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AN APPROXIMATE METHOD FOR THE ESTIMATION OF TOTAL π-ELECTRON ENERGIES OF ALTERNANT HYDROCARBONS

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Abstract. In the present study, firstly a generalized, McClelland type E_π formula has been derived then an angle θ is defined. Topologically variable upper and lower bounds for $\cos \theta_\pi$ are obtained and then used to get an approximate formula for E_π.

1. Introduction.

Total π-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 of E_π (3-18) . The McClelland's formula was the first of such bounds (3) . There are nowadays very many known bounds for the total π-electron energy (11-16) . 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 (19) .

2. Theory

Let E_n be an n-dimensional Euclidean linear space (20,21) and vectors A and B defined as,

$$A(X_1, X_2, \ldots X_n) \qquad B(1,1,\ldots\ldots 1)$$

Then, the following equations are true for the scalar product (21,22) of these vectors.

$$(A,B) = \sum_{i=1}^{n} X_i \tag{1}$$

$$(A,B) = \sqrt{n}\sqrt{\sum_{i=1}^{n} X_i^2}\cos\theta \tag{2}$$

where θ is the angle between the vectors A and B.

Now, suppose G is an undirected planar graph having r rings, e edges and N vertices such that N is an even number (N = 2n) and the degree (d_i) of every vertex of G is $1 \leqslant d_i \leqslant 3$ (a Hückel graph (23)) . Furthermore , let P(X) be the corresponding characteristic polynomial with the leading coefficient 1 (24) ,

$$P(X) = X^N + a_1X^{N-1} + \ldots + a_{N-1}X + a_N \tag{3}$$

Denote the graph eigenvalues by X_1, X_2, ..., X_N (counting multiplicities). For alternant hydrocarbons the following equations hold (25, 26) .

$$E_{\pi} = 2 \sum_{i=1}^{N/2} X_i \qquad (4)$$

$$e = \sum_{i=1}^{N/2} X_i^2 \qquad (5)$$

By using equations (2), (4) and (5) one obtains,

$$E_{\pi} = 2 \sqrt{ne} \cos \theta_{\pi} \qquad (6)$$

Obviously, equation (6) leads to McClelland's upper bound for E_{π} energy (3) (equation 7) if one considers that $\cos \theta_{\pi} \leqslant 1$.

$$E_{\pi} \leqslant 2 \sqrt{ne} \qquad (7)$$

A lower bound for $\cos \theta_{\pi}$.

Theorem 1. For alternant hydrocarbons having e edges and 2n vertices, $\cos \theta_{\pi}$ is greater than $((e + 2\sqrt{a_4})/en)^{1/2}$.

Proof. Squaring both sides of eqs. (4) and (6) and then equating to each other, one obtains

$$\sum_{i=1}^{n} X_i^2 + 2 \sum_{i<j}^{n} X_i X_j = ne \cos^2 \theta_{\pi} \qquad (8)$$

inserting eq.5 into eq.8 and solving for $\cos \theta_{\pi}$,

$$\cos \theta_{\pi} = \sqrt{(e + 2 \sum_{i<j}^{n} X_i X_j)/ne} \qquad (9)$$

On the other hand, $\sum_{i<j}^{n} X_i X_j$ term present in eq.9 can be expressed as

$$\left(\sum_{i<j}^{n} X_i\ X_i\right)^2 = \sum_{i<j}^{n} X_i^2 X_j^2 + 2\sum_{\substack{i<j\\k<l}}^{n} X_i\ X_j\ X_k\ X_l \qquad (10)$$

inserting $\sum_{i<j}^{n} X_i^2 X_j^2 = a_4$ (13) into eq.10 one gets

$$\left(\sum_{i<j}^{n} X_i\ X_j\right)^2 = a_4 + 2\sum_{\substack{i<j\\k<l}}^{n} X_i\ X_j\ X_k\ X_l \qquad (11)$$

Hence ,

$$\sum_{i<j}^{n} X_i\ X_j \geqslant (\ a_4\ )^{1/2} \qquad (12)$$

inserting ineq.12 into eq.9 , one gets

$$\cos \theta_\pi \geqslant \sqrt{(\ e + 2\ \sqrt{a_4})/ne} \equiv L \qquad (13)$$

Note that ineq.13 holds for $N \geqslant 2$ (Appendix I)

An upper bound for $\cos \theta_\pi$

Theorem 2. For alternant hydrocarbons having e edges and 2n vertices, $\cos \theta_\pi$ connot be greater than $((\ e + 2\ \sqrt{ma_4})/ne)^{1/2}$ where m is given by eq.14 .

Proof. Let E_m be an m-dimensional Euclidean space (20,21) and vectors C and D defined as

$$C(\ X_1\ X_2,\ X_1\ X_3,\ \dots\ ,\ X_{n-1}\ X_n\ )$$
$$D(\ 1,\ 1,\ \dots\ ,\ 1\ )$$

where $X_1,\ X_2,\ \dots\ ,\ X_n$ have the same meaning as stated above. Note that ,m is the number of components of vectors C and D. It is given by eq.14 .

$$m = (\ n^2 - n)/2 \qquad (14)$$

Then, the scalar product of vectors C and D becomes

$$(C,D) = \sum_{i<j}^{n} X_i \; X_j \qquad (15)$$

$$(C,D) = \sqrt{ma_4} \; \cos \alpha \qquad (16)$$

Inserting eq.16 into eq.9

$$\cos \theta_{\pi} = \sqrt{(e + 2 \; \sqrt{ma_4} \; \cos \alpha)/ne} \qquad (17)$$

which leads to ineq.18 (see appendix II).

$$\cos \theta_{\pi} \leqslant \sqrt{(e + 2 \; \sqrt{ma_4} \;)/ne} \quad \equiv U \qquad (18)$$

Note that by using ineq.18 and eq.6 one obtains the same upper bound for E_{π} which was previously reported based on a different approach (13).

Estimation of cos θ_{π} .

The inspection of cos θ_{π} values of alternant hydrocarbons reveals that they are closer to the upper bound, U . Hence , if one takes a special type of mean of averages, always keeping the upper bound constant , then gradually a value is obtained which should be a better estimate of cos θ_{π} than the upper bound. The method is actually based on iteration of the lower limit, L . Mathematically, the formula can be expressed as

$$y_i = \; (L + (2^i - 1)U)/2^i \qquad (19)$$

where , y_i is a new lower bound for cos θ_{π}. In the next step it is added to the upper bound ,U , and devided by 2, hence i which is the number of iterations in eq.19 has to be an integer. This process is repeated until a lower bound very close to cos θ_{π} is reached. Of course , the method remains to be obscure until any information about the value of i is available.

The difference between two successive y values are given by,

$$\delta_{ij} = (U - L)/2^{i} \qquad (20)$$
$$i = j - 1$$

Of course eq.20 gives the maximum error for $\cos\theta_\pi$ if the correct i value is known.

An approximate evaluation of i can be obtained by applying certain regression techniques or by using the already known McClelland's factor (3) which is about 0.92 . Let , the real value of $\cos\theta_\pi$ be c . Then by using eq.19 , substituting $y_i = c$ and solving for i , one gets,

$$i = \text{Log}((U - L)/(U - c)) \;/\; \log 2 \qquad (21)$$

It is known that for benzenoid hydrocarbons the lower bound is found to be 0.77 (17) . Inserting L= 0.77 , U = 1 and c=0.92 in eq.21 one obtains 3.2667 for the value of i . Hence, the nearest integer value ,3 ,can be used for the estimation of $\cos\theta_\pi$ values, and indeed very good approximate results are obtained for E_π values of very many alternant hydrocarbons. Then $\cos\theta_\pi$ can be estimated (eq.22) starting from eq.19 and inserting i= 3 .

$$\cos\theta_\pi \approx (L + 7U)/8 = \cos\theta_A \qquad (22)$$

Hence, one can obtain the approximate total π-energy (E_A) of alternant hydrocarbons (eq.23) by combining eq.6 and 22.

$$E_A = 2\sqrt{ne}\,\cos\theta_A \qquad (23)$$

3. Results and discussion.

The method presented above, enables one to estimate E_π energies by using eq.6 which in form resambles the McClelland's formula. Since, the approximate value of cos θ_π (eq.22) is the function of the lower and the upper bounds which have a common feature that both of them are expressed as certain functions of n, e and a_4, then the present method is almost compatible with McClelland's approach as long as the topological parameters are concerned. Note that calculation of a_4 is a straightforward process for alternant hydrocarbons (13) (see appendix I).

Table 1. displays the exact E_π values of certain alternant hydrocarbons together with the approximate values (E_A) obtained . By the inspection of table 1, one observes that E_A values are in most of the cases very close to the real ones and error is less than 5%.

Tables 2 and 3 tabulate the exact E_π and E_A values of some arbitrarily chosen alternant hydrocarbons together with some lower and upper bounds , respectively. One observes that E_A values are less than all the upper bounds (table 3) in all cases whereas, greater than all the lower bounds (table 2) except in few cases.

The supperiority of the present method lies in the fact that a topologically variable value ,cos θ_A , (eq.6) is used instead of a constant factor ,0.92 , of McClelland's approach (3,17) .

Since, in the present treatise, $\cos \Theta_\pi$ is estimated by the topologically variant upper and lower bounds (eq.22) , it is expected that the estimated E_π values should approximate E_π better than McClelland's lower and upper bounds.

Table 1

Approximate (E_A) and real (E_π) total π-electron energy values of some alternant hydrocarbons.

Molecule	E_A	E_π (27)	$\lvert E_\pi - E_A \rvert (100/E_\pi)$
Butadiene	4.472	4.472	0.00
2-Vinylbutadiene	7.017	6.900	1.69
Decapentaene	12.510	12.056	3.76
Cyclobutadiene	4.000	4.000	0.00
Styrene	10.503	10.424	0.75
Stilbene	18.992	18.878	0.60
Triphenylene	25.337	25.274	0.25
Biphenyl	16.393	16.382	0.06
3-Vinylhexatriene	9.759	9.445	3.32
2,3-Divinylbutadiene	9.633	9.331	3.23
3,4-Divinylhexatriene	12.384	11.924	3.85
Diphenylene	16.872	16.504	2.22
Octatetraene	9.878	9.516	3.80
Propenyl	2.828	2.828	0.00
Triphenylmethyl	25.428	25.800	1.44
Tri-m-biphenylmethyl	50.200	50.946	1.46

On the other hand, there have been many attempts to estimate the coefficient ,a , in the McClelland's formula, $a(2Ne)^{1/2}$. A function , $f(N)$, given by $f(N) = (N/2)(3/(N^2 - 1))^{1/2}$ is used to estimate the value of a (23) which corresponds to cos θ_π value in the present study. Table 4 tabulates the real cos θ_π values of various alternant hydrocarbons together with the estimated cos θ_π values (namely cos θ_A) and $f(N)$. It is evident that generally cos θ_A values obtained by using eq. 22 are supperior to $f(N)$ values.

Table 2

Comparision of E_A values with E_π and various lower bounds for certain alternant hydrocarbons.

Molecule	E_π (27)	E_A	Some lower bounds a	 b	 c	 d
Benzene	8.00	7.95	7.72	8.00	6.93	7.66
Naphthalene	13.68	13.77	12.71	13.48	11.68	11.55
Anthracene	19.31	19.57	17.39	18.69	16.53	15.17
Phenanthrene	19.45	19.57	17.90	19.04	16.53	16.21
Pyrene	22.51	22.75	20.33	21.80	19.13	17.67
Triphenylene	25.27	25.33	23.25	24.70	21.39	21.50
Perylene	28.25	28.50	25.25	27.13	24.00	21.37
Coronene	34.57	34.80	31.14	33.32	29.28	27.83
Ovalene	46.50	46.78	41.23	44.24	39.47	34.77

From, [a] Ref.(3), [b] Ref.(15), [c,d] Ref.(16)

Table 3

Comparision of E_A values with E_π and some upper bounds for alternant hydrocarbons.

Molecule	E_π(27)	E_A	Some upper bounds					
			a	b	c	d	e	f
Benzene	8.00	7.95	8.49	8.10	8.00	8.08	8.16	8.00
Naphthalene	13.68	13.77	14.83	14.35	14.01	13.98	14.19	13.84
Anthracene	19.31	19.57	21.17	20.66	20.09	19.99	20.38	19.67
Phenanthrene	19.45	19.57	21.17	20.66	20.09	20.09	20.39	19.71
Pyrene	22.51	22.75	24.66	24.13	23.43	23.41	23.81	22.91
Triphenylene	25.27	25.33	27.50	26.98	26.19	26.28	26.65	25.59
Perylene	28.25	28.50	30.98	30.45	29.54	29.61	30.03	28.79
Coronene	34.57	34.80	37.95	37.40	36.26	36.49	36.99	35.17
Ovalene	46.50	46.78	51.22	50.67	49.15	49.65	50.21	47.13

From ref. [a] (3), [b] (13) , [c] (11) , [d] (15) ,[e] (14), [f] (16)

Table 4

The real ($\cos \theta_{\pi}$), the estimated ($\cos \theta_{A}$) and f(N) values of various alternant hydrocarbons.

Molecule	$\cos \theta_{\pi}$	$\cos \theta_{A}$	f(N) (23)
Ethylene	1.0000	1.0000	1.0000
Butadiene	0.9128	0.9128	0.8944
2-Vinylbutadiene	0.8907	0.9059	0.8783
3-Vinylhexatriene	0.8925	0.9221	0.8728
Octatetraene	0.8991	0.9334	0.8728
Benzene	0.9428	0.9370	0.8783
Naphthalene	0.9225	0.9289	0.8703
Pyrene	0.9129	0.9226	0.8677
Perylene	0.9116	0.9198	0.8671
Stilbene	0.9211	0.9267	0.8682
Coronene	0.9110	0.9171	0.8667

4. Conclusion.

The generalized McClelland type formula (eq.6) is helpful to rationalize the origin of the factor, a, (which stands for $\cos \theta_{\pi}$ in the present study) in the McClelland's formula. Its lower and upper bounds (ineqs. 13 and 18 , respectively) are determined by the certain topological parameters.

The approximate formula ,E_A, (eq.23) reproduces E_{π} values quite well (table 1.). The comparision of E_A and E_{π} values reveals that although the former one is generally greater than the later, in most of the cases, it is less than the upper bounds present in the literature (table 3.).

Appendix I.

Since, $\cos \Theta_{\pi} \leqslant 1$, the right hand side of ineq. 13 requires that

$$(e + 2 \sqrt{a_4})/ne \leqslant 1$$

After rearranging and squaring both sides

$$4a_4 \leqslant n^2 e^2 - 2 n e^2 + e^2 \qquad (24)$$

Since a_4 is expressed as (13)

$$a_4 = ((e^2 - e)/2) - V_2 - 3V_3 - 2R_4 \qquad (25)$$

where , V_2, V_3 are the number of vertices having degree 2 and 3, respectively. In addition to this, R_4 stands for the number of 4-membered rings. Inserting eq.25 into ineq.24 and rearranging one obtains

$$1 - 2/e \leqslant n^2 - 2n$$

which is true for $e \geqslant 1$, then ineq.13 holds for every alternant hydrocarbon molecule.

Appendix II.

The condition $U \leqslant 1$ requires that

$$(e + 2(ma_4)^{1/2})/ne \leqslant 1$$

Rearranging, one gets

$$(ma_4)^{1/2} \leqslant ne(1 - 1/n)/2 \qquad (26)$$

Squaring both sides of ineq.26 and then inserting eq.14 , one obtains

$$a_4 \leqslant (1 - 1/n)e^2/2 \qquad (27)$$

Inserting eq.25 into ineq.27 and rearranging,

$$V_2 + 3V_3 + 2R_4 \geqslant (e^2 - en)/2n$$

Since, for a chemical graph (Hückel graph),

$$V_2 + V_3 = 2n - V_1$$

holds then,

$$2n - V_1 + 2V_3 + 2R_4 \geqslant (e^2 - en)/2n \qquad (28)$$

If,

$$2n - (V_1 - 2V_3) \geqslant (e^2 - en)/2n \qquad (29)$$

holds then ineq.28 is fulfilled.

Let, $V_1 - 2V_3 = k$ and insert it into ineq.29, then one gets

$$4n^2 - 2nk + en - e^2 \geqslant 0 \qquad (30)$$

solving for n,

$$n_{1,2} = (-(e - 2k) \mp \sqrt{(e - 2k)^2 + 16e^2})/8 \quad (31)$$

On the other hand, it is topologically evident that the maximum value of k is 2 for linear hydrocarbons and as the number of vertices having degree three (V_3) increaes , value of k decreases (see Fig.1). For k=2 , the discriminant of eq.31 becomes $17e^2 - 8e + 16$. Since,

$$17e^2 - 8e + 16 \leqslant 18e^2$$

for $e \geqslant 2$, the positive root becomes $n = 0.40e + 0.5$. On the other hand, ineq.30 is valid for values of n which are greater than the positive root (negative values are chemically meaningless) that is

$$2n \geqslant 0.80e + 1 \qquad (32)$$

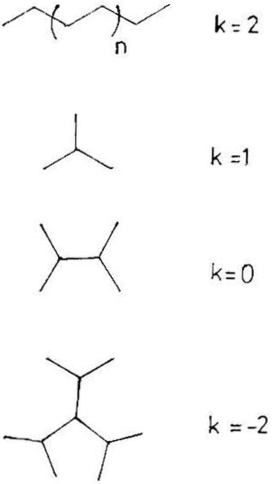

Fig.1 The topological variation of the value of k.

which is a sufficient condition for linear hydrocarbons. In a similar way, it can be proved that for $k = 1$

$$2n \geqslant 0.80e + 0.5 \tag{33}$$

and for $k \leqslant 0$

$$2n \geqslant 0.78e \tag{34}$$

Note that ineqs.33 and 34 are valid for systems having rings and branches. Although, ineqs. 32-34 are much simpler in form as compared to ineq.27 and fulfilled by many compounds ,the priority has to be given to ineq.27 for the test of the upper bound U for $\cos \theta_{\pi}$ whether it is a realistic bound ($U \leqslant 1$) or not.

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