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ON DISTRIBUTION OF π-ELECTRONS IN DOUBLE LINEAR HEXAGONAL CHAINS

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Abstract

In double linear hexagonal chains the distribution of π-electrons into rings (as computed by means of the Randić–Balaban method) is highly non-uniform: The electron contents monotonically decrease along each polyacene chain. As a somewhat surprising result we show that the sum of π-electron contents of two adjacent rings, belonging to different polyacene chains of the double chain is constant, irrespective of the nature of the terminal fragments. This regularity is a proper generalization of what earlier was observed for single linear hexagonal chains (polyacenes), and is not extendible to triple, quadruple, etc. linear hexagonal chains.

INTRODUCTION

The partition of π-electrons into the rings of polycyclic conjugated molecules, especially of benzenoid hydrocarbons, attracted recently much attention [1–23]. These studies were based on the concept of "algebraic Kekulé structures" [24], according to which each Kekulé structure of a benzenoid molecule may be characterized by indicating the number of π-electrons in each of its rings; for additional work along these lines see [25–27].

Based on the concept of "algebraic Kekulé structures", Randić and Balaban [1] put forward a method for assessing the π-electron content of a ring from the Kekulé structures of the respective molecule. This approach was eventually further elaborated and applied to a variety of conjugated systems [4–23].

According to [1], the π-electron content $EC(R)$ of a ring R 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. Details on how $EC(R)$ is computed (from its definition), illustrated by a pertinent example, can be found in another article in this book [28].

The calculation of $EC(R)$ was much facilitated by means of a simple formula [8]:

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

where p_{rs}^{P} is the Pauling bond order of the carbon–carbon bond rs, where $\sum_{*}$ indicates summation over bonds that belong solely to the ring R, and where $\sum_{**}$ indicates summation over bonds that are shared by the ring R and another ring. The Pauling bond orders of benzenoid hydrocarbons can be easily calculated thanks to a theorem by Ham [29], according to which in the case of benzenoid systems the Pauling bond orders coincide with the Ham–Ruedenberg bond orders [30].

In the work [20] 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.

Recently, other methods for estimating the π-electron content of a ring were put forward [7,9,15,17,18,22], but these will not be considered in the present article.

One of the earliest results [1,7] in the study of the distribution of π-electrons into the rings was the finding that in the case of linear polyacenes, all hexagons, except the two terminal hexagons, have equal EC-values (see Fig. 1). In other words, the distribution of π-electrons into the rings of the linear hexagonal chain (except the terminal rings) is uniform. In [14] 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.

A natural question that arises is if analogous uniformities in the π-electron distribution exist also in double, triple, etc. hexagonal chains. Problems of this kind were recently studied in due detail [17,18,23]. In this article we outline the main results obtained along these lines, restricting the consideration solely to the Randić–Balaban EC-values.

First of all, calculations show that in contrast with the single linear chains, the π-electron distribution in double–, triple–, etc. linear chains is highly non-uniform. An illustrative example is found in Fig. 1.

In this work we focus our attention to the double linear hexagonal chains $D(a)$ and their terminally substituted derivatives $G(a)$. The structure of $D(a)$ and $G(a)$, as well as the labelling of their rings in shown in Fig. 2.

π-ELECTRON CONTENTS OF RINGS OF $D(a)$ AND $G(a)$

The distribution of π-electrons into the rings of the double linear hexagonal chain $D(a)$ and its various derivatives of the type $G(a)$ is highly non-uniform; for examples see Figs. 1 and 2.

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

Rule 1. The total π-electron contents of two adjacent rings belonging to different linear chains of $D(a)$ or $G(a)$, provided that these are not the terminal rings, is constant.

In a more formal manner, Rule 1 can be stated as:

$$EC(k) + EC(k') = \Gamma \quad \text{for} \quad k = 2, 3, \ldots, a-1 \tag{1}$$

where the labelling of the rings is that shown in Fig. 2, and where Γ is a constant, depending on the length a of the linear hexagonal chains as well as (in the case of $G(a)$) on the nature of the terminal fragments X and Y.

In Figs. 1 and 2 the rings k and k' to which Rule 1 applies are indicated by the same color.

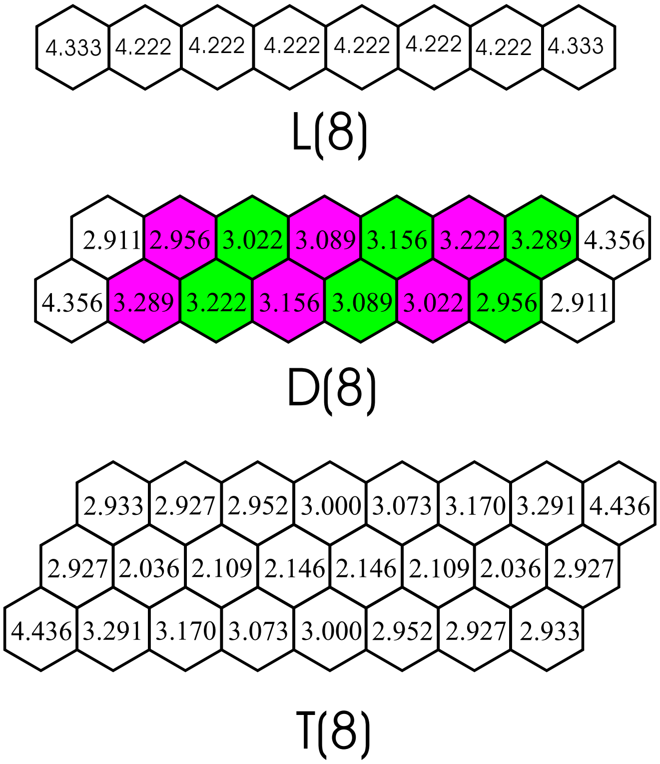

Fig. 1. The π-electron contents of rings of the linear hexagonal chain $L(8)$ with 8 hexagons, the double hexagonal chain $D(8)$ with $2 \times 8 = 16$ hexagons, and the triple hexagonal chain $T(8)$ with $3 \times 8 = 24$ hexagons. The uniformity of the π-electron distribution in $T(8)$ is obvious. In $D(8)$ the sum of two neighboring hexagons, lying in different linear chains is constant (for details see text). In $T(8)$ no similar regularity in the π-electron distribution could be envisaged.

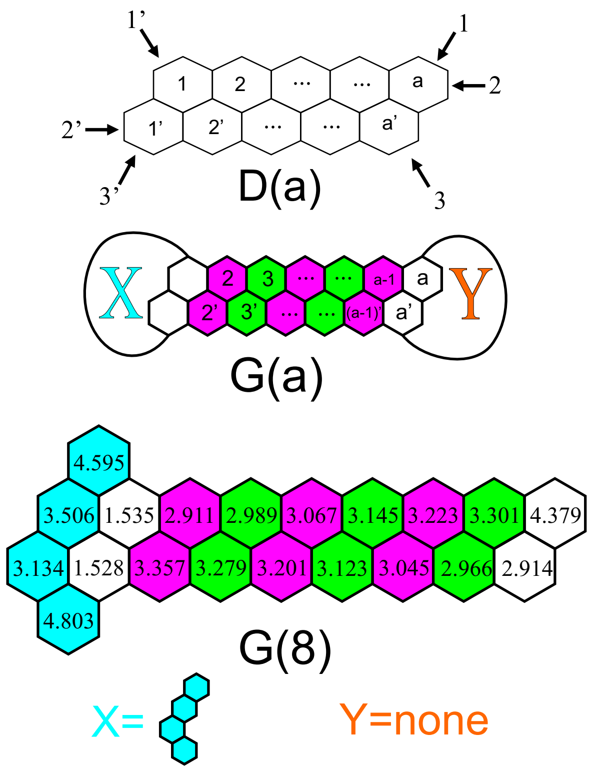

Fig. 2. The double linear hexagonal chain $D(a)$ and the general formula of its terminally annelated derivative $G(a)$, as well as the labelling of their relevant six-membered rings. The terminal fragments X and Y may be benzenoid systems, but need not. Irrespective of the nature of these terminal fragments, the sum $EC(k) + EC(k')$ is constant for $k = 2, 3, \ldots, a-1$, as can easily be checked on a special representative of $G(a)$ for $a = 8$.

Examples illustrating Rule 1 are found in Figs. 1 and 2. In particular, for $D(8)$, depicted in Fig. 1, $\Gamma = 6.244$ whereas for $G(8)$, depicted in Fig. 2, $\Gamma = 6.268$.

The validity of Eq. (1) was checked and verified on numerous examples, but its general mathematical proof has not yet been obtained. On the other hand, we determined explicit combinatorial expressions for Γ for a variety of benzenoid systems of the form $G(a)$. In what follows we give these expressions for all benzo-annelated derivatives of $D(a)$. The labelling of the sites of $D(a)$ where the benzo-annelations may take place is shown in Fig. 2.

$\Gamma = (6a^2 + 20a + 18)/(a^2 + 3a + 2)$ for unsubstituted $D(a)$
$\Gamma = (6a^2 + 14a + 11)/(a^2 + 2a + 1)$ for 1-benzo annelated $D(a)$
$\Gamma = (6a^2 + 32a + 32)/(a^2 + 5a + 4)$ for 2-benzo annelated $D(a)$
$\Gamma = (6a^2 + 20a + 12)/(a^2 + 3a + 1)$ for 3-benzo annelated $D(a)$
$\Gamma = (12a^2 + 28a + 16)/(2a^2 + 4a + 1)$ for 1,3-dibenzo annelated $D(a)$
$\Gamma = (6a^2 + 32a + 20)/(a^2 + 5a + 2)$ for 2,3-dibenzo annelated $D(a)$
$\Gamma = (6a^2 + 14a + 5)/(a^2 + 2a)$ for 1,1'-dibenzo annelated $D(a)$
$\Gamma = (6a^2 + 26a + 19)/(a^2 + 4a + 2)$ for 1,2'-dibenzo annelated $D(a)$
$\Gamma = (12a^2 + 16a + 14)/(2a^2 + 2a + 1)$ for 1,3'-dibenzo annelated $D(a)$
$\Gamma = (6a^2 + 32a + 26)/(a^2 + 5a + 3)$ for 2,1'-dibenzo annelated $D(a)$
$\Gamma = (6a^2 + 44a + 58)/(a^2 + 7a + 8)$ for 2,2'-dibenzo annelated $D(a)$
$\Gamma = (6a^2 + 20a + 6)/(a^2 + 3a)$ for 3,1'-dibenzo annelated $D(a)$
$\Gamma = (12a^2 + 28a + 4)/(2a^2 + 4a - 1)$ for 1,3,1'-tribenzo annelated $D(a)$

$\Gamma = (12a^2 + 52a + 32)/(2a^2 + 8a + 3)$ for 1,3,2'-tribenzo annelated $D(a)$
$\Gamma = (6a^2 + 8a + 4)/(a^2 + a)$ for 1,3,3'-tribenzo annelated $D(a)$
$\Gamma = (6a^2 + 32a + 14)/(a^2 + 5a + 1)$ for 2,3,1'-tribenzo annelated $D(a)$
$\Gamma = (6a^2 + 44a + 46)/(a^2 + 7a + 6)$ for 2,3,2'-tribenzo annelated $D(a)$
$\Gamma = (6a^2 + 26a + 7)/(a^2 + 4a)$ for 2,3,3'-tribenzo annelated $D(a)$
$\Gamma = (12a^2 + 52a + 8)/(2a^2 + 8a - 1)$ for 1,3,1',2'-tetrabenzo annelated $D(a)$
$\Gamma = (12a^2 + 16a + 2)/(2a^2 + 2a - 1)$ for 1,3,1',3'-tetrabenzo annelated $D(a)$
$\Gamma = (6a^2 + 44a + 34)/(a^2 + 7a + 4)$ for 2,3,1',2'-tetrabenzo annelated $D(a)$

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

Rule 2. With the increasing length of the double hexagonal chain in $G(a)$, irrespective of the nature of the terminal fragments X and Y, the sum of the π-electron contents of the rings k and k' (that is, Γ in Eq. (1)), monotonically decreases, approaching a limit value equal to 6.

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O RASPODELI π-ELEKTRONA U DVOSTRUKIM HEKSAGONALNIM LANCIMA

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IZVOD

U radu su izloženi rezultati istraživanja raspodele π-elektrona u šestočlanim prstenovima dvostrukih linearnih heksagonalnih lanaca. Primenjena je metoda koju su

2004. godine predložili Randić i Balaban, a koja za sadržaj π-elektrona u prstenu R uzima srednju (aritmetičku) vrednost sadržaja elektrona u prstenu R u pojedinačnim Kekuléovim strukturama.

Proračuni pokazuju da je raspodela elektrona u dvostrukim (a takođe i u trostrukim, četvorostrukim, ...) linearnim heksagonalnim lancima krajnje neuniformna, za razliku od onoga što važi u slučaju jednostrukih lanaca. Primeri koji ovo ilustruju dati su na Slici 1.

Međutim, pažljivijim proučavanjem elektronskih sadržaja prstenova u dvostrukim lancima uočeno je da važi sledeće:

Pravilo 1. Neka je a dužina dvostrukog heksagonalnog lanca, i neka su u tom lancu prsteni označeni kao na Slici 2. Tada jednakost

$$EC(k) + EC(k') = \Gamma$$

važi za $k = 2, 3, \ldots, a-1$. U navedenoj formuli $EC(k)$ je elektronski sadržaj prstena k (u prvom lancu), a $EC(k')$ elektronski sadržaj prstena k' (u drugom lancu), dok je Γ određena konstanta, nezavisna od vrednosti parametra k.

Na Slikama 1 i 2 prsteni k i k' na koje se odnosi Pravilo 1 su jednako obojeni.

Pravilo 1 znači da i u slučaju dvostrukih linearnih heksagonalnih lanaca postoji određena uniformnost u raspodeli π-elektrona, s tim da se ona ne odnosi na pojedinačne prstenove, nego na parove susednih prstenova koji se nalaze u različitim lancima. Pravilnost važi za unutrašnje prstenove lanca, ali ne i za njene terminalne delove (isto kao i u slučaju jednostrukih lanaca).

Pokazalo se da Pravilo 1 zadržava svoje važenje i ako se na krajeve dvostrukog linearnog heksagonalnog lanca dodaju proizvoljne grupe X i Y (prikazane na Slici 2). Iz niza ispitanih primera sledi i druga pravilnost:

Pravilo 2. Konstanta Γ monotono opada s porastom dužine dvostrukog heksagonalnog lanca (a), i njena granična vrednost kada $a \to \infty$ iznosi 6. Ova granična vrednost ne zavisi od prirodne bočnih grupa X i Y.

Pokušaji da se pravilnosti ovog tipa otkriju i kod trostrukih (i eventualno višestrukih) linearnih heksagonalnih lanaca nisu urodili plodom.