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Aromaticity of Diazaborines and Their Protonated Forms

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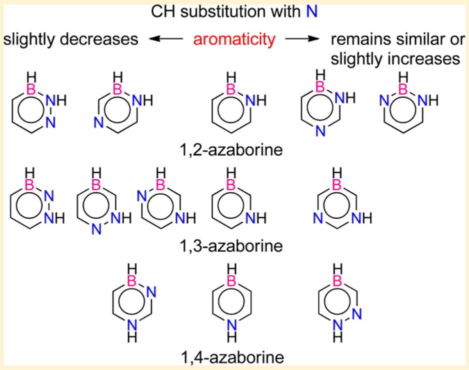
S *Supporting Information*

ABSTRACT: Substitution of a CH group in benzene with nitrogen has a little effect on its aromaticity (Wang et al., *Org. Lett.* **2010**, *12*, 4824). How does the same type of substitution affect aromatic character of the three isomeric azaborines? Does further protonation change aromaticity of diazaborines? This work is aimed at answering these questions. Such a knowledge should be of interest for further exploration and application of BN/CC isosterism. Aromaticity of diazaborines and their protonated forms is studied with the aid of four aromaticity indices, HOMA, $\mathrm{NICS}(0)_{\pi zz}$, PDI and ECRE. Generally, $\mathrm{NICS}(0)_{\pi zz}$ and PDI point to similar aromaticity of diazaborines and their parent azaborines, while HOMA and ECRE indicate some changes. Thus, aromaticity of 1,2-azaborine slightly decreases/increases when CH *meta*/*ortho*,*para* to B is substituted with nitrogen. Aromaticity of the most aromatic 1,3-azaborine remains almost unchanged when CH *meta* to B and N is replaced with nitrogen, and becomes slightly weaker when any other CH group is substituted with nitrogen. Replacement of the CH *ortho* to N in 1,4-azaborine does not change much its cyclic delocalization, while replacement of the CH *ortho* to B leads to smaller cyclic delocalization. Protonated forms are either of similar or decreased aromaticity compared with neutral molecules.



INTRODUCTION

Aromaticity is one of the most intriguing concepts in chemistry. Speaking about aromaticity, one often thinks of benzene, as a prototypical aromatic compound. It was isolated by Faraday in 1825, and its cyclic structure was proposed by Kekulé in 1865.[1] One year later, Kekulé began to write the cyclohexatriene formula, reminiscent of formula that we write today. In 1872, he suggested that benzene double bonds rapidly exchange their places, which produces a symmetric structure.[1b] Decades later, Hückel and Pauling explained benzene's structure and enhanced stability on the basis of quantum mechanical molecular-orbital (MO) and valence-bond (VB) theories, introducing the concept of electron delocalization.[2,3]

According to our traditional view, an aromatic compound is characterized as a stable, cyclic conjugated system with (nearly) equal bond lengths, tending to retain its cyclic delocalization by resisting addition reactions. The system is made such because of the tendency of π electrons to delocalize. However, a controversy about this topic has been arisen by evidence that benzene's symmetric structure is not caused by π electrons. It has been shown that the π electrons' delocalization is a consequnce of σ electrons' tendency to form a symmetric structure.[4] In any case, it is the cyclic conjugation of the π electrons which is responsible for enhanced stability of benzene. However, aromaticity and stability do not always go hand in hand and there are examples when the most aromatic isomer is not the most stable one.[5−9] Thus, a molecule can be characterized as aromatic when stability of its π electron system exceeds stability of π electrons in an appropriate acyclic molecule(s). On the basis of the prototype, benzene, four main aromaticity criteria have been developed: structure,[10,11] energy,[10,12] magnetic properties[10,13] and electron delocalization.[14] They may serve well for "classical" (anti)aromatic compounds, but the more usual lack of correlation has led to suggestions that aromaticity should be considered as a multidimensional phenomenon,[15,16] objected by other authors.[17]

Replacement of one or more CC units in benzene or other aromatic hydrocarbons by an isoelectronic, but polar BN unit alters the electronic structure of a system, thus allowing one to tune and control various properties of molecules.[6,9,18−22] Compounds having one BN unit and an additional N atom contained in a six-membered ring (diazaborines), have also been synthesized and characterized, in neutral or cationic forms.[23−25] These compounds were examined as boron-containing purine analogues,[23a] for their biological activities[23b−e] and for application in material science.[25a] Recently, relative stabilities of the six isomeric cationic NBN analogues of benzene were studied theoretically.[26] Despite the fact that both neutral and cationic NBN containing six-membered heterocycles are 6π-electron species, no aromaticity study on this type of compounds has been performed (the only data related to aromaticity are NICS(0) and NICS(1) values calculated for cationic N−B−N containing derivative, which indicated aromatic character of the ring[25c]). By contrast, influence of

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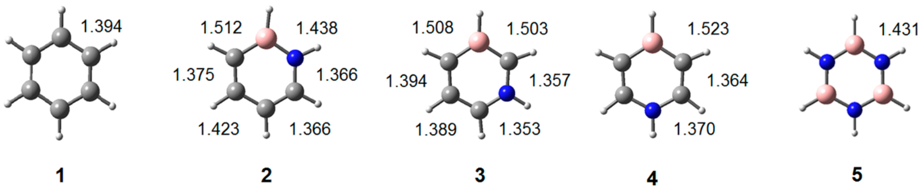


Figure 1. Optimized structures and calculated BC, BN, CC and CN bond lengths (Å) of benzene (**1**), 1,2-azaborine (**2**), 1,3-azaborine (**3**), 1,4-azaborine (**4**) and borazine (**5**).

substitution of one or more benzene carbon atoms by nitrogen on its aromatic character has been extensively studied.[27] Aromaticity of BN containing systems is important for understanding of their structure, physical properties, chemical reactivity and potential applications of BN/CC isosterism. In a recent paper, we have studied relative aromaticity of the three isomeric 1,2-, 1,3- and 1,4-azaborines.[9] Herein, we study how an additional nitrogen atom affects their aromaticity. This study comprises ten isomeric neutral diazaborines and six isomers of their protonated forms.

■ METHODS

Since comparison of aromaticity of a group of similar compounds can lead to divergent results,[15,16] we used all four criteria to characterize aromatic character of examined (protonated) diazaborines.

As a structural criterion, we used the HOMA index,[11] which is defined as shown in eq 1:

$$\text{HOMA} = 1 - \frac{\alpha}{n}\sum_{i}^{n}(R_{\text{opt},j} - R_{j,i})^2 \qquad (1)$$

In the equation, α is an empirical constant chosen to give HOMA = 0 for a nonaromatic system and HOMA = 1 for system where all bonds are equal to an optimal bond length (R_{opt}), n is the number of bonds taken into summation, R_i is an individual bond length and j represents the type of the bond. The following α/R_{opt} (Å) have been recommended and were used herein for HOMA calculations: 118.009/1.4378 (BC), 72.03/1.402 (BN), 257.7/1.388 (CC), 93.52/1.334 (CN) and 130.33/1.309 (NN).[11] In addition to HOMA index, we also discuss individual bond lengths in three ways, depending on a system in question. In fact, when one CH group in an azaborine is replaced with nitrogen, four bond types remain the same and two new bonds are formed. Thus, we compare: (1) bond length changes of the four bond types which remain the same, (2) bond length differences between two newly formed bonds, if they are of the same type, and (3) bond lengths of two newly formed bonds with optimal bond lengths used for HOMA calculations, when the type of two new bonds differ. Since bond length equalization and bond length closeness to optimal length of an aromatic system are considered as an indication of aromaticity (the basis of HOMA, as well), such comparisons give an idea about structural changes occurring on going from azaborine to diazaborine, the π-electron distribution in diazaborine system, and deviation of bond lengths from optimal lengths of an aromatic molecule.

As a magnetic criterion, the most refined NICS(0)$_{\pi zz}$ index was used. It measures the π electron contributions to the out-of-plane component of the magnetic shielding, and is more relevant to aromaticity studies than other NICS indices.[28] Significantly negative (shielded) NICS values indicate a diatropic ring current and aromaticity, while positive (deshielded) values denote a paratropic ring current and antiaromaticity.[29]

The *para*-delocalization (PDI) index was employed as an electron delocalization index.[14] It is derived from Bader's Atoms in Molecules (AIM) theory[30] and represents the average of delocalization indices (DI) of *para* related atoms in a given six-membered ring. The underlying idea of this index is that the delocalization of the electron density in benzene is greater between *para* related carbons, than between *meta* related carbons.[14] The delocalization index (DI) measures the number of electrons which are delocalized between two atoms. The PDI value inceases with increasing aromaticity of a ring.

As an energetic criterion, we used the extra cyclic resonance energy (ECRE), which measures extra stabilization of a cyclic system relative to an open-chain analogue having the same number and type of conjugations.[31] It represents difference between resonance energies (RE) of cyclic molecule and acyclic reference system(s). For benzene, for example, reference compound may be 1,3,5,7-octatetraene[31] or three butadienes.[27] The reference structures considered herein are suitably BNN substituted butadienes, taken in their planar forms and *s-cis* conformations to conform to the conformational arrangement of respective fragments in cyclic molecules. Although planar forms of many reference molecules are transition structures with one imaginary frequency corresponding to the out-of-plane rotation around the formal single bond, planarity ensures the σ/π separation, which was necessary for ECRE calculations (see Computational Details for more information). Positive ECRE values mean stabilization of a system by cyclic electron delocalization relative to acyclic reference molecule(s), while negative values denote destabilization of a system.

■ COMPUTATIONAL DETAILS

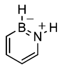
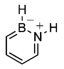
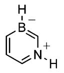
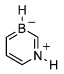
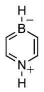
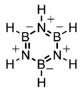
All calculations have been done at the B3LYP/6-311+G(d,p) level of theory.[32,33] Geometries of all molecules were fully optimized using Gaussian 09 program package.[34] All cyclic structures contained no imaginary frequencies. Five-decimal bond lengths used for HOMA calculations are given in Table S1 in the Supporting Information. NICS values were calculated by employing the GIAO method[35] and separated into contributions from natural localized molecular orbitals by using the natural chemical shielding-natural bond orbital (NCS-NBO) analysis.[36] ECREs were calculated as a difference between vertical resonance energies (VRE)[37] of cyclic system and sum of VREs of three acyclic reference molecules. VREs were calculated by disabling the $\pi \rightarrow \pi^*$ interactions employing the NBO deletion analysis[38] to resonance structures with three double bonds in cyclic molecules and with two double bonds in acyclic reference systems. Average ECRE values are based on relative weights of the two resonance structures of cyclic molecules, having three conjugated double bonds. The natural resonance theory (NRT) analysis[38] within the NBO program[39] was used to estimate resonance weights of individual resonance structures of the studied molecules. From these, the weights of the two structures with three double bonds were chosen to calculate their relative weight. DIs were derived from the Bader's Atoms in Molecules (AIM) theory,[30] using AIMAll program package.[40] Wave function files were created at the HF/6-311+G(d,p) level on B3LYP/6-311+G(d,p) optimized geometries. The PDIs calculated in this way predicted 1,3-azaborine/1,4-azaborine to be the most/least aromatic,[6] which is consistent with the previous examination of molecular geometries and bond lengths of azaborines[41] and later study based on ECRE and magnetic properties.[9]

■ RESULTS AND DISCUSSION

Figure 1 displays structures and calculated bond lengths of benzene (**1**), three isomeric azaborines **2**−**4** and borazine (**5**), for comparison purposes. The latter is considered to be nonaromatic or at most weakly aromatic.[8,20] Their respective ECRE, NICS(0)$_{\pi zz}$, PDI and HOMA values are listed in Table

1. The ECRE and NICS were discussed in detail in ref 9 and predicted the following aromaticity order: **1** > **3** > **2** > **4** > **5**.

Table 1. Calculated Extra Cyclic Resonance Energies (ECRE), NICS(0)$_{\pi zz}$, PDI and HOMA Values for Benzene (1), Three Isomeric Azaborines 2–4 and Borazine (5)[a]

Molecule		ECRE (kcal/mol)	NICS(0)$_{\pi zz}$ (ppm)	PDI (electrons)	HOMA
	**1**	93.99	−35.77	0.099	0.990
	**2-A** (93.1%)[b]	49.15 (55.69)[c]	−25.42	0.061	0.001
	**2-B** (6.9%)[b]	144.19 (55.69)[c]			
	**3-A** (51%)[b]	68.56 (76.66)[c]	−31.15	0.065	0.411
	**3-B** (49%)[b]	85.10 (76.66)[c]			
	**4**	33.51	−24.38	0.036	−0.115
	**5**	20.40	−7.87	0.009	0.940

[a] ECRE and NICS were taken from ref 9. [b] Relative weights of the two resonance structures having three double bonds. [c] Average values, obtained on the basis of relative weights of the two resonance structures with three double bonds.

The PDIs agree with this order and with those calculated previously.[6] The calculated HOMA classifies **3** as less aromatic than benzene, **2** as almost nonaromatic, while it becomes negative for **4**, which, in fact, shows the largest deviations of bond lengths from optimal values. Because of borazine's symmetric structure, HOMA incorrectly assigns its aromaticity as being higher than that of azaborines. In addition, HOMA values also depend on the choice of reference bond lengths and normalization constant, α.[11]

Structures of the studied diazaborines and their protonated forms are shown in Figure 2, along with the calculated bond lengths and their relative electronic energies, which are corrected for zero-point energies. Structures **6**–**9** are derived from 1,2-azaborine (**2**) by substitution of one CH unit by nitrogen. In the same manner, structures **10**–**13** are obtained from 1,3-azaborine (**3**) and structures **14** and **15** from 1,4-azaborine (**4**). Cationic forms, denoted as **6**-**15**-H$^+$, are obtained by H$^+$ addition to the neutral nitrogen atom in **6**–**15**. The most stable neutral diazaborine is **9**, having the N–B–N connectivity and the least stable one is **11** with the B–C–N–N linkage and BH and NH in 1,3-position (49.2 kcal/mol less stable **9**). Among isomers of azaborines[6,9] and diazadiborines,[18] those having the B–N and B–N–B–N sequences are also the most stable ones. Comparison of relative stabilities of tautomeric pairs, **6**/**10**, **7**/**14** and **8**/**13**, shows that structures having the BH–NH bond are by 12–19 kcal/mol more stable than those with the BH–N linkage. In the case of the tautomeric pair **11**/**15**, the one with the 1,4-BH,NH arrangement is by 2.5 kcal/mol lower in energy. Protonation increases difference in relative energies between isomers, but keeps the same relative order, except that **10**-H$^+$ becomes more stable than **12**-H$^+$, which is opposite to the stability order of their neutral forms. The least stable **11**/**15**-H$^+$ is by 78 kcal/mol higher in energy than the most stable **9**-H$^+$. The relative energies of cationic forms concur with those calculated previously.[26] Only compounds with the B–N–N, B–N–C–N and N–B–N linkages are known experimentally.[23–25]

In the following, we discuss aromaticity of the studied molecules, that is a degree of their stabilization by cyclic delocalization of 6 π electrons. This will be compared with their relative stabilities.

Table 2 lists calculated VRE, ECRE, NICS(0)$_{\pi zz}$, PDI and HOMA values for the studied (protonated) diazaborines and VREs for acyclic reference systems. Each cyclic molecule is represented by resonance structure involving three double bonds. For symmetric molecules **9**-H$^+$ and **12**-H$^+$, two equally populated resonance structures may be written, and only one is shown in the table. According to NRT, all cationic species except the two mentioned, **6** and **9** are characterized by only one structure with three double bonds. In the case of other compounds, relative weights of two such structures are given in the table. They are denoted by a capital letter. The letter **A** means that the given structure is also the leading resonance structure, the letter **B** means that the given structure's weight comes next to the leading one, and the letters **C**, **D** and **E** mean that the given resonance structure is at the third, the fourth and the fifth place according to its weight, as obtained by NRT analysis. Weights of individual resonance structures with respect to all resonance structures defined by NRT are included in discussion. All reference molecules, used for ECRE calculations, are shown as resonance structures with two double bonds, in the table.

Aromaticity of 6–9, Derived from 1,2-Azaborine (2). Replacement of CH, *meta* to B and *ortho* to N in **2**, with nitrogen to form **6** decreases the BN bond length by 0.013 Å, while changes of BC and two CC bonds do not exceed 0.01 Å. The newly formed CN bond (1.307 Å) and NN bond (1.349 Å) are by 0.027 and 0.04 Å shorter and longer, respectively, than optimal lengths used for HOMA calculations (1.334 Å for CN bond, 1.309 for NN bond). A slight decrease in the BN bond length indicates a somewhat increased NH to BH electron donation. The mentioned structural changes lead to the negative HOMA value, −0.295. ECRE decreases, as well, by 10.55 kcal/mol relative to average ECRE of **2**, while NICS and PDI are almost unchanged. Thus, it appears that aromaticity of **6** is either similar or somewhat weaker than that of **2**, with the π-electron distribution consisitent with its leading resonance structure **6-A** (54.9% of all resonance structures). According to all four criteria, protonated molecule **6**/**10**-H$^+$ is less cyclically delocalized than the neutral one, and it features the longest NN bond (1.353 Å) among all molecules studied.

Replacement of the CH group, *para* related to boron in **2**, by nitrogen to give **7** results in insignificant changes in the CC, BC, BN and CN bond lengths. The two newly formed CN bonds differ in length, the N(5)C(6) having more double bond character (1.299 Å) and the C(4)N(5) bond (1.373 Å), along with the N(1)C(6) bond (1.362 Å), more single bond character. This is consistent with the leading resonance structure **7-A**, shown in Table 2 and in Figure 3 (37.1% of all resonance structures). Weights of resonance structures **7-B** and **7-C** are smaller and similar (Figure 3). The structural HOMA index and ECRE point to a (slight) increase in electron

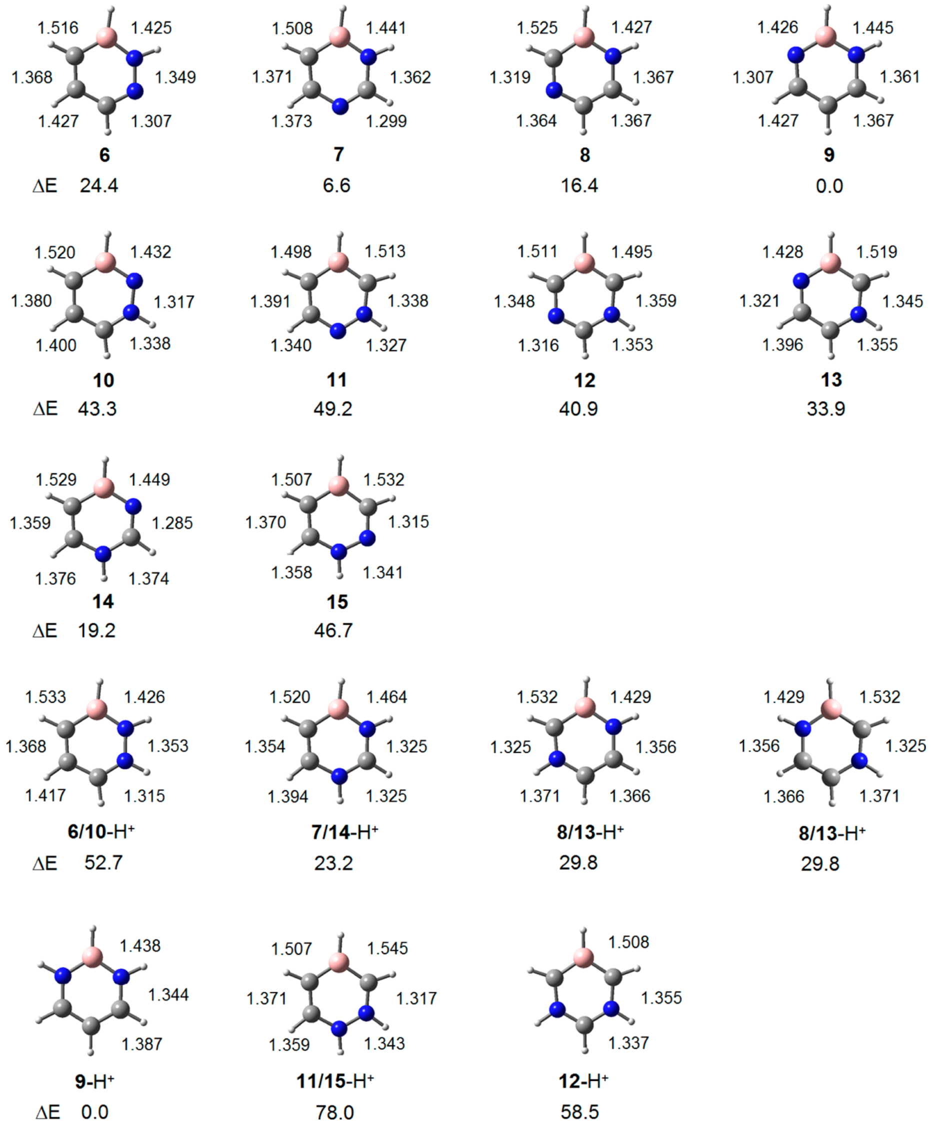


Figure 2. Optimized structures, calculated BC, BN, CC, CN and NN bond lengths (Å) and ZPE corrected relative energies (kcal/mol) of **6**−**15** and their protonated forms **6**-**15**-H$^+$. Cation **8**/**13**-H$^+$ is shown in two orientations to enable a direct comparison with both **8** and **13**.

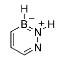
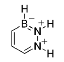
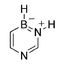
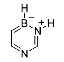
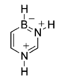
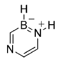
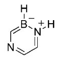
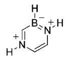
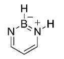
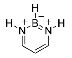
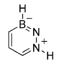
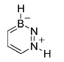
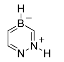
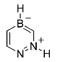
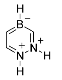
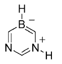
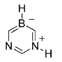
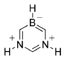
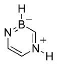
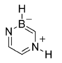
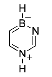
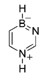
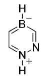
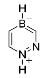
delocalization, relative to **2**. By contrast, both PDI and absolute NICS slightly decrease. On the basis of these results, it seems that aromaticity of **7** is similar to that of **2**, or just slightly larger.

Protonation of nitrogen atom in **7** to form **7**/**14**-H$^+$, localizes the π-electron distribution in the N(1)—B(2)—C(3)═C(4)—N(5) moiety, as evident from comparison of bond lengths in **7**/**14**-H$^+$ and **7** (Figure 2; the N(1)B(2), B(2)C(3) and C(4)N(5) bonds increase their lengths by 0.012−0.023 Å, while the C(3)C(4) bond shortens by 0.017 Å; the N(1)B(2) bond (1.464 Å) and the C(4)N(5) bond (1.394 Å) are the longest among all molecules studied). On the contrary, delocalization in the N(5)C(6)N(1) fragment is high and two CN bonds have the same length (1.325 Å). On the basis of structural considerations and all four indices (Table 2), aromatic character of cationic **7** is reduced relative to that of neutral **7**.

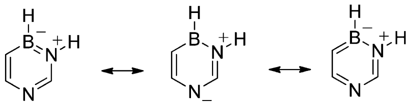
When nitrogen replaces the CH group oriented *meta* to BH and *para* to NH in **2** to give **8**, aromaticity indices change in a similar way as in the case of formation of **6**: HOMA becomes negative, −0.124 (though less than in the case of **6**), PDI and NICS increase very slightly and average ECRE decreases by 9.28 kcal/mol. Bond lengths consideration (Figures 1 and 2) shows that, similarly as in **6**, NH to BH lone pair donation slightly increases, while boron receives less electron density from the other side of the ring, compared with **2** (the BN bond length decreases by 0.011 Å and the BC bond length increases by 0.013 Å). The BC bond is long (1.525 Å), by only 0.022 Å shorter than the BC single bond in BH_2-CH_3 (1.5472 Å).[11] The CC and CN bonds retain almost the same lengths as in **2**. The bond length alternation between the two newly formed CN bonds, C(3)N(4) and N(4)C(5), is similar to the bond length alternation of the corresponding CC bonds in **2**, C(3)C(4) and C(4)C(5), 0.045 and 0.048 Å, respectively. Our impression is that aromaticity of **8** is either similar or somewhat weaker than that of **2**. In view of NRT, **8** is characterized by one leading structure, **8-A**, the weights of others being less than 7% with respect to all resonance structures.

Protonation of **8** to **8**/**13**-H$^+$ changes bond lengths by ≤0.011 Å. The structural HOMA index becomes more negative (−0.124 in **8**, −0.277 in **8**/**13**-H$^+$). Absolute NICS and PDI change negligibly, while ECRE increases by 19.19 kcal/mol relative to the average ECRE of **8**. It is even larger than ECRE

Table 2. Calculated Vertical Resonance Energies of Cyclic and Acyclic Structures (VRE$_{cyclic}$ and VRE$_{acyclic}$), Extra Cyclic Resonance Energies (ECRE), NICS(0)$_{\pi zz}$, PDI and HOMA Values for the Studied Molecules

Molecule		VRE$_{cyclic}$ (kcal/mol)	Reference molecules	VRE$_{acyclic}$ (kcal/mol)	ECRE (kcal/mol)	NICS(0)$_{\pi zz}$ (ppm)	PDI (electrons)	HOMA
	**6-A**	105.99	$H_2C=CH-CH=NH$ $H_2C=CH-BH^-=NH_2^+$ $H_2C=N-NH^+=BH_2^-$	21.83 16.72 22.30	45.14	−25.48	0.064	−0.295
	**6/10-A-**H$^+$	109.68	$H_2C=CH-CH=NH_2^+$ $H_2C=CH-BH^-=NH_2^+$ $H_2C=NH^+-NH^+=BH_2^-$	45.41 16.72 29.72	17.83	−22.59	0.049	−0.566
	**7-A** (74.7%)[a]	118.77 (158.57)[b]	$H_2C=CH-N=CH_2$ $HN=CH-NH^+=BH_2^-$ $H_2C=CH-BH^-=NH_2^+$	22.42 30.34 16.72	49.30 (74.51)[b]	−23.76	0.049	0.117
	**7-C** (25.3%)[a]	275.87 (158.57)[b]	$HN=CH-CH=BH_2^-$ $H_2C=BH^--NH^+=CH_2$ $H_2C=N-CH=NH_2^+$	52.03 33.42 41.59	148.83 (74.51)[b]			
	**7/14-A-**H$^+$	132.13	$H_2C=CH-NH^+=CH_2$ $H_2C=CH-BH^-=NH_2^+$ $H_2N^+=CH-NH^+=BH_2^-$	23.19 16.72 70.51	21.72	−20.18	0.036	−0.498
	**8-A** (91.6%)[a]	113.43 (111.42)[b]	$H_2C=CH-N=CH_2$ $H_2C=CH-NH^+=BH_2^-$ $HN=CH-BH^-=NH_2^+$	22.42 26.98 12.05	51.99 (46.41)[b]	−26.08	0.068	−0.124
	**8-C** (8.4%)[a]	89.45 (111.42)[b]	$H_2C=N-CH=BH_2^-$ $H_2C=BH^--NH^+=CH_2$ $HN=CH-CH=NH_2^+$	45.34 33.42 25.07	−14.38 (46.41)[b]			
	**8/13-A-**H$^+$	125.43	$H_2C=CH-NH^+=CH_2$ $H_2C=CH-NH^+=BH_2^-$ $H_2N^+=CH-BH^-=NH_2^+$	23.19 26.98 9.66	65.60	−25.72	0.065	−0.277
	**9-A**	124.63	$H_2C=CH-CH=NH$ $H_2C=CH-NH^+=BH_2^-$ $H_2C=N-BH^-=NH_2^+$	21.83 26.98 17.77	58.06	−23.52	0.056	0.587
	**9-A-**H$^+$	177.97	$H_2C=CH-CH=NH_2^+$ $H_2C=CH-NH^+=BH_2^-$ $H_2C=NH^+-BH^-=NH_2^+$	45.41 26.98 11.64	93.94	−21.84[c]	0.053	0.898
	**10-A** (66.6%)[a]	173.82 (161.45)[b]	$H_2C=CH-CH=NH_2^+$ $H_2C=CH-BH^-=NH$ $H_2C=NH^+-N=BH_2^-$	45.41 13.81 67.47	47.13 (23.97)[b]	−29.59	0.066	0.107
	**10-C** (33.4%)[a]	136.79 (161.45)[b]	$H_2C=CH-CH=BH_2^-$ $H_2C=CH-NH^+=NH$ $H_2C=BH^--N=NH_2^+$	47.48 33.09 78.42	−22.19 (23.97)[b]			
	**11-B** (60.9%)[a]	185.72 (187.64)[b]	$HN=CH-CH=BH_2^-$ $H_2C=BH^--CH=NH_2^+$ $H_2C=N-NH^+=CH_2$	52.03 62.47 18.08	53.14 (28.31)[b]	−30.25	0.056	0.409
	**11-C** (39.1%)[a]	190.62 (187.64)[b]	$H_2C=CH-BH^-=CH_2$ $H_2B^-=CH-NH^+=NH$ $H_2C=CH-N=NH_2^+$	17.76 126.59 56.64	−10.13 (28.31)[b]			
	**11/15-B-**H$^+$	206.28	$H_2N^+=CH-CH=BH_2^-$ $H_2C=BH^--CH=NH_2^+$ $H_2C=NH^+-NH^+=CH_2$	140.64 62.47 15.23	−12.05	−24.32	0.040	−0.233
	**12-A** (53.7%)[a]	210.37 (219.60)[b]	$HN=CH-BH^-=CH_2$ $H_2C=NH^+-CH=BH_2^-$ $H_2C=N-CH=NH_2^+$	18.34 85.55 41.59	64.89 (84.73)[b]	−31.17	0.072	0.454
	**12-B** (46.3%)[a]	230.33 (219.60)[b]	$H_2C=N-CH=BH_2^-$ $H_2C=BH^--CH=NH_2^+$ $HN=CH-NH^+=CH_2$	45.34 62.47 14.74	107.78 (84.73)[b]			
	**12-B-**H$^+$	236.38	$H_2C=NH^+-CH=NH_2^+$ $H_2C=NH^+-CH=BH_2^-$ $H_2C=BH^--CH=NH_2^+$	24.68 85.55 62.47	63.68	−29.91[c]	0.069	0.403
	**13-A** (55.2%)[a]	198.95 (214.78)[b]	$H_2C=CH-NH^+=CH_2$ $H_2C=CH-N=BH_2^-$ $HN=BH^--CH=NH_2^+$	23.19 47.93 31.96	95.87 (101.11)[b]	−29.89	0.067	0.139
	**13-B** (44.8%)[a]	234.29 (214.78)[b]	$HN=CH-CH=NH_2^+$ $H_2C=NH^+-CH=BH_2^-$ $H_2C=N-BH^-=CH_2$	25.07 85.55 16.10	107.57 (101.11)[b]			
	**14-D** (51.2%)[a]	230.70 (211.39)[b]	$H_2N^+=CH-CH=BH_2^-$ $HN=CH-NH^+=CH_2$ $H_2C=N-BH^-=CH_2$	140.64 14.74 16.10	59.22 (45.29)[b]	−21.88	0.034	−0.539
	**14-E** (48.8%)[a]	191.15 (211.39)[b]	$H_2C=CH-NH^+=CH_2$ $H_2B^-=N-CH=NH_2^+$ $H_2C=CH-BH^-=NH$	23.19 123.48 13.81	30.68 (45.29)[b]			
	**15-B** (79.2%)[a]	191.63 (212.53)[b]	$H_2N^+=CH-CH=BH_2^-$ $H_2C=N-NH^+=CH_2$ $H_2C=BH^--CH=NH$	140.64 18.08 18.34	14.57 (23.92)[b]	−25.62	0.040	−0.069
	**15-D** (20.8%)[a]	292.10 (212.53)[b]	$H_2C=CH-BH^-=CH_2$ $H_2C=CH-NH^+=NH$ $H_2B^-=CH-N=NH_2^+$	17.76 33.09 181.71	59.54 (23.92)[b]			

[a] Relative weights of the two resonance structures with three double bonds. [b] Obtained on the basis of relative weights of the two resonance structures with three double bonds. [c] NICS(0)$_{\pi xx}$ in this case.



37.1% **7-A** 13.1% **7-B** 12.6% **7-C**

Figure 3. Resonance structures of **7**, obtained by NRT analysis, having weights >10%. Given percent values refer to weights with respect to all resonance structures.

calculated for **2**. This is in contrast to ECRE behavior when **6** and **7** are protonated. Although, the current data do not allow one to reach to a conclusion, we offer an explanation for the increase in ECRE. Thus, cationic N(4) enhances the amount of positive charge next to the already electron deficient boron atom. To recover the lost electron density, π system increases its cyclic delocalization.

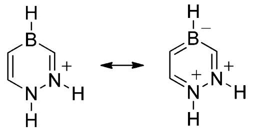
If nitrogen replaces the CH group next to boron in **2** to give **9**, bond lengths in the fragment BHNHCCC change negligibly, < 0.007 Å. The new CN bond is by 0.027 Å shorter than the CN$_{opt}$ (1.334 Å). The N−BH bond is shorter than the BH−NH bond, by 0.019 Å. According to NRT, this system is characterized by one leading structure shown in Table 2, 54.9% of all resonance structures, while weights of other individual resonance structures do not exceed 8%. The PDI and absolute NICS of **9** slightly decrease relative to **2**, while ECRE slightly increase pointing to a little change in aromaticity. On the other hand, HOMA increases significantly, from 0.001 in **2** to 0.587 in **9**. Hence, aromaticity of **9** appears to be similar or slightly increased relative to **2**.

Protonation of **9** to **9**-H$^+$ creates a symmetric structure, with two equally populated resonance structures, one of which is shown in Table 2. Because of symmetry (C_{2v}), there is no bond length alternation between bonds of the same type. The lengths of the CC bonds almost reach a value of 1.388 Å characteristic of an aromatic system, while the CN bonds are by only 0.01 Å larger than the CN$_{opt}$ bond length (1.334 Å). The BN bonds, however, are by 0.036 Å longer than the BN$_{opt}$ bond length (1.402 Å).[11] Thus, the HOMA value for this system is large, 0.898. The PDI changes insignificantly relative to the value of neutral **9**, absolute NICS drops slightly, but ECRE (93.94 kcal/mol) reaches the value calculated for benzene (93.99 kcal/mol). The bond length consideration, however, implies an unequal delocalization which is more pronounced in the NCCCN part, than in the NBN one.

Relative Aromaticity of 6−9. Apparently, the present data are not conclusive. Generally, PDI and NICS indicate similar aromatic character of **2** and **6**−**9**, while HOMA and ECRE indicate (slight) decrease/increase in aromaticity of **6**,**8**/**7**,**9**. The latter can be explained by an analysis of leading resonance structures of **6**-**9** and relative orientation of the C═N and B−N bonds. Thus, if the C═N bond directs more electron density toward NH than to BH (structures **6**-**A** and **8**-**A**), the system becomes more localized than when electron density is more directed toward BH than to NH (structures **7**-**A** and **9**-**A**). In the first two cases, two long bonds are formed, NN and BC, respectively, with smaller *π*-electron crossing over them, while the BN bonds are shorter than in **7** and **9**. According mainly to HOMA, the relative aromaticity order of **6**−**9** concurs with their relative stability order of **9** > **7** > **8** > **6**.

Aromaticity of 10−13, Derived from 1,3-Azaborine (3). Let us begin a discussion with structural changes accompanying the replacement of a CH group, *ortho* to both B and N in **3**, with nitrogen to form **10** (Figures 1 and 2). The CC bond length alternation increases from 0.005 Å in **3** to 0.02 Å in **10**, that is the C(4)C(5) bond shortens by 0.014 Å and C(5)C(6) bond lengthens by 0.011 Å. The length of the B(3)C(4) bond is increased by 0.012 Å and that of the N(1)C(6) bond decreased by 0.015 Å. This analysis points to a certain degree of increased electron localization, relative to **3**, also correctly followed by a decrease in the HOMA value, from 0.411 in **3** to 0.107 in **10** (Tables 1 and 2). PDI is almost the same as in **3**, absolute NICS drops only slightly (by ∼1.6 ppm) and still remains significantly negative, while ECRE significantly decreases, by 52.69 kcal/mol. Considering all these results, **10** can be characterized as being of similar (NICS and PDI) or somewhat weaker aromaticity than **3** (HOMA and ECRE), seemingly overestimated by ECRE. All four aromaticity indices (Table 2), as well as bond length changes occurring upon protonation of **10** to **6**/**10**-H$^+$ (Figure 2) agree that **6**/**10**-H$^+$ is more localized than **10**, and is best represented by its leading resonance structure **6**/**10**-**A**-H$^+$ shown in Table 2.

Substitution of the C(6)H group in **3** by nitrogen to give **11** increases the C(2)B(3) bond length and decreases the B(3)C(4) bond length in **3** by 0.01 Å, thus increasing the BC bond length alternation from 0.005 Å in **3** to 0.015 Å in **11** (Figures 1 and 2). The length of the N(1)C(2) bond in **3** shortens by 0.019 Å and becomes comparable with the CN_{opt} bond length (1.338 and 1.334 Å, respectively). The new C(6)N(1) bond in **11** is of comparable length, 1.340 Å. The C(4)C(5) bond in **3** retains almost the same length, which is close to the CC_{opt} bond length (1.388 Å), while the NN distance in **11** (1.327 Å) is somewhat increased relative to NN_{opt} (1.309 Å).[11] Structural HOMA index of **11** (0.409) is almost the same as that of **3** (0.411). The NICS and PDI are also comparable (slightly smaller) to those of **3**, while ECRE drops by 48.35 kcal/mol pointing to a decrease in the strength of the *π*-electron delocalization. On the basis of all presented data, **11** seems to be of similar or slightly weaker aromatic compared to **3**.



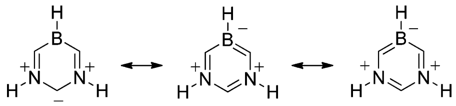
40%
11/**15**-**A**-H$^+$

18%
11/**15**-**B**-H$^+$

Figure 4. Resonance structures of **11**/**15**-H$^+$, obtained by NRT analysis, having weights of more than 10%. Given percent values refer to weights with respect to all resonance structures.

Protonation of **11** to form **11**/**15**-H$^+$ stabilizes **11**/**15**-**A**-H$^+$ resonance structure (Figure 4), as evident from an analysis of accompanying bond length changes (Figure 2). The C(3)B(4) bond, corresponding to the C(2)B(3) bond in azaborine **3**, is almost a single bond with the length of 1.545 Å (experimentally determined BC bond length in CH_3−BH_2 is 1.5472 Å[11]). This localization is followed by decrease in HOMA (from 0.409 in **11** to −0.233 in **11**/**15**-H$^+$), PDI (from 0.056 in **11** to 0.04 in **11**/**15**-H$^+$) and NICS (from −30.25 ppm in **11** to −24.32 ppm in **11**/**15**-H$^+$). Negative ECRE value of −12.05 kcal/mol also agrees with the *π*-electron localization and indicates that cyclic delocalization destabilizes the system, relative to acyclic reference molecules. In fact, **11**/**15**-H$^+$ appears to consist of two separately delocalized fragments, N(2)C(3) (corresponding to the N(1)C(2) bond in azaborine **3**) and B(4)C(5)-C(6)N(1), with little electron crossing between them over the C(3)−B(4) and N(1)−N(2) bonds (at least less than in acyclic reference systems). This can explain negative ECRE.

Compound **12** is obtained by substitution of the CH *meta* to B and N in **3** by nitrogen. Upon this substitution, the two BC bonds and the two CN bonds change their lengths negligibly, by <0.008 Å, while the two new CN bonds differ in lengths by 0.032 Å. The NICS value of **12** is almost the same as that of **3**, PDI and HOMA just slightly larger, and ECRE is increased by ∼8 kcal/mol. These data indicate similar aromaticity of **12** compared with **3**, or slightly larger. Protonation of **12** creates the C_{2v} symmetric structure **12**-H$^+$ with no bond length alternation between symmetrically disposed bonds. The two nonsymmetrically oriented CN bonds differ in length by 0.018 Å, those in the NCN fragment being the shorter ones. An NRT analysis slightly prefers structure **12**-**A**-H$^+$ over the two equally populated **12**-**B**-H$^+$ and **12**-**C**-H$^+$ (Figure 5). PDI is comparable with the value of **12**, NICS and HOMA drop very slightly, while ECRE decreases by 21.05 kcal/mol. It seems that protonation has a little effect on aromaticity of **12**, or slightly decreases it.



17.4%
12-**A**-H$^+$

15.6%
12-**B**-H$^+$

15.6%
12-**C**-H$^+$

Figure 5. Resonance structures of **12**-H$^+$, obtained by NRT analysis, having weights of more than 10%. Given percent values refer to weights with respect to all resonance structures.

Structural changes that accompany replacement of CH *ortho* to BH and *para* to NH in **3** with N to form **13** result in a decrease in the HOMA value from 0.411 to 0.139 (Tables 1 and 2). PDI indicates almost no change in aromaticity, NICS drops slightly by 1.26 ppm, while ECRE becomes very large, even larger than the value calculated for benzene. In this case, aromaticity indices lead to divergent results and the question about aromaticity of **13** should remain open. Protonation of **13** to **8**/**13**-H$^+$ has a localizing effect on *π*-electron density, consistent with the resonance structure shown in Table 2. Thus, the BC bond becomes very long, 1.532 Å, while the lengths of the C(3)N(4) and CC bonds decrease by 0.02 and 0.03 Å, respectively, relative to the corresponding bonds in **13**. The N(4)C(5) and N(1)C(6) bonds lengthen by 0.016–0.035 Å. This consideration together with all four indices agree that cationic **13** is less aromatic than the neutral **13**.

Relative Aromaticity of 10–13. The 1,3-azaborine (**3**) has been characterized as the most aromatic among the three isomeric forms, **2–4**, due to the charge separation in its π-electron system, inherent for the 1,3-NH,BH arrangement, which was considered as a driving force for strong delocalization.[9] This charge separation is represented with structures **3-I** to **3-IV** (Figure 6), in which charges reside on carbon atoms. On the basis of the preceding Results and Discussion, it appears that placement of nitrogen at positions carrying a charge stabilizes charge separation, which, in turn, diminishes the driving force for π-electron delocalization and slightly decreases aromaticity (compounds **10**, **11** and **13**; not quite clear for the latter). On the contrary, position C(5) is the only one that escapes any charge and its replacement with nitrogen does not influence much aromatic character (structure **12**). Stability order of **10–12** agrees with the larger aromaticity of **12** with respect to **10** and **11**, whereas **13** is the most stable among the four diazaborines derived from 1,3-azaborine (**3**).

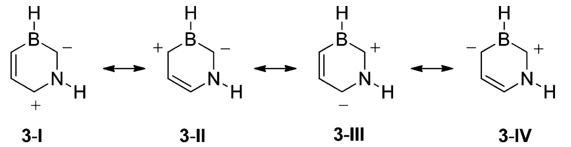


Figure 6. Resonance structures of 1,3-azaborine (**3**), with charges located on carbon atoms.

Aromaticity of 14 and 15. Aromatic character of 1,4-azaborine (**4**) was estimated to be the weakest among **2–4**, due to its one-directional π-electron delocalization (from N to B), rather than cyclic.[9] Indeed, its dominant resonance structure is **4-A** (Figure 7).

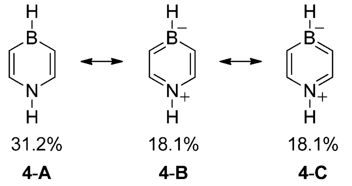


Figure 7. Resonance structures of 1,4-azaborine (**4**), obtained by NRT analysis, having weights of more than 10%. Given percent values refer to weights with respect to all resonance structures.

Replacement of the carbon, next to the boron atom in **4**, with nitrogen to form **14** (Figure 2), negligibly changes the BC, CC, and the two CN bond lengths. The newly formed C(6)N(1) bond, however, is very short (1.285 Å, by only 0.016 Å longer than the C=N double bond in CH_2=NH, 1.269 Å)[11] and the BN bond is the longest among all neutral molecules (1.449 Å). The HOMA and NICS indicate a decrease in cyclic delocalization with respect to **4**, PDI is almost the same as in **4**, while ECRE increases by 11.78 kcal/mol. As the bond length analysis suggests, the most populated resonance structure of **14** is **14-A**, having two double bonds (Figure 8). Other structures shown, imply partial delocalization across the two fragments, NCN and NCC, but not much cyclic delocalization. In addition, the C(6)=N(1) and BN bond lengths indicate that a little π-electron density goes from the C(6)=N(1) bond to boron, also supported by the very low population of structure **14-E**. It also seems that the π-electron density from the other side of the ring reaches boron to small extent (greater weight of **14-C** relative to **14-D** and long B(2)C(3) bond, 1.529 Å). Thus, all parameters, except ECRE, are consistent with smaller cyclic delocalization in **14**, relative to **4**. An analysis of calculated NBO charges on B and N in **4** (0.35 and −0.53, respectively) and **14** (0.54 and −0.57, respectively) indicates that B/N carries more positive/negative charge in **14** than in **4**, consistent with smaller charge transfer in **14**.

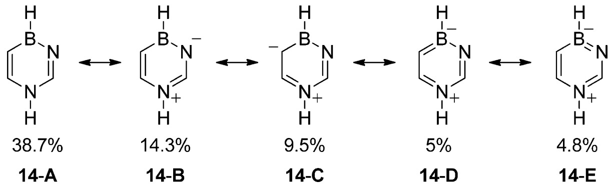


Figure 8. Resonance structures of **14**, obtained by NRT analysis. Given percent values refer to weights with respect to all resonance structures.

Protonation of **14** leads to the formation of **7/14**-H^+. As already discussed for this cation, there is an increased delocalization in the N(5)C(6)N(1) moiety of **7/14**-H^+, in which the two CN bonds have the same length. This is followed by an increase in lengths of the third C(4)N(5) bond and the BN bond by 0.018 and 0.015 Å, respectively, compared to neutral **14**. Lengths of the B(2)C(3) and C(3)C(4) bonds change by <0.01 Å. The PDI of cationic form is similar to that of the neutral one, absolute NICS is slightly smaller (by 1.7 ppm), HOMA slightly less negative (−0.539 for **14**, −0.498 for **7/14**-H^+) and ECRE is decreased by 23.57 kcal/mol. Structural changes and aromaticity indices indicate that there exists both partial increase and partial decrease in electron delocalization, resulting in similar or somewhat decreased aromaticity of **7/14**-H^+ compared to **14**.

A nitrogen introduction next to NH in **4** to give **15** results in a decrease in the CN and BC bonds in the NCCB moiety, by 0.012 and 0.016 Å, respectively. Another BC bond (1.532 Å) is slightly shorter than the BC single bond (1.5472 Å in CH_3–BH_2).[11] This points to a slight increase in delocalization in the NCCB part and decrease in the π-electron density in the longer BC bond. The PDI and NICS values are comparable to those of **4**, HOMA slightly less negative, while a drop of ECRE by 9.58 kcal/mol points to a slight decrease in the cyclic delocalization. It seems that **15** is best represented by its most populated resonance structure **15-A** (Figure 9), having similar cyclic delocalization as **4**.

Bond lengths in **15** do not change upon protonation to **11/15**-H^+, except the C(3)B(4) bond which becomes almost a single bond (1.545 Å in **11/15**-H^+, 1.5472 Å in CH_3–BH_2).[11]

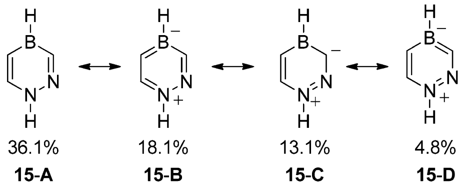


Figure 9. Resonance structures of **15**, obtained by NRT analysis. Given percent values refer to weights with respect to all resonance structures.

The PDI does not change upon protonation, absolute NICS decreases slightly (by 1.28 ppm), HOMA becomes more negative (−0.069 in **15**, −0.233 in **11**/**15**-H$^+$) and negative ECRE (−12.05 kcal/mol) indicates a destabilization of the π-electron system by cyclic delocalization, relative to acyclic reference molecules. As already discussed before and according to aromaticity indices, this molecule can be viewed as consisting of two separately delocalized fragments, N(2)C(3) and B(4)C(5)C(6)N(1), with little electron crossing between them, particularly over the C(3)B(4) bond.

In this case, the more stable **14** seems to be less cyclically delocalized than the less stable **15**.

CONCLUSIONS

This paper investigates how substitution of one CH group in azaborines with nitrogen, to form diazaborines, affects the strength of the cyclic π-electron delocalization (aromaticity). The influence of nitrogen protonation on the aromatic character of diazaborines is examined, too. Having in mind that there is an increasing interest in BN heterocycles and that some synthesized (cationic) diazaborines have already been examined as biologically active compounds and in material science, knowledge about their aromatic character is important for further exploration and application of BN/CC isosterism. Aromaticity of the studied molecules has been examined on the basis of bond length changes occurring upon CH → N substitution and further nitrogen protonation, and with the aid of aromaticity indices belonging to four groups: energy (ECRE), structure (HOMA), electron delocalization (PDI) and magnetic properties (NICS$(0)_{\pi zz}$). Generally, PDI and NICS and, in some cases HOMA, point to the little effect of CH → N substitution on the degree of cyclic delocalization. On the other hand, in most cases ECREs indicate some changes, which, with few exceptions (compounds **13**, **14** and **15**), point into the same direction as HOMA. It also appears that, in some cases, the NBO(del) derived ECREs overestimate aromaticity changes in the case of the studied diazaborines. The main conclusions of this work can be summarized as follows.

It appears that CH → N exchange does not affect much aromaticity of 1,2-azaborine (**2**) (PDI and NICS) or slightly decreases/increases it when CH *meta*/*ortho*,*para* to B is substituted with nitrogen. Aromaticity of the most aromatic 1,3-azaborine (**3**) becomes slightly weaker when any of the carbon atoms, carrying separated charges, is replaced with nitrogen (though not fully defined for **13**). On the other hand, substitution of the carbon *meta* to B and N, which escapes separated charges, does not affect aromaticity (or slightly inceases it). Diazaborine **14**, derived from the least cyclically delocalized 1,4-azaborine (**4**), appears to be even less cyclically delocalized (HOMA, NICS and bond lengths), while **15**, having the same parent compound, seems to be similarly delocalized as **4**.

Protonation either does not affect much the cyclic delocalzation (**8**-H$^+$, **12**-H$^+$ and **14**-H$^+$) or decreases it. Among the cationic species, the symmetric one having two 1,3-NH,BH arrangements appears to be the most cyclically delocalized, but not the most stable one (by 58.5 kcal/mol higher in energy than the most stable **9**-H$^+$). For the latter, aromaticity indices do not agree, and together with the bond lengths consideration imply an unequal delocalization, much more pronounced in the NCCCN moiety than in the NBN one. Cations **6**/**10**-H$^+$, **7**/**14**-H$^+$ and **11**/**15**-H$^+$, having long NN bond (**6**/**10**-H$^+$), BN and CN bonds (**7**/**14**-H$^+$) and BC bond (**11**/**15**-H$^+$) are the least cyclically delocalized. The latter is also the least stable one.

We predict that the extent of the π-electron delocalization of the three isomeric azaborines would be slightly affected by CH replacement with nitrogen, meaning that molecular properties associated with aromaticity, such as stability of the π-electron system and chemical reactivity, would more or less resemble those of parent azaborines. Differences in aromaticity between various diazaborines might affect their reactivity.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02499.

Bond lengths used for HOMA calculations, absolute energies and *x*, *y*, *z* coordinates of **6**−**15** and their protonated forms. (PDF)

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Notes

The authors declare no competing financial interest.

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