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JSCS–3874 *Original scientific paper*

On π-electron conjugation in the five-membered ring of fluoranthene-type benzenoid hydrocarbons

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Abstract: A fluoranthene-type benzenoid hydrocarbon (FTBH) is a polycyclic conjugated system obtained by joining two ordinary benzenoid hydrocarbons so as to form a five-membered ring. The main differences between the π-electron properties of FTBHs and those of ordinary benzenoid hydrocarbons are caused by this five-membered ring. The most important structural factors influencing the π-electron conjugation in the five-membered ring of FTBHs were analyzed and established.

Keywords: fluoranthene-type hydrocarbons; benzenoid hydrocarbons; PCP-effect; linear effect.

INTRODUCTION

Our recent theoretical studies[1–6] of fluoranthene-type benzenoid hydrocarbons (FTBHs) were motivated by the fact that whereas the π-electron properties of ordinary benzenoid hydrocarbons have been investigated for almost an entire century (see the books,[7–9] the reviews,[10–13] the recent papers,[14–18] and the references cited therein), the paper[1] seems to be the very first systematic research of FTBHs.

Fluoranthene-type benzenoid hydrocarbons (FTBHs) and ordinary benzenoid hydrocarbons are structurally closely related. The former can be viewed as being obtained by connecting two ordinary benzenoid fragments so as to form a new five-membered ring. The general structure of an FTBH is depicted in Fig. 1, in which the notation and terminology used throughout this work are also explained.

ON KEKULÉ STRUCTURES OF FLUORANTHENE-TYPE BENZENOIDS

If the two benzenoid fragments (denoted by **X** and **Y**, *cf.* Fig. 1) in an FTBH (denoted by **F**, *cf.* Fig. 1) both have Kekulé structures, then the Kekulé structure

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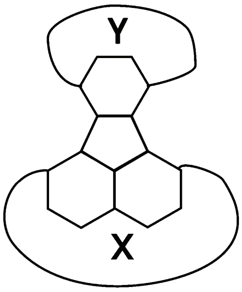
count of **F** is simply the product of the Kekulé structure counts of **X** and **Y**, $K(\mathbf{F}) = K(\mathbf{X})\cdot K(\mathbf{Y})$. In addition, the two carbon–carbon bonds by which **X** and **Y** are joined are single in all Kekulé structures. This gives the impression that the π-electron systems of the fragments **X** and **Y** are mutually independent and that the interaction between them (*via* the five-membered ring) is negligible. An illustrative example is provided in Fig. 2.



F

Fig. 1. The general form of a fluoranthene-type benzenoid hydrocarbon, **F**. It is obtained by joining two benzenoid systems (**X** and **Y**), so as to form a new five-membered ring. The fragments **X** and **Y** in **F** are referred to as “female” and “male”, respectively.

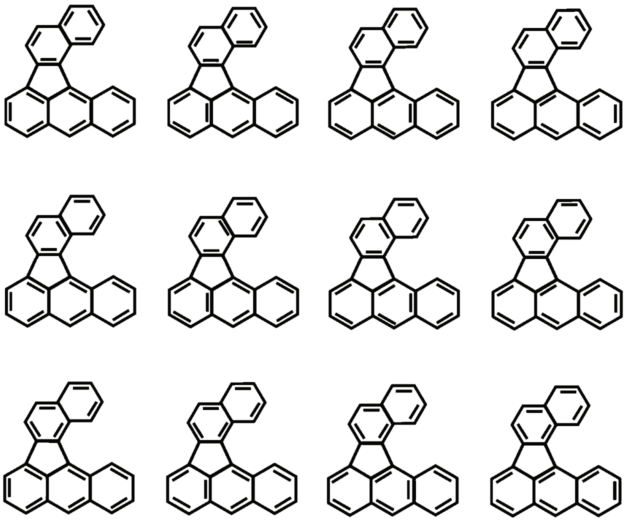


Fig. 2. The twelve (= 4×3) Kekulé structures of dibenzo[*a*,*l*]fluoranthene, composed of an anthracene (**X**) and a naphthalene (**Y**) fragment. The two carbon–carbon bonds connecting the anthracene and naphthalene fragments (thus belonging to the five-membered ring) are single in all Kekulé structures.

The fact that the two bonds connecting the benzenoid fragments **X** and **Y** are single in all Kekulé structures might be the main reason why theoreticians have for so long neglected FTBHs. Namely, according to the currently most often em-

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ployed approaches in the theory of benzenoid hydrocarbons (based on Kekulé structure counts, conjugated circuits, and Clar aromatic sextet formulas, for details see[7,12]), the π-electron conjugation in the five-membered ring of an FTBH would be zero or, saying this in a more cautious manner, very weak. In reality, the extent of π-electron conjugation in the five-membered ring of FTBHs is small, but far from negligible. The magnitude of this conjugation in a peculiar manner depends on the structure of **X** and **Y**, and on the manner in which these fragments are connected (see below).

At this point it should be mentioned that if the fragments **X** and **Y** are not Kekuléan, but **F** is, then either one or both the carbon–carbon bonds connecting **X** and **Y** must be double in all Kekulé structures of **F**. Examples illustrating this case are to be found in Fig. 3. An example of an FTBH in which all five carbon–carbon bonds of the five-membered ring are single in all Kekulé structures is also shown in Fig. 3.

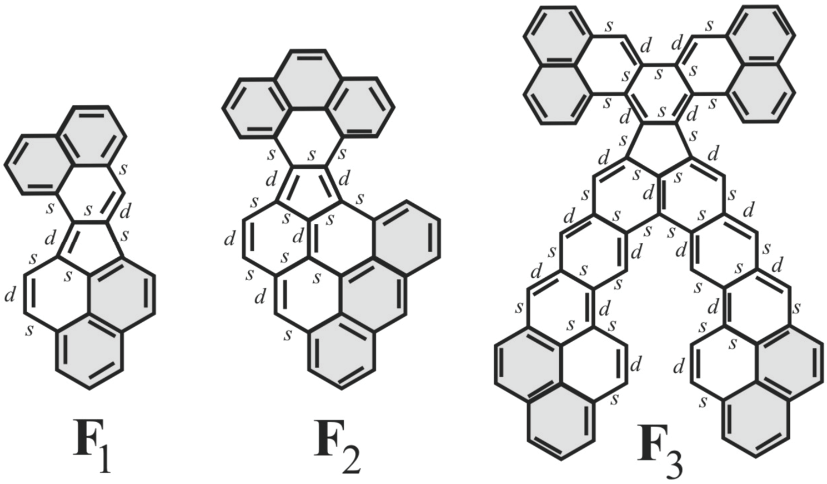

Fig. 3. Diagram $\mathbf{F}_1$ is a Kekulé structure (of the 9 possible) of an FTBH in which both benzenoid fragments **X** and **Y** are non-Kekuléan, $K(\mathbf{X}) = K(\mathbf{Y}) = 0$. Diagram $\mathbf{F}_2$ is a Kekulé structure (of the 20 possible) of an FTBH in which the benzenoid fragment **X** is non-Kekuléan, $K(\mathbf{X}) = 0$, whereas the fragment **Y** is Kekulèan, $K(\mathbf{Y}) > 0$. Diagram $\mathbf{F}_3$ is a Kekulé structure (of the 27 possible) of an FTBH in which both benzenoid fragments **X** and **Y** are Kekuléan, $K(\mathbf{X}) > 0$, $K(\mathbf{Y}) > 0$. In this FTBH, all the five carbon–carbon bonds of the five-membered ring are single in all Kekulé structures. The carbon–carbon bonds which are single and double in all Kekulé structures are marked by *s* and *d*, respectively. The domains without fixed single and double bonds are indicated by shading.

ON CYCLIC CONJUGATION IN THE FIVE-MEMBERED RING

The extent of cyclic conjugation in a ring of a polycyclic conjugated molecule can be assessed by means of its energy effect (*ef*). Details of the calculation

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of this energy effect can be found in the review,[19] recent papers,[3,5,20] and the references cited therein. For what follows, it is important that the *ef*-values are computed using a Coulson-integral based molecular orbital method, which is free of any *a priori* assumptions concerning Kekulé structures. Positive *ef*-values indicate stabilization, and the greater is the *ef*, the greater is the magnitude of the cyclic conjugation in the underlying ring.

Cyclic conjugation in the five-membered ring of FTBHs was studied in detail in previous papers.[3,5,6] Therefore, only the two main findings on its structure dependency are briefly repeated here.

PCP effect.[3] The five-membered ring and a six-membered ring in an FTBH are said to be in a phenyl-cyclopentadienyl (PCP) constellation if the two rings are connected by exactly one carbon–carbon bond. Six-membered rings in a PCP constellation increase the magnitude of cyclic conjugation in the five-membered ring. The greater is the number of such six-membered rings, the greater is the *ef*-value of the five-membered ring.

Linear effect.[6] The five-membered ring and a six-membered ring in an FTBH are said to be in a linear constellation if they are separated by a six-membered ring but are not in a PCP constellation. Six-membered rings in a linear constellation decrease the magnitude of the cyclic conjugation in the five-membered ring. The greater is the number of such six-membered rings, the smaller is the *ef*-value of the five-membered ring.

Simple examples illustrating the above two effects are given in Fig. 4. Some more complex situations are shown in Figs. 5 and 6.

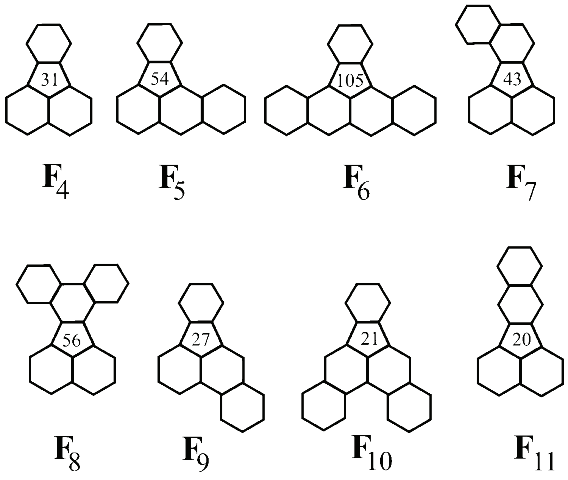

Fig. 4. Examples illustrating the PCP and linear effects in FTBHs: fluoranthene (**F**$_4$) and its congeners with one hexagon in the PCP constellation (**F**$_5$ and **F**$_7$), with two hexagons in the PCP constellation (**F**$_6$ and **F**$_8$), with one hexagon in the linear constellation (**F**$_9$ and **F**$_{11}$) and two hexagons in the linear constellation (**F**$_{10}$); in **F**$_4$–**F**$_8$, there are no linear constellations, in **F**$_4$ and **F**$_9$–**F**$_{11}$, there are no PCP constellations. The *ef*-value of the five-membered ring (multiplied by 10000 and expressed in the units of the HMO carbon–carbon resonance integral β) is inscribed into this ring; for details see text.

From the data shown in Figs. 4–6, especially in Fig. 4, it can be seen that the linear effect is much weaker than the PCP effect. Furthermore, the PCP effect caused by hexagons in the female benzenoid fragment (*e.g.*, in **F**$_6$ and **F**$_7$) is much

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stronger than the analogous effect caused by hexagons in the male benzenoid fragment (*e.g.*, in $\mathbf{F}_8$ and $\mathbf{F}_9$). This observation may be summarized as follows:

Male–female difference in the PCP effect.[6] A six-membered ring belonging to the female benzenoid fragment of an FTBH has a stronger PCP effect than a six-membered ring belonging to the male benzenoid fragment of the same FTBH.

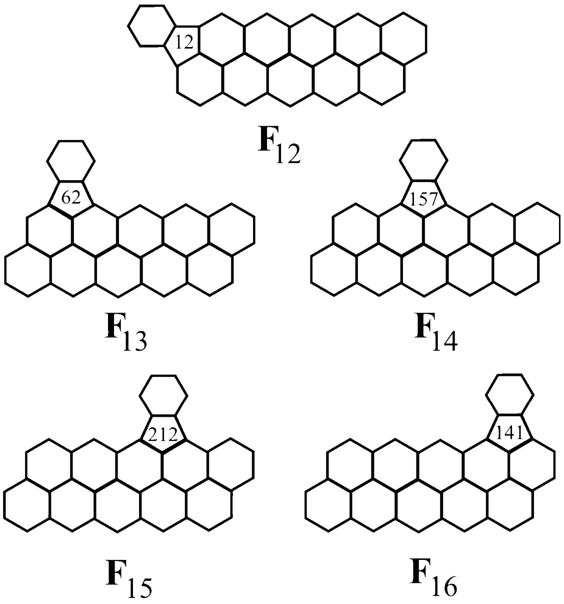

Fig. 5. The same data as in Fig. 4 for FTBHs the female and male benzenoid fragments of which are pentacenopentacene and benzene, respectively. $\mathbf{F}_{12}$–$\mathbf{F}_{16}$ have 1, 2, 3, 3, 2 PCP constellations, and 0, 2, 2, 2, 1 linear constellations, respectively. The *ef*-values of the five-membered ring follow the increase of the number of PCP constellations. Note, however, that the *ef*-value in $\mathbf{F}_{16}$ is signifycantly greater than in the case of $\mathbf{F}_{13}$, although both $\mathbf{F}_{13}$ and $\mathbf{F}_{16}$ have an equal number of PCP constellations.

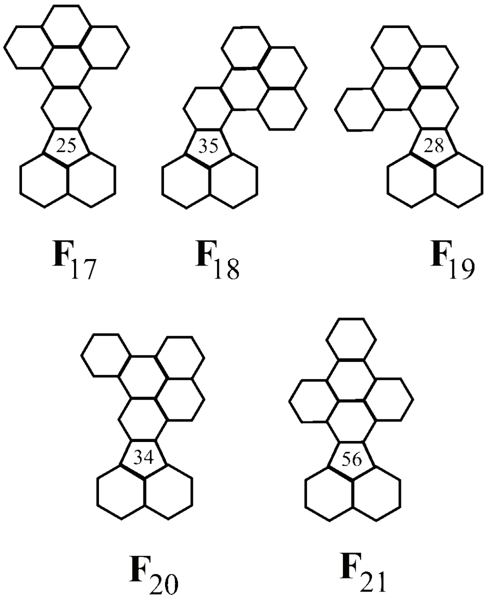

Fig. 6. The same data as in Fig. 4 for FTBHs the female and male benzenoid fragments of which are naphthalene and benzo[*b*]pyrene, respectively. $\mathbf{F}_{17}$–$\mathbf{F}_{21}$ have 0, 1, 1, 1, 2 PCP constellations, and 1, 0, 1, 1, 1 linear constellations, respectively. The *ef*-values of the five-membered ring follow the increase of the number of PCP constellations. In agreement with the linear effect, the *ef*-value in $\mathbf{F}_{18}$ is greater than that in $\mathbf{F}_{19}$ and $\mathbf{F}_{20}$.

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In order to convincingly demonstrate the validity of the above regularity, we examined pairs of FTBHs with an equal number of PCP and linear constellations, such that the female benzenoid fragment of one species and the male benzenoid fragment of the other species are identical, were examined. Two examples of this kind are depicted in Fig. 7.

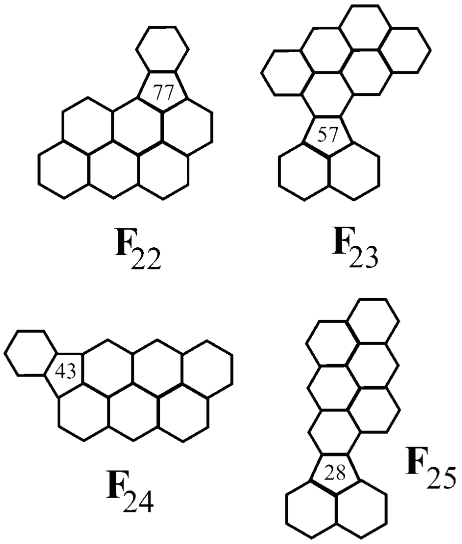

Fig. 7. The same data as in Fig. 4 for the pairs $\mathbf{F}_{22}$–$\mathbf{F}_{25}$. Both $\mathbf{F}_{22}$ and $\mathbf{F}_{23}$ possess two hexagons in the PCP constellation and one in the linear constellation. The female fragment of $\mathbf{F}_{22}$ and the male fragment of $\mathbf{F}_{23}$ are identical (= anthracenoanthracene), but the *ef*-value in $\mathbf{F}_{22}$ is much greater than in $\mathbf{F}_{23}$. Both $\mathbf{F}_{24}$ and $\mathbf{F}_{25}$ possess one hexagon in the PCP constellation and one in the linear constellation. The female fragment of $\mathbf{F}_{24}$ and the male fragment of $\mathbf{F}_{25}$ are identical (= anthracenoanthracene), but the *ef*-value in $\mathbf{F}_{24}$ is much greater than in $\mathbf{F}_{25}$. These examples confirm the existence of a male-female difference in the PCP effect.

CONCLUSIONS

The main conclusion of the present work is that, contrary to the inferences of the traditional, Kekulé-structure based, theoretical approaches,[7,12] the five-membered ring in fluoranthene-type benzenoid hydrocarbons is far from being "empty", and does possess a certain degree of π-electron conjugation. The magnitude of this conjugation, measured by its energy effect, depends in a perplexed manner on the structure and mode of condensation of the two benzenoid fragments which form the fluoranthene derivative. The most significant of these structural factors seems to have been identified.

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ИЗВОД

О π-ЕЛЕКТРОНСКОЈ КОНЈУГАЦИЈИ У ПЕТОЧЛАНОМ ПРСТЕНУ БЕНЗЕНОИДНИХ УГЉОВОДОНИКА ФЛУОРАНТЕНСКОГ ТИПА

ИВАН ГУТМАН и ЈЕЛЕНА ЂУРЂЕВИЋ

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Бензеноидни угљоводоници флуорантенског типа (FTBH) су полициклични конјуговани системи добијени спајањем два бензеноидна угљоводоника тако да се образује нови петочлани прстен. Главне разлике између π-електронских особина FTBH и бензеноидних угљоводоника узроковане су овим петочланим прстеном. У раду су анализирани и одређени најважнији структурни фактори који утичу на π-електронску конјугацију у петочланом прстену FTBH.

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