Relation between Pauling and Coulson Bond Orders in Benzenoid Hydrocarbons

Ivan Gutman, Boris Furtula, and Slavko Radenković

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

Reprint requests to Prof. I. G.; Fax: +381 34 335040; E-mail: gutman@knez.uis.kg.ac.yu

Z. Naturforsch. **59a,** 699 – 704 (2004); received July 14, 2004

The relation between Pauling and Coulson bond orders in benzenoid hydrocarbons is examined. The carbon–carbon bonds of benzenoid hydrocarbons have to be classified into three classes, depending on the number of attached hydrogen atoms. Within each class the correlation between the bond orders is linear. The results can be used to rationalize the recently discovered correlation between the energy and electron contents of rings. An approximate expression for the total π-electron energy is also deduced.

Key words: Pauling Bond Order; Coulson Bond Order; Benzenoid Hydrocarbons; Electron Content of Ring; Energy Content of Ring.

Introduction

The fact that in conjugated π-electron systems the carbon–carbon bonds are neither pure single nor pure double led to the introduction of the concept of bond order. Two bond orders put forward in the early days of quantum chemistry are those of Pauling [1, 2] (based on resonance theory) and of Coulson [3, 4] (based on molecular orbital theory). We denote them by P_{rs}^{P} and P_{rs}^{C}, respectively, with r and s indicating the two adjacent carbon atoms.

Both the Pauling [5 – 8] and the Coulson bond orders [9 – 12] were successfully used for predicting carbon–carbon bond lengths in aromatic molecules. Comparative studies revealed [10, 12] that both bond orders have essentially the same predictive power, as far as molecular geometry is concerned.

In view of this it is natural to seek for relations between P_{rs}^{P} and P_{rs}^{C}. Curiously, however, in spite of some attempts in the past [13–16], no generally valid connection between these two bond orders could be established. In a paper [10], that seems to be overlooked by later researchers [4 – 6, 15 – 17], Cruickshank and Sparks noticed that in the case of benzenoid hydrocarbons, the correlation between P_{rs}^{P} and P_{rs}^{C} is linear, but only if one restricts the consideration to carbon–carbon bonds of the same type. They distinguished between three types of carbon–carbon bonds: with two, with one, and without any hydrogen atoms attached. (Recall that in benzenoid systems only these three types of carbon–carbon bonds may occur [17].) If a graph–theoretical terminology is adopted [18 – 21], then the carbon–carbon bonds are represented by edges in the respective molecular graph; an edge is said to be of the (i, j)-type if it connects a vertex of degree i with a vertex of degree j. In the molecular graphs of benzenoid systems only edges of type (2,2), (2,3), and (3,3) are encountered [17]. Their number will be denoted by m_{22}, m_{23}, and m_{33}, respectively. It is known [17] that

$$m_{22} = 6 + b, \tag{1}$$

$$m_{23} = 4h - 4 - 2n_i - 2b, \tag{2}$$

$$m_{33} = h - 1 + n_i + b, \tag{3}$$

where h is the number of hexagons, n_i the number of internal vertices, and b the number of bay regions. The total number of edges (m) is equal to $m_{22} + m_{23} + m_{33}$, i. e.,

$$m = 5h + 1 - n_i. \tag{4}$$

The analogous expression for the number of vertices reads [17]

$$n = 4h + 2 - n_i. \tag{5}$$

0932–0784 / 04 / 1000–0699 $ 06.00

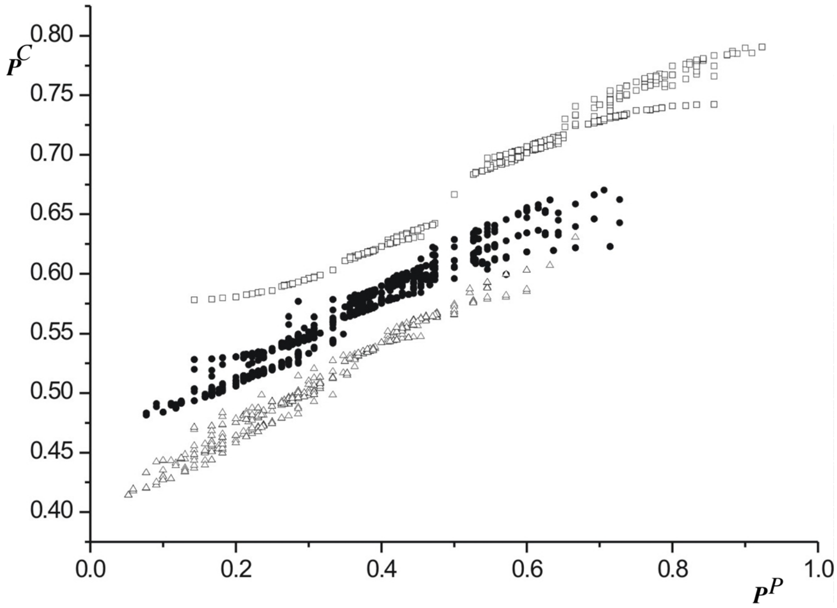

Fig. 1. Coulson bond orders (P^C) of the carbon–carbon bonds of catacondensed benzenoid hydrocarbons with up to 6 hexagons, versus the respective Pauling bond orders (P^P). The total number of data–points is 1582, but because of symmetry many of them coincide. The data–points are separated into three clusters, pertaining to edges of type (2,2) (squares), (2,3) (circles), and (3,3) (triangles)

.

The results reported by Cruickshank and Sparks [10] can now be stated as:

$$\begin{aligned} P_{rs}^C &\approx 0.30\,P_{rs}^P + 0.52 \quad \text{for edges } rs \text{ of type 22,} \\ P_{rs}^C &\approx 0.25\,P_{rs}^P + 0.48 \quad \text{for edges } rs \text{ of type 23,} \\ P_{rs}^C &\approx 0.33\,P_{rs}^P + 0.41 \quad \text{for edges } rs \text{ of type 33.} \end{aligned} \tag{6}$$

In the 1950s, when the formulas (6) were established, facilities for computing were limited. It is therefore understandable why the calculations leading to (6) were done on a sample consisting of only about 10 (small) benzenoid molecules; the actual molecules used for deducing (6) were not specified in [10]. In order to test and improve the accuracy of these correlations we have repeated the calculations on a much greater sample. The results obtained are outlined in the subsequent section.

Cruickshank–Sparks–Type Relations between Coulson and Pauling Bond Orders in Benzenoid Hydrocarbons

Coulson and Pauling bond orders were computed for all carbon–carbon bonds of all catacondensed benzenoid hydrocarbons with h hexagons, $1 \leq h \leq 6$, that is for 56 benzenoid hydrocarbons, and a total of 1582 bonds. The plot of Coulson bond order versus Pauling bond order thus obtained is shown in Figure 1.

As seen from Fig. 1, the data–points are grouped into three (and not more than three!) well–separated clusters. These clusters pertain to different types of (i,j)-bonds. From these data, instead of (6), we obtained

$$\begin{aligned} P_{rs}^C &\approx (0.325 \pm 0.003)\,P_{rs}^P + (0.503 \pm 0.002) \\ &\quad \text{for edges } rs \text{ of type 22,} \\ P_{rs}^C &\approx (0.297 \pm 0.003)\,P_{rs}^P + (0.460 \pm 0.001) \\ &\quad \text{for edges } rs \text{ of type 23,} \\ P_{rs}^C &\approx (0.351 \pm 0.003)\,P_{rs}^P + (0.398 \pm 0.001) \\ &\quad \text{for edges } rs \text{ of type 33.} \end{aligned} \tag{7}$$

The correlation coefficients of the three regression lines are equal to 0.984, 0.966, and 0.989, respectively.

Formulas (7) are similar to, but certainly not identical with, the earlier reported formulas (6).

In order to compare the precision of (6) and (7) we calculated the bond orders of the five heptacyclic ($h = 7$) catacondensed benzenoid hydrocarbons with two branched hexagons (annelation mode **7**, cf. Fig. 2), possessing a total of 180 carbon–carbon bonds. For this sample the standard deviations of (6) and (7) were found to be 0.0095 and 0.0073, respectively.

The regression lines (7) are certainly not parallel. Yet their deviation from parallelism is not very large. Therefore, as a not too drastic approximation, we may use three parallel lines to model the correlation of the (P^C, P^P) data–points, viz.,

$$P_{rs}^C \approx a\,P_{rs}^P + b_{ij} \tag{8}$$

with ij indicating the type of the edge rs (either 22, or 23, or 33). By least–squares fitting we obtained

$$\begin{aligned} a &= 0.3188, \\ b_{22} &= 0.5066 \quad \text{for edges } rs \text{ of type 22}, \\ b_{23} &= 0.4518 \quad \text{for edges } rs \text{ of type 23}, \\ b_{33} &= 0.4078 \quad \text{for edges } rs \text{ of type 33}. \end{aligned} \tag{9}$$

The loss of precision of (8) relative to (7) is minor. For instance, in the case of the above described sample of heptacyclic benzenoids, the standard deviation of (8) is 0.0080, only slightly greater than 0.0073 for (7), and well below 0.0095 for (6). As shown in the two subsequent sections, by imposing parallelism between the Cruickshank–Sparks regressions lines, several applications thereof become possible.

First Application: Electron and Energy Contents of Hexagons in Benzenoid Hydrocarbons

The concept of *π-electron content* of a six-membered ring (hexagon) R of a benzenoid hydrocarbon, denoted by $EC(R)$, was put forward in [21], based on previous theoretical studies of the distribution of π-electrons in polycyclic conjugated molecules [22–26]. According to [21],

$$EC(R) = 2\sum_{*} P^P_{rs} + \sum_{**} P^P_{rs}, \tag{10}$$

where $\sum_{*}$ and $\sum_{**}$ indicate, respectively, summation over the carbon–carbon bonds of the hexagon R which belong only to this hexagon, and over bonds which are shared by R and another hexagon.

Because the sum of Pauling bond orders over all bonds, times two, is equal to the total number n of π-electrons, the sum of π-electron contents of all hexagons of a benzenoid hydrocarbon is equal to n.

The sum of Coulson bond orders over all bonds, times two, is equal to the total π-electron energy E of the respective conjugated molecule [4]. Taking this into account, and in analogy with (10), we define the *π-electron energy content* of a hexagon R of a benzenoid hydrocarbon as

$$ec(R) = 2\sum_{*} P^C_{rs} + \sum_{**} P^C_{rs}. \tag{11}$$

From (11) directly follows that the sum of π-electron energy contents of all hexagons of a benzenoid hydrocarbon is equal to E.

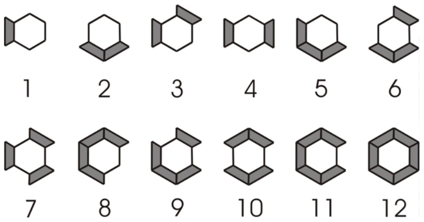

Fig. 2. The different annelation modes of hexagons in benzenoid systems.

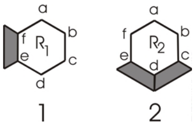

Fig. 3. Labelling of vertices of hexagons annelated in modes **1** and **2**, used to obtain the relations (12) and (13).

The basic properties of the π-electron energy contents of hexagons of benzenoid hydrocarbons were reported in [27]. In view of the close formal analogy between the definitions (10) and (11), the obvious question is whether the EC– and ec-values are mutually related. We now show that by means of Cruickshank–Sparks–type relations, in particular, by means of (8), we can establish such a connection.

A hexagon in a benzenoid hydrocarbon can be annelated to the rest of the molecule in 12 distinct ways [17]. These annelation modes are depicted in Figure 2.

Consider first the annelation mode **1**; let the vertices of the hexagon R_1 be labelled as shown in Figure 3.

The edges ab, bc, cd, de, and af of the hexagon R_1 belong solely to this hexagon, whereas the bond ef is shared by R_1 and its (unique) neighbor. Therefore

$$EC(R_1) = 2\left(P^P_{ab} + P^P_{bc} + P^P_{cd} + P^P_{de} + P^P_{af}\right) + P^P_{ef},$$

$$ec(R_1) = 2\left(P^C_{ab} + P^C_{bc} + P^C_{cd} + P^C_{de} + P^C_{af}\right) + P^C_{ef}.$$

The edges ab, bc, and cd are of type (2,2), the edges af and de are of type (2,3), whereas the edge ef is of type (3,3). By applying the approximations (8)–(9) we obtain

$$\begin{aligned} ec(R_1) &\approx 2\Big[\left(aP^P_{ab} + b_{22}\right) + \left(aP^P_{bc} + b_{22}\right) \\ &\quad + \left(aP^P_{cd} + b_{22}\right) + \left(aP^P_{de} + b_{23}\right) \\ &\quad + \left(aP^P_{af} + b_{23}\right)\Big] + \left(aP^P_{ef} + b_{33}\right) \\ &= a\Big[2\left(P^P_{ab} + P^P_{bc} + P^P_{cd} + P^P_{de} + P^P_{af}\right) + P^P_{ef}\Big] \\ &\quad + 6b_{22} + 4b_{23} + b_{33}, \end{aligned}$$

which finally yields

$$ec(R_1) \approx aEC(R_1) + (6b_{22} + 4b_{23} + b_{33}),$$

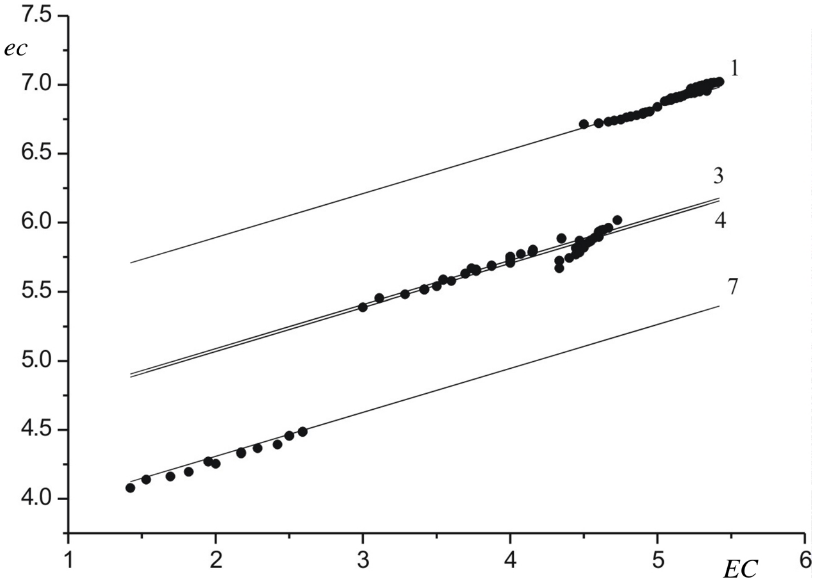

Fig. 4. The π-electron energy contents (ec) of the hexagons in catacondensed benzenoid hydrocarbons with up to 5 hexagons and in branched catacondensed benzenoid hydrocarbons with 6 hexagons, versus their π-electron contents (EC). The four lines pertain to the approximate formulas (14) for the annelation modes **1**, **3**, **4**, and **7.** Recall that in catacondensed benzenoids only these four annelation modes occur, cf. Figure 2. The agreement between the formulas (14) and the calculated EC- and ec-values is equally good also in the case of pericondensed benzenoids, in which all the 12 distinct annelation modes are encountered.

i. e.,

$$ec(R_1) \approx 0.3188\,EC(R_1) + 5.2546. \qquad (12)$$

In an analogous manner, for annelation mode **2**, shown in Fig. 3, we get

$$EC(R_2) = 2\left(P^P_{ab} + P^P_{bc} + P^P_{ef} + P^P_{af}\right) + \left(P^P_{cd} + P^P_{de}\right),$$
$$ec(R_2) = 2\left(P^C_{ab} + P^C_{bc} + P^C_{ef} + P^C_{af}\right) + \left(P^C_{cd} + P^C_{de}\right).$$

This time the edges ab and af are of type (2,2), bc and ef are of type (2,3), cd and de of type (3,3). Application of (8) – (9) results in

$$\begin{aligned} ec(R_2) \approx 2\Big[&\left(aP^P_{ab} + b_{22}\right) + \left(aP^P_{bc} + b_{22}\right) \\ &+ \left(aP^P_{ef} + b_{23}\right) + \left(aP^P_{af} + b_{23}\right)\Big] \\ &+ \Big[\left(aP^P_{cd} + b_{33}\right) + \left(aP^P_{de} + b_{33}\right)\Big] \\ = a\Big[&2\left(P^P_{ab} + P^P_{bc} + P^P_{ef} + P^P_{af}\right) + \left(P^P_{cd} + P^P_{de}\right)\Big] \\ &+ 4b_{22} + 4b_{23} + 2b_{33}, \end{aligned}$$

from which

$$ec(R_2) \approx a\,EC(R_2) + (4b_{22} + 4b_{23} + 2b_{33}),$$

i. e.,

$$ec(R_2) \approx 0.3188\,EC(R_2) + 4.6492. \qquad (13)$$

Repeating analogous calculations for all annelation modes (cf. Fig. 2), we arrive at

$$\begin{array}{ll}
\text{Mode } \mathbf{1}: & ec \approx a\,EC + (6b_{22} + 4b_{23} + b_{33}) \\
 & \quad = 0.3188\,EC + 5.2546 \\
\text{Mode } \mathbf{2}: & ec \approx a\,EC + (4b_{22} + 4b_{23} + 2b_{33}) \\
 & \quad = 0.3188\,EC + 4.6492 \\
\text{Mode } \mathbf{3}: & ec \approx a\,EC + (2b_{22} + 4b_{23} + 4b_{33}) \\
 & \quad = 0.3188\,EC + 4.4516 \\
\text{Mode } \mathbf{4}: & ec \approx a\,EC + (8b_{23} + 2b_{33}) \\
 & \quad = 0.3188\,EC + 4.4300 \\
\text{Mode } \mathbf{5}: & ec \approx a\,EC + (2b_{22} + 4b_{23} + 3b_{33}) \\
 & \quad = 0.3188\,EC + 4.0438 \\
\text{Mode } \mathbf{6}: & ec \approx a\,EC + (4b_{23} + 5b_{33}) \\
 & \quad = 0.3188\,EC + 3.8462 \\
\text{Mode } \mathbf{7}: & ec \approx a\,EC + (9b_{33}) \\
 & \quad = 0.3188\,EC + 3.6702 \\
\text{Mode } \mathbf{8}: & ec \approx a\,EC + (4b_{23} + 4b_{33}) \\
 & \quad = 0.3188\,EC + 3.4384 \\
\text{Mode } \mathbf{9}: & ec \approx a\,EC + (8b_{33}) \\
 & \quad = 0.3188\,EC + 3.2624 \\
\text{Mode } \mathbf{10}: & ec \approx a\,EC + (8b_{33}) \\
 & \quad = 0.3188\,EC + 3.2624 \\
\text{Mode } \mathbf{11}: & ec \approx a\,EC + (7b_{33}) \\
 & \quad = 0.3188\,EC + 2.8546 \\
\text{Mode } \mathbf{12}: & ec \approx a\,EC + (6b_{33}) \\
 & \quad = 0.3188\,EC + 2.4468
\end{array} \qquad (14)$$

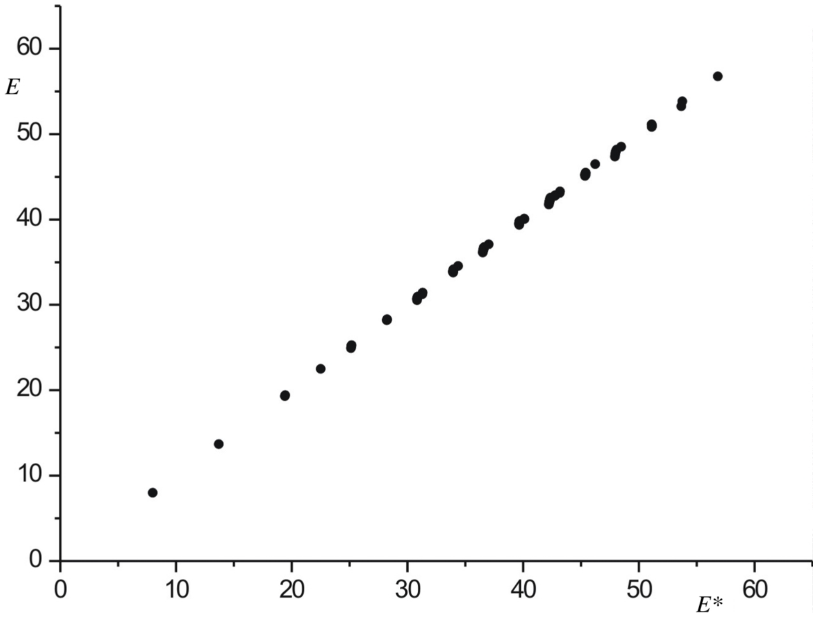

Fig. 5. The HMO total π-electron energies (E) of 106 benzenoid hydrocarbons from the book [33], vs. the approximate values (E^*), computed by means of (18).

The quality of the approximations (14) is seen from Figure 4.

Second Application: Total π-Electron Energy of Benzenoid Hydrocarbons

The dependence of the HMO total π-electron energy (E) on the molecular structure was much studied in the past; for details see [28,29] and the references cited therein. Much effort was applied to elucidate the structure–dependence of total π-electron energy of benzenoid hydrocarbons; for details see [30,31] and the references cited therein. In one of these studies [32] an approximation of the form

$$E \approx E^* = C_1 n + C_2 m + C_3 + C_4 b \tag{15}$$

was examined, where n, m, and b are the number of vertices, edges, and bay regions of the underlying benzenoid system. In [32] the numerical values of the coefficients C_i, $i = 1,2,3,4$, have not been determined.

We now show how (15) follows from the Cruickshank–Sparks–type relations (8). Our staring point is the well known expression [4]

$$E = 2\sum_{rs} P^C_{rs},$$

in which the summation embraces all edges. Benzenoid systems possess only edges of type (2,2), (2,3), and (3,3), and therefore

$$E = 2\left(\sum_{rs}^{22} P^C_{rs} + \sum_{rs}^{23} P^C_{rs} + \sum_{rs}^{33} P^C_{rs}\right), \tag{16}$$

where $\sum^{ij}$ indicates summation over edges of (i,j)-type. Using (8), we get

$$\sum_{rs}^{22} P^C_{rs} \approx a \sum_{rs}^{22} P^P_{rs} + b_{22}\, m_{22},$$
$$\sum_{rs}^{23} P^C_{rs} \approx a \sum_{rs}^{23} P^P_{rs} + b_{23}\, m_{23},$$
$$\sum_{rs}^{33} P^C_{rs} \approx a \sum_{rs}^{33} P^P_{rs} + b_{33}\, m_{33},$$

where m_{ij} stands for the number of edges of the type (i,j). Substituting the right–hand sides of the above three expressions back into (16) and bearing in mind that

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

we arrive at

$$E \approx E^* = a\,n + 2\,(b_{22}\, m_{22} + b_{23}\, m_{23} + b_{33}\, m_{33}),$$

which when combined with (1) – (3) and (5) yields

$$\begin{aligned} E \approx E^* = {} & (4a + 8b_{23} + 2b_{33})\,h \\ & - (a + 4b_{23} - 2b_{33})\,n_i \\ & + (2a + 12b_{22} - 8b_{23} - 2b_{33}) \\ & + (2b_{22} - 4b_{23} + 2b_{33})\,b \\ = {} & 5.7052h - 1.3104n_i \\ & + 2.2868 + 0.0216b. \end{aligned} \tag{17}$$

The relations $h = m - n + 1$ and $n_i = 4m - 5n + 6$ are immediate consequences of (4) and (5). When these are substituted into (17) we obtain

$$\begin{aligned} E \approx E^* = {} & (a + 12b_{23} - 12b_{33})\,n \\ & - (10b_{33} - 8b_{23})\,m \\ & + (12b_{22} - 24b_{23} + 12b_{33} \\ & + (2b_{22} - 4b_{23} + 2b_{33})\,b \\ = {} & 0.8468n + 0.4636m \\ & + 0.1296 + 0.0216b. \end{aligned} \tag{18}$$

Formula (18) has precisely the same form as (15), except that now the numerical values of the coefficients C_i, $i = 1, 2, 3, 4$, are known. The quality of the approximation (18) is seen from Figure 5.

[1] L. Pauling, L. O. Brockway, and J. Y. Beach, J. Amer. Chem. Soc. **57**, 2705 (1935).

[2] L. Pauling, The Nature of the Chemical Bond, Cornell Univ. Press, Ithaca 1960, pp. 234 – 239.

[3] C. A. Coulson, Proc. Roy. Soc. London **A169**, 413 (1939).

[4] C. A. Coulson, B. O'Leary, and R. B. Mallion, Hückel Theory for Organic Chemists, Academic Press, London 1978, pp. 60 – 69.

[5] W. C. Herndon, J. Amer. Chem. Soc. **96**, 7605 (1974).

[6] W. C. Herndon and C. Párkányi, J. Chem. Educ. **53**, 689 (1976).

[7] L. Pauling, Acta Cryst. **B36**, 1898 (1980).

[8] S. Narita, T. Morikawa, and T. Shibuya, J. Mol. Struct. (Theochem) **532**, 37 (2000).

[9] C. A. Coulson, Proc. Roy. Soc. London **A207**, 91 (1951).

[10] D. W. J. Cruickshank and R. A. Sparks, Proc. Roy. Soc. London **A258**, 270 (1960).

[11] D. W. J. Cruickshank, Tetrahedron **17**, 155 (1962).

[12] R. Goddard, M. W. Haenel, W. C. Herndon, C. Krüger, and M. Zander, J. Amer. Chem. Soc. **117**, 30 (1995).

[13] N. S. Ham and K. Ruedenberg, J. Chem. Phys. **29**, 1215 (1958).

[14] E. Heilbronner, Helv. Chim. Acta **50**, 1722 (1962).

[15] H. Hosoya and K. Hosoi, J. Chem. Phys. **64**, 1065 (1976).

[16] I. Gutman, J. Chem. Phys. **68**, 1321 (1978).

[17] I. Gutman and S. J. Cyvin, Introduction to the Theory of Benzenoid Hydrocarbons, Springer-Verlag, Berlin 1989.

[18] M. Zander, Z. Naturforsch. **40a**, 636 (1985).

[19] O. E. Polansky, Z. Naturforsch. **41a**, 560 (1986).

[20] M. Zander, Z. Naturforsch. **45a**, 1041 (1990).

[21] I. Gutman, T. Morikawa, and S. Narita, Z. Naturforsch. **59a**, 295 (2004).

[22] M. Randić and A. T. Balaban, Polyc. Arom. Comp. **24**, 173 (2004).

[23] A. T. Balaban and M. Randić, J. Chem. Inf. Comput. Sci. **44**, 50 (2004).

[24] I. Gutman, D. Vukičević, A. Graovac, and M. Randić, J. Chem. Inf. Comput. Sci. **44**, 296 (2004).

[25] M. Randić, J. Chem. Inf. Comput. Sci. **44**, 365 (2004).

[26] A. Miličević, S. Nikolić, and N. Trinajstić, J. Chem. Inf. Comput. Sci. **44**, 415 (2004).

[27] I. Gutman, B. Furtula, and N. Turković, Polyc. Arom. Comp., submitted.

[28] A. Graovac, I. Gutman, P. E. John, D. Vidović, and I. Vlah, Z. Naturforsch. **56a**, 307 (2001).

[29] H. Fripertinger, I. Gutman, A. Kerber, A. Kohnert, and D. Vidović, Z. Naturforsch. **56a**, 342 (2001).

[30] I. Gutman, Topics Curr. Chem. **162**, 29 (1992).

[31] I. Gutman, J. H. Koolen, V. Moulton, M. Parac, T. Soldatović, and D. Vidović, Z. Naturforsch. **55a**, 507 (2000).

[32] I. Gutman, G. G. Hall, S. Marković, Z. Stanković, and V. Radivojević, Polyc. Arom. Comp. **2**, 275 (1991).

[33] R. Zahradnik and J. Pancir, HMO Energy Characteristics, Plenum Press, New York 1970.