

Density Functional Theory Study on Stability of Monomer, Cyclic Dimers and Cyclic Trimers of RNHBH₂

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ABSTRACT: Ammonia-borane (AB, NH₃BH₃) has been known as a potential hydrogen storage material due to its high gravimetric capacity. However, there are some barriers to overcome for AB to be realized as a practically useful material. Among them, maximization of the utilization of H₂ in AB and regeneration of the used AB are the main problems, which are related to the forms of products after the first hydrogen extraction. After the first H₂ extraction is done, the products have various forms including monomer, cyclic oligomers, and polymers. The variety of products prohibits the further extraction of H₂ and regeneration of the used fuel. Therefore, the fuel should be designed to produce simply one or two forms of products of the first H₂ extraction. We investigated the stability of monomers, dimers, and trimers of alkyl substituted aminoborane (RNHBH₂) using density functional theory calculations. When no R group is present, cyclization of monomers is an exothermic process so that the cyclic trimers could be made preferentially. If the R groups are substituted, the general trend does not change and cyclic dimers and trimers are more stable than corresponding monomer. Phenyl ring substitution weakens the bond strength of B-N bonds and this makes the stabilization of cyclization smaller.

Keywords: hydrogen, storage, ammonia-borane, DFT

1. INTRODUCTION

There has been much effort to make hydrogen as an alternative energy carrier to overcome the sustainability problems made by burning fossil fuels. The fuel cell system, which needs hydrogen gas as its fuel, has been being developed as a clean energy source. One of critical issues for the fuel cell to be practically applicable is the need for efficient hydrogen storage materials.

Thus, many researchers have been trying to find materials to store hydrogen at high density. Ammonia-borane (AB) is one of the most potential materials for this purpose; it contains 19.6 wt% hydrogen which is far beyond the US Department of Energy (DOE) 2015 target 9 wt%.

However, as Marder pointed out [1], there are a few barriers for AB to be a practical hydrogen storage material: 1) to accelerate the hydrogen release rate; 2) to utilize the most content of hydrogen in AB; 3) to reduce volatile by-products; 4) to regenerate the used AB. Among them, to maximize the utilization of hydrogen in AB and to regenerate the used AB are the main problems and they are related to the forms of products after the first hydrogen extraction.

For the sake of the kinetics of hydrogen extraction, homogeneous dehydrogenation catalysts have been used in recent studies [2-9]. When neat AB is used as a fuel in the catalytic dehydrogenation reaction, the first H₂ extraction reaction produces various forms of products including NH₂BH₂ monomer, cyclic oligomers, and polymers. The resultant oligomers and polymers may prohibit further extraction of H₂ and regeneration of the used fuel.

Therefore, the fuel should be designed to produce simply one or two forms of products after the first H₂ extraction and the monomer is the most preferred form. In this work, in order to evaluate the effect of alkyl substitution on the composition of the first dehydrogenation products, we investigated the thermodynamic stability of monomers,

cyclic dimers and cyclic trimers of *N*-alkyl substituted aminoborane (RNHBH₂) using density functional theory (DFT) calculations.

2. COMPUTATIONAL DETAILS

2.1 Systems for Calculation

We examined 6 compounds of RNHBH₂, where R is H, CH₃ (Me), phenyl (Ph), *i*-propyl (*i*-Pr), *t*-butyl (*t*-Bu), or Si(CH₃)₃ (TMS). For each compound, monomer, cyclic dimers, and cyclic trimers could be generated and all the structures considered are summarized in Fig. 1. For the cyclic dimers, two conformations were modelled with the R groups on the same or opposite sides of the ring. For the cyclic trimers, four chair and eight twist-boat conformations were modelled for each compound considering the molecular symmetry.

2.2 Calculation Methods

All of the theoretical calculations were performed by DMol³ program, a quantum mechanical code using density functional theory, in the Materials Studio 4.3TM package [10]. The double numeric polarization basis set [11] was used in our calculations without any pseudopotential representation for the special treatment of core electrons. We used PWC exchange-correlation functional [12] for our DFT calculations and the results for cyclotriborazane are in good agreement with the MP2 results [13].

After we optimized the structures, we performed frequency analyses and confirmed that the obtained structures are the minimum-energy conformations. All energy values reported here are corrected for zero point energy.

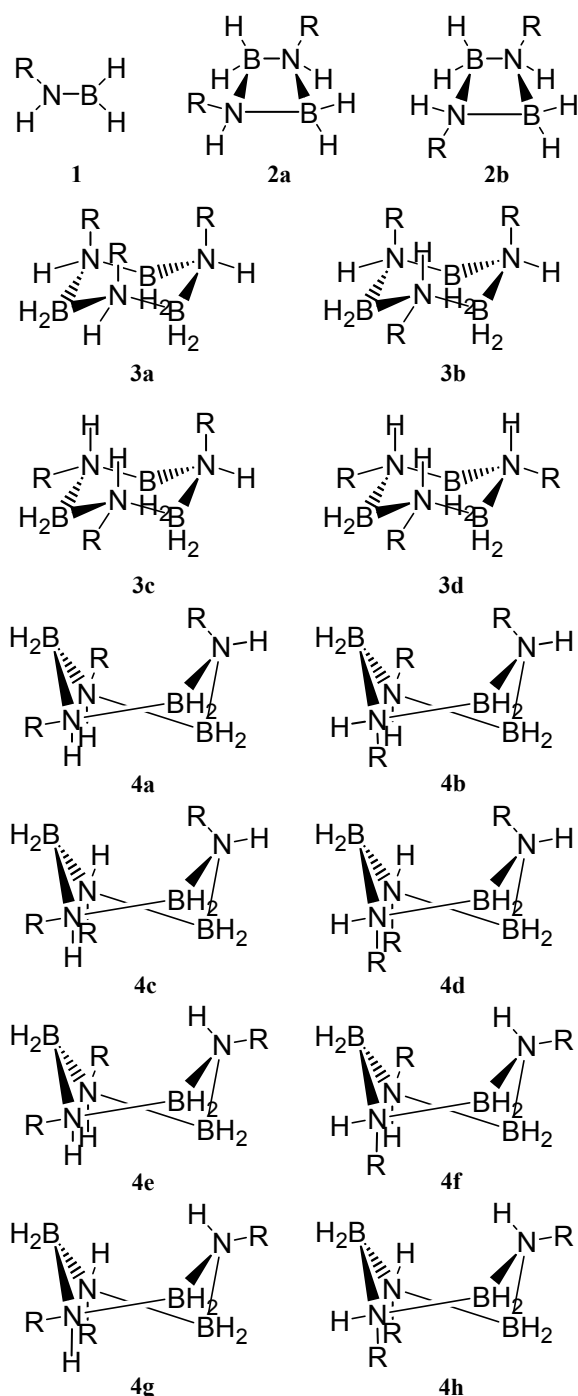


Figure 1: Chemical structures calculated in this work. R = -H, -CH₃, -Ph, -*i*-Pr, *t*-Bu, -TMS.

3. RESULTS AND DISCUSSION

3.1 Stability of NH₂BH₂, cyclic (NH₂BH₂)₂ and cyclic (NH₂BH₂)₃

Since AB was known for its possibility as a hydrogen storage material, thermodynamics of reactions involving AB has been studied theoretically [13-15] as well as experimentally [4,16]. In order to figure out the B-N bond character, we calculated the bond order for all structures (Table I). The B-N bond of the monomer NH₂BH₂, has strong σ bond and weak π -donor bond character [17], and the calculated bond order (1.465) confirms that this B-N bond has partial double bond character. For comparison, we also calculated the structure of ethylene, the carbon analogue of NH₂BH₂, using the same method and the bond order of the C=C bond was obtained as 1.944.

Table I: Averaged bond orders of B-N bonds.

	H	Me	Ph	<i>i</i> -Pr	<i>t</i> -Bu	TMS
1	1.465	1.494	1.417	1.491	1.494	1.465
2a	0.763	0.759	0.737	0.761	0.762	0.758
2b		0.761	0.742	0.762	0.764	0.760
3a	0.787	0.779	0.768	0.778	0.766	^a
3b		0.778	0.768	0.778	0.772	0.779
3c		0.775	0.759	0.770	0.768	0.769
3d		0.771	0.745	0.764	0.759	0.761
4a	0.788	0.779	0.766	0.773	0.765	0.764
4b		0.781	0.769	0.776	0.772	0.773
4c		0.780	0.759	0.776	0.772	0.770
4d		0.780	0.762	0.773	0.771	0.772
4e		0.777	0.756	0.772	0.767	0.763
4f		0.780	0.766	0.775	0.771	0.770
4g		0.778	0.757	0.771	0.767	0.764
4h		0.779	0.765	0.771	0.766	0.763

^aWe could not obtain the optimized structure.

When the cyclic dimer (NH₂BH₂)₂ is formed, the the B-N bond order is reduced to 0.763 and this bond has σ bond character only. The B-N bonds of the cyclic trimer (NH₂BH₂)₃ also have σ bond character. The B-N bonds in the twist-boat form have different bond orders and the averaged bond order is 0.788. For the chair form, all B-N bonds are equivalent and the bond order is 0.787 (the bond order of the C-C bond of cyclohexane was calculated as 0.979). The B-N bond order is slightly higher in the

cyclic trimer than in the cyclic dimer. The cyclic dimer has a ring strain due to the small bond angle, so that the strain free cyclic trimer could have stronger B-N bonds and lower conformation energies (Fig. 2) than the cyclic dimer.

3.2 Effect of R groups

According to our calculation results, there is no large change in relative stability during the cyclization of the monomers to the cyclic oligomers. Even bulky R groups such as *t*-butyl and TMS groups have little influence on the stability of the cyclic dimers and trimers. Fig.2 shows that all the compounds studied have similar structure-stability relationships with NH_2BH_2 . Small deviations are observed in the case of structure **4h**, which might have a small ring strain caused by the steric interaction between two bulky groups at the axial positions.

For *t*-butyl substitution structure of **3a**, all *t*-butyl groups are at the axial positions and the strain is larger than in other trimers. We could not obtain the optimized chair form structure **3a** with $\text{Si}(\text{CH}_3)_3$ substituents,

presumably because the structure is highly destabilized by the very large substituents.

With phenyl substituents, the cyclic oligomers are stabilized less than the other oligomers with different R groups (Fig. 2). Because a phenyl ring is not as bulky as a *t*-butyl group, the reduced stabilization is not due to the Ph-Ph steric interaction. In order to understand the effect of the Ph group, we analyzed the molecular orbitals of the related compounds.

As we can see in Fig. 3a, the HOMO of NH_2BH_2 shows the π bond character of the B-N bond as mentioned above. The substituted phenyl ring of PhNHBH_2 makes a coplanar surface with the NHBH_2 in the optimized structure (Fig. 3b). This coplanarity makes it easy to expand the conjugation system and the electrons on the nitrogen are in the conjugation with the π -system of the phenyl ring. In other words, the phenyl ring plays a role as an electron withdrawing group in this structure so the electron density of the B-N bond is reduced. The weakened bond strength of the B-N bond of PhNHBH_2 is validated by the bond order in Table I.

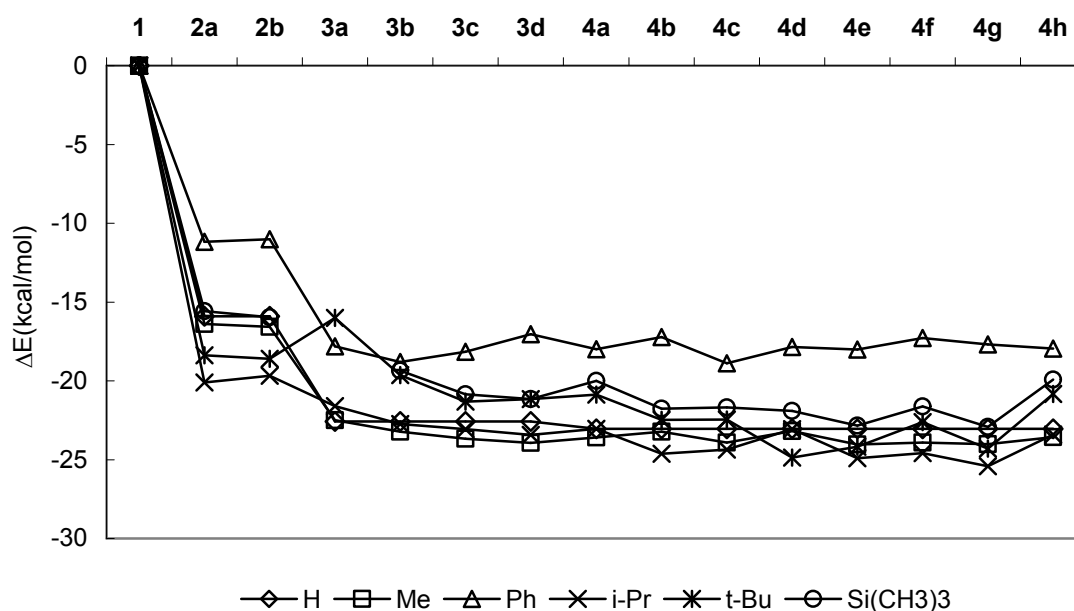


Figure 2: Relative energy of each structure with respect to the corresponding monomer. For the dimers and trimers, the energy is divided by 2 and 3 respectively to normalize the energy difference per monomer.

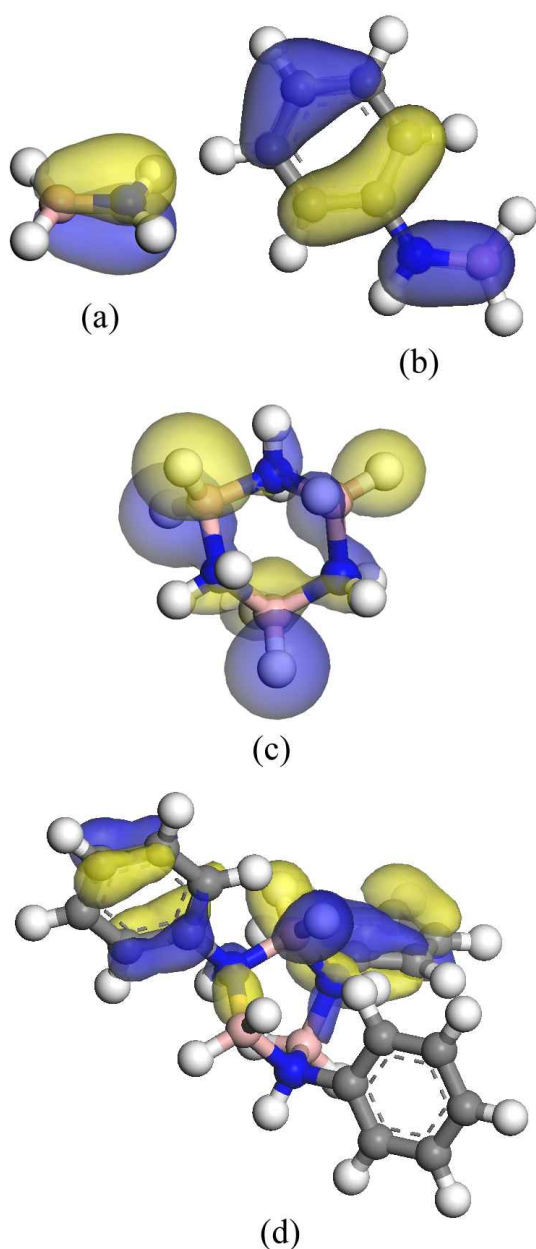


Figure 3: HOMO of (a) NH_2BH_2 , (b) PhNHBH_2 , (c) cyclic $(\text{NH}_2\text{BH}_2)_3$ and (d) cyclic $(\text{PhNHBH}_2)_3$. N: blue sphere, B: pink sphere, C: gray sphere, H: white sphere.

For the cyclic oligomers, the phenyl ring is also involved in the HOMO orbitals (Fig. 3c and 3d). Thus, the B-N bond order of the phenyl substituted structures is smaller than that of the other structures. Unlike *t*-butyl substituted compound, structure **3a** and **4h** of the phenyl substituted compound have similar energies with the other cyclic trimer structures. The phenyl rings at the axial

positions of structure **3a** and **4h** could make a π - π interaction which allows the phenyl rings get closer.

4. SUMMARY

We investigated the effect of alkyl group substitution in aminoborane on the stability of the RNHBH_2 monomer, cyclic dimers and cyclic trimers. Even bulky alkyl groups have little influence on the stability of the cyclic dimers and cyclic trimers. However, phenyl ring substitution makes the B-N bond weaker because the electron density of the nitrogen atom is delocalized into the phenyl ring so that the nitrogen contributes less to make the B-N bond. From this work, we can conclude that the alkyl group substitution hardly can change the results of dehydrogenation reactions of AB. In order to clarify the effect of the electron withdrawing group further, we are currently working on the compounds with other electron withdrawing substituents.

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