

A systematic study of the stabilities of cyclic boryl anions

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Abstract In this study, we perform several DFT functionals and post-SCF methods (MP2 and CCSD(T)) to investigate the stability of a series of virtual cyclic boryl anions. This investigation stems from two aspects: (1) the energetic difference between S_0 and T_1 states and (2) the electron affinity of the cyclic boryl anions. The results are systematically discussed in terms of substitution effect, influence of the steric effect, number of nitrogen atoms, the ring size and solvation inclusion. Moreover, the effect of the counter cation Li^+ on the singlet-triplet splitting is also investigated. Among various boryl anions studied, the results predict bulky-group substituted **5i** and **8**, shown in Schemes 3 and 4, respectively, to be stable anions in gas phase as well as in organic solvents. Since boryl anions may be exploited to synthesize new boron-containing compounds as well as to provide synthetic routes different from traditional protocols, the predicted thermodynamically stable **5i** and **8** are then of both synthetic interest and challenging for future applications of cyclic boryl anions.

Keywords Boryl anions · DFT · Electron affinity · Energetic difference · MP2

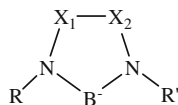
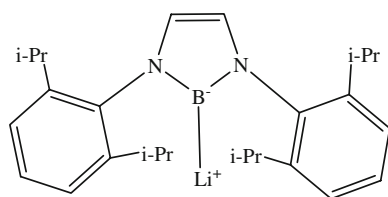
Introduction

Although boron sits just left of 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 [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]. Based on the theoretical prediction, Segawa et al. utilized a boron-bromide precursor to synthesize the first stable diamino-substituted boryllithium (see the upper part of Scheme 1). The ^{11}B NMR spectroscopy of the compound matched well with the prediction as a boryl anion [4]. To date, boryllithium has already shown a broad spectrum of utilizations [4–10]. For example, boryllithium behaves as an efficient nucleophile when it reacts with the electrophiles such as water, methyltrifluoromethanesulfonate, 1-chlorobutane and benzaldehyde [4]. In these approaches, a key reactive species clearly is ascribed to the anion containing boron, while Li^+ acts as a counterion.

Herein, we report a computational study on the stability of the diazaborole anion ($C_2H_4B_1N_2^-$, **1a**) and its various derivatives. Our focus of this approach is mainly on two folds, namely the energetic difference between S_0 and T_1 states (E_{ST}) and the electron affinity (EA) of the designated cyclic boryl anions. The justification is based on the fact that a species in triplet manifold tends to undergo facile radical reactions [11]. Since the intersystem crossing rate is

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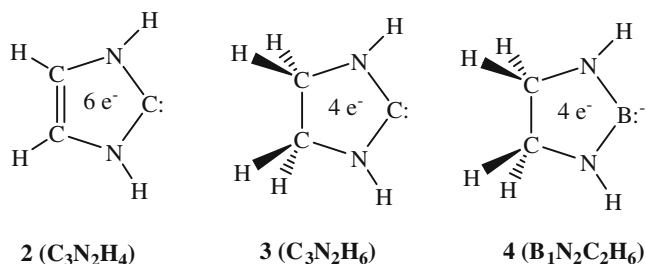


- 1 $X_1=X_2=CH$
 a $R=R'=H$ ($B_1N_2C_2H_4$)
 b $R=H, R'=Me$ ($B_1N_2C_3H_6$)
 c $R=R'=Me$ ($B_1N_2C_4H_8$)
 d $R=H, R'=Ph$ ($B_1N_2C_8H_8$)
 e. $R=R'=Ph$ ($B_1N_2C_{14}H_{12}$)

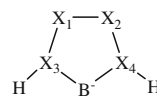
Scheme 1 The skeleton of the boryllithium synthesized by Segawa and coworkers and **1a~1e**

proportional to square of spin-orbit coupling matrix and inversely proportional to the energy gap between singlet and triplet manifold E_{ST} expressed as $\frac{\langle S|H_{so}|T \rangle^2}{E_{ST}}$ [12], 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 stability of boryl anions.

In this study, we also investigate the effects of substituents (**1b~1e** in Scheme 1), the steric effect (see e.g. **4** in Scheme 2), and the number of nitrogen atoms in the five-membered ring (**5a~5i** in Scheme 3). Currently available cyclic boryl anions possess a five-membered ring [4, 6], which is isoelectronic with the five-membered N-heterocyclic carbenes (NHC) that are widely exploited in catalysis [13–15]. Nevertheless, their four-, six- and seven-membered analogues have been synthesized and showed markedly different electronic structures from that of the five-membered analogues [16–18]. Thus, it is also of great interest to compare properties of the four-, six- and seven-membered diazaborole anions (**6~10** in Scheme 4) with those of the five-membered analogues, although they are synthetically unattainable at this stage [19]. Moreover, although the singlet state of a free boryl anion is only marginally more stable than the triplet, previous computa-



Scheme 2 The skeleton of the unsaturated (**2**) and saturated (**3**) carbenes and boryl anion **4**



- 5a $X_1=X_2=X_3=X_4=CH$ ($B_1C_4H_6$)
 5b $X_1=X_2=X_3=CH, X_4=N$ ($B_1N_1C_3H_6$)
 5c $X_1=N, X_2=X_3=X_4=CH$ ($B_1N_1C_3H_6$)
 5d $X_1=X_3=N, X_2=X_4=CH$ ($B_1N_2C_2H_4$)
 5e $X_2=X_3=N, X_1=X_4=CH$ ($B_1N_2C_2H_4$)
 5f $X_1=X_2=N, X_3=X_4=CH$ ($B_1N_2C_2H_4$)
 5g $X_1=X_2=X_3=N, X_4=CH$ ($B_1N_3C_1H_3$)
 5h $X_1=X_3=X_4=N, X_2=CH$ ($B_1N_3C_1H_3$)
 5i $X_1=X_2=X_3=X_4=N$ ($B_1N_4H_2$)

Scheme 3 The skeleton of the boryl anions **5a~5i**

tional approach [3] has drawn the conclusion that the addition of a lithium cation stabilizes the singlet state of a non-cyclic boryl anion more than the triplet one by ~ 20 kcal mol $^{-1}$. Therefore, the effect of a lithium cation on the singlet-triplet splitting of a cyclic boryl anion also receives considerable attention in this study.

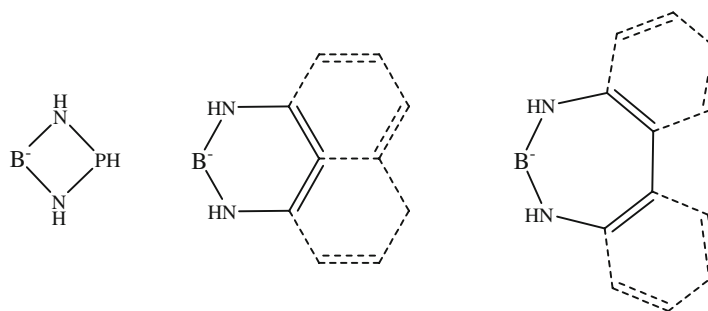
Theoretical methods

All calculations are done with the Gaussian 03 program [20]. MP2 and four DFT functionals, i.e. B3LYP, B3PW91, MPW1LYP and MPW1K are chosen and combined with the double- ζ basis set 6–31+G* in this study [21–26]. The core electron excitations are neglected in our MP2 calculation to save the computational span. Such a simplification can be rationalized by the fact that the core electrons are more inert than the valent ones, and has been adopted and proven to be acceptable in literatures [27]. All the stationary points are positively identified as equilibrium structures as evidenced by the lack of the numbers of imaginary frequency (NIMAG=0). 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 boryl anions [28]. 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. Moreover, realizing that Segawa and coworkers first synthesized boryllithium in tetrahydrofuran (THF) [4], from the viewpoint of practical applications, we further take solvent effect into account. In this approach, solvation effect of cyclohexane and THF on boryl anions was calculated by fully-optimized conductor-like polarizable continuum model (CPCM) [29].

Results and discussion

Evaluation of DFT functionals

Prior to presenting the results and discussion, we should focus on the suitability of the tested DFT functionals.

Scheme 4 The skeleton of the boryl anions **6**~**10****6** ($B_1N_2P_1H_3$) **7** ($B_1N_2C_3H_4$), **8** ($B_1N_2C_{10}H_8$) **9** ($B_1N_2C_4H_6$), **10** ($B_1N_2C_{12}H_{10}$)

Bearing this aim in mind, E_{ST} of **1a** is first taken into consideration. For the convenience of discussion, E_{ST} values estimated by various methods are summarized in Table 1. Furthermore, previous pertinent data regarding **1a** are also listed in Table 1 for a fair comparison [30]. It has been known that the calculated energies of MPn methods are oscillating [31]. Thus, the MP4 result, though being higher in level, may not be more reliable than, e.g. MP2. In this study, we adopt the MP2 optimized geometries and perform the frozen core CCSD(T)/6-31+G** theoretical level to calculate the E_{ST} of **1a**, the result of which is then taken as the reference value [32]. The results of calculation, independent of applied DFT functionals, all conclude the ground state of **1a** to be in singlet manifold. Among various tested DFT functionals, due to its least discrepancy from the most sophisticated CCSD(T) result ($E_{ST}=5.72$ kcal mol⁻¹), the MPW1K functional ($E_{ST}=28.3$ kcal mol⁻¹) is considered to perform the best. In our previous approach regarding the kinetic stability of **1a** and its derivatives, MPW1K was also found to be the most suitable DFT functional, despite the fact that it might underestimate the barrier height of isomerization [33]. Therefore, in the following discussion and throughout the text, we mainly rely on the results of MPW1K. In addition, in this study, 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 $\langle S^2 \rangle$ [34]. 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 [34]. 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 [35]. Additionally, when the negatively-charged boron of **1a** is replaced by a neutral carbon, forming imidazolin-2-ylidene ($C_3H_4N_2$), E_{ST} is calculated to be 78.5 kcal mol⁻¹, which is in agreement with the previous TCSCF and MP2 ones of 79.4 and 84.5 kcal mol⁻¹, respectively [36, 37]. Thiel and coworker, upon investigating a series of NHC, found a tendency in that the larger their E_{ST} , the more inert they are with respect to dimerization [37]. Comparing **1a**, the significant increase of E_{ST} in imidazolin-2-ylidene can be rationalized by the interaction strength of $P\pi(C)$ - $P\pi(N)$ being larger than that of $P\pi(B)$ - $P\pi(N)$ in **1a** ($P\pi(X)$ denotes the π -type p orbital of X atom).

The substitution effect of R and R'

Comparative studies are then made between the methyl- or phenyl-substituted diazaborole anions designated as **1b**~**1e** (see Scheme 1) and the parent diazaborole anion **1a**. Firstly, both bond length of B-N and bond angle $\angle N-B-N$ of **1a**~**1e** are taken into consideration. For a fair comparison, our MPW1K values and the previous data of HF, MP2, B3LYP and PBE1PBE for **1a**, **1b** and **1e** are depicted in Fig. 1 [30, 38–40]. **1c** and **1d** are strategically designed in this

Table 1 The values of E_{ST} (in kcal mol⁻¹) of the diazaborole anion **1a** calculated by various methods

Method	B3LYP	B3PW91	MPW1LYP	MPW1K	MP2	MP4 ^b	CCSD(T) ^c
E_{ST} ^a	31.3	29.5	31.0	28.3	35.8	23.1	5.72

^a The values are based on the energy of the triplet state – the one of the singlet manifold

^b The MP4SDTQ(fc)/6-31++G**//B3LYP/6-31++G** result in ref. [30]

^c The zero-point energies calculated by MP2 are taken into consideration

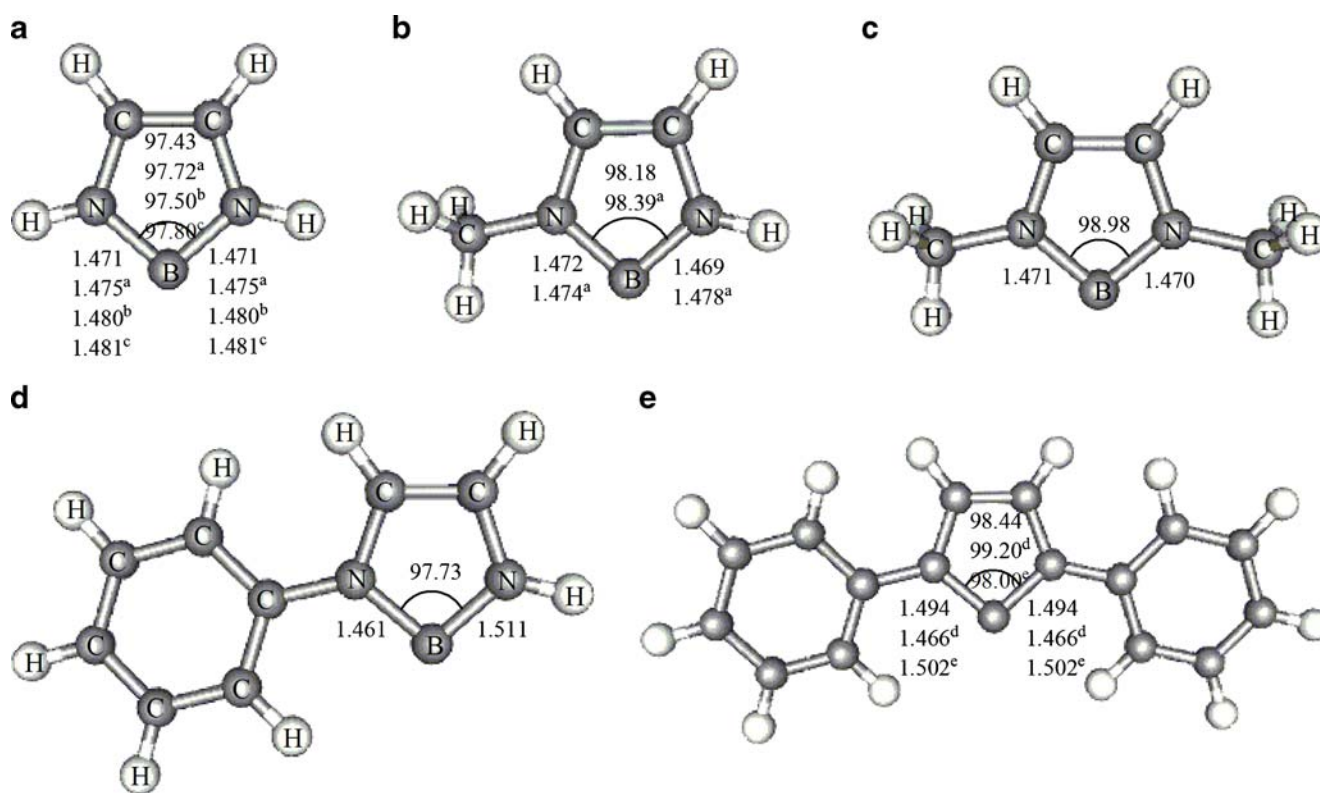


Fig. 1 The bond length of B-N (in Å) and bond angle \angle N-B-N (in $^{\circ}$) of **1a**~**1e**. (a) The value is calculated by HF/6-311+G*, see ref. [38]. (b) The value is calculated by MP2/6-311+G**, see ref. [39]. (c)

The value is calculated by B3LYP/6-31++G**, see ref. [30]. (d) The values are the ones of boryllithium (see the upper part of Scheme 1) in ref. [4]. (e). The value is calculated by PBE1PBE/TZVP, see ref. [40]

study to go through comprehensive investigation on the substituent effect of R and R' (see Scheme 1).

The geometry of **1a** derived from MPW1K, including the B-N bond distance and \angle N-B-N bond angle, is similar to that of the previous reports [30, 38–40]. Furthermore, B-N bond distance (1.494 Å) and \angle N-B-N bond angle (98.44 $^{\circ}$) calculated for **1e** only deviate from the analogous boryllithium synthesized by Segawa and coworkers by 0.03 Å and 0.76 $^{\circ}$, respectively [4]. Considering both B-N bond distance and \angle N-B-N bond angle, as shown in Fig. 1, it is evident that the phenyl ring has a stronger influence on the geometry of the boryl anion than that of the methyl group. Table 2 summarizes changes of B-N bond length and \angle N-B-N bond angle from the neutral radical (**1a**•~**1e**•) to **1a**~**1e**. Apparently, the addition of one electron, forming **1a**~**1e**, makes the B-N bond length (the \angle N-B-N bond angle) increased (decreased). Moreover, the results of our MPW1K approach for **1a** and **1b** summarized in Table 2 are in agreement with previous relevant data calculated based on HF and B3LYP [30, 38]. Finally, the results of natural population (NPA), natural localized molecular orbital (NLMO) analyses, E_{ST} and EA of **1a**~**1e** are all listed in Table 3. Based on the convergence, the T_1 states of **1a**~**1e** all stem from that

the electron transitions from σ -type lone pair to π -type lone pair on the negative charged B atom (see Fig. S 1 in Supporting Information).

As shown in Table 3, the boron atoms of **1a** and **1b** clearly possess anionic characters that are in agreement with the ^{11}B NMR spectrum experimentally reported [4]. Table 3 also shows a trend in that the negatively charged

Table 2 The differences of selected geometric parameters between neutral radical and negatively-charged **1a**~**1e** (bond length in Å and bond angle in $^{\circ}$)

	N(H)-B	N(Me or Ph)-B
1a	1.471/1.417 ^a 1.475/1.417 ^b 1.481/1.426 ^c	–
1b	1.469/1.410	1.472/1.410
1c	–	1.470/1.417
1d	1.461/1.410	1.511/1.420
1e	–	1.494/1.423

^a The values are arranged as 1a/ 1a•

^b The HF/6-311+G* result in ref. [38]

^c The B3LYP/6-31++G** result in ref. [30]

Table 3 The NPA/NLMO results, E_{ST} (in kcal mol⁻¹) and EA (in kcal mol⁻¹) of **1a**–**1e**

	Natural population analysis on B	The hybridization of B's lone pair	Occupancy of B's lone pair	E_{ST}	EA ^a
1a	-0.0349	s(62.56%),p(37.42%),d(0.02%)	1.931	28.7	1.2 3.3 ^b
1b	-0.0150	s(62.63%),p(37.34%),d(0.03%)	1.925	28.6	2.2 4.4 ^c
1c	0.0037	s(62.89%),p(37.08%),d(0.03%)	1.920	31.7	3.1
1d	0.0538	s(61.95%),p(38.01%),d(0.03%)	1.907	30.2	10.0

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

^b the value is obtained from ref. [30]

^c the value is obtained from ref. [38]

character of the boron atom decreases, i.e. becomes more positive, upon substituting the N-H hydrogen atom with a methyl or a phenyl ring. And, it further decreases as the number of the methyl (phenyl) substituent increases. Also, the effect induced by the phenyl ring is more significant than that of the methyl group. For example, the positively-charged character of boron increases by 0.0199 from **1a** to **1b** but it increases by as large as 0.0887 from **1a** to **1d**. We here tentatively attribute this result to the increase of the available volume occupied by the anion upon methyl or phenyl substitution. A closer examination of Table 3 also indicates that the occupancy of the boron's lone pair decreases from 1.931 of **1a** to 1.884 of **1e**. This is in accordance with the evidence that the negative charge of boron decreases from **1a** to **1e**, such that the basicity of the boron center may decrease upon the substitution of methyl or phenyl group. Furthermore, independent of the substitution of methyl or phenyl group, the contribution of d orbital to the hybridization on the boron's lone pair, in theory, is not of prime importance [40].

As for the calculation of EA, comparing with the previous EA estimated via HF and MP4 methods [30, 38], the resulting data using MPW1K are significantly lower. This is possibly due to the fact that a DFT functional cannot deal with the eigenvalue of LUMO very accurately [41]. Nevertheless, 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_{ST} s of **1a**–**1e** being estimated to be >24 kcal mol⁻¹ (see Table 3), indicates that they are stable and inert to radical reactions. From the viewpoint of reaction, both methyl and phenyl groups can induce higher barriers for 1,2-shift reactions and protect the boron atom from attack by neighboring molecules [33]. The consistency between current MPW1K and previous results leads us to believe that the comparative study between **1a** and **4**–**10** elaborated in the following sections should be fair and valuable.

The influence of the steric effect

In 1991, Arduengo and coworkers synthesized a stable carbene, designated as **2**, which was built via the skeleton depicted in Scheme 2 [13]. 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 [36, 37, 42–44]. In other words, rather than the thermodynamic stability, i.e. a deep minimum on the potential energy surface, NHCs are considered to be kinetically stable with respect to radical and electrophilic reactions [42]. Indeed, in 1995, Arduengo and coworkers successfully synthesized the corresponding saturated carbene, the structure of which is represented as **3** in Scheme 2 [45]. The difference between **2** and **3** is mainly caused by the twisting of the CH₂-CH₂ link in **3**, which is categorized as 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 the stability of a boryl anion; this can be done by comparing the calculated results of **1a** with those of **4**.

Accordingly, comparative studies are made by taking into consideration both bond length of B-N and bond angle \angle N-B-N of **1a** and **4**. As depicted in Fig. 2, the saturated diazaborole anion (**4**) has shorter B-N bond length by 0.06 Å and larger \angle N-B-N bond angle by 2.27° than that of the unsaturated **1a**. Also, the addition of one electron makes the B-N bond length (the \angle N-B-N bond angle) of **4** increased (decreased) similar to those mentioned above. The NPA/NLMO results on the boron atom, E_{ST} and EA of **1a** and **4** are summarized in Table 4. As shown in Table 4, the boron atom of **4** possesses less anionic character than that of **1a**, and the occupancy of boron's lone pair decreases from 1.931 of **1a** to 1.910 of **4**. It is also reasonable to assume that the contribution of d orbital to the hybridization on the boron's lone pair is negligible for both **1a** and **4** (vide supra). Further inspection on their respective EA values of **4** (-2.8) < **1a** (1.2, see Table 4) indicates that the steric effect

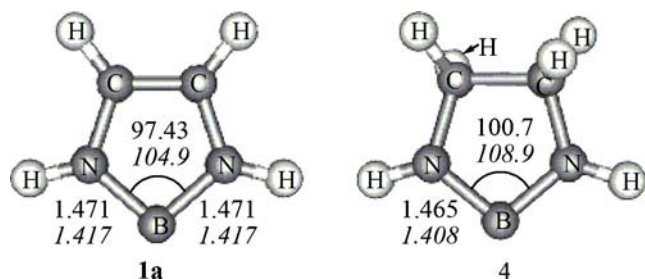
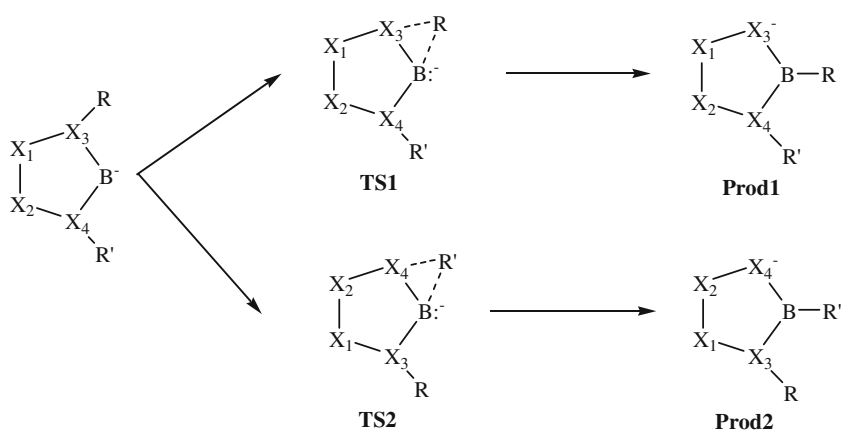


Fig. 2 The bond length of B-N (in Å) and bond angle \angle N-B-N (in $^{\circ}$) of **1a** and **4** (The results corresponding to the neutral radicals are in italic)

of the five-membered ring can significantly influence the stability of a diazaborole anion. This is in accordance with the decrease of E_{ST} calculated from $28.7 \text{ kcal mol}^{-1}$ in **1a** to $26.7 \text{ kcal mol}^{-1}$ in **4**. Similarly, the T_1 state of **4** involves the electronic transition from σ -type lone pair to π -type lone pair on the negative charged B atom (see Fig. S 1 in Supporting Information).

Influence of the number of nitrogen atoms

In our previous study on the diazaborole anions, we conclude that increase of the number of nitrogen atoms in the five-membered ring results in an increase of the barrier of 1,2-shift reaction (see Eq. 1) [33]. We herein then make further comparison between **5a**~**5i** (in Scheme 3) and **1a** from the viewpoints of E_{ST} s and EAs. Figure 3 depicts the structures calculated for **5a**~**5i**, while other pertinent parameters such as the NPA/NLMO results, E_{ST} and EA are summarized in Table 5.



(1)

As depicted in Fig. 3, the B-C bond distance is apparently longer than the B-N bond, the result of which is expected according to the difference in van der Waals radius between C and N. Also, 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) increased (decreased). As shown in Table 5, similar to that of other boryl anions (vide supra), among **5a**~**5i**, hybridization on the boron's lone pair is dominated by the s orbital. Also shown in Table 5, the charge on boron is not expected to decrease due to the fact that nitrogen acts as a σ - e^- acceptor. This can be rationalized by the fact that nitrogen can act not only as a σ - e^- acceptor but also as a π - e^- donor.

Interestingly, E_{ST} and EA predict certain inconsistency in stability trend among these anions. According to the calculated E_{ST} , the stability trend is in the order of **5i**>**5h**>**1a**>**5e**>**5d**>**5g**>**5b**>**5f**>**5c**>**5a**. In comparison, the trend of EA value is predicted to be **5i**>**5g**>**5f**>**5h**>**5e**>**5c**>**5d**>**1a**>**5b**>**5a**. Since E_{ST} and EA are two independent parameters, it is not surprising to render different tendency of stability predicted solely from each one. Nonetheless, both approaches consistently draw the conclusion that **5i** and **5a** are the most stable and labile anion species, respectively. It has been reported that only efficient π - e^- donors like nitrogen can stabilize boryl anion due to the existence of a strong P π -P π interaction [3]. Thus, the result of **5a** being the most unstable anion can be rationalized by the fact that carbon cannot act as a good π - e^- donor. Conversely, upon substitution of a HC=CH group in **1a** by a N=N group, **5i** becomes the most stable anion, although it is still synthetically unavailable at this stage. Lacking such strong P π -P π interaction may also cause the π -type lone pair on boron in **5a** to be more unstable than that in **1a**. Therefore, the T_1 state of **5a** involves the electronic transition from σ -type lone pair to the delocalized π system of the five-membered ring (see Fig. S 1 in Supporting Information). In a preliminary test, we have combined the keywords guess=alter

and vshift in Gaussian 03 in attempts to locate a triplet state of **5a**, which may be ascribed to the transition from the σ -type lone pair to π -type lone pair on the negative charged B atom. Unfortunately, we were unable to access the higher-lying triplet state via this approach.

Table 4 The NPA/NLMO results, E_{ST} (in kcal mol⁻¹) and EA (in kcal mol⁻¹) of **1a** and **4**

	Natural population analysis on B	The hybridization of B's lone pair	Occupancy of B's lone pair	E_{ST}	EA
1a	-0.0349	s(62.56%),p(37.42%),d(0.02%)	1.931	28.7	1.2
4	0.0441	s(59.88%),p(40.09%),d(0.02%)	1.910	26.7	-2.8

The influence of the ring size

In our previous study regarding the 1,2-shift reaction of boryl anions (see Eq. 1), six-membered ring anions (**7** and **8** in Scheme 4) are concluded to possess higher barrier than their four-, five- and seven-membered analogues [33]. In this study, we then made further attempts in an aim to probe their corresponding thermodynamics. Figure 4 compiles the bond length of B-N and bond angle $\angle N-B-N$ of compounds **6~10** (in Scheme 4) under consideration. The optimized

geometries of anionic **6~10** as well as their comparison have been elaborated in our previous study [33]. As depicted in Fig. 4, the addition of one electron makes the B-N bond length (the $\angle N-B-N$ bond angle) of **6~10** increased (decreased) as elaborated above.

Finally, the NPA/NLMO results on the boron atom, E_{ST} and EA of **1a** and **6~10** are summarized in Table 6. As shown in Table 6, the occupancy of the lone pair on boron for **1a** and **6~10** is around 1.90 and its hybridization is mainly dominated by the s orbital. However, the member of ring also

Fig. 3 The bond length of B-N (in Å) and bond angle $\angle N-B-N$ (in °) of **1a** and **5a~5i** (The results corresponding to the neutral radicals are in italic)

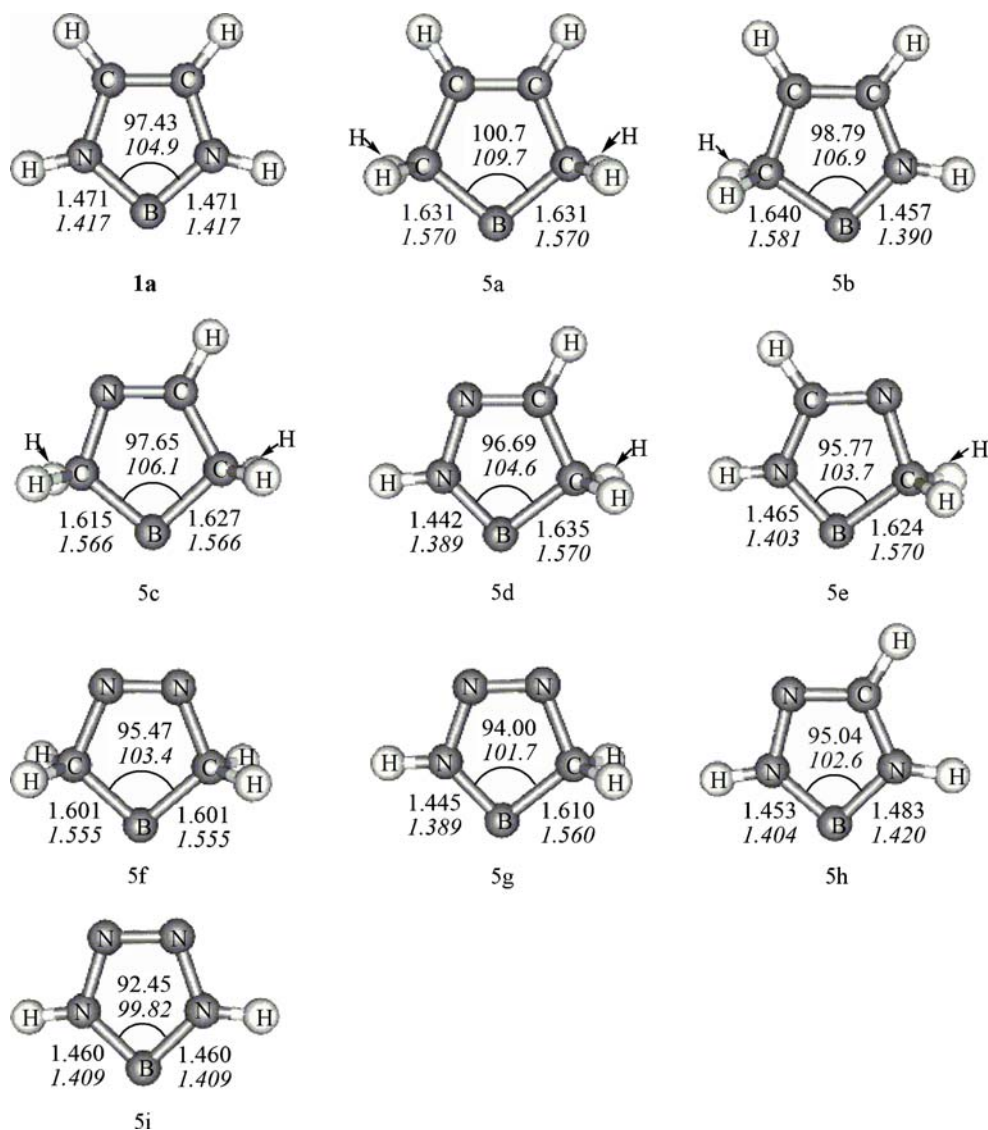


Table 5 The NPA/NLMO results, E_{ST} (in kcal mol⁻¹) and EA (in kcal mol⁻¹) of **1a** and **5a~5i**

	NPA on B	The hybridization of B's lone pair	Occupancy of B's lone pair	E_{ST}	EA
1a	-0.0349	s(62.56%),p(37.42%),d(0.02%)	1.931	28.7	1.2
5a	0.0278	s(57.91%),p(42.07%),d(0.02%)	1.934	10.0	-0.6
5b	-0.0019	s(60.37%),p(39.61%),d(0.02%)	1.931	23.3	-0.2
5c	-0.0094	s(57.42%),p(42.55%),d(0.03%)	1.926	11.2	7.2
5d	-0.0316	s(59.60%),p(40.38%),d(0.03%)	1.914	26.4	7.1
5e	-0.0291	s(60.21%),p(39.77%),d(0.03%)	1.931	27.6	8.3
5f	-0.0249	s(56.23%),p(43.73%),d(0.03%)	1.895	13.9	16.6
5g	-0.0450	s(58.99%),p(40.98%),d(0.03%)	1.901	24.7	17.3
5h	-0.0509	s(62.33%),p(37.64%),d(0.03%)	1.927	33.3	9.9
5i	-0.0631	s(61.94%),p(38.02%),d(0.03%)	1.917	45.2	20.6

influences the bonding pattern of the boron atom, as indicated by an additional lone pair orbital existing as a pure $P\pi$ on boron for **7**, **8** and **9**, which is not shown in Table 6 due to the occupancies of the additional lone pair <0.5 . Also, the different bonding pattern from **1a** causes the T_1 state of **6~9** originating from the σ -type lone pair transitions to the delocalized π system of the ring (see Fig. S 1 in Supporting Information). Again, E_{ST} and EA predict different stability trend among these anions. We thus introduced a parameter combining both effects of E_{ST} and EA, namely SF (see Eq. 2).

$$SF = E_{ST} + EA \quad (2)$$

As the SF value increases, the corresponding boryl anion becomes more stable. Calculated SFs values for compounds

1a and **6~10** are summarized in Table 6. According to SF listed in Table 6, the stability trend is in the order of **8** $>$ **1a** $>$ **7** $>$ **6** $>$ **10** $>$ **9**. Moreover, the comparison between **7** (**9**) and **8** (**10**) clearly shows that additional phenyl ring can increase the stability of a six- or seven-membered boryl anions. Likewise, **5i** and **8** are predicted to be rather stable boryl anion, although the corresponding synthetic routes have not yet been explored.

The inclusion of solvent

From the practical application point of view, we further performed the solvent effect using THF (dielectric constant $\epsilon=7.58$) by fully-optimized CPCM-MPW1K. This approach is necessary due to the fact that the first stable boryllithium

Fig. 4 The bond length of B-N (in Å) and bond angle $\angle N-B-N$ (in °) of **1a** and **6~10** (The results corresponding to the neutral radicals are in italic)

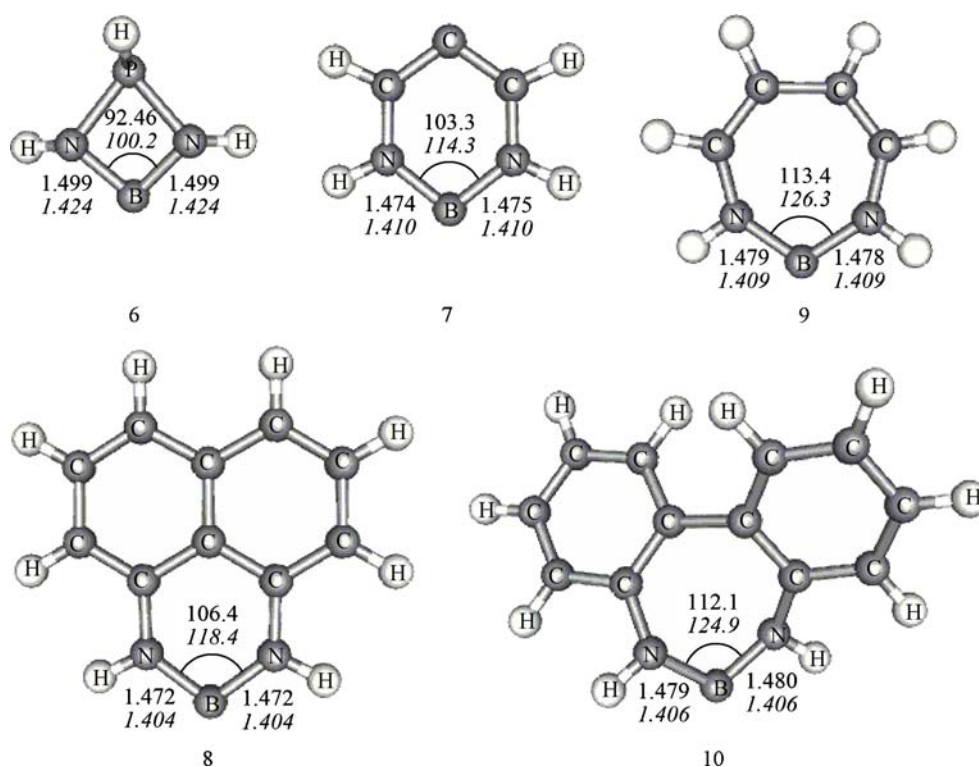


Table 6 The NPA/NLMO results, E_{ST} (in kcal mol⁻¹) and EA (in kcal mol⁻¹) of **1a** and **6–10**

	Natural population analysis on B	The hybridization of B's lone pair	Occupancy of B's lone pair	E_{ST}	EA	SF
1a	-0.0349	s(62.56%),p(37.42%),d(0.02%)	1.931	28.7	1.2	29.9
6	0.0679	s(65.56%),p(34.41%),d(0.03%)	1.942	14.7	4.3	19.0
7	0.0177	s(60.30%),p(39.67%),d(0.03%)	1.942	8.6	17.6	26.2
8	0.0695	s(61.01%),p(38.97%),d(0.03%)	1.939	22.5	12.3	34.8
9	0.0859	s(58.42%),p(41.55%),d(0.03%)	1.931	9.7	0.3	10.0
10	0.0441	s(59.88%),p(40.09%),d(0.02%)	1.910	9.7	7.2	16.9

was synthesized in THF [4]. Moreover, the effect of solvent polarity on the stability of a diazaborole anion can thus be investigated by a comparative study in cyclohexane ($\epsilon=2.02$) and THF ($\epsilon=7.58$). However, scanning all titled boryl anions would be a formidable process at this stage. Therefore, only three representative compounds **1a**, **5i** and **8** were carried out in this study. Comparison of the results of the three representatives in the gas phase with respect to the ones in cyclohexane and THF is depicted in Fig. 5. From both E_{ST}

and ET values, the stabilities of these anions increase as the dielectric constant of the medium increases. However, in comparison with the stability trend obtained in gas phase (**5i**>**8**>**1a**), the results show a different stability trend in cyclohexane and THF, being in the order of **5i**>**1a**>**8**. According to the NPA analyses, the negative charge of the anion is delocalized in a trend **8**>**1a**>**5i**. Therefore, the sensitivity to the solvation effect of a solvent is in a trend **5i**>**1a**>**8**. Moreover, the B-N bond distance decreases as ϵ increases. The results show that **1a**, **5i** and **8** are all stable boryl anions according to the calculated SFs in the gas phase, cyclohexane and THF. Since these are all anionic species, their stabilities are obviously influenced by the solvent polarity; upon increasing the solvent polarity, the stability of titled boryl anions **1a**, **5i** and **8** is expected to be increased.

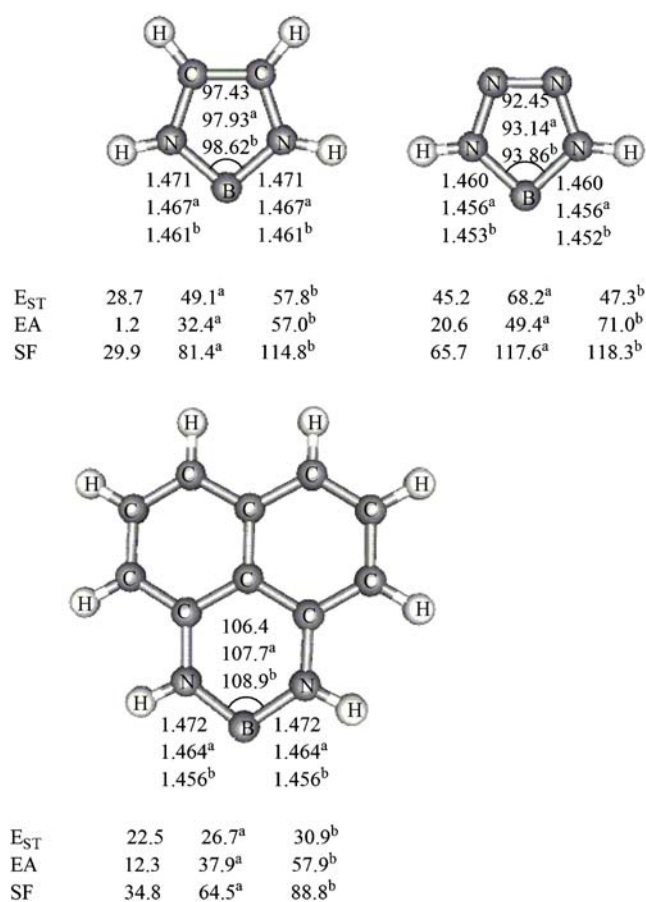


Fig. 5 The calculated results of **1a**, **5i** and **8** in THF (bond length in Å, bond angle in °) (a) The results are based on the fully-optimized CPCM model in cyclohexane. (b) The results are based on the fully-optimized CPCM model in THF

The influence of a lithium cation on E_{ST}

Similar to the non-cyclic boryl anions [3], as shown in Table 7, the singlet states of the cyclic ones are more strongly influenced by adding Li⁺ into the calculation than that of the triplet states. Accordingly, all E_{ST} of the anions shown in Table 7 increases as the ion pair is considered into the calculation. The results may indicate that the calculations regarding anionic and/or cationic species must consider the effect of the counter ion, especially in the gas phase or non-polar solvents. Upon close inspection of Table 7, E_{ST} of **5a** is the most strongly influenced by adding Li⁺ into the calculation. The value of E_{ST} for **5a** is 10.0 and 30.5 kcal mol⁻¹ for the free anion and ion pair, respectively. In comparison, E_{ST} is changed by 8.9 and 3.9 kcal mol⁻¹ for **1a** and **4**, respectively, as adding a lithium cation. Nonetheless, the stability still follows a trend of **5i**>**8**>**1a** upon addition of Li⁺.

Table 7 The E_{ST} (in kcal mol⁻¹) of Li**1a**, Li**4** and Li**5a**

	Li 1a	Li 4	Li 5a	Li 5i	Li 8
E_{ST}	37.6	30.7	30.5	49.6	39.1

Conclusions

Several remarks can be summarized according to our calculations on the boryl anions: (1) The lone pair of boron is mainly hybridized with its s orbital and the member of ring can influence the bonding pattern of the boron atom. (2) The steric effect of the ring may play a role to stabilize a cyclic boryl anion. (3) The singlet-triplet splitting (E_{ST}), electron affinity (EA) and their combination may predict trend of stability in a qualitative manner. (4) Except for **1a**, parent **5i** and **8** and their analogues shown in Scheme 3 and 4 should be candidates for stable cyclic boryl anions either in both gas phase and organic solvents such as cyclohexane and THF. (5) As the ion pair is considered, the energetics of singlet states are more strongly influenced than the triplet ones. Since the methyl and phenyl group can induce higher barriers for 1,2-shift reactions and protect the boron atom from attack by neighboring molecules, the bulky-group substituted **5i** and **8** are predicted to be stable boryl anions. Due to the fact that the boryl anion may be exploited to synthesize new boron-containing compounds as well as to provide different synthetic routes from traditional protocols, we hope that the results presented here can provide useful information for future applications.

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