

A NOVEL TOTAL π -ELECTRON ENERGY FORMULA
FOR ALTERNANT HYDROCARBONS - ANGLE OF TOTAL
 π -ELECTRON ENERGY

LEMI TÜRKER

Middle East Technical University,
Department of Chemistry, Ankara , Turkey.

(received: May 1993)

Abstract. The geometrical interpretation of E_{π} is presented. A new type of formula in parametric form is derived for the total n -electron energy of alternant hydrocarbons. It has been proved that E_{π} cannot be lower than $(ne)^{1/2}$ for alternant hydrocarbons. The concept of angle of total n -electron energy is developed.

1. Introduction.

Total n -electron energy (E_{π}) is one of the most important pieces of information about a conjugated molecule which can be obtained from simple Hückel molecular orbital (HMO) calculations (1,2) The investigation of general properties of E_{π} has attracted the attention of many researches and a great deal of effort has been made to derive rigorous upper and lower bounds for E_{π} (3-16). McClelland's formula was the first of such bounds (3). Nowadays, there are very many known bounds for total n -electron energy formula. A systematic study of all these approximate formulas revealed that they are mainly based on number of vertices, number of

edges and number of Kekule' structures (17,18).

In the present study, a generalized type of E_n formula which has been recently reported (19) is converted to a parametric form for total n -electron energies of alternant hydrocarbons. Then the concept of the angle of total n -electron energy is developed in the light of the parametric E_n formula derived.

2. Theory.

The total n -electron energy of an alternant hydrocarbon having e bonds and $2n$ atoms is expressed by eq.16 (19).

$$E_n = 2(ne)^{1/2} \cos \theta_n \quad (1)$$

where, θ_n is the angle between the vectors A and B defined in an n -dimensional Euclidean linear space (20) as follows,

$$A(X_1, X_2, \dots, X_n) \quad B(1, 1, \dots, 1)$$

where X_i stand for occupied molecular orbital energies of the molecule. Obviously eq.1 leads to McClelland's upper bound (eq.2) for E_n energy (3) if one considers that $\cos \theta_n \leq 1$.

$$E_n \leq 2(ne)^{1/2} \quad (2)$$

Theorem 1. Let G_0 be a Hückel graph having $2n$ vertices, e edges and R rings. Then, the total n -electron energy cannot be lower than $(ne)^{1/2}$.

Proof.

Draw a circle having radius of $2(ne)^{1/2}$ with centre at

the origin of the coordinates (Fig.1). Let ZOS angle be equal to θ . Then the projection of radius OS on the OY-axis for angle $\theta = \theta_n$ will be E_n energy of the conjugated molecule corresponding to graph G_n . Through the intersection of OY-axis with the circle (point Z) draw a perpendicular to OS . Then, project the point U (which is the foot of the previous perpendicular) on the OY-axis and let the intersection point be U' .

Since, $ZU \perp OS$ and $ES \perp OZ$, $OS = OZ = 2(ne)^{1/2}$ and $OE = OS \cos \theta$, $OU = OZ \cos \theta$ then $OE = OU$. Let it be $OE = E$. Obviously, the difference , h , which is equal to $E - OU'$ can be expressed as ,

$$h = (2(ne)^{1/2} - E) \cos \theta \quad (3)$$

Inserting $E = 2(ne)^{1/2} \cos \theta$, eq.3 becomes ,

$$h = 2(ne)^{1/2} (\cos \theta - \cos^2 \theta) \quad (4)$$

On the other hand, insertion of $\cos \theta = E/2(ne)^{1/2}$ converts eq.3 into eq.5 .

$$h = E - (E^2/2(ne)^{1/2}) \quad (5)$$

The function $h(E)$ is a parabolic function of E having its maximum at $E = (ne)^{1/2}/2$.

On the other hand, starting from eq.5 one gets

$$E^2 - 2(ne)^{1/2} E + 2(ne)^{1/2} h = 0 \quad (6)$$

which leads to

$$E = (ne)^{1/2} + (ne - 2(ne)^{1/2} h)^{1/2} \quad (7)$$

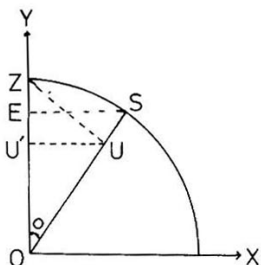


Figure 1. The geometrical meaning of E_n energy.

Obviously, eq.7 produces E_n if one substitutes $h = h_n$. Since, E_n and h_n are real positive quantities (see eqs.1 and 4) then the minimum value of eq.7 is obtained for the maximum value of h ($h_{\max} = (ne)^{1/2} / 2$) which leads to $(ne)^{1/2}$ for lower bound for E_n .

On the other hand, by substituting $E \geq (ne)^{1/2}$ into eq.1 and solving for D_n yields $0 \leq n/3$ which proves the following corollary.

Corollary 1. Let G_0 be a Hückel graph having $2n$ vertices and e edges. Then $D_n \leq n/3$ holds.

Theorem 2. Let G_0 be a Hückel graph having $2n$ vertices and e edges. Let A represent the adjacency matrix of G_0 . If $|\det A| \geq (e(n-1)/n(2n-1))^{n/2}$ holds then D_n for G_0 is less

than $n/4$.

Proof .

Consider eqs. 5 and 7 and let

$$Y = (ne)^{1/2} + (ne - 2(ne)^{1/2} h)^{1/2} \quad (8)$$

and

$$h = X - X^2/2(ne)^{1/2} \quad (9)$$

By substituting eq.9 into eq.8 one obtains

$$Y = (ne)^{1/2} + ((ne)^{1/2} - X) \quad (10)$$

which yields

$$Y_1 = X \quad (11)$$

and

$$Y_2 = 2(ne)^{1/2} - X \quad (12)$$

Now, draw a circle having radius of $2(ne)^{1/2}$ with centre at the origin of the coordinates (Fig.2) . From the intersection points of the circle with the axes draw parallel lines to X and Y axes to get a square. Let points D and G be the intersections of the diagonals with each other and one of the diagonal (the one having the positive slope) with the circle, respectively. \vec{OF} is the radius vector which sweeps angle θ . Note that its projection on the X-axis is equal E_n for $\theta = \theta_n$. The diagonals are analytically represented by eqs. 11 and 12 .

Since, eqs. 11 and 12 are obtained from eqs. 8 and 9 , then as X varies in the range of 0 and $2(ne)^{1/2}$, Y_1 also

varies in the same range and becomes E_n for $X = E_n$.

As vector \vec{OF} rotates in positive direction, point F approaches and coincides with point G which is a common point of the circle with the diagonal DC . The coordinates of point G can be found easily as $(2en)^{1/2}$ and $(2en)^{1/2}$, respectively. As it is seen from Fig.2, if $E_n \gg (2en)^{1/2}$ then point F on the circle has to lie in between points G and B . Since, McClelland's lower bound (3) is given as

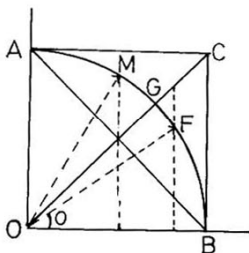


Figure 2. The geometrical interpretation of upper and lower bounds for E_n of alternant hydrocarbons.

$$E_n \geq (2e + 2n(2n-1) |\det A|^{2/n})^{1/2} = E_{ML} \quad (13)$$

Then, if

$$E_n \geq E_{ML} \geq (2en)^{1/2} \quad (14)$$

occurs, consequently $\widehat{FB} < \widehat{GB}$ which means $D_n \ll n/4$.

Combining ineqs. 13 and 14 in the desired way, one obtains

$$2e + 2n(2n-1) |\det A|^{2/n} \geq 2ne \quad (15)$$

which yields

$$|\det A| \geq (e(n-1)/n(2n-1))^{n/2} \quad (16)$$

Theorem 3. Let G_n be a benzenoid graph having $2n$ vertices and e edges. If $2e^2 - 9en + 12n^2 \geq 0$ holds then $\theta_n \leq \pi/4$.

Proof.

It is known that for benzenoid hydrocarbons ineq.17 is valid (16) .

$$E_n \geq (4e^3/(9e - 12n))^{1/2} \quad (17)$$

If,

$$(4e^3/(9e - 12n))^{1/2} \geq (2ne)^{1/2} \quad (18)$$

holds then from Fig.2 it is obvious that $\theta_n \leq \pi/4$.

Rearranging ineq.18 , one obtains

$$2e^2 - 9en + 12n^2 \geq 0 \quad (19)$$

which proves the theorem.

Conjecture 1. For alternant hydrocarbons having $2n$ atoms such that the numbers of starred and unstarred atoms obey $n^* - n^o = 0$ or 1 (Kekule type (2)) $\theta_n \leq \pi/4$ holds .

3. Results and Discussion.

The angle θ_n is an important topological parameters of molecules. All the variations in fine topology are included in $\cos \theta_n$ term. As it is proved above, for alternant hydrocarbons, θ_n , in theory, should vary in between 0 and 60 . However, a search involved very many alternant systems

revealed that $O_n \leq 45$. Cyclobutadiene and methylenepropenyl system are almost all the examples for which $O_n = 45$. On the

Table 1.

E_n and O_n values of certain alternant hydrocarbons.

Molecule	E_n (21)	O_n
Benzene	8.000	19.471
Naphthalene	13.684	22.694
Anthracene	19.312	24.160
Phenanthrene	19.448	23.244
Triphenylene	25.274	23.189
Perylene	28.245	24.272
Coronene	34.571	24.352
Ovalene	46.497	24.8104
Butadiene	4.472	24.098
Cyclobutadiene	4.000	45.000
Cyclooctatetraene	9.657	31.398
Biphenyl	16.383	21.950
1,1-Diphenylethylene	18.815	23.353
2-Vinylbutadiene	6.899	27.044

other hand, ethylene is on the other extreme having $O_n = 0$.

Table 1. displays the exact E_n and O_n values of certain alternant hydrocarbons which possess $O_n \leq 45$.

4. Conclusion.

The present work emphasizes the importance of the generalized McClelland type formula (eq.1) . It yields a brand new E_n formula (eq.7) which is the function of n , e and h . It appears to be a very potential formula to enlighten the importance of some mysterious topological parameters which dictate even the fine variations in total n -electron energies of alternant hydrocarbons. Note that all the theorems and formulas given above can be modified for odd alternant systems by replacing n with $N/2$ where N is the number of atoms.

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