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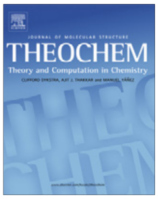

Boron–nitrogen- and boron-substituted anthracenes and -phenanthrenes as models for doped carbon-based materials

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ABSTRACT

The aim of this theoretical study is the investigation of hydrocarbon stability as a function of BN- and B-substitution degree. The targets are anthracene and phenanthrene because they resemble the zig-zag and armchair peripheries of graphene sheets. The computations are made at the RHF and MP2 level with various basis sets. The conclusions drawn are based on the results from calculations for more than 600 different structures created in a systematic way where pairs of carbon atoms are replaced by the respective number of B and N, or solely B-atoms. A common feature of all stable substituted molecules is the tendency for least fragmentation of the carbon skeleton, particularly, for preservation of maximum number of intact carbon aromatic cycles. The major dissimilarity between the BN- and B-substituted molecules are the preferred doping patterns and positions: the favorable structures feature alternation of B and N in the BN-derivatives and disjoint borons separated by C_2 fragments in the B-ones; the nitrogen atoms substitute predominantly secondary carbons, while borons prefer tertiary sites in the BN-substituted hydrocarbons and secondary positions in the B-modified structures. Overall, the anthracene isomers are more stable. The energy and AO contributions to the LUMOs of the studied species are rationalized in terms of electron-accepting properties of the latter, estimating their potential performance as oxidants. Energy depression of LUMOs is achieved mainly in B-substituted hydrocarbons due to large coefficients on the borons causing pronounced delocalization of the orbital. The findings can be used for directed synthesis of novel modified carbon-based materials for practical purposes.

1. Introduction

The development of anode materials with higher Li-ion capacity is a priority for advanced technologies [1,2]. Recently, heteroatom substitution into carbon materials has been addressed as a novel method for the enhancement of Li-ion capacities of carbon anodes. Many heteroatom-substituted carbon materials have been examined from experimental [3,4] and theoretical [5,6] viewpoints. BN- and B-doped systems attract most intense interest. The former are isoelectronic with the carbon precursors, while the latter are electron-deficient structures expected to be effective electron-acceptors.

Due to the non-uniform electron density distribution occurring upon substitution of carbon with boron and nitrogen, the BCN-compounds exhibit a number of specific properties. Besides a medium for Li intercalation in Li-ion batteries [7] they are also potential candidates for application in some modern technologies as semiconductors [8], source for production of boron nitride by means of gas phase deposition [9], medium for hydrogen storage [10], etc. Indeed, their electric [11,12], magnetic [13], intercalating [14] properties and electronic states [15] have been studied in detail. BCN-compounds have been synthesized by different experimental methods, including chemical vapor deposition (CVD) [16], precursor pyrolysis [17], metal-catalyzed laser ablation [18] and arc-discharge methods [19]. Depending on the synthetic method and raw materials used, two types of structures: domain (with partial separation of C and BN clusters) and mixed (more uniform distribution of C, B and N-atoms) have been observed [20]. Since atomic topology is essential for the suitability of BN-doped carbons as anode materials, preliminary theoretical characterizations providing important information are abundant. PBEPBE/DZ-PP geometry optimization [21] has been performed for infinite monolayers of BC2N stoichiometry and six various topologies of the B and N-atoms forming “islands” or “stripes” have been established. BC3 and BN3 with a single pattern have been calculated for comparison. The relative stability of the various topologies has been estimated based on heats of formation. Turker and Gumus [22] have performed AM1 calculations on cyclacenes substituted in one of the peripheral rings which contain a nitrogen atom in all the fusion points and a

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boron atom in all the peri-positions. Total energy values for the systems have been compared to the pristine cyclacenes proving that BN-substitutions have a stabilizing effect on the parent species. *Ab initio* calculations have been used to examine the robustness of various isomers of benzene and naphthalene after substitution of two carbon atoms with the isoelectronic boron–nitrogen pairs [23]. Enhanced stability has been found when B and N-atoms are adjacent to each other. When multiple BN-pairs are present, preferred consecutive ordering has been established. The energy has also been lowered by keeping the heteroatoms within the same benzene ring of naphthalene. However, the study is based on results for the benzene molecule where no tertiary carbons, typical for the bulk carbonaceous materials, exist. Thus the transferability of results is questionable. Moreover, naphthalene is representative only of a single type (acene) of periphery and does not allow examination of periphery-dependent properties.

The stability and aromaticity of benzene, naphthalene, anthracene, tetracene, pentacene and their BN-analogs have been evaluated using density functional theory [24]. The MESP topography patterns of acenes and BN-acenes are substantially different, with BN-acenes showing more localized π-electron features compared to those of acenes. The structural stability of BC2N has also been studied by Itoh and co-workers [25] using molecular mechanics simulations. Different structural models with various atomic arrangements have been considered. It has been predicted that the stable structures of BC2N are formed in a way maximizing the number of C–C and B–N bonds, C–B and C–N bonds being disfavored. Atomic arrangements with B–B and N–N bonds have been found to be less populated because of their higher energy compared to C–C and B–N bonds.

In particular, boron-doped carbon materials have been experimentally and theoretically investigated from different perspectives, not only as anode materials for Li-ion batteries, but also towards other potential applications, such as high-temperature oxidation protectors for carbon/carbon (C/C) composites. Since boron-substitution invokes the appearance of electron-accepting levels, enhanced Li capacity is expected. Alongside with ensuring superior electron uptake, boron acts as promoter of the graphitization of graphene sheets [11]. Another effect on the morphology of carbonaceous materials verified by XRD [26] is the reduced interlayer distance and increased bond length in the six-membered rings of graphite due to boron presence. The contraction of the graphene sheets separation obstructs the penetration of electrolyte and hampers solid electrolyte interphase formation. Thus, irreversible capacity could be eliminated. Regretfully, this drawback is still not removed because of the strong binding of Li to the electrode material, substantiated also by a number of theoretical investigations [27,28]. The strength of the interaction between Li and B-doped materials can be optimized by control of the C:B ratio. The successful design of better electrochemical parameters for this type of materials requires detailed investigation of the role of this ratio.

This study is a first stage in the search of optimal structures providing improved performance of prospective anode materials for Li-ion batteries. The investigation has two goals: (i) to outline the most stable isomers of the target molecules at different degrees of BN- and B-substitution; (ii) to find isomers with low-lying LUMOs as building blocks of prospective anode materials. To this end, *ab initio* calculations on structural isomers of boron–nitrogen- or boron-substituted anthracenes and phenanthrenes at different degrees of substitution were carried out and the features of the substituted molecules were compared to those of the pristine hydrocarbons. The results were rationalized on the basis of electron density distribution and MO analysis. The most favorable structures of each series of isomers are used for further investigations of Li adsorption [29]. The obtained results allow the formulation of rules for preferred positions and patterns of substitution of carbon atoms with nitrogen and/or boron atoms in the models and could be extended to larger hydrocarbons. This could aid the effective design of novel carbon-based materials, for example consisting of graphene sheets modified in accordance with the suggested heteroatom patterns.

2. Models and methods

Targets of this study are the molecules of anthracene and phenanthrene as they model two typical peripheries of the graphene materials (Fig. 1). It is well known [30] that the periphery type of polyaromatic hydrocarbons influences strongly their electronic features. Structural modifications, such as replacement of some carbon atoms with heteroatoms (substitution), occurrence of non-six-membered rings, etc., have also appreciable impact on the electronic parameters.

Two patterns of substitution were considered in this study. In the first case $2m$ carbons were replaced by m boron and m nitrogen atoms, thus obtaining an isoelectronic to the precursor structures. The second substitution scheme introduces solely $2m$ boron atoms. Thus, the appearance of electron-accepting levels could be expected from theoretical standpoint, which should enhance the capacity of the doped anode material.

The Restricted Hartree–Fock (RHF) method upgraded with second order Møller–Plesset calculations (MP2) was chosen. RHF is known to render unsatisfactory description of the electron–electron interaction, whereas MP2 accounts for the electron correlation by including the contribution of the doubly excited configurations. The results are compared to establish the dependence on the level of theory. Moreover, the computed data are sensitive to the size and type of basis set employed. It was important to find out whether the main descriptor of molecular stability assessed, i.e., the relative energy, depends essentially on the basis set. For the purpose, four basis sets were used for the energy calculations: 3-21G*, 6-31G*, cc-pVDZ, and cc-pVTZ. The first one (3-21G*) [31] is not very accurate but is good enough for a preliminary quick estimation of the relative stability of the substituted molecules. The second one (6-31G*) [32] is acknowledged as a standard in quantum chemistry calculations as it usually gives reliable results for the basic molecular characteristics and its use is mandatory in such detailed study. The higher-class basis sets, cc-pVDZ and cc-pVTZ [33], were employed only at the RHF level and solely for

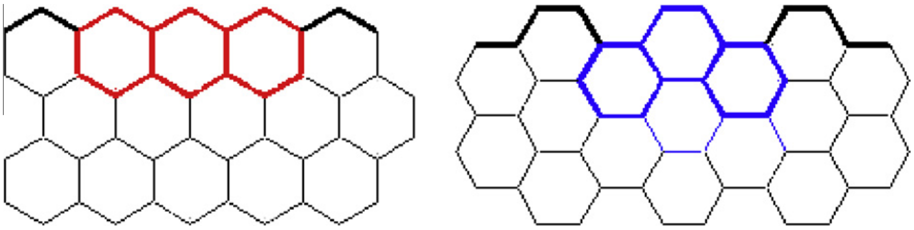


Fig. 1. Anthracene (left) and phenanthrene (right) as periphery prototypes of graphenes.

the most favorable isomers of each series since these sets of basis functions require longer computational times which would either encumber the systematic approach to the problem or constrict the number of isomers studied.

The tasks of the investigation are: (i) to find the lowest-energy isomers at each level of substitution and to outline rules for preferred positions or sequences of substitution in anthracene and phenanthrene; (ii) among the energetically favorable isomers at each degree of substitution to select the ones with the lowest-lying LUMOs as prospective candidates for substrates ensuring substantial charge transfer upon complex formation with alkali metals.

All calculations were made with GAUSSIAN 03 [34]. The RHF molecular orbitals were visualized at contour value 0.02. Mulliken atomic charges were used for description of the electron density distribution. The relative stability of the molecules was estimated from the energy difference (ΔE) of the current structure and the previous more stable one in a series with the same degree of substitution.

3. Results and discussion

3.1. Pristine hydrocarbons

Prior to investigating the substituted species, it is rational to compare the characteristics of the pristine hydrocarbons. Fig. 2 visualizes the canonic highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) and contains the total and frontier MO energies of anthracene and phenanthrene computed with RHF/6-31G*.

Several interesting features are worth pointing out. The total energies of the two structures differ by 6.90 kcal/mol, which implies higher stability of carbonaceous materials with phenanthrene periphery. On the other hand, the LUMO of anthracene has lower energy than that of phenanthrene which indicates that anthracene will have better electron-accepting properties. Hence, pristine hydrocarbons with acene type of periphery are expected to be more suitable anode materials. The differences between the two species are rooted in the dissimilar molecular symmetry which has an impact on the type and shape of the frontier MOs shown in Fig. 2. The HOMO of anthracene is more localized while delocalization spans almost the entire HOMO of phenanthrene with exception of two carbons. The situation is reverse in the first virtual MO: the considerable delocalized fragments in the LUMO of anthracene are an additional implication that the latter would be a more efficient electron-acceptor.

The atomic charges calculated according to the Mulliken scheme are often sufficiently informative about the preferred sites for initial substitution. As evident from the values (Fig. 3), they vary in a way that prevents the unambiguous defining of the most appropriate position for substitution. One would expect that the carbon with the largest negative atomic or group charge (with bound H-atom charge summed up) will be most easily substituted by a nitrogen atom and the one with least negative atomic charge (or positive group charge) is anticipated to be most effortlessly replaced by boron. As seen below, this assumption is not fully supported by the order of stability of neither 1BN-, nor 2B-hydrocarbons.

3.2. Boron–nitrogen substitution

The various BN-substituted isomers of anthracene and phenanthrene will be presented first. The computational protocol encompassed the following steps:

1. Each possible combination of two carbon atoms was replaced by equal number of boron and nitrogen atoms, gradually increasing the degree of substitution; all symmetry-unique topological isomers at the respective stoichiometric B:C:N ratio were built.
2. The energy of all model systems was calculated with the corresponding methods and basis sets (RHF/3-21G*; RHF/6-31G*; MP2/6-31G*). RHF/cc-pVDZ and RHF/cc-pVTZ calculations were performed for several lowest-energy isomers at each degree of substitution in order to check the stability of the solutions with the smaller basis sets.
3. The lowest-energy structures of each series were determined and analyzed.

The inspection of the results revealed that the ordering of the structures in terms of stability is independent of the method and the size of the basis set used with just two exceptions (see below).

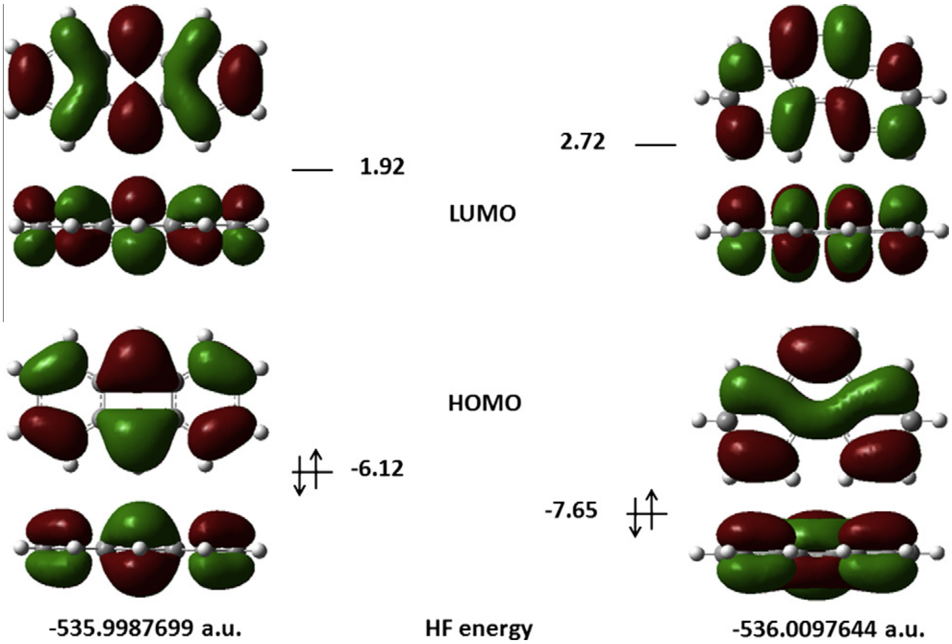


Fig. 2. Top and side view of the frontier MOs and their RHF/6-31G* energy (in eV) as well as total energy (bottom) of anthracene (left) and phenanthrene (right).

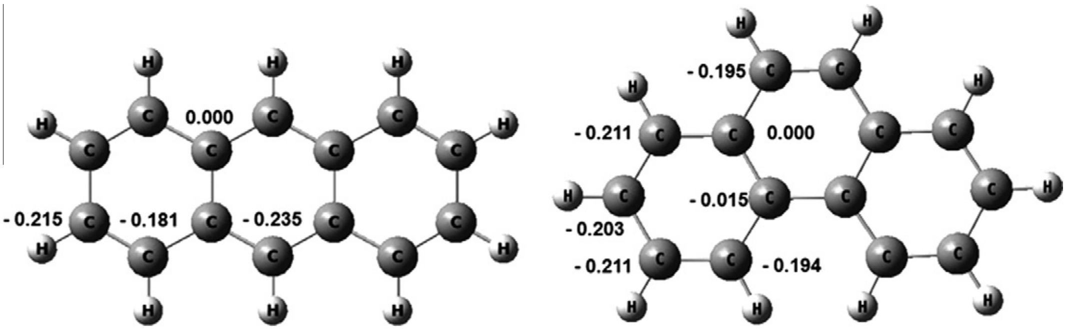


Fig. 3. RHF/6-31G* Mulliken atomic charges of anthracene (left) and phenanthrene (right). The charges on hydrogen atoms are omitted for clarity; their values vary between 0.200 and 0.210.

This is true for each series of isomers (Tables S1–S4). The most stable 4BN-substituted anthracenes are chosen to illustrate the above statement (Table 1).

The RHF/cc-pVTZ results for ΔE are fairly close to the MP2/6-31G* ones. Moreover, qualitatively the MP2 and the RHF estimates agree well, i.e., the account of electron correlation does not reorder the stability sequence.

The quantitative differences are of the same order of magnitude. Sophistication of the higher-level basis sets surprisingly yields results closer to the lower-level ones. This is an encouraging conclusion showing that such (and even larger) systems could be treated at lower computational cost without losing accuracy at the qualitative level. Therefore, the further considerations are based mainly on the RHF/6-31G* energy values.

3.2.1. BN-anthracenes

The total number of distinct topological BN-isomers of anthracene modeled is 235. All of them were optimized and checked for global energy minima. The two lowest-energy species at each degree of substitution are represented in Fig. 4. The RHF/6-31G* energy difference between them, ΔE, is given in Table 2. If the two 'favorites' are quasi-degenerate in energy, the third member of the respective series is included.

The energy difference between the first two isomers of *1BN-substituted* anthracenes is very small regardless of the method used (Table S1), which means that they are of equal probability. It is noteworthy that the boron and the nitrogen atom are adjacent and that substitution in the outer ring is preferred. These results were corroborated both by other *ab initio* calculations [23] and by experimental studies (B–N bond formation due to the presence of nitrogen impurities during the synthesis of boron-substituted carbonaceous materials proved by XPS) [4,26]. The third structure is much higher in energy although the two heteroatoms are still bonded. The most probable reason for that is the disturbed aromaticity of two carbon cycles in A.1.3 instead of only one in A.1.1 and A.1.2.

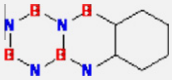
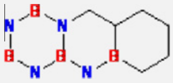
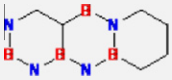
In the series of *2BN-substituted* anthracenes the difference between the two most stable isomers is substantial (17.532 kcal/mol), indicating that there is only one preferred structure (A.2.1), the one in which the conjugation of the remaining carbons is uninterrupted. Here borons and nitrogens alternate, the former occupying preferably the tertiary sites, whereas the latter substitute secondary carbons. In other words, borons more often 'choose' inner sites and nitrogens have a preference for the periphery. The only case among the BN-substituted anthracenes where MP2 calculations inverts the order of the second and the third structure is in this series. Instead of the unique stable molecule with one separated nitrogen atom (A.2.2), an isomer with two disjoint B–N bonds in the two outer rings becomes more favorable in energy (Table S1).

The outlining of a single most stable isomer is characteristic for most series with higher degree of substitution.

Most stable among the *3BN-substituted anthracenes* is the A.3.1 isomer, where the alternating boron and nitrogen atoms form a ring preserving a homonuclear carbon cycle intact, as found earlier by Kar and co-workers for the naphthalene molecule [23]. Next in energy is the structure featuring an alternating BN-chain spanning the three anthracene rings. Again the borons show preference towards tertiary and the nitrogens towards secondary sites.

Among the *4BN-substituted anthracenes* most stable are the isomers in which the alternating heteroatoms start forming a second ring adjacent to a completed first one. The BN-ring is one of the outer cycles and there are two alternatives for the fourth BN-pair. Lower energy has the isomer where the fourth BN-pair is split, the substituted carbons being secondary. Thus a carbon cycle remains intact. Next in energy is the structure in which the fourth BN-pair bridges the two outer rings in such a way that maximum number of tertiary carbons is replaced by borons.

Table 1
Total energy (in a.u.) and relative energy (ΔE, in kcal/mol) for 4BN-substituted anthracenes calculated with various methods and basis sets.

				
RHF/3-21G*	E_{tot}	−546.92497	−546.91062	−546.88131
	ΔE	–	9.005	18.392
RHF/6-31G*	E_{tot}	−549.93762	−549.91063	−549.88645
	ΔE	–	16.936	15.173
RHF/cc-pVDZ	E_{tot}	−549.98061	−549.95973	−549.93462
	ΔE	–	13.102	15.757
RHF/cc-pVTZ	E_{tot}	−550.12421	−550.10498	−550.07835
	ΔE	–	12.067	16.710
MP2/6-31G*	E_{tot}	−551.62113	−551.59867	−551.57014
	ΔE	–	14.094	17.903

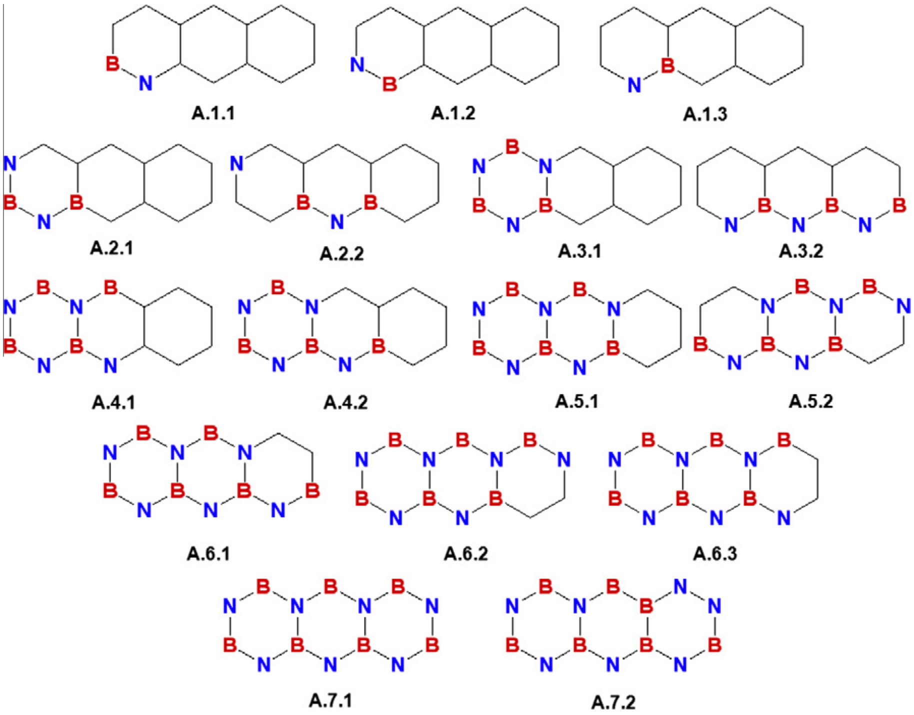


Fig. 4. Topology of the lowest-energy structures of BN-anthracenes at each degree of substitution.

Table 2
RHF/6-31G* total energy and energy difference (ΔE) of the lowest-energy structures of BN-anthracenes at each degree of substitution (see Fig. 4).

Structure	Energy (a.u.)	ΔE (kcal/mol)
A.1.1	−539.446131	–
A.1.2	−539.445607	0.329
A.1.3	−539.412023	21.074
A.2.1	−542.896922	–
A.2.2	−542.869001	17.521
A.3.1	−546.422360	–
A.3.2	−546.394837	17.271
A.4.1	−549.937663	–
A.4.2	−549.915525	13.892
A.5.1	−553.439410	–
A.5.2	−553.401237	23.954
A.6.1	−556.929304	–
A.6.2	−556.929147	0.099
A.6.3	−556.923135	3.773
A.7.1	−560.457286	–
A.7.2	−560.238094	137.545

The sizeable energy difference between the first two stable isomers of the *5BN-substituted anthracenes* justifies the conclusion that A.5.1 is the unrivaled structure of preference in this group. Two adjacent rings of alternating borons and nitrogens provide better stability than any other topology. Moreover, the remaining four carbons form a delocalized sequence in the preferred structure while in the less favorable one they are separated in two non-interacting pairs.

In contrast, the first three isomers in the series of the *6BN-substituted anthracenes* differ inconsequentially in energy and are close in terms of stability. A.6.1 and A.6.2 are practically identical in terms of substituted secondary and tertiary positions and accordingly are degenerate. Here again there are two patterns of extending the bicyclic BN-structure with a sixth BN-pair without interruption of the alternation: with or without BN-splitting. Unlike the 4BN-case, here the non-split variant has lower energy. Apparently, the BN-pair splitting is advantageous only when this guarantees the preservation of an unsubstituted carbon portion of the molecule with enhanced delocalization (a benzene ring in A.4.1); the carbon residue is practically identical in A.6.1 and A.6.2.

Last are the fully substituted hydrocarbons (*7BN-substituted anthracenes*). In this series the stable structure is definitely one (A.7.1), as the energy difference to the next candidate is huge, regardless of the computational method used (Table S1). This result is a convincing illustration of the BN-alternation advantage. The flip of just one BN-pair (A.7.2 in Fig. 4) leads to a drastic jump in energy.

3.2.2. BN-phenanthrenes

Calculations with the above listed methods and basis sets for all possible phenanthrene isomers at a given x-value of $(BN)_xC_{14-2x}$, $x = 0 \div 7$, were carried out too. The total number of 393 distinct structures was considered. The lowest-energy species at each x-value and the energy differences between them are represented in Fig. 5 and Table 3.

The most stable *1BN-phenanthrenes* are non-degenerate in energy, unlike in the anthracene 1BN-series, which outlines Ph.1.1 as a preferred pattern of substitution. The dissimilarity in 1BN-substitute of the two hydrocarbons evidently is due to their non-identical symmetry, since the interchange of the positions of boron and nitrogen in Ph.1.1 will not yield a different structure as it does in anthracene. The stability of this structure can be explained with the reactivity of the two carbon atoms of the middle ring of phenanthrene [35]. On the other hand, the preference of boron for tertiary sites is overridden by the stability of the carbon residue in Ph.1.1 and in Ph.1.2 but is demonstrated again in Ph.1.3, where two of the cycles are affected by the substitution, at the expense of energy increase. The latter structure is analogous to A.1.3. In all stable 1BN-phenanthrenes the boron and nitrogen atoms are adjacent (Table S2).

The energy difference between the first three *2BN-phenanthrenes* is insignificant and therefore, contrary to the 2BN-anthracenes, no definitely preferred structure can be outlined. The same

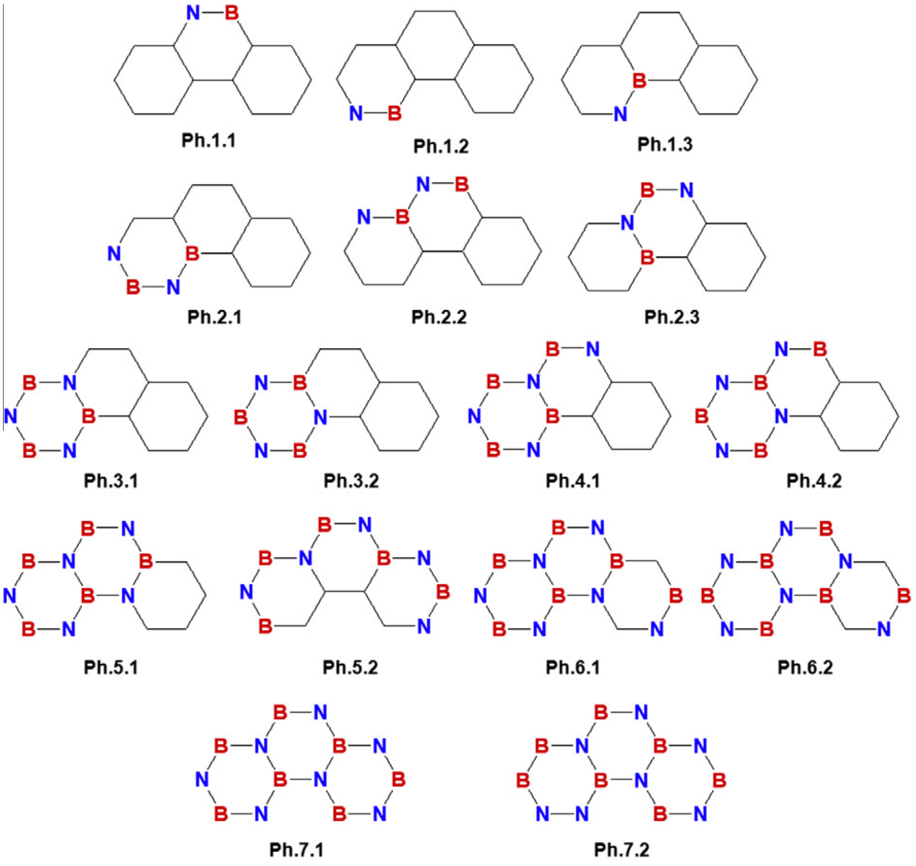


Fig. 5. Topology of the lowest-energy structures of BN-phenanthrenes at each degree of substitution.

Table 3
RHF/6-31G* total energy and energy difference (ΔE) of the lowest-energy structures of BN-phenanthrenes at each degree of substitution (see Fig. 5).

Structure	Energy (a.u.)	ΔE (kcal/mol)
Ph.1.1	−539.457341	–
Ph.1.2	−539.448958	5.261
Ph.1.3	−539.440697	5.184
Ph.2.1	−542.927992	–
Ph.2.2	−542.925884	1.323
Ph.2.3	−542.925221	0.416
Ph.3.1	−546.443547	–
Ph.3.2	−546.399040	27.929
Ph.4.1	−549.941543	–
Ph.4.2	−549.933372	5.127
Ph.5.1	−553.436636	–
Ph.5.2	−553.362579	46.472
Ph.6.1	−556.855758	–
Ph.6.2	−556.814469	25.909
Ph.7.1	−560.457478	–
Ph.7.2	−560.290665	104.677

tendency of small energy separation is preserved for the whole series (Table S2). There are also no favored substitution sites, i.e., the substitution of carbons from the outer and inner rings is equally probable, unlike the anthracene analogs where substitution of the outer ring is preferred. However, the carbon residues in both molecules with lowest energy have identical topology and differ only in geometry and position of one bridging bond, hence, the minor energy difference.

The stable isomers of *3BN-phenanthrene* match the substitution pattern of A.3.1: the alternating borons and nitrogens form an outer ring, each type of heteroatom substituting identical number of secondary and tertiary carbons. Due to the lower symmetry of phenanthrene, however, this substitution scheme produces two distinguishable isomers of similar stability. The carbon residues in both structures have identical topology but, unlike 2BN-phenanthrenes, they differ in the way of linking to the BN-substituted ring: the carbon cycle is bound directly to boron and indirectly to nitrogen in the lowest-energy isomer and vice versa in Ph.3.2. This binding scheme has stabilizing effect also in 1BN- and 2BN-substituted phenanthrenes. The analog of A.3.2 where the alternating BN-sequence forms a chain (Ph.3.3, Table S2) is the next in energy but its existence is less probable as evident from the energy difference with Ph.3.2 (Table S2).

ΔE between the first two stable *4BN-phenanthrenes* makes it clear that there are two close in energy 4BN-isomers (Ph.4.1 and Ph.4.2) unlike the 4BN-anthracenes. In the most favorable 4BN-anthracene there is at least one six-membered ring preserved, which is the same in both Ph.4.1 and Ph.4.2. Therefore, the energy difference between the isomers of the two species is so dissimilar. The stabilizing effect of the presence of six-membered rings, both homo- and heteronuclear, is as important as the BN-alternation rule. Our results are in agreement with Clar's theory [35,36] which describes the aromaticity of a benzenoid hydrocarbon on the basis of the maximum number of sextets drawn for a system. On the other hand, there are some noticeable differences in the substitution patterns of the lowest-energy structures: the fourth BN-pair was split in A.4.1 while in Ph.4.1 and Ph.4.2 it is non-split. One reason for this difference is again the molecular symmetry of the two hydrocarbons. The hypothesis that N-atoms substitute preferentially secondary carbons is also demonstrated by the topology of Ph.4.1 and Ph.4.2. The substitution first involves one of the outer rings and proceeds through the inner to the second outer one; if its propagation along the shortest route between the outer rings took place, two favorable factors would be attacked: more tertiary positions would be involved in N-substitution and the remaining carbon residue will be acyclic. Next in energy is the isomer consisting of a BN- and a C-sequence spanning the molecular periphery (Table S2).

Ph.5.1 is clearly the preferred structure in the series of *5BN-phenanthrenes*. As in the case of 5BN-anthracenes, more stable is the structure where the alternating borons and nitrogens form two adjacent rings. The combination of a BN- and C-chains is the second topology of preference as evidenced by the large difference between the energy of the second and the third lowest-energy 5BN-phenanthrenes (Table S2).

The energy difference between the most stable *6BN-phenanthrene* isomers is substantial, outlining again one preferred topology at this degree of substitution (Ph.6.1). Conservation of cycles (both homo- and heteronuclear) is clearly a more important factor than preservation of compact carbon residue, therefore the last carbon pair in this isomer is split. Obviously, it is more advantageous when identical dopants are separated by the two remaining carbon atoms. The breaking of the middle BN-ring (Ph.6.3) results in even more sizeable increase in energy (Table S2).

Ph.7.1 is the undisputable preferred structure of alternating borons and nitrogens in the series of *7BN-phenanthrenes*. A formidable rise in energy, yet milder than in anthracene, occurs in structures having just one violation of the BN-alternation (Ph.7.1–2 vs. A.7.1–2).

In the phenanthrene series there is a larger number of close in energy isomers in contrast to the anthracene analogs. This is an indication that phenanthrene peripheries are doped more easily than acene ones (Table S2). An additional evidence yields the comparison of the total energy of the most stable BN-substituted anthracenes and phenanthrenes with the same B:C:N ratio rendering the phenanthrene isomers as generally more stable, same as the pristine species.

3.3. Boron-substitution

This part of the study focuses on models of anthracene and phenanthrene in which combinations of two carbons are replaced by borons. Only systems containing 2, 4, 6, and 8 boron atoms were considered. This choice is substantiated by two arguments: on the one hand, as shown above, the adjacency of boron atoms (A.7.2) results in appreciable rise in energy, and the maximum number of disjoint positions in the target molecules is 7. On the other hand, according to some authors, B_xC_y structures where $x \leqslant y$ exhibit higher capacity for Li accommodation, the best stoichiometry being BC3 [37,38]. Since our models contain 14 non-hydrogen atoms, closest to this ratio are the isomers with four and six boron atoms. The latter are weighed against the molecules of higher and lower B-contents (two and eight borons) to find out how they compare and what they differ in. Further abundance of boron is ruled out as the existence of 2-D boron-rich structures is unrealistic from experimental standpoint and the pronounced non-planarity typical for B-enriched systems is inappropriate for Li accommodation. All B-substituted compounds are electron-deficient with respect to the parent and to the BN-substituted hydrocarbons and therefore enhanced electron-accepting properties are anticipated.

The calculations follow the protocol outlined in the previous section. RHF/6-31G* was the only method used because the computations carried out so far proved that the estimates are qualitatively independent of the method and basis set employed, i.e., the methods accounting for electron correlation order the lowest-energy isomers at each level of substitution in the same way as the standard RHF/6-31G*.

3.3.1. B-anthracenes

The systematic B-substitution of anthracene yielded 145 distinguishable structures. The two (three) most stable isomers at each degree of substitution and the RHF/6-31G* energy difference between them are collected in Fig. 6, Table 4 and Table S3.

First the isomers with two carbon atoms replaced by boron were considered (*2B-anthracenes*). Comparison with the 1BN-anthracenes reveals several differences. AB.2.1 is the only favorable isomer, having ~12 kcal/mol lower energy than AB.2.2, whereas the energy difference between the two most stable 1BN-isomers is ~0.3 kcal/mol. Another apparent dissimilarity is that while the heteroatoms are always adjacent in the stable BN-substituted hydrocarbons and substitutions in the outer ring is predominant, the borons in the B-substituted analogs are separated by at least two carbons and replacement in the inner ring is preferred. In AB.2.1 the carbons of the pristine anthracene having the most negative atomic and group charges are substituted (Fig. 3). In the second isomer (AB.2.2) the carbon atoms next in magnitude of the negative charge are replaced.

Table 4
RHF/6-31G* total energy and the energy difference (ΔE) of the lowest-energy structures of B-anthracenes (AB) and B-phenanthrenes (PhB) at each degree of substitution (see Fig. 6).

Structure	Energy (a.u.)	ΔE (kcal/mol)
AB.2.1	−509.648377	–
AB.2.2	−509.628894	12.226
AB.4.1	−483.241949	–
AB.4.2	−483.229417	7.864
AB.6.1	−456.809655	–
AB.6.2	−456.791086	11.652
AB.8.1	−430.301195	–
AB.8.2	−430.291759	5.921
PhB.2.1	−509.620036	–
PhB.2.2	−509.613959	3.814
PhB.4.1	−483.207041	–
PhB.4.2	−483.201317	3.592
PhB.6.1	−456.792499	–
PhB.6.2	−456.777342	9.511
PhB.8.1	−430.326752	–
PhB.8.2	−430.289565	23.335

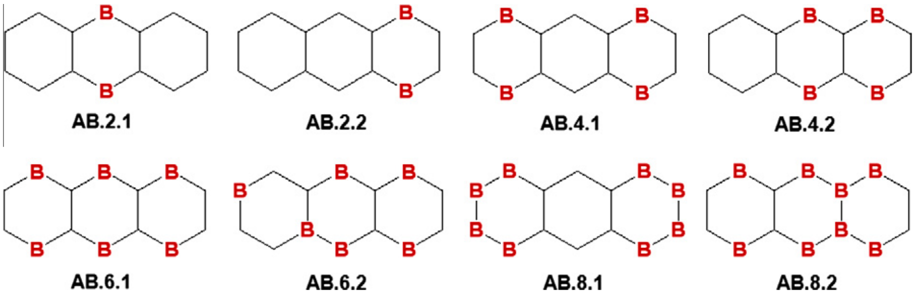

AB.2.1 AB.2.2 AB.4.1 AB.4.2
AB.6.1 AB.6.2 AB.8.1 AB.8.2

Fig. 6. Topology of the most stable isomers at each studied degree of 2 × B-substitution of anthracene.

In the *4B-substituted anthracenes* another interesting trend is observed: unlike the BN-species where the boron atoms show preference to the tertiary positions, in the B-substituted anthracenes they substitute secondary carbons. On the other hand, the outer rings are the substituted ones in AB.4.1, unlike the inner one in AB.2.1. Evidently, the structure providing more effective separation of the B-atoms leaving intact the central benzene ring is more advantageous. The carbon residues are the same in AB.4.1 and AB.4.2 which explains the smaller energy difference as compared to the stable 2B-anthracenes.

The isomers with *six boron atoms* allow the most regular distribution of boron and carbon atoms. Non-planarity is a new feature appearing at this degree of substitution and AB.6.1 has the shape of an arc. Substitution of mainly secondary carbons is preferred. There is only one possible structure (the most stable) in which the B-atoms are separated by carbons. In all the other isomers substitution of neighbouring positions occurs (Table S3) which apparently is a disadvantage causing loss of sp^2-character in these parts of the molecule.

The highest degree of substitution included in the study (*8B-isomers*) exhibits a tendency towards formation of boron cyclic and chain sequences. Due to the increased electron deficiency pronounced out-of-plane deformation of the B-substituted rings takes place (Fig. 7). Two seemingly very different structures have the lowest energy: one providing the maximum separation of two 4-atom boron chains followed by another with 6B-atomic structure and two disjoint borons. A more detailed inspection reveals that all possible secondary carbons in the end rings are substituted in the first, preserving the central benzene ring unbroken, while some tertiary sites are substituted in the second. The small energy difference raises doubts whether more precise methods would safeguard the order of stability. The MP2 check gave the same qualitative result. Substitution of more than two tertiary carbons invokes discernible jump in energy.

3.3.2. B-phenanthrenes

Phenanthrene was treated in analogous way yielding the total of 71 distinct structures. The favorites are shown in Fig. 8.

Like in the 1BN-phenanthrene series, the energy difference between the first two stable *2B-structures* is small. Advantage has the compound in which the substitution involves secondary carbons in one of the outer rings leaving an unsubstituted naphthalene residue.

Similar is the situation with the *4B-substituted phenanthrenes*: the energy difference between the most stable molecules is insignificant. The third member of the series is almost degenerate with the second one (Table S4) due to the same type of C–B-fragmentation. In the preferred structures the boron atoms are separated by 2–4 carbons.

The next series studied is the *6B-phenanthrenes*. They do not allow structures with disjoint boron atoms and therefore feature sizeable deformation (Fig. 7). Here the difference in the energy of the first two favorites is more substantial, demonstrating that compounds with two neighbouring borons are preferred to those with B_3-sequences.

It is obvious that further substitution should be discarded as unpractical for the purpose of the study. This is evidenced by the lowest-energy *8B-isomers* with abundant B–B contacts, featuring the most pronounced non-planarity (Fig. 7). Among the less stable isomers of this series even occurs regrouping of the cycles (Table S4).

Another group of inappropriate substrates are the odd-B-substituted hydrocarbons (See Supplementary Data).

The small energy differences between the most stable isomers at low degrees of BN- and B-substitution of phenanthrene indicates that a mixture of products is to be expected, whereas the respective preferred doped anthracenes are better defined.

At all realistic degrees of B-substitution the lowest-energy anthracene species are more stable than the corresponding phenanthrene ones, unlike the parent hydrocarbons (Table 4).

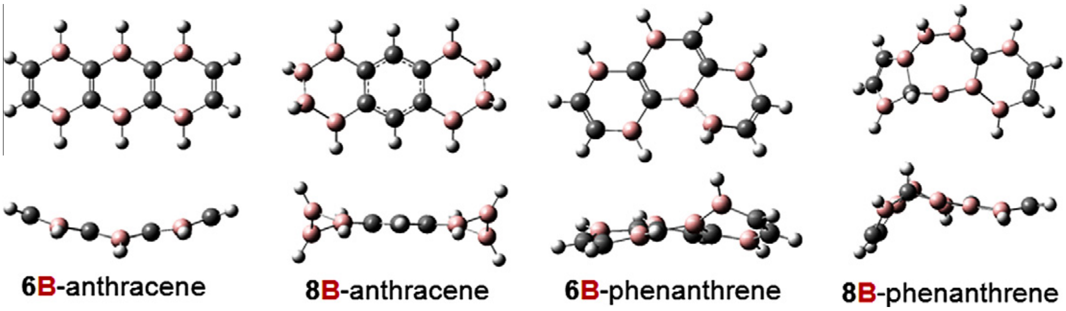


Fig. 7. Top and side view of the most stable optimized boron-rich anthracenes (left) and phenanthrenes (right).

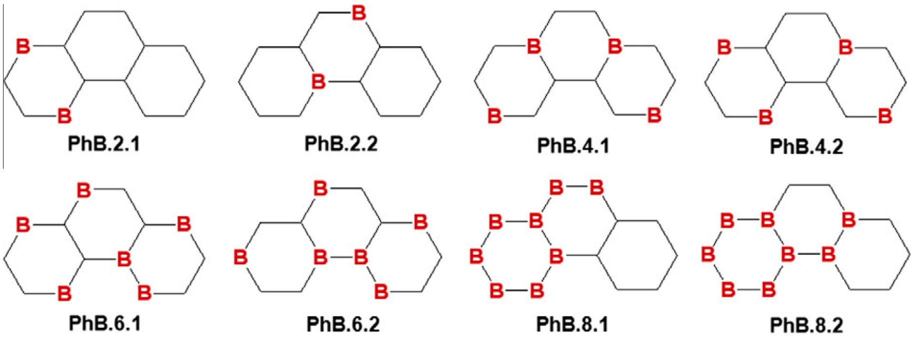


Fig. 8. Topology of the most stable isomers at each studied degree of 2 × B-substitution of phenanthrene.

3.4. MO analysis

In the normal charge cycle of a Li-ion battery the lithium atom donates an electron to the anode and turns into Li^+. Consequently, the best anode material will be the one with best electron-accepting properties. It is logical to expect that the molecules of this material will have vacant molecular orbital(s) of lowest possible energy. Therefore the lowest unoccupied molecular orbitals (LUMOs) of all stable substituted structures were compared to the pristine hydrocarbons. Another factor facilitating the effective charge transfer and ensuring low-lying LUMO is the delocalization of the latter. Hence, isomers suitable for the aims of this study are the ones possessing low-energy and well delocalized LUMOs.

Almost all BN-isomers have higher LUMOs than the parent hydrocarbon as evidenced by Fig. 9, which summarizes the results for the most stable isomers of each series. Thus, they are worse electron-acceptors than the pristine hydrocarbon. There is a tendency of increasing the energy of LUMO with the degree of BN-substitution.

The lowest LUMO (1.61 eV) among the BN-anthracenes belongs to the stable 2BN-species. It would be the most efficient electron-acceptor and it could be anticipated that hydrocarbon materials with such elementary unit would be superior to pristine acenes. The remaining degrees of substitution show no advantage with respect to the all-carbon substrate.

Only the favorites with lowest degrees of BN-substitution have lower-lying LUMOs than phenanthrene and all the rest are with worse electron-accepting parameters. The LUMO of the 1BN-isomer is practically equal in energy with the parent hydrocarbon. Fig. 9 shows that, similar to the anthracenes, only the 2BN-substituted isomer meets the requirement for enhanced electronegativity and would be the most promising electron-acceptor among all BN-phenanthrenes.

The studied stable B-substituted isomers of anthracene with no exception have lower-lying LUMOs than the precursor (Fig. 10); hence, all of them are better acceptors of electrons than the pristine and the BN-substituted anthracenes. The presence of energetically favorable LUMOs in B-substituted carbonaceous materials was also proved experimentally by XPS [4]. Here for the first time negative values of LUMOs are registered – the 4B- and the 6B-isomers, the latter having appreciably lower virtual orbital in both periphery types.

Among all the B-anthracenes considered in this study the most attractive in terms of electron-acceptance is the isomer in which in each aromatic ring two carbons in para-position are replaced by borons (AB.6.1). This is an indication that materials with acene

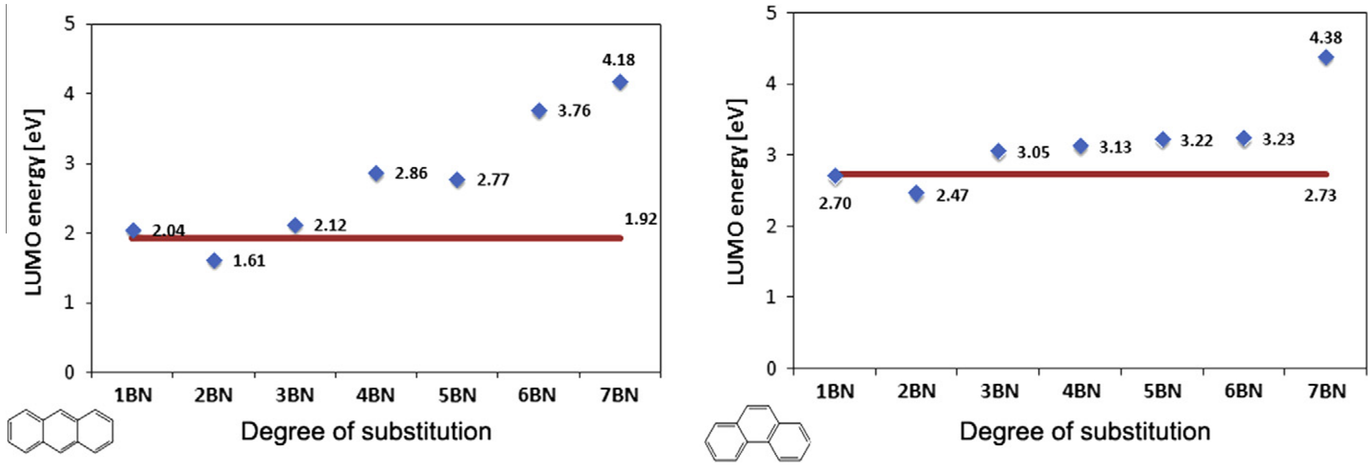


Fig. 9. RHF/6-31G* estimated LUMO energy of the most stable isomer at the respective degree of BN-substitution of anthracene (left) and phenanthrene (right); the baseline corresponds to the LUMO of the pristine hydrocarbon.

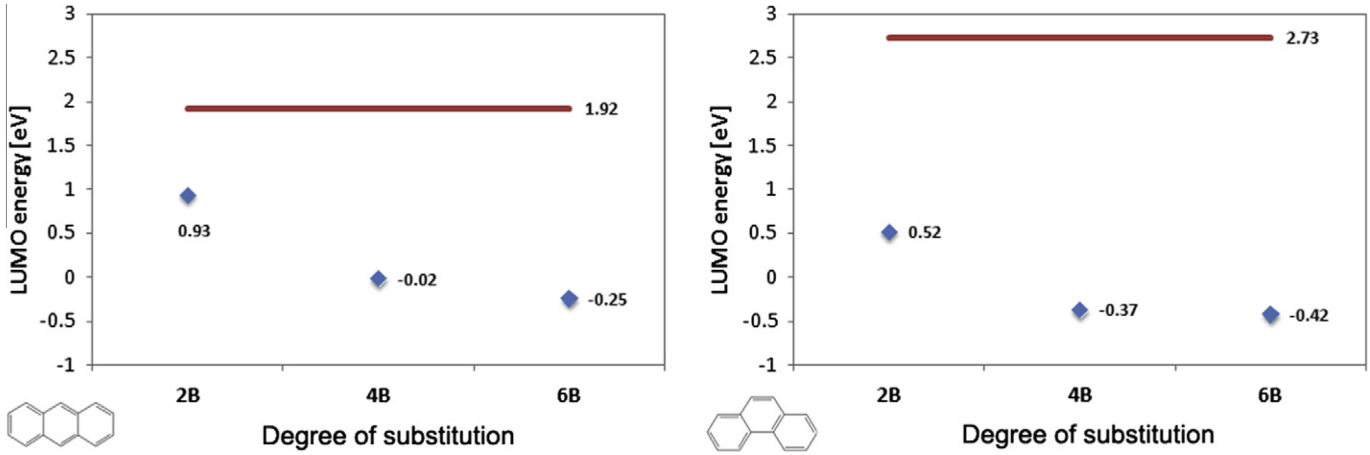


Fig. 10. RHF/6-31G* estimated LUMO energy of the most stable isomer at the respective degree of B-substitution of anthracene (left) and phenanthrene (right); the baseline corresponds to the LUMO of the pristine hydrocarbon.

periphery and building block of this type would be better electron-acceptors than all the carbon-based anode materials used to date. The stoichiometry of this isomer is close to the ratio BC_3 considered as most effective by the experimentalists but differs from the theoretical model suggested by them.

The stable B-phenanthrenes also have substantially lower LUMOs than both hydrocarbons considered and all the stable BN-derivatives of the latter. The LUMO of the 6B-isomer is again the lowest-lying not only among the phenanthrenes but also compared to all substituted anthracenes. If the energy of LUMO were the main factor determining the quality of the anode material, this would be the most appropriate unit cell of a prospective efficient substituted carbonaceous anode.

Based on the results obtained so far, the most favorable (in terms of total and LUMO energy) isomers in each series of structures were outlined. As stated above, the LUMO depression is related to its delocalization. In Fig. 11 are depicted the LUMOs of the BN- and B-isomers of anthracene with lowest-lying first vacant MO and are compared with LUMO of the parent hydrocarbon.

Slight modification of the delocalization pattern is witnessed in the LUMO of the 2BN-substituted species compared to the one of the pristine anthracene (Fig. 11) with more emphatic contribution of the boron from the electron-deficient central ring. This is confirmed by the charge distribution in A.2.1 (Fig. 12). Sizeable charge redistribution and substantial polarization in the doped ring is observed. In contrast, the low LUMO energy of AB.6.1 is due to the major contribution of the boron atoms and the superb delocalization, the highest possible for this number of π-centers (Fig. S1). In the latter isomer equalization of the moduli of alternating charges occurs (unlike the case of the pristine hydrocarbon – Fig. 3), in spite of the appreciable polarity of the C–B bonds, which ensures the strong delocalization in the B-substituted structures.

The phenanthrene structures exhibit similar behavior. In comparison to the precursor, the 2BN-isomer featuring the lowest LUMO has an analogous pattern of delocalization in the region of the tertiary boron (Fig. 13). In most of the isomers with higher degree of substitution the delocalization in the substituted ring is minimal (Figs. S3 and S4). In spite of the fact that the LUMO of the 6B-isomer is the lowest among all studied structures, its delocalization is poorer than the 6B-anthracene one, proving that delocalization alone is an insufficient token of low-energy virtual MO. The MO-results are supported by the charge values (Fig. 14 and Fig. S1). Unequal alternating charges characterize the substituted ring in the 2BN-isomer. Although the charges are of similar value

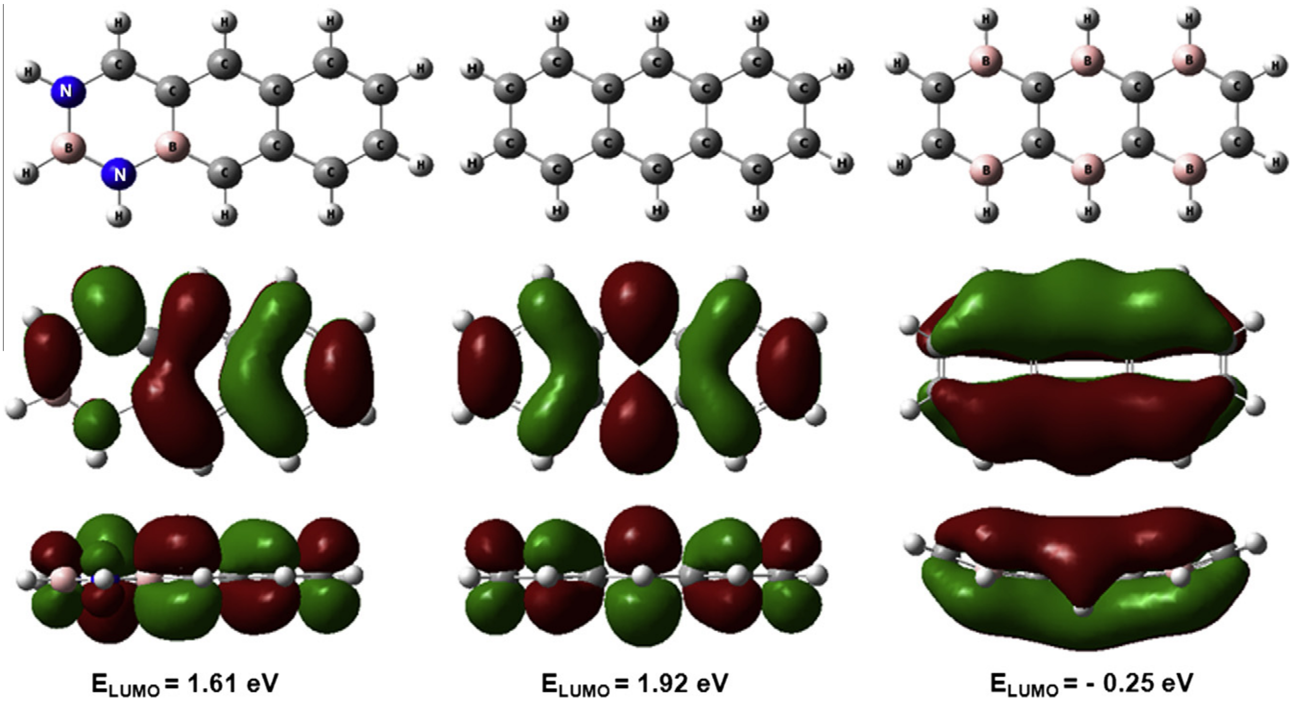


Fig. 11. Top and side view of the RHF/6-31G* computed LUMOs of the most stable 2BN- (left), 6B- (right) and pristine (center) anthracene.

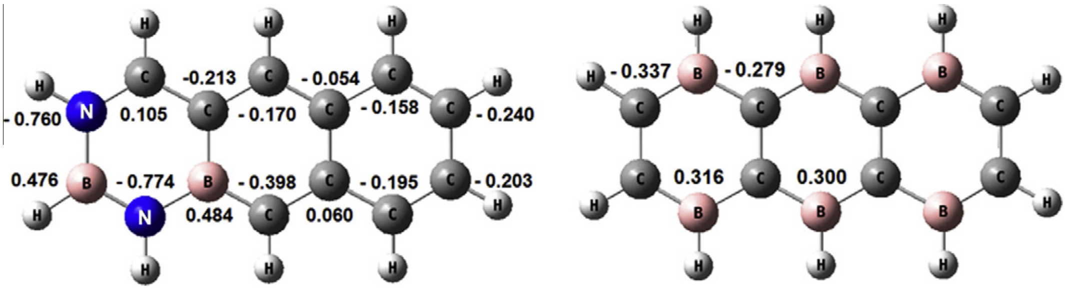


Fig. 12. RHF/6-31G* Mulliken atomic charges in the most stable 2BN- (left) and 6B- (right) substituted anthracenes. Hydrogen atom charges are shown in the Supplementary Data (Figure S2).

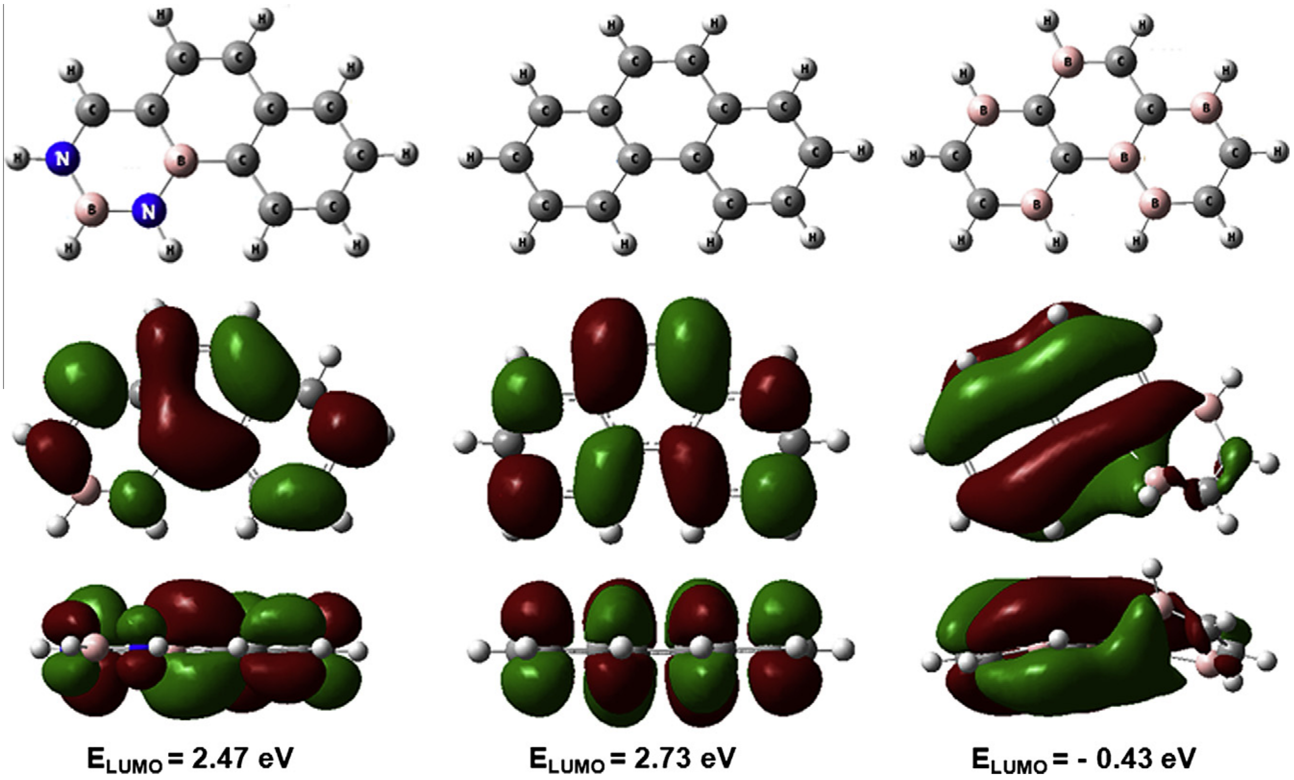


Fig. 13. Top and side view of the RHF/6-31G* computed LUMOs of the most stable 2BN- (left), 6B- (right) and pristine (center) phenanthrene.

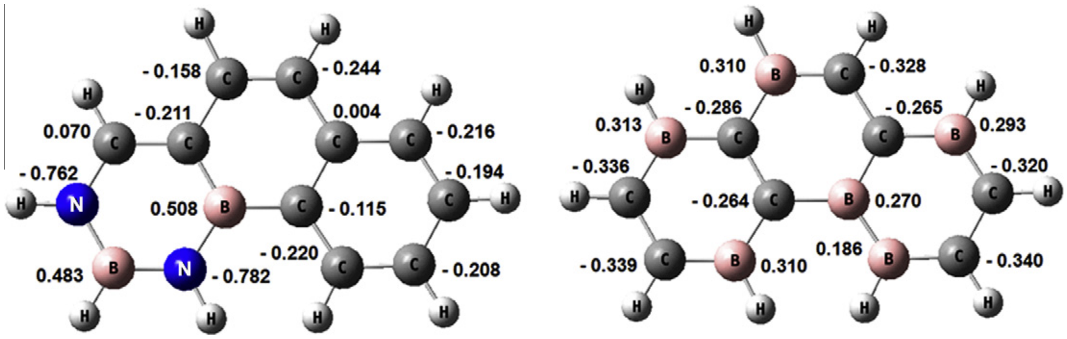


Fig. 14. RHF/6-31G* Mulliken atomic charges in the most stable 2BN- (left) and 6B- (right) substituted phenanthrenes. Hydrogen atom charges are shown in the Supplementary Data (Figure S2).

and opposite sign at the adjacent borons and carbons, the charge alternation is disturbed in all three rings of the 6B-phenanthrene, due to the low symmetry of the molecule.

Considerable contribution of the tertiary boron atom to the overall delocalization of the respective LUMO within the electron-deficient ring is notable for both 2BN-substituted hydrocarbons presented (Figs. 11 and 13). Most probably, this is the reason for the lower energy of the stable 2BN-species compared to the remaining isomers (Tables S1 and S2). There exist other structures having lower-lying LUMOs than that of the precursors where the boron atom takes part in the conjugation (Fig. S4) but they are unstable. At higher degrees of BN-substitution the preservation of delocalization in the unsubstituted portion of the compounds is less likely, hence, the electron-accepting properties deteriorate.

The 6B-substituted hydrocarbons have lower energy of LUMO with respect to the parent structure. Here most stable in the series is the compound with lowest-lying LUMO. These are the lowest values for LUMO among all the investigated isomers of the corresponding hydrocarbon. The share of the boron-containing fragments of the molecules to LUMO is the largest, whereas in the BN-structures the contribution of the electron-deficient portion of the molecule is not prevailing. This is the main cause for the depressed LUMO of the stable B-substituted hydrocarbons. The boron atoms do not participate in the LUMO of the less favorable isomers thus aggravating the electro-accepting features of the material.

4. Conclusions

Summarizing the results, the following major factors governing the stability of structures could be outlined:

4.1. For the BN-substituted structures

a. Formation of cyclic fragments; conservation of maximum number of carbon rings has higher priority as the enhanced aromaticity of the cycles stabilizes the structure.

b. Alternation of boron and nitrogen atoms; the adjacency of identical heteroatoms results in drastic increase of energy, whereas compactness of carbons has stabilizing effect.
c. Least fragmentation of the BN- and carbon portions of the molecules results in lower energy.
d. Preference of tertiary positions for B-substitution and secondary ones for N-substitution is marked.
e. Direct bond of the cyclic carbon residue to boron and through a linear (or branched) fragment to nitrogen is favored in all cases.

The importance of these factors is non-equivalent: the first two are much higher in hierarchy, whereas the next three are abided only when they do not contradict the former.

4.2. For the B-substituted structures

a. The tendency towards conservation of unbroken carbon rings is retained but not the one for minimum fragmentation of the carbon (boron) sequences; energy grows with the length of boron build-up and so does the deviation from planarity.
b. More stable are structures with disjoint boron atoms separated by C_2 spacers, thus ensuring regular distribution of the electron-deficient regions. B-substitution of tertiary sites has destabilizing effect.

The loss of planarity in phenanthrene structures occurs at lower degree of substitution and from this standpoint the anthracene isomers are preferred for accommodation of Li. Moreover, the latter have lower energy than the corresponding phenanthrene species.

Only few BN-hydrocarbons have LUMOs with lower energy than that of the precursors. In both anthracene and phenanthrene series of isomers the B-substituted compounds have lower-lying LUMOs than the pristine hydrocarbons and the BN-substituted ones. The substantial contribution of the boron atoms to this MO and the enhanced delocalization caused by them is recognized to be the reason for the energy depression of LUMO. Accordingly, B-substituted isomers will be better acceptors of electrons at any degree of substitution.

Among the entire set considered, anthracenes and phenanthrenes with four or six carbon atoms replaced by boron meet the requirements for building blocks of more efficient anode materials for Li-ion batteries.

Acknowledgements

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Appendix A. Supplementary data

The following supplementary material is available: structure, total energy and relative energy of BN-doped anthracenes (Table S1, multisheet), BN-doped phenanthrenes (Table S2, multisheet), 2 × B-doped anthracenes (Table S3, multisheet) and 2 × B-doped phenanthrenes (Table S4, multisheet); LUMO pattern of the three most stable 6B-anthracenes (Fig. S1); atomic charges of lowest-energy BN- and B-doped anthracene and phenanthrene (Fig. S2); LUMO pattern of the three most stable 6BN-anthracenes (Fig. S3); LUMO pattern of the three most stable 1BN-anthracenes (Fig. S4); structure (Fig. S5), energetics (Table S5) and parameters of Li adsorption (Table S6) of 1B-doped anthracenes and phenanthrenes. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.theochem.2010.06.003.

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