September, 1978] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (9), 2729—2731 (1978) 2729

Topological Properties of Benzenoid Systems. IV.[1] On Aihara's Resonance Energy

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(Received December 22, 1977)

Different mathematical properties of a resonance energy, recently defined by Aihara (This Bulletin, **50**, 2010 (1977)), are presented.

In a recent paper[2] Aihara defined a new resonance energy, RE^*, by

$$RE^* = K\sum_{k=1}^{m} X_k, \tag{1}$$

where X_k denotes the roots of the equation $A(X)=0$, arranged in descending order. The polynominal $A(X)$ is defined by

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

where $r(k)$ denotes the resonant sextet numbers.[3] The main properties of RE^* and its relation to the resonance energy of Dewar and that of Herndon were determined.[2] The present paper reports an attempt to establish further relations for this new concept, in order to clarify its mathematical meaning; Aihara's notations have been used. Sometimes notations $RE^*=RE^*(G)$, $A(X)=A(G, X)$ and $r(k)=r(G,k)$ are used to indicate quantities corresponding to a particular benzenoid molecule G.

Aihara noted[2] that in certain cases the X_k values become complex numbers. Equation 1 should thus be modified as

$$RE^* = K\sum_{k=1}^{m} x_k, \tag{1'}$$

where x_k is the real part of X_k. In the following this generalized definition of RE^* is considered. Equation 1′ is reduced to Eq. 1 when all X_k values are real.

*Identities, Bounds and Approximate Topological Formulas for RE**. There is a formal analogy between Eqs. 1 and 1′ and the definition of the total π-electron energy (E) in Hückel molecular orbital (HMO) theory. A number of known results for E can thus be applied and changed into relations valid for RE^*. For this it is important to recognize the analogy between $A(X)$ and the HMO characteristic polynominal.[2]

Let us denote the first derivative of the polynomial $A(X)$ by $A'(X)$ and a complex variable by z. Then according to Coulson,[4] the sum of the form (Eq. 1′) fulfills the equations

$$RE^* = \frac{K}{2\pi i}\int_C\left[2m-\frac{z\,A'(z)}{A(z)}\right]\mathrm{d}z \tag{2}$$

and

$$RE^* = \frac{K}{2\pi}\int_{-\infty}^{+\infty}\left[2m-\frac{iX\,A'(iX)}{A(iX)}\right]\mathrm{d}X, \tag{3}$$

where i is the imaginary unit, the contour C in Eq. 2 being chosen to encircle the non-negative part ($Re\ z\geqslant 0$) of the complex plain. Note that the polynominal $A(X)$ is constructed in such a manner that all its roots differ from zero.

Equation 3 is further transformed into[5]

$$RE^* = \frac{K}{2\pi}\int_{-\infty}^{+\infty} f(X)\mathrm{d}X, \tag{4}$$

where

$$f(X) = X^{-2}\ln\sum_{k=0}^{m} r(k)X^{2k} = X^{-2}\ln B(X^2)$$

and $B(X)$ is the sextet polynomial of Hosoya and Yamaguchi.[2,3]

Let G_1 and G_2 be two benzenoid systems and let their A-polynomials be of the order $2m_1$ and $2m_2$, respectively. Then another result of Coulson[6] gives the identity

$$RE^*(G_1) - RE^*(G_2) = \frac{K}{2\pi}\int_{-\infty}^{+\infty}\ln\left[(-X^2)^{m_2-m_1}\frac{A(G_1,\ iX)}{A(G_2,\ iX)}\right]\mathrm{d}X. \tag{5}$$

Three topological parameters of benzenoid systems are of importance in the following discussion. They are $r(G, 1)$—the number of resonant sextets in G, m—the maximal number of mutually resonant sextets in G and $r(G, m)$—the number of ways in which m resonant sextets are selected in G. Although no simple and general procedure exists for calculating these quantities, it is not difficult to determine them from an inspection of the molecular network of a benzenoid system.[7]

The significance of m, $r(1)$ and $r(m)$ becomes evident if one remembers that they play formally the same role in $A(X)$, as the number of carbon atoms, the number of carbon-carbon bonds and the algebraic structure count in the HMO characteristic polynomial.[8] Thus it is easy to transform the known[9] lower and upper bounds for E into bounds for RE^*. Hence we get

$$\begin{aligned} r(1) - mr(m)^{1/m} \leq mr(1) - (RE^*/K)^2 \leq \\ \leq (m-1)[r(1)-mr(m)^{1/m}]. \end{aligned} \tag{6}$$

A special case of the relation (Eq. 6) is the simple formula

$$m\leq RE^*/K\leq\sqrt{mr(1)}\ .$$

A class of approximate topological formulas for RE^* is obtained using a general method[10] which we will apply to Eq. 4. Similar conclusions can be reached from Eqs. 3 and 5.

The integrand $f(X)$ in Eq. 4 is a bell-shaped function, showing the following asymptotic behavior.

$$f(X) \approx \begin{cases} r(1) & \text{for } |X| \to 0 \\ 2m\, X^{-2} \ln X & \text{for } |X| \to \infty \end{cases} \tag{7}$$

Moreover, we have

$$f(1) = \ln SC, \tag{7'}$$

since $B(1)=r(0)+r(1)+\cdots\cdots+r(m)$ is equal to the structure count (SC) of the benzenoid system under consideration.[3]

If another function $g(X)$ fulfills the relations (Eqs. 7 and 7′), then the expression $\frac{K}{2\pi}\int_{-\infty}^{+\infty} g(X)\, \mathrm{d}X$ is expected[10] to give a good estimate of RE^*. A suitable function of this type is

$$g(X) = \frac{T^2\, r(1) + m \ln(1+X^2)}{T^2+X^2},$$

with

$$T^2 = (\ln SC - m \ln 2)/(r(1) - \ln SC).$$

Straightforward integration yields

$$RE^*/K \approx \frac{1}{2}T\, r(1) + m\frac{\ln(1+T)}{T}. \tag{8}$$

It can be shown that the above relation is suitable for numerical calculations. However, we are herewith mainly interested in the topological properties of Eq. 8, namely in the finding of the main structural factors which contribute to RE^*. We see that RE^* is grossly determined by three structural parameters $r(1)$, m, and SC. Since Eq. 8 does not depend explicitly on $r(m)$, we conclude that this quantity has only a second order influence on the value of RE^*. The functional dependence of RE^* on $r(1)$, m, and SC is rather complicated. In order to get a qualitative insight into this dependence, one can use the fact that T is small, which results in an essential simplification of Eq. 8.

$$RE^*/K \approx m + \frac{1}{2}T\, r(1) \tag{9}$$

Hence the main contribution to RE^* comes from the maximal number of mutually resonant sextets (m), while the number of simply resonant sextets ($r(1)$) has a smaller effect. An inspection of both Eqs. 8 and 9 suggests that RE^* is proportional to ln SC, but the functional dependence between RE^* and ln SC does not seem to be linear.

RE's of Non-Branched Cata-Condensed Benzenoid Systems.* For every non-branched cata-condensed benzenoid (NBCCB) system[11] G with n hexagons, an acyclic graph T with $n+1$ vertices can be constructed, such that its characteristic polynominal $P(T, X)$ fulfills the relation[12]

$$X^{n+1-2m}A(G, X) = P(T, X). \tag{10}$$

It follows from this relation that $RE^*(G)/K = E(T)/2$. Hence Aihara's resonance energy (in terms of K) of a NBCCB molecule is equal to half of the Hückel energy (in terms of β) of a particular acyclic graph. This simple result enables us to apply the numerous relations known for acyclic graphs and their Hückel energy[13] to the theory of RE^*. A few selected examples are given.

The way in which an "L, A-sequence" is associated with a NBCCB system and the procedure of the construction of the graph T have been reported.[12] As an example, in the case of a linear polyacene with n hexagons (an L^n-system), the corresponding T-graph is the star S_{n+1} with $n+1$ vertices. The characteristic polynomial of the star reads[13]: $P(S_{n+1}, X) = X^{n+1} - nX^{n-1}$. Consequently, it is $E(S_{n+1}) = 2\sqrt{n}$ and $RE^*(\mathrm{L}^n) = \sqrt{n}K$. This latter result is equivalent to Aihara's Eq. 15.[2]

By a similar argument we obtain general formulas for the RE 's of further classes of NBCCB molecules given below, where n denotes the total number of hexagons. RE^* is expressed in terms of K.

$$RE^*(\mathrm{L}^n) = \sqrt{n}$$

$$RE^*(\mathrm{L}^a\mathrm{A}\mathrm{L}^b) = \sqrt{n+2\sqrt{ab}} \qquad (a+b+1=n)$$

$$RE^*(\mathrm{L}^a\mathrm{A}^2\mathrm{L}^b) = \sqrt{n+2\sqrt{ab+n-2}} \qquad (a+b+2=n)$$

$$RE^*(\mathrm{L}^a(\mathrm{A}\mathrm{L}^a)^b) = \sum_{j=1}^{b+1} \sqrt{a+\cos^2\frac{\pi j}{b+2}} \qquad (a+b+ab=n)$$

$$RE^*(\mathrm{L}\mathrm{A}^{n-2}\mathrm{L}) = \begin{cases} \operatorname{cosec}\frac{\pi}{2n+4} - 1 & \text{if } n \text{ is odd} \\ \operatorname{cotg}\frac{\pi}{2n+4} - 1 & \text{if } n \text{ is even} \end{cases}$$

$$RE^*(\mathrm{L}^2\mathrm{A}^{n-3}\mathrm{L}) = \begin{cases} \operatorname{cotg}\frac{\pi}{2n+4} & \text{if } n \text{ is odd} \\ \operatorname{cosec}\frac{\pi}{2n+4} & \text{if } n \text{ is even} \end{cases}$$

$$RE^*(\mathrm{L}^2\mathrm{A}^{n-4}\mathrm{L}^2) = \begin{cases} \operatorname{cosec}\frac{\pi}{2n+4} + 1 & \text{if } n \text{ is odd} \\ \operatorname{cotg}\frac{\pi}{2n+4} + 1 & \text{if } n \text{ is even} \end{cases}$$

The T-graph associated with a NBCCB system of the type L^n and $\mathrm{L}\mathrm{A}^{n-2}\mathrm{L}$ is the star S_{n+1} and the path P_{n+1}, respectively, with $n+1$ vertices.[12] It has been proved[13] that for all acyclic graphs T with $n+1$ vertices, $E(S_{n+1}) \leq E(T) \leq E(P_{n+1})$. This implies that among NBCCB systems with n hexagons, the linear polyacene (L^n) has minimal and the angular polyacenes ($\mathrm{L}\mathrm{A}^{n-2}\mathrm{L}$) have maximal values of RE^*.

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