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WIENER NUMBERS OF DENDRIMERS

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Abstract

A method for the calculation of the Wiener number (W) of trees is outlined, by means of which it is relatively easy to find general formulas for W of various classes of branched molecules. The method is applied to dendrimers, whose molecular graphs are highly branched trees.

Introduction

The study of dendritic molecules is a relatively new and rapidly expanding field of experimental chemistry. Dendrimers are extremely branched molecules, mainly synthesized from identical building blocks that contain branching sites. The synthesis proceeds in repeatable steps, each reaction cycle resulting in a new, larger generation of the respective dendrimer. The majority of the known dendrimers are organic molecules (for review see [1,2]); the first inorganic systems of this kind (whose branching points are ruthenium atoms) were recently reported [3].

Because of their peculiar and unprecedented structural features, dendritic molecules are an evident challenge for theoretical and mathematical chemists. (For some recent theoretical work on dendrimers see [4].) According to the opinion of the authors of the review [2], "*the properties of strongly branched molecules are largely unknown and await discovery*".

A variety of methods for the description and quantification of the branching of the molecular skeleton is known in chemical graph theory (for a recent survey see [5]). Among them the Wiener index (W) plays an outstanding role. This topological index was put forward as early as in 1947 [6] and in the meantime became one of the most thoroughly investigated, and most frequently employed descriptors of molecular branching [7-12]. Of the numerous applications of the Wiener numbers in the modeling of physico-chemical and pharmacological properties of organic molecules we mention the recent studies in which W was related to such diverse quantities as the rates of electroreduction of chlorobenzenes [13], cytostatic and antihistaminic activities of certain drugs [14] and the n-octanol/water partition coefficient [15]; W was also used for distinguishing between fullerene isomers [16] as well as in recent approaches towards the quantification of molecular similarity [17].

In this paper we present a method that enables a relatively easy computation of the Wiener numbers of dendrimers, and establish expressions for W of some highly branched molecular graphs.

The Wiener number or Wiener index is defined as follows [8]. Let G be the molecular graph (which necessarily is connected) and V its vertex set. Let d(u,v) denote the distance [18] between the vertices u and v, $u,v \in V$. Then the Wiener number is equal to the sum of the distances between all pairs of vertices of the respective graph:

$$W = W(G) = \frac{1}{2} \sum_{u,v \in V} d(u,v) \quad .$$

A useful identity for the Wiener number of trees

It is a well known result [19-22] that among all trees with n vertices, the path P_n has maximal Wiener index, i.e., for any n-vertex tree T_n,

$$W(P_n) \geq W(T_n) \quad . \tag{1}$$

Equality in (1) occurs only if $T_n = P_n$. Furthermore,

$$W(P_n) = \frac{1}{6}(n^3 - n) = \binom{n+1}{3} \quad . \tag{2}$$

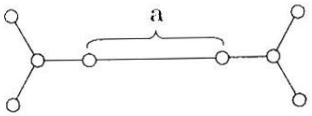
Every vertex of a tree, whose degree is greater than two, will be called a branching point of that tree. Consequently, P_n is the only n-vertex tree without branching points. In view of eq. (1), every branching point must have a decreasing effect on W. This effect was recently recognized [23] as being equal to the number of triplets of vertices that belong to different branches of the respective branching point. This observation led to the identity (3).

Let T be an n-vertex tree and u its branching point of dergee d(u), $d(u) \geq 3$. Let the branches attached to u have n_1, n_2, ..., $n_{d(u)}$ vertices, $n_1 + n_2 + \ldots + n_{d(u)} = n - 1$. Then,

$$W(T) = \binom{n+1}{3} - \sum_{u} \sum_{1 \leq i < j < k \leq d(u)} n_i \, n_j \, n_k \quad . \tag{3}$$

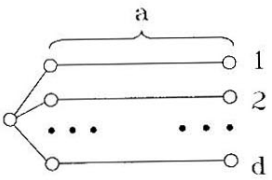
The first summation in (3) goes over all branching points of the tree T. The second summation embraces the $\binom{d(u)}{3}$ triple-products $n_i \, n_j \, n_k$.

As two elementary illustrations of formula (3) we compute the Wiener numbers of the trees T_1 and T_2, having two and one branching points, respectively.



T_1

$n = a + 6$



T_2

$n = da + 1$

In the case of T_1, the two branching points are symmetry-equivalent. For each of them, $n_1 = n_2 = 1$, $n_3 = a+3$. Because both branching points are of degree three, each of them is associated with only a single triple-product $n_i\, n_j\, n_k = 1 \times 1 \times (a+3) = a + 3$. Consequently,

$$W(T_1) = \binom{n+1}{3} - 2(a + 3).$$

In the case of T_2 , $n_i = a$ for all $i = 1,2,\ldots,d$. Therefore, all triple-products $n_i\, n_j\, n_k$ are equal to a^3 . Because the number of such triple-products is $\binom{d}{3}$, formula (3) results in:

$$W(T_2) = \binom{n+1}{3} - \binom{d}{3} a^3 .$$

For further details on the identity (3), including its proof, see [23].

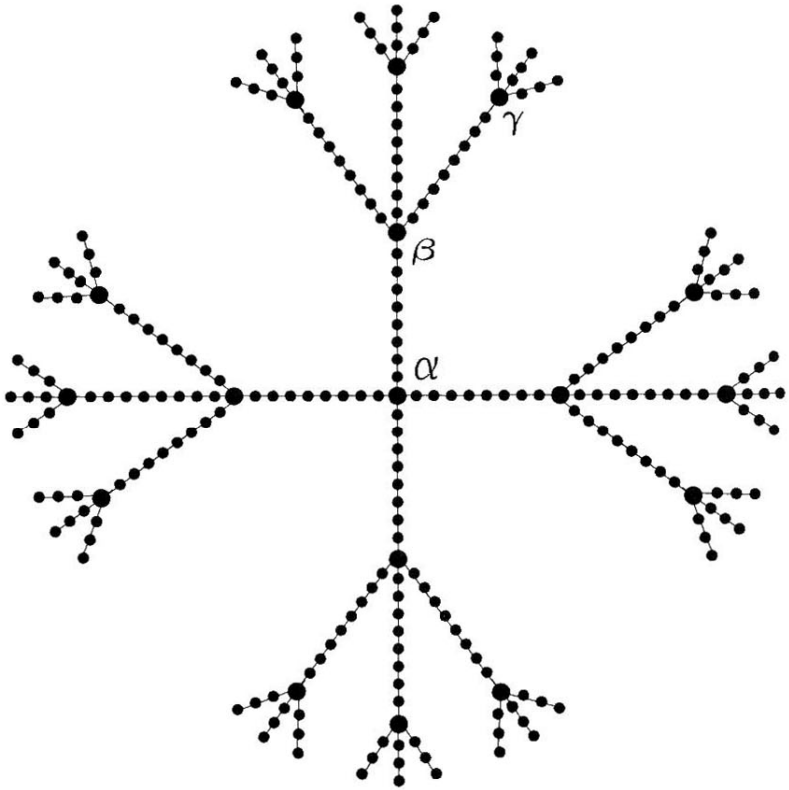
An example: The Wiener number of Newkome's arborol

Newkome and coworkers [24-27] synthesized a class of dendrimers which they called arborols. The arborol reported in [24] consists of a hydrocarbon skeleton, to the termini of which a total of $3 \times 3 \times 4 = 36$ OH groups are attached. In what follows we demonstrate the advantage of using formula (3) by calculating the Wiener number of the tree T_3 , shown in Fig. 1, that is just the graph of the carbon-atom skeleton of one of Newkome's arborols [24]. Observe that T_3 has $3 \times 3 \times 4 = 36$ vertices of degree one, and a total of 253 vertices.

In order to compute $W(T_3)$ we have to examine the branching points of T_3 . All branching points of T_3 are of degree four. They are of three types: α, β and γ (see Fig. 1). There is a single branching point of type α, four branching points of type β and $4 \times 3 = 12$ of type γ.

The branching point α has four identical branches, each with 63 vertices. Hence, it contributes to the right-hand side of (3) by $-\binom{4}{3} 63^3 = -1{,}000{,}188$.

A β-type branching point has three identical branches with 18 vertices each, and a branch with $253 - 3 \times 18 - 1 = 198$ vertices. Its contribution is thus equal to $-(18^3 + 3 \times 18^2 \times 198) = -198{,}288$.



T_3

Fig. 1. The molecular graph of Newkome's arborol

A γ-type branching point has three identical branches with 3 vertices each, and a branch with $253 - 3 \times 3 - 1 = 243$ vertices. Its contribution is equal to $-(3^3 + 3 \times 3^2 \times 243) = -6,588$.

According to formula (3), the Wiener number of T_3 is now equal to

$$W(T_3) = \binom{254}{3} - \left[1,000,188 + 4 \times 198,288 + 12 \times 6,588\right]$$

i.e.

$$W(T_3) = 826,608 \quad .$$

Some further highly branched molecular graphs and their Wiener numbers

In this section we determine the Wiener number of the highly branched trees $T_{k,d}$ which we call regular dendrimer graphs and for which $k \geq 0$ and $d \geq 3$. In particular, $T_{k,d}$ stands for the k-th regular dendrimer graph of degree d.

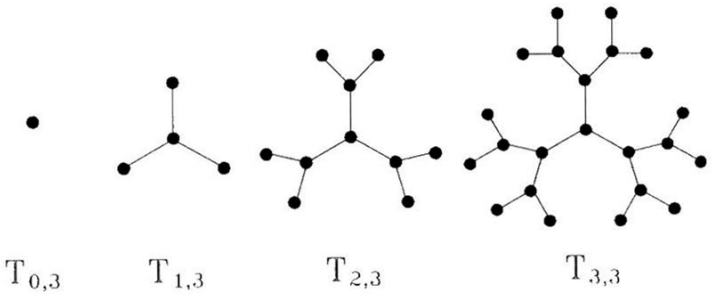
For any $d \geq 3$, $T_{0,d}$ is the one-vertex graph and $T_{1,d}$ is the star with d+1 vertices. Then for $k = 2,3,\ldots$ and $d \geq 3$, the tree $T_{k,d}$ is obtained by attaching d-1 new vertices of degree one to the vertices of degree one of $T_{k-1,d}$. Note that the parameter k corresponds to what in dendrimer chemistry is called "number of generations" [1,2].

For instance, in Fig. 2 are presented the first four regular dendrimer graphs of degrees three and four.

The number of vertices of the regular dendrimer graph $T_{k,d}$ is

$$n(T_{k,d}) = 1 + d + d(d-1) + d(d-1)^2 + \ldots + d(d-1)^{k-1}$$

$$= 1 + \frac{d}{d-2}\left[(d-1)^k - 1\right] \quad . \qquad (4)$$



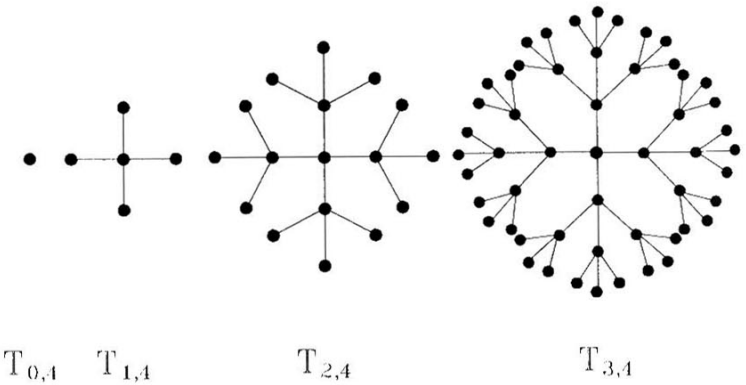
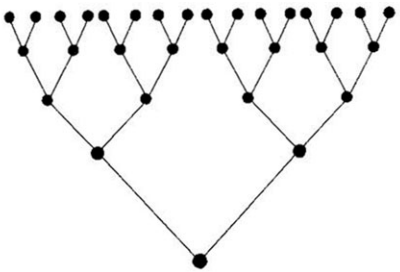


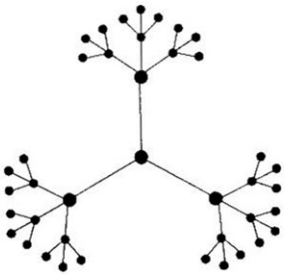
Fig. 2. Examples of regular dendrimer graphs

In order to compute $W(T_{k,d})$ it is convenient to introduce an auxiliary tree $B_{k,d}$, such that each of the d branches attached to the central vertex of $T_{k,d}$ is isomorphic to $B_{k-1,d}$. It is immediately seen that $B_{0,d}$ is the one-vertex graph whereas $B_{1,d}$ is the star with d vertices. Further, for k = 2,3,... and $d \geq 3$, the tree $B_{k,d}$ is obtained by attaching d-1 new vertices of degree one to the vertices of degree one of $B_{k-1,d}$. Observe that $B_{k,3}$, k = 1,2,..., are the well-known binary trees.

Two trees of the type $B_{k,d}$ are are given below:



$B_{4,3}$



$B_{3,4}$

Now, the number of vertices of $B_{k,d}$ is

$$n(B_{k,d}) = 1 + (d - 1) + (d - 1)^2 + \ldots + (d - 1)^k$$

$$= \frac{1}{d-2}\left[(d - 1)^{k+1} - 1\right] . \qquad (5)$$

Denote by u_0 the central vertex of $T_{k,d}$; u_0 is of degree d and is thus one of the branching points of $T_{k,d}$. From the construction of $T_{k,d}$ it is evident that the number of vertices that are at distance i from u_0 is equal to $d(d - 1)^{i-1}$, $i = 1,2,\ldots,k$. For $i = 1,\ldots,k-1$, all these vertices are branching points of $T_{k,d}$.

For the application of formula (3) it is crucial to observe that to each branching point u_i of $T_{k,d}$ that is at distance i from u_0 , $1 \le i \le k-1$, d branches are attached, d-1 of which are isomorphic to $B_{k-i-1,d}$. The number of vertices in each of these branches is $n(B_{k-i-1,d})$, cf. eq. (5). The remaining branch of u_i has n_i vertices, where

$$n_i = n(T_{k,d}) - (d - 1)\, n(B_{k-i-1,d}) - 1 \quad . \qquad (6)$$

The contribution of the branching point u_i to the right-hand side of (3) is thus

$$w_i = -\left[\binom{d-1}{3} n(B_{k-i-1,d})^3 + \binom{d-1}{2} n(B_{k-i-1,d})^2 \left[n(T_{k,d}) - n_i\right]\right] \quad . \qquad (7)$$

The analogous contribution of u_0 is simply

$$w_0 = -\left[\binom{d}{3} n(B_{k-1,d})^3\right] \quad . \qquad (8)$$

By applying formula (3) we obtain

$$W(T_{k,d}) = \binom{n(T_{k,d})-1}{3} + w_0 + \sum_{i=1}^{k-1} d(d - 1)^{i-1}\, w_i$$

which combined with eqs. (4)-(8) yields after a lengthy calculation

$$W(T_{k,d}) = \left[\left[kd^3 - 2(k+1)d^2 + d\right](d-1)^{2k} + 2d^2(d-1)^k - d\right](d-2)^{-3} \quad . \tag{9}$$

The chemically most interesting special cases of (9) are:

$$W(T_{k,3}) = (9k - 15)\, 2^{2k} + 18\, 2^k - 3$$

and

$$W(T_{k,4}) = (4k - \tfrac{7}{2})\, 3^{2k} + 4\, 3^k - \tfrac{1}{2} \quad .$$

For completeness we give here also the expression for the Wiener number of the auxiliary tree $B_{k,d}$:

$$W(B_{k,d}) = \left[\left[(k+2)d - 2(k+1)\right](d-1)^{k+1} + \left[kd - 2(k+1)\right](d-1)^{2k+2}\right](d-2)^{-3} \quad .$$

Its special case is the formula for the Wiener index of the binary trees:

$$W(B_{k,3}) = (k+4)\, 2^{k+1} + (k-2)\, 2^{2k+2} \quad .$$

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