Annelated perylenes: benzenoid molecules violating the Kekulé-structure-based cyclic conjugation models

IVAN GUTMAN*#, BORIS FURTULA, JELENA DJURDJEVIĆ, RADMILA KOVAČEVIĆ and SONJA STANKOVIĆ

Faculty of Science, University of Kragujevac, P. O. Box 60, 34000 Kragujevac, Serbia and Montenegro

Abstract: Several currently used models for assessing the extent of cyclic conjugation in benzenoid hydrocarbons, all based on Kekulé-type structural formulas, predict that there is no cyclic conjugation in the central, "empty", ring of perylene and its annelated derivatives. In this paper it is shown that in some annelated perylenes the cyclic conjugation in the "empty" ring (measured by its energy-effect) may be unexpectedly high. Therefore, in the case of these annelated perylenes, the Kekulé-structure-based models fail. The cause for such an "anomalous" behavior of annelated perylenes is discussed.

Keywords: cyclic conjugation, energy effect of cyclic conjugation, perylene, annelated perylenes.

INTRODUCTION

The fact that a cyclic arrangement of the π-electrons in conjugated molecules drastically influences their chemical and physical behavior was recognized already in the 1930s.[1–3] The respective theories, originally developed for monocyclic systems,[4,5] were eventually extended to polycyclic conjugated molecules.[6–9] Among the theoretical approaches put forward for quantifying cyclic conjugation in polycyclic conjugated molecules, the following are the most popular and most widely used:

(A) methods based on the number of Kekulé structures *(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;[10,11]

(B) methods based on the analysis of conjugated circuits,[12–16] which are just an alternative form of expressing interactions between pairs of Kekulé structures;[12,13,15,16]

(C) methods based on Clar aromatic sextet formulas,[17,18] which – again – are closely related (yet not equivalent) to the Kekulé structures.[19]

---

*   Corresponding author.

\#   Serbian Chemical Society active member.

Details of the approaches *(A)–(C)* are found in books[7,8] and reviews.[9,20,21] These approaches may be viewed as "classical" because they assume that the conjugation pattern is determined by means of the Kekulé structural formulas and only by them.

Another approach to cyclic conjugation, which is not based on the consideration of Kekulé structures, was put forward by one of the present authors[22,23] and, in a slightly different form, by Aihara.[24]

(D) The extent of conjugation in a cycle of a polycyclic conjugated π-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:

$$e\,f(G,\,Z) = \frac{2}{\pi} \int_{0}^{\infty} \ln \frac{\phi(G,\,ix)}{\phi(G,\,ix) + 2\phi(G - Z,\,ix)}\,\mathrm{d}x \tag{1}$$

where $\phi(G,x)$ is the characteristic polynomial of G, the subgraph $G - Z$ is obtained by deleting the cycle Z from G, and $i = \sqrt{-1}$. Further mathematical details are found elsewhere.[25–27] As in Eq. (1) the quantity $e\,f(G,Z)$ is expressed in the units of the HMO carbon–carbon resonance integral β, positive $e\,f$-values indicate thermodynamic stabilization, whereas cycles with a negative $e\,f$ destabilize the respective π-electron system. The greater $e\,f(G,Z)$ is, the greater is the extent of cyclic conjugation in the cycle Z.

PERYLENE AND ITS π-ELECTRON PROPERTIES

A carbon–carbon bond of a conjugated molecule is said to be "essentially single" if it is single in all Kekulé structures. All classical theories of cyclic conjugation predict that in rings containing essentially single carbon–carbon bonds there is no cyclic conjugation or that (at least) its intensity is very weak. Rings of this kind are usually referred to as empty. The simplest benzenoid hydrocarbon with an empty ring is perylene, see Fig. 1.

In this work a class of annelated perylenes, denoted here by $P(a,\,b,\,c,\,d)$, $a, b,$ c, $d \geq 0$, are considered. Their structure is shown in Fig. 1. From the point of view of classical theories, $P(a,\,b,$ c, $d)$ would be considered as consisting of two weakly coupled linear polyacene fragments (with $a + b + 2$ and c $+ d + 2$ hexagons), joined by two "essentially single" carbon–carbon bonds. Therefore, the two linear polyacene fragments of $P(a,\,b,$ c, $d)$ would be viewed as being almost independently conjugated and the hexagon connecting them as empty.

In this work the extent of cyclic conjugation in the central ring of $P(a,\,b,\,c,\,d)$ is considered and determined by means of Eq. (1). It is shown that the intensity of the cyclic conjugation in this ring is far from negligible, and that it significantly exceeds the cyclic conjugation in the hexagons of the linear polyacene fragments for certain values of the parameters $a,\,b,\,c,\,d$.

$P(0,0,0,0)$ $P(a,b,c,d)$
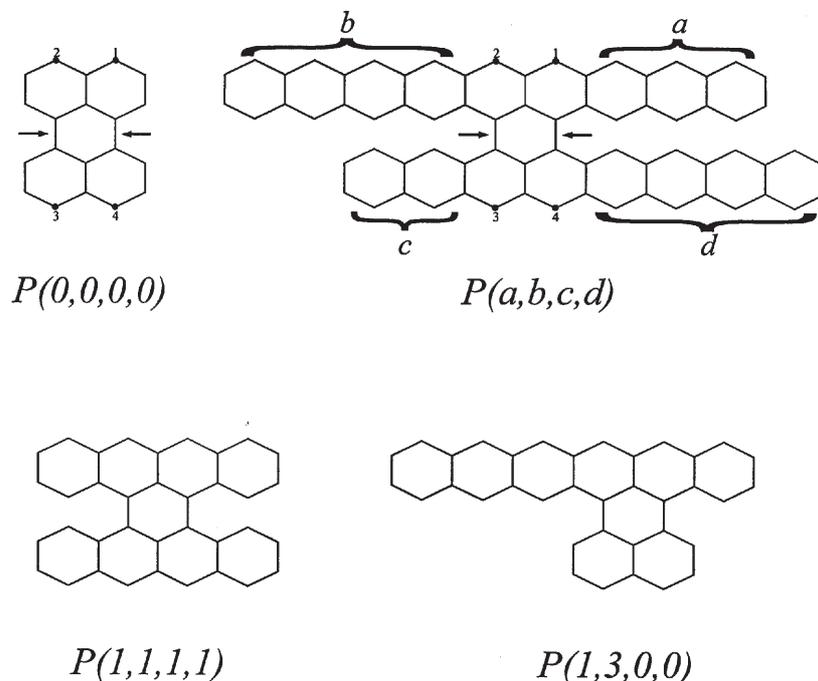

$P(1,1,1,1)$ $P(1,3,0,0)$

Fig. 1. Perylene $P(0, 0, 0, 0)$, the general formula $P(a, b, c, d)$ of its annelated derivatives considered in this work, $a,b,c,d \geq 0$, and two particular representatives of such benzenoid molecules: $P(1, 1, 1, 1)$ and $P(1, 3, 0, 0)$. The system $P(a, b, c, d)$ possesses $5 + a + b + c + d$ hexagons. The carbon–carbon bonds marked by arrows are "essentially single" because they are single in all Kekulé structures and in all Clar aromatic sextet formulas, and are not contained in any of the conjugated circuits of $P(a, b, c, d)$. "Classical" theories assume that these bonds, as well as the ring to which they belong, do not participate in cyclic conjugation. The carbon atoms that play a special role in the subsequent discussion are labelled by 1, 2, 3, and 4.

In an earlier work,[28] the same effects in benzo-annelated perylenes were studied, and it was found 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 that the central "empty" ring becomes one of the most intensely conjugated domains of the respective molecules; for details see Table I.

NUMERICAL WORK

In what follows the energy-effect, computed by means of Eq. (1), of the central ring of $P(a, b, c, d)$ is denoted by $ef(a, b, c, d)$. As already explained, in the classical theories this ring is "empty", *i.e.*, it is predicted to be devoid of any cyclic conjugation. For comparative purposes, we refer to the energy-effect of the ring to which atom 1 belongs (see Fig. 1), *i.e.*, to which the a-branch of $P(a,b,c,d)$ 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 $ef^*(a,b,c,d)$.

It was shown[28] that in perylene and its mono-, di-, and tribenzo-annelated derivatives, in full harmony with the classical theories,

$$e f(0, 0, 0, 0) < e f^*(0, 0, 0, 0)$$
$$e f(1, 0, 0, 0) < e f^*(1, 0, 0, 0)$$
$$e f(1, 1, 0, 0) < e f^*(1, 1, 0, 0)$$
$$e f(1, 1, 1, 0) < e f^*(1, 1, 1, 0).$$

However, in the case of tetabenzo-annelated perylene an inversion occurs:

$$e f(1, 1, 1, 1) > e f^*(1, 1, 1, 1)$$

In particular, $e f(1, 1, 1, 1) = 0.0522$ whereas $e f^*(1, 1, 1, 1) = 0.0437 \beta$-units. The aim of the present work was to investigate how far this breakdown of the classical picture can go and to try to find a rationalization for it.

Our numerical calculations revealed the following regularities.

Rule 1. If the length of a branch of $P(a, b, c, d)$ is increased, then $e f(a, b, c, d)$ increases. Symbolically,

$$e f(a + 1, b, c, d) > e f(a, b, c, d)$$
$$e f(a, b + 1, c, d) > e f(a, b, c, d)$$
$$e f(a, b, c + 1, d) > e f(a, b, c, d)$$
$$e f(a, b, c, d + 1) > e f(a, b, c, d).$$

Furthermore, with increasing length of a branch, $e f(a, b, c, d)$ rapidly tends to a limit value.

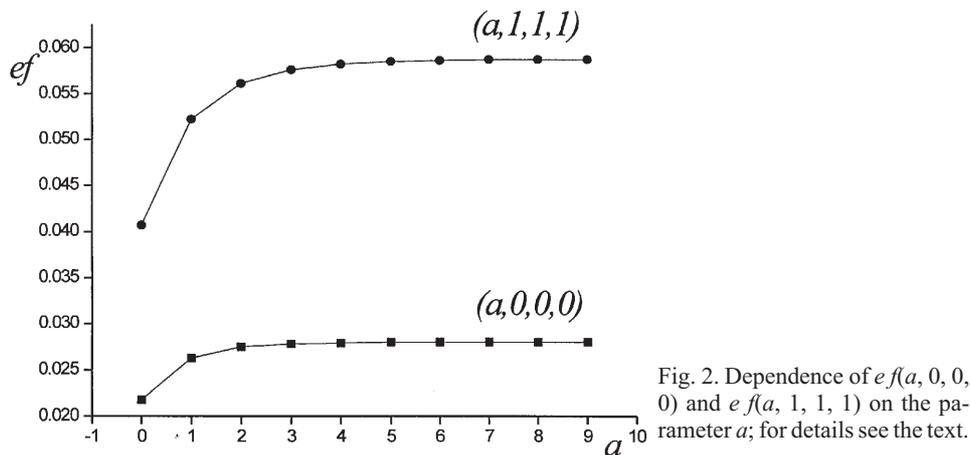Characteristic examples, illustrating Rule 1, are given in Fig. 2.

Fig. 2. Dependence of $e f(a, 0, 0, 0)$ and $e f(a, 1, 1, 1)$ on the parameter a; for details see the text.

Rule 2. By permuting the parameters a, b, c, d, the numerical value of $e f(a, b, c, d)$ is only slightly changed.

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

Rule 3. Let the sum $a + b = n$ be constant. Then $e\,f(a, b, c, d)$ is minimal for $a = 0$ or $b = 0$ (depending on the actual values of the parameters c and d); thus, by Rule 2, $e\,f(0, n, c, d) \approx e\,f(n, 0, c, d)$. If n is even, then $e\,f(a, b, c, d)$ is maximal for $a = b = n/2$. If n is odd, then $e\,f(a, b, c, d)$ is maximal for $a = (n-1)/2$ and $b = (n+1)/2$ or $a = (n+1)/2$ and $b = (n-1)/2$ (depending on the actual values of the parameters c and d); thus, by Rule 2, $e\,f((n-1)/2, (n+1)/2, c, d) \approx e\,f((n+1)/2, (n-1)/2, c, d)$.

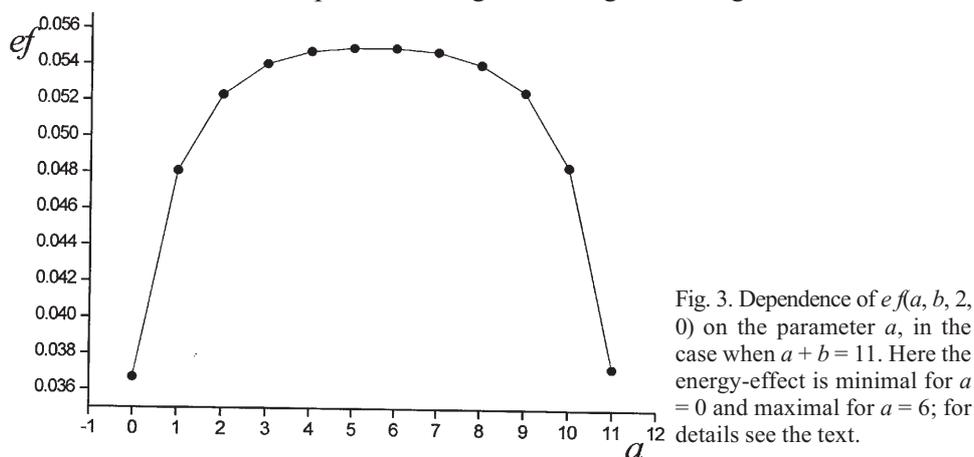A characteristic example illustrating Rule 3 is given in Fig. 3.

Fig. 3. Dependence of $e\,f(a, b, 2, 0)$ on the parameter a, in the case when $a + b = 11$. Here the energy-effect is minimal for $a = 0$ and maximal for $a = 6$; for details see the text.

Rule 4. Let the sum $a + b + c + d = N$ be constant. Then $e\,f(N, 0, 0, 0)$ is minimal whereas the maximal $e\,f$-value is attained for

$$
\begin{aligned}
a = b = c = d = k & \qquad \text{if } N = 4k \\
a = k + 1, b = c = d = k & \qquad \text{if } N = 4k + 1 \\
a = b = k + 1, c = d = k & \qquad \text{if } N = 4k + 2 \\
a = b = c = k + 1, d = k & \qquad \text{if } N = 4k + 3
\end{aligned}
$$

These maximal $e\,f$-values are given in Table I, together with the respective $e\,f^*$-values.

TABLE I. The maximal energy-effect $e\,f(a, b, c, d)$ of the central "empty" ring of the perylene derivatives to which N hexagons are attached ($N = a + b + c + d$, cf. Fig. 1 and Rule 4), for $N = 0, 1, 2, ..., 25$. These energy-effects should be compared with $e\,f^*(a, b, c, d)$, pertaining to a "full" ring of the same benzenoid species; for details see the text

N	a	b	c	d	$e\,f(a, b, c, d)$	$e\,f^*(a, b, c, d)$
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

TABLE I. Continued

N	a	b	c	d	e f(a, b, c, d)	e f*(a, b, c, d)
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

DISCUSSION

From Table I, it can be seen 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 a sufficiently large value of N, the intensity of the cyclic conjugation in the "empty" ring (measured by its energy-effect) is almost three times greater than in a "full" ring.

It is evident that the conjugation pattern of $P(a, b, c, d)$ cannot be satisfactorily described solely by means of Kekulé structures, but that some other resonance forms need to be taken into account. In our opinion, these resonance forms are ionic species of the type depicted in Fig. 4; an independent corroboration of this assertion is provided in the next section.

The annelated perylenes considered in this work have a small number of Kekulé structures, a total of $K\{P(a, b, c, d)\} = (a + b + 3)(c + d + 3)$. On the other hand, the number of ionic resonance forms of the type shown in Fig. 4 is equal to $K^{\pm}\{P(a, b, c, d)\} = 16(a + 1)(b + 1)(c + 1)(d + 1)$, which for any combination of the
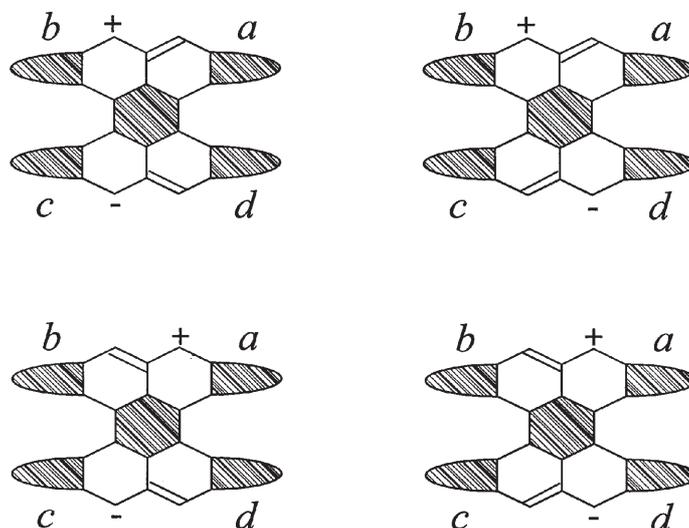
Fig. 4. Resonance structures of annelated perylenes which may be responsible for the high cyclic conjugation in the "empty" ring. There are eight types of such ionic structures, the four shown in this figure and an additional four with exchanged positive and negative charges. Note that the only charged atoms in these resonance structures are those labelled by 1, 2, 3 and 4 (*cf.*, Fig. 1). The classically conjugated domains, *i.e.*, domains in which the main conjugation modes are those described by the $2(a + 1)(b + 1)(c + 1)(d + 1)$ Kekulé structures, are indicated by dashing.

parameters a, b, c, d is much greater than $K\{P(a, b, c, d)\}$. For instance, if $a = b = c = d$ and $a = 0, 1, 2, 3, ...$, then $K = 9, 25, 49, 81, ...$, whereas $K^{\pm} = 16, 256, 1296, 4096, ...$, respectively. The effect of each ionic resonance structure is certainly much smaller than that of a Kekulé structure. However, because of the large number of ionic structures, as well as the small number of Kekulé structures, the effect of the former becomes dominant. This may be the cause of the observed large intensity of cyclic conjugation in the "empty" ring of $P(a, b, c, d)$.

<div align="center">VERIFICATION OF THE MODEL</div>

The above described explanation of the non-classical behavior of the conjugation pattern in annelated perylenes, whether convincing or not, needs an independent confirmation. Such a confirmation can be found in the distribution of π-electrons in the anion and cation of $P(a, b, c, d)$.

If the ionic resonance structures shown in Fig. 4 are really as important as anticipated, then the sites 1, 2, 3 and 4 of the molecule $P(a, b, c, d)$, on which the formal plus and minus charges are drawn, would be capable of accepting a true positive or negative charge. This indeed was found to be the case.

The distributions of the π-electron charge[29] in the anion $[P(a, b, c, d)]^-$ and cation $[P(a, b, c, d)]^+$ were determined. It was found that almost 50 % of the total charge is localized on the respective four sites of $P(a, b, c, d)$. An illustrative example is shown in Fig. 5, whereas the corresponding numerical data are given in Table II.
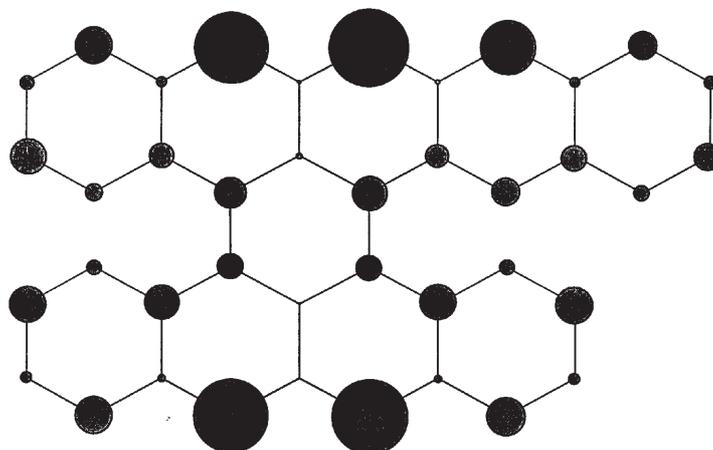
Fig. 5. The π-electron charge distribution in the anion (or cation)[29] of P(2, 1, 1, 1). The area of the circles is proportional to the π-electron charge on the corresponding carbon atoms. The greatest charges are located at the atoms 1, 2, 3, and 4 (*cf.*, Figs. 1 and 4).

TABLE II. The sum Q of the π-electron charges of the carbon atoms 1, 2, 3, and 4 of the perylene derivatives $P(a, b, c, d)$; *cf.* Fig. 1. The parameter N and the corresponding values of a, b, c, d are the same as in Table I. The quantity f shows how many times the sum Q exceeds its value in the (hypothetical) case of a uniform charge distribution

N	Q	f
0	0.431	2.2
1	0.423	2.5
2	0.431	3.0
3	0.464	3.7
4	0.497	4.5
5	0.484	4.8
6	0.475	5.2
7	0.478	5.7
8	0.479	6.2
9	0.465	6.5
10	0.454	6.8
11	0.446	7.1
12	0.439	7.5

ИЗВОД

АНЕЛИРАНИ ПЕРИЛЕНИ: БЕНЗЕНОИДНИ МОЛЕКУЛИ КОД КОЈИХ СУ НАРУШЕНИ МОДЕЛИ ЦИКЛИЧНЕ КОНЈУГАЦИЈЕ ЗАСНОВАНИ НА КЕКУЛЕОВИМ СТРУКТУРАМА

ИВАН ГУТМАН, БОРИС ФУРТУЛА, ЈЕЛЕНА ЂУРЂЕВИЋ, РАДМИЛА КОВАЧЕВИЋ и СОЊА СТАНКОВИЋ

Природно-математички факултет у Крагујевцу

Неколико постојећих модела за процену јачине цикличне конјугације у бензено-идним угљоводоницима, који се сви заснивају на Кекулеовим структурним формулама, предвиђају непостојање цикличне конјугације у централном, празном, прстену пери-лена и његових анелираних деривата. У раду је показано да у неким анелираним периленима циклична конјугација у празном прстену (мерена преко њеног енергетског ефекта) може да буде неочекивано велика. Због тога, у случају ових анелираних пери-лена модели засновани на Кекулеовим структурама постају неадекватни. Разматран је узрок оваквог аномалног понашања анелираних перилена.

(Примљено 12. јануара 2005)

REFERENCES

1. E. Hückel, *Z. Phys.* **70** (1931) 204
2. E. Hückel, *Z. Phys.* **76** (1932) 628
3. E. Hückel, *Grundzüge der Theorie ungesättiger and aromatischer Verbindungen,* Verlag Chemie, Berlin, 1940
4. R. Breslow, E. Mohásci, *J. Am. Chem. Soc.* **85** (1963) 431
5. G. M. Badger, *Aromatic Character and Aromaticity*, Cambridge Univ. Press, Cambridge, 1969
6. M. J. S. Dewar, R. C. Dougherty, *The PMO Theory of Organic Chemistry*, Plenum Press, New York, 1975
7. E. Clar, *The Aromatic Sextet*, Wiley, London, 1972
8. I. Gutman, S. J. Cyvin, *Introduction to the Theory of Benzenoid Hydrocarbons*, Springer-Verlag, Berlin, 1989
9. M. Randić, *Chem. Rev.* **103** (2003) 3449
10. W. C. Herndon, *J. Chem. Educ.* **51** (1974) 10
11. M. Randić, *Tetrahedron* **30** (1974) 2067
12. W. T. Simpson, *J. Am. Chem. Soc.* **75** (1953) 597
13. I. Gutman, W. C. Herndon, *Chem. Phys. Lett.* **34** (1975) 387
14. M. Randić, *Chem. Phys. Lett.* **38** (1976) 68
15. W. C. Herndon, *MATCH Commun. Math. Comput. Chem.* **11** (1981) 3
16. I. Gutman, S. El-Basil, *Chem. Phys. Lett.* **115** (1985) 416
17. W. C. Herndon, H. Hosoya, Tetrahedron **40** (1984) 3987
18. H. Hosoya, *Topics Curr. Chem.* **153** (1990) 255
19. I. Gutman, S. Obenland, W. Schmidt, *MATCH Commun. Math. Comput. Chem.* **17** (1985) 57
20. I. Gutman, *J. Serb. Chem. Soc.* **47** (1982) 453
21. J. A. N. F. Gomes, R. B. Mallion, *Chem. Rev.* **101** (2001) 1349
22. I. Gutman, S. Bosanac, *J. Serb. Chem. Soc.* **42** (1977) 499
23. I. Gutman, S. Bosanac, *Tetrahedron* **33** (1977) 1809
24. J. Aihara, *J. Am. Chem. Soc.* **99** (1977) 2048
25. I. Gutman, O. E. Polansky, *Theor. Chim. Acta* **60** (1981) 203
26. I. Gutman, *Theor. Chim. Acta* **66** (1984) 43
27. I. Gutman, *Monatsh. Chem.* **136** (2005), 1055
28. I. Gutman, N. Turković, J. Jovičić, *Monatsh. Chem.* **135** (2004) 1389
29. Because of the pairing theorem, the charge distributions in $[P(a, b, c, d)]^-$ and $[P(a, b, c, d)]^+$ are equal, except that the sign of the charges is opposite.