

## DEPENDENCE OF HESS–SCHAAD RESONANCE ENERGY ON KEKULÉ STRUCTURES

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ABSTRACT. The Hess–Schaad resonance energy is defined as  $RE = E - E^{ref}$  where  $E$  is the total  $\pi$ -electron energy and  $E^{ref}$  is the reference energy computed by adding double- and single-bond contributions pertaining to some Kekulé structure. Therefore  $RE$  depends on the Kekulé structure considered. We show that in the case of benzenoid molecules the number of only one double-bond type determines  $RE$ . Furthermore,  $RE$  is a monotonically increasing function of the number of double bonds of type 3–3 or 2–2, and a monotonically decreasing function of the number of double bonds of type 2–3. This implies that  $RE$  is maximal if the respective Kekulé structure has the greatest possible number of double bonds of type 3–3, or the greatest possible number of double bonds of type 2–2, or the smallest possible number of double bonds of type 2–3.

### INTRODUCTION

In the 1970s Hess and Schaad invented a method for calculating reliable resonance energies within the Hückel molecular orbital (HMO) approximation [1,2]. Eventually, these “*Hess–Schaad resonance energies*” found numerous chemical applications whose details are found in the reviews [3–6] and books [7,8]. The Hess–Schaad resonance energy is a variant of the Dewar resonance energy [9,10], adjusted to the HMO model. Therefore, it is often referred to as “*Dewar resonance energy*”. (Recall that Dewar-type resonance energies are constructed so as to assume zero or near-zero values for acyclic conjugated molecules.)

The Hess–Schaad resonance energy is defined as

$$RE = E - E^{ref} \quad (1)$$

where  $E$  is the HMO total  $\pi$ -electron energy [11,12] and  $E^{ref}$  is the reference energy. This reference energy is an additive function of bond increments  $E_{ij}$ , such that

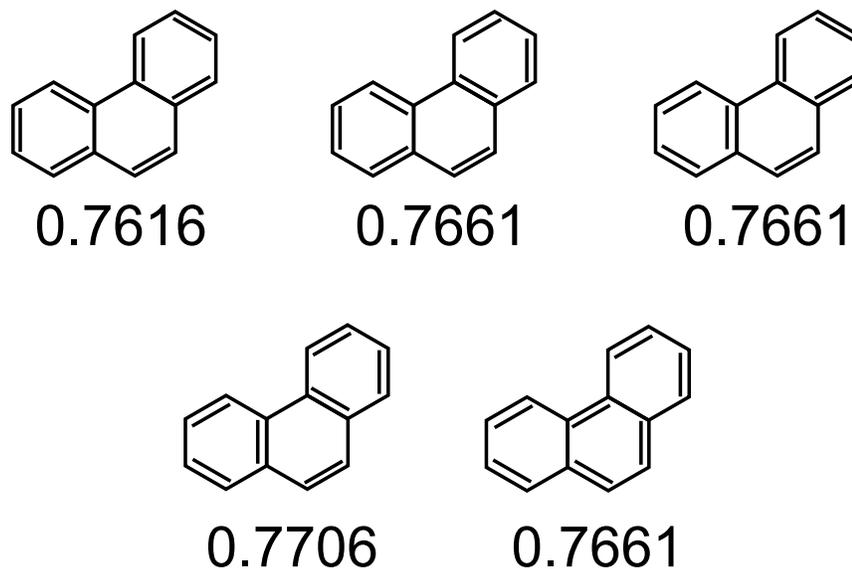
$$E^{ref} = \sum_{ij} E_{ij} \quad (2)$$

with the summation going over all conjugated bonds  $ij$  of a chosen Kekulé structure of the underlying conjugated molecule. In the case of benzenoid hydrocarbons only the following six bond increments are needed [1,2]:

$$\begin{aligned} E_{ij} &= 2.0699 && \text{for a HC=CH bond} \\ E_{ij} &= 2.1083 && \text{for a HC=C bond} \\ E_{ij} &= 2.1716 && \text{for a C=C bond} \\ E_{ij} &= 0.4660 && \text{for a HC-CH bond} \\ E_{ij} &= 0.4362 && \text{for a HC-C bond} \\ E_{ij} &= 0.4358 && \text{for a C-C bond .} \end{aligned}$$

From the above definition follows that the actual value of  $RE$  depends on the choice of the Kekulé structure used for its calculation. Hess and Schaad were aware of this shortcoming [1] and their  $RE$ -values were averaged over all Kekulé structures. Such an averaging makes the application of the Hess–Schaad resonance energy model much more difficult than it looks from the simple expressions (1) and (2). Anyway, the difficulties connected with the dependence of  $RE$  on Kekulé structures are not mentioned in the most recent surveys on this matter [5,6].

In Fig. 1 are depicted the five Kekulé structures of anthracene together with the respective  $RE$ -values. In this case, as well as for all other benzenoid hydrocarbons studied, the greatest differences between the  $RE$ -values are of the order 0.01  $\beta$  units, which cannot be considered as negligibly small [11,12].



**Figure 1.** The five Kekulé structures of anthracene and the respective Hess–Schaad resonance energies. The maximum  $RE$ -value ( $= 0.7704$ ) is for the Kekulé structure with 4 double bonds of type 2–2, two double bonds of type 3–3 and no double bond of type 2–3. The minimum  $RE$ -value ( $= 0.7616$ ) is for the Kekulé structure with only 3 double bonds of type 2–2, no double bond of type 3–3, but 4 double bonds of type 2–3. This illustrates the general rule that maximum (resp. minimum)  $RE$  is attained for the Kekulé structure(s) with maximum (resp. minimum) number of double bonds of type 2–2, maximum (resp. minimum) number of double bonds of type 3–3, and minimum (resp. maximum) number of double bonds of type 2–3.

## BOND TYPES IN KEKULÉ STRUCTURES OF BENZENOID HYDROCARBONS

In benzenoid hydrocarbons there are carbon–carbon bonds to which 2, 1, and 0 hydrogen atoms are attached [13,14]. These will be referred to as bonds of type 2–2, 2–3, and 3–3, respectively. (Recall that a bond of type  $i$ – $j$  corresponds to an edge of the molecular graph, connecting a vertex of degree  $i$  with a vertex of degree  $j$  [14].) Therefore, in the Kekulé structures of a benzenoid hydrocarbon there may

exist double bonds of type 2–2, 2–3, and 3–3, and single bonds of type 2–2, 2–3, and 3–3.

Denote the number of bonds of type  $i$ – $j$  (in the benzenoid hydrocarbon considered) by  $m_{ij}$ . Denote the number of double bonds of type  $i$ – $j$  (in a particular Kekulé structure of the benzenoid hydrocarbon considered) by  $n_{ij}$ . Note that the number of single bonds of type  $i$ – $j$  in the same Kekulé structure is then  $m_{ij} - n_{ij}$ .

In the theory of benzenoid systems it is known [13] that the numbers  $m_{ij}$  satisfy the following relations:

$$m_{22} = b + 6 \quad (3)$$

$$m_{23} = 4h - 2n_i - 2b - 4 \quad (4)$$

$$m_{33} = h + n_i + b - 1 \quad (5)$$

where  $h$  is the number of hexagons,  $n_i$  the number of internal carbon atoms, and  $b$  the number of bays [13]. Bearing these relations in mind we may express the Hess–Schaad resonance energy as

$$\begin{aligned} RE = E & - [2.0699 n_{22} + 0.4660 (b + 6 - n_{22}) \\ & + 2.1083 n_{23} + 0.4362 (4h - 2n_i - 2b - 4 - n_{23}) \\ & + 2.1716 n_{33} + 0.4358 (h + n_i + b - 1 - n_{33})] . \end{aligned} \quad (6)$$

The parameters  $n_{22}$ ,  $n_{23}$ , and  $n_{33}$  are related as follows.

In any Kekulé structure each carbon atom is incident to exactly one double bond. Therefore, since each double bond is incident to two carbon atoms, two times the number of double bonds, i. e.,  $2(n_{22} + n_{23} + n_{33})$ , is equal to the number  $n$  of carbon atoms. On the other hand [13,14],  $n = 4h + 2 - n_i$ . Therefore,

$$n_{22} + n_{23} + n_{33} = 2h - \frac{1}{2}n_i + 1 . \quad (7)$$

Each double bond of the type 2–3 is incident to one tertiary carbon atom (i. e., carbon atom having three carbon–atom neighbors, i. e., carbon atom to which no hydrogen is attached). Each double bond of the type 3–3 is incident to two tertiary carbon atoms. Therefore, the total number of tertiary carbon atoms is equal to

$n_{23} + 2n_{33}$ . On the other hand, the number of tertiary carbon atoms in a benzenoid hydrocarbon is known [13] to be equal to  $2(h - 1)$ . Therefore,

$$n_{23} + 2n_{33} = 2h - 2 . \quad (8)$$

Because of the relations (7) and (8), only one of the parameters  $n_{22}$ ,  $n_{23}$ , and  $n_{33}$  can be independently varied. In other words, if in a given Kekulé structure one of the parameters  $n_{22}$ ,  $n_{23}$ , and  $n_{33}$  attains a fixed value, then in that Kekulé structure also the other two parameters have a fixed value, as determined by (7) and (8).

### DEPENDENCE OF $RE$ ON KEKULÉ STRUCTURES

Combining formula (6) with the identities (7) and (8) we arrive at the following expressions for the Hess–Schaad resonance energy:

$$RE = E + 0.0045 n_{22} - 5.5248 h + 1.2408 n_i - 0.0294 b - 2.0964 \quad (9)$$

$$RE = E - 0.00225 n_{23} - 5.5203 h + 1.23855 n_i - 0.0294 b - 2.0874 \quad (10)$$

$$RE = E + 0.0045 n_{33} - 5.5248 h + 1.23855 n_i - 0.0294 b - 2.0829 . \quad (11)$$

From Eqs. (9)–(11) one immediately concludes:

- $RE$  is a monotonically increasing function of the number of double bonds of type 2–2.
- $RE$  is a monotonically decreasing function of the number of double bonds of type 2–3.
- $RE$  is a monotonically increasing function of the number of double bonds of type 3–3.
- $RE$  is maximum for those Kekulé structures that have a maximum number of double bonds of type 2–2.
- $RE$  is maximum for those Kekulé structures that have a minimum number of double bonds of type 2–3.
- $RE$  is maximum for those Kekulé structures that have a maximum number of double bonds of type 3–3.

- $RE$  is minimum for those Kekulé structures that have a minimum number of double bonds of type 2–2.
- $RE$  is minimum for those Kekulé structures that have a maximum number of double bonds of type 2–2.
- $RE$  is minimum for those Kekulé structures that have a minimum number of double bonds of type 3–3.

In Kekulé structures of benzenoid hydrocarbons it is always easier to count and classify the double bonds than the single bonds. If, nevertheless, one prefers to reformulate the above rules in terms of single bonds, then these read as follows:

- $RE$  is a monotonically decreasing function of the number of single bonds of type 2–2.
- $RE$  is a monotonically increasing function of the number of single bonds of type 2–3.
- $RE$  is a monotonically decreasing function of the number of single bonds of type 3–3.
- $RE$  is maximum for those Kekulé structures that have a minimum number of single bonds of type 2–2.
- $RE$  is maximum for those Kekulé structures that have a maximum number of single bonds of type 2–3.
- $RE$  is maximum for those Kekulé structures that have a minimum number of single bonds of type 3–3.
- $RE$  is minimum for those Kekulé structures that have a maximum number of single bonds of type 2–2.
- $RE$  is minimum for those Kekulé structures that have a minimum number of single bonds of type 2–2.
- $RE$  is minimum for those Kekulé structures that have a maximum number of single bonds of type 3–3.

It deserves to note that in Eqs. (9)–(11) the numerical value of the multipliers associated with the terms  $n_{ij}$  is relatively small. As a consequence of this, the Hess–Schaad resonance energies (of benzenoid hydrocarbons, at least) do not vary much when the Kekulé structure chosen for their calculation is changed. Yet, these variations can exceed 0.01  $\beta$  units, which is around the limit of accuracy of the HMO model [11,12,15].

In our recent studies of resonance energy [16–19] we computed  $RE$  for Fries–type Kekulé structures, for which  $n_{33}$  is maximal, and therefore also  $RE$  is maximal.

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