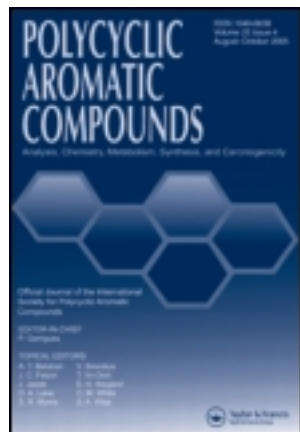


This article was downloaded by: [Svetlana Markovic]

On: 27 October 2011, At: 23:03

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Polycyclic Aromatic Compounds

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gpol20>

Local Aromaticity in Benzo- and Benzocyclobutadieno-Annulated Phenanthrenes

ALEXANDRU T. BALABAN^a, IVAN GUTMAN^b, SVETLANA MARKOVIĆ^b,
DuŠICA SIMIJONOVIĆ^b & Jelena ĐURĐEVIĆ^b

^a Texas A&M University at Galveston, 200 Seawolf Parkway,
Galveston, TX, USA

^b Faculty of Science, University of Kragujevac, P. O. Box 60,
Kragujevac, Serbia

Available online: 27 Oct 2011

To cite this article: ALEXANDRU T. BALABAN, IVAN GUTMAN, SVETLANA MARKOVIĆ, DuŠICA SIMIJONOVIĆ & Jelena ĐURĐEVIĆ (2011): Local Aromaticity in Benzo- and Benzocyclobutadieno-Annulated Phenanthrenes, *Polycyclic Aromatic Compounds*, 31:5, 339-349

To link to this article: <http://dx.doi.org/10.1080/10406638.2011.614179>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Local Aromaticity in Benzo- and Benzocyclobutadieno-Annulated Phenanthrenes

Alexandru T. Balaban,¹ Ivan Gutman,² Svetlana Marković,²
Dušica Simijonović,² and Jelena Đurđević²

¹Texas A&M University at Galveston, 200 Seawolf Parkway, Galveston, TX, USA

²Faculty of Science, University of Kragujevac, P. O. Box 60, Kragujevac, Serbia

The effects of benzo- and benzocyclobutadieno-(BCBD-)annulation on the local aromaticity of the central ring (X) of phenanthrene were examined. The local aromaticity of the ring X was estimated using a graph-theory-based index and two geometry-based indices. DFT calculations of phenanthrene congeners showed that many of these molecules are nonplanar, with significant steric strain. All three indices indicate that the effect of benzo-annulation is opposite to that of BCBD-annulation. The deviation of some phenanthrene derivatives from planarity does not influence the effects of annulation. This finding is in accord with some previously reported studies on the dependence of the aromaticity of the ring(s) on distortion from planarity.

Key Words: phenanthrene, benzo-annulated phenanthrenes, benzocyclobutadieno-annulated phenanthrenes, aromaticity, deviation from planarity

INTRODUCTION

The effects of benzo- and benzocyclobutadieno-(BCBD-)annulation on local aromaticity of a particular six-membered ring in benzenoid hydrocarbons have been investigated in several recent papers [1–6]. In Figure 1, diagrams 2 and 3 illustrate linear and angular benzo-annulation of an arbitrary benzenoid hydrocarbon (diagram 1), whereas diagrams 4 and 5 illustrate linear and angular BCBD-annulation of the same hydrocarbon. The six-membered ring whose local aromaticity has been examined is marked by X. Note that the congeners

Received 1 May 2011; accepted 4 May 2011.

The authors thank the support of the Ministry of Science of Serbia, through Grant no. 174033 and 172016.

Address correspondence to Svetlana Marković, Faculty of Science, P.O. Box 60 34000, Kragujevac, Serbia. E-mail: mark@kg.ac.rs

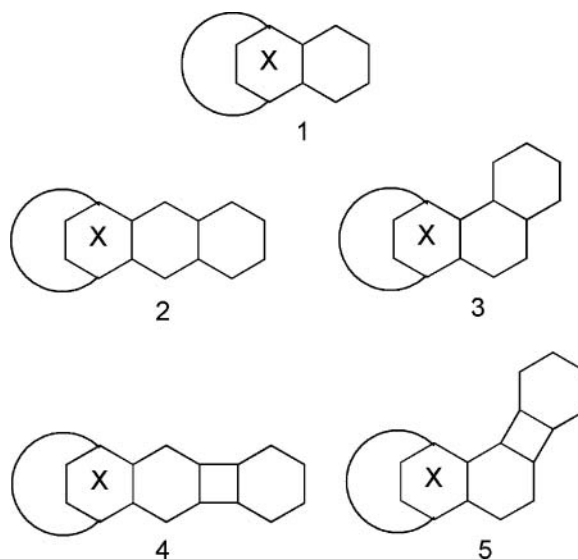


Figure 1: A benzenoid molecule (1), its benzo-annelated congeners (2 and 3), and its BCBD-annelated congeners (4 and 5). In this work we are focused on the local aromaticity of the six-membered ring marked by X.

obtained by BCBD-annulation are structurally similar to the earlier, much-studied phenylenes [7].

The effects of benzo- and BCBD- annulation on the central ring X of anthracene have recently been studied in detail [6]. For this purpose, three local aromaticity indices were applied: *ef* (energy effect), HOMA (Harmonic Oscillator Model of Aromaticity), and Σ (see Equation 4 further below). These indices are well suited for studies of the dependence of local aromaticity on the environment of the molecule or its fragment.

Before we introduce the energy effect, we need to present the result of Coulson, concerning the total π -electron energy [8]:

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

In Equation (1), $E(G)$ stands for the total π -electron energy of the conjugated molecule whose molecular graph is G . In Equation (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 [9, 10], 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 by Eq. (2) [11, 12]:

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

where $G-X$ 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 [13]. The positive ef values indicate that the cycle X stabilizes the molecule, whereas negative ef values imply destabilization. More details on the energy effect can be found in the review [3].

The HOMA index is defined as [14–16]:

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

where n is the number of bonds taken into the summation ($n = 6$ [6]), and α is an empirical constant ($\alpha = 25.77 \cdot 10^{-3}$) chosen to give $\text{HOMA} = 0$ 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} . The quantity R_{opt} is defined as a length of the C-C bond for which the energy (estimated by use of the harmonic potential) of the compression to the length of a double bond and expansion to the length of a single bond in 1,3-butadiene is minimal ($R_{\text{opt}} = 138.8$ pm). The individual bond lengths are denoted by R_i . Their values were determined [6] using density functional theory (DFT).

The Σ index is simply defined as the sum of the lengths of the six C-C bonds of the ring X (in picometers) [6]

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

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 congeners [6].

It was found that the agreement between the graph-theory-based ef results, and geometry-based HOMA and Σ results is reasonably good [6]. The main conclusion was surprising: The effect of benzo-annulation is opposite to that of BCBD-annulation. In particular, the following rules were revealed.

1. Linear benzo-annulation (diagram **2** in Figure 1) decreases the local aromaticity in the ring X in comparison to that in the non annulated parent species **1**.

2. Angular benzo-annulation (diagram **3** in Figure 1) increases the local aromaticity in the ring X in comparison to that in the non annelated parent species **1**.
3. Linear BCBD-annulation (diagram **4** in Figure 1) increases the local aromaticity in the ring X in comparison to that in the non annelated parent species **1**.
4. Angular BCBD-annulation (diagram **5** in Figure 1) decreases the local aromaticity in the ring X in comparison to that in the non annelated parent species **1**.

It is worth pointing out that anthracene and its all congeners are perfectly planar molecules with negligible steric strain. A logical question arises: How does the deviation from planarity influence the local aromaticity of the ring X , and the above-stated rules 1–4? The answer to this question can be obtained by examining the effects of benzo- and BCBD-annulation in a case where some congeners are non planar. In this work, we present the results of the investigation of the effects of benzo- and BCBD-annulation on the central ring (X) of phenanthrene. As expected, some of the phenanthrene derivatives are found to be non planar, with significant steric strain. Our ultimate goal is to establish whether the non planarity of the annelated molecules influences the local aromaticity of the ring X of phenanthrene, and its change due to benzo- and BCBD-annulation.

COMPUTATIONAL DETAILS

Phenanthrene and its benzo- and BCBD-annelated congeners are studied in this work. Phenanthrene is a relatively small and symmetric molecule, and has a total of 14 benzo-annelated and 14 BCBD-annelated congeners, that makes the DFT calculations of all possible molecules practical.

The geometries of all investigated molecules were optimized using the Gaussian 09 program package [17], at the B3LYP/6-311+G(d,p) level of theory [18, 19]. The applied 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 [6, 20], this theoretical model yields reliable molecular geometries, especially for such stable, singlet ground state species as those studied in the present work. Details of the calculated geometries of phenanthrene and its benzo- and BCBD-annelated congeners can be obtained from autho, Svetlana Marković, upon request.

After determining the geometries of the investigated molecules, the HOMA and Σ values of the ring X were calculated using Equations (3) and (4). The corresponding ef values were calculated using an in-house software, based on Equation (2) [21].

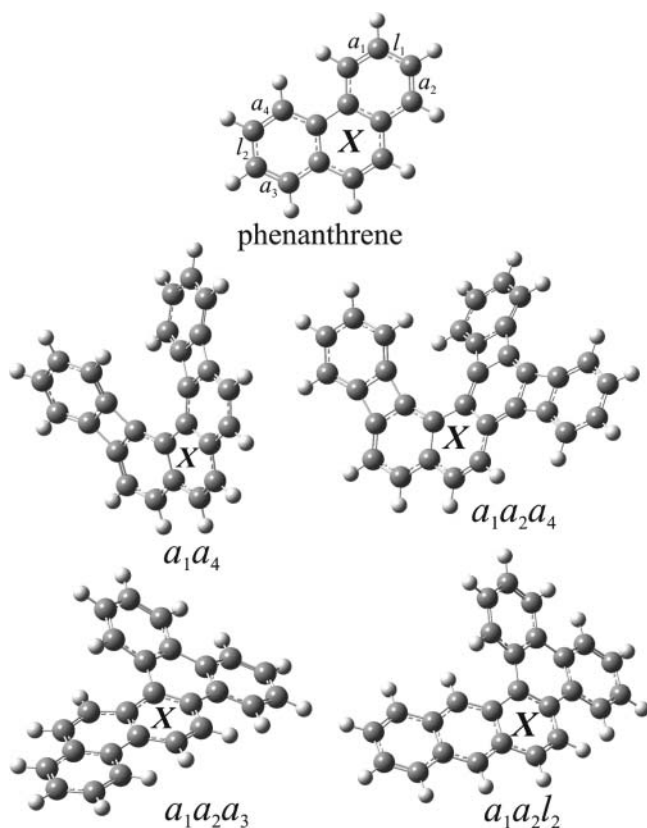


Figure 2: Optimized geometries of phenanthrene (with labeled sites of annelation) and some BCBD-annulated (a_1a_4 and $a_1a_2a_4$) and benzo-annulated ($a_1a_2a_3$ and $a_1a_2l_2$) congeners. *X* indicates the ring whose local aromaticity is examined.

RESULTS AND DISCUSSION

Before we present our results, we need to introduce the notation used in this work. Namely, the sites of annelation in phenanthrene are labeled as shown in Figure 2. The labeling of phenanthrene congeners is illustrated by optimized geometries of some BCBD- and benzo-annulated derivatives of phenanthrene. The examples presented in Figure 2 confirm our assumption that some phenanthrene derivatives are non planar. Careful examination of the geometries of all non planar molecules showed that the ring *X* is particularly twisted, where the bond angles considerably deviate from the dihedral bond angle characteristic for sp^2 hybridized carbon atoms. This structural feature necessarily induces significant strain in the non planar benzo- and BCBD-annulated phenanthrenes. These facts justify our choice of phenanthrene congeners in order to examine the influence of non planarity to the local aromaticity of the ring *X*.

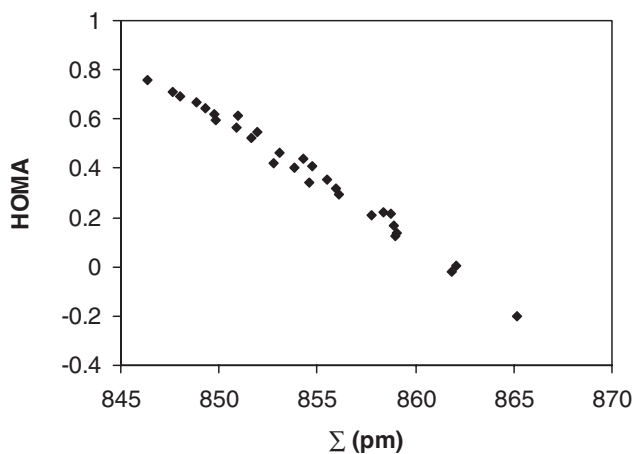


Figure 3: Correlation between the HOMA and Σ values of the ring X of phenanthrene, and its benzo- and BCBD-annelated derivatives.

As expected, the linear correlation between HOMA and Σ is fairly good, with the correlation coefficient of -0.993 (Figure 3). The data points pertaining to both benzo- and BCBD-annulation form a single correlation line, without any visible separation between the points associated to the two different annulation modes. This result confirms the earlier finding [6] that HOMA and Σ reproduce the same π -electron property of the ring X , which can be considered as its local aromaticity.

The correlation between HOMA and ef is curvilinear and much weaker, although one can observe that the HOMA values increase with increasing ef values (Figure 4). The deviation from curvilinearity is more pronounced in the

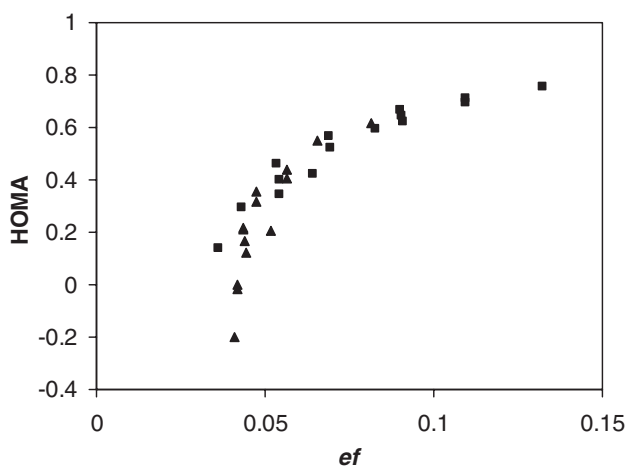


Figure 4: Correlation between the HOMA and ef values of the ring X of phenanthrene, and its benzo- (squares) and BCBD-annelated (triangles) derivatives.

Table 1: The change of the ef , HOMA and Σ indices of the ring X caused by benzo- and BCBD-annelation. $\Delta ef(\text{benzo})$ is the difference between the ef value of the ring X of the benzo-annelated congener and the ef value of the same ring in phenanthrene. The meanings of $\Delta ef(\text{BCBD})$, $\Delta\text{HOMA}(\text{benzo})$, $\Delta\text{HOMA}(\text{BCBD})$, $\Delta\Sigma(\text{benzo})$, and $\Delta\Sigma(\text{BCBD})$ are analogous. The labeling of the compounds is presented in Figure 2. The ef , HOMA, and Σ values of phenanthrene amount 0.0534 β , 0.4621, and 853.083 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.

| molecule | Δef (benzo) | Δef (BCBD) | ΔHOMA (benzo) | ΔHOMA (BCBD) | $\Delta\Sigma$ (benzo) (pm) | $\Delta\Sigma$ (BCBD) (pm) |
|----------------|------------------------|-----------------------|--------------------------------|-------------------------------|--------------------------------|-------------------------------|
| l_1 | -0.0103 | 0.0120 | -0.1684 | 0.0856 | 3.014 (P) | -1.139 (P) |
| $l_{1/2}$ | -0.0173 | 0.0281 | -0.3221 | 0.1536 | 5.940 (P) | -2.116 (P) |
| a_1 | 0.0159 | -0.0059 | 0.0609 | -0.1066 | -1.428 (P) | 2.427 (P) |
| a_2 | 0.0155 | -0.0058 | 0.1048 | -0.1452 | -2.154 (P) | 2.905 (P) |
| a_1a_2 | 0.0295 | -0.0088 | 0.1321 | -0.3896 | -3.226 (NP) | 5.919 (P) |
| a_1a_3 | 0.0373 | -0.0097 | 0.1848 | -0.2436 | -3.800 (NP) | 5.308 (P) |
| a_1a_4 | 0.0375 | -0.0098 | 0.1588 | -0.2494 | -3.317 (NP) | 5.683 (NP) |
| a_2a_3 | 0.0369 | -0.0096 | 0.2059 | -0.2933 | -4.211 (P) | 5.850 (P) |
| $a_1a_2a_3$ | 0.0559 | -0.0114 | 0.2474 | -0.4792 | -5.444 (NP) | 8.791 (P) |
| $a_1a_2a_4$ | 0.0562 | -0.0115 | 0.2321 | -0.4604 | -5.093 (NP) | 8.980 (NP) |
| $a_1a_2a_3a_4$ | 0.0790 | -0.0126 | 0.2951 | -0.6622 | -6.736 (NP) | 12.047 (NP) |
| $a_{1/2}$ | 0.0011 | 0.0029 | -0.1170 | -0.0249 | 1.543 (NP) | 1.187 (P) |
| $a_{2/2}$ | 0.0008 | 0.0030 | -0.0595 | -0.0560 | 0.736 (P) | 1.651 (P) |
| $a_{1/2/2}$ | 0.0109 | -0.0018 | -0.0426 | -0.2550 | -0.306 (NP) | 4.653 (P) |

case of BCBD-annelated molecules (triangles). The correlation between Σ and ef is of similar quality (except that the HOMA values decrease with increasing ef values), and is not presented here.

The results of the investigation are summarized in Table 1. The authors first consider the molecules obtained by linear or angular annelation (first 11 pairs of molecules). In this case, all three indices are in agreement (the sign of the HOMA value is the same as the sign of the respective ef value, and 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. This implies that the rules 1–4, stated in the Introduction, are obeyed with no exceptions. Furthermore, the higher the number of linear (resp. angular) benzo-annelations, the weaker (resp. stronger) is the local aromaticity of the ring X . This finding is documented with the ef and HOMA values that decrease (resp. increase) with increasing number of linear (resp. angular) annelations, and Σ values that increase (resp. decrease) with increasing number of linear (resp. angular) annelations. The situation with BCBD-annelation is completely opposite. Namely, the higher the number of linear (resp. angular) BCBD-annelations, the stronger (resp. weaker) is the local aromaticity of the ring X .

As a consequence, the local aromaticity of the ring X is the highest in benzo-annelated $a_1a_2a_3a_4$, and lowest in BCBD-annelated $a_1a_2a_3a_4$. By inspecting the $\Delta ef(\text{BCBD})$ values in Table 1, one can observe that for a certain number of angular annelations the ef values are mutually nearly equal. On the other hand, the ranges of the ΔHOMA and $\Delta\Sigma$ values for a certain number of angular BCBD-annelations are much wider. This fact explains the deviation of the BCBD-annelated molecules from curvilinearity in Figure 4.

As for the a_1l_2 and a_2l_2 pairs of molecules, where both linearly and angularly annelated fragments are involved, the values of the ef , HOMA and Σ indices lie between those for linearly and angularly annelated molecules. In particular, the ef and HOMA values of benzo-annelated congeners are higher (resp. lower) than those of linearly (resp. angularly) annelated derivatives, whereas their Σ values are lower (resp. higher) than those of linearly (resp. angularly) annelated molecules. The situation with the BCBD-annelated a_1l_2 and a_2l_2 is quite opposite. But, the sign of the Δef values is opposite to the sign of the ΔHOMA values, and the same as the sign of the $\Delta\Sigma$ values. It turns out that HOMA and Σ indices predict that the effect of linear benzo-annelation dominates over that of angular benzo-annelation, whereas the effect of linear BCBD-annelation is weaker than that of angular BCBD-annelation. The prediction based on the ef index is opposite. Finally, in the case of BCBD-annelated $a_1a_2l_2$ all indices predict that the angular effect is dominant over linear effect. The ef value lies between those for linearly and angularly BCBD-annelated congeners, whereas the HOMA (resp. Σ) value is lower (resp. higher) than the corresponding values of some angularly BCBD-annelated molecules. The values of the three indices for benzo-annelated $a_1a_2l_2$ are mutually contradictory, but lie between those for linearly and angularly annelated molecules. All these "irregularities" are the consequence of the competition between the stabilizing and destabilizing modes of annelation.

CONCLUDING REMARKS

Examination of local aromaticity of the ring X in benzo- and BCBD-annelated phenanthrenes confirms the rules 1–4 [6] presented in the Introduction. In short, the effects of benzo-annelation are opposite to those of BCBD-annelation. The agreement between the graph-theory based ef results and the geometry-based HOMA and Σ results is remarkably good. The fact that many phenanthrene derivatives are non planar (Figure 2 and Table 1) does not affect the effects of annelation. This finding is in accord with some previously reported studies on the dependence of the aromaticity of the ring(s) on distortion from planarity [22, 23]. Peri-substituted naphthalene derivatives are convenient examples of molecules where the changes in aromaticity due to the folding of the aromatic moiety can be studied. It was shown [16] that small folding of the naphthalene moiety does not substantially affect the

aromaticity. Analysis of the experimental molecular geometry of 1,4-dichloro-2,6[5]metacyclophane [22] showed its high aromaticity, despite substantial distortions from the planar conformation. A similar situation was found in the case of [5]-*p*-cyclophane [23], where a substantial folding of the ring was observed.

It is worth pointing out that there are fewer examples of (non planar) phenanthrene derivatives that violate the rules 1–4 in comparison to (planar) anthracene congeners. In the case of some anthracene derivatives (for example perfectly planar BCBD-annulated a_1l_2 [6]), the repulsion between the hydrogen atoms that lie on the bays necessarily gives rise to the elongation of some C-C bonds of the ring *X*. This elongation leads to the increased Σ values, and decreased HOMA values. In the case of phenanthrene congeners, the deviation from planarity allows the bonds to take the lengths close to their optimal values.

The few molecules where disagreement among the values of applied indices exists, contain both linearly and angularly annulated fragments. These examples confirm the fact that energetic and geometric criteria of aromaticity [24–27] may lead to contradictory conclusions [16, 28–30].

REFERENCES

1. Balaban, A. T., J. Đurđević, I. Gutman, S. Jeremić, and S. Radenković. 2010. Correlations between local aromaticity indices of bipartite conjugated hydrocarbons. *J. Phys. Chem. A* 114:5870–77.
2. Balaban, A. T., I. Gutman, S. Jeremić, and J. Đurđević. 2011. Effect of benzo-annulation on cyclic conjugation. *Monatsh. Chem.* 142:53–7.
3. Gutman, I. 2005. Cyclic conjugation energy effects in polycyclic π -electron systems. *Monatsh. Chem.* 136:1055–69.
4. Đurđević, J., S. Radenković, I. Gutman, and S. Marković. 2009. Testing the PCP-rule. *Monatsh. Chem.* 140:1305–9.
5. Gutman, I., B. Furtula, and A. T. Balaban. 2011. Effect of benzocyclobutadieno-annulation on cyclic conjugation in fluoranthene congeners. *J. Serb. Chem. Soc.* 76: 733–41.
6. Balaban, A. T., I. Gutman, S. Marković, and D. Simijonović. 2011. Local aromaticity in benzo- and benzocyclobutadieno-annulated anthracenes. *Monatsh. Chem.* 142:797–800.
7. Trinajstić, N., T. G. Schmalz, T. P. Živković, S. Nikolić, G. E. Hite, D. J. Klein, and W. A. Seitz. 1991. [*N*]phenylenes: A theoretical study. *New J. Chem.* 15:27–31.
8. Coulson, C. A. 1940. Calculation of the energy in unsaturated hydrocarbon molecules. *Proc. Cambridge Phil. Soc.* 36:201–3.
9. Graovac, A., I. Gutman, N. Trinajstić, and T. Živković. 1972. Graph theory and molecular orbitals. Application of Sachs theorem. *Theor. Chim. Acta* 26:67–78.
10. Gutman, I. 2003. Impact of the Sachs theorem on theoretical chemistry: a participant's testimony. *MATCH Commun. Math. Comput. Chem.* 48:17–34.

11. S. Bosanac, and I. Gutman. 1977. Effect of a ring on the stability of polycyclic conjugated molecules. *Z. Naturforsch.* 32a:10–12.
12. Gutman, I., and S. Bosanac. 1977. Quantitative approach to Hückel rule. The relations between the cycles of a molecular graph and the thermodynamic stability of a conjugated molecule. *Tetrahedron* 33:1809–12.
13. Schaad, L. J., and B. A. Hess. 1972. Hückel molecular orbital π -resonance energies. Question of the σ structure. *J. Am. Chem. Soc.* 94:3068–74.
14. Kruszewski, J., and T. M. Krygowski. 1972. Definition of aromaticity basing on the harmonic oscillator model. *Tetrahedron Lett.* 13:3839–42.
15. Krygowski, T. M. 1993. Crystallographic studies of inter- and intramolecular interactions reflected in aromatic character of π -electron systems. *J. Chem. Inf. Comput. Sci.* 33:70–8.
16. Krygowski, T. M., and M. K. Cyranski. 2001. Structural aspects of aromaticity. *Chem. Rev.* 101:1385–1419.
17. Frisch, M. J., G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox. 2009. Gaussian, Inc., Wallingford, CT.
18. Lee, C., W. Yang, and R. G. Parr. 1988. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* 37:785–9.
19. Becke, A. D. 1993. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* 98:5648–52.
20. Vijayalakshmi, K. P., and C. H. Suresh. 2008. Theoretical studies on the carcinogenicity of the polycyclic aromatic hydrocarbons. *J. Comput. Sci.* 29:1808–17.
21. Gutman, I. 2010. On a class of integrals encountered in theoretical chemistry. *Int. J. Chem. Model.* 2:335–41.
22. Jenneskens, L. W., J. C. Klamer, H. J. R. de Boer, W. H. de Wolf, F. Bickelhaupt, and C. H. Stam. 1984. Molecular structure of 8,11-dichloro[5]metacyclophane: A strongly bent benzene ring. *Angew. Chem. Int. Ed.* 23:238–9.
23. Rice, J. E., T. J. Lee, R. B. Remington, W. D. Allen, D. A. Clabo, and H. F. Schaefer. 1987. [5]Paracyclophane. An important example of ring strain and aromaticity in hydrocarbon compounds. *J. Am. Chem. Soc.* 109:2902–9.
24. Balaban, A. T. 1980. Is aromaticity outmoded? *Pure Appl. Chem.* 52:1409–29.
25. Balaban, A. T., and T. G. Schmalz. 2006. Strain-free sextet-resonant benzenoids and their antisextet dualists. *J. Chem. Inf. Model.* 46:1563–79.
26. Balaban, A. T. 2009. Aromaticity of six-membered rings with one heteroatom, in *Aromaticity in heterocyclic compounds*, eds. T. M. Krygowski and M. K. Cyranski (Berlin: Springer), 203–46.

27. Balaban, A. T. 2010. Monocyclic hetarenes with π -electron aromatic sextet, in *Advances in Heterocyclic Chemistry*, ed. A. R. Katritzky (Chennai, India: Academic Press), 61–105.
28. Minkin, V. I., M. N. Glukhovtsev, and B. Y. Simkin. 1994. *Aromaticity and antiaromaticity. Electronic and structural aspects* (New York: Wiley).
29. Schaad, L. J., and B. A. Hess. 2001. Dewar resonance energy. *Chem. Rev.* 101: 1465–76.
30. Stanger, A. 2009. What is . . . aromaticity: A critique of the concept of aromaticity - can it really be defined? *Chem. Commun.* 1939–47.