Indian Journal of Chemistry
Vol. 45A, February 2006, pp. 347-351

On π-electron excess of rings of benzenoid molecules

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Received 15 November 2005; accepted 26 December 2005

In a previous paper [Gutman I, *Indian J Chem* 43A (2004) 1615], the concept of π-electron excess of rings of benzenoid hydrocarbons has been introduced, aimed at amending the π-electron contents of rings computed on the basis of Pauling bond orders. We now show how a π-electron-content-like quantity can be computed from the Hosoya bond orders and establish its close relation with the π-electron excess.

Randić and Balaban[1-3] have recently invented a method for partitioning of the π-electrons of a benzenoid hydrocarbon into its rings. This method utilizes Kekulé structures and the respective electron content of a ring R can be expressed in terms of Pauling bond orders as[4]:

$$EC_{RB}(R) = 2\sum_{*} p_{rs}^{P} + \sum_{**} p_{rs}^{P} \qquad \ldots(1)$$

where the first summation goes over bonds rs that belong solely to the ring R, whereas the second summation is over bonds rs shared by the ring R and another ring. However, the Pauling bond order of the bond rs between the atoms r and s is defined as[5,6]:

$$p_{rs}^{P} = K(B-r-s)/K(B) \qquad \ldots(2)$$

where $K(B)$ stands for the Kekulé structure count of the underlying benzenoid system B. $K(B\text{-}r\text{-}s)$ denotes the number of those Kekulé structures in which the bond rs is double, i.e. $K(B\text{-}r\text{-}s)$ is the number of Kekulé structures of the subgraph $B\text{-}r\text{-}s$, obtained by deleting from B the vertices r and s. Some recent applications of the Pauling bond orders are also known[4,7-9].

Theoretical

The success of Eq. (1) is based on the relation[10]:

$$2\sum_{rs} p_{rs}^{P} = n \qquad \ldots(3)$$

in which the summation goes over all bonds rs and n is the total number of π-electrons of the conjugated molecule considered. Eq. (3) may be interpreted as a distribution of the π-electrons into the bonds of the respective conjugated molecule, so that the term $2\,p_{rs}^{P}$ is the π-electron content of the bond rs.

Bearing in mind the analogous relation for the Coulson bond order p_{rs}^{C}, as reported earlier[10]:

$$2\sum_{rs} p_{rs}^{C} = E \qquad \ldots(4)$$

where E is the total π-electron energy, we recently conceived the energy content of a ring as[11,12]:

$$ec(R) = 2\sum_{*} p_{rs}^{C} + \sum_{**} p_{rs}^{C} \qquad \ldots(5)$$

In view of relations (1) and (5), it is reasonable to ask if other bond-order-like quantities may also be employed in the analysis of the local π-electron properties of conjugated molecules[13-15]. We now focus our attention to the Hosoya bond order[16,17] and derive a Hosoya-bond-order-based electron content of a ring, $EC_{\mathrm{H}}(R)$. Some recent applications of the Hosoya bond orders can be found in the papers[18-20]. We can generalize this approach by finding a connection between $EC_{\mathrm{RB}}(R)$ and $EC_{\mathrm{H}}(R)$, which sheds new light on the recently introduced concept of π-electron excess[21].

Hosoya bond order and its physical interpretation

In an attempt to extend the applications of his "topological index" (nowadays known under the name

'Hosoya index') to conjugated π-electron systems, Hosoya defined a bond order p_{rs}^{H} as[16,17,20]:

$$p_{rs}^{H} = Z(B-r-s)/Z(B) \qquad \ldots(6)$$

where $Z(G)$ stands for the Hosoya index of the graph G. The analogy between Eqs (2) and (6) is evident. One should recall that $Z(G)$ is equal to the total number of matchings of the graph G, whereas $K(G)$ is equal to the number of its perfect matchings. The main difference between the Pauling and Hosoya bond orders is that in contrast with Eq. (3), the sum (7)

$$2\sum_{rs} p_{rs}^{H} \qquad \ldots(7)$$

has no visible relation to the electron characteristics of the underlying conjugated molecule.

We now offer a result that could fill this gap.

The Hosoya index of any graph G conforms to the recurrence relation[22,23]:

$$Z(G) = Z(G-e) + Z(G-r-s) \qquad \ldots(8)$$

where e is an edge (any edge) of G, and r and s are the two end vertices of e. Further, if the graph G consists of two disjoint components G_1 and G_2, then:

$$Z(G) = Z(G_1)\,Z(G_2) \qquad \ldots(9)$$

Let $e_1, e_2, \ldots, e_d$ be the edges of G, terminating at the vertex r. Let $s_1, s_2, \ldots, s_d$ be, respectively, the other end vertices of the edges $e_1, e_2, \ldots, e_d$. Then by applying relation (8) consecutively to all edges that terminate at the vertex r, we get:

$$Z(G) = Z(G-e_1-e_2-\cdots-e_d) + \sum_{i=1}^{d} Z(G-r-s_i)$$

The subgraph G-e_1-e_2-...-e_d is disconnected, consisting of G-r and an isolated vertex. Then, using Eq.(9), we get

$$Z(G-e_1-e_2-\cdots-e_d) = (G-r)$$

because the Z-index of a single-vertex graph is equal to unity.

Combining the above relations, we arrive at

$$Z(G) = Z(G-r) + \sum_{s\to r} Z(G-r-s) \qquad \ldots(10)$$

where $\sum_{s\to r}$ indicates summation over all vertices s that are adjacent to the vertex r. Summing Eq. (10) over all n vertices of the graph G and bearing in mind that every edge has two end vertices, we obtain the identity

$$n\,Z(G) = \sum_{r} Z(G-r) + 2\sum_{rs} Z(G-r-s) \qquad \ldots(11)$$

which can be rewritten as:

$$2\sum_{rs} Z(G-r-s)/Z(G) + \sum_{r} Z(G-r)/Z(G) = n \ \ldots(12)$$

Applied to a benzenoid system B, this identity becomes:

$$2\sum_{rs} p_{rs}^{H} + \sum_{r} p_{rr}^{H} = n \qquad \ldots(13)$$

where, in analogy to Eq. (6), we define $p_{rr}^{H} = Z(G-r)/Z(G)$.

Relation (13) should be compared with Eq. (3). It immediately implies a natural interpretation of the Hosoya bond order. Eq. (13) may be viewed as a distribution of the π-electrons into the bonds and atoms of the respective conjugated molecule, so that the term $2\,p_{rs}^{H}$ is the π-electron content of the bond rs, and the term p_{rr}^{H} the π-electron content of the atom r.

Thus, we shall see that this Hosoya-bond-order-based electron distribution pertains to the case when the π-electron conjugation effects are (almost) completely disregarded.

Hosoya-bond-order based π-electron content of rings

In full analogy with the Kekulé-structure-based π-electron content of a ring, Eq. (1), bearing in mind Eq.(13) and its interpretation, we define the Hosoya-index-based π-electron content as:

$$EC_{H}(R) = 2\sum_{*} p_{rs}^{H} + \sum_{**} p_{rs}^{H} + \sum_{o} p_{rr}^{H} + \frac{1}{2}\sum_{oo} p_{rr}^{H} + \frac{1}{3}\sum_{ooo} p_{rr}^{H} \qquad \ldots(14)$$

Table 1—Hosoya-bond-order-based π-electron contents [EC_H, Eq. (14)] of rings of benzenoid hydrocarbons, depicted in Fig. 1 [ν is the number of first neighbours of the ring considered. For comparative purposes also, the Kekulé-structure-based π-electron contents [EC_{RB}, Eq. (1)] are given]

Molecule	Ring	EC_H	ν	EC_{RB}
1	A	4.979	1	4.750
	B	4.041	2	4.500
2	A	5.030	1	5.200
	B	3.939	2	3.600
3	A	4.978	1	4.500
	B	4.021	2	4.333
	C	4.003	2	4.333
4	A	5.030	1	5.147
	B	3.969	2	3.794
	C	4.000	2	4.088
	D	3.998	2	3.941
5	A	4.335	2	4.667
	B	3.665	3	3.333
6	A	4.362	2	4.667
	B	2.550	4	1.333
7	A	5.059	1	5.302
	B	2.887	3	2.191
	C	3.035	3	3.619

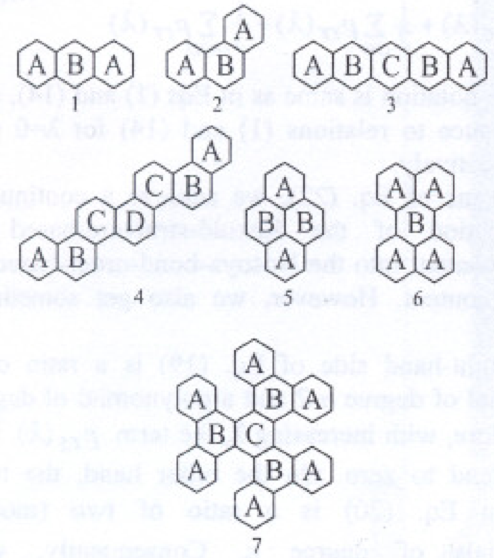

Fig. 1—Benzenoid systems encountered in Table 1 and the labelling of their rings.

where sum $\sum_{o}$, $\sum_{oo}$ and $\sum_{ooo}$ indicate, respectively, summation over atoms belonging solely to the ring R, shared by R and another ring, and shared by R and two other rings.

In Table 1 are found the EC_H-values of some typical benzenoid hydrocarbons, whose formulas are depicted in Fig. 1 and whose Clar formulas are depicted in Fig. 2. For comparative reasons also the respective EC_{RB}-values are also given.

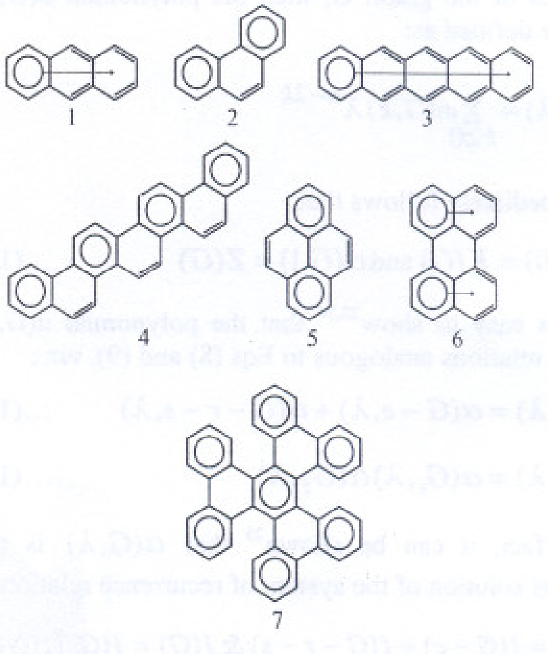

Fig. 2—Clar aromatic sextet formulas of the benzenoid systems encountered in Table 1. Note that rings in which aromatic sextets are located have increased EC_{RB}-values, relative to the EC_{RB}-values of analogously annelated "empty" rings. This is not the case with the EC_H-values.

Comparing the data given in Table 1 with Fig. 2, it is seen that the EC_H-values do not reflect the π-electron distribution predicted by Clar theory. From the same data, we also see that the main structural factor determining $EC_H(R)$ is the number ν of rings adjacent to the ring R. In this respect, EC_H resembles much the earlier introduced[21] "atom-based π-electron content", EC_a. The reason for this coincidence will be clarified in the subsequent discussions.

Because $EC_H \approx EC_a$, one may use the difference EC_{RB}-EC_H for computing the π-electron excess of a ring (discussed in detail elsewhere[21]). Such an approach to the concept of π-electron excess would be theoretically justified, bearing in mind that EC_H is based on the consideration of all matchings of the underlying molecular graph, whereas EC_{RB} reflects only the effects of the (chemically most relevant) perfect matchings[23,24].

A generalization: Relating EC_{RB}, EC_H and EC_a

Denote by $m(G,k)$ the number of k-matchings[22,23] of the graph G (= the number of ways in which k mutually non-touching edges can be selected in G). By definition, $m(G,0)=1$ for all graphs, and $m(G,1)$ = the number of edges of G. If n is the number of vertices of the graph G, then the polynomial $\alpha(G,\lambda)$ will be defined as:

$$\alpha(G,\lambda) = \sum_{k \geq 0} m(G,k)\,\lambda^{n-2k}$$

It immediately follows that:

$$\alpha(G,0) = K(G) \text{ and } \alpha(G,1) = Z(G) \qquad \ldots(15)$$

It is easy to show[23,24] that the polynomial $\alpha(G,\lambda)$ obeys relations analogous to Eqs (8) and (9), viz.:

$$\alpha(G,\lambda) = \alpha(G-e,\lambda) + \alpha(G-r-s,\lambda) \qquad \ldots(16)$$

$$\alpha(G,\lambda) = \alpha(G_1,\lambda)\,\alpha(G_2,\lambda) \qquad \ldots(17)$$

In fact, it can be shown[25] that $\alpha(G,\lambda)$ is the general solution of the system of recurrence relations:

$$I(G) = I(G-e) + I(G-r-s) \;\&\; I(G) = I(G_1)\,I(G_2)$$

Starting with Eqs (16) and (17) and following a reasoning fully analogous to what was used for deducing Eq. (12), we get:

$$2\sum_{rs} \alpha(G-r-s,\lambda)/\alpha(G,\lambda) + \lambda \sum_{r} \alpha(G-r,\lambda)/\alpha(G,\lambda) = n \qquad \ldots(18)$$

The multiplier λ before the second summation on the left-hand side of (18) comes from the fact that the α-polynomial of the single-vertex graph is λ.

In view of relations (15), we easily conclude that Eqs (3) and (13) are special cases of Eq. (18), for λ=0 and λ=1, respectively. Bearing this in mind, we introduce the following λ-dependent bond-order like quantities:

$$p_{rs}(\lambda) = \alpha(G-r-s,\lambda)/\alpha(G,\lambda) \qquad \ldots(19)$$

and

$$p_{rr}(\lambda) = \lambda\,\alpha(G-r,\lambda)/\alpha(G,\lambda) \qquad \ldots(20)$$

and then identity (18) becomes,

$$2\sum_{rs} p_{rs}(\lambda) + \sum_{r} p_{rr}(\lambda) = n \qquad \ldots(21)$$

Based on this analogy, we now conceive a λ-dependent π-electron content of a ring R,

$$EC(R,\lambda) = 2\sum_{*} p_{rs}(\lambda) + \sum_{**} p_{rs}(\lambda) + \sum_{o} p_{rr}(\lambda) + \frac{1}{2}\sum_{oo} p_{rr}(\lambda) + \frac{1}{3}\sum_{ooo} p_{rr}(\lambda) \qquad \ldots(22)$$

where the notation is same as in Eqs (1) and (14), and which reduce to relations (1) and (14) for λ=0 and λ=1, respectively.

By means of Eq. (22), we achieve a continuous transformation of the Kekulé-structure-based π-electron content into the Hosoya-bond-order-based π-electron content. However, we also get something more.

The right-hand side of Eq. (19) is a ratio of a polynomial of degree n-2 and a polynomial of degree n. Therefore, with increasing λ, the term $p_{rs}(\lambda)$ will rapidly tend to zero. On the other hand, the term $p_{rr}(\lambda)$ in Eq. (20) is a ratio of two (monic) polynomials of degree n. Consequently, with increasing λ, it will tend to unity. This means that in the limit case $\lambda \to \infty$, the π-electron distribution described by means of Eq. (21) reduces to the earlier studied[21] uniform electron distribution: one π-electron on each carbon atom, and no π-electrons associated with the carbon-carbon bonds. Therefore, the limit value of $EC(\lambda)$ is just the earlier studied[21] atom-based π-electron content EC_a.

Numerical studies reveal that with increasing value of the parameter λ, the π-electron content $EC(\lambda)$ tends to EC_a very rapidly, and that already at $\lambda \approx 1$, the difference between $EC(\lambda)$ and EC_a becomes insignificant. A characteristic example is shown in Fig. 3.

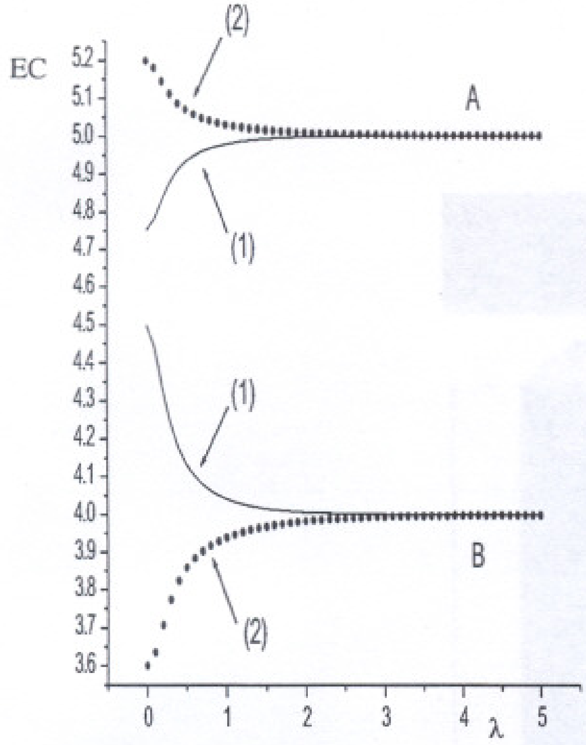

Fig. 3—The λ-dependence of the π-electron contents of the rings of anthracene (1) and phenanthrene (2), *cf.* Fig. 1. Note that $EC(-\lambda)=EC(\lambda)$ and therefore only the case $\lambda \geq 0$ needs to be examined. The curves pertaining to rings *B* of both anthracene and phenanthrene approach the same limit value, implying that this limit value depends solely on the parameter v. The same is true for the rings *A*.

Discussion

Extending the Randić-Balaban approach to the calculation of the π-electron content of rings in benzenoid hydrocarbons, and knowing the role which the Pauling bond order plays in this approach, we put forward a novel π-electron content, EC_H, Eq. (14), based on the Hosoya bond order. This quantity was, however, found to be insensitive to effects of π-electron conjugation, and mainly determined by the annelation mode of the respective ring. Therefore, EC_H could be used for determining the π-electron excess of the ring[21].

Conclusions

The main results of our study are obtained by utilizing the auxiliary π-electron content $EC(\lambda)$, depending on a variable parameter λ. By means of EC(λ), it is possible to achieve a continuous transformation of the Pauling-bond-order-based π-electron content (at λ=0) into its Hosoya-bond-order-based variant (at λ=1). By further increasing λ, $EC(\lambda)$ becomes equal to the earlier introduced[21] atom-based π-electron content. By this, we get a better understanding of the concept of π-electron excess, which is now seen to be the difference between the π-electron content of a ring calculated on the basis of perfect matchings, and the analogous π-electron-like quantity, obtained by considering all matchings of the underlying molecular graph.

Acknowledgement

This work was supported in part by the Ministry of Sciences, Technologies and Development of Serbia (Project No. 1389), and the Ministry of Education, Science and Sport of Slovenia, Research Program P1-0297 and Research Project J1-6150.

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