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# CONTEMPLATION ON THE TOTAL II-ELECTRON ENERGIES OF ALTERNANT HYDROCARBONS

LEMİ TÜRKER

Middle East Technical University
Department of Chemistry
Ankara, Turkey

Abstract. Within the constraints of the Hückel molecular orbital theory, the generalized formula of McClelland-type for the total π-electron energies (E) of alternant hydrocarbons has been modified and separated into two subfunctions which should yield E values of alternant hydrocarbons in the different ranges of the angle of total π-electron energy.

## 1. Introduction

The finding (1) that there exists a precise linear relationship between the total π-electron energy (E) and the kinetic energy of the π-electrons in a conjugated molecule caused the investigations to focus on the topological backgrounds of E to acquire a great interest and importance in the last decade (2-14).

Although, the structural factors that determine the gross part of E are now identified , a complete solution of

the question that is how fine topological changes influence E still preserves its mystery.

In the present study, some interesting findings on E values of alternant hydrocarbons are mentioned within the constraints of Hückel molecular orbital (HMO) approach (15).

## 2. Theory

It is known that E of alternant hydrocarbons is expressed (9) as

$$E = 2(ne)^{1/2} \cos O_{\pi} \qquad (1)$$

where the number of carbon-carbon bonds and half the number of carbon atoms are represented by e and n , respectively whereas the angle $O_{\pi}$ is called the angle of total $\pi$-electron energy which reflects the fine topology of the system. Since, $\cos O_{\pi} \leq 1$ , eq.1 yields McClelland's upper bound (16) , ineq.2 .

$$E \leq 2(ne)^{1/2} \qquad (2)$$

In the period before the derivation of eq.1 , E values were estimated by using a formula based on ineq.2 that is

$$E \approx 2a(ne)^{1/2} \qquad (3)$$

where a, inherently related to $\cos O_{\pi}$ was determined from the known values of E for some group of conjugated molecules (2,6). McClelland-type nonlinear lower bounds for E are also common in the literature. For example, it was proved by

Gutman (6) that

$$E \geq 2g(ne)^{1/2} \quad ; \quad g = (16/27)^{1/2} \qquad (4)$$

holds for all benzenoid molecules. Cioslowski also reported (17) another lower bound of the above type (ineq.4) with the g value which is equal to 0.6734 . Some more bounds of the same type are obtained by Babic' and Gutman (18). Recently, it has been proved (13) that the lowest bound for E of alternant hydrocarbons possesses the g value of 0.5 .

Below, it will be pointed out that alternant hydrocarbons ought to be grouped, at least theoretically, into two classes, depending on the mathematical functions which yield their E values .

Modification of the McClelland-type formula

For the purpose of the modification of the generalized McClelland formula (eq.1), construct an oblique cartesian coordinate system, having an acute angle which is equal to $O_\pi$ of the alternant hydrocarbon being considered (Fig.1).

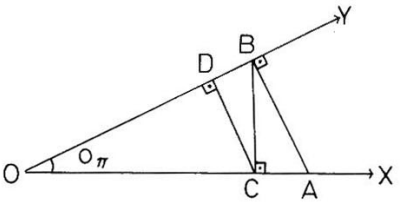


Fig.1 An oblique cartesian system used for the derivations.

On the X-axis, choose a point A such that OA = E .Then draw a perpendicular from point A to the Y-axis. After that, from the foot (B) of the first perpendicular draw another one to the X-axis and finally from the intersection point (C) of the second perpendicular and the X-axis draw a perpendicular to the Y-axis. Let the foot of the third perpendicular be point D. From Fig.1 obviously, $OB = E \cos O_{\pi}$ , $OD = E \cos^3 O_{\pi}$ and

$$DB = E \cos O_{\pi} - E \cos^3 O_{\pi} \equiv t \qquad (5)$$

Solving eq.1 for $\cos O_{\pi}$ and inserting into eq.5 one gets

$$t = E^2/2(ne)^{1/2} - E^4/8ne(ne)^{1/2} \qquad (6)$$

solving for E yields

$$E_1 = (2ne + u)^{1/2} \quad \text{and} \quad E_2 = (2ne - u)^{1/2} \qquad (7)$$

where

$$u = (4n^2e^2 - 8ne(ne)^{1/2}\, t\,)^{1/2} \qquad (8)$$

Evidently, the real values of u require $t \leqslant (ne)^{1/2}/2$ .

On the other hand, inserting eq.1 into eq.5 one obtains,

$$t = 2(ne)^{1/2}( \cos^2 O_{\pi} - \cos^4 O_{\pi} ) \qquad (9)$$

Substitution of eq.9 into eq.8 and then eq.8 into eq.7 yields

$$E_{1,2} = (2ne)^{1/2} (1 \mp (1 - 4(\cos^2 O_{\pi} - \cos^4 O_{\pi} ))^{1/2} )^{1/2} \qquad (10)$$

Figures 2 and 3 display E vs. u and E vs. $O_{\pi}$ graphs for alternant hydrocarbons.

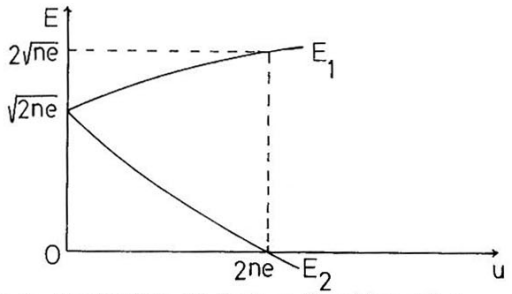


Fig.2 Variation of E as a function of u.

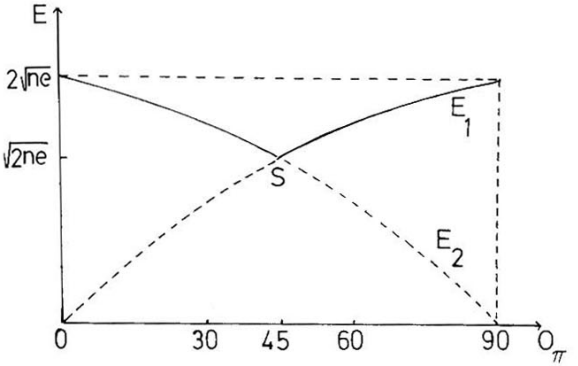


Fig.3 Variation of E as a function of $O_{\pi}$ .

Estimation of the q value.

Figure 2 shows that as u varies from zero to 2ne , $E_1$ increases smoothly from $(2ne)^{1/2}$ to $2(ne)^{1/2}$. Thus, its

functional average (19)

$$E_1 = (1/2ne) \int_0^{2ne} (2ne + u)^{1/2} \, du \qquad (11)$$

is equal to

$$E_1 = (2^{3/2}/3)(2^{3/2}-1)(ne)^{1/2} \qquad (12)$$

On the other hand, as u varies between 0 and ne, $E_2$ smoothly decreases such that $(2ne)^{1/2} \geq E_2 \geq (ne)^{1/2}$ . The functional average of $E_2$ yields the g value as $(2^{3/2}-1)/3$ .

## 3. Results and discussion

The generalized McClelland-type formula (eq.1) in its modified form (eq.10) consists of two complementary equations , $E_1$ and $E_2$ . Figure 3 displays graphs of these as the function of $\theta_\pi$ . As it is evident from the figure, the combination of arcs of $E_1$ and $E_2$ engenders $E= 2(ne)^{1/2} \cos \theta_\pi$ graph in the range of $0 \leq \theta_\pi \leq \pi/2$ . Thus , the approach utilized in the present study unveils some hidden topological factors which are effective on the total π-electron energies of alternant hydrocarbons. For instance, one can visualize the geometrical meaning of various upper and lower bounds for E. Obviously, E should mimic $E_1$ curve (solid curve in Fig.3) in the region of $0 \leq \theta_\pi \leq \pi/4$ in order to be single-valued in the range of $0 \leq \theta_\pi \leq \pi/3$ (the maximum value of $\theta_\pi$ is 60° (13)), whence $E_2$ curve (dashed curve) should be mimiced for $\pi/4 \leq \theta_\pi \leq \pi/3$ . Note that, although $E_1$ produces E in the range of $(2ne)^{1/2}$ to $2(ne)^{1/2}$, $E_2$ yields E values only in between $(ne)^{1/2}$ and $(2ne)^{1/2}$ . The abrupt character changes

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(S is the spinode (cusp) point (19) in Fig.3) of $E_1$ and $E_2$ curves occur at $\theta = \pi/4$ .

In the light of the present treatise, the angle corresponding to cusps of $E_1$ and $E_2$ curves is critical and it is equal to $\pi/4$. There are a few molecules having $\theta_\pi = \pi/4$ . For instance, cyclobutadiene and methylenepropenyl system (which is a non-Kekulean structure (20)) have to be cited.

On the other hand, the g values obtained from the functional averages of $E_1$ and $E_2$ are 0.8619 and 0.6095 , respectively. The former value is greater than the one obtained by Gutman (6) which is 0.7698 and holds for all benzenoid compounds. Whereas the value obtained from $E_2$ function is less than Cioslowski's bound (17), 0.6734 .

## 4. Conclusion

Within the HMO framework, the total $\pi$-electron energies of alternant hydrocarbons fall on the curves of $E_1$ or $E_2$ if $\theta_\pi$ lies in between 0 and $\pi/4$ or $\pi/4$ and $\pi/3$ , respectively . However, E vs u curve (Fig.2) implies that in order to have a single value for the total $\pi$-electron energy for the same value of u , either $E_1$ or $E_2$ should be abandoned or alternant hydrocarbons should be grouped into two classes depending on whether $E_1$ or $E_2$ reproduces their E values.

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