PAPER

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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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All isomeric BN isosteres of naphthalene have been studied theoretically, at the B3LYP/6-311+G(d,p) level, in order to investigate the effect of the BN position in a molecule on relative stability, aromaticity and frontier orbital energies. The results show that the 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 the nitrogen-polarized naphthalenic system and is related to partial atomic charges at the boron and nitrogen atoms in a BN-heterocycle. The HOMO–LUMO gap of the parental hydrocarbon is retained only in the **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. The aromaticity of a benzene unit in naphthalene is retained/increased only in a carbocycle, when it can be represented as having a π-electronic sextet. The aromaticity of heterocyclic rings is more or less reduced relative to naphthalene and is the weakest in the rings featuring the push–pull π-electronic structure while the BN pair resides at the external ring positions.

Introduction

There is increasing interest in compounds having one or more CC units replaced by an isoelectronic BN pair.[1] The polarity of the BN unit endows such compounds with unique electronic properties giving potential for application in various fields, such 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 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 the 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 reactivities, with minimal changes in molecular shape compared with a known

hydrocarbon, or to synthesize a molecule that adopts 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 the three isomers have been synthesized.[1,6c,e,7] In the naphthalenic system, which is the simplest polycyclic aromatic hydrocarbon (PAH), only those BN isosteres that feature 1,2- and 1,4-BN relationships are experimentally known. While five, out of six, isomers have been prepared in the case of the former,[8] only one isomeric species having a 1,4-BN relation has been isolated.[5,9] A fundamental question about the 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.

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Computational details

The optimization of molecular structures and NICS calculations have been performed 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 the structures were energy minima (no imaginary frequencies). Electronic energies are corrected for zero-point energies.

A degree of aromaticity was estimated at the same level of theory on the basis of π-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 (σ and inner shell orbitals) and contributions from the parallel orientations of a molecule with respect to the magnetic field direction. A more negative NICS value means a 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 π orbitals which belong to one ring were taken into account when calculating the 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. A 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 eqn (1):

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

α is an empirical constant chosen to give HOMA = 0 for a non-aromatic system and HOMA = 1 for a system where all the bonds are equal to an optimal bond length (R_{opt}), n is the number of bonds taken into summation, R_i is an individual bond length and j represents the type of the bond. We have used the following α/R_{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 Fig. 1.
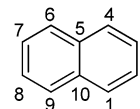

Fig. 1   Numbering system used in this study.

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]

Table 1 lists the 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.
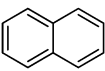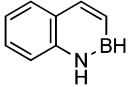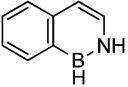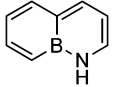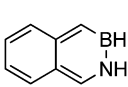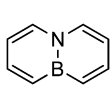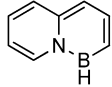
There are six isomers with a 1,2-BN relationship denoted as **1,2, 1,10, 2,1, 2,3, 5,10** and **10,1** (Table 1, the first row showing structures), seven isomeric 1,3-BN-related species denoted as **1,3, 1,5, 1,9, 2,10, 3,1, 5,1** and **10,2** (Table 1, the second row showing structures), six isomers featuring the 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 denoted as **1,7, 2,8** and **7,1**, and one isomer having a BN pair in a 1,6-relationship (Table 1, the last row showing structures). All the isomers having the BN unit in 1,2-, 1,4- and 1,6-relationships can be represented by neutral structures, while those having the BN unit in the 1,3- and 1,5-positions are intrinsically charge-separated (no neutral resonance structure can be written).
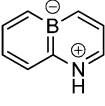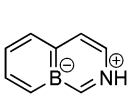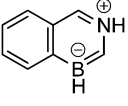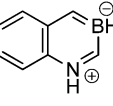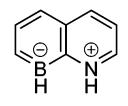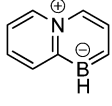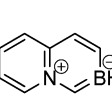
Stability analysis

The relative energies of BN naphthalenes span a range of 48 kcal mol^{-1}. 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^{-1}. The energies of the 1,4-BN-related isomers span a similar range of 18.09 kcal mol^{-1} (22.61–40.71 kcal mol^{-1} relative to the most stable **1,2** isomer). The energy of the 1,6-BN-related **2,7** isomer is just slightly higher than the last cited value and amounts 41.72 kcal mol^{-1}, relative to the **1,2** isomer. A narrower range of energies, 11.54 kcal mol^{-1}, is observed for the group containing 1,3-BN-related charge-separated species, and they are 32.43–43.97 kcal mol^{-1} relative to the **1,2** isomer. An even narrower range of energies, 1.44 kcal mol^{-1}, is found in the other group comprising the charge-separated 1,5-BN-related isomers, which are 46.56–48.00 kcal mol^{-1} 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]

The stability trend of the most stable members of the 1,2-, 1,3- and 1,4-BN-related groups, that is the **1,2** (0.00 kcal mol^{-1}), **1,5** (32.43 kcal mol^{-1}) and **1,4** isomers (22.61 kcal mol^{-1}), is the same as that previously reported for the 1,2-, 1,3- and 1,4-azaborine isomers (0.00 kcal mol^{-1}, 29.56 kcal mol^{-1} and 21.88 kcal mol^{-1}, respectively),[6e] and can be similarly rationalized by the charge-separation instability of the π-system in the **1,5** isomer, created
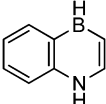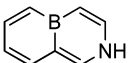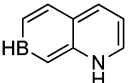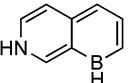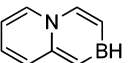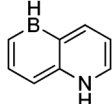
Table 1 Relative energies^a (kcal mol^{-1}), HOMO/LUMO energies (eV), NICS values (ppm), HOMA and PDI (electrons) of naphthalene and BN-naphthalenes

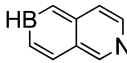| Compound	naphthalene	1,2	2,1	1,10	2,3	5,10	10,1
Isomer		**1,2**	**2,1**	**1,10**	**2,3**	**5,10**	**10,1**
E_{rel}		0.00	0.40	7.87	10.68	12.85	17.96
E_{LUMO}	−1.40	−1.51	−1.04	−1.87	−1.83	−1.33	−1.56
E_{HOMO}	−6.15	−6.45	−5.97	−5.89	−5.59	−6.28	−5.55
$\Delta E_{HOMO-LUMO}$	4.75	4.93	4.93	4.02	3.76	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
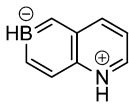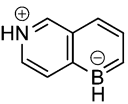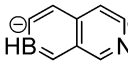
Compound	1,5	2,10	3,1	1,3	1,9	5,1	10,2
Isomer	**1,5**	**2,10**	**3,1**	**1,3**	**1,9**	**5,1**	**10,2**
E_{rel}	0.00	1.46	1.53	2.00	8.58	10.37	11.54
$E_{rel}{}^b$	32.43	33.88	33.96	34.43	41.01	42.80	43.97
E_{LUMO}	−2.01	−1.73	−1.67	−1.99	−2.30	−1.69	−1.61
E_{HOMO}	−5.83	−5.91	−5.55	−5.75	−5.16	−5.47	−5.76
$\Delta E_{HOMO-LUMO}$	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	1,4	2,5	1,8	8,1	5,2	1,6
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
$\Delta E_{HOMO-LUMO}$	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	1,7	7,1	2,8	2,7
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.

by the 1,3-BN relationship, and an increased steric repulsion between the lone pair of nitrogen and the π-electronic system in the **1,4** isomer relative to lower repulsion when boron and nitrogen are directly connected, as in the **1,2** isomer. The separation of the BN unit into two rings decreases the stability further, giving the following trend of decreasing stability: 1,2-relation (**1,2** isomer, 0.00 kcal mol^{-1}) > 1,4-relation (**1,4** isomer, 22.61 kcal mol^{-1}) > 1,3-relation (**1,5** isomer, 32.43 kcal mol^{-1}) > 1,6-relation (**2,7** isomer, 41.72 kcal mol^{-1}) > 1,5-relation (**1,7** isomer, 46.56 kcal mol^{-1}).

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
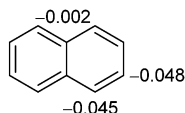
Fig. 2   Hirshfeld partial atomic charges in naphthalene.

and nitrogen atoms at the 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 denoted, herein, as the internal/external isomers). The energy difference between the two corresponding external isomers is small (0.4–1.1 kcal mol^{-1}), while the energy difference between the two corresponding internal/external isomers is much larger and amounts to 10.1–10.5 kcal mol^{-1}. The less stable isomer always contains a 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 (Fig. 2). As seen from the figure, external carbon atoms carry more negative charge than the internal ones. If we had to substitute the carbon atoms with nitrogen and boron, placing the more electronegative nitrogen at the external position and the less electronegative boron at the internal position would be more favoured than the opposite arrangement. Hence, there is a large energy difference between the two internal/external isomers. The partial atomic charges of the two different external positions, α and β, are similar, so that the stability difference between the two corresponding external isomers is small.

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

The substitution of a carbon atom in naphthalene by the nitrogen atom polarizes the system further and the obtained charge distribution could help to decide 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 Fig. 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 naphthalenes can be predicted by considering that the boron atom prefers to be placed at the electropositive sites. Beginning with the quinolinium cation, the most favoured position for
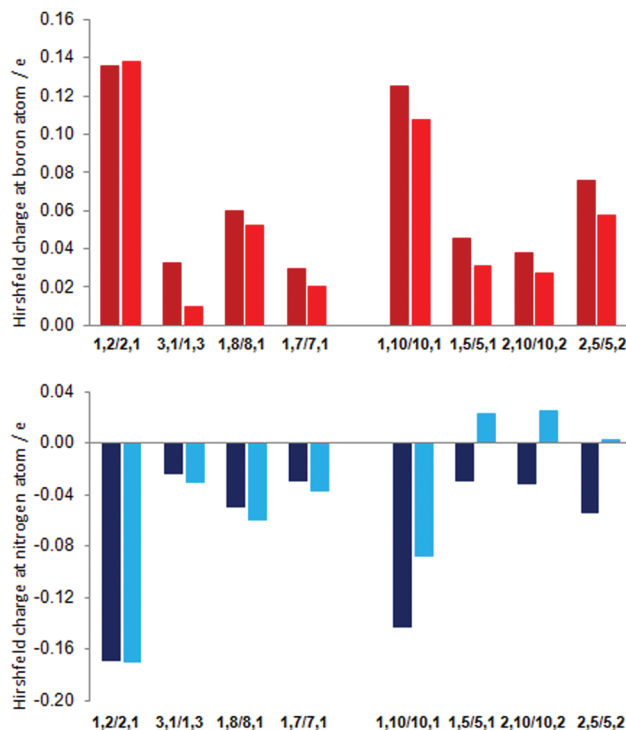
Fig. 3   Hirshfeld charges at the boron atom (the upper part) and the nitrogen atom (the lower part) in the eight orientational isomers of BN naphthalenes: dark red/dark blue colour represents charges in the more stable of the two isomers.
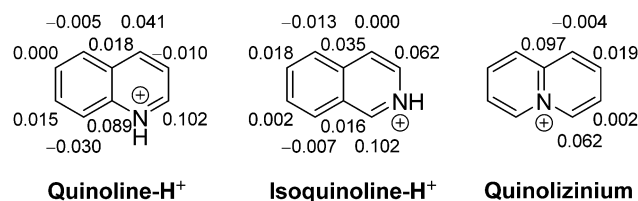
Fig. 4   Hirshfeld partial atomic charges in protonated quinoline and iso-quinoline, and quinolizinium cations.

boron would be 2 and the **1,2** isomer is indeed the most stable one. Next comes position 10 leading to the **1,10** isomer with a relative energy of 7.87 kcal mol^{-1}. The *para*-related site is the next preferred place and the formed **1,4** isomer is by 22.61 kcal mol^{-1} less stable. Among the two *meta*-positions, the one at the ring-junction is a better place for boron, so that the relative energies of the **1,5** and **1,3** isomers are 32.43 kcal mol^{-1} and 34.43 kcal mol^{-1}. By placing the boron atom in another ring decreases the stability further (40.71–46.56 kcal mol^{-1}) and is not in a simple relation with the partial atomic charges. The same analysis beginning with the isoquinolinium cation predicts the stability trend which is in accord with the obtained results: **2,1** (0.00 kcal mol^{-1}), **2,3** (10.28 kcal mol^{-1}), **2,5** (29.56 kcal mol^{-1}), **2,10** (33.48 kcal mol^{-1}) and **3,1** (33.96 kcal). Here, too, the substitution of a carbon atom by the boron atom in another ring decreases the stability further (39.69–48.00 kcal mol^{-1}). If we begin from the 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
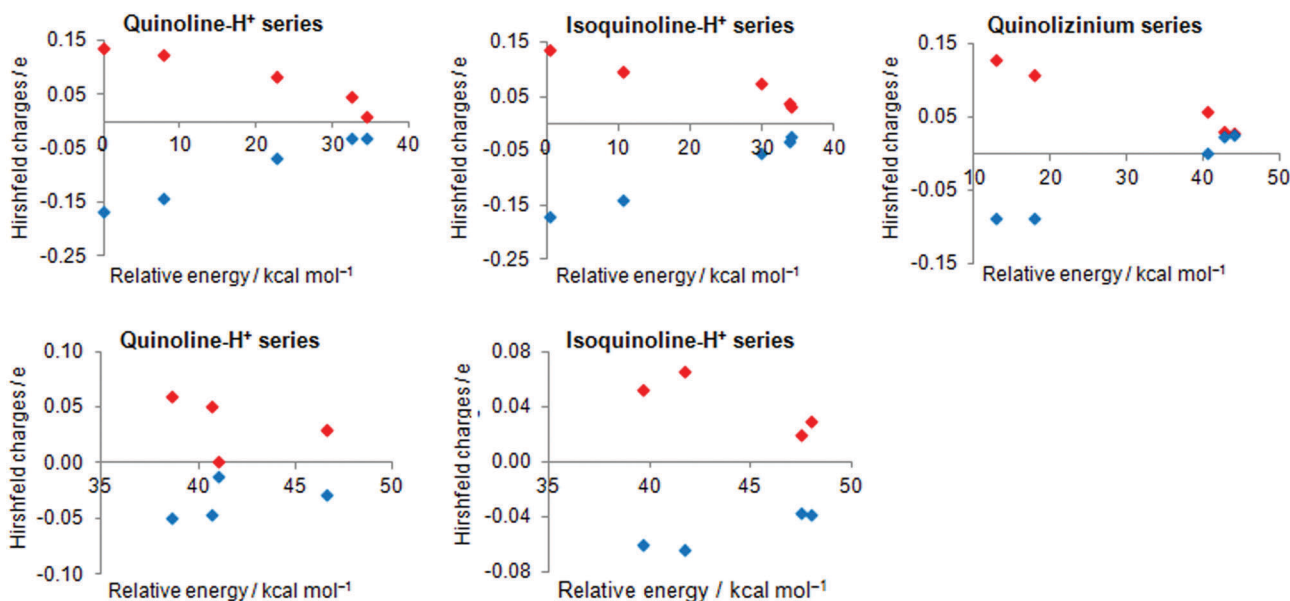
Fig. 5 Hirshfeld charges at the boron atom (red colour) and the nitrogen atom (blue colour) in the BN naphthalenes derived from quinoline-H$^+$, isoquinoline-H$^+$ and quinolizinium cations. Upper part: The isomers having heteroatoms in one ring. Lower part: The isomers having heteroatoms in separate rings.

the partial charges of the two *meta*-positions: **5,10** (0.00 kcal mol^{-1}), **10,1** (5.11 kcal mol^{-1}), **5,2** (27.61 kcal mol^{-1}), **10,2** (31.12 kcal mol^{-1}) and **5,1** (29.95 kcal mol^{-1}).

In BN naphthalenes having both the heteroatoms in one ring, the stability order is related with charges at both the boron and nitrogen atoms, for each series derived from quinoline-H$^+$, isoquinoline-H$^+$ and quinolizinium cations. As the charge at boron/nitrogen becomes less positive/negative, the energy of the molecule increases (Fig. 5, the 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 (Fig. 4).

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^{-1}, for both series).

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

HOMO/LUMO energies

The trend of the calculated HOMO/LUMO energy levels and energy gaps for the 1,2-BN-related isomers is in accord with previous experimental and theoretical results.[8e] The previous observation that the isomers of the *m,n/n,m* type (*m*, *n* = 1, 2 and 10)[8e] have similar HOMO–LUMO gaps holds for all the 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 a 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 the higher HOMO and LUMO energy (**3,1** and **2,5**).

The 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 the charge-separated and neutral structure series, the HOMO–LUMO gaps are the smallest when both heteroatoms occupy the α-positions (1, 4, 6 and 9 in Fig. 1) and steadily increase when one or both heteroatoms are moved to the most external ring site, that is the β-position (2, 3, 7 and 8 in Fig. 1). Also, the 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 β-site (**2,3** isomer) and 4.94 eV when both heteroatoms occupy the internal sites (**5,10** isomer).

The 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 the **1,4** isomer retains a similar HOMO–LUMO gap. It is slightly increased in the **1,2/2,1** isomeric pair and the **5,10** isomer, all featuring the 1,2-BN relationship, and is lowered in all the other isomers.

Aromaticity analysis

The NICS(0)$_{\pi zz}$ index suggests a similar aromaticity of the corresponding rings in the 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 the nitrogen *vs.* boron heterocycle in the isomers having two heterocyclic rings (all, but **1,2/2,1** and **1,3/3,1** pairs).

According to all the three indices, the 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 the boron and nitrogen atoms are shown in their trivalent forms (in the case of **1,3/3,1**, charges would reside on the carbon atoms). The lack of the π-sextet in a carbocycle reduces aromaticity, as in the **2,3**-isomer. In this kind of BN naphthalene, which has one carbocycle and one heterocycle, the heterocyclic ring is characterized by decreased aromaticity which is more prominent for the 1,2- and 1,4-BN-related species (**1,2/2,1** and **1,4**) than for the 1,3-BN-related isomers (**1,3/3,1**). These findings agree with our previous results[6e] and the results of another group[7f] which classified the 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 the heterocycle results in the larger aromaticity of the carbocycle (**1,2/2,1** and **1,4** isomers), while the larger aromaticity of the heterocycle retains naphthalene's aromaticity of a carbocycle (**1,3/3,1** isomeric pair). In the case of the **2,3** isomer, where six π-electrons belong to the heterocyclic part, it is more aromatic than the carbocycle and its aromaticity approaches that of naphthalene.

When a BN naphthalene contains two monoheterocycles (the BN pair is separated into two rings; the **1,9**, **1,8/8,1**, **1,6**, **1,7/7,1**, **2,8** and **2,7** isomers), the aromaticity of the two rings is similar (NICS and PDI), except in the case of the **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 a more push–pull nature[24] than cyclic electron delocalization (the left ring). The HOMA index, however, always characterizes the nitrogen-containing ring as more bond length equalized than boron-containing ring. The aromaticity of these species is more or less reduced relative to naphthalene and is weakest in the rings with a push–pull π-electronic arrangement (the 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 ring (*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 the 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 the three indices agree that the diheterocycle is more aromatic, even though it contains a direct connection between two heteroatoms with a 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**), the HOMA index characterizes the diheterocycle as more aromatic than the monoheterocycle when boron occupies the ring-junction site (**1,5**, **2,10** and **2,5**), but the monoheterocycle is more aromatic than the diheterocycle when nitrogen occupies the ring-junction site (**5,1**, **10,2** and **5,2**). NICS(0)$_{\pi zz}$ assigns (slightly) greater aromaticity to the diheterocycle, while the PDI values are comparable for both the rings except for the **2,5/5,2** isomeric pair for which they characterize the monoheterocycle as more aromatic.

Now, considering a degree of aromaticity of individual rings and all the three aromaticity indices, we can distinguish three groups of compounds among the isomeric BN naphthalenes: (1) the first group involves the isomers in which the aromaticity of the two rings differs significantly, (2) the second group includes isomers with a smaller difference in the 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 a neutral π-system and consist of one carbocycle and one heterocycle (**1,2/2,1** isomeric pair and the **1,4** isomer). Here, a decrease of aromaticity of the heterocycle increases the aromaticity of the 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 bonds (**1,10/10,1** isomeric pair and the **2,3** isomer), or a 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 a 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 the three compounds the BN-containing ring is the one with the π-electronic sextet. In the case of the **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 the isomers having a charge-separated π-electronic system, two isomers with the neutral π-system (**1,6** and **2,7**) and the symmetrical **5,10** isomer. The least aromatic isomer within this group is **2,7** having a 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 isosteres of naphthalene, there is no direct relationship between aromaticity and stability, either. As an example, we can consider the internal/external type of orientational isomers. As discussed above, the degree of their aromaticity is similar, but they differ in energy by ~10 kcal mol^{-1} which is related to partial charges at the two heteroatoms (Fig. 3).

The 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 the **5,1** and **10,2** isomers (Fig. 3). However, when the nitrogen atom occupies the 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 the **1,2/2,1** isomeric pair and **1,4** isomer), the aromaticity of the corresponding rings is similar, but the **1,4** isomer is less stable which can be ascribed to the smaller positive and negative charges at the boron and nitrogen atoms (Fig. 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 the isomeric BN isosteres of naphthalene have been studied theoretically at the B3LYP/6-311+G(d,p) level in order to investigate how the position and orientation of the BN unit affect their fundamental properties such as stability, aromaticity and frontier orbital energies.

It was found that the 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, the energy difference increases to ~10 kcal mol^{-1}. 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, the substitution of ring-junction sites by the boron and external atoms by nitrogen is energetically more favourable than the opposite arrangement. Furthermore, the more stable isomer always contains a more positively charged boron atom and a more negatively charged nitrogen atom. In most of the orientational isomers, the more stable one has lower energy frontier orbitals.

The stability trend of the studied compounds is predictable on the basis of the charge distribution analysis of nitrogen polarized naphthalene, that is quinolinium, isoquinolinium and quinolizinium cations and is related with partial atomic charges at the boron and nitrogen atoms, when they share the same ring. A decrease in the positive/negative charge at B/N increases the energy of a system. In addition, sharing the same

ring is an energetically more favourable arrangement for the BN unit than their separation into two rings, by at least 6 kcal mol^{-1}. 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 retained in the **1,4**-isomer. It is slightly increased in the 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 (carbocycle with π-electronic sextet is more aromatic than naphthalene, the heterocycle is less aromatic and has the 1,2- and 1,4-BN relationship), (2) aromaticity of the two rings differs by a smaller extent (when the 1,2-BN relation forms the π-electronic sextet in the BN-heterocycle, 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 the other isomers; among them, the one having a 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, the 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 orientations has little effect. We hope that the established relations may lead experimental chemists to synthesize compounds with the desired and predictable properties.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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