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RELATION BETWEEN WIENER INDEX AND SPECTRAL RADIUS

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ABSTRACT. Among the variety of molecular-graph-based structure-descriptors, aimed at measuring the extent of branching of the skeleton of organic molecules, there are the Wiener index W and the spectral radius λ_1 i. e., the greatest eigenvalue of the molecular graph. Although, these indices are used for decades, they have never been compared. Our computational studies show that within series of the isomeric chemical trees there exists a decreasing linear correlation between W and λ_1. The relation between W and λ_1 is also examined for benzenoid molecules.

INTRODUCTION

Already in the 19th century it was known that the extent of branching of the carbon-atom skeleton of an organic molecule is related to its molecular surface area [1, 2]. The molecular surface area is of crucial importance for physical and chemical properties of nonpolar organic molecules, such as alkanes. Therefore, a quantitative measure of branching is needful for finding connections between molecular structure and physico-chemical properties of chemical compounds, which is the main task in QSAR (quantitative structure-activity relations) and QSPR (quantitative structure-property relations) researches. Starting from the 1970s numerous topological indices aimed at quantifying the extent of branching were proposed [3-9].

Here, we are concerned with two branching indices: the Wiener index W and the spectral radius λ_1 i. e., the greatest eigenvalue of the molecular graph. These were among the first structure-descriptors that were proposed for measuring molecular branching. Also, these indices are among the most often used molecular structure-descriptors in QSPR and QSAR.

The Wiener index [10] is the oldest structure-descriptor that still attracts much attention [11]. The Wiener index is defined as

$$W = W(G) = \sum_{u>v} d(u,v|G)$$

where $d(u, v|G)$ is the distance (= length of the shortest path) between the vertices u and v of the molecular graph G, and the summation goes over all pairs of vertices.

If G is a molecular graph with n vertices, then its adjacency matrix $A = \|A_{rs}\|$ is a square matrix of order n defined as

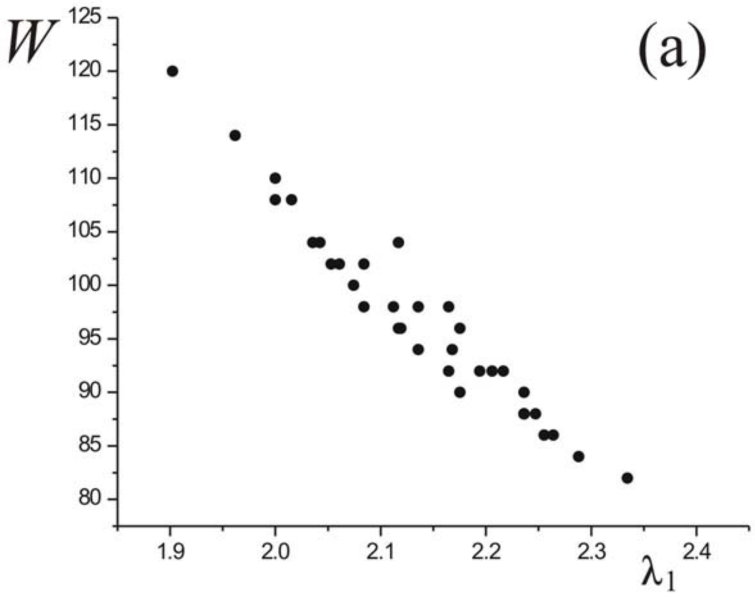
$$A_{rs} = \begin{cases} 1 & \text{if the vertices } r \text{ and } s \text{ are adjacent} \\ 0 & \text{otherwise.} \end{cases}$$

The eigenvalues of the adjacency matrix of G are usually called to be the eigenvalues of G [12]. The largest eigenvalue of G, referred to as the spectral radius of G, will be labeled by λ_1. Using λ_1 as a measure of branching was proposed by one of the present authors as early as in 1977 [13]. For decades this branching index has not attracted much attention of theoretical chemists. Recently, studies of the spectral radius as the measure of branching became attractive again [14-16].

Although W and λ_1 are the oldest branching indices (together with Randić's connectivity index [3]), until now the relation between them has not been duly investigated. The present paper is aimed at contributing towards filling this gap.

RELATION BETWEEN W AND λ_1 FOR ALKANES

Because W depends on the size (number of carbon atoms) of the molecules examined, it is purposeful to restrict the consideration to classes of alkane isomers. Our investigation of the relation between W and λ_1 was preformed on several sets of isomeric chemical trees i. e., graph representation of alkanes. Chemical trees with n vertices represent alkane isomers with the formula C_nH_{2n+2}.



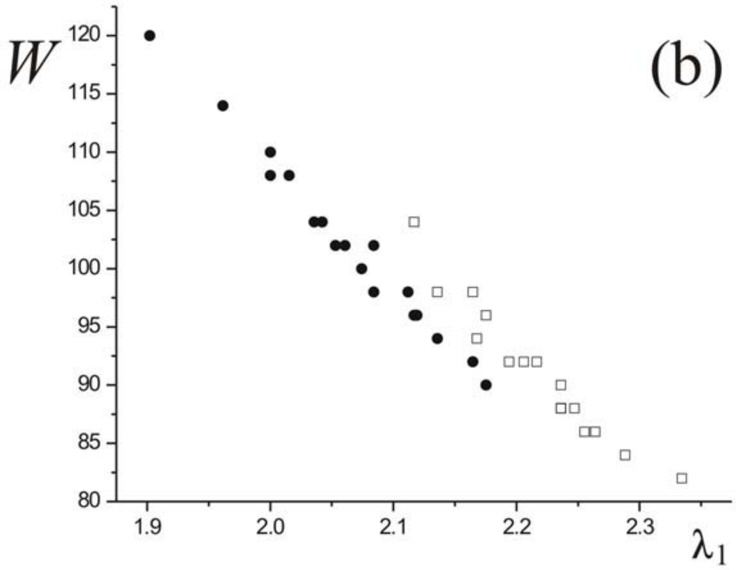


Figure 1. a) The Wiener index *W* of the molecular graphs of the 35 isomeric nonanes C_9H_{20} versus the spectral radius λ_1 (correlation coefficient is -0.9721). b) The same correlation between *W* and λ_1; squares and circles correspond to molecules having quaternary carbon atoms and having no quaternary carbon atoms, respectively. The corresponding regression formulas are $W=(-100\pm7)\lambda_1 + (310\pm10)$ for squares, and $W=(-109\pm4)\lambda_1 + (327\pm7)$ for circles, with correlation coefficients -0.9677 and -0.9914, respectively.

For all examined series of isomeric chemical trees starting from trees with six vertices we observed the same regularities. One characteristic example is given in Fig. 1.

The first impression is that the correlation between W and λ_1 is decreasing, linear, but not particularly good (Fig. 1a).

The fundamental property of W is that the star S_n has minimal and the path P_n maximal value of W among trees with n vertices [17]. Among chemical trees the highly branched, so-called Volkmann tree has minimal W-value [16]. This means that within sets of isomeric trees, the value of W decreases with the increasing extent of branching. On the other hand in series of n-vertex trees, the star S_n has maximal λ_1, whereas the path P_n minimal λ_1 [18]. Furthermore, among chemical trees the Volkmann tree has maximal spectral radius [19]. These finding imply that the spectral radius increases with the increasing extent of branching. Consequently, one can anticipate that between W and λ_1 there exists a decreasing correlation. This indeed is the case (Fig. 1a).

By a closer examination of the correlation between W and λ_1 we found that the (W, λ_1)-points are divided into two groups (Fig. 1b). It was recognized that the parameter determining to which group a given (W, λ_1)-point belongs is the presence of quaternary carbon atoms in the molecule considered. Within each group of data points there is a relatively good linear correlation. Moreover, these regression lines are almost parallel (see Fig. 1). The existence of these linear correlations indicates that within series of isomeric chemical trees that have about the same extent of branching both W and λ_1 in the same manner quantify the extent of branching.

RELATION BETWEEN W AND λ_1 FOR BENZENOID COMPOUNDS

The Wiener index W and the spectral radius λ_1 are popular topological indices and they found numerous QSAR and QSPR applications [9]. W and λ_1 are used for modeling of properties of many types of chemical compounds. The vast majority of molecules of interest in chemistry are cyclic. Therefore finding relation between W and λ_1 is important not only in the case of alkanes, but also for other classes of organic compounds.

In this section we analyze the relation between W and λ_1 for benzenoid hydrocarbons. The structural dependence of W and (separately) of λ_1 of benzenoid hydrocarbons was studied previously [20,21]. The carbon-atom skeleton of these hydrocarbons consists of mutually fused hexagons. The electron properties of benzenoid compounds are attracting the interest of chemist for over 150 years [22-24]. They are also much studied in environmental chemistry because benzenoid hydrocarbons are dangerous pollutants [24, 25].

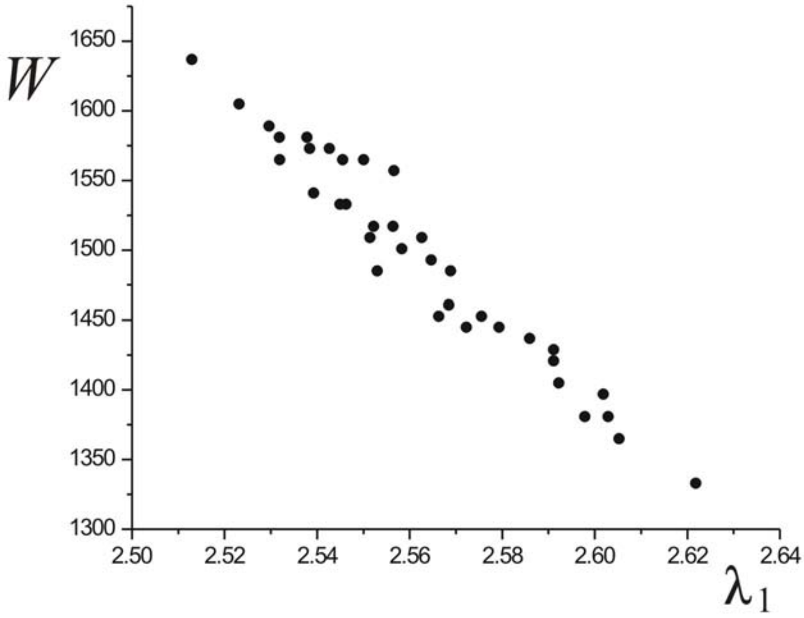


Figure 2. The Wiener index *W* of the 36 isomeric hexacyclic catacondesed benzenoid hydrocarbons $C_{26}H_{16}$ plotted versus their spectral radius λ_1 (the correlation coefficient is -0.9746).

In order to avoid the size-dependence of *W* and λ_1, the correlation between these two quantities was examined within sets of isomers. In Fig. 2 a characteristic W/λ_1-plot for the set of the 36 catacondensed benzenoid molecules with six hexagons is shown. These isomeric hydrocarbons have the formula $C_{26}H_{16}$. From Fig. 2 it is seen that between *W* and λ_1 there exists a reasonably good linear correlation. This is the case for several other examined sets of isomeric benzenoid hydrocarbons.

The observed linear correlation between *W* and λ_1 means that these two topological indices in a very similar way reflect the characteristic features of the molecular structure of benzenoid hydrocarbons, and the use of both of them in modeling properties of these compounds in QSAR and QSPR researches would give the same results.

CONCLUSIONS

We studied the relation between *W* and λ_1. It was found that in sets of isomeric alkanes the data points are clustered into two groups, depending on the presence or absence of quaternary carbon atoms. Within each of these groups W and λ_1 are relatively well linearly correlated. The existence of such linear correlations implies that both topological indices provide comparable measures of branching of the carbon skeleton of alkanes. Linear correlation between W and λ_1 was found also in the case of benzenoid hydrocarbons. This means that these two topological indices depend in the same manner on the structure of benzenoid molecules and that the usage of these indices in QSAR/QSPR researches will lead to equivalent results.

We checked these regularities on several sets of chemical trees and benzenoid systems and we did not find any violation. These regularities are established by means of computer experiments, whereas some theoretical rationalization thereof remains a task for the future.

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