



*J. Serb. Chem. Soc.* 77 (6) 751–759 (2012)  
JSCS–4306

## Cyclic conjugation in benzo- and benzocyclobutadieno-annelated terrylenes and higher rylenes

MARIJA MARKOVIĆ, JELENA ĐURĐEVIĆ and IVAN GUTMAN<sup>\*#</sup>

*Faculty of Science, University of Kragujevac, P. O. Box 60, 34000 Kragujevac, Serbia*

(Received 31 January 2012)

**Abstract:** The effect of benzo- and benzocyclobutadieno-annulation on cyclic conjugation in terrylene and the higher members of the rylene homologous series are examined. Some peculiar regularities are established, which could not be observed in the case of perylene (the first member of the rylene series).

**Keywords:** cyclic conjugation; energy effect (of cyclic conjugation); terrylene; quaterrylene; rylenes.

### INTRODUCTION

In this work, we are concerned with the cyclic conjugation in the benzo- and benzocyclobutadieno-annelated derivatives of the rylene homologous series of benzenoid hydrocarbons, Fig. 1. What is meant under “linear” and “angular” benzo- and benzocyclobutadieno-annulation is clarified in Fig. 2.

A method for calculating the energy effect *ef* of cyclic conjugation in individual rings of polycyclic conjugated compounds was conceived in the 1970s by one of the present authors.<sup>1</sup> Its details and an exhaustive bibliography can be found in the reviews,<sup>2,3</sup> whereas the mathematical details by which the quantity *ef* is computed are outlined in recent articles.<sup>4,5</sup>

When the *ef*-method was applied to benzo-annelated perylenes,<sup>6,7</sup> a remarkable phenomenon was discovered: Contrary to what standard methods<sup>8–10</sup> predict, benzo-annulation significantly influences the intensity of cyclic conjugation in the “empty” central ring of perylene; in some cases it even exceeds the intensity of cyclic conjugation in the “full” rings. Characteristic results of this kind are shown in Fig. 3.

Eventually, systematic studies<sup>11–15</sup> revealed that the first observations made in the case of perylene are general regularities that can be stated as follows:

**Rule 1.** Angular benzo-annulation increases the intensity of cyclic conjugation.

\* Corresponding author. E-mail: gutman@kg.ac.rs; jddjurdjevic@gmail.com

# Serbian Chemical Society member.

doi: 10.2298/JSC120131012M

*Rule 2.* Linear benzo-annellation decreases the intensity of cyclic conjugation.

*Rule 3.* The effect of angular benzo-annellation is stronger than the effect of linear benzo-annellation.

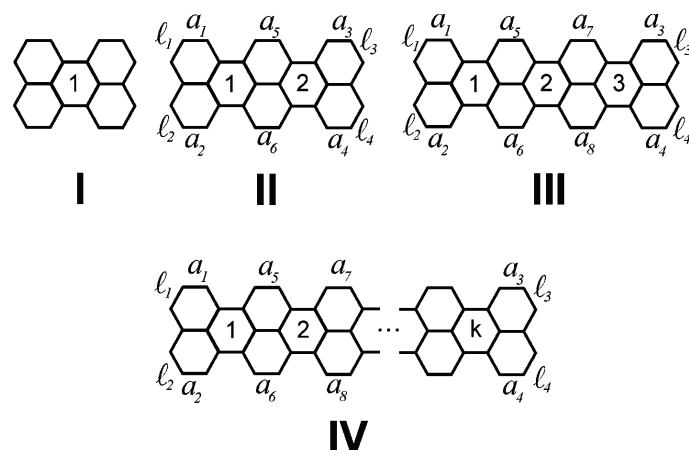


Fig. 1. The first three members of the rylene homologous series: perylene (I), terrylene (II), and quaterrylene (III), their general formula (IV), and the labeling of their annellation sites; sites marked by *a* pertain to angular, and those marked by *l* to linear annellation, *cf.* Fig. 2. The “empty” rings are labeled by 1, 2, ..., *k*. According to classical Kekulé-structure-based theories, the “empty” rings are devoid of any cyclic conjugation, implying that rylenes should be viewed as consisting of several independent naphthalene fragments. The present approach shows that this is an oversimplification and that cyclic conjugation in the “empty” rings is far from negligible, and is much influenced by benzo- and benzocyclobutadieno-annellation.

Rules 1–3 summarize the results of a large number of calculations. In addition, their general validity was recently confirmed by means of theoretical arguments.<sup>16</sup> Recalling that in some polycyclic conjugated systems (*e.g.*, in perylene<sup>6,7</sup>), as a consequence of Rules 1–3, the conjugation pattern significantly differs from what previous theories<sup>8–10</sup> based on the analysis of Kekulé structures would predict. One could even speak of the “breakdown of the Kekulé-structure model”.<sup>17</sup>

Another way to attach a six-membered ring to a conjugated system is the benzocyclobutadieno-annellation, Fig. 2. The effect of such an annellation was also studied in due detail.<sup>18–23</sup> In many cases, but not all,<sup>22,23</sup> the following regularities could be envisaged:

*Rule 4.* Angular benzocyclobutadieno-annellation decreases the intensity of cyclic conjugation.

*Rule 5.* Linear benzocyclobutadieno-annellation increases the intensity of cyclic conjugation.

*Rule 6.* The effect of linear benzocyclobutadieno-annellation is stronger than the effect of angular benzocyclobutadieno-annellation.

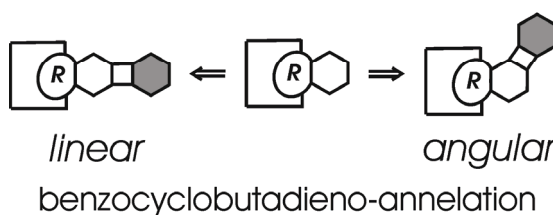
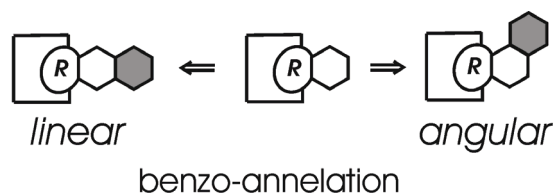


Fig. 2. Modes of benzo- and benzocyclobutadieno-annulation with regard to the ring *R*.

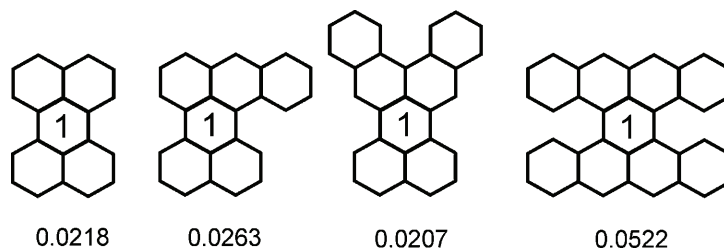


Fig. 3. Energy effects of the central “empty” ring (1) of perylene and its angularly annelated benzo-derivatives. The greater is the number of angular benzo-annulations, the greater is *ef*. In tetra-angularly annelated perylene, each of the four six-membered rings adjacent to ring 1 has  $ef = 0.0437$ , which is smaller than  $ef(1) = 0.0522$ . This contradicts the predictions of classical theories,<sup>8–10</sup> according to which there is no cyclic conjugation in the “empty” ring.

A remarkable violation of Rule 4 was found in the case of benzocyclobutadieno-annelated perylenes.<sup>23</sup> Surprisingly, in these polycyclic systems, angularly annelated benzocyclobutadieno-fragments have practically no effect on the *ef*-value of the “empty” central ring. Characteristic results of this kind are shown in Fig. 4.

The evident question that could be asked at this point is whether analogous regularities also exist in the higher members of the rylene series, in particular in terrylene and quaterrylene, *cf.* Fig. 1. The importance of knowing the answer to this question lies in the fact that oligorylenes (the first few, experimentally available, members of the rylene series) possess interesting and non-standard optical and optoelectronic properties.<sup>24–26</sup> These are primarily caused by the  $\pi$ -electrons, the degree of delocalization of which is significantly influenced by conjugation in the “empty” rings. Thus, by means of appropriately combined benzo- and benzocyclobutadieno-annulation, a fine-tuning of the optical and optoelectronic pro-

properties of these compounds could be achieved, which would be of evident value for their practical (technical) applications.

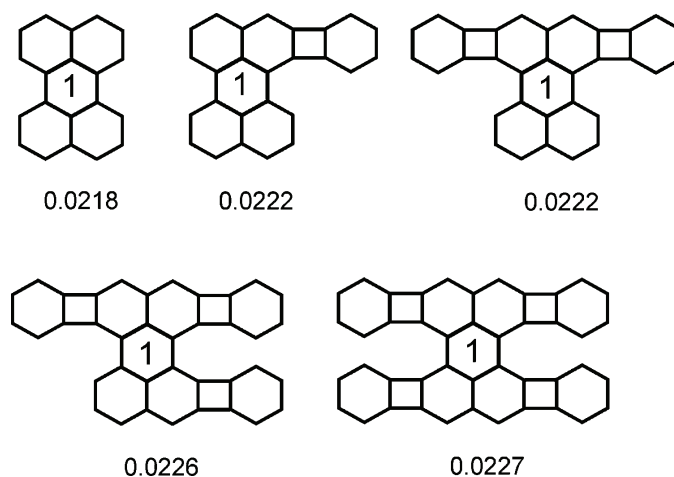


Fig. 4. Energy effects  $ef$  of the central ring (1) of various angularly benzocyclobutadieno-annelated perylenes. Practically, angular benzocyclobutadieno-annellation has an influence on the value of  $ef$ . These results should be compared with those in Fig. 6.

In what follows, some partial answers to the above question are offered.

#### NUMERICAL WORK

The energy effects,  $ef$ , of the six-membered rings were calculated by means of a several times previously described<sup>1-7</sup> graph-theoretical method, using in-house software. As usual, the  $ef$  values are given in the units of the HMO carbon-carbon resonance integral  $\beta$ . Thus, positive  $ef$  values indicate thermodynamic stabilization caused by cyclic conjugation. The greater is  $ef$ , the greater is the intensity of cyclic conjugation in the underlying ring.

There are 3 monobenzo-, 14 dibenzo-, 24 tribenzo-, 32 tetrabenzo-, 18 pentabenzo- and 7 hexabenzo-annelated terylenes, *i.e.*, a total of 98 benzo-annelated congeners. Exactly the same counts apply to benzocyclobutadieno-annelated terylenes. All calculated  $ef$ -values of the six-membered rings of these derivatives of terylene are available from the authors (M.M.) upon request.

The number of terylene derivatives possessing both benzo- and benzocyclobutadieno-annelations is several hundred. Their  $ef$  values were not calculated.

#### CONJUGATION IN BENZO-ANNELATED TERRYLENE AND HIGHER RYLENES

The  $ef$ -values of benzo-annelated terylenes and higher rylenes are found to obey fully the Rules 1–3. A few characteristic examples are depicted in Fig. 5.

A structural feature that does not exist in perylene is the sites  $a_5, a_6, \dots$  (see Fig. 1).

Benzo-annellation on these sites also obeys Rules 1 and 3, but the effect is somewhat weaker than at the terminal sites  $a_1$ – $a_4$ . Examples: For  $a_1$ - and  $(a_1, a_2)$ -annellation  $ef = 0.0293$  and  $ef = 0.0367$ , whereas for  $a_5$ - and  $(a_5, a_6)$ -annellation  $ef$

= 0.0287 and  $ef = 0.0352$ . Consistently, the  $ef$  values for  $(a_1, a_5)$ - and  $(a_1, a_6)$ -annulation are 0.0355 and 0.0358, which lie between 0.0287 and 0.0367.

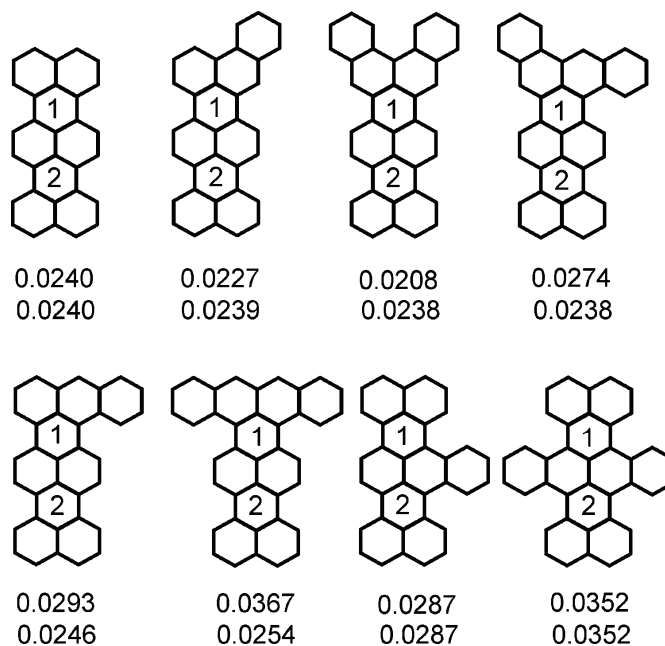


Fig. 5. Energy effects,  $ef$ , of the two “empty” rings in benzo-annulated terrylenes; the numbers below the structures are  $ef(1)$  and  $ef(2)$ , in that order. Rules 1–3 are satisfied in all cases.

In the higher rylene, there are several “empty” rings and annulation influences all their energy effects. This can be seen from the examples depicted in Fig. 5. In order to show how fast this “transmission” of annulation effect decreases, the sixth member of the rylene series ( $k=6$ , see Fig. 1) is considered. For the non-annulated species,  $ef(1) = ef(6) = 0.0252$ ,  $ef(2) = ef(5) = 0.0282$  and  $ef(3) = ef(4) = 0.0290$ . For the  $(a_1, a_2)$ -dibenzo derivative,  $ef(1) = 0.0396$ ,  $ef(2) = 0.0305$ ,  $ef(3) = 0.0301$ ,  $ef(4) = 0.0296$ ,  $ef(5) = 0.0285$  and  $ef(6) = 0.0253$ .

For the  $(l_1, l_2)$ -dibenzo derivative, the attenuation of the annulation effect is even faster:  $ef(1) = 0.0216$ ,  $ef(2) = 0.0279$ ,  $ef(3) = 0.0289$ ,  $ef(4) = 0.0289$ ,  $ef(5) = 0.0281$  and  $ef(6) = 0.0252$ .

#### CONJUGATION IN BENZOCYCLOBUTADIENO-ANNELATED TERRYLENE AND HIGHER RYLENES

In the case of benzocyclobutadieno-annulation, the first point to be examined is whether violation of Rule 4 also occurs at the higher members of the rylene series. The findings are surprising: the same as in the case of perylene, angular benzocyclobutadieno-annulation in the terminal positions  $a_1$ – $a_4$  has a negligible influence on cyclic conjugation in the “empty” rings of terrylene; examples are

given in Fig. 6. On the other hand, angular benzocyclobutadieno-annellation in the lateral positions  $a_5, a_6, \dots$  diminishes the  $ef$  values, thus obeying Rule 4; examples are given in Fig. 7. From the examples given in Fig. 7, it is seen that the same regularity also applies to benzocyclobutadieno-annellated quaterrylenes.

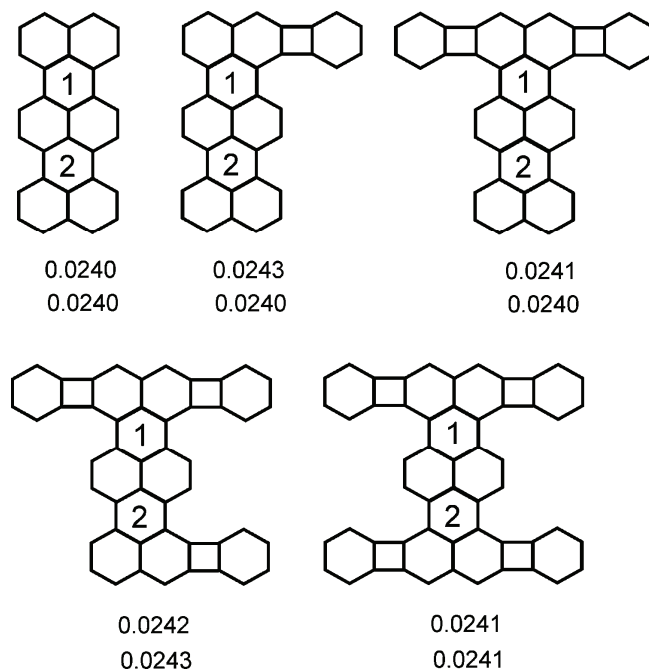


Fig. 6. Energy effects,  $ef$ , of the “empty” rings of benzocyclobutadieno-derivatives of terylene, annellated in terminal positions  $a_1, a_2, a_3$  and  $a_4$ . The numbers below the structures are  $ef(1)$  and  $ef(2)$ , in that order. Practically, such angular benzocyclobutadieno-annellation has an influence on the value of  $ef$ . These results should be compared with those in Fig. 4.

The present calculations confirmed that Rules 5 and 6 apply without a single exception. A few illustrative examples are provided in Fig. 8.

The results of the present work indicate that there exists an annellation mode (or, more precisely, an angular benzocyclobutadieno-annellation mode) that leaves the pattern of cyclic conjugation in the members of the rylene homologous series essentially unchanged. The theoretical explanation of why this is so remains a task for the future. Other annellation modes obey the relatively “reasonable” regularities stated here as Rules 1–6. By employment of these rules, it would be possible to design oligorylenes with the desired conjugation patterns, thus possessing optical and optoelectronic properties required for technical applications.

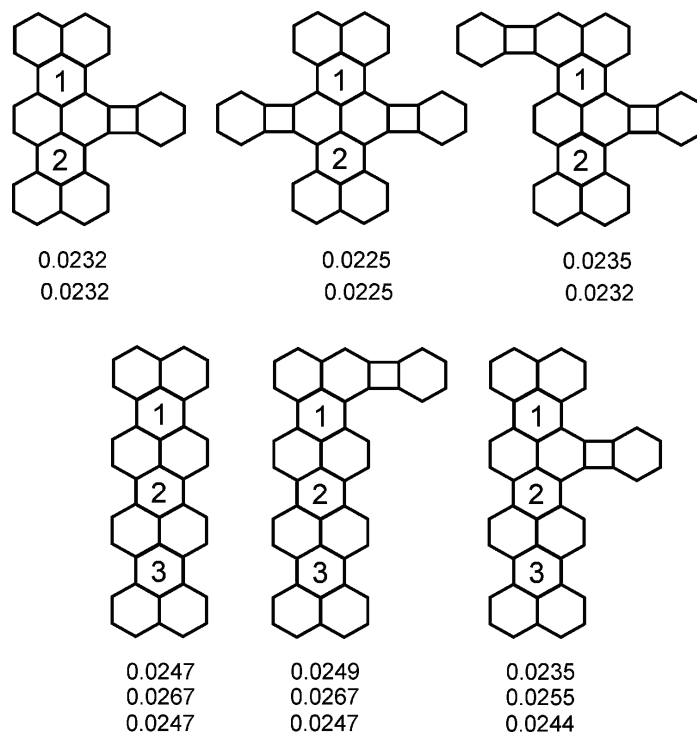


Fig. 7. The above three examples illustrate that contrary to angular benzocyclobutadieno-annellation in terminal positions, annellation in lateral positions  $a_5, a_6, \dots$  obeys Rule 4 and diminishes the intensity of cyclic conjugation in the "empty" rings of terrylene. The three examples below show that the same regularities also hold in the case of higher members of the rylene homologous series. The numbers below the structures are  $ef(1)$ ,  $ef(2)$ , and, where applicable,  $ef(3)$ , in that order.

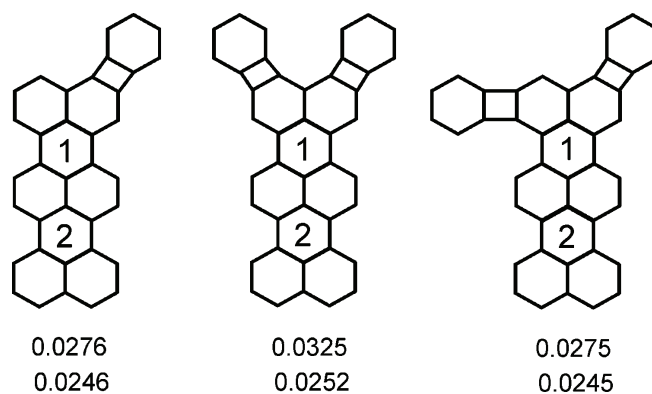


Fig. 8. Examples confirming that Rules 5 and 6 hold in the case of benzocyclobutadieno-annelated terrylenes. The numbers below the structures are  $ef(1)$  and  $ef(2)$ , in that order. Note that the  $ef$ -values in the  $\ell_1$ - and  $(\ell_1, a_2)$ -derivatives are practically identical; this is the consequence of the non-validity of Rule 4, cf. Fig. 6.

*Acknowledgement.* The authors thank the Ministry of Education and Science of the Republic of Serbia for support (Grant No. 174033).

## ИЗВОД

ЦИКЛИЧНА КОНЈУГАЦИЈА У БЕНЗО- И БЕНЗОЦИКЛОБУТАДИЕНО-АНЕЛИРАНИМ  
ТЕРИЛЕНИМА И ВИШИМ РИЛЕНИМА

МАРИЈА МАРКОВИЋ, ЈЕЛЕНА ЂУРЂЕВИЋ и ИВАН ГУТМАН

*Природно–математички факултет Универзитета у Краљевцу*

Испитиван је утицај бензо- и бензоциклобутатиенске аелације на цикличну конјугацију у териленима и вишим члановима риленског хомологног низа. Установљене су извесне неочекиване правилности, које нису могле бити уочене у случају перилена (првог члана риленског низа).

(Примљено 31. јануара 2012)

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