PARTITIONING OF π-ELECTRONS IN THE RINGS OF BENZENOID HYDROCARBONS USING FRIES STRUCTURAL FORMULAS

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Abstract

The recently introduced concept of electron contents (*EC*) of the rings in benzenoid hydrocarbons initiated detailed investigations in that area. There are numerous papers considering this particular topic [1-19]. Calculation of electron contents of the rings is based on Kekulé structures. In this paper, we propose a new way for distributing π-electrons into the hexagons of benzenoid molecules using Fries structures. In addition, we compared our results with those obtained by original the Randić-Balaban model.

INTRODUCTION

The distribution of π-electrons in conjugated chemical compounds is very important because it gives a better insight into their molecular structure and physico-chemical properties. Theoretical chemists have investigated this problem and there is a large literature considering this particular topic. Until recently, partitioning of π-electrons was investigating exclusively between atoms in conjugated molecules. M. Randić and A. T. Balaban introduced a concept of electron contents [1,18] of the rings in benzenoid hydrocarbons. For the first time, the distribution of π-electrons in polycyclic aromatic molecules was considered among rings. They used Kekulé structures as the basis for calculation of electron contents of the rings in benzenoid hydrocarbon. The first step is to convert "geometrical" Kekulé structures into algebraic Kekulé structures. This can be done by following rule: the double bonds (in the considered Kekulé structure) that belong solely to the ring *R* contribute to that ring with two π-electrons and those double bonds that are shared with other rings contribute to the ring *R* with one π-electron. It has to be done for every ring in benzenoid molecule. By that way, we

transformed the considered Kekulé structure into its algebraic model. The above-mentioned rule should be applied to every Kekulé structure of the benzenoid molecule. For catacondensed benzenoid systems, there is a one-to-one correspondence between the classical Kekulé structures and theirs algebraic analogs [15]. In Fig. 1 is shown benzo[a]phenanthrene, its Kekulé and algebraic Kekulé structures.
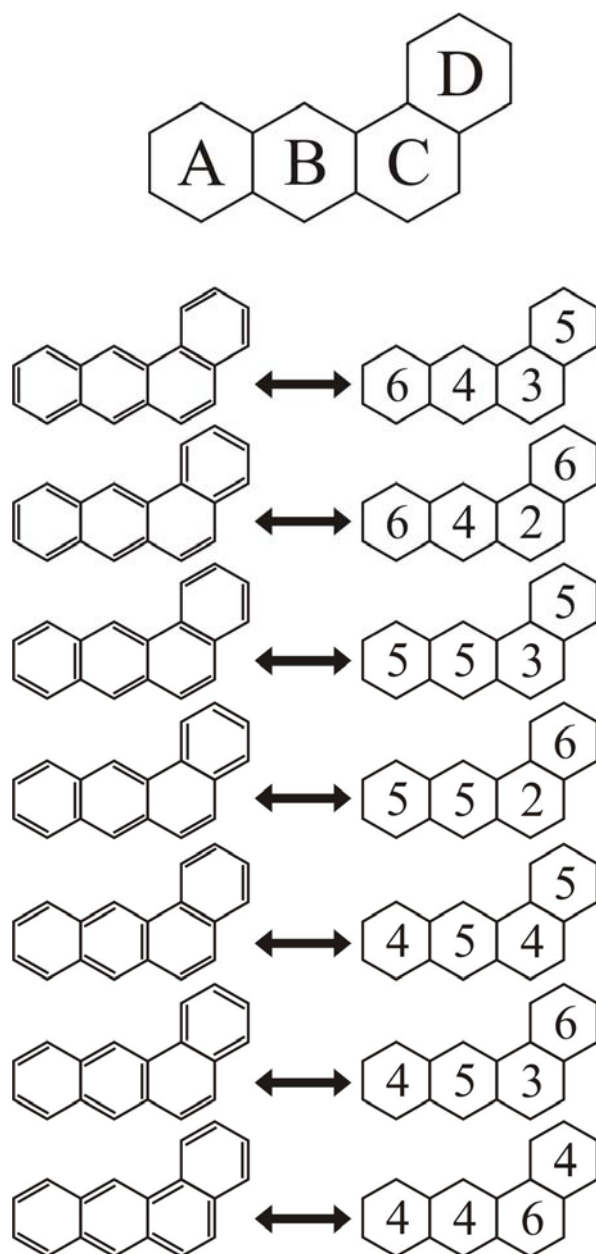

Fig. 1. All "geometrical" Kekulé and theirs correspondent algebraic Kekulé structures of benzo[a]phenanthrene.

When the algebraic Kekulé structures are obtained, the electron content of the ring R is calculated as the average of integers inscribed in that ring in all algebraic Kekulé structures. Below are the calculated electron contents of all rings in benzo[a]phenanthrene:

$$EC(A) = (6+6+5+5+4+4+4)/7 = 4.857$$
$$EC(B) = (4+4+5+5+5+5+4)/7 = 4.571$$
$$EC(C) = (3+2+3+2+4+3+6)/7 = 3.286$$
$$EC(D) = (5+6+5+6+5+6+4)/7 = 5.286$$

It should be pointed out that the sum of the electron contents of all rings in benzenoid hydrocarbons is equal to the number of carbon-atoms (i.e., π-electrons).

This way of calculation of electron contents of the rings can be applied only for benzenoid molecules with considerably small number of Kekulé structures. Electron contents of rings can be also calculated by the following formula:

$$EC(R) = 2\sum_{*} p_{rs}^{P} + \sum_{**} p_{rs}^{P} \tag{1}$$

where, p_{rs}^{P} is the Pauling bond order of the bond rs, $\sum_{*}$ is the sum of all bonds that belong solely to the ring R, and $\sum_{**}$ is the sum of bonds which are shared between ring R and some other rings.

Using formula (1) one can develop a software for the calculation of electron contents of the rings in benzenoid hydrocarbons.

Since Kekulé structures had been introduced in organic chemistry, scientists tried to rationalize them. In other words, among all Kekulé structures, they tried to pick those which, by their opinion, describe the molecule in the best possible way. K. Fries [20] was the one of these scientists who tried to reduce the number of Kekulé structures of benzenoid hydrocarbons. He thought that one should pick Kekulé structures with the greatest number of hexagons with three double bonds, because they are the best possible representation of true nature of benzenoid molecule. By Fries, if the double bond is shared between two rings, it should be counted for each of two rings. He hoped that this approach to the problem would lead to only one structure (nowadays known as Fries structure, see Fig. 2(b)). Unfortunately,

there is rather small number of benzenoid molecules that have only one Fries structure, but he succeeded to reduce the number of Kekulé structures of all benzenoid hydrocarbons. The number of hexagons, in Fries structure, in which are inscribed three double bonds is called the Fries number. In Fig. 2(a) are depicted Fries structures of benzo[a]phenanthrene.
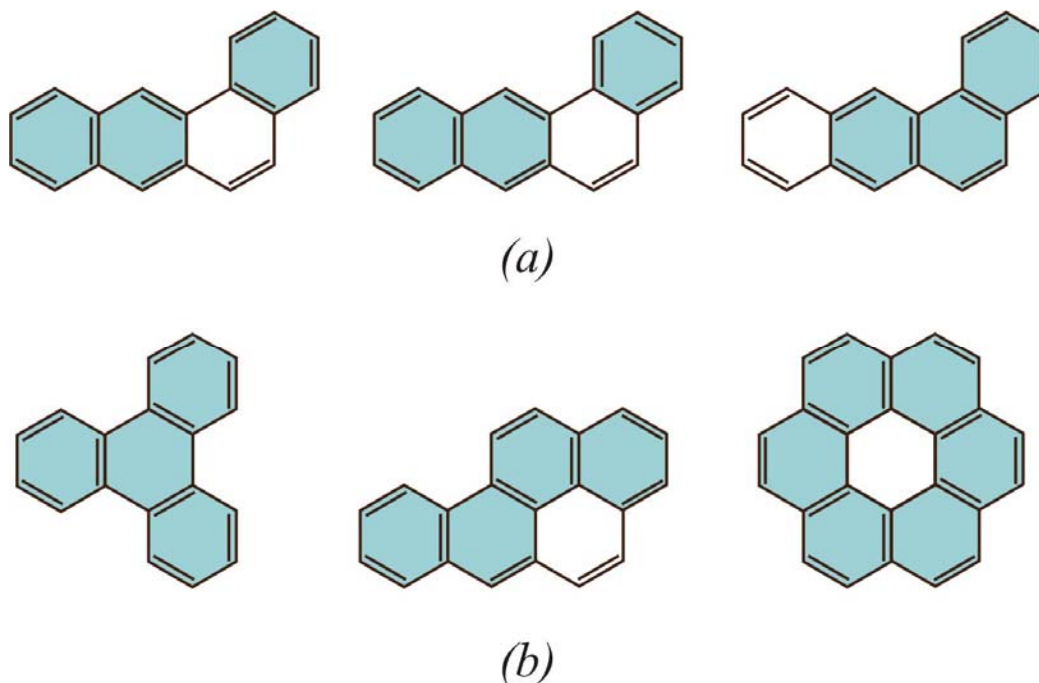

Fig. 2. *(a)* The Fries structures of benzo[a]phenanthrene; their Fries number is 3. *(b)* The unique Fries structures of triphenylene, benzo[a]pyrene, and coronene. Hexagons containing three double bonds are colored.

RESULTS AND DISCUSSION

The main contribution of this paper is a proposal of a new method for distribution of π-electrons by the rings in benzenoid hydrocarbons. This method uses Fries structures as the basis for calculation of electron contents of the rings in benzenoid hydrocarbons. In order to get Fries electron contents (EC^F) one should obey the following rules:

Rule 1. Convert "classical" (geometrical) Fries structures into algebraic Fries structures by the procedure explained in previous section. More about construction of algebraic Kekulé structures and theirs properties can be found elsewhere [18].

Rule 2. Integers that are inscribed in the considered ring, *R*, in all algebraic Fries structures have to be added, and then divided by the number of Fries structures.

Below is shown how the Fries electron contents of rings of benzo[a]phenathrene are computed:

$$EC^F(A) = (5+5+4)/3 = 4.667$$
$$EC^F(B) = (5+5+5)/3 = 5.000$$
$$EC^F(C) = (3+2+4)/3 = 3.000$$
$$EC^F(D) = (5+6+5)/3 = 5.333$$

The sum of Fries electron contents of all rings in the examined benzenoid hydrocarbon is (like in the case of the ordinary Randić-Balaban electron contents) equal to the number of carbon atoms. In Figs. 3 and 4 are shown a few benzenoid hydrocarbons and their Fries electron contents (Fig. 3) and Randić-Balaban electron contents (Fig. 4). In most cases, both methods qualitatively describe the distribution of π-electrons into rings in a nearly same manner. The correlation between the two electron contents is shown in Fig. 5.

The main difference between these two methods is noticed in the case of polyacenes. While the Randić-Balaban method gives larger values of electron contents for terminal hexagons than for inner ones, the Fries method gives opposite results. In Table 1 the values of the terminal and inner rings of polyacenes are given up to 10 hexagons.

In Ref. [5] the authors found relations for the calculation of the electron content of rings in polyacenes that depend only of the number of hexagons. One can obtain similar relations for Fries electron contents that depend only of the number of hexagons. In other words, in the case of polyacenes, if one calculates the Randić-Balaban electron contents, he also may obtain from this result the Fries electron contents. Equation (2) shows the formulas for calculating the Fries electron contents of terminal and inner rings:

$$EC^F(T) = 4 + \frac{1}{h-1}$$
$$EC^F(I) = 4 + \frac{2}{h-1}$$

(2)
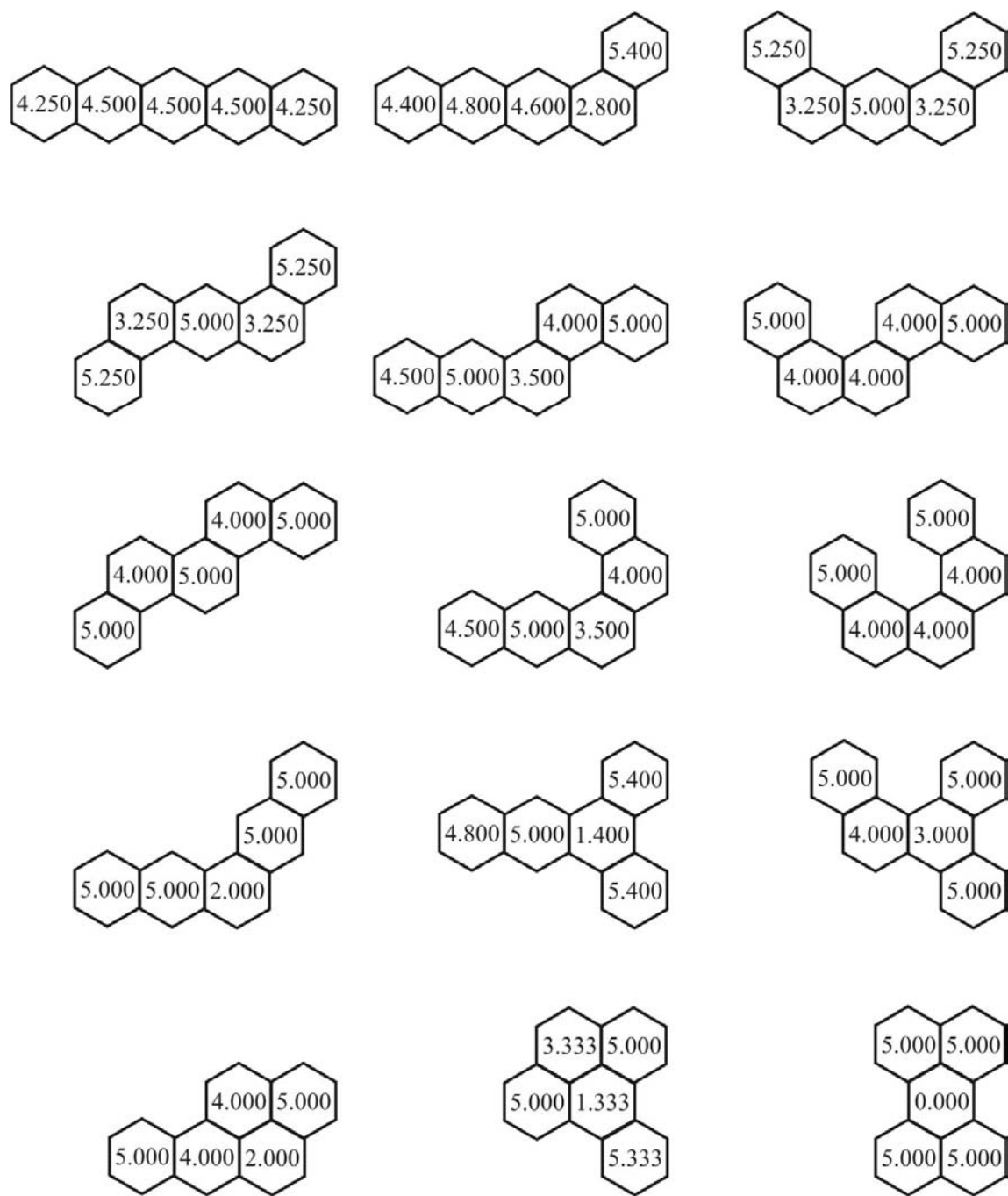
where *h* is the number of hexagons.

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Fig. 3. The Fries electron contents of rings of all Kekuléan bezenoid hydrocarbons with five hexagons
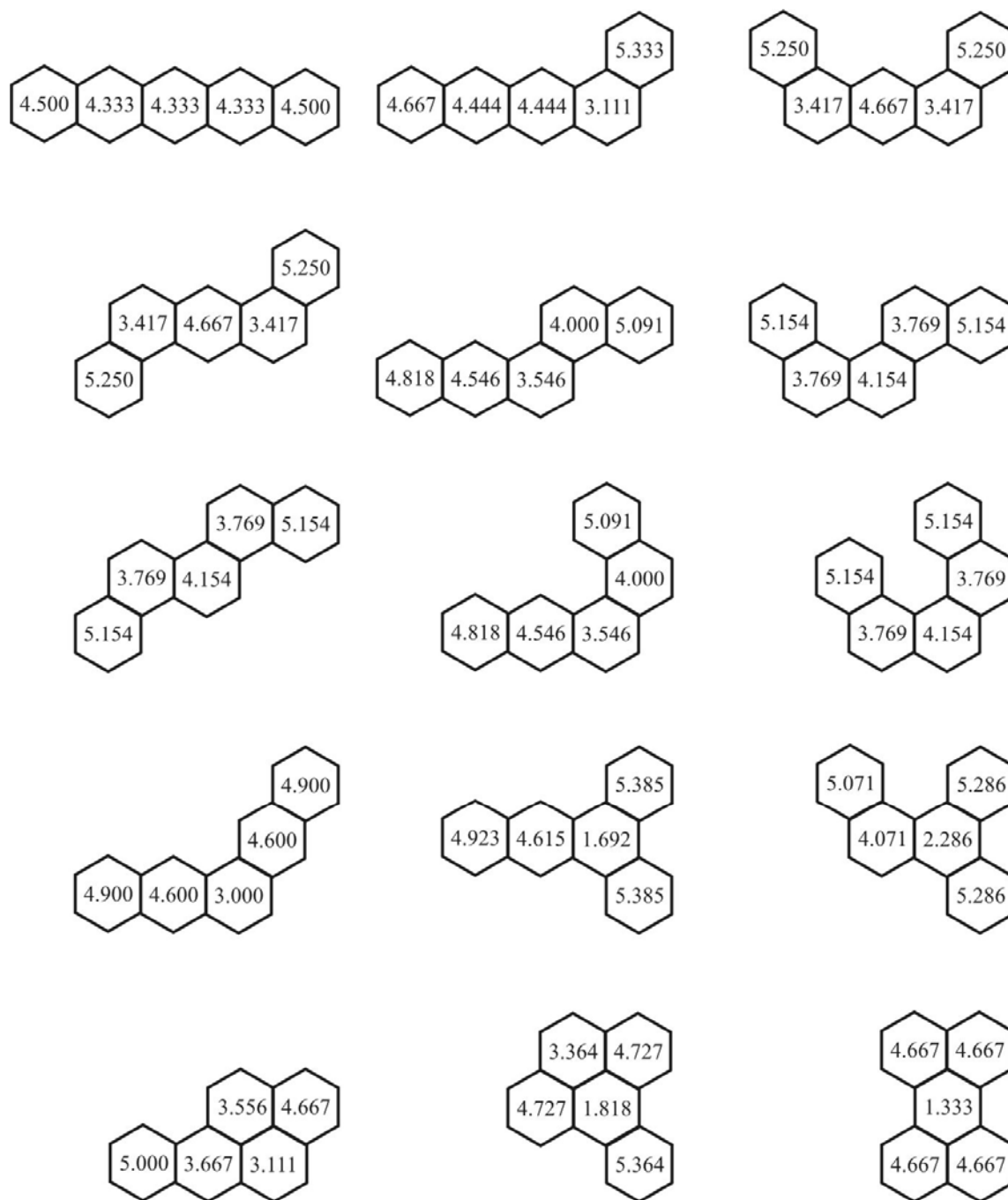
Fig. 4. The Randić-Balaban electron contents of rings of all Kekuléan bezenoid hydrocarbons with five hexagons
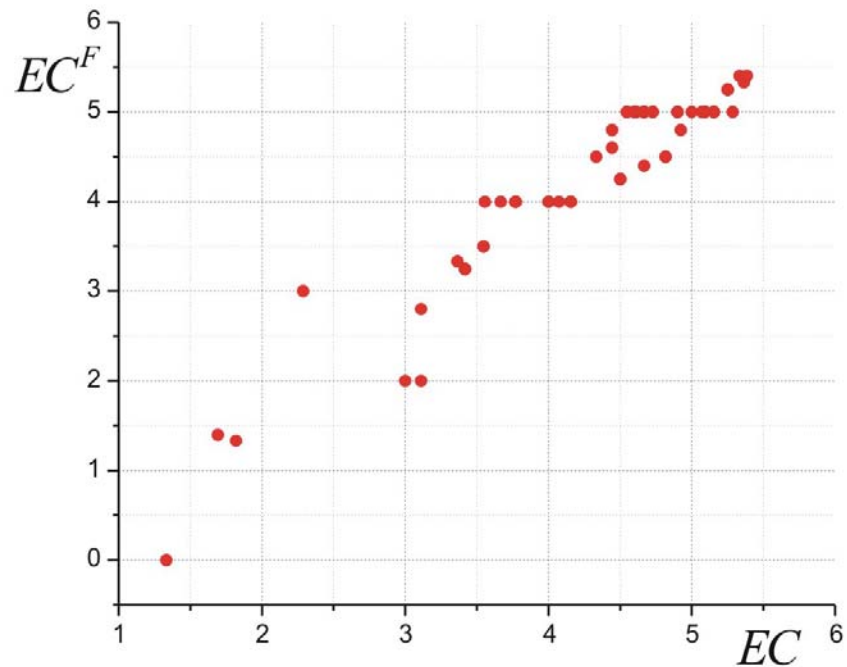
Fig. 5. Correlation between the Fries-structure-based and the Kekulé-structure-based π-electron contents of the rings in the benzenoid hydrocarbons shown in Figs. 3 and 4.

h	EC(T)	$EC^F(T)$	EC(I)	$EC^F(I)$
3	4.75	4.50	4.50	5.00
4	4.60	4.33	4.40	4.67
5	4.50	4.25	4.33	4.50
6	4.43	4.20	4.29	4.40
7	4.38	4.17	4.25	4.33
8	4.33	4.14	4.22	4.29
9	4.30	4.12	4.20	4.25
10	4.27	4.11	4.18	4.22

Table 1. Randić-Balaban electron contents (*EC*) and Fries electron contents (EC^F) of of the terminal (*T*) and inner (*I*) rings of polyacenes up to 10 hexagons.

The Fries electron contents of rings do not show satisfactory results in the case of homologous series whose first member is perylene. The Fries electron content of the central hexagon in perylene is equal to zero (see Fig. 3). Literally speaking, this result is chemically impossible. However, this result is relative and it only tells us that the considered ring is poor in its π-electron content.

As it has been pointed out above, the electron contents, calculated by means of Fries structures, give nearly the same results as EC and it can be used for analyzing electron structure of benzenoid molecule as well as Ranić-Balaban method. Calculation of EC^F using the concept of algebraic Kekulé structures is somewhat easier than the calculation of the original EC, and that is the main reason for introducing the method outlined in the present paper.

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RASPODELA π-ELEKTRONA PO PRSTENOVIMA U BENZENOIDNIM UGLJOVODONICIMA POMOĆU FRIESOVIH STRUKTURNIH FORMULA

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IZVOD

Dva američka naučnika, Milan Randić i Alexandru T. Balaban, su pre dve godine uveli u teorijsku hemiju koncept rapodele π-elektrona po prstenovima u benzenoidnim molekulima i nazvali ga elektronski sadržaj prstenova (*EC*). Pre ove ideje raspodela elektrona u molekulima je razmatrana isključivo među susednim atomima. Elektronski sadržaj je ubrzo privukao pažnju naučnika širom sveta i danas postoji obimna literaturna građa koja razmatra ovu oblast teorijske hemije. Izračunavanje orginalnog Randić-Balabanovog elektronskog sadržaja prstenova je bazirano na Kekuléovim strukturama. Da bi se dobio *EC*, prethodno se „geometrijske" Kekuléove formule moraju pretvoriti u tzv. algebarske Kekuléove strukture. Konverzija geometrijskih Kekuléovih formula u algebarske radi se po sledećem pravilu: dvostruke veze određene „geometrijske" Kekuléove strukture koje pripadaju samo posmatranom prstenu doprinose tom prstenu sa dva π-elektrona, a one koje su zajedničke sa drugim prstenovima doprinose tom prstenu sa jednim π-elektronom. Ovo pravilo mora da se primeni za sve prstenove i sve Kekuléove strukture kao što je to prikazano na Slici 1. Aritmetička sredina brojeva koji su upisani u posmatrani prsten u svim dobijenim algebarskim Kekuléovim strukturama predstavlja Randić-Balabanov elektronski sadržaj tog prstena.

Tokom vremena koncept elektronskog sadržaja prstenova u benzenoidnim molekulima je razrađivan i pokušavano je da se on što je moguće više usavrši. Takva istraživanja dovela su i do novih metoda za raspodelu π-elektrona po prstenovima. Ovaj rad predlaže korišćenje Friesovih struktura kao osnove za računanje elektronskog sadržaja prstenova umesto Kekuléovih struktura. Razlog za ovaj predlog je što Friesovih struktura ima znatno manje nego Kekuléovih struktura, a to olakšava izračunavanje elektronskog sadržaja prstenova u

benzenoidnim ugljovodonicima. Ovu metodu raspodele π-elektrona po prstenovima smo nazvali Friesov elektronski sadržaj *(EC^F)*. Na Slici 3 su izračunati elektronski sadržaji za sve prstenove benzenoidnih sistema sa 5 heksagona, a na Slici 4 su prikazani Randić-Balabanovi elektronski sadržaji prstenova za isti skup jedinjenja. Upoređivanjem se može ustanoviti da u najvećem broju slučajeva Randić-Balabanov i Friesov elektronski sadržaj prstenova daju kvalitativno iste rezultate. Najveća diskrepancija između ove dve metode se javlja kod poliacena. Naime, Randić-Balabanov elektronski sadržaj pokazuje da u terminalnim heksagonima ima više π-elektrona nego u unutrašnjim, dok kod Friesovog elektronskog sadržaja je obrnut slučaj. I u slučaju Friesovog elektronskog sadržaja raspodela π-elektrona u unutrašnjim prstenovima poliacena je uniformna. Utvrđeno je da Friesov elektronski sadržaj terminalnih i unutrašnjih heksagona kod poliacena zavisi samo od broja heksagona. Slične formule su već nađene i u slučaju Randić-Balabanog elektronskog sadržaja. Dakle, iako se u slučaju poliacena ove dve metode potpuno različito ponašaju, određivanjem jednog elektronskog sadržaja poznat nam je i drugi.

Kod perilena i njegovih homologa se javlja slučaj da neki heksagoni imaju Friesov elektronski sadržaj jednak 0 (vidi Sliku 3). Bukvalno gledano, to je krupna greška, međutim treba imati u vidu da nam ove metode ne daju informaciju koliko je tačno raspodeljeno elektrona po prstenu, što je nemoguće, već samo da li ima više ili manje elektrona u jednom prstenu u proseku u odnosu na druge.

Friesova raspodela π-elektrona po prstenovima u benzenoidnim ugljovodonicima i pored navedenih ograničenja daje uvid u elektronsku strukturu molekula na sličan način kao i Randić-Balabanova metoda. Friesove strukture se mogu posmatrati kao „destilat" Kekuléovih struktura, pa je samim tim i računanje Friesovog elektronskog sadržaja olakšano u odnosu na orginalnu metodu.