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Verifying the modes of cyclic conjugation in tetrabenzo[bc,ef,op,rs]circumanthracene

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Abstract: Cyclic conjugation in the “empty” central ring of tetrabenzo-[bc,ef,op,rs]circumanthracene (TBCA) is stronger than in its neighboring “non-empty” rings, contradicting the predictions of Kekulé-structure-based theoretical models. Earlier examples of such anomalous cyclic conjugation were observed in highly strained, non-planar benzenoid systems. As the molecule of TBCA is perfectly planar and strain-free, it was possible to test and verify its cyclic conjugation pattern by means of high-level, B3LYP/6-311+G(d,p), *ab initio* DFT calculations.

Keywords: cyclic conjugation; energy effect (of cyclic conjugation); Kekulé-structure-based models; DFT calculation; benzo-annelated perylene; tetrabenzo-circumanthracene.

INTRODUCTION

Kekulé-structure-based models of cyclic conjugation

In polycyclic conjugated molecules, the location of the π -electrons usually cannot be represented by a single structural formula, but by several so-called Kekulé structures. In the 1970s and later, several approaches were put forward, aimed at quantitatively describing the π -electron properties of conjugated molecules, based on counting and analyzing their Kekulé structures. In particular, the Kekulé structure count K was used to predict the total π -electron energy^{1–3} and thermodynamic stability of benzenoid hydrocarbons.^{4–6} The aromaticity of an individual ring R in the conjugated system the molecular graph of which is G was assessed^{7,8} by means of the quantity $2K(G-R)/K(G)$. This idea was eventually elaborated in the so-called theory of conjugated circuits.^{9–12} A conjugated circuit in a Kekulé structure is a cycle in which single and double bonds alternate. Within the theory of conjugated circuits, cyclic conjugation in a ring R is assumed the consequence of the existence of conjugated circuits pertaining to R in

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the Kekulé structures. Clar¹³ proposed a diagrammatical method for drawing structural formulas, in which the most important cyclic conjugation modes (originating from the Kekulé structures) were indicated.¹⁴ Eventually, a quantitative version of the Clar theory was put forward.^{15,16} Kekulé structures were used to assess the distribution of π -electrons in polycyclic conjugated hydrocarbons and to estimate the π -electron content of individual rings.^{17–19} A similar approach based on the Clar formulas was also offered.^{20,21} Recently, ring currents in benzenoid hydrocarbons were also modeled by means of conjugated circuits.²²

Details on these Kekulé-structure-based models of cyclic conjugation can be found in a book²³ and in reviews.^{24–28}

Energy effect of cyclic conjugation

Also in the 1970s, a molecular-orbital- and graph-theory-based method for calculating the energy effect of individual cycles in polycyclic conjugated molecules was developed.²⁹ Its details can be found in the reviews^{30,31} and elsewhere.^{32–35} The energy effect ef of the ring R in the conjugated system whose molecular graph is G is computed by means of the formula

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

where $\phi(G, x)$ is the characteristic polynomial of G and $i = \sqrt{-1}$.

The ef -values calculated by Eq. (1) are expressed in units of the HMO carbon–carbon resonance integral β . Therefore, positive ef -values indicate thermodynamic stabilization caused by cyclic conjugation. The greater is $ef(R)$, the stronger is the intensity of cyclic conjugation in the ring R .

For the considerations in the present paper, it is important to note that the ef -method is independent of any assumption based on Kekulé structures. Yet, in the majority of cases, its results are in full harmony with those obtained by means of Kekulé-structure-based approaches.^{30,31} In some cases, however, the ef -method leads to conclusions that differ from those implied by the Kekulé-structure-based models.^{32,33} These “anomalies” are outlined in the subsequent section, and then further elaborated and corroborated in the later parts of this article.

CYCLIC CONJUGATION IN PERYLENE AND ITS CONGENERS

The application of the ef -method to the six-membered rings of perylene is of particular interest because this benzenoid molecule possesses a so-called “empty” ring, namely a ring in which according to Kekulé-structure- and Clar-structure-based models, there is no cyclic conjugation. This is illustrated in Fig. 1 in which all the nine Kekulé structures of perylene are depicted. None of these has a conjugated circuit (*i.e.*, three double bonds) in the central ring. In fact, the two vertical carbon–carbon bonds in the central ring are single in all Kekulé structures.

Rings of this kind are referred to as “empty”.^{13,14,23} The central rings in perylene and all its congeners examined in this paper are “empty”. Recall that for such rings, the Randić local aromaticity index $2K(G-R)/K(G)$ is equal to zero, indicating a complete absence of cyclic conjugation.

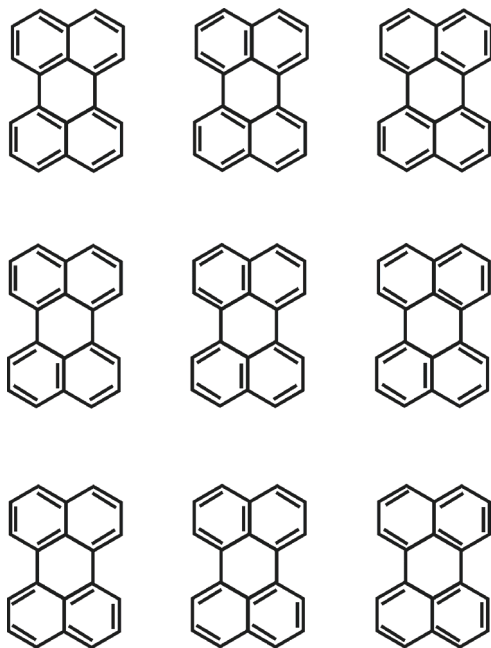


Fig. 1. The Kekulé structures of perylene. The two vertical carbon–carbon bonds in the central ring are always single. Therefore, within the Kekulé-structure-based models, this ring is claimed to be devoid of any cyclic conjugation.

In the case of perylene (**1** in Fig. 2), calculations based on the *ef*-model are in good agreement with the predictions of the Kekulé-structure- and Clar-structure-based models. Although the *ef*-value of the central “empty” ring (A) is not zero, it is nevertheless some five times smaller than the *ef*-value of the other four neighboring rings (B).

Due to a generally valid regularity,^{8,36} benzo-annulation (in the position indicated in **2** in Fig. 2) increases the intensity of cyclic conjugation in the central ring of perylene. When the same type of benzo-annulation is realized at all the four sites of perylene (**3**), then cyclic conjugation in the central “empty” ring is increased so much that it exceeds the magnitude of cyclic conjugation in the four neighboring rings. This phenomenon, discovered several years ago,³² was the first example when the pattern of cyclic conjugation in a benzenoid hydrocarbon violates the predictions of Kekulé-structure-based models. The “anomaly” of this kind can be strengthened by considering naphthalene-annulation (as shown in **4**). Although the *ef*-values of the central ring of benzoperylene (**3**) and naphthalenoperylene (**4**) differ only slightly, the cumulative effect in tetranaphthalenoperylene (**5**) is remarkable: in **5** the cyclic conjugation in the “empty” ring (A) is

found to be more than two times stronger than in the neighboring rings (B), and is also significantly greater than the analogous effect in the rings C, *cf.* Fig. 2.

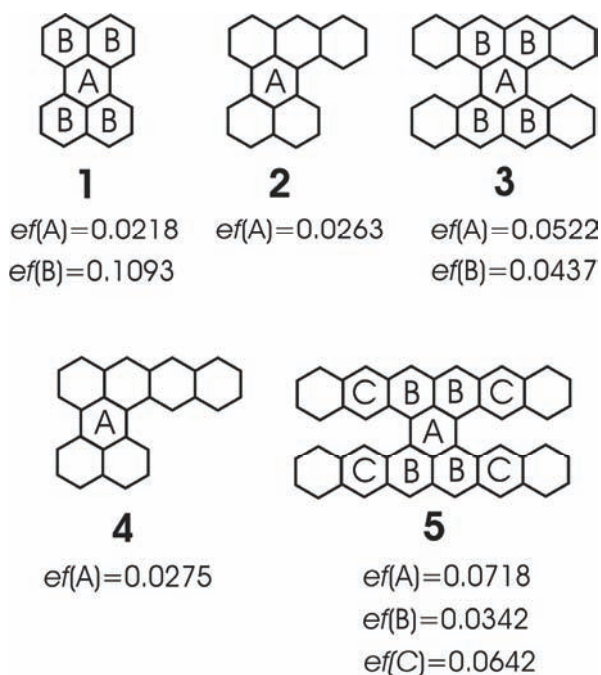


Fig. 2. Energy effects (in β units) of some six-membered rings of perylene (**1**) and its congeners. For details, see text.

HOW REALISTIC IS THE *ef*-METHOD?

The conclusions concerning cyclic conjugation in perylene and its congeners outlined in the preceding section are based on the energy effects *ef*, calculated according to formula (1). The natural dilemma is whether these results reflect real features of the π -electrons in the underlying molecules or whether they are artifacts originating from the crudeness of the HMO approximation. In order to resolve this problem, these conclusions have to be verified by means of more reliable theoretical approaches.

However, first a serious objection to the calculated cyclic conjugation patterns of tetrabenzo- and tetranaphtho-perylenes (**3** and **5**) needs to be addressed.

In HMO calculations, only the topology of the carbon-atom skeleton is taken into account. Consequently, steric effects are fully disregarded. In tetrabenzo- and tetranaphtho-perylenes, the near-lying hydrogen atoms impose a strong steric repulsion, which necessarily causes an extension of some carbon-carbon bonds, deformation of some six-membered rings and non-planarity of the entire molecule (Fig. 3). This, in turn, makes the results of any HMO-based calculation doubtful and inapplicable.

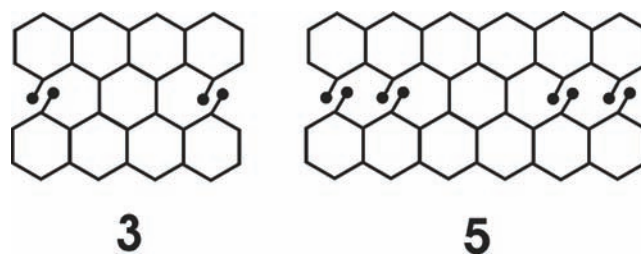


Fig. 3. Tetrabenzoperylene (**3**) and tetranaphthalenoperylene (**5**) in which the near-lying hydrogen atoms are indicated. Their repulsion causes strong sterical strain and deviation from planarity.

This difficulty would be overcome if instead of **3** and **5**, similar, but strain-free and strictly planar benzenoid systems would be considered. Such are obtained by replacing the overcrowded hydrogen atoms (indicated in Fig. 3) by carbon-carbon bonds. By this, one arrives at tetrabenzo[*bc,ef,kl,no*]coronene (**6**) and tetrabenzo[*bc,ef,op,rs*]circumanthracene (**7**), depicted in Fig. 4.

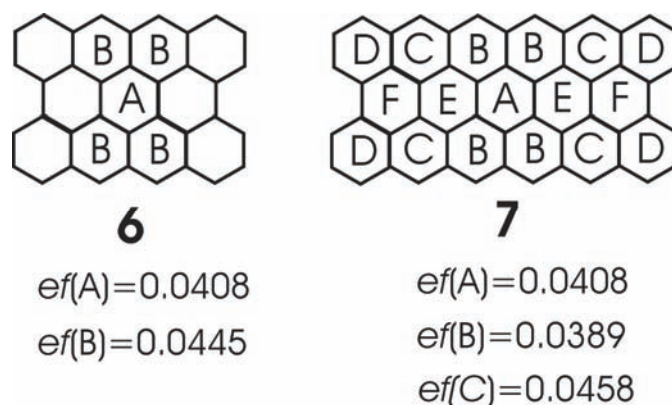


Fig. 4. Energy effects (in β units) of some six-membered rings of tetrabenzo[*bc,ef,kl,no*]coronene (**6**) and tetrabenzo[*bc,ef,op,rs*]circumanthracene (**7**).

These *ef*-values show that in **6**, the pattern of cyclic conjugation does not violate the predictions of the Kekulé-structure-based theoretical models, whereas in **7** it does, because $ef(A) > ef(B)$.

From the calculated *ef*-values of **6**, it can be seen that the transformation **3** \rightarrow **6** reduces the intensity of cyclic conjugation in the central ring A and increases it in the neighboring rings B. Consequently, $ef(A)$ becomes smaller than $ef(B)$, and the disagreement with the Kekulé-structure-based theories is lost. Fortunately, in **7**, the “anomaly” in the cyclic conjugation pattern remains, although much less pronounced than in the case of **5** (Fig. 4). Bearing these observations in mind, it was decided to test the modes of cyclic conjugation in tetrabenzo[*bc,ef,op,rs*]cir-

cumanthracene (TBCA) by independent, much more reliable quantum-theoretical methods.

A DENSITY-FUNCTION-THEORETICAL STUDY OF TBCA

The DFT calculations on tetrabenzo[*bc,ef,op,rs*]circumanthracene (TBCA) were realized using the Gaussian 09W package, version 0.1, at the B3LYP/6-311+G(d,p) level of theory.³⁷ Geometry optimization confirmed that the molecule is perfectly planar. Bond lengths were taken from the optimized geometry. The frequency calculations showed that the examined molecule has no imaginary vibration frequencies, *i.e.*, that the geometry determined corresponds to a true energy minimum. Nucleus independent chemical shift (NICS) values were calculated at the B3LYP/6-311+G(d,p) level through the gauge-including atomic orbital method (GIAO).³⁸

The results of the DFT study that are representative for the cyclic conjugation pattern of TBCA are presented in Table I. Full computational details can be obtained from the authors (J.Đ.) upon request.

From the data in Table I, it can be seen that the NICS method³⁹ indicates that the cyclic conjugation in ring A is stronger than that in ring B and even in ring C. Needless to say that the cyclic conjugation in ring A much exceeds also those in rings E and F. In fact, according to the NICS-values, only in the peripheral rings D is the cyclic conjugation more intense than in A. (Recall that the more negative a NICS-value is, the higher is the local aromaticity and cyclic conjugation in the underlying ring.^{39–41})

TABLE I. Properties of the rings of TBCA (7) according to the labeling indicated in Fig. 4. NICS(0) and NICS(1) are, respectively, the NICS values for the virtual charge located in the center of the ring and 1 Å above its center; Σ is the sum of the lengths (in pm) of the six carbon–carbon bonds forming the respective ring; Δ is the change of Σ relative to ring A ($\Delta < 0$ indicates bond compression and increased cyclic conjugation relative to ring A, $\Delta > 0$ indicates bond extension and decreased cyclic conjugation relative to ring A); *ef* is the energy effect computed by Eq. (1)

Ring	NICS(0)	NICS(1)	Σ	Δ	<i>ef</i>
A	−3.74	−7.09	852.8	0.0	0.0408
B	+2.11	−2.00	854.0	+1.2	0.0389
C	−2.47	−5.73	852.3	−0.5	0.0458
D	−5.74	−8.30	846.4	−6.4	0.0982
E	+0.26	−3.69	854.6	+1.8	0.0391
F	+8.03	2.81	861.8	+9.0	0.0277

Bond lengths may serve as another indicator of cyclic conjugation: With increasing magnitude of cyclic conjugation, the carbon–carbon bonds forming the respective ring will gain in double-bond character and thus become shorter. This effect is clearly seen from the bonds lengths of TBCA. The sums Σ of the lengths

of the six carbon–carbon bonds of the respective ring are given in Table I. Indeed, the Σ -value of ring A is smaller than those of the rings B, nearly equal to those of the rings C, and only exceeds those of the rings D. To see this effect better, the difference Δ between the Σ -value of a ring and the Σ -value of ring A are also presented.

For the sake of completeness, the *ef*-values of all six-membered rings of TBCA are also included in Table I.

CONCLUDING REMARKS

Based on the above-described DFT calculations and the data collected in Table I, it has been demonstrated that the results of the presented *ef*-method provide a reliable and realistic picture of the cyclic conjugation pattern of TBCA. Attention was focused on TBCA as a benzenoid molecule for which a breakdown of the Kekulé-structure-based theories is predicted by the *ef*-method. Therefore, by confirming the validity of the predictions of the *ef*-method, a case was also found for which, by considering Kekulé structures, one arrives at fallacious conclusions on the modes of cyclic conjugation and thus on local aromaticity. The example provided in this work, namely tetrabenzo[*bc,ef,op,rs*]circumanthracene (7), is a strain-free and planar benzenoid hydrocarbon, with a π -electron system for which Kekulé-structure-based theories were hitherto believed to be perfectly applicable. It can now be seen that the domain of applicability of these theories is somewhat more restricted than was previously thought.

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ИЗВОД

ПОТВРЂИВАЊЕ НАЧИНА ЦИКЛИЧНЕ КОНЈУГАЦИЈЕ У ТЕТРАБЕНЗО[*bc,ef,op,rs*]ЦИРКУМАНТРАЦЕНУ

ИВАН ГУТМАН, ЈЕЛЕНА ЂУРЂЕВИЋ, ЗОРАН МАТОВИЋ и МАРИЈА МАРКОВИЋ

Природно–математички факултет Универзитета у Крагујевцу

Циклична конјугација у “празном” централом прстену тетрабензо[*bc,ef,op,rs*]циркумантрацена (ТВСА) је јача него у суседним “не-празним” прстеновима, што противречи предвиђањима добијеним помоћу модела заснованих на Кекулеовим структурама. Ранији примери овакве аномалне цикличне конјугације нађени су код непланарних бензеноидних система са великим стерним напонима. Будући да је молекул ТВСА потпуно планаран и лишен стерног напона, модови његове цикличне конјугација могли су се проверити и потврдити помоћу *ab initio* DFT прорачуна, на нивоу B3LYP/6-311+G(d,p).

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