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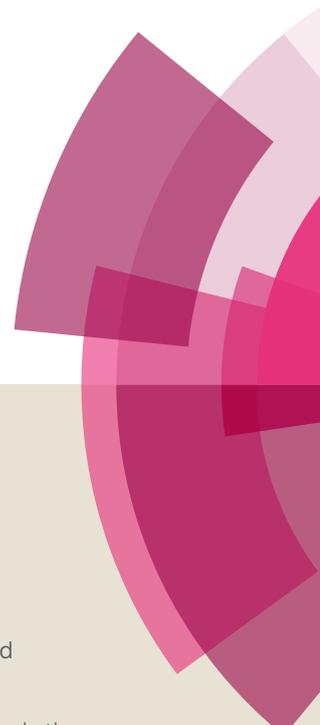
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# Mono BN-Substituted Analogues of Naphthalene: A Theoretical Analysis of the Effect of BN Position on Stability, Aromaticity and Frontier Orbital Energies

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## Abstract

All isomeric BN isosters of naphthalene have been studied theoretically, at the B3LYP/6-311+G(d,p) level, in order to investigate the effect of BN position in a molecule on relative stability, aromaticity and frontier orbital energies. The results show that orientational isomers of m,n/n,m type have similar aromaticity, similar HOMO-LUMO gaps and similar stability, though the latter only when both heteroatoms occupy external ring positions. This latter finding is explained by an analysis of partial atomic charges in the parent hydrocarbon and final BN-compound. Placing the BN pair in one ring results in larger stability and larger HOMO-LUMO gaps than when it is placed in separate rings. The stability order of the former series is predictable on the basis of charge distribution in nitrogen-polarized naphthalenic system and is related to partial atomic charges at boron and nitrogen atoms in BN-heterocycle. The HOMO-LUMO gap of the parental hydrocarbon is retained only in **1,4**-isomer, it is slightly increased in **1,2**/**2,1** and **5,10** isomers and more or less decreased in all other isomers. Aromaticity of a benzene unit in naphthalene is retained/increased only in a carbocyle, when it can be represented as having the π-electronic sextet. Aromaticity of heterocyclic rings is more or

less reduced relative to naphtahlene and is the weakest in the rings featuring the push-pull π-electronic structure while the BN pair resides at external ring positions.

## Introduction

There is an increasing interest in compounds having one or more CC units replaced by the isoelectronic BN pair.[1] The polarity of the BN unit endows such compounds with unique electronic properties giving a potential for application in various fields, as, for example, in biomedicine,[2] hydrogen storage,[3] organic electronics[4] and synthetic chemistry.[5] Thus, many BN-containing compounds have been synthesized and studied theoretically, where a particular attention has been paid to analysis of their fundamental properties such as stability, (anti)aromaticity, frontier orbital energies and conformation, all of which are affected by the position of BN pair(s) in a molecule.[6] Understanding of the relation between these two, for a particular molecular framework, makes it possible to design and prepare molecules with tunable and predictable physical properties and chemical reactivity, with minimal changes in molecular shape compared with the known hydrocarbon, or to synthesize a molecule that adopt a specific conformation (different from the parent hydrocarbon).

The mono BN-substituted analogues of the prototypical aromatic compound, benzene, have received great attention from both experimental and theoretical chemists, and all three isomers have been synthesized.[1,6c,e,7] In the naphthalenic system, which is the simplest polycyclic aromatic hydrocarbon (PAH), only those BN isosters that feature 1,2- and 1,4-BN relationship are experimentally known. While five, out of six, isomers have been prepared in the case of the former,[8] only one isomeric species having 1,4-BN-relation has been isolated.[5,9] A fundamental question about consequences of BN/CC substitution on the electronic structure in this system is largely unexplored. Thus, apart from the detailed experimental and theoretical analysis of frontier orbital energetics in 1,2-BN-related naphthalenes[8e] and their stability analysis,[10,11] no systematic investigation on how the BN

relation and position influence basic molecular properties has been carried out. This missing information prompted us to perform a detailed theoretical study in which we examine all possible isomeric BN naphthalenes and relate the BN position with their fundamental properties, such as stability, aromaticity and frontier orbital energies. This simplest BN-substituted PAH may also serve as a model for higher BN-containing PAHs and initiate further studies.

## Computational Details

Optimization of molecular structures and NICS calculations have been done by using the Gaussian 09 program package.[12] Molecular structures were optimized by using the B3LYP density functional[13] and 6-311+G(d,p) basis set,[14] followed by frequency calculations which confirmed that all structures were enegy minima (no imaginary frequences). Electronic energies are corrected for zero-point energies.

A degree of aromaticity was estimated at the same level of theory on the basis of $\pi$-electron contribution to the out-of-plane component of magnetic shielding calculated at the geometric center of each ring, NICS(0)$_{\pi zz}$.[15] This index is known as the most refined NICS index, since it avoids contributions from other orbitals ($\sigma$ and inner shell orbitals) and contributions from parallel orientations of a molecule with respect to magnetic field direction. More negative NICS value means greater degree of aromaticity. Magnetic shielding values were obtained by employing the GIAO method,[16] and they were partitioned into contributions from natural localized molecular orbitals (NLMOs), created by the NBO program,[17] by using the natural chemical shielding (NCS) analysis.[18] The NICS(0)$_{\pi zz}$ index, used in this work, is based on the relative weights of the three resonance structures, having five double bonds, which were obtained by the natural resonance theory analysis, within the NBO program.[17] Only $\pi$ orbitals which belong to one ring were taken into account when calculating NICS value.

Another aromaticity index used, the *para*-delocalization index PDI,[19] belongs to the group of indices based on electron delocalization. It is derived from Bader's Atoms in Molecules (AIM) theory[20] and represents the average of delocalization indices of *para*-related atoms in a 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. Higher value of PDI means larger aromaticity.

A degree of aromaticity was also assessed by using the structural HOMA index,[21] which is based on the reduction of bond length alternation in aromatic systems vs nonaromatic and antiaromatic ones. The HOMA index is defined as shown in Eq. 1:

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

The $\alpha$ is an empirical constant chosen to give HOMA = 0 for a non-aromatic system and HOMA = 1 for a system where all bonds are equal to an optimal bond length ($R_{\text{opt}}$), $n$ is the number of bonds taken into summation, $R_i$ is an individual bond length and $j$ represents the type of the bond. We have used the following $\alpha/R_{\text{opt}}$ (Å) to compute the HOMA values: 118.009/1.4378 (BC), 72.03/1.402 (BN), 257.7/1.388 (CC) and 93.52/1.334 (CN).[21c] The HOMA index and PDI were computed by using the Multiwfn program.[22]

## Results and discussion

In order to avoid repetition in the labeling of some isomers, the numbering system used throughout this work is shown in Figure 1. Thus, the isomeric BN naphthalenes are denoted as, for example, **1,2** which means that nitrogen occupies position 1 and boron position 2, **2,1** which means that nitrogen is placed at position 2 and boron at position 1, etc. (see Table 1). In the literature, and according to the IUPAC nomenclature for fused systems, the **1,10/10,1** isomeric pair is labeled as **1,9/9,1** and **5,10** isomer as **9,10**.[8e]
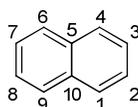
**Figure 1.** Numbering system used in this study.

Table 1 lists calculated relative energies of all isomeric BN naphthalenes, HOMO/LUMO energies and HOMO-LUMO gaps, NICS(0)$_{\pi zz}$, HOMA and PDI values. Data for naphthalene are included for comparison.
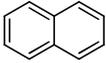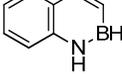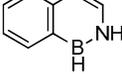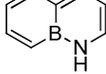
There are six isomers with 1,2-BN-relationship denoted as **1,2**, **1,10**, **2,1**, **2,3**, **5,10** and **10,1** (Table 1, the first row showing structures), seven isomeric 1,3-BN-related species denoted as **1,3**, **1,5**, **1,9**, **2,10**, **3,1**, **5,1** and **10,2** (Table 1, the second row showing structures), six isomers featuring 1,4-BN-position, labeled as **1,4**, **1,6**, **1,8**, **2,5**, **5,2** and **8,1** (Table 1, the third row showing structures), three 1,5-BN-related isomers named as **1,7**, **2,8** and **7,1**, and one isomer having BN pair in 1,6-relationship (Table 1, the last row showing structures). All isomers having BN unit in 1,2-, 1,4- and 1,6-relationship can be represented by neutral structures, while those having BN unit in 1,3- and 1,5-position are intrinsically charge-separated (no neutral resonance structure can be written).

**Stability Analysis**

Relative energies of BN naphthalenes span a range of 48 kcal/mol. The most stable isomer is **1,2** and the least stable is the charge-separated **2,8** isomer, having the 1,5-BN-relationship. The most stable group of isomers features the 1,2-BN-relation and their energies are in the range of 0-17.96 kcal/mol. Energies of the 1,4-BN-related isomers span a similar range of 18.09 kcal/mol (22.61-40.71 kcal/mol relative to the most stable **1,2** isomer). Energy of 1,6-BN-related **2,7** isomer is just slightly higher than the last cited value and amounts 41.72 kcal/mol, relative to **1,2** isomer. A narrower range of energies, 11.54 kcal/mol, is observed for the group containing 1,3-BN-related charge-separated species, and they are 32.43-43.97 kcal/mol relative to **1,2** isomer. Even the narrower range of

energies, 1.44 kcal/mol, is found for the other group comprising charge-separated 1,5-BN-related isomers, which are 46.56-48.00 kcal/mol relative to the most stable **1,2** isomer. The stability order of the 1,2-BN-related series obtained in this work is the same as that predicted by previous calculations.[8e]

**Table 1.** Relative energies[a] (kcal/mol), HOMO/LUMO energies (eV), NICS values (ppm), HOMA and PDI (electrons) of naphthalene and BN-naphthalenes.

| compound | | | | | | | |
|---|---|---|---|---|---|---|---|
| isomer | | **1,2** | **2,1** | **1,10** | **2,3** | **5,10** | **10,1** |
| $E_{rel}$ | | 0.00 | 0.40 | 7.87 | 10.68 | 12.85 | 17.96 |
| $E_{LUMO}$ | -1.40 | -1.51 | -1.04 | -1.87 | -1.83 | -1.33 | -1.56 |
| $E_{HOMO}$ | -6.15 | -6.45 | -5.97 | -5.89 | -5.59 | -6.28 | -5.55 |
| $\Delta E_{HOMO\text{-}LUMO}$ | 4.75 | 4.93 | 4.93 | 4.02 | 3.76 | 4.94 | 3.99 |
| $NICS(0)_{\pi zz}$ | -33.62/-33.62 | -35.75/-19.46 | -35.65/-18.67 | -22.30/-28.78 | -25.75/-28.73 | -25.52/-25.51 | -24.97/-30.37 |
| HOMA | 0.782/0.782 | 0.906/0.617 | 0.872/0.561 | 0.490/0.782 | 0.517/0.731 | 0.636/0.636 | 0.673/0.814 |
| PDI | 0.076/0.076 | 0.082/0.052 | 0.085/0.053 | 0.062/0.067 | 0.064/0.074 | 0.068/0.068 | 0.063/0.068 |

| compound | | | | | | | |
|---|---|---|---|---|---|---|---|
| isomer | **1,5** | **2,10** | **3,1** | **1,3** | **1,9** | **5,1** | **10,2** |
| $E_{rel}$ | 0.00 | 1.46 | 1.53 | 2.00 | 8.58 | 10.37 | 11.54 |
| $E_{rel}{}^{b}$ | 32.43 | 33.88 | 33.96 | 34.43 | 41.01 | 42.80 | 43.97 |
| $E_{LUMO}$ | -2.01 | -1.73 | -1.67 | -1.99 | -2.30 | -1.69 | -1.61 |
| $E_{HOMO}$ | -5.83 | -5.91 | -5.55 | -5.75 | -5.16 | -5.47 | -5.76 |
| $\Delta E_{HOMO\text{-}LUMO}$ | 3.82 | 4.18 | 3.88 | 3.76 | 2.86 | 3.78 | 4.15 |
| $NICS(0)_{\pi zz}$ | -27.49/-31.29 | -27.85/-31.36 | -33.90/-29.56 | -32.64/-31.12 | -35.48/-31.59 | -30.53/-32.88 | -30.23/-32.30 |
| HOMA | 0.564/0.700 | 0.541/0.673 | 0.757/0.642 | 0.777/0.716 | 0.621/0.794 | 0.755/0.679 | 0.763/0.685 |
| PDI | 0.066/0.065 | 0.066/0.062 | 0.077/0.066 | 0.073/0.065 | 0.066/0.066 | 0.068/0.065 | 0.066/0.060 |

| compound | | | | | | |
|---|---|---|---|---|---|---|
| isomer | **1,4** | **2,5** | **1,8** | **8,1** | **5,2** | **1,6** |
| $E_{rel}$ | 0.00 | 7.35 | 15.97 | 17.07 | 17.85 | 18.09 |
| $E_{rel}{}^{b}$ | 22.61 | 29.96 | 38.59 | 39.69 | 40.46 | 40.71 |
| $E_{LUMO}$ | -1.39 | -1.57 | -2.15 | -1.71 | -1.69 | -2.17 |
| $E_{HOMO}$ | -6.17 | -5.85 | -5.71 | -5.26 | -5.88 | -5.28 |
| $\Delta E_{HOMO\text{-}LUMO}$ | 4.77 | 4.28 | 3.55 | 3.55 | 4.19 | 3.11 |
| $NICS(0)_{\pi zz}$ | -33.10/-19.98 | -21.86/-26.56 | -24.35/-27.34 | -23.74/-28.33 | -23.45/-28.07 | -28.01/-26.48 |
| HOMA | 0.895/0.580 | 0.372/0.554 | 0.360/0.704 | 0.570/0.442 | 0.597/0.580 | 0.500/0.750 |
| PDI | 0.085/0.049 | 0.062/0.054 | 0.045/0.059 | 0.047/0.061 | 0.060/0.053 | 0.062/0.063 |

| compound |  |  |  |  |
|---|---|---|---|---|
| isomer | **1,7** | **7,1** | **2,8** | **2,7** |
| $E_{rel}$ | 0.00 | 0.88 | 1.44 | 0.00 |
| $E_{rel}{}^{b}$ | 46.56 | 47.44 | 48.00 | 41.72 |
| $E_{LUMO}$ | -2.37 | -2.07 | -2.12 | -1.71 |
| $E_{HOMO}$ | -5.33 | -5.04 | -5.28 | -5.65 |
| $\Delta E_{HOMO-LUMO}$ | 2.96 | 2.97 | 3.16 | 3.95 |
| $NICS(0)_{\pi zz}$ | -32.18/-31.57 | -31.42/-34.69 | -33.14/-30.54 | -23.86/-23.87 |
| HOMA | 0.516/0.748 | 0.703/0.508 | 0.451/0.682 | 0.292/0.520 |
| PDI | 0.053/0.059 | 0.056/0.062 | 0.052/0.052 | 0.044/0.043 |
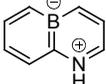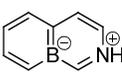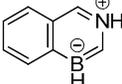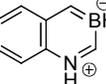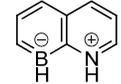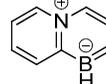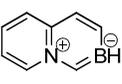
[a] Corrected for ZPE. [b] Relative to the most stable **1,2**-isomer.

The stability trend of the most stable members of 1,2-, 1,3- and 1,4-BN-related groups, that is **1,2** (0.00 kcal/mol), **1,5** (32.43 kcal/mol) and **1,4** isomers (22.61 kcal/mol), is the same as that previously reported for 1,2-, 1,3- and 1,4-azaborine isomers (0.00 kcal/mol, 29.56 kcal/mol and 21.88 kcal/mol, respectively),[6e] and can be similarly rationalized by the charge-separation instability of the π-system in **1,5** isomer, created by the 1,3-BN-relationship, and an increased steric repulsion between the lone pair of nitrogen and the π-electronic system in **1,4** isomer relative to lower repulsion when boron and nitrogen are directly connected, as in **1,2** isomer. Separation of BN unit into two rings decreases stability further, giving the following trend of decreasing stability: 1,2-relation (**1,2** isomer, 0.00 kcal/mol) > 1,4-relation (**1,4** isomer, 22.61 kcal/mol) > 1,3-relation (**1,5** isomer, 32.43 kcal/mol) > 1,6-relation (**2,7** isomer, 41.72 kcal/mol) > 1,5-relation (**1,7** isomer, 46.56 kcal/mol).

There is a total of eight orientational isomers of the m,n/n,m type (m, n = 1, 2, 3, 5, 7, 8, 10). Four of them contain both boron and nitrogen atoms at external ring positions (**1,2/2,1**, **1,3/3,1**, **1,8/8,1** and **1,7/7,1**) and the other four have one heteroatom at the ring-junction (internal) position (**1,10/10,1**, **1,5/5,1**, **2,10/10,2** and **2,5/5,2**; they will be named, herein, as internal/external isomers). Energy difference between the two corresponding external isomers is small (0.4-1.1 kcal/mol), while energy difference between the two corresponding internal/external isomers is much larger and amounts 10.1-10.5 kcal/mol. The less stable isomer always contain nitrogen atom at the ring-fusion position (Table

1). The observed trend can be explained by an analysis of Hirshfeld partial atomic charges[23] in the parent naphthalene system (Figure 2). As can be seen from the figure, external carbon atoms carry more negative charge than internal ones. If we had to substitute carbon atoms with nitrogen and boron, placing the more electronegative nitrogen at an external position and the less electronegative boron at the internal position would be more favoured than the opposite arrangement. Hence the large energy difference between the two internal/external isomers. Partial atomic charges of the two different external positions, α and β, are similar, so that stability difference between the two corresponding external isomers is small.
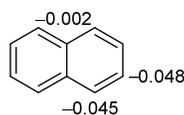


**Figure 2.** Hirshfeld partial atomic charges in naphthalene.

In BN naphthalenes, there is a clear correlation between charge at boron and nitrogen atoms in internal/external isomers and their relative stability. The more stable isomer, with boron at the ring-junction site, always has more positive charge at boron atom and more negative charge at nitrogen atom (Figure 3, right part of each graphic). Difference in charges is more pronounced for nitrogen than for boron atoms (0.052-0.057e for the former and 0.010-0.018e for the latter). Situation is different in two external isomers. While the more stable one has more positively charged boron atom (with exception of **1,2/2,1** isomeric pair, where difference in charges is very small), the more stable isomer contains less negatively charged nitrogen atom (Figure 3, left part of each graphic). This trend may also be responsible for the small energy difference between the two external isomers.

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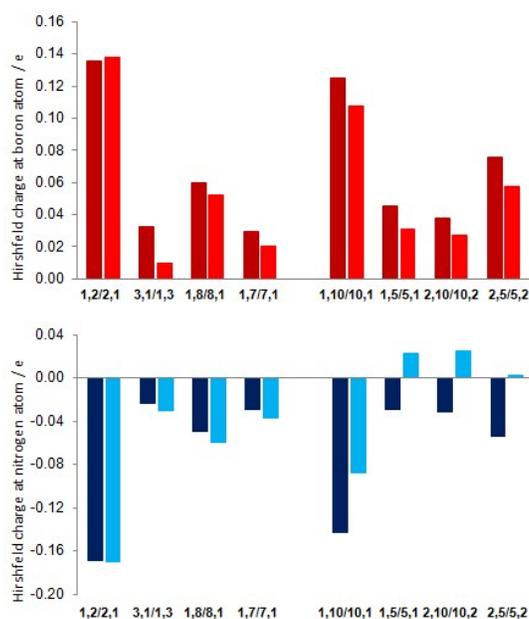
**Figure 3.** Hirshfeld charges at boron atom (upper part) and nitrogen atom (lower part) in eight orientational isomers of BN naphthalenes: dark red/dark blue colour represents charges in the more stable of the two isomers.

Substitution of a carbon atom in naphthalene by nitrogen atom polarizes system further and the obtained charge distribution could help deciding the preferred positions of the incoming boron atom. As can be expected, the most positive positions in the so-formed quinolinium, isoquinolinium and quinolizinium cations, shown in Figure 4, are those *ortho*-related to nitrogen, followed by the *para*-related atoms. The two *meta*-positions carry the smallest positive charge, or a small negative charge. Thus, the stability trend of various isomeric BN naphthalens can be predicted by considering that the boron atom prefers to be placed at electropositive sites. Beginning with quinolinium cation, the most favoured position for boron would be 2 and **1,2** isomer is indeed the most stable one. Next comes position 10 leading to **1,10** isomer with relative energy of 7.87 kcal/mol. The *para*-related site is the next preferred place and the formed **1,4** isomer is by 22.61 kcal/mol less stable. Among the two *meta*-positions, the one at the ring-junction is a better place for boron, so that relative energies of **1,5** and **1,3** isomers are 32.43 kcal/mol and 34.43 kcal/mol. Placing boron atom in another ring decreases stability further (40.71-46.56 kcal/mol) and is not in a simple relation with the partial atomic charges.

The same analysis beginning with the isoquinolinium cation predict the stability trend which is in accord with the obtained results: **2,1** (0.00 kcal/mol), **2,3** (10.28 kcal/mol), **2,5** (29.56 kcal/mol), **2,10** (33.48 kcal/mol) and **3,1** (33.96 kcal). Here, too, substitution of a carbon atom by boron atom in another ring decreases stability further (39.69-48.00 kcal/mol). If we start from quinolizinium cation the predicted and the observed stability trend differs only for the last two isomers, which is due to the very small difference in partial charges of the two *meta*-positions: **5,10** (0.00 kcal/mol), **10,1** (5.11 kcal/mol), **5,2** (27.61 kcal/mol), **10,2** (31.12 kcal/mol) and **5,1** (29.95 kcal/mol).
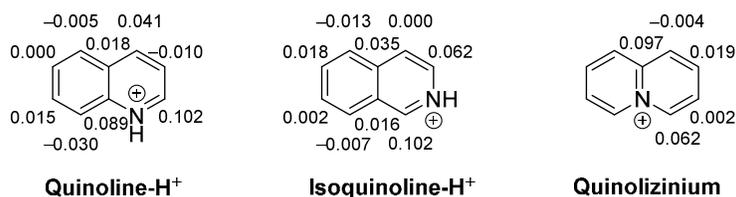


**Figure 4.** Hirshfeld partial atomic charges in protonated quinoline and isoquinoline, and quinolizinium cation.

In BN naphthalenes having both heteroatoms in one ring, the stability order is related with charges at both boron and nitrogen atoms, for each series derived from quinoline-H$^+$, isoquinoline-H$^+$ and quinolizinium cation. As charge at boron/nitrogen becomes less positive/negative, the energy of the molecule increases (Figure 5, upper part). No such relationship exists when heteroatoms are situated in separate rings, as was also suggested by the analysis of partial atomic charges in the parent nitrogen-substituted naphthalene (Figure 4).
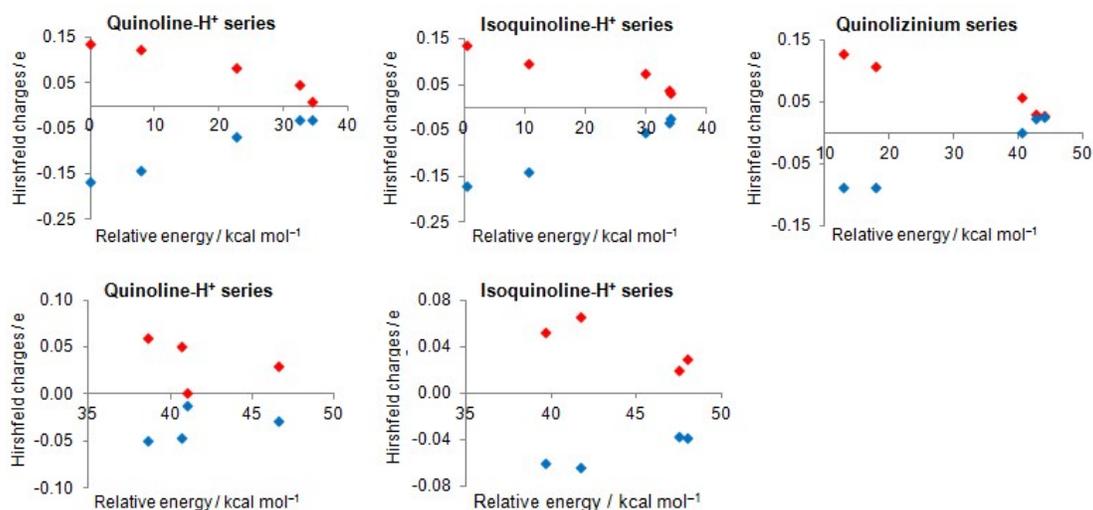
**Figure 5.** Hirshfeld charges at boron atom (red colour) and nitrogen atom (blue colour) in BN naphthalenes derived from quinoline-H$^+$, isoquinoline-H$^+$ and quinolizinium cation. Upper part: isomers having heteroatoms in one ring. Lower part: isomers having heteroatoms in separate rings.

In short, placing a boron atom in the same ring with nitrogen in the parent (iso)quinolinium results in a more stable system than placing a boron atom in another ring (difference in energy between the least stable same-ring isomer and the most stable separate-rings isomer is around 6 kcal/mol, for both series).

Charge distribution analysis in heteroatom-polarized hydrocarbon was used previously to explain stability order of cationic/anionic NBN/BNB substituted benzene analogues[6d] and BN substituted lower polyenes.[6i]

## HOMO/LUMO Energies

The trend of calculated HOMO/LUMO energy levels and energy gaps for 1,2-BN-related isomers is in accord with previous experimental and theoretical results.[8e] The previous observation that isomers of the m,n/n,m type (m,n = 1, 2 and 10)[8e] have similar HOMO-LUMO gaps holds for all isomeric BN naphthalenes (m,n = 1, 2, 3, 5, 7, 8, 10), as is shown in Table 1. In most of these pairs the

more stable isomer has lower HOMO and LUMO energy (**1,2**, **1,10**, **1,5**, **2,10**, **1,8** and **1,7**), while for the two pairs the more stable isomer has higher HOMO and LUMO energy (**3,1** and **2,5**).

Separation of two heteroatoms, boron and nitrogen, into two rings results in lower HOMO-LUMO energy gaps (2.86-3.95 eV) than when they are part of the same ring (3.76-4.94 eV). Among the former, in both charge-separated and neutral structure series the HOMO-LUMO gaps are the smallest when both heteroatoms occupy $\alpha$-positions (1, 4, 6 and 9 in Figure 1) and steadily increase when one or both heteroatoms are moved at the most external ring site, that is $\beta$-position (2, 3, 7 and 8 in Figure 1). Also, charge-separated isomers are characterized by smaller gaps compared with the related neutral structures (Table 1): **1,9** (2.86 eV)/**1,6** (3.11 eV), **1,7**/**7,1** (2.96 eV)/**1,8**/**8,1** (3.55 eV) and **2,8** (3.16 eV)/**2,7** (3.95 eV). When the two heteroatoms are part of one ring, the smallest and the largest HOMO-LUMO gaps belong to the 1,2-BN-related group: 3.76 eV when both heteroatoms are at the external $\beta$-site (**2,3** isomer) and 4.94 eV when both heteroatoms occupy internal sites (**5,10** isomer).

Charge separated 1,5-BN-related isomeric pair, **1,7**/**7,1**, features the lowest/highest energy frontier orbitals. The more stable **1,7** isomer has the lowest energy LUMO orbital ($-2.37$ eV) and would be the compound which is easiest to reduce. The less stable **7,1** isomer has the highest energy HOMO orbital ($-5.04$ eV) and would be the compound which is easiest to ionize.

Compared with the parent hydrocarbon, naphthalene, only **1,4** isomer retains similar HOMO-LUMO gap. It is slightly increased in the **1,2**/**2,1** isomeric pair and **5,10** isomer, all featuring 1,2-BN-relationship, and is lowered in all other isomers.

## Aromaticity Analysis

The NICS(0)$_{\pi zz}$ index suggests similar aromaticity of the corresponding rings in orientational isomers of the m,n/n,m type (**1,2**/**2,1**, **1,10**/**10,1**, **1,5**/**5,1**, **2,10**/**10,2**, **1,3**/**3,1**, **2,5**/**5,2**, **1,8**/**8,1** and **1,7**/**7,1** in Table 1) and this is fully supported by the PDI values. The HOMA index, however, assigns

increased bond length equalization for nitrogen vs boron heterocycle in isomers having two heterocyclic rings (all, but **1,2**/**2,1** and **1,3**/**3,1** pairs).

According to all three indices, aromaticity of a benzene unit in the parent naphthalene changes little (**1,3**/**3,1**) or becomes slightly larger (**1,2**/**2,1** and **1,4**) when the carbocyclic ring can be represented as having the aromatic π-electronic sextet, while boron and nitrogen atoms are shown in their trivalent forms (in the case of **1,3**/**3,1**, charges would reside on carbon atoms). Lack of the π-sextet in carbocyle reduces aromaticity, as in **2,3**-isomer. In this kind of BN naphthalenes, which have one carbocycle and one heterocycle, the heterocyclic ring is characterized by decreased aromaticity which is more prominent for 1,2- and 1,4-BN-related species (**1,2**/**2,1** and **1,4**) than for 1,3-BN-related isomers (**1,3**/**3,1**). These findings agree with our previous results[6e] and results of other group[7f] which classified 1,3-azaborine isomer as the most aromatic, among the three isomers, due to its inherent charge-separation instability of the π-system which acts as a driving force for the strongest delocalization.[6e] The smaller aromaticity of heterocycle results in larger aromaticity of carbocycle (**1,2**/**2,1** and **1,4** isomers), while larger aromaticity of heterocycle retains naphthalene's aromaticity of a carbocycle (**1,3**/**3,1** isomeric pair). In the case of **2,3** isomer, where six π-electrons belong to the heterocyclic part, it is more aromatic than the carbocyle and its aromaticity approaches that of naphthalene.

When a BN naphthalene contains two monoheterocycles (the BN pair is separated into two rings; **1,9**, **1,8**/**8,1**, **1,6**, **1,7**/**7,1**, **2,8** and **2,7** isomers), aromaticity of the two rings is similar (NICS and PDI), except in the case of **1,8**/**8,1** isomeric pair where the more cyclically delocalized ring, according to the neutral resonance structure shown in Table 1 (the right ring), is more aromatic than the other ring having more push-pull nature[24] than cyclic electron delocalization (the left ring). HOMA index, however, always characterizes nitrogen-containing ring as more bond length equalized than boron-containing ring. Aromaticity of these species is more or less reduced relative to naphthalene and is the weakest in the rings with push-pull π-electronic arrangement (left ring in **1,8**/**8,1** and both rings in

**2,7**). As we have shown previously for azaborine systems,[6e] in this kind of rings (i.e. 1,4-azaborine) the π-electron flow is more one-directional, toward electron-deficient boron, than cyclic. Only NICS(0)$_{\pi zz}$ characterizes charge-separated isomers, consisting of two monoheterocycles, to be as aromatic as naphthalene is.

In isomers belonging to 1,2-BN-related series, which have one heteroatom at the ring-fusion site, that is, those which consist of one monoheterocycle and one diheterocycle (**1,10/10,1** isomeric pair), all three inidices agree that diheterocycle is more aromatic, even though it contains a direct connection between two heteroatoms with large difference in electronegativity. Its aromaticity degree is close to that of naphthalene (NICS and HOMA). If both heteroatoms are at the ring-junction sites (**5,10** isomer), a decrease of aromaticity relative to naphthalene is observed.

In the 1,3- and 1,4-BN-related series having one heteroatom at the ring-junction site (**1,5/5,1**, **2,10/10,2** and **2,5/5,2**), HOMA index characterizes diheterocycle as more aromatic than monoheterocycle when boron occupies the ring-junction site (**1,5**, **2,10** and **2,5**), but monoheterocycle more aromatic than diheterocycle when nitrogen occupies the ring-junction site (**5,1**, **10,2** and **5,2**). NICS(0)$_{\pi zz}$ assigns (slightly) greater aromaticity to diheterocycle, while PDI values are comparable for both rings except for the **2,5/5,2** isomeric pair for which they characterize monoheterocycle as more aromatic.

Now, considering a degree of aromaticity of individual rings and all three aromaticity indices, we can distinguish three groups of compounds among the isomeric BN naphthalenes: 1) the first group involves isomers in which aromaticity of the two rings differs significantly, 2) the second group includes isomers with smaller difference in aromaticity degree between the two rings and 3) the third group comprises compounds which contain two rings of comparable aromaticity. 1) Molecules that belong to the first group have neutral π-system and consist of one carbocyle and one heterocycle (**1,2/2,1** isomeric pair and **1,4** isomer). Here, a decrease of aromaticity of heterocycle increases aromaticity of benzene ring to the extent which is larger than that in naphthalene. 2) The second group

also involves molecules with the neutral π-electronic system and they have B−N bond (**1,10**/**10,1** isomeric pair and **2,3** isomer), or 1,4-BN-relation and one ring with the push-pull electronic arrangement (**1,8**/**8,1** isomeric pair). Interestingly, among the former, the BN-containing ring is more aromatic even though the B−N bond includes atoms with large difference in electronegativity and one would expect little electron delocalization over this bond. Larger aromaticity can be explained by an examination of the main resonance structures given in Table 1, which show that in all three compounds the BN-containing ring is the one with the π-electronic sextet. In the case of **1,8**/**8,1** isomeric pair, the push-pull π-electronic structure of one ring decreases its aromaticity by involving one-directional π-electron flow, while the other ring having cyclic electron arrangement is characterized by somewhat larger aromaticity. 3) The third group involves all isomers having charge-separated π-electronic system, two isomers with the neutral π-system (**1,6** and **2,7**) and symmetrical **5,10** isomer. The least aromatic isomer within this group is **2,7** having push-pull electronic structure in both rings.

## Comparison of Aromaticity and Stability

Aromaticity is often associated with an increased thermodynamic stability of the molecule. However, there are a number of exceptions to this rule, because aromaticity is a kind of stabilizing effect while energetic stability is influenced by other factors, as well.[6c,e,7a,25] In the case of the studied BN isosters of naphthalene, there is no direct relationship between aromaticity and stability, either. As an example, we can consider internal/external type of orientational isomers. As discussed above, a degree of their aromaticity is similar, but they differ in energy by ~10 kcal/mol which is related to partial charges at the two heteroatoms (Figure 3).

Isomers consisting of two rings with similar aromaticity (group 3, from the previous section) can serve as another example. Thus, the charge-separated isomers having two monoheterocycles (**1,9**, **1,7**/**7,1** and **2,8**) and those having electronegative nitrogen at the ring-junction site (**5,1** and **10,2**) are

more aromatic than the push-pull arranged **2,7** isomer, but are of similar (**1,9**, **5,1** and **10,2**) or lower stability (**1,7**/**7,1** and **2,8**). Here, aromatic stabilization does not overcome charge-separation instability of the π-electronic system, as well as instability due to the partial positive charge at the nitrogen atom in **5,1** and **10,2** isomers (Figure 3). However, when nitrogen atom occupies external ring position and is negatively charged, the more aromatic charge-separated isomers **1,5** and **2,10** are more stable than the push-pull **2,7** one.

In group 1 from the previous section (carbocycle and heterocycle, that is **1,2**/**2,1** isomeric pair and **1,4** isomer), aromaticity of the corresponding rings is similar, but **1,4** isomer is less stable which can be ascribed to the smaller positive and negative charges at boron and nitrogen atoms (Figure 5) and an increased Pauli repulsion in 1,4- vs 1,2-BN-relation.[6e]

Thus, while aromaticity always acts as a stabilizing factor, it is the interplay of aromatic stabilization, charge-separation and Pauli destabilization, and the amount of charges at boron and nitrogen that determines the stability trend of BN naphthalenes.

## Conclusions

All isomeric BN isosters of naphthalene have been studied theoretically at the B3LYP/6-311+G(d,p) level in order to investigate how position and orientation of the BN unit affect their fundamental properties such as stability, aromaticity and frontier orbital energies.

It was found that orientational isomers of the m,n/n,m type (m, n = 1, 2, 3, 5, 7, 8, 10) have similar aromaticity (according to $NICS(0)_{\pi zz}$ and PDI), similar HOMO-LUMO gaps and similar relative energies, the latter only when both heteroatoms occupy external ring positions. If one heteroatom resides at the ring-junction site, energy difference increases to ~10 kcal/mol. This is explained by an analysis of partial atomic charges in the parent naphthalene, where the two common carbon atoms carry much less negative charge than the eight external atoms. Thus, substitution of ring-junction sites by boron and external atoms by nitrogen is energetically more favourable than the

opposite arrangement. Furthermore, the more stable isomer always contains more positively charged boron atom and more negatively charged nitrogen atom. In most of orientational isomers, the more stable one has lower energy frontier orbitals.

The stability trend of the studied compounds is predictable on the basis of charge distribution analysis of nitrogen polarized naphthalene, that is quinolinium, isoquinolinium and quinolizinium cations and is related with partial atomic charges at boron and nitrogen atoms, when they share the same ring. A decrease in positive/negative charge at B/N increases the energy of a system. In addition, sharing the same ring is energetically more favourable arrangement for the BN unit than their separation into two rings, by at least 6 kcal/mol. The latter arrangement creates smaller HOMO-LUMO gaps (2.86-3.95 eV) than putting the BN pair into the one ring (3.76-4.94 eV). The HOMO-LUMO gap of the parent hydrocarbon (4.75 eV) is retaind in **1,4**-isomer. It is slightly increased in 1,2-BN-related **1,2**/**2,1** and **5,10** isomers (4.9 eV), and is more or less decreased in all others.

By varying the BN position in the naphthalenic system, three kinds of compounds with respect to their aromaticity degree can be created: 1) aromaticity of the two rings differs significantly (carbocyle with π-electronic sextet is more aromatic than naphthalene, heterocycle is less aromatic and has 1,2- and 1,4-BN-relationship), 2) aromaticity of the two rings differs by smaller extent (when the 1,2-BN-relation forms the π-electronic sextet in BN-heterocyle, while the other ring, carbocyclic or monoheterocyclic lacks the π-sextet: the former is more aromatic than the latter; when the BN pair occupy external ring sites and a molecule consists of one ring with cyclic electronic arrangement and the other with the push-pull electronic structure, the latter being less aromatic) and 3) the two rings are of comparable aromaticity (all other isomers; among them, the one having push-pull electronic structure in both rings is the least aromatic). Aromaticity and stability are not directly related to each other since stability is determined by several factors, such as the amount of partial charges at heteroatoms, a degree of aromatic stabilization, and degree of charge-separation and Pauli destabilization.

The results of this work show that some fundamental properties of the smallest member of PAHs, naphthalene, can be tuned by varying the position of the BN unit within the molecule, while its different orientation has little effect. We hope that the established relations may lead experimental chemists to synthesize compounds with the desired and predictable properties.

## Acknowledgements

## Conflicts of Interest

There are no conflicts to declare.

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### TOC Graphic
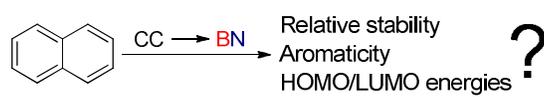


An insight into the electronic structure changes driven by CC → BN substitution in naphthalene system has been given by quantum chemical calculations.