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Note

Corroborating a Modification of the Wiener Index*

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In a recent work [*Chem. Phys. Lett.* **333** (2001) 319–321] Nikolić, Trinajstić, and Randić put forward a novel modification ${}^{m}W$ of the Wiener index. We now show that ${}^{m}W$ possesses the basic properties required by a topological index to be acceptable as a measure of the extent of branching of the carbon-atom skeleton of the respective molecule (and therefore to be a structure-descriptor, potentially applicable in QSPR and QSAR studies). In particular, if T_n is any n-vertex tree, different from the n-vertex path P_n and the n-vertex star S_n, then ${}^{m}W(\mathrm{P}_n) < {}^{m}W(\mathrm{T}_n) < {}^{m}W(\mathrm{S}_n)$. We also show how the concept of the modified Wiener index can be extended to weighted molecular graphs.

Key words: Wiener index, modified Wiener index, weighted modified Wiener index, branching, chemical graph theory.

INTRODUCTION

In connection with QSPR and QSAR studies, hundreds of molecular-structure-descriptors have been considered in the chemical literature.[1] Many of these are defined *via* the molecular graph[2,3] and are usually re-

* Dedicated to Professor Milan Randić on the occassion of his 70th birthday.

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ferred to as topological indiced, TIs.[2,4–7] The Wiener index W (= the sum of distances between all pairs of vertices of the molecular graph) is the oldest topological index.[8] Its applicability for predicting physico-chemical and pharmacologic properties of organic compounds is well documented and was outlined in quite a few reviews;[9–12] there is also a recent survey[13] on the mathematical research on W.

In the last 10–15 years a remarkably large number of modifications and extensions of the Wiener index was put forward and studied by mathematical chemists.[14–33] In the case of acyclic systems many of these modifications coincide with the original Wiener index[14–20] or are linearly related with it.[21–26] No surprise that numerous relations exist between these distance-based TIs.[34–38]

The »modified Wiener index« ${}^{m}W$, recently proposed by Nikolić, Trinajstić, and Randić,[33] has a few noteworthy properties, which distinguish it among the plethora of other TIs of the same kind:

(i) ${}^{m}W$ is not integer-valued (in contrast to practically all other Wiener-type indices);

(ii) ${}^{m}W$ is an additive function of edge-contributions;

(iii) the relative magnitude of these edge-contributions is in harmony with chemical intuition (in contrast to what is found in the case of the original Wiener index).

In this paper we add to this list also the following:

(iv) ${}^{m}W$ correctly reflects the extent of branching of the carbon-atom skeleton of an alkane;

(v) ${}^{m}W$ can in a natural manner be extended to weighted molecular graphs (representing chemical species different from hydrocarbons).

For trees, the modified Wiener index is defined as follows:[33]

$$ {}^{m}W = {}^{m}W(\mathrm{G}) = \sum_{e} \frac{1}{n_1(e) \cdot n_2(e)} \tag{1} $$

where $n_1(e)$ and $n_2(e)$ are the number of vertices lying on the two sides of the edge e, and the summation goes over all edges of the respective (acyclic) molecular graph. Recall that if this graph has n vertices, then $n_1(e) + n_2(e) = n$ and the number of edges is n–1. Formula (1) should be compared with relation (2):

$$ W = W(\mathrm{G}) = \sum_{e} n_1(e) \cdot n_2(e) \tag{2} $$

which was discovered already by Wiener[8] and which is applicable to all trees, but not to cycle-containing graphs.

Eq. (1) may be understood as a sum of increments, each associated with a particular edge of the molecular graph. Clearly, the contribution of the edge e, denoted by ${}^{m}W_e = {}^{m}W_e(\mathrm{G})$, is equal to $1/[n_1(e)n_2(e)]$.

The quantities $n_1(e)$ and $n_2(e)$ may be defined in a somewhat more formal manner:[18,35] Let G be an arbitrary graph and let its edge e connect the vertices u and v. Then $n_1(e)$ is the number of vertices of G whose distance to u is smaller than the distance to v. Similarly, $n_2(e)$ is the number of vertices of G whose distance to u is greater than the distance to v. If so, then the modified Wiener index, Eq. (1), is a well-defined quantity for all graphs G.

In the work[33] as well as in this paper the considerations will be restricted to trees.

There is no general agreement about what »branching« is and how the extent of branching of the carbon-atoms skeleton of an organic molecule can

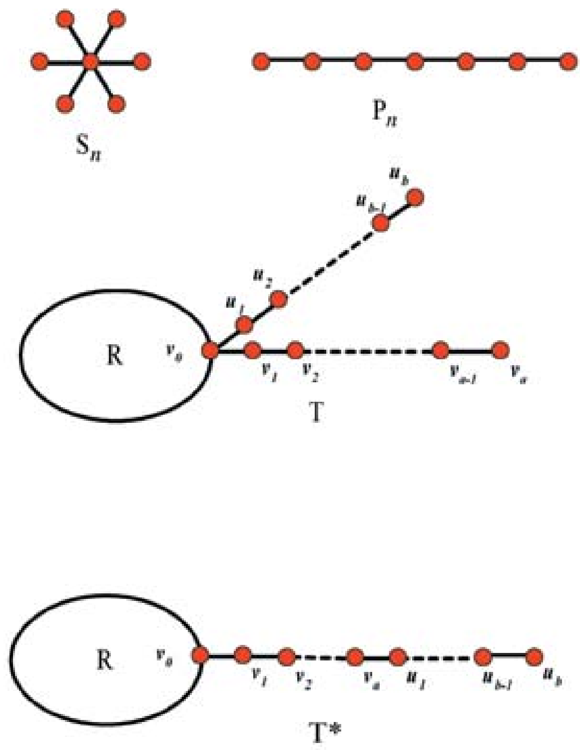

Figure 1. The trees encountered in Eqs. (3) and (4) and in Theorems 1 and 2. The star and path graphs depicted are S_9 and P_7.

be represented by some scalar quantity; more details on this matter can be found elsewhere.[39–42] Anyway, certain conditions that a measure of branching must obey are out of dispute.

First, in order that a topological index TI be acceptable as a measure of branching it must satisfy the inequalities

$$\mathrm{TI}(\mathrm{P}_n) < \mathrm{TI}(\mathrm{T}_n) < \mathrm{TI}(\mathrm{S}_n), \quad n = 5, 6, \ldots \tag{3}$$

where P_n and S_n are the n-vertex path graph and star, respectively (see Figure 1), and where T_n is any n-vertex tree, different from P_n and S_n. Indeed, among n-vertex trees P_n is the least branched and S_n the most branched species.

Second, if T and T* are graphs whose structure is depicted in Figure 1, then one requires that the inequality

$$\mathrm{TI}(\mathrm{T}^*) < \mathrm{TI}(\mathrm{T}) \tag{4}$$

holds irrespective of the actual form of the fragment R. This is because the vertex v_0 in T^* is more branched (has greater degree) than the vertex v_0 in T whereas the other structural details in T and T^* are the same.

Of course, if in Eqs. (3) and (4) all < signs are exchanged by >, then the respective TI is equally suitable to measure branching.

In what follows we show that Eqs. (3) and (4) are obeyed by ${}^mW$.

PROOF OF EQ. (3) FOR THE MODIFIED WIENER INDEX

Theorem 1. If T_n is an arbitrary tree on n vertices, different from P_n and S_n, then

$${}^mW(\mathrm{P}_n) < {}^mW(\mathrm{T}_n) < {}^mW(\mathrm{S}_n) \tag{5}$$

holds for all $n \geq 5$.

Proof. (a) The inequality ${}^mW(\mathrm{T}_n) < {}^mW(\mathrm{S}_n)$

Any n-vertex tree has $n-1$ edges and, consequently, there are $n-1$ summands on the right-hand side of Eq. (1). Each of these summands is of the form $1/[p(n-p)]$ for some $p = 1, 2, \ldots, \lfloor n/2 \rfloor$. Clearly, p is the number of vertices lying on one side of the respective edge.

Now, an elementary result from arithmetics reads:

$$1 \cdot (n-1) < 2 \cdot (n-2) < 3 \cdot (n-3) < \cdots < \left\lfloor \frac{n}{2} \right\rfloor \cdot \left\lceil \frac{n}{2} \right\rceil . \tag{6}$$

Bearing this in mind, we see that if there is a tree, such that $p = 1$ for all of its edges, then this tree will necessarily have maximal ${}^{m}W$-value. It is immediate to realize that the star is such a tree, and that no other tree has this property.

(b) The inequality ${}^{m}W(\mathrm{P}_n) < {}^{m}W(\mathrm{T}_n)$

Suppose that the relation (4) is obeyed by the modified Wiener index, *i.e.*, that ${}^{m}W(\mathrm{T}^*) < {}^{m}W(\mathrm{T})$ holds for all trees (*cf.* Figure 1). In any n-vertex tree T, except the path graph P_n, there is a branching vertex v_0 (a vertex whose degree is greater than two), to which (at least) two unbranched chains are attached. The transformation $\mathrm{T} \Rightarrow \mathrm{T}^*$ decreases the degree of vertex v_0 and decreases the number of unbranched chains attached to it. In the same time, it also diminishes the value of ${}^{m}W$. If $\mathrm{T}^* = \mathrm{P}_n$, then we are done. If $\mathrm{T}^* \neq \mathrm{P}_n$, then T^* must possess another branching vertex to which (at least) two unbranched chains are attached and the previous transformation may be repeated. By it the value of ${}^{m}W$ will further be diminished. Ultimately we arrive at the tree without branching vertices *i.e.*, at P_n, which therefore has the minimal value of the modified Wiener index.

Thus in order to complete the proof of the left-hand side inequality in Eq. (5), it remains to demonstrate that Eq. (4) holds for the modified Wiener index.

PROOF OF EQ. (4) FOR THE MODIFIED WIENER INDEX

Theorem 2. If T and T* are trees with equal number (n) of vertices, whose structure is shown in Figure 1, then for any $a > 0$ and $b > 0$, such that $a < n - a - b$, and for arbitrary R,

$$ {}^{m}W(\mathrm{T}^*) < {}^{m}W(\mathrm{T}). \tag{7}$$

In any tree T, different from P_n it is possible to find a vertex v_0 (*cf.* Figure 1), with properties required in the statement of Theorem 2.

Proof. Label the vertices of the trees T and T* as indicated in Figure 1. Consider the difference ${}^{m}W(\mathrm{T}^*) - {}^{m}W(\mathrm{T})$. Bearing in mind Eq. (1) and the structure of the trees T and T*, we see that the contributions of all edges will cancel out, except of the edges involving the vertices $v_0, v_1, v_2, \ldots, v_a$. Thus, if e_i is the edge connecting the vertices v_{i-1} and v_i, then

$$ {}^{m}W(\mathrm{T}^*) - {}^{m}W(\mathrm{T}) = \sum_{i=1}^{a} \left[{}^{m}W_{e_i}(\mathrm{T}^*) - {}^{m}W_{e_i}(\mathrm{T}) \right] . \tag{8}$$

Inspection of Figure 1 readily yields

$$^{m}W_{e_i}(\mathrm{T}^*) = \frac{1}{(a+b-i+1)(n-a-b+i-1)}$$

$$^{m}W_{e_i}(\mathrm{T}) = \frac{1}{(a-i+1)(n-a+i-1)} .$$

Now, if

$$(a - i + 1)(n - a + i - 1) < (a + b - i + 1)(n - a - b + i - 1) \tag{9}$$

holds for all values of $i = a, a - 1,..., 1$, then the relation (7) will follow from (8). For $i = a$, $i = a - 1,...,$ $i = 1$ relation (9) reduces to

$$1(n - 1) < (b + 1)(n - b - 1)$$

$$2(n - 2) < (b + 2)(n - b - 2)$$

$$\ldots\ldots$$

$$a(n - a) < (a + b)(n - a - b).$$

In view of Eq. (6), the first and second among the above inequalities are certainly obeyed. In order that all these inequalities be obeyed it is necessary that also the last one holds. This will happen if $a < n - a - b$, *i.e.*, if the branch which is moved in the transformation $\mathrm{T} \Rightarrow \mathrm{T}^*$ has fewer vertices than the fragment R.

Inequalities (9) are tantamount to

$$^{m}W_{e_i}(\mathrm{T}) > {}^{m}W_{e_i}(\mathrm{T}^*), \quad i = 1, 2, ..., a$$

which in view of (8) imply Eq. (7).

This completes the proofs of both Theorem 2 and Theorem 1.

WEIGHTED MODIFIED WIENER INDEX

A vertex-weighted graph G_w is a graph in which to every vertex v a positive real number $w(v)$ is assigned. Then the weighted modified Wiener index of such a weighted graph is defined as

$$^{m}\mathrm{W}(\mathrm{G}_w) = \sum_{e} \frac{1}{s_u(e) s_v(e)} \tag{10}$$

where e is an edge connecting the vertices u and v, $s_u(e)$ is the sum of weights of the vertices of G_w lying closer to u than to v, $s_v(e)$ is the sum of weights of the vertices of G_w lying closer to v than to u, and the summation goes over all edges of G_w.

The definition used here is clearly a generalization of the definition of the (non-weighted) modified Wiener index.[33] More precisely, if the weights of all vertices are equal to unity, then ${}^mW(G_w)$ coincides with the ordinary modified Wiener index.

Theorem 2 can now be generalized to vertex-weighted trees. For a set of vertices A let $w(A)$ be the sum of weights of all vertices from A.

Theorem 3. Let the trees T and T* be defined and labeled as before (see Figure 1). Let $A = \{v_1, v_2,\ldots,v_a\}$ and $B = \{u_1, u_2,\ldots u_b\}$ be the vertex sets of the two paths attached to the vertex v_0 and C the vertex set of the fragment R, formally $C = V(T) - A - B$. Then

$$ {}^mW(T_w^*) < {}^mW(T_w) \tag{11} $$

provided $w(A) < w(C)$.

Proof. Recall the labelling of the vertices of the trees T and T* as indicated in Figure 1. As in the proof of Theorem 2 consider the difference ${}^mW(T^*) - {}^mW(T)$. From Eq. (10) and the structure of the trees T and T*, we see that the contributions of all edges will cancel out, except of the edges e_i connecting the vertices v_{i-1} and v_i for $i = 1,2,\ldots,a$. Thus,

$$ {}^mW(T_w^*) - {}^mW(T_w) = \sum_{i=1}^{a}\left[{}^mW_{e_i}(T_w^*) - {}^mW_{e_i}(T_w)\right] . \tag{12} $$

Let the sum of weights of all vertices be

$$ S = \sum_{v\in V(T_w)} w(v) . $$

Clearly, for e_i in T_w we have (introducing the symbols Δ_i for brevity)

$$ s_{v_i}(e_i) = \sum_{j=i}^{a} w(v_j) = \Delta_i $$

$$ s_{v_{i-1}}(e_i) = S - s_{v_i}(e_i) = S - \Delta_i $$

while for edges e_i in T_w^*

$$ s_{v_i}^*(e_i) = \Delta_i + w(B) $$

$$ s_{v_{i-1}}^*(e_i) = S - \Delta_i - w(B). $$

The contribution of the edge e_i can now be written as

$$ {}^{m}W_{e_i}(\mathrm{T}_w^*) = \frac{1}{(\Delta_i + w(\mathrm{B}))(S - \Delta_i - w(\mathrm{B}))} $$

$$ {}^{m}W_{e_i}(\mathrm{T}_w) = \frac{1}{\Delta_i (S - \Delta_i)}. $$

Now, if

$$ \Delta_i (S - \Delta_i) < (\Delta_i + w(\mathrm{B}))(S - \Delta_i - w(\mathrm{B})) \tag{13} $$

holds for all values of $i = 1,2,...,a$, then the relation (11) will follow from (12). The values on the left and right sides of the inequality (13) can be seen as the values of the real function $f(x) = x(S - x)$. From elementary properties of the quadratic function f (*i.e.*, $x(S - x) < z(S - z)$ if and only if $x < z < S - x$), it follows that Eq. (13) is obeyed for all i provided $\Delta_i < \Delta_i + w(\mathrm{B}) < S - \Delta_i$. As $0 < \Delta_i \le w(\mathrm{A})$, a sufficient condition reads $w(\mathrm{A}) + w(\mathrm{B}) < S - w(\mathrm{A})$, or $w(\mathrm{B}) < S - w(\mathrm{A}) - w(\mathrm{B})$. Therefore, Eq. (11) holds if $w(\mathrm{B})$, the weight of the branch which is moved in the transformation $\mathrm{T}_w \Rightarrow \mathrm{T}_w^*$, is less than $w(\mathrm{C}) = S - w(\mathrm{A}) - w(\mathrm{B})$, the weight of the fragment R.

This concludes the proof of Theorem 3.

Remark. Extremal cases over all trees on a given set of n vertices with prescribed weights cannot always be obtained using only the transformation considered in this paper. It is not difficult to observe that among weighted stars S_n, the extremal species is the star in which the central vertex has the greatest weight. Among weighted paths the extremal value of ${}^{m}W(\mathrm{P}_w)$ is attained for P_w being the path with maximally weighted end-vertices. (More precisely, such a path can be constructed by ordering weights, and then putting the weights in this order as far from the center as possible.)

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SAŽETAK

Potvrda modifikacije Wienerova indeksa

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U nedavnom su članku (*Chem. Phys. Lett.* **333** (2001) 319–321) Nikolić, Trinajstić i Randić predložili novu modifikaciju, ^{m}W, Wienerova indeksa. U ovom je članku pokazano da ^{m}W posjeduje osnovna svojstva koja mora imati topologijski indeks da bi bio prihvatljiv kao mjera grananja ugljikova kostura pojedine molekule (pa da bi bio primjenjiv u QSPR i QSAR modeliranju). Ako je T_n bilo koje stablo s n čvorova, koje se razlikuje od staze P_n s n čvorova i zvijezde S_n s n čvorova, tada je $^{m}W(P_n) < {}^{m}W(T_n) < {}^{m}W(S_n)$. Također je pokazano da se koncepcija o modificiranom Wienerovu indeksu može proširiti na vagane molekulske grafove.