Aromatic Sextets and Aromaticity in Benzenoid Hydrocarbons

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The aromatic sextet theory of Clar was used to estimate the degree of aromaticity in benzenoid hydrocarbons. The resonance energies obtained correlate well with the Dewar-type resonance energies calculated in a previous paper.

An aromatic sextet is defined as a benzene unit (six sp^2 carbon atoms arranged in a hexagon) which can be chosen from a benzenoid hydrocarbon, on condition that when the benzene unit and all the adjacent π bonds are removed from the π system, one or more Kekulé structures can be written for the residual π system.[1] One or more aromatic sextets may further be chosen from the residual π system. Clar long ago stressed the importance of writing the structural formula of a benzenoid hydrocarbon with a maximum number of aromatic sextets.[1] These aromatic sextets, isolated from each other in the same π system, are considered to be the main origin of aromatic stabilization.[1–7] A structural formula thus defined is termed a sextet formula.[4] In this paper, the degree of aromaticity in a benzenoid hydrocarbon is examined on the basis of the Clar aromatic sextet theory.[1]

Theoretical

First, a new polynomial $A(X)$ characterizing the aromaticity of a benzenoid hydrocarbon is proposed in the form

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

where $r(k)$ denotes the number of ways in which k disconnected aromatic sextets can be chosen from the π system. Each coefficient of this polynomial has exactly the same meaning as the corresponding coefficient of a sextet polynomial $B(X)$ defined by Hosoya and Yamaguchi.[5] By definition $r(0)$ is equal to unity. Therefore, k is less than, or equal to, the number of aromatic sextets m in the sextet formula. This type of polynomial is termed a resonance polynomial. For example, the resonance polynomial for triphenylene is

$$A(X) = X^6 - 4X^4 + 3X^2 - 1. \qquad (2)$$

Furthermore, the sextet polynomial[5] for this compound is

$$B(X) = 1 + 4X + 3X^2 + X^3. \qquad (3)$$

Next, the roots of the equation, $A(X)=0$, are arranged in decreasing order,

$$X = X_1, X_2, \cdots, X_m, X_{m+1}, \cdots, X_{2m-1}, X_{2m}. \qquad (4)$$

We then define a new quantity, RE^*, as

$$RE^* = K\sum_{k=1}^{m} X_k, \qquad (5)$$

where the proportionality constant, K, is equal to the resonance energy of benzene (*i.e.*, of a single aromatic sextet).

Let us consider the physical meaning of this equation. We remember that, for an acyclic polyene, the HMO characteristic polynomial $P(X)$ can be written as[8]

$$P(X) = \sum_{k=0}^{n}(-1)^k p(k) X^{2n-2k}, \qquad (6)$$

where $p(k)$ is the number of ways in which k disconnected π bonds are chosen from the π system, and n is the number of formal double bonds in the canonical structure. The roots of the secular equation $P(X)=0$ can be related to the π energy of the formal double bonds plus the additional π energy associated with a migration of this double bond character throughout the π system. By close analogy in form with this secular equation, the roots of the equation $A(X)=0$ can be formally expected to give some energetic quantity related to the aromatic sextets and their migration throughout the π system. To be more concrete, RE^* in Eq. 5 can be interpreted as the resonance energy induced by the aromatic sextets in a benzenoid hydrocarbon. This quantity refers to the resonance energy in Dewar's sense.[9–12]

Discussion

The following considerations help one to interpret RE^* as the resonance energy. The resonance energy for a π system composed of aromatic fragments, connected by essentially single bonds, should be additive. This requirement is fulfilled by the definition of RE^*. For example, a resonance polynomial for a polyphenyl (*p*-polyphenyl) composed of m phenyl groups is written in the form

$$A(X) = \sum_{k=0}^{m}\frac{m!}{k!(m-k)!}X^{2m-2k} = (X^2-1)^m. \qquad (7)$$

Therefore, for the polyphenyl,

$$RE^* = mK. \qquad (8)$$

This result is consistent with the two resonance theoretical approaches proposed by Herndon and others.[2,3,13,14]

Further support for RE^* is given by the close relationship found between the resonance energy and the Kekulé structure count for benzenoid hydrocarbons. As mentioned in a previous paper,[12] the following approximation holds fairly well for any polynomial $Q(X)$, if all the roots of equation $Q(X)=0$ lie in the interval between -3.0 and 3.0;

$$\sum_{k=1}^{2m}|X_k| \approx 6.0846 \log |Q(i)|, \qquad (9)$$

where $2m$ indicates the degree of the equation and $i=\sqrt{-1}$. For most benzenoid hydrocarbons, the resonance polynomial $A(X)$ fulfils the prerequisite for this approximation. Accordingly,

$$RE^* \approx 3.0423K \log |A(i)|. \qquad (10)$$

Here, the fact was used that if X' is a root of the equation $A(X)=0$, $-X'$ is also a root. By comparing $A(X)$ with the corresponding sextet polynomial $B(X)$ defined by Hosoya and Yamaguchi,[5] $|A(i)|$ is evaluated as

$$|A(i)| = B(1) = SC, \qquad (11)$$

where SC is the Kekulé structure count. We then arrive at the interesting expression

$$RE^* \approx 3.0423K \log SC. \qquad (12)$$

This is none other than one of the expressions previously proposed by Herndon *et al.*[13,14] The confluence of their resonance theory and the present approach obviously provides mutual support for arguing the essential correctness of both approaches.

Table 1. Resonance energies of benzenoid hydrocarbons

Compound	m	RE^*/K	Resonance energy (β) RE^*	 RE
Benzene	1	1.000	0.273$^{a)}$	0.273
Naphthalene	1	1.414	0.385$^{a)}$	0.389
Anthracene	1	1.732	0.472$^{a)}$	0.475
Naphthacene	1	2.000	0.545$^{a)}$	0.553
Pentacene	1	2.236	0.610$^{a)}$	0.626
Hexacene	1	2.449	0.668$^{a)}$	0.706
Phenanthrene	2	2.236	0.560$^{b)}$	0.546
Pyrene	2	2.449	0.613$^{b)}$	0.598
Benz[*a*]anthracene	2	2.613	0.654$^{b)}$	0.643
Benzo[*c*]phenanthrene	2	2.732	0.684$^{b)}$	0.687
Chrysene	2	2.732	0.684$^{b)}$	0.688
Perylene	2	2.828	0.708$^{b)}$	0.740
Benzo[*a*]naphthacene	2	2.909	0.728$^{b)}$	0.725
Benzo[*a*]pyrene	2	2.909	0.728$^{b)}$	0.725
Pentaphene	2	3.000	0.751$^{b)}$	0.746
Dibenzo[*def,mno*]chrysene	2	3.076	0.770$^{b)}$	0.766
Benzo[*b*]chrysene	2	3.078	0.770$^{b)}$	0.781
Triphenylene	3	3.181	0.745$^{b)}$	0.739
Benzo[*e*]pyrene	3	3.402	0.797$^{c)}$	0.791
Dibenzo[*a,j*]anthracene	3	3.449	0.808$^{c)}$	0.806
Dibenzo[*a,h*]anthracene	3	3.449	0.808$^{c)}$	0.807
Dibenzo[*c,g*]-phenanthrene	3	3.494	0.819$^{c)}$	0.832
Picene	3	3.494	0.819$^{c)}$	0.835
Benzo[*b*]triphenylene	3	3.574	0.837$^{c)}$	0.845
Benzo[*ghi*]perylene	3	3.646	0.854$^{c)}$	0.853
Dibenzo[*a,c*]naphthacene	3	3.878	0.909$^{c)}$	0.929
Benzo[*c*]picene	3	4.078	0.955$^{c)}$	0.980
Coronene	3	4.135	0.969$^{c)}$	0.947
Dibenzo[*fg,op*]-naphthacene	4	4.351	1.019$^{c)}$	0.983
Dibenzo[*g,p*]chrysene	4	4.449	1.042$^{c)}$	1.041

a) $K=0.2726\beta$. b) $K=0.2503\beta$. c) $K=0.2343\beta$.

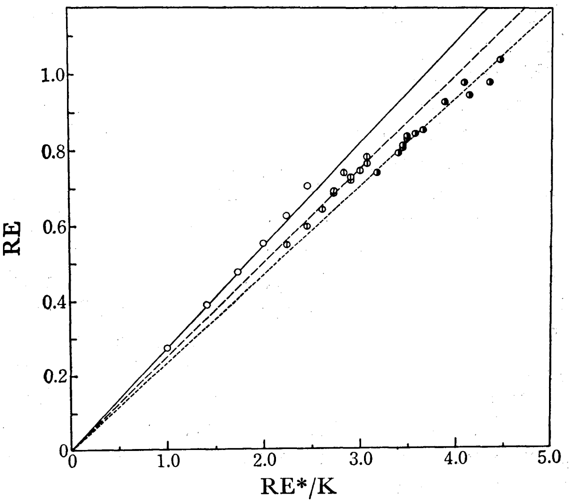

Fig. 1. Plot of RE *versus* RE^*/K for benzenoid hydrocarbons. Compounds with $m=1$ are marked by ○, those with $m=2$ by ⦶, and those with $m\geq 3$ by ◑.

Extensive numerical analysis gives definite support to the view that RE^* represents the resonance energy of a benzenoid hydrocarbon. For this purpose, the equation $A(X)=0$ were solved for 30 typical benzenoid hydrocarbons. The RE^* values obtained were compared with the Dewar-type resonance energies, RE, analytically obtained by Aihara[11] (see Table 1 and Fig. 1). A refined definition of RE is given in the Appendix. Figure 1 shows fairly good correlation between the values for RE and RE^*/K. As indicated by Eq. 5, RE^*/K signifies the sum of the first m roots of equation $A(X)=0$. On the basis of this figure, the coefficient K actually appears close to the resonance energy of benzene (0.2726β).[11] These facts firmly establish the above view of RE^*, namely,

$$RE \approx RE^*. \qquad (13)$$

However, if Fig. 1 is examined in detail, it is found that the benzenoid hydrocarbons investigated must be classified into groups, depending on the number of aromatic sextets, m, in the sextet formula. First, compounds with $m=1$ (polyacenes) form the first group. The resonance polynomial for a polyacene with n hexagons is

$$A(X) = X^2 - n. \qquad (14)$$

RE^* can be expressed as

$$RE^* = \sqrt{n}K. \qquad (15)$$

The solid line in Fig. 1 indicates that the resonance energies of the polyacenes fit Eq. 15 well if the resonance energy of benzene is assigned to K. This suggests that the aromatic character of benzene is fully retained in the aromatic sextet of all polyacenes.

Moreover, the present interpretation of Clar's aromatic sextets shows that the migration of a single aromatic sextet in a polyacene considerably increases the overall resonance energy. This is in marked contrast to the structure-resonance theory of Herndon,[2,3] which predicts the limiting resonance energy of a polyacene to be 2.8 times the resonance energy of benzene. Equation 15 strongly suggests that such a small value for the resonance energy of an infinitely large polyacene is rather doubtful.

Compounds with $m=2$ form the second group of benzenoid hydrocarbons, in the sense that the RE^* values correlate differently with the RE values. In this case, if the coefficient K in Eq. 5 is slightly decreased, good linear correlation is maintained. As indicated by the slope of long dashes in Fig. 1, the best K value is $0.2503\,\beta$ for compounds with $m=2$.

In this context, there is some evidence showing that each aromatic sextet in a polycyclic π system should rather be considered as a kind of substituted benzene. The resonance energy of any substituted benzene is somewhat smaller than that of benzene itself.[11] This effect can readily be understood by comparing the resonance energies of benzene and biphenyl. The resonance energy of biphenyl ($0.5017\,\beta$) is somewhat smaller than twice the resonance energy of benzene ($0.2726\,\beta$).[11] Accordingly, the effective resonance energy assignable to each aromatic sextet in a polycyclic π system should be somewhat smaller than that of benzene. This may be the reason why the K-value for compounds with $m\geq 2$ becomes somewhat smaller than the resonance energy of benzene.

Compounds with $m\geq 3$ constitute the third group of benzenoid hydrocarbons. For these compounds, the good linear relationship between the values for RE and RE^* is characterized by a K-value of $0.2343\,\beta$. The short-segmented broken line in Fig. 1 represents this situation. Here, it is noteworthy that 86% of the resonance energy of benzene is still retained in the K for such large benzenoid systems.

Concluding Remarks

As seen above, an analysis of Clar's aromatic sextet theory[1] appears to form the important basis for a resonance-theoretical consideration of conjugated hydrocarbons. It is interesting to note that some energetic quantities can be derived from such polynomials as Eqs. 1 and 6. Finally, one minor difficulty must be admitted in the present approach. This is caused by the fact that some roots of the equation $A(X)=0$ for certain compounds have a small imaginary part. Considering that the value of RE^* is always real and is a good approximation to the exact resonance energy RE, this aspect of the approach need not be a cause for concern.

Appendix

The definition of resonance energy previously given by Aihara[11] can be refined within the HMO theory as follows. Let the characteristic polynomial for a conjugated compound $P(X)$ and the corresponding reference polynomial $R(X)$ be written, respectively, as

$$P(X) = X^N + \sum_{k=1}^{N} a_k X^{N-k}, \tag{A1}$$

and

$$R(X) = X^N + \sum_{k=1}^{N} b_k X^{N-k}, \tag{A2}$$

where N is the number of atoms in the π system. The roots of the secular equation $P(X)=0$, arranged in decreasing order, are

$$X = X_1, X_2, \cdots, X_{N-1}, X_N. \tag{A3}$$

Each root, X_t, can be considered to be a function of N coefficients of $P(X)$, *i.e.*,

$$X_t = X_t(a_1, a_2, \cdots, a_{N-1}, a_N). \tag{A4}$$

If each variable a_k in the function X_t takes the value for a corresponding coefficient b_k of $R(X)$, X_t becomes the energy of the reference orbital related to the t-th molecular orbital in an actual π system. The resonance energy of the compound, RE, is then defined as

$$\begin{aligned} RE = \sum_{t}^{\text{occ}} g_t \{ & X_t(a_1, a_2, \cdots, a_{N-1}, a_N) \\ & - X_t(b_1, b_2, \cdots, b_{N-1}, b_N)\}, \end{aligned} \tag{A5}$$

where t extends over all occupied π-molecular orbitals, and g_t is the number of electrons which occupy the t-th orbital. The resonance energies given in Table 1 are, of course, in agreement with this definition.

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