



## On the cation– $\pi$ interactions in 1,2-dihydro-1,2-azaborine

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**Abstract.** In recent years, it has become a strategy, and important area of research, to incorporate heteroatom into polycyclic aromatic compounds. Especially B/N containing aromatic compounds have been the topic of interest over the years, because of the isoelectronic nature of B–N bond with C=C bond. The substitution of B–N in place of C=C brings many important electronic and structural changes in the system. This work presents the investigation of the interaction between different cations and the  $\pi$ -cloud of the 1,2-dihydro-1,2-azaborine molecule using quantum chemical investigations at the MP2/aug-cc-pVDZ level of theory. The nature of interactions has been gauged by employing the energy decomposition analysis and molecular electron density critical point calculations. Further, the changes in N–H, B–H and C–H bond vibrational frequencies due to the cation binding were also investigated. Among the cations studied in this work,  $\text{Be}^{2+}$  is found to provide the best compromise between size and charge as revealed by its high interaction energy and presence of electron density three critical points.

**Keywords.** Interaction energy; energy decomposition analysis; vibrational frequency; critical points.

### 1. Introduction

Molecular level investigations of noncovalent interactions such as hydrogen bonding,  $\pi$ – $\pi$  interaction, cation– $\pi$  interaction, hydrophobic, ionic, and van der Waals, have gained significant importance. In particular, cation– $\pi$  interactions have been the topic of interest in molecular recognition.<sup>1–4</sup> Because these ion–molecule interaction is known to be one of the strong noncovalent interactions in molecular systems.<sup>1–10</sup> A large number of reports exist in the literature on cation– $\pi$  interactions involving benzene and heterocycles and these have been studied extensively by quantum chemical methods.<sup>1,4,8,9</sup>

The isoelectronic inorganic analogue of benzene *viz.*, borazine (*c*- $\text{B}_3\text{N}_3\text{H}_6$ ), have also been the topic of interest and has been studied extensively over the years.<sup>11,12</sup> Though B–N bond is isoelectronic with the C=C bond, it imparts various electronic effects such as aromaticity which is different from benzene.<sup>11,12</sup> Because of this, in recent years, it has become an emerging strategy of incorporation of B/N unit in organic structures by the

substitution of an isoelectronic C=C bond. As mentioned above, the total valence electron count is same but the substitution causes the differences in molecular and structural properties.<sup>13</sup>

One such very early attempt leads to the synthesis of 1,2-Dihydro-1,2-azaborine (abbreviated as 1,2-azaborine) where one C=C in benzene is replaced by the B–N bond. This hybrid organic/inorganic structure 1,2-azaborines were popularized by Dewar and White<sup>14</sup> in the 1960s, and recent contributions from the groups of Ashe,<sup>15</sup> Piers,<sup>16</sup> Paetzold,<sup>17</sup> and Liu.<sup>13,18</sup> Over the years a number of synthetic routes have been devised for synthesizing the B/N containing aromatic compounds by making use of 1,2-azaborine.<sup>13,19–22</sup> With such a significant role in synthetic chemistry, it becomes important to study the properties of 1,2-azaborine which may help in devising more synthetic routes.

In view of this, the current work presents the investigation of the cation interaction with a 1,2-azaborine molecule, in particular with the  $\pi$ -cloud of the molecule. In this work, the complexes of 1,2-azaborine with various cations e.g.,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Be}^{2+}$ ,  $\text{NH}_4^+$ , *etc.* have been studied by using Second order Møller-Plesset

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Perturbation (MP2) theory and correlated consistent basis sets. The nature of the interactions has been gauged by employing the energy decomposition analysis.

## 2. Computational details

In order to capture the fundamental aspects of interactions in 1,2-azaborine and cation complexes, *ab initio* calculations were carried out at MP2 level with Dunning's correlated consistent aug-cc-pVDZ basis set.<sup>23,24</sup> First, the geometry optimizations and vibrational frequency calculations of the complexes were carried out at the all electron MP2/aug-cc-pVDZ level of theory.<sup>25</sup> The interaction energies were analyzed by using LMO-EDA (localized molecular orbital-energy decomposition analysis) available in the 2016 version of Gamess.<sup>26,27</sup> Further, the molecular electron density (MED) critical points were calculated at the same level of theory, for the interactions between the cation and azaborine molecule. The results thus obtained are discussed in the next section.

## 3. Results and Discussion

The cation- $\pi$  complexes of 1,2-azaborine with various cations were studied by quantum chemical investigations. In this work, the complexes of 1,2-azaborine with  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Be}^{2+}$ ,  $\text{NH}_4^+$  and  $\text{H}_3\text{O}^+$ , were studied at the MP2/aug-cc-pVDZ level of theory. The optimized geometries of the complexes of 1,2-azaborine with the chosen cations are shown in Figure 1. The presence of nitrogen atoms makes the interactions interesting and different from the interactions in benzene-cation complexes.

### 3.1 Energy decomposition analysis

The nature of the interactions between 1,2-azaborine and cations was investigated by LMO-EDA method available in Gamess software. The total interaction energy of the complex is decomposed into electrostatic, exchange, repulsion, polarization and dispersion energy terms. The decomposition of interaction energy of the 1,2-azaborine-cation complexes is presented in Table 1. As can be seen from the table,  $\text{Be}^{2+}$ , and  $\text{Mg}^{2+}$  complexes have very strong interactions with 1,2-azaborine as revealed by their total interaction energies. Also, in all of the cations, except  $\text{H}_3\text{O}^+$ , the electrostatic contribution is seen to stabilize the bonding. The interaction between  $\text{Mg}^{2+}$  cation and 1,2-azaborine also has high polarization contribution which suggests that the interaction is also close to a covalent bond.<sup>26</sup>

Among the singly charged cations,  $\text{Li}^+$  ( $\Delta E = -34.29$  kcal/mol) binds stronger to 1,2-azaborine than  $\text{Na}^+$  cation ( $\Delta E = -22.25$  kcal/mol). Both the cations have comparable electrostatic and exchange contribution. However, the magnitude of the polarization component in  $\text{Li}^+$  is larger than that in  $\text{Na}^+$  complex (*cf.* Table 1). This high contribution due to polarization makes the total interaction energy in  $\text{Li}^+$  complex lower than that of  $\text{Na}^+$  complex even though the repulsion contribution is higher in the former. The magnitude of total interaction energy in the  $\text{Be}^{2+}$  complex is the highest. However, it is interesting to note that the magnitude of electrostatic contribution in the  $\text{Be}^{2+}$  complex is lower than that of the  $\text{Mg}^{2+}$  complex while the magnitude of polarization contribution is less than that in  $\text{Li}^+$  complex (*cf.* Table 1). This suggests that most of the part of total interaction energy has come from Hartree-Fock contribution.

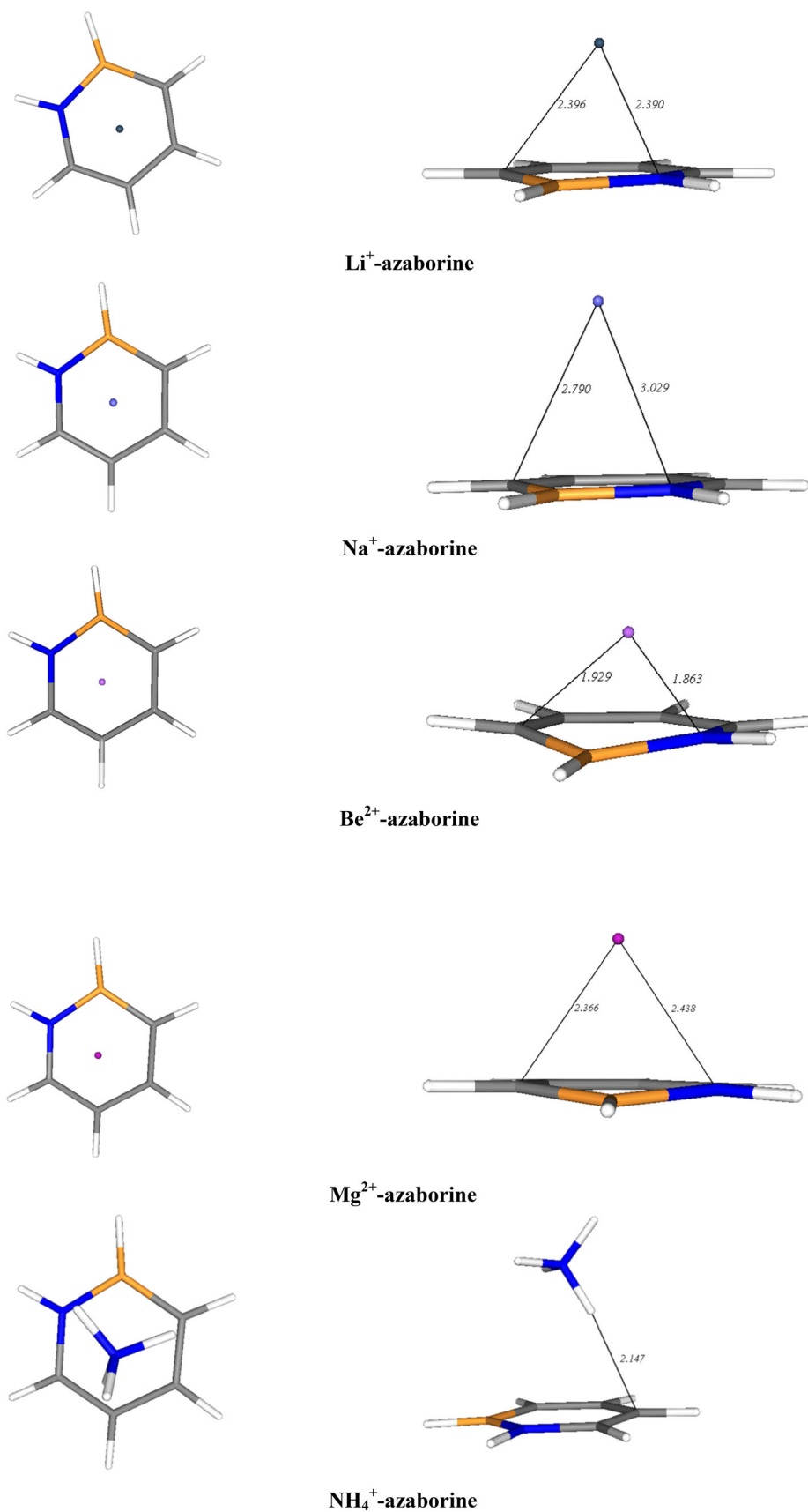
Among all the cations, the  $\text{NH}_4^+$ -azaborine complex is the least stable one. This may be due to its bulky nature. It is worth to note here that for all of the cations the dispersion component has positive value while in  $\text{NH}_4^+$  complex it is negative; *viz.*,  $-4.48$  kcal/mol meaning that it is stabilizing the interaction.

In  $\text{H}_3\text{O}^+$  complex the electrostatic contribution is positive, hence it is destabilizing the interaction. But at the same time,  $\text{H}_3\text{O}^+$  complex has very high polarization contribution ( $\Delta E_{\text{polar}} = -212.37$  kcal/mol) which makes the total interaction stronger. This high polarization shows that the cation is bonded with the 1,2-azaborine by a covalent bond. An attempt has been made to study the nature of the interaction between  $\text{Al}^{3+}$  and 1,2-azaborine. But it was found that there exists no interaction ( $\Delta E = -0.02$  kcal/mol) with no contribution from any of the components of the interaction energy.

As can be seen from the values, among the singly charged cations, azaborine favors  $\text{Li}^+$  which is smaller in size. Again, in doubly charged cations azaborine shows an affinity towards  $\text{Be}^{2+}$  which is also smaller in size than  $\text{Mg}^{2+}$ . Here, as the charge is increased, the magnitude of the interaction energy also increased. However, in the case of  $\text{Al}^{3+}$ , the charge is higher but it does not show any binding to azaborine ring. Thus, it can be said that the azaborine ring favors the compromise between size and charge and hence the  $\text{Be}^{2+}$  cation complex has maximum stability amongst all.

### 3.2 Vibrational frequencies

One of the main reason behind the growing interest in azaborine chemistry is a synthesis of B/N



**Figure 1.** Structures of the 1,2-azaborine-cation complexes (top view left and side view right) optimized at the MP2/aug-cc-pVDZ level of theory.

**Table 1.** Decomposition of 1,2-azaborine-cation Interaction Energies (in kcal/mol) into electrostatic, exchange, repulsion, polarization and dispersion contributions.

|                      | $\Delta E_{\text{electro}}$ | $\Delta E_{\text{exchange}}$ | $\Delta E_{\text{repu}}$ | $\Delta E_{\text{polar}}$ | $\Delta E_{\text{disp}}$ | $\Delta E_{\text{Total}}$ |
|----------------------|-----------------------------|------------------------------|--------------------------|---------------------------|--------------------------|---------------------------|
| Aza-Li               | -17.57                      | -5.26                        | 15.55                    | -29.40                    | 2.40                     | -34.29                    |
| Aza-Na               | -16.10                      | -4.89                        | 12.18                    | -14.25                    | 0.80                     | -22.25                    |
| Aza-Be               | -32.32                      | -12.42                       | 53.16                    | -28.15                    | 8.28                     | -221.46                   |
| Aza-Mg               | -42.07                      | -12.77                       | 40.27                    | -104.26                   | 3.50                     | -115.42                   |
| Aza-Al               | 0.0                         | 0.0                          | 0.0                      | -0.01                     | -0.01                    | -0.02                     |
| Aza-H <sub>3</sub> O | 1.88                        | -33.50                       | 64.85                    | -212.37                   | 24.55                    | -154.61                   |
| Aza-NH <sub>4</sub>  | -14.42                      | -16.03                       | 31.06                    | -14.09                    | -4.48                    | -17.97                    |

**Table 2.** The N–H stretch frequencies (in  $\text{cm}^{-1}$ ) of 1,2-azaborine-cation complexes calculated at the MP2/aug-cc-pVDZ level of theory. See text for details.

|                     | N–H     | B–H     | C–H (Avg) |
|---------------------|---------|---------|-----------|
| Azaborine           | 3605.15 | 2652.83 | 3213.76   |
| Aza-Li              | 3554.18 | 2728.12 | 3230.69   |
| Aza-Na              | 3566.60 | 2705.93 | 3221.61   |
| Aza-Be              | 3431.12 | 2798.49 | 3213.90   |
| Aza-Mg              | 3478.32 | 2767.18 | 3216.85   |
| Aza-NH <sub>4</sub> | 3571.79 | 2693.79 | 3218.90   |

containing aromatic compounds starting from 1,2-azaborine.<sup>13,19–22</sup> In this, the aromatic rings are constructed by substituting the hydrogens connected to B–N bond. Thus, it is important to investigate what makes the N–H or B–H bond stronger or weaker. In view of this, the current article also analyzes the changes in N–H, B–H and average of C–H stretching frequency due to its interaction with various cations. The stretching frequencies in the chosen azaborine-cation complexes calculated at the MP2/aug-cc-pVDZ level of theory are listed in Table 2.

As can be seen from the table, for  $\text{Be}^{2+}$ -azaborine complex the N–H frequency value is minimum and increases as we go to the complexes above or below in the table. However, there is a clear trend observed for B–H stretch frequency. For  $\text{Be}^{2+}$ -azaborine complex, the B–H stretch is highest and for  $\text{Li}^+$ -azaborine complex it is lowest. As seen in the above discussion,  $\text{Be}^{2+}$  has the maximum interaction energy. This suggests that the N atom also contributes its electron density for binding a cation. Such a contribution is maximum for  $\text{Be}^{2+}$  atom and because of that, the N–H bond shows lower frequency as compared to other complexes. On the other hand, as N atoms take part in bonding with  $\text{Be}^{2+}$  cation, it seems that electron density of B–H bond increases which makes the frequency higher than others. On the

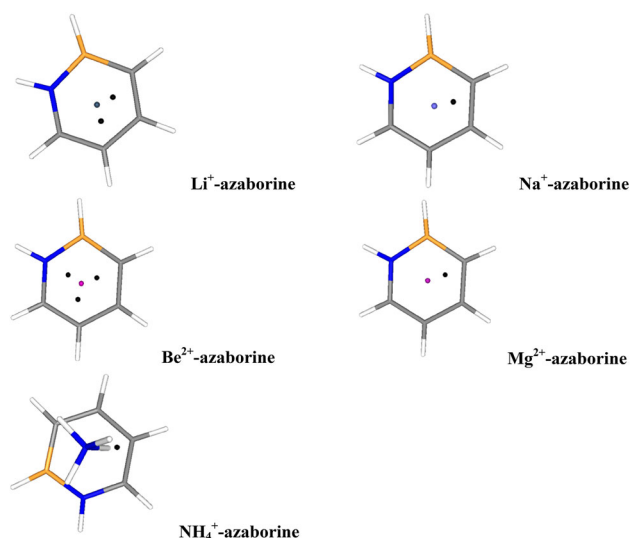
other hand,  $\text{NH}_4$  cation has a large size which makes it less favourable for interaction with 1,2-azaborine, as revealed by highest N–H frequency band.

The trend in average C–H frequencies is observed to be similar to that of N–H stretch. Among the complexes, the azaborine- $\text{Be}^{2+}$  complex exhibits the minimum C–H stretch frequency. But in case of N–H stretch, the azaborine- $\text{Mg}^{2+}$  complex has the highest frequency while for the C–H stretch azaborine- $\text{Li}^+$  has the highest frequency. However, the overall change in frequency of C–H stretch is smaller than that in N–H stretch.

### 3.3 Electron density topology analysis

Molecular Electron Density (MED) is a scalar function of chemical interest because it gives the vital information about the bonding in a molecular system. The scalar field of MED and its topology has been popularized by Bader and co-workers<sup>28,29</sup> through their fundamental and exhaustive investigations. It was suggested that a chemical bond is represented by (3, –1) critical point (CP). The topology of MED has been extensively used for investigating the structure and bonding in molecular systems.<sup>30,31</sup> In view of this, the MED topology of cation-azaborine complexes have been carried out at MP2/aug-cc-pVDZ level by using DAMQT software<sup>32</sup> to understand the nature of bonding between the cation and the azaborine ring.

As can be seen from Figure 2, the  $\text{Be}^{2+}$ -azaborine complex shows the maximum number of (3, –1) CP which suggests strong bonding of  $\text{Be}^{2+}$  with azaborine ring. This finding is in agreement with the maximum interaction energy for the complex as seen above (*cf.* Table 1). These three CP's, indicate the binding of  $\text{Be}^{2+}$  with two C atoms and Nitrogen atoms. This is again in agreement with the above observation of minimum value of N–H stretch frequency. Among all other cations, Li-azaborine complex exhibits two CP's for Li



**Figure 2.** Molecular electron density (3,  $-1$ ) critical points (denoted as black dots) of the 1,2-azaborine-cation complexes at the MP2/aug-cc-pVDZ level of theory.

and azaborine ring interaction while all other complexes show only one CP for the cation-azaborine ring.

### 3.4 Aromaticity

The changes in the aromatic character of azaborine ring after binding to cations is investigated by calculating the Nucleus Independent Chemical Shift (NICS) values of the parent and complexes. The NICS is the negative magnetic shielding calculated at the centre of the ring. This descriptor of aromaticity was proposed by Schleyer *et al.*,<sup>33,34</sup> as a magnetic index of aromaticity. A large negative NICS value indicates aromatic character while non-aromatic species have NICS values close to zero and positive NICS values indicate antiaromaticity.<sup>33</sup> The NICS values provide a simple and effective tool for studying the aromaticity of the molecular systems. The NICS values calculated for the azaborine and its complexes by GIAO method are reported in Table 3. There is clear increasing trend observed in the NICS values. It suggests that after binding of cations the aromatic character of azaborine ring increases in case of  $\text{Li}^+$  and  $\text{Be}^{2+}$  cations. On the other hand, the NICS values for  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{NH}_4^+$  are observed to be less than that of the bare azaborine ring. These trends are similar to the total interaction energy. Hence, once again it has been found that the azaborine ring favors  $\text{Be}^{2+}$  cation where NICS value is highest suggesting the more aromatic character.

**Table 3.** The NICS values (in ppm) of 1,2-azaborine-cation complexes calculated at the MP2/aug-cc-pVDZ level of theory. See text for details.

|                    | NICS    |
|--------------------|---------|
| Azaborine          | $-5.36$ |
| Aza-Li             | $-6.03$ |
| Aza-Na             | $-4.50$ |
| Aza-Be             | $-6.53$ |
| Aza-Mg             | $-1.54$ |
| Aza- $\text{NH}_4$ | $-5.11$ |

## 4. Conclusions

A significant number of investigations have emerged in the last few years showing the importance of heteroatom-doped polycyclic aromatic compounds. In particular, B/N containing aromatic compounds have been the topic of interest in recent years, because of the isoelectronic nature of B–N bond with the C=C bond. One such attempt leads to the synthesis of hybrid benzene *viz.*, 1,2-azaborine where one C=C in benzene is replaced by the B–N bond. In the last few years, this molecule has emerged as a good starting point for synthesizing B/N containing polycyclic aromatic compounds.<sup>12,18–21</sup> In view of the importance of 1,2-azaborine, this work investigated the interaction of different cations with the  $\pi$ -cloud of the 1,2-azaborine molecule at the MP2/aug-cc-pVDZ level of theory.

Among the cations studied in this work,  $\text{Be}^{2+}$  is found to provide the best compromise between charge and size and form a complex with maximum interaction energy. The  $\text{NH}_4^+$  shows the minimum interaction energy which may be due to the large size of the cation. The energy decomposition analysis shows that the electrostatics and polarization contributions are the dominant components of the total interaction energy in all the complexes. Further, the changes in N–H, B–H and average of C–H stretching frequency, due to its interaction with various cations were studied. The changes in aromaticity of the azaborine ring were also studied by making use of the NICS values and it was found that azaborine- $\text{Be}^{2+}$  complex has maximum aromatic character. It was found that the  $\text{Be}^{2+}$ -azaborine complex shows the smallest N–H and C–H stretch and largest B–H stretch frequency. This may be due to the interaction of  $\text{Be}^{2+}$  cation with nitrogen atom along with the carbons in the ring. This observation was further validated by MED analysis which shows the presence of three CP's indicating the interaction of cation with two carbons and a nitrogen

atom. This frequency and MED analysis show how the nature of the cations changes the bond strength of N–H, B–H and C–H bond. This could be of help in identifying the possibilities for hydrogen substitution and increasing the aromatic framework through N–H bond or B–H bond.

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