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4 π -Electron BN-monocycles: stability and (anti)aromaticity

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Abstract: This is a theoretical (DFT) study of an impact of electronic structure changes, induced by BN/CC isosterism, on two basic properties of 4 π -electron antiaromatic system: stability and antiaromaticity. It was found that the main driving force to nonplanarity of B₂N₂ rings is electrostatic energy, and in the case of ring with one B–N unit it is the Pauli repulsion relief. The charge-separation instability, inherent for 1,3-B,N relationship, turns the ground state of BCNC system to aromatic triplet which is less stable than the isomeric BNCC system, mostly because of larger Pauli interactions. The alternating BNBN connectivity is favoured primarily by orbital interaction energy, and secondarily by better electrostatic attraction. The CC \rightarrow BN substitution weakens the antiaromatic character except for 1,3-B,N relationship, which, in the closed-shell state increases antiaromaticity relative to cyclobutadiene.

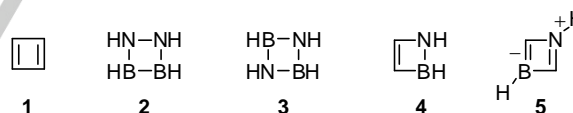
Introduction

Aromaticity is one of the most intriguing and much debated concepts in chemistry. It results from cyclic 4n+2 electron delocalization, which provides for an enhanced thermodynamic stability of compounds (relative to acyclic reference systems) and specific chemical reactivity (a tendency to retain the cyclical delocalization).^[1] Consequently, a considerable effort has been directed to its deeper understanding and quantification,^[2] though the latter proved not to be an easy task. Various aromaticity indices, based on structural, energetic, magnetic and electronic properties, often do not agree with one another, which has led to aromaticity being considered as a multidimensional phenomenon.^[3] Antiaromaticity, on the other hand, is described as a reduced thermodynamic stability of molecules (with respect to appropriate acyclic reference) and enhanced chemical reactivity,^[4] tending to disrupt its source, that is, the cyclic 4n electron delocalization. Unlike aromaticity, it is less explored, which may be due to the short-living character of truly antiaromatic compounds.^[5]

Replacement of one, or more CC units in an organic molecule with an isoelectronic, but polar BN pair changes the electronic structure, thus forming a basis for development of compounds and materials with altered properties. For example, while ethylbenzene acts as a substrate for ethylbenzene dehydrogenase, its BN analogues, *B*- and *N*-ethyl-1,2-azaborines, are strong inhibitors.^[6] The zero-band gap of graphene, that hinders its applications in electronic devices, opens up in BN-doped materials and hexagonal boron nitride, making them as semiconductors.^[7] In fact, variation of BN content and its position in molecules is increasingly exploited to

tune and control various properties, particularly in aromatic systems.^[8] Antiaromatic ones are much less explored. Recently, the synthesis of B₂N₂ isosters of benzopentalene^[9] and dibenzopentalene,^[10] exhibiting distinct optical and electronic properties, has been reported. Optoelectronic properties were shown to be dependent on the BN orientation pattern.^[10]

There are four possible B_nN_n (n = 1,2) isosters of the prototypical antiaromatic molecule, cyclobutadiene (**1**). Compounds **2** (1,2,3,4-diazadiboretidine) and **3** (1,3,2,4-diazadiboretidine) contain two BN units, which are connected in the head-to-head and head-to-tail fashion, respectively. Compounds **4** (1,2-dihydro-1,2-azaborete) and **5** (2,3-dihydro-1,3-azaborete-1-ium-2-ide) contain one BN pair, which is, in the case of **5**, separated by two carbon atoms (one at each side). While parent **2** and **3** were studied only theoretically,^[11] their substituted derivatives are experimentally known.^[12,13] The complexation behaviour of substituted **3** was also examined.^[14] The BNBN ring in derivatives of **3** was found to be planar, or nonplanar, with the BN bond lengths ranging from 1.45-1.49 Å.^[13b,e,g] Substituted **4** was isolated only as an intermediate Rh-complex, en route to substituted 1,4-azaborine^[15] and 1,2-azaborine.^[16] In the complexes, the BNCC ring is distorted, with two longer bonds (BC and CN, 1.53-1.55 Å and 1.44-1.47 Å, respectively) and two shorter bonds (BN and CC, 1.52-1.54 Å and 1.42-1.43 Å, respectively). Substituted **4** was also studied theoretically as a product of pericyclic reactions between iminoboranes and alkynes. The BNCC ring was found to be nonplanar, to avoid 4 π antiaromaticity, with two double bonds (BN and CC, 1.48-1.49 Å and 1.37 Å, respectively) and two single bonds (BC and CN, 1.52 Å and 1.45 Å, respectively).^[17] No data are available for the inherently charge-separated **5**.^[18]



It is generally believed that CC substitution with BN decreases (anti)aromaticity, mainly because of electronegativity difference between boron and nitrogen. Thus, **3** was theoretically predicted to be weakly antiaromatic,^[11b,11e] nonaromatic (like six-membered borazine),^[11f] or even aromatic.^[11g] Compound **2** was described as having two localized BN bonds and two long and weak BB and NN bonds.^[11d] The BN rings in (di)benzopentalene derivatives were found to be nonaromatic in the case of NN fusion, nonaromatic (NBN ring) and less antiaromatic (BNB ring) than the corresponding hydrocarbon in the case of BN fusion.^[9,10]

Given the recently discovered potential of the BN/CC isosterism to develop novel antiaromatic compounds with tunable optoelectronic properties^[9,10] and the relatively unexplored area, it is the aim of the present paper to provide answers to fundamental questions about the influence of B_nN_n (n = 1,2) orientation on antiaromaticity and stability of 4 π -electron monocycles, derived from the prototypical antiaromatic hydrocarbon, cyclobutadiene.

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Computational Details

Molecular geometries were optimized at the RB3LYP/6-311+G(d,p) level^[19,20] by using the Gaussian 09 program package.^[21] Compound **5** was also examined at the UB3LYP/6-311+G(d,p) level. The nature of each stationary point was verified by frequency calculations, done at the same level of theory as used for geometry optimization.

Stability Analysis

This work compares relative stability between the following species: (1) planar transition structure vs nonplanar minimum of the same compound, or closed shell vs triplet state in the case of **5**, (2) two isomeric, closed-shell planar forms (**2** vs **3** and **4** vs **5**) and (3) two isomeric most stable structures (**2** vs **3** and **4** vs **5**). The origin of the relative stability is examined on the basis of an energy decomposition analysis (EDA), in which each molecule was built from four fragments: **2** and **3** from two BH and two NH groups in their electronic triplet state, **4** and **5** from two CH groups in their electronic quartet state, one BH and one NH groups in their electronic triplet states. Neighbouring fragments are taken with opposite spin, so that they can form a bond (Figure 1). Since the **2/3** pair, as well as **4/5** pair, are composed of identical fragments, their relative stability (or isomerization energy) corresponds to energy change occurring when these identical fragments exchange their position (compare **2/3** and **4/5** pairs, in Figure 1). When comparing relative stability of different conformations of the same compound (or conformational energy), the connectivity between fragments remains the same, only their spatial position within a molecule is changed.

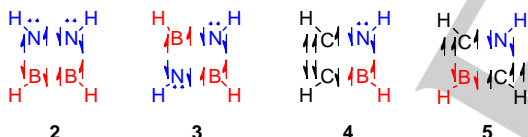


Figure 1. Formation of studied compounds from four fragments in energy decomposition analysis.

Isomerization or conformation energy (both denoted herein as ΔE_{iso}) consists of two major parts, interaction energy change ($\Delta\Delta E_{\text{int}}$) and deformation energy change ($\Delta\Delta E_{\text{def}}$), as shown in Eq. 1.

$$\Delta E_{\text{iso}} = \Delta\Delta E_{\text{int}} + \Delta\Delta E_{\text{def}} \quad (1)$$

The $\Delta\Delta E_{\text{int}}$ corresponds to energy change due to changes in bonding nature, while $\Delta\Delta E_{\text{def}}$ reflects energy change due to structural and electronic changes within the constituting fragments.

The $\Delta\Delta E_{\text{def}}$ was calculated as a difference between the four fragment deformation energy in final and starting structures, where deformation energy (ΔE_{def}) represents an energy required to deform an isolated radical fragment from its equilibrium state into the state it has in a structure in question.

The $\Delta\Delta E_{\text{int}}$ can be further decomposed into five energy terms (Eq. 2), by using the localized molecular orbital analysis

(LMOEDA), developed by Su and Li,^[22] and implemented in the Gamess programe package.^[23]

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{ex}} + \Delta E_{\text{rep}} + \Delta E_{\text{pol}} + \Delta E_{\text{disp}} \quad (2)$$

In the equation 2, electrostatic energy (ΔE_{elstat}) corresponds to all attractive (nucleus-electron) and repulsive (nucleus-nucleus, electron-electron) electrostatic interactions between the fragments having geometry and position as in the optimized molecule. This energy is usually stabilizing (negative energy contribution), because attractive electrostatic forces overcome the repulsive ones. The exchange energy (ΔE_{ex}) refers to the quantum-mechanical exchange between the same-spin electrons and is simultaneously counteracted by the repulsion energy (ΔE_{rep}). Taken together, they form the exchange-repulsion^[24] or Pauli repulsion^[25] of other EDA schemes, which is a destabilizing interaction (positive energy contribution). Herein, the sum of ΔE_{ex} and ΔE_{rep} is used to represent the Pauli repulsion and it is refer to as ΔE_{Pauli} . The polarization energy (ΔE_{pol}) is an orbital relaxation energy that accounts for the bond formation, charge transfer (donor-acceptor interactions between occupied orbitals on one fragment with empty orbitals on the other) and polarization (empty-occupied orbital mixing within one fragment due to the presence of another fragment). Herein, the original labeling ΔE_{pol} ^[22] is changed into ΔE_{oi} to refer to the all orbital interactions. Dispersion energy (ΔE_{disp}) comes from electron correlation. Both ΔE_{oi} and ΔE_{disp} are stabilizing interactions. In the performed analysis, the individual energy changes occurring during the conformational change or constitutional isomerization are expressed as a difference between the corresponding energies of final and starting structures, and are denoted as $\Delta\Delta E$ values (Table S1).

The EDA was done at the UB3LYP/6-311+G(d,p) level employing the Gamess program package.^[23] Analysis of the interaction energy between two or more radical fragments constituting a molecule has been applied before to study the torsional potential of ethane,^[22,26] butane^[27] and group 13-elements ($E = B - \text{Ti}$),^[28] fluorine *gauche* effect^[29] and azido *gauche* effect,^[30] distortion to the trans-bent geometry in heavier ethylene homologues,^[31] the isomerization energy of heterocyclic^[32] and polycyclic^[33] compounds, the strength of conjugation and hyperconjugation,^[34] and the nature of covalent bonds.^[35]

Antiaromaticity Analysis

A degree of antiaromaticity in the studied molecules was estimated by using magnetic and energetic criteria.

As a magnetic criterion, the π -electron contribution to the out-of-plane component of magnetic shielding, computed in the geometric center of the ring, was used. It is known as the most refined NICS index and is denoted as $\text{NICS}(0)_{\pi\text{zz}}$.^[36] This index avoids superfluous effects such as contributions from σ electrons and from parallel orientations of a molecule with respect to magnetic field direction, which do not create a π -electron ring current. Significantly negative NICS values reflect an induced diatropic ring current and aromaticity, while positive values denote an induced paratropic ring current and

antiaromaticity. Magnetic shieldings were computed by using the GIAO method^[37] and were partitioned into contributions from natural localized molecular orbitals (NLMOs) by using the natural chemical shielding (NCS) analysis^[38] within the NBO program.^[39] In the case of open-shell system, the out-of-plane component of magnetic shielding 1 Å above the ring center (NICS(1)_{zz}) was computed.

As an energetic criterion, the extra cyclic resonance energy (ECRE) was used. It represents resonance energy difference between cyclic molecule and acyclic reference system(s), where positive values mean aromatic stabilization, negative values show an antiaromatic destabilization, while values close to zero are associated with a nonaromatic system.^[40] The π -electron resonance energy was computed by using (1) the second-order perturbation analysis of natural bond orbitals (NBOs) and (2) by disabling $\pi \rightarrow \pi^*$ interactions, employing the NBO deletion analysis,^[39,41] to resonance structures having two double bonds (as shown in Tables 2 and S1; abbreviated as Del and E2 values, respectively). The reference structures were chosen to be two appropriately BN-substituted *cis*-butadienes, having the same number and type of conjugations as in cyclic molecule. The *cis*-butadiene conformation was chosen to conform to conformational arrangement of respective fragments in cyclic systems. The resonance energy (RE), representing an energy difference between delocalized and localized state of a molecule, was computed at an optimal geometry of a delocalized system and is thus termed as vertical resonance energy (VRE). In the case of planar cyclic structures, the planar reference forms were used, though most of them represent transition structures with one imaginary frequency. In the case of nonplanar cyclic structures, reference molecules were optimized to their energy minimum forms (due to nonplanarity, the clear σ - π separation was not possible). Both Del and E2 values correlate well with NICS index and only the former are discussed. They are given in Tables S2 and S3, respectively.

Results and Discussion

Molecular structures and energies

Optimized structures of cyclobutadiene (**1**), 1,2,3,4-diazadiboretidine (**2**), 1,3,2,4-diazadiboretidine (**3**), 1,2-azaborete (**4**) and 1,3-azaborete (**5**) are shown in Figure 2, along with their bond lengths and relative energies. The most stable form of **2** shows C_2 symmetry and slightly deviates from planarity ($\varphi_{\text{NBNN}} = 5.3^\circ$, $\varphi_{\text{BNNB}} = 6.4^\circ$ and $\varphi_{\text{BBNN}} = -5.1^\circ$), with somewhat pyramidalized nitrogen atoms (the sum of bond angles around nitrogen amounts 348.8°). The planar form having C_{2v} symmetry is a transition structure, by 0.76 kcal/mol higher in energy. It has slightly shorter BN bonds (by 0.01 Å) and slightly longer BB bond (by 0.014 Å), which might result from larger $N_{\text{LP}} \rightarrow \text{B}$ electron delocalization. Both forms have long BB and NN bonds, which are by ~ 0.12 Å and 0.05 Å, respectively, longer than the corresponding single bonds (1.65 Å, BB, and 1.42 Å, NN).^[2c] The BN bond lengths (~ 1.41 Å) are intermediate between single (1.56 Å)^[2c] and double (1.36 Å)^[2c] BN bond. Thus, both forms of **2** are significantly less stable (by ~ 87 kcal/mol) than the isomeric **3**, the most stable form of which is a wing-shaped structure of C_{2v} symmetry ($\varphi_{\text{BNBN}} = -17.3^\circ$, the sum of bond angles around nitrogen is 346.1°). The D_{2h} planar form of **3** is a transition structure, by 1 kcal/mol higher in energy. Planar and nonplanar forms of **3** have almost equal BN bond lengths of 1.45 Å, which is in excellent agreement with the above mentioned experimental data,^[13b,e,g] and they are by 0.05 Å longer than the BN bonds in **2** obviously exhibiting more double bond character.

The planar form of **4** is a transition structure, by 4.06 kcal/mol higher in energy than the nonplanar form with significantly pyramidalized N atom (312.9°), pyramidalized boron (355.9°) and carbon next to boron (351.8°). The CBNC, CCBN, CCNB and BCCN dihedral angles are -20.8° , 21.9° , 24.1° and -23.5° , respectively. The CC and BN bonds in nonplanar form are longer (by 0.02 Å and 0.07 Å) and BC and CN bonds shorter (by 0.089 Å and 0.026 Å) than in the planar structure. This is indicative of weaker $N_{\text{LP}} \rightarrow \text{B}$ electron delocalization, but larger delocalization in the N-C=C-B fragment in nonplanar form. The

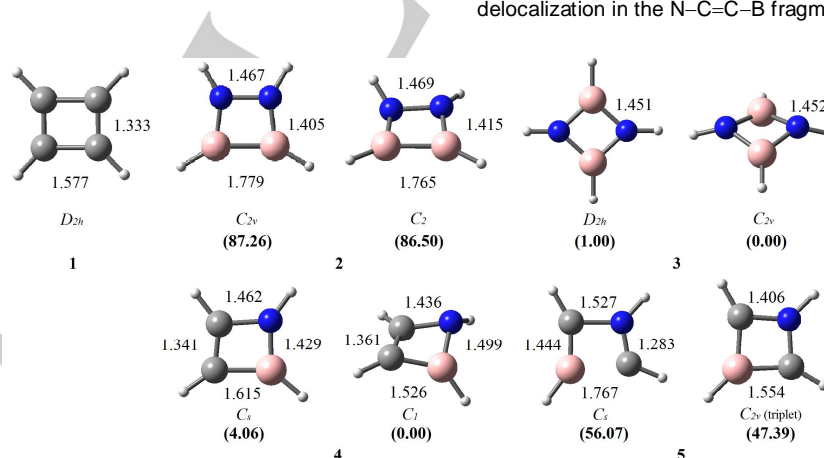


Figure 2. Optimized structures of 1-5 (B3LYP/6-311+G(d,p)), bond lengths (Å) and relative energies (values in brackets, kcal/mol).

CC bond lengths in both forms of **4** are longer than in **1** (by 0.008 Å in planar **4** and by 0.028 Å in nonplanar **4**), suggesting more electron delocalization. The planar form of the isomeric **5** is energy minimum, though significantly distorted and by 56.07 kcal/mol higher in energy than the most stable **4**. It has two short BC and BN bonds, and two very long BC and CN bonds, the first one is almost broken (1.767 Å). Nonplanar **5** is even higher in energy (by 8.68 kcal/mol). Re-optimization of **5** as the open-shell singlet and triplet states resulted in more compact structures of C_s and C_{2v} symmetry, which are by 1.44 kcal/mol and 8.68 kcal/mol, respectively, lower in energy. Thus, the theory level employed predicts triplet ground state for **5**. The BC bond lengths (1.554 Å) in the ground state structure correspond to the single BC bond length (1.55 Å)^[2c] and the CN bond lengths (1.406 Å) are close to the CN single bond (1.46 Å).^[2c] Test calculations run with other functionals,^[42] as well as at the MP2(full) level,^[43] with the same 6-311+G(d,p) basis set, all predict triplet ground state for **5**, with the following singlet-triplet energy difference: CAM-B3LYP -9.61 kcal/mol, M06-2X -6.48 kcal/mol, BHandHLYP -12.86 kcal/mol and MP2 -3.54 kcal/mol. Single point energy calculations at the CCSD(T)/aug-cc-pVDZ/B3LYP/6-311+G(d,p)^[44] level predict triplet to be by 3.13 kcal/mol lower in energy than the singlet state.

Stability and antiaromaticity analysis

The EDA results for studied BN analogues of cyclobutadiene **2-5** are given in Table S1. Table S2 lists π resonance energies of cyclic structures (VRE_{cyclic}), acyclic reference molecules ($VRE_{acyclic}$), extra cyclic resonance energies (ECRE) and NICS(0) _{π_{zz}} values. Data for cyclobutadiene (**1**), nonaromatic borazine (**6**) and benzene (**7**) are included for comparison.

Planar vs nonplanar forms of 2-4

As the data in Figure 2 show, nonplanar forms of all **2-4** are more stable than their planar forms. The energy difference is small in the case of **2** and **3** (0.76 kcal/mol and 1 kcal/mol, respectively), but larger in the case of **4** (4.06 kcal/mol). The EDA results reveal that nonplanar forms benefit from both geometric relaxation and larger bonding interactions, the latter being the major contribution to energy decrease upon planar \rightarrow nonplanar conformational change (64% for **2**(C_{2v}) \rightarrow **2**(C_2), 72% for **3**(D_{2h}) \rightarrow **3**(C_{2v}) and 88% for **4**(C_s) \rightarrow **4**(C_1)). In the case of **2** and **3**, the major stabilizing effect of nonplanar forms is electrostatic energy, somewhat more pronounced in the BN-alternating **3** (70% for **2** and 76% for **3**). The rest comes from orbital interaction energy (30% for **2** and 24% for **3**), whereas contribution of dispersion interactions is negligible in both systems. In the performed EDA, the orbital interaction energy mainly involves electron-pair bonding and $N_{LP} \rightarrow B$ charge transfer interactions.

It is a general thought that $4n\pi$ cyclic molecules tend to adopt a nonplanar structure in order to avoid antiaromatic destabilization. The calculated VREs of **2** and **3** show that the π system is more delocalized in nonplanar than in planar forms (by 0.4 kcal/mol in **2** and by 6.1 kcal/mol in **3**) and a weak antiaromaticity, evaluated as $NICS(2/3)_{planar} = 18.6/15.7$ ppm for

vs $NICS(1) = 56.9$ ppm and $ECRE(2) = -17.2$ kcal/mol vs $ECRE(1) = -46.6$ is, indeed, reduced upon planar \rightarrow nonplanar transition, $NICS(2/3)_{nonplanar} = 8.8/7.9$ ppm and $ECRE(2)_{nonplanar} = -2.9$ kcal/mol. In fact, according to $ECRE = 6.9$ kcal/mol, planar **3** appears to be somewhat more delocalized than its reference system and this delocalization increases upon ring puckering to $ECRE = 13.0$ kcal/mol. Generally, according to the presented data, the main driving force toward the nonplanar geometry in fully BN-substituted cyclobutadiene analogues is electrostatic energy, while orbital interactions that involve the σ bond strengths and π -electron delocalization play a secondary role.

In the case of **4**, however, it is the all-electron Pauli repulsion which decreases upon ring puckering (**4**(C_s) \rightarrow **4**(C_1) conformational change), on account of a decrease in both electrostatic and orbital stabilization. Even though the moderate antiaromaticity of planar **4** ($ECRE/NICS = -16.9/34.9$ vs $ECRE/NICS = -46.6/56.9$ for **1**) turns into nonaromaticity in nonplanar form ($ECRE/NICS = 17.8/8.7$ vs $ECRE/NICS = 20.5/-7.9$ for borazine and $90.4/-35.8$ for benzene) all orbital interactions are larger in the former. This can be ascribed to the two stronger (shorter) CC and BN (double) bonds in the planar form (Figure 2). Calculated bond dissociation energies of the CC and BN double bonds are 171 kcal/mol and 139.7 kcal/mol,^[45] respectively, both with the strong σ -component (106 kcal/mol, CC, and 109.8 kcal/mol, BN). Thus, even though the π -electron system is more than twice as delocalized in nonplanar **4** as in the planar **4** (Table S2), it is the π -electron localization, along with the stronger σ CC and BN bond component that is responsible for larger orbital interactions in the less stable form of **4**.

Triplet vs singlet of 5

Data in Table S1 show that the larger stability of triplet electronic state of **5** vs closed-shell singlet state (**5**(C_s) \rightarrow **5**(C_{2v}) change) originates solely from $\Delta\Delta E_{def}$, while bonding interactions are stronger in the singlet state mainly due to larger orbital interactions (~72%), followed by stronger electrostatic interactions (~28%). In other words, the charge-separation instability of closed-shell **5**, inherent for 1,3-B,N relationship and reflected in large $\Delta E_{def} = 205.4$ kcal/mol (Table S1), drives the electronic state of **5** toward diradical. Now, left with only two paired electrons, the ground state of **5** reverses to aromatic. Indeed, the $NICS(1)_{zz}$ ^[46] of triplet **5** is negative and amounts -10.4 ppm, compared with the value of -29.2 ppm for the ground state of benzene. The idea of a reversal of aromaticity/antiaromaticity for closed-shell \rightarrow open-shell transitions dates back to 1972, when Baird theoretically predicted that $(4n+2)\pi/4n\pi$ -electron systems become antiaromatic/aromatic in their lowest triplet state,^[47] and it has been in the focus of recent research interest.^[48] In fact, contrary to the general thought that CC \rightarrow BN substitution decreases (anti)aromaticity, the closed-shell **5** is more antiaromatic than cyclobutadiene (**1**), $NICS(5/1) = 79.1/56.9$ ppm, $ECRE(5/1) = -145.6/-46.6$ kcal/mol. The triplet state of **5** is, however, less aromatic than the triplet state of **1**, $NICS(5/1) = -10.4/-17.2$ ppm. An average aromatic stabilization energy ASE = -7.37 kcal/mol of triplet **5**, based on two isogyric reactions (2) and (3) shown in

Figure 3, confirm its aromatic character, which is, again, smaller than that of triplet **1** (ASE = -10.27 kcal/mol), based on reaction (1).

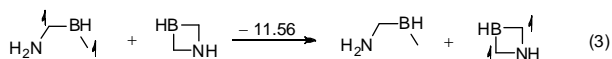
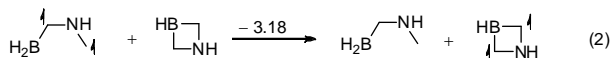
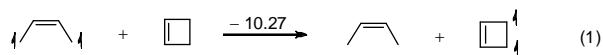


Figure 3. Aromatic stabilization energies (kcal/mol) estimated from isogyric reactions at the B3LYP/6-311+G(d,p) level of theory. The $\text{H}_2\text{BCH}_2\text{NHCH}_3$ and $\text{H}_2\text{NCH}_2\text{BHCH}_3$ are taken in their optimized synperiplanar form.

Thus, while the charge-separation instability in the 6π -electron 1,3-azaborine induces strong π -electron ring current that makes it the most aromatic among the three six-membered isomers,^[32b,49] the same effect turns 4π -electron heterocycle **5** into an aromatic diradical.

Comparison between isomers: 2 vs 3 and 4 vs 5 1,2,3,4-diazadiboretidine (**2**) and 1,3,2,4-diazadiboretidine (**3**)

As can be seen in Figure 2 and in Table S1 the BN alternation is energetically more favoured than the presence of BB and NN bonds, in both planar and nonplanar conformations (by ~86 kcal/mol). This is in accord with previous computations on four- and six-membered BN-heterocycles.^[11d,50] The EDA results show that the BNB-type connectivity is favoured mainly due to larger orbital interactions (82% in planar and 60% in nonplanar forms), which is followed by electrostatic attractive interactions (17% in planar and 39% in nonplanar forms). Contribution of dispersion effects to the relative energy of two isomers, **2** and **3**, is negligible (1%). Probably in contrast to our intuitive reasoning, the Pauli repulsion, coming from neighbouring nitrogen lone pair interaction, is not the source of the higher energy of **2**. In fact, the long NN and BB bonds in **2** can be the result of molecular tendency to lower the Pauli repulsion between N \rightarrow B delocalized lone pairs of nitrogen, in a similar way as in cyclobutadiene (**1**) where π/π repulsion lengthens the CC single bonds.^[5a] This bond lengthening reduces the BB and NN σ -bond strengths, resulting in smaller orbital interaction energy compared to **3**, even though the two BN bonds in **2** possess more double bond character. The smaller electrostatic attraction in **2** can easily be explained on the basis of almost parallel orientation of $\text{B}^{\delta+}-\text{N}^{\delta-}$ bond dipoles.

Both ECRE and NICS indicate that **2** is less delocalized than **3**, $\text{ECRE}(\mathbf{2}/\mathbf{3}) = -17.2/6.95$ kcal/mol and $\text{NICS}(\mathbf{2}/\mathbf{3}) = 18.6/15.7$ ppm for planar systems, $\text{ECRE}(\mathbf{2}/\mathbf{3}) = -2.9/13.0$ kcal/mol and $\text{NICS}(\mathbf{2}/\mathbf{3}) = 8.8/7.9$ ppm for nonplanar conformations. Compared with **1**, planar **2** can be regarded as weakly antiaromatic. According to ECRE calculations, the planar **3** (ECRE = 6.9 kcal/mol) is somewhat more delocalized than its acyclic reference and should be considered as nonaromatic (as

a comparison, ECRE = 20.5 kcal/mol for nonaromatic borazine). According to NICS, however, planar **3** appears to be weakly antiaromatic, so that it can be considered mostly as nonaromatic. Nonplanar forms of both compounds are nonaromatic.

1,2-dihydro-1,2-azaborete (**4**) and 2,3-dihydro-1,3-azaborete (**5**)

Among the two closed-shell planar species **4** and **5** the former, which is a transition structure, is by -52 kcal/mol lower in energy, solely because of the charge-separation present in **5** (ΔE_{def} in Table S1 mostly reflects energy needed to separate charges in this molecule). Interaction energy is larger in **5** due to more favourable orbital and electrostatic interactions. The former can be ascribed to two short CN and BC bonds: the length of the first (1.28 Å) corresponds to the length of the CN double bond (1.27 Å),^[2c] while the length of the second (1.44 Å) is intermediate between the BC single and double bonds (1.55 Å and 1.36 Å, respectively). The π -electron delocalization between these two bonds is very small and closed-shell **5** would be more antiaromatic than cyclobutadiene (**1**), Table S2. In the case of **4**, the substitution of one CC pair by the BN pair, weakens antiaromaticity and planar **4** can be characterized as moderately antiaromatic.

Energy difference between the most stable nonplanar **4** and triplet **5** is such that the latter is still significantly higher in energy (~47 kcal/mol), even though it can be regarded as aromatic ($\text{NICS}(1)_{zz} = -10.4$ ppm, ASE = -7.4 kcal/mol), while nonplanar **4** is certainly nonaromatic ($\text{NICS}_{\text{av}}(1)_{zz} = -4.3$ ppm, $\text{NICS}(0)_{\pi zz} = 8.7$ ppm and ECRE = 17.8 kcal/mol). The nonplanar **4** benefits almost entirely (99.6%) from favourable interaction energy mostly coming from its lower Pauli repulsion (91%), followed by dispersion interactions (8%), whereas difference in orbital interaction energy between nonplanar **4** and triplet **5** is small and contributes only 1% to more favourable ΔE_{int} of **4**.

Conclusions

This work presents a theoretical analysis of two basic properties of a 4π -electron system, stability and antiaromaticity, perturbed by $\text{C}_n\text{C}_n \rightarrow \text{B}_n\text{N}_n$ ($n = 1, 2$) substitution. The results show that nonplanarity of B_2N_2 systems **2** and **3** is driven mainly by better electrostatic interactions, though the difference in energy between planar and nonplanar forms is small (≤ 1 kcal/mol), which means that their derivatives might adopt both conformations, depending on steric and electronic properties of substituents. In the case of 1,2-azaborete (**4**) the nonplanar ground state results from lowering of the Pauli repulsion. The inherent charge-separation of 1,3-B,N relationship, present in 1,3-azaborete (**5**), drives the ground state to aromatic triplet, which is less stable than the isomeric 1,2-azaborete due to Pauli destabilization. In the case of B_2N_2 molecules **2** and **3** the BN alternation is more favoured mainly due to orbital energy stabilization, followed by better electrostatic interactions.

Despite the general belief that CC \rightarrow BN substitution decreases (anti)aromaticity, the closed-shell 1,3-azaborete (**5**) would be more antiaromatic than cyclobutadiene (**1**). All other

BN combinations, indeed, attenuate antiaromaticity making planar **4** as moderately antiaromatic, planar **2** as weakly antiaromatic and planar **3** as nonaromatic. Antiaromaticity is lost in all nonplanar systems.

The given deeper insight into the origin of B,N position impact on some fundamental molecular properties should be useful for further exploration and practical application of BN/CC isosterism in antiaromatic systems, which is an emerging area of research.

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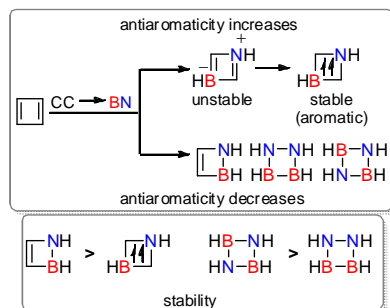
Keywords: antiaromaticity • bond theory • conjugation • density functional calculations • heterocycles

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FULL PAPER

While BN/CC isosterism is widely studied and applied in aromatic compounds, antiaromatic ones are rather unexplored. Thus, the influence of $C_nC_n \rightarrow B_nN_n$ ($n = 1, 2$) substitution on two basic properties of 4π -electron monocycle, stability and antiaromaticity, is analysed in detail, on the basis of DFT calculations. The results and their rationalization could initiate further theoretical and experimental studies on $4n\pi$ BN-heterocycles.



Antiaromatic BN-monocycles

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