On the Relation between the *P′*/*P* Index and the Wiener Number[†]

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It is shown analytically that the recently introduced P'/P index and the Wiener number are closely related graph-theoretical invariants for connected undirected acyclic structures and cycles.

INTRODUCTION

Molecular structure is the central theme of chemistry.[1−3] According to the principle of molecular structure, properties and behaviour of molecules follow from their structures. This statement has also been a subject of some criticisms.[4,5] If one considers nonmetric properties of a molecule, then the molecule can be represented by a (molecular) graph, which is essentially a nonnumerical mathematical object. Measurable properties of a molecule are usually expressed by means of numbers. Hence, to correlate property or activity of a molecule with its topology, one must first convert by an algorithm the information contained in the graph to a numerical characteristic. A scalar numerical descriptor uniquely determined by a molecular graph is named a topological (graph-theoretical) index.[6,7]

In the past the selection of graph matrices used for deriving of molecular indices was limited to the adjacency matrix $\boldsymbol{A}$ and the distance matrix $\boldsymbol{D}$.[8,9] The situation has been changed in the last few years, and quite a few novel graph-theoretical matrices have been proposed.[10−15] Randić has recently put forward a novel structure - explicit graph matrix $\boldsymbol{P}$ as well as the novel molecular index P′/P derived from it.[16,17] He also tested the new index by examining the octane numbers of octanes and empirically found a linear relationship between the P'/P index and the Wiener number[18,19] in octanes.

The representation of a molecule by a single number (topological index) entailes a considerable loss of information concerning the molecular structure. In search of new invariants which would improve the graph-theoretical characterization of molecular structure, a great number of indices have been proposed so far.[20,21] To make the evaluation of the existing and the future indices easier, Randić put forward a list of desirable attributes for topological indices.[16] A particularly important requirement is that an index is not trivially related to, or highly intercorrelated with, other indices. If an index does not fulfill this condition then its informational content is either entirely or in major part comprised in other indices, as for instance in case of the Schultz index and the Wiener number[22,23] or the Hosoya Z index and the ^1Z index.[24]

In this article we will discuss the relationship between the P′/P index and the Wiener number for connected undirected acyclic graphs and cycles.

DEFINITIONS

***P* Matrix**. The $\boldsymbol{P}$ matrix of a labeled connected undirected graph G with N vertices, $\boldsymbol{P} = \boldsymbol{P}(\mathrm{G})$ is the square symmetric matrix of order N whose entry in the ith row and jth column is defined as

$$(\boldsymbol{P})_{ij} = \begin{cases} p'_{ij}/p \text{ if the vertices } \mathrm{v}_i \text{ and } \mathrm{v}_j \text{ are adjacent in } G \\ 0 \text{ otherwise} \end{cases} \tag{1}$$

where p'_{ij} is the total number of paths in the subgraph G' obtained by the removal of the edge e_{ij} from G, and p is the total number of paths in G. "Otherwise" means that either the vertices $\mathrm{v_i}$ and $\mathrm{v_j}$ are not adjacent or $i = j$. If G' is disjoint then the contributions of each component could be for instance, added[16] or multiplied.[25] Here we follow the Randić's route, i.e., the addition of contributions. The $\boldsymbol{P}$ matrix can be the source of quite a few novel graph invariants-molecular indices. The process of finding $\boldsymbol{P}$ matrix is ilustrated for 2,3-dimethylpentane in Figure 1.

***P′*/*P* Index**. The P′/P index, $P'/P = P'/P(G)$, of a graph G is defined by means of the $\boldsymbol{P}$ matrix entries as

$$P'/P = \sum_{i=1}^{N-1}\sum_{j>i}^{N}(\boldsymbol{P})_{ij} \tag{2}$$

The quantity p'_{ij}/p could be understood as a graphical bond order,[26] $\pi_{e_{ij}}$ of the edge (bond) e_{ij} of G. It is a measure of relative "importance" of an edge in a graph. Using the sum over all edges in G of these local quantities

$$P'/P = \sum_{e_{ij}} \pi_{e_{ij}} \tag{3}$$

one obtains the graph invariant—molecular index P'/P.

Wiener Number. The Wiener number, $W = W(G)$, of a graph G was introduced as the path number.[18] H. Wiener defined the path number as the number of bonds between all pairs of atoms in an acyclic molecule. Later W was defined in the framework of graph theory[19] by means of the

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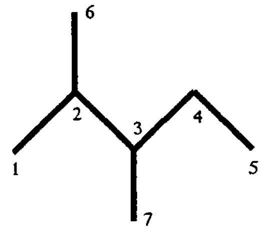

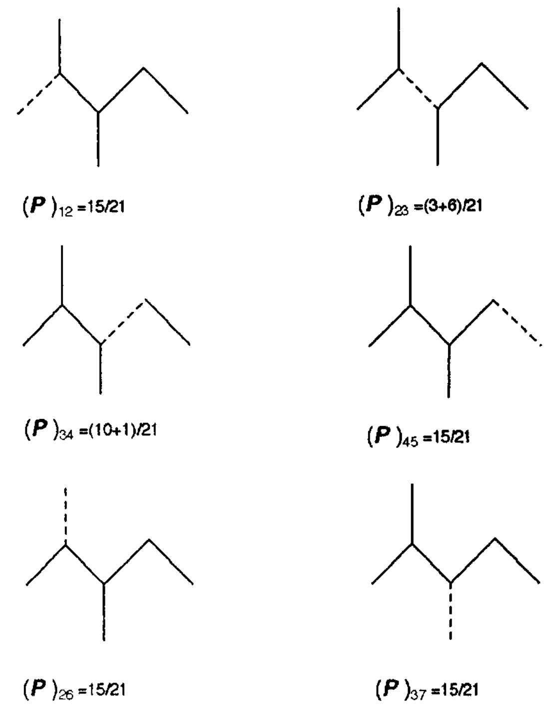

$$\boldsymbol{P} = \begin{bmatrix} 0 & 15/21 & 0 & 0 & 0 & 0 & 0 \\ 15/21 & 0 & 9/21 & 0 & 0 & 15/21 & 0 \\ 0 & 9/21 & 0 & 11/21 & 0 & 0 & 15/21 \\ 0 & 0 & 11/21 & 0 & 15/21 & 0 & 0 \\ 0 & 0 & 0 & 15/21 & 0 & 0 & 0 \\ 0 & 15/21 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 15/21 & 0 & 0 & 0 & 0 \end{bmatrix}$$

Figure 1. Calculation of the elements of the ***P*** matrix for 2,3-dimethylpentane. The broken lines represent erased bonds.

elements of the distance matrix $\boldsymbol{D} = \boldsymbol{D}(G)$ of G as

$$W = \sum_{i=1}^{N-1} \sum_{j>i}^{N} (D)_{ij} \tag{4}$$

RELATIONSHIP BETWEEN P'/P INDEX AND W NUMBER

Let T be a connected undirected acyclic graph (tree) with N vertices. Consider a given edge e_{ij} of T. By deletion of e_{ij}, T breaks into two components, whose numbers of vertices are $X_{e_{ij}}$ and $N - X_{e_{ij}}$, respectively. It is well-known that the Wiener number of T is given by

$$W = \sum_{e_{ij}} W_{e_{ij}} \tag{5}$$

where

$$W_{e_{ij}} = X_{e_{ij}}(N - X_{e_{ij}});\ 1 \le X_{e_{ij}} \le N - 1 \tag{6}$$

The total number of paths in T is

$$p = (N^2 - N)/2 \tag{7}$$

The graphical bond order of an edge e_{ij} of T, $\pi_{e_{ij}}$ is given by

$$\pi_{e_{ij}} = [(N - X_{e_{ij}})^2 - (N - X_{e_{ij}}) + X_{e_{ij}}^{\ 2} - X_{e_{ij}}]/(N^2 - N) \tag{8}$$

Combining eq 8 with eq 6 one finds the link between $\pi_{e_{ij}}$ and $W_{e_{ij}}$,

$$\pi_{e_{ij}} = 1 - [2/(N^2 - N)]W_{e_{ij}} \tag{9}$$

and the relationship between the P'/P index and the Wiener number of T immediately follows:

$$P'/P = (N - 1) - [2/(N^2 - N)]W \tag{10}$$

To calculate the P'/P index of a tree it is necessary and sufficient to have knowledge of the number of vertices and the value of W. The Wiener number of T can be computed in many ways.[18,23,27−36] If one selects the route[27]

$$W = \sum_{n=1}^{n \le N-1} n\,{}^{n}p \tag{11}$$

where ${}^{n}p$ is the number of paths of length n in T, then it is possible to find out the explicit formula for computing the Wiener number of T. We will show in the further text that one can derive the analytical expressions for ${}^{n}p$'s of T. The problem has been also considered by Kier, Hall et al. but from the aspect of graph reconstruction and only for paths up to length three.[37−39]

We have derived the explicit formulas for computing the number of paths of a given length in a tree with N vertices:

$${}^{1}p = N - 1 \tag{12}$$

$${}^{2}p = (1/2)\sum_i v_i^2 - (N - 1) \tag{13}$$

$${}^{3}p = \sum_{\substack{d(i,j)=1 \\ i<j}} v_i v_j - \sum_i v_i^2 + (N - 1) \tag{14}$$

$${}^{4}p = \sum_{\substack{d(i,j)=2 \\ i<j}} v_i v_j - 2 \sum_{\substack{d(i,j)=1 \\ i<j}} v_i v_j + (3/2)\sum_i v_i^2 - (N - 1) \tag{15}$$

$${}^{5}p = \sum_{\substack{d(i,j)=3 \\ i<j}} v_i v_j - 2 \sum_{\substack{d(i,j)=2 \\ i<j}} v_i v_j + 3 \sum_{\substack{d(i,j)=1 \\ i<j}} v_i v_j - 2\sum_i v_i^2 + (N - 1) \tag{16}$$

etc. where v_i is the valency of the vertex i, and $d(i,j) = 1, 2, 3, ...$ denotes that the distances between the vertices i and j are 1, 2, 3, ..., respectively. By noting that

$$\sum_{d(i,j)=0} v_i v_j = \sum_i v_i^2 \tag{17}$$

the general analytical expression for the number of paths of length n in T reads as follows:

$$^{n}p = \sum_{m=0}^{n-2+k} (-1)^{m+1}(n-m-1) \sum_{\substack{d(i,j)=m \\ i<j}} v_i v_j + (-1)^{n+1}\{[(n-1)/2] \sum_{d(i,j)=0} v_i v_j + (N-1)\} \tag{18}$$

The parameters k and l take the following values:

$$k = \begin{cases} 1 & \text{for } n = 1 \\ 0 & \text{for } n \geq 2 \end{cases} \tag{19}$$

and

$$l = \begin{cases} 1 & \text{for } n = \text{odd} \\ 0 & \text{for } n = \text{even} \end{cases} \tag{20}$$

A closer examination of eqs 12−16 reveals that for the number of paths of a given length, $n \geq 3$, the following recursion relation holds:

$$^{n}p = \sum_{\substack{d(i,j)=n-2 \\ i<j}} v_i v_j - 2(^{n-1}p) - {}^{n-2}p \tag{21}$$

where the initial conditions are given by eqs 12 and 13.

Combining eqs 10 and 11, with eq 18 one obtains the general formula for computing the P'/P index of T

$$P'/P = (\mathrm{N}-1) - [2/(N^2-N)] \sum_{n=1}^{n \leq N-1} n\{ \sum_{m=0}^{n-2+k} (-1)^{m+1}(n-m-1) \sum_{\substack{d(i,j)=m \\ i<j}} v_i v_j + (-1)^{n+1}[[(n-1)/2] \sum_{d(i,j)=0} v_i v_j + (N-1)]\} \tag{22}$$

where the parameters k and l take the values from eqs 19 and 20.

Chains. A special case of connected undirected acyclic graphs is the chain graph, L_N.[7] The relationship between P'/P and W for chains is rather simple and can be given only in terms of N. Since the Wiener number of L_N is given by[27]

$$W = (N^3 - N)/6 \tag{23}$$

the P'/P index for a chain is

$$P'/P = (2/3)(N-2); \quad N \geq 2 \tag{24}$$

Cycles. For a general connected undirected graph, what means a graph containing ring(s) as well, it is not possible to find out the explicit formula for the P'/P index. However, it is possible to derive the analytical expressions for P'/P in some special cases if ring(s) are present in G. For cycles (regular graphs of degree 2)[7] the formula is simple, and is given by

$$P'/P = N/2 \tag{25}$$

The relationship between P'/P and W for cycles depends on the parity of N. The expression for W reads as follows:[23,36]

$$W = \begin{cases} (N/2)^3 & \text{for } N = \text{even} \\ (N/8)(N^2-1) & \text{for } N = \text{odd} \end{cases} \tag{26}$$

Hence, the relationship between P'/P and W for cycles is given by

$$P'/P = \begin{cases} (4/N^2)W & \text{for } N = \text{even} \\ [4/(N^2-1)]W & \text{for } N = \text{odd} \end{cases} \tag{27}$$

CONCLUDING REMARKS

In this report we have shown that the novel P'/P index is functionally related to the Wiener number in simple classes of chemical graphs such as trees and cycles. It is also demonstrated that P'/P for these classes can be expressed simply in terms of the number of vertices and their valences.

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