

Rapid Communication

Assessing the distribution of π -electrons into rings of phenylenes

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We propose a novel method for assessing the distribution of π -electrons into rings of phenylenes. This method is equivalent to, but significantly simpler than, the original approach of Randić and Balaban.

Randić and Balaban introduced recently^{1,2} the concept of distribution of π -electrons into rings in polycyclic conjugated hydrocarbons. Their approach was soon elaborated and extended by other authors³⁻¹⁰. Practically, all hitherto published studies in this area are concerned with benzenoid hydrocarbons. In this paper, we attempt to go beyond this important, yet restricted, class of conjugated molecules.

Theoretical

The original Randić-Balaban model for partitioning π -electrons into the rings of benzenoid hydrocarbons is based on Kekulé structures. For calculation of the electron content (EC) of a ring R , it is needed to transform all Kekulé structures into their algebraic form. This is done by¹¹: (i) Every double bond in the respective Kekulé structure that belongs solely to the ring R , contributes to R with two π -electrons; (ii) Those double bonds that are shared between the ring R and some other ring, contribute to R with one π -electron; and, (iii) The arithmetic average of the π -electron counts, obtained by rules (i) and (ii) taken over all Kekulé structures, is interpreted as the part of all π -electrons that belong to the ring R , and is referred³ as the (Randić-Balaban) electron content of R , denoted by $EC = EC(R)$.

It can be shown³ that

$$EC(R) = 2 \sum_{rs \in R} p_{rs}^p + \sum_{rs \notin R} p_{rs}^p \quad \dots(1)$$

where p_{rs}^p is the Pauling bond order of bond rs , $\sum_{rs \in R}$ is the sum of all bonds that belong solely to the ring R ,

and $\sum_{rs \notin R}$ is the sum of all bonds that are shared between R and some other ring. Recall that the Pauling bond order of the bond rs is equal to the ratio between the number K_{rs} of Kekulé structures in which rs is a double bond, and the total number K of Kekulé structures^{3,6}.

The EC -values give a reasonably good description of the electron structure of benzenoid hydrocarbons and are in fair agreement with the available experimental results⁴.

It is well known that the Kekulé structure count and the Pauling bond orders are related to numerous physico-chemical properties of benzenoid hydrocarbons¹². Such relations fail to exist in the case of non-benzenoid polycyclic conjugated systems. The way out of these difficulties was found long time ago by Dewar and Longuet-Higgins¹³. They showed that for alternant non-benzenoid hydrocarbons, instead of the Kekulé structure count K , one has to use the so-called algebraic structure count (ASC). This latter quantity is defined as¹⁴⁻¹⁶

$$ASC = \sqrt{|\det A|} \quad \dots(2)$$

where A is the adjacency matrix. Recall that for benzenoid systems, the right-hand side of Eq. (2) is equal to K . In the general case, $ASC \leq K$.

In view of the above, if we want to assess the π -electron content of a ring of an alternant non-benzenoid hydrocarbon, then it seems to be purposeful to try to construct a Kekulé-structure-basis consisting of exactly ASC Kekulé structures, and then to use a formula analogous to Eq. (1). We offer here a solution of this problem for the case of phenylenes.

Phenylenes

Phenylenes form a class of polycyclic alternant conjugated hydrocarbons that consist of benzene and cyclobutadiene rings. Every cyclobutadiene ring is adjacent to two benzene rings, and two benzene rings are never adjacent to each other. Data on the synthesis and basic physico-chemical properties of phenylenes are reviewed¹⁷ already. Examples of phenylenes are given in Fig. 1.

To every phenylene a benzenoid system, called hexagonal squeeze¹⁶, can be associated in a natural

manner. Construction of the hexagonal squeeze should be evident from the examples given in Fig. 1. Of the numerous known relations between properties of phenylenes and their hexagonal squeezes, we mention here only that the *ASC* of a phenylene is equal to the *K*-value of the corresponding hexagonal squeeze^{15,16}.

As explained above, our goal is to construct a resonance-theoretical basis of phenylenes, consisting of exactly *ASC* Kekulé structures. One such choice was recently proposed¹⁰. It is based on an intuitively agreeable and chemically understandable idea: the basis K^F consists of all Kekulé structures of the respective phenylenes that do not have the structural details shown in Fig. 2. The Kekulé structures possessing structural details shown in Fig. 2 are abandoned. It has been shown¹⁰ that the size K^F of the basis thus constructed is equal to *ASC*.

The Pauling-type bond order for phenylenes is now defined by the following relation:

$$p_{rs}^F = \frac{K_{rs}^F}{K^F}$$

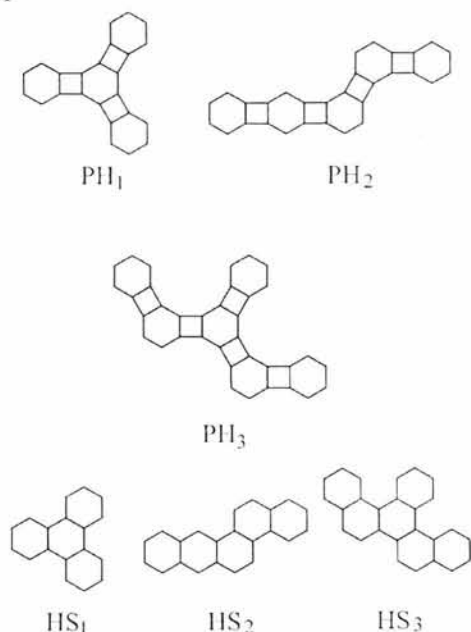


Fig 1 — Examples of phenylenes, *PH*, and their hexagonal squeezes, *HS*.



Fig. 2 — The structural details that are not permitted in the Kekulé-structure-basis K^F .

where K_{rs}^F is the number of elements of K^F in which the bond *rs* is double.

Let *rs* be a carbon-carbon bond of a phenylene that belongs solely to a hexagon. It was shown¹⁰ that the sum of the bond order p_{rs}^F and of the Pauling bond order p_{rs}^P of the respective bond in the hexagonal squeeze is equal to 1.

Results and discussion

The modified π -electron content of a ring *R* of a phenylene, denoted by EC^F , can be defined in a manner analogous to Eq. (1):

$$EC^F(R) = 2 \sum_{*} p_{rs}^F + \sum_{**} p_{rs}^F \quad \dots(3)$$

While comparing relations (1) and (3), one should note that it is much easier to calculate EC^F than the original Randić-Balaban *EC*-values. For instance, in order to obtain the EC^F -values of the phenylene **2** from Fig. 4, it is necessary to examine only 7 of its Kekulé structures. For the calculation of *EC* one would need to consider all the 31 Kekulé structures of **2**.

Using the fact that $p_{rs}^P + p_{rs}^F = 1$, we found simple algebraic relations between the modified π -electron contents of the ring *R* of a phenylene and a certain Pauling bond order of the respective hexagonal squeeze *HS* (Fig. 3):

$$\left. \begin{aligned} EC^F(R) &= 6 - p_{xy}^P(HS) && \text{for annelation mode A} \\ EC^F(R) &= 5 && \text{for annelation mode B} \\ EC^F(R) &= 6 - 2 p_{xy}^P(HS) && \text{for annelation mode C} \\ EC^F(R) &= 6 - 3 p_{xy}^P(HS) && \text{for annelation mode D} \end{aligned} \right\} \dots(4)$$

Eqs (4) enable us to relatively easy compute $EC^F(R)$ and estimate the distribution of π -electrons into the six-membered rings of phenylenes. Based on these, we calculated the π -electron contents of phenylenes for all phenylenes up to 5 hexagons. All phenylenes with 4 hexagons are shown in Fig. 4, whereas the

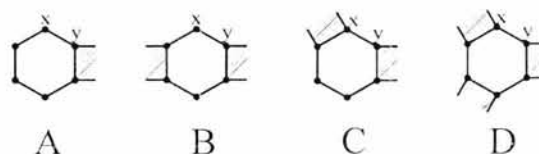


Fig 3 — Structural details of phenylenes and the notation used in Eq. (4).

Table 1 — Randić-Balaban π -electron contents, $EC(R)$, and the modified π -electron contents, $EC^F(R)$, of rings of phenylenes (PH) depicted in Fig. 4

PH	Benzene rings	$EC(R)$	$EC^F(R)$	Cyclobutadiene rings	$EC(R)$	$EC^F(R)$
1	A	5.241	5.800	a	1.448	0.800
	B	4.690	5.000	b	1.242	0.800
2	A	5.258	5.714	a	1.387	0.714
	B	4.645	5.000	b	1.581	0.714
	C	4.226	5.714	c	1.742	0.571
	D	5.161	5.571			
3	A	5.147	5.625	a	1.794	0.625
	B	4.088	5.500	b	1.942	0.500
4	A	5.147	5.625	a	1.794	0.625
	B	4.088	5.500	b	1.942	0.500
5	A	5.114	5.556	a	1.914	0.556
	B	2.914	5.667			

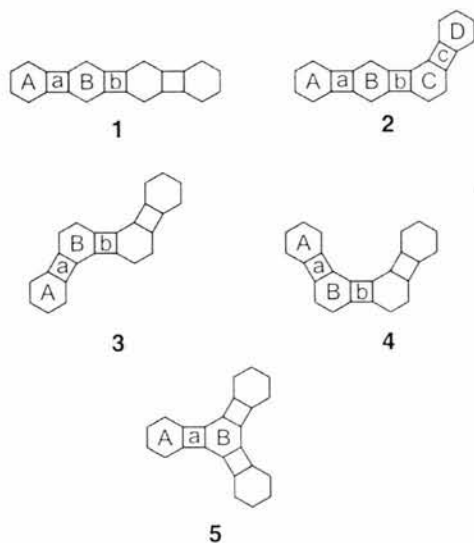


Fig. 4 — Phenylenes with four hexagons and the labelling of their rings (All the phenylenes have been synthesized¹⁷⁻¹⁹. Also, the phenylenes are isomeric with coronene, all having the formula $C_{24}H_{12}$. At this moment we see no connection between the π -electron properties of coronene and its phenylenic isomers).

original Randić-Balaban $EC(R)$ - as well as the $EC^F(R)$ -values of all their rings are shown in Table 1. The results for phenylenes with 5 hexagons are analogous.

The data given in Table 1 show that both π -electron contents give similar predictions. Benzene rings are relatively rich with π -electrons and cyclobutadiene rings are relatively poor. In addition, some more delicate details can be observed: $EC^F(R)$ of hexagons has always a greater value than $EC(R)$. In the case of cyclobutadiene rings (contrary to benzene rings), $EC(R)$ has always a greater value than $EC^F(R)$. In cyclobutadiene rings where the $EC(R)$ has greater

values, $EC^F(R)$ has smaller values and vice versa; this rule is valid also for hexagons of some (but not all) phenylenes. For instance, in molecule **5** (Fig. 4) the hexagon with three neighbors has significantly smaller value of $EC(R)$ compared to the analogous values of the peripheral rings. This can be explained by the greater impact of the number of neighbors on Randić-Balaban electron contents. In contrary to Randić-Balaban electron contents in the molecule **5**, the hexagon with three neighbors has a greater value of $EC^F(R)$ than the value of $EC^F(R)$ of others hexagons.

In general, the complex relations between $EC^F(R)$ of phenylenes and $EC(R)$ of theirs hexagonal squeezes depend of the Pauling bond orders of the respective bonds in the hexagon considered. In particular, in the case of terminal hexagons, there exists a simple linear relation:

$$EC_{PH}^F(R) = -\frac{1}{3}EC_{HS}(R) + \frac{22}{3}$$

By it the calculation of π -electron contents of terminal rings of phenylenes becomes remarkably easy.

Conclusions

The $EC^F(R)$ -values, described here, provide a partition of π -electrons into the rings of phenylenes nearly identical to the results of the standard Randić-Balaban method. However, the calculation of $EC^F(R)$ is significantly easier. The other advantage of the present method is a smaller impact of neighboring rings on the π -electron contents of the ring considered.

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