

Partition of π -Electrons in Rings of Double Linear Hexagonal Chains

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Two methods for assessing the π -electron content of a ring of a benzenoid hydrocarbon were recently proposed: one based on the averaging of the π -electron contents of the Kekulé structural formulas, and the other based on an analogous treatment of the Clar aromatic sextet formulas. We apply these two methods to the homologous series consisting of two condensed linear polyacene units (whose first members are pyrene, anthanthrene, peri-naphthacenonaphthacene, ...). The two approaches give essentially the same results. Contrary to the case of linear polyacenes (in which the partition of π -electrons into rings is uniform), in their double-chain analogs the partition of π -electrons is found to be highly non-uniform. The electron contents monotonically decrease along each polyacene chain, being maximal in the hexagons having the smallest number (= 2) of neighbors. Several other regularities of the π -electron distribution are also established.

Key Words: Electron content of ring; Kekulé structures; Clar aromatic sextet formulas; benzenoid hydrocarbons; double linear hexagonal chains

1. INTRODUCTION

In this paper we examine the partition of the π -electrons in the rings of double linear hexagonal chains. The structure of this homologous series of benzenoid hydrocarbons is shown in Figure 1. In the same figure is shown also the structure of linear polyacenes, namely of the single hexagonal chains. The double hexagonal chain consisting of $2a$ hexagons will be denoted by D_a .

Slika 1 (Figure 1) dolazi otprilike ovde

In the recent years the partition of π -electrons in the rings of polycyclic conjugated molecules was much studied [1-19]. These researches were initiated by the paper [18], in which a method was proposed for assessing the π -electron content of a ring from the Kekulé structures of the respective molecule. (The theoretical foundation of the method was established in [15, 17].) This Kekulé-structure-based approach, that in the following we refer to as Model 1, was eventually further elaborated and applied to a variety of conjugated systems [1-11, 13, 14].

In Model 1 the π -electron content of a ring in a polycyclic conjugated molecule is obtained by averaging the respective electron contents of the individual Kekulé structures. In each Kekulé structure the π -electrons are assumed to be distributed in the rings according to the positions of the double bonds: a double bond belonging to a ring, contributes to this ring by two π -electrons; a double bond shared by two rings contributes by one π -electron to each of these rings. The final electron content of a ring k , denoted here as $EC_1(k)$, is computed as the arithmetic average of the respective electron contents of all Kekulé structures.

Model 1 is illustrated in Figure 2 on the example of anthanthrene.

Slika 2 (Figure 2) dolazi otprilike ovde

In the work [13] it was demonstrated that in the case of large polycyclic aromatic hydrocarbons, the theoretically established electron-distribution pattern is in good agreement with the experimentally observed submolecularly resolved patterns seen in the high-resolution images, obtained by scanning tunneling microscopy.

Long before Model 1 was conceived, Clar proposed [20] a graphical representation of the π -electron structure of benzenoid hydrocarbons, nowadays known as the Clar aromatic sextet theory [21]. The aromatic sextet formulas in Clar theory may be viewed and treated in a similar manner as the Kekulé structures in Model 1. In particular: an aromatic sextet drawn in a ring contributes to this ring by six π -electrons; a double bond belonging to a ring, contributes to this ring by two π -electrons; a double bond shared by two rings contributes by one π -electron to each of these rings. The final electron content of a ring k , denoted here as $EC_2(k)$, is the arithmetic average of the respective electron contents of all Clar aromatic sextet formulas [5]. We call this method for assessing the π -electron content of a ring Model 2.

Model 2 is illustrated in Figure 3 on the example of anthanthrene.

Slika 3 (Figure 3) dolazi otprilike ovde

We mention in passing that also the distribution of total π -electron energy in rings of polycyclic conjugated molecules was studied [4, 8, 10], as well as possible refinements of Model 1 [6, 13]. Partition of π -Electrons in Rings of Linear Polyacenes From a structural point of view, linear polyacenes L_h are the simplest benzenoid hydrocarbons [21], cf. Figure 1. The π -electron contents of their rings were among the first to be determined both by means of Model 2 [5] and Model 1 [18]. It was found that within Model 2 the electron distribution is completely uniform. Within Model 1 all non-terminal hexagons have equal electron contents, whereas the two terminal hexagons have a slight excess of π -electrons relative to the non-terminal hexagons. It was easy to find the following analytical expressions for EC_1 and EC_2 of L_h :

$$\begin{aligned} EC_1(1) = EC_1(h) &= 4 + \frac{3}{h+1} \\ EC_1(k) &= 4 + \frac{2}{h+1} \quad \text{for } k = 2, 3, \dots, h-1 \\ EC_2(k) &= 4 + \frac{2}{h} \quad \text{for } k = 1, 2, \dots, h \end{aligned}$$

2. PARTITION OF π -ELECTRONS IN RINGS OF DOUBLE HEXAGONAL CHAINS

The structure of the homologous series D_a , considered in this paper, is shown in Figure 1. D_a has $2a$ hexagons. The respective benzenoid hydrocarbons have a general formula $C_{6a+4}H_{2a+6}$. Its Kekulé structure count is $K(D_a) = (a+1)(a+2)/2$ whereas its Clar formula count is $C(D_a) = a(a-1)/2$. The parameter a may assume the values $1, 2, 3, \dots$. The case $a=1$ (naphthalene) is exceptional and will

be excluded from consideration. Therefore in what follows, a will denote an integer greater than or equal to 2.

Because the double hexagonal chains have much fewer Clar formulas than Kekulé structures, the application of Model 2 to them is significantly easier than the application of Model 1.

Comparing Figures 2 and 3 we see that Models 1 and 2 result in different partitioning of π -electrons in double chains, but that these differences are not very large. The same conclusion is reached by the inspection of Table 1, in which the EC_1 - and EC_2 -values of all rings of D_a , up to $a=10$ are given.

Tabela 1 (Table 1) dolazi otprilike ovde

The results of both Models 1 and 2 clearly indicate that, in stark contrast with the single chains, the partition of π -electrons in the systems D_a is highly non-uniform. The rings 1 and 1' have a much higher EC-value than the other rings, and when k increases from 1 to a , then the electron contents $EC(k)$ monotonically decrease. Thus the rings a and a' have the smallest π -electron contents.

A typical dependence of $EC(k)$ on k is shown in Figure 4.

Slika 4 (Figure 4) dolazi otprilike ovde

By means of a tedious computation and trial-and-error testing we arrived at the following general expressions for the EC_1 - and EC_2 -values of the rings D_a , $a=2, 3, \dots$. (The labeling of the hexagons agrees with that in Figure 1.)

$$EC_1(1) = 4 + \frac{4a}{(a+1)(a+2)} = 4 + \frac{2a}{K(D_a)} \quad (1)$$

$$EC_1(k) = 3 + \frac{4a+6-6k}{(a+1)(a+2)} = 3 + \frac{2a+3-3k}{K(D_a)} \quad \text{for } k = 2, 3, \dots, a-1 \quad (2)$$

$$EC_1(a) = 3 - \frac{2a-8}{(a+1)(a+2)} = 3 - \frac{a-4}{K(D_a)} \quad (3)$$

$$EC_2(1) = 4 + \frac{4}{a} = 4 + \frac{2(a-1)}{C(D_a)} \quad (4)$$

$$EC_2(k) = 3 + \frac{6a+6-10k}{a(a-1)} = 3 + \frac{3a+3-5k}{C(D_a)} \quad \text{for } k = 2, 3, \dots, a \quad (5)$$

Only formula (4) and formula (5) for $k=2$ were proven in a rigorous mathematical manner. The form of the other expressions was guessed from the available numerical data. Nevertheless, there should be no doubt that all the formulas (1)-(5) are correct and valid for all values of a , $a \geq 2$.

Formulas (1)-(5) reproduce, of course, the data given in Table 1 and the features shown in Figure 4. From them also another, difficult-to-envisage, regularity can be deduced.

Because the expressions (2) and (5) are linear functions of the parameter k , and in view of the symmetry of the systems D_a (cf. Figure 1), we obtain the following:

(a) For $k=2, 3, \dots, a-1$, the sum of the π -electron contents of the rings k and $(a-k+1)'$ is constant, i. e., independent of k . In particular, within Model 1:

$$EC_1(k) + EC_1((a-k+1)') = 6 + \frac{2a+6}{(a+1)(a+2)}$$

whereas within Model 2:

$$EC_2(k) + EC_2((a-k+1)') = 6 + \frac{2}{a}$$

(b) Within Model 2 for $k=2, 3, \dots, a$, and within Model 1 for $k=3, 4, \dots, a-1$, also the sum of the π -electron contents of the rings k and $(a-k+2)'$ is constant, i. e., independent of k :

$$EC_1(k) + EC_1((a-k+2)') = 6 + \frac{2a}{(a+1)(a+2)}$$

$$EC_2(k) + EC_2((a-k+2)') = 6 + \frac{2a-8}{a(a+1)}$$

Thus in the case of double hexagonal chains the partition of π -electrons in rings is non-uniform, but the partition of π -electrons into two adjacent rings (belonging to two different chains) is uniform, except for the rings located at the ends of the chain. This, unexpected property of the π -electron distribution in double chains, should be compared with the (above mentioned) uniformness of the π -electron distribution in the single chains.

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POTPISI ISPOD SLIKA I TABELE

Figure 1. The structure of linear polyacenes L_h (single hexagonal chains) and of double hexagonal chains D_a , as well as the labeling of their hexagons. The first members of the L_h series are naphthalene ($h=2$), anthracene ($h=3$), naphthacene ($h=4$), The first members of the D_a series are pyrene ($a=2$), anthanthrene ($a=3$), naphthaceno[4, 5, 6, 7, 8-defghij]naphthacene or simply perinaphthacenonaphthacene ($a=4$), Note that for $k=1, 2, \dots, a$, the rings of D_a labelled by k and k' are symmetry-equivalent.

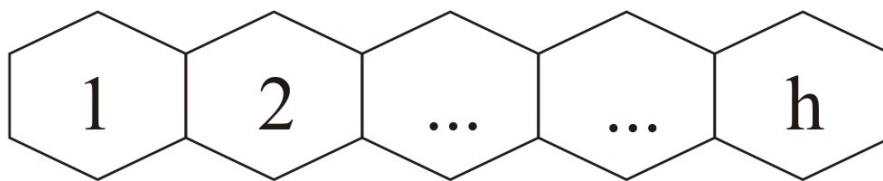
Figure 2. The ten Kekulé structures of anthanthrene (D_3) with the respective π -electron contents indicated in their rings. In the bottom diagram the arithmetic averages of these electron contents are given, that are just the π -electron contents of the rings of anthanthrene, computed according to Model 1. The sum of the six EC_1 -values is equal to 22, the total number of π -electrons of D_3 .

Figure 3. The three Clar aromatic sextet formulas of anthanthrene (D_3) with the respective π -electron contents indicated in their rings. In the bottom diagram the arithmetic averages of these electron contents are given, that are just the π -electron contents of the rings of anthanthrene, computed according to Model The sum of the six EC_2 -values is equal to 22, the total number of π -electrons of D_3 . Note that it is significantly simpler to compute EC_2 than EC_1 , a conclusion applying to all members of the D_a series.

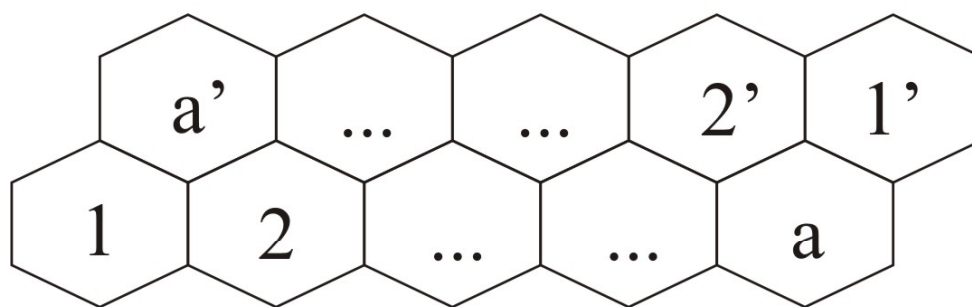
Figure 4. Dependence of the π -electron content on the position of the ring in the double hexagonal chain D_a with $a=8$. The labeling of the rings is same as in Figure 1. The EC -values monotonically decrease with increasing k . Diagram (a): Results obtained with Model 1. The data points for $k=2, 3$,

..., $a-1$ lie on an exact straight line. The point pertaining to $k=a$ only slightly deviates from this line, cf. Eqs. (2) and (3). Diagram (b): Analogous results obtained with Model 2. In this case the linear relation holds for $k=2, 3, \dots, a$, cf. Eq. (5). For details see text.

Table 1. The π -electron content of the k -th ring of the double hexagonal chain D_a , $a=2, 3, \dots, 10$. Labelling of the hexagons is same as in Figure 1. For each values of a , in the upper row are the results of Model 2 (EC_2) whereas in the lower row those of Model 1 (EC_1). Except for the first few values of a , the differences between the two models are negligible.

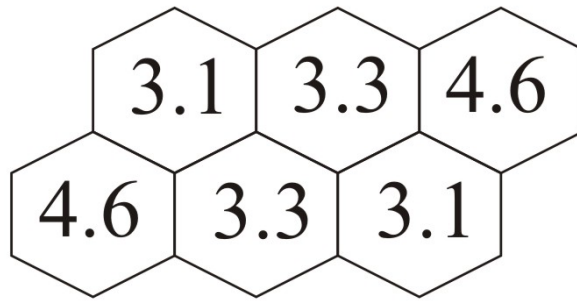
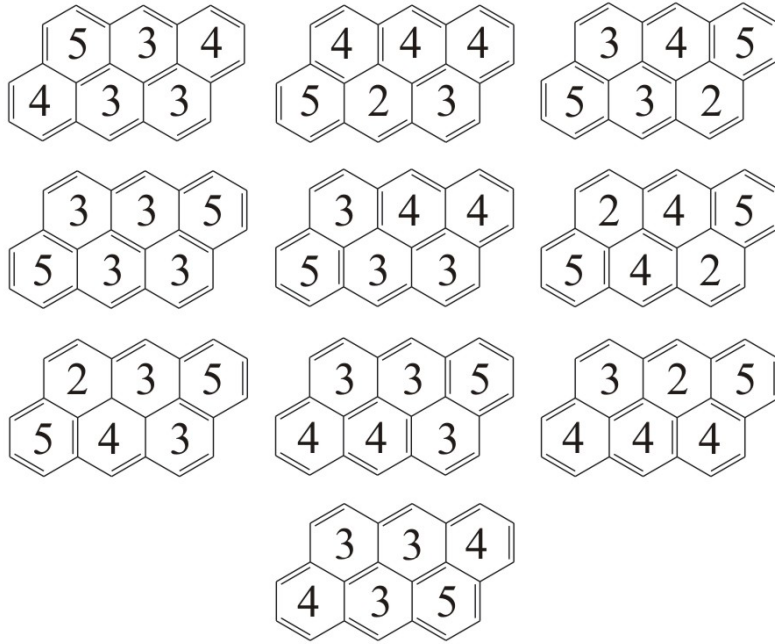


L_h



D_a

Figure 1

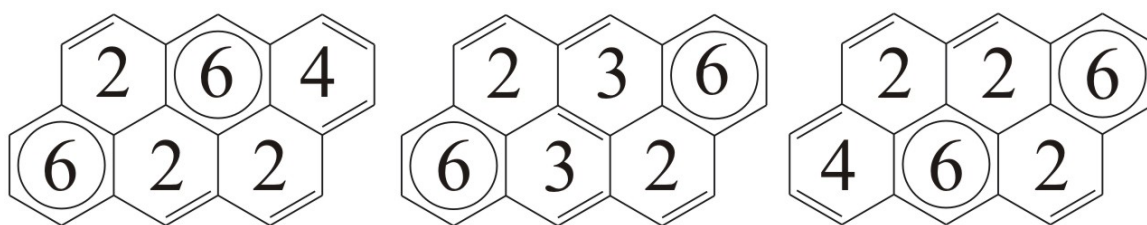


$$EC_1(1) = \frac{1}{10} (4 + 5 + 5 + 5 + 5 + 5 + 5 + 4 + 4 + 4) = 4.6$$

$$EC_1(2) = \frac{1}{10} (3 + 2 + 3 + 3 + 3 + 4 + 4 + 4 + 4 + 3) = 3.3$$

$$EC_1(3) = \frac{1}{10} (3 + 3 + 2 + 3 + 3 + 2 + 3 + 3 + 4 + 5) = 3.1$$

Figure 2



$$EC_2(1) = \frac{1}{3}(6 + 6 + 4) = 5.33$$

$$EC_2(2) = \frac{1}{3}(2 + 3 + 6) = 3.67$$

$$EC_2(3) = \frac{1}{3}(2 + 2 + 2) = 2.00$$

Figure 3

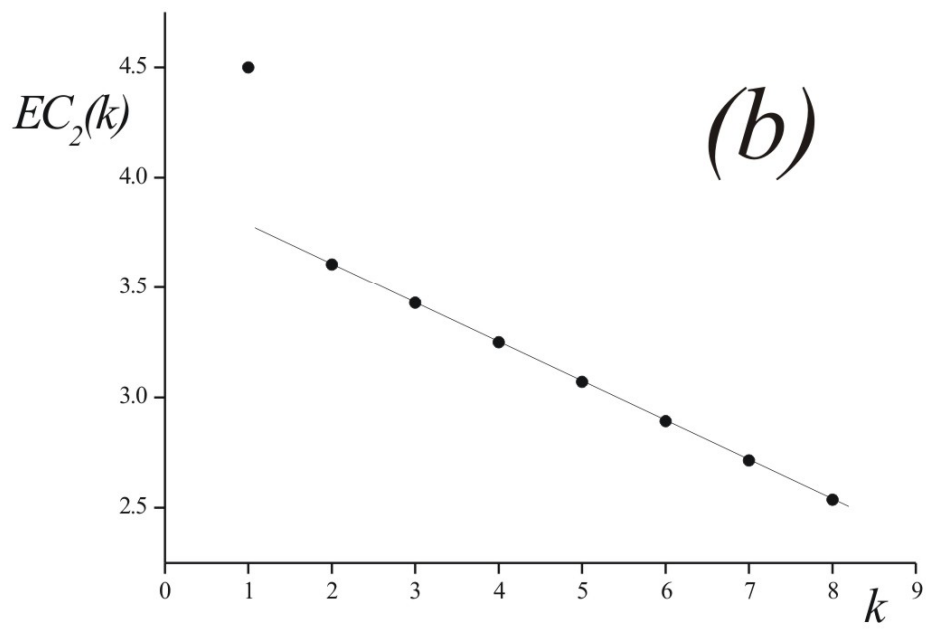
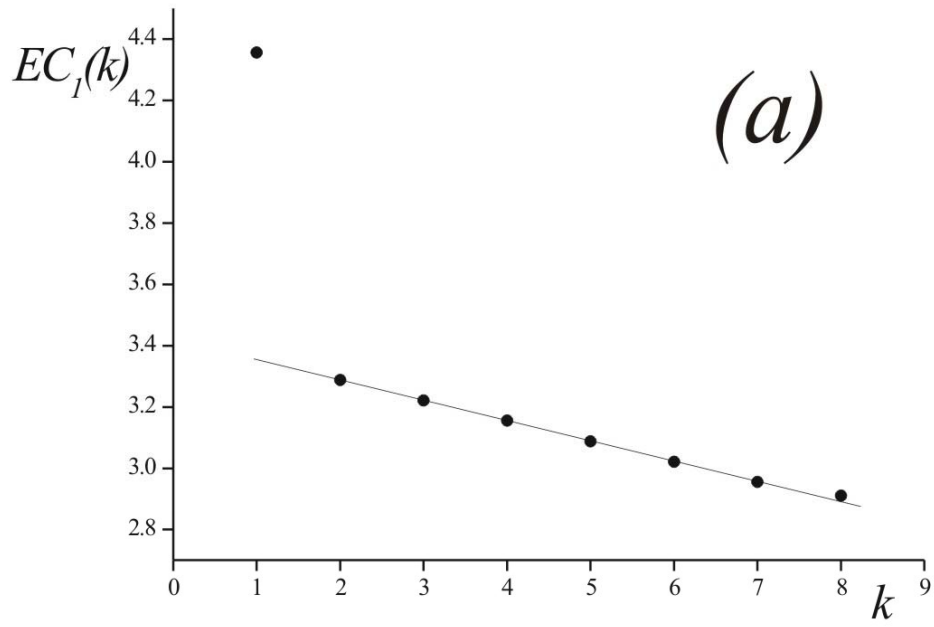


Figure 4

a	k=1	k=2	k=3	k=4	k=5	k=6	k=7	k=8	k=9	k=10
2	6.000	2.000								
	4.667	3.333								
3	5.333	3.667	2.000							
	4.600	3.300	3.100							
4	5.000	3.833	3.000	2.167						
	4.533	3.333	3.133	3.000						
5	4.800	3.800	3.300	2.800	2.300					
	4.476	3.333	3.190	3.048	2.952					
6	4.667	3.733	3.400	3.067	2.733	2.400				
	4.429	3.321	3.214	3.107	3.000	2.929				
7	4.571	3.667	3.429	3.190	2.952	2.714	2.476			
	4.389	3.306	3.222	3.139	3.056	2.972	2.917			
8	4.500	3.607	3.429	3.250	3.071	2.893	2.714	2.536		
	4.356	3.289	3.222	3.156	3.089	3.022	2.956	2.911		
9	4.444	3.556	3.417	3.278	3.139	3.000	2.861	2.722	2.583	
	4.327	3.273	3.218	3.164	3.109	3.055	3.000	2.945	2.909	
10	4.400	3.511	3.400	3.289	3.178	3.067	2.956	2.844	2.733	2.622
	4.303	3.258	3.212	3.167	3.121	3.076	3.030	2.985	2.939	2.909

Table 1