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Validity of a Linear Estimator for the Total π-Electron Energy of Alternant Hydrocarbons

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The validity of a linear topological estimator formula which possesses a slope k such that $0 < k < 1$, where k is dependent on the topology of the system, is proved for the totol π-electron energy of alternant hydrocarbons.

Introduction

So far, numereous topological formulas have been derived [1-15] for the totol π-electron energy, E, (or bounds of E) of alternant hydrocarbons. Although, starting from different standing points and using quite dissimilar approaches, most of these derivations resulted in McClelland-type[1] topological formulas (eq. $E = g(ne)^{1/2}$, g is a constant) in which E is determined by only two topological invariants, namely, the number of carbon atoms, N, and the number of carbon-carbon bonds [9,16], e. So far, the role of other graph invariants preserve their mystery and their effects collectively made use of in the angle of total π- electron energy[13,17]. On the other hand, Hall's formula[10,11] for E of benzenoid hydrocarbons has linear dependence on N, e and the number of Kekule structures. In that sense, it differs from the McClelland-type formulas which are known as nonlinear E forulas. Below, within the Hückel molecular orbital (HMO) framework, a novel linear estimator for E of alternant hydrocarbons is derived and tested for its validity.

Theory

Let, $G(2n, e)$ be a molecular grap[18] of an even alternant hydrocarbon, A. Suppose, the occupied molecular orbital energies of A are $X_1 =< X_2 =< \ldots =< X_n$ and its total π-electron energy, E, is defined [18] as

$$E = 2\sum_{i=1}^{n} X_i, \tag{1}$$

where n is half the number of carbon atoms, N.

Suppose, E is linear in n and e such as

$$E = k(e + n), \tag{2}$$

where $k > 0$ is a topological parameter. Squaring both sides of Eq. 2 one obtains

$$k^2(e+n)^2 = E^2 \tag{3}$$

Now, using a property of ratios, namely adding the right hand side of Eq. 3 into the left hand side one gets

$$(k^2(e+n)^2 + E^2)/2 = E^2 \tag{4}$$

Dividing both sides of Eq. 4 by E^2 yields

$$(k^2(e+n)^2 + E^2)/2E^2 = 1 \tag{5}$$

Now, substitute Eq. 2 in the denominator of Eq. 5 as follows:

$$(k^2(e+n)^2 + E^2)/2E(e+n)k = 1. \tag{6}$$

An Upper Bound For k

To estimate the value of k, let

$$((e+n)^2 + E^2)/2E(e+n) = R \tag{7}$$

Note that Eq. 7 is the limit of Eq. 6 for $k = 1$. It is quite easily proved that $R >= 1$. By rearranging Eq. 7, one obtains an equation for a parabola in the parametric form:

$$E^2 - 2(e+n)RE + (e+n)^2 = 0. \tag{8}$$

One can easily prove that only the smallest root of Eq. 8 stands for E value of alternant hydrocarbons, that is

$$E = (e+n)(R - (R^2-1)^{1/2}) \tag{9}$$

thus

$$k = R - (R^2-1)^{1/2} \tag{10}$$

Since $R >= 1$, let $R = 1 + p$ where p stands for a small perturbation, $p >= 0$. Then, express Eq. 9 in terms of p:

$$E = (e+n)(1 + p - (p^2 + 2p)^{1/2}). \tag{11}$$

using the binomial expansion[19] of the term in the square root, Eq. 11 becomes

$$E = (e+n)(1/2(1+p)^2 + 1/8(1+p)^4 + 1/16(1+p)^6 + \ldots). \tag{12}$$

Since p is positive then each summand in the parenthesis is smaller than the corresponding term obtained by inserting $p = 0$. So the whole sum in Eq. 12 is less than

$$S = \lim_{t \to \infty} \sum_{i=1}^{t} (1/t!) \prod_{i=1}^{t-i} (i - 1/2), \tag{13}$$

which can be derived quite easily by using the binomial expansion[19]. Then, obviously, Eq. 12 becomes

$$E =< (e+n)S \tag{14}$$

On the other hand, substitution of $p = 0$ into Eq. 11 reveals that $S = 1$. Hence, by using Eq. 14, one can indeed satisfactorily estimate E as

$$E = (e+n)k, \tag{15}$$

where it is expacted to be $0 < k =< 1$.

Topological Bounds For k

Since, for alternant hydrocarbons Eq. 16 holds [13] as

$$e = 2(en)^{1/2} \cos Q, \tag{16}$$

where Q is the angle of total n-electron energy, inserting Eq. 16 into Eq.15 one obtains

$$2(ne)^{1/2} \cos Q = (e+n)k, \tag{17}$$

Rearranging Eq.17 it becomes

$$\cos Q/k = \left((e)^{1/2} - (n)^{1/2}\right)^2 /2(ne)^{1/2} + 1. \tag{18}$$

Since $\cos Q =< 1$ Eq. 18 clearly shows that k cannot be equal to 1. On the other hand, it is known [17] that $\cos Q >= 1/2$. inserting this value into Eq. 17 and solving for k yields

$$k >= (ne)^{1/2}/(e+n). \tag{19}$$

A better but more complicated lower bound for k is obtained by inserting Eq.20 (see Ref. 13) into Eq. 17 and solving for k

$$\cos Q >= ((e + 2(a_4)^{1/2})/ne)^{1/2} \tag{20}$$

where a_4 is expressed [4] as

$$a_4 = \binom{e}{2} - V_2 - 3V_3 - 2R_4, \tag{21}$$

where V_2, V_3 and R_4 stand for the number of vertices of degree 2,3 and the number of 4-membered rings, respectively. Thus,

$$k >= 2\left(e + 2(a_4)^{1/2}\right)^{1/2} /(e+n) \tag{22}$$

On the other hand, it is known [13] that

$$\cos Q =< \left[\left[e + 2(ma_4)^{1/2}\right) /ne)\right]^{1/2} , \tag{23}$$

where m is given [4] as $m = \binom{n}{2}$. Inserting Eq. 23 into Eq.17 and solving for k yields

$$k =< 2(e + 2(ma_4)^{1/2})^{1/2}/(e + n) \tag{24}$$

Results and Discussion

Eq. 15 is a linear topological formula for E of alternant hydrocarbons based on invariants of the molecular graph being considered. The slope, k which lies between 0 and 1 is also dependent on topology. The upper and lower bounds, in eqs. 19, 22 and 24 enable one to estimate the range of k of a system. In general, the value of k is close to 1. For instance, a set of benzeneoid hydrocarbons (20) possesses 0.828535 (SDEV : 0.008752) as the mean of k. All of these imply that eq 15 can be used as a good estimator for E of alternant hydrocarbons.

On the other hand, Eq. 15 clearly shows that variations of E values of isomeric compounds which possess obviously the same e and n values are dictated by k values only. Since, the range of k is quite narrow, E values of isomeric compounds should not differ much from each other.

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