



Antiaromatic B–N Monocycles

4π-Electron B–N Monocycles: Stability and (Anti)aromaticity

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Abstract: This is a theoretical (DFT) study of the impact of electronic structural changes, induced by B–N/C–C isosterism, on two basic properties of 4π -electron antiaromatic system, that is, stability and antiaromaticity. The main driving force for the nonplanarity of B₂N₂ rings is electrostatic energy, and that for a ring with one B–N unit is the relief of Pauli repulsion. The charge-separation instability, inherent for a 1,3-B,N relationship, turns the ground state of the BCNC system to an aromatic trip-

Introduction

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

The replacement of one or more C–C units in an organic molecule with an isoelectronic, but polar B–N pair changes the electronic structure and, thus, forms a basis for the development of compounds and materials with altered properties. For example, although ethylbenzene acts as a substrate for ethylbenzene dehydrogenase, its B–N analogues, *B*- and *N*-ethyl-1,2-azaborine, are strong inhibitors.^[6] The zero band gap of graphene, which hinders its applications in electronic devices, opens up in B,N-doped materials and hexagonal boron nitride and they become semiconductors.^[7] The variation of the B,N content and its position in molecules is increasingly exploited to

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let, 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 C–C \rightarrow B–N substitution weakens the antiaromatic character, except that for a 1,3-B,N relationship, which results in increased antiaromaticity in the closed-shell state relative to that of cyclobutadiene.q

tune and control various properties, particularly in aromatic systems.^[8] Antiaromatic ones are much less explored. Recently, the syntheses of B₂N₂ isosters of benzopentalene^[9] and dibenzopentalene were reported,^[10] and these molecules exhibit distinct optical and electronic properties, which are dependent on the BN orientation pattern.^[10]

There are four possible $B_n N_n$ (n = 1,2) isosters of the prototypical antiaromatic molecule, cyclobutadiene (1). 1,2,3,4-Diazadiboretidine (2) and 1,3,2,4-diazadiboretidine (3) contain two B-N units, which are connected in head-to-head and head-totail fashions, respectively. 1,2-Dihydro-1,2-azaborete (4) and 2,3dihydro-1,3-azaborete-1-ium-2-ide (5) contain one B-N pair, and that of 5 is separated by two carbon atoms (one at each side). Although the parent molecules 2 and 3 have been studied only theoretically,^[11] their substituted derivatives are known experimentally.^[12,13] The complexation behaviour of substituted **3** was also examined.^[14] The BNBN ring in derivatives of **3** can be planar or nonplanar, and the B-N bond lengths are in the range 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 and has two longer bonds (B-C and C-N, 1.53-1.55 and 1.44–1.47 Å, respectively) and two shorter bonds (B-N and C-C, 1.52-1.54 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 is nonplanar to avoid 4π antiaromaticity and has two double bonds (B=N and C=C, 1.48-1.49 and 1.37 Å, respectively) and two single bonds (B-C and C-N, 1.52 and 1.45 Å, respectively).^[17] No data are available for the inherently charge-separated 5.^[18]



It is generally believed that the C–C/B–N substitution decreases (anti)aromaticity, mainly because of the electronegativ-

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ity 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 with two localized B–N bonds and two long and weak B–B and N–N bonds.^[11d] The B–N rings in (di)benzopentalene derivatives are nonaromatic for N–N fusion or nonaromatic (NBN ring) and less antiaromatic (BNB ring) than the corresponding hydrocarbon for B–N fusion.^[9,10]

Owing to the recently discovered potential of B–N/C–C isosterism to produce new antiaromatic compounds with tuneable optoelectronic properties^[9,10] and as this area is relatively unexplored, it is the aim of this paper to provide answers to fundamental questions about the influence of the B_nN_n (n = 1, 2) orientation on the antiaromaticity and stability of 4π -electron monocycles derived from the prototypical antiaromatic hydrocarbon, cyclobutadiene.

Computational Details

The molecular geometries were optimized at the RB3LYP/6-311+G(d,p) level^[19,20] with 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, which were performed at the same level of theory as that used for geometry optimization.

Stability Analysis

In this work, the relative stabilities of the following species were compared: (1) the planar transition structure versus the nonplanar minimum of the same compound or the closed-shell versus triplet state for 5, (2) two isomeric, closed-shell planar forms (2 vs. 3 and 4 vs. 5), and (3) the two most stable isomeric 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 were built from two B-H groups and two N-H groups in their electronic triplet state, and 4 and 5 were built from two C-H groups in their electronic quartet state and one B-H group and one N-H group in their electronic triplet states. Neighbouring fragments are taken with opposite spin to enable bond formation (Figure 1). As the 2/3 pair as well as the 4/5 pair are composed of identical fragments, their relative stabilities (or isomerization energies) correspond to the energy change that occurs when these identical fragments exchange their positions (compare the 2/3 and 4/5 pairs in Figure 1). For comparisons of the relative stabilities of different conformations of the same compound (or conformational energies), the connectivity between the fragments remains the same, and only their spatial position within a molecule changes.



Figure 1. Formation of studied compounds from four fragments in EDA.

The isomerization or conformation energy (both denoted herein as ΔE_{iso}) consists of two major parts, the interaction-

energy change $(\Delta \Delta E_{int})$ and the deformation-energy change $(\Delta \Delta E_{def})$, as shown in Equation (1).

$$\Delta E_{\rm iso} = \Delta \Delta E_{\rm int} + \Delta \Delta E_{\rm def} \tag{1}$$

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

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

The $\Delta\Delta E_{int}$ value can be further decomposed into five energy terms [Equation (2)] through localized molecular orbital analysis (LMOEDA), developed by Su and Li^[22] and implemented in the Gamess program package.^[23]

$$\Delta E_{\rm int} = \Delta E_{\rm elstat} + \Delta E_{\rm ex} + \Delta E_{\rm rep} + \Delta E_{\rm pol} + \Delta E_{\rm disp} \tag{2}$$

In Equation (2), the electrostatic energy (ΔE_{elstat}) corresponds to all attractive (nucleus-electron) and repulsive (nucleusnucleus, electron-electron) electrostatic interactions between the fragments with geometries and positions the same as those 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 referred to as ΔE_{Pauli} . The polarization energy (ΔE_{pol}) is an orbital relaxation energy that accounts for the bond formation, charge transfer (donoracceptor interactions between occupied orbitals on one fragment with empty orbitals on the other), and polarization (empty-occupied orbital mixing within one fragment owing to the presence of another fragment). Herein, the original labeling $\Delta E_{pol}^{[22]}$ is changed to ΔE_{oi} to refer to all orbital interactions. The dispersion energy (ΔE_{disp}) comes from electron correlation. Both ΔE_{oi} and ΔE_{disp} are stabilizing interactions. In the analysis performed, the individual energy changes that occur during the conformational changes or constitutional isomerization are expressed as the differences between the corresponding energies of the final and starting structures and are denoted as the $\Delta\Delta E$ values (Table S1).

The EDA was performed at the UB3LYP/6-311+G(d,p) level with the Gamess program package.^[23] The analysis of the interaction energy between two or more radical fragments that constitute a molecule has been applied before to study the torsional potential of ethane,^[22,26] butane^[27] and group 13-elements (B–TI);^[28] the fluorine *gauche* effect^[29] and the azido *gauche* effect;^[30] the 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 co-valent bonds.^[35]

Antiaromaticity Analysis

The degrees of antiaromaticity in the studied molecules were estimated from magnetic and energetic criteria.

As a magnetic criterion, the π -electron contribution to the out-of-plane component of magnetic shielding, computed at the geometric centre of the ring, was used. It is considered to be the most refined nucleus-independent chemical shift (NICS) index and is denoted as NICS(0)_{π zz}.^[36] This index avoids superfluous effects such as contributions from σ electrons and from parallel orientations of a molecule with respect to the magnetic field direction, which do not create a π -electron ring current. Significantly negative NICS values reflect an induced diatropic ring current and aromaticity, whereas positive values denote an induced paratropic ring current and antiaromaticity. The magnetic shieldings were computed by the gauge-including atomic orbital (GIAO) method^[37] and partitioned into contributions from natural localized molecular orbitals (NLMOs) through natural chemical shielding (NCS) analysis^[38] within the NBO program.^[39] For open-shell systems, the out-of-plane component of magnetic shielding 1 Å above the ring centre $[NICS(1)_{zz}]$ was computed.

As an energetic criterion, the extracyclic resonance energy (ECRE) was used. It represents the resonance energy difference between a cyclic molecule and an acyclic reference system; positives values indicate aromatic stabilization, negative values show antiaromatic destabilization, and values close to zero are associated with nonaromatic systems.^[40] The π -electron resonance energy was computed through (1) the second-order perturbation analysis of natural bond orbitals (NBOs) and (2) NBO deletion analysis with $\pi \rightarrow \pi^*$ interactions disabled^[39,41] for resonance structures with two double bonds (as shown in Tables S2 and S3, abbreviated as Del and E2 values, respectively). The reference structures were chosen to be two appropriately B,N-

substituted *cis*-butadienes with the same number and type of conjugations as the cyclic molecule. The *cis*-butadiene conformation was chosen to conform to the conformational arrangements of the respective fragments in the cyclic systems. The resonance energy (RE), which represents the energy difference between the delocalized and localized state of a molecule, was computed at the optimal geometry of a delocalized system and is, thus, termed the vertical resonance energy (VRE). For planar cyclic structures, the planar reference forms were used, though most of these represent transition structures with one imaginary frequency. For nonplanar cyclic structures, the reference molecules were optimized to their energy-minimum forms (owing to nonplanarity, clear σ - π separation was not possible). The Del and E2 values both correlate well with the NICS index, and only the former are discussed.

Results and Discussion

Molecular Structures and Energies

The 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 C₂ symmetry and deviates slightly from planarity ($\varphi_{\text{NBBN}} = 5.3^\circ$, $\varphi_{\text{BNNB}} = 6.4^\circ$ and $\varphi_{\text{BBNN}} = -5.1^\circ$), and the nitrogen atoms are somewhat pyramidalized (the sum of the bond angles around the nitrogen atoms is 348.8°). The planar form with C_{2v} symmetry is a transition structure that is 0.76 kcal/mol higher in energy. It has slightly shorter B–N bonds (by 0.01 Å) and a slightly longer B–B bond (by 0.014 Å), which might result from larger $N_{IP} \rightarrow B$ electron delocalization. Both forms have long B-B and N-N bonds, which are longer than the corresponding single bonds by ca. 0.12 and 0.05 Å, respectively (B-B 1.65 Å, N-N 1.42 Å).^[2c] The B-N bond lengths (ca. 1.41 Å) are intermediate between those of single (1.56 Å)^[2c] and double (1.36 Å)^[2c] B–N bonds. Thus, both forms of **2** are significantly



Figure 2. The optimized structures of 1-5 [B3LYP/6-311+G(d,p)] with bond lengths [Å] and relative energies in parentheses [kcal/mo]].

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less stable (by ca. 87 kcal/mol) than the isomeric **3**, the most stable form of which is a wing-shaped structure with C_{2v} symmetry ($\varphi_{\text{BNBN}} = -17.3^{\circ}$, the sum of the bond angles around the nitrogen atoms is 346.1°). The D_{2h} planar form of **3** is a transition structure that is 1 kcal/mol higher in energy. The planar and nonplanar forms of **3** have almost equal B–N bond lengths of 1.45 Å, which are in excellent agreement with the abovementioned experimental data^[13b,e,g] and are longer than the B–N bonds in **2** by 0.05 Å; therefore, the latter clearly exhibit more double-bond character.

The planar form of 4 is a transition structure that is 4.06 kcal/ mol higher in energy than the nonplanar form, which has a significantly pyramidalized N atom (312.9°), a pyramidalized boron (355.9°) atom, and a pyramidalized carbon atom next to the boron atom (351.8°). The CBNC, CCBN, CCNB and BCCN dihedral angles are -20.8, 21.9, 24.1 and -23.5°, respectively. The C-C and B-N bonds in nonplanar form are longer (by 0.02 and 0.07 Å) and the B-C and C-N bonds are shorter (by 0.089 and 0.026 Å) than those in the planar structure. This is indicative of weaker $N_{IP} \rightarrow B$ electron delocalization but larger delocalization in the N–C=C–B fragment in the nonplanar form. The C–C bond lengths in both forms of 4 are longer than that in 1 (by 0.008 Å in planar 4 and 0.028 Å in nonplanar 4), which suggests that more electron delocalization occurs in 4. The planar form of the isomeric 5 is an energy minimum, but it is significantly distorted and 56.07 kcal/mol higher in energy than the most stable form of 4. It has two short B-C and B-N bonds and two very long B-C and C-N bonds, and the first of these is almost broken (1.767 Å). Nonplanar 5 is even higher in energy (by 8.68 kcal/ mol). The reoptimization of 5 in the open-shell singlet and triplet states resulted in more compact structures with C_s and $C_{2\nu}$ symmetry, which are 1.44 and 8.68 kcal/mol, respectively, lower in energy. Thus, the level of theory employed predicts a triplet ground state for 5. The B-C bond lengths (1.554 Å) in the ground-state structure correspond to a single B-C bond (1.55 Å),^[2c] and the C–N bond lengths (1.406 Å) are close to that of a C-N 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 a triplet ground state for 5 with the following singlet-triplet energy differences: 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 the triplet to be by 3.13 kcal/mol lower in energy than the singlet state.

Stability and Antiaromaticity Analysis

The EDA results for the studied B–N analogues of cyclobutadiene **2–5** are given in Table S1. The π resonance energies of cyclic structures (VRE_{cyclic}), acyclic reference molecules (VRE_{acyclic}), extracyclic resonance energies (ECRE) and NICS(0)_{π zz} values are listed in Table S2. The data for **1**, nonaromatic borazine (**6**), and benzene (**7**) are included for comparison.

Planar versus Nonplanar Forms of 2-4

As the data in Figure 2 show, the nonplanar forms of **2–4** are all more stable than their planar forms. The energy differences

are small for **2** and **3** (0.76 and 1 kcal/mol, respectively), but that for **4** is larger (4.06 kcal/mol). The EDA results reveal that the nonplanar forms benefit from both geometric relaxation and larger bonding interactions, and the latter makes the major contribution to the energy decrease for the planar to nonplanar conformational change [64 % for $2(C_{2v}) \rightarrow 2(C_2)$, 72 % for $3(D_{2h})$ $\rightarrow 3(C_{2v})$ and 88 % for $4(C_s) \rightarrow 4(C_1)$]. For **2** and **3**, the major stabilizing effect of the nonplanar forms is electrostatic energy, which is somewhat more pronounced in the B–N-alternating **3** (70 % for **2** and 76 % for **3**). The rest of the stabilization comes from the orbital interaction energy (30 % for **2** and 24 % for **3**), and the contributions from dispersion interactions are 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 generally thought that $4n\pi$ cyclic molecules tend to adopt nonplanar structures to avoid antiaromatic destabilization. The calculated VREs of **2** and **3** show that the π system is more delocalized in the nonplanar forms than in the planar forms (by 0.4 kcal/mol for 2 and by 6.1 kcal/mol for 3), and a weak antiaromaticity, evaluated as $NICS(2/3)_{planar}$ = 18.6/15.7 ppm versus NICS(1) = 56.9 ppm and ECRE(2) = -17.2 kcal/mol versus ECRE(1) = -46.6 kcal/mol, is reduced by the planar to nonplanar transition [NICS(2/3)_{nonplanar} 8.8/7.9 ppm and ECRE(2)_{nonplanar} = -2.9 kcal/mol]. On the basis of the ECRE value of 6.9 kcal/mol, planar 3 appears to be somewhat more delocalized than its reference system, and this delocalization increases through ring puckering (ECRE = 13.0 kcal/ mol). Generally, according to the presented data, the main driving force toward the nonplanar geometry in fully B,N-substituted cyclobutadiene analogues is electrostatic energy, whereas orbital interactions that involve the σ bond strengths and π electron delocalization play a secondary role.

For 4, however, it is the all-electron Pauli repulsion that decreases upon ring puckering $[\mathbf{4}(C_s) \rightarrow \mathbf{4}(C_1) \text{ conformational}]$ change] on account of decreased 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 the 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 of the orbital interactions are larger in the former. This can be ascribed to the two stronger (shorter) C-C and B=N (double) bonds in the planar form (Figure 2). The calculated bond dissociation energies of the C=C and B=N double bonds are 171 and 139.7 kcal/mol,^[45] respectively, both with a strong σ component (106 kcal/mol for C–C and 109.8 kcal/mol for B=N). Thus, even though the π -electron system in nonplanar 4 is more than twice as delocalized as that in planar 4 (Table S2), it is the π -electron localization and the stronger σ C–C and B=N bond components that are responsible for the larger orbital interactions in the less stable form of 4.

Triplet versus Singlet of 5

The data in Table S1 show that the larger stability of the triplet electronic state of **5** relative to the closed-shell singlet state $[\mathbf{5}(C_s) \rightarrow \mathbf{5}(C_{2\nu}) \text{ change}]$ originates solely from $\Delta\Delta E_{defr}$ whereas



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the bonding interactions are stronger in the singlet state mainly because of larger orbital interactions (ca.72 %), followed by stronger electrostatic interactions (ca. 28 %). In other words, the charge-separation instability of closed-shell 5, inherent for the 1,3-B,N relationship and reflected in a large ΔE_{def} value of 205.4 kcal/mol (Table S1), drives the electronic state of 5 toward a diradical. With only two paired electrons left, the ground state of **5** reverses to an aromatic from. Indeed, the NICS(1)₇₇^[46] value of triplet 5 is negative and amounts to -10.4 ppm compared with a value of -29.2 ppm for the ground state of benzene. The idea of a reversal of aromaticity/antiaromaticity for closed-shell to 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 has been the focus of recent research interest.^[48] In contrast to the general thought that C-C/B-N substitution deceases (anti)aromaticity, the closed-shell 5 is more antiaromatic than cyclobutadiene [NICS(5/1) = 79.1/56.9 ppm, ECRE(5/1) = -145.6/ -46.6 kcal/mol]. However, the triplet state of 5 is less aromatic than the triplet state of 1 [NICS(5/1) = -10.4/-17.2 ppm]. An average aromatic stabilization energy (ASE) of -7.37 kcal/mol for triplet 5 [for isogyric reactions (2) and (3) in Figure 3] confirms its aromatic character, which is again smaller than that of triplet **1** [ASE = -10.27 kcal/mol for reaction (1) in Figure 3].

$$H_{2B} \xrightarrow{I} H_{2B} \xrightarrow{HB} H_{2B} \xrightarrow{-3.18} H_{2B} \xrightarrow{-NH} H_{2B} \xrightarrow{HB} (2)$$

$$\begin{array}{c} \begin{array}{c} \begin{array}{c} H \\ H_2 N \end{array} & \begin{array}{c} H \\ H_2 N H \\ & \begin{array}{c} H \\ H_2 N \end{array} & \begin{array}{c} H \\ H_2 N H \\ & \begin{array}{c} H \\ H_2 N H \end{array} & \begin{array}{c} H \\ H_2 N H \\ & \begin{array}{c} H \\ H_2 N H \\ & \begin{array}{c} H \\ H_2 N H H \\ & \begin{array}{c} H \\ H_2 N H \\ & \begin{array}{c} H \\ & H \\ & \begin{array}{c} H \\ H_2 N H \\ & \begin{array}{c} H \\ & H \\ & H \\ & \begin{array}{c} H \\ & H \\ &$$

Figure 3. Aromatic stabilization energies [kcal/mol] estimated from isogyric reactions at the B3LYP/6-311+G(d,p) level of theory. The $H_2BCH_2NHCH_3$ and $H_2NCH_2BHCH_3$ molecules are taken in their optimized synperiplanar forms.

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

Comparison between Isomers - 2 versus 3 and 4 versus 5

1,2,3,4-Diazadiboretidine (2) and 1,3,2,4-Diazadiboretidine (3)

As can be seen in Figure 2 and Table S1, the system with B–N alternation is energetically more favoured than that with B–B and N–N bonds in the planar and nonplanar conformations (by ca. 86 kcal/mol). This is in accord with previous computations on four- and six-membered B,N-heterocycles.^[11d,50] The EDA results show that the BNBN-type connectivity is favoured mainly because of the larger orbital interactions (82 % in the planar form and 60 % in the nonplanar form), followed by electrostatic attractive interactions (17 % in the planar form and 39 % in the nonplanar form). The contribution of dispersion effects to the

relative energies of the two isomers, **2** and **3**, are negligible (1%). Probably in contrast to our intuitive reasoning, the Pauli repulsion from neighbouring nitrogen lone-pair interactions is not the source of the higher energy of **2**. The long N–N and B–B bonds in **2** could be the result of molecular tendency to lower the Pauli repulsion between N→B delocalized lone pairs of the nitrogen atom, in a similar way to that in cyclobutadiene, in which π - π repulsion lengthens the C–C single bonds.^[5a] This bond lengthening reduces the B–B and N–N σ -bond strengths and results in a smaller orbital interaction energy compared with that for **3**, even though the two B–N bonds in **2** possess more double-bond character. The smaller electrostatic attraction in **2** can be explained readily on the basis of the almost parallel orientation of the B^{δ +}–N^{δ -} bond dipoles.

Both the ECRE and the NICS indicate that **2** is less delocalized than **3** [ECRE(**2**/**3**) = -17.2/6.95 kcal/mol and NICS(**2**/**3**) = 18.6/ 15.7 ppm for planar systems, ECRE(**2**/**3**) = -2.9/13.0 kcal/mol and NICS(**2**/**3**) = 8.8/7.9 ppm for nonplanar conformations]. Compared with **1**, planar **2** can be regarded as weakly antiaromatic. According to the ECRE calculations, the planar **3** (ECRE = 6.9 kcal/mol) is somewhat more delocalized than its acyclic reference and should be considered as nonaromatic (for comparison, ECRE = 20.5 kcal/mol for nonaromatic borazine). According to the NICS results, however, planar **3** appears to be weakly antiaromatic and can be considered mostly as nonaromatic. The nonplanar forms of both compounds are nonaromatic.

1,2-Dihydro-1,2-azaborete (4) and 2,3-Dihydro-1,3azaborete (5)

Among the two closed-shell planar species 4 and 5, the former, which is a transition structure, is ca. 52 kcal/mol lower in energy, solely because of the charge-separation present in **5** (the ΔE_{def} value in Table S1 mostly reflects the energy needed to separate the charges in this molecule). The interaction energy is larger in 5 owing to more favourable orbital and electrostatic interactions. The former can be ascribed to two short C-N and B-C bonds: the length of the first (1.28 Å) corresponds to the length of a C=N double bond (1.27 Å),^[2c] whereas the length of the second (1.44 Å) is intermediate between B-C single and double bonds (1.55 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 (Table S2). For 4, the substitution of one C-C pair by a B-N pair weakens the antiaromaticity, and planar 4 can be characterized as moderately antiaromatic.

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





Conclusions

Theoretical analysis has shown how two basic properties of a 4π-electron system, stability and antiaromaticity, are perturbed by $C_n C_n \rightarrow B_n N_n$ (n = 1,2) substitution. The results show that the nonplanarity of the B_2N_2 systems **2** and **3** is driven mainly by better electrostatic interactions, though the difference in energy between the planar and nonplanar forms is small (≤ 1 kcal/ mol); therefore, their derivatives might adopt both conformations, depending on the steric and electronic properties of the substituents. For 1,2-azaborete (4), a nonplanar ground state results from decreased Pauli repulsion. The inherent charge separation of the 1,3-B,N relationship, present in 1,3-azaborete (5), drives the ground state to an aromatic triplet, which is less stable than the isomeric 1,2-azaborete owing to Pauli destabilization. For the B_2N_2 molecules 2 and 3, the B–N alternation is more favourable, mainly because of orbital energy stabilization, followed by better electrostatic interactions.

Despite the general belief that $C-C \rightarrow B-N$ substitution decreases (anti)aromaticity, the closed-shell 1,3-azaborete (**5**) would be more antiaromatic than cyclobutadiene (**1**). All other B-N combinations attenuate antiaromaticity; planar **4** is moderately antiaromatic, planar **2** is weakly antiaromatic, and planar **3** as nonaromatic. Antiaromaticity is lost in all nonplanar systems.

The deeper insights provided into the origin of the impact of the B and N positions on some fundamental molecular properties should be useful for the further exploration and practical application of B–N/C–C isosterism in antiaromatic systems, which is an emerging area of research.

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