Equivalence of Two Models for Partitioning of π-Electrons in Rings of Benzenoid Hydrocarbons

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Two recently proposed methods for assessing the π-electron contents of rings of benzenoid hydrocarbons are shown to be equivalent.

Key words: Electron Distribution; Electron Content (of Ring); Clar Theory; Kekulé Structures; Benzenoid Hydrocarbons.

1. Introduction

Kekulé structures belong to the classical concepts of theoretical chemistry of polycyclic conjugated molecules and, in particular, of benzenoid hydrocarbons [1 – 3]. Nevertheless, it was only quite recently recognized [4] that in addition to the standard representation of a Kekulé structure (in which the locations of the double bonds are indicated), also an "algebraic" representation is possible. For a given Kekulé structure k of a polycyclic conjugated molecule consisting of rings $R_1, R_2, \ldots, R_h$, its algebraic representation is constructed by inscribing a number $EC(k|R_j)$ into the ring R_j for $j = 1, 2, \ldots, h$. These numbers count the π-electrons which (in the Kekulé structure k) belong to the respective rings.

Let b be a carbon-carbon bond belonging to the ring R. Then its contribution to the π-electron content of R (in the Kekulé structure k) is determined by the following rules:

(1) If b is a double bond of the Kekulé structure k, and if it belongs solely to the ring R, then it contributes two π-electrons to R.

(2) If b is a double bond of the Kekulé structure k, and if it is shared by R and another ring, then it contributes one π-electron to R.

(3) If b is a single bond of the Kekulé structure k, then it does not contribute π-electrons to R.

The quantity $EC(k|R)$ is the sum of the above specified contributions over all bonds b that belong to the ring
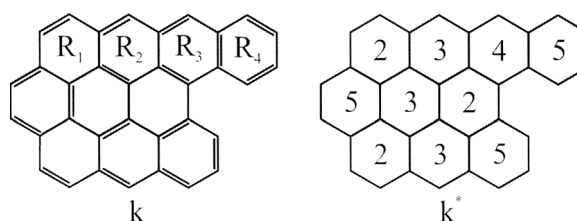

Fig. 1. An ordinary Kekulé structure (k) and its algebraic representation (k^*). There is only one double bond in the ring R_1, and it is not shared by other rings; therefore $EC(k|R_1) = 2$. The ring R_2 has two double bonds, one of which is shared by R_2 and another ring; therefore $EC(k|R_2) = 2 + 1 = 3$. The ring R_3 has three double bonds, one of which belongs solely to R_3 whereas two are shared by R_3 and another ring; therefore $EC(k|R_3) = 2 + 2 \times 1 = 4$. The ring R_4 has also three double bonds, but only one is shared; therefore $EC(k|R_4) = 2 \times 2 + 1 = 5$.

R. It can be viewed as the "π-electron content" of the ring R in the Kekulé structure k.

An example illustrating the construction of the algebraic Kekulé structure is given in Figure 1.

For the majority of benzenoid hydrocarbons there is a one-to-one correspondence between the ordinary and the algebraic Kekulé structures [5].

Randić and Balaban [6, 7] proposed to assess the distribution of π-electrons in rings of polycyclic conjugated molecules by taking the arithmetic average of the π-electron contents of the respective rings over all Kekulé structures. This method for partitioning of π-electrons in rings was eventually elaborated and applied to numerous classes of benzenoid molecules; for details and additional references see [8 – 12].
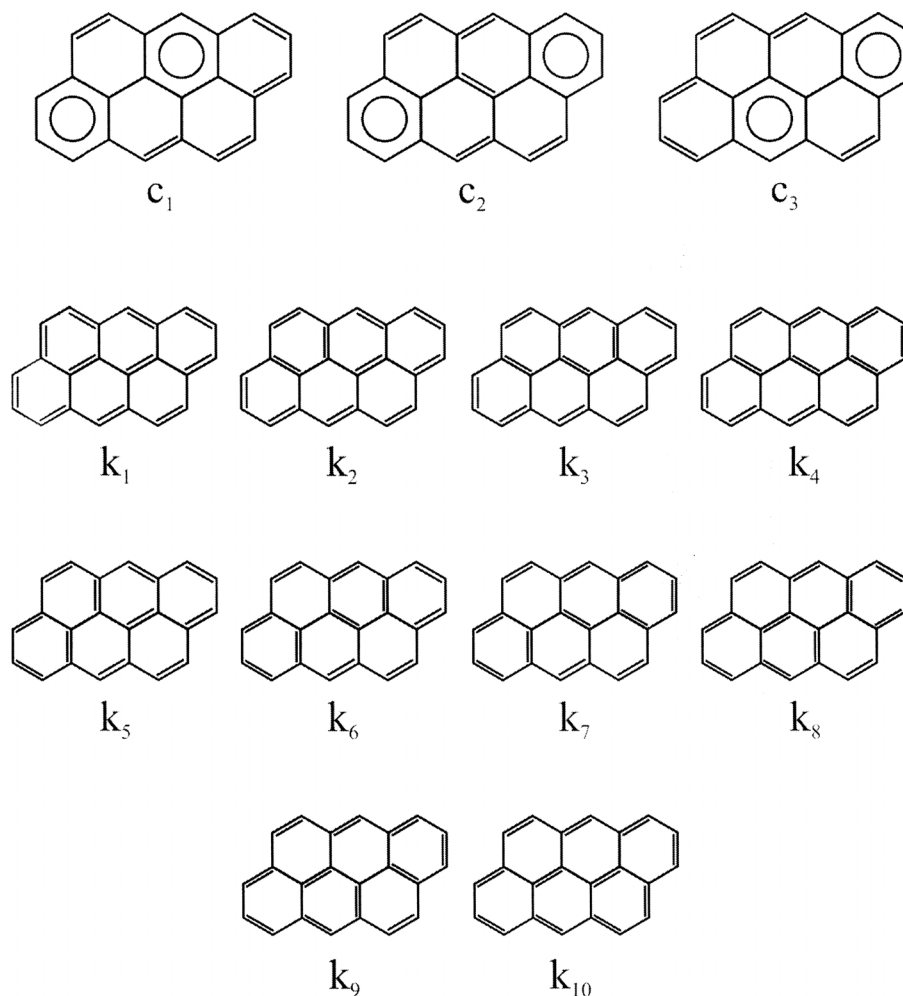
Fig. 2. The Clar (c) and Kekulé (k) structures of anthanthrene. Each Clar formula (c_1, c_2, c_3) possesses $\gamma = 2$ aromatic sextets. Each Clar formula can be viewed as representing $2^\gamma = 4$ Kekulé structures. For instance, c_1 would be the joint representation of the Kekulé structures k_2, k_3, k_5, and k_6, or symbolically, $\mathcal{K}(c_1) = \{k_2, k_3, k_5, k_6\}$; for details see text.

Suppose that a conjugated molecule has K Kekulé structures, $k_1, k_2, \ldots, k_K$. Then, according to the original Randić-Balaban model [6, 7], the π-electron content of the ring R is computed as

$$EC(R) = \frac{1}{K} \sum_{i=1}^{K} EC(k_i|R). \qquad (1)$$

In (1) it is assumed that all Kekulé structures are equally important, as far as the π-electron distribution is concerned. Such an assumption, that evidently was made for the sake of simplicity, is far from being satisfactory. Therefore several modified approaches to the π-electron content of rings were put forward [12–16].

2. Modified π-Electron Contents of Rings of Benzenoid Molecules

It is straightforward to generalize (1) by giving each Kekulé structure a certain weight w:

$$EC_w(R) = \frac{\sum\limits_{i=1}^{K} w_i EC(k_i|R)}{\sum\limits_{i=1}^{K} w_i}. \qquad (2)$$

Evidently, for $w_1 = w_2 = \cdots = w_K$, (2) reduces to (1).

By choosing appropriate weights for the Kekulé structures one may hope to arrive at electron contents

that agree better with the experiment [17] than the original EC-values. Two such weighting procedures were recently proposed by Randić and Balaban [12], applicable to benzenoid hydrocarbons.

According to [12], one considers the Clar aromatic sextet formulas of the underlying benzenoid molecule; for details on the Clar aromatic sextet theory see [2, 3, 18, 19]. In Fig. 2 the Clar formulas of anthanthrene are shown.

Consider a benzenoid system B having $C = C(B)$ Clar aromatic sextet formulas, $c_1, c_2, \ldots, c_C$. Each of these formulas possesses an equal number of aromatic sextets, denoted by $\gamma = \gamma(B)$ (and usually called "the Clar number" of B).

Each aromatic sextet in a Clar formula may be viewed as representing two different arrangements of three double bonds. Consequently, if a Clar formula c_j possesses γ aromatic sextets, then it could be viewed as representing 2^γ distinct Kekulé structures of the corresponding benzenoid molecule. The set of Kekulé structures represented by a Clar formula c_j will be denoted by $\mathcal{K}(c_j)$.

For instance, in the case of anthanthrene (see Fig. 2),

$$\mathcal{K}(c_1) = \{k_2, k_3, k_5, k_6\},$$
$$\mathcal{K}(c_2) = \{k_3, k_4, k_6, k_7\},$$
$$\mathcal{K}(c_3) = \{k_6, k_7, k_8, k_9\}.$$

Note that there may exist Kekulé structures that do not belong to any of the sets $\mathcal{K}(c_j)$, $j = 1, 2, \ldots, C$. (In the case of anthanthrene, such are k_1 and k_{10}.) On the other hand, some Kekulé structures may be contained in several sets $\mathcal{K}(c_j)$. (In the case of anthanthrene, such are k_3, k_6, and k_7.)

The two models for the calculation of the π-electron content of the rings of benzenoid hydrocarbons, put forward in [12], are in fact special cases of (2) if the Kekulé structures are weighted in the following manner:

Model 1: $w_i = 1$ if the Kekulé structure k_i is contained in at least one of the sets $\mathcal{K}(c_j)$, $j = 1, 2, \ldots, C$, and $w_i = 0$ if it is not contained in any of the sets $\mathcal{K}(c_j)$, $j = 1, 2, \ldots, C$.

Model 2: w_i is equal to the number of times the Kekulé structure k_i occurs in the sets $\mathcal{K}(c_j)$, $j = 1, 2, \ldots, C$.

For instance, in the case of anthanthrene (see Fig. 2) we would have in Model 1: $w_2 = w_3 = w_4 = w_5 = w_6 = w_7 = w_8 = w_9 = 1$ and $w_1 = w_{10} = 0$, whereas

in Model 2: $w_1 = w_{10} = 0$, $w_2 = w_4 = w_5 = w_8 = w_9 = 1$, $w_3 = w_7 = 2$, and $w_6 = 3$. Needless to say that the Models 1 and 2 result in π-electron contents different from what would be obtained by means of the original Randić-Balaban method, (equation (1) [6, 7]).

In order to avoid misunderstanding: In [12] the Models 1 and 2 were described by words and examples. The above statement for these models, via (2) and by specifying the weights of the Kekulé structures, is given here for the first time.

A seemingly different method for assessing the π-electron content of rings in benzenoid hydrocarbons was proposed in [14, 15]. This method considers only Clar formulas and proceeds as follows:

In analogy with the "algebraic Kekulé structures", for a given Clar formula c of a benzenoid molecule consisting of rings $R_1, R_2, \ldots, R_h$, we inscribe a number $EC^*(c|R_j)$ into the ring R_j for $j = 1, 2, \ldots, h$.

Let b be a carbon-carbon bond belonging to the ring R. Then its contribution to the π-electron content of R (in the Clar formula c) is determined by the following rules:

(1*) If b is a double bond of the Clar formula c, and if it belongs solely to the ring R, then it contributes two π-electrons to R.

(2*) If b is a double bond of the Clar formula c, and if it is shared by R and another ring, then it contributes one π-electron to R.

(3*) If b is a single bond of the Clar formula c, then it does not contribute π-electrons to R.

(4*) If b belongs to an aromatic sextet of the Clar formula c, and if b belongs solely to the ring R, then it contributes one π-electron to R.

(5*) If b belongs to an aromatic sextet of the Clar formula c, and if it is shared by R and another ring, then it contributes 0.5 π-electrons to R.

The quantity $EC^*(c|R)$ is the sum of the above specified contributions over all bonds b that belong to the ring R.

One should note the full analogy between the above points (1*)–(3*) and the rules (1)–(3) by which the algebraic Kekulé structures are constructed.

An example illustrating the construction of the above specified "algebraic" Clar formulas is given in Figure 3.
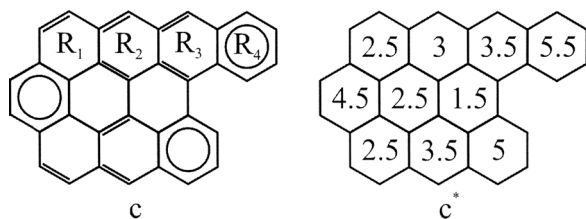
Fig. 3. An ordinary Clar formula (c) and its algebraic representation (c^*). In the ring R_1 there is one double bond, not shared by other rings, and a bond belonging to an aromatic sextet; therefore $EC^*(c|R_1) = 2 + 0.5 = 2.5$. The ring R_2 has two double bonds, one of which is shared by R_2 and another ring; therefore $EC(c|R_2) = 2 + 1 = 3$. The ring R_3 has two double bonds, one of which belongs solely to R_3 and one is shared by R_3 and another ring, and a bond belonging to an aromatic sextet; therefore $EC(c|R_3) = 2 + 1 + 0.5 = 3.5$. An aromatic sextet is located in the ring R_4, which shares only one bond with another ring; therefore $EC(c|R_4) = 5 \times 1 + 0.5 = 5.5$.

Model 2*: In analogy to (1), the π-electron content of the ring R is computed by means of the formula

$$EC_2^*(R) = \frac{1}{C} \sum_{j=1}^{C} EC^*(c_j|R). \tag{3}$$

3. Models 2 and 2* Are Equivalent

We now demonstrate that, in spite of their apparent formal differences, Models 2 and 2* are equivalent. In order to do this, bearing in mind the way in which the weighting of the Kekulé structures is achieved, we express the π-electron contents of Model 2 as

$$EC_2(R) = \frac{1}{C \cdot 2^\gamma} \sum_{j=1}^{C} \sum_{k \in \mathcal{K}(c_j)} EC(k|R). \tag{4}$$

Recall that the total number of Kekulé structures that need to be considered in Model 2 is $C \cdot |\mathcal{K}(c)| = c \cdot 2^\gamma$.

From (4) we get

$$EC_2(R) = \frac{1}{C} \sum_{j=1}^{C} \left[\frac{1}{2^\gamma} \sum_{k \in \mathcal{K}(c_j)} EC(k|R) \right], \tag{5}$$

and in view of (3) it is sufficient to show that

$$\frac{1}{2^\gamma} \sum_{k \in \mathcal{K}(c_j)} EC(k|R) = EC^*(c_j|R). \tag{6}$$

Let b be a carbon-carbon bond of a benzenoid molecule B belonging to a ring R of B. We examine a particular Clar formula c_j of B. We have to distinguish between three cases:

Case (a): b is a single bond in the Clar formula c_j. Thus b does not belong to an aromatic sextet of c_j.

If so, then b is single also in all Kekulé structures k, $k \in \mathcal{K}(c_j)$.

Consequently the contribution of b to $EC^*(c_j|R)$ is zero, and its contribution is zero also to any $EC(k|R)$, $k \in \mathcal{K}(c_j)$.

Case (b): b is a double bond in the Clar formula c_j. Thus b does not belong to an aromatic sextet of c_j.

If so, then b is double also in all 2^γ Kekulé structures k, $k \in \mathcal{K}(c_j)$.

Consequently, if b belongs solely to R, then its contribution to $EC^*(c_j|R)$ is two, and it contributes two also to any $EC(k|R)$, $k \in \mathcal{K}(c_j)$. Therefore its contribution to the left-hand side of (6) is two. If, on the other hand, b is shared by R and another ring, then its contribution to $EC^*(c_j|R)$ is one, and it contributes one also to any $EC(k|R)$, $k \in \mathcal{K}(c_j)$. Therefore its contribution to the left-hand side of (6) is one.

Case (c): b belongs to an aromatic sextet of c_j.

If so, then b is a double bond in half of the 2^γ Kekulé structures from $\mathcal{K}(c_j)$, and a single bond in the other half of the members of $\mathcal{K}(c_j)$. Therefore its contribution to the left-hand side of (6) is $(2+0)/2 = 1$ if b belongs solely to R, and $(1+0)/2 = 1/2$ if b is shared by R and another ring. This is exactly the same as the contribution of b to $EC^*(c_j|R)$.

By this, all possible cases have been exhausted, and in each of them we found that the contribution of any carbon-carbon bond to the left-hand side of (6) is equal to the contribution of the same bond to the right-hand side of (6). Therefore the equality (6) holds. Consequently – in view of (3) and (5) – we conclude that $EC_2(R) = EC_2^*(R)$, i.e., that the Models 2 and 2* are equivalent.

Model 2 requires the examination of $C \cdot 2^\gamma$ Kekulé structures, whereas in Model 2* only C Clar formulas need to be considered. For instance, in order to assess the π-electron content of the rings of anthanthrene, by using Model 2 one would have to construct 12 algebraic Kekulé structures (as in Fig. 1), whereas by using Model 2* only 3 algebraic Clar structures would be required (as in Fig. 3).

Bearing this in mind, it is obvious that Model 2* is more suitable than Model 2 for studying the distribution of π-electrons in benzenoid molecules. Several such studies, based on Model 2*, have already been reported [14, 15].

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