

行政院國家科學委員會專題研究計畫 成果報告

含氮雜環碳烯基及其等電子系統與一氧化氮提供者之理論 研究 研究成果報告(精簡版)

計畫類別：個別型
計畫編號：NSC 99-2113-M-040-004-
執行期間：99年08月01日至100年10月31日
執行單位：中山醫學大學應用化學系(所)

計畫主持人：賴金宏

計畫參與人員：此計畫無其他參與人員

公開資訊：本計畫可公開查詢

中華民國 100 年 12 月 29 日

中文摘要： 在 2006 年，Segawa 等人以一個含有硼溴鍵的前驅物合成了第一個含有雙氨基(diamino)取代且含有 B⁻-Li⁺的物質。經由 X 射線結晶學以及硼-11 核磁共振光譜證明此物質裡的硼原子上帶有一負電荷。這些含硼物質可以用來合成新的含硼物質或提供一些不同以往的合成路徑。例如，它們可當成親核劑與親電子劑(H₂O, methyltrifluoromethanesulfonate, 1-chlorobutane, and benzaldehyde)反應。最近，Segawa 等人用它們來合成了含硼的 Grignard 試劑。這些物質也可當成親核劑攻擊一些第 11 族金屬含氯錯合物。所以，本計畫也擬以一些計算方法來探討它們的電子性質。

中文關鍵詞： 含有 B⁻-Li⁺的物質

英文摘要： In 2006, Nozaki, Yamashita and Segawa, firstly utilized a boron-bromide precursor to synthesize a stable diamino-substituted boryllithium. X-ray crystallography and ¹¹B NMR spectroscopy of the compound matched with the prediction of a boron anion. Boryllithium can be used to synthesize new boron-containing compounds or to provide a different synthetic route from the traditional ones. For example, boryllithium behaves as an efficient nucleophile when it reacts with the electrophiles such as water, methyltrifluoromethanesulfonate, 1-chlorobutane, and benzaldehyde. Recently, Segawa and coworkers synthesized a borylmagnesium that may be served as a boron-containing Grignard reagent. In yet another approach, boryllithium may act as a nucleophile and attack on Group 11 metal chloride complexes. On this basis, Segawa and coworkers reported the examples of borylsilver and borylgold complexes. Therefore, the intrinsic properties and the substituent effect of this anionic boron species are interesting and of importance. Herein, I propose to investigate the corresponding properties computationally via DFT functionals.

英文關鍵詞： boryllithium

國科會專題研究計畫成果報告撰寫格式

99年5月5日本會第304次學術會報修正通過

一、說明

國科會基於學術公開之立場，鼓勵一般專題研究計畫主持人發表其研究成果，但主持人對於研究成果之內容應負完全責任。計畫內容及研究成果如涉及專利或其他智慧財產權、違異現行醫藥衛生規範、影響公序良俗或政治社會安定等顧慮者，應事先通知國科會不宜將所繳交之成果報告蒐錄於學門成果報告彙編或公開查詢，以免造成無謂之困擾。另外，各學門在製作成果報告彙編時，將直接使用主持人提供的成果報告，因此主持人在繳交報告之前，應對內容詳細校對，以確定其正確性。

本格式說明之目的為統一成果報告之格式，精簡報告內容之篇幅以4至10頁為原則，完整報告內容之篇幅不得少於10頁。

成果報告繳交之期限及種類(精簡報告、完整報告、期中精簡報告、期中完整報告等)，應依本會補助專題研究計畫作業要點及專題研究計畫經費核定清單之規定辦理。

二、報告格式：依序為封面、目錄(精簡報告得省略)、中英文摘要及關鍵詞、報告內容、參考文獻、計畫成果自評、可供推廣之研發成果資料表、附錄。

(一)報告封面：請至本會網站(<http://www.nsc.gov.tw>)線上製作(格式如附件一)。

(二)中、英文摘要及關鍵詞(keywords)。

(三)報告內容：包括前言、研究目的、文獻探討、研究方法、結果與討論(含結論與建議)……等。

(四)計畫成果自評部分：請就研究內容與原計畫相符程度、達成預期目標情況、研究成果之學術或應用價值(簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性)、是否適合在學術期刊發表或申請專利、主要發現或其他有關價值等，作一綜合評估，並請至本會網站線上製作。(格式如附件二)

(五)頁碼編寫：請對摘要及目錄部分用羅馬字I、II、III……標在每頁下方中央；報告內容至附錄部分請以阿拉伯數字1.2.3……順序標在每頁下方中央。

(六)附表及附圖可列在文中或參考文獻之後，各表、圖請說明內容。

(七)可供推廣之研發成果資料表：

1.研究計畫所產生之研發成果，應至國科會科技研發成果資訊系統(STRIKE系統，<https://nscnt66.nsc.gov.tw/strike/>)填列研發成果資料表(如附件三)，循執行機構行政程序，由研發成果推廣單位(如技轉中心)線上繳交送出。

2.每項研發成果填寫一份。

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三、計畫中獲補助國外或大陸地區差旅費、出席國際學術會議差旅費或國際合作研究計畫差旅費者，須依規定分別撰寫心得報告，並至本會網站線上繳交電子檔，心得報告格式如附件四、五、六。

四、報告編排注意事項

(一)版面設定：A4紙，即長29.7公分，寬21公分。

(二)格式：中文打字規格為每行繕打(行間不另留間距)，英文打字規格為Single Space。

(三)字體：以中英文撰寫均可。英文使用Times New Roman Font，中文使用標楷體，字體大小以12號為主。

行政院國家科學委員會補助專題研究計畫 成果報告
 期中進度報告

(計畫名稱)

計畫類別： 個別型計畫 整合型計畫

計畫編號：NSC 99-2113-M-040-004-

執行期間：99年08月01日至100年10月31日

執行機構及系所：中山醫學大學應用化學系

計畫主持人：賴金宏

共同主持人：

計畫參與人員：

成果報告類型(依經費核定清單規定繳交)： 精簡報告 完整報告

本計畫除繳交成果報告外，另須繳交以下出國心得報告：

赴國外出差或研習心得報告

赴大陸地區出差或研習心得報告

出席國際學術會議心得報告

國際合作研究計畫國外研究報告

處理方式：除列管計畫及下列情形者外，得立即公開查詢

涉及專利或其他智慧財產權， 一年 二年後可公開查詢

中華民國 100 年 12 月 29 日

國科會補助專題研究計畫成果報告自評表

請就研究內容與原計畫相符程度、達成預期目標情況、研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）、是否適合在學術期刊發表或申請專利、主要發現或其他有關價值等，作一綜合評估。

1. 請就研究內容與原計畫相符程度、達成預期目標情況作一綜合評估

達成目標

未達成目標（請說明，以 100 字為限）

實驗失敗

因故實驗中斷

其他原因

說明：

2. 研究成果在學術期刊發表或申請專利等情形：

論文：已發表 未發表之文稿 撰寫中 無

專利：已獲得 申請中 無

技轉：已技轉 洽談中 無

其他：（以 100 字為限）

所發表的論文(請見附錄文件):

1. Lai, Chin-Hung; Chou, Pi-Tai. "A computational study on the capability of borane-cyclic boryl anion adducts to act as hydrogen atom donors." *Journal of Computational Chemistry* 2010, 31, 2258 – 2262.
2. Lai, Chin-Hung; Chou, Pi-Tai. "Borylene – Boron Bearing a Negative Charge" In "Boron: Compounds, Production and Application" Gary L. Perkins Ed. , Nova publisher: New York, 2011.

3. 請依學術成就、技術創新、社會影響等方面，評估研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）（以500字為限）

在2006年，Segawa等人以一個含有硼溴鍵的前驅物合成了第一個以雙氫基作取代的 boryllithium (1)。¹ 由硼-11核磁共振光譜的檢測結果可得知 boryllithium 可看成是鋰離子(Li⁺)與一個含有負電性硼原子(B⁻)的含氮雜環（此雜環稱為 borylene）所形成的離子對(ion pair)。此物質已經展示了它們許多的用途。¹⁻⁵ 例如它們可以扮演親核劑去攻擊一些親電子劑。在台大化學系周必泰老師實驗室做博士後研究員的期間(2008/10~2010/02)，我們已經用了密度泛函數理論(density functional theory)的方法對 borylene 熱力學及動力學穩定性作了系統性的研究並已經刊登在國際期刊上，⁶⁻⁷ 所以接著在台大做助理研究學者(2010/08/01~2010/09/12)以及在中山醫學大學擔任助理教授(2010/09/13~至今)我們繼續對這個含負電性硼原子的雜環進行理論研究，根據我們的計算結果發現，borylene 這類物質可以扮演路易斯鹼(Lewis base)與BH₃形成路易斯酸鹼對進而減弱BH₃中B-H的鍵能使得氫原子容易被釋放出去。傳統上，在有機合成中常常使用含有Sn-H鍵的化合物當作氫原子的提供者，但不幸的是，這類化合物含有相當的毒性，而H₃B-borylene 這類路易斯酸鹼對的毒性相對地小了很多。所以可說，我們預測了一個有效且毒性小的氫原子提供者，相信對於有機合成會有所助益。

參考文獻：

1. Segawa, Y.; Yamashita, M.; Nozaki, K. *Science* **2006**, *314*, 113-115.
2. Yamashita, M.; Suzuki, Y.; Segawa, Y.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 9570-9571.
3. Segawa, Y.; Yamashita, M.; Nozaki, K. *Angew. Chem. Int. Ed.* **2007**, *46*, 6710-6713.
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5. Yamashita, M.; Nozaki, K. *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1377-1392.
6. Lai, C.-H.; Chou, P.-T. *The Open Chem. Phys. J.* **2008**, *1*, 51-61.
7. Lai, C.-H.; Chou, P.-T. *J. Mol. Mod.* **2010**, *16*, 713-723.

國科會補助計畫衍生研發成果推廣資料表

日期：__年__月__日

| | | | |
|--------------------------|-------------|----------------------|--|
| 國科會補助計畫 | 計畫名稱： | | |
| | 計畫主持人： | | |
| | 計畫編號： | 領域： | |
| 研發成果名稱 | (中文) | | |
| | (英文) | | |
| 成果歸屬機構 | | 發明人 (創作人) | |
| 技術說明 | (中文) | | |
| | (200-500 字) | | |
| | (英文) | | |
| 產業別 | | | |
| 技術/產品應用範圍 | | | |
| 技術移轉可行性及預期 效益 | | | |

註：本項研發成果若尚未申請專利，請勿揭露可申請專利之主要內容。

國科會補助專題研究計畫項下出席國際學術會議心得報告

日期：__年__月__日

| | | | |
|------------|-----------------|-------------|--|
| 計畫編號 | NSC — — — — | | |
| 計畫名稱 | | | |
| 出國人員 姓名 | | 服務機構 及職稱 | |
| 會議時間 | 年 月 日至 年 月 日 | 會議地點 | |
| 會議名稱 | (中文) (英文) | | |
| 發表論文 題目 | (中文) (英文) | | |

一、參加會議經過

二、與會心得

三、考察參觀活動(無是項活動者略)

四、建議

五、攜回資料名稱及內容

六、其他

國科會補助專題研究計畫項下赴國外(或大陸地區)出差或研習心得報告

日期：__年__月__日

| | | | |
|------------|-----------------|-------------|--|
| 計畫編號 | NSC — — — — — | | |
| 計畫名稱 | | | |
| 出國人員 姓名 | | 服務機構 及職稱 | |
| 出國時間 | 年 月 日至 年 月 日 | 出國地點 | |

一、國外(大陸)研究過程

二、研究成果

三、建議

四、其他

國科會補助專題研究計畫項下國際合作研究計畫國外研究報告

日期：__年__月__日

| | | | |
|------------|-----------------|-------------|--|
| 計畫編號 | NSC — — — — — | | |
| 計畫名稱 | | | |
| 出國人員 姓名 | | 服務機構 及職稱 | |
| 合作國家 | | 合作機構 | |
| 出國時間 | 年 月 日至 年 月 日 | 出國地點 | |

一、國際合作研究過程

二、研究成果

三、建議

四、其他

A Computational Study on the Capability of Borane-Cyclic Boryl Anion Adducts to Act as Hydrogen Atom Donors

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Abstract: According to our theoretical approaches, a cyclic boryl anion can act as a Lewis base like its isoelectronic counterpart N-heterocyclic carbene, reducing the homolytic bond dissociation energy of B–H in BH₃. However, the donating efficiency is affected by the counter cation in both gas phase and nonpolar solvents. Moreover, we also predict the seven-membered ring boryl anion **5**, although it has not yet synthesized, to be the most efficient reagent to reduce the bond dissociation energy of a B–H bond in BH₃. This study may thus pave another avenue toward Lewis base induced hydrogen atom abstraction in BH₃.

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Key words: N-heterocyclic carbene; cyclic boryl anion; Lewis base; boryllithium

Introduction

Because of its high hydrogen content, BH₃ has been considered as a latent candidate to donate hydrogen atoms. Unfortunately, the homolytic bond dissociation energy (BDE) of the B–H bond is too high to release a hydrogen atom in a radical reaction.¹ Via a computational approach, Rablen computed that a Lewis base can aid in the dissociation of the B–H bond by complexation with BH₃.² From the experimental aspect, radical reactions involving amine-borane and phosphine-borane pairs have been studied by Roberts and coworkers.³ Although BDE of the B–H bond in BH₃ (106.6 kcal/mol) has been reduced modestly to 94 and 104 kcal/mol by complexation with NH₃ and PH₃, respectively,² it is unfortunately still higher than BDE of, for example, Sn–H bond in Bu₃Sn–H (74 kcal/mol), a popular tin hydride for donating a hydrogen atom.⁴ Theory also predicts that BDE of the B–H bond can be further reduced by a π -conjugated Lewis base (cf. a nonconjugated Lewis base).² Recently, Curran and coworkers reported that the complex formed by an N-heterocyclic carbene (NHC) and BH₃ may serve as a new source of hydrogen atom donors.⁵ They calculated that an NHC dramatically reduces BDE of the B–H bond from 111.7 to 74–80 kcal/mol, which is within the BDE range of tin hydrides.^{4,5} Walton pointed out that this is due to the formation of a stable NHC-BH₂· radical by π -delocalization/resonance.⁶ Very recently, such radical has been detected by EPR spectroscopy.⁷

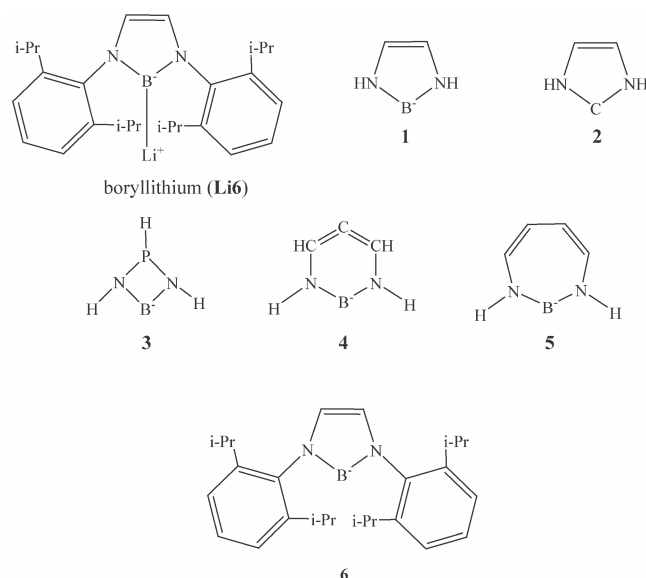
In yet another approach, the boryllithium (see Scheme 1) synthesized by Segawa et al. can be viewed as an ion pair

between Li⁺ and a five-membered boryl anion, that is, isoelectronic to an NHC.^{8,9} Our previous studies regarding the kinetic stability of boryl anions have shown that nitrogen is an efficient π -donor that stabilizes the boryl anions. The six-membered ring boryl anion is kinetically more stable than a five-membered one.¹⁰ To continue our efforts on cyclic boryl anions, we herein investigate the capability of diazaborole anion (C₂H₄B₁N₂[−], **1**) to complex with BH₃ and conduct comparative studies with respect to that of imidazolin-2-ylidene (C₃H₄N₂, **2**) and its analogues. Our goal is to examine whether borane-cyclic boryl anion adduct can serve as an effective hydrogen-atom donor for radical reactions.

Based on G3 and/or MPW1K calculations, thermodynamics values^{11,12} and other pertinent parameters for complexes **H₃B-1**, **H₃B-2** and their hydrogen-atom abstracted products **H₂B-1** and **H₂B-2**, respectively, are listed in Table 1. Upon careful inspection of Table 1, the MPW1K results are found to be in agreement with G3. Note that previous study about the kinetic stability of cyclic boryl anions also pointed out that the MPW1K functional performed better than other tested DFT functionals.¹⁰ MPW1K-optimized geometries of **H₃B-1**, **H₃B-2**, and their hydrogen atom abstracted products are depicted in Figure 1.

Additional Supporting Information may be found in the online version of this article.

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Scheme 1. Structures of boryllithium and compounds **1–6**.

When one hydrogen atom of B–H group is abstracted, as depicted in Figure 1, the B–B bond length shortens by 0.05 Å and the $\angle\text{N–B–N}$ bond angle remains unchanged for $\text{H}_3\text{B-1}$. Correspondingly, for $\text{H}_3\text{B-2}$, the B–C bond length shortens by 0.09 Å and the $\angle\text{N–C–N}$ bond angle decreases by 0.93°. The B–H bond length of BH_3 increases from 1.189 to 1.233 and 1.219 Å for $\text{H}_3\text{B-1}$ and $\text{H}_3\text{B-2}$, respectively. Moreover, the B–B bond in $\text{H}_3\text{B-1}$ is longer than that of the B–C bond in $\text{H}_3\text{B-2}$, the result of which can be expected, because the van der Waals radius of boron (2.08 Å) is larger than that of carbon (1.85 Å).

Table 1. The G3 or MPW1K Calculated $\Delta E(\text{H}_3\text{B-1-6})$, $\Delta E(\text{H}_2\text{B-1-6})$, $\Delta\text{BDE}_{\text{B-H}}$ (all in kcal/mol), and the B–X (X = B or C) Bond Length of $\text{H}_3\text{B-1-6}$ (in Å).

| | $\Delta E(\text{H}_3\text{B-1-6})^a$ | $\Delta E(\text{H}_2\text{B-1-6})^b$ | $\Delta\text{BDE}_{\text{B-H}}^c$ | B–X bond length |
|------------|--------------------------------------|--------------------------------------|-----------------------------------|--------------------|
| 1 | –79.8 | –2.5 | 20.4 | 1.710 |
| | –86.3 ^d | –6.0 ^d | 20.0 ^d | 1.707 ^d |
| 2 | –49.1 | 22.4 | 26.3 | 1.595 |
| | –54.3 ^d | 19.4 ^d | 26.6 ^d | 1.587 ^d |
| 3 | –86.3 ^d | –7.8 ^d | 21.9 ^d | 1.691 ^d |
| 4 | –86.4 ^d | –8.0 ^d | 21.9 ^d | 1.692 ^d |
| 5 | –91.1 ^d | –16.3 ^d | 25.4 ^d | 1.696 ^d |
| 6 | –83.0 ^d | –4.1 ^d | 21.5 ^d | 1.700 ^d |
| Li1 | –69.3 ^d | 12.3 ^d | 18.8 ^d | 1.713 ^d |
| Li3 | –73.8 ^d | 5.8 ^d | 20.8 ^d | 1.697 ^d |
| Li4 | –67.0 ^d | 14.8 ^d | 18.6 ^d | 1.721 ^d |
| Li5 | –75.1 ^d | 3.5 ^d | 21.7 ^d | 1.713 ^d |
| Li6 | –77.8 ^d | 7.6 ^d | 14.9 ^d | 1.713 ^d |

^aTaking **1** as an example, $\Delta E(\text{H}_3\text{B-1}) = E(\text{H}_3\text{B-1}) - E(\text{H}_3\text{B}) - E(\mathbf{1})$.

^bTaking **1** as an example, $\Delta E(\text{H}_2\text{B-1}) = E(\text{H}_2\text{B-1}) + E(\text{H}) - E(\text{H}_3\text{B}) - E(\mathbf{1})$.

^c $\Delta\text{BDE}_{\text{B-H}} = [E(\text{H}_2\text{B}) - E(\text{H}_3\text{B})] - [E(\text{H}_2\text{B-1}) - E(\text{H}_3\text{B-1})]$.

^dThe value is calculated by the MPW1K/6–31+G* level.

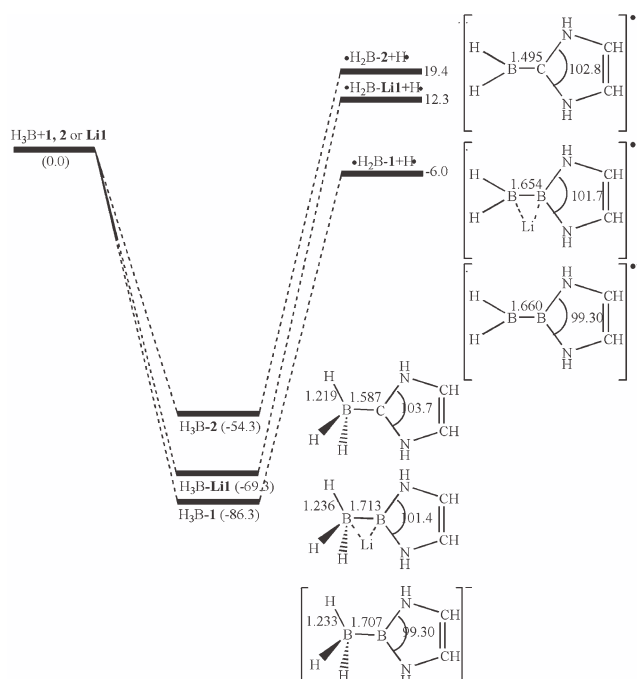


Figure 1. The schematic energy diagram and selected geometric parameters of $\text{H}_3\text{B-1}$, $\text{H}_3\text{B-2}$, $\text{H}_3\text{B-Li1}$ and their hydrogen atom abstracted products.

Incorporating zero-point energy, BDE of the B–H bond in BH_3 is estimated to be 97.77 kcal/mol by G3.¹¹ To quantify the efficiency of **1** and **2** in view of the decrease of BDE of the B–H bond, a parameter $\Delta\text{BDE}_{\text{B-H}}$ is introduced, which is defined as

$$\Delta\text{BDE}_{\text{B-H}} = [E(\text{BH}_2) + E(\text{H}) - E(\text{BH}_3)] - [E(\text{H}_2\text{B-X}) + E(\text{H}) - E(\text{H}_3\text{B-X})] \quad (1)$$

where X stands for **1** or **2**. Accordingly, $\Delta\text{BDE}_{\text{B-H}}$ for **1** and **2** is estimated to be 20.4 kcal/mol and 26.3 kcal/mol (Table 1), respectively, indicating that BDE of the B–H bond is influenced more strongly by complexing **2**. Conversely, as shown in Table 1, the reaction $\text{H}_3\text{B} + \mathbf{2} \rightarrow \cdot\text{H}_2\text{B-2} + \text{H}\cdot$ is highly endothermic, whereas the reaction $\text{H}_3\text{B} + \mathbf{1} \rightarrow \cdot\text{H}_2\text{B-1} + \text{H}\cdot$ is more thermodynamically favorable by 24.8 kcal/mol. Moreover, **1** forms a more stable complex with BH_3 than **2**, as evidenced by the calculated $\Delta E(\text{H}_3\text{B-1})$ (–79.8 kcal/mol) being more negative than $\Delta E(\text{H}_3\text{B-2})$ (–49.1 kcal/mol) by ~30 kcal/mol (See Table 1). The result can be qualitatively rationalized by the fact that the interaction between the empty orbital (EO_B) and lone pair (LP_B) of boron is stronger than that with LP_C of carbon. The calculated energy of LP_B (–0.02 eV) is closer to the value of EO_B (0.56 eV) than that of LP_C (–0.33 eV).

We then extended our investigations to how the four-, six-, and seven-membered ring boryl anions (see **3–5** in Scheme 1) complex with BH_3 according to MPW1K results corrected by zero-point energy. Note that the corresponding carbenes were synthesized and showed markedly different electronic structures from those of the five-membered analogues.¹³ For a

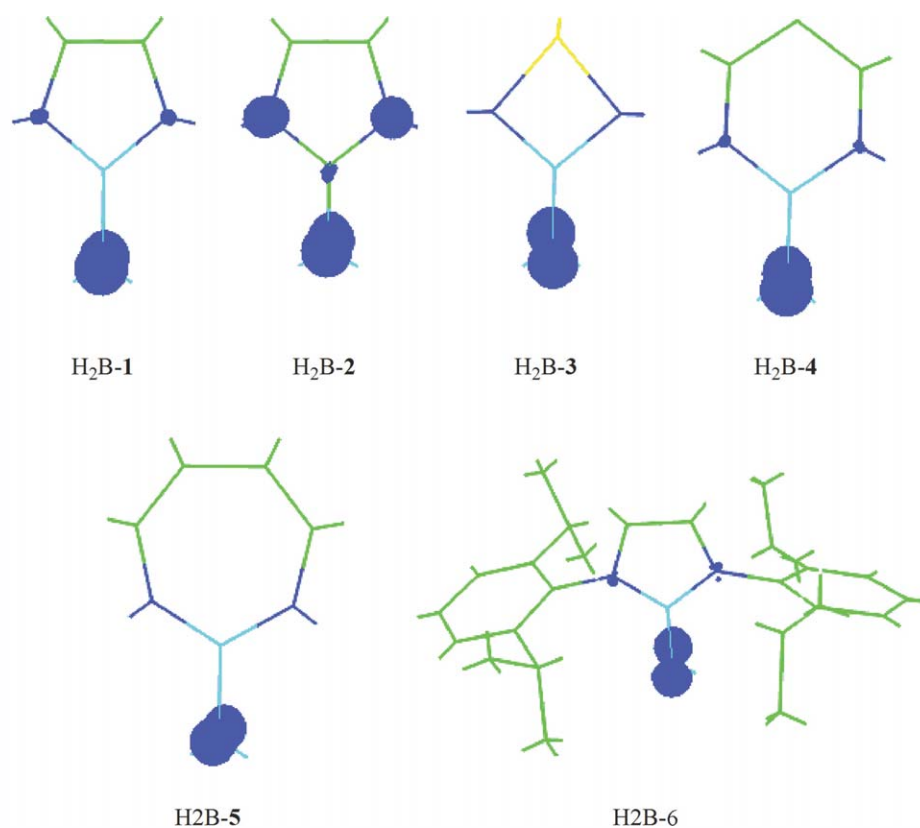


Figure 2. The SOMOs of **H₂B-1-6** (the isodensity value = 0.02).

fair comparison, the spin density of the singly occupied molecular orbital (SOMO) around **H₂B** and **1** and **2** is depicted in Figure 2. Clearly, the results show partial delocalization for both **1** and **2**. It is worthy to note that the result for **2** is in agreement with Walton's viewpoint on **H₂B-2** complex.⁶ Relevant data for **3-5** are also summarized in Table 1 and Figure 2.

Because the reaction enthalpy of $\text{H}_3\text{B} + \text{boryl anion} \rightarrow \text{H}_3\text{B-boryl anion}$ can be viewed as an indicator of the Lewis basicity of a boryl anion ($-RT\ln K_{\text{eq}} = \Delta G = \Delta H - T\Delta S \approx \Delta H$),¹⁴ the seven-membered ring boryl anion (**5**), having the largest reaction enthalpy of -91.1 kcal/mol, is concluded to be the strongest base among **1**, **3**, **4**, and **5**. In addition, the four- (**3**) and six-membered analogue (**4**) possess almost the same basicity as the five-membered **1**. The optimized B—B bond lengths of the complexes **H₃B-3**, **H₃B-4**, and **H₃B-5** are also summarized in Table 1. The results indicate that Lewis basicities of boryl anions only slightly affect the B—B bond lengths. As Figure 2 depicts, the spin densities of **H₂B-3**, **H₂B-4**, and **H₂B-5** are mainly localized on **H₂B** fragments and not significantly shifted to **3-5**.

We then made an attempt to examine the thermodynamics of currently existing boryllithium to form a borane-cyclic boryl anion adduct. As Li^+ behaves as a bystander, *N,N'*-bis(2,6-diisopropylphenyl)-2,3-dihydro-1H-1,3,2-diazaborole anion (**6** in Scheme 1) can form a stable complex with BH_3 , which decreases BDE of the B—H bond by 21.5 kcal/mol (see Table 1). The spin density of **H₂B-6** is similar to that of **H₂B-1** (see Fig. 2). When

compared with **1**, the substitution of hydrogens by 2,6-diisopropylphenyl groups does not alter the B—B bond length of the complex significantly (Table 1). The result indicates that the Lewis basicity of the boron atom in a five-membered boryl anion may be influenced only slightly by bulky substituents.

Moreover, as Li^+ is taken into the calculation, $\Delta\text{BDE}_{\text{B-H}}$ are all decreased for **1-6** (the Cartesian coordinates of the complexes in this study can be seen in Additional Supporting Information). For example, the reduction of the B—H bond energy by **1** is decreased from 20.4 to 18.8 kcal/mol when Li^+ is taken into the MPW1K calculation. This may indicate that the chemical behavior of a cyclic boryl anion is influenced by the counter cation, especially in both gas phase and nonpolar solvents. However, the reaction $\text{H}_3\text{B} + \text{cyclic boryl anion} \rightarrow \cdot\text{H}_2\text{B-cyclic boryl anion} + \text{H}\cdot$ is still more thermodynamically favorable than that of $\text{H}_3\text{B} + \text{NHC} \rightarrow \cdot\text{H}_2\text{B-NHC} + \text{H}\cdot$ no matter Li^+ is considered or not. Similarly, the effects of **3-5** on the decrease of the B—H bond energy are influenced by the addition of Li^+ into the calculation. Taking $\Delta\text{BDE}_{\text{B-H}}$ as the reference, the efficiencies of the titled boron species in Scheme 1 to decrease the B—H bond's BDE are in the trend of **Li5** > **Li3** > **Li1** \approx **Li4** > **Li6**. This trend may be influenced by the binding energy of the cyclic boryl anion with cation Li^+ and the Lewis basicity of the cyclic boryl anion. For a fair comparison, the spin density of the singly occupied molecular orbitals (SOMO) around **H₂B** and **Li1-Li6** is depicted in Figure 3. As shown in Figure 3, the spin density of **H₂B-Li5** is

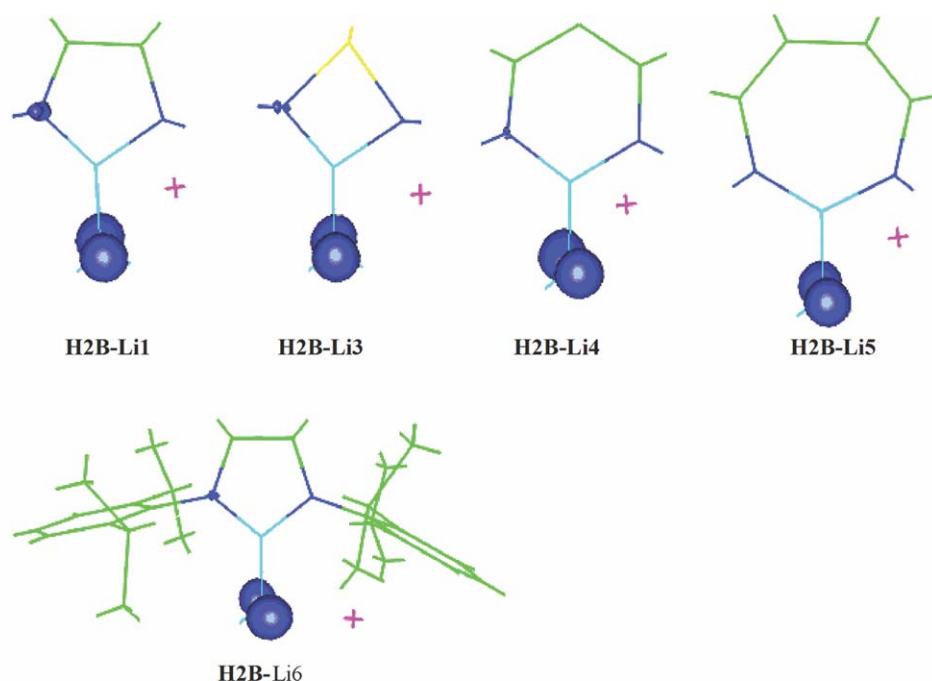


Figure 3. The SOMOs of $\text{H}_2\text{B-Li1}$ and $\text{H}_2\text{B-Li3-Li6}$ (the isodensity value = 0.02).

not delocalized at the seven-membered ring, although **Li5** is the most efficient one to reduce the BDE of B–H bond.

In sum, several remarks can be made according to the above approaches. According to our calculated results, boryl anions which are isoelectronic analogues to NHCs can lower BDE of B–H bond and make the hydrogen abstraction from BH_3 more favorable even under the counter cation being considered (see Table 1 and Fig. 1). Moreover, the seven-membered ring boryl anion **5** acts most efficiently to decrease BDE of the B–H bond; although it has not yet been synthesized. Knowing that substitution of BH_3 by other boranes (BR_2H) or the N–H group in **1** (**3–5**) by other N–R groups is feasible, sizeable reductions in the strengths of the B–H bond could also be achieved via Lewis acid–base interactions. The results presented here may thus pave another avenue toward boryl anion induced hydrogen atom abstraction in BH_3 .

Acknowledgments

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Chapter 11

BORYLENE – BORON BEARING A NEGATIVE CHARGE

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ABSTRACT

Although boron sits just left to carbon on the periodic table, this atom does not share its neighbor's versatility in reactivity. Due to its empty p orbital, which is in contrast to the partially filled p orbital in carbon, boron containing compounds almost behave as Lewis acids and are ready to accept electrons from others during the reaction. In one approach, anionic organoboron alkali metal salts were reported as possible reactive intermediates in some reactions, but none could be isolated or conclusively characterized. Based on the theoretical prediction by Schleyer and coworkers, Segawa and coworkers utilized a boron-bromide precursor to synthesize the first stable diamino-substituted boryllithium. To date, boryllithium has already shown a broad spectrum of utilizations and can be viewed as an ion pair between lithium and a five-membered ring containing negative-charge boron (borylene). In this context, we summarize our previous investigations regarding the thermodynamic and kinetic stabilities and Lewis basicities of borylenes. By the hybrid DFT functional, MPW1K, we studied a series of borylenes and found that nitrogen can act as a good π donor to stabilize a borylene and the not-yet synthesized six-membered analogue is more stable than the known five-membered borylene. Moreover, like the isoelectronic counterparts, N-heterocyclic carbenes, borylenes can act as Lewis bases to complex with BH_3 and reduce the bond dissociation energy of the B-H bond in BH_3 . The Lewis acid-base pair then can donate hydrogen atoms during a radical reaction.

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1. INTRODUCTION

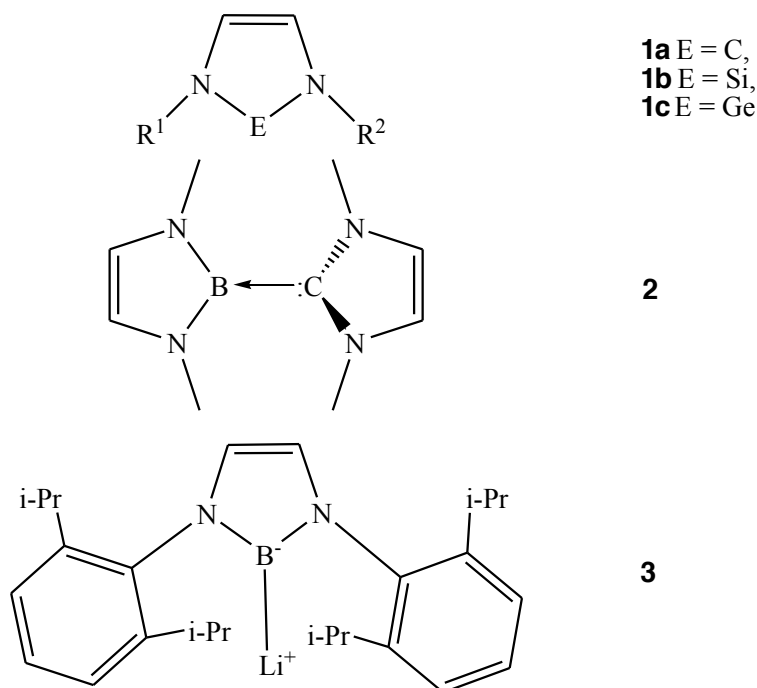
Since Arduengo and coworkers successfully isolated a nucleophilic carbene (**1a** in Scheme 1) in 1991 [1], the relevant carbenes have played a pivotal role in a variety of chemical reactions [2]. For example, these nucleophilic carbenes have attracted much attention as reagents in a variety of transesterification, nucleophilic aromatic substitution and cycloaddition chemistry [3]. Various quantum chemical calculations have been performed to investigate the peculiar stability of these Arduengo-type carbenes which are also called N-heterocyclic carbenes (NHCs) [4-10]. Subsequently, their analogues silylene (**1b**) and germylene (**1c** in Scheme 1) have also been studied experimentally [11, 12]. In stark contrast, analogues of Arduengo-type carbenes containing boron, which are named borylenes, were much less investigated. Borylenes are isoelectronic with Arduengo-type carbenes and, in theory, would bear a negative charge at the boron atom. Although anionic organoboron alkali metal salts were reported to be possible reactive intermediates in certain reactions [13], none have been isolated and conclusively characterized [14]. Indeed, the first experimental evidence about borylenes was provided by the synthesis and structural elucidation of **2** depicted in Scheme 1 [15]. In 1995, Schleyer and coworkers, on the basis of theoretical calculation, predicted that diamino groups on the boron atom should stabilize a boryllithium [16]. In 2006, Nozaki, Yamashita and Segawa firstly utilized a boron-bromide precursor to synthesize a stable diamino-substituted boryllithium (**3**, see Scheme 1). X-ray crystallography and ^{11}B NMR spectroscopy of **3** matched with the prediction of a boron anion [17]. They also made a comparison between the structure of **3** and the ones of hydroborane and free boryl anions. The comparison showed that the boron-lithium bond was polarized where the boron atom was anionic [18]. **3** has been utilized to synthesize new boron-containing compounds with synthetic routes differing from traditional ones [17-20]. For example, borylene could behave as an efficient nucleophile as it reacted with electrophiles such as water, methyltrifluoromethanesulfonate, 1-chlorobutane, and benzaldehyde in tetrahydrofuran (THF) [17].

Motivated by their intriguing chemistry, we have been investigating the structure, stability and electronic properties of the parent borylene (**4a**) and its derivatives (see Scheme 2) from theoretical viewpoint. Furthermore, due to the fact that carbenes bearing four-, six- and seven-membered ring (see in Scheme 3) have been synthesized and they showed quite different electronic structures from that of the more famous five-membered carbene (NHC) [21-23], their analogous borylenes bearing four-, six- and seven-membered ring (see **8-12** in Scheme 3) are also studied. We then compared these results with that of the five-membered borylene which has been successfully synthesized. Finally, summary and perspective about borylenes are made mainly based on our previous theoretical results [24-26].

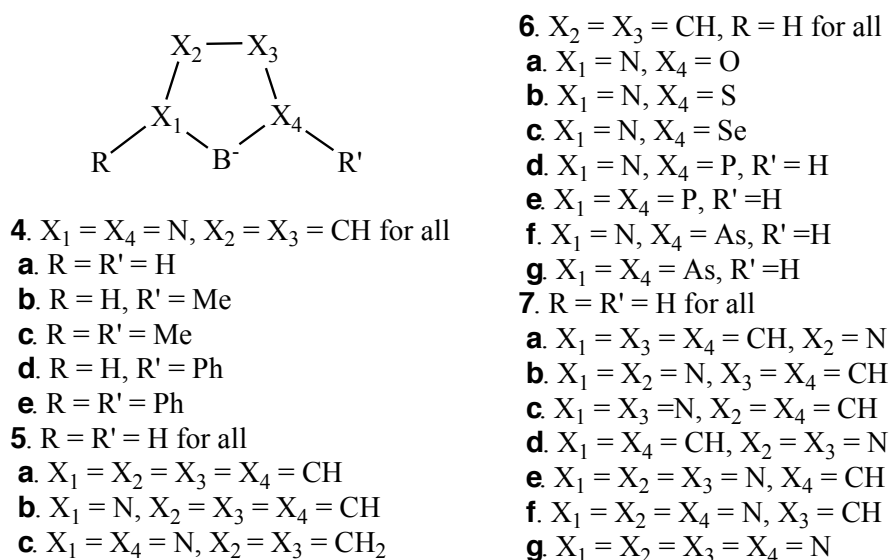
2. THEORETICAL METHOD

All calculations are done with the Gaussian 03 program [27]. All the stationary points are calculated by the hybrid DFT MPW1K functional and positively identified as equilibrium structures or transition states as evidenced by the lack of the numbers of imaginary frequency (NIMAG=0) or NIMAG=1 [28]. All energetic values listed in this study are corrected for

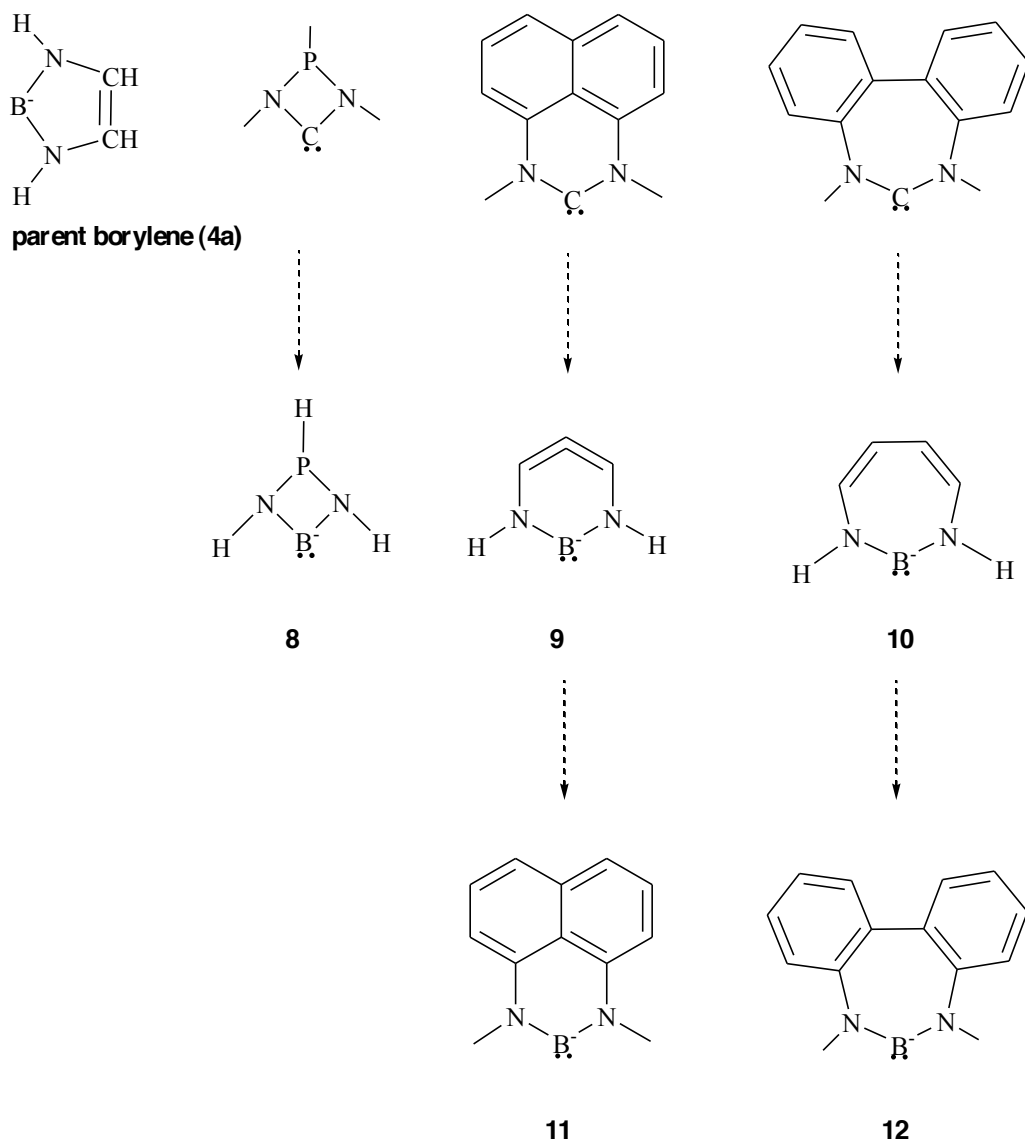
zero-point vibrational energies. Furthermore, NBO 3.1 implemented in Gaussian 03 is performed to survey the properties of the borylenes [29]. Natural bond orbitals (NBOs) are an orthonormal set of localized "maximum occupancy" orbitals, which describe the molecular bonding pattern of electron pairs to give the most accurate Lewis-like description of the total N-electron density.



Scheme 1. The structures of 1~3.



Scheme 2. The structures of borylenes 4, 5, 6 and 7.



Scheme 3. The scaffolds of four-, six- and seven-membered Arudengo-type carbene and the structures of the parent borylene (**4a**), the corresponding analogues **8**, **9**, **10**, **11** and **12**.

The UMPW1K/6-31+G* theoretical level is adopted to optimize the open shell species. Although unrestricted calculations can be performed efficiently, it should be noted that their wavefunctions are no longer eigenfunctions of the total spin $\langle S^2 \rangle$ [30]. Thus, certain error, namely the spin contamination, may be introduced throughout the calculation. For all open shell species in this study, the expectation values of $\langle S^2 \rangle$ are close to 0.75 and 2.00, which are located at values expected for a radical and a triplet species, respectively [30]. The result indicates that spin contamination is not serious in this study, possibly due to the fact that the effect of spin contamination on densities and energies by a DFT functional is less than those obtained by the unrestricted HF method [31,32]. In an attempt to obtain the second triplet

state (T_2), the keywords “guess=alter” and “vshift” in Gaussian are both used to change the orbital ordering of a borylene.

3. THE PROPERTIES OF BORYLENES

3.1. The Electronic Structures of Borylenes

Based on the previous theoretical results, the stabilities of borylenes are due to their high electron affinity [33]. Other computational studies on the reactivity of borylenes predicted that the thermodynamic stability of these species and their high reactivity toward electrophiles are mainly due to the availability of the lone pair and the high energy of the highest occupied molecular orbital (HOMO) [34]. According to our NPA/NLMO analysis among the titled borylenes, the lone pair of boron is mainly hybridized by its s and p orbitals, while the contributions of its d orbitals are negligible [25]. Based on the NPA/NLMO analyses, there exists a lone pair and its occupancy is < 0.5 on boron for **9**, **10** and **11**. A more detailed inspection unveils that this additional lone pair can be viewed as a pure p_π orbital. Accordingly, the electronic structures of the four-, six- and seven-membered borylenes may be different from that of the known five-membered borylene. This result is in agreement with the previous studies regarding their isoelectronic counterparts, NHCs, which showed the four-, six- and seven-membered NHCs were different from that of the famous five-membered one.

According to the natural population analyses (NPA) among the titled borylenes, almost all the five-membered borylenes bear a negative charge on boron, except for borylenes **4c**, **4d**, **4e**, **5a** and **5c**. Moreover, NPA on boron are 0.0679, 0.0177, 0.0859, 0.0695 and 0.0441, for **8**, **9**, **10**, **11** and **12**, respectively and different from that (-0.0349) of **4a**. The results illustrate that the negatively-charged character of boron is in a trend of **4a** $>$ **9** $>$ **12** $>$ **8** $>$ **11** $>$ **10**. Therefore, the binding strength with Li^+ and the stabilities of the ion-pair Li-borylene should be in the order of **4a** $>$ **9** $>$ **12** $>$ **8** $>$ **11** $>$ **10**.

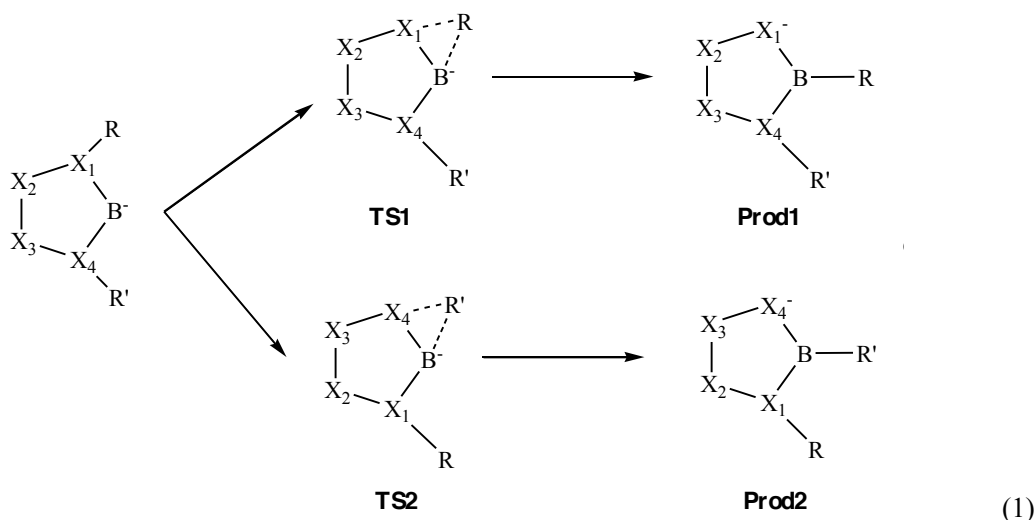
According to the converged geometries, **8** has the longest B-N bonds among the titled borylenes (c.f. **4a**, **9**, **10**, **11** and **12**). This may imply that **8** has the weakest $\text{EP}_\pi(\text{B})\text{-FP}_\pi(\text{N})$ interactions among these borylenes (EP_π and FP_π present the empty and filled p_π orbitals). Moreover, the bond angles around the nitrogen atom are taken as a parameter to investigate whether the ring is planar or not. For a planar conformation, the sum of the bond angles around the nitrogen atom is 360° . Otherwise, a value deviated from 360° is obtained. As a result of calculation, they are 360° , 341° , 360° , 356° , 360° and 349° for **4a**, **8**, **9**, **10**, **11** and **12**, respectively. That is to say, **4a** (five-membered), **9** and **11** (six-membered) are planar. In contrast, **8** (four-membered), **10** and **12** (seven-membered) are in twisted forms, the results of which are in agreement with the previous reports regarding the four-, six- and seven-membered NHCs [21-23,35,36]. Moreover, additional aromatic rings in **11** and **12** do not change the geometries of the borylenes as compared with **9** and **10**. We then make a fair comparison among **4a**, **6e** and **6g** and find that the dihedral angles $\angle\text{H-X}_1\text{-C-C}$ ($\text{X}_1 = \text{N, P or As}$) are 180° , 133° and 122° for N (**4a**), P (**6e**) and As (**6g**), respectively. Since phosphorus and arsenic atoms are pyramidized in **6e** and **6g**, the filled p orbital (lone pair) of phosphorus and arsenic is not purely π -oriented, i.e. they are not perpendicular to the molecular plane.

This may be due to the fact that the interaction strength is in the order $EP_{\pi}(\text{B})\text{-FP}_{\pi}(\text{N}) > EP_{\pi}(\text{B})\text{-FP}_{\pi}(\text{P}) > EP_{\pi}(\text{B})\text{-FP}_{\pi}(\text{As})$ [37].

The strength of the interaction between EP_{π} of boron and FP_{π} of the neighboring atoms also influence the origin of the electronic transition from S_0 to T_1 . According to our calculation [25], the electronic $S_0 \rightarrow T_1$ transition for borylenes **5a**, **7f**, **7g**, **8**, **9**, **10** and **11** results from the σ -type lone pair on boron to the π^* orbital of the heterocycle, as the interaction is weak. In contrast, for the rest of titled boron complexes borylenes the transition originates from the σ -type lone pair to EP_{π} on boron, as the interaction is strong.

3.2. The Stabilities of Borylenes

The stabilities of borylenes from both the kinetic [24] and thermodynamic viewpoints [25] are then discussed according to our previous calculated results. We have investigated the kinetic stabilities of borylenes from five aspects: (3.2-1) the substitute effect of R and R' (**4a-4e**), (3.2-2) the stabilizing efficiency of nitrogen atom and the steric effect of $\text{CH}_2\text{-CH}_2$ link (**4a**, **5a**, **5b** and **5c**), (3.2-3) the stabilizing effects of other π -donating elements (**4a** and **6a-6g**), (3.2-4) the influences of numbers and positions of nitrogen on the stability of a five-membered ring borylene (**4a** and **7a-7g**) and (3.2-5) the comparison of four- **8**, six- (**9**, **11**) and seven-membered borylenes (**10**, **12**) with the five-membered one **4a** [24]. For a clear comparison, the 1,2-R or 1,2-R' group transfer reactions (see eq. (1)) are chosen as a prototype. Note that the higher the reaction barrier, the more stable the borylene could be.



According to the results [24], nitrogen is the most efficient π donor to stabilize a borylene. Therefore, the comparisons of the thermodynamic stabilities of the titled borylenes neglect the effect of other π -donating elements and are from four aspects, i.e. (3.2-1), (3.2-2), (3.2-4) and (3.2-5). Two parameters, i.e. singlet-triplet splitting and electron affinity, are then chosen to compare the thermodynamic stabilities of borylenes shown in Scheme 2 and 3. According to the results of Schleyer and ours [16, 25], the ground state of a borylene is in singlet manifold. The justification is based on the fact that a species in triplet manifold tends

to undergo facile radical reactions [38]. Since the intersystem crossing rate is proportional to square of spin-orbit coupling matrix and inversely proportional to the energy gap between

singlet and triplet manifold E_{ST} expressed as $\frac{|\langle S_0 | H_{so} | T_1 \rangle|^2}{E_{ST}}$ [39], the increase of

intersystem crossing rate is expected with a smaller E_{ST} and hence a radical reaction should be facilitated. Moreover, EA of a species is defined as $-\Delta H$ of the reaction $A + e^- \rightarrow A^-$; thus a stable anion must have a positive value of EA. These two factors, in combination, should govern the thermodynamic stabilities of borylenes.

The results of systematic comparisons can be categorized and elaborated as follows.

3.2.1. The Substitute Effect of R and R'

The transition states of isomerization reactions of **4a-e** are depicted in Figure 1. According to the results of MPW1K, **4a** must overcome a barrier height of 127.5 kJ/mol, which was even higher (198.2 kJ/mol) calculated based on MP4/6-311+G*//HF/6-311+G* [33]. Furthermore, the Miller parameter (χ^\ddagger) is introduced (see eq. (2)) to investigate the chemical reactivities of **4a-e** [40].

$$\chi^\ddagger \text{ Miller} = \frac{1}{2 - \left(\frac{\Delta H_r}{\Delta H^\ddagger} \right)} \approx \frac{1}{2 - \left(\frac{\Delta G_r}{\Delta G^\ddagger} \right)} \quad (2)$$

where ΔH_r and ΔH^\ddagger are the reaction and activation enthalpies, respectively. According to the reaction free energy (ΔG_r) = $\Delta H_r - T\Delta S_r \approx \Delta H_r$ and the activation free energy (ΔG^\ddagger) = $\Delta H^\ddagger - T\Delta S^\ddagger \approx \Delta H^\ddagger$, the Miller parameter can thus be obtained via eq. (2) and the results are listed in Table 1. For the Miller parameter, the smaller (larger) χ^\ddagger value indicates that the transition state is close to the reactant (product). Evidently, the barrier of the hydrogen atom transfer reaction does not alter significantly, upon substituting the other N-H hydrogen atom in **4a**, with a methyl group (Me) in **4b** or a phenyl ring (ph) in **4d**. Similar results are concluded for the methyl group or phenyl ring transfer reaction. Clearly, the migration barrier is in a trend of Me > ph > H. This can be rationalized by the fact that hydrogen migration involves a spherical s orbital, whereas the one with e.g. CH₃ involves a directional p/sp³ orbital. Moreover, there may exist a resonance effect between the π orbital of a phenyl ring and EP $_{\pi}$ of the boron atom, and/or repulsion between the π orbital of a phenyl ring and FP $_{\pi}$ of the nitrogen atom in TS (see Scheme 4), causing the barrier of the phenyl group transfer to be smaller than that of the methyl group transfer. For a fair comparison, the previous B3LYP results for NHCs are also summarized in Table 1 [41]. The comparison between the boryl anions (**4a** and **4c**) and their carbon analogs (**4a-C** and **4c-C**) shows that both borylenes and NHCs are kinetically stable, with respect to their 1,2-H or Me shifted isomers. In addition to the 1,2-R group shifted reactions, it has been reported that there is a lower barrier of dimerization process for NHC [41]. Such dimerization reaction should not occur for a borylene due to the repulsion between the two negative boron centers. According to the above results, the stability of the boryllithium synthesized by Segawa and coworkers (see **3** in Scheme 1) can be rationalized by the two bulky groups on the two nitrogen atoms, which induce a large barrier if the borylene undergoes such isomerization [17]. On the other hand,

these two bulky groups can protect the boron atom from attack by neighboring molecules. Also, **4a-e** are found to be kinetically stable with respect to their isomers; that is they must overcome large barrier heights, prior to the isomerization. However, their isomers, for which the negative charge is mainly located on nitrogen, are thermodynamically more stable than **4a-e**. This should be due to nitrogen being more electronegative than boron. Interestingly, the Miller parameters, χ^\ddagger , are all between 0.28 and 0.33; thus, substitution of the hydrogen atom of N-H group by a methyl group or a phenyl ring does not affect the location of TS on the potential energy surface, along the isomerization reaction.

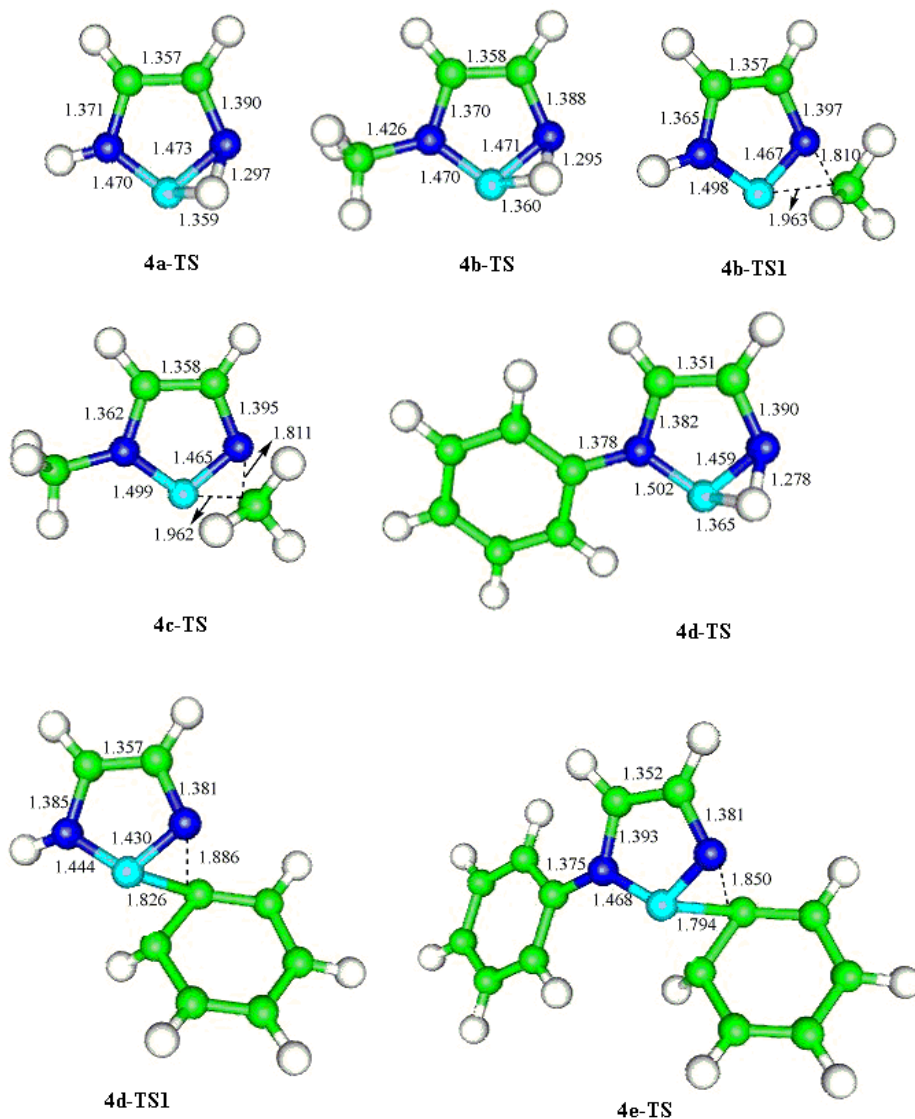


Figure 1. The critical geometrical parameters of TSs of the isomerization reactions of **4a-e** (bond length in Å, boron in sky blue, nitrogen in navy blue, carbon in green and hydrogen in white). a. The previous HF/6-311+G* results (see ref. [33]).

Table 1. The activation free energies (ΔG^\ddagger in kJ/mol), reaction free energies (ΔG_r in kJ/mol) and Miller parameters (χ^\ddagger) of the isomerization reaction of **4a-e**

| | ΔG^\ddagger | ΔG_r | χ^\ddagger |
|-------------------------|---------------------|---------------------|---------------------|
| 4a | 127.8 | -186.2 | 0.2893 |
| 4a-C | 160.9 ^d | -111.7 ^d | 0.3711 ^d |
| 4b^a | 127.8 | -186.0 | 0.2894 |
| 4b^b | 216.6 | -232.7 | 0.3253 |
| 4c^b | 216.1 | -231.5 | 0.3256 |
| 4c-C^b | 218.8 ^d | -136.9 ^d | 0.3809 ^d |
| 4d^a | 130.4 | -192.1 | 0.2879 |
| 4d^c | 183.5 | -220.8 | 0.3122 |
| 4e^c | 182.6 | -210.7 | 0.3171 |

^a The hydrogen atom transfer.

^b The methyl group transfer reaction.

^c The phenyl ring transfer reaction.

^d The ZPVE corrected results of E_a and ΔH_r in ref. [41].

Table 2. The differences of selected geometric parameters between neutral radical and negatively-charged **4a~4e** (bond length in Å)

| | N(H)-B | N(Me or Ph)-B |
|-----------|--------------------------|---------------|
| 4a | 1.471/1.417 ^a | – |
| 4b | 1.469/1.410 | 1.472/1.410 |
| 4c | – | 1.470/1.417 |
| 4d | 1.461/1.410 | 1.511/1.420 |
| 4e | – | 1.494/1.423 |

^a The values are arranged as 4a/ 4a.

Table 3. The E_{ST} (in kJ/mol) and EA (in kJ/mol) of **4a~4e**

| | E_{ST} | EA ^a |
|-----------|----------|-----------------|
| 4a | 120.1 | 5.2 |
| 4b | 119.8 | 9.3 |
| 4c | 132.4 | 13.1 |
| 4d | 126.3 | 41.8 |
| 4e | 103.3 | 70.5 |

^a EA= E(neutral form) – E(anionic form).

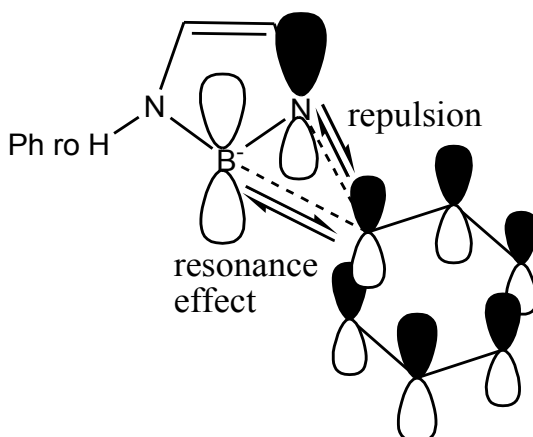
According to our MPW1K results, the addition of one electron, forming **4a~4e**, makes the B-N bond length (the \angle N-B-N bond angle) of **4a~4e** increased (decreased). Changes of B-N bond length from the neutral radical (**4a~4e**) to **4a~4e** are summarized in Table 2. Finally, the results of E_{ST} and EA of **4a~4e** are all listed in Table 3. Although the DFT functional cannot deal with the eigenvalue of LUMO very accurately [42,43], the electron

affinity of a species cannot be thus predicted accurately. However, the present calculation still renders valuable EA values suited for predicting their trend in a qualitative manner. According to EA values, the stability of diazaborole anions increases upon substituting the N-H hydrogen atom with a methyl or a phenyl group. This, in combination with E_{STS} of **4a-4e** being estimated to be $> 100 \text{ kJ mol}^{-1}$ (see Table 3), indicates that they are stable and inert to radical reactions.

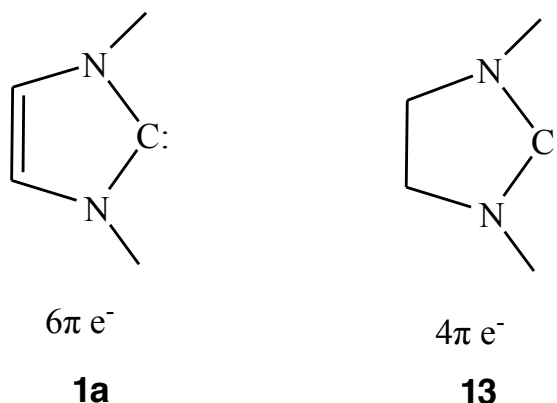
3.2.2. The Stabilizing Efficiency of Nitrogen Atom and the Steric Effect of $\text{CH}_2\text{-CH}_2$ Link

According to the results of Schleyer and coworkers [16], nitrogen can stabilize a boryllithium. This may be due to the fact that nitrogen can act as a π donor to interact with EP_π of boron. The stabilizing efficiency of nitrogen has been investigated by comparing the kinetic stability of **4a**, **5a** and **5b**. The number of nitrogen on the five-membered ring is zero, one and two for **5a**, **5b** and **4a**, respectively. Ever since 1991, a number of theoretical calculations and physical studies have been performed and the results pointed out that cyclic delocalization and/or resonance ($6\pi e^-$) in the imidazole ring was not a dominant factor to stabilize Arduengo-type carbene [4-10]. Indeed, in 1995, Arduengo and coworkers successfully synthesized the corresponding saturated carbene, the structure of which is represented as **13** in Scheme 5 [44]. The difference between **1a** and **13** is mainly caused by the twisting of the $\text{CH}_2\text{-CH}_2$ link in **13**, resulting in a steric effect. In this study, we are also interested in finding whether the steric effect of the five-membered ring plays a role in stabilizing a borylene; this can be done by comparing the calculated results of **4a** with those of **5c**. The relevant results are summarized in Figure 2 and Table 4.

Owing to the lack of a π -donating capacity, carbon cannot stabilize the borylene. Therefore, hydrogen atom transfer of CH_2 group (**5a**) has a lower barrier than that of the NH group (**4a**) by 81.3 kJ/mol. The bond length of the B-H bond in **5a-TS** is longer than the bond length in **4a-TS** the result of which is in agreement with the fact that **5a** has a smaller Miller parameter. According to the similar H-shifted barrier of N-H group for both **5b** and **4a**, the existence of one nitrogen atom (in **5b**) may be sufficient to stabilize the five-membered boryl anion kinetically.



Scheme 4. The illustration of orbital interactions in **4d-TS1** or **4e-TS**.



Scheme 5. The skeletons of Arduengo-type carbenes.

As shown in Table 4, the borylene **5c** has a similar isomerization barrier with **4a**. Furthermore, the Miller parameter of **5c** is calculated to be larger than that of **4a**, indicating that TS of **5c** is leaner toward the isomer. The B3LYP results regarding the 1,2-H shifted reaction of **13** (see Scheme 5) are also listed in Table 4 [41]. As listed in Table 4, the carbon counterpart of **5c**, which is designated as **5c-C**, has a similar barrier as **4a-C**. Considering the exothermicities of 1,2-H shifted reaction, the saturated borylene (**5c**) and NHC (**5c-C**) have lower exothermicities than that of the unsaturated ones. Moreover, TS of **5c** has a longer N-transferred H but shorter B-transferred H bond than that of **4a** (see Figure 2).

Similarly, the addition of one electron causes the B-C or B-N bond length (the \angle C-B-C, \angle C-B-N or \angle N-B-N bond angle) of **5a**~**5c** increased (decreased). The pertinent parameters such as E_{ST} and EA are summarized in Table 5. Interestingly, E_{ST} and EA predict certain inconsistency in thermodynamic stability trend among these anions. According to the calculated E_{ST} , the thermodynamic stability trend is in the order of **4a** > **5c** > **5b** > **5a**. In comparison, the trend of EA value is predicted to be **4a** > **5b** > **5a** > **5c**. Since E_{ST} and EA are two independent parameters, it is not surprising to render different tendency of stability predicted solely from each factor. Nonetheless, both parameters consistently draw the conclusion that **4a** is the most stable species, which is in agreement with the result that only efficient π - e^- donors like nitrogen can stabilize borylenes due to the existence of a strong p_π - p_π interaction [16]. For further investigation, a stability factor SF is introduced and defined as shown in eq. (3) to investigate the thermodynamic stabilities of borylenes:

$$SF = E_{ST} + EA \quad (3)$$

Undoubtedly, upon increasing SF an anionic species becomes more thermodynamically stable. Accordingly, SF of **4a**, **5a**, **5b** and **5c** are calculated to be 125.3, 39.2, 96.7 and 100.4 kJ/mol, respectively. This indicates that the steric effect of the CH_2 - CH_2 link can significantly influence the stability of a diazaborole anion.

Table 4. The activation free energies (ΔG^\ddagger in kJ/mol), reaction free energies (ΔG_r in kJ/mol) and Miller parameters (χ^\ddagger) of the isomerization reactions of **5a-c**

| | ΔG^\ddagger | ΔG_r | χ^\ddagger |
|-------------------------|---------------------|--------------------|---------------------|
| 5a^a | 46.5 | -232.2 | 0.1429 |
| 5b^a | 51.9 | -214.4 | 0.1630 |
| 5b^b | 129.1 | -196.7 | 0.2838 |
| 5c^b | 133.5 | -153.9 | 0.3171 |
| 5c-C^b | 162.5 ^c | -88.6 ^c | 0.3929 ^c |

^a The hydrogen atom transfer of the CH₂ group.

^b The hydrogen atom transfer of the N-H group.

^c The ZPVE corrected results of E_a and ΔH_r in ref. [41].

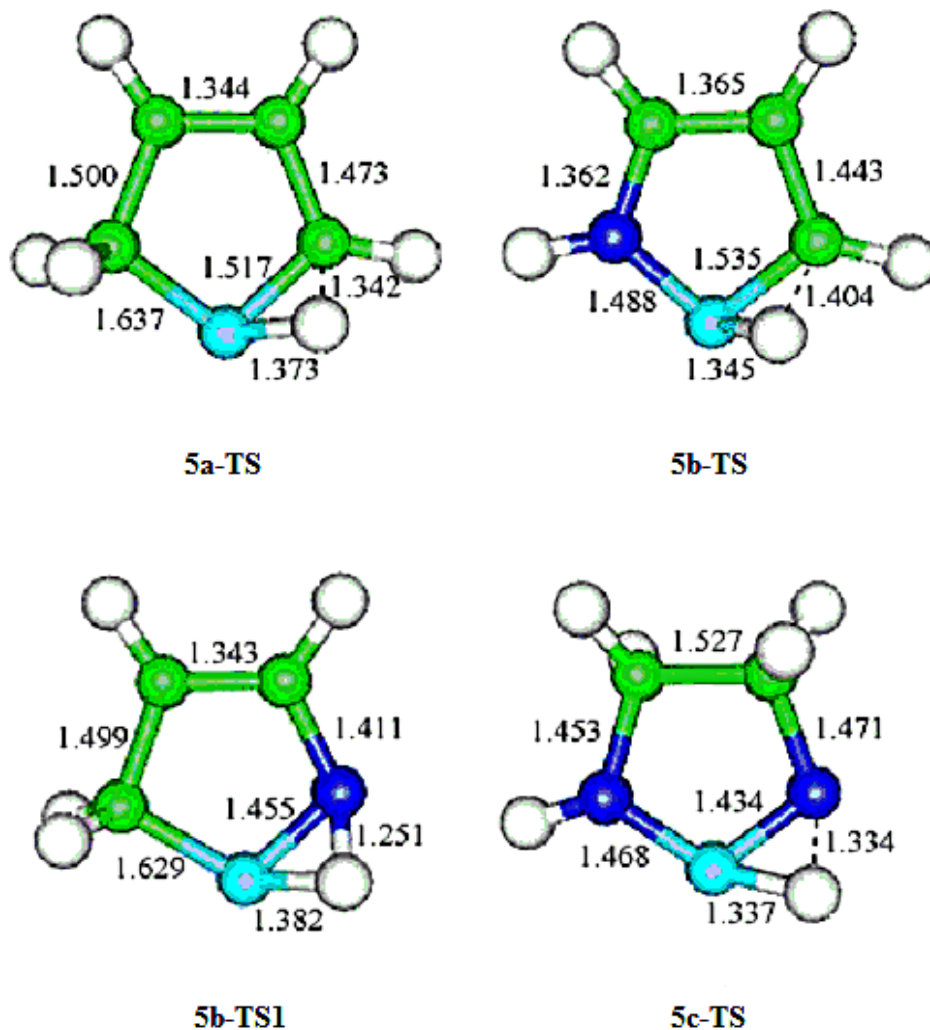


Figure 2. The critical geometrical parameters of TSs of the isomerization reactions of **5a-c** (bond length in Å, boron in sky blue, nitrogen in navy blue, carbon in green and hydrogen in white).

Table 5. E_{ST} (in kJ/mol), EA (in kJ/mol) and SF (in kJ/mol) of 4a and 5a~5c

| | E_{ST} | EA | SF |
|-----------|----------|-------|-------|
| 4a | 120.1 | 5.2 | 125.3 |
| 5a | 41.7 | -2.5 | 39.2 |
| 5b | 97.4 | -0.7 | 96.7 |
| 5c | 111.9 | -11.6 | 100.4 |

3.2.3. The Stabilizing Effects of α her π -donating Elements

In 3.2-2, the π -donating efficiency of nitrogen is investigated by comparing **4a**, **5a** and **5b**. According to MPW1K results, the existence of one nitrogen atom (in **5b**) may be sufficient to stabilize the five-membered borylene kinetically. Moreover, the other pnicogen (P, As) and chalcogen (O, S and Se) elements which also act as π donors are investigated to compare their efficiencies to stabilize a borylene with nitrogen. As **6a~g** depicted in Scheme 2, one or two nitrogen atoms are replaced by pnicogen (P, As) or chalcogen (O, S and Se) elements. Relevant results are summarized in Figure 3 and Table 6.

As shown in Table 6, the kinetic stability of a five-membered boryl anion decreases when the nitrogen atom is replaced by other group 15 elements. Comparing the data between **4a** and **6e**, in the gas phase, ΔG^\ddagger of hydrogen atom migration of P-H group (**6e**) is calculated to be 43.6 kJ/mol, which is less than that of N-H group (**4a**) by 84.2 kJ/mol. Moreover, ΔG^\ddagger of the hydrogen atom transfer of the As-H group (**6g**) is calculated to be 31.4 kJ/mol, which is less than that of the hydrogen atom migration of N-H group (**4a**) by 96.4 kJ/mol. This may be rationalized by the difference in interaction strengths between the empty p_π orbital of the boron atom ($EP_\pi(B)$) and the filled p_π orbital of the group 15 element ($FP_\pi(X_1$ or $X_4)$, X_1 or $X_4 = N, P$ and As) as well as the interaction strength, which is in the order $EP_\pi(B)-FP_\pi(N) > EP_\pi(B)-FP_\pi(P) > EP_\pi(B)-FP_\pi(As)$ [37]. Furthermore, comparing the results of **4a**, **6e** and **6g**, the isomerization barriers are found to have a correlation with respect to the Miller parameters, in which a larger barrier corresponds to a larger Miller parameter, i.e. TS is leaner toward the product.

Table 6. The activation free energies (ΔG^\ddagger in kJ/mol), reaction free energies (ΔG_r in kJ/mol) and Miller parameters (χ^\ddagger) of the isomerization reactions of 6a-g

| | ΔG^\ddagger | ΔG_r | χ^\ddagger |
|-----------------------|---------------------|--------------|-----------------|
| 6a | 123.1 | -202.0 | 0.2747 |
| 6b | 133.7 | -201.8 | 0.2849 |
| 6c | 135.2 | -198.0 | 0.2886 |
| 6d^a | 135.1 | -201.3 | 0.2866 |
| 6d^b | 28.1 | -265.6 | 0.0873 |
| 6e^b | 43.6 | -254.8 | 0.1274 |
| 6f^a | 136.3 | -198.5 | 0.2893 |
| 6f^b | 24.6 | -274.4 | 0.0760 |
| 6g^b | 31.4 | -269.7 | 0.0944 |

^a The hydrogen atom transfer of the N-H group.

^b The hydrogen atom transfer of the P-H or As-H group.

As depicted in Figure 3, the B-H bond lengths in TS are in the order of *6g-TS* > *6e-TS* > *4a-TS*. As the other N-H group is replaced by a group 16 element, according to our calculation; the migration of the hydrogen atom of N-H group is not significantly influenced from both thermodynamic and kinetic viewpoints. However, due to the lack of a protecting group, the boron atom in *6a-c* is subject to attack by neighboring molecules. We thus, expect that *6a-c* may be less stable than *4a*. Among these π -donating elements, nitrogen atom seems to be the most efficient π donor to stabilize a borylene.

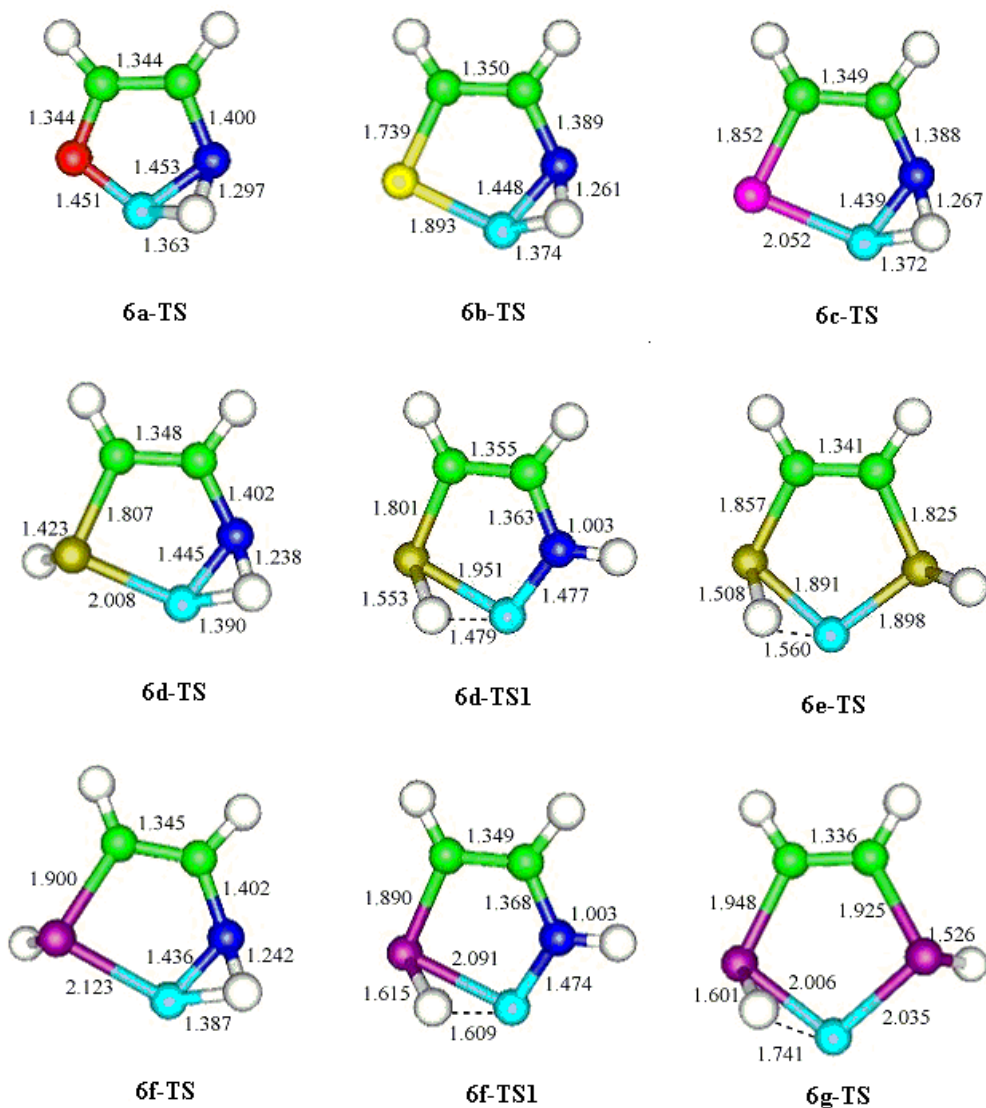


Figure 3. The critical geometrical parameters of TSs of the isomerization reactions of *6a-g* (bond length in Å, boron in sky blue, oxygen in red, sulfur in yellow, selenium in pink, nitrogen in navy blue, phosphorous in gold, arsenic in purple, carbon in green and hydrogen in white).

Table 7. The Activation Free Energies (ΔG^\ddagger in kJ/mol), Reaction Free Energies (ΔG_r in kJ/mol) and Miller Parameters (χ^\ddagger) of the isomerization Reactions of 7a-g

| | ΔG^\ddagger | ΔG_r | χ^\ddagger |
|--------------------------------|---------------------|--------------|-----------------|
| 7a (Path 1)^a | 45.8 | -220.2 | 0.1468 |
| 7a (Path 2)^a | 42.6 | -253.0 | 0.1260 |
| 7b^a | 48.56 | -243.6 | 0.1425 |
| 7b^b | 144.5 | -160.3 | 0.3216 |
| 7c^a | 51.5 | -203.9 | 0.1677 |
| 7c^b | 135.6 | -205.1 | 0.2847 |
| 7d^a | 39.6 | -246.9 | 0.1215 |
| 7e^a | 43.0 | -243.8 | 0.1303 |
| 7e^b | 146.1 | -172.0 | 0.3147 |
| 7f (Path 1)^b | 147.3 | -147.3 | 0.3334 |
| 7f (Path 2)^b | 135.4 | -201.6 | 0.2866 |
| 7g^b | 221.3 | -169.5 | 0.3616 |

^a The hydrogen atom transfer of the CH₂ group.

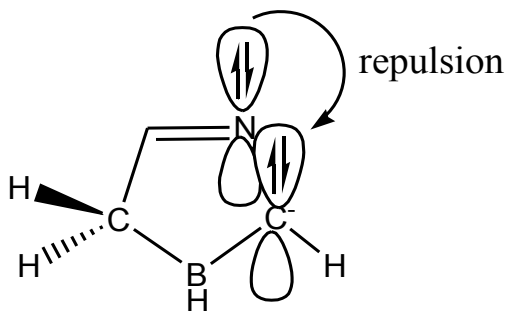
^b The hydrogen atom transfer of the N-H group.

3.2.4. The Influences of the Numbers and Positions of Nitrogen on the Stability of a Five-membered Borylene

Having one filled lone pair, nitrogen is the most efficient π donor to stabilize a five-membered borylene (vide supra). However, due to its large electronegativity, nitrogen can also behave as an σ acceptor. Accordingly, the effects of the numbers and positions of nitrogen in the five-membered ring on the kinetic stability of a borylene are also investigated. The relevant results are summarized in Figure 4 and Table 7. Notably, **7a** has two kinds of CH₂ groups, which can undergo the H atom migration to the boron atom. One is close to nitrogen and the other is to the CH group. Similar condition can be seen in **7f**, for which one NH group is close to the CH group and the other is close to nitrogen. As listed in Table 7, **7a-Prod2**, which is the product of the second isomerization reaction of **7a**, is more stable than **7a-Prod1** by 32.8 kJ/mol, despite that the two reactions have similar barriers. This can be rationalized by the repulsion between the filled p_π orbitals of nitrogen and carbon anion (see Scheme 6). Similar explanation can be applied to the difference in energetics between **7f-Prod1** and **7f-Prod2**. Furthermore, as shown in Table 7, all H-shifted reactions of the CH₂ group have smaller Miller parameters and barriers than those of the NH group. When comparing with **4a**, the bond length of X₂-X₃ in Scheme 2 decreases from 1.351 Å to 1.255 Å, as the number of nitrogen atom increases from zero to two. This result is qualitatively in agreement with the van-der Waals radius of carbon and nitrogen. Thus, nitrogen atom seems only to behave as a π donor in the five-membered borylene. The 1,2-H shifted activation free energy ΔG^\ddagger increases as the number of nitrogen atom in the five-membered ring increases.

Again, similar with that mentioned above, the addition of one electron causes the B-N or B-C bond length (the \angle C-B-C, \angle C-B-N or \angle N-B-N bond angle) of **7a-7g** increased (decreased). Moreover, their E_{ST} and EA, which are listed in Table 8, also show an inconsistent prediction about their stability trend. According to the singlet-triplet splitting, their stabilities are in the order of **7g** > **7f** > **4a** > **7c** > **7b** > **7e** > **7d** > **7a**. However, the electron affinity predicts a sharply different stability trend of **7g** > **7e** > **7d** > **7f** > **7c** > **7a** > **7b**

> **4a**. Due to the nitrogen atoms acting as efficient π - e^- donors, **7g** is predicted as the most stable species by both E_{ST} and EA. Likewise, we can use SF to investigate the relative stabilities between **4a** and **7a**~**7g**. And, the stability trend is in the order of **7g** > **7f** > **7e** > **7c** > **7b** > **7d** > **4a** > **7a**. Both **7a** and **5b** have only one nitrogen atom, but **5b** (SF = 96.7 kJ/mol) is more stable than **7a** (76.7 kJ/mol). This may be due to the fact that nitrogen atom is closer to the negatively-charged boron in **5b**; thus FP_π of nitrogen can interact more efficiently with EP_π of boron.



Scheme 6. The repulsive interaction in **7a-Prod1**.

3.2.5. The Comparison of Four-, Five-, Six- and Seven-membered Borylenes

The calculated free energies of activation, the reaction free energies and the Miller parameters of the H-shifted reactions of **8**, **9**, **10**, **11** and **12** are summarized in Table 9. The geometries of TSs of the H atom migration reactions of **8**, **9**, **10**, **11** and **12** are depicted in Figure 5. As shown in Table 9, **11** is the most stable species due to the fact that it has the largest isomerization barrier. Surprisingly, although **8** has a larger ring strain, it is as stable as **4a** kinetically due to the similar activation free energy. Although the additional aromatic rings of **11** and **12** do not alter their geometries, they induce larger activation free energies during the H-shifted reactions (c.f. comparison between **9** and **11**, or between **10** and **12**).

Like their five-membered analogues, the addition of one electron makes the B-N bond length (the \angle N-B-N bond angle) of **8**~**12** increased (decreased). The calculated values of E_{ST} , EA and SF of **8**~**12** are summarized in Table 10. According to SF, their relative stabilities are in the order of **11** > **4a** > **9** > **8** > **12** > **10**. A comparison between **9** (**10**) and **11** (**12**) shows that additional phenyl rings can increase the stability of a six- or seven-membered borylene. Possibly due to the ring strain, both **8** and **10** are less stable than **4a**.

Table 8. E_{ST} (in kJ/mol), EA (in kJ/mol) and SF (in kJ/mol) of **7a** ~ **7g**

| | E_{ST} | EA | SF |
|-----------|----------|------|-------|
| 7a | 46.7 | 30.0 | 76.7 |
| 7b | 110.4 | 29.6 | 139.9 |
| 7c | 115.4 | 34.6 | 150.0 |
| 7d | 58.3 | 69.4 | 127.7 |
| 7e | 103.2 | 72.6 | 175.8 |
| 7f | 139.3 | 41.2 | 180.5 |
| 7g | 189.1 | 86.0 | 275.1 |

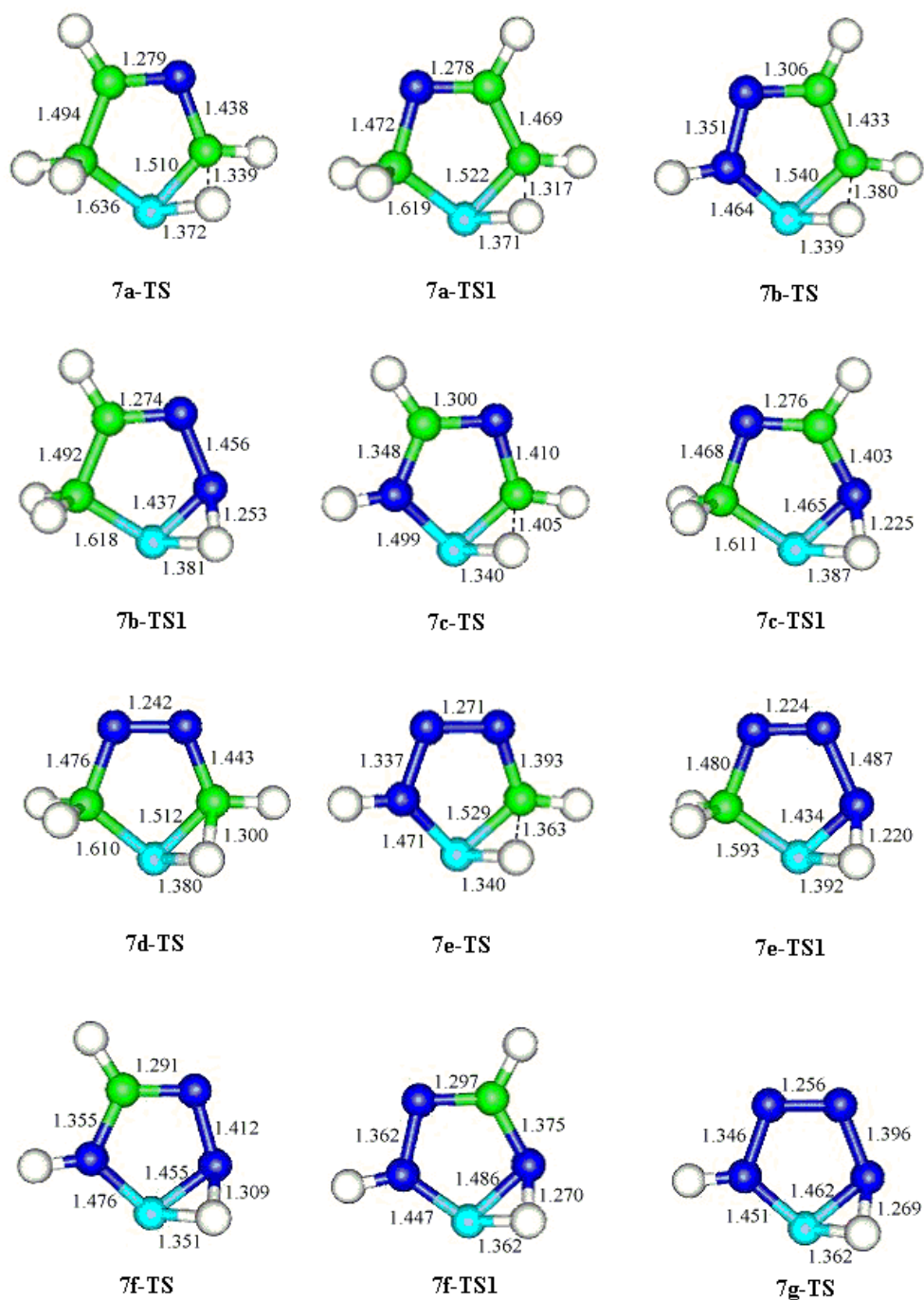


Figure 4. The critical geometrical parameters of TSs of the isomerization reactions of **7a-f** (bond length in Å, boron in sky blue, nitrogen in navy blue, carbon in green and hydrogen in white).

Table 9. The Activation Free Energies (ΔG^\ddagger in kJ/mol), Reaction Free Energies (ΔG_r in kJ/mol) and Miller Parameters (χ^\ddagger) of the isomerization Reactions of **8**, **9**, **10**, **11** and **12**

| | ΔG^\ddagger | ΔG_r | χ^\ddagger |
|-----------|---------------------|--------------|-----------------|
| 8 | 128.1 | -175.6 | 0.2967 |
| 9 | 134.3 | -215.7 | 0.2774 |
| 10 | 118.5 | -197.6 | 0.2726 |
| 11 | 148.0 | -210.4 | 0.2923 |
| 12 | 144.3 | -207.2 | 0.2910 |

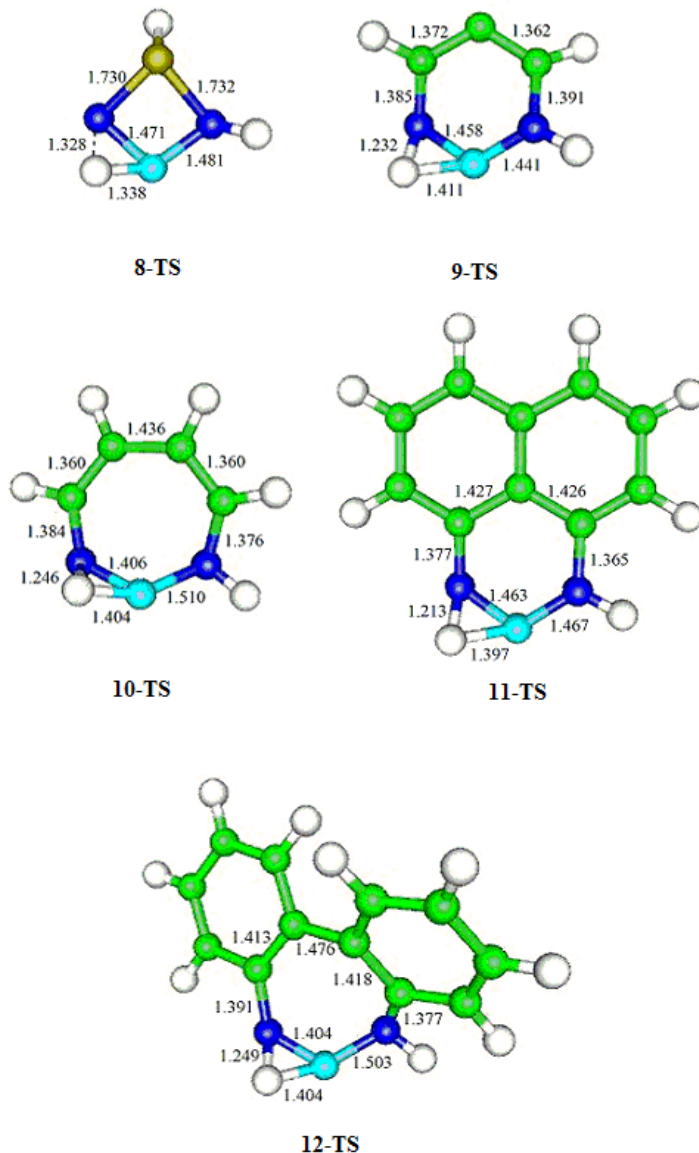


Figure 5. The critical geometrical parameters of TSs of the isomerization reactions of **8**, **9**, **10**, **11** and **12** (bond length in Å, boron in sky blue, nitrogen in navy blue, phosphorus in gold, carbon in green and hydrogen in white).

Table 10. E_{ST} (in kJ/mol), EA (in kJ/mol) and SF (in kJ/mol) of 8 ~ 12

| | E_{ST} | EA | SF |
|-----------|----------|------|-------|
| 8 | 61.5 | 18.0 | 79.5 |
| 9 | 36.2 | 73.5 | 109.6 |
| 10 | 40.4 | 1.4 | 41.8 |
| 11 | 94.2 | 51.4 | 145.6 |
| 12 | 40.7 | 30.1 | 70.7 |

For further advancement, the solvent effect of tetrahydrofuran (THF; dielectric constant $\epsilon = 7.58$) and acetonitrile (ACN; $\epsilon = 36.64$) on the kinetic stabilities of the borylenes is considered by a single-point MPW1K-PCM calculation [45]. According to our calculated results, the activation free energies of the H-shifted reactions all increase by adding either THF or ACN into the calculation. Upon changes from THF to ACN, it is found that the activation free energy ΔG^\ddagger increases as the dielectric constant of the solvent increases. Taking **4a** as an example, ΔG^\ddagger of the 1,2-H sifted reaction is calculated to be 127.8, 145.6 and 149.6 kJ/mol in gas phase, THF and ACN, respectively. Therefore, a negatively-charged boron compound may be stable in polar solvents.

Although **7g** (in Scheme 2) and **11** (in Scheme 3) have not successfully been synthesized yet, we predict that they are stable borylenes from both thermodynamic and kinetic viewpoints. Because borylenes are anionic species, they usually exist as an ion pair with counter ions like Li^+ in **3**. Therefore, the stabilities of borylenes should be influenced by various counter cations. Indeed, on the theoretical basis, Schleyer and coworkers found that the addition of Li^+ increases the singlet-triplet splittings (E_{ST}) of acyclic boryl anions [16]. Based on our calculated results, E_{ST} of cyclic analogues, i.e. **4a** and titled borylenes shown in Schemes 2 and 3 are also increased by adding lithium into the calculation. For example, E_{ST} increases by 37.1 kJ/mol, 18.6 kJ/mol and 69.5 kJ/mol for **4a**, **7g** and **11**, respectively as Li^+ is taken into the consideration. For E_{ST} , **7g** is the less sensitive to the addition of a counter cation. In contrast, the stability of **11** is significantly influenced by the cation.

The stability of an anion, in theory, should be greatly influenced by the solvent. Based on the fully-optimized MPW1K-CPCM theoretical method, the solvent effect of cyclohexane ($\epsilon = 2.02$) and THF ($\epsilon = 7.58$) on SF of **4a**, **7g** and **11** are thus investigated [46]. From the gas phase to cyclohexane, SF increases by 215.5 kJ/mol, 124.4 kJ/mol and 217.0 kJ/mol for **4a**, **11** and **7g**, respectively. In THF, SF increases by 354.9 kJ/mol, 226.1 kJ/mol and 219.9 kJ/mol for **4a**, **11** and **7g**, respectively. This indicates that the stabilities of these anions increase as the dielectric constant of the medium increases. However, in comparison to the stability trend obtained in gas phase (**7g** > **11** > **4a**), the results show a different stability trend in cyclohexane and THF, being in the order of **7g** > **4a** > **11**. Applying NPA analyses, the negative charge of the anion is delocalized in a trend of **11** > **4a** > **7g**. Therefore, the sensitivity to the solvation effect of a solvent is in the order of **7g** > **4a** > **11**.

Table 11. EDP (in 10^{-3} eV) of titled borylenes

| Borylenes | EDP | Borylenes | EDP | Borylenes | EDP |
|-----------|------|-----------|------|-----------|------|
| 4a | 19.8 | 6b | 7.9 | 7d | 9.0 |
| 4b | 17.7 | 6c | 6.0 | 7e | 8.7 |
| 4c | 15.8 | 6d | 9.8 | 7f | 12.8 |
| 4d | 7.0 | 6e | 1.6 | 7g | 7.4 |
| 4e | 1.6 | 6f | 8.1 | 8 | 14.6 |
| 5a | 22.7 | 6g | 0.6 | 9 | 4.9 |
| 5b | 21.3 | 7a | 15.3 | 10 | 15.6 |
| 5c | 24.0 | 7b | 15.4 | 11 | 3.7 |
| 6a | 14.2 | 7c | 13.9 | 12 | 5.6 |

3.3. The Chemical Reactivities of Borylenes

Very recently, Jaramillo and coworkers performed density functional theory and certain global (the electrophilicity index, nucleophilicity index and electron donating power) and local descriptors (the Fukui function, philicity concept and local nucleophilicity) to investigate the chemical reactivity of boryllithium [47-54]. According to their results, boryllithium compounds revealed to be strong bases and nucleophiles [47]. The nucleophilicity of a boryllithium should be ascribed to the negatively-charged moiety, borylene. Among these descriptors, the electron donating power (EDP), which is a measure of the propensity of a system to donate electrons, can be taken as an index to sense the nucleophilic character of species and represented by the first ionization potential I and electron affinity A of the species [49].

$$EDP \equiv \frac{I^-}{2\eta^-} = \frac{I + A}{16(I - A)} \approx \frac{\epsilon_L + 3\epsilon_H}{16(\epsilon_L - \epsilon_H)} \quad (4)$$

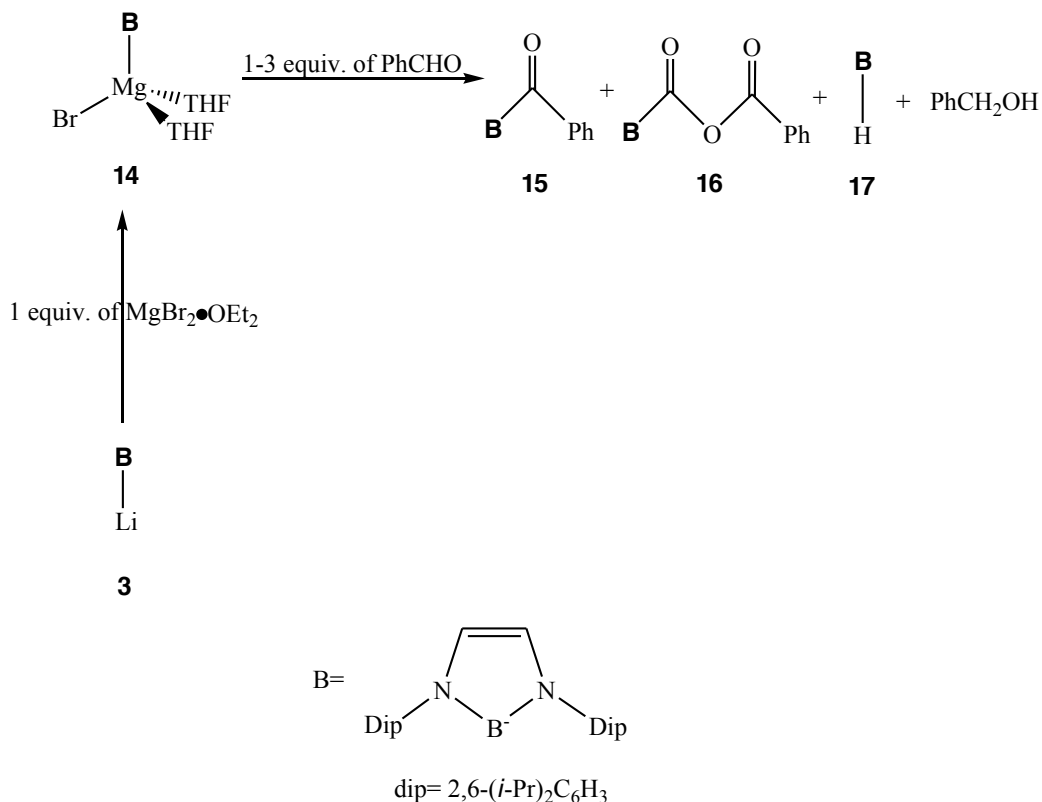
In eq. (4), we further apply the Koopmans' theorem in which the first ionization potential I of a species is equal to the negative of the energy of the highest-occupied molecular orbital (ϵ_H) and the electron affinity of a species equals to the negative of the energy of the lowest-unoccupied molecular orbital (ϵ_L). We then use EDP to examine the effects of substituents (R and R'), types of atoms in the ring (X_1 , X_2 , X_3 and X_4 in Scheme 2) and ring sizes on the nucleophilicities of borylenes and the results are summarized in Table 11. As shown in Table 11, the five-membered ring borylene (**4a**) is more nucleophilic than its four- (**8**), six- (**9**) and seven-membered (**10**) analogues. This may be rationalized by the fact that their electronic structures are very different. If one makes a comparison between **9** (**10**) and **11** (**12**), the additional phenyl rings have a reducing effect on the nucleophilicity of a borylene. In agreement with the experimental finding, the unsaturated (**4a**) and saturated (**5c**) have different nucleophilicities [18]. A more detailed inspection (see Table 11) reveals that the nucleophilicity of a borylene decreases as the neighboring elements to boron changes from a second-row element to a third or fourth one. For example, EDP decreases from 19.8×10^{-3} eV (**4a**) to 9.8×10^{-3} eV (**6d**) as a nitrogen atom is replaced by a phosphorus atom. A further decrease can be seen from 9.8×10^{-3} eV (**6d**) to 8.1×10^{-3} eV (**6e**) as the phosphorus atom is

substituted by an arsenic atom. This result can be explained by the interaction strengths that are in the order of $EP_{\pi}(\text{B})\text{-FP}_{\pi}(\text{N}) > EP_{\pi}(\text{B})\text{-FP}_{\pi}(\text{P}) > EP_{\pi}(\text{B})\text{-FP}_{\pi}(\text{As})$ [37]. As the interaction strength becomes weaker, the electronic configuration on the boron center changes from σ^2 to $\sigma^1 p_{\pi}^1$ more easily, the nucleophilicity of a borylene thus decreases. Nevertheless, the nucleophilicity of a species is known to be influenced by a solvent. This effect is not considered herein and should be investigated more detail in the future.

CONCLUSION

Several salient points can be summarized according to the above results and discussion: (1) From both the thermodynamic and kinetic points of view, the bulkier the R and R' groups are, the more stable a five-membered borylene may be. (2) Nitrogen should be the most efficient π donor to stabilize a borylene, and **7g** is thus the most stable five-membered borylene from both the thermodynamic and kinetic viewpoints. (3) The six-membered borylene **11** is predicted to be more stable than the five-membered one that has been successfully synthesized. However, its nucleophilicity is predicted to be less than **4a**.

Due to the fact that the boryllithium **3** has shown a broad spectrum of utilization [17-20,55,56] in synthesis, we believe that the results presented here can provide useful information for future applications. For example, borylmagnesium (**14** in Scheme 7), which can be viewed as a Grignard reagent containing boron, has already been synthesized by the transmetalation of boryllithium **3** with 1 equiv of $\text{MgBr}_2 \cdot \text{OEt}_2$ powder in THF at room temperature [20]. **14** is reactive with respect to benzaldehyde, affording a mixture of benzoylborane **15**, boron-substituted ester **16**, hydroborane **17** and benzyl alcohol. In addition to these synthetic applicabilities [17-20,55,56], borylenes are found to be hydrogen storage materials and Lewis bases to induce the B-H bond of BH_3 to dissociate more feasibly [24,26]. According to our computational approach, the titled boryl anions can spontaneously react with hydrogen gas to form dihydrogen adducts [24]. For example, the reaction between **4a** and H_2 , forming two new B-H bonds is proven to be a spontaneous reaction by $\Delta G = -146.0$ kJ/mol. Applying Le Châtelier's principle, the equilibrium reaction may be shifted by removing H_2 . In other words, pressurizing H_2 will be useful in regenerating the H_2 storage system. Like their isoelectronic analogues, NHCs, borylene **4a** can lower BDE of the B-H bond and makes the hydrogen abstraction from BH_3 more favorable even considering counter cation. Finally, we extend our investigation to the four- **8**, six- **9** and seven-membered borylenes **10** and find that **10** acts most efficiently to decrease BDE of the B-H bond; although it has not yet been synthesized. This is due to the formation a stable radical like **4a**- $\text{BH}_2\cdot$ or **10**- $\text{BH}_2\cdot$. Owing to the increasing importance for borylenes in the field of synthetic chemistry and perhaps hydrogen and hence energy storage, we believe that our advancement on structure-versus-reactivity relationship of borylenes should provide timely and valuable information on their future applications.



Scheme 7. The schematic representation of the synthesis of borylmagnesium **14** and its reaction with benzaldehyde.

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國科會補助計畫衍生研發成果推廣資料表

日期:2011/12/28

| | |
|-----------|-------------------------------------|
| 國科會補助計畫 | 計畫名稱: 含氮雜環碳烯基及其等電子系統與一氧化氮提供者之理論研究 |
| | 計畫主持人: 賴金宏 |
| | 計畫編號: 99-2113-M-040-004- 學門領域: 物理化學 |
| 無研發成果推廣資料 | |

99 年度專題研究計畫研究成果彙整表

| 計畫主持人：賴金宏 | | 計畫編號：99-2113-M-040-004- | | | | | |
|----------------------------------|-------------|-------------------------|-----------------|------------|------|-------------------------------------|--|
| 計畫名稱：含氮雜環碳烯基及其等電子系統與一氧化氮提供者之理論研究 | | | | | | | |
| 成果項目 | | 量化 | | | 單位 | 備註（質化說明：如數個計畫共同成果、成果列為該期刊之封面故事...等） | |
| | | 實際已達成數（被接受或已發表） | 預期總達成數（含實際已達成數） | 本計畫實際貢獻百分比 | | | |
| 國內 | 論文著作 | 期刊論文 | 0 | 0 | 100% | 篇 | |
| | | 研究報告/技術報告 | 0 | 0 | 100% | | |
| | | 研討會論文 | 0 | 0 | 100% | | |
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| | 技術移轉 | 件數 | 0 | 0 | 100% | 件 | |
| | | 權利金 | 0 | 0 | 100% | 千元 | |
| | 參與計畫人力（本國籍） | 碩士生 | 0 | 0 | 100% | 人次 | |
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| | | 權利金 | 0 | 0 | 100% | 千元 | |
| | 參與計畫人力（外國籍） | 碩士生 | 0 | 0 | 100% | 人次 | |
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| <p>其他成果 (無法以量化表達之成果如辦理學術活動、獲得獎項、重要國際合作、研究成果國際影響力及其他協助產業技術發展之具體效益事項等，請以文字敘述填列。)</p> | <p>截至目前為止，此篇期刊論文已經被引用了四次</p> |
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| | 成果項目 | 量化 | 名稱或內容性質簡述 |
|---|-----------------|----|-----------|
| 科 教 處 計 畫 加 填 項 目 | 測驗工具(含質性與量性) | 0 | |
| | 課程/模組 | 0 | |
| | 電腦及網路系統或工具 | 0 | |
| | 教材 | 0 | |
| | 舉辦之活動/競賽 | 0 | |
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請就研究內容與原計畫相符程度、達成預期目標情況、研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）、是否適合在學術期刊發表或申請專利、主要發現或其他有關價值等，作一綜合評估。

1. 請就研究內容與原計畫相符程度、達成預期目標情況作一綜合評估

達成目標

未達成目標（請說明，以 100 字為限）

實驗失敗

因故實驗中斷

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說明：

2. 研究成果在學術期刊發表或申請專利等情形：

論文： 已發表 未發表之文稿 撰寫中 無

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所發表的論文請見附錄文件

3. 請依學術成就、技術創新、社會影響等方面，評估研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）（以 500 字為限）

在 2006 年，Segawa 等人以一個含有硼溴鍵的前驅物合成了第一個以雙氨基作取代的 boryllithium (1)。1 由硼-11 核磁共振光譜的檢測結果可得知 boryllithium 可看成是鋰離子(Li+)與一個含有負電性硼原子(B-)的含氮雜環(此雜環稱為 borylene)所形成的離子對(ion pair)。此物質已經展示了它們許多的用途。1-5 例如它們可以扮演親核劑去攻擊一些親電子劑。在台大化學系周必泰老師實驗室做博士後研究員的期間(2008/10~2010/02)，我們已經用了密度泛函理論(density functional theory)的方法對 borylene 熱力學及動力學穩定性作了系統性的研究並已經刊登在國際期刊上，6-7 所以接著在台大做助理研究學者(2010/08/01~2010/09/12)以及在中山醫學大學擔任助理教授(2010/09/13~至今)我們繼續對這個含負電性硼原子的雜環進行理論研究，根據我們的計算結果發現，borylene 這類物質可以扮演路易士鹼(Lewis base)與 BH₃ 形成路易士酸鹼對進而減弱 BH₃ 中 B-H 的鍵能使得氫原子容易被釋放出去。傳統上，在有機合成中常常使用含有 Sn-H 鍵的化合物當作氫原子的提供者，但不幸的是，這類化合物含有相當的毒性，而 H₃B-borylene 這類路易士酸鹼對的毒性相對地小了很多。所以可說，我們預測了一個有效且毒性小的氫原子提供者，相信對於有機合成會有所助益。

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