# Effect of a ring on the cyclic conjugation in another ring: applications to acenaphthylene-type polycyclic conjugated molecules

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*Abstract*: In a recent work, a method was developed for assessing the influence $ief(G, Z_0 \mid Z_1)$ of a ring $Z_1$ on the energy effect of another ring $Z_0$ in a polycyclic conjugated molecule $G$. Herein, a report is given of detailed numerical investigations of $ief(G, Z_0 \mid Z_1)$ aimed at the elucidation of the influence of various six-membered rings on the intensity of cyclic conjugation in the five-membered ring of acenaphthylene-type molecules. The earlier discovered regularities for cyclic conjugation in acenaphthylene-type molecules (in particular, the PCP rule and the linear rule) could thus not only be rationalized, but also a number of hitherto concealed regularities could be envisaged.

*Keywords*: cyclic conjugation; energy effect of cyclic conjugation; acenaphthylene-type hydrocarbons; PCP-rule.

## INTRODUCTION

In the theory of polycyclic conjugated molecules,[1–3] it is well known that the size and mutual arrangement of the rings have a profound influence on the behavior of the π-electrons and, therefore, on practically all physical and chemical properties of the respective compounds. A method for assessing the effect of individual rings on the total π-electron energy was already elaborated in the 1970s and since then found numerous chemical applications; for details see the review[4] and the recent papers.[5–12] The energy effect (*ef*) of a ring can be viewed as a measure of the intensity of cyclic conjugation in this ring.

Most of the investigations of the π-electron properties of polycyclic conjugated molecules were focused on benzenoid hydrocarbons.[3,4] Acenaphthylenes and fluoranthenes are structurally very similar to benzenoid systems, differing from them by the presence of a single five-membered ring. Yet, their systematic

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study commenced only quite recently[13] and was eventually extended to species the odd-membered ring of which has a size greater than five.[12] A number of general properties of these benzenoid-like systems could be established,[8–12,14,15] of which the most interesting are those related to cyclic conjugation in the five--membered ring.[8–11]

In this paper, acenaphthylene-type conjugated molecules are considered. Their structure is evident from Fig. 1 and the subsequent figures; a more formal definition can be found elsewhere.[13]
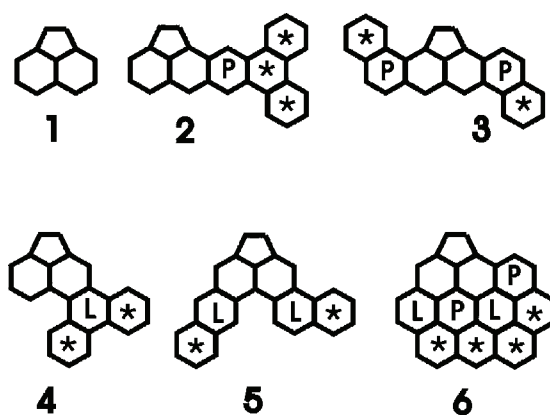


Fig. 1. Acenaphthylene (**1**) and some of its congeners (**2**–**6**). The six-membered rings attached to the parent hydrocarbon (**1**) that are in a PCP and a linear constellation are marked by P and L, respectively; the other rings are marked by asterisks. A six-membered ring is said to be in a PCP constellation if it is connected to the five-membered ring by a single carbon–carbon bond. A six-membered ring is said to be in a linear constellation if it is separated from the five-membered ring by two carbon–carbon bonds.[8,9,11]

According to their position with regard to the five-membered ring, three types of six-membered rings can be distinguished in acenaphthylenes: rings in a PCP constellation, rings in a linear constellation, and rings that neither are in a PCP nor in a linear constellation; for explanation and examples see Fig. 1.

Based on a large number of calculations, it has been established[8–11] that six--membered rings in a PCP constellation significantly increase the *ef*-value, *i.e.*, the magnitude of the cyclic conjugation, in the five-membered ring (the so-called PCP rule), whereas rings in a linear constellation slightly decrease it (the so-called linear rule). However, a theoretical explanation of these empirical regularities was not possible to find. Namely, by introducing a new six-membered ring into the acenaphthylene molecule, a large number of structural features (*e.g.*, the number of carbon and hydrogen atoms, the number of carbon–carbon bonds, *etc*.) are simultaneously changed and it is not easy to separate cyclic from non-cyclic effects. A way out of this problem was recently proposed.[16] Its essence is that

instead of comparing cyclic conjugation in two acenaphthylene species of diffe-rent size and structure, one extracts the influence of a ring on the *ef*-value of ano-ther ring within the same molecule.

If, as usual,[4] the energy effect of a ring (or cycle) $Z_0$ of a polycyclic conju-gated molecule the molecular graph of which is $G$ is denoted by $ef(G, Z_0)$, then the influence of another ring (or cycle) $Z_1$ on the value of $ef(G, Z_0)$ will be denoted by $ief(G, Z_0 | Z_1)$. How this latter quantity is calculated is briefly des-cribed in the subsequent section.

## THEORY

Let $G$ be the molecular graph[13,17] of an acenaphthylene-type system, posses-sing $n$ vertices. Let $Z_0$ be its (unique) five-membered ring and $Z_1$ another ring of $G$, which necessarily must be of size six. Denote by $\phi(G, x)$ the characteristic polynomial[17] of the graph $G$ and let $\varphi(G - Z_0, x)$, $\varphi(G - Z_1, x)$, and $\varphi(G - Z_0 - Z_1, x)$ be, respectively, the characteristic polynomials of the sub-graphs $G - Z_0$, $G - Z_1$, and $G - Z_0$. Let further $i$ be the imaginary unit, $i = \sqrt{-1}$.

It was shown[16] that the influence of ring $Z_1$ on the energy effect of ring $Z_0$ can be expressed as:

$$ief(G, Z_0 | Z_1) = \frac{2}{\pi} \int_{-\infty}^{+\infty} \left[ \frac{A_1(x) + iB_1(x)}{A(x) + iB(x)} - \frac{A_1(x) + iB_1(x) - 2iA_{01}(x)}{A(x) + iB(x) - 2iA_0(x)} \right] dx \quad (1)$$

where

$$\varphi(G, ix) = i^n \left[ A(x) + iB(x) \right]$$

$$\varphi(G - Z_0, ix) = i^{n-5} \left[ A_0(x) \right]$$

$$\varphi(G - Z_1, ix) = i^{n-6} \left[ A_1(x) + iB_1(x) \right]$$

$$\varphi(G - Z_0 - Z_1, ix) = i^{n-11} \left[ A_{01}(x) \right]$$

and where $A$, $B$, $A_0$, $A_1$, $B_1$ and $A_{01}$ are polynomials (in the variable $x$) all coef-ficients of which are positive or zero; for more details see Ref. 16.

The calculation of the right-hand side of Eq. (1) is not easy. However, the true problem with Eq. (1) is that its structure-dependency is so complicated that no generally valid conclusion could be deduced from it. Using certain, pertinently chosen by not very accurate, approximations, the right-hand side of Eq. (1) could be simplified as:[16]

$$ief(G, Z_0 | Z_1) \approx \frac{8}{\pi} \int_0^\infty \frac{A_0(x) \left[ A(x) A_{01}(x) - A_0(x) A_1(x) \right]}{A(x) \left[ A(x)^2 + 4A_0(x)^2 \right]} dx \quad (2)$$

The advantage of formula (2) is that all terms in it, except the difference:

$$A(x) A_{01}(x) - A_0(x) A_1(x) \quad (3)$$

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are necessarily positive-valued for all $x > 0$. Therefore, the sign of the right-hand side of Eq. (2), and thus also of *ief*, depends on the sign of Eq. (3).

It could be demonstrated[16] that if the ring $Z_1$ is in a PCP constellation to the five-membered ring $Z_0$, then Eq. (3) is a polynomial of degree $2n$–13 with a positive leading coefficient. Consequently, Eq. (3) gives positive values for, at least, sufficiently large $x$, implying that the right-hand side of Eq. (2) is also positive--valued, in good agreement with the PCP rule. If the ring $Z_1$ is in a linear constellation to the five-membered ring $Z_0$, then Eq. (3) is a polynomial of degree $2n$–15 with a negative leading coefficient, implying that the right-hand side of Eq. (2) is negative-valued, in harmony with the linear rule. If the ring $Z_1$ neither is in a PCP nor in a linear constellation to the five-membered ring $Z_0$, then Eq. (3) is a polynomial of degree $2n$–17 or lower, but the sign of its leading coefficient is not always the same. In other words, in this case the *ief* may assume both positive and negative values. The following numerical studies gave examples for both $ief > 0$ and $ief < 0$.

## NUMERICAL WORK

In view of the fact that all the general regularities for $ief(G, Z_0 \mid Z_1)$, outlined in the preceding section,[16] were deduced employing the approximate expression (2), the first point that needs to be checked by numerical calculation is whether there is any agreement between the approximate and exact *ief*-values. That such an agreement does indeed exist is seen from Fig. 2.
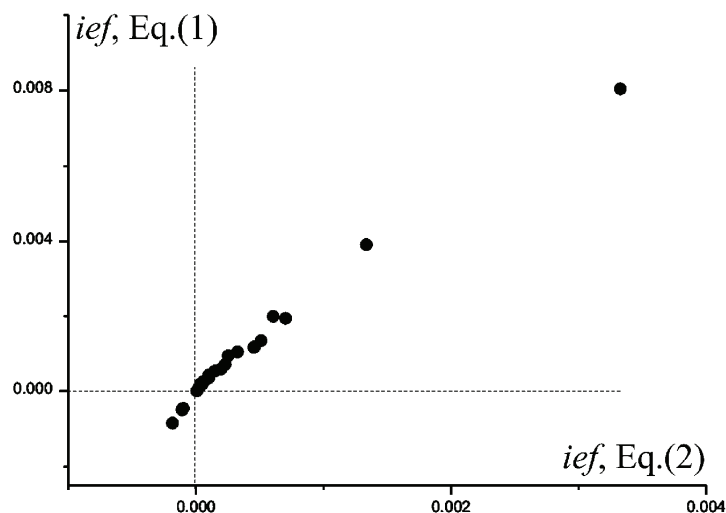


Fig. 2. Correlation between the exact (Eq. (1)) and approximate (Eq. (2)) values of $ief(G, Z_0 \mid Z_1)$ for acenaphthylene congeners, where $Z_0$ is the five-membered and $Z_1$ some six-membered ring, numerical values are available from the authors upon request. It should be noted that in no case do the approximate and exact *ief*-values differ in sign.

The data presented in Fig. 2 show that from a quantitative point of view, the approximation (2) is not particularly good: the *ief*-values computed by means of Eq. (2) are about two-times smaller than the exact *ief*-values. On the other hand, the correlation between the approximate and exact *ief*-values is remarkably good. For qualitative considerations, it is of greatest importance that whenever the right-hand side of Eq. (2) is positive (resp. negative), then the right-hand side of Eq. (1) is also found to be positive (resp. negative). This implies that the inferences made based on Eq. (2) and the sign of the polynomial (3), specified in the preceding section, remain valid also if the *ief* is calculated by means of Eq. (1). In particular, our earlier offered[16] proofs of the PCP rule and the linear rule are now seen to hold at the exact level of the theory.

In order to learn about the long-range influences on cyclic conjugation, the $ief(G, Z_0 | Z_k)$-values were examined for the six-membered rings $Z_k$, $k = 1,2,…,h$ of the acenaphthylene congeners $\mathbf{A}_h$ and $\mathbf{B}_h$ depicted in Fig. 3. The respective *ief*-values are plotted in Figs. 4 and 5.
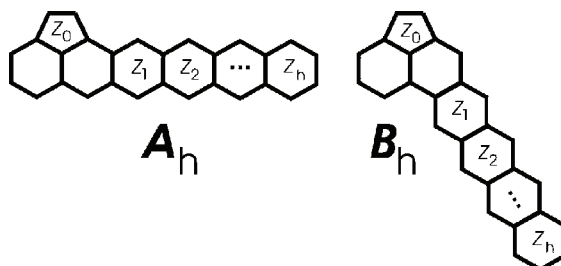


Fig. 3. The acenaphthylene congeners used for testing the influence of far-lying six-membered rings, $Z_k$, $k = 1,2,…,h$, on the cyclic conjugation in the five-membered ring $Z_0$, see Figs. 4 and 5.

The ring $Z_1$ in the system $\mathbf{A}_h$ is in a PCP constellation and, in harmony with the PCP rule, $ief(A_h, Z_0 | Z_1)$ is positive-valued. The rings $Z_k$, $k = 2,…,h$, may be viewed as extending the PCP constellation. As seen from Fig. 4, the influence of these latter rings is also positive and monotonically decreases with increasing $k$, *i.e.*, with the increasing distance from the five-membered ring. It may be said that the *ief*-values of the rings $Z_k$, $k = 1,2,…,h$ in $\mathbf{A}_h$ have a regular behavior.

The case $h = 2$ is exceptional since in $\mathbf{A}_2$, the influence of the ring $Z_2$ is greater than that of $Z_1$. One should note that $\mathbf{A}_2$ is the same as the naphthaleno-acenaphthylene **7**, depicted in Fig. 6. Its *ief*-values will be discussed in more detail in connection with Fig. 6 and Table I.

The situation with the system $\boldsymbol{B}_h$ is somewhat more complex. The ring $Z_1$ in $\boldsymbol{B}_h$ is in a linear constellation and, in harmony with the linear rule, $ief(B_h, Z_0 | Z_1)$ is negative-valued. The rings $Z_k$, $k = 2,…,h$, may be viewed as extending the linear constellation. However, their *ief*-values are positive or near-zero. As seen from Fig. 5, the influence of these latter rings increases with increasing distance

from the five-membered ring and slightly decreases only at very large distances. It is difficult to understand such an irregular behavior and its rationalization will remain a task for the future.
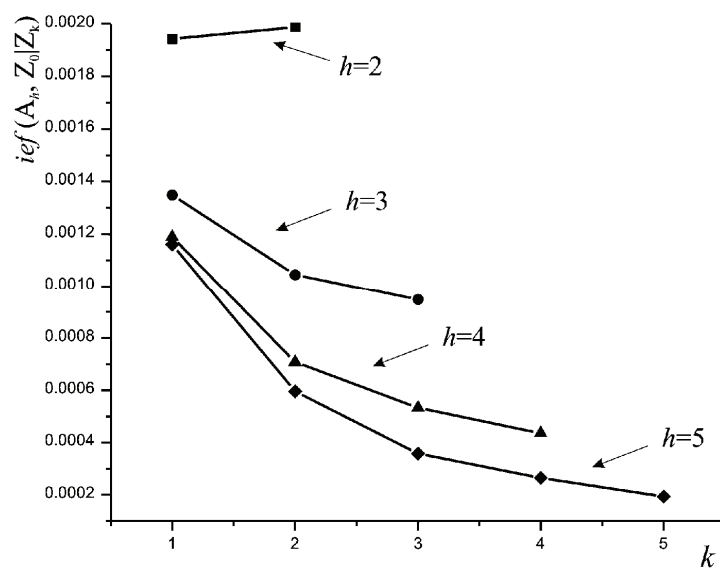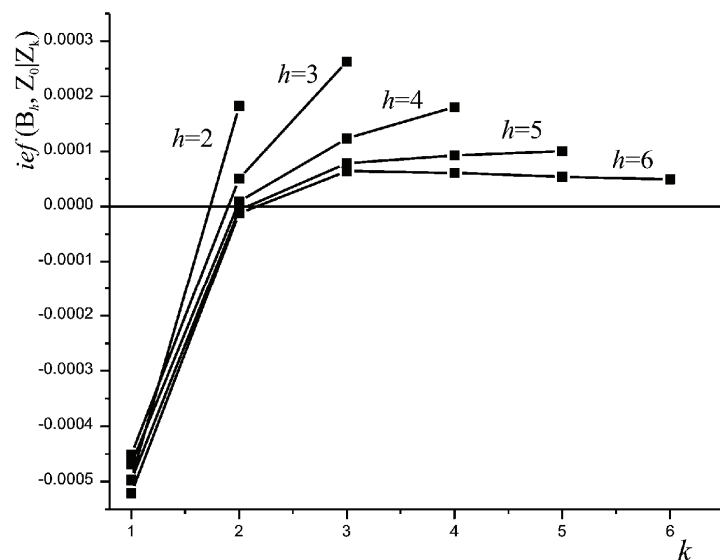


Fig. 4. Influence of the ring $Z_k$ of the acenaphthylene congeners $A_h$ on the magnitude of the cyclic conjugation in the five-membered ring $Z_0$, *cf*. Fig. 3.



Fig. 5. Influence of the ring $Z_k$ of the acenaphthylene congeners $\boldsymbol{B}_h$ on the magnitude of the cyclic conjugation in the five-membered ring $Z_0$, *cf*. Fig. 3.

Motivated by the above-described peculiarities of the *ief*-values of distant-lying rings, their detailed study was undertaken. From the numerous examples examined, in the following, only the results for the six naphthalenoacenaphthylenes, species **7**–**12** depicted in Fig. 6, will be presented. The respective *ief*-values are given in Table I. Note that $A_2$ and $B_2$ in Fig. 3 are the same as **7** and **10** in Fig. 6.
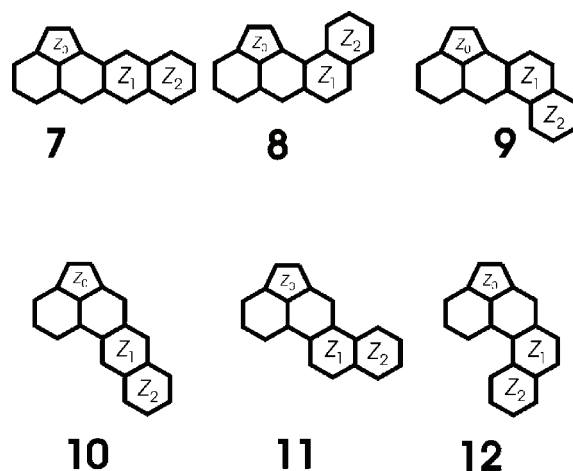


Fig. 6. The six possible naphthaleno-annelated acenaphthylenes; their $ief(G, Z_0 \mid Z_1)$ - and $ief(G, Z_0 \mid Z_2)$ -values are given in Table I.

TABLE I. Influence of the six-membered rings in the naphthalene fragment on the magnitude of the cyclic conjugation of the five-membered ring of the naphthalenoacenaphthylenes depicted in Fig. 6. The $ief(G, Z_0 \mid Z_1)$ -values clearly obey the PCP rule (in the case of **7**, **8** and **9**) and the linear rule (in the case of **10**, **11** and **12**). For a discussion on $ief(G, Z_0 \mid Z_2)$ see text

| Compound | $ief(G, Z_0 \mid Z_1)$ | $ief(G, Z_0 \mid Z_2)$ |
|---|---|---|
| **7** | 0.00194 | 0.00199 |
| **8** | 0.00158 | –0.00154 |
| **9** | 0.00154 | –0.00106 |
| **10** | –0.00050 | 0.00018 |
| **11** | –0.00053 | 0.00048 |
| **12** | –0.00042 | 0.00015 |

As can be seen from Table I, the $ief(G, Z_0 \mid Z_1)$ -values behave just as expected based on the PCP rule and the linear rule. A general regularity for the $ief(G, Z_0 \mid Z_2)$ -values could not be envisaged. As already noted, in the case of molecule **7**, $ief(G, Z_0 \mid Z_2) > ief(G, Z_0 \mid Z_1)$ in spite of the fact that $Z_2$ is more distant from $Z_0$ than $Z_1$. For the systems **8** and **9**, $ief(G, Z_0 \mid Z_2)$ is negative, whereas for **7**, **10**, **11** and **12**, it is positive. Furthermore, although molecules **11** and **12** are known to have very similar π-electron properties, their $ief(G, Z_0 \mid Z_2)$ -values differ significantly.

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In view of the above, it can be concluded that in the case of six-membered rings in the PCP and linear constellation, the simple and generally valid rules exist for their influence on the cyclic conjugation in the five-membered ring of acenaphthylene congeners. In contrast to this, rings at a greater distance from the five-membered ring (those marked by asterisks in Fig. 1) exhibit a quite irregular and "counterintuitive" behavior.

ИЗВОД

УТИЦАЈ ПРСТЕНА НА ЦИКЛИЧНУ КОНЈУГАЦИЈУ У ДРУГОМ ПРСТЕНУ: ПРИМЕНА НА ПОЛИЦИКЛИЧНЕ МОЛЕКУЛЕ АЦЕНАФТИЛЕНСКОГ ТИПА

БОРИС ФУРТУЛА, ИВАН ГУТМАН, СВЕТЛАНА ЈЕРЕМИЋ и СЛАВКО РАДЕНКОВИЋ

*Природно-машемашички факулшеш Универзишеша у Крагујевцу*

Недавно је развијена метода за процену утицаја $ief(G, Z_0 | Z_1)$ прстена $Z_1$ на енергетски ефекат неког другог прстена $Z_0$ у полицикличном конјугованом молекулу $G$. У овом раду саопштавамо резултате детаљних нумеричких истраживања $ief(G, Z_0 | Z_1)$, усмерених на проучавање утицаја разних шесточланих прстенова на интензитет цикличне конјугације у петочланом прстену молекула аценафтиленског типа. Овим су могле бити разјашњене раније откривене правилности за цикличну конјугацију у једињењима аценафтиленског типа (нарочито, ПЦП правило и линеарно правило), али су уочене и неке друге законитости.

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