CYCLIC CONJUGATION IN ANNELATED PERYLENES

Jelena Đurđević,[a] **Boris Furtula,**[a] **Ivan Gutman,**[a]
Radmila Kovačević,[a] **Sonja Stanković**[a]
and **Nedžad Turković**[b]

[a]*Faculty of Science, University of Kragujevac,
Kragujevac, Serbia and Montenegro*, and
[b]*City Assembly, 31300 Prijepolje, Serbia & Montenegro*

Abstract

Cyclic conjugation in benzo-annelated perylenes was studied by means of the energy–effects of their six-membered rings. Several currently used models for assessing the extent of cyclic conjugation in benzenoid hydrocarbons, based on Kekulé structures, Clar formulas, or conjugated circuits, predict that there is no cyclic conjugation in the central, "empty", ring of perylene and its annelated derivatives. We show that in some annelated perylenes the extent of cyclic conjugation in the "empty" ring becomes unexpectedly high. Therefore, in the case of these annelated perylenes the Kekulé–structure–based models fail.

INTRODUCTION

Cyclic arrangement of π-electrons drastically influences the chemical and physical behavior of conjugated molecules. Theories aimed at explaining the effects of cyclic conjugation were first developed for monocyclic systems [1,2] and were only somewhat later extended to polycyclic conjugated molecules [3–6] Among the theoretical approaches put forward for quantifying cyclic conjugation in polycyclic conjugated molecules the following are the most popular and most widely used:

- methods based on the Kekulé structure count (K), in particular on comparing the K-value of the molecule considered, with the K-value of the fragment obtained by deleting the cycle considered [7,8];

- methods based on the analysis of conjugated circuits,[9–11] that are just an alternative form of expressing interactions between pairs of Kekulé structures;

- methods based on Clar aromatic sextet formulas [12], that – again – are closely related (yet not equivalent) to the Kekulé structures.

Details of these approaches can be found in the books [3,4] and the reviews [5,7,13,14]. These approaches may be considered as "classical" because they assume that the conjugation pattern is determined by the Kekulé structural formulas and only by them.

Another approach to cyclic conjugation, that is not based on the consideration of Kekulé structures, was put forward by one of the present authors [6,15] and, in a slightly different form, by Aihara [16]. In this approach the extent of conjugation in a cycle of a polycyclic conjugatedπ-electron system can be measured by its energy–effect, computed within the framework of the Hückel molecular orbital (HMO) approximation.

The energy–effect of a cycle Z of a (polycyclic) conjugated molecule whose molecular graph is G, satisfies the expression

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

where $\phi(G, x)$ is the characteristic polynomial of G, the subgraph $G - Z$ is obtained by deleting from G the cycle Z, and $i = \sqrt{-1}$. Details on ef can be found elsewhere [6,17–20]. Recall that positive ef-values indicate thermodynamic stabilization, whereas cycles with negative ef destabilize the respective π-electron system. The greater is $ef(G, Z)$, the greater is the extent of cyclic conjugation in the cycle Z.

A carbon–carbon bond of a conjugated molecule is said to be "essentially single" if it is single in all Kekulé structures. Six-membered rings of benzenoid hydrocarbons that contain essentially single carbon–carbons bonds are referred to as "empty". The above specified "classical" theories predict that in "empty" rings there is no cyclic conjugation or — to say the same in a more cautious manner — that their extent of cyclic conjugation is very weak.

The simplest benzenoid hydrocarbon with an "empty" ring is perylene, depicted in Fig. 1. This benzenoid hydrocarbon is usually considered as composed of two naphthalene units that have almost independent π-electron conjugation modes. The central rings in perylene is thus viewed as devoid (or almost devoid) of any cyclic conjugation, cf. Fig. 1. The same viewpoint would then be applicable also to the benzo-annelated derivatives of perylene.

Examining the various annelated perylenes [21,22] we found that the claim that there is no or little cyclic conjugation in their "empty" rings is not always true. In some benzo– and polyaceno-annelated perylenes, the extent of π-electron conjugation in the "empty" ring (measured by means of its energy–effect) significantly exceeds the conjugation in "non-empty" rings. This, in turn, implies that the "classical" models of π-electron conjugation have their limitations and, in some cases, are not capable to correctly describe all the existing modes of cyclic conjugation.

In the subsequent section we outline the results pertaining to benzo-annelated perylenes [21], whereas in the following section we discuss the ef-values of some polyaceno-annelated perylenes.
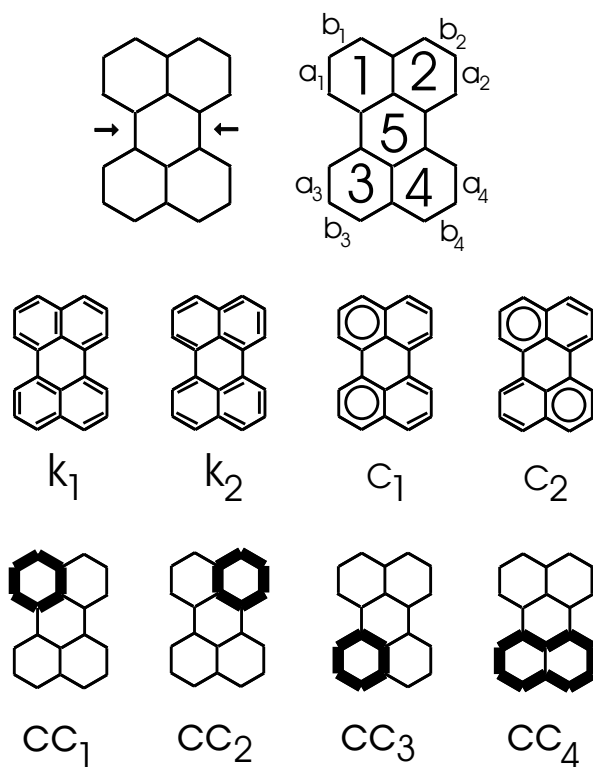
Fig. 1. Perylene and the labelling of its rings and annelation sites. From the point of view of the central ring (5) annelation may be either angular (in positions a_1, a_2, a_3, and/or a_4) or linear (in positions b_1, b_2, b_3, and/or b_4). The diagrams k_1 and k_2 represent two Kekulé structures, whereas c_1 and c_2 the two Clar aromatic sextet formulas of perylene. In the diagrams cc_1–cc_4 are indicated the conjugated circuits contained in the Kekulé structure k_1. The carbon–carbon bonds of perylene marked by arrows are "essentially single" because they are single in all (nine) Kekulé structures, all (four) Clar aromatic sextet formulas, and are not contained in any of the (six) conjugated circuits.

ON CYCLIC CONJUGATION IN BENZO-ANNELATED PERYLENES

For the present considerations it important to recall that the energy–effect–based theory of cyclic conjugation is not *a priori* restricted to the "classical" conjugation modes, implied by the Kekulé–type or Clar–type structural formulas. The fact is that in most cases the energy–effects are in harmony with the predictions of the "classical" theories [20]. There are, however, exceptions, revealing the limitations of the "classical" approaches. A simple case of this kind is analyzed in this section.

There exist two mono–, nine di–, eight tri–, and seven tetra-benzo-perylenes, a total of 26 distinct benzo-annelated derivatives, cf. Tables 1 and 2. For all rings of these benzenoid systems the ef-values, as given by Eq. (1), were computed. The results obtained are given in Tables 1 and 2.

The first regularity that easily can be seen from Tables 1 and 2 is that the extent and modes of conjugation in the region formed by the rings 1'-1-2-2' is not much dependent on the conjugation in the region 3'-3-4-4', in full harmony with the "classical" picture (namely that perylene consists of two weakly coupled naphthalene subunits). For instance, consider the species in which the ring 1', attached to ring 1, is in angular position, and no ring is attached to ring 2. Then the ef-values of 1' in the systems a_1, $a_1 a_3$, $a_1 b_3$, $a_1 a_4$, $a_1 b_4$, and $a_1 b_3 b_4$ are 0.1086, 0.1130, 0.1085, 0.1111, 0.1083, and 0.1079, respectively, all being nearly equal and all insignificantly differing from 0.11.

The next regularity that we wish to emphasize is that the energy effects of the rings annelated in a given position (either angular or linear) vary within very narrow limits. Thus, the ef-values of all angularly annelated rings lie between 0.1056 and 0.1232, whereas those of linearly annelated rings between 0.1390 and 0.1653. In all cases angularly annelated rings have smaller energy–effects than the linearly annelated ones. Such a cyclic–conjugation–effect is no surprise whatsoever, and is easily rationalized (or predicted) by means arguments from Clar aromatic sextet theory.

The third regularity envisaged from the data given in Table 1 is inexplicable in terms of "classical" theories.

In perylene the "empty" central ring 5 has an energy–effect of 0.0218, significantly smaller than 0.1093 — the energy–effects of the other four rings. This is a finding acceptable by the "classical" approaches (although their strict application would require a zero energy–effect in the ring 5).

The annelation of a ring in angular position increases the energy–effect of the ring 5 by 20%. This contradicts the "classical" picture, which would predict no (or very small) effect of such an annelation on the extent of cyclic conjugation. Only angular annelation causes a non-classical intensification of cyclic conjugation in the central ring of perylene. The analogous annelation in linear position results in a much smaller effect: it decreases the ef-value of the ring 5 by only 5%.

compound	$ef(1)$	$ef(2)$	$ef(3)$	$ef(4)$	$ef(5)$
perylene	0.1093	0.1093	0.1093	0.1093	0.0218
a_1	0.0563	0.0873	0.1048	0.1091	0.0263
b_1	0.0482	0.1429	0.1094	0.1098	0.0207
$a_1 a_2$	0.0465	0.0465	0.1040	0.1040	0.0325
$a_1 a_3$	0.0534	0.0885	0.0534	0.0885	0.0322
$a_1 a_4$	0.0556	0.0837	0.0837	0.0556	0.0324
$a_1 b_2$	0.0690	0.0396	0.1058	0.1096	0.0247
$a_1 b_3$	0.0564	0.0878	0.0464	0.1421	0.0248
$a_1 b_4$	0.0566	0.0873	0.1369	0.0482	0.0248
$b_1 b_2$	0.0626	0.0626	0.1101	0.1101	0.0193
$b_1 b_3$	0.0482	0.1435	0.0482	0.1435	0.0197
$b_1 b_4$	0.0483	0.1431	0.1431	0.0483	0.0197
$a_1 a_2 a_3$	0.0439	0.0465	0.0523	0.0846	0.0407
$a_1 a_2 b_3$	0.0465	0.0468	0.0462	0.1352	0.0304
$a_1 a_3 b_2$	0.0654	0.0402	0.0540	0.0888	0.0300
$a_1 a_4 b_2$	0.0681	0.0383	0.0844	0.0561	0.0302
$a_1 b_2 b_3$	0.0691	0.0398	0.0468	0.1429	0.0234
$a_1 b_2 b_4$	0.0693	0.0396	0.1382	0.0484	0.0234
$a_1 b_3 b_4$	0.0568	0.0880	0.0604	0.0625	0.0227
$b_1 b_2 b_3$	0.0627	0.0629	0.0484	0.1439	0.0184
$a_1 a_2 a_3 a_4$	0.0437	0.0437	0.0437	0.0437	0.0522
$a_1 a_2 a_3 b_4$	0.0445	0.0468	0.0641	0.0388	0.0376
$a_1 a_2 b_3 b_4$	0.0469	0.0469	0.0599	0.0599	0.0274
$a_1 a_3 b_2 b_4$	0.0662	0.0403	0.0662	0.0403	0.0281
$a_1 a_4 b_2 b_3$	0.0687	0.0385	0.0385	0.0687	0.0283
$a_1 b_2 b_3 b_4$	0.0696	0.0399	0.0608	0.0628	0.0216
$b_1 b_2 b_3 b_4$	0.0630	0.0630	0.0630	0.0630	0.0173

Table 1. Energy–effects of the rings 1–5 in perylene and its benzo-annelated derivatives; for notation see Fig. 1. The symbols in the column "*compound*" indicate the positions of the annelated benzene rings.

compound	$ef(1')$	$ef(2')$	$ef(3')$	$ef(4')$
a_1	0.1086	—	—	—
b_1	0.1546	—	—	—
$a_1\,a_2$	0.1066	0.1066	—	—
$a_1\,a_3$	0.1130	—	0.1130	—
$a_1\,a_4$	0.1111	—	—	0.1111
$a_1\,b_2$	0.1167	0.1647	—	—
$a_1\,b_3$	0.1085	—	0.1534	—
$a_1\,b_4$	0.1083	—	—	0.1536
$b_1\,b_2$	0.1413	0.1413	—	—
$b_1\,b_3$	0.1547	—	0.1547	—
$b_1\,b_4$	0.1547	—	—	0.1547
$a_1\,a_2\,a_3$	0.1118	0.1099	0.1163	—
$a_1\,a_2\,b_3$	0.1064	0.1062	0.1521	—
$a_1\,a_3\,b_2$	0.1206	0.1627	0.1119	—
$a_1\,a_4\,b_2$	0.1186	0.1626	—	0.1102
$a_1\,b_2\,b_3$	0.1166	0.1649	0.1538	—
$a_1\,b_2\,b_4$	0.1164	0.1649	—	0.1540
$a_1\,b_3\,b_4$	0.1079	—	0.1403	0.1404
$b_1\,b_2\,b_3$	0.1414	0.1414	0.1549	—
$a_1\,a_2\,a_3\,a_4$	0.1161	0.1161	0.1161	0.1161
$a_1\,a_2\,a_3\,b_4$	0.1105	0.1087	0.1232	0.1599
$a_1\,a_2\,b_3\,b_4$	0.1056	0.1056	0.1390	0.1390
$a_1\,a_3\,b_2\,b_4$	0.1198	0.1634	0.1198	0.1634
$a_1\,a_4\,b_2\,b_3$	0.1179	0.1632	0.1632	0.1179
$a_1\,b_2\,b_3\,b_4$	0.1161	0.1653	0.1406	0.1407
$b_1\,b_2\,b_3\,b_4$	0.1416	0.1416	0.1416	0.1416

Table 2. Energy–effects of the benzene rings 1', 2', 3', and/or 4', attached to the rings 1, 2, 3, and/or 4 of perylene, at position(s) indicated in the column "*compound*"; for notation see Fig. 1.

In the case of monobenzo-perylenes the angular–annelation–effect may look small and, perhaps, negligible. However, in multiply annelated perylenes the same effect becomes remarkably stronger. With two angularly annelated rings the extent of conjugation in the central ring is by 49% greater than in the parent compound, with three by 87%, whereas in the extreme case, namely for the $a_1\,a_2\,a_3\,a_4$ tetrabenzo-perylene, the ef-value of the ring 5 is 0.0522, implying an increase of cyclic conjugation by 140%. Moreover, in this latter molecule, cyclic conjugation in the "empty" ring 5 is found to be significantly more intense than in the rings 1, 2, 3, and 4.

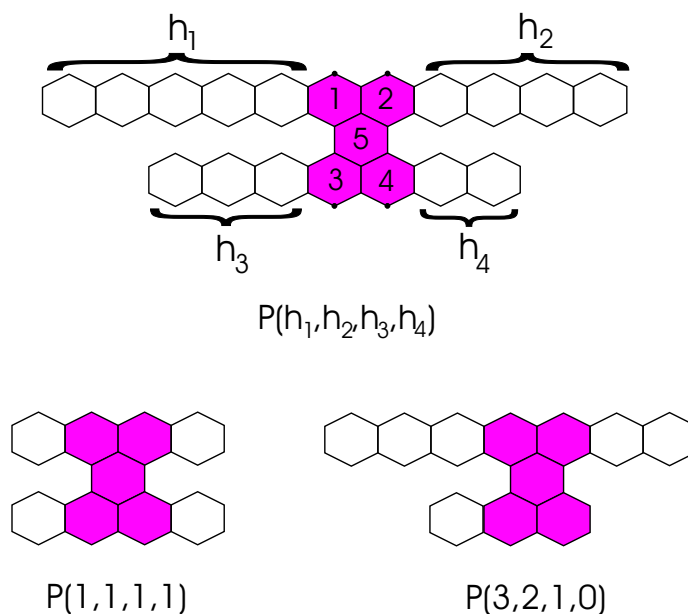## ON CYCLIC CONJUGATION IN POLYACENO-ANNELATED PERYLENES

Bearing in mind the results obtained in the preceding section, we focused our attention to perylene derivatives in which linear polyacene fragments are annelated in the (angular) positions a_1, a_2, a_3, and/or a_4, cf. Figs. 1 and 2. By this we expect to be able to find examples in which the violations from the "classical" picture of cyclic conjugation are even greater than in the case of benzo-annelated species.

In this section we are concerned with a class of annelated perylenes, whose general member is denoted by $P(h_1, h_2, h_3, h_4)$, see Fig. 2.

From the point of view of "classical" theories, $P(h_1, h_2, h_3, h_4)$ would be considered as consisting of two weakly coupled linear polyacene fragments (with $h_1 + h_2 + 2$ and $h_3 + h_4 + 2$ hexagons), joined by two "essentially single" carbon–carbon bonds. Therefore, the two linear polyacene fragments of $P(h_1, h_2, h_3, h_4)$ would be viewed as almost independently conjugated and the hexagon connecting them as "empty".

We now examine the extent of cyclic conjugation in the central ring of $P(h_1, h_2, h_3, h_4)$, and determine it by means of Eq. (1). We show that the intensity of cyclic conjugation in this ring is far from negligible, and that for certain values of the parameters h_1, h_2, h_3, h_4 it significantly exceeds the cyclic conjugation in the hexagons of the linear polyacene fragments.

Fig. 2. The polyaceno-annelated perylenes whose cyclic conjugation is studied in this work. The species $P(h_1, h_2, h_3, h_4)$ is obtained from perylene by attaching to its site a_i (cf. Fig. 1) an h_i-cyclic linear polyacene fragment, $i = 1, 2, 3, 4$. Thus, $P(h_1, h_2, h_3, h_4)$ has $5 + h_1 + h_2 + h_3 + h_4$ six-membered rings. For instance, $P(0, 0, 0, 0)$ is perylene itself, and $P(1, 1, 1, 1)$ is the $a_1 \, a_2 \, a_3 \, a_4$ tetrabenzo-perylene, whose anomalous cyclic conjugation pattern is established in the previous section.

In the notation just introduced, the main result of the preceding section is that in the series $P(1, 0, 0, 0)$, $P(1, 1, 0, 0)$, $P(1, 1, 1, 0)$, $P(1, 1, 1, 1)$ one encounters a complete breakdown of the "classical" theories of cyclic conjugation, namely the central "empty" ring becomes one of the most intensely conjugated domains of the respective molecules; for details see Table 1.

In what follows we denote by $ef(h_1, h_2, h_3, h_4)$ the energy–effect, computed by means of Eq. (1), of the central ring of $P(h_1, h_2, h_3, h_4)$. As already explained, in the classical theories this ring is considered to be "empty" and devoid of any cyclic conjugation. For comparative purposes we refer to the energy–effect of the ring 1 of the perylene core (see Fig. 2), i. e., to which the h_1-branch of $P(h_1, h_2, h_3, h_4)$ is attached. This latter ring is a typical representative of "full" rings, in which the "classical" theories forecast a significant amount of cyclic conjugation. Its energy–effect will be denoted by $ef^*(h_1, h_2, h_3, h_4)$.

It was shown above that in perylene and its mono–, di–, and tribenzo–annelated

derivatives, in full harmony with the classical theories,

$$
\begin{aligned}
ef(0,0,0,0) &< ef^*(0,0,0,0) \\
ef(1,0,0,0) &< ef^*(1,0,0,0) \\
ef(1,1,0,0) &< ef^*(1,1,0,0) \\
ef(1,1,1,0) &< ef^*(1,1,1,0) \ .
\end{aligned}
$$

However, in the case of tetrabenzo–annelated perylene an inversion happens:

$$
ef(1,1,1,1) \ > \ ef^*(1,1,1,1) \ .
$$

In particular, $ef(1,1,1,1) = 0.0522$ whereas $ef^*(1,1,1,1) = 0.0437$. Our aim is to investigate how far this breakdown of the classical picture can go.

Our numerical calculations revealed the following regularities.

Rule 1. If the length of a branch of $P(h_1, h_2, h_3, h_4)$ is increased, then the energy–effect $ef(h_1, h_2, h_3, h_4)$ of the central ring increases. Symbolically,

$$
\begin{aligned}
ef(h_1 + 1, h_2, h_3, h_4) &> ef(h_1, h_2, h_3, h_4) \\
ef(h_1, h_2 + 1, h_3, h_4) &> ef(h_1, h_2, h_3, h_4) \\
ef(h_1, h_2, h_3 + 1, h_4) &> ef(h_1, h_2, h_3, h_4) \\
ef(h_1, h_2, h_3, h_4 + 1) &> ef(h_1, h_2, h_3, h_4) \ .
\end{aligned}
$$

Furthermore, with the increasing length of a branch, $ef(h_1, h_2, h_3, h_4)$ rapidly tends to a limit value.

Rule 2. By permuting the parameters h_1, h_2, h_3, h_4, the numerical value of $ef(h_1, h_2, h_3, h_4)$ is only slightly changed.

As an illustration of Rule 2 we have $ef(3,2,1,0) = 0.0478$, $ef(3,2,0,1) = 0.0477$, $ef(3,1,2,0) = 0.0476$, $ef(3,1,0,2) = 0.0473$, $ef(3,0,2,1) = 0.0475$, $ef(3,0,1,2) = 0.0472$.

Rule 3. Let the sum $h_1 + h_2 = n$ be constant. Then $ef(h_1, h_2, h_3, h_4)$ is minimal for $a = 0$ or $b = 0$ (depending on the actual values of the parameters c and d); anyway, by Rule 2, $ef(0, n, h_3, h_4) \approx ef(n, 0, h_3, h_4)$. If n is even, then $ef(h_1, h_2, h_3, h_4)$ is

maximal for $h_1 = h_2 = n/2$. If n is odd, then $ef(h_1, h_2, h_3, h_4)$ is maximal for $h_1 = (n-1)/2$ and $h_2 = (n+1)/2$ or $h_1 = (n+1)/2$ and $h_2 = (n-1)/2$ (depending on the actual values of the parameters h_3 and h_4); anyway, by Rule 2,

$$ef((n-1)/2, (n+1)/2, h_3, h_4) \approx ef((n+1)/2, (n-1)/2, h_3, h_4) \ .$$

Rule 4. Let the sum $h_1 + h_2 + h_3 + h_5 = N$ be constant. Then $ef(N, 0, 0, 0)$ is minimal, whereas the maximal ef-value is attained for

$$h_1 = h_2 = h_3 = h_4 = k \qquad \text{if } N = 4\,k$$
$$h_1 = k+1\,, \ h_2 = h_3 = h_4 = k \qquad \text{if } N = 4\,k+1$$
$$h_1 = h_2 = k+1\,, \ h_3 = h_4 = k \qquad \text{if } N = 4\,k+2$$
$$h_1 = h_2 = h_3 = k+1\,, \ h_4 = k \qquad \text{if } N = 4\,k+3\ .$$

These maximal ef-values are given in Table 3, together with the respective ef^*-values.

From Table 3 we see that the energy–effect of the "empty" ring can significantly exceed the energy–effect of a "full" ring. In particular, in the case of the annelated perylenes, this inversion of the classical picture begins at $N = 4$ and gradually increases. For sufficiently large N the energy–effect of the cyclic conjugation in the "empty" ring is almost three times greater than in a "full" ring.

It is evident that in the conjugation pattern of $P(h_1, h_2, h_3, h_4)$ cannot be satisfactorily described solely by means of Kekulé structures, but that some other resonance forms need to be taken into account. We could show [22] these resonance forms are the ionic species of a particular type.

CONCLUDING REMARKS

Within the "classical" approaches the above described angular–annelation–effect is not anticipated and cannot be explained. In order to offer an "explanation" we must go beyond the simple Kekulé–structure–based models. At this moment it is not our aim to propose a new class of structural formulas that would compete with (and sometimes outperform) the Kekulé– and Clar–type formulas. We, however, want to

N	h_1	h_2	h_3	h_4	$ef(h_1, h_2, h_3, h_4)$	$ef^*(h_1, h_2, h_3, h_4)$
0	0	0	0	0	0.0218	0.1093
1	1	0	0	0	0.0263	0.0563
2	1	1	0	0	0.0325	0.0465
3	1	1	1	0	0.0407	0.0439
4	1	1	1	1	0.0522	0.0437
5	2	1	1	1	0.0561	0.0360
6	2	2	1	1	0.0607	0.0349
7	2	2	2	1	0.0659	0.0342
8	2	2	2	2	0.0718	0.0342
9	3	2	2	2	0.0742	0.0328
10	3	3	2	2	0.0769	0.0328
11	3	3	3	2	0.0796	0.0326
12	3	3	3	3	0.0826	0.0326
13	4	3	3	3	0.0839	0.0324
14	4	4	3	3	0.0854	0.0325
15	4	4	4	3	0.0868	0.0325
16	4	4	4	4	0.0884	0.0325
17	5	4	4	4	0.0891	0.0325
18	5	5	4	4	0.0899	0.0326
19	5	5	5	4	0.0907	0.0326
20	5	5	5	5	0.0915	0.0326
21	6	5	5	5	0.0920	0.0327
22	6	6	5	5	0.0924	0.0327
23	6	6	6	5	0.0929	0.0327
24	6	6	6	6	0.0933	0.0327

Table 3. The maximal energy–effect $ef(h_1, h_2, h_3, h_4)$ of the central "empty" ring of the perylene derivatives to which N hexagons are attached ($N = h_1 + h_2 + h_3 + h_4$, cf. Rule 4). These energy–effects should be compared with $ef^*(h_1, h_2, h_3, h_4)$, pertaining to a "full" ring of the same benzenoid species.

call the attention the fact that the "classical" picture of π-electron conjugation is not complete and sometimes fully unsatisfactory. As shown by our analysis of benzo-annelated perylenes, discrepancies seem to occur already in the case of benzenoid hydrocarbons, the class of polycyclic conjugated molecules whose theory was most extensively studied in the past [3–5].

Anyway, the central ring in perylene and its benzo-annelated derivatives, especially

those in which the annelation is angular, is much less "empty" than assumed by theories based (solely) on Kekulé structures, Clar aromatic sextet formulas and/or conjugated circuits.

REFERENCES

[1] O. E. Polansky, Über ungesättigte Monocyclen mit durchlaufender Konjugation, 2. Mitt.: Berechnung der Elektronenstruktur mit hilfe der einfachen LCAO-MO-Methode und allgemeine gruppentheoretische Betrchtungen, *Monatsh. Chem.* **91** (1960) 916–962.

[2] R. Breslow, E. Mohácsi, Studies on d-orbital conjugation. III. Non-aromaticity of a derivative of the 1,3 dithiepinyl anion, a ten π-electron conjugated system, *J. Am. Chem. Soc.* **85** (1963) 431–434.

[3] E. Clar, *The Aromatic Sextet*, Wiley, London, 1972.

[4] I. Gutman, S. J. Cyvin, *Introduction to the Theory of Benzenoid Hydrocarbons*, Springer–Verlag, Berlin, 1989.

[5] M. Randić, Aromaticity of polycyclic conjugated hydrocarbons, *Chem. Rev.* **103** (2003) 3449–3606.

[6] I. Gutman, Cyclic conjugation energy effects in polycyclic π-electron systems, *Monatsh. Chem.* **136** (2005) 1055–1069.

[7] W. C. Herndon, Resonance theory and the enumeration of Kekulé structures, *J. Chem. Educ.* **51** (1974) 10–15.

[8] M. Randić, On the characterization of local aromatic properties of benzenoid hydrocarbons, *Tetrahedron* **30** (1974) 2067–2074.

[9] W. T. Simpson, On the use of structures as an aid in understanding π-electron spectra, *J. Am. Chem. Soc.* **75** (1953) 597–603.

[10] M. Randić, Conjugated circuits and resonance energies of benzenoid hydrocarbons, *Chem. Phys. Lett.* **38** (1976) 68–70.

[11] W. C. Herndon, Notes on valence bond theory, structure–resonance theory, and graph theory, *MATCH Commun. Math. Chem.* **11** (1981) 3–11.

[12] W. C. Herndon, H. Hosoya, Parametrized valence bond calculations for benzenoid hydrocarbons using Clar structures, *Tetrahedron* **40** (1984) 3987–3995.

[13] I. Gutman, Topological properties of benzenoid molecules, *Bull. Soc. Chim. Beograd* **47** (1982) 453–471.

[14] J. A. N. F. Gomes, R. B. Mallion, Aromaticity and ring currents, *Chem. Rev.* **101** (2001) 1349–1383.

[15] I. Gutman, S. Bosanac, Quantitative approach to Hückel rule. The relations between the cycles of a molecular graph and the thermodynamic stability of a conjugated molecule, *Tetrahedron* **33** (1977) 1809–1812.

[16] J. Aihara, Resonance energies of benzenoid hydrocarbons, *J. Am. Chem. Soc.* **99** (1977) 2048–2053.

[17] I. Gutman, O. E. Polansky, Cyclic conjugation and the Hückel molecular orbital model, *Theor. Chim. Acta* **60** (1981) 203–226.

[18] I. Gutman, On cyclic conjugation, *Theor. Chim. Acta* **66** (1984) 43–49.

[19] I. Gutman, V. Petrović, B. Mohar, Cyclic conjugation effects: individual, collective and overall, *Chem. Phys. Lett.* **203** (1993) 378–382.

[20] I. Gutman, Cyclic conjugation in benzenoid hydrocarbons, *Bull. Acad. Serbe Sci. Arts* (Cl. Math. Natur.) **106** (1993) 37–50.

[21] I. Gutman, N. Turković, J. Jovičić, Cyclic conjugation in benzo-annelated perylenes: How empty is the "empty" ring ?, *Monatsh. Chem.* **135** (2004) 1389–1394.

[22] I. Gutman, B. Furtula, J. Đurđević, R. Kovačević, S. Stanković, Annelated perylenes: Benzenoid molecules violating the Kekulé–structure–based cyclic conjugation models, *J. Serb. Chem. Soc.* **70** (2005) 1023–1031.

CIKLIČNA KONJUGACIJA U ANELIRANIM PERILENIMA

Jelena Đurđević, Boris Furtula, Ivan Gutman, Radmila Kovačević, Sonja Stanković i Nedžad Turković

IZVOD

U radu su izloženi rezultati istraživanja ciklične konjugacije u benzo-aneliranim perilenima. Za tu svrhu su izračunati energetski efekti ciklične konjugacije u šestočlanim prstenovima odgovarajućih benzenoidnih sistema.

Formula perilena kao i način na koji su njegovi prstenovi i položaji anelacije označeni prikazani su na Slici 1. Na toj slici se nalaze i po dve Kekuléove strukture i Clarove formule perilena, te konjugovani krugovi koji su sadržani u prvoj od ovih Kekuléovih struktura. Ovim primerima ilustrujemo pojam "esencijalno jednostruke" ugljenik–ugljenik veze, koje postoje u perilenu (označene strelicame). Za prsten u kojem se nalaze "esencijalno jednostruke" veze kaže se da je "prazan".

Energetski efekat π-elektronske konjugacije u ciklu Z (policikličnog) konjugovanog molekula čiji molekulski graf je G, izračunava se pomoću formule

$$ef = ef(G, Z) = \frac{2}{\pi} \int\limits_0^\infty \ln \frac{\phi(G, ix)}{\phi(G, ix) + 2\,\phi(G - Z, ix)} \, dx$$

gde je $\phi(G, x)$ karakteristični polinom grafa G, podgraf $G - Z$ je dobiven izbacivanjem iz G cikla Z, a $i = \sqrt{-1}$.

U savremenoj teorijskoj hemiji benzenoidnih ugljovodonika za procenu ciklične konjugacije u širokoj upotrebi su modeli zasnovani na Kekuléovim strukturama, Clarovim formulama i konjugovanim krugovima. Svi ovi modeli jednoglasno predviđaju da ciklična konjugacija u centralnom "praznom" prstenu perilena i njegovih aneliranih derivata uopšte ne postoji ili, opreznije govoreći, da treba da bude veoma slaba.

Naša istraživanja su pokazala da kod nekih benzo– i poliaceno-aneliranih derivata perilena to uopšte nije slučaj, pod uslovom za se intenzitet ciklične konjugacije procenjuje metodom u koju nije ugrađena pretpostavka o *a priori* nepostojanju ciklične

konjugacije u "praznim" prstenovima. Energetski efekat ciklične konjugacije se upravo izračunava na takav nepristrasni način.

Prvo su ispitivani benzo-anelirani perileni, i to sve moguće mono–, di-, tri– i tetra-anelirane specije. Najvažniji dobiveni rezultati navedeni su u Tablicama 1 i 2.

Ciklična konjugacija u perilenu (merena svojim energetskim efektom) je u punoj saglasnosti sa klasičnim teorijama: ef-vrednost "praznog" centralnog prstena 5 znatno je manja od ef-vrednosti "punih" prstenova 1, 2, 3 i 4. Ako se na perilen doda benzenov prsten u linearnom položaju u odnosu na centralni prsten, ef-vrednost centralnog prstena se još više smanji. Ako se, međutim, anelacija izvrši u položaju koji je angularan u odnosu na centralni prsten, onda se ef-vrednost centralnog prstena povećava. Kumulativno dejstvo ovakvih angularnih anelacionih efekata dovodi do "anomalije" koja se u radu istražuje.

Pokazujemo da se odstupanje od klasične (na Kekuléovim strukturama i/ili Clarovim formulama zasnovane) slike prvi put javlja kod tetrabenzo-aneliranog perilena, kod koga su sva četiri anelirana benzenska prstena u angularnom položaju u odnosu na centralni "prazni" prsten. U tom molekulu, u centralnom "praznom" prstenu ciklična konjugacija (merena preko svog energetskog efekta) prevazilazi cikličnu konjugaciju u prstenovima koji su prema klasičnim teorijama "puni". Time smo otkrili slučaj kada teorijski modeli, zasnovani na Kekuléovim strukturama i/ili Clarovim formulama (i samo na njima) daju nezadovoljavajući opis ciklične konjugacije u benzenoidnim ugljovodonicima.

Da bismo ovu "anomaliju" u cikličnoj konjugaciji (ili tačnije: anomaliju u teoriji ciklične konjugacije) ilustrovali i drugim primerima, ispitivali smo i poliaceno-anelirane derivate perilena. Imajući u vidu pravilnosti uočene kod benzo-aneliranih perilena, proučavali smo samo sisteme koji se dobivaju dodavanjem poliacenskih fragmenata u angularnom položaju u odnosu na centralni "prazni" prsten. Struktura poliaceno-aneliranih perilena koje smo u ovom radu ispitivali prikazana je na Slici 2.

Dobiveni rezultati omogućili su da se formulišu četiri pravila. Za proučavanje "anomalne" ciklične konjugacije najvažnije je Pravilo 4, koje određuje uslove pod kojima je ciklična konjugacija u centralnom prstenu poliaceno-aneliranih derivata perilena maksimalna. Ako su na prstene 1, 2, 3 i 4 perilenskog jezgra (v. Sliku 2)

zakačeni poliaceni sa h_1, h_2, h_3 i h_4 šestočlana prstena, i ako je $h_1 + h_2 + h_3 + h_4 = N$ konstantno, onda je u centralnom prstenu 5 ciklična konjugacija maksimalna ako su ispunjeni uslovi:

$$h_1 = h_2 = h_3 = h_4 = k \qquad \text{ako je } N = 4\,k$$

$$h_1 = k + 1\,,\ h_2 = h_3 = h_4 = k \qquad \text{ako je } N = 4\,k + 1$$

$$h_1 = h_2 = k + 1\,,\ h_3 = h_4 = k \qquad \text{ako je } N = 4\,k + 2$$

$$h_1 = h_2 = h_3 = k + 1\,,\ h_4 = k \qquad \text{ako je } N = 4\,k + 3\,.$$

Odgovarajuće maksimalne vrednosti energetskog efekta prikazane su u Tablici 3, zajedno sa energetskim efektom "punog" prstena 1. Vidi se da se porastom broja aneliranih prstenova anomalija jako povećava: intenzitet ciklične konjugacije u "praznom" prstenu 5 postaje skoro tri puta veći od intenziteta ciklične konjugacije u "punom" prstenu 1.