# A Generalized Total $\pi$-Energy Index for a Conjugated Hydrocarbon

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A total $\pi$-energy index $Z^*$ is defined as $Z^* = |\mathrm{P}(i)|$ for a conjugated hydrocarbon, where $\mathrm{P}(X)$ is an HMO characteristic polynomial of the compound, and $i = \sqrt{-1}$. It is found that the HMO total $\pi$ energy $E_\pi$ is proportional to the logarithm of this index: $E_\pi \approx 6.0846 \log Z^*$. With the use of an analogous $\pi$-energy index $Z_0{}^*$ for the reference structure previously defined by us, the resonance energy RE for the conjugated hydrocarbon can be expressed in the form RE $\approx 6.0846 \log Z^*/Z_0{}^*$.

Total $\pi$ energy is one of the key quantities in chemistry of a conjugated hydrocarbon, and is especially important when its thermochemical stability and reactivity are examined.[1,2] So far, molecular orbital theories have provided much of the information concerning the total $\pi$ energy of the conjugated system.[3] In parallel with this, a considerable amount of effort has been devoted to correlating the total $\pi$ energy with particular structural features of the conjugated system.[4,5] The problem of prime interest has been to find a formula which would express the total $\pi$ energy as a function of topological parameters, such as sp$^2$ carbon atoms, $\pi$ bonds, and numbers and types of $\pi$ electron rings. Although in 1974 Gutman verified that no exact topological formulas can exist for the total $\pi$ energy,[5] this problem does not cease to attract us.

Since 1968, Wilcox et al. have stressed that the algebraic structure count (ASC) and not the number of Kekulé structures plays an essential role in determining stability of a conjugated hydrocarbon.[6] Not a few expressions in terms of the ASC and/or the numbers of sp$^2$ carbon atoms and $\pi$ bonds have skillfully been presented to duplicate the total $\pi$ energy[5,7] and the resonance energy[8] as well for the conjugated hydrocarbon. McClelland attempted to reproduce the total $\pi$ energy in terms of the Frobenius norm of an adjacency matrix for the conjugated system.[9]. The coefficients of an HMO characteristic polynomial can graph-theoretically be enumerated from the $\pi$-electron framework,[10,11] and hence are topological quantities of a different kind. Last year, Hosoya et al. ingeniously showed that these coefficients also reflect the total $\pi$ energy for most conjugated hydrocarbons.[12] In this paper, I would like to generalize and verify their formula for the total $\pi$ energy, with its application to a variety of conjugated hydrocarbons. An HMO theory is used in its simplest form. All energies are given in units of $\beta$.

**Definition of a Generalized Total $\pi$-Energy Index $Z^*$.** In general, an HMO secular determinant for a conjugated hydrocarbon can be expanded into a polynomial $\mathrm{P}(X)$, which is termed an HMO characteristic polynomial, i.e.,

$$\mathrm{P}(X) = \det|EX - A| = \sum_{k=0}^{N} a_k X^{N-k} \qquad (1)$$

Here, $A$ is an adjacency matrix which specifies the connectivity of sp$^2$ carbon atoms in the compound,[13] and therefore is a square matrix of the same order as the number of sp$^2$ carbon atoms ($N = 2m$); $E$ is a unit matrix of the same order. The coefficients $a_k$ can readily be evaluated either by enumerating the Sachs graphs[10] or by counting the nonadjacent numbers concerned.[11] The secular variable $X$ is related to an HMO eigenvalue variable $\epsilon$ in this manner:

$$X = (\epsilon - \alpha)/\beta \qquad (2)$$

The roots of $\mathrm{P}(X) = 0$ are arranged in a decreasing order as

$$X = X_1, X_2, \ldots, X_m, X_{m+1}, \ldots, X_{N-1}, X_N \qquad (3)$$

All these roots are real, and lie in the interval between $-3.0$ and 3.0[14] The first $m$ roots correspond to the energies of the occupied $\pi$ molecular orbitals. The $\pi$ energy of the entire compound $E_\pi$ is then given by

$$E_\pi = 2 \sum_{k=1}^{m} X_k \qquad (4)$$

Equation 1 is expressed by means of the roots of $\mathrm{P}(X) = 0$ as

$$\mathrm{P}(X) = \prod_{k=1}^{N} (X - X_k) \qquad (5)$$

Now, let us consider a new quantity $Z^*$ defined as

$$Z^* = |\mathrm{P}(i)| = \left| \sum_{k=0}^{N} a_k i^{N-k} \right| \qquad (6)$$

where $i = \sqrt{-1}$. This expression can be rewritten by the use of the roots of $\mathrm{P}(X) = 0$ as

$$Z^* = \left| \prod_{k=1}^{N} (i - X_k) \right| = \prod_{k=1}^{N} (|i - X_k|) = \prod_{k=1}^{N} (1 + X_k{}^2)^{1/2} \qquad (7)$$

The logarithm of $Z^*$ is

$$\log Z^* = \frac{1}{2} \sum_{k=1}^{N} \log (1 + X_k{}^2) \qquad (8)$$

In order to visualize the physical image of eq 8, we introduce the approximation

$$\log (1 + X^2) \approx h|X| \qquad (9)$$

where $h$ is a quasi-proportionality constant for this relation. The validity of this expression for $|X| \leq 3.0$ can straightforwardly be seen from Figure 1. It is especially noteworthy that this approximation holds very well within the same region ($|X| \leq 3.0$) as covered by the roots of $\mathrm{P}(X) = 0$. The constant $h$ is obtained by equating the following integral $I$ to zero:

$$I = \int_{-3}^{3} \{\log (1 + X^2) - h|X|\}\, \mathrm{d}X \qquad (10)$$

This means that the $h$ is so determined that eq 9 holds best within the same region as covered by the roots of $\mathrm{P}(X) = 0$. The $h$ value thus derived is 0.32870. With this approximation, eq 8 can be made linear with respect to every $X_k$:

$$\log Z^* \approx \frac{h}{2} \sum_{k=1}^{N} |X_k| \qquad (11)$$

On this basis, we defined $E_{Z^*}$ as

$$E_{Z^*} = \frac{2}{h} \log Z^* = 6.0846 \log Z^* \qquad (12)$$

We can show that this quantity is closely related to the HMO total $\pi$ energy $E_\pi$ of the conjugated hydrocarbon as follows. The sum of all roots of $\mathrm{P}(X) = 0$ always vanishes for any conjugated hydrocarbons. Accordingly as far as the product $X_m \cdot X_{m+1}$ is less than, or equal to, zero,

$$E_\pi = \sum_{k=1}^{N} |X_k| \qquad (13)$$

This formula exactly holds for all alternant and most nonalternant hydrocarbons, because the product $X_m \cdot X_{m+1}$ is not positive for them. Then, we arrive at a desired expression for the total π energy:

$$E_\pi \approx E_{Z*} \qquad (14)$$

i.e., for these compounds, the total π energy is said to approximate to $E_{Z*}$. The $Z^*$ values and the total π energies thus obtained for 20 typical conjugated hydrocarbons are presented in Table I. The agreement with HMO total π energies is quite satisfactory for all the hydrocarbons investigated.

For nonalternant hydrocarbons with $X_m \cdot X_{m+1} > 0$, eq 13 and 14 no longer hold. Among such rare hydrocarbons are symmetric fulvalenes and fulvadienes, and *as*-indacene.[15] With the intention of including these exceptions, we might most safely say that, as shown by eq 11, the logarithm of $Z^*$ is linearly related to the sum of the absolute values of all the HMO π orbital energies. The correlation between these two quantities is excellent even for these exceptional compounds. However, as eq 14 holds very well for most conjugated hydrocarbons, we term $Z^*$ a total π-energy index.

**Comparison with Hosoya's Total π-Energy Index $\tilde{Z}$.** An HMO characteristic polynomial P($X$) is divided into an even function S($X$) and an odd function A($X$) with respect to $X$, namely,

$$\mathrm{P}(X) = \mathrm{S}(X) + \mathrm{A}(X) = \sum_{k=0}^{m} a_{2k} X^{N-2k} + \sum_{k=0}^{m-1} a_{2k+1} X^{N-2k-1} \qquad (15)$$

The present index $Z^*$ is rewritten in terms of these functions as

$$Z^* = \{|\mathrm{S}(i)|^2 + |\mathrm{A}(i)|^2\}^{1/2} \qquad (16)$$

On the other hand, Hosoya et al. defined an analogous π-energy index $\tilde{Z}$ simply as[12]

$$\tilde{Z} = |\mathrm{S}(i)| \qquad (17)$$

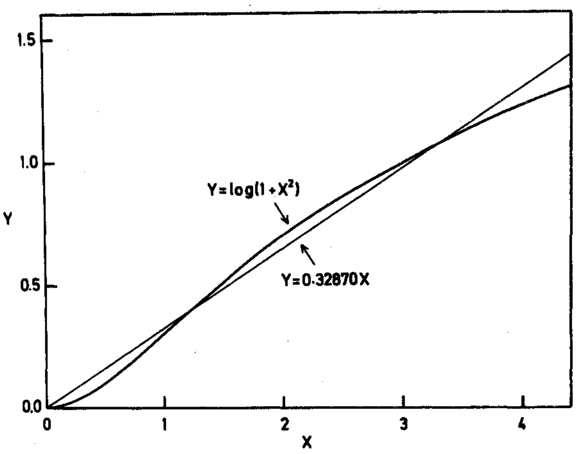

**Figure 1.** Plots of $Y = \log(1 + X^2)$ and its approximate form $Y = 0.32870X$.

where the contribution from the odd function A($i$) is missing. Contrary to $Z^*$, $\tilde{Z}$ is always an integral number. After practicing extensive numerical analysis, they showed that the logarithm of $\tilde{Z}$ is approximately proportional to the total π energy of the conjugated hydrocarbon. It is broadly true that, as the contribution from A($i$) is relatively small for most hydrocarbons (see Table I), Hosoya's index $\tilde{Z}$ is evidently comparable to our index $Z^*$. However, the mathematical justification for $\tilde{Z}$ and the limit of its utility remained obscure. As mentioned in a previous section, the derivation of $Z^*$ has overcome these difficulties. In this sense, our total π-energy index can be considered as a more general index for the HMO total π energy. From a mathematical standpoint, any other topological formula for the total π energy[4-9] is not so straightforward as ours.

For any alternant hydrocarbon, $Z^*$ is an integer, and agrees with $\tilde{Z}$ because A($X$) = 0. Conversely, for any nonalternant hydrocarbon, $Z^*$ is never an integer, and hence disagrees with $\tilde{Z}$. The decimal fraction of $Z^*$ obviously comes from A($i$). By correlating the coefficients of the HMO characteristic polynomial with corresponding Sachs graphs,[10,11] $Z^*$ can com-

**Table I. Total π-Energy Indices and Related Quantities for Typical Conjugated Hydrocarbons**

| Registry no. | Compd | \|S($i$)\| | \|A($i$)\| | $Z^*$ | $Z_0^*$ | Estimated total π energy ($\beta$)[a] | Estimated resonance energy ($\beta$)[b] |
|---|---|---|---|---|---|---|---|
| 1120-53-2 | Cyclobutadiene | 5 | 0 | 5.00 | 7 | 4.253 (4.000) | −0.889 (−1.226) |
| 71-43-2 | Benzene | 20 | 0 | 20.00 | 18 | 7.916 (8.000) | 0.278 (0.273) |
| 629-20-9 | Cyclooctatetraene | 45 | 0 | 45.00 | 47 | 10.059 (9.657) | −0.115 (−0.595) |
| 3227-76-7 | [10]Annulene | 125 | 0 | 125.00 | 123 | 12.759 (12.944) | 0.043 (0.159) |
| 497-20-1 | Fulvene | 16 | 2 | 16.12 | 15 | 7.436 (7.466) | 0.190 (0.020) |
| 5291-90-7 | Dimethylenecyclobutene | 13 | 0 | 13.00 | 15 | 6.778 (7.208) | −0.378 (−0.163) |
| 250-25-9 | Pentalene | 54 | 12 | 55.32 | 56 | 10.605 (10.456) | −0.032 (−0.215) |
| 257-24-9 | Heptalene | 384 | 32 | 385.33 | 386 | 15.734 (15.618) | −0.005 (−0.141) |
| 275-51-4 | Azulene | 149 | 10 | 149.34 | 147 | 13.229 (13.364) | 0.042 (0.151) |
| 267-21-0 | *s*-Indacene | 469 | 108 | 481.27 | 457 | 16.321 (16.231) | 0.137 (0.055) |
| 208-96-8 | Acenaphthylene | 522 | 52 | 524.58 | 466 | 16.549 (16.619) | 0.313 (0.354) |
| 209-86-9 | Cyclopent[*cd*]azulene | 464 | 66 | 468.67 | 466 | 16.251 (16.366) | 0.015 (0.101) |
| 209-42-7 | Aceheptylene | 1236 | 28 | 1236.32 | 1220 | 18.814 (18.911) | 0.035 (0.106) |
| 92-52-4 | Biphenyl | 464 | 0 | 464.00 | 388 | 16.225 (16.383) | 0.473 (0.502) |
| 4026-23-7 | Benzocyclobutadiene | 49 | 0 | 49.00 | 57 | 10.284 (10.381) | −0.400 (−0.393) |
| 259-79-0 | Biphenylene | 481 | 0 | 481.00 | 477 | 16.320 (16.505) | 0.022 (0.123) |
| 91-20-3 | Naphthalene | 170 | 0 | 170.00 | 148 | 13.571 (13.683) | 0.366 (0.389) |
| 120-12-7 | Anthracene | 1440 | 0 | 1440.00 | 1208 | 19.217 (19.314) | 0.464 (0.475) |
| 85-01-8 | Phenanthrene | 1489 | 0 | 1489.00 | 1233 | 19.306 (19.448) | 0.499 (0.546) |
| 129-00-0 | Pyrene | 4810 | 0 | 4810.00 | 3888 | 22.404 (22.505) | 0.562 (0.598) |

[a] See eq 14; exact values are placed in parentheses. [b] See eq 21; exact values are placed in parentheses.

pletely be assigned to individual $\pi$ bonds and $\pi$-electron rings in the conjugated system. Our expression for the total $\pi$ energy (eq 14) has a particular advantage in that the total $\pi$ energy can necessarily be assigned to the individual $\pi$ bonds and $\pi$-electron rings.[16,17] Especially, the coefficients of $\mathrm{A}(X)$ are attributed mainly to the odd-membered $\pi$-electron rings.[10] Therefore, eq 16 strongly suggests that the existence of such odd-membered rings increases, more or less, the total $\pi$ energy of the system. It goes without saying that the even-membered rings influence the total $\pi$ energy to much more extent.[12,16]

**Derivation of Dewar-Type Resonance Energy.** In a previous paper,[16] we graph-theoretically formulated Dewar's theory of aromaticity.[1,2] We therein proposed an HMO reference polynomial $\mathrm{R}(X)$ for a conjugated hydrocarbon defined as

$$\mathrm{R}(X) = \sum_{k=0}^{m} (-1)^k p(2k) X^{N-2k} \tag{18}$$

where $N$ and $m$ bear the same meanings as in eq 1–4. The coefficient $p(2k)$ is indicative of the number of ways in which $k$ $\pi$ bonds are so chosen from the conjugated system that no two of them are connected to each other.[11] By definition, $p(0) = 1$. The roots of $\mathrm{R}(X) = 0$ are supposed to represent the energies of the $\pi$ molecular orbitals which the hydrocarbon would possess if it were absolutely olefinic in nature. The reference energy $E_\pi°$, relative to which aromatic stabilization is calculated, can be estimated from the coefficients of this polynomial in the same manner as the actual total $\pi$ energy, i.e.,

$$E_\pi° \approx 6.0846 \log Z_0^* \tag{19}$$

where

$$Z_0^* = |\mathrm{R}(i)| = \sum_{k=0}^{m} p(2k) \tag{20}$$

Dewar-type resonance energy has been considered as the best measure of aromaticity available at present.[1,2] It has widely been accepted that it correlates very well with experimental stability for a variety of conjugated systems.[1,2,16] The resonance energy is defined as the difference between the total $\pi$ energy of the conjugated hydrocarbon and its reference energy.[2,16] These two $\pi$ energies were shown above to be estimated from eq 14 and 19, respectively. On this basis, the resonance energy RE of this type can now be estimated as

$$\mathrm{RE} = E_\pi - E_\pi° \approx 6.0846 \log \frac{Z^*}{Z_0^*} \tag{21}$$

The resonance energies thus obtained for the 20 conjugated hydrocarbons, together with their exact resonance energies (A-II resonance energies),[16] are also listed in Table I.

As may easily be seen from this table, the estimated resonance energy is in fairly good agreement with the exact one for all the hydrocarbons investigated. When the absolute value of the resonance energy is small, a discrepancy between these two resonance energies may be large. However, a better agreement is naturally attained as the size of the conjugated system increases. It is especially noteworthy that the sign of the estimated resonance energy is always in accord with that of the exact one. This fact means that aromaticity or antiaromaticity can assuredly be inferred from the sign of the former resonance energy.

As stated before, the coefficients of the HMO characteristic polynomial can manually be enumerated with little difficulty from the geometry of the conjugated system.[10,11] The coefficients of the HMO reference polynomial can more easily be obtained as nonadjacent numbers for the same system.[11] It should hence be emphasized that the total $\pi$ energy and the resonance energy for a conjugated hydrocarbon, both usually obtained by complicated MO calculations, can accurately be reproduced merely by inspecting the $\pi$-electron framework. This implies that the present approach can be employed as a practical and instructive basis for chemistry of a conjugated hydrocarbon.

## References and Notes

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