

A NOVEL APPROACH TO THE ESTIMATION OF TOTAL π -ELECTRON
ENERGIES OF CYCLIC ALTERNANT HYDROCARBONS

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Abstract. The concept of auxiliary graphs is introduced and some theorems are given for the design of the upper and the lower auxiliary graphs, especially the fundamental graphs. Then, a novel approach is presented in order to estimate total n -electron energies of cyclic alternant hydrocarbons.

1. Introduction.

The total n -electron energy, E_n , has been rigorously studied for more than a couple of decades (1-15). It depends on a variety of structural invariants of the respective molecule. Coulson pointed out that a relationship existed between E_n and the coefficients of the characteristic polynomial of the molecular graph (16). McClelland's formula which is based on the number of atoms and the number of bonds is the simplest of all the topological formulas for total n -electron energy (1). In the last decade very many upper and lower bounds for E_n have been derived at various levels of

sophistication (6-15,17).

In the present study, a completely different approach is presented for the estimation of total n -electron energy of certain alternant hydrocarbons which are structurally convertible into their suitable partial graphs (18) again of Hückel type (18,19). The approach is based on an upper bound for E_n of alternant hydrocarbons reported previously by L.Türker (7).

2. Theory.

Suppose, $G(A)$ is a connected planar graph having e edges, R rings and $2n$ vertices, such that the degree, d_i , of every vertex of $G(A)$ is $1 \leq d_i \leq 3$ (a Hückel graph (17)). For alternant hydrocarbons the following equations hold (18-20).

$$E_n = 2 \sum_{i=1}^n X_i \quad (1)$$

$$e = \sum_{i=1}^n X_i^2 \quad (2)$$

where, X_1, X_2, \dots, X_n are eigenvalues standing for the occupied molecular orbitals of the respective molecular graph, ordered so that $X_i \geq X_j$ for $i \leq j$.

It is known that eq.3 holds for alternant hydrocarbons (7).

$$E_n \leq 2 \sqrt{4ma_4 + e} \equiv E_T \quad (3)$$

where a_4 is the respective coefficient of the characteristic

polynomial of the given molecule expressed by eqs.4 and 5 (7).

$$a_4 = \sum_{\substack{i=1 \\ i < j}}^n x_i^2 x_j^2 \quad (4)$$

$$a_4 = \binom{e}{2} - v_2 - 3v_3 - 2R_4 \quad (5)$$

where, v_2 , v_3 and R_4 stand for the numbers of vertices having degree two, three and number of 4-membered rings, respectively. In eq.3, m is given by

$$m = \binom{n}{2} \quad (6)$$

Although, the upper bound, E_T (eq.3) is a suitable one to estimate E_n of small and moderately large systems, it diverges from the real n -electron energy for huge molecules. Thus, for these systems an improvement of ineq.3 is needed. Instead of deriving new but probably more complicated formulas just to obtain better bounds for E_n which require many topological parameters sometimes difficult to get, below a different approach is presented which enables one still to make use of the same upper bound formula (ineq.3) for gross systems.

Definition 1. A connected partial graph of $G(A)$, denoted by $G(U)$, which possesses an upper bound, $E_{T(U)}$, such that $E_{T(U)} \geq E_{n(A)}$ is called an upper auxiliary graph. Conversely, a lower auxiliary graph denoted by $G(L)$ is defined such that $E_{T(L)} \leq E_{n(A)}$.

Note that, $G(A)$ can have more than one upper or lower

auxiliary graphs. Since, by definition $G(U)$ is a partial graph of $G(A)$ and therefore, has the same number of vertices ($2n$) as $G(A)$.

Definition 2. An upper auxiliary graph of $G(A)$ having the smallest $E_{T(U)}$ value is called the upper boundary graph of $G(A)$. Analogously, a lower boundary graph is a lower auxiliary graph such that $E_{T(L)}$ is as close to $E_{\pi(A)}$ as possible.

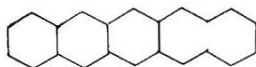
Definition 3. All auxiliary graphs fulfilling the properties of a boundary graph of $G(A)$ and having the same $E_{T(U)}$ or $E_{T(L)}$ values are upper or lower isoboundary graphs (or isoboundary structures).

Figure 1. shows the boundary graph and some auxiliary graphs of pentacene. The isoboundary graphs and some auxiliary graphs of coronene is illustrated in Fig.2 .

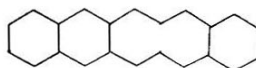
Note that , usually isoboundary structures have the same number of vertices characterized by degree 2 and 3, besides the same number of 4-membered rings because necessarily they have to possess the same E_T value. This constraint generally does not allow respective a_4 and e values to deviate from each other for a set of isoboundary structures.

Definition 4. The lower auxiliary graph of $G(A)$ having the smallest possible E_T value is called the fundamental graph of $G(A)$.

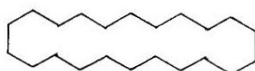
Note that $G(A)$ might have more than one fundamental graphs. Fig.3 shows some fundamental graphs of coronene.



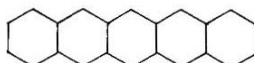
$$E_{T(U)} = 32.6747$$



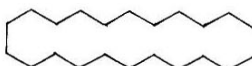
$$E_{T(U)} = 32.6747$$



$$E_{T(U)} = 30.7225$$



$$E_{\pi} = 30.5440$$

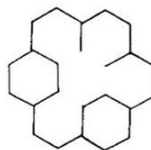


$$E_{T(L)} = 30.0300$$

Fig.1 The boundary graph and some auxiliary graphs of pentacene.



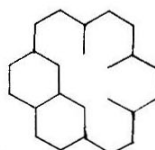
$$E_{T(U)} = 34.8782$$



$$E_{T(U)} = 34.8236$$



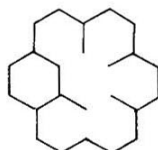
$$E_{T(U)} = 34.7962$$



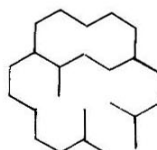
$$E_{T(U)} = 34.6283$$



$$E_n = 34.5718$$



$$E_{T(L)} = 34.1170$$



$$E_{T(L)} = 33.4280$$

Fig.2 The upper and lower boundary structures and some auxiliary graphs of coronene.



$$E_{T(L)} = 32.6963$$

Fig.3 Some fundamental graphs of coronene.

Design of Auxiliary Graphs.

The theorems presented below enable one to design various types of auxiliary graphs.

Lemma 1. Let $G(A)$ be a Hückel graph having $2n$ vertices, e edges and R rings. Then, the maximum number of edges (k_{\max}) which can be removed to get a fundamental graph is determined by the number of rings present in $G(A)$.

Proof :

Since, by definition, the numbers of vertices in $G(A)$ and in any auxiliary graph are the same, as the number of edges decreases the number of rings has to decrease just to fulfill the requirement of Euler equation (18), $2n = e - R + 1$.

Now, suppose vectors A and B in an n -dimensional Euclidean space (21) are defined as follows,

$$A(x_1, x_2, \dots, x_n) \quad B(1, 1, \dots, 1)$$

Then, the following is true for the scalar product, (A, B) ,

of these vectors (22).

$$(A, B) = \sum_{i=1}^n x_i \quad (7)$$

$$(A, B) = \sqrt{n \sum_{i=1}^n x_i^2} \cos \theta_A \quad (8)$$

where θ_A is the angle between vectors A and B. By using eqs.1,2,7 and 8 one gets

$$E_{\pi(A)} = 2 \sqrt{ne} \cos \theta_A \quad (9)$$

Theorem 2. Let $G(A)$ be a Hückel graph having $2n$ vertices e edges and R rings. Furthermore, suppose $G(U)$ is a connected partial graph of $G(A)$ obtained by deleting certain number (k) of edges ($R \geq k \geq 1$) and characterized by $2n$ vertices, $e' = e - k$ edges and r rings. If $2n \geq 4R + 1$ and $\cos \theta_A \leq (1 - k/e)^{1/2}$ then $G(U)$ is an upper auxiliary graph of $G(A)$ such that $E_{\pi(A)} \leq E_{T(U)}$.

Proof:

Suppose, k edges are deleted for the transformation of $G(A) \implies G(U)$. Thus, the number of edges in $G(U)$ is simply $e' = e - k$. The required condition $E_{\pi(A)} \leq E_{T(U)}$ holds if (using eq.9 and ineq.3).

$$2 \sqrt{ne} \cos \theta_A \leq 2 \sqrt{\sqrt{4ma'_4} + e'} \quad (10)$$

where a'_4 is the respective coefficient of the characteristic polynomial of $G(U)$. Rearranging ineq.10,

$$\cos \theta_A \leq \sqrt{(\sqrt{4ma'_4} + e') / ne} \quad (11)$$

Since, ineq.12 holds for Hückel graphs having $r \leq 0.2 e'$ (17) ,

$$a_4' \leq (n-1)(e')^2 / 2n \quad (12)$$

then by substituting ineq.12 into ineq.11, one obtains

$$\cos \theta_A \leq \sqrt{(1 - k/e)} \quad (13)$$

On the other hand, in the light of lemma 1, the requirement, $r \leq 0.2 e'$ for ineq.12 can be written as

$$R - k \leq 0.2 (e - k) \quad (14)$$

Substituting $e = 2n + R - 1$ (Euler eq.) into ineq.14 and rearranging one gets,

$$4R \leq 2n - 1 + 4k \quad (15)$$

which holds if $2n \geq 4R + 1$.

Corollary 1. Let $G(A)$ be a Hückel graph having $2n$ vertices , e edges and R rings. If $2n \geq 4R + 1$ and $\cos \theta_A \leq (1 - k/e)^{1/2}$ for $k \geq 1$ then there exists at least k upper auxiliary graphs of $G(A)$.

Note that $G(A)$ possesses at least R auxiliary graphs (upper or lower type) and obviously acyclic graphs cannot have any auxiliary graphs.

Theorem 3. Let $G(A)$ be a Hückel graph $(2n, e, R)$. Suppose $G(L)$ is a connected partial graph of $G(A)$ obtained by deleting certain number $(k \leq R)$ of edges. If $k \geq e \sin^2 \theta_A$ then $G(L)$ is a lower auxiliary graph of $G(A)$ such that $E_{n(A)} \geq E_{T(L)}$.

Proof:

The theorem requires $E_{\pi(A)} \geq E_{T(L)}$. Since, for alternant graphs, McClelland's upper bound, $E_M = 2(ne)^{1/2}$, is greater than the corresponding E_T value (7) then $E_{M(L)} \geq E_{T(L)}$ where $E_{M(L)}$ stands for E_M value of $G(L)$. On the other hand, the condition, $E_{\pi(A)} \geq E_{M(L)}$ requires that (using eq.9 and noting that $e - k$ edges exist in a lower auxiliary graph),

$$2\sqrt{ne \cos \theta_A} \geq 2\sqrt{n(e - k)} \quad (16)$$

solving for k ,

$$k \geq e(1 - \cos^2 \theta_A) \quad (17)$$

$$k \geq e \sin^2 \theta_A \quad (18)$$

Theorem 4. Let $G(A)$ be a Hückel graph having $2n$ vertices, e edges and R rings. Then the fundamental graph(s) of $G(A)$ is an acyclic graph having the highest possible branching (a tree).

Proof:

Since, the fundamental graph of $G(A)$ possesses the lowest possible E_T value, then it is obvious from eq.3 that the number of edges, e' and a_4' coefficient for the fundamental graph have to be the lowest possible values and Euler formula has to be fulfilled ($2n = e' - r + 1$, where r is the number of rings in the fundamental graph). It is evident that the minimum value of $\binom{e'}{2}$ is obtained for $r = 0$. Hence, a_4' becomes

$$a_4' = \binom{e'}{2} - v_2' - 3v_3' \quad (19)$$

where V'_2 and V'_3 are the numbers of the corresponding types of vertices of the auxiliary graph and $e' = e - R$ (see lemma 1).

In eq.19 as V'_3 increases a'_4 decreases more sharply than the corresponding response to decrease in V'_2 . Thus, it is possible to deduce that if it is structurally permissible, the fundamental graph should possess $3V'_3 \gg V'_2$. Then the necessary requirement for the design of the fundamental graph(s) of $G(A)$ involves the destruction of all types of rings in such a way that one gets the maximum number of vertices having degree 3.

Corollary 2. All the auxiliary graphs of $G(A)$ have E_T values ($E_{T(U)}$ or $E_{T(L)}$ type) lower than E_T of the parent system, $G(A)$.

Conjecture. Polycyclic Hückel graphs possess at least one fundamental graph .

3. Results and Discussion.

Although, there are many formulas and methods in the literature to estimate the total n - electron energies of molecules, each one has its particular drawbacks. McClelland's formula (1) is the simplest one but it cannot reproduce E_n accurately enough .

All the above theorems, although stated for even alternant hydrocarbons ($N = 2n$) in the present treatise , are adaptable to odd alternant systems having M vertices simply by replacing M with $2n = M - 1$, because inevitably $X_{(M+1)/2} = 0$ for odd alternant hydrocarbons. Hence, all the

summands in eq.4 including this eigenvalue vanish, decreasing the number of summands, m , (7).

In the light of the above definitions and theorems the following rules can be stated related to design of various auxiliary graphs.

Rule 1: The auxiliary graphs are obtained by the destruction of rings, successively.

Rule 2: The fundamental graphs are designed by destroying all types of rings present so that the maximum number of vertices having degree 3 is obtained.

The structures of the upper and lower boundary graphs remain to be obscure as long as any information about the value of $\cos \theta_A$ is present. Although, recently the upper and lower bounds of $\cos \theta_A$ have become available topologically (17), the point in the present study is to get accurate results by using a simple treatment as much as possible. Therefore, two methods are given below to estimate E_π of alternant hydrocarbons.

Method 1. Calculate the E_T values of the given system and its fundamental graph and then get the arithmetic mean of them.

Method 2. Inserting 0.92 into ineq.16 as the average value of $\cos \theta_A$ (McClelland's factor (1,17)) one obtains an approximate value of k . That is

$$k_{av} = 0.1536 \quad (20)$$

Integer part (k) of k_{av} is the number of edges to be deleted. The resultant graph is used together with eq.3 to estimate the total n -electron energy for the original system. Note that by using integer k , increasing and decreasing it one by one each time and getting the average of the corresponding E_T values, it is possible to devise various approximation methods for E_n of alternant systems.

Table 1. tabulates the real and the estimated total n -electron energies of various systems, there E_1 and E_2 stand for the estimated values of E_n by methods 1 and 2, respectively. E_2 values in table 1. are based on the structure characterized by the smallest possible a_4 coefficient within the set of structures specified by k -deleted edges. As it is seen in table 1. the comparison to the precise n -electron energy of 17 benzenoid hydrocarbons shows mean absolute errors of 1.46 and 1.70 % for methods 1 and 2, respectively. Although, these results are inferior as compared to some other approximation methods (14,15,23) available for E_n , the advantage of methods 1 and 2 is rather in the simple structural interpretation.

4. Conclusion.

Total n -electron energies of alternant hydrocarbons may be calculated at different level of precision by using various topological approaches. However, most of these methods are either impractical or have low precision for large systems. In the present study, the methods given for cyclic alternant hydrocarbons are straightforward and require

Table 1.

The real and the approximate total n -electron energies of various alternant hydrocarbons.

Compound	e	N	$E_n(20,24)$	E_1	E_2^a	Abs. % error E_1 E_2
Diphenylethylene	15	14	18.815	19.2596	18.5198	2.36 1.56
Coronene	30	24	34.571	35.0467	34.7962	1.37 0.64
1,2-Diphenylene	15	14	18.878	19.2528	18.4571	1.98 2.22
1,2-Benz-anthracene	21	18	25.101	25.5606	24.8430	1.83 1.02
3,4-benz-phenanthrene	21	18	25.187	25.5373	24.8430	1.38 1.36
2,3-Benzo-biphenylene	19	16	22.251	22.6912	22.6270	1.97 1.68
Perylene	24	20	28.245	28.7047	28.3548	1.62 0.38
1,2-Benzo-biphenylene	19	16	22.166	22.6912	22.6270	2.36 2.07
Chrysene	21	18	25.192	25.5373	24.8430	1.36 1.38
Triphenylene	21	18	25.274	25.5837	24.8430	1.22 1.70
Bisanthanthrene	35	28	40.077	41.0109	40.3373	2.32 0.64
1,2,4,5-Dibenz-pyrene	29	24	34.064	34.7035	34.0000	1.87 0.18
Peropyrene	32	26	37.089	37.8195	37.5114	1.96 1.13
Diphenylmethyl	14	13	17.301	17.2495	16.5398	0.29 4.39
1-Naphthylallyl	14	13	17.131	17.1919	16.4750	0.35 3.82
2-phenylbenzyl	14	13	17.151	17.1919	16.4750	0.28 3.94
1,9,2,3-Dibenz-anthranyl	25	21	29.340	29.4434	29.1023	0.35 0.81

^a Based on the structure having the smallest possible a_4 coefficient within the set specified by k -deleted edges.

very simple topological parameters (N , e , R and a_4). The comparison of methods 1 and 2 implies that the former one is characterized by absolute percent errors scattered comparatively in much more narrow range. However, the second method in most of the cases reproduces E_n values better, especially for large condensed systems. On the other hand, it would be interesting to develop the concept of auxiliary graphs introduced above for the investigation of other topological properties of cyclic systems.

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