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Edge Structure Index for Evaluating the Ground State Properties of One–Dimensional Macro– to Suprabenzenoid Hydrocarbons as Examined by DMRG VB Calculations

Haibo Ma, Yi Gao, Xin Li, Jing Ma, Chungeng Liu, and Yuansheng Jiang
Institute of Theoretical and Computational Chemistry, Department of Chemistry, Nanjing
University, Nanjing, 210093, P. R. China

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Edge Structure Index for Evaluating the Ground State Properties of One–Dimensional Macro– to Suprabenzenoid Hydrocarbons as Examined by DMRG VB Calculations[#]

Haibo Ma, Yi Gao, Xin Li, Jing Ma, Chungen Liu, and Yuansheng Jiang*

Institute of Theoretical and Computational Chemistry, Department of Chemistry, Nanjing University, Nanjing, 210093, P. R. China

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Abstract

A new topological index, the edge structure index (ESI), was proposed in this paper for evaluating the ground-state properties of one–dimensional macro– to suprabenzenoid hydrocarbons. The ESI was shown to be effective in providing good correlations with the ground state properties, such as the ground state energy (E_{π}) and resonance energy per π electron (REPE) obtained by density matrix renormalization group (DMRG) using valence bond (VB) calculation within the JTH parametric scheme. It was also demonstrated that for one–dimensional macro– to suprabenzenoid hydrocarbons the edge structure index gives better correlations than the connectivity index χ .

Keywords. Density matrix renormalization group; valence bond; aromaticity; benzenoid hydrocarbon; topology; edge structure index.

1 INTRODUCTION

Because of their important impact on public health and the environment, benzenoid hydrocarbons have attracted for a long time the attention of both experimental and theoretical chemists [1–4]. Recently, the potential applications of macro– to suprabenzenoid hydrocarbons as nanostructures and electronic materials have become a focus of scientific community's research interests [5–7]. Some *ab initio* calculations have been carried out on benzenoid hydrocarbons [8–14], but they were limited only to small to medium sized systems due to the computational difficulties. Thus, the semi–empirical approaches are still desirable for the systematic study of large to infinite sized benzenoid hydrocarbons. Although the Hückel molecular orbital (HMO) theory can treat very large systems [15–18], it is not satisfactory because of the neglect of electron correlations in this one–electron model. On the other hand, under certain conditions, the valence bond (VB)

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* Correspondence author; E–mail: ysjiang@netra.nju.edu.cn.

theory has been able to successfully describe some physical and chemical properties such as the bond lengths, kinetic reactivities, low-lying electronic spectra, and aromaticities of various conjugated systems [19–23]. However, the exact solution of the classical VB model of conjugated hydrocarbons is currently available only for systems with not more than 30 π -electrons due to the exponential increase in the number of configuration states with the system size [23–24]. According to the resonance theory, by restricting attention just to Kekulé structures, a number of quantitative resonance-theoretic VB approaches [25–30] extended the size limitations. But the number of Kekulé structures still increases fairly rapidly with the system size. Recently, mean-field resonating VB theory [31] was advocated for the description of a variety of conjugated π -network species as an efficient qualitative resonance-theoretic method.

Another distinguishing feature of the benzenoid hydrocarbons is their topological dependences [32–42], which make it possible to carry out some simple calculations just by the “pen-and-paper” approach based on some well-behaved topological indices and to rationalize some interesting properties. Wiener introduced the first topological index, the Wiener index W [43] in 1947, and Hosoya introduced the Hosoya Z index [44] in 1971. Subsequently, various other topological methods [27,28,45–54] for evaluating the properties of benzenoid hydrocarbons, such as the Randić connectivity index [45] and the conjugated-circuit model [48,49] were proposed. These topological indices are especially used by experimental chemists due to their remarkable computational and theoretical advantages. However, they suffer from a number of limitations. One important limitation is that, when system is very large, it is difficult to enumerate the vertexes or edges, Kekulé structures, conjugated circuits, etc. Therefore, the properties of large benzenoid hydrocarbons are still difficult to predict. Another important limitation is that these traditional topological indices cannot distinguish some isomeric molecules. For example, chrysene and benzo[*c*]phenanthrene are considered to be identical according to all topological indices defined so far.

To overcome these limitations, we propose an efficient topological index, the edge structure index (ESI) to evaluate the ground-state properties of one-dimensional macro- to suprabenzenoid hydrocarbons. To test the efficiency of our edge structure index within the classical VB models, we perform density matrix renormalization group (DMRG) [55,56] calculations, which have been demonstrated to be able to yield nearly exact results for large benzenoid hydrocarbons [57].

2 COMPUTATIONAL DETAILS

2.1 Classical VB Model

For neutral conjugated hydrocarbons, as all carbon atoms and all conjugated π bonds are supposed to be identical in the classical VB model, hence, the Hamiltonian takes the Heisenberg form [58]:

$$H = -J \sum_{i \sim j} (2S_i \cdot S_j - 1/2) \quad (1)$$

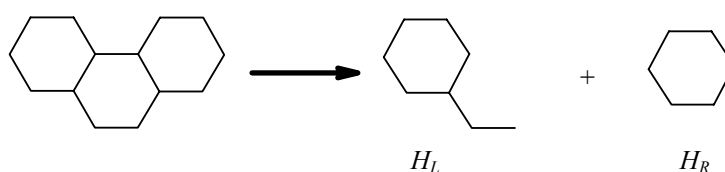
where $i \sim j$ specifies that the summation is over all the bonded atom pairs for the π -electron skeleton of the molecule, S_i denoting the spin operator of the i -th site and J is an (positive) exchange parameter.

It has been demonstrated that for the large benzenoid hydrocarbons, the classical VB model can give reasonable results [59]. Using this classical VB model, we perform DMRG calculations to obtain the ground state energies for the selected series.

2.2 Density Matrix Renormalization Group (DMRG) Method

The difficulty of obtaining the exact solution of VB models for large conjugated systems lies in the exponential increase in the number of configuration states with the system size. Our physical intuition suggests that not all of those numerous configuration states contribute significantly to the low-lying states. There are several schemes proposed for efficiently truncating the configuration space. In 1992, White developed a very powerful and accurate numerical method, the density matrix renormalization group (DMRG), for many-electron models treating one-dimensional lattice systems [55].

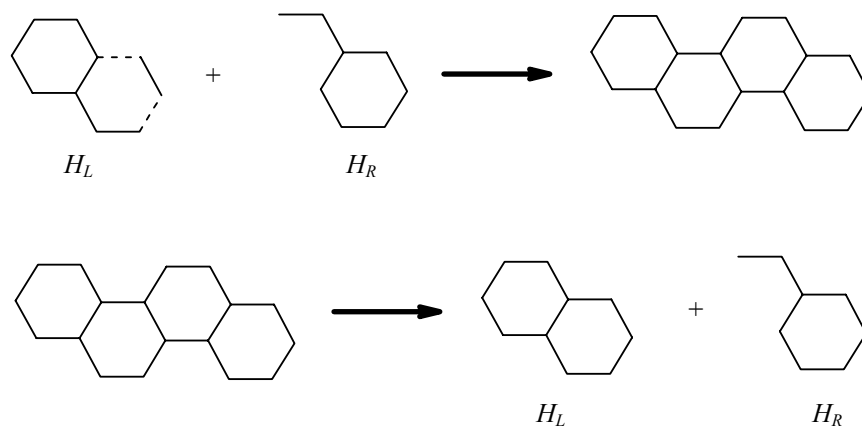
Recently, we performed DMRG calculations on classical VB models to study polyacene and polyphenanthrene series [59]. Here, we extended the DMRG VB calculations to several one-dimensional benzenoid hydrocarbons by choosing different blocks. Let us take polyphenanthenes as an illustration. We begin with phenanthrene. In the first step, we calculate the ground state of phenanthrene using the standard method. Then we divide the phenanthrene into two parts, L (left) and R (right), as shown in Scheme 1.



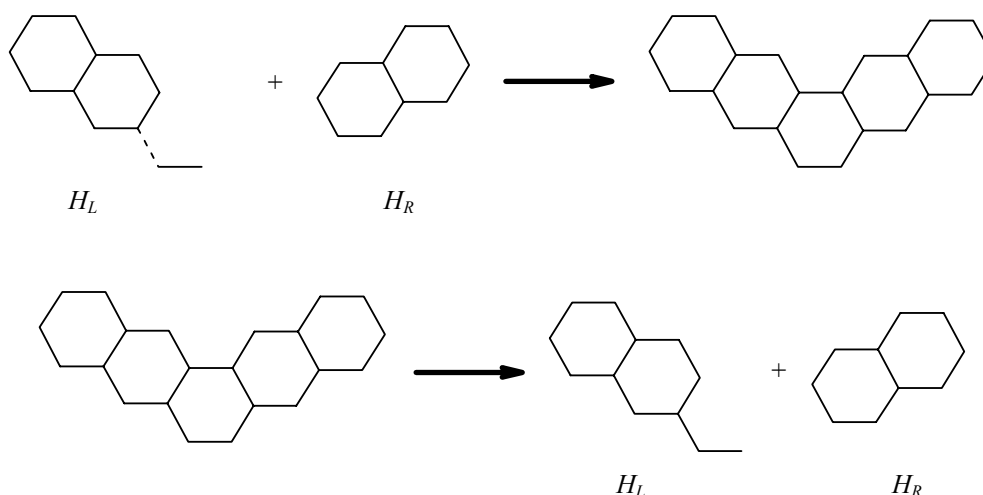
Scheme 1

Then we form the density matrix of the left block, $\rho_{ii} = \sum_j \Psi_{ij}^* \Psi_{ij}$ where $\Psi_{ij} = c_{ij} |i\rangle |j\rangle$, $|i\rangle$ is the set of vectors in the left block and $|j\rangle$ is the set of vectors in the right block. The density matrix is diagonalized for choosing m eigenvectors with the largest eigenvalues to induce a new system block, $H_L' = O H_L O^+$, where O is specified by the m eigenvectors with the largest eigenvalues of ρ as columns. In the next step, we form a larger superblock as shown in Scheme 2 using H_L' , an extra ethylene (added block), and H_R' , which is the reflection of the left block H_L . We use H_L' plus

an extra ethylene (added block) as the new H_L and H_R' as the new H_R . Then we diagonalize the combined blocks displayed above and obtain the ground state of chrysene. A further repetition of the step (as shown in Scheme 3) leads to the ground state of pentaphene.



Scheme 2



Scheme 3

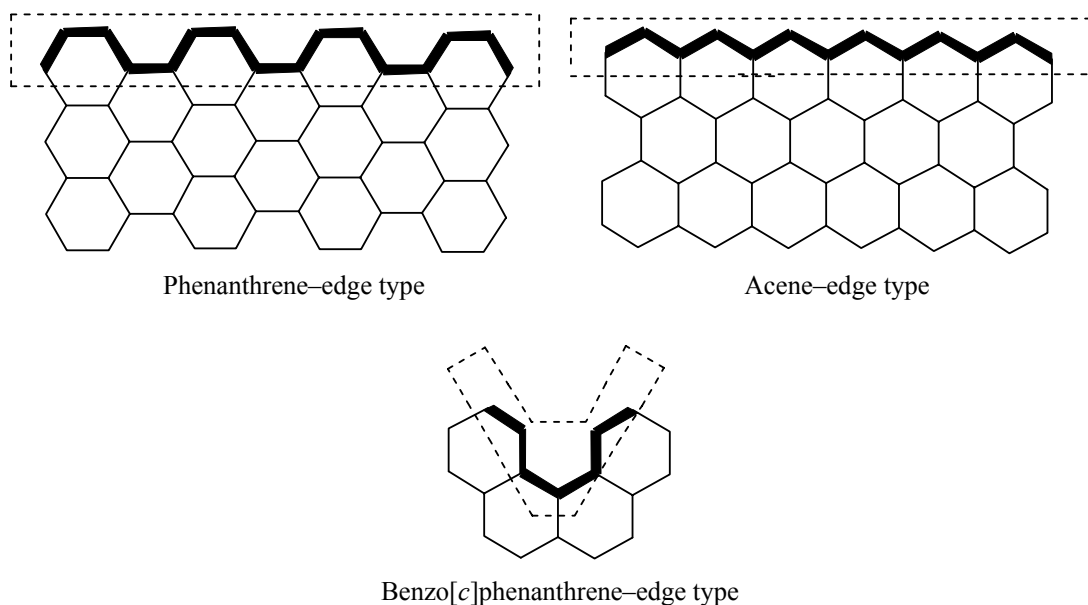
By analogy to the repeating steps as described above, we can locate the ground states of higher members of the series one by one. Similar treatment can be done for other conjugated systems.

3 EDGE STRUCTURE INDEX

3.1 Definition of Edge Structure Index

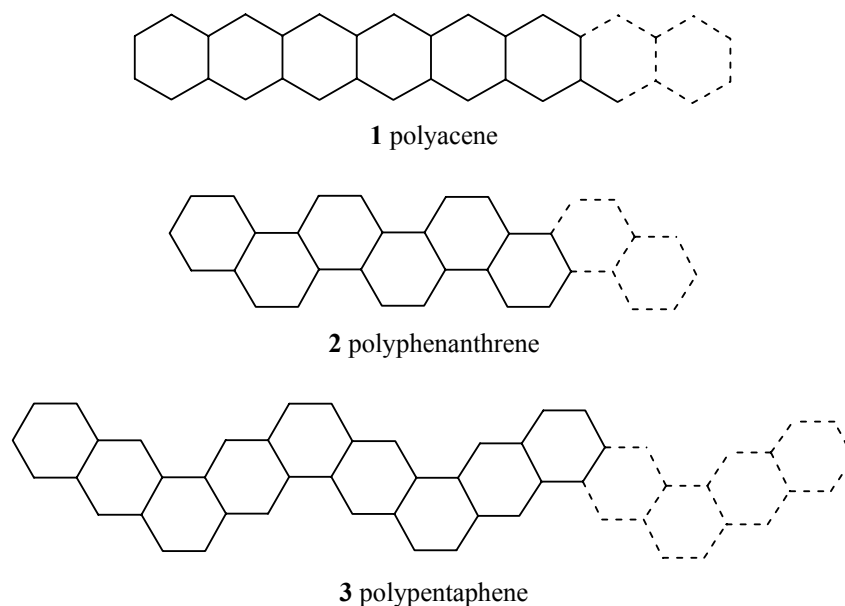
It has been well established by theoretical studies at various levels that the electronic properties of benzenoid hydrocarbons depend significantly on their molecular sizes and edge structures [32–39,42]. There are several prototypes for the edge structures of benzenoid hydrocarbons: one of the

most important edge structure is “phenanthrene–edge type” (or armchair–edge type) and another is “acene–edge type” (or zigzag–edge type) [60], as shown in Scheme 4. For one–dimensional benzenoid hydrocarbons, another edge structure, benzo[*c*]phenanthrene–edge type as shown in Scheme 4, is also assumed to be very important.

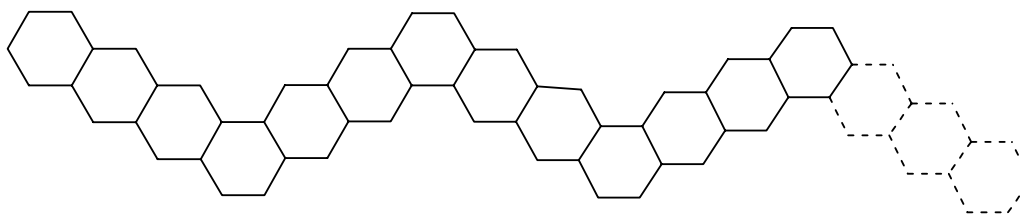


Scheme 4

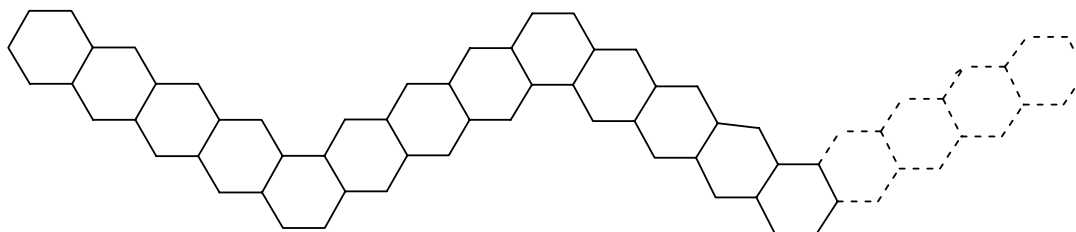
We propose a new scheme to evaluate the ground state properties of one–dimensional macro– to suprabenzenoid hydrocarbons by their edge structures. The series **1–9** (shown in Scheme 5) have been selected for our study.



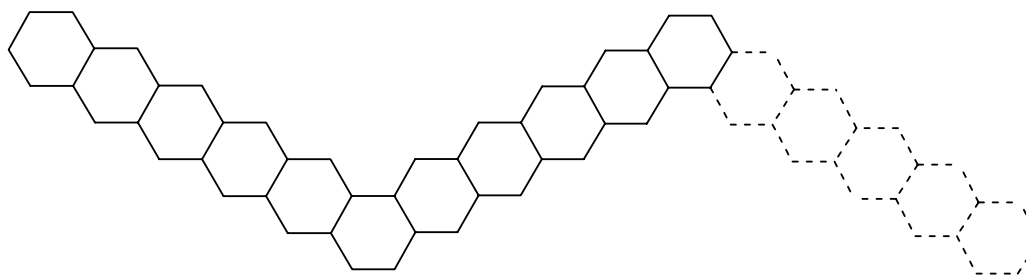
Scheme 5



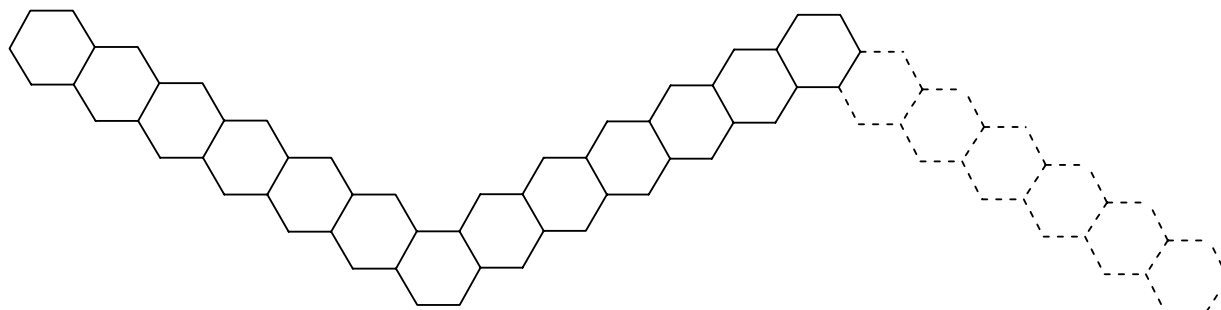
4 polyheptaphene



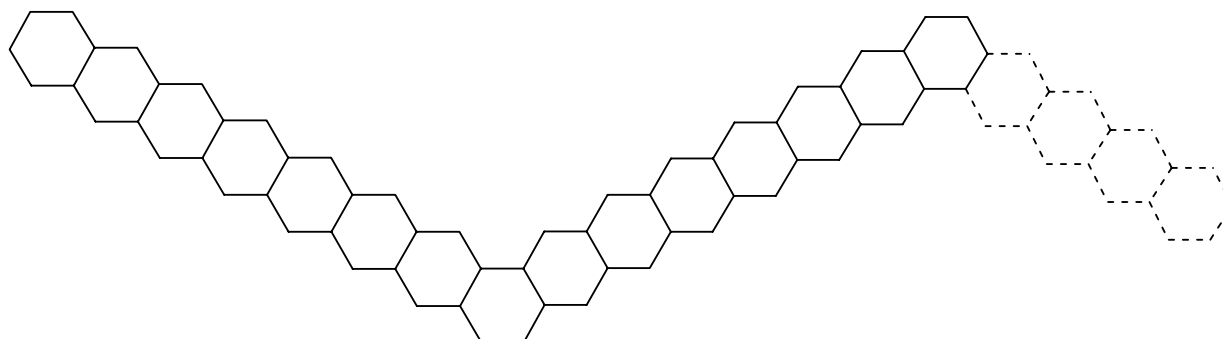
5 polyenneaphene



6 polyhendecaphene

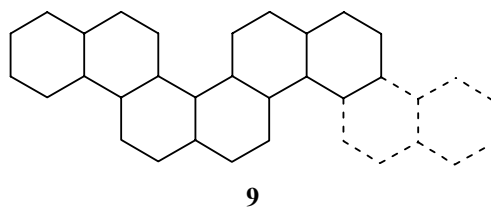


7 polytridecaphene



8 polypentadecaphene

Scheme 5 (Continued)



Scheme 5 (Continued)

According to the classification of edge types as shown in Scheme 4, polyacene **1** can be taken as entirely composed of acene–edge structures, and polyphenanthrene **2** is entirely composed of phenanthrene–edge structures and other one–dimensional macro– to suprabenzenoid hydrocarbons, such as series **3–8**, as a mixture of acene–edge structures and phenanthrene–edge structures. Interestingly, series **9** and polyphenanthrene **2** have identical acene– and phenanthrene–edge structures, so they may have very similar properties. Many topological indices, like the connectivity index χ , also predict identical ground-state properties. However, their real properties are somewhat different [61]. We thought that the difference might be contributed as due to the benzo[*c*]phenanthrene–edge structures in series **9**.

Here, we define the edge structure index ESI by the following formula:

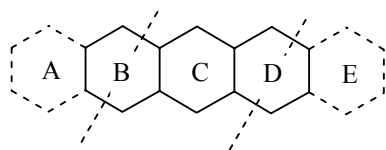
$$ESI = (n_p - c \times n_b) / (n_p + n_a) \quad (2)$$

where n_p , n_a and n_b are defined as the number of phenanthrene–edge structures, acene–edge structures and benzo[*c*]phenanthrene–edge structures, respectively, and c is an empirical parameter which in this paper is taken as 0.064 [62].

We have studied the units of series **1–9**, as shown in Scheme 6. Series **1–8** actually do not have benzo[*c*]phenanthrene–edge structures. Let us take polyheptaphene **4** as an example. The hexagons C and D are the only integral hexagons in the duplicational unit of polyheptaphene. There are two kinds of edge structures: A–B–C and D–E–F form 2 phenanthrene–edge structures; B–C–D and C–D–E form 2 acene–edge structures. So that for polyheptaphene **4**, $n_p = 2$, $n_a = 2$, and $n_b = 0$. The series **9** is different from the others because it has benzo[*c*]phenanthrene–edge structures. In its duplicational unit, B–C–D, C–D–E, D–E–F, E–F–G, F–G–H form 5 phenanthrene–edge structures and B–C–D–E, D–E–F–G–H, F–G–H–I form 3 benzo[*c*]phenanthrene–edge structures, therefore we obtain $n_p = 5$, $n_a = 0$, and $n_b = 3$.

3.2 Correlation to Quantitative Indices of the Ground State Properties

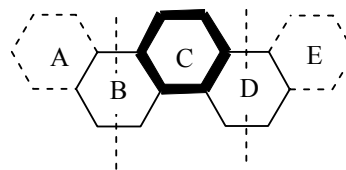
According to the above defined edge structure index ESI, we have studied the topological dependences of the ground state properties of series **1–9**. The calculated ESIs of series **1–9** are shown in Table 1. To test the efficiency of our edge structure index ESI, we perform DMRG VB calculations to obtain the ground state energies per π electron (E_π/N , where N is the number of π electrons), in the infinite sized limits of series **1–9**, as shown in Table 1.



$$n_p = 0$$

1 polyacene $n_a = 3$

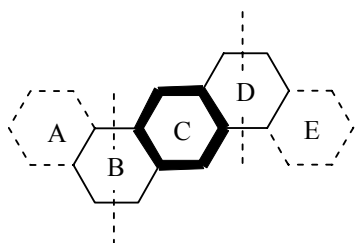
$$n_b = 0$$



$$n_p = 3$$

2 polyphenanthrene $n_a = 0$

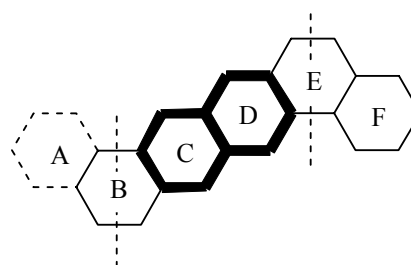
$$n_b = 0$$



$$n_p = 2$$

3 polypentaphene $n_a = 1$

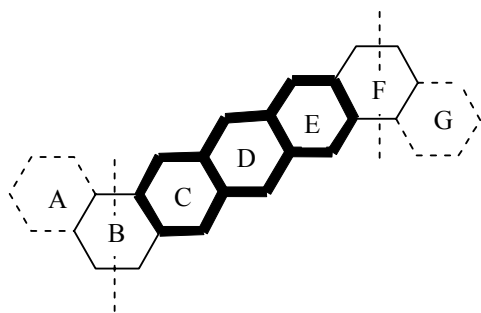
$$n_b = 0$$



$$n_p = 2$$

4 polyheptaphene $n_a = 2$

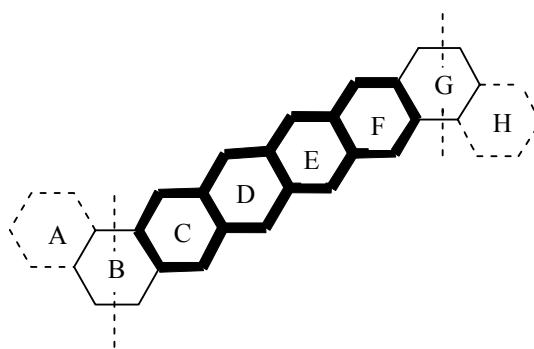
$$n_b = 0$$



$$n_p = 2$$

5 polyenneaphene $n_a = 3$

$$n_b = 0$$

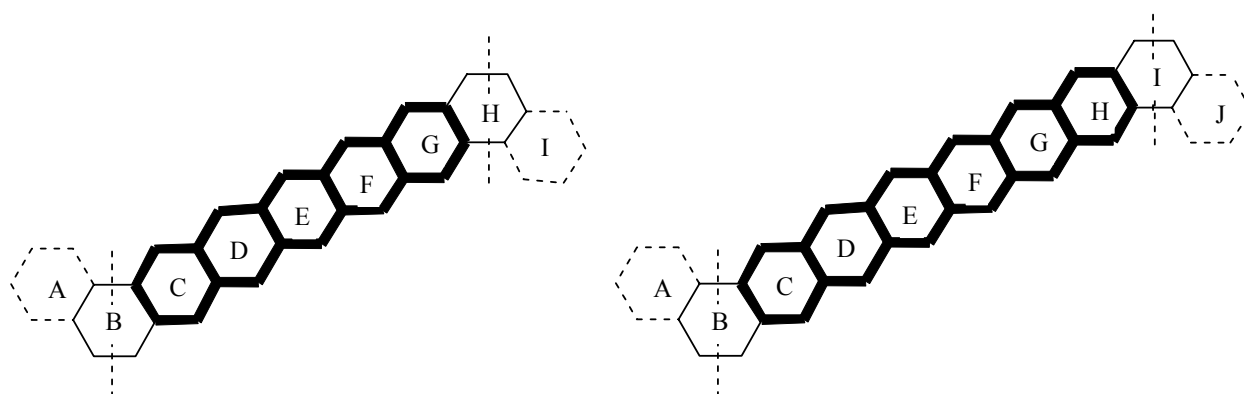


$$n_p = 2$$

6 polyhendecaphene $n_a = 4$

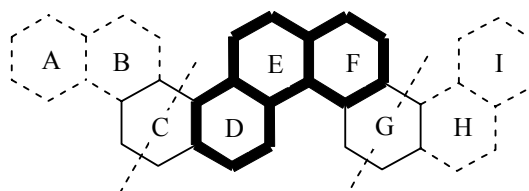
$$n_b = 0$$

Scheme 6



$$\begin{aligned}
 & n_p = 2 \\
 \text{7 polytridecaphene } & n_a = 5 \\
 & n_b = 0
 \end{aligned}$$

$$\begin{aligned}
 & n_p = 2 \\
 \text{8 polypentadecaphene } & n_a = 6 \\
 & n_b = 0
 \end{aligned}$$



$$\begin{aligned}
 & n_p = 5 \\
 \text{9 } & n_a = 0 \\
 & n_b = 3
 \end{aligned}$$

Scheme 6 (Continued)

Table 1. Edge structure indices and REPE of series 1–9.

series	edge structure			ESI	χ / n_{edge}	E_{π}/N ^a	REPE ^b
	n_p	n_a	n_b				
1	0	3	0	0.0000	0.3933	-1.60249	-0.03172
2	3	0	0	1.0000	0.3966	-1.61882	-0.04535
3	2	1	0	0.6667	0.3950	-1.61431	-0.04179
4	2	2	0	0.5000	0.3944	-1.61111	-0.03894
5	2	3	0	0.4000	0.3941	-1.60908	-0.03711
6	2	4	0	0.3333	0.3940	-1.60778	-0.03593
7	2	5	0	0.2857	0.3939	-1.60689	-0.03513
8	2	6	0	0.2500	0.3938	-1.60627	-0.03457
9	2	0	3	0.9616	0.3966	-1.61865	-0.04521

^a E_{π}/N values obtained by DMRG VB calculations are in J units

^b REPE values obtained by DMRG VB calculations are in J units

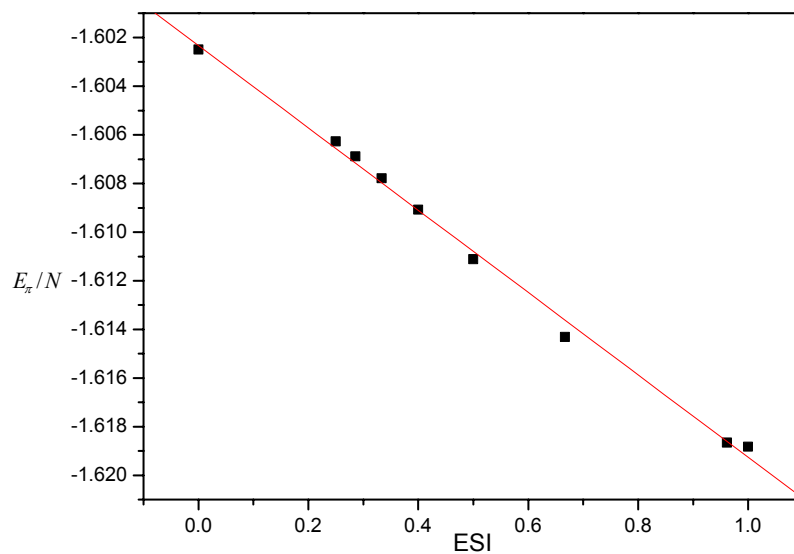


Figure 1. Plot of E_{π}/N versus ESI of series 1–9.

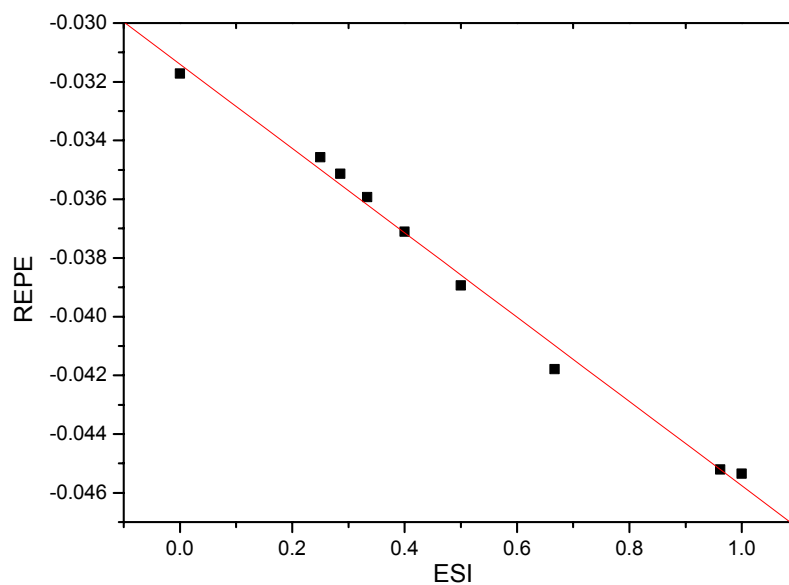


Figure 2. Plot of REPE versus ESI of series 1–9.

We see from Figure 1 that there exists a good linear relationship between ESI and E_{π}/N . Thus, E_{π}/N can be easily correlated by the following formula:

$$E_{\pi} / N = -1.60233 - 0.01693 \times ESI \quad (3)$$

The resonance energy per π electron (REPE) [63–68] has been widely used as a criterion of

aromaticity for conjugated molecules [26,69–78]. We have also calculated REPEs of series 1–9 in the infinite sized limits by DMRG VB calculations within the JTH parametric scheme [66], which were listed in Table 1. In fact, ESI also correlates well with REPE (shown in Figure 2). The relationship between ESI and REPE approximately satisfies the following formula:

$$REPE = -0.03140 - 0.01436 \times ESI \quad (4)$$

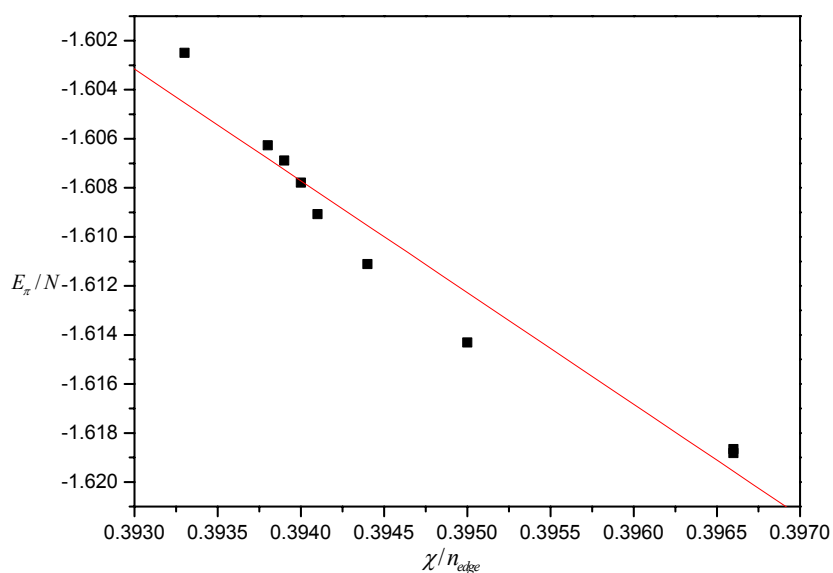


Figure 3. Plot of E_{π}/N versus χ/n_{edge} of series 1–9.

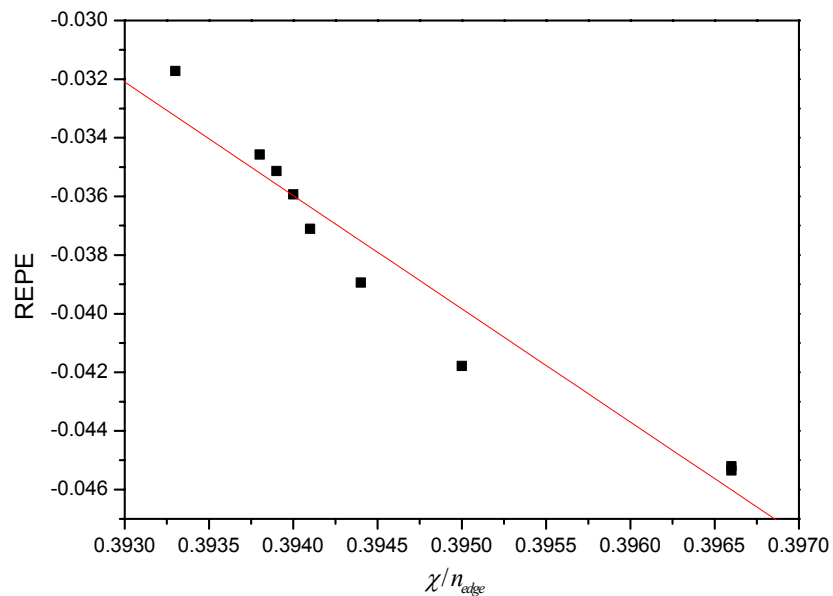


Figure 4. Plot of REPE versus χ/n_{edge} of series 1–9.

It is also worthwhile comparing our ESI with other topological indices. The connectivity index χ is a widely used topological index, so we also computed χ/n_{edge} (n_{edge} , the number of edges, is introduced to compare systems of different sizes), with the results in Table 1. Similarly, we studied the correlation between χ/n_{edge} and E_{π}/N , REPE of series **1–9** as shown in Figure 3–4.

It is clearly shown that ESI has advantages in that: (1) ESI does suggest polyphenanthrene **2** should be thermodynamically more stable than series **9**; (2) our ESI gives better correlations with E_{π}/N and REPE. In conclusion, the edge structure index ESI is a good topological index for evaluating the ground state properties of one-dimensional macro- to suprabenzenoid hydrocarbons. This scheme provides a convenient way with error ratio less than 2% for experimental chemists to predict E_{π} and REPE of one-dimensional macro- to suprabenzenoid hydrocarbons. It would be especially useful for synthetic chemistry of nanostructures and electronic materials.

4 CONCLUSIONS

Macro- to suprabenzenoid hydrocarbons play an increasingly important role in today's material chemistry, but they are difficult to characterize experimentally and theoretically. As demonstrated in this study, the DMRG method provides an efficient and powerful tool for implementing calculations within many-electron models for macro- to suprabenzenoid hydrocarbons. Our edge structure index ESI was demonstrated to be a useful parameter in quantitative structure-property (QSPR) and quantitative structure-activity (QSAR) studies. Since ESI is closely related to edge structures and it touches the duplicational units of the molecules directly, it is very convenient for predictions of the ground-state properties of large benzenoid hydrocarbons and it has good discrimination of isomers. We hope that ESI can be applied to more interesting systems in our future work.

Acknowledgment

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