

Local aromaticity in benzo- and benzocyclobutadieno-annelated perylenes

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Abstract

The effects of benzo- and benzocyclobutadieno- (BCBD-) annelation on the local aromaticity of the central ring *X* of perylene were examined. The local aromaticity of the ring *X* was estimated using a graph-theory based index, *ef*, and two geometry-based indices, *HOMA* and Σ . The findings resulting from the application of the *ef* index are to some extent contradictory to those obtained on the basis of *HOMA* and Σ . Namely, the geometry-based indices indicate that the effect of benzo-annelation is opposite to that of BCBD-annelation, whereas *ef* predicts that angular BCBD-annelation has very little influence to the local aromaticity of the central ring of perylene. Since the geometry-based indices are more sophisticated than the graph-theory-based index, one should conclude that the predictions emanating from the application of *HOMA* and Σ are more reliable.

Keywords: Aromaticity, molecular geometry, benzo-annelated perylenes, benzocyclobutadieno-annelated perylenes, DFT calculations

1. Introduction

Aromaticity is an important concept in modern organic chemistry. This term is related either to some typical properties or to a specific structure. It has been almost generally accepted that aromaticity is associated with the ground-state properties of polycyclic π -electron compounds which are more stable than their chain analogues, have bond lengths between those typical for single and double ones, and have a π -electron ring current that is induced when the system is exposed to external magnetic fields, leading to increased values of the magnetic susceptibility and specific values of ¹H NMR chemical shifts. These properties are easily measurable and concern molecules in their ground electronic state. Thus, they can be readily transformed into the numerical parameters describing the aromatic character (aromaticity indices) of molecules or their fragments.

A more subtle problem is that what one calls “aromaticity”, needs not be (as is usually not) uniformly distributed over the entire conjugated π -electron system. To overcome this difficulty, so-called local aromaticity indices have been introduced, capable of measuring the extent of aromaticity in some pertinently selected domains of the underlying π -electron system.

The local aromaticity indices: *ef* (energy effect) (Gutman 2005a), *HOMA* (Harmonic Oscillator Model of Aromaticity) (Kruszewski and Krygowski 1972; Krygowski 1993;

Krygowski and Cyranski 2001), and Σ (Balaban et al. 2011a; Balaban et al. 2011b) are well suited for studies of the dependence of local aromaticity on the environment of the molecule or its fragment. They have been used in several recent papers (Gutman 2005b; Đurđević et al. 2009; Balaban et al. 2010; Balaban et al. 2011a; Balaban et al. 2011b; Balaban et al. 2011c; Gutman et al. 2011a; Gutman et al. 2011b; Gutman 2011; Gutman and Stojanovska 2011; Gutman and Balaban 2011; Marković et al. 2012) to investigate the effects of benzo- and benzocyclobutadieno- (BCBD-) annelation on local aromaticity of a particular six-membered ring in benzenoid hydrocarbons. In Fig. 1, diagrams 2 and 3 illustrate linear and angular benzo-annelation of an arbitrary benzenoid hydrocarbon (diagram 1), whereas diagrams 4 and 5 illustrate linear and angular BCBD-annelation of the same hydrocarbon. The six-membered ring whose local aromaticity is under investigation is marked by X .

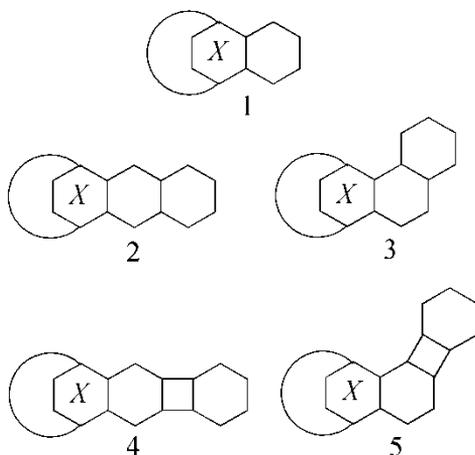


Fig. 1. A benzenoid molecule (1), its benzo-annelated congeners (2 and 3), and its BCBD-annelated congeners (4 and 5).

Perylene was the first benzenoid hydrocarbon on which the effects of benzo-annelation were considered using the ef index (Gutman et al. 2004). The analogous effects of benzocyclobutadieno-annelation were examined only recently (Gutman and Stojanovska 2011). The results obtained by means of the ef -method could be summarized as follows:

Rule 1. Benzo-annelation in angular position to the central six-membered ring increases the intensity of cyclic conjugation in this ring.

Rule 2. Benzo-annelation in linear position to the central six-membered ring decreases the intensity of cyclic conjugation in this ring.

Rule 3. The effects specified in Rules 1 and 2 are proportional to the number of benzo-annelated rings.

Rule 1*. BCBD-annelation in angular position to the central six-membered ring has almost no effect on the intensity of cyclic conjugation in this ring.

Rule 2*. BCBD-annelation in linear position to the central six-membered ring increases the intensity of cyclic conjugation in this ring.

Rule 3*. The effect specified in Rule 2* is proportional to the number of linearly BCBD-annelated rings. Irrespective of the number of angularly BCBD-annelated rings, their effect on cyclic conjugation remains negligible.

Rule 4*. The intensity of cyclic conjugation in the central six-membered ring is almost completely determined by the number of linear BCBD-annelations, and is almost independent on both the number of angular BCBD-annelations and on the position of the annelated BCBD-fragments.

In a series of recent studies (Balaban et al. 2010; Jeremić et al. 2010a; Jeremić et al. 2010b; Balaban et al. 2011b; Balaban et al. 2011c; Gutman and Balaban 2011; Gutman et al. 2011b; Gutman 2011; Marković et al. 2012), it was established that the above rules seem to be quite general and to be applicable to the majority of polycyclic aromatic molecules.

Returning to perylene congeners, we note that rules 1-3 indicate a remarkable variation of the magnitude of cyclic conjugation in its central ring. Note that, according to the standard theoretical approaches based solely on Kekulé or Clar structures (Clar 1972; Gutman and Cyvin 1989; Randić 2003), in this ring there would be no cyclic conjugation at all. In addition, rules 1* - 4* are quite surprising. Namely, comparison of rules 1-3 to rules 1*-4* reveals that the two types of annelation influence the cyclic conjugation in the rings of perylene in profoundly different manner. What readily comes to mind is that these differences are caused by the 4-membered rings, known to have a destabilizing (antiaromatic) effect and negative-valued energy effect. In order to further test (and possibly corroborate) these somewhat unusual findings, in this paper we approach the local-aromaticity problem from another direction, based on the geometry of the benzo- and BCBD-annelated perylene congeners, as determined by means of advanced DFT calculations.

2. Numerical work

Calculations of the ef-values of the ring X were performed by means of the formula (2) using our in-house software. Before we introduce the energy effect, we need to recall a seminal result of Coulson, concerning the total π -electron energy (Coulson 1940; Li et al. 2012):

$$E(G) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \left[n - ix \frac{\phi'(G, ix)}{\phi(G, ix)} \right] dx \quad (1)$$

In Eq. (1), $E(G)$ stands for the total π -electron energy of the conjugated molecule whose molecular graph is G , possessing n vertices. In formula (1), $\phi(G, x)$ and $\phi'(G, x)$ denote the characteristic polynomial of G and its first derivative, whereas i is the imaginary unit. Taking into account the Sachs theorem (Graovac et al. 1972; Gutman 2003), it is possible to express the energy effect $ef(X)$ of a particular ring X, contained in the molecular graph G , on the respective E value, resulting in Eq. (2) (Bosanac and Gutman 1977; Gutman and Bosanac 1977):

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

in which $G-X$ is the subgraph obtained by deleting the ring X from the graph G . The ef values are expressed in the units of the HMO resonance integral β , whose recommended value for thermochemical purposes amounts -137 kJ/mol. Positive ef values indicate that the cycle X stabilizes the molecule, whereas negative ef values imply destabilization.

In order to calculate the *HOMA* and Σ indices it was necessary to determine the geometries of the underlying molecules. The optimizations were performed with the Gaussian 09 program package (Frisch et al. 2009), using the B3LYP hybrid functional (Lee et al. 1988; Becke 1993), and 6-311+G(d,p) basis set. This triple split basis set adds p functions to hydrogen atoms in

addition to the d functions and diffuse functions on carbon atoms. As previously documented (see e. g. (Balaban et al. 2011a; Balaban et al. 2011b)), this theoretical model yields reliable molecular geometries for such stable, singlet ground state species as those studied in the present work. The details of the calculated geometries of perylene and its annelated congeners can be obtained from an author (S. M.) upon request.

The HOMA index values were calculated using the formula (Kruszewski and Krygowski 1972; Krygowski 1993; Krygowski and Cyranski 2001):

$$HOMA(X) = 1 - \frac{\alpha}{n} \sum_i (R_{opt} - R_i)^2 \quad (3)$$

where n is the number of bonds taken into the summation (6 in this case), and α is an empirical constant ($\alpha = 25.77 \cdot 10^{-3}$) chosen to give $HOMA = 0$ for a hypothetical Kekulé structure of an aromatic system (with the lengths for C-C bonds as in 1,3-butadiene) and 1 for the system with all bonds equal to the optimal value R_{opt} . In this work, R_{opt} was taken to be equal to the calculated length of the C-C bonds in an ideal aromatic system – benzene ($R_{opt} = 139.4$ pm). The individual bond lengths are denoted by R_i . Positive $HOMA$ values indicate that the cycle X stabilizes the molecule, whereas negative $HOMA$ values imply destabilization.

The Σ index was simply calculated as the sum of the lengths (in picometers) of the six C-C bonds of the ring X (Balaban et al. 2011a, Balaban et al. 2011b).

$$\Sigma(X) = \sum_i R_i \quad (4)$$

It is supposed that if cyclic conjugation in a ring increases (resp. decreases), then the double-bond character of the involved C-C bonds increases (resp. decreases), causing in average a shortening (resp. extension) of the C-C bonds of X . Such an assumption was confirmed in the investigation of the anthracene and phenanthrene congeners (Balaban et al. 2011a; Balaban et al. 2011b).

3. Results and discussion

The considerations in this paper pertain to benzo- and BCBD-annelated perylenes. In order to simplify our notation, the sites of annelation in perylene are labeled as indicated in Fig. 2. The labeling of the BCBD-derivatives is analogous to that of the benzo-annelated congeners, and should be evident from the examples depicted in Fig. 2. Perylene is a relatively small molecule of C_s symmetry, but the majority of its 26 benzo-annelated and 26 BCBD-annelated congeners are non-planar molecules, with significant steric strain (Fig. 2, Table 1). The results of our investigation are collected in Table 1, and illustrated with Fig. 3.

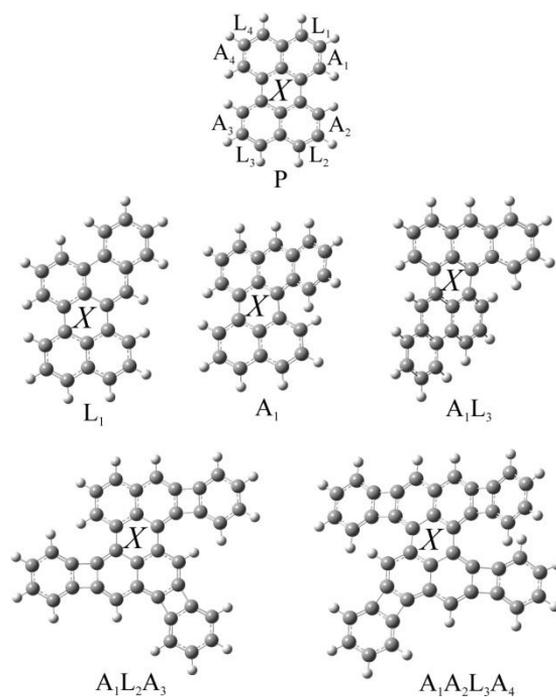


Fig. 2. Perylene (P) and the labeling of its annelation sites (A = angular, L = linear with regard to the central ring X). The benzo- and BCBD-annelated congeners of perylene are denoted by indicating the sites of annelation.

molecule	Δef (benzo)	Δef (BCBD)	$\Delta HOMA$ (benzo)	$\Delta HOMA$ (BCBD)	$\Delta \Sigma$ (benzo)	$\Delta \Sigma$ (BCBD)
L ₁	-0.0011	+0.0029	-0.0596	+0.0120	+1.180 (P)	-0.046 (P)
L ₁ L ₂	-0.0021	+0.0067	-0.1242	+0.0313	+2.485 (P)	-0.121 (P)
L ₁ L ₃	-0.0021	+0.0068	-0.1156	+0.0327	+2.302 (P)	-0.240 (P)
L ₁ L ₄	-0.0025	+0.0067	-0.0795	+0.0228	+1.904 (NP)	-0.036 (P)
L ₁ L ₂ L ₃	-0.0034	+0.0121	-0.1090	+0.0494	+2.613 (NP)	-0.257 (P)
L ₁ L ₂ L ₃ L ₄	-0.0045	+0.0197	-0.1391	+0.1201	+3.640 (NP)	-1.449 (NP)
A ₁	+0.0045	+0.0004	+0.0811	-0.0443	-1.934 (NP)	+1.028 (P)
A ₁ A ₂	+0.0104	+0.0007	+0.1381	-0.0680	-3.399 (NP)	+1.541 (NP)
A ₁ A ₃	+0.0106	+0.0007	+0.1282	-0.0538	-3.461 (NP)	+1.464 (NP)
A ₁ A ₄	+0.0107	+0.0004	+0.1567	-0.0442	-3.198 (NP)	+1.818 (NP)
A ₁ A ₂ A ₃	+0.0189	+0.0008	+0.2070	-0.0793	-4.762 (NP)	+2.723 (NP)
A ₁ A ₂ A ₃ A ₄	+0.0304	+0.0009	+0.2870	-0.1123	-6.330 (NP)	+4.334 (NP)
A ₁ L ₂	+0.0030	+0.0031	+0.0406	-0.0136	-1.162 (NP)	+0.526 (NP)
A ₁ L ₃	+0.0030	+0.0032	+0.0365	-0.0195	-0.951 (NP)	+0.853 (NP)
A ₁ L ₄	+0.0029	+0.0029	+0.0251	-0.0172	-1.238 (NP)	+0.363 (NP)
A ₁ A ₂ L ₃	+0.0082	+0.0033	+0.0771	-0.0404	-2.601 (NP)	+1.003 (NP)
A ₁ L ₂ A ₃	+0.0084	+0.0032	+0.0726	-0.0355	-2.780 (NP)	+0.901 (NP)
A ₁ L ₂ A ₄	+0.0086	+0.0029	+0.1154	-0.0197	-2.329 (NP)	+1.564 (NP)
A ₁ L ₂ L ₃	+0.0009	+0.0069	-0.0516	+0.0163	+0.194 (NP)	+0.286 (NP)
A ₁ L ₂ L ₄	+0.0016	+0.0066	-0.0121	-0.0241	-0.472 (NP)	+0.644 (P)
A ₁ L ₃ L ₄	+0.0016	+0.0066	-0.0150	+0.0180	-0.299 (NP)	+0.109 (NP)
A ₁ A ₂ A ₃ L ₄	+0.0158	+0.0031	+0.1459	-0.0569	-3.932 (NP)	+2.185 (NP)
A ₁ A ₂ L ₃ L ₄	+0.0063	+0.0065	+0.0170	-0.0050	-1.822 (NP)	+0.443 (NP)
A ₁ L ₂ A ₃ L ₄	+0.0065	+0.0066	+0.0184	-0.0133	-2.105 (NP)	+0.268 (NP)
A ₁ L ₂ L ₃ A ₄	+0.0056	+0.0062	+0.0631	+0.0513	-0.966 (NP)	-0.421 (NP)
A ₁ L ₂ L ₃ L ₄	-0.0002	+0.0116	-0.0431	+0.0102	+0.664 (NP)	+1.248 (NP)

¹ The ef values were taken from Ref. (Gutman et al. 2004). The same holds for Fig. 3.

² The ef values were taken from Ref. (Gutman and Stojanovska 2011). The same holds for Fig. 3

Table 1. The change of the ef (β), $HOMA$ and Σ (pm) indices of the ring X caused by benzo- and BCBD-annulation. $\Delta ef(\text{benzo})$ is the difference between the ef value of the ring X of the benzo-annulated congener and the ef value of the same ring in perylene. The meanings of $\Delta ef(\text{BCBD})$, $\Delta HOMA(\text{benzo})$, $\Delta HOMA(\text{BCBD})$, $\Delta \Sigma(\text{benzo})$, and $\Delta \Sigma(\text{BCBD})$ are analogous. The labeling of the compounds is presented in Fig. 2. The ef , $HOMA$, and Σ values of perylene amount 0.0218 β , 0.1898, and 867.712 pm, respectively. The symbols P and NP in the $\Delta \Sigma(\text{benzo})$ and $\Delta \Sigma(\text{BCBD})$ columns indicate planarity/non-planarity of the molecule in question.

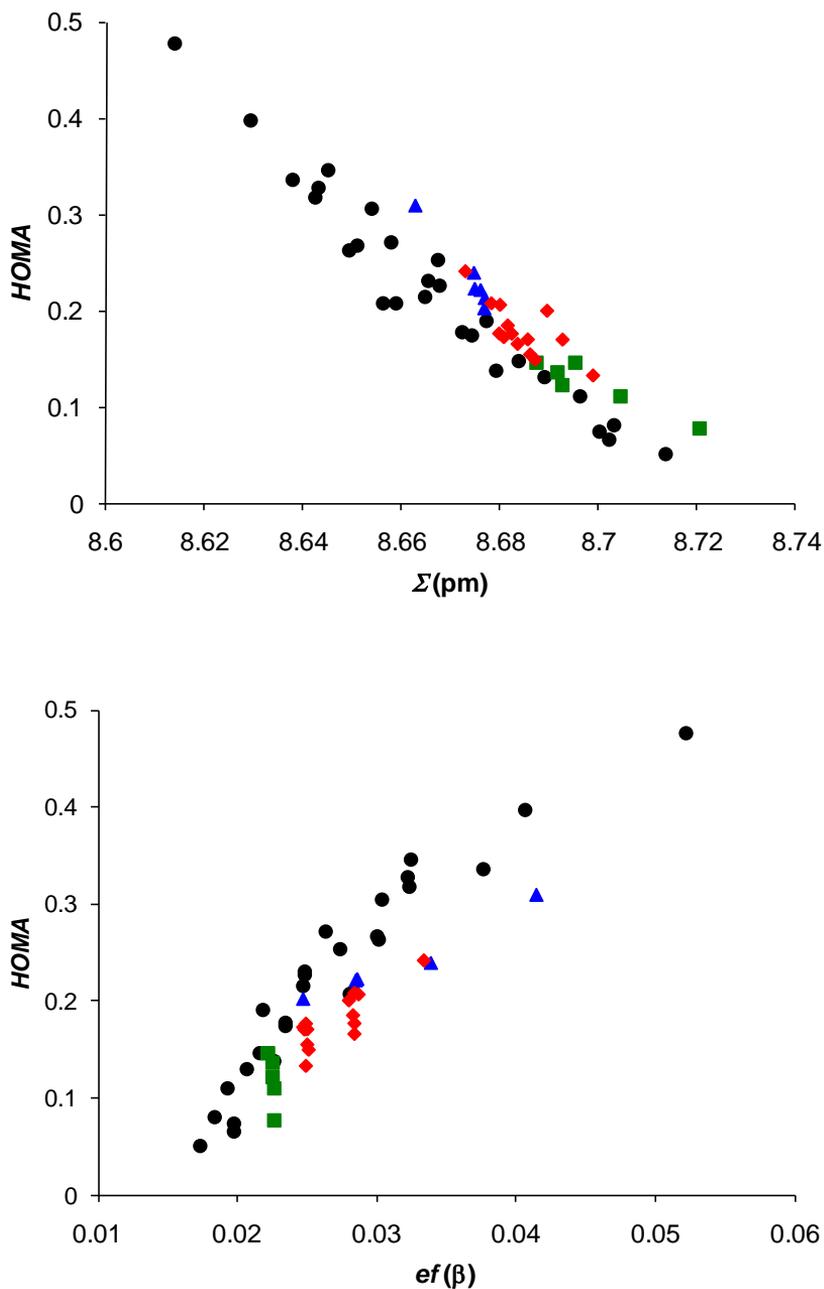


Fig. 3. Correlation between the *HOMA* and Σ values (top), and *HOMA* and ef values (bottom) of the ring *X* of perylene and its benzo- and BCBd-annulated derivatives. Circles denote all benzo-annulated perylenes, whereas triangles, rectangles, and squares stand for linearly, angularly, and medley BCBd-annulated derivatives, respectively.

As expected, linear correlation between the *HOMA* and Σ values is reasonably good, with the correlation coefficient of -0.95 (Fig. 3). The data points pertaining to both benzo- and BCBD-annelation form a single correlation line, without visible separation between the points associated to two different annelation modes. This result confirms our earlier findings (Balaban et al. 2011a; Balaban et al. 2011b) that *HOMA* and Σ reproduce very similar π -electron properties of the ring *X*, which can be considered as its local aromaticity. As in the case of the phenanthrene congeners (Balaban et al. 2011b) the fact that many perylene derivatives are nonplanar does not affect the effects of annelation. Obviously, the deviation from planarity allows the bonds to take the lengths close to their optimal values.

Consider now the *HOMA* and Σ values of the molecules obtained by linear and angular annelation (first 12 pairs of molecules in Table 1). In this case the two indices are in agreement (the sign of the *HOMA* value is opposite to the sign of the Σ value), and their values indicate that the effect of benzo-annelation is opposite to that of BCBD-annelation. Furthermore, the *HOMA* values decrease (resp. increase) with increasing number of linear (resp. angular) benzo-annelations, and the Σ values increase (resp. decrease) with increasing number of linear (resp. angular) benzo-annelations. The situation with BCBD-annelation is completely opposite. Namely, the *HOMA* values increase (resp. decrease) with increasing number of linear (resp. angular) BCBD-annelations, and Σ values decrease (resp. increase) with increasing number of linear (resp. angular) BCBD-annelations. In addition, one can observe that the effects of angular annelation are stronger, so that the local aromaticity of the ring *X* is the highest in benzo-annelated A1A2A3A4, and lowest in BCBD-annelated A1A2A3A4. As a consequence of the competition between the stabilizing and destabilizing modes of annelation, the values of the *HOMA* and Σ indices of the pairs of molecules where both linearly and angularly annelated fragments are involved lie between those for linearly and angularly annelated molecules. In the majority of cases, $\Delta HOMA$ and $\Delta \Sigma$ take positive and negative values, respectively, for the benzo-annelated molecules, whereas the situation is opposite in the case of the BCBD-annelation. This finding again confirms the stronger effect of both benzo- and BCBD-annelations in angular position. These facts imply that *HOMA* and Σ obey the rules 1-3 and 2*, but not the rules 1*, 3*, and 4*.

The *ef* values of the benzo-annelated perylenes obey the rules 1-3, implying that they show very similar behavior to that of the *HOMA* values (Table 1). The only negative Δef value among the medley annelated molecules is that for the congener containing three linear fragments. The dependence of *HOMA* of the benzo-annelated perylene derivatives on *ef* is curvilinear, without significant deviations from curvilinearity (Fig. 3). On the other hand, the *ef* values of the BCBD-annelated derivatives conform to the rules 1*-4*, implying that angular annelation has very weak influence to the local aromaticity of the central ring. Such behavior of the *ef* values of the BCBD-annelated perylenes is quite contradictory to those of the *HOMA* and Σ indices. Namely, the *ef* values are almost identical for a certain number of angular annelations, while the ranges of the *HOMA* and Σ values are much wider. This fact explains the appearance of “vertical lines” in the *HOMA* vs. *ef* plot (Fig. 3). The correlation between Σ and *ef* is of similar quality (except that the Σ values increase with the increasing *ef* values), and is not presented here.

4. Conclusions

Our assessment of local aromaticity, based on DFT molecular geometry, confirmed the validity of the rules 1-3 and 2* emanating from the simple graph-theory-based energy effects *ef*. On the other hand, severe violations from the rules 1*, 3*, and 4* were observed. This finding is not surprising, since the fact that energetic and geometric criteria of aromaticity may lead to

contradictory conclusions has been recognized many times (see e. g. (Krygowski 1993; Schaad and Hess 2001; Stanger 2009)). As the presently used DFT-method provides a far more accurate description of the electronic structure of polycyclic conjugated molecules than a graph-theory-based approach, we are inclined to conclude that the predictions concerning the angular BCBD-annulation, made by means of the *ef*-method, should be taken and interpreted with due caution.

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Извод

Локална ароматичност код бензо- и бензоциклобутатиено-анелираних перилена

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Резиме

Испитани су ефекти бензо- и бензоциклобутатиено- (BCBD-) анелације на локалну ароматичност централног прстена *X* перилена. Локална ароматичност прстена *X* је процењена помоћу индекса *ef*, заснованог на теорији графова, и помоћу два индекса који се заснивају на геометрији молекула, *НОМА* и Σ . Резултати настали применом индекса *ef* са једне стране и индекса *НОМА* и Σ са друге стране су донекле контрадикторни. Наиме, индекси засновани на геометрији показују да је ефекат бензо-анелације супротан ефекту BCBD-анелације, док *ef* предвиђа да ангуларна BCBD-анелација има веома мали утицај на локалну ароматичност централног прстена перилена. Пошто су индекси засновани на молекулској геометрији софистициранији у односу на индекс који се заснива на теорији графова, може се закључити да су поузданија предвиђања проистекла из примене индекса *НОМА* и Σ .

Кључне речи: Ароматичност, молекулска геометрија, бензо-анелирани перилени, бензоциклобутатиено-анелирани перилени, DFT израчунавања

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