On distribution of π-electrons in rhombus-shaped benzenoid hydrocarbons

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The distribution of π-electrons into rings of rhombus-shaped benzenoid hydrocarbons is reported here. In this class of benzenoid systems, the (unique) Clar formula represents only a minute fraction of the total number of Kekulè structures, and therefore a breakdown of the Clar model could be expected. It is found that the π-electron distribution follows a pattern different from what is predicted by the Clar model: the greatest π-electron content is in the two "full" peak hexagons (around 4.5 electrons). In the other boundary hexagons, the π-electrons are distributed almost uniformly (around 3 electrons per hexagon). In the internal hexagons, the π-electrons are also distributed in an almost uniform manner (around 2 electrons per hexagon), the π-electron content of the "full" hexagons insignificantly exceeding the π-electron contents of the "empty" hexagons.

Randić and Balaban recently proposed a method for assessing the π-electron content of rings in polycyclic conjugated molecules[1,2]. This approach proved to be particularly suitable in the case of benzenoid hydrocarbons[1-14], where its agreement with experimentally measured electron distributions could be demonstrated[15].

Theoretical

For a given Kekulè structure of a benzenoid hydrocarbon B, the π-electron content of a hexagon H, denoted by $EC(H,B,k)$ is equal to twice the number of double bonds that belong solely to H plus the number of double bonds that are shared by H and its neighbours. The π-electron content of H, denoted by $EC(H,B)$, is then computed by averaging the $EC(H,B,k)$-values over all K Kekulè structures of the benzenoid molecule B:

$$EC(H,B) = \frac{1}{K}\sum_{k=1}^{K} EC(H,B,k).$$

Details of the calculation of EC, including the usage of Pauling bond orders[6], as well as pertinent examples, can be found elsewhere[7-9].

Among many other applications, the EC-values may serve to independently test the validity of the Clar aromatic sextet theory[16] or, equivalently, the Clar aromatic sextet theory may serve to test the adequacy of the EC-values computed by the Randić-Balaban method. Within Clar theory, the π-electron

configuration of a benzenoid hydrocarbon is presented by means of Clar formulas, in which circles drawn in certain hexagons indicate that six π-electrons (called "*aromatic sextets*") are located in these hexagons. These "*full*" hexagons are then expected to
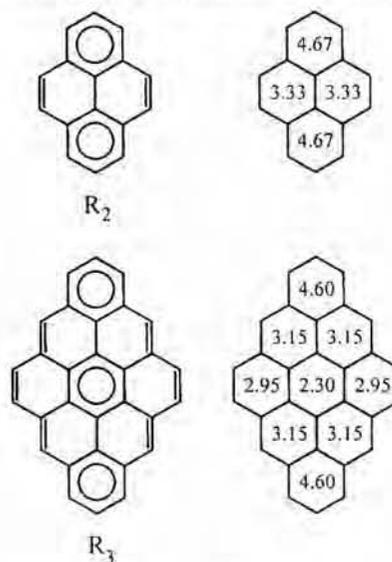

Fig. 1—Two benzenoid hydrocarbons with unique Clar aromatic sextet formulas (R_2 = pyrene, R_3 = benzo[bc,kl]coronene) and the distribution of their π-electrons computed according to the Randić-Balaban method. In the case of R_2 Clar theory is satisfied: the two "full" hexagons have higher π-electron contents than the two "empty" hexagons. In the case of the central "full" hexagon of R_3 Clar theory is violated, since the π-electron content of that hexagon is smaller than the π-electron contents of any of the six "empty" hexagons.

have significantly greater π-electron content than the other hexagons that in the jargon of theoretical chemistry are referred to as "*empty*". [The latter hexagons are, of course, not really empty, and their π-electron content is certainly much greater than zero.] Two characteristic examples are shown in Fig. 1 revealing that the predictions of Clar theory may, but need not agree with the π-electron distribution estimated on the basis of the Randić-Balaban method.

In view of the results shown in Fig. 1, we have undertaken a systematic study of the π-electron distribution in rhombus-shaped benzenoid hydrocarbons whose first members are R_1 = benzene, R_2 = pyrene, R_3 = dibenzo[*bc,kl*]coronene, and whose general member R_a is depicted in Fig. 2.

The rhombus-shaped benzenoids were chosen because they have a unique Clar formula. The Clar formula for R_a has a aromatic sextets, which means that this Clar formula may be viewed as representing 2^a distinct Kekulè structures[1,5]. On the other hand, it is known for a long time[18] that R_a has a total of $\binom{2a}{a}$ Kekulè structures. Because $\binom{2a}{a}$ is much larger than 2^a (Table 1), we conclude that the Clar formula of R_a represents only an insignificant fraction of its Kekulè structures. Consequently, the Clar-theory-based π-electron distribution in rhombus-shaped benzenoids is unlikely to be a realistic one. Indeed, we have found that this π-electron distribution is quite different from what would be predicted on the basis of Clar theory.
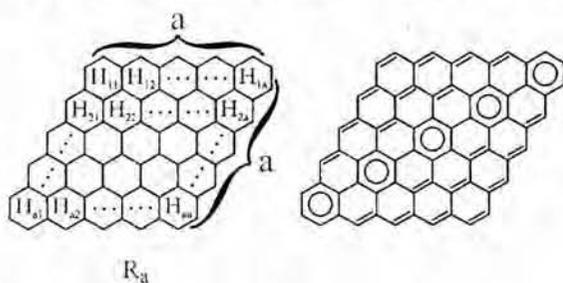

Fig. 2—The general member R_a of the homologous series of rhombus-shaped benzenoid hydrocarbons, and the labelling of its hexagons. The right-hand side diagram is the (unique) Clar formula of R_a. Recall that R_1 = benzene, R_2 = pyrene, R_3 = benzo[*bc,kl*]coronene. The *peak hexagons* of R_a are H_{1a} and H_{a1}. The other hexagons adjacent to the perimeter of R_a are referred to as its *boundary hexagons*; those not adjacent to the perimeter are the *internal hexagons*. In the unique Clar formula of R_a, the hexagons H_{1a}, $H_{2,a-1}$, $H_{3,a-2}$, ..., $H_{a-1,2}$ and H_{a1} are "full" whereas all others are "empty".

Numerical studies

π-Electron contents were calculated for all hexagons of the rhombus-shaped benzenoid systems R_a for a=2,3,...,10. The EC-values of R_2 and R_3 are depicted in Fig. 1. As a characteristic example, the EC-values of all hexagons of R_8 are given in Table 2. Analogous results for other values of a; can be obtained from the authors upon request.

The first thing that is noticed by inspection of the data in Table 2 is that all EC-values, except $EC(H_{18})$ and $EC(H_{81})$, i.e. except the π-electron contents of the peak hexagons, are decimal numbers whose values are remarkably close to integers. Boundary hexagons, except the peak ones, have EC-values very close to 3, whereas the EC-values of all internal hexagons are very close to 2.

From our numerical data, it is fully obvious that in the limit $a \to \infty$, EC=3 for all boundary non-peak hexagons and EC=2 for all internal hexagons. This is illustrated in Fig. 3.

For the peak hexagons of R_a, we have found that:

$$EC = 4 + \frac{2a}{4a-2}$$

whose limit value is equal to 4.5 .

According to the Clar formula of R_a (Fig. 2), the π-electron content of the "full" hexagons H_{1a}, $H_{2,a-1}$, $H_{3,a-2}$...., $H_{a-1,2}$ and H_{a1} should exceed the π-electron contents of the other "empty" hexagons. This certainly happens in the case of H_{1a} and H_{a1} (whose EC-values are greater than 4.5). If a>2, all "full" hexagons other than H_{1a} and H_{a1} have π-electron contents around 2 which is significantly less than the π-electron contents of the boundary "empty" hexagons (which

Table 1—The number K of Kekulè structures of the rhombus-shaped benzenoid hydrocarbons R_a and the fraction f of Kekulè structures that are represented by the unique Clar formula of R_a. As explained in the text, $K = \binom{2a}{a}$ and $f = 2^a \binom{2a}{a}^{-1} \cdot 100$

a	K	f (%)
1	2	100.00
2	6	66.67
3	20	40.00
4	70	22.86
5	252	12.70
6	894	7.16
7	3432	3.73
8	12870	1.99
9	48620	1.05
10	149226	0.69

Table 2—The electron contents of the hexagons H_{ij} of the rhombus-shaped benzenoid molecule R_8. The labelling of the hexagons is same as indicated in Fig. 2

| i	j=1	j=2	j=3	j=4	j=5	j=6	j=7	j=8
1	2.9964	2.9882	2.9730	2.9534	2.9436	2.9795	3.1333	4.5333
2	2.9882	1.9733	1.9602	1.9646	2.0037	2.0821	2.1642	3.1333
3	2.9730	1.9602	1.9695	2.0087	2.0653	2.1044	2.0821	2.9795
4	2.9534	1.9646	2.0087	2.0609	2.0870	2.0653	2.0037	2.9436
5	2.9436	2.0037	2.0653	2.0870	2.0609	2.0087	1.9646	2.9534
6	2.9795	2.0821	2.1044	2.0653	2.0087	1.9695	1.9602	2.9730
7	3.1333	2.1642	2.0821	2.0037	1.9646	1.9602	1.9733	2.9882
8	4.5333	3.1333	2.9795	2.9436	2.9534	2.9730	2.9882	2.9964
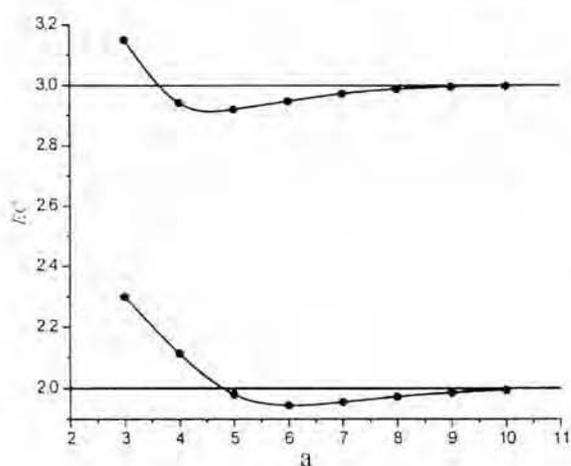
Fig. 3—Dependence of the π-electron contents of the hexagons H_{12} and H_{22} of R_a on the parameter a, $a \geq 3$. Note that H_{12} is a boundary, whereas H_{22} an internal hexagon. As $a \to \infty$, the two curves asymptotically approach the values 3 and 2, respectively.

are around 3). Thus, in all rhombus-shaped benzenoids R_a ($a>2$), the internal "full" hexagons violate the predictions of Clar theory.

It should, nevertheless, be noted that if a "full" hexagon is adjacent only to internal "empty" hexagons, then the EC-value of the "full" hexagon is slightly greater than the EC-value of any of its "empty" neighbours. Examples for this are given in Table 2. As another example may serve the EC-value of the "full" hexagon H_{38} in R_{10} (equal to 2.0929), which should be compared with the π-electron contents 2.0077, 2.0774, 2.0774, 2.0077, 2.0580, and 2.0580 of its six "empty" neighbours. This effect, although formally in harmony with Clar theory, is negligibly small and chemically insignificant.

Conclusions

Numerous previously studied examples imply that the distribution of π-electrons into rings of benzenoid hydrocarbons is highly non-uniform[2-10,12,13,15]. Such a

non-uniformity is now found to occur also in the case of rhombus-shaped benzenoids.

The greatest π-electron content is in the two peak hexagons each containing around 4.5 electrons. In the other boundary hexagons, there are around 3 π-electrons. Internal hexagons contain around 2 π-electrons each. This kind of electron distribution is found in all members of the rhombus-shaped homologous series R_a, $a \geq 3$, and varies very little with the actual position of the hexagon within the molecule and with the parameter a.

This kind of electron distribution contradicts the inferences made on the basis of the Clar aromatic sextet theory[16,17]. Therefore, in the case of rhombus-shaped benzenoids, Clar theory is found to be inadequate. The reason for this should be sought in the fact that the Clar structure of R_a represents only a minute fraction of the total number of Kekulé structures, as shown by Table 1.

In some benzenoid systems, the distribution of π-electrons into rings was found to exhibit certain uniformity[11,14]. Also in the case of rhombus-shaped benzenoids, we encounter a novel kind of uniformity:

The distribution of the π-electrons into boundary hexagons (except the two peak hexagons) is nearly uniform, each such hexagon containing around 3 electrons. Analogously, also the distribution of the π-electrons into the internal hexagons is nearly uniform, each such hexagons (no matter whether it is "full" or "empty") containing around 2 electrons. In the limit $a \to \infty$, the small deviations from uniformity completely vanish.

The present investigations reveal certain concealed and hitherto unnoticed peculiarities in the π-electron properties of a class of benzenoid hydrocarbons. Our findings may serve as another example for the ability of chemical graph theory to deduce non-trivial and chemically relevant results[19].

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