PARTITIONING OF π-ELECTRONS IN RINGS OF POLYCYCLIC CONJUGATED MOLECULES CONTAINING HETEROATOMS

Ivan Gutman

Faculty of Science, University of Kragujevac, Serbia
e-mail: `gutman@kg.ac.yu`

(Received June 8, 2006)

Abstract

It is shown how the Randić–Balaban method for partitioning of π-electrons in rings of polycyclic benzenoid hydrocarbons can be modified so as to be applicable to conjugated molecules containing heteroatoms

INTRODUCTION

A method for partitioning of π-electrons in rings of polycyclic conjugated hydrocarbons was put forward by Randić and Balaban in 2004 [1–3]. It assesses the π-electron content of a ring of a conjugated molecule using its Kekulé structures. The method is based on an earlier observation [4,5] that instead of the standard way of

drawing a Kekulé structure (by specifying the position of the double bonds) one may represent it by indicating the total number of π-electrons in each ring.

According to Randić [4,5], the number $EC(R, k)$ of π-electrons in the ring R of the Kekulé structure k is defined as two times the number of double bonds that belong solely to R plus the number of double bonds that are shared by R and another ring. In most cases there is a one–to–one correspondence between the standard and the "algebraic" representation of Kekulé structures, i. e., the $EC(R, k)$-values fully determine the position of the double bonds in the Kekulé structure k. Exceptional cases, when several Kekulé structures have the same "algebraic" representation, were analyzed in [6,7]. Some other properties of the numbers $EC(R, k)$ are considered in [6,8,9].

The Randić–Balaban (RB) approach computes the π-electron content $EC_{RB}(R)$ of a ring R as the arithmetic average of the $EC(R, k)$-values, i. e.,

$$EC_{RB}(R) = \frac{1}{|\mathcal{K}|} \sum_{k \in \mathcal{K}} EC(R, k) \tag{1}$$

where $\mathcal{K}$ is the set of all Kekulé structures of the conjugated molecule considered. It was immediately recognized [10] that the right–hand side of (1) can be expressed in terms of the Pauling bond orders P_{rs}^P so that

$$EC_{RB}(R) = 2 \sum_{*} P_{rs}^P + \sum_{**} P_{rs}^P \tag{2}$$

where $\sum_{*}$ indicates summation over those bonds rs that belong solely to the ring R whereas $\sum_{**}$ indicates summation over the bonds rs that are shared by the ring R and another ring.

Although by means of the RB approach one could estimate the π-electron content of any ring in any conjugated hydrocarbon, the vast majority of reported applications was concerned with the six–membered rings of benzenoid and coronoid systems [1–3,10–26], and only in a single paper [27] with non-benzenoids. The original RB model is not applicable to conjugated molecules containing heteroatoms, or – even worse – its application would give results identical to those for the parent hydrocarbon.

The distribution defined via Eqs. (1) or (2) is not the only possible and several other options were put forward. Some of these were based on Clar aromatic sextet formulas [17,18,28,29], which was eventually shown [30] to be equivalent to using in formula (1) a particular subset of $\mathcal{K}$ instead of $\mathcal{K}$ itself. Distributions based on other

subsets of $\mathcal{K}$ were also considered [31,32], whereas in the paper [33] a bond order different from Pauling's was used in formula (2).

A necessary condition for the success of the RB approach, and in particular, of formula (2) is that the sum over all bonds of the Pauling bond orders, times two, is equal to the total number n_π of π-electrons. If so, then the "book–keeping" relation

$$\sum_R EC_{RB}(R) = n_\pi$$

is satisfied. Now, it was established long time ago [34–36] that

$$2 \sum_{rs} P_{rs}^P = n \tag{3}$$

where n is the number of carbon atoms (i. e., the number of vertices in the molecular graph [37]). Evidently, for conjugated hydrocarbons, $n_\pi = n$.

In formula (3) and elsewhere in this article, $\sum\limits_{rs}$ indicates summation over all conjugated bonds rs in the molecule considered, i. e., over all pairs of atoms labelled by r and s that participate in the conjugation and are connected by a covalent bond. In the language of graph–theoretical formalism [37], $\sum\limits_{rs}$ indicates summation over all pairs of adjacent vertices r and s of the Hückel molecular graph.

GENERALIZING THE RANDIĆ–BALABAN APPROACH

Analysis of the Randić–Balaban approach [1–3] and its various recently proposed variants [28–33] reveals that if we have a bond order P_{rs}, satisfying the condition

$$2 \sum_{rs} P_{rs} = n_\pi \tag{4}$$

then the quantity

$$EC_{gen}(R) = 2 \sum_* P_{rs} + \sum_{**} P_{rs} \tag{5}$$

defined in a manner analogous to Eq. (2), may be interpreted as some kind of π-electron content of the ring R, and then

$$\sum_R EC_{gen}(R) = n_\pi \tag{6}$$

will hold.

Of the infinitely many of such "electron contents" preference should be given to those

- that in the case of benzenoid hydrocarbons coincide with the Randić–Balaban EC-values,

- that yield results in harmony with the known regularities for the π-electron distribution in conjugated molecules,

- that agree with the available experimental data (cf. [13]), and

- that could be applied to a variety of conjugated systems, in particular to both hydrocarbons and heteroatom–containing species.

In our opinion the Ham–Ruedenberg bond order may satisfy both Eq. (4) and the above listed requirements.

A HAM–RUEDENBERG–BOND–ORDER–BASED π-ELECTRON CONTENT OF A RING

The bond order introduced long time ago by Ham and Ruedenberg [38] is defined as follows.

Let $C_i = (C_{i1}, C_{i2}, \ldots, C_{in})$ be a normalized eigenvector of the adjacency matrix $A = ||A_{ij}||$ of the molecular (Hückel) graph representing the conjugated system under consideration [37,39,40]; here n stands for the number of vertices of the molecular graph. There exist n linearly independent eigenvectors, and therefore $i = 1, 2, \ldots, n$. Let λ_i be the eigenvalue of A, corresponding to the eigenvector C_i, $i = 1, 2, \ldots, n$.

As well known [39,40], within the Hückel molecular orbital (HMO) theory, C_i and λ_i are in a simple manner related to, respectively, the i-th molecular orbital and the i-the molecular orbital energy level. Let g_i be the occupation number of the i-th MO, and recall that

$$\sum_{i=1}^{n} g_i = n_\pi \ . \tag{7}$$

Relation (7) holds in the most general case, including both arbitrarily charged species, arbitrarily excited states, and – of course – conjugated molecules containing heteroatoms.

Then the Ham–Ruedenberg bond order is defined as [38,41–43]:

$$P_{rs}^{HR} = \sum_{i=1}^{n} g_i \frac{C_{ir} C_{is}}{\lambda_i} \tag{8}$$

where it is assumed that no eigenvalue is equal to zero (i. e., that there are no non-bonding MOs).

In the case of conjugated hydrocarbons, all diagonal elements of the adjacency matrix A are equal to zero. Then (as we show below), for conjugated hydrocarbons (both benzenoid and non-benzenoid),

$$2 \sum_{rs} P_{rs}^{HR} = n_{\pi} \tag{9}$$

and therefore we may use P_{rs}^{HR} in formula (5). This is additionally justified by the fact that for (Kekuléan) benzenoid hydrocarbons, and for r and s being adjacent vertices [41,44],

$$P_{rs}^{HR} = P_{rs}^{P} \ .$$

This means that in the case of benzenoid systems, the Ham–Ruedenberg–bond–order–based π-electron content of a ring coincides with the original Randić–Balaban EC-value.

Unfortunately, relation (9) does not hold for heteroatom–containing conjugated molecules and therefore for such molecules instead of the ordinary Ham–Ruedenberg bond order we need to use its modified version. This is achieved by means of the following:

Lemma 1. If the elements of the adjacency matrix $A = ||A_{ij}||$ of a (molecular) graph satisfy the conditions

$$A_{ij} = A_{ji} \qquad \text{for all } i, j = 1, 2, \ldots, n \tag{10}$$

$$A_{ij} = 1 \qquad \text{if the vertices } i \text{ and } j \ (i \neq j) \text{ are adjacent} \tag{11}$$

$$A_{ij} = 0 \qquad \text{if the vertices } i \text{ and } j \ (i \neq j) \text{ are not adjacent} \tag{12}$$

whereas the diagonal elements A_{ii}, $i = 1, 2, \ldots, n$, need not be equal to zero, then

$$2 \sum_{rs} P_{rs}^{HR} = n_{\pi} - \sum_{r=1}^{n} A_{rr} P_{rr}^{HR} \ . \tag{13}$$

Proof. Let C be the square matrix of order n whose (ij)-entry is C_{ij} – the j-th component of the i-th eigenvector. Then

$$C A C^{\dagger} = \Lambda \tag{14}$$

where

$$(C^\dagger)_{ij} = C_{ji}^* \quad \text{and} \quad \Lambda = diag(\lambda_1, \lambda_2, \ldots, \lambda_n) \, .$$

The graph eigenvectors can always be chosen so as to have real–valued components and then $C_{ji}^* = C_{ji}$.

Now, in view of (10)–(12),

$$2 \sum_{rs} P_{rs}^{HR} = \sum_{r=1}^{n} \sum_{s=1}^{n} A_{rs} P_{rs}^{HR} - \sum_{r=1}^{n} A_{rr} P_{rr}^{HR} \tag{15}$$

and by taking into account (8) and (14),

$$\sum_{r=1}^{n} \sum_{s=1}^{n} A_{rs} P_{rs}^{HR} = \sum_{r=1}^{n} \sum_{s=1}^{n} A_{rs} \sum_{i=1}^{n} g_i \frac{C_{ir} C_{is}}{\lambda_i} = \sum_{i=1}^{n} \frac{g_i}{\lambda_i} \sum_{r=1}^{n} \sum_{s=1}^{n} C_{ir} A_{rs} (C^\dagger)_{si}$$

$$= \sum_{i=1}^{n} \frac{g_i}{\lambda_i} \left(C \, A \, C^\dagger \right)_{ii} = \sum_{i=1}^{n} \frac{g_i}{\lambda_i} \Lambda_{ii} = \sum_{i=1}^{n} g_i$$

i. e., by (7),

$$\sum_{r=1}^{n} \sum_{s=1}^{n} A_{rs} P_{rs}^{HR} = n_\pi \, . \tag{16}$$

By combining (15) and (16) we arrive at (13). □

Corollary 1.1. If all diagonal elements of the adjacency matrix are equal to zero (as in the case of molecular graphs of conjugated hydrocarbons), then (13) reduces to the earlier known [34,35] formula (9).

From formula (13) we see why the Ham–Ruedenberg bond order is not suitable for modelling, via Eq. (5), the π-electron content of rings in heteroatom–containing polycyclic conjugated molecules. However, a way out of this difficulty is easily found:

Define a modified Ham–Ruedenberg bond order as

$$P_{rs}^{HR'} = P_{rs}^{HR} + \frac{A_{rr}}{\delta_r} P_{rr}^{HR} + \frac{A_{rr}}{\delta_s} P_{ss}^{HR} \tag{17}$$

where δ_r and δ_s are, respectively, the degrees (number of first neighbors) of the vertices r and s. Then from (13) it immediately follows that

$$2 \sum_{rs} P_{rs}^{HR'} = n_\pi$$

implying that

$$EC_{HR}(R) = 2 \sum_* P_{rs}^{HR'} + \sum_{**} P_{rs}^{HR'} \tag{18}$$

is a well chosen model for the π-electron content of rings, applicable to arbitrary heteroatom–containing polycyclic conjugated species. For benzenoid hydrocarbons, $EC_{HR}(R)$ coincides with the Randić–Balaban $EC_{RB}(R)$-values.

Results of numerical calculations based on Eq. (18) will be reported elsewhere.

Remark 1.2. In the case of edge–weighted molecular graphs (for which conditions (10) and (12) are obeyed, but not necessarily condition (11)), Eqs. (13) and (17) need to be modified as

$$2 \sum_{rs} A_{rs} P_{rs}^{HR} = n_{\pi} - \sum_{r=1}^{n} A_{rr} P_{rr}^{HR}$$

and

$$P_{rs}^{HR'} = A_{rs} P_{rs}^{HR} + \frac{A_{rr}}{\delta_r} P_{rr}^{HR} + \frac{A_{rr}}{\delta_s} P_{ss}^{HR}$$

where now

$$\delta_r = \sum_{i=1}^{n} A_{ir} - A_{rr} \quad \text{and} \quad \delta_s = \sum_{i=1}^{n} A_{is} - A_{ss} \ .$$

Then formula (18) is still applicable.

ON THE COULSON–BOND–ORDER–BASED π-ELECTRON ENERGY CONTENT OF A RING

We have seen that whenever a bond order satisfies the relation (4), then by means of the formula (5) it is possible to conceive a model for the π-electron content of rings of the considered polycyclic conjugated molecule. This π-electron content will then satisfy the "book–keeping" relation (6).

The Coulson bond order is defined as [45–47]

$$P_{rs}^C = \sum_{i=1}^{n} g_i \, C_{ir} \, C_{is} \ . \tag{19}$$

In the case of conjugated hydrocarbons it satisfies a relation analogous to (4), namely,

$$2 \sum_{rs} P_{rs}^C = E_{\pi} \tag{20}$$

where E_{π} is the HMO total π-electron energy [48,49],

$$E_{\pi} = \sum_{i=1}^{n} g_i \, \lambda_i \ .$$

In view of this, the Coulson bond order was used to assess the π-electron energy contents of rings [11,16,23,24], based on a formula analogous to Eqs. (2) and (5):

$$ec(R) = 2 \sum_* P_{rs}^C + \sum_{**} P_{rs}^C \ . \tag{21}$$

This time the "book–keeping" relation (analogous to (6)) is

$$\sum_R ec(R) = E_\pi \ .$$

The relation (20) does not hold for heteroatom–containing conjugated systems. Therefore the π-electron energy content of a ring, defined by Eq. (21), cannot be applied. The resolution of this difficulty is similar and analogous to what we already did for π-electron content, and requires the following:

Lemma 2. If the adjacency matrix $A = ||A_{ij}||$ of a (molecular) graph satisfies the same conditions as specified in Lemma 1, then

$$2 \sum_{rs} P_{rs}^C = E_\pi - \sum_{r=1}^n A_{rr} P_{rr}^C \ . \tag{22}$$

Proof proceeds in full analogy with the proof of Lemma 1. In view of (10)–(12),

$$2 \sum_{rs} P_{rs}^C = \sum_{r=1}^n \sum_{s=1}^n A_{rs} P_{rs}^C - \sum_{r=1}^n A_{rr} P_{rr}^C \tag{23}$$

and by taking into account the definition (19) of the Coulson bond order,

$$\sum_{r=1}^n \sum_{s=1}^n A_{rs} P_{rs}^C = \sum_{r=1}^n \sum_{s=1}^n A_{rs} \sum_{i=1}^n g_i C_{ir} C_{is} = \sum_{i=1}^n g_i \sum_{r=1}^n \sum_{s=1}^n C_{ir} A_{rs} (C^\dagger)_{si}$$

$$= \sum_{i=1}^n g_i \left(C A C^\dagger \right)_{ii} = \sum_{i=1}^n g_i \lambda_i$$

i. e.,

$$\sum_{r=1}^n \sum_{s=1}^n A_{rs} P_{rs}^C = E_\pi \ . \tag{24}$$

By combining (23) and (24) we arrive at (22). □

Corollary 2.1. If all diagonal elements of the adjacency matrix are equal to zero (as in the case of molecular graphs of conjugated hydrocarbons), then (22) reduces to the long time known [46,47] formula (20).

Bearing in mind Lemma 2, we need to introduce a modified Coulson bond order

$$P_{rs}^{C'} = P_{rs}^C + \frac{A_{rr}}{\delta_r} P_{rr}^C + \frac{A_{rr}}{\delta_s} P_{ss}^C \tag{25}$$

where the notation is same as in Eq. (17), and then to calculate the π-electron energy content by means of an expression analogous to (21), viz.:

$$ec'(R) = 2 \sum_* P_{rs}^{C'} + \sum_{**} P_{rs}^{C'} . \tag{26}$$

Remark 2.2. In the case of edge–weighted molecular graphs (for which conditions (10) and (12) are obeyed, but not necessarily condition (11)), Eqs. (22) and (25) need to be modified as

$$2 \sum_{rs} A_{rs} P_{rs}^C = E_\pi - \sum_{r=1}^n A_{rr} P_{rr}^C$$

and

$$P_{rs}^{C'} = A_{rs} P_{rs}^C + \frac{A_{rr}}{\delta_r} P_{rr}^C + \frac{A_{rr}}{\delta_s} P_{ss}^C$$

with δ_r and δ_s having the same meanings as in Remark 1.2. Then formula (26) is still applicable.

References

[1] M. Randić, A. T. Balaban, Partitioning of π-electrons in rings of polycyclic conjugated hydrocarbons. Part 1: Catacondensed benzenoids, *Polyc. Arom. Comp.* **24** (2004) 173–193.

[2] A. T. Balaban, M. Randić, Partitioning of π-electrons in rings of polycyclic benzenoid hydrocarbons. 2. Catacondensed coronoids, *J. Chem. Inf. Comput. Sci.* **44** (2004) 50–59.

[3] A. T. Balaban, M. Randić, Partitioning of π-electrons in rings of polycyclic conjugated hydrocarbons. Part 3. Perifusenes, *New J. Chem.* **28** (2004) 800–806.

[4] M. Randić, Aromaticity of polycyclic conjugated hydrocarbons, *Chem. Rev.* **103** (2003) 3449–3606.

[5] M. Randić, Algebraic Kekulé formulas for benzenoid hydrocarbons, *J. Chem. Inf. Comput. Sci.* **44** (2004) 365–372.

[6] I. Gutman, D. Vukičević, A. Graovac, M. Randić, Algebraic Kekulé structures of benzenoid hydrocarbons, *J. Chem. Inf. Comput. Sci.* **44** (2004) 296–299.

[7] D. Vukičević, M. Randić, A. T. Balaban, Partitioning of π-electrons in rings of polycyclic conjugated hydrocarbons. Part 4. Benzenoids with more than one geometric Kekulé structure corresponding to the same algebraic Kekulé structure, *J. Math. Chem.* **36** (2004) 271–279.

[8] A. Miličević, S. Nikolić, N. Trinajstić, Coding and ordering Kekulé structures, *J. Chem. Inf. Comput. Sci.* **44** (2004) 415–421.

[9] D. Vukičević, D. J. Klein, Characterization of distribution of π-electrons amongst benzenoid rings for Randić's "algebraic" Kekulé structures, *J. Math. Chem.* **37** (2005) 163–170.

[10] I. Gutman, T. Morikawa, S. Narita, On π-electron content of bonds and rings in benzenoid hydrocarbons, *Z. Naturforsch.* **59a** (2004) 295–298.

[11] I. Gutman, B. Furtula, S. Radenković, Relation between Pauling and Coulson bond orders in benzenoid hydrocarbons, *Z. Naturforsch.* **59a** (2004) 699–704.

[12] I. Gutman, Electron content and electron excess of rings of benzenoid hydrocarbons, *Indian J. Chem.* **43A** (2004) 1615–1618.

[13] I. Gutman, Ž. Tomović, K. Müllen, J. P. Rabe, On the distribution of π-electrons in large polycyclic aromatic hydrocarbons, *Chem. Phys. Lett.* **397** (2004) 412–416.

[14] A. T. Balaban, M. Randić, Partitioning of π-electrons in rings of polycyclic conjugated hydrocarbons. 6. Comparisons with other methods for estimating the local aromaticity of rings in polycyclic benzenoids, *J. Math. Chem.* **37** (2005) 443–453.

[15] I. Gutman, S. Gojak, N. Turković, B. Furtula, Polansky's benzenoid character and the electron content of rings of benzenoid hydrocarbons, *MATCH Commun. Math. Comput. Chem.* **53** (2005) 139–145.

[16] I. Gutman, B. Furtula, N. Turković, Electron and energy contents of hexagons in benzenoid hydrocarbons, *Polyc. Arom. Comp.* **25** (2005) 87–94.

[17] I. Gutman, M. Randić, A. T. Balaban, B. Furtula, V. Vučković, π-Electron contents of rings in the double–hexagonal–chain homologous series (pyrene, anthanthrene, . . .), *Polyc. Arom. Comp.* **25** (2005) 215–226.

[18] I. Gutman, G. Stojanović, Ž. Bošković, N. Radulović, P. Rašić, Comparing the Randić–Balaban and the Clar models for partitioning of π-electrons in rings of benzenoid hydrocarbons. The case of phenes and starphenes, *Polyc. Arom. Comp.* **25** (2005) 345–355.

[19] I. Gutman, B. Furtula, S. Jeremić, N. Turković, Electron content of rings of fully benzenoid hydrocarbons, *J. Serb. Chem. Soc.* **70** (2005) 1199–1204.

[20] I. Gutman, B. Furtula, V. Vučković, B. Arsić, M. Ranđelović, Partition of π-electrons in rings of double linear hexagonal chains, *Bull. Acad. Serbe Sci. Arts (Cl. Math. Natur.)* **130** (2005) 97–105.

[21] I. Gutman, A. T. Balaban, M. Randić, C. Kiss–Tóth, Partitioning of π-electrons in rings of fibonacenes, *Z. Naturforsch.* **60a** (2005) 171–176.

[22] I. Gutman, N. Turković, On the distribution of π-electrons into rings of conjugated hydrocarbons containing a linear polyacene fragment, *Monatsh. Chem.* **136** (2005) 713–717.

[23] B. Furtula, I. Gutman, N. Turković, Relation between electron and energy contents of hexagons in catacondensed benzenoid hydrocarbons, *Indian J. Chem.* **44A** (2005) 9–12.

[24] I. Gutman, S. Milosavljević, B. Furtula, N. Cmiljanović, Relation between electron and energy contents of hexagons in pericondensed benzenoid hydrocarbons, *Indian J. Chem.* **44A** (2005) 13–17.

[25] I. Gutman, N. Turković, B. Furtula, On distribution of π-electrons in rhombus–shaped benzenoid hydrocarbons, *Indian J. Chem.* **45** (2006) 000–000.

[26] I. Gutman, S. Gojak, N. Radulović, B. Furtula, Benzenoid molecules with uniform distribution of π-electrons within rings, *Monatsh. Chem.* **137** (2006) 277–284.

[27] A. T. Balaban, M. Randić, Partitioning of π-electrons in rings of polycyclic conjugated hydrocarbons. 5. Nonalternant hydrocarbons, *J. Chem. Inf. Comput. Sci.* **44** (2004) 1701–1707.

[28] I. Gutman, On the distribution of π-electrons in benzenoid hydrocarbons, *Bull. Chem. Technol. Maced.* **22** (2003) 105–110.

[29] M. Randić, A. T. Balaban, Partitioning of π-electrons in rings for Clar structures of benzenoid hydrocarbons, *J. Chem. Inf. Model.* **46** (2006) 57–64.

[30] I. Gutman, B. Furtula, Equivalence of two models for partitioning of π-electrons in rings of benzenoid hydrocarbons, *Z. Naturforsch.* **61** (2006) 000–000.

[31] B. Furtula, I. Gutman, Partitioning of π-electrons in the rings of benzenoid hydrocarbons using Fries structural formulas, in: I. Gutman (Ed.), *Mathematical Methods in Chemistry*, Prijepolje Museum, Prijepolje, 2006, pp. 89–100.

[32] I. Gutman, B. Furtula, A Kekulé structure basis for phenylenes, *J Mol. Struct. (Theochem)*, in press.

[33] I. Gutman, A. Vodopivec, S. Radenković, B. Furtula, On π-electron excess of rings of benzenoid molecules, *Indian J. Chem.* **45A** (2006) 347–351.

[34] I. Gutman, A comparative study of bond orders, *MATCH Commun. Math. Comput. Chem.* **3** (1977) 121–132.

[35] I. Gutman, Relations between bond orders, *J. Serb. Chem. Soc.* **43** (1978) 379–384.

[36] I. Gutman, H. Sachs, New approach to the Pauling bond order concept, *Z. Phys. Chem. (Leipzig)* **268** (1987) 257–266.

[37] I. Gutman, O. E. Polansky, *Mathematical Concepts in Organic Chemistry*, Springer–Verlag, Berlin, 1986.

[38] N. S. Ham, K. Ruedenberg, Mobile bond orders in conjugated systems, *J. Chem. Phys.* **29** (1958) 1215–1223.

[39] J. R. Dias, *Molecular Orbital Calculations Using Chemical Graph Theory*, Springer–Verlag, Berlin, 1993.

[40] A. Graovac, I. Gutman, N. Trinajstić, *Topological Approach to the Chemistry of Conjugated Molecules*, Springer–Verlag, Berlin, 1977.

[41] N. S. Ham, Mobile bond orders in the resonance and molecular orbital theories, *J. Chem. Phys.* **29** (1958) 1229–1231.

[42] K. Ruedenberg, Theorem on the mobile bond orders of alternant conjugated systems, *J. Chem. Phys.* **29** (1958) 1232–1233.

[43] K. Ruedenberg, Quantum mechanics of mobile electrons in conjugated bond systems. III. Topological matrix as generatrix of bond orders, *J. Chem. Phys.* **34** (1961) 1884–1891.

[44] D. Cvetković, I. Gutman, N. Trinajstić, Graph theory and molecular orbitals. VII. The role of resonance structures, *J. Chem. Phys.* **61** (1974) 2700–2706.

[45] C. A. Coulson, The electronic structure of some polyenes and aromatic molecules. VII. Bonds of fractional order by the molecular orbital method, *Proc. Roy. Soc. London* **A169** (1939) 413–428.

[46] C. A. Coulson, H. C. Longuet–Higgins, The electronic structure of conjugated systems. I. General theory, *Proc. Roy. Soc. London* **A191** (1947) 39–60.

[47] C. A. Coulson, H. C. Longuet–Higgins, The electronic structure of conjugated systems. III. Bond orders in unsaturated molecules, *Proc. Roy. Soc. London* **A193** (1948) 447–456.

[48] I. Gutman, The energy of a graph: Old and new results, in: A. Betten, A. Kohnert, R. Laue, A. Wassermann (Eds.), *Algebraic Combinatorics and Applications*, Springer–Verlag, Berlin, 2001, pp. 196–211.

[49] I. Gutman, Topology and stability of conjugated hydrocarbons. The dependence of total π-electron energy on molecular topology, *J. Serb. Chem. Soc.* **70** (2005) 441–456.