

# On cyclic conjugation of the members of the pyrene/pyropyrene series and their formally $\pi$ -localized derivatives

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## ON CYCLIC CONJUGATION OF THE MEMBERS OF THE PYRENE/PEROPYRENE SERIES AND THEIR FORMALLY $\pi$ -LOCALIZED DERIVATIVES

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In the pyrene/peropyrene homologous series cyclic conjugation is found to follow a pattern different from what the classical Kekulé-structure-based theories would predict. In the derivatives of these benzenoid systems, in which the  $\pi$ -electrons formally belong to localized double bonds, the Kekulé-structure-based picture is fully violated.

**Key words:** cyclic conjugation; benzenoid hydrocarbons; Kekulé structures; energy effect of cyclic conjugation

### INTRODUCTION

A significant part of the current theory of benzenoid molecules [1–5] is based on the examination of their Kekulé structures. It is nowadays accepted as a firmly established fact that the overall aromaticity of a benzenoid hydrocarbon (measured via its resonance energy) is proportional to its Kekulé structure count [6–8]. Further, the aromaticity of an individual ring in a benzenoid hydrocarbon is proportional to the number of conjugated circuits (pertaining to that ring), contained in the Kekulé structures [9–12]. Another way to assess local aromaticity in benzenoid molecules is via Clar aromatic sextet theory [13–15], which – again – is based on Kekulé structures [16].

Any of the mentioned approaches would predict that a domain in a benzenoid molecule in which the double bonds are (formally) localized, is devoid of cyclic conjugation of the  $\pi$ -electrons and is therefore non-aromatic. Under *formally localized* is meant that in all Kekulé structures certain double bonds have a fixed position. In what follows we shall refer to such systems as *formally  $\pi$ -localized*.

Some time ago a molecular-orbital method was developed [17] for the calculation of the effect of individual cycles in polycyclic conjugated molecules on the total  $\pi$ -electron energy. This method is not based on the Kekulé-structure para-

digm, and may therefore be used for a non-biased testing of the validity of conclusions drawn by means of the Kekulé-structure-based approaches.

In the vast majority of cases examined (see, for instance, [15, 17–19] and the references cited therein), the agreement between the results obtained by the classical (Kekulé-structure-based and Clar-theory-based) methods and our method is remarkably good, providing thus an independent justification of the former. However, there exist certain benzenoid molecules for which the two approaches significantly disagree, indicating that the Kekulé picture of these molecules is inadequate.

These exceptional benzenoid systems are of interest not only from a theoretician's point of view, but are of potential value for applications in electronics (as conductors, semiconductors, photoemitters and similar). We are currently undertaking a detailed study thereof. In this paper we report some novel results obtained along these lines.

We examined cyclic conjugation in the homologous series  $P_n$  of which the first few members are pyrene ( $n = 1$ ), peropyrene ( $n = 2$ ), teropyrene ( $n = 3$ ), quateropyrene ( $n = 4$ ), ... , see Fig. 1. The first few members of this series are known compounds [1] and their physico-chemical properties are typical for aromatic benzenoid hydrocarbons: low chemical reactivity, high

low chemical reactivity, high thermodynamic stability, insensitivity to air, heat and light [1]. This behavior is consistent with a large Kekulé structure count:  $P_n$  has  $2 \cdot 3^n$  Kekulé structures [20]. Also the energy-effects due to cyclic conjugation in  $P_n$  can be described as usual for benzenoid molecules.

The reason for studying cyclic conjugation in the benzenoid molecules  $P_n$ ,  $n = 1, 2, \dots$ , is their following peculiar topological property: In these molecules there are two sites (tentatively denoted as "top",  $t$ , and "bottom",  $b$ , see diagram I in Fig. 1). By pertinently modifying  $P_n$  in positions  $t$  and  $b$  the resulting  $\pi$ -electron system becomes formally  $\pi$ -localized, i.e. has a single Kekulé structure. Various such modifications are possible, some depicted in Fig. 2.

We found that, provided  $n$  is sufficiently large ( $n \geq 3$ ), the intensity of cyclic conjugation in  $P_n$  and in its formally  $\pi$ -localized derivatives is nearly equal. This finding is contradictory to what one would expect from the large number of Kekulé structures of  $P_n$  and a single Kekulé structure of its

formally  $\pi$ -localized derivative. Details are given in the subsequent sections.

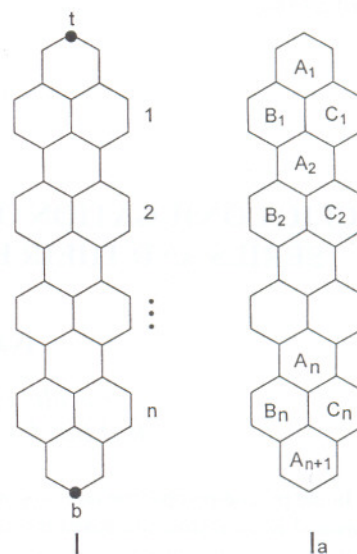


Fig. 1. The homologous series of benzenoid molecules studied in this work; diagram I depicts the structure of  $P_n$ , a benzenoid system with  $3n + 1$  hexagons; in diagram Ia the labeling of the hexagons of  $P_n$  is indicated

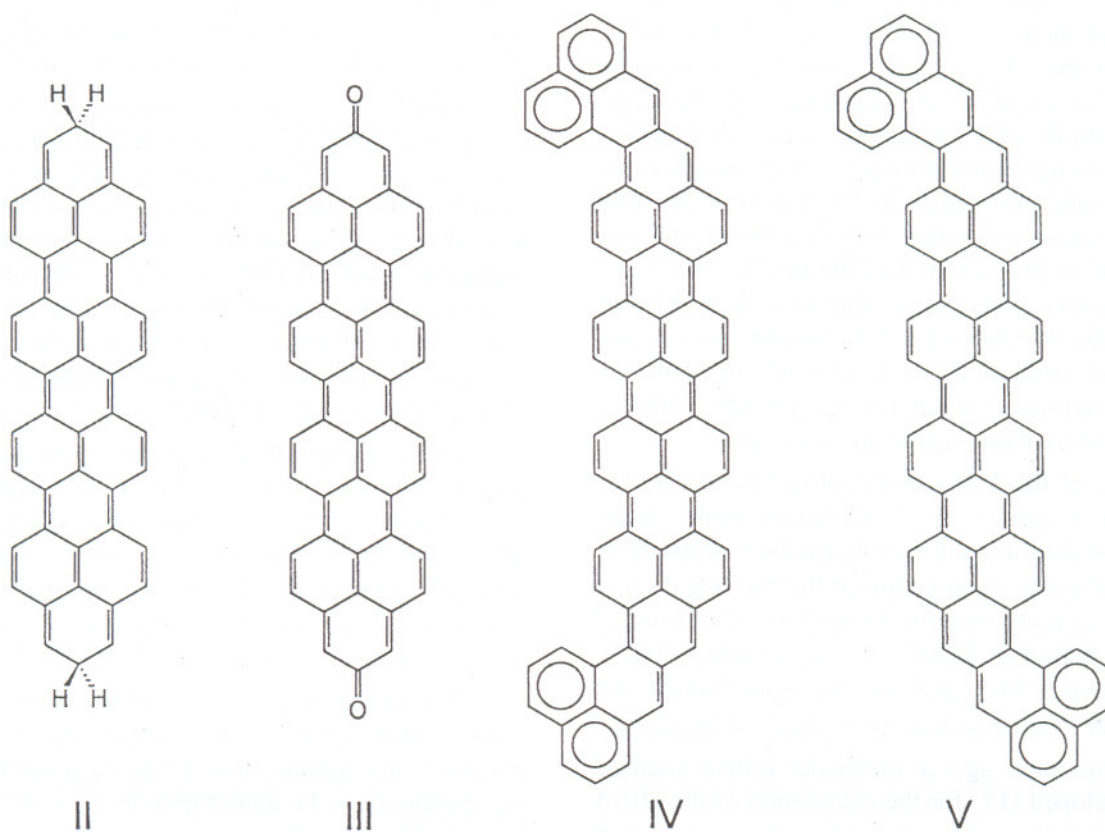


Fig. 2. Various formally  $\pi$ -localized derivatives of  $P_n$

## CYCLIC CONJUGATION IN PEROPYRENES

The effect that a particular cycle  $Z$  has on the total  $\pi$ -electron energy of a polycyclic conjugated molecule is calculated by means of the formula [17] (see also [21])

$$ef(G, Z) = \frac{2}{\pi} \int_0^{\infty} \ln \left| \frac{\phi(G, ix)}{\phi(G, ix) + 2\phi(G - Z, ix)} \right| dx \quad (1)$$

where  $G - Z$  is the subgraph obtained by deleting  $Z$  from the molecular graph  $G$  and where  $\phi$  stands for the respective characteristic polynomial. As usual in this field of theoretical chemistry, the  $ef$ -values, as defined by means of eq. (1), are expressed in the units of the carbon-carbon resonance integral  $\beta$  of the Hückel molecular orbital theory [22]. The resonance integral  $\beta$  is negative. Consequently, positive values of  $ef$  imply thermodynamic stabilization. The greater is  $ef(G, Z)$ , the greater is the intensity of cyclic conjugation in the cycle  $Z$ .

Characteristic values of  $ef$  are +0.2726 for benzene, +0.1211 and +0.0709 for the 6- and 10-membered cycles in naphthalene, -0.0017, -0.0109, +0.1467 for the 5-, 7- and 10-membered cycles in azulene, and -1.2257 for cyclobutadiene [17].

In column I of Table 1 are given the  $ef$ -values of all (symmetry non-equivalent) six-membered rings of the first few members of the pyrene/peropyrene series [23]. From these data it is seen that, with the exception of the rings  $A_1$  and  $A_{n+1}$ , the contribution of all hexagons to total  $\pi$ -electron energy is roughly the same, i.e. all hexagons have roughly the same extent of cyclic conjugation. Thus the intensity of cyclic conjugation of the  $\pi$ -electrons is nearly equal in all parts of the molecule  $P_n$ , except that it is stronger in its peaks (hexagons  $A_1$  and  $A_{n+1}$ ). Such a behavior, characteristic for aromatic molecules, is usually rationalized by the large number ( $= 2 \cdot 3^n$ ) of Kekulé structures of  $P_n$ .

Table 1

The energy-effects, calculated by means of eq. (1) and expressed in  $\beta$ -units, of the six-membered rings of the first six members of the pyrene/peropyrene series as well as of various formally  $\pi$ -localized derivatives thereof (cf. Figs. 1 and 2) [23]; the labeling of the rings is indicated in diagram 1a in Fig. 1

System	Cycle	I	II	III	IV	V
$P_1$	$A_1$	0.1063	–	0.0551	0.0530	0.0536
	$B_1$	0.0528	0.0438	0.0493	0.0706	0.0560
	$C_1$	0.0528	0.0438	0.0493	0.0454	0.0560
$P_2$	$A_1$	0.1032	–	0.0599	0.0548	0.0550
	$B_1$	0.0595	0.0579	0.0591	0.0718	0.0687
	$C_1$	0.0595	0.0579	0.0591	0.0553	0.0573
	$A_2$	0.0423	0.0358	0.0392	0.0397	0.0399
$P_3$	$A_1$	0.1021	–	0.0620	0.0555	0.0556
	$B_1$	0.0611	0.0616	0.0615	0.0726	0.0718
	$C_1$	0.0611	0.0616	0.0615	0.0576	0.0581
	$A_2$	0.0404	0.0378	0.0392	0.0391	0.0391
	$B_2$	0.0678	0.0692	0.0685	0.0720	0.0693
	$C_2$	0.0678	0.0692	0.0685	0.0669	0.0693
$P_4$	$A_1$	0.1017	–	0.0626	0.0557	0.0557
	$B_1$	0.0618	0.0632	0.0625	0.0732	0.0730
	$C_1$	0.0618	0.0632	0.0625	0.0584	0.0586
	$A_2$	0.0397	0.0386	0.0392	0.0388	0.0388
	$B_2$	0.0700	0.0713	0.0705	0.0728	0.0721
	$C_2$	0.0700	0.0713	0.0705	0.0696	0.0701
	$A_3$	0.0382	0.0373	0.0378	0.0376	0.0376
$P_5$	$A_1$	0.1014	–	0.0628	0.0557	0.0557
	$B_1$	0.0621	0.0639	0.0630	0.0736	0.0735
	$C_1$	0.0621	0.0639	0.0630	0.0588	0.0589
	$A_2$	0.0393	0.0388	0.0391	0.0386	0.0386
	$B_2$	0.0709	0.0723	0.0715	0.0734	0.0732
	$C_2$	0.0709	0.0723	0.0715	0.0706	0.0708
	$A_3$	0.0374	0.0371	0.0373	0.0370	0.0370
	$B_3$	0.0724	0.0728	0.0726	0.0736	0.0730
	$C_3$	0.0724	0.0728	0.0726	0.0724	0.0730
$P_6$	$A_1$	0.1013	–	0.0629	0.0556	0.0556
	$B_1$	0.0623	0.0642	0.0632	0.0738	0.0738
	$C_1$	0.0623	0.0642	0.0632	0.0590	0.0590
	$A_2$	0.0391	0.0388	0.0390	0.0384	0.0384
	$B_2$	0.0714	0.0729	0.0720	0.0738	0.0738
	$C_2$	0.0714	0.0729	0.0720	0.0712	0.0712
	$A_3$	0.0370	0.0369	0.0369	0.0367	0.0367
	$B_3$	0.0735	0.0737	0.0736	0.0743	0.0741
	$C_3$	0.0735	0.0737	0.0736	0.0736	0.0737
	$A_4$	0.0365	0.0364	0.0365	0.0363	0.0363

CYCLIC CONJUGATION IN THE FORMALLY  $\pi$ -LOCALIZED DERIVATIVES OF PEROPYRENES

In columns II–V of Table 1 are given the  $ef$ -values of all (symmetry non-equivalent) six-membered rings of the formally  $\pi$ -localized domains of the derivatives of  $P_n$  depicted in Fig. 2. Based on the fact that these all have a single Kekulé structural formula (indicated in Fig. 2), one would expect that all the  $\pi$ -electrons are confined in localized double bonds and that the intensity of cyclic conjugation is either very small or nil. The results obtained by means of eq. (1) show that this is far from reality. Some decrease of  $ef$ -values of the hexagons of the systems II–V is found only for  $n=1$  and, to a lesser degree, for  $n=2$ . For  $n \geq 3$  the intensity of cyclic conjugation in the derivatives II–V is practically the same as in the parent compound I. (This, of course, does not apply to the hexagons  $A_1$  and  $A_{n+1}$  on which the sites  $t$  and  $b$  are located, where the perturbation of the  $\pi$ -electron system of  $P_n$  is maximal.)

We also see that the cyclic conjugation in the formally  $\pi$ -localized derivatives of  $P_n$  (for  $n \geq 3$ ) is

almost independent of the kind of chemical modification of the sites  $t$  and  $b$ . This suggests that cyclic conjugation (at least in benzenoid molecules, and at least as measured by the energy-effects, eq. (1) is primarily determined by local (short-range), rather than by global (long-range) structural details.

The anonymous referee of this paper pointed out that according to his semiempirical (AM1) calculations, some double-bond localization was found in the parent compound I. In ring  $B$  (or  $C$ ) the external longitudinal bond was always found to be double, whereas the central bond (joining the rings  $B$  and  $C$ ) was always single. In the molecule I the rings  $A$  are aromatic. The longitudinal bonds in II–V are double, and the other bonds single. In the referee's opinion it is amazing that these rings contribute to the energy of the molecules in a similar extent in all the structures. We share the referee's opinion: one of the reasons for publishing this paper was just to communicate these (from the classical point of view) unusual findings.

## CONCLUDING REMARKS

The example studied in this paper shows that cyclic conjugation may be quite intense also in benzenoid systems with a single Kekulé structure. In our example, when the perturbed sites  $t$  and  $b$  were sufficiently far from each other (when  $n \geq 3$ ), the intensity of cyclic conjugation was found to be insensitive of the perturbation and, consequently, insensitive of the Kekulé structure count.

It is not our intention to claim that Kekulé structures are not important for the understanding and quantifying the  $\pi$ -electron properties of benzenoid molecules and that a big part of the existing theory of benzenoid molecules needs to be revisited.

However, we wish to point out that there exist exceptional ("pathological") cases, in which the classical picture, based on Kekulé structures, needs to be applied with due caution. In other words, there exist benzenoid systems in which the dominant modes of cyclic conjugation cannot be described by classical arguments. The formally  $\pi$ -localized derivatives of the members of the pyrene/peropyrene series may serve as an example for such an exceptional behavior.

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- [23] The  $ef$ -values of the 10- and higher-membered cycles of  $P_n$  and its formally  $\pi$ -localized derivatives (cf. diagrams I–V in Figs. 1 and 2), for  $n$  up to 10, are available from the authors upon request. The  $ef$ -values of 10- and higher-membered cycles are much smaller (usually one or two orders of magnitude) than those pertaining to 6-membered cycles [17, 19].

## Резиме

**ЗА ЦИКЛИЧНАТА КОНЈУГАЦИЈА НА ЧЛЕНОВИТЕ НА НИЗАТА ПИРЕН/ПЕРОПИРЕН И НИВНИ ДЕРИВАТИ СО  $\pi$ -ЕЛЕКТРОНИ КОИ ФОРМАЛНО ПРИПАЃААТ НА ЛОКАЛИЗИРАНИ ДВОЈНИ ВРСКИ**

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**Клучни зборови:** циклична конјугација; бензеноидни јагледороди; Кекулéови структури; енергетски ефект на цикличната конјугација

Во хомологната серија пирен/перопирен е најде-но дека цикличната конјугација се однесува различно од она што го предвидува класичната теорија засно-вана на Кекулéовите структури. Во дериватите на

овие бензеноидни системи, во кои  $\pi$ -електроните фор-мално им припаѓаат на локализираните двојни врски, сликата заснована на Кекулéовите структури е пот-полно нарушена.