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FLUORANTHENE AND ITS CONGENERS — A GRAPH THEORETICAL STUDY

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Abstract

Fluoranthene and its congeners are compounds which, in view of their chemical and physical properties, belong among benzenoid hydrocarbons. However, because of the presence of a five–membered ring, in all chemical–graph–theoretical considerations of benzenoid systems, fluoranthenes have been disregarded. The aim of this work is to establish the basic characteristics of the molecular graphs of fluoranthene–type benzenoid hydrocarbons. By this we prepare the theoretic framework for a systematic study of the topology–based physico–chemical properties of this class of polycyclic aromatic hydrocarbons.

INTRODUCTION

Benzenoid systems (also referred to as hexagonal systems, polyhexses, fusenes, or hexagonal animals) are one of the most thoroughly studied class of molecular graphs (see the reviews [1–7], the books [8–12], and the references cited therein). A precise definition of benzenoid systems, as well as a survey of their basic graph–theoretical properties can be found in the book [10]. In view of the way in which the concept of benzenoid systems is conceived, the respective molecular graphs must not possess odd-membered cycles. Consequently, fluoranthene and its congeners were from the beginning excluded from consideration, and not a single graph–theory–based property thereof seems to have been reported in the chemical or mathematical literature.

The aim of the present work is to contribute towards filling of this gap.

FLUORANTHENE–TYPE BENZENOIDS

In Fig. 1 are depicted fluoranthene (**1**) and a few of its congeners. From these examples the readers will immediately get an idea of their general structure.

A more formal definition of this class of polycyclic aromatic compounds is as follows.

Let X be a benzenoid system [10]. Let u and v be two vertices of X whose degree is two, and which both are adjacent to a vertex w of degree 3.

Let Y be another benzenoid system. Let a and b be two adjacent vertices of Y whose degree is two.

The fluoranthene–type benzenoid system F is obtained by joining (with a new edge) the vertices u and a, and by joining (with a new edge) the vertices v and b, see Fig. 2.

What first needs to be noticed is that the vertices a, b, v, w, u of F form a five-membered cycle. Each fluoranthene–type benzenoid system possesses (by definition) exactly one five-membered cycle.

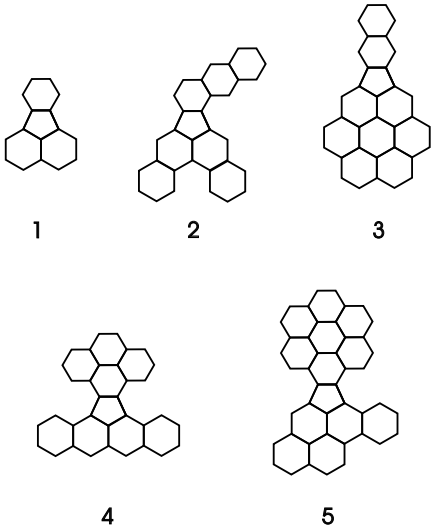

Fig. 1. Fluoranthene (**1**) and examples of fluoranthene–type benzenoid systems. **1** and **2** are cata-catacondensed, **3** is peri-catacondensed, **4** is cata-pericondensed, and **5** is peri-pericondensed; for details see text.

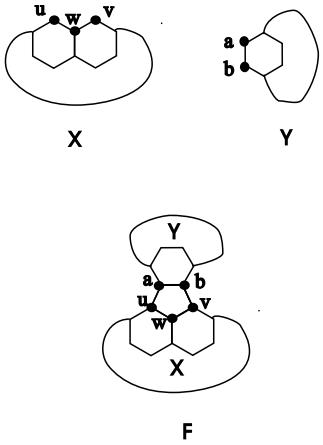

Fig. 2. The general form of a fluoranthene–type benzenoid system (F) and its construction from two benzenoid systems X and Y .

It is a matter of choice whether helicenic and other geometrically non-planar species (such as those depicted in Fig. 3) should be permitted in the above definition. We prefer that such "pathological" congeners of fluoranthene be disregarded. Thus the fluoranthene–type benzenoid systems considered by us must pertain to plane graphs composed of regular hexagons and a regular pentagon, all having same edge lengths. Non-adjacent hexagon–hexagon and hexagon–pentagon pairs must neither touch nor overlap.

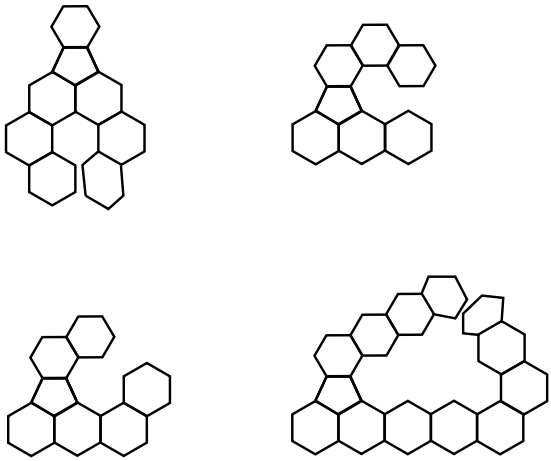

Fig. 3. Examples of fluoranthene–type species that are (by definition) excluded from consideration.

In what follows, instead of "*fluoranthene–type benzenoid system*" we shall say "*f-benzenoid system*" or shorter, "*f-benzenoid*".

BASIC STRUCTURAL DETAILS AND CLASSIFICATION OF f-BENZENOIDS

Let F be an f-benzenoid system. The number of its vertices, edges, and hexagons will be denoted by n, m, and h, respectively. In view of the fact that F possesses

$h + 1$ independent cycles (h hexagons and a pentagon), these three quantities are related as

$$m = n + h \ .$$

Some vertices and edges of F lie on its boundary (perimeter). These will be referred to as external vertices and external edges. Their numbers are denoted by n_{ex} and m_{ex}, respectively. Evidently, $n_{ex} = m_{ex}$, and the size of the boundary of F is equal to n_{ex}.

The vertices and edges that are not external are said to be internal. Their numbers are denoted by n_i and m_i. Clearly, $n_{ex} + n_i = n$ and $m_{ex} + m_i = m$.

The vertex w of F (see Fig. 2) does not lie on the boundary (perimeter) of F. Thus w is an internal vertex of F, and every f-benzenoid system possesses at least one internal vertex.

By elementary combinatorial reasoning we arrive at the following:

Theorem 1. If an f-benzenoid system has n vertices, m edges, h hexagons, and n_i internal vertices, then

$$n = 4h + 5 - n_i \tag{1}$$

$$m = 5h + 5 - n_i \ . \tag{2}$$

Corollary 1.1. The size of the perimeter of the f-benzenoid system specified in Theorem 1 is equal to

$$n_{ex} = m_{ex} = 4h + 5 - 2\,n_i \ . \tag{3}$$

In connection with the size of the boundary see also Corollary 2.1, which, in fact, can be deduced from Eq. (3).

Combining Eqs. (2) and (3), we arrive at:

Corollary 1.2. The number of internal edges of the f-benzenoid system specified in Theorem 1 is equal to $h + n_i$.

Recall that all internal edges connect vertices of degree 3, a detail that will be needed later.

A benzenoid system is said to be catacondensed if it has no internal vertices; otherwise it is pericondensed [10]. In view of this, we propose the following classification of f-benzenoid systems.

If the f-benzenoid system F has just a single internal vertex, then it is said to be cata-catacondensed. This happens when both fragments X and Y (as shown in Fig. 2) are catacondensed benzenoids. If X is pericondensed, and Y is catacondensed, then F is peri-catacondensed. If X is catacondensed, and Y is pericondensed then F is cata-pericondensed. If both X and Y are pericondensed, then F is said to be peri-pericondensed.

Examples of cata-cata–, peri-cata–, cata-peri–, and peri-pericondensed f-benzenoids are found in Fig. 2.

For cata-catacondensed f-benzenoids, $n_i = 1$. For peri-cata– and cata-pericondensed species, $n_i \geq 2$. For peri-pericondensed f-benzenoids, $n_i \geq 3$.

MORE STRUCTURAL DETAILS

Benzenoid systems are bipartite graphs and therefore possess only cycles of even size. f-Benzenoids possess a (single) five-membered cycle and are thus non-bipartite. In fact, f-benzenoids necessarily possess 5-, 6-, 9-, 10-, 11-, 13-, and 15-membered cycles, and may (but need not) possess also 12- and 14-membered cycles, as well as k-membered cycles for any $k \geq 16$. Only cycles of size 3, 4, 7, and 8 can never occur in an f-benzenoid system.

In Fig. 4 are depicted some cycles of the f-benzenoid system **3**.

By means of a proof technique analogous to what earlier was used for benzenoid systems [13,14] we can demonstrate the validity of the following:

Theorem 2. Let F be an f-benzenoid system and Z its cycle of size $|Z|$. If $|Z| \equiv 0$ $(mod\ 4)$ or $|Z| \equiv 3$ $(mod\ 4)$, then in the interior of Z there is an odd number of vertices. Otherwise, i. e., if $|Z| \equiv 1$ $(mod\ 4)$ or $|Z| \equiv 2$ $(mod\ 4)$, then in the interior of Z there is an even number of vertices or there are no vertices at all.

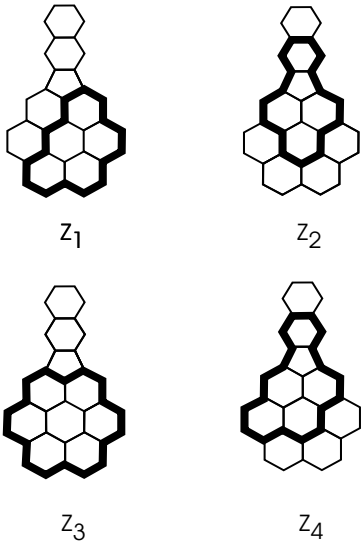

Fig. 4. The cycles Z_1, Z_2, Z_3, Z_4 of the f-benzenoid system **3** (cf. Fig. 1), indicated by heavy lines. Note that their sizes are 16, 17, 18, and 19, respectively. Note also that in the interior of Z_2 and Z_3 there is an even number (2 and 6) of vertices, whereas in the interior of Z_1 and Z_4 there is an odd number (3 and 3) of vertices. This illustrates Theorem 2.

Corollary 2.1. If $n_i(F)$ is odd, then the boundary of F is either of the size $4k$ or $4k+3$. If $n_i(F)$ is even, then the boundary of F is either of the size $4k+1$ or $4k+2$. All these four cases may happen, as shown in Fig. 5.

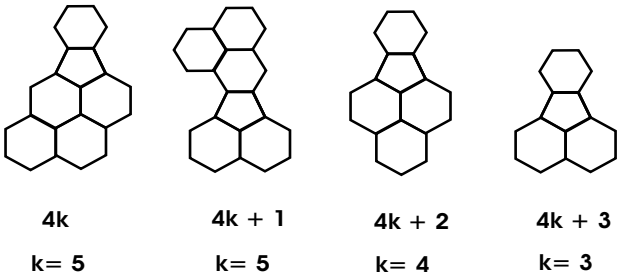

Fig. 5. f-Benzenoids with the smallest boundaries of sizes $4k$, $4k+1$, $4k+2$, and $4k+3$. The sizes of the boundaries are indicated.

An f-benzenoid system has vertices of degree 2 or 3. Let their number be n_2 and n_3, respectively, $n_2+n_3 = n$. By mathematical induction on the number of hexagons we easily verify that

$$n_3 = 2h$$

which, combined with Eq. (1) yields

$$n_2 = 2h + 5 - n_i \ . \tag{4}$$

From Eqs. (1) and (4) we conclude that the formula of a fluoranthene–type benzenoid hydrocarbon with h six-membered rings and n_i internal carbon atoms is $C_{4h+5-n_i}H_{2h+5-n_i}$. The formula of all cata-catacondensed f-benzenoids with h six-membered rings is then $C_{4h+4}H_{2h+4}$ and, consequently, all these hydrocarbons are isomers.

All vertices of degree two lie on the boundary. Therefore, the boundary contains $n_{ex} - n_2$ vertices of degree three, which by Eqs. (3) and (4) is equal to $2h - n_i$.

We say that an edge of a graph is of (i,j)-type if it connects a vertex of degree i with a vertex of degree j. In f-benzenoids only edges of type $(2,2)$, $(2,3)$, and $(3,3)$ occur. Their number is denoted by m_{22}, m_{23}, and m_{33}, respectively. Then

$$m_{22} + m_{23} + m_{33} = m \tag{5}$$

and

$$\begin{aligned} 2\,m_{22} + m_{23} &= 2\,n_2 \\ m_{23} + 2\,m_{33} &= 3\,n_3 \end{aligned}$$

from which

$$\frac{1}{2}\,(2\,m_{22} + m_{23}) + \frac{1}{3}\,(m_{23} + 2\,m_{33}) = n$$

i. e.,

$$6\,m_{22} + 5\,m_{23} + 4\,m_{33} = 6n \ . \tag{6}$$

In order to be able to solve the system of two equations (5) and (6) in three unknowns (m_{22}, m_{23}, and m_{33}) we need to examine the structural features occurring on the boundary of an f-benzenoid system.

We already know that on the boundary there are $2h+5-n_i$ vertices of degree two and $2h-n_i$ vertices of degree three. If we move along the boundary then the vertex degrees form one of the following sequences: 232 , 2332 , 23332 , 233332 , and 2333332 . These sequences pertain to structural features called "fissure", "bay", "cove", "fjord", and "lagoon" [10,15], see Fig. 6.

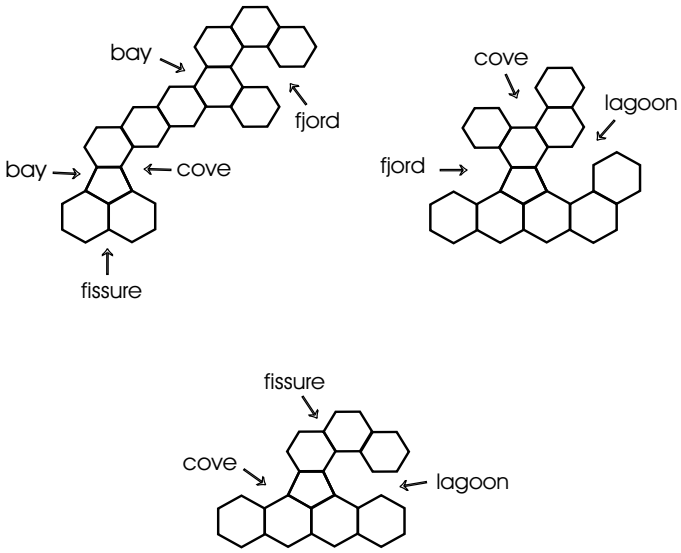

Fig. 6. Structural features occurring on the boundary of f-benzenoid systems.

The number of fissures, bays, coves, fjords, and lagoons will be denoted by n_{fi} , n_b , n_c , n_{fj} , and n_ℓ , respectively. Then, evidently, $n_{fi}+2\,n_b+3\,n_c+4\,n_{fj}+5\,n_\ell$ is the number of vertices of degree 3 on the boundary. In addition, $n_b+2\,n_c+3\,n_{fj}+4\,n_\ell$ is the number of $(3,3)$-type edges on the boundary. In the theory of benzenoid systems (in which lagoons cannot occur) $n_b+2\,n_c+3\,n_{fj}$ is called the "number of bay regions" [10]. In view of this, we call $n_b+2\,n_c+3\,n_{fj}+4\,n_\ell$ the number of bay regions of the underlying f-benzenoid, and denote it by b . Thus, b is just the number of $(3,3)$-type edges on the boundary.

By inspecting Fig. 2 it is seen that $b \geq 2$ holds for all f-benzenoid systems.

By Corollary 1.2 we know that the number of $(3,3)$-type edges that do not lie on

the boundary is $h + n_i$. Consequently,

$$m_{33} = h + n_i + b \ . \tag{7}$$

From Eqs. (5) and (6) we get

$$\begin{aligned} n_{22} &= 6n - 5m + m_{33} \\ n_{23} &= 6m - 6n - 2\,m_{33} \end{aligned}$$

which combined with Eqs. (1), (2), and (7) yield:

Theorem 3. If an f-benzenoid system has h hexagons, n_i internal vertices, and b bay regions, then the counts of edges of type $(2,2)$ and $(2,3)$ are

$$\begin{aligned} m_{22} &= b + 5 \\ m_{23} &= 4h - 2\,n_i - 2b \end{aligned}$$

whereas the analogous expression for the count of $(3,3)$-type edges is given by Eq. (7).

SPECTRAL PROPERTIES

In this section we are concerned with the eigenvalues of the adjacency matrix of the molecular graphs of fluoranthene–type benzenoid hydrocarbons. These eigenvalues will be denoted by λ_i , $i = 1, 2, \ldots, n$, and assumed to be labelled in a non-increasing order as

$$\lambda_1 \geq \lambda_2 \geq \cdots \geq \lambda_n \ .$$

At the present moment not much is known on the spectral properties of f-benzenoids. Because these are not bipartite graphs, the pairing theorem, namely $\lambda_i = -\lambda_{n-i+1}$ for all $i = 1, 2, \ldots, n$, is not obeyed.

We can nevertheless prove:

Theorem 4. If F is an f-benzenoid system with even number of vertices, and if F has a perfect matching (i. e., a Kekulé structure), then $\lambda_{n/2} > 0 > \lambda_{n/2+1}$. Furthermore, if F has K perfect matchings (Kekulé structures), then

$$\prod_{i=1}^{n} \lambda_i = (-1)^{n/2}\, K^2 \ .$$

The proof of Theorem 4 is lengthy and complicated. Its details will be communicated elsewhere.

The k-th spectral moment is defined as

$$M_k = \sum_{i=1}^{n} (\lambda_i)^k \ .$$

In the theory of benzenoid systems much attention was paid to the spectral moments (see [3,16] and the references cited therein). We anticipate that spectral moments will play a similar role also in the theory of f-benzenoid systems.

Based on the fact that the k-th spectral moment is equal to the number of closed walks of length k, we have established the following results:

Theorem 5. If F is an f-benzenoid system with n vertices, m edges, and b bay regions, then its first six spectral moments satisfy the relations:

$$\begin{aligned} M_1 &= 0 \\ M_2 &= 2m \\ M_3 &= 0 \\ M_4 &= 18\,m - 12\,n \\ M_5 &= 10 \\ M_6 &= 158\,m - 144\,n + 6b + 30 \ . \end{aligned}$$

It is worth noting that the formula for M_4 holds also for benzenoid systems, whereas the sixth spectral moment of benzenoid systems is equal to $158\,m - 144\,n + 6b + 48$.

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