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Acyclic Systems with Extremal Hückel π-Electron Energy

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The main result of the present work is the proof that among acyclic polyenes C_nH_{n+2}, the linear isomer $H_2C{=}(CH)_{n-2}{=}CH_2$ has maximal HMO π-electron energy. The 1,1-divinyl isomer $(H_2C{=}CH)_2C(CH)_{n-6}{=}CH_2$ has maximal π-energy among branched acyclic systems. Among trees with n vertices, the star has minimal energy. A number of additional inequalities for HMO total π-electron energy of acyclic conjugated systems are proved.

Key words: Acyclic polyenes – Graph theory

1. Introduction

From the pioneering work of Coulson [1] there exists a continuous interest towards the general mathematical properties of total π-electron energy (E) as calculated within the framework of the Hückel molecular orbital (HMO) model [2–19]. These efforts enabled one to get an insight into the dependence of E on the details of molecular structure, although a complete solution of the problem is not to be expected [13].

It has been shown that E is a bounded quantity and various upper and lower bounds were derived [8, 12]. A related problem is which conjugated molecules (within a given class of conjugated systems) have extremal (maximal and minimal) values of total π-electron energy. Evidently, the answer to this question would provide the best possible bounds for E (within the class considered).

In the present paper we offer a solution of the above problem for acyclic conjugated systems. The proof technique which we shall develop yields numerous further inequalities between the E values of different acyclic structures. In this respect, the present work contains proofs of several relations which have been found empirically in Ref. [17].

A starting point in our considerations is the following integral expression for E (in β units) of *alternant* conjugated hydrocarbons [18, 19].

$$E=\frac{1}{\pi}\int_{-\infty}^{+\infty}\frac{dx}{x^2}\log\left(1+b_1x^2+b_2x^4+\cdots+b_kx^{2k}\right) \tag{1}$$

where

$$P(G, x)=x^n-b_1x^{n-2}+b_2x^{n-4}-\cdots+(-1)^k b_k x^{n-2k} \tag{2}$$

is the characteristic polynomial of the corresponding molecular graph G. n is the number of vertices in G and

$$k=\begin{cases} n/2 & \text{if } n \text{ is even} \\ (n-1)/2 & \text{if } n \text{ is odd.} \end{cases} \tag{3}$$

If the characteristic polynomial is written as in Eq. (2), then $b_j \equiv b_j(G) \geqslant 0$ for all $j=1, 2, \ldots, k$. For further details of graph theory and its applications in the theory of conjugated compounds see Ref. [20].

Let G and H be the molecular graphs of two alternant molecules with the same number n of conjugated atoms. Suppose the coefficients b_j of these two graphs fulfil the inequalities

$$b_j(G) \geqslant b_j(H) \quad \text{for all } j=1, 2, \ldots, k. \tag{4}$$

Then from Eq. (1) it follows immediately that $E(G) \geqslant E(H)$. Moreover, if G and H are not isospectral (that is, if the characteristic polynomials of G and H are not equal), the relations (4) imply $E(G) > E(H)$. Of course, if G and H are isospectral, then $E(G)=E(H)$.

We will write the set of inequalities (4) in an abbreviated form as $G \succ H$ (or $H \prec G$). Hence, if G and H are not isospectral,

$$G \succ H \Rightarrow E(G) > E(H). \tag{5}$$

In the present work several relations $\succ$ will be demonstrated for molecular graphs of acyclic systems. These graphs are called trees. In the next section is presented a survey of necessary graph theoretical results valid for trees.

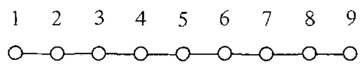
A graph which represents a conjugated system cannot contain vertices, the degrees of which exceed three [20]. Although in the subsequent discussion this restriction will not be taken into account, our results apply in the great majority of cases to molecular graphs. In particular, note that the tree $n(v)m$ is a molecular graph for all values of n, m and v (see later).

2. Trees and Their Spectral Properties

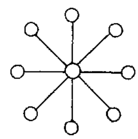
We shall use the following notation and terminology. A connected acyclic graph is called a tree. A tree with n vertices contains $n-1$ edges. Let $\mathscr{T}_n$ be the set of all trees with (exactly) n vertices.

A tree possesses necessarily vertices of degree one. Such vertices are, for obvious reasons, called terminal. The tree with minimal number ($=2$) of terminal vertices is the path (P_n), while that with maximal number ($=n-1$) of terminal vertices is the star (S_n). Let the vertices $1, 2, \ldots, n$ of the path P_n be labelled so that vertices 1 and n are terminal and the vertices j and $j+1$ are adjacent ($j=1, 2, \ldots, n-1$).

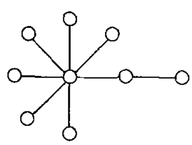
Let the trees A_n, B_n, and C_n be defined as follows. A_n is obtained by joining a vertex to a terminal vertex of S_{n-1}. B_n is obtained by joining a vertex to the vertex of degree two of A_{n-1}. C_n is obtained by joining a vertex of P_2 to a terminal vertex of S_{n-2}. For example, we present P_9 (labelled), S_9, A_9, B_9 and C_9.



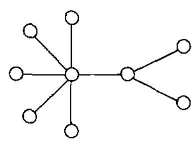
P_9



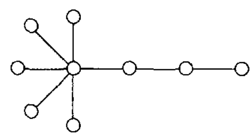
S_9



A_9

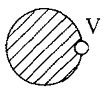


B_9

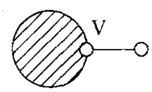


C_9

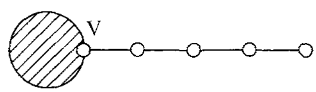
Further, let G be an arbitrary graph and v its arbitrary vertex. Then we denote by $G(v)m$ the graph obtained by joining the terminal vertex of P_m to the vertex v of G.



G

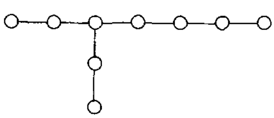


G(v)1

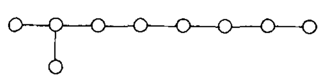


G(v)4

In particular, $P_n(v)m$ is obtained by joining the terminal vertex of P_m to the vth vertex of P_n. For convenience we shall denote $P_n(v)m$ in an abbreviated manner as $n(v)m$. As an example we present $P_7(3)2 \equiv 7(3)2$ and $P_8(2)1 \equiv 8(2)1$.



$P_7(3)2 \equiv 7(3)2$



$P_8(2)1 \equiv 8(2)1$

Let A be the adjacency matrix of the graph G. Then $P(G, x) = \det(xI - A)$ is the characteristic polynomial of G. A tree is bipartite since it is acyclic. Therefore [20], if $T \in \mathcal{T}_n$, $P(T, x)$ can be written in the form (2). Moreover, the coefficients $b_j(T)$ have the following property [21–23]

$$b_j(T) = p(T, j) \tag{6}$$

where $p(G, j)$ is the number of ways in which j non-incident edges can be selected in a graph G. Consequently, for all trees, $b_1(T)$ = number of edges in $T = n-1$.

Let T be a representation of an acyclic conjugated system. The spectrum of T are the roots $x_1 \geqslant x_2 \geqslant \cdots \geqslant x_n$ of $P(T, x)$. Then the total π-electron energy (in β units) of the corresponding system is [6, 9, 20]

$$E = E(T) = 2 \sum_{j=1}^{k} x_j = \sum_{j=1}^{n} |x_j|.$$

In the following we will call the sum of the absolute values of the elements of the graph spectrum "the energy of the graph". We use this term regardless of whether a graph represents a conjugated system or not.

The characteristic polynomial of a tree T fulfils the equation [23, 24]

$$P(T, x) = P(T-e, x) - P(T-(e), x)$$

where $T-e$ is the graph obtained by deletion of an (arbitrary) edge e from T, while $T-(e)$ is obtained by deletion from T the edge e and its two incident vertices. This is a proper consequence of a relation [22]

$$b_j(T) = b_j(T-e) + b_{j-1}(T-(e)). \tag{7}$$

In order to prove (7) remember that any selection of j non-incident edges from T either contains the edge e or not. Now there are exactly $p(T-e, j)$ selections without the edge e and $p(T-(e), j-1)$ such selections with the edge e. Then Eq. (7) follows from Eq. (6).

Let v be a terminal vertex of T, adjacent to another vertex w. Let e be the edge connecting these two vertices. Then a special case of Eq. (7) is

$$b_j(T) = b_j(T-v) + b_{j-1}(T-v-w) \tag{8}$$

with $T-v$ and $T-v-w$ being the graphs obtained by deletion of the vertex v and the vertices v and w, respectively, from T. In particular, if $T = T_0(v)m$,

$$b_j(T) = b_j(T_0(v)m-1) + b_{j-1}(T_0(v)m-2).$$

For several proofs in the following discussion it is important to remember that if $T \in \mathscr{T}_n$, then $T-v \in \mathscr{T}_{n-1}$ and $T-v-w \in \mathscr{T}_{n-2}$.

3. The Trees with Maximal and Minimal Energies

3.1. Proposition 1. $S_n \prec T$ for all $T \in \mathscr{T}_n$

Proof. The characteristic polynomial of the star is $P(S_n, x) = x^n - (n-1)x^{n-2}$. But all other trees from $\mathscr{T}_n$ have also $b_1 = n-1$, but $b_2 > 0$. Hence, inequalities (4) are fulfilled.

3.2. Proposition 2. $P_n \succ T$ *for all* $T \in \mathscr{T}_n$

Proof. It is easy to check the above statement for small values of n ($n=2, 3, 4$). Now suppose that proposition 2 is true for $n=2, 3, \ldots, m-1$. Let T_0 be the tree such that $T_0 \succ T$ for all $T \in \mathscr{T}_m$. We prove that $T_0 = P_m$.

Let v be a terminal vertex of T_0 adjacent to the vertex w. Then Eq. (8) holds. Now, $b_j(T_0)$ is maximal if both $b_j(T_0 - v)$ and $b_{j-1}(T_0 - v - w)$ are maximal. According to our assumption, this implies $T_0 - v = P_{m-1}$ and $T_0 - v - w = P_{m-2}$. This, however, is possible only if $T_0 = P_m$.

3.3. Proposition 3. $T \in \mathscr{T}_n$

$$E(S_n) < E(T) < E(P_n) \tag{9}$$

This is a proper consequence of the above two propositions, Eq. (5) and the fact that there are no trees isospectral with S_n or P_n.

Thus we have found that among all trees, the non-branched path has maximal, and the maximally branched star has minimal energy. The fact that the linear polyene should be the most stable isomer among all acyclic conjugated systems has been first pointed out in Ref. [9]. Proposition 3 is a new indication that branching is a destabilizing factor in conjugated molecules [17].

Lovász and Pelikán [23] proved the intriguing result that for all trees T with n vertices,

$$x_1(S_n) \geqslant x_1(T) \geqslant x_1(P_n) \tag{10}$$

The analogy between Eqs. (9) and (10) is evident. However, the readers attention is drawn to the fact that a naïve extension of inequalities (10) would lead to a conclusion which is just the contrary of proposition 3, namely $E(S_n) \geqslant E(T) \geqslant E(P_n)$. Therefore, proposition 3 seems to be a non-trivial result with reference to inequalities (10).

4. Further Inequalities

It is not difficult to find additional trees with minimal energy.

4.1. Proposition 4

If $T \in \mathscr{T}_n$, but $T \neq S_n, A_n, B_n, C_n$, then

$$S_n \prec A_n \prec B_n \prec C_n \prec T$$

and therefore

$$E(S_n) < E(A_n) < E(B_n) < E(C_n) < E(T).$$

Proof is analogous to that of proposition 1 and is based on the knowledge of the characteristic polynomials of A_n, B_n and C_n: $P(A_n, x) = x^n - (n-1)x^{n-2} + (n-3)x^{n-4}$; $P(B_n, x) = x^n - (n-1)x^{n-2} + (2n-8)x^{n-4}$; $P(C_n, x) = x^n - (n-1)x^{n-2} + (2n-7)x^{n-4}$.

4.2. Proposition 5

Let t be an integer. Then

a) if $n=4t$,
$$n-1(2)1<n-1(4)1<\cdots<n-1(k)1<n-1(k-1)1< \\ <n-1(k-3)1<\cdots<n-1(3)1<n-1(1)1\equiv P_n \tag{11a}$$
b) if $n=4t+2$,
$$n-1(2)1<n-1(4)1<\cdots<n-1(k-1)1<n-1(k)1< \\ <n-1(k-2)1<\cdots<n-1(3)1<n-1(1)1\equiv P_n \tag{11b}$$
c) if $n=4t+1$,
$$n-1(2)1<n-1(4)1<\cdots<n-1(k)1<n-1(k+1)1< \\ <n-1(k-1)1<\cdots<n-1(3)1<n-1(1)1\equiv P_n \tag{11c}$$
d) if $n=4t+3$,
$$n-1(2)1<n-1(4)1<\cdots<n-1(k+1)1<n-1(k)1< \\ <n-1(k-2)1<\cdots<n-1(3)1<n-1(1)1\equiv P_n. \tag{11d}$$

Here k is defined by Eq. (3).

In accordance with Eq. (5), relations (11) imply a set of inequalities for E. These have been first noticed in Ref. [17] (see Fig. 1 in this reference), where also a perturbation-theoretical argument is given for their justification. In order to prove proposition 5, we shall need the following proposition 6.

4.3. Proposition 6

Let $n(+)m$ be the graph, the (only) components of which are P_n and P_m. Then for $i=1, 2, \ldots, n$,

$$1(+)n-1<i(+)n-i<2(+)n-2<0(+)n\equiv P_n \tag{12}$$

Proof. The inequalities (12) can be easily verified for $n=6, 7$. Suppose they hold for all $n=6, 7, \ldots, m-1$. We prove that Eq. (12) holds then for $n=m$ too.

Because of Eq. (8), we have for arbitrary i,

$$b_j(P_m)=b_j(i(+)m-i)+b_{j-1}(i-1(+)m-i-1).$$

Since obviously $b_j(P_m)$ is independent of i, $b_j(i(+)m-i)$ is minimal if $b_{j-1}(i-1(+)m-i-1)$ is maximal. According to proposition 2, this occurs when $i-1=0$. Hence, $1(+)m-1<i(+)m-i$. Further, for $i\neq 0$ and $i\neq n$, $b_j(i(+)m-i)$ is maximal if $b_{j-1}(i-1(+)m-i-1)$ is minimal. According to our assumption, this occurs when $i-1=1$. Hence, $2(+)m-2>i(+)m-i$.

4.4. Proof of Proposition 5

Application of Eq. (8) gives

$$b_j(n-1(i)1)=b_j(P_{n-1})+b_{j-1}(i-1(+)n-i-1)$$

Since $b_j(P_{n-1})$ is independent of i, $b_j(n-1(i)1)$ will be minimal if $b_{j-1}(i-1(+)n-i-1)$ is minimal, that is if $i-1=1$. Therefore, $n-1(2)1<n-1(i)1$.

Similarly, $b_j(n-1(i)1)$ is maximal if $b_{j-1}(i-1(+)n-i-1)$ is maximal, that is if $i-1=2$. Therefore, if $i \neq 1$, $n-1(3)1 \succ n-1(i)1$.

All other statements of proposition 5 can be proved analogously.

The relation $n-1(3)1 \succ n-1(i)1$ implies, of course, $E(n-1(3)1) > E(n-1(i)1)$. Translated into the language of organic chemistry, this means that among isomers with the same number of branches, the one which contains a vinyl group (or the maximal number of such groups) is the most stable. Moreover, the presence of vinyl groups turns out to be the most favourable, while the presence of methylene groups the most unfavourable case in acyclic polyenes. Examples from the polyene chemistry and especially from naturally occurring conjugated systems come rapidly to mind.

Later we shall see that the search of the most stable branched acyclic polyene will lead also to vinyl compounds.

The following simple argument enables one to find numerous new inequalities between the energies of trees.

4.5. Proposition 7

Let G and H be trees with n vertices and g and h their arbitrary vertices. If $G \succ H$ and $G(g)1 \succ H(h)1$, then also for arbitrary i it holds

$$G(g)i \succ H(h)i$$

Proof can be performed by total induction, using the facts that

$$b_j(G(g)i) = b_j(G(g)i-1) + b_{j-1}(G(g)i-2)$$
$$b_j(H(h)i) = b_j(H(h)i-1) + b_{j-1}(H(h)i-2)$$

Then from $b_j(G(g)i-1) \geq b_j(H(h)i-1)$ and $b_{j-1}(G(g)i-2) \geq b_{j-1}(H(h)i-2)$ it follows immediately that $b_j(G(g)i) \geq b_j(H(h)i)$.

As a consequence of this proposition, we can set $n-1(v)i$ instead of $n-1(v)1$ in Eqs. (11).

Now we are able to determine the tree with second maximal energy. First we prove the simple proposition 8.

4.6. Proposition 8. $n-1(i)1 \prec n-2(3)2$ *for all* $i \neq 1, n$

Proof. Because of proposition 5, it is sufficient to show that $n-1(3)1 \prec n-2(3)2$. But this follows immediately from

$$b_j(n-2(3)2) = b_j(n-2(3)1) + b_{j-1}(P_{n-2})$$

and

$$b_j(n-1(3)1) = b_j(n-2(3)1) + b_{j-1}(n-3(3)1)$$

and the fact that $b_{j-1}(P_{n-2}) \geq b_{j-1}(n-3(3)1)$ by proposition 2.

4.7. Proposition 9

If $T \in \mathscr{T}_n$, but $T \neq P_n$,

$$n-2(3)2 \succ T \tag{13}$$

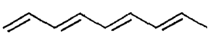
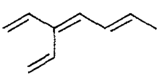
Proof. For small values of $n(n=6, 7)$ relation (13) can be checked by considering the characteristic polynomials of all trees. Suppose that Eq. (13) holds for all $n=6, 7, \ldots, m-1$ and let T_0 be a tree which fulfils the relation $T_0 \succ T$ for all $T \in \mathscr{T}_m$, $T \neq P_m$. We prove that $T_0 = m-2(3)2$.

Let v be a terminal vertex of T_0 adjacent to the vertex w. Then $b_j(T_0) = b_j(T_0 - v) + b_{j-1}(T_0 - v - w)$. *Since*

$$b_j(n-2(3)2) = b_j(n-3(3)2) + b_{j-1}(n-4(3)2)$$

the inequalities $b_j(T_0) \geqslant b_j(n-2(3)2)$ will be fulfilled if either $T_0 = n-2(3)2$ or $T_0 - v = P_{n-1}$ or $T_0 - v - w = P_{n-2}$. If $T_0 - v = P_{n-1}$, it must be $T_0 = n-1(i)1$. According to proposition 8, this implies $T_0 \prec n-2(3)2$, which is impossible. If $T_0 - v - w = P_{n-2}$, it must be $T_0 = n-2(i)2$. From the consequence of proposition 7, $n-2(3)2 \succ n-2(i)2$ and therefore $T_0 = n-2(3)2$.

In the language of organic chemistry, this proposition means that the most stable non-linear acyclic polyene is the 1,1-divinyl isomer:

E( ...) > E( ..) > E(any other acyclic polyene)

5. Inequalities for the Topological Index of Hosoya

Hosoya introduced [25] the topological index $Z = Z(G)$, which is by definition

$$Z(G) = 1 + p(G, 1) + p(G, 2) + \cdots + p(G, k).$$

Later it has been demonstrated [26] that $Z(G)$ is a rather sensitive measure for certain thermodynamic properties of saturated hydrocarbons. The relations between $Z(G)$ and the characteristic polynomial of the molecular graph G have been also established [27]. Because of Eq. (6), for a tree T

$$Z(T) = 1 + b_1(T) + b_2(T) + \cdots + b_k(T).$$

Hence, $T_1 \succ T_2$ implies also $Z(T_1) > Z(T_2)$, unless T_1 and T_2 are isospectral (when, of course, it is $Z(T_1) = Z(T_2)$). Every relation between trees which has been derived in the present paper results in a corresponding inequality for the topological index. We list only one set of such inequalities.

If $T \in \mathscr{T}_n$, but $T \neq S_n$, A_n, $n-2(3)2$, P_n, then

$$Z(S_n) < Z(A_n) < Z(T) < Z(n-2(3)2) < Z(P_n).$$

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