Graph Theoretical Invariant of Randić Revisited

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The mathematical properties of the graph theoretical invariant of Randić for a series of regular graphs was studied, taking as examples the calculation of vertex and edge connectivity indices. Mathematical relations that explain the degeneracy of both indices for this type of graphs are obtained. The exponent −1/2 used in the graph invariant of Randić was identified as the main cause of this accidental degeneracy of studied topological indices. Several examples of this kind of degeneracy for edge and vertex connectivity indices in graphs representing alkanes and cycloalkanes are presented. Degeneracy in all studied graphs was eliminated by using an exponent of −1/3 in the graph invariant, given a mathematical basis for the empirical generalization of connectivity index carried out by Altenburg. The importance of using regular graphs to test novel graph invariants was also analyzed.

INTRODUCTION

One of the most intensive fields of research in chemical graph theory is the development and application of topological indices.[1,2] These indices are numbers generated from several invariants of molecular graphs that encode important information about the chemical structures of molecules.

There are many topological indexes described in the literature,[3] and new ones are invented,[4,5] but only a few of them have been extensively applied in quantitative structure−property relationship (QSPR) and quantitative structure−activity relationship (QSAR) studies.[3,6]

The molecular connectivity index χ introduced by Randić 20 years ago[7] appears to be one of the most successful indices in producing structure−property correlations and regressions, especially when suitably expanded to account for heteroatoms differentiation.[8,9]

This index is based on bond additivity, using different weights for bonds. The weights are given by $(mn)^{-1/2}$ where m and n are degrees of two adjacent vertices in the graph. This simple graph-theoretical invariant was adopted as a solution of a set of inequalities constructed to reproduce the correct ordering of alkane structures.[7] The invariant of Randić is also used in calculation of several topological indexes. Among these indices we can mention Balaban J index,[10] ID[11] numbers, topographic Ω index,[12] as well as the edge connectivity index ϵ.[13] The last index was introduced recently by this author, and it is calculated like Randić's index but uses edge degrees instead of vertex degrees.

Altenburg[14] generalized Randić's invariant considering different values for exponent g in the expression $(mn)^{-g}$. On the other hand, Randić[15] studied values of $g = -1/3$ and $g = -1/4$ in the calculation of χ index using an empirical approach. He observed that molecular connectivity index calculated by using $g = -1/3$ and $g = -1/4$ produced better correlations with boiling points of alkanes than with the use of $g = -1/2$.

The purpose of this paper is to analyze the graph theoretical invariant of Randić from the mathematical point of view, using as examples the calculation of χ and ϵ indices for regular graphs. This selection is motivated by the observation of Kunz[16] that cyclooctane and cubane, two regular graphs with vertex connectivities of 2 and 3, have the same value of χ index.

CONNECTIVITY INDICES AND REGULAR GRAPHS

Regular graphs are those in which all vertices are of same degree.[17] This type of graph has many applications in chemistry, for example, several molecules can be represented by hydrogen-depleted regular graphs. In Figure 1, we illustrate three of these graphs representing molecules of cyclooctane, prismane (tetracyclo[2.2.0.$0^{2,6}$.$0^{3,5}$]hexane), and cubane (pentacyclo[4.2.0.0^{2,5}.$0^{3,8}$.$0^{4,7}$]octane).

Vertex and edge connectivity indices are calculated using the same graph theoretical invariant. Randić's index is defined as follows:[7]

$$\chi = \sum_{e=1}^{m} [\delta(\nu_i)\delta(\nu_j)]_e^{-1/2} \qquad (1)$$

Vertex degree, $\delta(\nu_i)$, is the number of vertices with which the vertex ν_i is adjacent, and the summation $\sum_e$ is over all adjacent vertices in the molecule. Edge connectivity index ϵ is defined similarly to χ index, but uses edge degrees instead of vertex degrees:[13]

$$\epsilon = \sum_{s} [\delta(e_i)\delta(e_j)]_s^{-1/2} \qquad (2)$$

Edge degree, $\delta(e_k)$, is the number of edges with which e_k is adjacent, and here the sum $\sum_s$ is over all adjacent edges in the graph. A trivial mathematical relationship between edge and vertex degree can be found:[13]

$$\delta(e_l) = \delta(\nu_i) + \delta(\nu_j) - 2 \qquad (3)$$

where vertices ν_i and ν_j are incident with edge e_l in the graph.

In Figure 2, we illustrate the values of both indices calculated for several regular graphs with four to eight vertices and having different vertex and edge connectivities. As can be appreciated, the χ index has identical values for non-isomorphic regular graphs with different connectivities

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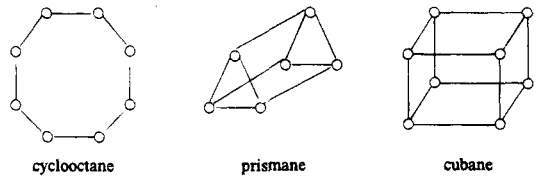

Figure 1. Regular graphs representing the hydrogen-depleted graphs of several molecules.

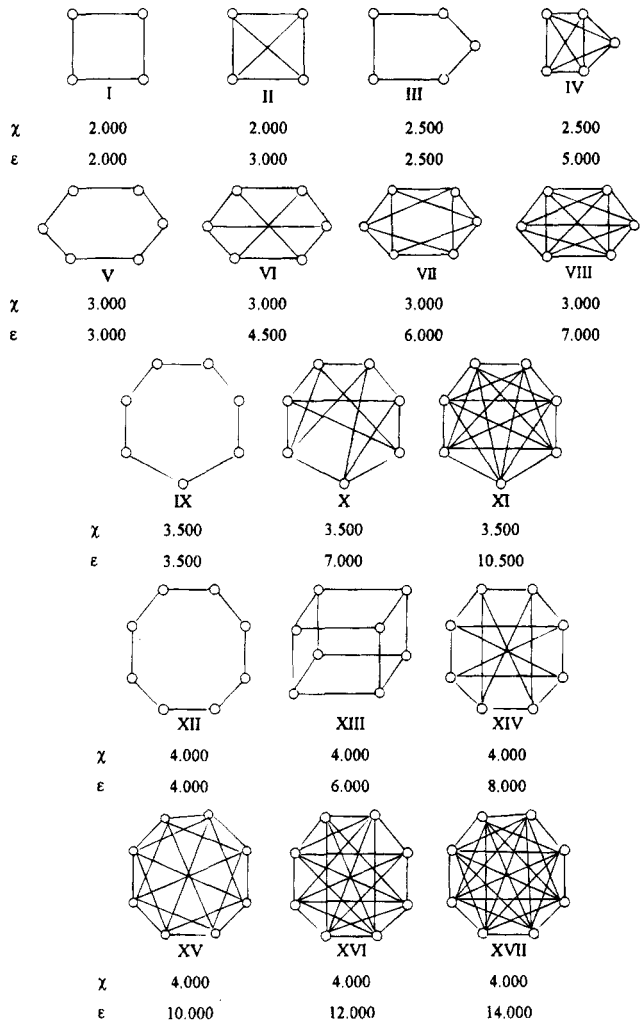

Figure 2. Regular graphs of sizes 4−8 and its values of χ and ϵ indexes.

but with the same number of vertices. This observation can be generalized in a more elaborated form exposed as follows:

LEMMA 1: The number of edges, m, in a k-regular graph is $kn/2$, where k is the regularity and n is the number of vertices of the graph.

Proof: In a regular graph, all vertices have the same degree, k, and we get

$$\sum_{i=1}^{n}\delta(v_i) = nk \tag{4}$$

As proved elsewhere,[18] the sum of degrees of each vertex in the graph is equal to $2m$:

$$\sum_{i=1}^{n}\delta(v_i) = 2m \tag{5}$$

by combination of expressions 4 and 5, we obtain:

$$m = kn/2 \tag{6}$$

THEOREM 1: The vertex connectivity index of a k-regular graph is $n/2$.

Proof: For a k-regular graph, expression 1 is transformed in

$$\chi = mk^{-1} \tag{7}$$

because of the identical value for all vertex degree. Substituting expression 6 in expression 7, we have

$$\chi = n/2 \tag{8}$$

An important consequence related to theorem 1 is that all regular graphs with the same number of vertices have identical values of the Randić index. This theorem generalizes the empirical observation of Kunz about the degenerated values for χ index in cubane and cyclooctane.[16]

In Figure 2, we can also appreciate that the ϵ index is also degenerated for some non-isomorphic regular graphs. This index is more discriminant than the χ index for both regular graphs and alkane trees. Degeneracy in the ϵ index appears for regular graphs having the same number of edges, for instance, graphs II and V have six edges and a value of $\epsilon = 3.000$. The 4-regular graph with six vertices and the 3-regular graph with eight vertices both having 12 edges (graphs VII and XIII) have an identical value of ϵ ($\epsilon = 6.000$). Generalization of this regult is straightforward and worth stating as another theorem.

LEMMA 2: In a k-regular graph, the number of pairs of adjacent edges is $m(k-1)$.

Proof: The number of adjacent edge in a graph is the half sum of its edge degrees:

$$s = \frac{1}{2}\sum_{\rho=1}^{m}\delta(e_\rho) \tag{9}$$

Using expression 3 and transforming them for regular graphs, where $\delta(v_i) = \delta(v_j) = k$, we get

$$\delta(e) = 2k - 1 \tag{10}$$

Substituting expression 10 in expression 9

$$s = \frac{1}{2}\sum_{l=1}^{m}2k - 1 = m(k-1) \tag{11}$$

THEOREM 2: Edge connectivity index of a k-regular graph is equal to $m/2$.

Proof: Using expression 11 in eq 2, we obtain for regular graphs

$$\epsilon = \sum_{s}^{m(k-1)}[\delta(e_i)\delta(e_j)]_s^{-1/2} \tag{12}$$

$$\epsilon = m(k-1)[\delta(e)]^{-1} \tag{13}$$

Using expression 10 in eq 13, we get

$$\epsilon = m/2 \tag{14}$$

DISCUSSION

In order to analyze the degeneracy of vertex and edge connectivity indices in regular graphs, we return to the

Table 1. Values of Connectivity Indices Using $g = -1/3$ for Regular Graphs Presented in Figure 2

graph	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	XVII
$\chi(-1/3)$	2.5198	2.8845	3.1498	3.6056	3.7798	4.3267	4.7622	5.1299	4.4097	5.5559	6.3599	5.0397	5.7690	6.3496	6.8399	7.2685	7.6517
$\epsilon(-1/3)$	2.5198	4.7622	3.1498	9.0856	3.7798	7.1433	10.9027	15.0000	4.4097	12.7198	22.6215	5.0397	9.5244	14.5370	20.0000	25.8532	32.0520

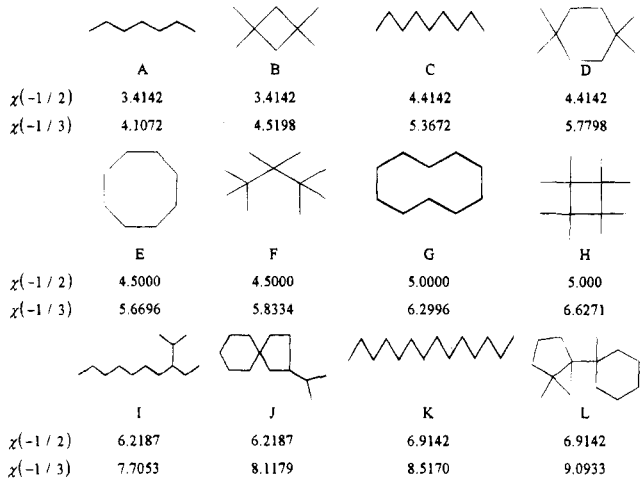

Figure 3. Some alkanes and cycloalkanes with "accidental" degeneracy of the Randić index.

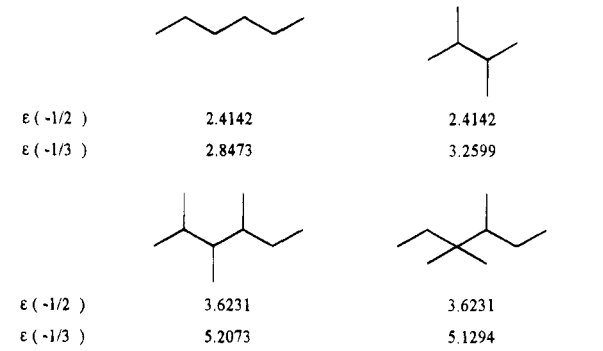

Figure 4. Examples of alkanes with degenerated values of edge connectivity index.

example of cubane and cyclooctane. In the cubane graph, the product of vertex degrees, $\delta(v_i)\delta(v_j)$, is equal to 9, corresponding to the number of self-avoiding paths of length 1, 2, and 3 in which the edge i,j is incident as the central edge; this number is equal to 4 in the graph representing cyclooctane. The number of adjacent vertices in the first graph is 12, while in the second it is only 8; hence, the total number of self-avoiding paths of length 1, 2, and 3 for both graphs is very different (108 and 32, respectively).

An examination of expression 7 obtained in the proof of theorem 1 permits us to conclude that the degeneration is a consequence of exponent $-1/2$ in graph theoretical expression used to calculate χ and ϵ indices. If we use the generalized expression of Altenburg in the calculation of the χ index, we obtain

$$\chi = \sum_{i=1}^{m} [\delta(v_i)\delta(v_j)]^g \tag{15}$$

and expression 7 is transformed to

$$\chi = \frac{n}{2} k^{(1+2g)} \tag{16}$$

when $g = -1/2$, as in the original definition of Randić index, we obtain expression 8 that justifies the degeneracy of χ for a regular graph with the same number of vertices. Using a similar procedure for the ϵ index, we transform expression 13 into the following:

$$\epsilon = 2^{2g}\, m(k-1)^{1+2g} \tag{17}$$

Values of χ and ϵ indices using $g = -1/3$ for graphs illustrated in Figure 2 are shown in Table 1. The discriminative power of both indices has been increased considerably by the modification of the exponent in expressions 1 and 2, which defines the way to calculate both indices.

Degeneracy of connectivity indices due to exponent $g = -1/2$ in the graph theoretical invariant is not exclusive for regular graphs. If we consider cyclic and acyclic graphs together, i.e., alkanes and cycloalkanes, several examples of the degenerated χ index can be found. In Figure 3, we illustrate some of these pairs of graphs.

On the other hand, among the 74 alkane trees with C2−C9 atoms there are only two pairs of isomers with degenerated values of $\epsilon(-1/2)$ index. When the exponent g is changed to $-1/3$, these graphs are discriminated by the ϵ index, as depicted in Figure 4.

The observed degeneracy in connectivity indices is a consequence of the trivial relationships between some of the weights used to differentiate bonds in the calculation of the χ and ϵ indices. For instance, two examples of these equalities are the following: $2 \times (4 \times 4)^{-1/2} = (2 \times 2)^{-1/2} = (4 \times 1)^{-1/2}$ and $2 \times (4 \times 2)^{-1/2} = (2 \times 1)^{-1/2}$. These equalities permit the construction of graphs with degenerated values of topological indices similar to the ones illustrated in Figures 3 and 4.

CONCLUDING REMARKS

Considering the characterization of structures, regular graphs represent a more challenging group because many properties and procedures valid for the acyclic system no longer hold for this type of polycyclic structures. A proof to this statement is the high degeneracy of the molecular connectivity index of Randić for regular graphs having the same number of vertices.

We propose a mathematical basis for degeneracy of the χ index in regular graphs, and we find that the cause of this degeneracy is the use of an exponent $-1/2$ in expression used to calculate the connectivity index. By changing this exponent by another value, for instance, $-1/3$, we discriminate a greater number of structures having different connectivities of its vertices. Empirical approaches used by Altenburg[14] and Randić et. al.[15] now have a mathematical basis that justifies the introduction of another exponent in the graph theoretical invariant of Randić.

Degeneracy in topological indices produced by mathematical "accidents" in graph theoretical invariants can be considered as an undesirable "noise" that should be eliminated. To avoid this kind of degeneracy, the investigation of topological indices for regular graphs appears to be a prominent test that can be added to the calculation of topological indices for alkane trees. Among the desirable

attributes recently proposed by Randić for topological indices, we can find the good discrimination of isomers.[18] This important attribute of topological indices is commonly proved in analyzing a series of alkane isomers, but as can be concluded from the present work, this is not sufficient to detect some kind of degeneracy in graph invariants.

Finally, we will comment on a statement of Kunz about the molecular connectivity index of Randić. Kunz[16] stressed that "the Randić index does not measure connectivity but it is a very elegant measure of the regularity of a graph". After the analysis carried out here, we can conclude that the χ index is really a measure of connectivity in a graph. When "accidental" degeneracy produced by exponent $-1/2$ in the graph invariant is eliminated, the index can differentiate between regular graphs with different connectivities, and it can have identical values for all non-isomorphic regular graphs with the same connectivity (for instance, the 85 cubic graphs with 12 vertices have the same value of the χ index).

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