

Chemical applications of the Laplacian spectrum. VI. On the largest Laplacian eigenvalue of alkanes

IVAN GUTMAN^{a#}, DUŠICA VIDOVIĆ^{a#} and DRAGAN STEVANOVIĆ^b

^aFaculty of Science, University of Kragujevac, P.O. Box 60, YU-34000 Kragujevac, and ^bDepartment of Mathematics, Faculty of Science, University of Niš, Yugoslavia

(Received 28 February 2002)

The largest Laplacian eigenvalue μ_1 of the molecular graph is a quantity important in the theory of the photoelectron spectra of saturated hydrocarbons. It is shown that in the case of alkanes, the presence or absence of quaternary carbon atoms is the main structural feature on which μ_1 depends. Within sets of all alkanes with a given number of carbon atoms the species (with and without quaternary carbon atoms) whose μ_1 -values are minimal and maximal are determined.

Keywords: Laplacian spectrum, molecular graph, alkanes.

Let G be a graph with n vertices. The Laplacian matrix of G is defined as $L(G) = D(G) - A(G)$, where $A(G)$ is the adjacency matrix of G and $D(G)$ is the diagonal matrix of the vertex degrees of G . The eigenvalues of $L(G)$, denoted by $\mu_1, \mu_2, \dots, \mu_n$, form the Laplacian spectrum of G . If they are labeled so that $\mu_1 \geq \mu_2 \geq \dots \geq \mu_n$, then μ_n is always 0, whereas $\mu_{n-1} > 0$ if and only if the graph G is connected. The largest Laplacian eigenvalue of G is thus $\mu_1 = \mu_1(G)$.

Two recent discoveries in theoretical chemistry resulted in a significant increase of the interest in the Laplacian spectra of molecular graphs. First, the Wiener topological index W of alkanes was shown to conform to the formula

$$W = n \sum_{i=1}^{n-1} \frac{1}{\mu_i} \quad (1)$$

Second, within the Heilbronner model, the ionization potentials of alkanes (as measured *via* the high-energy bands in their photoelectron spectra) are expressed as

$$\alpha + (\mu_i - 2) \beta; i = 1, 2, 3, \dots \quad (2)$$

where α and β are pertinently chosen semiempirical constants. It follows from Eq. (2) that μ_1 determines the first ionization potential of the respective alkane.

Serbian Chemical Society active member.

For details about Eq. (1) see the papers¹⁻³ and the references cited therein. For details about Eq. (2) see the papers⁴⁻⁶ and the references cited therein. Parts I-V of the series *Chemical Applications of the Laplacian Spectrum* are the papers.^{2,4-7} Details of the theory of Laplacian eigenvalues can be found in the reviews.⁸⁻¹⁰

A REGULARITY IN THE STRUCTURE-DEPENDENCY OF THE LARGEST LAPLACIAN EIGENVALUE OF ALKANES

A tree is a connected acyclic graph. A chemical tree is a tree in which no vertex has a degree (= number of first neighbors) greater than 4. Chemical trees are molecular graphs representing constitutional isomers of alkanes. If n is the number of vertices, then each chemical tree represents a particular isomer of C_nH_{2n+2} .

Continuing our research on the Laplacian eigenvalues of molecular graphs, and, in particular, of the dependence of the largest Laplacian eigenvalue on molecular structure,⁷ the μ_1 -values of all chemical trees with 20 and fewer vertices have been computed. When the isomeric alkanes are ordered according to their μ_1 -values a remarkable regularity is observed.

Denote the maximal degree of a vertex of the graph G by Δ . For molecular graphs Δ is equal to either 2 or 3 or 4. (The condition $\Delta = 1$ is satisfied only by ethane and is, therefore, irrelevant for the present study.) In the case of alkanes, only the normal (unbranched) isomers have $\Delta = 2$. If the molecule possesses tertiary carbon atoms, but no quaternary carbon atom, then $\Delta = 3$. If there is at least one quaternary carbon atom in the molecule, then $\Delta = 4$.

The chemical trees pertaining to the 18 isomeric octanes, ordered by increasing μ_1 , are depicted in Fig. 1. The isomer with the smallest μ_1 -value is the unbranched normal octane (the unique species with $\Delta = 2$). It is followed by 10 other isomers, with various extents of branching, none of which possesses a quaternary carbon atom ($\Delta = 3$). The remaining 7 octane isomers, with the largest μ_1 -values, all possess a quaternary carbon atom ($\Delta = 4$). Thus, by means of the largest Laplacian eigenvalue, the isomeric octanes are separated into three groups according to their μ -values.

The same regularity is found to exist for sets of isomeric alkanes with n carbon atoms, $4 \leq n \leq 12$: *The normal alkane (with $\Delta = 2$) has the smallest μ_1 . All alkanes with $\Delta = 3$ have smaller μ_1 values than any isomer with $\Delta = 4$.* This regularity is corroborated by the data shown in Fig. 2, depicting the distribution of the μ_1 -values of alkanes with $6 \leq n \leq 10$ carbon atoms.

It can, thus, be concluded that Δ (the parameter indicating the presence or absence of quaternary carbon atoms) is the main molecular structure-descriptor¹¹ affecting the value of the largest Laplacian eigenvalue of an alkane.

For $n \geq 13$ a slight violation of the above rule is found which is discussed in more detail in the subsequent section.

The fact that the largest Laplacian eigenvalue of trees is bound from below by $\Delta + 1$ and from above by some linear function of the parameter Δ has been known for some time.⁸⁻¹⁰

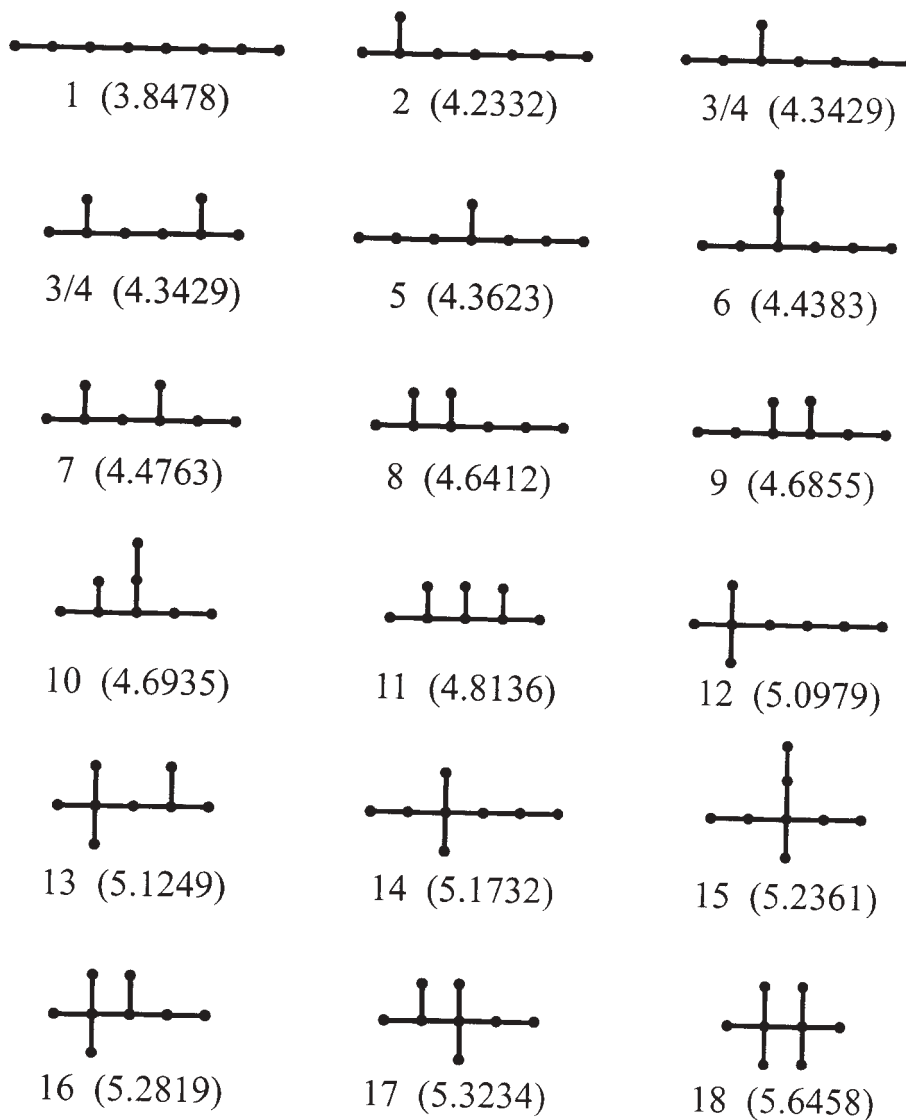


Fig. 1. The molecular graphs representing isomeric octanes ordered according to increasing largest Laplacian eigenvalue (given in parentheses); graphs 1, 2–11, and 12–18 have $\Delta = 2$, $\Delta = 3$ and $\Delta = 4$, respectively.

Recently one of the present authors improved the upper boundary¹² so that one now has

$$\Delta + 1 < \mu_1 < \Delta + 1 + 2\sqrt{\Delta - 1} \quad (3)$$

The estimates (3) are in qualitative agreement with our finding that Δ significantly influences the value of the largest Laplacian eigenvalue. These estimates suggest that a

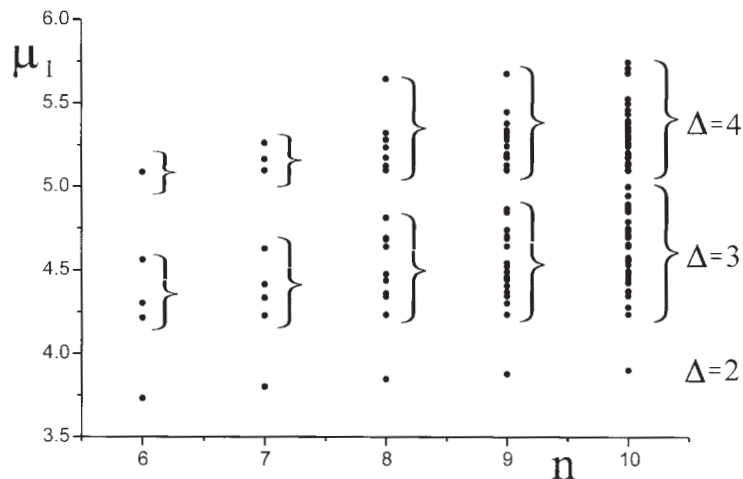


Fig. 2. The distribution of the largest Laplacian eigenvalues (μ_1) of isomeric hexanes ($n=6$), heptanes ($n=7$), octanes ($n=8$), nonanes ($n=9$), and decanes ($n=10$). In all these cases the data points are strictly separated into groups with different Δ values.

(rough) approximation for μ_1 could be obtained by a linear combination of the lower and upper boundary in (3):

$$\mu_1 \approx \frac{C_1 (\Delta + 1) + C_2 (\Delta + 1 + 2\sqrt{\Delta - 1})}{C_1 + C_2}$$

i.e.,

$$\mu_1 \approx \Delta + 1 + \gamma \sqrt{\Delta - 1} \quad (4)$$

for some pertinently chosen constant $\gamma = 2C_2/(C_1 + C_2)$. By numerical testing it was found that for alkane graphs, $\gamma \approx 0.2$. A more detailed examination reveals that γ would depend on both n and Δ , making the usage of formula (4) unnecessarily complicated.

ALKANES WITH MAXIMAL AND MINIMAL LARGEST LAPLACIAN EIGENVALUES

As already mentioned, we calculated μ_1 for all alkanes with 20 and fewer carbon atoms. From these data it is easy to see that among alkanes with a fixed values of n the normal alkane (whose graph representation is the path P_n , see Fig. 3) has minimal μ_1 . It can be shown that $\mu_1(P_n) = 2 + 2 \cos(\pi/n)$. This, of course, is the alkane with $\Delta = 2$ and minimal μ_1 .

The structure of the alkane isomers with $\Delta = 3$ and $\Delta = 4$, having minimal μ_1 is also easily established. The respective chemical trees (T_n^{\min} for $\Delta = 3$ and Q_n^{\min} for $\Delta = 4$) are depicted in Fig. 3.

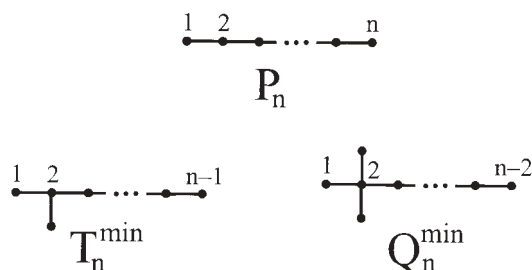


Fig. 3. The n -vertex trees with $\Delta = 2, 3, 4$ having minimal μ_1 . Graphs 1, 2, and 12 in Fig. 1 are the same as P_n , T_n^{\min} and Q_n^{\min} for $n = 8$.

The structure of the chemical trees T_n^{\max} (for $\Delta = 3$) and Q_n^{\max} (for $\Delta = 4$), having maximal μ_1 , turns out to be much harder to characterize. Fortunately, however, the analogous problem was earlier considered for a number of other molecular structure-descriptors.^{13–15} In particular, we determined the chemical trees with minimal Wiener index (W),^{13,15} minimal connectivity index,¹⁴ maximal largest (ordinary) graph eigenvalue (λ_1),¹⁵ minimal Hosoya index,¹⁵ and minimal energy.¹⁵ What has now been established is that T_n^{\max} and Q_n^{\max} coincide with the chemical trees with the same n and Δ , having minimal W and maximal λ_1 . These extreme $\Delta = 3$ and $\Delta = 4$ species are depicted in Figs. 4 and 5 for a few values of n . The precise characterization of the structure of T_n^{\max} and Q_n^{\max} (which is far from being elementary) can be found elsewhere.¹⁵

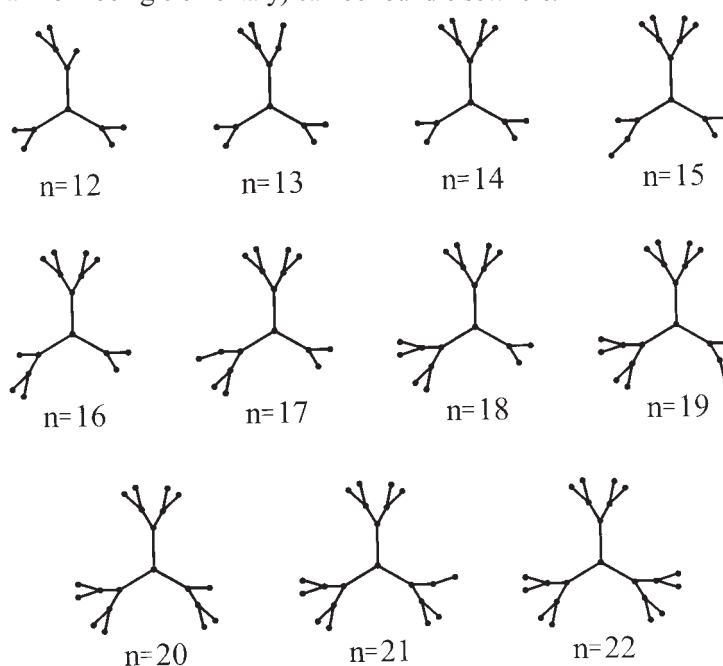


Fig. 4. The n -vertex trees T_n^{\max} with $\Delta = 3$ having maximal μ_1 , for $n = 12, 13, \dots, 22$. Graph 11 in Fig. 1 is such a tree for $n = 8$.

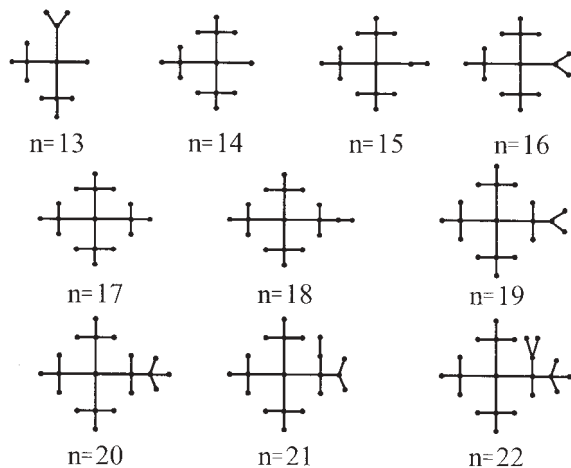


Fig. 5. The n -vertex trees Q_n^{\max} with $\Delta = 4$ having maximal μ_1 , for $n = 13, 14, \dots, 22$. Graph 18 in Fig. 1 is such a tree for $n = 8$.

In order to have a complete separation of alkane isomers without and with quaternary carbon atoms (as shown in Fig. 2 and exemplified in Fig. 1), it is necessary that

- (a) $\mu_1(P_n)$ be smaller than $\mu_1(T_n^{\min})$, cf. Fig. 3, and
- (b) $\mu_1(T_n^{\max})$ be smaller than $\mu_1(Q_n^{\min})$, cf. Figs. 3 and 4.

Condition (a) is always obeyed. Moreover, $\mu_1(P_n) < 4$ whereas all other n -vertex trees have $\mu_1 > 4$.

By direct calculation we have verified that condition (b) is obeyed for all $n \leq 12$, but is violated for $n \geq 13$. In particular, $\mu_1(T_{12}^{\max}) = 5.0825$ and $\mu_1(Q_{12}^{\min}) = 5.0981$ whereas $\mu_1(T_{13}^{\max}) = 5.1084$ and $\mu_1(Q_{13}^{\min}) = 5.0981$.

Thus the rule formulated in the preceding section is not strictly obeyed. Violations may occur for pairs of alkanes with a large number of carbon atoms, one of which (the species with $\Delta = 3$) must be highly branched. However, these cases of violations are of little practical relevance, because highly branched alkanes (such as those corresponding to the chemical trees depicted in Fig. 3) are hardly ever encountered in real-life chemistry.

ИЗВОД

ХЕМИЈСКЕ ПРИМЕНЕ ЛАПЛАСОВОГ СПЕКТРА. VI. О НАЈВЕЋОЈ ЛАПЛАСОВОЈ СОПСТВЕНОЈ ВРЕДНОСТИ АЛКАНА

ИВАН ГУТМАН, ДУШИЦА ВИДОВИЋ и ДРАГАН СТЕВАНОВИЋ

Природно-математички факултет у Крагујевцу и Природно-математички факултет у Нишу

Највећа Лапласова сопствена вредност μ_1 молекулског графа је од значаја у теорији фотоелектронских спектра засићених угљоводоника. Показано је да је, у случају алкана, присуство или одсуство кватернерних угљеникових атома најважнији структурни детаљ од којег зависи μ_1 . Одређени су изомери који међу алканима са фиксираним бројем угљеникових атома (са кватернерним угљениковим атомима и без њих) имају најмању и највећу вредност параметра μ_1 .

(Примљено 28. фебруара 2002)

REFERENCES

1. B. Mohar, D. Babić, N. Trinajstić, *J. Chem. Inf. Comput. Sci.* **33** (1993) 153
2. I. Gutman, S. L. Lee, C. H. Chu, Y. N. Luo, *Indian J. Chem.* **33A** (1994) 603
3. S. Marković, I. Gutman, Ž. Bančević, *J. Serb. Chem. Soc.* **60** (1995) 633
4. C. D. Godsil, I. Gutman, *ACH Models Chem.* **136** (1999) 503
5. I. Gutman, V. Gineityte, M. Lepović, M. Petrović, *J. Serb. Chem. Soc.* **64** (1999) 673
6. R. Merris, I. Gutman, *Z. Naturforsch.* **55a** (2000) 973
7. I. Gutman, D. Vidović, *Indian J. Chem.* **41A** (2002), in press
8. R. Grone, R. Merris, V. S. Sunder, *SIAM J. Matrix Anal. Appl.* **11** (1990) 218
9. R. Merris, *Lin. Algebra Appl.* **197** (1994) 143
10. R. Merris, *Lin. Multilin. Algebra* **39** (1995) 19
11. R. Todeschini, V. Consonni, *Handbook of Molecular Descriptors*, Wiley-VCH, Weinheim, 2000
12. D. Stevanović, *Lin. Algebra Appl.*, in press
13. M. Lepović, I., Gutman, *J. Chem. Inf. Comput. Sci.* **38** (1998) 823
14. I. Gutman, O. Miljković, G. Caporossi, P. Hansen, *Chem. Phys. Lett.* **306** (1999) 366
15. M. Fischermann, I. Gutman, A. Hoffmann, D. Rautenbach, D. Vidović, L. Volkmann, *Z. Naturforsch.* **57a** (2002) 49.