# Partitioning of $\pi$-Electrons in Rings of Fibonacenes

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The partitioning of $\pi$-electrons into rings of benzenoid hydrocarbons is examined in the case of fibonacenes. It is demonstrated that the $\pi$-electron contents (*ECs*) of the hexagons of fibonacenes satisfy the following peculiar regularities: Let $h$ be the number of hexagons, and $EC(i)$ the electron content of the $i$-th hexagon. Then $EC(i)$ is maximal for $i = 1$ and $i = h$, and minimal for $i = 2$ and $i = h - 1$. Going from the end towards the center of the fibonacene chain, $EC(1) > EC(3) > EC(5) > \cdots$ and $EC(2) < EC(4) < EC(6) < \cdots$ and $EC(1) > EC(2) < EC(3) > EC(4) < EC(5) > EC(6) < \cdots$. For large values of $h$, the asymptotic values of $EC(1)$ and $EC(2)$ are 5.146 and 3.798, whereas of the central ring(s) 4 $\pi$-electrons.

*Key words:* Benzenoid Hydrocarbon; Fibonacene; Partition of $\pi$-Electrons; $\pi$-Electron Content (of a Ring).

## 1. Introduction

Recently two of the present authors proposed a method for partitioning of $\pi$-electrons in rings of polycyclic aromatic compounds [1] and eventually applied it to numerous benzenoid [1, 2], coronoid [3], and nonalternant conjugated species [4]. Some general properties of the $\pi$-electron contents of rings in benzenoid molecules were also established [5 – 8].

According to [1], the fraction of the total number of $\pi$-electrons that is attributed to a ring $R$ of a polycyclic conjugated hydrocarbon $H$, named "$\pi$-electron content" ($EC$) [5], can be computed by means of the expression

$$EC = EC(R) = 2\sum_{*} P_{\mathrm{rs}} + \sum_{**} P_{\mathrm{rs}} \tag{1}$$

where $P_{\mathrm{rs}}$ denotes the Pauling bond order of the carbon–carbon bond rs, and where $\sum_{*}$ and $\sum_{**}$ indicate summation over bonds belonging solely to $R$, and shared by $R$ and another ring of $H$, respectively.

The Pauling bond order is defined as

$$P_{\mathrm{rs}} = \frac{K_{\mathrm{rs}}\{H\}}{K\{H\}}, \tag{2}$$

where $K\{H\}$ is the number of Kekulé structures of $H$, whereas $K_{\mathrm{rs}}\{H\}$ is the number of those Kekulé structures of $H$ in which the bond rs is double. For more details on the Pauling bond order see [5, 6, 9] and the references cited therein.

From (1) and (2) we see that the $EC$-values are fully determined by the Kekulé structures of the underlying conjugated molecule. From this fact it follows that isoarithmic benzenoid hydrocarbons [10, 11] will have an identical partitioning of $\pi$-electrons into rings. (Note that in the recent review [11] the term "iso-Kekuléan" is being used instead of "isoarithmic".)

Fibonacenes are unbranched catacondensed benzenoid hydrocarbons in which all non-terminal hexagons are angularly annelated [9]. Their name was coined [10, 12], bearing in mind that the number of Kekulé structures of any fibonacene with $h$ hexagons is equal to the $(h+1)$-th Fibonacci number [9]. All fibonacenes with the same number of hexagons are isoarithmic [10]. Therefore, all fibonacenes with the same number of hexagons have an identical partitioning of $\pi$-electrons into rings.

In Fig. 1 the five distinct hexacyclic fibonacenes are depicted, starting with fulminene (**1**), together with their helicenic congener hexahelicene (**6**). For more details on fibonacenes see [10, 13 – 16].

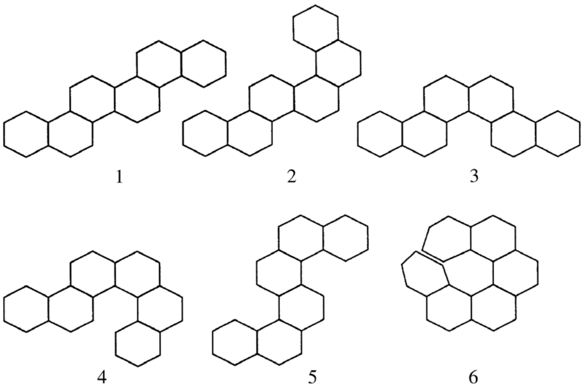

Fig. 1. The five distinct fibonacenes (**1**−**5**) and hexahelicene (**6**) with six hexagons. These are unbranched catacondensed systems with two terminal hexagons and four angularly annelated hexagons. Fibonacenes are isoarithmic [10], which means that all their properties that are deduced solely from Kekulé structures are identical. In particular, fibonacenes have identical partitioning of their $\pi$-electrons, as computed by means of (1).

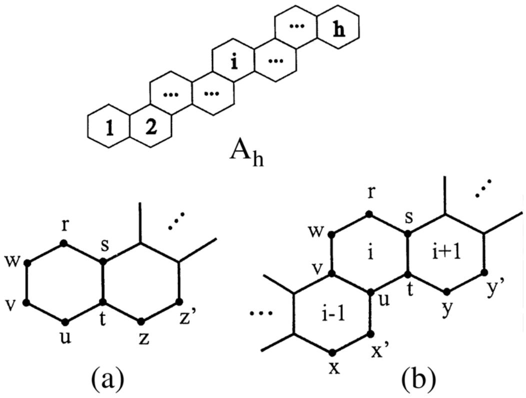

Fig. 2. The $h$-cyclic zig-zag fibonacene $A_h$ and the numbering of its hexagons. The labeling of the carbon atoms, used in the computation of the $\pi$-electron contents of the hexagons of $A_h$ is indicated in diagram $(a)$ for the terminal hexagon ($i=1$) and in diagram $(b)$ for the $i$-th hexagon ($i = 2,3,\ldots,h-1$).

Table 1. The $\pi$-electron contents $EC(i)$ of the hexagons of fibonacenes with 12, 13, 14, and 15 hexagons. The labeling of the hexagons is shown in Figure 2. These examples illustrate the four different cases $h \equiv k \pmod 4, k = 0,1,2,3$. Italics denote $EC$-values of the central rings.

| $i$ | $h=12$ | $h=13$ | $h=14$ | $h=15$ |
|---|---|---|---|---|
| 1 | 5.1459 | 5.1459 | 5.1459 | 5.1459 |
| 2 | 3.7984 | 3.7984 | 3.7984 | 3.7984 |
| 3 | 4.0769 | 4.0770 | 4.0770 | 4.0770 |
| 4 | 3.9708 | 3.9705 | 3.9706 | 3.9706 |
| 5 | 4.0106 | 4.0115 | 4.0111 | 4.0113 |
| 6 | *3.9973* | 3.9951 | 3.9959 | 3.9956 |
| 7 | *3.9973* | *4.0033* | *4.0010* | 4.0019 |
| 8 | 4.0106 | 3.9951 | *4.0010* | *3.9987* |
| 9 | 3.9708 | 4.0115 | 3.9959 | 4.0019 |
| 10 | 4.0769 | 3.9705 | 4.0111 | 3.9956 |
| 11 | 3.7984 | 4.0770 | 3.9706 | 4.0113 |
| 12 | 5.1459 | 3.7984 | 4.0770 | 3.9706 |
| 13 |  | 5.1459 | 3.7984 | 4.0770 |
| 14 |  |  | 5.1459 | 3.7984 |
| 15 |  |  |  | 5.1459 |

Because all fibonacenes (with the same number $h$ of hexagons) are mutually isoarithmic, it suffices to determine the $\pi$-electron contents in any of them. In what follows, we consider the zig-zag fibonacene series $\{A_h \,|\, h = 2,3,\ldots\}$, whose first members are naphthalene ($h=2$), phenanthrene ($h=3$), chrysene ($h=4$), picene ($h=5$), fulminene ($h=6$), $\ldots$ . The general formula of the zig-zag fibonacene is shown in Fig. 2, where also the numbering of its hexagons is indicated.

In what follows, the $\pi$-electron content of the $i$-th hexagon of $A_h$, computed according to (1), will be denoted by $EC(i)$ or, if the number of hexagons needs to be specified, by $EC(i,h)$. In both cases, $i = 1,2,\ldots,h$. Because of the molecular symmetry, the relation

$$EC(i) = EC(h-i+1) \tag{3}$$

holds for all $i = 1,2,\ldots,h$.

As already explained, $EC(i,h)$ is equal to the $\pi$-electron content of the $i$-th hexagon not only of $A_h$, but of any $h$-cyclic fibonacene.

Numerical calculations of the $EC$-values of hexagons of fibonacenes, based on (1), revealed [1] certain regularities that are illustrated in Table 1.

By inspection of the data given in Table 1 we readily conclude the following: $EC(i)$ is maximal for $i=1$ and $i=h$, and minimal for $i=2$ and $i=h-1$. Going from the first hexagon ($i=1$) towards the center of the fibonacene chain, the sequence $EC(1), EC(3), EC(5), \ldots$ monotonically decreases whereas the sequence $EC(2), EC(4), EC(6), \ldots$ monotonically increases. Furthermore,

$$\begin{aligned} EC(1) &> EC(2) < EC(3) \\ &> EC(4) < EC(5) > EC(6) < \cdots . \end{aligned}$$

Bearing the above in mind, as well as the symmetry condition (3), we see that four (slightly) different cases occur, depending on the remainder after dividing $h$ by 4.

**Case 1:** $h = 4k$, i. e. $h \equiv 0 \pmod 4$

$$\begin{aligned} &EC(1) > EC(3) > \cdots > EC(2k-1) \\ &= EC(2k+2) < EC(2k+4) < \cdots < EC(h), \end{aligned} \tag{4}$$

$$\begin{aligned}&EC(2) < EC(4) < \cdots < EC(2k)\\ &= EC(2k+1) > EC(2k+3) > \cdots > EC(h-1),\end{aligned} \tag{5}$$

$$\begin{aligned}&EC(1) > EC(2) < EC(3) > EC(4) < \cdots\\ &\quad < EC(2k-1) > EC(2k) =\\ &EC(2k+1) < EC(2k+2) > \cdots\\ &\quad > EC(h-1) < EC(h).\end{aligned} \tag{6}$$

**Case 2:** $h = 4k+1$, i. e. $h \equiv 1 \pmod 4$

$$\begin{aligned}&EC(1) > EC(3) > \cdots > EC(2k-1)\\ &\quad > EC(2k+1) < EC(2k+3) < \cdots\\ &\quad < EC(h),\end{aligned} \tag{7}$$

$$\begin{aligned}&EC(2) < EC(4) < \cdots < EC(2k)\\ &= EC(2k+2) > EC(2k+4) > \cdots > EC(h-1),\end{aligned} \tag{8}$$

$$\begin{aligned}&EC(1) > EC(2) < EC(3) > EC(4) < \cdots\\ &\quad < EC(2k-1) > EC(2k) < EC(2k+1)\\ &\quad > EC(2k+2) < \cdots > EC(h-1) < EC(h).\end{aligned} \tag{9}$$

**Case 3:** $h = 4k+2$, i. e. $h \equiv 2 \pmod 4$

$$\begin{aligned}&EC(1) > EC(3) > \cdots > EC(2k+1)\\ &= EC(2k+2) < EC(2k+4) < \cdots < EC(h),\end{aligned} \tag{10}$$

$$\begin{aligned}&EC(2) < EC(4) < \cdots < EC(2k)\\ &= EC(2k+3) > EC(2k+5) > \cdots > EC(h-1),\end{aligned} \tag{11}$$

$$\begin{aligned}&EC(1) > EC(2) < EC(3) > EC(4) < \cdots\\ &\quad > EC(2k) < EC(2k+1) = EC(2k+2)\\ &\quad > EC(2k+3) < E(2k+4) > \cdots\\ &\quad > EC(h-1) < EC(h).\end{aligned} \tag{12}$$

**Case 4:** $h = 4k+3$, i. e. $h \equiv 3 \pmod 4$

$$\begin{aligned}&EC(1) > EC(3) > \cdots > EC(2k+1)\\ &= EC(2k+3) < EC(2k+5) < \cdots < EC(h),\end{aligned} \tag{13}$$

$$\begin{aligned}&EC(2) < EC(4) < \cdots < EC(2k) < EC(2k+2)\\ &\quad > EC(2k+4) > \cdots > EC(h-1),\end{aligned} \tag{14}$$

$$\begin{aligned}&EC(1) > EC(2) < EC(3) > EC(4) < \cdots\\ &< EC(2k+1) > EC(2k+2) < EC(2k+3)\\ &> EC(2k+4) < \cdots > EC(h-1) < EC(h).\end{aligned} \tag{15}$$

In this paper we demonstrate the general validity of the above relations.

## 2. Computing the $\pi$-Electron Contents of Rings of Fibonacenes

The Fibonacci numbers $F_k$ are defined by means of the recursion relation $F_{k+2} = F_{k+1} + F_k$ and the initial conditions $F_0 = F_1 = 1$. Consequently, $F_2 = 2$, $F_3 = 3$, $F_4 = 5$, $F_6 = 8$, etc.

The starting point of our consideration is the well known relation [9]

$$K\{A_h\} = F_{h+1}\ . \tag{16}$$

We note in passing that $F_{h+1}$ is the maximal number of Kekulé structures of a $h$-cyclic unbranched catacondensed benzenoid molecule [17].

In order to compute the Pauling bond orders of the carbon bonds in the $i$-th ring of a fibonacene, $2 \le i \le h-1$, we refer to diagram $(b)$ in Figure 2.

Consider the bond rs. If rs is chosen to be double, then also the bonds tu, vw, xx', and yy' must be double. (The bonds ty and ux' cannot be double when rs and vw are double because of bonding conflict at the terminal rings of the chain.) By deleting the bonds rs, tu, vw, xx', and yy' from $A_h$, the molecule decomposes into two fragments, both of which being fibonacenes: $A_{i-2}$ and $A_{h-i-1}$. Consequently,

$$K_{\mathrm{rs}}\{A_h\} = K\{A_{i-2}\} \times K\{A_{h-i-1}\}$$

and, bearing in mind (16),

$$K_{\mathrm{rs}}\{A_h\} = F_{i-1}F_{h-i}\ .$$

This finally results in

$$P_{\mathrm{rs}} = \frac{F_{i-1}F_{h-i}}{F_{h+1}}\ . \tag{17}$$

In a fully analogous manner we compute the Pauling bond orders for the other five bonds of the ring $i$:

$$P_{\mathrm{st}} = \frac{F_i F_{h-i}}{F_{h+1}}, \tag{18}$$

$$P_{\mathrm{tu}} = \frac{F_{i-1}F_{h-i}}{F_{h+1}} = P_{\mathrm{rs}}, \tag{19}$$

$$P_{\mathrm{uv}} = \frac{F_{i-1}F_{h-i+1}}{F_{h+1}}, \tag{20}$$

$$P_{\mathrm{vw}} = \frac{F_{i-1}F_{h-i}}{F_{h+1}} = P_{\mathrm{rs}}, \tag{21}$$

$$P_{\mathrm{wr}} = \frac{F_i F_{h-i+1}}{F_{h+1}}. \tag{22}$$

Using the relations (17) – (22) it is possible to express $EC(i)$ in terms of Fibonacci numbers. Indeed, in view of formula (1),

$$EC(i) = 2\,[P_{\mathrm{rs}} + P_{\mathrm{tu}} + P_{\mathrm{vw}} + P_{\mathrm{wr}}] + [P_{\mathrm{st}} + P_{\mathrm{uv}}]\,,$$

which combined with (17) – (22) yields

$$EC(i) = 2 + 4\,\frac{F_{i-1}F_{h-i}}{F_{h+1}} + \frac{F_i F_{h-i} + F_{i-1}F_{h-i+1}}{F_{h+1}}$$

because $P_{\mathrm{vw}} + P_{\mathrm{wr}} = 1$. (Recall that the sum of Pauling bond orders over all bonds ending at a given atom equals to unity [6, 18].)

Now, by applying the identity

$$F_h = F_i F_{h-i} + F_{i-1}F_{h-i-1}$$

we get

$$\begin{aligned} &F_i F_{h-i} + F_{i-1}F_{h-i+1} \\ &\quad = F_h - F_{i-1}F_{h-i-1} + F_{i-1}F_{h-i+1} \\ &\quad = F_h + F_{i-1}\,(F_{h-i+1} - F_{h-i-1}) \\ &\quad = F_h + F_{i-1}\,(F_{h-i} + F_{h-i-1} - F_{h-i-1}) \\ &\quad = F_h + F_{i-1}F_{h-i}. \end{aligned}$$

Therefore

$$\begin{aligned} EC(i) &= 2 + 4\,\frac{F_{i-1}F_{h-i}}{F_{h+1}} + \frac{F_h + F_{i-1}F_{h-i}}{F_{h+1}} \\ &= 2 + \frac{F_h}{F_{h+1}} + 5\,\frac{F_{i-1}F_{h-i}}{F_{h+1}}\ . \end{aligned}$$

In order to deduce the analogous formula valid for $i = 1$ (and, by symmetry, also for $i = h$), consider diagram $(a)$ in Figure 2. This time

$$EC(1) = 2\,[P_{\mathrm{rs}} + P_{\mathrm{tu}} + + P_{\mathrm{uv}} + P_{\mathrm{vw}} + P_{\mathrm{wr}}] + [P_{\mathrm{st}}]\,,$$

which in view of $P_{\mathrm{vw}} + P_{\mathrm{wr}} = 1$ and $P_{\mathrm{tu}} + P_{\mathrm{uv}} = 1$ is simplified as

$$EC(1) = 4 + 2P_{\mathrm{rs}} + P_{\mathrm{st}}.$$

From diagram $(a)$ is seen that, if the bond rs is fixed to be double, then so are also the bonds tu, vw, and zz'. By deleting them from $A_h$, what remains is $A_{h-2}$. Consequently

$$K_{\mathrm{rs}}\{A_h\} = K\{A_{h-2}\} = F_{h-1}$$

and

$$P_{\mathrm{rs}} = \frac{F_{h-1}}{F_{h+1}}\ .$$

In a fully analogous manner we conclude that $P_{\mathrm{st}} = P_{\mathrm{rs}}$, from which it follows

$$EC(1) = 4 + 3\,\frac{F_{h-1}}{F_{h+1}} = 4 + 3\,\frac{F_{h+1} - F_h}{F_{h+1}} = 7 - 3\,\frac{F_h}{F_{h+1}}\ .$$

In summary, the $\pi$-electron content of the $i$-th hexagon of a fibonacene with $h$ hexagons, $h \geq 2$, is given by

$$EC(i) = \begin{cases} 7 - 3\,\dfrac{F_h}{F_{h+1}} \\ \text{for } i = 1 \text{ and } i = h \\ 2 + \dfrac{F_h}{F_{h+1}} + 5\,\dfrac{F_{i-1}F_{h-i}}{F_{h+1}} \\ \text{for } i = 2, 3, \ldots, h-1 \end{cases}\ . \tag{23}$$

It remains now to show that the relations (4) – (15) follow from (23).

## 3. Proving the Relations (4) – (15)

The fact, that the symmetry relation (3) is satisfied, is evident from the expressions (23). Bearing in mind (3) as well as (4) – (15), it is sufficient to show that

$$\begin{aligned} &EC(1) > EC(2) < EC(3) > EC(4) < \cdots \\ &\quad > EC(h-1) < EC(h) \end{aligned} \tag{24}$$

with

$$EC(h/2) = EC(h/2+1)$$

in the case when $h$ is even, and

$$\begin{aligned} &EC(1) > EC(3) > \cdots > EC(\alpha); \\ &\alpha = 2\,\lfloor (h-1)/4 \rfloor + 1, \end{aligned} \tag{25}$$

$$\begin{aligned} &EC(2) < EC(4) < \cdots < EC(\beta); \\ &\beta = 2\,\lfloor (h+1)/4 \rfloor. \end{aligned} \tag{26}$$

Recall that, as usual, $\lfloor x \rfloor$ denotes the greatest integer that is not greater than $x$.

Because the expression for $EC(1)$ has a different algebraic form than the expressions for $EC(i)$ $,i = 2, 3, \ldots, h-1$, we first show that $EC(1) > EC(2)$ and $EC(1) > EC(3)$, i. e. that

$$\begin{aligned} 7 - 3\,\frac{F_h}{F_{h+1}} &> 2 + \frac{F_h}{F_{h+1}} + 5\,\frac{F_1 F_{h-2}}{F_{h+1}}, \\ 7 - 3\,\frac{F_h}{F_{h+1}} &> 2 + \frac{F_h}{F_{h+1}} + 5\,\frac{F_2 F_{h-3}}{F_{h+1}}, \end{aligned}$$

which are equivalent to

$$5 > 4\,\frac{F_h}{F_{h+1}} + 5\,\frac{F_{h-2}}{F_{h+1}}\,,$$
$$5 > 4\,\frac{F_h}{F_{h+1}} + 10\,\frac{F_{h-3}}{F_{h+1}}\,,$$

and

$$5F_{h+1} > 4F_h + 5F_{h-2}\,,$$
$$5F_{h+1} > 4F_h + 10F_{h-3}\,.$$

The latter inequalities hold because

$$\begin{aligned}5F_{h+1} &= 5F_h+5F_{h-1}>4F_h+5F_{h-1}>4F_h+5F_{h-2}\,,\\ 5F_{h+1} &= 5F_h+5F_{h-1}>4F_h+5F_{h-1}\\ &= 4F_h+5F_{h-2}+5F_{h-3}>4F_h+5F_{h-3}+5F_{h-3}\,.\end{aligned}$$

From formulas (23) we see that for $i > 1$, the sign of the difference $EC(i) - EC(i+1)$ depends solely on the sign of the difference $F_{i-1}F_{h-i} - F_i F_{h-i-1}$. In the Appendix we deduce the identity (29). By means of it we get

$$F_{i-1}F_{h-i} - F_i F_{h-i-1} = (-1)^{i+1} F_{h-2i-1}\,. \qquad (27)$$

Relation (27) is applicable for $h - 2i - 1 \geq 0$, i. e. for $i \leq (h-1)/2$, i. e. for the hexagons lying in the first half of the fibonacene chain.

The right-hand side of (27) is negative-valued for $i = 2,4,6,\ldots$, and therefore $EC(2) < EC(3)$, $EC(4) < EC(5)$, $EC(6) < EC(7)$, etc. The right–hand side of (27) is positive–valued for $i = 3,5,7,\ldots$, implying $EC(3) > EC(4)$, $EC(5) > EC(6)$, $EC(7) < EC(8)$, etc.

Combining the above inequalities with the symmetry relation (3) we arrive at (24).

The inequalities (25) and (26) are verified by means of a similar reasoning, based on identity (30). Indeed, for $i > 1$ the sign of the difference $EC(i) - EC(i+2)$ is determined by the sign of $F_{i-1}F_{h-i} - F_{i+1}F_{h-i-2}$. Applying (30) we get

$$F_{i-1}F_{h-i} - F_{i+1}F_{h-i-2} = (-1)^{i+1} F_{h-2i-2} \qquad (28)$$

valid for $h - 2i - 2 \geq 0$, i. e. for the hexagons lying in the first half of the fibonacene chain.

If $i$ is odd, then the right-hand side of (28) is positive-valued, implying $EC(3) > EC(5)$, $EC(5) > EC(7)$, etc., proving the validity of (25). If $i$ is even, then the right–hand side of (28) is negative–valued, from which it follows $EC(2) < EC(4)$, $EC(4) < EC(6)$, etc. Thus also the relations (26) are proven.

## 4. Discussion

From the formulas (23) the earlier observed [1] method for the recursive calculation of $EC$-values is readily deduced and rationalized: Consider the auxiliary quantity $\eta(i,h) = EC(i,h)\cdot K\{A_h\} = EC(i,h)\cdot F_{h+1}$. From (23) we immediately see that

$$\eta(i,h) = \begin{cases} 7F_{h+1} - 3F_h \\ \text{for } i = 1 \text{ and } i = h \\ 2F_{h+1} + F_h + 5F_{i-1}F_{h-i} \\ \text{for } i = 2,3,\ldots,h-1 \end{cases}.$$

For any value of $i$, from the fundamental property of the Fibonacci numbers (namely, $F_k = F_{k-1} + F_{k-2}$), it follows

$$\eta(i,h) = \eta(i,h-1) + \eta(i,h-2)$$

and therefore

$$EC(i,h) = \frac{F_h}{F_{h+1}}\,EC(i,h-1) + \frac{F_{h-1}}{F_{h+1}}\,EC(i,h-2)\,,$$

which makes it possible to recursively compute the $\pi$-electron contents of rings of the $h$-cyclic fibonacene from the $\pi$-electron contents of the rings of the $(h-1)$-cyclic and $(h-2)$-cyclic fibonacenes [1].

The limit values (for $h \to \infty$) of the $\pi$-electrons contents are computed as follows. Starting with the asymptotic expression (valid for large values of $k$),

$$F_k \sim \frac{1}{\sqrt{5}}\left(\frac{\sqrt{5}+1}{2}\right)^k,$$

and using the formulas (23) we straightforwardly obtain

$$\lim_{h\to\infty} EC(1,h) = 7 - 3\,\tfrac{\sqrt{5}-1}{2} = 5.145898\ldots,$$
$$\lim_{h\to\infty} EC(2,h) = 2 + \tfrac{\sqrt{5}-1}{2} + 5\left(\tfrac{\sqrt{5}-1}{2}\right)^3 = 3.798374\ldots,$$
$$\lim_{h\to\infty} EC(3,h) = 2 + \tfrac{\sqrt{5}-1}{2} + 10\left(\tfrac{\sqrt{5}-1}{2}\right)^4 = 4.070014\ldots,$$
$$\lim_{h\to\infty} EC(4,h) = 2 + \tfrac{\sqrt{5}-1}{2} + 15\left(\tfrac{\sqrt{5}-1}{2}\right)^5 = 3.970583\ldots,$$
$$\lim_{h\to\infty} EC(5,h) = 2 + \tfrac{\sqrt{5}-1}{2} + 25\left(\tfrac{\sqrt{5}-1}{2}\right)^6 = 4.011236\ldots.$$

For hexagons around the middle of the fibonacene chain, that is, for $i \sim h/2$ the limit value of $EC(i,h)$ is 4.

Note that this is the *EC*-value of any ring in fibonacenic coronoids in which there is no beginning or end of the fibonacenic chain [3].

Any $h$-cyclic catacondensed benzenoid hydrocarbon possesses $4h+2$ $\pi$-electrons. Therefore the average electron content of a ring is $4+2/h$. Its limit value is 4, which coincides with the electron content of rings in the middle of (long) fibonacene chains.

From Table 1 we see that these limit values are (almost) achieved already at fibonacenes with ten and more hexagons.

## Appendix: Two Identities for Fibonacci Numbers

Let, as before, $F_k$ denote the $k$-th Fibonacci number. Let $a$ and $b$ be positive integers, such that $a > b$. Then

$$F_a F_b - F_{a+1} F_{b-1} = (-1)^b F_{a-b} \tag{29}$$

and

$$F_a F_b - F_{a+2} F_{b-2} = (-1)^{b-1} F_{a-b+1}\ . \tag{30}$$

In order to deduce (29) note that

$$\begin{aligned} F_aF_b - F_{a+1}F_{b-1} &= F_a(F_{b-1}+F_{b-2}) + (F_a + F_{a-1})F_{b-1} \\ &= -(F_{a-1}F_{b-1} - F_aF_{b-2}). \end{aligned}$$

Continuing the same transformation an additional $p-1$ times, we arrive at

$$F_aF_b - F_{a+1}F_{b-1} = (-1)^p (F_{a-p}F_{b-p} - F_{a+1-p}F_{b-1-p}).$$

Choosing $p = b-1$ and bearing in mind that $F_0 = F_1 = 1$ we get

$$F_a F_b - F_{a+1} F_{b-1} = (-1)^{b-1} (F_{a-b+1} - F_{a-b+2}),$$

from which identity (29) is obtained by taking into account that $F_{a-b+2} = F_{a-b+1} + F_{a-b}$.

In order to deduce (30), rewrite its left–hand side as

$$(F_a F_b - F_{a+1} F_{b-1}) + (F_{a+1} F_{b-1} - F_{a+2} F_{b-2})$$

and apply (29) to get

$$\begin{aligned} F_a F_b - F_{a+2} F_{b-2} &= (-1)^b F_{a-b} + (-1)^{b-1} F_{a-b+2} \\ &= (-1)^{b-1} (F_{a-b+2} - F_{a-b}). \end{aligned}$$

The identity (30) follows now because $F_{a-b+2} = F_{a-b+1} + F_{a-b}$.

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