

Alkanes with Greatest Estrada Index

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If $\lambda_1 > \lambda_2 \geq \lambda_3 \geq \dots \geq \lambda_n$ are the eigenvalues of the molecular graph, then the Estrada index, a recently conceived molecular structure-descriptor is $EE = \sum_{i=1}^n e^{\lambda_i}$. The same alkanes, whose molecular graphs have extremal Wiener indices and λ_1 , are shown to be also extremal with regard to the Estrada index.

Key words: Estrada Index; Alkanes; Extremally Branched Alkanes; Molecular Graph; Volkmann Tree.

1. Introduction

Several hundreds of so-called *molecular structure-descriptors* were proposed in the chemical literature [1] and are used for modeling of various physical and chemical properties of (mainly) organic molecules. In general, a molecular structure-descriptor is a number, usually computed from the molecular graph [2, 3], that reflects certain topological features [4, 5] of the underlying molecule. Many of the currently used structure-descriptors quantify (and thus measure) a property of acyclic molecules that in chemistry is referred to as “*branching*” [6–10]. In connection with this, the question may be asked which are the most branched alkanes [11]. Recently this problem was examined in due detail [12]. It could be shown [12] that several molecular structure-descriptors imply that the most branched alkanes are those represented by the (below described) molecular graphs which we propose to be called *Volkmann trees*.

It has been proven that Volkmann trees represent alkanes with a minimal Wiener index [13], and that these trees have the maximal greatest eigenvalue [14]. It was also empirically established [15] (but so far not proven) that Volkmann trees have the maximal greatest Laplacian eigenvalue [16, 17]. The reality of the existence of alkanes pertaining to Volkmann trees was tested by means of advanced quantum-chemical calculations [18].

In this paper we demonstrate that Volkmann trees are also the molecular graphs of alkanes with a maximal Estrada index.

The Estrada index (EE) is a recently conceived molecular structure-descriptor. Details on its theory and applications can be found in recent articles [19, 20] as well as in Ernesto Estrada’s original papers [21–26]. It is defined as follows:

Let G be a molecular graph [2, 3], and let its eigenvalues [27] be $\lambda_1 > \lambda_2 \geq \lambda_3 \geq \dots \geq \lambda_n$, then

$$EE = EE(G) = \sum_{i=1}^n e^{\lambda_i}. \quad (1)$$

2. Volkmann Trees

A tree is a connected acyclic graph. A chemical tree is a tree in which the maximal vertex degree does not exceed 4. The maximal vertex degree will be denoted by Δ . Hence, a chemical tree is a tree for which $\Delta \leq 4$.

The Wiener index $W(G)$ is the sum of distances between all pairs of vertices of the graph G . The n -vertex tree with maximal vertex degree Δ , having a minimal W value, was determined by a group of German mathematicians whose leader was Lutz Volkmann [13]. By them, also the chemical trees with a minimal W value have been characterized [12]. For this reason we propose that these trees be named *Volkmann trees* and denoted by $VT_n(\Delta)$.

The definition and construction of Volkmann trees was described in detail in [12, 13]. In [12] a figure showing the Volkmann trees with $n = 5, 6, \dots, 22$ vertices can be found. For the sake of completeness we, nevertheless, briefly repeat the construction of Volkmann trees (for the case $\Delta = 4$).

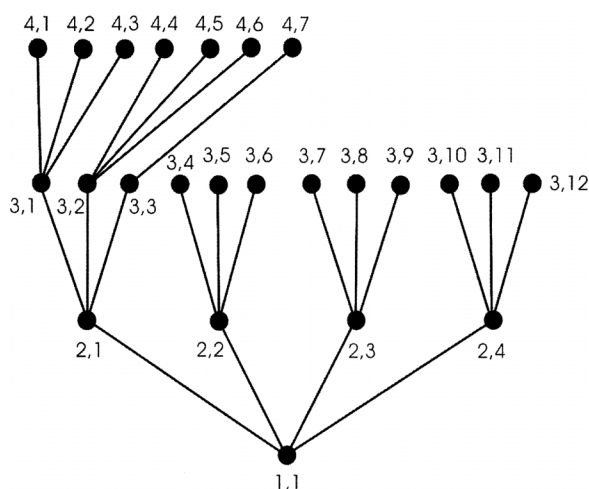


Fig. 1. The Volkman tree $VT_n(\Delta)$ for $\Delta = 4$ and $n = 24$. For $n = 24$, from (2) one obtains $k = 1$ and $h = 7$. The vertices of $VT_{24}(4)$ are labelled as explained in the text.

The Volkman tree $VT_n(4)$ with n vertices is obtained as follows:

- For given n , determine the integers k and h from the conditions

$$\begin{aligned} 2 \cdot 3^{k+1} - 1 &\leq n < 2 \cdot 3^{k+2} - 1, \\ h &= n - 2 \cdot 3^{k+1} + 1. \end{aligned} \quad (2)$$

- Arrange the n vertices of VT_n into $k + 2$ rows, so that
 - in the first row there is one vertex, labelled by v_{11} ;
 - in the i -th row, $i = 2, 3, \dots, k + 1$, there are $r_i = 4 \cdot 3^{i-2}$ vertices, labelled by $v_{i,1}, v_{i,2}, \dots, v_{i,r_i}$;
 - in the $(k + 2)$ -th row there are h vertices, labelled by $v_{k+2,1}, \dots, v_{k+2,h}$. If $h = 0$, then the $(k + 2)$ -th row is empty.
- Connect the vertices from the first and second row.
- For $i = 2, 3, \dots, k + 1$ and $j = 1, 2, \dots, r_i$ connect the vertex $v_{i,j}$ with the vertices $v_{i+1,3j-2}$, $v_{i+1,3j-1}$, and $v_{i+1,3j}$, provided (in the case $i = k + 1$) that such vertices exist.

The above definition is illustrated in Figure 1.

It is easy to verify that the Volkman tree $VT_n(4)$ has the following property:

If $n \equiv 0 \pmod{3}$, then $VT_n(4)$ has vertices of degree 1 and 4, and a single vertex of degree 2.

If $n \equiv 1 \pmod{3}$, then $VT_n(4)$ has vertices of degree 1 and 4, and a single vertex of degree 3.

If $n \equiv 2 \pmod{3}$, then $VT_n(4)$ has only vertices of degree 1 and 4.

3. An Auxiliary Result

The Zagreb index of a graph G is defined as [1]

$$Zg = Zg(G) = \sum_{i=1}^n (\delta_i)^2,$$

where δ_i is the degree (= number of first neighbors) of the i -th vertex of G . For molecular graphs, for which $\delta_i \in \{1, 2, 3, 4\}$,

$$Zg = n_1 + 4n_2 + 9n_3 + 16n_4, \quad (3)$$

where n_i ($i = 1, 2, 3, 4$) is the number of vertices of degree i . In this notation, $n_1 + n_2 + n_3 + n_4$ and $(n_1 + 2n_2 + 3n_3 + 4n_4)/2$ are equal to the number of vertices and edges, respectively, of the molecular graph G . If G is an n -vertex chemical tree, then it has $n - 1$ edges, and we have the following relations:

$$n_1 + n_2 + n_3 + n_4 = n, \quad (4)$$

$$n_1 + 2n_2 + 3n_3 + 4n_4 = 2n - 2. \quad (5)$$

By solving (4) and (5) in n_1 and n_4 and substituting the solutions into (3), one obtains

$$Zg = 6n - 10 - 2n_2 - 2n_3. \quad (6)$$

Equation (6) implies that the Zagreb index of chemical trees attains its greatest possible value if either there are no vertices of degree 2 and 3, or if their number is as small as possible. A more detailed analysis of (6) leads to:

Theorem 1. Let T be a chemical tree and n the number of its vertices, then

$$Zg(T) \leq 6n - 12, \text{ if } n \equiv 0 \pmod{3}, \quad (7)$$

$$Zg(T) \leq 6n - 12, \text{ if } n \equiv 1 \pmod{3}, \quad (8)$$

$$Zg(T) \leq 6n - 10, \text{ if } n \equiv 2 \pmod{3}. \quad (9)$$

Equality in (7) is attained for trees possessing vertices of degree 1 and 4 and a single vertex of degree 2. Equality in (8) is attained for trees possessing vertices of degree 1 and 4 and a single vertex of degree 3.

Equality in (9) is attained for trees possessing only vertices of degree 1 and 4.

From Theorem 1 we see that the Volkmann trees $VT_n(4)$ have the greatest possible Zagreb indices. However, in addition to $VT_n(4)$ there are other chemical trees with the same (extremal) Zg value.

4. An Approximate Expression for the Estrada Index of Chemical Trees

The k -th spectral moment of a graph G is defined as [27]

$$M_k = M_k(G) = \sum_{i=1}^n (\lambda_i)^k, \quad (10)$$

and for chemical trees the following identities are known [27–29]:

$$\begin{aligned} M_0 = n, \quad M_1 = 0, \quad M_2 = 2n - 2, \quad M_3 = 0, \\ M_4 = 2Zg - 2n + 2 \end{aligned} \quad (11)$$

A closer inspection of (1) reveals that the main contribution to EE comes from the greatest graph eigenvalue, λ_1 , which – for the sake of simplicity – from now on will be denoted by r . One should note that for all connected graphs $r > \lambda_2$. Besides, all trees with $\Delta \geq 3$ have $r > 2$ [27]. As already mentioned, it has been proven [14] that among n -vertex chemical trees, the Volkmann tree $VT_n(4)$ has a maximal r value.

Bearing the latter in mind, we rewrite (1) as

$$\frac{EE}{e^r} = \sum_{i=1}^n e^{\lambda_i - r}$$

and expand the functions $e^{\lambda_i - r}$ into power series, which results in

$$\sum_{i=1}^n \left[1 + (\lambda_i - r) + \frac{(\lambda_i - r)^2}{2} + \frac{(\lambda_i - r)^3}{6} + \frac{(\lambda_i - r)^4}{24} \right] + \text{higher-order terms.}$$

Combined with the relations (10) and (11) this yields

$$\begin{aligned} \frac{n}{24} (r^4 - 4r^3 + 24r^2 - 48r + 46) - \frac{1}{2} (r^2 - 2r) \\ + \frac{1}{12} Zg - \frac{11}{12} + \text{higher-order terms.} \end{aligned}$$

We thus arrive at the approximation

$$EE \approx EE^*, \quad (12)$$

where

$$\begin{aligned} EE^* = e^r \left[\frac{n}{24} (r^4 - 4r^3 + 24r^2 - 48r + 46) \right. \\ \left. - \frac{1}{2} (r^2 - 2r) + \frac{1}{12} Zg - \frac{11}{12} \right]. \end{aligned}$$

5. Volkmann Trees Have Greatest Estrada Index

Formula (12) relates the Estrada index of a chemical tree with two other graph invariants, namely the greatest eigenvalue (r) and the Zagreb index (Zg). For us the most important feature of (12) is that the approximate expression EE^* is a monotonically increasing function of both r and Zg .

The monotonicity of the Zg dependence is immediate since

$$\frac{\partial EE^*}{\partial Zg} = \frac{e^r}{12} > 0.$$

This suggests that the chemical trees with the greatest Estrada index might be those with a maximal Zg value. Recall that chemical trees with maximal Zg value are characterized by Theorem 1.

In order to see that EE^* is a monotonically increasing function of the parameter r , we calculate

$$\begin{aligned} \frac{\partial EE^*}{\partial r} = e^r \left[\frac{n}{24} (r^4 + 12r^2 - 2) \right. \\ \left. - \frac{1}{2} (r^2 - 2) + \frac{1}{12} Zg - \frac{11}{12} \right], \end{aligned}$$

which for $r > 2$ is evidently positive-valued.

From

$$\frac{\partial EE^*}{\partial Zg} > 0 \quad \text{and} \quad \frac{\partial EE^*}{\partial r} > 0$$

follows that the n -vertex chemical tree having the greatest value of EE^* is the chemical tree with the greatest r and Zg value, which is known (from [14] and Theorem 1) to be the Volkmann tree $VT_n(4)$.

In view of relation (12), we claim that $VT_n(4)$ is also the n -vertex chemical tree with the greatest Estrada index. However, because of the approximate nature of (12), the latter assertion cannot be considered as proven in a rigorous mathematical manner. Such a proof awaits to be achieved in the future.

To additionally corroborate our claim, we have performed a systematic computer search for the chemical trees with the greatest Estrada index, embracing all

such trees with n vertices, $n \leq 20$. Indeed, for each value of n examined, we found that the chemical tree

with the greatest Estrada index is $VT_n(4)$, and that this tree is unique.

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