

A Computational Study on the Kinetic Stability of Cyclic Boryl Anions

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Abstract: In this study, we perform an MPW1K investigation on the kinetic stability of a cyclic boryl anion. According to our calculation, the bulkier the R and R' groups are, the more kinetically stable a five-membered boryl anion may be. Nitrogen should be a more efficient π donor to increase the kinetic stability of a cyclic boryl anion than P, As, O, S and Se. Although, one nitrogen atom is enough to stabilize a cyclic boryl anion from the kinetic aspect, the stability of a cyclic boryl anion increases as the number of nitrogen in the ring increases. The six-membered boryl anion is calculated to be more stable kinetically than the five-membered one that has been synthesized successfully.

INTRODUCTION

Although boron sits just left to the carbon on the periodic table, this atom does not share its neighbor's reactive versatility. Due to its empty p orbital, which is in contrast to the partially filled p orbital in carbon, boron compounds are almost found to be electrophilic; i.e. they act as a Lewis acid 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 [1], but none could be isolated or conclusively characterized [2]. In 1995, Schleyer and coworkers, on the basis of theoretical calculation, predicted that diamino groups on the boron atom should stabilize a boryllithium [3]. The stabilization mainly results from the interaction between the empty p orbital of boron and the lone pair/ p_π orbital of the nitrogen atoms. In 2006, Nozaki, Yamashita and Segawa, firstly utilized a boron-bromide precursor to synthesize a stable diamino-substituted boryllithium (see the upper part of Scheme 1). X-ray crystallography and ^{11}B NMR spectroscopy of the compound matched with the prediction of a boron anion [4].

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 [4]. Very recently, Segawa and coworkers synthesized a borylmagnesium that may be served as a boron-containing Grignard reagent [5]. In 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 [6].

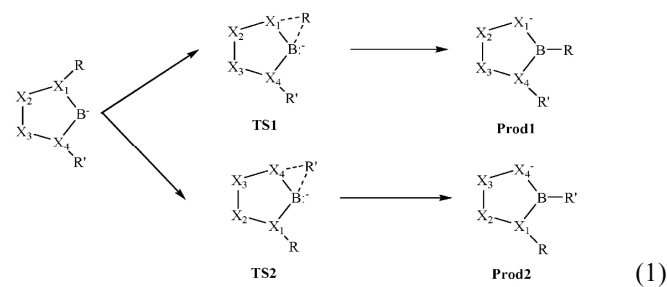
Traditionally, the methodologies to introduce a boryl ligand into a transition-metal complex can be classified into three types of reactions: 1) salt elimination through the reaction of anionic metal carbonyl complexes with haloboranes [7]; 2) oxidative addition of a boron-heteroatom bond

to low-valent transition metals [8], and 3) σ -bond metathesis reactions between alkyl metal complexes and hydroboranes in the presence of light or oxygen-substituted metal complexes and diborane [9-11].

Herein, we report a computational study on the kinetic stability of cyclic boryl anions. The effects of substituents (R and R') and types of atoms in the ring (X_1 , X_2 , X_3 and X_4 in Scheme 1) are investigated. Currently available cyclic boryl anions possess a five-membered ring [4, 6], which is isoelectronic with the five-membered N-heterocyclic carbene (NHC) [12]. Five-membered N-heterocyclic carbenes (NHCs) are widely used in catalysis [12-14]. Nevertheless, their four-, six- and seven-membered analogs have been synthesized and showed marked different electronic structures from that of the five-membered analogues [15-17]. Thus, it is also important to investigate the cyclic boryl anions other than five membered ones, although, they are synthetically unattainable at this stage. Accordingly, in addition to five-membered boryl anions (1-4), the four-, six- and seven-membered analogs (5-7 in Scheme 1) are also taken into consideration. Furthermore, the effects of additional aromatic rings on 6 and 7 denoted by 8 and 9, are also studied, respectively.

THEORETICAL BASIS

All calculations are done with the Gaussian 03 program [18]. Four DFT functionals, i.e. B3LYP, MPWB1K, MPW1B95 and MPW1K are chose; and combined with the double- ζ basis set 6-31+G*, in this study [19-22]. The 1,2-R or R' shifted isomerization reaction (R and R' = H, CH₃ and Ph) is chosen for the comparative studies of the kinetic stability. These reactions can be expressed as Eq. (1):



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All three points of interest, including reactants, transition states (TS), and products on the potential energy surfaces (PES) of the isomerization reactions, have been investigated. All stationary points have been positively identified as equilibrium structures (the numbers of imaginary frequency (NIMAG=0)), or transition states (NIMAG=1). For the transition states, motion corresponding to the imaginary frequency is checked visually. All mentioned energetic values are corrected for zero point energies (ZPE). To aid in the experimental characterization of such anions, the ^{11}B chemical tensor of each minimum is calculated by the gauge-independent atomic orbitals (GIAO) method [23]. Theoretically, the chemical shielding depends on the orientation of the molecule, in relation to the applied magnetic field. Therefore, the chemical shielding can be described by a nine-component cartesian tensor, σ .

$$\sigma = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix} \quad (2)$$

Unfortunately, in conventional NMR experiments, the trace of the tensor can only be determined. Then the isotropic chemical shielding, σ^{iso} , is defined as (3)

$$\sigma^{iso} = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33}) \quad (3)$$

Usually, the calculated chemical tensor of a compound is reported in relation with a reference. Thus, the complex $\text{BF}_3:\text{OEt}_2$ is taken as the standard of ^{11}B chemical tensor. The solvent effect of tetrahydrofuran (THF) and acetonitrile is considered by a single-point MPW1K-PCM calculation [24].

RESULTS AND DISCUSSION

1. The Performance of DFT Functional

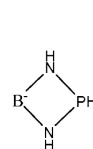
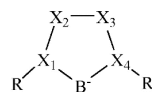
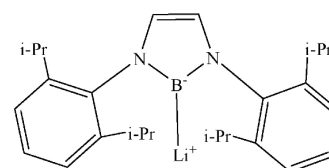
The results of isomerization reaction of **1a** using four different DFT functionals, are summarized in Table 1. As shown in Table 1, although the MPW1K functional underestimates the isomerization barrier of **1a** by 70.70 kJ/mol, its average deviation is the smallest among the tested DFT functionals as compared with the previous MP4 result [25]. Therefore, we believe that MPW1K should provide a decent analysis for those boryl anions depicted in Scheme 1.

Table 1. The Activation Energies (E_a in kJ/mol), Reaction Enthalpies (ΔH_r in kJ/mol) of the Isomerization Reaction of **1a**

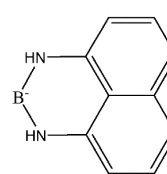
	B3LYP	MPWB1K	MPW1B95	MPW1K	The Previous Results
E_a	117.2	115.7	124.0	127.5	198.2 ^a
ΔH_r	-185.3	-185.6	-186.8	-186.2	-175.6 ^a -178.1 ^b

a. The MP4/6-311+G**//HF/6-311+G* results in ref. [25].

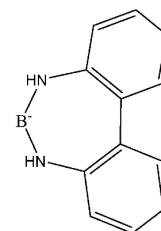
b. The B3LYP/6-31++G(d,p)+ZPE results in ref. [26].



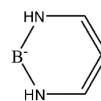
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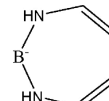
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Scheme 1. The boryllithium reported in ref. 4 and the boryl anions discussed in this study.

2. The Substituent Effect of R or R' on the Stability of a Boryl Anion

The transition states of isomerization reactions of **1a-e** are depicted in Fig. (1). For a comparison, the previous HF/6-311+G* results are also listed in Fig. (1) [25]. As depicted in Fig. (1), the distance between N and the migrated H atom of **1a-TS** is calculated to be longer by MPW1K than that calculated by HF; in contrast, the bond distance between B and the migrated H atom of **1a-TS** is shorter by MPW1K (c.f. HF).

By MPW1K, **1a** must overcome a barrier height of 127.5 kJ/mol, which was calculated to be 198.2 kJ/mol based on MP4/6-311+G**//HF/6-311+G*. A more detailed comparison between MPW1K and the previous results can be seen in Table 2 [25, 26]. Furthermore, the Miller parameter (χ^\ddagger) is introduced (see Eq (4)) to investigate the chemical reactivities of **1a-e** [27, 28].

$$\chi^\ddagger(\text{Miller}) = \frac{1}{2 - \left(\frac{\Delta H_r}{\Delta H^\ddagger} \right)} \approx \frac{1}{2 - \left(\frac{\Delta G_r}{\Delta G^\ddagger} \right)} \quad (4)$$

where ΔH_r and ΔH^\ddagger are the reaction and activation enthalpies, respectively. For the Miller parameter, the smaller (larger) χ^\ddagger value indicates that the transition state is close to the reactant (product). Since, the reaction free energy (ΔG_r) = $\Delta H_r - T\Delta S_r \approx \Delta H_r$, and the activation free energy (ΔG^\ddagger) = $\Delta H^\ddagger - T\Delta S^\ddagger \approx \Delta H^\ddagger$, then the Miller parameter can be calculated by Eq (4). If the shape of the potential energy surface is not altered by solvation, the location of TS on the solvated potential energy surface can also be calculated by Eq. (4). The results are listed in Table 2. Evidently, the barrier of the hydrogen atom transfer reaction does not alter significantly, upon substituting the other N-H hydrogen atom in **1a**, with a methyl group (Me) in **1b** or a phenyl ring (ph) in **1d**. Similar results can be concluded in 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 CH₃ involves a directed p/sp³ orbital. Moreover, there may exist a resonance effect between the π orbital of a phenyl ring and the empty p _{π} orbital of the boron atom, and/or repulsion between the π orbital of a phenyl ring and the filled p _{π} orbital of the nitrogen atom in TS (see Scheme 2), causing the barrier of the phenyl group transfer to be smaller than that of the methyl group transfer.

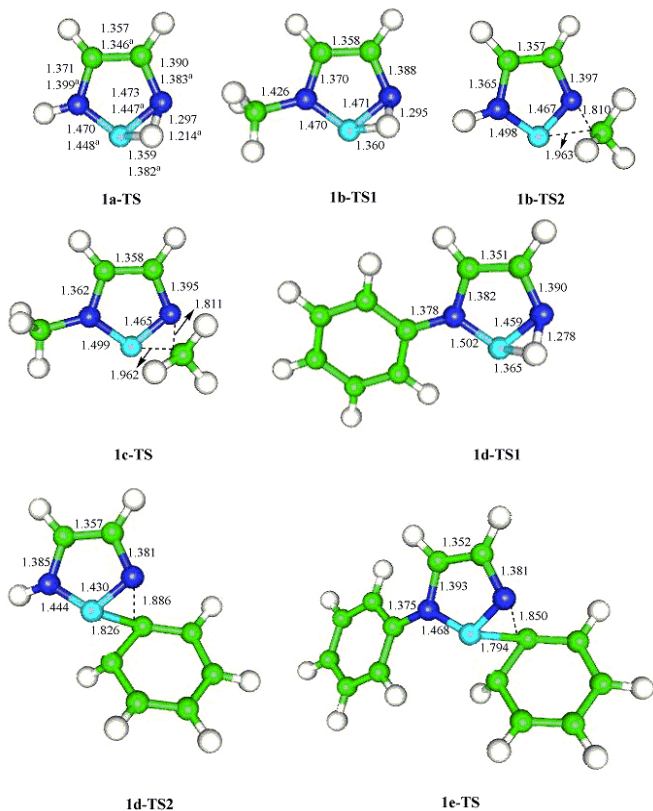
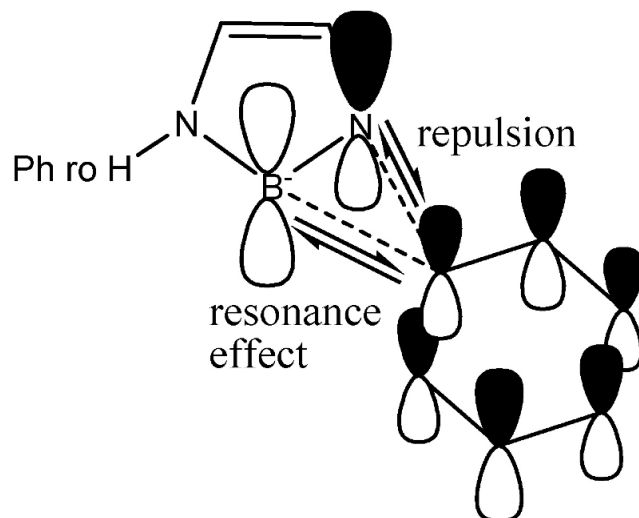


Fig. (1). The critical geometrical parameters of TSs of the isomerization reactions of **1a-e** (bond length in Å, boron in sky blue, nitrogen in navy blue, carbon in green and hydrogen in white). a. The previous HF/6-311+G* results (see ref. [25]).

Recently, it has been reported that the incorporation of boron atoms into the backbone of a polymer can extend its π -conjugation length through the vacant p _{π} orbital of the boron atom [29]. For a fair comparison, the previous B3LYP results for NHCs are also summarized in Table 2 [30]. The

comparison between the boryl anions (**1a** and **1c**) and their carbon analogs (**1a-C** and **1c-C**), shows that both the boryl anions and the NHCs are kinetically stable, with respect to their 1,2-H or Me shifted isomers. It has been reported that there is a lower-barrier dimerization process for a NHC [30]. Such dimerization should not occur for a five-membered boryl anion due to the repulsion between the two negative boron centers.



Scheme 2. The illustration of orbital interactions in **1d** or **1e-TS**.

The boryllithium synthesized by Segawa and coworkers has two bulky groups on the two nitrogen atoms (see the upper part of Scheme 1) [4]. These two bulky groups should induce a large barrier if the boryl anion undergoes such isomerization. On the other hand, these two bulky groups can protect the boron atom from attack by neighboring molecules. Accordingly, **1a-e** are kinetically stable with respect to their isomers, i.e. they must overcome large barrier heights, prior to the isomerization. However, their isomers, for which the negative charge is mainly located on nitrogen, are more stable than **1a-e**. This should be due to nitrogen being more electronegative than boron. **1a-e**, all have early TSs during the isomerization reactions. The result is in agreement with that of Sastry and coworkers, who have reported the H-shifted reactions in many five-membered rings [31]. Accordingly, the Miller parameter, χ^\ddagger , is between 0.28 and 0.33; thus, the 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. Comparing the results in gas phase and the ones in solvents, it is clear that increasing the solvent polarity leads to the increase in ΔG^\ddagger and the decrease in ΔG_r . Therefore, χ^\ddagger increases as the isomerized reaction occurs in polar solvents. The calculated ¹¹B NMR signals of **1a-e** and their isomerized products are summarized in Table 3. Undoubtedly, the isomerized products are less downfield than **1a-e**.

3. The Stabilizing Effects of Other π -Donating Elements

In 1995, Schleyer and coworkers estimated the energy difference between the singlet and triplet state of a boryl anion to be 3.9 kJ/mol in favor of the singlet state [3]. It has

already been reported that a singlet carbene, which is isoelectronic with a singlet boryl anion, can be stabilized by π -donating substituents, like halogens and amines [32]. Herein, we investigate further the stabilizing efficiencies of π -donating substituents on a five-membered boryl anion. We replace one or two nitrogen atoms by other pnictogen (P, As), or chalcogen (O, S and Se) elements, i.e. **2a-g** depicted in Scheme 1. The relevant results are summarized in Fig. (2) and Tables 4 and 5.

Table 2. 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 **1a-e**

	ΔG^\ddagger	ΔG_r	χ^\ddagger
1a	127.8	-186.2	0.2893
	145.6 ^d	-163.5 ^d	0.3202 ^d
	149.6 ^e	-156.8 ^e	0.3281 ^e
1a-C	160.9 ^f	-111.7 ^f	0.3711 ^f
1b^a	127.8	-186.0	0.2894
	144.4 ^d	-165.0 ^d	0.3182 ^d
	148.3 ^e	-158.3 ^e	0.3260 ^e
1b^b	216.6	-232.7	0.3253
	221.7 ^d	-216.1 ^d	0.3362 ^d
	222.7 ^e	-210.7 ^e	0.3394 ^e
1c^b	216.1	-231.5	0.3256
	220.1 ^d	-219.5 ^d	0.3337 ^d
	221.0 ^e	-213.5 ^e	0.3372 ^e
1c-C^b	218.8 ^f	-136.9 ^f	0.3809 ^f
1d^a	130.4	-192.1	0.2879
	147.5 ^d	-169.3 ^d	0.3176 ^d
	151.6 ^e	-162.3 ^e	0.3256 ^e
1d^c	183.5	-220.8	0.3122
	197.5 ^d	-208.5 ^d	0.3272 ^d
	201.4 ^e	-204.6 ^e	0.3315 ^e
1e^c	182.6	-210.7	0.3171
	190.8 ^d	-202.8 ^d	0.3265 ^d
	194.1 ^e	-199.2 ^e	0.3304 ^e

a. The hydrogen atom transfer.

b. The methyl group transfer reaction.

c. The phenyl ring transfer reaction.

d. The values are calculated in THF by PCM model.

e. The values are calculated in acetonitrile by PCM model.

f. The ZPVE corrected results of E_a and ΔH , in ref. [30].

As shown in Table 4, the kinetic stability of a five-membered boryl anion decreases when the nitrogen atom is replaced by the other group 15 elements. By comparing the data between **1a** and **2e**, in the gas phase, the ΔG^\ddagger of hydrogen atom migration of P-H group (**2e**) is calculated to be 43.55 kJ/mol, which is less than that of N-H group (**1a**) by 84.21 kJ/mol. Moreover, ΔG^\ddagger of the hydrogen atom transfer of As-H group (**2g**) is calculated to be 31.40 kJ/mol, which is less than the hydrogen atom migration of N-H group (**1a**) by 96.36 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). The interaction strengths are in the order $EP_\pi(B)-FP_\pi(N) > EP_\pi(B)-FP_\pi(P) > EP_\pi(B)-FP_\pi(As)$ [33]. This can be seen from the calculated dihedral angle $\angle H-X_1-C-C$ ($X_1 = N, P, As$) in the boryl anions **1a**, **2e** and **2g**. The dihedral angles $\angle H-X_1-C-C$ are 180.0° , 132.9° and 121.6° for N, P and As, respectively. The phosphorus and arsenic atoms are pyramidized in **2e** and **2g**. 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. Furthermore, by comparing the results of **1a**, **2e** and **2g**, 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. The calculated $\Delta\sigma^{iso}$ of **2e**, **2g** and their H-shifted isomers show similar trends as **1a** and its isomers.

Table 3. The $\Delta\sigma^{iso}$ on Boron (in ppm) of **1a-e and Their Isomerized Products**

	$\Delta\sigma^{iso}$
1a	-41.40
1a-Prod1	-18.00
1b	-47.11
1b-Prod1	-20.94
1b-Prod2	-22.65
1c	-52.45
1c-Prod1	-23.97
1d	-53.41
1d-Prod1	-21.65
1d-Prod2	-23.49
1e	-66.87
1e-Prod1	-24.94

a. The values are taken as σ^{iso} of the compound- σ^{iso} of $BF_3 \cdot OEt_2$.

As depicted in Fig. (2), the B-H bond lengths in TS are in the order of **2g-TS** > **2e-TS** > **1a-TS**. This result is in agreement with the Hammond postulate [34]. 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 either thermodynamically or kinetically. However, due to the lack of a protecting group, the boron atom in **2a-c** is subject to attack by neighboring molecules. We thus, expect that **2a-c** may be more unstable than **1a**. Among these π -donating elements, nitrogen atom should be the most efficient π donor to stabilize a boryl anion.

4. The Influence of Aromaticity and the Stabilizing Efficiency of Nitrogen Atom

In 1991, Arduengo and coworkers synthesized a stable carbene, which was built by the skeleton, designated as **10** in Scheme 3 [12]. From then on, a number of theoretical calculations and physical studies had 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 such carbene [35-39]. Indeed, in 1995, Arduengo and coworkers successfully synthesized the corresponding saturated carbene, the structure of which is represented as **11** in Scheme 3 [40]. In this study, we are interested in finding whether the aromaticity of the five-membered ring plays a role in the stability of a boryl anion; this can be done by comparing the calculated results of **1a** with those of **3a**. As discussed in the above section, nitrogen is the most efficient π -donating element to stabilize a five-membered boryl anion. The boryl anions **3b-c** are also added to investigate the efficiency of this atom. The relevant results are summarized in Fig. (3) and Tables 6 and 7. As Table 7 shows, the C=C double bond of **1a** is saturated to be **3a**, $\Delta\sigma^{\text{iso}}$ of boron changes from -41.40 ppm to -50.72 ppm. The absolute values of $\Delta\sigma^{\text{iso}}$ are calculated to be 198.9, 91.61 and 41.40 for **3b**, **3c** and **1a**, respectively.

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 2a-g

	ΔG^\ddagger	ΔG_r	χ^\ddagger
2a	123.1	-202.0	0.2747
	148.3 ^c	-172.0 ^c	0.3165 ^c
	154.2 ^d	-163.4 ^d	0.3268 ^d
2b	133.7	-201.8	0.2849
	160.1 ^c	-169.6 ^c	0.3269 ^c
	166.0 ^d	-161.0 ^d	0.3367 ^d
2c	135.2	-198.0	0.2886
	160.9 ^c	-167.8 ^c	0.3286 ^c
	166.5 ^d	-159.8 ^d	0.3379 ^d
2d^a	135.1	-201.3	0.2866
	157.8 ^c	-171.8 ^c	0.3238 ^c
	162.5 ^d	-164.0 ^d	0.3323 ^d
2d^b	28.08	-265.6	0.0873
	26.76 ^c	-255.4 ^c	0.0866 ^c
	26.64 ^d	-252.1 ^d	0.0872 ^d
2e^b	43.55	-254.8	0.1274
	43.55 ^c	-238.0 ^c	0.1340 ^c
	43.55 ^d	-233.1 ^d	0.1360 ^d
2f^a	136.3	-198.5	0.2893
	159.6 ^c	-170.5 ^c	0.3260 ^c
	164.7 ^d	-162.9 ^d	0.3345 ^d
2f^b	24.59	-274.4	0.0760
	20.40 ^c	-266.4 ^c	0.0664 ^c
	19.78 ^d	-263.7 ^d	0.0652 ^d
2g^b	31.40	-269.7	0.0944
	28.08 ^c	-257.5 ^c	0.0895 ^c
	27.50 ^d	-253.8 ^d	0.0891 ^d

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

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

c. The values are calculated in THF by PCM model.

d. The values are calculated in acetonitrile by PCM model.

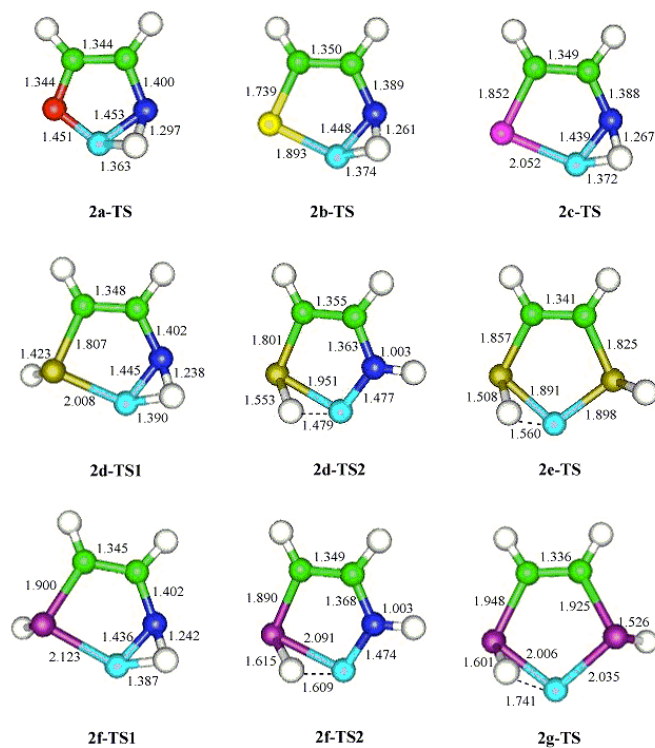


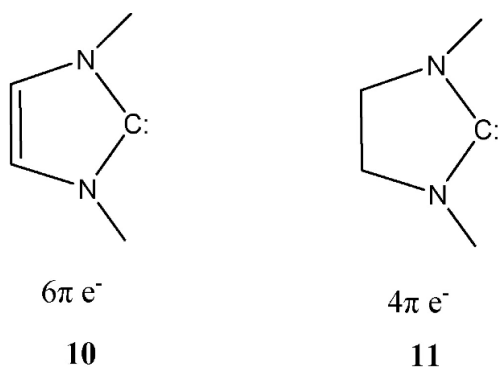
Fig. (2). The critical geometrical parameters of TSs of the isomerization reactions of 2a-g (bond length in Å, boron in sky blue, oxygen in red, sulfur in yellow, selenium in pink, nitrogen in navy blue, phosphorous in gold, arsenic in purple, carbon in green and hydrogen in white).

Table 5. The $\Delta\sigma^{\text{iso}}$ on Boron (in ppm) of 2a-g and Their Isomerized Products

	$\Delta\sigma^{\text{iso}}$
2a	-48.57
2a-Prod1	-25.19
2b	-63.21
2b-Prod1	-29.91
2c	-69.95
2c-Prod1	-31.66
2d	-103.0
2d-Prod1	-43.25
2d-Prod2	-34.75
2e	-185.6
2e-Prod1	-61.79
2f	-107.5
2f-Prod1	-43.42
2f-Prod2	-38.50
2g	-244.3
2g-Prod1	-70.93

a. The values are taken as σ^{iso} of the compound - σ^{iso} of $\text{BF}_3\cdot\text{OEt}_2$.

As shown in Table 6, the boryl anion **3a** has a similar isomerization barrier, as **1a**. Furthermore, the Miller parameter of **3a** is calculated to be larger than that of **1a**, indicating that TS of **3a** is leaner toward the isomer. The B3LYP results, regarding the 1,2-H shifted reaction of **11** in Scheme 3 are also listed in Table 6 [30]. As listed in Table 6, the carbon counterpart of **3a**, which is designated as **3a-C**, has a similar barrier as **1a-C**. Considering the exothermicities the saturated boryl anion (**3a**) and NHC (**3a-C**) have lower exothermicities than that of the unsaturated ones. In fact, the bulky-group substituted **3a**, has been synthesized successfully and shows little influence on its donor ability with group 11 metals [6]. Moreover, TS of **3a** has a longer N-transferred H but shorter B-transferred H bond than that of **1a** (see Fig. 3). Owing to the lack of a π -donating capacity, carbon cannot stabilize the boryl anion. According to our calculation, the hydrogen atom transfer of CH₂ group has a lower barrier than that of the NH group by 81.31 kJ/mol. The bond length of the B-H bond in **3b-TS** is longer than the bond length in **1a-TS**, the result of which is in agreement with the fact that **3b** has a smaller Miller parameter. According to the similar H-shifted barrier of N-H group for both **3c** and **1a**, the existence of one nitrogen atom (in **3c**) may be sufficient to stabilize the five-membered boryl anion kinetically.



Scheme 3. The skeletons of Arduengo carbenes.

5. The Influences of the Numbers and Positions of Nitrogen on the Stability of a Five-Membered Boryl Anion

Nitrogen is considered to play dual roles. On one hand, having one filled lone pair, it can behave as a π -donor. On the other hand, it also acts as a σ -acceptor owing to its large electronegativity. In this section, we thus investigate how the numbers and positions of nitrogen on the five-membered ring affect the stability of a five-membered boryl anion. The relevant results are summarized in Fig. (4) and Tables 8 and 9. Notably, **4a** has two kinds of CH₂ groups, which can undergo the H atom migration. One is close to nitrogen and the other is close to the CH group. Similar condition can be seen in **4f**, for which one NH group is close to the CH group and the other is close to nitrogen. As listed in Table 4, **4a-Prod2**, which is the product of the second isomerization reaction of **4a**, is more stable than **4a-Prod1** by 32.79 kJ/mol, despite 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 4). Similar explanation

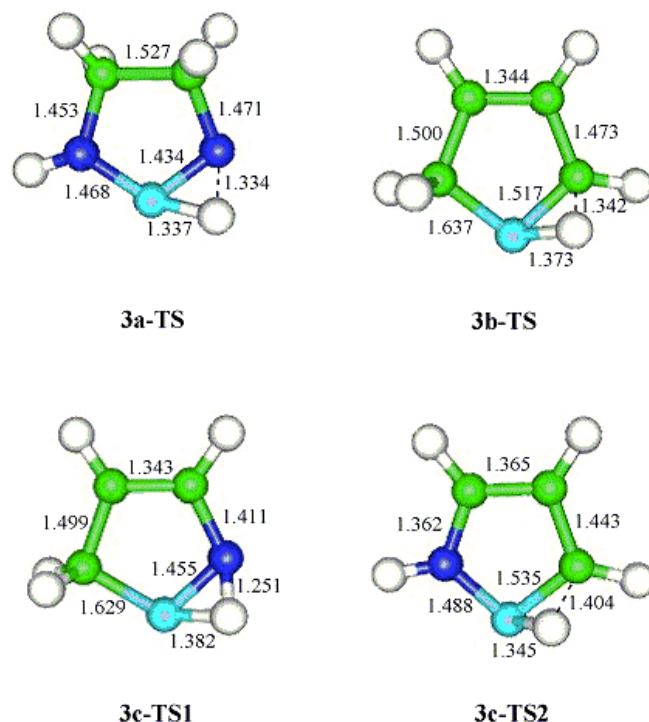


Fig. (3). The critical geometrical parameters of TSs of the isomerization reactions of **3a-c** (bond length in Å, boron in sky blue, nitrogen in navy blue, carbon in green and hydrogen in white).

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 **3a-c**

	ΔG^\ddagger	ΔG_r	χ^\ddagger
3a^a	133.5	-153.9	0.3171
	153.7 ^c	-136.2 ^c	0.3465 ^c
	158.8 ^d	-130.5 ^d	0.3544 ^d
3a-C^a	162.5 ^c	-88.62 ^c	0.3929 ^c
3b^b	46.45	-232.2	0.1429
	46.70 ^c	-208.3 ^c	0.1548 ^c
	47.01 ^d	-200.2 ^d	0.1598 ^d
3c^a	129.1	-196.7	0.2838
	150.2 ^c	-172.7 ^c	0.3175 ^c
	154.9 ^d	-165.4 ^d	0.3260 ^d
3c^b	51.85	-214.4	0.1630
	50.95 ^c	-193.7 ^c	0.1724 ^c
	50.81 ^d	-187.0 ^d	0.1761 ^d

- a. The hydrogen atom transfer of the N-H group.
 b. The hydrogen atom transfer of the CH₂ group.
 c. The values are calculated in THF by PCM model.
 d. The values are calculated in acetonitrile by PCM model.
 e. The ZPVE corrected results of E_a and ΔH_r in ref. [30].

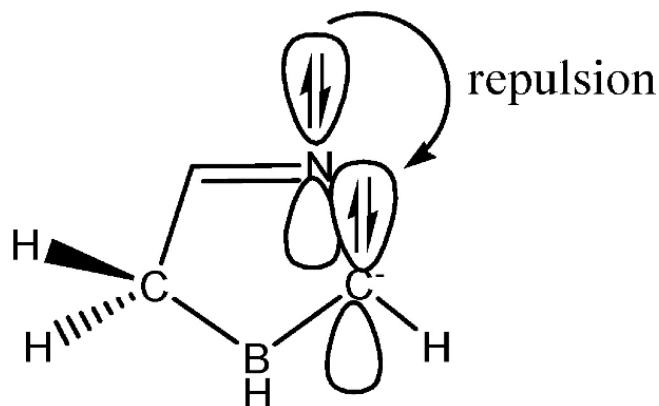
can be applied to the difference in energetics between **4f-Prod1** and **4f-Prod2**. Furthermore, as shown in Table 8, all H-shifted reactions of the CH₂ group, have smaller Miller parameters and barriers than those of the NH group. This is again consistent with the Hammond postulate [34]. When

comparing with **1a**, the bond length of X₂-X₃ in Scheme 1 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 boryl anion. The 1,2-H shifted barrier E_a increases as the number of nitrogen atom in the five member ring increases.

Table 7. The $\Delta\sigma^{\text{iso}}$ on Boron (in ppm) of **3a-c** and Their Isomerized Products

	$\Delta\sigma^{\text{isoa}}$
3a	-50.72
3a-Prod1	-26.26
3b	-198.9
3b-Prod1	-34.71
3c	-91.61
3c-Prod1	-41.59
3c-Prod2	-13.17

a. The values are taken as σ^{iso} of the compound - σ^{iso} of BF₃·OEt₂.



Scheme 4. The repulsive interaction in **4a-Prod1**.

6. The Comparison of Four-, Five-, Six- and Seven-Membered Boryl Anion

Due to the ability to transform an electron-deficient carbene into the realm of isolable compounds [12], they have already acted as powerful tools for synthetic chemists. So far, only five membered NHCs (see **10** and **11** in Scheme 3) have been widely applied as catalysts [13]. Therefore, it is interesting to design new stable cyclic diamino carbenes, possessing different scaffolds and electronic structures. Very recently, Grubbs and coworkers synthesized a stable four-membered NHC **12** (in Scheme 5), and found that the ring was not strictly planar [15]. The six- (**13** in Scheme 5) and seven-membered (**14** in scheme 5) NHCs have been synthesized by Präsaug and Scarborough, respectively [16,17].

In 2006, the synthesized boryllithium was built by a five-membered ring scaffold. In this study, the corresponding

Table 8. 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 **4a-g**

	ΔG^\ddagger	ΔG_r	χ^\ddagger
4a (Path 1)^b	45.75	-220.2	0.1468
	46.93 ^c	-202.0 ^c	0.1586 ^c
	47.49 ^d	-195.9 ^d	0.1633 ^d
4a (Path 2)^b	42.63	-253.0	0.1260
	47.81 ^c	-234.6 ^c	0.1448 ^c
	49.40 ^d	-228.2 ^d	0.1511 ^d
4b^a	144.5	-160.3	0.3216
	154.8 ^c	-155.0 ^c	0.3332 ^c
	156.8 ^d	-152.7 ^d	0.3363 ^d
4b^b	48.56	-243.6	0.1425
	54.50 ^c	-228.1 ^c	0.1617 ^c
	56.50 ^d	-222.2 ^d	0.1685 ^d
4c^a	135.6	-205.1	0.2847
	162.4 ^c	-182.9 ^c	0.3199 ^c
	168.7 ^d	-176.0 ^d	0.3286 ^d
4c^b	51.45	-203.9	0.1677
	50.45 ^c	-191.3 ^c	0.1726 ^c
	50.76 ^d	-186.7 ^d	0.1761 ^d
4d^b	39.62	-246.9	0.1215
	44.35 ^c	-237.5 ^c	0.1360 ^c
	46.11 ^d	-233.3 ^d	0.1416 ^d
4ea	146.1	-172.0	0.3147
	162.3 ^c	-167.6 ^c	0.3298 ^c
	165.7 ^d	-165.4 ^d	0.3335 ^d
4eb	42.95	-243.8	0.1303
	43.79 ^c	-242.2 ^c	0.1328 ^c
	44.70 ^d	-240.0 ^d	0.1357 ^d
4f (Path 1)^a	147.3	-147.3	0.3334
	155.8 ^c	-145.7 ^c	0.3406 ^c
	157.4 ^d	-144.6 ^d	0.3426 ^d
4f (Path 2)^a	135.4	-201.6	0.2866
	162.9 ^c	-178.8 ^c	0.3229 ^c
	169.3 ^d	-171.6 ^d	0.3318 ^d
4g^a	221.3	-169.5	0.3616
	168.9 ^c	-166.3 ^c	0.3351 ^c
	172.3 ^d	-164.4 ^d	0.3385 ^d

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

b. The hydrogen atom transfer of the CH₂ group.

c. The values are calculated in THF by PCM model.

d. The values are calculated in acetonitrile by PCM model.

four-, six- and seven-membered boryl anions (**5**, **6**, **7**, **8** and **9** in Scheme 1) are compared with **1a**. In the first place, the bond lengths of B-N and bond angle, \angle N-B-N, of each species are collected in Fig. (5). Previous results of **1a** are also depicted in Fig. (5), for a comparison [25, 26, 41]. The geometry of **1a** derived from MPW1K, such as the B-N bond distances and N-B-N bond angle, is similar to that of the

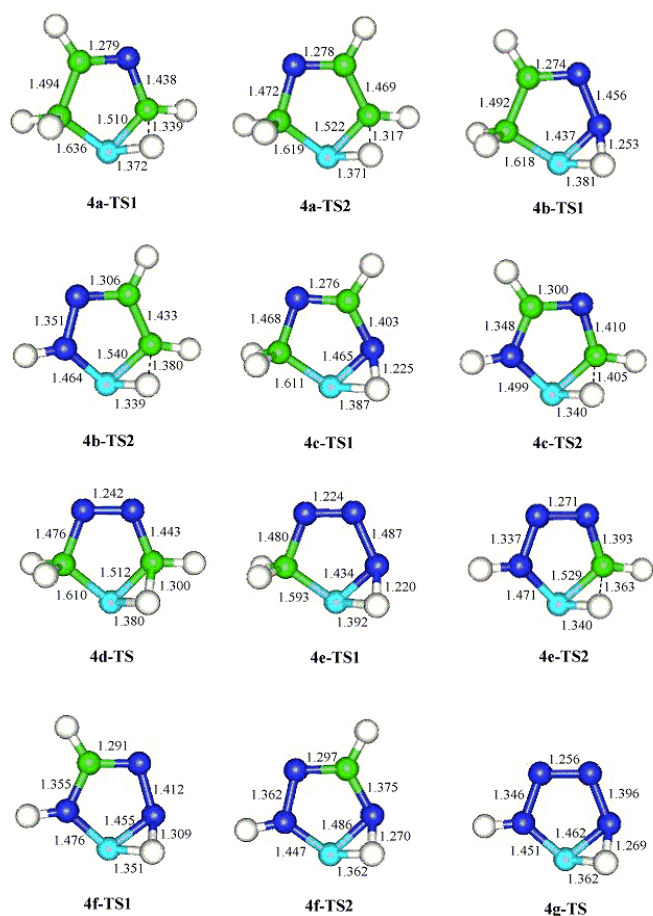


Fig. (4). The critical geometrical parameters of TSs of the isomerization reactions of 4a-f (bond length in Å, boron in sky blue, nitrogen in navy blue, carbon in green and hydrogen in white).

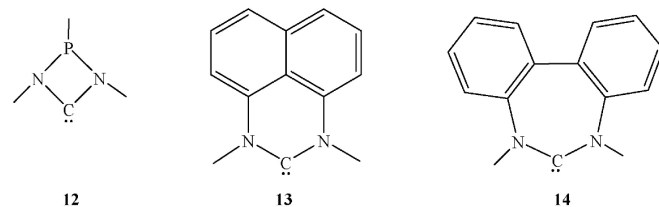
previous reports [25, 26, 41]. As depicted in Fig. (5), **5** has the longest B-N bonds among these boryl anions (**1a**, **5**, **6**, **7**, **8** and **9**). This may imply that **5** has the weakest $EP_{\pi}(B)-FP_{\pi}(N)$ interactions among these boryl anions. The sum of the bond angles around the nitrogen atom is 360° , if the ring is in a planar conformation. Otherwise, a value deviated from 360.0° is obtained. As a result of calculation, they are 360.0° , 340.6° , 360° , 349.2° , 360.0° and 356.0° for **1a**, **5**, **6**, **7**, **8** and **9**, respectively. Accordingly, **1a** (five-membered), **6** and **8** (six-membered) are planar, while, **5** (four-membered), **7** and **9** (seven-membered) are in twisted forms, the results of which are in agreement with the previous reports regarding **12**, **13** and **14**, depicted in Scheme 5 [15-17, 42, 43]. The sum of the bond angles around nitrogen was 348.2° for the four-membered NHC **12** [15]. Rzepa and coworkers used DFT computational methods to analyze a series of 8π -electron heterocycles, including seven-membered NHC [42, 43]. Such antiaromatic heterocyclic rings were found to gain Möbius aromatic stabilization and release of the ring strain intrinsic to seven-membered rings by undergoing torsional twist. Presumably due to the ring strain, the four-membered boryl anion (**5**) and NHC (**12**) are not planar [15]. Accordingly, it can be said that the additional aromatic rings of **6** and **7** do not change the geometries of the boryl anions as compared with **8** and **9**. The calculated free energies of activation, the reaction free energies, and the Miller param-

eters of the H-shifted reactions of **5**, **6**, **7**, **8** and **9** are summarized in Table 10. The geometries of TSs of the H atom migration reactions of **5**, **6**, **7**, **8** and **9** are depicted in Fig. (6). As shown in Table 10, **6** is kinetically most stable due to the fact that it has the largest isomerization barrier. Due to the similar activation free energy, **5** is nearly stable to **1a** kinetically although it has a larger ring strain. Although the additional aromatic rings of **6** and **7** do not change their geometries, they induce larger activation free energies of the H-shifted reactions, if making a comparison between **6** and **8**, or between **7** and **9**. Finally, the calculated $\Delta\sigma^{\text{iso}}$ s of **5-9** are summarized in Table 11. As given in Table 11, the ring size can alter the calculated $\Delta\sigma^{\text{iso}}$ of the boryl anion, this may indicate the negatively charged character of boron of the boryl anion is influenced by the ring size.

Table 9. The $\Delta\sigma^{\text{iso}}$ on Boron (in ppm) of 4a-g and Their Isomerized Products

	$\Delta\sigma^{\text{isoa}}$
4a	-188.8
4a-Prod1	-26.65
4a-Prod2	-40.53
4b	-75.20
4b-Prod1	-34.26
4b-Prod2	-14.24
4c	-92.50
4c-Prod1	-46.48
4c-Prod2	-10.80
4d	-171.3
4d-Prod1	-34.89
4e	-74.09
4e-Prod1	-39.76
4e-Prod2	-11.21
4f	-33.87
4f-Prod1	-18.22
4f-Prod2	-18.43
4g	-26.15
4g-Prod1	-17.61

a. The values are taken as σ^{iso} of the compound- σ^{iso} of $\text{BF}_3\cdot\text{OEt}_2$.



Scheme 5. The scaffolds of four-, six- and seven-membered N-heterocyclic carbene

In 2006, Dixon and coworkers found that NHCs could be good candidates, to act as hydrogen storage materials, by a

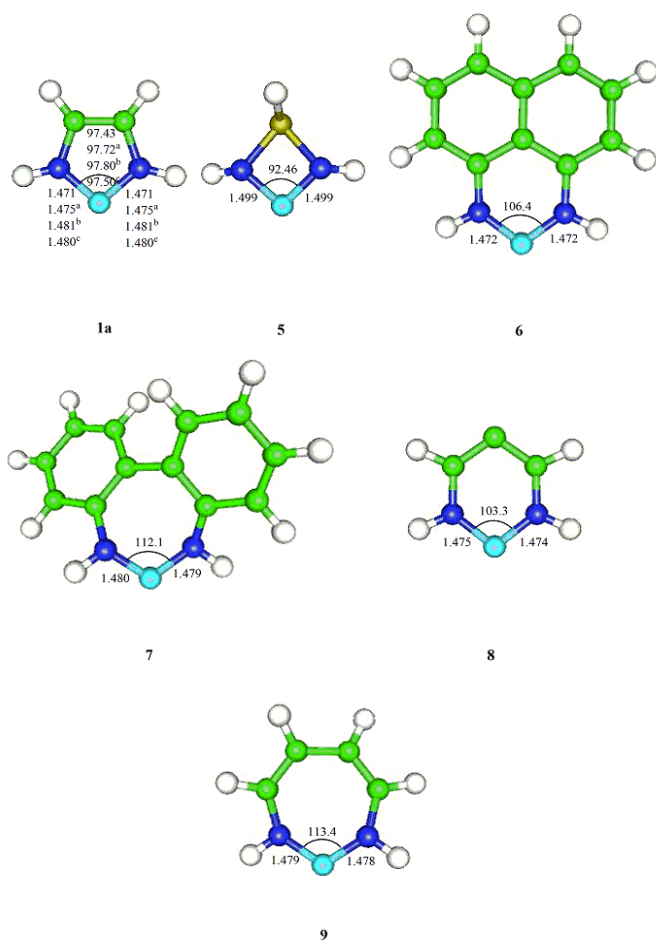


Fig. (5). The critical geometry parameters of 1a, 5, 6, 7, 8 and 9 (bond lengths in Å, bond angles in °, boron in sky blue, nitrogen in navy blue, phosphorus in gold, carbon in green and hydrogen in white). a. The value is calculated by HF/6-311+G*, see ref. [25]. b. The value is calculated by DFT/6-31++G**, see ref. [26]. c. The value is calculated by MP2/6-311++G**, see ref. [41].

Table 10. 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 5, 6, 7, 8 and 9

	ΔG^\ddagger	ΔG_r	χ^\ddagger
5	128.1	-175.6	0.2967
	148.2 ^a	-161.7 ^a	0.3236 ^a
	153.0 ^b	-157.1 ^b	0.3303 ^b
6	148.0	-210.4	0.2923
	169.3 ^a	-182.8 ^a	0.3247 ^a
	172.9 ^b	-177.3 ^b	0.3306 ^b
7	144.3	-207.2	0.2910
	164.7 ^a	-179.3 ^a	0.3238 ^a
	168.9 ^b	-173.3 ^b	0.3305 ^b
8	134.3	-215.7	0.2774
	170.4 ^a	-198.1 ^a	0.3162 ^a
	178.3 ^b	-193.6 ^b	0.3240 ^b
9	118.5	-197.6	0.2726
	144.6 ^a	-174.5 ^a	0.3118 ^a
	149.9 ^b	-169.1 ^b	0.3197 ^b

a. The values are calculated in THF by PCM model.
b. The values are calculated in acetonitrile by PCM model.

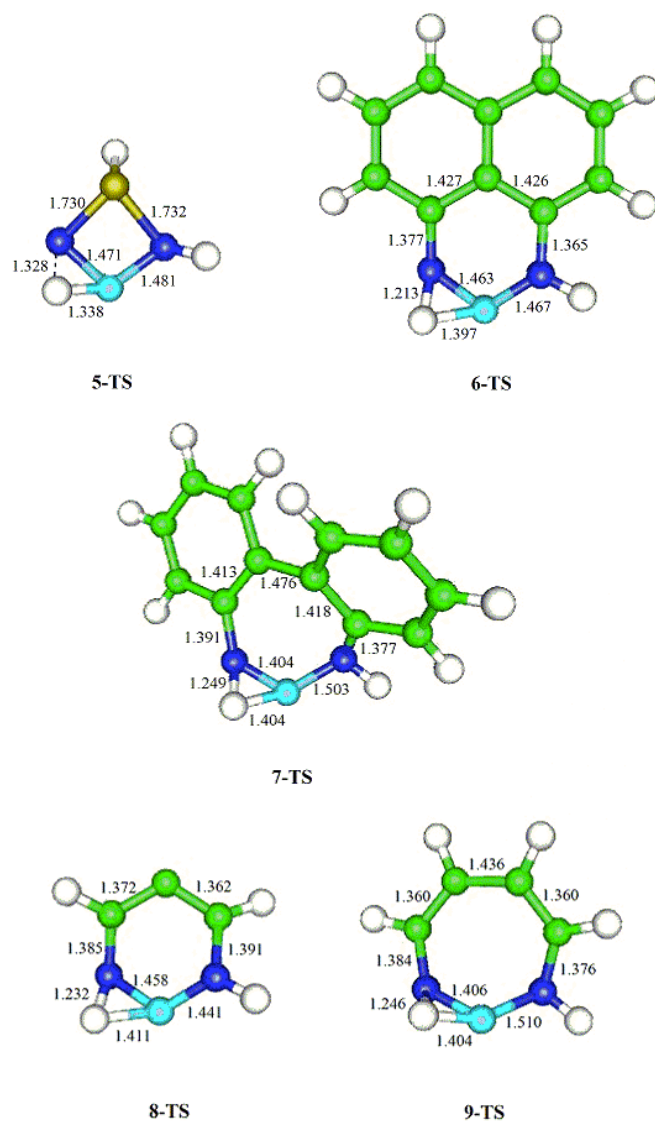


Fig. (6). The critical geometrical parameters of TSs of the isomerization reactions of 5, 6, 7, 8 and 9 (bond length in Å, boron in sky blue, nitrogen in navy blue, phosphorus in gold, carbon in green and hydrogen in white).

Table 11. The $\Delta\sigma^{\text{iso}}$ on Boron (in ppm) of 5-9 and Their Isomerized Products

	$\Delta\sigma^{\text{isoa}}$
5	-107.4
5-Prod1	-32.86
6	-62.57
6-Prod1	-24.21
7	-98.29
7-Prod1	-26.75
8	-55.32
8-Prod1	-22.75
9	-96.58
9-Prod1	-26.75

a. The values are taken as σ^{iso} of the compound- σ^{iso} of $\text{BF}_3\cdot\text{OEt}_2$.

sophisticated theoretical level [44]. According to our results, the titled boryl anions can spontaneously react with hydrogen gas to form dihydrogen adducts. For example, **1a** reacts with H₂, to form two new B-H bonds is a spontaneous reaction, by $\Delta G = -146.0$ kJ/mol. Applying Le Chatelier's principle, the equilibrium reaction may be shifted by pumping to remove H₂. In other words, pressurizing with H₂ will be useful in regenerating the H₂ storage system. Moreover, this reaction can provide another method to investigate the relative stability between **1a** and **3a**. According to our calculation, the reaction free energy of **1a** + H₂ → **3a** is -35.44 kJ/mol, and this indicates that **1a** reacts with H₂ to form **3a** spontaneously.

CONCLUSIONS

To sum up, several salient points can be noted according to our calculations on the boryl anions: (1) The bulkier, the R₁ and R₂ groups are, the more kinetically stable a five-membered boryl anion may be. (2) Nitrogen should be the most efficient π donor to stabilize a boryl anion, and the stability of a boryl anion increases as the number of nitrogen atom increases from a kinetic viewpoint. (3) A six-membered boryl anion is predicted to be more kinetically stable than the five-membered one, that has been successfully synthesized [4, 6]. (4) Similar to their isoelectronic analogues N-heterocyclic carbenes, boryl anions could be good candidates to store hydrogen. Work focusing on the reactivity of nucleophilicities is in progress.

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