On the π-Electron Content of Rings in Benzenoid Parallelograms

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We make use of the classical correspondence between Kekulé structures and lattice paths to obtain explicit formulas for the Pauling bond order of edges in benzenoid parallelograms. These formulas are further used to establish the average π-electron content of hexagonal rings in such benzenoids. We then compare this quantity with the atom-based π-electron content of rings, and study the local and the asymptotic behaviour of their difference.

Key words: Benzenoid Graph; Kekulé Structure; π-Electron Partition; π-Electron Content; π-Electron Excess.

1. Introduction

In this paper we are concerned with the average π-electron content in the rings of a particular class of benzenoid hydrocarbons. There are several ways to define and compute this quantity. Here we follow a method proposed and developed in a series of recent papers [1 – 8], where it was applied to various cata- and pericondensed benzenoid and coronoid species. The method makes use of the Pauling bond order and, hence, boils down to counting Kekulé structures in the considered benzenoids. We take further this line of research first by revisiting the folklore correspondence between Kekulé structures and lattice paths and deriving simple explicit formulas for the Pauling bond order of edges in benzenoid parallelograms, and then by presenting explicit formulas for the average π-electron content of rings in such benzenoids. These formulas then allow us to study the deviation of so computed π-electron content from the uniform distribution, where an atom shared by k rings contributes $1/k$ electrons to each ring. It is shown that for large enough parallelograms this deviation is most prominent in a rather narrow band along the longer diagonal, and that there is a small net migration of electrons from the periphery toward the interior.

2. Preliminaries

2.1. Benzenoid Parallelograms

Let us consider a configuration of $m \times n$ congruent regular hexagons arranged in m rows, each row of
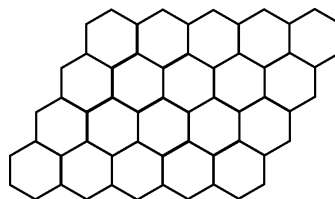

Fig. 1. Benzenoid parallelogram $B_{4,5}$.

n hexagons, shifted for half a hexagon to the right from the row immediately below. An example is shown in Figure 1. The arrangement is such that two hexagons either share a whole edge or are completely disjoint. To each such configuration we assign a graph by taking the vertices of hexagons as vertices of the graph, and the edges of hexagons as its edges. The resulting planar and bipartite graph is called a **benzenoid parallelogram** and denoted by $B_{m,n}$. It has mn hexagonal rings as its faces, $2(mn + m + n)$ vertices, and $3mn + 2m + 2n - 1$ edges. For $m = n$ we obtain a **benzenoid rhombus B_m**.

Let $B_{m,n}$ be embedded in the plane as in Figure 1. To each of its mn hexagons we assign two integer labels indicating its position within the graph. The first label indicates the row, the second one the column. The labels increase from lower to higher rows and from left to right for the columns. We also label the edges. First, we observe that they are partitioned into three classes. We denote the classes by v (vertical), d (descending), and a (ascending). To each vertical edge we assign two labels: The first one denotes the row, the second one the number of hexagons in that row left from the considered edge. By specifying $1 \leq i \leq m$ and $0 \leq j \leq n$
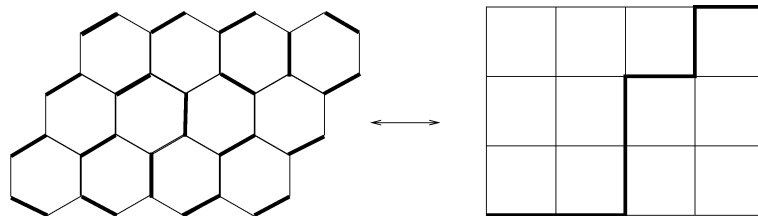
the position of edge $v_{i,j}$ is fully determined. The meaning of labels i, j assigned to other two types of edges is similar: $d_{i,j}$ denotes the descending edge in the j-th column with i hexagons below it, while $a_{i,j}$ stands for the ascending edge such that there are i hexagons below it and j hexagons left of it. The label ranges are $0 \leq i \leq m$ and $1 \leq j \leq n$ for descending edges and $0 \leq i \leq m$ and $0 \leq j \leq n$ for the ascending ones.

Let F be a face of a planar graph G. The set of all edges of G incident with F is called its **boundary** and denoted by ∂F. For any hexagonal face $H_{i,j}$ of $B_{m,n}$ its boundary can be described in a compact way using our labelling scheme:

$$\partial H_{i,j} = \{v_{i,j-1}, v_{i,j}, d_{i-1,j}, d_{i,j}, a_{i-1,j}, a_{i,j-1}\}.$$

2.2. Importance, Redundancy, and Pauling Bond Order

A **matching** in a graph G is a set M of edges of G such that no two edges from M share a vertex. A matching M is called **perfect** if every vertex of G is incident with some edge from M. The number of perfect matchings in G we denote by $K(G)$.

Let e be an edge of G. Its **importance** $\iota(e)$ is defined as the number of perfect matchings in G that contain e. The concept of importance of an edge is closely related to its Pauling bond order: The **Pauling bond order** $p(e)$ of an edge e is obtained by dividing its importance by the total number of perfect matchings in G, $p(e) = \iota(e)/K(G)$. Another related concept is **redundancy** of an edge. It is defined as the number of perfect matchings in G that do not contain e, and is denoted by $\rho(e)$. Obviously, $\iota(e) + \rho(e) = K(G)$, for any edge e of G.

The number of perfect matchings in $B_{m,n}$ is given by $K(B_{m,n}) = \binom{m+n}{m}$. This classical result [9] has been rediscovered many times; the formula is a direct consequence of a bijective correspondence between perfect matchings in $B_{m,n}$ and directed lattice paths with steps $(1,0)$ and $(0,1)$ from $(0,0)$ to (n,m) in $\mathbb{Z}^2$. We refer the reader to [10] where the proof has been worked

out in full detail. The correspondence is illustrated in Figure 2. The literature on the enumeration of perfect matchings in benzenoid graphs is vast. We refer the reader to the monograph [11] for a comprehensive survey.

2.3. π-Electron Distribution

Benzenoid graphs were introduced as mathematical models of compounds known as polycyclic aromatic hydrocarbons or benzenoids. Carbon atoms of such compounds are represented by vertices, and the chemical bonds between them by edges of the corresponding graphs. Each carbon atom is adjacent either to three carbon atoms, or to two carbons and one hydrogen. This leaves one π-electron per carbon atom for forming carbon-carbon double bonds. The pattern of double bonds is called a **Kekulé structure**. Since in benzenoids no carbon atom can participate in more than one double bond, a Kekulé structure is mathematically represented by a perfect matching.

The number of π-electrons that participate in Kekulé structures is equal to the number of atoms in the compound. The pattern of their distribution among the bonds is quantified by the Pauling bond order [6]. Hence, one can look at this quantity as a measure of the π-electron content of a given bond. The Pauling bond order also enables us to measure the π-electron content of hexagonal rings of benzenoid compounds.

Let G be a planar graph with a perfect matching and H one of its bounded faces. Let U denote the unbounded face of G. An edge $e \in \partial H$ can be shared either with U or with another bounded face of G. Let M be a perfect matching of G. Each edge from ∂H participating in M carries two electrons. If e is not shared with another bounded face of G, both its electrons are assigned to H; if the edge is shared between two bounded faces, each of them gets one of its electrons. Under such scheme, the total number of electrons given to H by M is obtained by counting edges from ∂H in M, counting the edges shared by the unbounded side twice. The **total π-electron content** of H, $\pi(H)$, is ob-
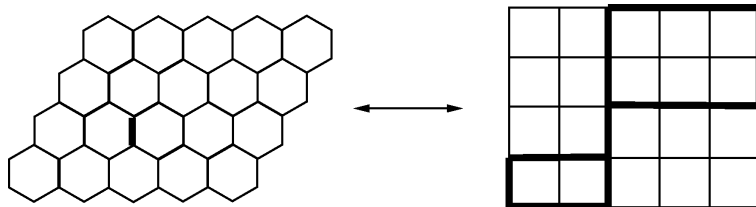
Fig. 3. Importance of a vertical edge.

tained by summing such contributions over all perfect matchings of G. The **average π-electron content** of a bounded face H, $\overline{\pi}(H)$, is then obtained by dividing its total π-electron content by the number of perfect matchings in G. Hence, $\overline{\pi}(H) = \frac{\pi(H)}{K(G)}$.

By double counting of edges one can obtain a simple expression for the total π-electron content of a face in terms of importances of edges from ∂H.

Theorem A:

$$\pi(H) = \sum_{e \in \partial H} \iota(e) + \sum_{e \in \partial H \cap \partial U} \iota(e). \qquad \square$$

By dividing the above expression by $K(G)$ we obtain a formula for $\overline{\pi}(H)$ equivalent to formula (1) of reference [6]. However, we find the formula from Theorem A more convenient for the computations that follow.

There are also other ways of defining the π-electron content of a face of G. The simplest one is to assume that an atom (i. e., a vertex) shared by k rings gives $1/k$ of its π-electron to each ring. This formula depends only on the local modes of annelation, hence, it is very coarse. For example, it gives two electrons to all internal rings. Nevertheless, it was considered in [12] as a useful baseline for comparisons with other, more refined, distributions. Since it is atom-based, we denote the π-electron content of a ring H based on this distribution by $\pi_a(H)$. Following the reference cited above, the **π-electron excess** of a bounded face H of G is defined as the difference between $\overline{\pi}(H)$ and $\pi_a(H)$. We denote this quantity by $\varepsilon_\pi(H)$. Hence, $\varepsilon_\pi(H) = \overline{\pi}(H) - \pi_a(H)$. In the next section we compute $\overline{\pi}(H)$ and $\varepsilon_\pi(H)$ for all hexagons of a benzenoid parallelogram $B_{m,n}$.

3. Main Results

Let us consider a benzenoid parallelogram $B_{m,n}$. We assume $m > 1$; the case $m = 1$ was considered in [6]. This section generalizes the results of the special case $m = n$ considered in [8]. We start by establishing explicit formulas for importances of edges in $B_{m,n}$. Those importances depend on the edge type (v, d, or a) and position in $B_{m,n}$. The case of vertical edges is the simplest and we treat it first.

Lemma 1:

$$\iota(v_{i,j}) = \binom{i+j-1}{i-1}\binom{m+n-(i+j)}{m-i}.$$

Proof: The nature of the above-mentioned correspondence between perfect matchings and lattice paths is such that the vertical edges in a perfect matching are mapped to vertical steps in the corresponding lattice path. Hence, the number of perfect matchings of $B_{m,n}$ containing a given vertical edge $v_{i,j}$ is equal to the number of lattice paths containing the vertical edge corresponding to $v_{i,j}$. This, in turn, is equal to the product of the numbers of lattice paths in two smaller rectangles. Depending on the position of $v_{i,j}$ within $B_{m,n}$, one of the rectangles can be degenerated. The claim now follows from the well-known formula for the number of lattice paths in such rectangles. The correspondence and the resulting rectangles are shown in Figure 3. $\qquad \square$

Importances of descending edges can be related to the importances of vertical edges using a transformation mapping $B_{m,n}$ to $B_{n,m}$.

Lemma 2:

$$\iota(d_{i,j}) = \binom{i+j-1}{j-1}\binom{m+n-(i+j)}{n-j}.$$

Proof: By rotating $B_{m,n}$ clockwise for $\pi/3$ and reflecting the result across a horizontal line in a way shown in Figure 4 we obtain a benzenoid parallelogram $B_{n,m}$. Descending edges of $B_{m,n}$ are mapped to the vertical edges of $B_{n,m}$ so that $d_{i,j}$ becomes $v_{j,i}$. The claim now follows from Lemma 1. $\qquad \square$

Although no similar trick can be employed to map the ascending edges of $B_{m,n}$ to vertical edges of some other benzenoid parallelogram, their importances can
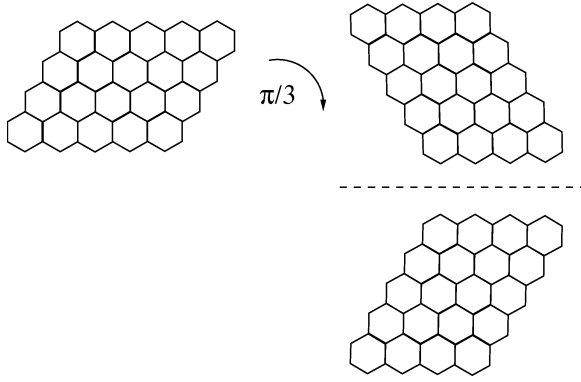
Fig. 4. Mapping descending edges to the vertical ones.

Fig. 5 (colour online). π-electron excess of internal hexagons.

still be expressed in terms of importances of vertical edges.

Lemma 3:

$$\iota(a_{i,j}) = \binom{m+n}{m} - \iota(v_{i,j}) - \iota(v_{j,i}).$$

Proof: The edges $v_{i,j}$, $d_{i,j}$, and $a_{i,j}$ meet at the vertex in the upper right corner of $H_{i,j}$. Since the importances of all edges incident to any vertex must add up to the total number of perfect matchings in the graph, the claim follows from Lemmas 1 and 2.   □

Now we can determine the total π-electron content of an internal hexagon of $B_{m,n}$.

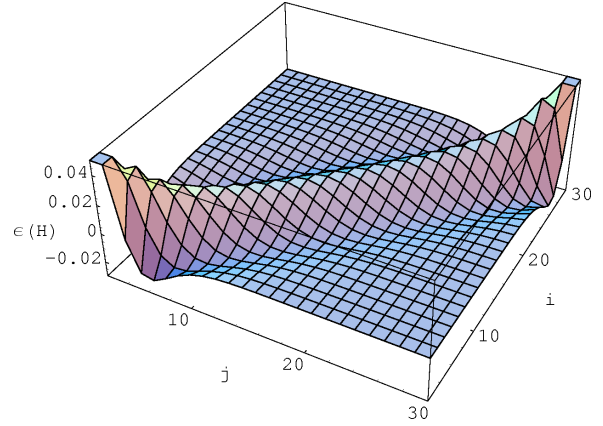**Lemma 4:** Let $H_{i,j}$ be an internal hexagon of $B_{m,n}$. Then

$$\pi(H) = 2\binom{m+n}{m} + \iota(v_{i,j}) - \iota(v_{i-1,j})$$
$$+ \iota(v_{i,j-1}) - \iota(v_{i+1,j-1}).   □$$

The result follows immediately from the above lemmas and Theorem A. By dividing the above expression by $\binom{m+n}{m}$ we obtain an explicit formula for the average π-electron content of an internal hexagon.

Theorem 5: Let $H_{i,j}$ be an internal hexagon of $B_{m,n}$. Then

$$\overline{\pi}(H) = 2 + [\iota(v_{i,j}) - \iota(v_{i-1,j}) + \iota(v_{i,j-1})$$
$$- \iota(v_{i+1,j-1})] \Big/ \binom{m+n}{m}.   □$$

By noticing that 2 is exactly equal to $\pi_a(H_{i,j})$, we immediately obtain an expression for the π-electron excess of an internal hexagon.

Corollary 6: Let $H_{i,j}$ be an internal hexagon of $B_{m,n}$. Then

$$\varepsilon_\pi(H_{i,j}) = [\iota(v_{i,j}) - \iota(v_{i-1,j}) + \iota(v_{i,j-1})$$
$$- \iota(v_{i+1,j-1})] \Big/ \binom{m+n}{m}.   □$$

Closer examination of the above expression for large m and n reveals some interesting numerical patterns. In Figure 5 we show the plot of $\varepsilon_\pi(H_{i,j})$ for internal hexagons of $B_{31,31}$. We see that there is a prominent ridge along the longer diagonal of the parallelogram, accompanied by two ditches running parallel to it on each side and gradually flattening out toward zero near the other two corners of the parallelogram. Those observations can be verified by direct computations. The choice $m = n$ is not essential – it was introduced to eliminate one parameter and simplify the computation. Even so simplified it remains tedious and does not offer any new insights, so we omit the details.

Figure 5 is in agreement with the fact that in benzenoid rhombi Clar formulas show that the π-electron sextets are along their longer diagonal. We refer the reader to [13] for more information on Clar π-sextets.

Let us now look at the border hexagons. It suffices to consider $H_{1,1}$, $H_{1,n}$, and $H_{1,j}$, $j = 2, \ldots, n-1$.

Lemma 7:

$$\overline{\pi}(H_{1,1}) = 4 + 2\frac{mn}{(m+n)(m+n-1)}$$
$$\overline{\pi}(H_{1,n}) = 3 + \frac{m+n-mn+2}{\binom{m+n}{m}}.   □$$

Both results follow straightforwardly from previous lemmas and Theorem A. For $m = n$ the first formula

reproduces the result of reference [8] for the corner hexagons of benzenoid rhombi. We notice that the non-constant term of the right-hand side of the formula for $\overline{\pi}(H_{1,n})$ is negative for $m+n > 5$.

Lemma 8: Let $2 \leq j \leq n-1$. Then

$$\overline{\pi}(H_{1,j}) = 3 + \frac{m+2n+1}{m-1} \binom{m+n-j-1}{m-2} \bigg/ \binom{m+n}{m}. \quad \Box$$

The result follows by simplifying the expression resulting from application of Theorem A. The non-constant term on the right-hand side is equal to $\varepsilon_{\pi}(H_{1,j})$. Let us denote its numerator by $p(j)$, hence $p(j) = \frac{m+2n+1}{m-1} \binom{m+n-j-1}{m-2}$. This is a polynomial in j of degree $m-1$. It has exactly $m-1$ real zeros; the smallest one is $\frac{m+2n-1}{m-1}$, the next largest is $n+2$. Between them must be exactly one zero of $p'(j)$, where $p(j)$ has a local minimum. Hence, there must be an index j_0 between 2 and $n-1$ such that $p(j_0) \leq p(j_0+1)$. It follows by a straightforward calculation that j_0 must satisfy $j_0 \geq \frac{(m-2)(m+2n+1)+(m+1)(n+1)}{m^2-1}$. By setting $m = n$ we obtain $j_0 = \lceil \frac{4m+1}{m-1} \rceil$. For large m it tends toward 4, hence, the minimum π-electron excess is achieved on $H_{1,4}$ for all m big enough. This is fully consistent with the position of the sub-diagonal ditch for internal hexagons. Indeed, a similar analysis shows that $\varepsilon_{\pi}(H_{2,j})$ is minimized for $j_0 = \lceil \frac{7m+1+\sqrt{25m^2-34m-23}}{2(m+1)} \rceil$, and this tends to 6 for large m. The positions of both minima are consistent with the results reported in Table 2 of reference [8] for $n = m = 8$.

On the whole, our analysis shows that for large $m \approx n$ both internal hexagons and border hexagons that are not in the corners of $B_{m,n}$ receive roughly the same share of π-electrons as allotted to them by the atom-based distribution π_a. The situation is different with corner hexagons. It is easy to see that $\pi_a(H_{1,1}) = 13/3$ and $\pi_a(H_{1,n}) = 11/3$. Taken together, the four corner hexagons receive 16 electrons under the atom-based distribution. On the other hand, from our formulas it follows that they collectively receive only 15 electrons. The hexagons $H_{1,1}$ and $H_{n,n}$ receive, in the limit, 4.5 electrons each, while the other two corner hexagons receive 3 electrons each. Hence, there is a net migration of 4/3 electrons from the hexagons at the ends of the shorter diagonal of $B_{m,n}$. One-third of one electron is shared between the other two corner hexagons, and the remaining one electron is distributed among non-corner hexagons. The exact nature of this distribution depends on the ratio of m and n.

Let us set $n = km$. It suffices to consider $k \geq 1$. It is easy to see that the average electron contents of the corner hexagons are not affected and remain 4.5 and 3, respectively, in the limit for large m and n. Let us look at the non-corner hexagons of the longer side of $B_{m,n}$. By summing $\overline{\pi}(H_{1,j})$ over $2 \leq j \leq n-1$ we get

$$\sum_{j=2}^{n-1} \overline{\pi}(H_{1,j}) = 3(n-2) + \frac{(m^2+n)(m+2n+1)}{(m-1)(n+1)(m+n)} - \frac{2mn}{(m+n)(m+n-1)} - \frac{m+1}{m-1} + R(m,n).$$

Here $R(m,n)$ denotes some terms quadratic and linear in m and n divided by $\binom{m+n}{m}$ that vanish for large m and n. By setting $m = n$ we obtain that $\sum_{j=2}^{n-1} \overline{\pi}(H_{1,j}) \longrightarrow 3(m-2)$, hence the non-corner hexagons of the longer side do not profit from the electron migration from $H_{1,n}$. However, for general $k > 1$, simplifying the right-hand side of the above expression yields the total π-electron excess of the longer side as $\frac{3k+1}{k(k+1)^2} - 1$. This quantity is negative for all $k > 1$ and tends to -1 as $k \longrightarrow \infty$. Hence, for long benzenoid parallelograms there is also a net migration of electrons from their longer sides. This is intuitively clear, since, in accordance with our previous results, as the parallelogram is stretched, more and more hexagons of the bottom row fall deeper into the sub-diagonal ditch. The electrons cannot go to the hexagons on the shorter sides, since they too fall either in a ditch or in the flat but still slightly negative area. Hence they must end in the diagonal ridge, in particular near its end-hexagons.

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