Kragujevac J. Sci. 28 (2006) 39-46.

ON HOSOYA BOND ORDER OF ALTERNANT NONBENZENOID MOLECULES

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(Received November 24, 2005)

ABSTRACT. The *Hosoya bond order* is defined as $p_{rs}^{H} = Z(G_{rs})/Z(G)$, where G is a molecular graph, G_{rs} is the graph obtained from G by deleting its vertices *r* and *s*, and *Z* denotes the respective Hosoya index. In the past this bond-order-like quantity was not much studied, what can be explained by the difficulties in its calculation. These difficulties motivated us to define a new bond order, named the *modified Hosoya bond order,* $\widetilde{p}_{rs}^{H}$, which can be easily calculated. In the case of acyclic molecular graphs, $\widetilde{p}_{rs}^{H} = p_{rs}^{H}$. For benzenoid hydrocarbons there exists a good linear corelation between $\widetilde{p}_{rs}^{H}$ and p_{rs}^{H}, and it was also found that in usual chemical applications, one may accept that $p_{rs}^{H} \approx \widetilde{p}_{rs}^{H}$. We now show that in the case of nonbenzenoid polycyclic systems the relation between p_{rs}^{H} and $\widetilde{p}_{rs}^{H}$ is less simple and that p_{rs}^{H} cannot be approximated by means of $\widetilde{p}_{rs}^{H}$.

INTRODUCTION

In contemporary theoretical organic chemistry several bond-order-like quantites have been studied. The bond-order concept is aimed at describing the variations of the lenght of the carbon-carbon bonds in conjugated molecules. As early as in the 1930s, on the beginning of quantum chemistry, two bond orders were put forward. Those are the Pauling [1] and the Coulson [2] bond orders, which are the best known today. In the 1970s Hosoya introduced the *topological bond order* [3-6], which is nowadays referred to as the *Hosoya bond order*. The Hosoya bond order for a bond between the atoms *r* and *s*, denoted by p_{rs}^{H}, is defined as

$$p_{rs}^{H} = \frac{Z(G_{rs})}{Z(G)} \qquad (1)$$

where G is the molecular graph, G_{rs} is the graph obtained from G by deleting its adjacent vertices r and s, and Z stands for the respective Hosoya index [7]. The Hosoya index, $Z(G)$, is equal to the total number of matchings of the graph G, i. e.,

$$Z(G) = \sum_{k \geq 0} m(G,k) \tag{2}$$

where $m(G,k)$ is the number of selections of k mutually independent edges in the graph G. In addition, $m(G,0) = 1$ and $m(G,1)$ = number of edges of G.

Formula (2) is not suitable for the calculation of the Hosoya index, unless the molecular graph studied is very small. Another expression that needs to be mentioned here is:

$$Z(G) = \sqrt{\prod_{i=1}^{n} [1 + (\mu_i)^2]} \tag{3}$$

where μ_1, μ_2 ,..., μ_n are the zeros of the matching polynomial of the graph G [8,9], and n is the number of its vertices. The matching polynomial, $\alpha(G,\lambda)$ is a mathematical object closely related to $Z(G)$, and it is defined as:

$$\alpha(G,\lambda) = \sum_{k \geq 0} (-1)^k m(G,k) \lambda^{n-2k} \ . \tag{4}$$

Unfortunately, also the computing of the zeros of the matching polinomial is quite difficult.

In order to skip these obstacles, we tried to use the known relations between the matching polynomial, $\alpha(G,\lambda)$ and the characteristic polynomial, $\phi(G,\lambda)$. For acyclic molecular graphs $\alpha(G,\lambda)$ is equal to $\phi(G,\lambda)$. Then, from (3) we have:

$$Z(G) = \sqrt{\prod_{i=1}^{n} [1 + (\lambda_i)^2]} \tag{5}$$

where λ_1, λ_2,..., λ_n are the eigenvalues of G, which can be easily calculated. Formula (5) cannot be used for polycyclic graphs. To evade this difficulty, we proposed the *modified Hosoya index* [10], $\widetilde{Z}$:

$$\widetilde{Z}(G)=\sqrt{\prod_{i=1}^{n}[1+(\lambda_i)^2]}\quad . \tag{6}$$

Formula (6) is applicable to all molecular graphs, both acyclic and polycyclic. For acyclic molecular graphs $\widetilde{Z}(G)=Z(G)$. By menas of the modified Hosoya index, the *modified Hosoya bond order,* $\widetilde{p}_{rs}^{H}$, was defined as [11]:

$$\widetilde{p}_{rs}^{H}=\frac{\widetilde{Z}(G_{rs})}{\widetilde{Z}(G)}. \tag{7}$$

Directly from this definition we see that for of acyclic systems, $\widetilde{p}_{rs}^{H}=p_{rs}^{H}$.

In the paper [11] some properties of the modified Hosoya bond order were established. It was shown that the relation between the Hosoya bond order and the modified Hosoya bond order reads:

$$p_{rs}^{H}=\frac{\widetilde{p}_{rs}^{H}-\Delta Z(G_{rs})/\widetilde{Z}(G)}{1-\Delta Z(G)/\widetilde{Z}(G)}\quad \text{or}\quad \widetilde{p}_{rs}^{H}=\frac{p_{rs}^{H}+\Delta Z(G_{rs})/Z(G)}{1+\Delta Z(G)/Z(G)} \tag{8}$$

where $\Delta Z=\widetilde{Z}-Z$.

As one can see from Eqs. (8), in the general case the connection between $\widetilde{p}_{rs}^{H}$ and p_{rs}^{H} is relatively complicated. However, numerical testing [11] revealed that for benzenoid molecules there exists a much simpler, linear, correlation between $\widetilde{p}_{rs}^{H}$ and p_{rs}^{H}, viz.:

$$p_{rs}^{H}=(0.929\pm 0.006)\widetilde{p}_{rs}^{H}+(0.036\pm 0.001) \tag{9}$$

with correlation coefficinent as large as 0.993. From (9) it follows that if the accuracy required is not to high, then one may accept that $p_{rs}^{H}\approx\widetilde{p}_{rs}^{H}$.

RESULTS AND DISCUSSION

In this paper we report the results of the studies of the correlation between $\widetilde{p}_{rs}^{H}$ and p_{rs}^{H} for two classes of alternant nonbenzenoid hydrocarbons: (1) phenylenes with four and fewer six-membered rings, and (2) cyclobutadieno-annelated derivatives of benzene and naphthalenes, shown in Fig.1. All those conjugated molecules posses cycles of size 4*k*, *k*=1,2,3,... .

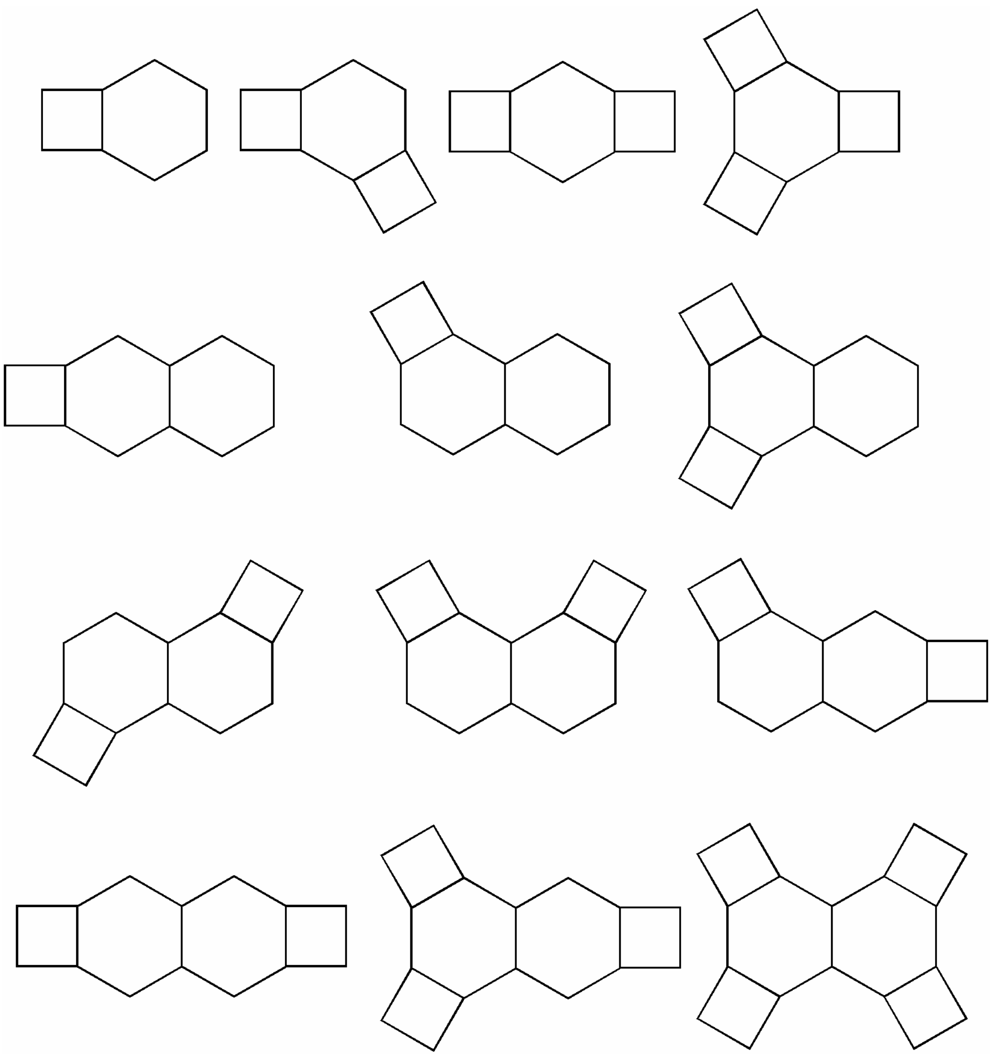

Figure 1. The cyclobutadieno-annelated derivatives of benzene and naphthalene investigated in this work.

In Fig. 2 are plotted the Hosoya bond orders versus the respective modified Hosoya bond orders of all carbon-carbon bonds in the mentioned molecules; the data-points pertaining to phenylenes are indicated by circles, those for the cyclobutadieno-annelated species by triangles. A total of 23 compounds with a total of 238 non-equivalent carbon-carbon bonds were considered. Two features are immediately recognized. First, there is no linear correlation of the kind given by Eq. (9), and there is lacking any other kind of correlation. Second, there is no grouping of the data-points pertaining to phenylenes relative to those representing the cyclobutadieno-annelated benzenes and naphthalenes.

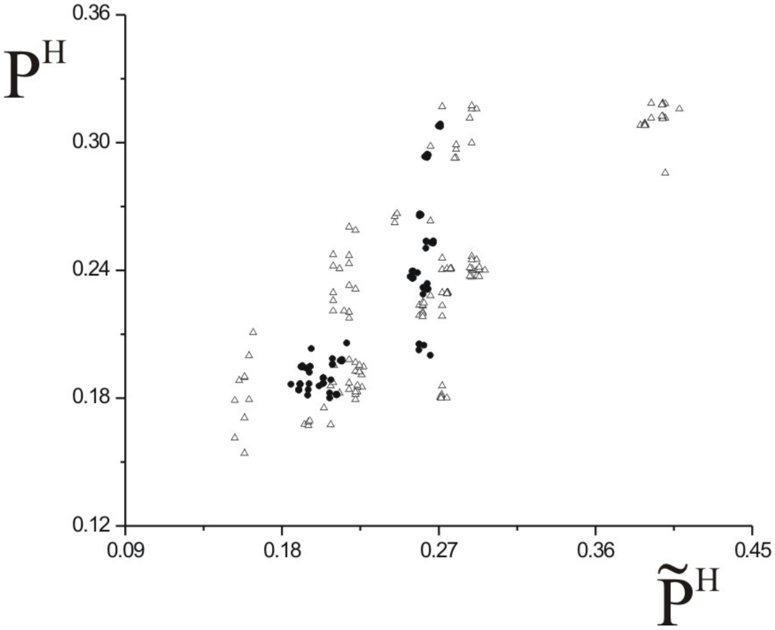

Figure 2. Correlation between Hosoya bond orders (p^H) and modified Hosoya bond orders ($\tilde{p}^H$) pertaining to phenylenes with 4 and fewer six-membered rings (circles) and the molecules shown in Fig. 1 (triangles).

A detailed analysis shows that the data-points are separated into three clusters The molecular graphs of the systems we investigated have three types of edges depending on the degrees of the end-vertices. These are the edges of the type 3-3, 3-2, and 2-2, indicated in Fig. 3 by triangles, circles, and squares, respectively.

Some other properties of the correlation between Hosoya and modified Hosoya bond orders are shown in Fig. 4. We found that the data-points are grouped depending on the ring to which the respective carbon-carbon bond belongs. There are two clusters of data points, one pertaining to the edges lying on six-membered rings (triangles) and the other pertaining to edges lying on four-membered rings (squares). This regularity was noticed only in the case of phenylenes and not for the cyclobutadieno-annelated species.

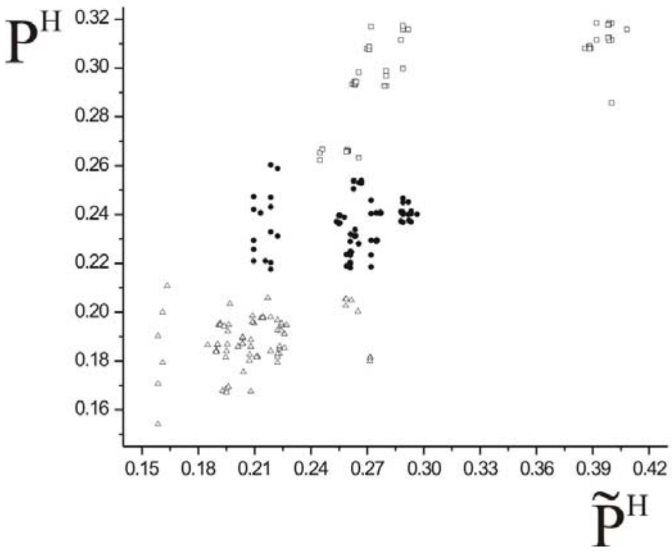

Figure 3. Same data as in Fig. 2. The data-points are separated into three clusters, pertaining to edges of type 3-3 (triangles), 3-2 (circles), and 2-2 (squares).

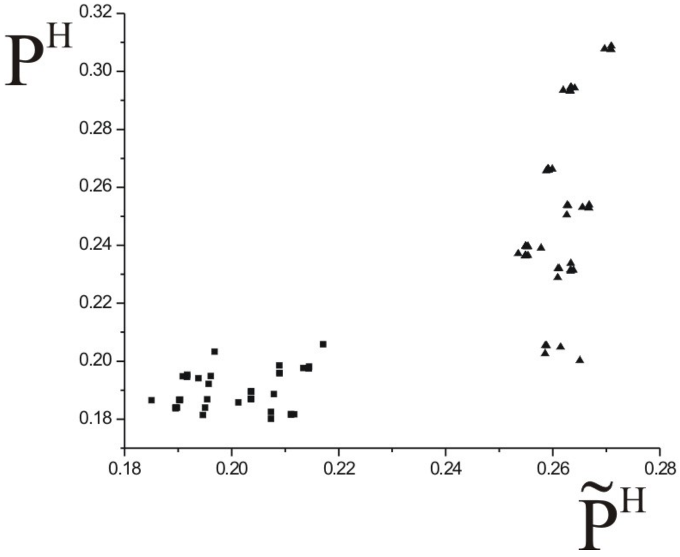

Figure 4. Correlation between p^H and $\tilde{p}^H$ in the case of all phenylenes with 4 and fewer six-membered rings (a total of 103 pairs of bond orders). The data-points are separated into two clusters, pertaining to edges belonging to six-membered rings (triangles) and edges belonging to four-membered rings (squares).

CONCLUSIONS

We studied the relations between the Hosoya bond order and its modified version for two well-defined classes of alternant nonbenzenoid polycyclic conjugated molecules. These differ from the earlier studied [11] benzenoids by possessing cycles of size 4, 8, 12, … . The good linear correlation between the two bond orders in the case of benzenoids [11], and the lack of such correlation in the presently studied conjugated species must be explained by the presence of antiaromatic, destabliziling ($4k$)-membered rings. This implies not only that the modified Hosoya index (whose calculation is easy) cannot be used instead of the original Hosoya index (whose calculation is difficult), but also calls for caution when the Hosoya-bond-order concept is applied to nonbenzenoid polycyclic molecules.

Instead of a correlation between the two bond orders we only could establish certain clustering of the data points: one caused by the type of carbon-carbon bonds (illustrated in Fig. 3), the other caused by the size of the ring to which the carbon-carbon bond belongs (illustrated in Fig. 4).

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