

## A new theoretical approach to the empirical resonance energies of the aromatic hydrocarbons

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**Abstract.** In the framework of the Hückel MO approximation, the differences in total binding energy between a given molecule and the corresponding distorted Kekulé-type structure are calculated for a variety of benzenoid hydrocarbons. The total binding energy is assumed to be given by the sum of the  $\pi$ -electron and  $\sigma$ -electron binding energies. It is shown that there is a good linear relationship between the calculated differences in total binding energy and the  $\pi$ -electron delocalization energies (DE) as obtained by using the simple Hückel MO method. This provides a physical basis for the use of the  $\pi$ -electron DE as a theoretical index to the empirical resonance energy (RE). Further, by examining the changes in  $\pi$ -electron binding energy between a given molecule and the corresponding distorted Kekulé-type structure, it is concluded that in benzenoid hydrocarbons the main contributor to the RE is not the  $\pi$ -electron DE but the compressional energy of  $\sigma$  bonds.

**Key words:** Delocalization energy – Resonance energy – Compressional energy of  $\sigma$  bonds

### 1. Introduction

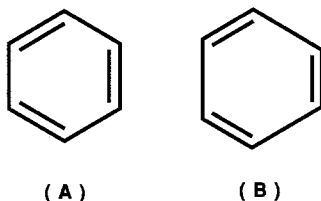
In most of the textbooks of quantum chemistry [1], it is remarked that in benzenoid hydrocarbons, there exists an excellent correlation between the  $\pi$ -electron delocalization energies (DE) as calculated by using the simple Hückel MO method and the empirical resonance energies (RE) as obtained from the difference in heat of formation or hydrogenation between a given molecule and the corresponding Kekulé-type structure. Thus, most of the chemists who had studied quantum chemistry have naturally come to believe that the thermodynamical stabilities of benzenoid hydrocarbons are entirely due to the  $\pi$ -electron delocalization.

Recently, the well-accepted concept mentioned above has been challenged by several authors [2–7]: especially Shaik et al. [3] have provided, using the *ab initio*

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SCF MO method, the computational evidence that the symmetrical hexagonal structure of benzene is driven by the  $\sigma$  framework alone, the  $\pi$ -electron system favoring a bond-alternating and distorted Kekulé structure.

It should be remembered that in calculating the DE value of a given molecule, the reference Kekulé-type structure is assumed to have the same geometrical structure as the molecule in question. For example, the Kekulé structure for benzene is assumed to have the symmetrical hexagonal arrangement of C atoms, all the lengths of CC bonds being taken to be the same as that of benzene (A). On the other hand, in obtaining the RE value of benzene by using, for example, the heats of hydrogenation, the heat of hydrogenation of the Kekulé structure is assumed to be given by three times that of *cis*-2-butene.<sup>1</sup> Therefore, in this case the Kekulé structure is considered to be composed of three nearly pure CC double bonds linked with three nearly pure single bonds and hence has a distorted arrangement of C atoms (B).



It is evident that an energy contribution from the compression of CC  $\sigma$  bonds should duly be taken into account in a theoretical index to be compared with the empirical RE.<sup>2</sup> Thus, the theoretical basis for the existence of a good correlation between the conventional  $\pi$ -electron DE values and the empirical RE values is no way clear, and the reason for the existence of the above apparent correlation should be explained. In this paper we are concerned with the total binding energy taken to be the sum of the  $\sigma$ -electron and  $\pi$ -electron binding energies. Our theoretical index to the empirical RE is the difference in total binding energy between a given molecule and the corresponding distorted localized Kekulé-type structure.

## 2. Method of calculation

In order to calculate the total binding energy of a conjugated hydrocarbon in a most unsophisticated way, we use the method in the framework of the Hückel MO approximation proposed by Longuet-Higgins and Salem [9]. The resonance integral  $\beta_i(r_i)$  for the *i*th CC bond is assumed to be an exponential function of the form:

$$\beta_i(r_i) = \beta_b \exp[a(r_b - r_i)] \quad (1)$$

<sup>1</sup> The empirical RE of benzene contains an energy contribution from changes in hybridization between the  $sp^2$ - $sp^3$  single bond in *cis*-2-butene and the  $sp^2$ - $sp^2$  single bond in the Kekulé structure [1a, 8]. In this paper, we do not consider this relatively minor factor.

<sup>2</sup> That the  $\sigma$ -bond compression energy plays an important part of the empirical RE of benzene has already been pointed out by Dewar [8, 1a]

where  $r_i$  is the length of the  $i$ th bond and  $\beta_b$  and  $r_b$  indicate the values in benzene. Further, the equilibrium bond length  $r_i$  is assumed to be related to the  $\pi$ -bond order  $p_i$  by the equation:

$$r_i = r_s - bp_i \quad (2)$$

where  $r_s$  is the length of the CC single bond. According to Longuet-Higgins and Salem, the total binding energy,  $E_{\text{tot}}$ , taken to be the sum of  $\sigma$ -electron and  $\pi$ -electron binding energies, is given simply by the equation:

$$E_{\text{tot}} = \frac{2}{ab} \sum_i \beta_i + \text{const.} \quad (3)$$

On the other hand, it is well known that the binding energy of  $\pi$  electrons,  $E_\pi$ , is given by:

$$E_\pi = \sum_i 2p_i \beta_i \quad (4)$$

It is noted that in order for benzene to keep the  $D_{6h}$  symmetry, the values of constants  $a$  and  $b$  must satisfy the following condition [10]:

$$ab \leq 1 \quad (5)$$

In this paper we use the values  $4.4/\text{\AA}$  for  $a$  [11] and  $0.186 \text{\AA}$  for  $b$ , together with  $r_s = 1.520 \text{\AA}$  [10].

### 3. Results and discussion

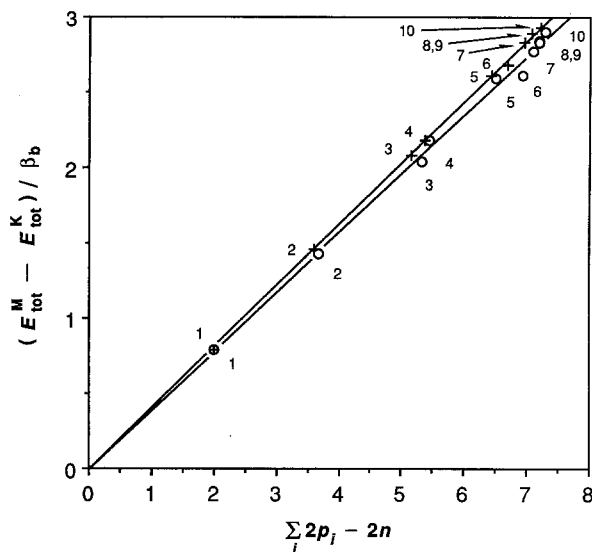
For a given benzenoid hydrocarbon, the total binding energy  $E_{\text{tot}}^{\text{M}}$  is calculated by using the bond lengths obtained from the simple Hückel  $\pi$ -bond orders by the use of Eq. (2). For a Kekulé-type structure by using  $r_s = 1.520 \text{\AA}$  and  $r_d = 1.344 \text{\AA}$ , we have  $\beta_s = 0.582 \beta_b$  and  $\beta_d = 1.319 \beta_b$  for the single and double bonds, respectively. For benzene, for example,  $E_{\text{tot}}^{\text{M}}$  and the total binding energy for the Kekulé structure,  $E_{\text{tot}}^{\text{K}}$ , are calculated to be  $14.727 \beta_b + \text{Const.}$  and  $13.940 \beta_b + \text{Const.}$ , respectively. We then have  $E_{\text{tot}}^{\text{M}} - E_{\text{tot}}^{\text{K}} = 0.787 \beta_b$ .

In Fig. 1 for various benzenoid hydrocarbons the  $(E_{\text{tot}}^{\text{M}} - E_{\text{tot}}^{\text{K}})/\beta_b$  values are plotted against the conventional  $\pi$ -electron DE values in units of  $\beta_0$ ,  $(\sum_i 2p_i - 2n)$ , where  $n$  is the number of double bond in a Kekulé-type structure,  $\beta_0$  being the resonance integral taken to be common not only to all the CC bonds in a molecule but also to all the double bonds in a Kekulé-type structure (see page 30). Figure 1 shows that there exists a good linear relationship between the two quantities. This is the reason that we can use, instead of  $(E_{\text{tot}}^{\text{M}} - E_{\text{tot}}^{\text{K}})$ , the  $\pi$ -electron DE as a theoretical index to the empirical RE. We have recently shown analytically that if we expand Eq. (1) in the power series of  $a(r_b - r_i)$  and neglect the terms higher than the first power, that is, if we assume  $\beta_i(r_i)$  to be a linear function of  $r_i$ , we obtain [12]:

$$E_{\text{tot}}^{\text{M}} - E_{\text{tot}}^{\text{K}} \propto \left( \sum_i 2p_i - 2n \right) \beta_0 \quad (6)$$

The present results indicate that the above approximation is reasonable in practice.

Strictly speaking, Eq. (3) is valid only for a conjugated molecule in which the CC bond lengths are optimized. Such being the case, we recalculated  $E_{\text{tot}}^{\text{M}}$  by the



**Fig. 1.** The correlation of the difference in total binding energy between a molecule and the corresponding distorted Kekulé-type structure,  $(E_{\text{tot}}^{\text{M}} - E_{\text{tot}}^{\text{K}})$ , with the conventional DE,  $(\sum 2p_i - 2n)\beta_0$ , for benzenoid hydrocarbons. The circles represent the  $(E_{\text{tot}}^{\text{M}} - E_{\text{tot}}^{\text{K}})/\beta_b$  values calculated by using the simple Hückel CC bond lengths and the crosses those calculated by using the optimized bond lengths.  
 1: Benzene, 2: naphthalene, 3: anthracene, 4: phenanthrene, 5: pyrene, 6: tetracene, 7: 1,2-benzanthracene, 8: 3,4-benzphenanthrene, 9: chrysene, 10: triphenylene

use of optimized bond lengths obtained by the repeated use of Eqs. (1) and (2). The newly calculated  $(E_{\text{tot}}^{\text{M}} - E_{\text{tot}}^{\text{K}})$  values are plotted against the  $\pi$ -electron DE values also in Fig. 1, the  $(\sum 2p_i - 2n)$  values being calculated by using the optimized bond orders in this case. There is a very good linear relationship between the two quantities, and the inclination of the newly obtained line is somewhat larger than that obtained above.

The inclinations of the  $(E_{\text{tot}}^{\text{M}} - E_{\text{tot}}^{\text{K}})/\beta_b$  versus  $(\sum 2p_i - 2n)$  lines are ca. 0.4. This leads to:

$$\beta_b \simeq 2.5 \beta_0 \quad (7)$$

This means that the  $\beta_b$  value determined so that the  $(E_{\text{tot}}^{\text{M}} - E_{\text{tot}}^{\text{K}})$  values may reproduce the empirical RE values is considerably larger than the  $\beta_0$  value determined so that the apparent theoretical index,  $(\sum 2p_i - 2n)$ , may reproduce the empirical RE.

We then examine the difference in  $\pi$ -electron binding energy, between a given molecule and the corresponding distorted Kekulé-type structure. The  $(E_{\pi}^{\text{M}} - E_{\pi}^{\text{K}})$  values calculated by using Eq. (4) are  $0.119 \beta_b$ ,  $0.205 \beta_b$ ,  $0.188 \beta_b$ ,  $0.401 \beta_b$  and  $0.145 \beta_b$  for benzene, naphthalene, anthracene, phenanthrene, and tetracene, respectively. The ratio  $(E_{\pi}^{\text{M}} - E_{\pi}^{\text{K}})/(E_{\text{tot}}^{\text{M}} - E_{\text{tot}}^{\text{K}})$  is then calculated to be 0.151 for benzene, 0.143 for naphthalene, 0.093 for anthracene, 0.184 for phenanthrene, and 0.055 for tetracene. This shows that in benzenoid hydrocarbons, the energy depression due to the  $\pi$ -electron delocalization from a localized, distorted Kekulé-type structure does not play an important part of  $(E_{\text{tot}}^{\text{M}} - E_{\text{tot}}^{\text{K}})$  and hence of RE.

The  $(E_{\pi}^{\text{M}} - E_{\pi}^{\text{K}})$  value depends sensitively on the value of parameter  $a$  used. In benzene, if we use the  $a$  Å values, 4.5, 4.6, 4.7 and 4.8, all of which satisfy Eq. (5), the  $(E_{\pi}^{\text{M}} - E_{\pi}^{\text{K}})$  values are calculated to be  $0.069 \beta_b$ ,  $0.020 \beta_b$ ,  $-0.030 \beta_b$  and  $-0.081 \beta_b$ , respectively. It turns out that if an  $a$  Å value larger than ca. 4.65 is used, the  $(E_{\pi}^{\text{M}} - E_{\pi}^{\text{K}})$  value becomes negative in unit of  $\beta_b$ . In such a case, the

$\pi$ -electron system favors the localized and distorted Kekulé structure, the  $D_{6h}$  benzene being brought about by the compression of  $\sigma$  bonds alone. Of course, this does not mean that the  $\pi$  electrons in the  $D_{6h}$  benzene are not delocalized: they are forced to be delocalized by the  $\sigma$ -electron framework, which prefers a symmetric hexagonal structure.

We can thus show, even by using the Hückel MO approximation, that the main contributor to the empirical RE values of benzenoid hydrocarbons and hence, if we consider  $(E_{\text{tot}}^{\text{M}} - E_{\text{tot}}^{\text{K}})$  to be the theoretical index to the aromaticity, to the aromatic stabilities of these molecules is not the  $\pi$ -electron DE but the compressional energy of  $\sigma$  bonds.

In 1972 Schaad and Hess [13] succeeded in reproducing Dewar's RE [14] in the framework of the simple Hückel MO approximation. However, their conclusion that in benzenoid hydrocarbons the main contributor to the RE is not the compression energy of the  $\sigma$  bonds but the  $\pi$ -electron DE directly contradicts the present result. Their results show further that the difference in  $\sigma$ -compression energy between a molecule and the corresponding reference structure favors the latter. These discrepancies are due mainly to the fact that their reference structure is different from ours: they take a polyene-like structure in which single bonds have considerable double bond character as a reference system. The ratio of the  $\pi$ -electron binding energy or of the  $\sigma$ -electron binding energy to the total binding energy is naturally changed by the choice of the reference structure [15]. Moreover, they have not used the variable- $\beta$  technique but used the HMO approximation in the simplest form. This inevitably brings about a larger  $\pi$ -electron DE value.

Although it is out of the main subject of this paper to refer to  $4n$  aromatic hydrocarbons, it would be interesting to note finally that the  $(E_{\text{tot}}^{\text{M}} - E_{\text{tot}}^{\text{K}})$  values for cyclobutadiene and cyclooctatetraene are calculated to be  $-0.727 \beta_{\text{b}}$  and  $-0.906 \beta_{\text{b}}$ , respectively. In these molecules, a localized, distorted Kekulé-type structure is distinctly lower in energy than the corresponding delocalized, symmetrical structure. They are thus placed in the antiaromatic category in agreement with Dewar's classification [14].

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