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Benzenoid Molecules with Uniform Distribution of π-Electrons within Rings

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Summary. In a recent work it was demonstrated that in linear hexagonal chains the distribution of π-electrons into rings (as computed by means of the *Randić–Balaban* method) is uniform, irrespective of the nature of the terminal fragments. We now establish that an analogous, yet somewhat more complex, uniformity in the π-electron distribution exists also in double linear hexagonal chains, as well as in some other benzenoid systems.

Keywords. π-Electron content; π-Electron distribution; Benzenoid hydrocarbons.

Introduction

The partition of π-electrons within the rings of polycyclic conjugated molecules, especially of benzenoid hydrocarbons, attracted recently much attention [1–16]. These studies were initiated by an article of *Randić* [17], followed by papers, in which *Randić* and *Balaban* put forward a method for assessing the π-electron content of a ring from the *Kekulé* structures of the respective molecule [1, 14]. This approach was eventually further elaborated and applied to a variety of conjugated systems [2–13].

According to [1, 14, 17], the π-electron content $EC(\rho)$ of a ring ρ in a polycyclic conjugated molecule is the arithmetic average of the respective electron contents of individual *Kekulé* structures. In each *Kekulé* structure the π-electrons are assumed to be distributed as follows: a double bond belonging solely 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 calculation of $EC(\rho)$ is illustrated in Fig. 1 on the example of the prolate rectangle $R(2,6)$. The actual distribution of π-electrons into rings is shown in Fig. 2

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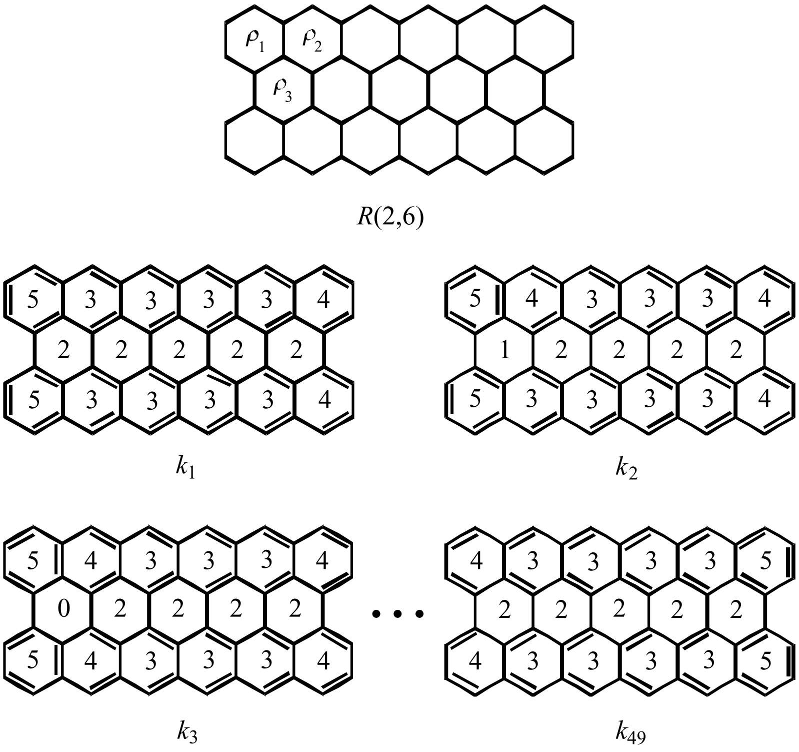

$$EC(\rho_1) = \frac{1}{49}(5 + 5 + 5 + \cdots + 4) = 4.2857$$

$$EC(\rho_2) = \frac{1}{49}(3 + 4 + 4 + \cdots + 3) = 3.2857$$

$$EC(\rho_3) = \frac{1}{49}(2 + 1 + 0 + \cdots + 2) = 1.7143$$

Fig. 1. Four *Kekulé* structures of the prolate rectangle $R(2,6)$ whose *Kekulé* structure count is 49; the numerals inscribed in the rings stand for the π-electron contents, pertaining to the respective *Kekulé* structure (for details see text); the way by which the $EC(\rho)$-values are computed is indicated for the rings ρ_1, ρ_2, and ρ_3: these are the arithmetic averages of the π-electron contents of the individual *Kekulé* structures; the entire distribution of the π-electrons within the rings of $R(2,6)$ is shown in Fig. 2

for $R(2,6)$ and for a dibenzo-annelated derivative of the double linear hexagonal chain $D(6)$. For further details see elsewhere [1–3, 8, 14].

In earlier work [12] 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 tunnelling microscopy.

One of the earliest results [5, 14] in the study of the distribution of π-electrons within the rings was the finding that in the case of linear polyacenes, all hexagons,

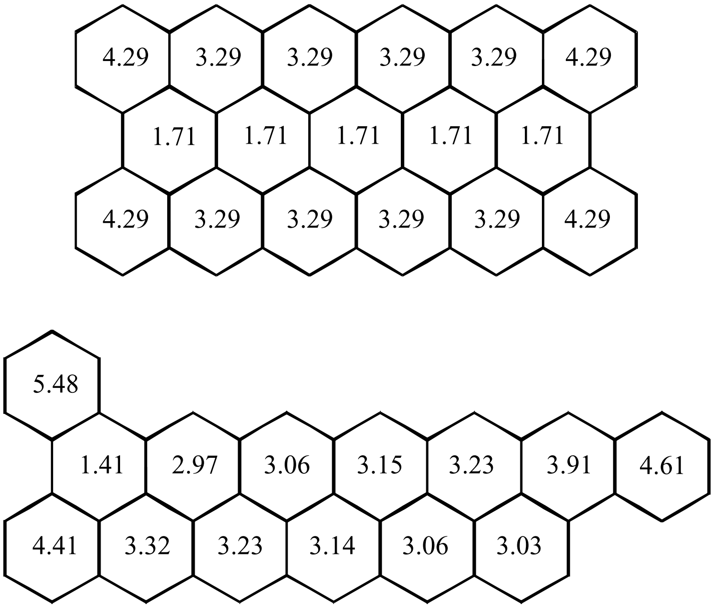

Fig. 2. The distribution of π-electrons within the rings of the prolate rectangle $R(2,6)$ and of the 2,1′-dibenzo derivative of the double linear hexagonal chain $D(6)$, calculated according to the *Randić-Balaban* method [1, 14]; note that within each row of hexagons of $R(2,6)$ (except the terminal hexagons) the π-electron distribution is uniform; in the 2,1′-dibenzo derivative of $D(6)$ the distribution of the π-electrons appears to be highly non-uniform; yet, also here a concealed uniformity can be established (see Rule 2a and Eq. (2))

except the two terminal hexagons, have equal *EC*-values. In other words, the distribution of π-electrons within the rings of the linear hexagonal chain (except the terminal rings) is uniform. In Ref. [13] this uniformity was shown to hold for all conjugated species containing a linear hexagonal chain, irrespective of the nature of the fragments attached to its ends.

The aim of the present study is to examine if analogous uniformities in the π-electron distribution exist also in other classes of benzenoid molecules. We first describe such a class – the oblate rectangles $R(m,n)$. The regularities found to hold for $R(m,n)$ are no surprise whatsoever since these benzenoids may be viewed as consisting of m linear hexagonal chains, joined by essentially single carbon–carbon bonds [18]. The other homologous series analyzed in this work – the double linear hexagonal chains $D(n)$ – could serve as examples of benzenoid systems in which the distribution of π-electrons into rings is highly non-uniform (*cf.* Figs. 2 and 4). Yet, in $D(n)$ a concealed uniformity in the π-electron distribution could be established, which – again – is independent of the nature of the fragments attached to its ends.

The general formulas of the benzenoid systems we are concerned with are shown in Fig. 3, together with the notation used throughout the present paper. These are the prolate rectangle $R(m,n)$ (*cf.* p. 201 in Ref. [18]), the double linear hexagonal chain $D(n)$, and its terminally annelated derivatives $G(n)$, as well as the triple linear hexagonal chain $T(n)$. The meaning of the parameters m and n is

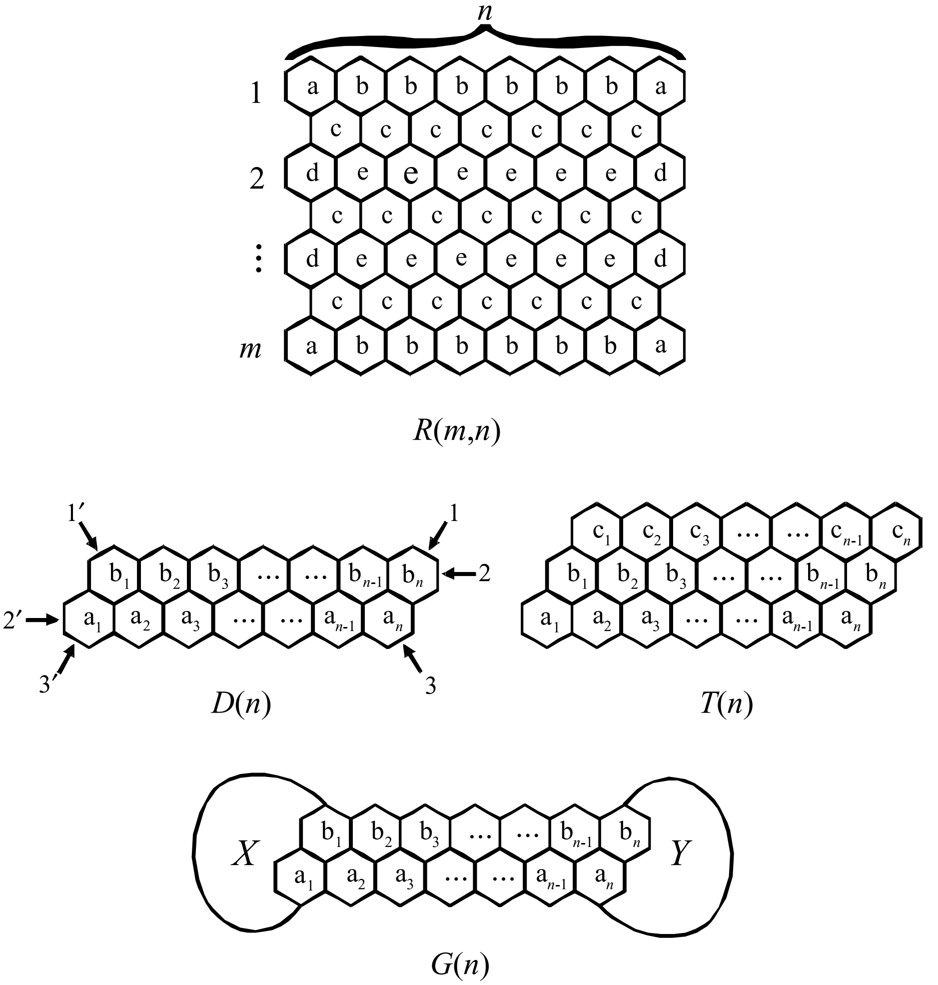

Fig. 3. General formulas of some benzenoid systems, and the labelling of their rings; arrows indicate the sites of possible benzo-annelation of $D(n)$; in $R(m, n)$ the rings labelled by the same letter have mutually equal EC-values; in $D(n)$ and $G(n)$ the distribution of π-electrons within rings is non-uniform, but $EC(\mathrm{a}_i) + EC(\mathrm{b}_i)$ is constant for $i = 2, 3, \dots, n-1$, see Eq. (2); in $T(n)$ no regularity of this kind could be envisaged

indicated in Fig. 3. Thus $R(m, n)$, $D(n)$, and $T(n)$ have $mn + (m-1)(n-1)$, $2n$, and $3n$ hexagons, respectively.

Results and Discussion

π-Electron Contents of Rings of R(m, n)

As already mentioned, the prolate rectangle $R(m, n)$ may be viewed as consisting of m linear polyacene chains, connected by essentially single carbon–carbon bonds. Bearing this in mind, and knowing the rules for the distribution of π-electrons in linear polyacenes [5, 13, 14], we readily arrive at the following expressions, pertaining to any $R(m, n)$, $n \geq 2$, $m \geq 2$ (Eqs. (1)), where the labelling of the rings is indicated in Fig. 3.

$$EC(\rho) = \begin{cases} (4n+6)/(n+1) & \text{for all rings } \rho \text{ of type a} \\ (3n+5)/(n+1) & \text{for all rings } \rho \text{ of type b} \\ 2n/(n+1) & \text{for all rings } \rho \text{ of type c} \\ (4n+5)/(n+1) & \text{for all rings } \rho \text{ of type d} \\ (2n+4)/(n+1) & \text{for all rings } \rho \text{ of type e} \end{cases} \tag{1}$$

Of course, if $n = 2$, then there are no rings of the type b, whereas if $m = 2$, then there are no rings of the type d and e.

It should be noted that the π-electron contents of the rings of $R(m, n)$ are independent of the value of the parameter m.

The chemically most significant consequences of Eqs. (1) can be formulated as follows:

Rule 1a. Within each of the horizontal arrays of hexagons of $R(m, n)$ (except in the terminal hexagons of the linear polyacene fragments) the distribution of π-electrons within rings is uniform.

Rule 1b. With increasing length of each linear polyacene chain in $R(m, n)$, the π-electron content of the rings of type b monotonically decreases, approaching a limit value equal to 3. The same holds also for the rings of type c and e, except that for these the limit value is 2.

An example illustrating Rule 1a is found in Fig. 2.

π-Electron Contents of Rings of $D(n)$ and $G(n)$

The distribution of π-electrons within the rings of the double linear hexagonal chain $D(n)$ and its various derivatives of the type $G(n)$ is highly non-uniform; for an example see Fig. 2; two more examples are given in Fig. 4.

A detailed examination of the calculated EC-values reveals a surprising regularity:

Rule 2a. The total π-electron contents of two adjacent rings belonging to different linear chains of $D(n)$ or $G(n)$, provided that these are not the terminal rings, is constant.

In a more formal manner, Rule 2a can be stated as shown by Eq. (2) where the labelling of the rings is that shown in Fig. 3, and where Γ is a constant, depending on the length n of the linear hexagonal chains as well as (in the case of $G(n)$) on the nature of the terminal fragments X and Y.

$$EC(\mathrm{a}_i) + EC(\mathrm{b}_i) = \Gamma \quad \text{for } i = 2, 3, \ldots, n-1 \tag{2}$$

Examples illustrating Rule 2a are found in Figs. 2 and 4. In particular, for $G(6)$ depicted in Fig. 2, $\Gamma = 6.290$; in the examples shown in Fig. 4, $\Gamma = 6.244$ for $D(8)$ and $\Gamma = 6.268$ for $G(8)$.

The validity of Eq. (2) was checked and verified on numerous examples, but its mathematical proof (for the case of arbitrary substituents X and Y in $G(n)$, *cf.* Fig. 3) could not be achieved. On the other hand, we determined explicit

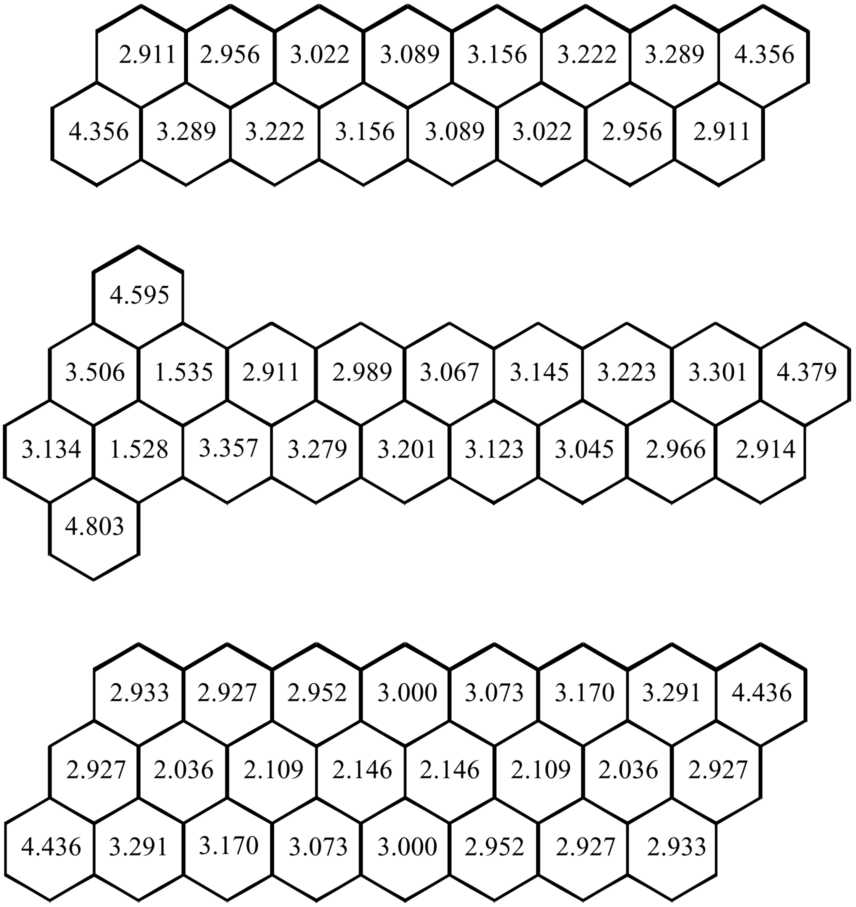

Fig. 4. The distribution of the π-electrons within the rings of the double linear hexagonal chain $D(8)$, its derivative $G(8)$, and of the triple linear hexagonal chain $T(8)$

combinatorial expressions for Γ for a variety of benzenoid systems of the form $G(n)$. In what follows we give these expressions for all benzo-annelated derivatives of $D(n)$. The labelling of the sites of $D(n)$ where the benzo-annelations may take place is shown in Fig. 3.

$\Gamma = (6n^2 + 20n + 18)/(n^2 + 3n + 2)$ for unsubstituted $D(n)$
$\Gamma = (6n^2 + 14n + 11)/(n^2 + 2n + 1)$ for 1-benzo annelated $D(n)$
$\Gamma = (6n^2 + 32n + 32)/(n^2 + 5n + 4)$ for 2-benzo annelated $D(n)$
$\Gamma = (6n^2 + 20n + 12)/(n^2 + 3n + 1)$ for 3-benzo annelated $D(n)$
$\Gamma = (12n^2 + 28n + 16)/(2n^2 + 4n + 1)$ for $1,3$-dibenzo annelated $D(n)$
$\Gamma = (6n^2 + 32n + 20)/(n^2 + 5n + 2)$ for $2,3$-dibenzo annelated $D(n)$
$\Gamma = (6n^2 + 14n + 5)/(n^2 + 2n)$ for, $1'$-dibenzo annelated $D(n)$
$\Gamma = (6n^2 + 26n + 19)/(n^2 + 4n + 2)$ for $1,2'$-dibenzo annelated $D(n)$

$\Gamma = (12n^2 + 16n + 14)/(2n^2 + 2n + 1)$ for $1, 3'$-dibenzo annelated $D(n)$

$\Gamma = (6n^2 + 32n + 26)/(n^2 + 5n + 3)$ for $2, 1'$-dibenzo annelated $D(n)$

$\Gamma = (6n^2 + 44n + 58)/(n^2 + 7n + 8)$ for $2, 2'$-dibenzo annelated $D(n)$

$\Gamma = (6n^2 + 20n + 6)/(n^2 + 3n)$ for $3, 1'$-dibenzo annelated $D(n)$

$\Gamma = (12n^2 + 28n + 4)/(2n^2 + 4n - 1)$ for $1, 3, 1'$-tribenzo annelated $D(n)$

$\Gamma = (12n^2 + 52n + 32)/(2n^2 + 8n + 3)$ for $1, 3, 2'$-tribenzo annelated $D(n)$

$\Gamma = (6n^2 + 8n + 4)/(n^2 + n)$ for $1, 3, 3'$-tribenzo annelated $D(n)$

$\Gamma = (6n^2 + 32n + 14)/(n^2 + 5n + 1)$ for $2, 3, 1'$-tribenzo annelated $D(n)$

$\Gamma = (6n^2 + 44n + 46)/(n^2 + 7n + 6)$ for $2, 3, 2'$-tribenzo annelated $D(n)$

$\Gamma = (6n^2 + 26n + 7)/(n^2 + 4n)$ for $2, 3, 3'$-tribenzo annelated $D(n)$

$\Gamma = (12n^2 + 52n + 8)/(2n^2 + 8n - 1)$ for $1, 3, 1', 2'$-tetrabenzo annelated $D(n)$

$\Gamma = (12n^2 + 16n + 2)/(2n^2 + 2n - 1)$ for $1, 3, 1', 3'$-tetrabenzo annelated $D(n)$

$\Gamma = (6n^2 + 44n + 34)/(n^2 + 7n + 4)$ for $2, 3, 1', 2'$-tetrabenzo annelated $D(n)$

The above formulas (as well as others not reported here) indicate that the following general regularity holds:

Rule 2b. With the increasing length of the double hexagonal chain in $G(n)$, irrespective of the nature of the terminal fragments X and Y, the sum of the π-electron contents of the rings a_i and b_i (that is, Γ in Eq. (2)), monotonically decreases, approaching a limit value equal to 6.

Concluding Remarks

The Case of the Triple Hexagonal Chains T(n)

Rules 2a and 2b may be viewed as a proper, but by no means straightforward, extension to double linear hexagonal chains of the results established in Ref. [13] for single hexagonal chains: Whereas in single linear chains the distribution of π-electrons within rings is uniform, in double chains the distribution of π-electrons within two adjacent rings is uniform (in the sense of Eq. (2)).

In view of this, the obvious question is: Is there any analogous regularity in triple linear chains $T(n)$ and their terminally substituted derivatives? Is there a relation, analogous to Eq. (2), applicable to triple chains? This relation should be of the form $\alpha EC(\mathrm{a}_i) + \beta EC(\mathrm{b}_i) + \gamma EC(\mathrm{c}_i) = const$ for $i = 2, 3, \ldots, n-1$, with α, β, γ being some constants, or, more generally, $f(EC(\mathrm{a}_i), EC(\mathrm{b}_i), EC(\mathrm{c}_i)) = const$ for $f(x, y, z)$ being some function.

In spite of detailed examination we could not envisage any such relation, which we find not only disappointing, but also surprising. Such a regularity may nevertheless exist, awaiting to be discovered. In Fig. 4 are presented the EC-values of the rings of a sufficiently long triple hexagonal chain, $T(8)$, based on which a reader of this paper may try to arrive at the desired extension of Eq. (2).

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