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FACTORS INFLUENCING THE FMO ENERGIES OF ALTERNANT HYDROCARBONS

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Abstract: Within the Hückel molecular orbital theory, the angle of frontier molecular orbital energy is defined and an expression for the highest occupied molecular orbital (HOMO) energy of alternant hydrocarbons is derived. Conditions for the highest and the lowest values of HOMO energy are discussed.

1. Introduction.

The frontier molecular orbital (FMO) energies[1] of molecules attracted a great deal of attention because even within the framework of Hückel molecular orbital theory (HMO), many physico-chemical properties of molecules are determined by, or are at least highly dependent upon the frontier molecular orbital energy gap that is the separation between the highest occupied and the lowest unoccupied molecular orbital energies, namely HOMO-LUMO energy difference[2,3]. Also, some physico-chemical properties such as light absorption depend on HOMO-LUMO energy separation, some other directly correlate with HOMO or LUMO

energies itself, for instance the oxidation or reduction potentials[2,3] etc. In recent decades, many graph theoretical techniques have been developed which are helpful to analyse and partially understand the dependence of the π-electron properties of conjugated molecules on molecular topology[4-8] .

In the present study, using the classical HMO approach first , an expression for the HOMO energy of alternant hydrocarbons has been derived. Second , the conditions for the maximum and minimum values of FMO energies are sought.

2. Theory.

Suppose G(2n,e) is the molecular graph of an even alternant hydrocarbon within the constraints of the Hückel molecular orbital theory. Let the occupied molecular orbital energies be $X_1 \geq X_2 \geq \ldots \geq X_{n-1} \geq X_n$ in units of β.[2,3].

Now, consider an n-1 dimensional Euclidean linear space[9] and let vectors A and B be defined as follows.

$$A(1,1,\ldots,1) \quad \text{and} \quad B(X_1X_n, X_2X_n, \ldots, X_{n-1}X_n)$$

Then, the scalar product[10] of these vectors can be expressed as,

$$A.B = \sum_{i=1}^{n-1} X_iX_n$$

It is equivalent to

$$X_n \sum_{i=1}^{n-1} X_i = \left((n-1)\sum_{i=1}^{n-1} X_i^2X_n^2\right)^{1/2} \cos L_n \qquad (1)$$

which can be simplified into

$$\sum_{i=1}^{n-1} X_i = ((n-1) \sum_{i=1}^{n-1} X_i^2)^{1/2} \cos L_n \qquad (2)$$

Definition 1: The angle, L_n, is called the angle of frontier molecular energy.

It is known that the total π-electron energy[2,3] (E_π) for alternant hydrocarbons can be expressed as[11],

$$E_\pi = 2 \sum_{i=1}^{n} X_i = 2(ne)^{1/2} \cos O_\pi \qquad (3)$$

where O_π is called the angle of total π-electron energy[11].

Multiplying both sides of eq.2 by 2 and considering[12] that $\sum_{i=1}^{n} X_i^2 = e$ and

$$2\sum_{i=1}^{n-1} X_i = E_\pi - 2X_n \qquad (4)$$

one obtains

$$E_\pi - 2X_n = 2((n-1)(e - X_n^2))^{1/2} \cos L_n \qquad (5)$$

Squaring both sides of eq.5 and solving for X_n, eq.6 is produced.

$$X_n = (E_\pi - D)/2P \qquad (6)$$

where

$$D=((n-1)(4eP - E_\pi^2))^{1/2} \cos L_n \qquad (7)$$

and

$$P = 1 + (n-1)(\cos L_n)^2 \qquad (8)$$

Hence, eq.6 ,in form, is a certain combination of E_π , n , e and cos L_n. Therefore, the variations of X_n values of

isomeric compounds are dictated merely by E_π and cos L_n values. On the other hand, from eqs. 7 and 8 , the necessary condition for a real X_n is obtained as

$$(\cos L_n)^2 \geq (E_\pi^2 - 4e)/4e(n-1) \qquad (9)$$

Substitution of $P = E_\pi /2y$ into eqs. 8,7 and then into eq.6 produces a more informative and suitable expression for X_n as a function of y that is

$$X_n = y - ((2E_\pi y^2 - (E_\pi^2 + 4e)y + 2eE_\pi)/2E_\pi)^{1/2} \qquad (10)$$

On the other hand, using eq.10 and taking the derivative of X_n with respect to L_n (using the chain rule) and equating to zero produces $L= 0, (2k+1)\pi$. Hence, insertion of cos $L_n=1$ into eqs.8 through 6 yields

$$(X_n)_{min} = (E_\pi /2n) -((1- 1/n)(e- E_\pi^2 /4n))^{1/2} \qquad (11)$$

Note that ineq.9 requires $D\geq 0$ thus, the maximum value of X_n can be obtained by inserting ineq.9 into eq.6 that is

$$(X_n)_{max} = 2e/E_\pi \qquad (12)$$

Theorem 1. Let A be an even alternant hydrocarbon having molecular graph G(2n,e). If the total π-electron energy is greater than $2(e(n-1))^{1/2}$ then A cannot have any nonbonding molecular orbitals (NBMO).

Proof.

Since, an NBMO possesses $X_n = 0$, by inserting this value into eq.6 and using eq.7 and 8 one gets

$$(\cos L_n)^2 = E_\pi^2 / 4e(n-1) \qquad (13)$$

but obviously, $\cos L_n \leq 1$ thus , eq.13 yields

$$E_\pi \leq 2(e(n-1))^{1/2} \qquad (14)$$

Hence, any even alternant hydrocarbon which does not fulfill the above inequality cannot have $X_n = 0$. Note that ineq.14 necessitates $\cos O_\pi \leq ((n-1)/n)^{1/2}$. For instance, in the case of benzene which does not conform to the condition, the possibility of having $X_n=0$ is definitely excluded (also true for naphthalene, anthracene etc.) whereas it is possible for cyclobutadiene, cyclooctatetraene etc. Indeed they possess $X_n = 0$.

Corollary 2. Let A be an even alternant hydrocarbon whose molecular graph possesses e edges and 2n vertices. If $E_\pi^2 - 4E_\pi + 4 \leq 4(e-1)(n-1)$ does not hold for A then its X_n value cannot be equal to unity.

Note that corollary 2 is true for systems for which the required condition fails. On the other hand , inserting eq.3 for E_π , the condition for corollary 2 can be expressed in the form of

$$\cos O_\pi \leq (1/en)^{1/2} (1 + ((e-1)(n-1))^{1/2}) \qquad (15)$$

Theorem 3. Let G(N,e) be the molecular graph of an odd alternant hydrocarbon. Then, $\cos O_\pi \leq ((N-1)/(N+1))^{1/2}$.

Proof.

Since, an odd alternant hydrocarbon possesses an NBMO, it has (N+1)/2 occupied molecular orbitals thus the number of

components of vectors A and B considered above is (N-1)/2 . Consequently, n in ineq.14 has to be replaced by (N+1)/2 . Then, ineq.14 becomes ineq.16 for odd alternant systems.

$$E_{\pi} \leqslant (2e(N-1))^{1/2} \qquad (16)$$

whereas E_{π} (eq.3) becomes

$$E_{\pi} = (2e(N+1))^{1/2} \cos O_{\pi} \qquad (17)$$

In the light of theorem 1 (to have an NBMO) , substituting eq.17 into ineq.16 and simplifying one obtains

$$\cos O_{\pi} \leqslant ((N-1)/N+1))^{1/2} \qquad (18)$$

3. Results and Discussion.

Equation 6 is a topological expression for the HOMO energy of alternant hydrocarbons within the framework of Hückel molecular orbital theory. It is a function of E_n , n , e and cos L_n only. It is obvious that what have been proved and discussed so far is true for the absolute value of LUMO energy because of the nature of FMO energies of alternant hydrocarbons[2,3].

Since, E_{π} is the function of the angle of total π-electron energy, O_{π} , then the FMO energies of alternant hydrocarbons are dictated by n and e which are related to gross topology of the system and two angles, O_{π} and L_n which reflect the fine topological changes.

Inasmuch as , E_{π} can be topologically evaluated[12] quite accurately, the value of cos L_n has the main importance if

one wishes to estimate X_n via eq.6. A search for the approximate value of cos L_n has been carried out in the present study for the pool of 106 benzenoid compounds[13] which yields mean of .930466 having $5.68542\ 10^{-3}$ and $3.23240\ 10^{-5}$ for the standard deviation and variance, repectively. For all the benzenoid compounds studied, it has been found that $|\cos O_\pi - \cos L_n| \leq .1$ and for some of them this difference is even much less (ca. .015) . Whereas, the mean of cos O_π /cos L_n is .966256 for the same class of compounds (standard deviation: .0136999). All these imply that the values of angle of FMO energy of benzenoid hydrocarbons are quite comparable with their angle of total π-electron energy values.

For the arbitrarily chosen 25 alternant hydrocarbons the mean of cos L_n yields the value of .954127 (having standard deviation of .0204463).

As it is clear from eqs. 6-8, X_n values of isomeric compounds vary only because of their E_π and cos L_n values. For isomeric sets of compounds the upper and lower limits of X_n are given by eqs.11 and 12, respectively. Of these, the former one is obtained in a classical way namely by differentiating eq.10 with respect to L_n using the chain rule and inserting the root of the derivative into eq.10 . However, the derivative also becomes zero for $E_\pi = 2(e)^{1/2}$. If this happens for an alternant hydrocarbon then X_n does not have any extremum whatever the value of L_n is . This situation arises for cyclobutadiene (X_n function is a straight line , $E_\pi = 4.000\ \beta$) which possesses two

nonbonding molecular orbitals[14].

A search , involving more than a hundred alternant hydrocarbons for the validity of the condition formulated in ineq.15 implies that indeed their cos O_π values fulfill the requirement of ineq.15 . Hence, the following conjecture can be asserted.

Conjecture 1. For all the alternant hydrocarbons $E_\pi^2 - 4E_\pi + 4 \leq 4(e-1)(n-1)$.

Since, $X_n=1$ for ethylene, then corollary 2 in an indirect way leads to the principle already known that is the extended conjugation narrows the interfrontier energy gap[1].

4. Conclusion.

The angle of FMO energy of an alternant hydrocarbon is confined to the range of 0 to arccos $((E_\pi^2 - 4e)/4e(n-1))^{1/2}$. In the case of benzenoid hydrocarbons L_n is quite close to the corresponding O_π values. The FMO energies of isomeric compounds are merely dictated by O_π and L_n which should be interrelated with each other implicitly.

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