JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
pubs.acs.org/JACS

Ionic N−B−N- and B−N−B-Substituted Benzene Analogues: A Theoretical Analysis

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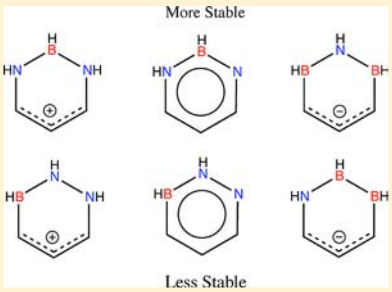
Supporting Information

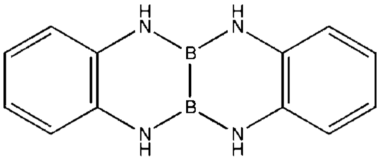
ABSTRACT: Calculations are presented on six-π-electron N−B−N- and B−N−B-substituted benzene rings, $[C_3BN_2H_6]^+$ and $[C_3NB_2H_6]^-$, and their isomers. These compounds display a wide range of thermodynamic stability in those molecules, with N−B−N connectivity favored strongly in the cation, B−N−B in the anion. That stability order is easily understood using the charge distribution in a benzene polarized by heteroatom substitutions or the underlying allyl anion and cation. Deprotonation at N in $[C_3BN_2H_6]^+$ leads to a set of BN-substituted pyridines. The calculations predicted three B−N-substituted pyridines clearly more stable thermodynamically than those synthesized so far. The order of stability of the B−N−B-substituted benzenoid systems, which are as yet not well known experimentally, shows similar features. We investigated in a preliminary way the reactivity and potential stabilization by substitution of the energetically most stable structures and by examining possible escape routes by dimerization. Our study suggests new N−B−N and B−N−B molecules that could be made.



INTRODUCTION

Boron, nitrogen substitutions in benzene and other cyclic hydrocarbons have been an active and productive field of study for more than 50 years.[1] With applications in pharmacology,[2] electronic materials,[3] and nanoscience,[4] many B,N-containing organic compounds have been synthesized and studied theoretically.[5−7] Their utility stems from the fact that B−N is isoelectronic to C−C. This makes it possible to prepare systems that are similar in structure to known hydrocarbons, but with different, tunable chemical reactivity and physical properties. In this paper, we look at two such B,N-substituted systems from a theoretical point of view.

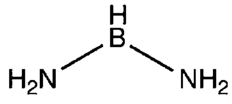
Our study was motivated initially by a report of a preparation of diazaborines of the kind shown in structure **1**.[8]



1

One N−B−N fragment of molecule **1** is extracted in **2**; this is N_2BH_5, isoelectronic to an allyl anion, $[C_3H_5]^-$. Like allyl anion, N_2BH_5 has four π-electrons. We imagined a hypothetical condensation of structure **2** with allyl cation, $[C_3H_5]^+$, in a six-membered ring. The resulting molecule is cation **3**, $[C_3BN_2H_6]^+$, isoelectronic to benzene.[9,10]

Analogously, one could think of constructing another molecule that is isoelectronic to benzene, using a B−N−B-π system with two π-electrons, NB_2H_5, **4**. **4** is isoelectronic to allyl cation. Such B−N−B systems are less common than N−B−N ones, but a few are known.[11,12] A condensation of **4**, now with an allyl anion, leads to anionic structure **5**, $[C_3B_2NH_6]^-$ also isoelectronic with benzene. In this paper, we study the chemical bonding and the stability of these hypothetical molecules, and their isomers and derivatives. We also study deprotonated isomers of **3** and their derivatives, in order to compare their stabilities with, as we shall see, known systems.



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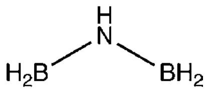

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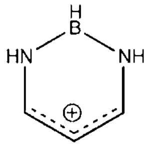

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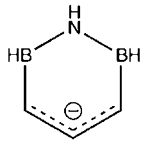


5

COMPUTATIONAL METHODOLOGY

All the structures we have studied were calculated in the framework of density functional theory (DFT). Becke's three-parameter hybrid functional as modified by Lee, Yang, and Parr (B3LYP), and the split-valence 6-31+G (d,p) basis set was used, as implemented in the Gaussian 09 program.[13] Harmonic vibration frequencies were calculated for all structures at the same level (B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p)); all the molecules reported were found to be minima on

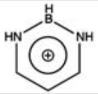
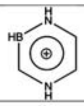
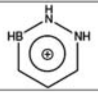
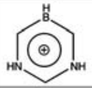
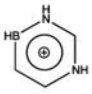
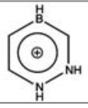
Received: May 21, 2012
Published: June 27, 2012

their potential energy surface. The electronic energies are corrected for the zero-point energies.

RESULTS AND DISCUSSION

$[C_3BN_2H_6]^+$. There are a number of possible positional isomers of **3**, **6–10**.[14] These isomers are shown in Table 1, along with their calculated energies. Although not all isomers are known experimentally, derivatives of **3**,[3,15–18] **6**,[2,19] and **7**[15] were synthesized and crystallographically characterized.

Table 1. Structures 3, 6–10 and Their Relative Energies

Structure #	Structure	E (kcal/mol)	Structure #	Structure	E (kcal/mol)
3		0	8		30
6		53	9		59
7		24	10		78

Among the isomers, **3** is calculated to have by far the lowest energy. Despite the high thermodynamic stability of **3**, it is its other isomers that have received greater attention. So, derivatives of **6** (calculated to be 53 kcal/mol less stable than **3**) have been prepared experimentally.[2] We will return to a detailed consideration of these compounds below. Structure **3** has N–B–N connectivity of the heteroatoms, while the much less stable **6** contains B–N–N.

Let us first see what clues to the stability and aromaticity of the various species are to be found in the calculated equilibrium bond lengths of the molecules. Figure 1 shows the calculated bond lengths of **3** and **6** and, as references, benzene, borazine, allyl cation, **2**, and the BN_2H_5 models **11a**,**b**. **11a** is the optimized H_2BNHNH_2 geometry, nonplanar and to be discussed in the next section. **11b** is a planar, higher energy conformation of **11a**, more suitable for comparison with the benzenoid structures.

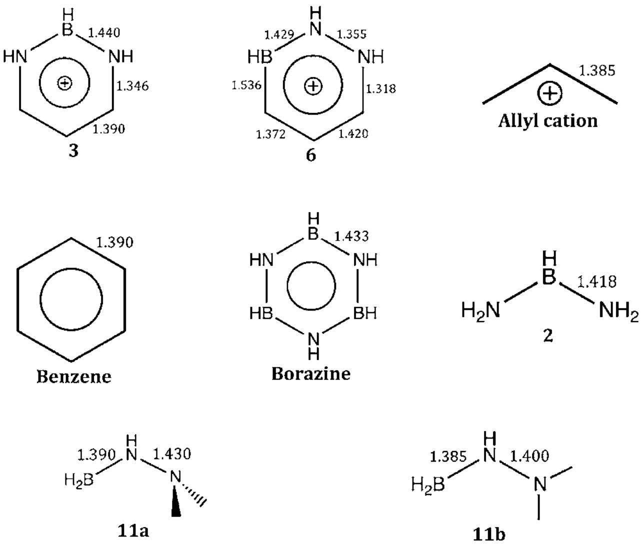
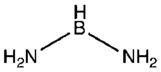
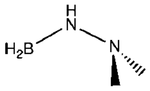
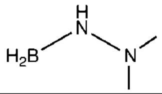


Figure 1. Calculated bond lengths (in Å) of **3** and **6** and, as references, benzene, borazine, allyl cation, and the BN_2H_5 models.

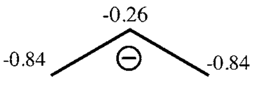
Equalization of bond lengths is one criterion of aromaticity, and (perhaps) an indicator of stability.[20] The calculated bond lengths in **3** are reasonably equalized, and consistent with models of **2**, borazine, and allyl cation. For the less stable **6**, the calculated bond lengths appear to be contradictory in the information they give us. On one hand, the bond lengths in the B–N–N segment of **6** are very different from the ones in a B–N–N model **11a**,**b**. So the mixing with allyl cation segment has a large effect. On the other hand, we see signs of destabilization in the unequal C–C distances of 1.372 and 1.420 Å in **6** (or is it just inherent asymmetry?), and the very long B–C distance of 1.536 Å.

Order of Stability of the $[C_3BN_2H_6]^+$ Isomers. In seeking an explanation of the great difference in stability of **3** and **6**, we thought to go back to the positional isomer of BN_2H_5 **2**, namely **11**. **11**, however, has a degree of structural complexity, in that it prefers to be nonplanar, **11a**, by about 9 kcal/mol relative to the planar conformation **11b**. As Table 2 shows, both **11a** and **11b** are very high in energy above **2**. The rotation of the terminal NH_2 out of plane and its pyramidalization are indicative of a tendency for the lone pairs (full on terminal NH_2, partial on the central N) to get out of each other's way as they do in, for example, hydrazine.

Table 2. Structures 2, 11a, and 11b and Their Relative Energies

Structure #	Structure	E (kcal/mole)
2		0
11a		60
11b		69

The order of stability of **2** and **11** can be understood by analyzing the charge distribution in allyl anion, isoelectronic to the BN_2H_5 models. The charge distribution of allyl anion, using the natural bond orbital (NBO) analysis (on wave functions calculated with the B3LYP 6-31+G(d,p) method), is shown in **12**.

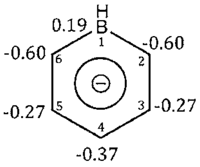


12

As expected from the four-π-electron system, the negative charge is highly localized on the two carbon atoms at the ends of the molecule. If we were to make a substitution (e.g., B,N) in allyl anion, placing the more electronegative atoms in the positions where there are most electrons (the outer atoms) should be favored.[21] The less electronegative atoms should go into the site of less electron density. The N–B–N substitution fits the predicted pattern best, B–N–N less so. The calculated energetics of the various $[C_3BN_2H_6]^+$ isomers in Table 1 are reasonably consistent with this analysis.

There is another way to approach the observed order of stability in **3** vs **6**. The electron density in benzene is equally distributed between the carbon atoms. However, if we were to polarize benzene by substituting a single heteroatom, the charge distribution would change, and the resulting polarization would indicate where subsequent substituent would prefer to go. We take the case of a B-substituted benzene ($[BC_5H_6]^-$) as one starting point for our analysis.

13 shows the charge distribution in the anionic ring, isoelectronic to benzene. Positions 2 and 6 have the highest electron density, making them the most favored positions for substitution by high electronegative atoms. Positions 3 and 5 are less negative. Therefore, nitrogen atoms would favor positions 2, 4, and 6. This is consistent with the energy order found in Table 1. For example, structure **9**, which has nitrogens substituted in positions 3 and 5, is less stable than **3** by about 59 kcal/mol.



13

Alternatively, one could begin with a N-substituted benzene (the pyridinium cation, $[C_5NH_6]^+$). We then find electron deficiency at the *ortho* and *para* positions (2, 4, and 6), now favoring B substitution there.

In summary, arguments based on either the inherent charge asymmetry in the allyl anion or the polarization caused in an N- or B-substituted benzene ring, explain the calculated preference for N−B−N over B−N−N connectivity in the molecules under consideration. There are signs of destabilizing lone pair−lone pair repulsion in the B−N−N isomers.

Functionalization of Deprotonated 3 and 6. Most of the experimentally known derivatives of our molecules are based not on the parent cationic system, but a formally deprotonated $[C_3BN_2H_6]^+$, i.e., $C_3BN_2H_5$. As Figure 2 shows, such molecules are neutral B,N-substituted pyridines with a B−N−N topology. These molecules were found to inhibit the synthesis of lipopolysaccharides in Gram-negative bacteria.[2] We begin our analysis by comparing deprotonated structures of **3** and **6**, which are shown in **14** and **15**, respectively.

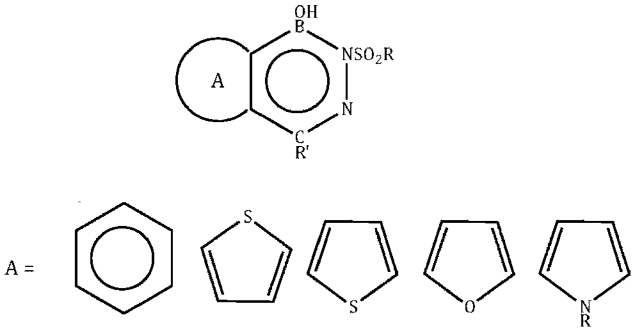
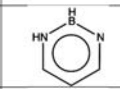
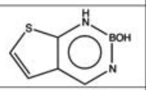
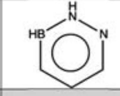
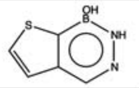
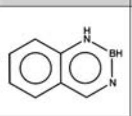
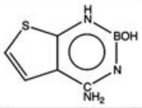
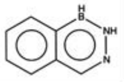
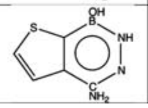


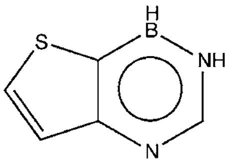
Figure 2. Generic structures of the biologically active diazaborines. (Adapted from ref 2a.)

As Table 3 shows, **14** is about 24 kcal/mol lower in energy than **15**. The N−B−N connectivity remains significantly more stable than B−N−N in the pyridines, though the energy difference is about 50% lower in comparison to the protonated structures. To get closer to the observed biologically active molecules, we also calculated the pairs **16** and **17**, **18** and **19**, **20** and **21**. In all cases the molecules with N−B−N connectivity are more than 20 kcal/mol more stable than the ones with B−N−N.

Table 3. Structures 14−21 and Their Relative Energies

Structure #	Structure	E (kcal/mol)	Structure #	Structure	E (kcal/mol)
14		[0]	**18**		[0]
15		24	**19**		23
16		[0]	**20**		[0]
17		24	**21**		33

We also constructed structures isomeric to those shown in Table 3, now derived from deprotonated **7** and **8**. Surprisingly, these were calculated to be more stable than **6** as well as being more stable than the experimentally known pharmaceutically active molecules. For instance, structure **22**, shown below, was calculated to be more stable than its isomeric structure with N−B−N connectivity by 1 kcal/mol. When additional functional groups were added to **22** (guided by the known pyridine substitutions) to construct, for example, the isomeric structure of **18**, the initial stability order was restored (derivatives of **14** most stable); **18** is now more stable by about 5 kcal/mol.



22

It is fascinating that generally the less stable (thermodynamically) isomers are those that are known and pharmacologically active. It could be that their very instability makes them kinetically more reactive at some enzyme active sites. The mechanism of the diazaborine inhibiting process and the kinetic stability of these molecules is beyond the scope of this study.[2] We think it would be worthwhile, however, to synthesize the B−N-substituted pyridines **14**, **16**, **18**, **20**, and their isomers, derivatives of **7** and **8**, predicted, in some cases clearly so, as the more stable isomers. And for the cases where isomeric structures are known, it would be important to have experimental measures of their relative stability to test our theoretical predictions.

It is interesting that one can generate neutral analogues of **3** and **5** by fusing a naphthalene unit to the three carbons of the six-membered ring. **3** and **5** then become B−N derivatives of a phenalenium cation and anion respectively. In fact, two of the known compounds, Figure 3, are of this type.[3,8,11]

Isomers of $[C_3B_2NH_6]^-$. In the second part of this paper, we consider the anionic benzene analogue $[C_3B_2NH_6]^-$, formed conceptually by a condensation of allyl anion, $[C_3H_5]^-$, with NB_2H_5 **4**, in a six-membered ring. All possible positional isomers,

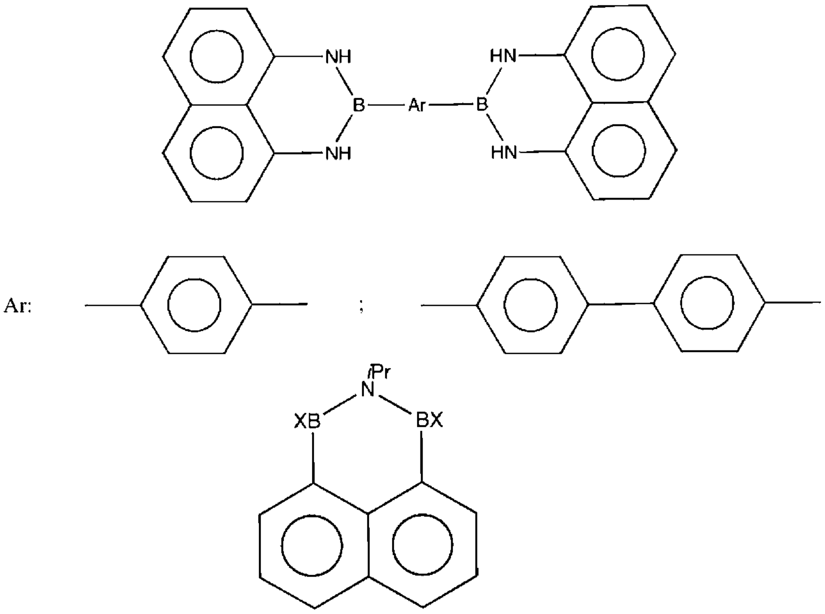
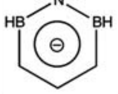
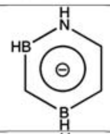
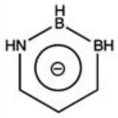
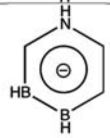
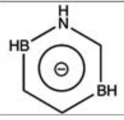
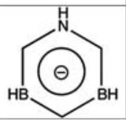


Figure 3. Known neutral analogues of **3** and **5** generated by fusing a naphthalene unit to the six-membered rings. Ar could also be blank, that is, a direct B−B bond.[8]

Table 4. Structures 5, 23−27 and Their Relative Energies

Structure #	Structure	E (kcal/mole)	Structure #	Structure	E (kcal/mole)
5		0	25		22
23		42	26		65
24		28	27		54

23−27, are drawn in Table 4 along with their relative energies. Now the B−N−B connectivity emerges as the most stable. To the best of our knowledge, no such B−N−B systems are known; in general, B−N−B systems are not common, and have not received much attention.[11,12]

Following an analysis similar to that in the first part of our paper, we compare **5** and **23** with various model systems in Figure 4.

Figure 4 shows the calculated bond lengths of **5** and **23** and, as references, benzene, borazine, allyl anion, **4**, and **28a,b** of the NB_2H_5 model. **28a** is the optimized H_2NBHBH_2 geometry, nonplanar. **28b** is a planar, rotated 90° with respect to the molecular plane, higher energy conformation of **28a**, for comparison with **4** and **5**.

The calculated bond lengths in **5** are reasonably equalized, and consistent with models of **4**, borazine, and allyl anion. On the other hand, signs of destabilization are clear in **23**, in that the C−C bonds are very different from the ones found in allyl anion, and that the N−B bond length does not follow that of N−B−B model **28a,b**. In examining the energetics of the model systems, **4** (planar) emerges as 30 kcal/mol below the optimum structure of its NBB isomer **28a** (nonplanar), while a planar **28b** is 4 kcal/mol higher.

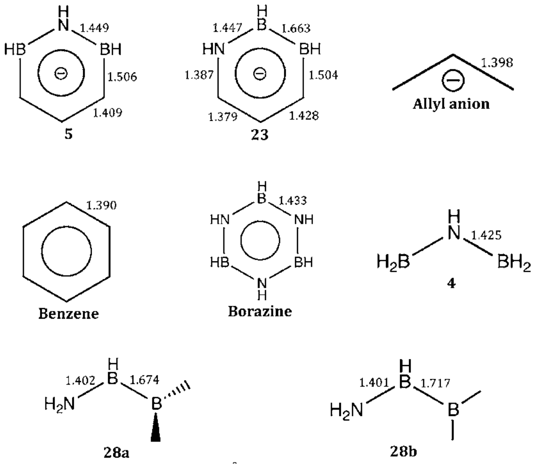
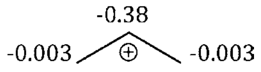


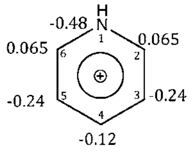
Figure 4. Calculated bond lengths (in Å) of **5** and **23** and, as references, benzene, borazine, allyl anion, and the NB_2H_5 models.

Allyl cation, isoelectronic to the NB_2H_5 models, has the NBO charge distribution shown in **29**. As expected for the two-π-electron system, the electron density peaks on the middle atom. If one were to make a substitution in allyl cation, the most electronegative atom(s) should go in the middle; the B−N−B substitution fits the predicted pattern best, N−B−B less so.



29

Proceeding to the other way we have found of explaining substitution, if we polarize benzene by substituting a nitrogen atom, we can predict which sites favor boron substitution by analyzing the electron density distribution of the substituted ring. **30** shows the charge distribution of cationic ring $[NC_5H_6]^+$, isoelectronic to benzene. Positions 2 and 6 have the lowest electron density, making them the most favored positions for substitution by less electronegative atoms. This is consistent with the energy order of the $[C_3B_2NH_6]^-$ isomers calculated. Analogous conclusions are reached if one begins with a B-substituted benzene (shown in **13** above).



30

Again, arguments based on either the inherent charge asymmetry in the allyl cation, or on the polarization caused by a heteroatom in a N- or B-substituted benzene ring explain the calculated preference for B−N−B over N−B−B connectivity in their molecules.

Strategies for Stabilizing 3 and 5. We have seen that among their isomers, **3** and **5** are quite stable. But could one stabilize these ions further by substitution?

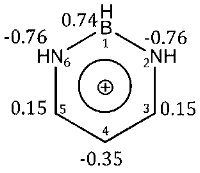
It is difficult to come up with a quantitative measure of stabilization. We think we can find one in characteristic acid and base reactions of these molecules. For the cations we will look at the heat of hydride addition reaction

$$C_3N_2BH_6^+ + H^- \rightarrow C_3N_2BH_7$$

and compare that heat for a substituted and unsubstituted molecule. For the anion we will examine a corresponding protonation,

$$C_3B_2NH_6^- + H^+ \rightarrow C_3B_2NH_7$$

31 shows the charge distribution in cation **3**. Positions 3 and 5 on the allyl segment have low electron density. This is a consequence of the proximity of these to N atoms, and the memory of the polarization of the π-system of an allyl cation. Substituting a π-electron donor group for the hydrogen at one (or both) of these positions should have a stabilizing effect on the molecule. An NH_2^- serves us as potential stabilizing substituent; our model is **32**, which has NH_2^- groups substituted at positions 3 and 5.



31

There are several possible positions for attack by H^-; we considered the ones that result in the most stable molecules, **33** and **34**. The hypothetical reactions that were used to generate **33** and **34** are shown in Figure 5, along with their calculated heats of reaction. Since hydride addition to **32** is much less exothermic than that of **3**, we reason that electron donor substitution had a stabilizing effect on **3**. The assumption here is that the NH_2^- substituent in **34** has little effect on the stability of the π-system remaining.

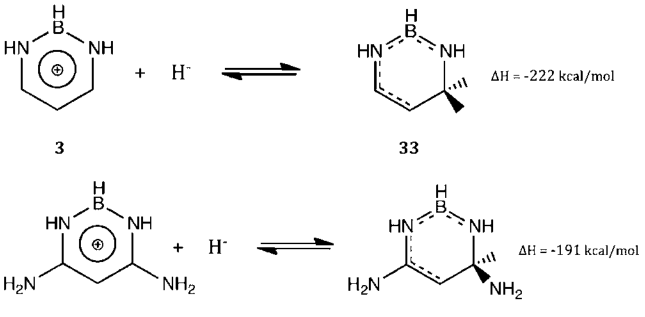
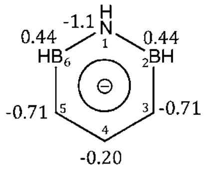


Figure 5. Hypothetical hydride addition reactions of **3** and the NH_2^--stabilized derivative **32**.

The charge distribution in anion **5**, shown in **35**, suggests π-acceptor substitutions at positions 3 and 5 for stabilization. **36** models this, with ^-CN groups as acceptors. Protonation of anions **5** and **36** would result in neutral molecules as shown in Figure 6, along with the corresponding heats of reaction. The lower heat of protonation of **36** is indicative of stabilization, again under the assumption of little effect of the remaining cyanide substituent on the π-systems.



35

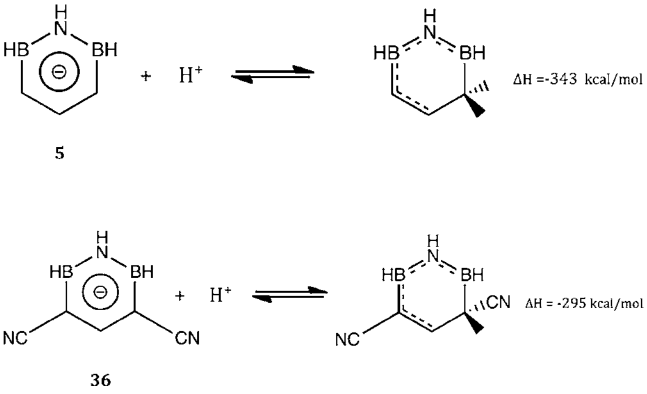


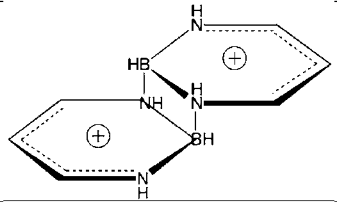
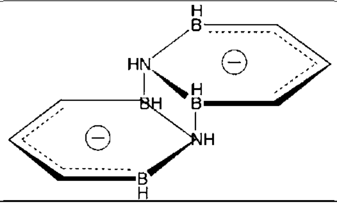
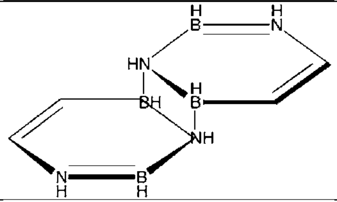
Figure 6. Hypothetical protonation reactions of **5** and the ^-CN-stabilized derivative **36**.

Note that the two heats of reaction, for H^+ and H^- addition, are very negative. This is because they are ionic recombinations; were solvents included in the calculations, the heats of reaction would be much reduced.

Dimerization Escape Routes for 3 and 5. In order to assess the stability of **3** and **5** further, we studied one escape route, dimerization. While these rings partake of some of the features of aromaticity, the boron atoms retain their π-acceptor character, through their only partially filled p-orbital. The N atom's π-type lone pair is only partially depleted by delocalization. Thus, one would expect B−N bond formation to feature in hypothetical dimerization, as indicated by structures **37**−**39**. Such a dimerization has been postulated in the literature for a B−N−B system.[12] As Table 5 shows, such dimerizations are computed to be highly endothermic.

Before we use these large endothermicities as a proof of stability of the monomers, we need to consider whether the

Table 5. Structures 37−39 along with Their Heats of Dimerization

Structure #	Structure	ΔH (kcal/mol)
37		109
38		106
39		30

charge repulsion in **37** and **38** could be the reason behind the instability of the dimers. So we also looked at the neutral dimer, **39**, isoelectronic to **37** and **38**, resulting from substituting two carbon atoms by boron or nitrogen in **37** and **38**, respectively. The heat of dimerization of **39** is calculated to be much less than that of the previous dimers, but is still positive. Thus, while Coulomb forces are clearly at work, these results point to a thermodynamic factor working against dimerization

■ CONCLUSION

The stabilities of the six-π-electron cationic $[C_3BN_2H_6]^+$ and anionic $[C_3NB_2H_6]^-$ systems were investigated theoretically. Among all the studied structures of $[C_3BN_2H_6]^+$, N−B−N connectivity corresponded to the most stable configuration. Based on the bond equalization criterion, such N−B−N systems could be said to be aromatic. Extending our calculations to the deprotonated analogues, we predicted three B−N-substituted pyridines more stable than the ones found to be biologically active. $[C_3NB_2H_6]^-$ follows a similar stability trend to that found in the cationic system, with B−N−B connectivity the most stable. To the best of our knowledge, no such B−N−B systems are known.

The stability of those systems was explained by analyzing at the charge distribution in allyl anion and cation, as well as that of heteroatom polarized benzenes.

We also investigated the means of further stabilization of these ions by donor or acceptor substitution, respectively, of the energetically most stable structures, **3** and **5**, and examined possible escape routes by means of dimerization. An obvious strategy for substituent stabilization is confirmed. And dimerization is endothermic.

We think it would be worthwhile to synthesize the most stable N−B−N and B−N−B structures, **3** and **5**, as well as the neutral B−N-substituted pyridines **14**, **16**, **18**, **20**, and their isomers, derivatives of **7** and **8**.

■ ASSOCIATED CONTENT

Supporting Information

Additional structures that were studied but not included in the main text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Saudi Aramco for supporting K.A. in pursuing his degree. We are grateful to Walter Siebert for making us aware of some research. Our work at Cornell was supported by NSF Research Grant CHE-0910623.

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