Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 75 (8) 1093–1098 (2010)
JSCS–4034
UDC 547.53:547.686:54.02
Original scientific paper

On the number of Kekulé structures of fluoranthene congeners

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(Received 7 December 2009)

Abstract: The Kekulé structure count K of fluoranthene congeners is studied. It is shown that for such polycyclic conjugated π-electron systems, either $K = 0$ or $K \geq 3$. Moreover, for every $t \geq 3$, there are infinitely many fluoranthene congeners having exactly t Kekulé structures. Three classes of Kekuléan fluoranthenes are distinguished: *i*) Φ_0 – fluoranthene congeners in which neither the male nor the female benzenoid fragment has Kekulé structures, *ii*) Φ_m – fluoranthene congeners in which the male benzenoid fragment has Kekulé structures, but the female does not, and *iii*) Φ_{fm} – fluoranthene congeners in which both the male and female benzenoid fragments have Kekulé structures. Necessary and sufficient conditions are established for each class, $\Phi = \Phi_0, \Phi_m, \Phi_{fm}$, such that for a given positive integer t, there exist fluoranthene congeners in Φ with the property $K = t$.

Keywords: fluoranthenes; Kekulé structure; polycyclic aromatic hydrocarbons.

INTRODUCTION

Continuing our studies of the π-electron properties of polycyclic conjugated molecules of the fluoranthene-type,[1–8] in this work, attention was focused on their Kekulé structures. As explained in detail elsewhere,[1,6] the systems considered consist of two benzenoid fragments, joined so as to form an additional five-membered ring (*cf*. Fig. 1). Thus, fluoranthene congeners are, from a structural point of view, closely similar to benzenoid systems.[9–13] The Kekulé structures and various Kekulé-structure-based properties of benzenoid molecules have been extensively studied in the past; for details see the books,[13–16] review[17] and recent papers.[18–21] Analogous properties of the fluoranthene-type systems were, so far, analyzed only to a limited extent.[8] In this paper, we are concerned with the possible number of Kekulé structures (Kekulé structure count, K) of fluoranthene congeners. If $K > 0$, the respective molecule is said to be Kekuléan.[13,16]

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doi: 10.2298/JSC091207077V

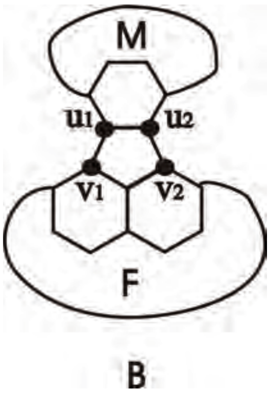

Fig. 1. The general form of a fluoranthene congener B; it is obtained by joining two benzenoid fragments (M and F) so as to form a five-membered ring. The fragments M and F are referred to as male and female, respectively. For details see text.

Following the terminology of an earlier work,[6] the benzenoid fragments of a fluoranthene-type system are called "male" and "female", so that the male fragment (M in Fig. 1) is connected to the female fragment (F in Fig. 1) by two adjacent vertices (u_1 and u_2 in Fig. 1), whereas the female fragment is connected to the male fragment *via* two vertices at distance 2 (v_1 and v_2 in Fig. 1). In other words, three vertices of the five-membered ring belong to the female fragment and two vertices to the male fragment.

Bearing in mind the notation specified in Fig. 1, if *B* is a fluoranthene congener, then be deleting from B the edges u_1v_1 and u_2v_2, a subgraph is obtained consisting of two disconnected benzenoids, referred to as male $M = M_B$ and female $F = F_B$. Denote *i*) by Φ_0 the class of Kekuléan fluoranthenes in which neither the female nor the male benzenoid fragment have Kekulé structures, *ii*) by Φ_m the class of Kekuléan fluoranthenes in which the male fragment has Kekulé structures, but the female does not, and *iii*) by Φ_{fm} the class of fluoranthenes in which both the male and female fragments have Kekulé structures.

The main results obtained are the following:

i) there exist fluoranthenes of the type Φ_0 with *K* Kekulé structures if and only if *K* is the product of two integers both greater than 2;

ii) a fluoranthene of type Φ_m can have *K* Kekulé structures if and only if $K \geq 3$;

iii) a fluoranthene of the type Φ_{fm} can have *K* Kekulé structures if and only if $K \geq 6$, and *K* is not a prime number, *i.e.*, $K \neq 7, 11, 13, 17, 19, 23, \ldots$

NOTATION AND PRELIMINARIES

Let B be the molecular graph[22] of a benzenoid or fluoranthene system, and let κ be a Kekulé structure of B. Denote by $d_1 = d_1(B) = d_1(B,\kappa)$ the number of double bonds of κ belonging to only one ring and by $d_2 = d_2(B) = d_2(B,\kappa)$ the number of double bonds that are shared by two rings. Let R be a ring of B and $D(R) = D(R,\kappa)$ the number of double bonds belonging to *R*. Then,

$$\sum_{\mathrm{R}} D(\mathrm{R}) = d_1 + 2d_2$$

where the summation goes over all rings of B.

Denote by $n = n(\mathrm{B})$ the number of vertices of B, by $n_\mathrm{i} = n_\mathrm{i}(\mathrm{B})$ the number of internal vertices of B and by $h = h(\mathrm{B})$ number of hexagons of B. The number of Kekulé structures of B is $K = K(\mathrm{B})$.

Let B' be a subgraph of B and let κ be a Kekulé structure of B. Then, κ(B') denotes the set of double bonds of κ that belong to B'.

In the proof of the main results, the following theorems were used.

Theorem A.[1,16] If B is a benzenoid system, then $n = 4h + 2 - n_\mathrm{i}$. If B is a fluoranthene-like system, then $n = 4h + 5 - n_\mathrm{i}$.

Theorem B.[8] *i*) Let $\mathrm{B} \in \Phi_0$. Then $K(\mathrm{B}) = K(F_\mathrm{B} - v_i) \cdot K(M_\mathrm{B} - u_i)$ for either $i = 1$ or $i = 2$. Moreover, for $i \neq j$, $K(F_\mathrm{B} - v_j) = K(M_\mathrm{B} - u_j) = 0$; *ii*) let $\mathrm{B} \in \Phi_\mathrm{m}$. Then $K(\mathrm{B}) = K(F_\mathrm{B} - v_1 - v_2)K(M_\mathrm{B})$. Moreover, if κ is a Kekulé structure of B, then $\kappa(F_\mathrm{B} - v_1 - v_2)$ is a Kekulé structure of $F_\mathrm{B} - v_1 - v_2$; *iii*) let $\mathrm{B} \in \Phi_\mathrm{fm}$. Then $K(\mathrm{B}) = K(F_\mathrm{B})K(M_\mathrm{B})$.

MAIN RESULTS

The main results obtained are stated in the following three theorems.

Theorem 1. Let $B \in \Phi_0$. Then $K(\mathrm{B})$ is equal to the product of two numbers, each greater than 2. Moreover, for every number t that is a product of two numbers greater than 2, there are infinitely many fluoranthenes $\mathrm{B} \in \Phi_0$ for which $K(\mathrm{B}) = t$.

Theorem 2. Let $\mathrm{B} \in \Phi_\mathrm{m}$. Then $K(\mathrm{B}) \geq 3$. Moreover, for every $t \geq 3$, there are infinitely many fluoranthenes $\mathrm{B} \in \Phi_\mathrm{m}$ for which $K(\mathrm{B}) = t$.

Theorem 3. Let $B \in \Phi_\mathrm{fm}$. Then, $K(\mathrm{B}) \geq 6$ and $K(\mathrm{B})$ is not a prime number. For every $t \geq 6$ which is not a prime number, there is at least one $\mathrm{B} \in \Phi_\mathrm{fm}$, such that $K(\mathrm{B}) = t$. Moreover, for every positive integer t there are infinitely many fluoranthenes with t Kekulé structures in Φ_fm if and only if $t = t_1t_2t_3$, such that $t_1 \geq 3$, $t_2 \geq 3$ and $t_3 \geq 2$.

Proof of Theorem 1. Let $B \in \Phi_0$ and κ be a Kekulé structure of B. It will be shown that $K(\mathrm{B})$ is the product of two numbers, each of which being greater than 2.

From Theorem B for *i*), it follows that $K(\mathrm{B}) = K(M_\mathrm{B} - u_i)K(F_\mathrm{B} - v_i)$. Therefore, it is sufficient to prove that $K(M_\mathrm{B} - u_i) \geq 3$ and $K(F_\mathrm{B} - v_i) \geq 3$. Both proofs are completely analogous and, therefore, only the validity of $K(F_\mathrm{B} - v_i) \geq 3$ will be demonstrated. Note that $\kappa(F_\mathrm{B} - v_i)$ is a Kekulé structure of $F_\mathrm{B} - v_i$. Furthermore, $n(F_\mathrm{B} - v_i) = n(F_\mathrm{B}) - 1$. Then by Theorem A:

$$d_1(F_\mathrm{B}) + d_2(F_\mathrm{B}) = \frac{\left(4h(F_\mathrm{B}) + 2 - n_i(F_\mathrm{B})\right) - 1}{2} = 2h(F_\mathrm{B}) - \frac{n_i(F_\mathrm{B})}{2} + \frac{1}{2}$$

As, evidently, $d_2(F_\mathrm{B}) \geq \frac{1}{2} n_i(F_\mathrm{B})$, one obtains:

$$\sum_{\mathrm{R}} D(\mathrm{R},\kappa) = d_1(F_{\mathrm{B}}) + 2d_2(F_{\mathrm{B}}) \geq 2h(F_{\mathrm{B}}) + \frac{1}{2}$$

with the left-hand side summation going over all rings of F_{B}. Since this sum is an integer, it follows that:

$$\sum_{\mathrm{R}} D(\mathrm{R},\kappa) \geq 2h(F_{\mathrm{B}}) + 1$$

Hence, at least one hexagon of F_{B} contains three double bonds of the Kekulé structure κ.

It is necessary to distinguish between two cases:

Case 1. In F_{B}, the relation $D(\mathrm{R}_1,\kappa) = D(\mathrm{R}_2,\kappa) = 3$ holds for (at least) two six-membered rings, R_1 and R_2.

Let κ_1 and κ_2 be the Kekulé structures obtained by rotation of the double bonds of $\kappa(F_{\mathrm{B}} - v_i)$ in the rings R_1 and R_2, respectively. Then, κ_1, κ_2 and $\kappa(F_{\mathrm{B}} - v_i)$ are three distinct Kekulé structures on $F_{\mathrm{B}} - v_i$, which means that $K(F_{\mathrm{B}} - v_i) \geq 3$.

Case 2. In F_{B}, the relation $D(\mathrm{R},\kappa) = 3$ holds for only one six-membered ring R.

Then, $D(\mathrm{R}') = 2$ for all other six-membered rings R'. Let κ' be the Kekulé structure obtained by rotating the double bonds in *R*. Then:

$$\sum_{\mathrm{R}} D(R,\kappa') \geq 2h(F_{\mathrm{B}}) + 1$$

Hence, either κ' has at least two hexagons R_1 and R_2 for which $D(\mathrm{R}_1,\kappa') = D(\mathrm{R}_2,\kappa') = 3$ or $D(\mathrm{R},\kappa') = 3$ and $D(\mathrm{R}',\kappa') = 2$ for all other hexagons R'. In the latter case, $D(\mathrm{R}',\kappa(F_{\mathrm{B}}))$ and $D(\mathrm{R}',\kappa')$ would coincide for all hexagons R'. However, these two terms differ in the hexagon(s) adjacent to R, which is a contradiction. Therefore, it must be $D(\mathrm{R}_1,\kappa') = D(\mathrm{R}_2,\kappa') = 3$.

Let κ_1 and κ_2 be the Kekulé structures obtained by rotation of the double bonds of κ' in the rings R_1 and R_2, respectively. Then, κ_1, κ_2 and κ' are three Kekulé structures of $F_{\mathrm{B}} - v_i$, which means that also in this case $K(F_{\mathrm{B}} - v_i) \geq 3$.

This proves that $K(\mathrm{B})$ is a product of two numbers, each of which is greater than 2. The example depicted in Fig. 2 shows that it is possible to design arbitrarily many fluoranthenes of class Φ_0 for which $K = t_1t_2$, $t_1 \geq 3$, $t_2 \geq 3$.

This concludes the proof of the Theorem.

Proofs of Theorems 2 and 3 are analogous, except that instead of Theorem B (i), it is necessary to use Theorem B (ii) and (iii), respectively.

By combining Theorems 1–3, one obtains:

Corollary 4. Let B be a Kekuléan fluoranthene. Then $K(\mathrm{B}) \geq 3$. Moreover, for every number $t \geq 3$, there are infinitely many fluoranthenes B such that $K(\mathrm{B}) = t$.

According to Theorems 1–3, the minimal Kekulé structure count of a fluoranthene in class Φ_0, Φ_{m} and Φ_{fm} is 9, 3 and 6, respectively. The smallest such minimal-*K* fluoranthenes are depicted in Fig. 3.

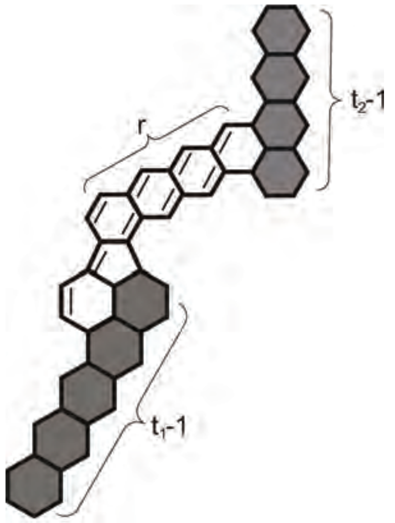

Fig. 2. Fluoranthenes belonging to the class Φ_0, having t_1t_2 Kekulé structures, $t_1 \geq 3$ and $t_2 \geq 3$, irrespective of the value of the parameter r, r = 1, 2, 3,… The fixed double bonds are indicated, whereas the shaded areas are domains in which the π–electrons are delocalized. In this example the shaded areas pertain to polyacenes with $t_1 - 1$ and $t_2 - 1$ hexagons; recall that a polyacene with h hexagons has $h + 1$ Kekulé structures.

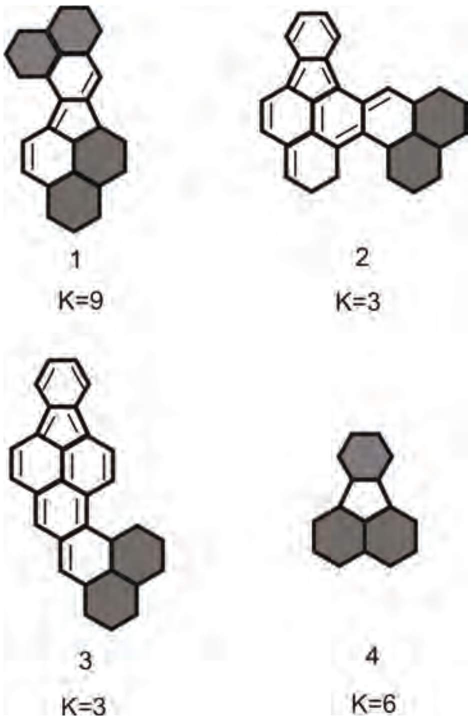

Fig. 3. Fluoranthenes **1**, **2** **3** and **4** are the smallest members of the classes Φ_0, Φ_m and Φ_{fm}, respectively, having the smallest possible number of Kekulé structures (K). In these formulas the fixed double bonds are indicated, whereas the shaded areas are domains in which the π–electrons are delocalized.

Acknowledgements. The partial support of Croatian Ministry of Science, Education and Sport (Grant Nos. 177-0000000-0884 and 037-0000000-2779) is gratefully acknowledged. The authors also thank the Ministry of Science and Technological Development of the Republic of Serbia for partial support of this work through Grant No. 144015G.

И З В О Д

О БРОЈУ KEKULÉ СТРУКТУРА У ЈЕДИЊЕЊИМА ФЛУОРАНТЕНСКОГ ТИПА

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Проучаван је број Kekulé структура K у једињењима флуорантенског типа. Показано је да је код ових полицикличних конјугованих π-електронских система $K = 0$ или $K \geq 3$. Осим тога, за свако $K \geq 3$ постоји бесконачно много флуорантена са тачно K Kekulé структура. Разликују се три класе Kekulé флуорантена: *i*) Φ_0 – флуорантене код који ни мушки ни женски бензеноидни фрагмент немају Kekulé структуре, *ii*) Φ_m – флуорантене код којих мушки бензеноидни фрагмент има Kekulé структуре, а женски нема, и *iii*) Φ_{fm} – флуорантене код којих и мушки и женски бензеноидни фрагмент имају Kekulé структуре. Одређени су неопходни и довољни услови за сваку класу $\Phi = \Phi_0, \Phi_m, \Phi_{fm}$, да за задани позитивни цео број m, постоји једињење флуорантенског типа у Φ са особином $K = m$.

(Примљено 7. децембра 2009)

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