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ORIGINAL RESEARCH

Aromaticity of benzenoid hydrocarbons with inserted –B=B– and –BH–BH– groups: a comparison

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Abstract Structures of selected polycyclic conjugated hydrocarbons with –B=B– and –BH–BH– moieties inserted in different places were calculated at the B3LYP/6-311++G** level and their aromatic properties evaluated. HOMA, NICS(0), NICS(1)zz, Λ and PDI indices were used for studying their aromatic properties. Both optimized planar (as in parent hydrocarbons) and non-planar structures were taken into account. It is shown that insertion of both types of boron groups disturbs and decreases the aromaticity of the corresponding hydrocarbons. The decreasing effect of the –BH–BH– group is much stronger. What is quite intriguing is that it appears that non-planar structures of the studied compounds have a little higher aromaticity than the strictly planar ones. Mutual correlations between results obtained by different aromaticity indices are calculated and thoroughly discussed.

Keywords Aromaticity · Substituted benzenoid hydrocarbons · Boron compounds · HOMA · NICS

Introduction

Replacement of one or more carbon atom(s) in benzene and in polycyclic aromatic hydrocarbons (PAH) by heteroatoms other than the typical "heterocyclic" elements like nitrogen, oxygen, phosphorus and sulfur has been recently a topic of several studies [1–6]. Such structural modifications are important because they can create compounds with unusual properties. The preparation of the (poly)cyclic hydrocarbons doped by boron(s) discussed in the present work would be difficult. However, some publications report the syntheses of other types of hydrocarbons with inserted BB bonds [7–12]. Very important for further development of the chemistry of substituted boron(s) hydrocarbons is the understanding of the effects of the replacement of C by B^- [13, 14].

Among others, introduction of boron into a carbon place in the hydrocarbon skeleton provides the possibility of obtaining new materials with potentially useful properties. Boron is one of the key elements [15]; it forms enormous number of compounds, and the riches of its chemistry can be compared only with chemistries of such basic elements like carbon, silicon, nitrogen or oxygen. The main groups of boron compounds are borates [16] and borosilicates [17]. Many compounds built from boron and hydrogen atoms (boranes), and from boron, hydrogen and carbon atoms (carboranes) are also well known [18].

As indicated, even in the commonly used name of "aromatic hydrocarbons," the aromaticity is one of the most significant properties defining these compounds. The aromaticity defines their structure as well as their reactivity. Thus, increasing or decreasing the aromatic properties in substituted hydrocarbons is very important for their properties and potential applications. Therefore, the influence of heteroatoms on the aromaticity of conjugated hydrocarbons is a subject worth studying.

In this work, we examined the aromatic properties of several aromatic hydrocarbons, such as benzene, naphthalene, anthracene, phenanthrene, pyrene and coronene, substituted by –B=B– and –BH–BH– moieties in various positions. Recently we have published two papers in which

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aromaticity of some conjugated hydrocarbons doped by a single boron atom (–B=) [19] and by two boron atoms –B=B– [20] was briefly studied. Those publications resulted in arising the question of what will happen concerning substitution by the –BH–BH– group [21], something that cannot be predicted. Thus, we decided to study in more detail the aromaticity of hydrocarbons with structures disturbed by replacing a CC bond by –B=B– or –BH–BH– groups.

The question of the aromatic properties of compounds containing boron is not new. Borazine, $B_3N_3H_6$, the most famous member of the azaborines group, is even named "inorganic benzene" [22]. Aromaticity of other boron compounds was also reported several times [23–28]. Thus, we think that investigation of the aromatic properties of boron-substituted hydrocarbons and the evaluation of the usefulness of different aromaticity indices for the description of such compounds' aromaticity was a really interesting topic.

Computational details

Manifestations of strong cyclic electronic delocalization, commonly known under the little confusing name of "aromaticity," are an intriguing but still not fully characterized phenomenon. Its definition is still under vivid disputation [29], and as a result of this ambiguously definition, there is no single method that is generally accepted for aromaticity strength evaluation. So-called aromaticity indices are a set of very different methods based on three main aromaticity criteria: energetic, geometric and magnetic [30], as well as electronic indices that derive aromatic properties directly from molecular wave functions analysis [31]. It is recommended to use more than one aromaticity index of aromaticity in order to consider all aspects of aromaticity [32, 33].

That is why, in order to obtain a wide range of information about aromatic properties of the structures studied in this paper, we will use different sets of aromaticity indices, namely: harmonic oscillator model of aromaticity (HOMA) [34], nucleus-independent chemical shift (NICS) [35, 36], para delocalization index (PDI) [37] and magnetic susceptibility (Λ) [38]. Parameters of the HOMA model (optimum aromatic bond length R_{opt} and normalization constant α) for the CC ($R_{opt} = 1.388$ Å, $\alpha = 257.70$), BC ($R_{opt} = 1.4378$ Å, $\alpha = 118.009$) and BB ($R_{opt} = 1.5665$ Å, $\alpha = 244.147$) bonds were taken from references [19, 20, 39]. Values of the delocalization indices [40] between atoms in *para* position, necessary for PDI calculations, were obtained with the AIMAll package [41]. Indices used in this work can be divided into two groups. HOMA, NICS and PDI indices were used to determine aromatic properties of all single rings of studied structures. On the other hand, HOMA (again) and Λ provided the total aromaticity of the compounds.

The B3LYP [42] /6-311++G(d,p) [43] level of computation was used in this work. This level of theory had been used in our previous papers for calculations of the structures of boron-substituted hydrocarbons [19, 20]. Thus, such a basis set enabled the direct comparison between the results obtained in this work and those published previously. Strictly planar (like for the parent hydrocarbons) and relaxed unplanar structures were examined. All structural optimizations were executed using the Gaussian'09 Revision A.02 package [44].

Results and discussion

All compounds studied in this work obtained by substituting the CC bonds in cyclic conjugated hydrocarbons by –B=B– or –BH–BH– groups are presented in Fig. 1, compounds **1** to **12**; series **a** corresponds to –B=B– derivatives and series **b** to –BH–BH– ones. Ring labeling is also provided.

Geometry optimization procedure was performed for all compounds. In general, insertion of boron fragments into the flat hydrocarbon's structures results in destroying the planarity of the ring. Thus, the boron derivatives of the studied hydrocarbons are not planar. The CBBC dihedral angle in boron compounds is about 40° for **a** series and 30° for the **b** series. Due to the non-planar structures of the compounds, we decided to determine the aromaticities of boron derivatives with a plane of symmetry (like in the parent hydrocarbons) and without it (like in relaxed structures of boron derivatives). There are two exceptions from this typical behavior for boron-substituted hydrocarbons, in both cases for –BH–BH– substituted derivatives. The structure of compound **10b** is flat; no loss of planarity is observed. On the other hand, in compound **5b**, the boron-containing ring transforms, upon optimization, into a pyramidal structure with a five-membered ring (four carbons and a BH group) in the base of the pyramid and a second BH group at the top. Due to its unusual structure, this "ring" has been excluded from further analyses. For all other than **5b** and **10b** compounds, the planar structures are transition states between two equivalent non-planar minima. The energy barriers between planar and non-planar structures are different, from about 0.1 kJ mol^{-1} (for compounds **2a**, **9a** and **12b**) up to about 43 kJ mol^{-1} for compound **5a**.

Aromaticity data for the whole structures of boron-substituted hydrocarbons will be presented first. The analysis is based on the values of the HOMA index for all bonds ($HOMA_{total}$) as well as on values of magnetic

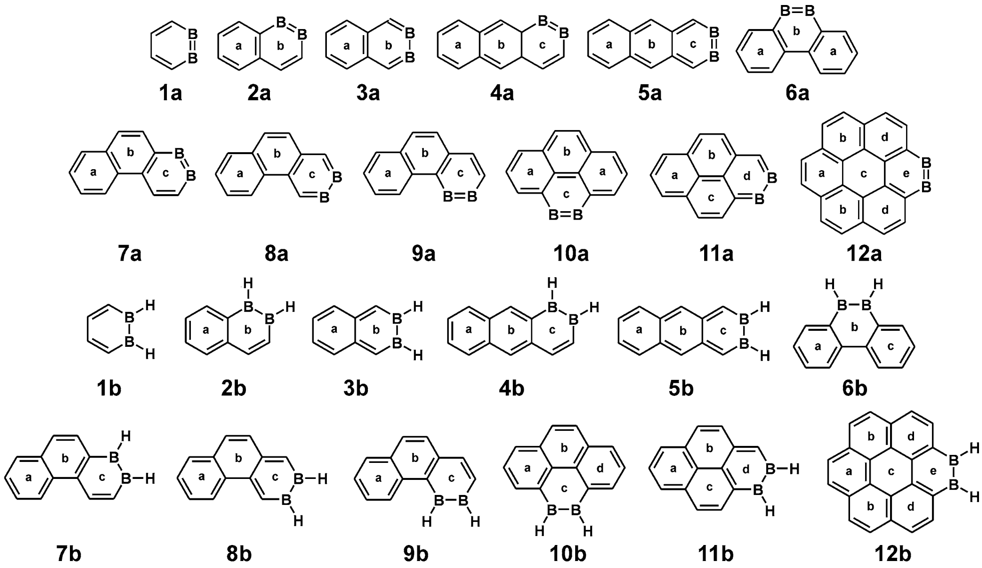

Fig. 1 Molecular structures and individual ring labeling of the studied hydrocarbons with inserted –B=B– groups, a series, and inserted –BH–BH– groups, b series. Hydrogen atoms connected to the carbon atoms are omitted for clarity

susceptibility (Λ). Data obtained by these two methods are collected in Table 1 and presented in Fig. 2.

Variations of the $\mathrm{HOMA}_{\mathrm{total}}$ index for hydrocarbons of the **a** series are surprisingly small. Most $\mathrm{HOMA}_{\mathrm{total}}$ values for this group of compounds are between 0.67 (compound **9a**) and 0.53 (compound **5a**). Thus, all these compounds can be classified as moderate aromatic. Only compound **1a** (the benzene derivative) has higher $\mathrm{HOMA}_{\mathrm{total}}$ value (0.79) and from this point of view can be described as almost highly aromatic. Also the aromaticity of compound **3a** (HOMA = 0.68) is quite high. On the other side, $\mathrm{HOMA}_{\mathrm{total}}$ values for the compounds of the **b** series span over a much larger region. They are antiaromatic (compounds **1b** and **3b**) or non-aromatic (**2b**, **7b**, **8b**, **9b**, **11b**); small aromatic properties are suggested by the $\mathrm{HOMA}_{\mathrm{total}}$ values for compounds **4b**, **5b**, **6b**, **10b** and especially **12b**. The last compound can be considered as moderate aromatic. However, its moderate aromaticity is due to the fact that compound **12b**, a derivative of coronene, is much larger than the other studied systems. Thus, boron substitution strongly disturbs electronic structure probably only in a part of its carbon skeleton. The biggest difference in aromatic properties is observed between benzene derivatives of both series. One (benzene with a –B=B– group, **1a**) is aromatic, while strong antiaromaticity is observed for its –BH–BH– counterpart, **1b**. Benzene is the smaller hydrocarbon considered in this work, so it is reasonable that in this case, introduction of the boron atoms can change completely its electronic structure. Differences between $\mathrm{HOMA}_{\mathrm{total}}$ values for planar and non-planar structures of **a** series are always small or very small. Bigger changes between planar and non-planar systems are observed for

Table 1 Aromaticity data for whole structures of substituted hydrocarbons (values for planar structures underlined)

Compound	–B=B– substitution				–BH–BH– substitution			
	$\mathrm{HOMA}_{\mathrm{total}}$		Λ [10^{-30} J/T^2]		$\mathrm{HOMA}_{\mathrm{total}}$		Λ [10^{-30} J/T^2]	
1	0.79	0.73	−644.3	−728.0	−1.28	−0.45	−392.0	−368.0
2	0.64	0.65	−165.7	−468.4	−0.06	0.13	−846.1	−846.3
3	0.56	0.68	−1022.4	−1220.0	−0.65	−0.26	104.5	−137.2
4	0.61	0.64	−3020.5	6144.6	0.21	0.28	−833.8	−895.0
5	0.53	0.63	−1458.9	−1378.5	0.46	–	4034.2	–
6	0.54	0.62	−2723.7	−817.2	0.25	0.32	−1132.9	−1423.0
7	0.61	0.62	−1193.5	−1649.7	0.12	0.28	−949.0	−1279.3
8	0.59	0.67	−1613.0	−1536.0	−0.17	0.07	−330.8	−853.7
9	0.67	0.67	−1073.7	−1438.8	0.10	0.30	−498.0	−1156.5
10	0.55	0.60	−2613.3	−8450.5	0.34	–	−1578.5	–
11	0.57	0.65	−1657.4	−1770.8	0.17	0.26	−751.1	−790.4
12	0.59	0.65	−6184.0	−2371.2	0.44	0.44	−569.3	−210.3

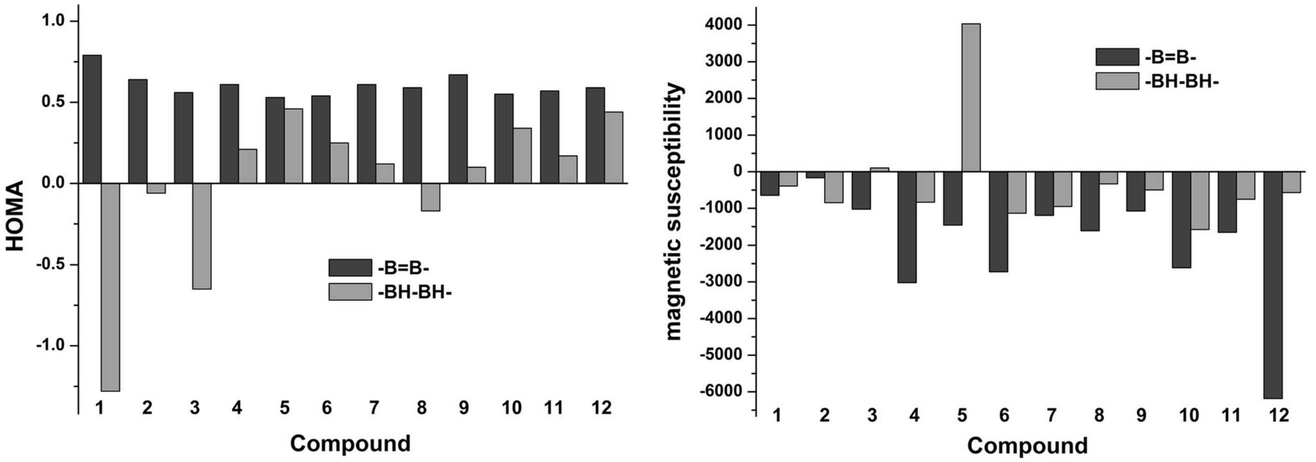

Fig. 2 Aromaticity data for entire studied systems

the **b** series (up to -0.83). What is intriguing is that $\text{HOMA}_{\text{total}}$ values are usually a bit higher for relaxed non-planar structures. This behavior is in opposite to the pure hydrocarbons where destroying the planar structure results in decreasing aromatic properties [45].

In general, calculated Λ values follow $\text{HOMA}_{\text{total}}$ data, i.e., compounds of the **a** series are more aromatic than their **b** series counterparts. However, differences between magnetic susceptibilities of the same compound in its planar and non-planar structures are much greater than for the $\text{HOMA}_{\text{total}}$ results. In addition, magnetic susceptibility calculations afforded sometimes quite unexpected values. Such an unexpected case is compound **2**, where significantly more negative values are predicted for the hydrocarbon with the –BH–BH– insertion, **2b**. Another somewhat strange case is that of compound **4**. For this compound, a very huge, difficult to explain, change in magnetic properties occurred during transition from the flat to the relaxed structure without symmetry plane. Such a huge change is not observed for any other structure reported in this work. The origin of such unexpected artifact in the magnetic susceptibility data is worth of a future more detailed study.

Low correlations are observed between $\text{HOMA}_{\text{total}}$ and Λ data presented in Table 1. For both series, correlation coefficients between $\text{HOMA}_{\text{total}}$ and Λ are almost zero. Such a result can support the thesis about the multidimensional character of aromaticity, where structural and magnetic indices correspond to different manifestations of this property [32]. What is even more intriguing is that there is no correlation between magnetic susceptibilities (Λ) determined for the –B=B– substituted compounds and their –BH–BH– analogs (correlation coefficients, c.c., equal to -0.07 for planar and -0.11 for non-planar structures). At the same time, there is some correlation between $\text{HOMA}_{\text{total}}$ data for two groups of boron-doped hydrocarbons, correlation coefficients being 0.46 and 0.66 for planar and non-planar structures, respectively.

Now the aromatic properties of individual rings in the structures of boron-substituted hydrocarbons will be discussed. The data are collected in Table 2 (for compounds containing –B=B– group, **1**) and in Table 3 (compounds with the –BH–BH– group, **2**). Figure 3 reports the aromaticity data for all rings with boron atoms.

It should be mentioned at this moment that there are some problems with using some standard aromaticity indices for the compounds containing boron atoms. First of all, NICS index data look sometimes unreliable for these rings. This can be the result of the fact that electrons close to B atoms are freer to move than those of C atoms and create ring currents that produce these high NICS(0) values. The fact that electrons close to B atoms are more diffuse can influence also the PDI data, due to the higher values of para delocalization indices obtained in these rings. Thus, PDIs for rings containing B atoms are likely to be somewhat overestimated.

HOMA values for the individual rings with only carbon atoms are usually quite “stable” during “transition” from planar to non-planar structures. Some changes appear for the rings that have a boundary with the ring containing boron atoms. For rings with boron atoms, transforming the molecular structure from planar to non-planar results sometimes in a substantial change. It can be noticed that in non-planar structures, some rings containing boron atoms, compounds **3a** and **6a** as well as **1b**, **2b** and **3b**, switch their antiaromatic properties into non-aromatic ones. Almost all rings increase their HOMA values in non-planar structures, and this is the rule for all the rings with boron atoms. The exception from this rule occurs only for benzene derivative **1a**. There are no dramatic changes after the plane of the symmetry disappears in the case of the PDI data. Higher PDI values are observed for the non-planar structures for

Table 2 Aromaticity data for individual rings in the –B=B–substituted hydrocarbons (values for planar structures underlined, values for rings containing boron atoms in bold)

Compound/ring	HOMA*		NICS(0) [ppm]		NICS(1)zz [ppm]	PDI	
1a/a	**0.79**	**0.73**	**−27.30**	**−11.99**	**−27.44**	**0.0925**	**0.1145**
2a/a	0.46	0.48	−6.28	−5.96	−26.39	0.0700	0.0700
2a/b	**0.53**	**0.55**	**−69.38**	**−53.46**	**−31.71**	**0.0730**	**0.0753**
3a/a	0.73	0.89	−8.91	−6.93	−29.57	0.0776	0.7870
3a/b	**−1.33**	**0.43**	**−23.42**	**−7.54**	**−23.80**	**0.0629**	**0.0771**
4a/a	0.61	0.66	−6.14	−8.43	−24.02	0.0632	0.0647
4a/b	0.40	0.47	−19.31	39.12	−33.41	0.0623	0.0602
4a/c	**0.38**	**0.41**	**25.22**	**−303.02**	**−31.08**	**0.0656**	**0.0703**
5a/a	0.70	0.54	−7.95	−7.83	−26.72	0.0674	0.0716
5a/b	0.62	0.60	−10.34	−7.52	−33.82	0.0636	0.0597
5a/c	**0.06**	**0.31**	**−20.61**	**−6.17**	**−19.75**	**0.0542**	**0.0665**
6a/a	0.65	0.70	−11.88	−1.19	−28.55	0.0781	0.0764
6a/b	**−1.04**	**0.19**	**30.28**	**−50.69**	**−24.80**	**0.0479**	**0.0598**
7a/a	0.87	0.90	−8.43	−7.54	−27.58	0.0814	0.0825
7a/b	0.13	0.16	−5.87	−0.99	−17.07	0.0430	0.0358
7a/c	**0.62**	**0.62**	**−43.81**	**−10.49**	**−29.89**	**0.0772**	**0.1054**
8a/a	0.84	0.80	−8.61	−8.00	−28.36	0.0789	0.0753
8a/b	0.40	0.68	−6.67	−6.35	−22.84	0.0544	0.0568
8a/c	**0.48**	**0.53**	**−25.04**	**−7.06**	**−24.21**	**0.0698**	**0.0874**
9a/a	0.90	0.90	−8.14	−7.30	−27.83	0.0810	0.0807
9a/b	0.27	0.28	−7.05	−3.29	−18.05	0.0424	0.0399
9a/c	**0.64**	**0.67**	**−42.60**	**−18.77**	**−30.09**	**0.0756**	**0.0883**
10a/a	0.57	0.62	−15.49	−54.87	−33.30	0.0667	0.0657
10a/b	0.40	0.45	−2.02	6.74	−16.74	0.0447	0.0443
10a/c	**0.05**	**0.21**	**30.64**	**253.26**	**78.70**	**0.0444**	**0.0507**
11a/a	0.81	0.82	−11.73	−7.43	−34.58	0.0676	0.0652
11a/b	0.48	0.74	−7.46	−5.00	−19.74	0.0477	0.0558
11a/c	0.24	0.37	−4.29	1.25	−12.45	0.0407	0.0352
11a/d	**0.38**	**0.50**	**−40.48**	**−7.88**	**−33.60**	**0.0617**	**0.0793**
12a/a	0.70	0.70	−8.78	−7.17	−30.48	0.0518	0.0497
12a/b	0.70	0.76	−6.13	−8.43	−33.26	0.0528	0.0537
12a/c	0.39	0.59	13.59	−1.02	−10.16	0.0335	0.0352
12a/d	0.43	0.50	−17.04	−2.77	−29.38	0.0502	0.0452
12a/e	**0.20**	**0.44**	**167.85**	**−10.00**	**−36.26**	**0.0524**	**0.0696**

* HOMA values for planar compounds taken from reference 20

almost all rings with only carbon atoms and for all rings containing boron (even for **1a**). A different behavior is observed for the NICS(0) and NICS(1)zz models of aromaticity evaluation. In these cases, it is difficult to predict what is more probable is decreasing or increasing in aromatic properties in non-planar structures in comparison with the planar ones. In addition, sometimes very huge values, both very positive and very negative, are predicted by the NICS calculations.

In general, more significant perturbations of aromatic properties are observed in the rings with boron atoms than in those consisting of only carbon atoms. Depending on the position of the carbocyclic ring in the structures of the compounds, either increasing or decreasing in the aromatic properties can be observed. In general, aromatic properties of pure carbon rings that border with carbon–boron ones are more affected (decreased) than those located far from boron groups. It is difficult to decide about the way of aromatic properties affecting of pure carbon rings directly connected with carbon–boron rings. There is a very variable relationship between aromaticity and the structure of the studied hydrocarbons. For some structures, aromaticity of such rings is higher in hydrocarbons with the –B=B– group (**a** series), and for others, the opposite effect is observed.

We will examine now the rings in which boron atoms are present. Insertion of the –B=B– group into the

Table 3 Aromaticity data for individual rings of the –BH–BH– substituted hydrocarbons (values for planar structures underlined, values for rings containing boron atoms in bold)

Compound/Ring	HOMA		NICS(0) [ppm]		NICS(1)zz [ppm]	PDI	
1b/a	**−1.28**	**−0.45**	**15.40**	**11.16**	**23.92**	**0.0454**	**0.0465**
2b/a	0.92	0.92	−2.67	−3.25	−16.13	0.0893	0.0900
2b/b	**−0.93**	**−0.58**	**14.30**	**12.78**	**21.48**	**0.0234**	**0.0244**
3b/a	−0.22	−0.34	18.33	14.34	38.28	0.0435	0.0442
3b/b	**−1.33**	**−0.61**	**30.37**	**22.41**	**67.10**	**0.0507**	**0.0515**
4b/a	0.86	0.85	−6.47	−6.58	−24.33	0.0752	0.0752
4b/b	0.75	0.66	−6.80	−2.44	−13.45	0.0557	0.0566
4b/c	**−0.83**	**−0.63**	**13.04**	**12.20**	**17.86**	**0.0196**	**0.0150**
5b/a	0.93	0.54	49.61	−5.97	119.839	0.0773	0.0622
5b/b	0.41	0.60	96.18	−9.01	241.62	0.0282	0.0647
5b/c	**−0.07**	**–**	**103.17**	**–**	**262.46**	**0.0718**	**–**
6b/a	0.89	0.91	−2.77	−3.15	−16.37	0.0903	0.0911
6b/b	**−0.95**	**−0.78**	**13.24**	**−3.15**	**19.20**	**0.0155**	**0.0169**
7b/a	0.71	0.72	−6.62	−7.16	−24.51	0.0708	0.0717
7b/b	0.69	0.69	−4.68	−5.20	−19.72	0.0666	0.0665
7b/c	**−0.72**	**−0.48**	**16.53**	**14.40**	**27.90**	**0.0270**	**0.0283**
8b/a	0.95	0.95	−2.65	−4.16	−13.87	0.0850	0.0856
8b/b	−0.65	−0.56	12.10	9.39	23.13	0.0229	0.0237
8b/c	**−1.19**	**−0.56**	**23.33**	**16.95**	**47.29**	**0.0421**	**0.0437**
9b/a	0.74	0.76	−6.60	−6.99	−24.62	0.0715	0.0723
9b/b	0.70	0.73	−4.29	−5.27	−19.21	0.0682	0.0681
9b/c	**−0.95**	**−0.45**	**15.74**	**13.61**	**26.89**	**0.0277**	**0.0292**
10b/a	0.78	–	−3.78	–	−18.19	0.0757	–
10b/b	0.46	–	−6.03	–	−22.12	0.0516	–
10b/c	**−0.65**	**–**	**14.35**	**–**	**21.43**	**0.0147**	**–**
11b/a	0.73	0.74	1.46	0.56	−3.10	0.0611	0.0620
11b/b	0.00	−0.02	10.36	10.04	19.11	0.0252	0.0250
11b/c	0.79	0.79	−2.81	−3.47	−14.67	0.0720	0.0715
11b/d	**−0.87**	**−0.58**	**23.91**	**22.01**	**49.04**	**0.0277**	**0.0288**
12b/a	0.81	0.81	−9.03	−9.07	−29.18	0.0599	0.0599
12b/b	0.57	0.57	0.81	0.74	−4.49	0.0442	0.0443
12b/c	0.28	0.28	3.58	3.64	2.52	0.0291	0.0291
12b/d	0.75	0.75	−3.26	−3.32	−16.10	0.0677	0.0677
12b/e	**−0.65**	**−0.63**	**22.22**	**22.16**	**43.89**	**0.0172**	**0.0173**

hydrocarbons structures results in carbon–boron rings with different aromatic properties. Most of them are moderate aromatic. However, in some rings, non-aromatic or antiaromatic properties are calculated. As it was mentioned above, aromatic properties of the boron-containing rings increase in their non-planar structures. On the contrary, insertion of the –BH–BH– group, **b** series, leads to obtain carbon–boron rings with clearly antiaromatic properties (negative HOMA, positive NICS(0) and NICS(1)zz as well as low PDI values); see Table 3.

As it was mentioned earlier, not always different indices of aromaticity describe aromatic properties of chemical species in the same way. Thus, it is interesting to check whether their results correlate or not in such a difficult case as the aromaticity of rings with boron atoms in structures of PAHs.

An attempt to find mutual correlations between different indices describing the same set of compounds (substituted hydrocarbons assumed as planar structures, substituted hydrocarbons in their relaxed non-planar structures or both these groups together) provides following results. Very high correlation (c.c. 0.99) is observed between NICS(0) and NICS(1)zz data in planar structures (NICS(1)zz data were calculated only in this case). Significant correlation is noticed also between HOMA and PDI for **b** series and all studied substituted hydrocarbons in planar structures (correlation coefficients higher than 0.80). Unfortunately this correlation does not exist for planar –BH–BH– species.

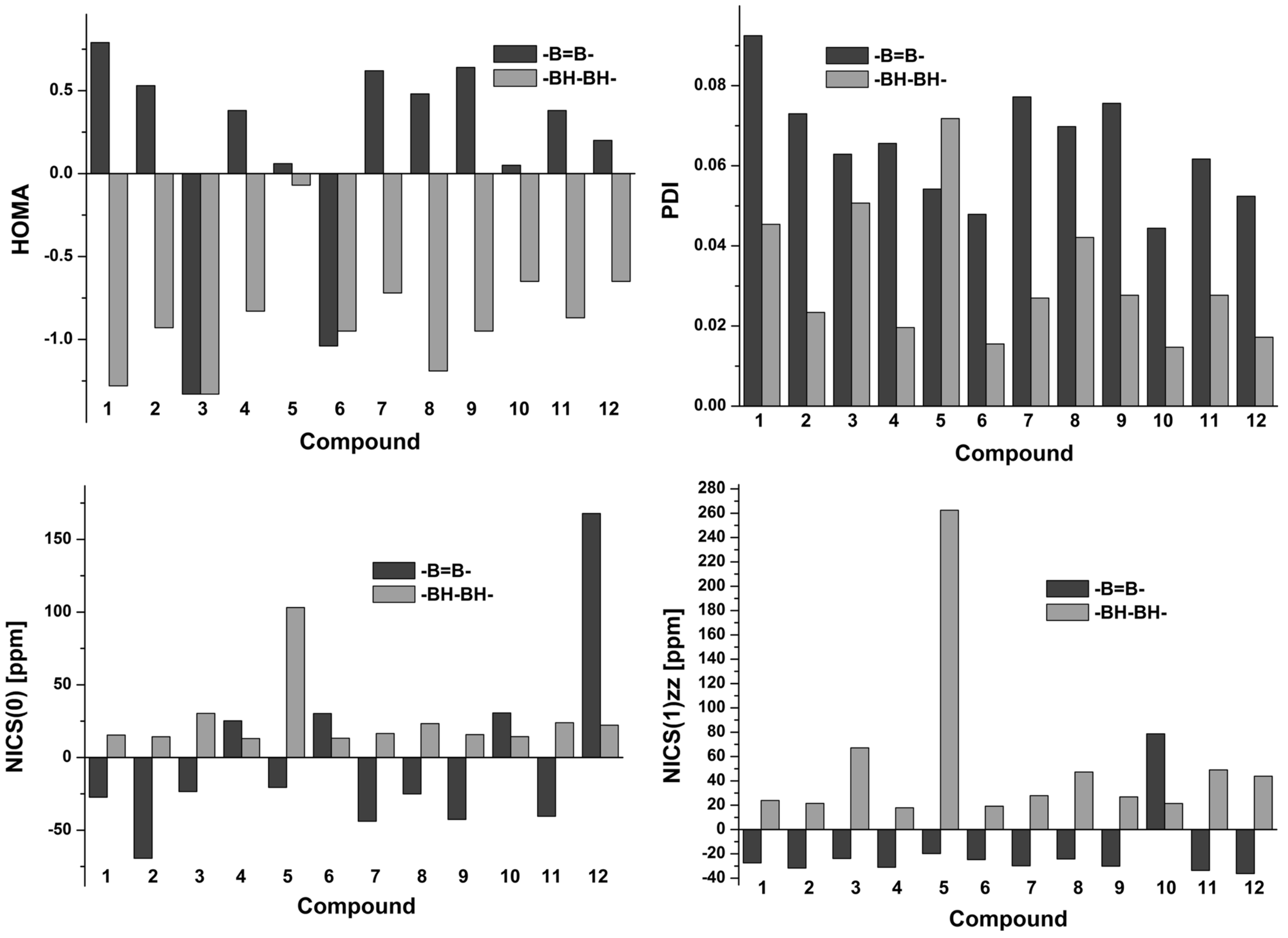

Fig. 3 Aromaticity data for studied system's rings containing boron atoms

Weak correlations (c.c. from the range 0.4–0.6) are obtained for some groups of compounds between HOMA–PDI and NICS–PDI results. Only small correlations are observed between HOMA and both NICS indices.

We have also checked how the results provided by the same indices for carbon–boron rings in both groups of substituted hydrocarbons correlate. The results are rather poor, i.e., in most cases, very low correlations are found. Contrary to this general trend, strong correlation (c.c. 0.97) is observed between HOMA data for rings with –B=B– and –BH–BH– groups in non-planar structures. This result is interesting because in a recent paper [46], it was shown that in polycyclic conjugated hydrocarbons, in which two carbon atoms are replaced by various pairs of heteroatoms, peripheral lengths of the heteroatomic bonds are strictly correlated with the corresponding CC bond lengths in the native hydrocarbons. However, in the mentioned paper, only planar structures were considered. HOMA index, as other structural indices of aromaticity, is based on bond lengths. Thus, it was interesting to check whether there is a correlation between the BB bond lengths in both series of compounds. The result is curious. There is a strong correlation (c.c. −0.99) between BB bond lengths in planar structures, while there is lack of correlation (c.c. −0.03) in non-planar ones. Thus, there is the strong correlation between HOMA data and no correlation between BB bond lengths for non-planar carbon–boron rings, and the opposite situation occurs for these rings in planar structures.

Conclusions

Structures of several PAHs with inserted –B=B– or –BH–BH– groups, series **a** and **b**, have been investigated. We have clearly shown that insertion of both types of boron groups disturbs and decreases aromaticity of the precursor hydrocarbons. However, the decreasing influence of the –BH–BH– group is much stronger and leads in all cases to carbon–boron rings with antiaromatic properties. If one changes C–H by B in a benzenoid structure, the number of valence electrons available for σ and π bonding does not change and as a result, the change of –CH=CH– by B=B in benzene leads to a 6-π-electron system which in principle should be aromatic according to Hückel's rule. On the other hand, if one changes C–H by B–H, then one electron less is present for σ and π bonding, and since σ is preferred over π bonding, then the change of –CH=CH– by –BH–BH– reduces the number of available π-electrons in a substituted benzene ring to 4 and this should lead to antiaromatic species. Thus, it is reasonable that aromaticity should disappear in –BH–BH– derivatives.

Insertion of the –B=B– moiety gives rings with different aromatic properties. Antiaromatic, non-aromatic, slightly aromatic rings and even one with quite strong aromaticity were observed. What is quite unexpected is that non-planar structures have a bit higher aromaticity than strictly planar ones. This is observed despite the fact that parent hydrocarbons, as well as some boron clusters in which aromaticity was postulated, are planar. It is possible, even if it sounds quite strange, that in hydrocarbons substituted by boron groups, the aromaticity is a driving force for the rings to lose their planarity.

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