

π -ELECTRON CONTENTS OF RINGS IN THE DOUBLE-HEXAGONAL-CHAIN HOMOLOGOUS SERIES (PYRENE, ANTHANTHRENE AND OTHER ACENOACENES)

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Recently three methods for calculating the π -electron content of rings of benzenoid hydrocarbons were put forward: one based on the consideration of Kekulé structural formulas, and the other two based on an analogous treatment of the Clar aromatic sextet formulas. These three methods are applied to the homologous series consisting of two condensed acene chains (whose first members are pyrene, anthanthrene, peri-naphthacenonaphthacene, ...), leading to basically identical results. In contrast to acenes (in which the partition of π -electrons into rings is uniform), in the double-hexagonal-chain species the partition of π -electrons is highly non-uniform. The electron content monotonically decreases, in opposite directions, along the two acene chains, being maximal in the least annelated rings. Some other generally valid regularities in the π -electron properties of the double-hexagonal-chain benzenoids are also pointed out.

Keywords: π -Electron distribution; electron content of ring; Kekulé structures, Clar theory; benzenoid hydrocarbons; double hexagonal chains

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INTRODUCTION

In this paper we are concerned with the partition of the π -electrons in the rings of double linear hexagonal chains (peri-acenoacenes). The structure of the members of this homologous series of benzenoid hydrocarbons we show in Fig. 1. In the same figure is shown also the structure of acenes, namely of single hexagonal chains. The double hexagonal chain consisting of $2a$ rings will be denoted by D_a .

Fig. 1 comes about here

The partition of π -electrons in the rings of polycyclic conjugated molecules was recently much studied [1–14]. These researches were initiated by two of the present authors [1,2], who proposed a method for assessing the π -electron content of a ring by examining the Kekulé structures of the respective molecule. This Kekulé–structure–based approach, that in the following we refer to as *Method 1*, was eventually further elaborated and applied to a variety of conjugated systems [3–8,10,13,14].

In Method 1 the π -electron content of a ring in a polycyclic conjugated molecule is computed as follows. In each Kekulé structure the π -electrons are assumed to be distributed in the rings according to the positions of the double bonds [1]: a double bond belonging to a ring contributes two π -electrons to this ring; a double bond shared by two rings contributes 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.

Method 1 is illustrated in Fig. 2 on the example of anthanthrene.

Fig. 2 comes about here

In the work [14] it was proposed to treat the aromatic sextet formulas in Clar theory [15–18] in a similar manner as the Kekulé structures in Method 1. In particular, according to [14], an aromatic sextet drawn in a ring contributes six π -electrons to this ring; a double bond belonging to a ring contributes two π -electrons to this ring; a double bond shared by two rings contributes 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. We call this procedure for assessing the π -electron content of a ring *Method 2*.

Method 2 is illustrated in Fig. 3 on the example of anthanthrene.

Fig. 3 comes about here

An evident consequence of Method 2 is that for the rings that in Clar theory are “empty”, it predicts a zero π -electron content, which might does not agree with Clar’s original views on localization of π -sextets. Anyway, other quantum mechanical and graph-theoretical approaches, for instance [19–21], assign to so-called “empty” rings certain amount of “conjugation”. This restriction imposed by Model 2 on “empty” was recently overcome [22,23] by its following pertinent modification: An aromatic sextet drawn in a ring contributes $(6 - \frac{1}{2}\nu)$ π -electrons to this ring, where ν is the number of adjacent rings, and contributes $\frac{1}{2}$ π -electrons to each adjacent ring; a double bond belonging to a ring contributes two π -electrons to this ring; a double bond shared by two rings contributes one π -electron to each of these rings. The final electron content of a ring k , denoted here as $EC_3(k)$, is the arithmetic average of the respective electron contents of all Clar aromatic sextet formulas. We call this procedure for assessing the π -electron content of a ring *Method 3*. Its application to anthanthrene is shown in Fig. 3.

A fourth method, which will be mentioned only in passing, assigns in a benzenoid ring to each atom shared with 0, 1, or 2 other rings 1, 1/2, and 1/3 π -electrons, respectively [9]. This results in π -electron counts for D_a -systems of 4.333 π -electrons for $k = 1$, 3.000 π -electrons for $k = 2, 3, \dots, a - 1$, and 3.667 π -electrons for $k = a$.

PARTITION OF π -ELECTRONS OF RINGS OF ACENES

From a structural point of view, acenes L_h form the simplest homologous series of benzenoid hydrocarbons [16], cf. Fig. 1. The π -electron content of the rings of L_h was among the first to be examined. It was found that within Method 1, all non-terminal rings have equal π -electron contents, whereas the two terminal rings have a slight excess of π -electrons relative to the non-terminal rings. By means of Methods 2 and 3, the electron distribution is predicted to be completely uniform. It is easy to

establish the following analytical expressions for EC_1 , EC_2 , and EC_3 of L_h :

$$EC_1(k) = \begin{cases} \frac{4h+7}{h+1} & \text{for } k = 1 \text{ and } k = h \\ \frac{4h+6}{h+1} & \text{for } k = 2, 3, \dots, h-1 \end{cases} .$$

$$EC_2(k) = EC_3(k) = \frac{4h+2}{h} \quad \text{for } k = 1, 2, \dots, h .$$

PARTITION OF π -ELECTRONS IN RINGS OF DOUBLE HEXAGONAL CHAINS

The double hexagonal chain D_a (cf. Fig. 1) has $2a$ rings. The formula of the respective benzenoid hydrocarbon is $C_{6a+4}H_{2a+6}$. D_a has $K(D_a) = (a+1)(a+2)/2$ Kekulé structures. If $a > 1$ then D_a has $C(D_a) = a(a-1)/2$ Clar aromatic sextet formulas, each with two aromatic sextets [24]. Exceptionally, if $a = 1$ (naphthalene), then $C(D_a) = 2$ with a single aromatic sextet in the Clar formulas. Therefore, in what follows the case $a = 1$ will be excluded from our considerations and the parameter a is assumed to be greater than or equal to 2.

From Figs. 2 and 3 we see that Methods 1, 2, and 3 yield different partitionings of π -electrons in the rings of the double-chain benzenoids, but that these differences are not very large. This conclusion is corroborated by the data given in Table 1, that contains the EC_1 -, EC_2 -, and EC_3 -values of all rings of D_a up to $a = 10$.

Table 1 comes about here

The results of both Methods 1, 2, and 3 agree in the following general regularity in the π -electron distribution of double hexagonal chains. Note that it is in stark contrast with the analogous property of the single chains (acenes), in which the π -electrons are uniformly distributed among the rings.

Rule 1. In the double-chain benzenoid systems D_a the partition of π -electrons in rings is highly non-uniform. The rings 1 and 1' of D_a have a somewhat higher EC -values than the other rings, and for $k = 1, 2, \dots, a$, the $EC(k)$ -values monotonically decrease. Thus the rings a and a' of D_a have the smallest π -electron contents.

A typical dependence of $EC(k)$ on k , illustrating Rule 1, is shown in Fig. 4.

Fig. 4 comes about here

A detailed examination revealed that the π -electron contents of the rings of D_a conform to the following general expressions. (The numbering of the rings agrees with that in Fig. 1.)

$$EC_1(k) = \begin{cases} \frac{4a^2 + 16a + 2}{(a+1)(a+2)} = 4 + \frac{2a}{K(D_a)} & \text{for } k = 1 \\ \frac{3a^2 + 13a + 12 - 6k}{(a+1)(a+2)} = 3 + \frac{2a + 3 - 3k}{K(D_a)} & \text{for } k = 2, 3, \dots, a-1 \\ \frac{3a^2 + 7a + 14}{(a+1)(a+2)} = 3 + \frac{a-4}{K(D_a)} & \text{for } k = a \end{cases} \quad (1)$$

$$EC_2(k) = \begin{cases} \frac{4a+4}{a} = 4 + \frac{2a-2}{C(D_a)} & \text{for } k = 1 \\ \frac{3a^2 + 3a + 6 - 10k}{a(a-1)} = 3 + \frac{3a+3-10k}{C(D_a)} & \text{for } k = 2, 3, \dots, a \end{cases} \quad (2)$$

$$EC_3(k) = \begin{cases} \frac{4a^2 - a - 4}{a(a-1)} = 4 + \frac{1.5a-2}{C(D_a)} & \text{for } k = 1 \\ \frac{3a^2 + a + 3 - 6k}{a(a-1)} = 3 + \frac{2a+1.5-3k}{C(D_a)} & \text{for } k = 2, 3, \dots, a-1 \\ \frac{3a^2 - 5a + 4}{a(a-1)} = 3 - \frac{a-2}{C(D_a)} & \text{for } k = a \end{cases} \quad (3)$$

Formulas (1)–(3) hold for all values of $a \geq 2$.

Formulas (1)–(3) reproduce, of course the data given in Table 1 as well as Rule 1. From them also some other, less-easy-to-envisage, regularities can be deduced.

For $k = 2, 3, \dots, a-1$, the expressions (1) and (3) are linear functions of the parameter k . The same is true for the expression (2), except that here linearity holds up to $k = a$. As a consequence of this, and in view of the symmetry of the system D_a (cf. Fig. 1), we arrive at the following peculiar, but generally valid, conclusions.

Rule 2. 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,

$$EC_1(k) + EC_1((a - k + 1)') = \frac{6a^2 + 20a + 18}{(a + 1)(a + 2)}$$

$$EC_2(k) + EC_2((a - k + 1)') = \frac{6a^2 - 4a - 4}{a(a - 1)}$$

$$EC_3(k) + EC_3((a - k + 1)') = \frac{6a - 4}{a(a - 1)}.$$

Rule 3. For $k = 3, 4, \dots, a - 1$, the sum of the π -electron contents of the rings k and $(a - k + 2)'$ is constant, i. e., independent of k .

Rule 4. In the limit case $a \rightarrow \infty$ the electron contents of the rings 1 and 1' of D_a become equal to 4, whereas the limit value of the electron contents of all other rings is equal to 3.

Note that Rules 2–4 follow from both Methods 1, 2, and 3. (According to Method 2, Rule 3 would hold also for $k = 2$.)

Rules 2 and 3 imply the following. 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.

The above described π -electron properties of the double-chain benzenoid molecules, formulated as Rules 1–4, could be deduced from either Method 1 or Method 2 or Method 3. Therefore we trust that these are not artifacts of our approaches, but that they reflect chemical reality.

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a	$k = 1$	$k = 2$	$k = 3$	$k = 4$	$k = 5$	$k = 6$	$k = 7$	$k = 8$	$k = 9$	$k = 10$
2	4.67	3.33								
	6.00	2.00								
	5.00	3.00								
3	4.60	3.30	3.10							
	5.33	3.67	2.00							
	4.83	3.50	2.67							
4	4.53	3.33	3.13	3.00						
	5.00	3.83	3.00	2.17						
	4.67	3.58	3.08	2.67						
5	4.48	3.33	3.19	3.05	2.95					
	4.80	3.80	3.30	2.80	2.30					
	4.55	3.55	3.25	2.95	2.70					
6	4.43	3.32	3.21	3.11	3.00	2.93				
	4.67	3.73	3.40	3.07	2.73	2.40				
	4.47	3.50	3.30	3.10	2.90	2.73				
7	4.39	3.31	3.22	3.14	3.06	2.97	2.92			
	4.57	3.67	3.43	3.19	2.95	2.71	2.48			
	4.40	3.45	3.31	3.17	3.02	2.88	2.76			
8	4.36	3.29	3.22	3.16	3.09	3.02	2.96	2.91		
	4.50	3.61	3.43	3.25	3.07	2.89	2.71	2.54		
	4.36	3.41	3.30	3.20	3.09	2.98	2.88	2.79		
9	4.33	3.27	3.22	3.16	3.11	3.05	3.00	2.95	2.91	
	4.44	3.56	3.42	3.28	3.14	3.00	2.86	2.72	2.58	
	4.32	3.38	3.29	3.21	3.13	3.04	2.96	2.88	2.81	
10	4.30	3.26	3.21	3.17	3.12	3.08	3.03	2.98	2.94	2.91
	4.40	3.51	3.40	3.29	3.18	3.07	2.96	2.84	2.73	2.62
	4.29	3.34	3.28	3.21	3.14	3.08	3.01	2.94	2.88	2.82

TABLE 1 The π -electron content of the ring k of the double hexagonal chain D_a , $a = 2, 3, \dots, 10$ (and, by symmetry, also of the ring $(a - k + 1)'$, see Fig. 1. For each value of a , in the upper, middle, and lower rows are the results of Methods 1, 2, and 3, respectively, i. e., EC_1 , EC_2 , and EC_3 , respectively. Except for $a = 2$ and, perhaps, $a = 3$, the differences between the outcomes of the three models are insignificant.

Figure and Table Captions

FIGURE 1 The structure of acenes L_h (single hexagonal chains) and of double hexagonal chains D_a , as well as the labelling 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, *peri*-naphthacenonaphthacene ($a = 4$), ... 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 Method 1. The sum of the six EC_1 -values is equal to 22, the total number of π -electrons of anthanthrene.

FIGURE 3 The three Clar aromatic sextet formulas of anthanthrene (D_3) and the respective π -electron contents of their rings, calculated according to Method 2 (upper numbers) and Method 3 (lower numbers). In the bottom diagrams the arithmetic averages of these electron contents are given, that are just the π -electron contents of the rings of anthanthrene, computed according to Methods 2 and 3. The sum of both the six EC_2 - and the six EC_3 -values is equal to 22, the total number of π -electrons of anthanthrene.

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 labelling of the rings is same as in Fig. 1. The EC -values monotonically decrease with increasing k . Diagram (a): Results obtained by Method 1. The data points for $k = 2, 3, \dots, a - 1$ lie on an exact straight line. The point pertaining to $k = a$ only slightly deviates from this line, cf. Eq. (1). Diagram (b): Analogous results obtained by Method 2. In this case the linear relation holds for $k = 2, 3, \dots, a$, cf. Eq. (2). Diagram (c): Analogous results obtained by Method 3. Here again the data points for $k = 2, 3, \dots, a - 1$ lie on an exact straight line, whereas the point at $k = a$ only slightly deviates from it, cf. Eq. (3).

TABLE 1 The π -electron content of the ring k of the double hexagonal chain D_a , $a = 2, 3, \dots, 10$ (and, by symmetry, also of the ring $(a - k + 1)'$, see Fig. 1. For each value of a , in the upper, middle, and lower rows are the results of Methods 1, 2, and 3, respectively, i. e., EC_1 , EC_2 , and EC_3 , respectively. Except for $a = 2$ and, perhaps, $a = 3$, the differences between the outcomes of the three models are insignificant.