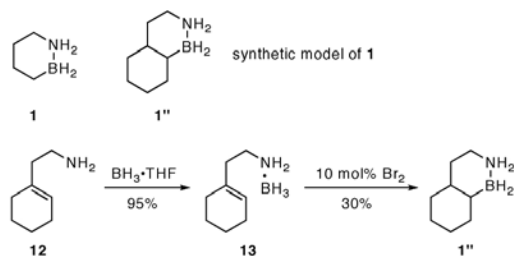
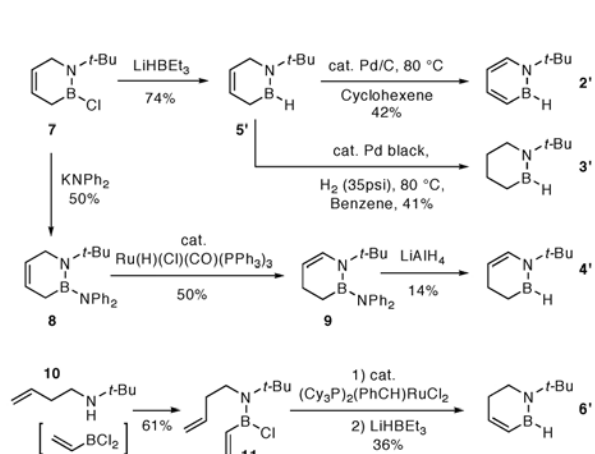
The hydrogen release from heterocycle 1 can potentially involve partially spent-fuel intermediates 3-6 (Scheme 2, top). Synthetic access to all compounds on the pathway from the fully charged material 1 to the discharged fuel 2 will be essential to understand and improve the H_2 release and uptake properties of this particular storage system. Heterocycle 1 has been reported but it has not been isolated [3]. To the best of our knowledge, intermediates 3-6 are still elusive. We recently successfully prepared the fully discharged material, 1,2-dihydro-1,2-azaborine 2 [4]. One challenge we encountered in the synthesis of 2 is the removal of a protecting group from nitrogen to introduce the N-H bond. To avoid the synthetically challenging deprotection step, we pursued the preparation of *N*-protected derivatives 2'-6' ($\text{R} = t\text{-Bu}$, Scheme 2, bottom) as models for 2-6. High-level calculations show that the thermodynamic properties of CBN Material (1) do not change significantly when the nitrogen is protected with a *t*-Bu group (Scheme 2) [2].



SCHEME 2. CBN Heterocycle Material (1) and its Model System

Scheme 3 (top) illustrates the synthesis of **2'**-**6'**. We previously reported the preparation of heterocycle **7** [5], which reacts with LiHBEt_3 to furnish one of the desired intermediates **5'**. Compound **5'** subsequently serves as a common precursor to **2'** and **3'** under catalytic dehydrogenation and hydrogenation conditions, respectively. Treatment of **7** with KNPh_2 produces compound **8**, which isomerizes to the *N*-vinyl isomer **9** in the presence of a ruthenium catalyst. Displacement of the diphenylamino group with LiAlH_4 generates isomer **4'**. The synthesis of **6'** commences with the condensation of homoallylic amine **10** with the in situ generated vinylboron dichloride to yield **11**. Subsequent ring-closing metathesis of **11** using Grubbs 1st generation catalyst followed by nucleophilic substitution of the B-Cl bond with LiHBEt_3 generates CBN heterocycle **6'**. All these syntheses are preliminary, and the yields have not been optimized. Compounds **2'**-**6'** are all liquids with melting points below -30°C .

We chose to prepare **1''** as a synthetic model for **1**. Scheme 3 (bottom) illustrates our synthetic pathway to **1''**, which was adapted and optimized from the route reported by Vedejs et al. [3]. Treatment of homoallylic amine **12** with $\text{BH}_3\cdot\text{THF}$ furnished the amine-borane complex **13** in high yield. Subsequent reaction of **13** with a catalytic amount of elemental bromine resulted in a directed intramolecular hydroboration to yield the desired **1''**. Thus, we have accomplished the synthesis of representative model compounds on the pathway from

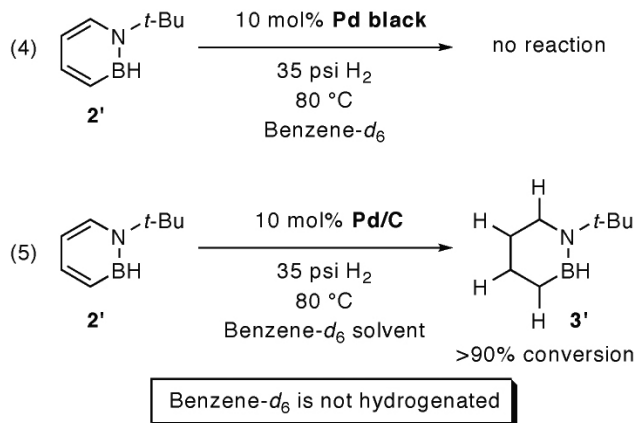


SCHEME 3. Synthesis of Model Compounds of CBN Material (1)

the fully charged material **1** to the discharged fuel **2**. Compounds **2'**-**6'** have been delivered to our CHSCoE partners at University of Washington for catalytic H_2 absorption/desorption studies. The synthesis of compound **1''** will be scaled up and delivered to our center partners as well.

Development of Conditions/Catalysts that will Recharge the Spent Fuel

With CBN heterocycles **2'**-**6'** in hand (see Scheme 2), we began to investigate the regeneration of spent-fuel material **2'** using molecular H_2 . Our initial attempt met with failure. Treatment of **2'** in the presence of Pd black as a catalyst under 35 psi H_2 pressure at 80°C in deuterated benzene did not result in any hydrogen uptake (Eq. 4). However, upon further investigation, we subsequently determined that the choice of the catalyst is crucial for reactivity. Under identical conditions as illustrated in Eq. 4, the spent-fuel material **2'** readily takes up two equivalents of H_2 to furnish **3'** when Pd/C is used as a catalyst instead of Pd black (Eq. 5). The reaction solvent benzene- d_6 is not hydrogenated under the reaction conditions. Given that compound **2'** is an aromatic molecule – **2'** is isoelectronic and isostructural with benzene – Eq. 5 suggests that the activation barrier for hydrogen uptake is substantially lower for CBN heterocycle material **2'** than for the corresponding aromatic carbocycles.



Conclusions and Future Directions

In summary, we developed a versatile synthetic toolbox that led to the preparation of CBN H_2 storage materials. We determined that 1) model compounds of CBN hydrogen storage Material (1) are low-melting liquids, and 2) regeneration of its spent fuel can be accomplished using molecular H_2 under mild conditions (80°C and 35 psi H_2 pressure for 2 out of 3 possible H_2 equivalents).

In Fiscal Year 2010, we will:

- Optimize our current synthetic toolbox with regard to yields and efficiency.
- Prepare CBN Material (1).
- Prepare CBN heterocycles related to Material (7).
- Determine experimental thermodynamic properties for model CBN heterocycles.
- Continue develop conditions/catalysts for recharging the spent fuel.
- Develop conditions/catalysts for H₂ desorption.

FY 2009 Publications/Presentations

1. “A Hybrid Organic/Inorganic Benzene”; A.J.V. Marwitz, M.H. Matus, L.N. Zakharov, D.A. Dixon, S.-Y. Liu, *Angew. Chem. Int. Ed.* **2009**, *48*, 973-977.
2. “1,2-Dihydro-1,2-Azaborine: An Organometallic Benzene”; S.-Y. Liu, *IMEBoron XIII International Boron Conference*, Platja d'Aro, Spain, September 2008.
3. “Hydrogen Storage by Novel CBN Heterocycle Materials”; S.-Y. Liu et al.; poster presented at the *D.O.E. Hydrogen Annual Review*, Washington, D.C., May 2009.
4. “Hydrogen: A Drive to the Future”; Kshitij Parab, Patrick Campbell, Shih-Yuan Liu; poster presented at the *Hydrogen Road Tour '09 Eugene Stop*, Eugene, OR, May 2009.

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2. D.A. Dixon, University of Alabama, Tuscaloosa, AL. Personal communication, 2008.
3. M. Scheideman, G. Wang, E. Vedejs, *J. Am. Chem. Soc.* **2008**, *130*, 8669-8676.
4. A.J.V. Marwitz, M.H. Matus, L.N. Zakharov, D.A. Dixon, S.-Y. Liu, *Angew. Chem. Int. Ed.* **2009**, *48*, 973-977.
5. E.R. Abbey, L.N. Zakharov, S.-Y. Liu, *J. Am. Chem. Soc.* **2008**, *130*, 7250-7252.