Kekulé Structures in Fluoranthenes

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Fluoranthenes are polycyclic conjugated molecules consisting of two benzenoid fragments, connected by two carbon–carbon bonds so as to form a five-membered ring. Fluoranthenes possessing Kekulé structures are classified into three types, depending on the nature of the two carbon–carbon bonds connecting the two benzenoid fragments. Either both these bonds are essentially single (i. e., single in all Kekulé structures), or both are essentially double (i. e., double in all Kekulé structures), or one is essentially single and the other is essentially double. All Kekuléan fluoranthenes have equal number of bonding and antibonding molecular orbitals (MO), and no non-bonding MO.

Key words: Kekulé Structures; Fluoranthenes.

1. Introduction

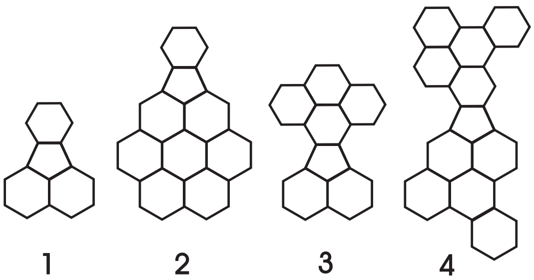
From a theoretical point of view, benzenoid molecules are the most thoroughly studied class of polycyclic aromatic hydrocarbons (PAHs) [1 – 6]. These molecules are assumed to be composed of mutually condensed six-membered rings. Other types of PAHs have attracted much less attention of theoretical chemists. Thus, in spite of the fact that fluoranthene and its congeners are structurally very similar to benzenoids (see below), the systematic elaboration of their theory has started only quite recently [7].

For theoretical considerations of PAHs, the fact that they have a large number of Kekulé structural formulas is of profound importance [1, 2, 6].

Until now, Kekulé structures in fluoranthenes have not been systematically analyzed. The aim of the present work is to contribute towards filling this gap.

2. Fluoranthenes and their Molecular Graphs

In Figure 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 fluoranthene is a conjugated π-electron system, consisting of two benzenoid fragments which are joined so as to form a five-membered ring. From the classical point of view [2 – 4, 6], the π-electrons in fluoranthenes behave as two disconnected conjugated systems, with two disconnected sets of conjugated circuits, each set lying completely inside one of the benzenoid fragments.



1 2 3 4

Fig. 1. Fluoranthene (**1**) and examples of its congeners. Note that these PAHs are obtained by joining two benzenoid fragments, so as to form a new five-membered ring. The general structure of fluoranthenes is depicted in Figure 2.

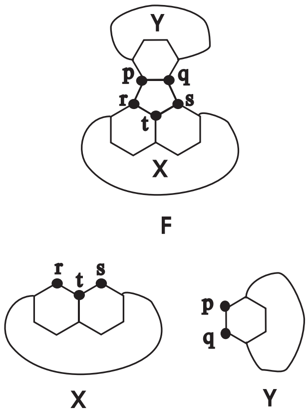


Fig. 2. General form of a fluoranthene-type system (F) and its construction from two benzenoid fragments X and Y.

In what follows we will represent the fluoranthenes by means of their molecular graphs [7, 8]. This, in particular, means that the carbon atoms are represented by vertices, and the carbon–carbon bonds by edges.

The molecular graphs of fluoranthenes are then defined in the following manner (see Fig. 2). Let X be a benzenoid system [2]. Let r and s be two vertices of X whose degrees are two, and which both are adjacent to a vertex t of degree 3.

Let Y be another benzenoid system. Let p and q be two adjacent vertices of Y whose degrees are two.

The fluoranthene-type system F is obtained by joining (with a new edge) the vertices p and r, and by joining (with a new edge) the vertices q and s, see Figure 2. The vertices p,q,r,s,t of F form a five-membered ring. By definition, each fluoranthene-type system possesses exactly one five-membered ring.

3. Kekuléan Fluoranthenes

The number of Kekulé structures of a fluoranthene F will be denoted by $K\{F\}$. Fluoranthenes having Kekulé structures (i. e., having the property $K\{F\} > 0$) are said to be Kekuléan (cf. [2]). All chemically relevant fluoranthene congeners are necessarily Kekuléan.

In the molecular-graph formalism, Kekulé structures are represented by perfect matchings [8], i. e., by selections of mutually non-touching edges which cover all vertices.

In what follows the edge connecting the vertices u and v will be denoted by uv. If an edge belongs to a perfect matching, it is said to be a "double bond" (of the respective Kekulé structure). Otherwise it is a "single bond" (of the respective Kekulé structure).

An edge which is single in all Kekulé structures is said to be an "essentially single bond". Analogously, an edge which is double in all Kekulé structures is said to be an "essentially double bond" [9 – 12].

The existence and number of Kekulé structures in a fluoranthene F is determined by the two benzenoid fragments (X and Y in Fig. 2), from which F is composed. Therefore, in order to establish the basic regularities for $K\{F\}$, we need to recall some well-known properties of benzenoid systems and their Kekulé structures [2, 13].

Benzenoid systems are bipartite graphs and therefore their vertices can be colored by two colors, say black and white, so that no two adjacent vertices have the same color. We denote the number of black and white vertices of a (bipartite) molecular graph G by $n_b(G)$ and $n_w(G)$, respectively. For an example see Figure 3.

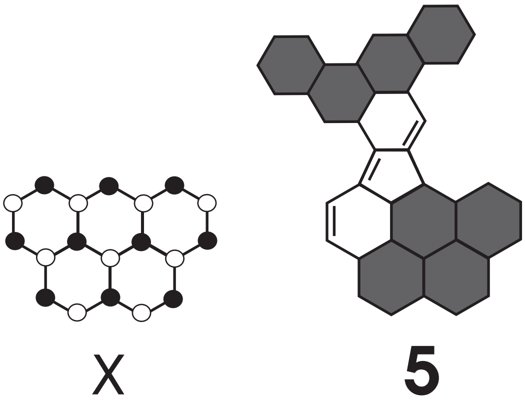


Fig. 3. Benzenoid system X with $n_b(X) = 10$ black and $n_w(X) = 9$ white vertices. Since $n_b(X) \neq n_w(X)$, this benzenoid system has no Kekulé structures. Nevertheless, there exist Kekuléan fluoranthenes (for instance **5**), in which X is one of the two benzenoid fragments; for details see text.

The condition $n_b = n_w$ is necessary (but not sufficient) for the existence of Kekulé structures of a benzenoid hydrocarbon [2, 13].

In order to simplify our considerations, we will assume that the vertices of the benzenoid fragments X and Y (as shown in Fig. 2) are colored as follows: The vertices r and s of X are black (in which case vertex t white). Further, vertex p of Y is black (in which case vertex q is white).

With regard to the coloring of vertices in the benzenoid fragments X and Y, and with regard to the Kekulé structures of the respective fluoranthene F, four cases need to be distinguished.

Case 1. $n_b(X) = n_w(X)$ and $n_b(Y) = n_w(Y)$. This is the regular case embracing the majority of Kekuléan fluoranthenes (e. g., all examples depicted in Fig. 1). Because of $n_b(X) = n_w(X)$, in all Kekulé structures of F, all double bonds ending at vertices r and s lie in the fragment X. Consequently, in all Kekulé structures the edges pr and qs are single, i. e., these edges are essentially single bonds. Therefore,

$$K\{F\} = K\{X\} \cdot K\{Y\}. \tag{1}$$

In Case 1 the fluoranthene F is Kekuléan if and only if both benzenoid systems X and Y are Kekuléan.

Case 2. $n_b(X) = n_w(X) + 1$ and $n_b(Y) = n_w(Y) + 1$. Because $n_b \neq n_w$ for both X and Y, neither X nor Y can have Kekulé structures. However, the fluoranthene F may nevertheless be Kekuléan, as shown by example **5** in Figure 3.

Indeed, since the vertices r and p are black, the subgraphs $X - r$ and $Y - p$ have equal number of black and white vertices, $n_\mathrm{b}(X-r) = n_\mathrm{w}(X-r)$ and $n_\mathrm{b}(Y-p) = n_\mathrm{w}(Y-p)$, and therefore $X - r$ and $Y - p$ may be Kekuléan. If so, then in the corresponding fluoranthene pr is an essentially double bond whereas qs is essentially single. Then

$$K\{F\} = K\{X-r\} \cdot K\{Y-p\}.$$

In Case 2 the fluoranthene F is Kekuléan if and only if both benzenoid subgraphs $X - r$ and $Y - p$ are Kekuléan.

Case 3. $n_\mathrm{b}(X) = n_\mathrm{w}(X) + 2$ and $n_\mathrm{b}(Y) = n_\mathrm{w}(Y)$. This time the benzenoid system X cannot have Kekulé structures, but its subgraph $X - r - s$ may be Kekuléan. If so, then both pr and qs are essentially double bonds, and therefore

$$K\{F\} = K\{X-r-s\} \cdot K\{Y\}.$$

In Case 3 the fluoranthene F is Kekuléan if and only if the benzenoid fragment Y as well as the benzenoid subgraph $X - r - s$ are Kekuléan.

An example of a Kekuléan fluoranthene pertaining to Case 2 is the species **5**, depicted in Figure 3. Further examples, for both Cases 2 and 3 are **6**, **8**, and **9** in Figure 4. In these diagrams only the essentially single and essentially double bonds are indicated. Those parts of the fluoranthene molecule in which the carbon–carbon bonds have intermediate double- and single-bond characters are indicated by gray shading.

It is worth noting that the π-electron content [12, 14 – 17] of the five membered ring in the Case 1, 2, and 3 fluoranthenes differs significantly. In Case 1 its value is between 0 and 2, in Case 2 is between 2 and 3, and in Case 3 it is always equal to 4.

Cases 1 – 3 exhaust all possibilities for fluoranthenes being Kekuléan. In view of this, what remains is:

Case 4. If the colouring of the vertices of the benzenoid systems X and Y does not satisfy any of the conditions required in Cases 1 – 3, then the respective fluoranthene F is non-Kekuléan, $K\{F\} = 0$.

An example of a fluoranthene-type species to which Case 4 applies is **10** in Figure 4.

4. Kekuléan Fluoranthenes are Closed-Shell Systems

In the previous section we demonstrated that in all Kekuléan fluoranthenes the two carbon–carbon bonds (pr and qs) which connect the two benzenoid fragments (X and Y) are either essentially single or essentially double. Now, if a carbon–carbon bond is essentially double, then all carbon–carbon bonds incident to it must be essentially single. Thus, all Kekuléan fluoranthenes possess essentially single carbon–carbon bonds.

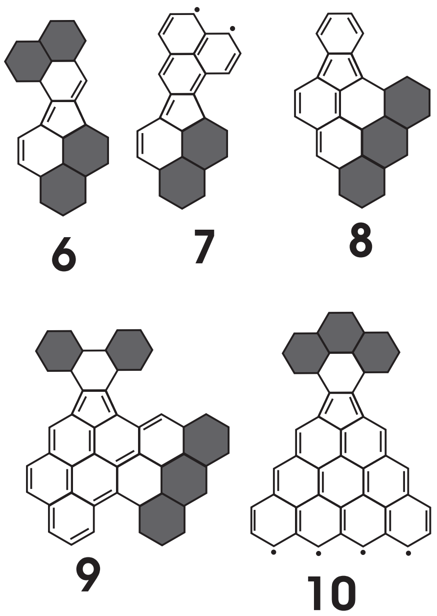


Fig. 4. Molecules **5** (in Fig. 3) and **6** are examples of Case 2 Kekuléan fluoranthenes. Molecules **8** and **9** are examples of Case 3 Kekuléan fluoranthenes. Case 2 applies also to the species **7**, which is non-Kekuléan because of $K\{Y-p\} = 0$. The species **10** is non-Kekuléan because $n_\mathrm{b}(X) = n_\mathrm{w}(X) - 2$. For more details see text.

Within the tight-binding Hückel molecular orbital (HMO) model, the bonding, non-bonding, and antibonding molecular orbitals pertain, respectively, to positive, zero, and negative eigenvalues of the adjacency matrix of the molecular graph [18 – 20]. As a consequence, conjugated π-electron systems have equal number of positive and negative eigenvalues, and no zero eigenvalues are predicted to have a closed-shell electron configuration.

We now show that all Kekuléan fluoranthenes satisfy this condition.

Let F be a fluoranthene and $\mathbf{A}(F)$ its adjacency matrix. As well known, the determinant of the adjacency matrix is equal to the product of the graph eigenvalues.

The determinant of the adjacency matrix of a graph G with n vertices can be calculated by using the Sachs theorem, whose details can be found in [8, 18 – 20]. We only recall that a Sachs graph consists of disjoint edges and/or disjoined cycles. The determinant of the adjacency matrix of G is expressed as a sum of terms, each pertaining to a Sachs graph with n vertices. Edges that are essentially single may be contained only in odd-membered cycles of n-vertex Sachs graphs. If a molecular graph is Kekuléan, then it must possess an even number of vertices. In this case, each n-vertex Sachs graph possesses either no odd-membered cycle or possesses an even number of odd-membered cycles. Since fluoranthenes have no two disjoint odd-membered cycles, none of their n-vertex Sachs graphs contain odd-membered cycles. Consequently, none of their n-vertex Sachs graphs contain the essentially single edges. Therefore, we may associate an arbitrary weight [21] to the essentially single edges of F, without influencing the value of $\det \mathbf{A}(F)$.

In what follows we consider only Case 1 Kekuléan fluoranthenes. However, the precisely same reasoning applies also in Cases 2 and 3.

Thus, let F be a Case 1 Kekuléan fluoranthene, in which the edges pr and qs are essentially single (see Figure 2). Let $F(w)$ be the weighted molecular graph [21], in which the edges pr and qs have weights w. Then $F(1)$ is the usual molecular graph, whereas $F(0)$ is the graph consisting of disconnected benzenoid systems X and Y. Recall that in view of (1), X and Y must be Kekuléan. Therefore,

$$\begin{aligned}\det \mathbf{A}(F(0)) &= \det \mathbf{A}(X) \times \det \mathbf{A}(Y) \\ &= K\{X\}^2 \times K\{Y\}^2 > 0.\end{aligned}$$

For $w = 0$ we have two benzenoid graphs, which being bipartite necessarily have equal number of positive and negative eigenvalues, and being Kekuléan have no zero eigenvalues. Since $\det \mathbf{A}(F(w))$ is independent of w, we may continuously change w from zero to one, without changing the value of the determinant. This means that the number of positive and negative eigenvalues of $\mathbf{A}(F(w))$ are independent of w, and that $\mathbf{A}(F(w))$ has no zero eigenvalues. Applying this argument to the case $w = 1$ we arrive at the conclusion that (within the HMO approximation) the Case 1 Kekuléan fluoranthenes have equal number of bonding and antibonding MOs, and no non-bonding MO, i. e., have a closed shell π-electron configuration.

The proof of the same property for Case 2 and Case 3 Kekuléan fluoranthenes is analogous, yet slightly more complicated.

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