

I. Gutman (Ed.)
Mathematical Methods in Chemistry
Prijepolje Museum, Prijepolje, 2006, pp. 73-87.

ELECTRON AND ENERGY CONTENT OF HEXAGONS IN BENZENOID HYDROCARBONS

Nedžad Turković,¹ Boris Furtula² and Ivan Gutman²

¹*City Assembly, 31300 Prijepolje, Serbia & Montenegro*

²*Faculty of Science, P. O. Box 60, 34000 Kragujevac, Serbia & Montenegro*

Abstract

In this paper we first define the recently proposed (by Randić and Balaban, in 2004) π -electron content (EC) of hexagons in benzenoid hydrocarbons. In full analogy to it one may conceive also the π -electron energy content (ec) of hexagons. These contents are mutually related, but in a somewhat perplexed manner. We establish the actual relation between EC and ec in the case of catacondensed benzenoid hydrocarbons. In catacondensed benzenoid systems there are only four types of hexagons: terminal, linearly annelated, angularly annelated, and branched. We show that within hexagons of the same type the relation between ec and EC is nearly linear and the respective regression lines are nearly parallel and equidistant. The analogous relations between EC and ec in pericondensed benzenoids are essentially the same, yet significantly more complicated because in pericondensed benzenoids there exist 12 distinct annelation modes of hexagons.

INTRODUCTION

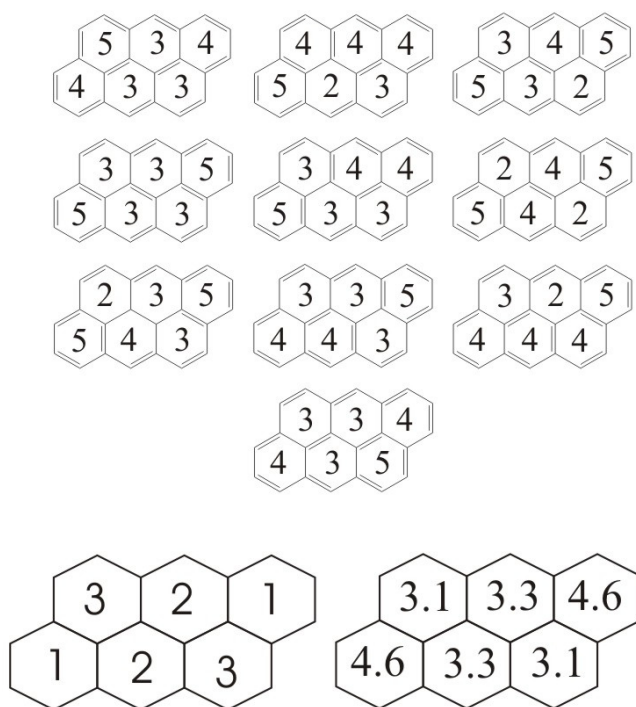
The concept of π -electron content (EC) of a ring of a polycyclic conjugated molecule was recently put forward by two American mathematical chemists - Milan Randić (of Croatian origin) and Alexandru T. Balaban (of Rumanian origin) [1,2]. Their idea attracted much attention and was further examined, elaborated, and extended by several authors. A complete bibliography of works dealing with the π -electron content of rings and its various congeners is given in another article in this book [3] and will not be repeated here.

Throughout this paper we are concerned only with π -electrons and therefore, in what follows, the symbol π will be (in most cases) omitted. One should recall that a benzenoid hydrocarbon with n carbon atoms possess a total of n π -electrons, which are spread over the entire molecule. Finding out the distribution of π -electrons in benzenoid hydrocarbons (and, more generally, in polycyclic conjugated molecules) is one of the main goals of theoretical organic chemistry. Usually one considers such a distribution over the carbon atoms and/or the carbon-carbon bonds. The true novelty of the Randić-Balaban approach is that it considers the distribution of electrons into rings. In the case of benzenoid hydrocarbons all rings are six-membered and therefore, in what follows, we refer to them as “hexagons”.

The starting point in the definition of EC is the concept of “algebraic Kekulé structures”, invented by Randić [4] and further elaborated in [5]. According to it, each Kekulé structure of a benzenoid molecule may be characterized by indicating the number of π -electrons in each of its hexagons. This is achieved by the following simple and obvious counting procedure. Consider a hexagon H of a benzenoid system B , and a Kekulé structure k of B . Each double bond of k that solely belongs to H contributes two electrons to H . Each double bond of k that is shared by H and another hexagon contributes one electron to H . The total number of electrons belonging to the hexagon H (in the considered Kekulé structure k) is denoted by $EC(H,k)$. By inscribing the numbers $EC(H,k)$ in all hexagons of B we obtain the so-called “algebraic Kekulé structure” [4]. It could be shown [5] that for all catacondensed and for the majority of pericondensed benzenoids, algebraic Kekulé structures and ordinary Kekulé structures are in a one-to-one correspondence.

Now, the electron content $EC(H)$ of the hexagon H of the benzenoid molecule B is, by definition [1,2], equal to the arithmetic average of the numbers $EC(H,k)$, taken over all Kekulé structures.

An example illustrating the calculation of the electron contents of the hexagons of a benzenoid hydrocarbon (anthanthrene) is shown in Fig. 1.



$$EC(1) = \frac{1}{10}(4 + 5 + 5 + 5 + 5 + 5 + 5 + 4 + 4 + 4) = 4.6$$

$$EC(2) = \frac{1}{10}(3 + 2 + 3 + 3 + 3 + 4 + 4 + 4 + 4 + 3) = 3.3$$

$$EC(3) = \frac{1}{10}(3 + 3 + 2 + 3 + 3 + 2 + 3 + 3 + 4 + 5) = 3.1$$

Fig. 1. The numerals inscribed in the hexagons of the ten “algebraic” Kekulé structures of anthanthrene pertain to the π -electron contents of the respective hexagons in individual Kekulé structures. The Randić-Balaban π -electron content (EC) of a hexagon is the arithmetic mean of the respective numerals taken over all Kekulé structures. The calculation of the EC -values of the hexagons 1, 2, and 3 of anthanthrene is shown explicitly.

The Pauling bond order was introduced in the 1930s and was used for the prediction the lengths of chemical bonds in organic molecules. We denote it by p_{rs}^P , where r and s indicate adjacent atoms in the respective molecule. It is equal to the ratio of the number of Kekulé structures in which the bond rs is double, and the number of all Kekulé structures. The sum of Pauling bond orders over all bonds, times two, is equal to the total number of π -electrons in the conjugated system considered:

$$2 \sum_{rs} p_{rs}^P = n \quad (1)$$

Based on the relation (1), one may use the Pauling bond orders to (formally) distribute the π -electrons of a polycyclic conjugated hydrocarbon into its rings.

It has been shown [6] that the electron content of a hexagon can be expressed in terms of Pauling bond orders as:

$$EC(H) = 2 \sum_{*} p_{rs}^P + \sum_{**} p_{rs}^P \quad (2)$$

with \sum_{*} and \sum_{**} indicating summations over bonds belonging solely to H , and over bonds shared by H and another hexagon, respectively. (Recall that the total number of summands on the r.h.s. of Eq. (2) is six, because a hexagon has six edges.) The sum of EC -values over all rings of a benzenoid system B is equal to the total number n of its π -electrons, i. e.,

$$\sum_{i=1}^h EC_i = n \quad (3)$$

where h stands for the number of hexagons of B .

The most frequently employed bond order for prediction of bond lengths is the molecular-orbital-based Coulson bond order, which we denote by p_{rs}^C . It is known that the sum of Coulson bond orders over all bonds of a conjugated π -electron system, times two, is

equal to the total π -electron energy of that system (expressed in units of the carbon-carbon resonance integral β):

$$2\sum_{rs} p_{rs}^C = E_{\pi}. \quad (4)$$

One should recognize the deep analogy between Eqs. (1) and (4). Relation (4) for the Coulson bond order makes it possible to employ a procedure analogous to the one described above, and partition the total π -electron energy into rings. The *energy content* of a hexagon H , denoted by $ec(H)$, is thus defined by means of the expression

$$ec(H) = 2\sum_{*} p_{rs}^C + \sum_{**} p_{rs}^C \quad (5)$$

in which the notation is analogous to that in Eq. (2). The sum of energy contents of all rings is equal to the total π -electron energy E_{π} . In the case of benzenoid systems, in full analogy to Eq. (3) we have

$$\sum_{i=1}^h ec_i = E_{\pi}. \quad (6)$$

The quantity ec was invented by the present authors and first communicated in the paper [8]. Extensive studies of the relations between ec and EC were eventually reported in the papers [9] (for catacondensed benzenoids) and [10] (for pericondensed benzenoids). One should bear in mind the relations between ec and EC can be rationalized by knowing the relation between the Pauling and Coulson bond orders [11].

COMPUTER EXPERIMENTS WITH CATACONDENSED BENZENOIDS

Before we describe the main results obtained by our computer experiments done on benzenoid molecules, it is necessary to recall some details on their structure [7,12].

Benzenoid systems are classified as catacondensed and pericondensed. A pericondensed benzenoid system possesses at least one vertex that belongs to three hexagons (or, what is the same: at least one triplet of mutually adjacent hexagons). If such structural features are absent, then the benzenoid system is said to be catacondensed. From the theoretical point of view, catacondensed benzenoid systems are much simpler than pericondensed. For instance, all cycles in a catacondensed benzenoid are of size $4k+2$, whereas pericondensed benzenoids possess also cycles of size $4k$. All catacondensed benzenoids are Kekuléan, whereas among pericondensed benzenoids there exist also non-Kekuléan species.

The hexagons in benzenoid systems can be annelated in 12 distinct ways. These annelation modes are depicted in Fig. 2. For what follows it is important to notice that in catacondensed benzenoids the number of possible annelation modes is much smaller – only 4.

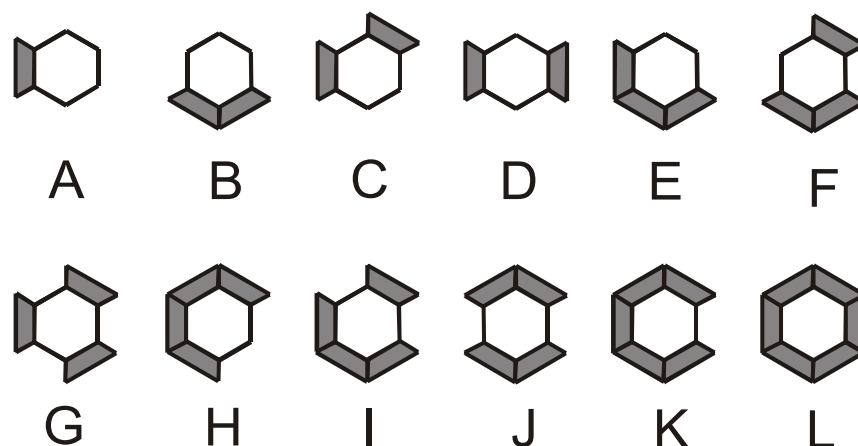


Fig. 2. The twelve different annelation modes of hexagons in benzenoid systems. In catacondensed benzenoids only modes **A**, **C**, **D**, and **G** can occur, whereas in pericondensed systems all the twelve modes are encountered.

In order to investigate the possible relation between $ec(R)$ and $EC(R)$ it was necessary to compute the electron and energy contents of hexagons for a reasonably large set of polycyclic benzenoid molecules. This task required the usage of a specially designed computer program, which we named *CELER* (= Content of **E**lectrons and **E**nergy in **R**ing); details on *CELER* will be published elsewhere.

By means of *CELER* we calculated the electron and energy contents of the hexagons of all catacondensed benzenoid systems with up to five rings, and of all catacondensed systems with six rings, containing a branched hexagon. The thus obtained energy contents versus electron contents are plotted in Fig. 3.

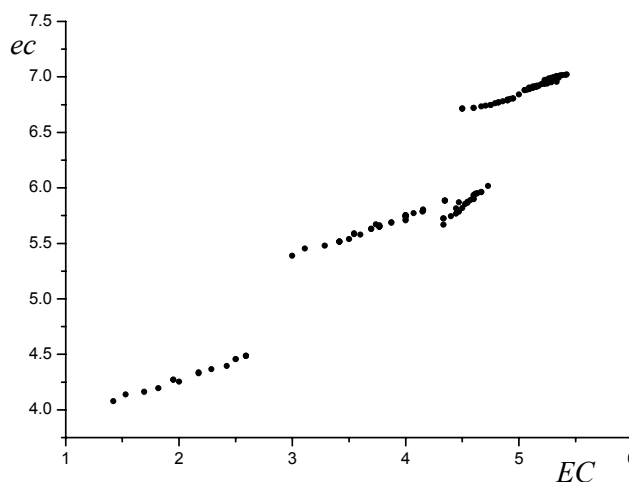


Fig. 3. The energy contents (ec) of the hexagons of all catacondensed benzenoid systems with 5 and fewer hexagons and all branched catacondensed systems with 6 hexagons, versus the respective electron contents (EC).

From Fig. 3 it is obvious that the data-points are separated into three groups. By direct checking we established that the data-points are clustered with regard to the number of neighbouring hexagons. The points with $ec < 5$ correspond to branched hexagons (annelation mode **G**, hexagons having three neighbours). The points with $ec > 6.5$ pertain to terminal hexagons (annelation mode **A**, hexagons having a single neighbour). In the middle are lying the points that correspond to hexagons possessing two neighbours (annelation modes **C** and **D**). This central cluster is further separated into two groups. The left-hand-side points pertain to angularly (mode **C**), and the right-hand side points to linearly annelated (mode **D**) hexagons.

These findings lead to the conclusion that the structural feature having the strongest influence on the relation between $ec(R)$ and $EC(R)$ is the number of neighbours. The simplest way to take into account such a neighbour-effect is to add to ec an increment, proportional to

the number v of neighbouring rings ($v = 1$ for terminal, $v = 2$ for linearly or angularly annelated rings, $v = 3$ for branched rings). This leads to the regression model:

$$ec + v\gamma = aEC + b \quad (7)$$

By least-squares fitting it was found that the optimal value of the parameter γ is 0.7897. For this value of γ , we obtained $a = 0.339 \pm 0.003$, $b = 5.95 \pm 0.01$, with correlation coefficient equal to 0.9945. This reasonably good correlation between the electron and energy contents is shown in Fig.4.

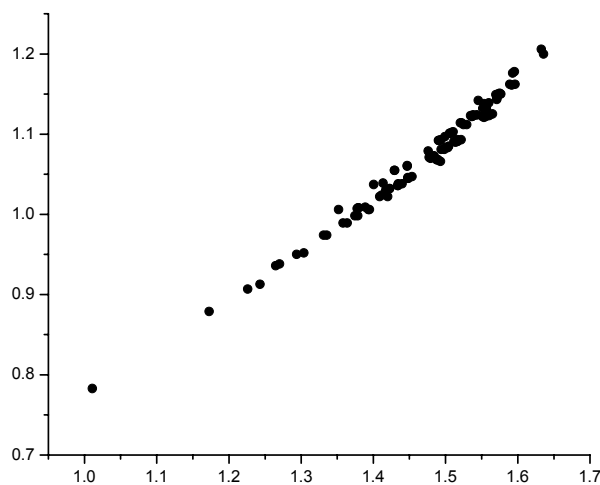


Fig. 4. The same data as in Fig. 3, except that $0.7897v$ was added to each ec -value; v is the number of neighboring rings.

COMPUTER EXPERIMENTS WITH PERICONDENSED BENZENOIDS

In this section we report our research one with pericondensed benzenoid molecules. In this case all the 12 annelation modes, shown in Fig. 2, may occur and therefore a rather complicated EC/ec -correlation pattern is expected. To make things a bit clearer we first construct an approximate mathematical model for the EC - ec dependence. For this we use a

modified version of the Cruickshank-Sparks equations, which relate the Coulson and Pauling bond orders in benzenoid hydrocarbons.

Although both the Pauling and the Coulson bond orders are classical notions of theoretical (quantum) chemistry, their relation was much studied. No generally valid connection between p_{rs}^P and p_{rs}^C could be established so far. Cruickshank and Sparks [13] discovered that in the case of benzenoid hydrocarbons there exists a not very accurate relation between the two bond orders, but only within carbon-carbon bonds of the same type. These relations were further studied in the paper [11].

One has to distinguish between three types of carbon-carbon bonds: with two, with one, and without any hydrogen atoms attached. We refer to these bond types as 2-2, 2-3, and 3-3, respectively (see also [14]).

The original Cruickshank-Sparks formulas (obtained by a standard least-squares optimization) read [13]:

$$\begin{aligned} p_{rs}^C &= 0.30 p_{rs}^P + 0.52 && \text{for (2-2)-type bonds} \\ p_{rs}^C &= 0.25 p_{rs}^P + 0.48 && \text{for (2-3)-type bonds} \\ p_{rs}^C &= 0.33 p_{rs}^P + 0.41 && \text{for (3-3)-type bonds} \end{aligned}$$

As seen, the above three regression lines are not parallel.

We have repeated the required calculation, employing a data set consisting exclusively of bond orders of pericondensed benzenoids. Further, in view of what we experienced with catacondensed systems, the least-squares optimization was adjusted so that the regression lines be parallel. The following expressions were obtained:

$$\left. \begin{aligned} p_{rs}^C &= 0.275 p_{rs}^P + 0.532 && \text{for (2-2)-type bonds} \\ p_{rs}^C &= 0.275 p_{rs}^P + 0.465 && \text{for (2-3)-type bonds} \\ p_{rs}^C &= 0.275 p_{rs}^P + 0.428 && \text{for (3-3)-type bonds} \end{aligned} \right\} \quad (8)$$

In view of Eqs. (2) and (5), the modified Cruickshank-Sparks formulas (8) can be used to model the relations between the electron content and electron energy content of hexagons of benzenoid molecules. Indeed, by combining Eqs. (8) with (2) and (5) we obtain

the following approximate relations between ec and EC for hexagons of a given annelation mode (cf. Fig. 2) [10,11]:

$$ec = 0.2746 EC + 5.4795 \quad \text{for hexagons of mode A} \quad (9a)$$

$$ec = 0.2746 EC + 4.8430 \quad \text{for hexagons of mode B} \quad (9b)$$

$$ec = 0.2746 EC + 4.6342 \quad \text{for hexagons of mode C} \quad (9c)$$

$$ec = 0.2746 EC + 4.5738 \quad \text{for hexagons of mode D} \quad (9d)$$

$$ec = 0.2746 EC + 4.2065 \quad \text{for hexagons of mode E} \quad (9e)$$

$$ec = 0.2746 EC + 3.9977 \quad \text{for hexagons of mode F} \quad (9f)$$

$$ec = 0.2746 EC + 3.8493 \quad \text{for hexagons of mode G} \quad (9g)$$

$$ec = 0.2746 EC + 3.5700 \quad \text{for hexagons of mode H} \quad (9h)$$

$$ec = 0.2746 EC + 3.4216 \quad \text{for hexagons of mode I} \quad (9i)$$

$$ec = 0.2746 EC + 3.4216 \quad \text{for hexagons of mode J} \quad (9j)$$

$$ec = 0.2746 EC + 2.9939 \quad \text{for hexagons of mode K} \quad (9k)$$

$$ec = 0.2746 EC + 2.5662 \quad \text{for hexagons of mode L} \quad (9l)$$

Note that the relations (9i) and (9j) coincide.

Using the computer package CELER the EC - and ec -values of the hexagons of 63 pericondensed benzenoid molecules were calculated. The molecules were taken from tables found in the book [15] and the review [16]. Plots of the data thus obtained are displayed in Figs. 5a and 5b. Because the ec/EC -dependence of the hexagons of type A, C, D, and G was already discussed (see Fig. 2), the results obtained for these annelation modes are not shown.

CONCLUSIONS

Our theoretical model is in fairly good agreement with the calculated data points. Thus, our calculations lead to the following conclusions: (a) It is necessary to separately consider hexagons with different modes of annelation. (b) Within each group of equally annelated hexagons of benzenoid hydrocarbons, a reasonably good linear correlation

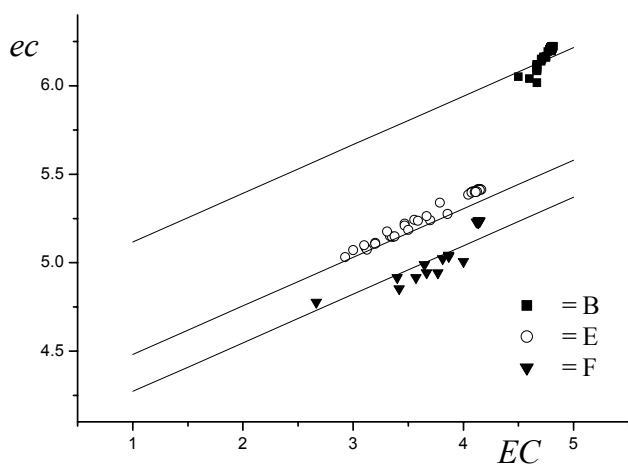


Fig. 5a. Energy contents of the hexagons of type **B**, **E**, and **F** of pericondensed benzenoid hydrocarbons, versus their electron contents. Note that these hexagons are adjacent to 2 and 3 other hexagons. The lines correspond to the theoretical models (9b), (9e), and (9f), obtained by means of the Cruickshank-Sparks equations.

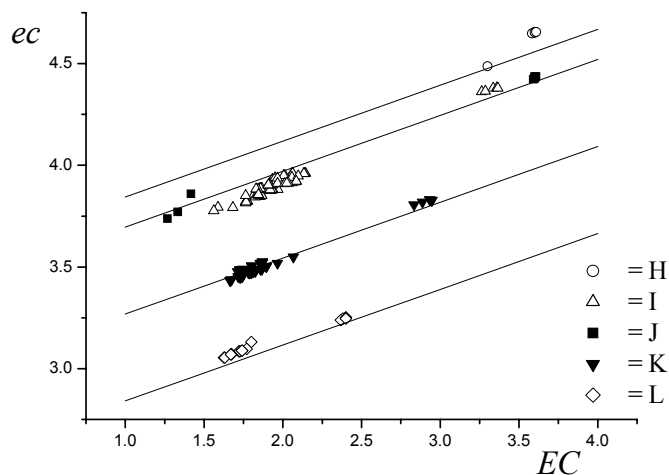


Fig. 5b. Same data as in Fig. 5a, for the hexagons of the type **H**, **I**, **J**, **K**, and **L**, and Eqs. The lines corresponding to Eqs. (9h), (9i)=(9j), (9k), and (9l). The hexagons considered here are adjacent to 4, 5, and 6 other hexagons. Note that the ec/EC -dependence of the hexagons of type **I** and **J** is modeled by one and the same line, which agrees well with the calculated data points.

exists between the π -electron content and the π -electron energy content ec and EC (in both cata- and pericondensed systems), Eqs. (9). This means that the domains of a benzenoid hydrocarbon that are electron-rich are also energy-rich. (c) The Cruickshank-Sparks-type formulas provide a clue for the understanding why and how the mode of annelation of a hexagon influences the mutual dependence of its electron and energy contents.

REFERENCES

1. M. Randić, A. T. Balaban, Partitioning of π -electrons in rings of polycyclic conjugated hydrocarbons. Part 1: Catacondensed benzenoids, *Polyc. Arom. Comp.* **24** (2004) 173-193.
2. A. T. Balaban, M. Randić, Partitioning of π -electrons in rings of polycyclic benzenoid hydrocarbons. 2. Catacondensed coronoids, *J. Chem. Inf. Comput. Sci.* **44** (2004) 50-59.
3. S. Gojak, I. Gutman, B. Furtula, On distribution of π -electrons in double linear hexagonal chains, this book, pp. 00-00.
4. M. Randić, Algebraic Kekulé formulas for benzenoid hydrocarbons, *J. Chem. Inf. Comput. Sci.* **44** (2004) 365-372.
5. I. Gutman, D. Vukičević, A. Graovac, M. Randić, Algebraic Kekulé structures of benzenoid hydrocarbons, *J. Chem. Inf. Comput. Sci.* **44** (2004) 296-299.
6. I. Gutman, T. Morikawa, S. Narita, On π -electron content of bonds and rings in benzenoid hydrocarbons, *Z. Naturforsch.* **59a** (2004) 295-298.
7. I. Gutman, S. J. Cyvin, *Introduction to the Theory of Benzenoid Hydrocarbons*, Springer-Verlag, Berlin, 1989.
8. I. Gutman, B. Furtula, N. Turković, Electron and energy contents of hexagons in benzenoid hydrocarbons, *Polyc. Arom. Comp.* **25** (2005) 87-94.
9. B. Furtula, I. Gutman, N. Turković, Relation between electron and energy contents of hexagons in catacondensed benzenoid hydrocarbons, *Indian J. Chem.* **44A** (2005) 9-12.

10. I. Gutman, S. Milosavljević, B. Furtula, N. Cmiljanović, Relation between electron and energy contents of hexagons in pericondensed benzenoid hydrocarbons, *Indian J. Chem.* **44A** (2005) 13-17.
11. I. Gutman, B. Furtula, S. Radenković, Relation between Pauling and Coulson bond orders in benzenoid hydrocarbons, *Z. Naturforsch.* **59a** (2004) 699-704.
12. I. Gutman, *Uvod u hemijsku teoriju grafova*, PMF Kragujevac, Kragujevac, 2003.
13. D. W. J. Cruickshank, R. A. Sparks, Experimental and theoretical determination of bond lengths in naphthalene, anthracene and other hydrocarbons, *Proc. Roy. Soc. London* **A258** (1960) 270-285.
14. I. Gutman, S. Radenković, Investigation of Hosoya bond order, this book, pp. 00-00.
15. J. V. Knop, W. R. Müller, K. Szymanski, N. Trinajstić, *Computer Generation of Certain Classes of Molecules*, SKTH, Zagreb, 1985.
16. B. N. Cyvin, J. Brunvoll, S. J. Cyvin, Enumeration of benzenoid systems and other polyhexes, *Topics Curr. Chem.* **162** (1992) 65-180.

ELEKTRONSKI I ENERGETSKI SADRŽAJ HEKSAGONA U BENZENOIDNIM UGLJOVODONICIMA

Nedžad Turković, Boris Furtula i Ivan Gutman

IZVOD

Godine 2004. Balaban i Randić su koncipirali postupak pomoću kojeg se može proceniti sadržaj π -elektrona (EC) u pojedinačnim prstenovima policikličnih konjugovanih jedinjenja. U ovom radu se prvo daje definicija π -elektronskog sadržaja prstena i detaljno opisuje kako se on izračunava. Jedan primer ovakvog izračunavanja prikazan je na Slici 1.

U ovom radu bavimo se isključivo benzenoidnim ugljovodonicima. U njima postoje samo šestočlani prstenovi, koji se u naslovu rada, kao i u daljem tekstu označavaju kao “heksagoni”.

Može se pokazati da se EC -vrednost heksagona H može odrediti preko Paulingovih redova veze (p_{rs}^P), po formuli

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

gde prvo sumiranje s desne strane ide preko onih ugljenik-ugljenik veza rs koje u potpunosti pripadaju posmatranom heksagonu (H), dok drugo sumiranje ide preko onih veza rs koje se nalaze na granici između heksagona H i nekog od njegovih suseda. Uočavajući određene analogije između Paulingovog i Coulsonovog reda veze (p_{rs}^C), i uzimajući u obzir da se Coulsonov red veze odnosi na raspodelu ukupne π -elektronske energije po ugljenik-ugljenik vezama, definiše se veličina ec :

$$ec(H) = 2 \sum_{*} p_{rs}^C + \sum_{**} p_{rs}^C$$

koja predstavlja energetska sadržaj heksagona H .

Prvo pitanje koje se posle definisanja elektronskog i energetskog sadržaja prstena postavlja jeste kakva veza postoji među njima. Mi smo pokušali da na ovo pitanje odgovorimo u slučaju benzenoidnih ugljovodonika.

Veze između EC i ec su prvo ispitivane kod katakondenzovanih benzenoidnih molekula. Dobiveni rezultati prikazani su na Slici 3. Vidljivo je grupisanje tačaka, za koje je pokazano da odražava različite načine aneliranja heksagona. Kod katakondenzovanih molekula postoje tačno četiri takva načina, koji odgovaraju dijagramima **A**, **C**, **D** i **G** na Slici 2. Budući da su tačke na Slici 3, koje odgovaraju anelacionim modovima **C** i **D** slabo razdvojene, zaključuje se da je osnovni parametar koji određuje grupisanje, broj suseda posmatranog prstena. (Taj broj je jedan u slučaju **A**, dva u slučajevima **C** i **D**, i tri u slučaju **G**). Kada se izvrši korekcija na broj suseda (v), pomoću jednačine

$$ec + v\gamma = aEC + b$$

uz $\gamma=0.7897$, postiže se da sve tačke (približno) leže na istoj pravoj (Slika 4).

Istraživanja veza između elektronskog i energetskeg sadržaja heksagona kod perikondenzovanih benzenoidnih ugljovodonika dovode do, u suštini, istih rezultata. Ovde je situacija komplikovanija zato što kod perikondenzovanih sistema može da postoji 12 različitih načina anelacije heksagona (prikazanih na Slici 2). Da bi se situacija donekle razjasnila, konstruisali smo matematički model koji, posebno za svaki način anelacije, povezuje ec i EC . Ove formule se dobivaju primenom, na pogodan način modifikovanih, Cruickshank-Sparksovih formula i glase:

$ec = 0.2746 EC + 5.4795$	za heksagone tipa A
$ec = 0.2746 EC + 4.8430$	za heksagone tipa B
$ec = 0.2746 EC + 4.6342$	za heksagone tipa C
$ec = 0.2746 EC + 4.5738$	za heksagone tipa D
$ec = 0.2746 EC + 4.2065$	za heksagone tipa E
$ec = 0.2746 EC + 3.9977$	za heksagone tipa F
$ec = 0.2746 EC + 3.8493$	za heksagone tipa G
$ec = 0.2746 EC + 3.5700$	za heksagone tipa H
$ec = 0.2746 EC + 3.4216$	za heksagone tipa I
$ec = 0.2746 EC + 3.4216$	za heksagone tipa J
$ec = 0.2746 EC + 2.9939$	za heksagone tipa K
$ec = 0.2746 EC + 2.5662$	za heksagone tipa L

Rezultati prikazani na Slikama 5a i 5b potvrđuju da navedene jednačine zadovoljavajuće dobro opisuju računskim putem dobivene grupe tačaka.

Na osnovu opisanih kompjuterskih eksperimenata dolazimo do sledećih zaključaka.

- (a) Potrebno je odvojeno proučavati heksagone koji imaju različite tipove anelacije (Slika 2).
- (b) Unutar svake grupe jednako aneliranih heksagona, postoji relativno dobra linearna korelacija između π -elektronskog sadržaja (EC) i π -elektronskog energetskeg sadržaja (ec). Prave koje odgovaraju ovim korelacijama su skoro paralelne.
- (c) Način na koji različiti anelacioni modovi heksagona nekog benzenoidnog ugljovodonika utiču na međusobni odnos elektronskog i energetskeg sadržaja tog heksagona, moguće je opisati i donekle razumeti pomoću formula Cruickshank-Sparksovog tipa.

