

AN UPPER BOUND FOR TOTAL π -ELECTRON ENERGY
OF ALTERNANT HYDROCARBONS

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Abstract. An upper bound for total π -electron energy of alternant hydrocarbons is derived which reflects the topology of the molecules much better than the McClelland's formula.

1. Introduction

The total π -electron energy (E_{π}) is an important property of conjugated molecules and has attracted much attention in the last few decades [1-3]. Coulson found the relationship which exists between E_{π} and the coefficients of the molecular graph [4]. Gutman et al have made several efforts to modify the original complicated analytical form of Coulson's formula [5]. The McClelland's formula is the simplest of all the topological total π -electron energy formulae [6] but it contains insufficient

topological parameters to reproduce E_π with an accuracy which is required for chemical purposes [5].

In this work a rather simple formula for the upper bound of E_π has been derived for alternating hydrocarbons (AH) which is more accurate than the McClelland's topological formula.

2. Theory

Combinatorially, r -combinations of n distinct things are given by (1)[7]. So pairwise combinations of e disjoint edges are expressed by (2).

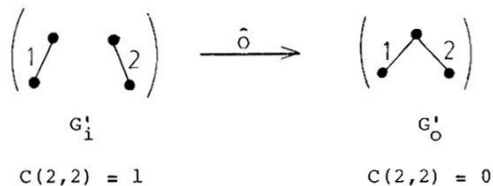
$$C(n,r) = \frac{n!}{r!(n-r)!} \quad (1)$$

$$= \binom{n}{r}$$

$$C(e,2) = \binom{e}{2} \quad (2)$$

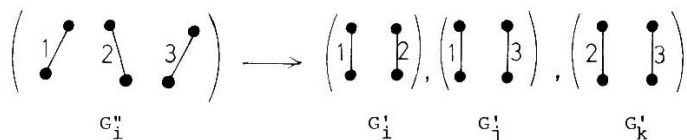
Suppose G_0 is an undirected planar graph, having e edges and N vertices such that the degree (d_i) of every vertex in G_0 is $1 \leq d_i \leq 3$ (a Hückel graph [8,9]). Let G'_i be one of the partial subgraphs of G_0 such that it has four vertices of degree-one only.

Now, consider that two disjoint edges in G'_i become incident or from the same vertex, through operation \hat{O} .

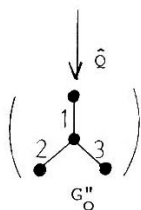


Therefore, the appearance of every vertex having degree two ($d_i = 2$) in G'_0 , decreases the degree of freedom of the pairwise combination of e disjoint edges by one.

Now, let G''_i be a partial subgraph of G_0 such that it has six vertices of degree-one only. The pairwise combination process of three disjoint edges is shown below. The operation \hat{Q} on G''_i



$$C(3,2) = 3$$



$$C(3,2) = 0$$

produces G''_0 in which all the three edges are incident or from the same vertex. So every vertex having $d_i = 3$ decreases the degree of freedom of the above mentioned pairwise combination of edges by three.

Let S be a set of partial subgraphs (G'_i -type) of G_0 . The number of set elements can be formulated by considering the above arguments as follows.

$$C(e,2) = \binom{e}{2} - V_2 - 3V_3 \tag{3}$$

where, V_2 and V_3 stand for number of vertices having degree-two

and three.

According to Coulson-Sachs graphical method [10,11,12], a_4 coefficient of characteristic polynomial of a Hückel graph is given by,

$$a_4 = \sum_J \left(\begin{array}{c} \bullet \text{---} \bullet \\ \bullet \text{---} \bullet \end{array} \right) - 2R_4 \quad (4)$$

where, R_4 represents the total number of 4-membered rings and indice J indicates that summation is over all such kind of sets. It is evident that in (4) summation term is equal to $C(e,2)$. Therefore, a_4 is expressed by (5).

$$a_4 = \binom{e}{2} - V_2 - 3V_3 - 2R_4 \quad (5)$$

Now, consider a polynomial $P(x)$ of degree N (an even number) with leading coefficient 1,

$$P(x) = x^N + a_1 x^{N-1} + a_2 x^{N-2} + \dots + a_{N-1} x + a_N \quad (6)$$

and let $x_1, x_2 \dots x_N$ be its roots (counting multiplicities), then $P(x)$ has the following expansion:

$$P(x) = (x-x_1)(x-x_2)\dots(x-x_N) \quad (7)$$

Suppose roots of $P(x)$ are symmetrically distributed about the zero such that,

$$x_1 = -x_N \quad (8)$$

$$x_{N/2} = -x_{N/2+1}$$

then $P(x)$ becomes,

$$P(x) = (x^2 - x_1^2)(x^2 - x_2^2)\dots(x^2 - x_{N/2}^2) \quad (9)$$

Multiplying out the paranthesis on the right and then collecting like terms and comparing the resulting coefficients. With the coefficients of (6), one gets Vieta's formulae [13], modified for a polynomial which has N symmetrical roots. Where,

$$a_2 = - \sum_{i=1}^{N/2} x_i^2 \quad (10)$$

$$a_4 = \sum_{i < j}^{N/2} x_i^2 x_j^2 \quad (11)$$

Since, eigen values are symmetrical in even alternant hydrocarbons [14], (10) and (11) hold for secular polynomials of this class of compounds. For odd alternant hydrocarbons having M atoms upper indices of (10) and (11) are expressed by $\frac{M-1}{2}$, because inevitably $x_{(M+1)/2} = 0$ for this class of compounds. Inserting $N=M-1$, equations (10) and (11) can be used for odd AHs as well.

The following inequality holds for mean and mean power of order α of the positive numbers k_1, k_2, \dots, k_n [15].

$$\left(\frac{k_1^\alpha + k_2^\alpha + \dots + k_m^\alpha}{m} \right)^{1/\alpha} \geq \frac{k_1 + k_2 + \dots + k_m}{m} \quad (12)$$

for $\alpha = 2$, it becomes,

$$\sqrt{\frac{\sum_{i=1}^m k_i^2}{m}} \geq \frac{1}{m} \sum_{i=1}^m k_i \quad (13)$$

Let,

$$\sum_{i < j}^m k_i = \sum_{i < j}^{N/2} x_i x_j \quad (14)$$

$$\sum_{i=1}^m k_i = \frac{(\sum_{i=1}^{N/2} x_i)^2 - \sum_{i=1}^{N/2} x_i^2}{2} \quad (15)$$

On the other hand, the total π -electron energy E_π within the Hückel framework is given by [16].

$$E_\pi = \sum_{i=1}^{\text{occ}} b_i x_i \quad (16)$$

where b_i is the occupancy number and for closed shell systems its value is equal to 2. Since the followings hold for Hückel graphs [10],

$$\begin{aligned} a_2 &= -e \\ \sum_{i=1}^{N/2} x_i^2 &= e \end{aligned} \quad (17)$$

by inserting (16) and (17) into (15) one gets (18) for alternant hydrocarbons.

$$\sum_{i=1}^m k_i = \frac{(\frac{1}{2}E_\pi)^2 - e}{2} \quad (18)$$

On the other hand, (14) leads to,

$$\begin{aligned} \sum_{i=1}^m k_i^2 &= \sum_{i < j}^{N/2} x_i^2 x_j^2 \\ &= a_4 \end{aligned} \quad (19)$$

So, (13) becomes,

$$\sqrt{\frac{a_4}{m}} \geq \frac{E_\pi^2}{8m} - \frac{e}{2m} \quad (20)$$

By rearranging (20) one gets (21).

$$E_{\pi} \leq 2 \sqrt{\sqrt{4ma_4} + e} \quad (21)$$

where $m = \binom{N/2}{2}$. Algebraically m is equal to number of summands in the expression of $\sum_{i < j}^{N/2} x_i x_j$.

Let, $E_M = \sqrt{2Ne}$ (McClelland's formula [6]) and E_L be total π -electron energy calculated by (21). If $E_L \leq E_M$, then $E_L^2 \leq E_M^2$, ($E_L, E_M > 0$) and,

$$E_L^2 - E_M^2 \leq 0 \quad (22)$$

It means that E_L approximates the value of E_{π} better than E_M does. By substituting equivalents of E_L and E_M into (22), equations (23) and (24) are obtained. Dividing both sides of (24) by $Ne/2$,

$$4\sqrt{4ma_4} + 4e - 2Ne \leq 0 \quad (23)$$

$$2\sqrt{4ma_4} + 2e \leq Ne \quad (24)$$

rearranging, one gets (25).

$$\sqrt{\frac{4ma_4}{N^2 e^2}} \leq \frac{1}{2} - \frac{1}{N} \quad (25)$$

By substituting,

$$\begin{aligned} m &= \binom{N/2}{2} \\ &= \frac{N}{4} \left(\frac{N}{2} - 1 \right) \end{aligned} \quad (26)$$

and,

$$a_4 = \frac{e^2 - e}{2} - V_2 - 3V_3 - 2R_4 \quad (27)$$

into (25), one obtains,

$$\sqrt{\left(\frac{1}{2}-\frac{1}{N}\right)\left[\frac{1}{2}-\frac{1}{2e}-\frac{(V_2+3V_3+2R_4)}{e^2}\right]} \leq \frac{1}{2}-\frac{1}{N} \quad (28)$$

Simplifying and rearranging,

$$2e^2 \leq Ne + 2N(V_2+3V_3+2R_4) \quad (29)$$

The validity of (22) depends on whether (29) holds or not. Since the followings are true for a Hückel graph [10],

$$\sum d_i = 2e \quad (30)$$

$$3V_3+2V_2+V_1 = 2e \quad (31)$$

$$V_1+V_2+V_3 = N \quad (32)$$

one gets,

$$2V_3+V_2 = 2e-N \quad (33)$$

On the other hand, it is obvious that,

$$\begin{aligned} 3V_3+V_2+2R_4 &\geq 2V_3+V_2 \\ &\geq 2e-N \end{aligned} \quad (34)$$

Therefore, (29) is valid if (35) holds.

$$\begin{aligned} 2e^2 &\leq Ne + 2N(2e-N) \\ &\leq 5Ne-2N^2 \end{aligned} \quad (35)$$

By using the Euler formula ($e = N+r-1$) [10], (35) is converted to (36),

$$2r^2 + 2 - 4r \leq N^2 + Nr - N \quad (36)$$

Since, $2 \leq N^2 - N$ and $2r^2 - 4r \leq Nr$ for a Hückel graph having $N \geq 2$, then (35) is true. This result proves the validities of (29) and (22). Therefore, E_L which is derived in this work and expressed by (21) gives a better upper bound for the total π -electron energy of alternant hydrocarbons.




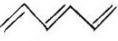

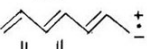


3. Result and Discussion

The total π -electron energy, E_π , can be calculated with the desired accuracy by applying Sachs' theorem through tedious calculations [1]. On the other hand, McClelland's formula is simple but contains insufficient topological parameters to reproduce E_π with an accuracy which is required for chemical purposes. Table 1 tabulates upper bounds of E_π (E_{\max}) for certain alternant hydrocarbons, estimated by (21), E_L and McClelland's formula, E_M , together with true values of E_π within the Hückel framework. As proved above, all the values predicted by formula (21) are much closer to real E_π values compared to results given by McClelland's E_{\max} formula.

By inspection of formula (21), it can be seen that as the number of edges and carbon atoms increase, the upper bound of E_π increases, whereas increasing number of 4-membered rings and branching decrease the E_{\max} .

Table 1

E_{π} and E_{\max} values for certain alternant hydrocarbons.

Compound	E_{\max} Values		E_{π} [17]
	E_M	E_L	
	3.46	2.82	2.82
	4.89	4.47	4.47
	4.89	3.46	3.46
	7.74	7.34	6.98
	5.65	4.00	4.00
	9.16	8.23	8.05
	7.74	7.14	6.89
	8.48	8.09	8.00

Formula (21) can also be used for isomeric alternant hydrocarbons having different a_4 values to predict the trend of E_{π} (Table 1). Also, a regression analysis of formula (21) for specific type of alternant hydrocarbons can be done to correlate the E_{π} and the topology of similar type of molecules.

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