

Dedicated to Professor Alexandru T. Balaban
on the occasion of his 85th anniversary

STRAIN IN STRAIN-FREE BENZENOID HYDROCARBONS: THE CASE OF CHRYSENE AND TRIPHENYLENE

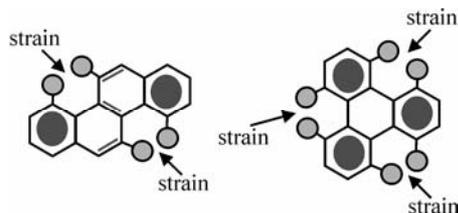
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Benzenoid molecules possessing bays, but no coves and fjords, are traditionally considered as “strain-free”. Yet, repulsion between the two bay *H*-atoms affects the length of the near-lying carbon-carbon bonds as well as the corresponding bond angles. A method is developed to estimate the energy of this strain. In the case of chrysene and triphenylene, its values were found to be about 7 and 13 kJ/mol, respectively.



INTRODUCTION

Over almost a half of a century, Alexandru T. Balaban studied benzenoid hydrocarbons and made significant contributions to their theory (see, for example, the papers¹⁻⁶). One of the numerous topics he examined were the so-called “*strain-free benzenoids*”⁷, namely benzenoid systems in which steric strain is absent or minimal. The present study is an attempt to better understand strain in such benzenoid hydrocarbons, and to estimate its magnitude.

Benzenoid hydrocarbons form a class of conjugated molecules whose π -electron properties have been extensively studied. These studies started as early as in the 1930s,^{8,9} and were eventually enhanced by applying the mathematical apparatus of graph theory.¹⁰⁻¹⁴ The main concepts used in the topological theory of benzenoid hydrocarbons are graph spectra,^{11,14,15} especially in connection with

total π -electron energy¹⁶ and resonance energy,^{17,18} Kekulé structures (= perfect matchings),^{13,19-22} Clar aromatic sextet structures,^{19,23,24} and conjugated circuits.^{19,25,26} All these approaches assume that the underlying benzenoid molecules are planar, and disregard the steric strain that may be present. In other words, the topological theories of benzenoid hydrocarbons are applicable, and yield results that agree with experimental findings, only in the case of molecules with negligible non-planarity and negligible steric strain. In view of this, of particular interest for the topological theory of benzenoid hydrocarbons are those referred to as *strain-free*, namely benzenoids whose perimeters do not contain coves and fjords, but may possess bays.

The structural features named “*bay*”, “*cove*” and “*fjord*”, which may occur on the perimeter of a benzenoid molecule, are explained in Fig. 1; for details see elsewhere.¹⁸

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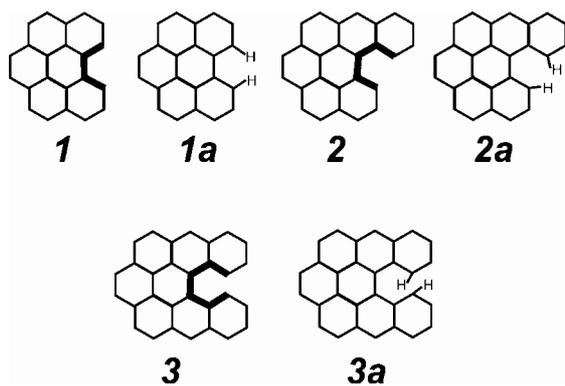


Fig. 1 – By heavy lines are indicated the structural features on the perimeter of a benzenoid molecule referred to as *bay* (1), *cove* (2), and *fjord* (3). The hydrogen atoms, indicated in diagrams 1a, 2a, and 3a are said to be, respectively, in bay-, cove- and fjord-constellation.

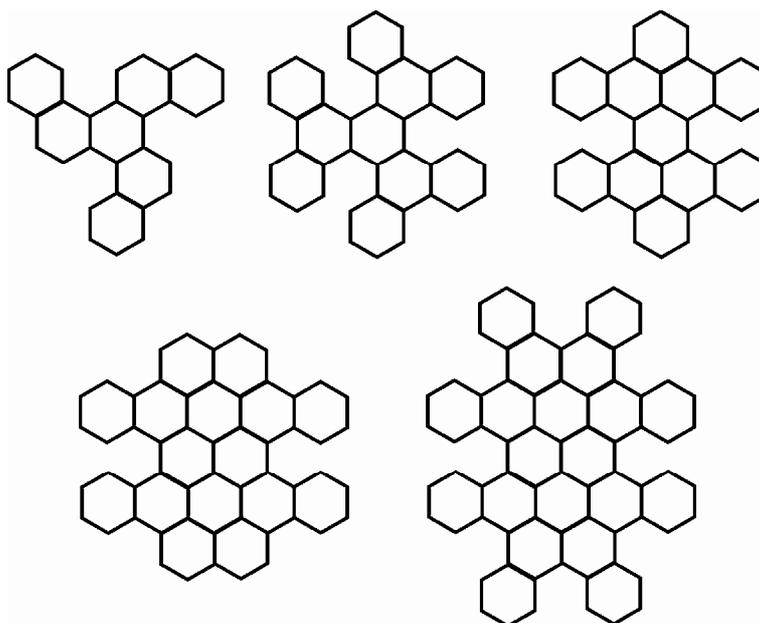


Fig. 2 – Some recently synthesized benzenoid hydrocarbons.²⁸⁻³¹ These all possess coves and/or fjords and are non-planar.

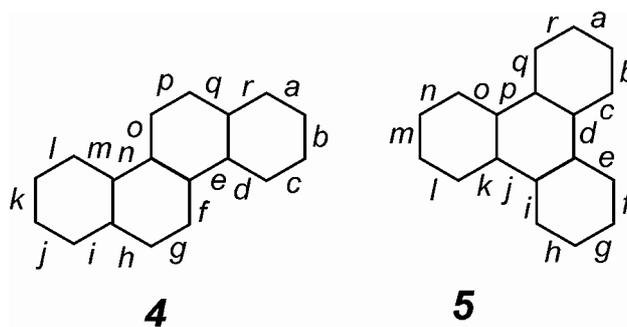


Fig. 3 – Chrysene (4) and triphenylene (5) and the labeling of their carbon-carbon bonds according to IUPAC rules. Note that the bonds *e* and *n* in 4 are symmetry-equivalent, and the same is the case with the bonds *d*, *j*, *p* in 5. Symmetry-equivalent are also the bond pairs (*d,e*), (*m,n*) and (*e,f*), (*n,o*) in 4, as well as (*c,d*), (*d,e*), (*i,j*), (*j,k*), (*o,p*), (*p,q*) in 5. In chrysene, the two pairs of overcrowded hydrogen atoms (*cf.* diagram 1a in Fig 1) are attached to the bonds *d* and *f* as well as *m* and *o*. In triphenylene, the three pairs of overcrowded hydrogen atoms are attached to the bonds *c* and *e*, *i* and *k*, as well as *o* and *q*.

On the other hand, it is known for quite some time that a large part of the known benzenoid hydrocarbons are highly strained and non-planar.²⁷ Recently, several new representatives of such benzenoid systems have been obtained²⁸⁻³¹ (see Fig. 2).

As usual, when writing the structural formula of a benzenoid hydrocarbon (as in Fig. 2), the hydrogen atoms are not indicated. This has the consequence that one may miss to immediately recognize that if there are coves and fjords on the perimeter, then the respective hydrogen atoms

come so close to each other that the molecule necessarily becomes non-planar and possesses a large steric strain.

In the chemical literature, benzenoid molecules without coves and fjords (cf. Fig. 1) are traditionally referred to as “strain-free” (see, for example,³²⁻³⁵ and especially pp. 86-96 in the book.¹³ These molecules are believed to be perfectly planar and devoid of any steric strain. In particular, in the recent tutorial review,³⁶ it is explicitly claimed that “*chrysene and triphenylene with nonadjacent bay regions are essentially strain-free*”. There is no doubt that this is true for *convex benzenoids*,^{37,38} i.e., benzenoids in which in addition to coves and fjords, also bays are absent.

In the case of benzenoids with bays, the distance between the two hydrogen atoms in a bay-constellation is typically 198-199 pm, which is significantly smaller than twice the van der Waals radius of the H-atom (109 pm). Therefore, a non-negligible repulsion between the bay H-atoms is to be expected, causing deformation of the carbon-atom skeleton. Therefore, whether “strain-free benzenoids” with bay regions are really strain-free is doubtful and - at least - deserves to be checked and verified.

Indeed, the fact that there must be some strain in benzenoid systems with bays was recognized quite some time ago; see^{7,39-42} and the references cited therein. We have recently elaborated⁴² a new method for estimating and quantifying strain in such benzenoids and applied it to their simplest representative - phenanthrene. The strain in this benzenoid hydrocarbon, possessing just a single bay, was estimated to be around 7 kJ/mol. We now extend our studies to the (again, simplest) benzenoids with two and three bay regions, namely to chrysene and triphenylene.

Our approach⁴² is based on the examining the energy effect of the strain-caused deformation of the carbon-atom skeleton of the underlying benzenoid hydrocarbon, paying attention to carbon-carbon bond lengths and bond angles in the bay region(s). Thus, we estimate the energy needed to change the bond lengths and bond angles in the bay region(s) from their ideal “strain-free” values to the actual ones. The “strain-free” carbon-carbon bond lengths are calculated from the Pauling bond orders as

$$d_{rs}^{(0)} = 145.65 - 10.05 P_{rs} \quad (1)$$

$$d_{rs}^{(1)} = 144.62 - 9.19 P_{rs} \quad (2)$$

$$d_{rs}^{(2)} = 144.19 - 10.34 P_{rs} \quad (3)$$

where for $h = 0, 1, 2$, $d_{rs}^{(h)}$ is the length [in pm] of the bond rs to which h hydrogen atoms are attached, and where P_{rs} is the respective Pauling bond order.^{19,43-45} Formulas (1)-(3) were obtained⁴² so as to reproduce the true bond lengths of convex benzenoids.

Determining the “strain-free” bond angles is straightforward: 120°.

NUMERICAL WORK

Assuming that the benzenoid molecule possessing one or more bay regions is geometrically planar, strain in its carbon-atom skeleton can be assessed as the sum of the bond-component (the effect of deviation of the carbon-carbon bond lengths in the bay region(s) from their “strain-free” values), and the angle-component (the effect of deviation of the carbon-carbon bond angles in the bay region(s) from their “strain-free” values). These deviations, the result of repulsion between bay H-atoms, are considered to be the *principal strain-caused geometry change*, and its energy-effect the *strain energy*. All other bond lengths and bond angles in the molecule accommodate to the new geometry in bay region(s), *resulting in a secondary strain-caused geometry change*, which in our opinion should not be directly associated with strain.

Geometries of the examined benzenoid systems were calculated at the B3LYP/def2-TZVP level of theory. The data relevant for our study are given in Tables 1 and 2.

All calculations were performed with the Gaussian 09 program package.⁴⁶ The geometries of the studied molecules were optimized by means of the B3LYP density functional method^{47,48} in combination with the def2-TZVP Ahlrichs type basis set.⁴⁹ Harmonic frequency calculations were carried out to verify that the optimized structures correspond to minima on the potential energy surface.

Table 1

Lengths of the carbon-carbon bonds (in pm) and of the perimeter bond angles (in degrees) of chrysene (according to the labeling indicated in Fig. 3). The deviation of a bond length from its "strain-free" value is calculated by means of Eqs. (1), (2) or (3), for h equal to 0, 1 or 2, respectively, using the Pauling bond order P_{rs} . All angles are in degrees. The deviation of a bond angle is obtained by assuming that its "strain-free" value is 120°

bond or angle	optimized value	h	P_{rs}	deviation
a, j	137.3	2	5/8	-0.43
b, k	140.5	2	3/8	0.09
c, l	137.6	2	5/8	-0.13
d, m	141.3	1	3/8	0.13
e, n	144.9	0	2/8	1.77
f, o	142.7	1	2/8	0.38
g, p	135.8	2	6/8	-0.63
h, q	142.2	1	2/8	-0.12
i, r	141.2	1	3/8	0.03
$(a,b), (j,k)$	119.5			-0.5
$(b,c), (k,l)$	120.5			0.5
$(c,d), (l,m)$	121.5			1.5
$(d,e), (m,n)$	123.2			3.2
$(e,f), (n,o)$	121.4			1.4
$(f,g), (o,p)$	121.8			1.8
$(g,h), (p,q)$	121.3			1.3
$(h,i), (q,r)$	121.1			1.1
$(i,j), (a,r)$	121.0			1.0

Table 2

Same data as in Table 1 for triphenylene (according to the labeling indicated in Fig. 3)

bond or angle	optimized value	h	P_{rs}	Deviation
a, g, m	139.6	2	4/9	0.01
b, f, h, l, n, r	137.7	2	5/9	-0.75
c, e, i, k, o, q	140.8	1	4/9	0.26
d, j, p	146.3	0	1/9	1.78
$(a,b), (a,r), (f,g), (g,h), (l,m), (m,n)$	119.6			-0.4
$(b,c), (e,f), (h,i), (k,l), (n,o), (q,r)$	121.9			1.9
$(c,d), (d,e), (i,j), (j,k), (o,p), (p,q)$	121.5			1.5

The potential energy surface for the stretching models of the bonds e and n in chrysene (**4**) and of the bonds d, j, p in triphenylene (**5**), see Fig. 3, were obtained by simultaneously fixing the lengths of these bonds to $d_0 + \Delta d$, and performing partial optimization for the rest of the molecule. For d_0 we used the optimized bond length (see Tables 1 and 2), and for $\Delta d = -0.4, -0.3, -0.2, -0.1, 0.0, 0.1, 0.2, 0.3, 0.4$ pm. In the case of chrysene, analogous calculations were done by simultaneously fixing the bond angles (d,e) and (m,n) to $\theta_{0,1} + \Delta\theta_1$, and (in separate calculations) the bond angles (e,f) and (n,o) to $\theta_{0,2} + \Delta\theta_2$, where $\theta_{0,1}$ and $\theta_{0,2}$ are the optimized bond angles (see Table 1), whereas $\Delta\theta_1, \Delta\theta_2 = -0.4, -0.3, -0.2, -0.1, 0.0, 0.1, 0.2, 0.3, 0.4$ degrees. In the case of

triphenylene, all the six symmetry-equivalent bond angles $(c,d), (d,e), (i,j), (j,k), (o,p), (p,q)$ were simultaneously fixed to $\theta_0 + \Delta\theta$, for θ_0 being the optimized bond angle (see Table 2), whereas $\Delta\theta = -0.4, -0.3, -0.2, -0.1, 0.0, 0.1, 0.2, 0.3, 0.4$ degrees.

STRAIN ENERGY OF CHRYSENE

Bond-component of strain in chrysene

In order to estimate the energy-effect of the bond-component, we have calculated the electron energy of chrysene in which the length of the (symmetry-equivalent) bonds e and n were fixed at a given value $d_0 + \Delta d$, and all other geometric

parameters were optimized. Here $d_0 = 144.9$ pm is the length of the bonds e and n in the fully optimized geometry of chrysene, see Table 1. We then calculate the difference ΔE_{bond} , between the energy of the optimized geometry and of the geometry with fixed bonds e and n . The

dependence of ΔE_{bond} [in kJ/mol] on Δd is shown in Fig. 4a. It is well reproduced by the formula

$$\Delta E_{bond} = a \Delta d^2 + b \Delta d^3 \quad (4)$$

for $a = 0.3189$ and $b = 0.0027$. Setting $\Delta d = 1.77$ pm (see Table 1), we get $\Delta E_{bond} = 1.01$ kJ/mol.

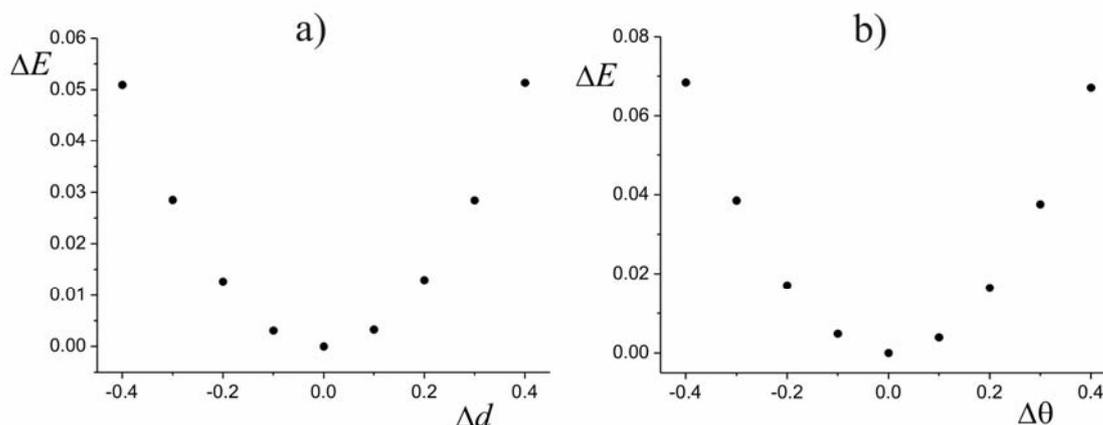


Fig. 4 – (a) Dependence on the parameter Δd [in pm] of the electronic energy [in kJ/mol] of chrysene with fixed length of the bonds e and n , relative to the energy of its fully optimized geometry. (b) Analogous dependence on the parameter $\Delta \theta_1$ [in degrees]. These dependencies are almost harmonic, with a very small anharmonicity. For details see text.

Angle-component of strain in chrysene

The bay regions of chrysene have two pairs of symmetry-equivalent bond angles, (d,e) , (m,n) and (e,f) , (n,o) , see Fig. 3 and Table 1. Therefore, the angle-component of its strain has to be separated into two parts, $\Delta E_{angle} = \Delta E_{angle,1} + \Delta E_{angle,2}$, where $\Delta E_{angle,1}$ pertains to (d,e) and (m,n) , whereas $\Delta E_{angle,2}$ pertains to (e,f) and (n,o) . Pursuing a strategy fully analogous as in the case of bond-component, we arrive at

$$\Delta E_{angle,1} = a_1 \Delta \theta_1^2 + b_1 \Delta \theta_1^3$$

and

$$\Delta E_{angle,2} = a_2 \Delta \theta_2^2 + b_2 \Delta \theta_2^3$$

where $a_1 = 0.4233$, $b_1 = -0.0122$, $a_2 = 0.6867$, $b_2 = 0.1669$. Setting into the above relations $\Delta \theta_1 = 3.2^\circ$ and $\Delta \theta_2 = 1.4^\circ$, we obtain $\Delta E_{angle,1} = 3.93$ kJ/mol and $\Delta E_{angle,2} = 1.80$ kJ/mol, which yields for the angle-component of chrysene: $\Delta E_{angle} = 5.73$ kJ/mol.

Finally, from $\Delta E = \Delta E_{bond} + \Delta E_{angle}$, we get our estimate of the strain energy in chrysene, equal to $1.01 + 5.73 \approx 6.7$ kJ/mol, or, to remain on the safe side, around 7 kJ/mol.

STRAIN ENERGY OF TRIPHENYLENE

Bond-component of strain in triphenylene

The procedure was analogous as in the case of chrysene, except that here the lengths of the three symmetry-equivalent bay bonds d , j , p were simultaneously fixed at $d_0 + \Delta d$, for $d_0 = 146.3$ pm being the length of these bonds in the fully optimized geometry, see Table 2. The respective energy difference, ΔE_{bond} is well reproduced by the formula (4) for $a = 0.4091$ and $b = 0.0899$. Setting $\Delta d = 1.78$ pm (see Table 2), we get $\Delta E_{bond} = 1.80$ kJ/mol.

Angle-component of strain in triphenylene

The bay regions of triphenylene six symmetry-equivalent bond angles, (c,d) , (d,e) , (i,j) , (j,k) ,

(*o,p*), (*p,q*), see Fig. 3 and Table 2. These were simultaneously fixed at $\theta_0 + \Delta\theta$, for $\theta_0 = 121.5^\circ$ being the bond angle in the fully optimized geometry. The energy difference ΔE_{angle} satisfies the formula

$$\Delta E_{angle} = a \Delta\theta^2 + b \Delta\theta^3 \quad (5)$$

for $a = 4.0723$ and $b = 0.6954$. Setting $\Delta\theta = 1.5^\circ$ (see Table 2), we get $\Delta E_{angle} = 11.51$ kJ/mol.

This finally yields our estimate of the strain energy in triphenylene, equal to $1.80 + 11.51 \approx 13.3$ kJ/mol, or, to remain on the safe side, between 13 and 14 kJ/mol.

DISCUSSION AND CONCLUDING REMARKS

In the earlier paper,⁴³ the strain energy of phenanthrene was estimated to be about 7 kJ/mol. Bearing in mind that phenanthrene has a single bay region, whereas chrysene and triphenylene have two and three, it could be expected that the strain energy of chrysene and phenanthrene would be, respectively, nearly two and three times as large as that of phenanthrene. Our calculations, using the exactly same method as in the paper,⁴³ show that the strain energy of chrysene is nearly equal to that of phenanthrene, and is nearly two times greater in the case of triphenylene. These somewhat surprising results require a detailed analysis and some rationalization.

As explained above, the method used in the present work determined two components of the strain energy, or more precisely of the energy effect of the principal strain-caused geometry change in the bay regions of the considered benzenoids. The first component, ΔE_{bond} , pertains to the extension of the bay carbon-carbon bond(s). Its values for phenanthrene, chrysene, and triphenylene are, respectively, 0.47, 1.01, and 1.80 kJ/mol. Remarkably, the bond-components to the strain energy are fairly well related as 1:2:3.

Both in the earlier work⁴² and in the present study, the angle-component of the strain energy, ΔE_{angle} , is found to be much (almost one order of magnitude) greater than the bond-component. This, in turn, implies that the deformation of bond angles is much more energy demanding than the

deformation of the bond lengths. Therefore, whenever possible, the angle deformations will be “distributed” over a larger domain of the molecule. As the data in Table 1 indicate, this happens in the case of chrysene. Whereas the bay-bond-angles (*d,e*) and (*m,n*) are significantly extended, the deformations of the other two bay-bond-angles (*e,f*) and (*n,o*) are not different from the deformations of bond angles outside the bay regions. This seems to cause that the angle-component of strain energy (calculated within the bay regions) is less than what one would expect based on “chemical intuition”.

The situation with triphenylene is exceptional from another point of view. Namely, the three bay regions in this molecule are positioned so close to each other, that a simultaneous extension of the six symmetry-equivalent bay-bond-angles would require the compression of all other carbon-carbon bond angles, which would be very energy demanding. This fact is seen from the value of the parameter a in Eq. (5), which is an order of magnitude greater than the analogous a -values for chrysene. In Table 2 we see that the deformation of the six bay-bond-angles in triphenylene is again “distributed” over other non-bay bond-angles, making the angle-component of the strain energy smaller than one would expect on the basis of “chemical intuition”. Anyway, because of the large a -value in Eq. (5), ΔE_{bond} is more than twice as large as in the case of chrysene.

In summary: Our studies confirm that “strain-free” benzenoid hydrocarbons with bay regions are not truly strain-free. In case of several bay regions, the bond-component of the strain energy is approximately additive, i.e., proportional to the number of bay regions. On the other hand, the angle-component of the strain energy follows a pattern that is not yet possible to fully comprehend.

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REFERENCES

1. A. T. Balaban and F. Harary, *Tetrahedron*, **1968**, *24*, 2505-2516.
2. A. T. Balaban, *Rev. Roum. Chim.*, **1970**, *15*, 1243-1250.
3. A. T. Balaban, *Pure Appl. Chem.*, **1982**, *54*, 1075-1096.
4. A. T. Balaban, *Pure Appl. Chem.*, **1993**, *65*, 1-9.
5. A. T. Balaban, I. Gutman, S. Marković, D. Simijonović and J. Đurđević, *Polyc. Arom. Comp.*, **2011**, *31*, 339-349.

6. J. Kovič, T. Pisanski, A. T. Balaban and P. W. Fowler, *MATCH Commun. Math. Comput. Chem.*, **2014**, *72*, 3-26.
7. A. T. Balaban and T. G. Schmalz, *J. Chem. Inf. Model.*, **2006**, *46*, 1563-1579.
8. E. Hückel, *Z. Phys.*, **1931**, *70*, 204-286.
9. E. Hückel, "Grundzüge der Theorie ungesättigter und aromatischer Verbindungen", Verlag Chemie, Berlin, 1940.
10. A. T. Balaban (Ed.), "Chemical Applications of Graph Theory", Academic Press, London, 1976.
11. A. Graovac, I. Gutman and N. Trinajstić, "Topological Approach to the Chemistry of Conjugated Molecules", Springer, Berlin, 1977.
12. I. Gutman and O. E. Polansky, "Mathematical Concepts in Organic Chemistry", Springer, Berlin, 1986.
13. J. R. Dias, "Handbook of Polycyclic Hydrocarbons. Part A. Benzenoid Hydrocarbons", Elsevier, Amsterdam, 1987.
14. J. R. Dias, "Molecular Orbital Calculations Using Chemical Graph Theory", Springer, Berlin, 1993.
15. Z. Lou, Q. Huang and D. Yiu, *MATCH Commun. Math. Comput. Chem.*, **2014**, *72*, 153-164.
16. I. Gutman, *Topics Curr. Chem.*, **1992**, *162*, 29-63.
17. N. C. Baird, *J. Chem. Educ.*, **1971**, *48*, 509-514.
18. L. J. Schaad and B. A. Hess, *Chem. Rev.*, **2001**, *101*, 1465-1476.
19. I. Gutman and S. J. Cyvin, "Introduction to the Theory of Benzenoid Hydrocarbons", Springer, Berlin, 1989.
20. S. J. Cyvin and I. Gutman, "Kekulé Structures in Benzenoid Hydrocarbons", Springer, Berlin, 1988.
21. W. C. Herndon, *J. Chem. Educ.*, **1974**, *51*, 10-15.
22. A. T. Balaban and M. Randić, *New J. Chem.*, **2004**, *28*, 800-806.
23. E. Clar, "The Aromatic Sextet", Wiley, London, 1972.
24. X. Zhou and H. Zhang, *MATCH Commun. Math. Comput. Chem.*, **2015**, *74*, 161-174.
25. D. J. Klein, *J. Chem. Educ.*, **1992**, *69*, 691-694.
26. V. Gineityte, *MATCH Commun. Math. Comput. Chem.*, **2014**, *72*, 39-73.
27. W. C. Herndon, P. C. Norwalk, D. A. Connor and P. Lin, *J. Am. Chem. Soc.*, **1992**, *114*, 41-47.
28. D. Peña, D. Pérez, E. Guitián and L. Castedo, *Org. Lett.*, **1999**, *1*, 1555-1557.
29. C. Lütke Eversloh, Z. Liu, B. Müller, M. Stangl, C. Li and K. Müllen, *Org. Lett.*, **2011**, *13*, 5528-5531.
30. J. Luo, X. Xu, R. Mao and Q. Miao, *J. Am. Chem. Soc.*, **2012**, *134*, 13796-13803.
31. S. Xiao, S. J. Kang, Y. Wu, S. Ahn, J. B. Kim, Y. L. Loo, T. Siegrist, M. L. Steigerwald, H. Li and C. Nuckolls, *Chem. Sci.*, **2013**, *4*, 2018-2023.
32. J. R. Dias, S. J. Cyvin and J. Brunvoll, *Polyc. Arom. Comp.*, **1991**, *2*, 195-208.
33. J. R. Dias, *J. Chem. Inf. Comput. Sci.*, **2004**, *44*, 1210-1220.
34. J. R. Dias, *J. Chem. Inf. Model.*, **2007**, *47*, 20-24.
35. J. R. Dias, *Chem. Soc. Rev.*, **2010**, *39*, 1913-1924.
36. R. Cruz, I. Gutman and J. Rada, *MATCH Commun. Math. Comput. Chem.*, **2012**, *68*, 97-108.
37. R. Cruz, I. Gutman and J. Rada, *J. Serb. Chem. Soc.*, **2013**, *78*, 1351-1357.
38. C. F. Matta, J. Hernández-Trujillo, T. H. Tang and R. F. W. Bader, *Chem. Eur. J.*, **2003**, *9*, 1940-1951.
39. J. Poater, M. Solá and F. M. Bickelhaupt, *Chem. Eur. J.*, **2006**, *12*, 2889-2895.
40. J. Poater, M. Solá and F. M. Bickelhaupt, *Chem. Eur. J.*, **2006**, *12*, 2902-2905.
41. J. Poater, F. M. Bickelhaupt and M. Solá, *J. Phys. Chem.*, **2007**, *A111*, 5063-5070.
42. J. Poater, R. Visser, M. Solá and F. M. Bickelhaupt, *J. Org. Chem.*, **2007**, *72*, 1134-1142.
43. S. Radenković, I. Gutman and S. Đorđević, *Chem. Phys. Lett.*, **2015**, *625*, 69-72.
44. L. Pauling, *Acta Cryst.*, **1980**, *B36*, 1898-1901.
45. R. Goddard, M. W. Haenel, W. C. Herndon, C. Krüger and M. Zander, *J. Am. Chem. Soc.*, **1995**, *117*, 30-41.
46. M. J. Frisch, 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, Gaussian 09, Rev A.1 Gaussian Inc., Wallingford, 2009.
47. C. Lee, W. Yang and R. G. Parr, *Phys. Rev.*, **1988**, *B37*, 785-789.
48. A. D. Becke, *J. Chem. Phys.*, **1993**, *98*, 5648-5652.
49. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, **2005**, *7*, 3297-3305.