A Method for Calculation of Resonance Energy of Benzenoid Hydrocarbons

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A semiempirical topological formula (2) is derived, which reproduces Aihara's resonance energy [1] of benzenoid hydrocarbons with a chemically negligible error of 2—3%.

In a recent work Aihara [1] proposed a new approach to the problem of aromaticity. He introduced a new concept of resonance energy based on the aromatic sextet theory of Clar. This resonance energy, RE*, is defined for benzenoid hydrocarbons only and can be calculated from the roots of the polynomial

$$A(X) = \sum_{k=0}^{m} (-1)^k r(k) X^{2m-2k} .$$

Hosoya and Yamaguchi [2] have previously considered another polynomial of the same type, namely

$$B(X) = \sum_{k=0}^{m} r(k) X^k .$$

Evidently, $A(X) = X^{2m} B(-X^{-2})$. The coefficient $r(k)$ in the above formulas is called [2] the resonant sextet number. It is equal to the number of ways in which k mutually disconnected aromatic sextets can be selected from a benzenoid system ($k = 1, 2, \ldots, m$). In addition, $r(0) = 1$.

Hence, m ist the maximal number of aromatic sextets which can be simultaneously drawn in a Clar formula. $r(1)$ is the number of those rings in a benzenoid molecule which possess an aromatic sextet in at least one Clar formula. In many, but certainly not in all cases $r(1)$ coincides with the number of hexagons in the benzenoid system. An additional property of the resonant sextet numbers, which will be important in the present consideration, is [2]

$$B(1) = \sum_{k=0}^{m} r(k) = \mathrm{SC} ,$$

where SC is the Kekulé structure count, i.e. the number of Kekulé structures of the benzenoid molecule. SC, m and $r(1)$ are easily determined by inspection of the topology of the corresponding conjugated system [3].

In the general case the roots of the polynomial $A(X)$ are complex numbers. Let X_k ($k = 1, 2, \ldots, 2m$) denote the real part of these roots, arranged in non-increasing order. Then the Aihara's resonance energy (in suitably chosen units) reads

$$\mathrm{RE}^* = \sum_{k=1}^{m} X_k . \qquad (1)$$

There exist [1] few techniques for the calculation of RE*. In the present work we offer another method for approximate evaluation of this quantity, based on a relatively simple topological formula. Although the formula depends only on the three topological parameters m, $r(1)$ and SC, it reproduces RE* with a chemically unimportant error of less than 2—3%. Besides, our result provides some insight into the relations between the structure of a benzenoid molecule and its aromatic properties.

There is evidently a close formal analogy between the definition (1) of RE* and the expression for the total electron energy in simple MO theories. This enables one to utilize the mathematical apparatus which was developed for the study of the total π-electron energy, also in the Aihara's theory. In particular, we shall need the integral formula [4]

$$E = \langle U \rangle \quad \text{where} \quad U = X^{-2} \ln |X^N P(i/X)| ,$$

relating the total π-electron energy E to the secular polynomial $P(X)$ of a molecule with N conjugated centers; i is the imaginary unit. Here and later we shall adopt the notation

$$1/\pi \int_{-\infty}^{+\infty} F(X)\,\mathrm{d}X \equiv \langle F(X) \rangle \equiv \langle F \rangle .$$

Now RE* obeys the identity

$$\mathrm{RE}^* = \tfrac{1}{2} \langle U^* \rangle \quad \text{where}$$
$$U^* = X^{-2} \ln |X^{2m} A(i/X)| .$$

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The function U^* is further transformed into

$$U^* = X^{-2} \ln B(X^2)$$
$$= X^{-2} \ln [1 + r(1) X^2 + \cdots + r(m) X^{2m}].$$

Analysis shows that U^* is a bell-shaped even function with the properties

$$U^*(0) = r(1),$$
$$U^*(1) = 1 + r(1) + \cdots + r(m) = \mathrm{SC},$$
$$U^*(X) \sim 2m X^{-2} \ln X \quad \text{for large } X.$$

In order to estimate the integral $\langle U^* \rangle$, we apply a method developed in Reference [5]. Thus another bell-shaped function $V = V(X)$ will be constructed, namely

$$V(X) = \frac{r(1) + m t^2 \ln (u^2 X^2 + 1)}{t^2 X^2 + 1}.$$

This function obeys the relations

$$V(0) = r(1),$$
$$V(X) \sim 2m X^{-2} \ln X \quad \text{for large } X$$

for arbitrary values of the (positive) parameters u and t. The requirement

$$V(1) = U^*(1) = \mathrm{SC}$$

results in the condition

$$t^2 = \frac{r(1) - \ln \mathrm{SC}}{\ln \mathrm{SC} - m \ln (1 + u^2)}.$$

Since always $r(1) > \ln \mathrm{SC}$, the parameter u is bounded as follows:

$$0 < u^2 < (\mathrm{SC})^{1/m} - 1.$$

The function $V(X)$ is now adjusted to have the same analytical behaviour as $U^*(X)$ for small and large values of X, and moreover it is equal to U^* for $X = 1$. Therefore the integrals $\langle U^* \rangle$ and $\langle V \rangle$ must have nearly the same value [5]. Straightforward integration yields $\langle V \rangle$ and hence the desired approximate formula for RE*:

$$\mathrm{RE}^* \doteq \frac{r(1)}{2t} + m t \ln \left(1 + \frac{u}{t}\right). \tag{2}$$

Numerical examination shows that the value of the expression (2) is not very sensitive to small variations of the parameter u and that $u^2 = 0.5$ provides a fairly accurate approximate formula for Aihara's resonance energy.

In Table 1 exact values [1] of RE* are compared with values calculated from Eq. (2) for $u^2 = 0.5$. In all the studied cases the agreement is found to be rather good. The deviations of 2—3% from the exact value of RE* have hardly any significance in chemical applications.

Table I. Aihara's resonance energies of selected benzenoid hydrocarbons.

Molecule	RE* Eq. (1)	RE* Eq. (2)	Error (%)
benzene	1.000	1.023	+ 2.3
naphthalene	1.414	1.427	+ 0.9
anthracene	1.732	1.733	+ 0.05
phenanthrene	2.236	2.269	+ 1.5
pyrene	2.449	2.492	+ 1.8
benz[a]anthracene	2.613	2.623	+ 0.4
chrysene	2.732	2.743	+ 0.4
perylene	2.828	2.854	+ 0.9
benzo[a]pyrene	2.909	2.906	— 0.1
pentaphene	3.000	3.074	+ 2.5
triphenylene	3.181	3.183	+ 0.06
benzo[e]pyrene	3.402	3.420	+ 0.5
picene	3.494	3.565	+ 2.0
dibenz[a, c]anthracene	3.574	3.565	— 0.2
coronene	4.135	4.072	— 1.5

From Eq. (2) is seen that the resonance energy of benzenoid hydrocarbons is mainly determined by three simple topological parameters. Since Eq. (2) is a decreasing function of the parameter t, one can conclude that the resonance energy is proportional to the logarithm of the number of Kekulé structures. However, in spite of the Aihara's claim [1], this proportionality is by no means a linear one.

The fact that RE* is also an increasing function of $r(1)$ and m is in full agreement with the basic ideas of the aromatic sextet theory of Clar.

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