The Multiplicative Version of the Wiener Index

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The classical Wiener index, $W(G)$, is equal to the sum of the distances between all pairs of vertexes of a (molecular) graph, G. We now consider a related topological index, $\pi(G)$, equal to the product of distances between all pairs of vertexes of G. The basic properties of the π index are established and its possible physicochemical applications examined. In the case of alkanes, π and W are highly correlated; a slightly curvilinear correlation exists between ln π and W.

INTRODUCTION

Since 1947, when Harold Wiener conceived[1] the first molecular-graph-based structure descriptor, eventually named the "Wiener index", a plethora of so-called topological indexes have been put forward.[2] The Wiener index is usually defined in terms of the distances between vertexes of the molecular graph.[3,4] Let u and v be two vertexes of a (connected) graph G. Then the distance[5−7] between u and v is the number of edges in a shortest path whose endpoints are u and v. This quantity is denoted by $d(u,v)$ or $d(u,v|G)$. Clearly, $d(u,v)$ is a positive integer; if the vertexes u and v ($u \neq v$) are adjacent, then $d(u,v) = 1$; otherwise, $d(u,v)$ is greater than unity. The Wiener index is defined as[4]

$$W = W(G) = \sum_{u<v} d(u,v|G) \tag{1}$$

with the summation going over all pairs of vertexes of the molecular graph G. As explained below, it is purposeful to generalize eq 1 in the following manner:[8]

$$W_\lambda = W_\lambda(G) = \sum_{u<v} d(u,v|G)^\lambda \tag{2}$$

where λ is some parameter. Evidently, if $\lambda = +1$, then W_λ coincides with the ordinary Wiener index W.

The motivation for the generalization (2) is the following. Somewhat earlier than eq 2 was put forward,[8] the quantity W_λ for $\lambda = -2$ was introduced and named the "Harary index".[9] Eventually, W_λ for $\lambda = -1$ was also considered[10] and named the "reciprocal Wiener index". The quantity W_λ for $\lambda = +2$ is closely related to the hyper-Wiener index, WW; namely,[11] $WW = (W_2 + W_1)/2$. Another topological index, proposed by Tratch et al.,[12] is expressed in terms of W_3, W_2, and W_1 as[13] $(W_3 + 3W_2 + 2W_1)/6$. More connections of the same kind can be found in refs 13 and 14.

Bearing the above in mind, we may consider W_λ to be a unification of all the above-mentioned distance-based topological indexes and of the Wiener index in particular. Some general properties of W_λ have already been established.[8,15]

The parameter λ may assume any real value (i.e., it need not necessarily be an integer). However, if $\lambda = 0$, then, in a trivial manner, we obtain that for all (connected) graphs with n vertexes,

$$W_0 = \binom{n}{2} = n(n-1)/2$$

(Recall that in a graph with n vertexes, there are $n(n-1)/2$ vertex pairs.) In view of this, the new index W_λ was examined only in the case of $\lambda \neq 0$. We now show that it is profitable to examine the behavior of W_λ in the vicinity of $\lambda = 0$, i.e., in the case when λ has near-zero values. Then, somewhat surprisingly, W_λ is related to the product of distances.

PROPERTY OF W_Λ

As well-known from calculus, $e^x = 1 + x + x^2/2 + x^3/6 + ...$, implying that for near-zero values of x, as a good approximation,

$$e^x \approx 1 + x$$

Because, for any positive number a,

$$a^x = e^{x \ln a}$$

we get that for near-zero values of

$$d(u,v|G)^\lambda \approx 1 + \lambda \ln d(u,v|G)$$

substitution back into eq (2) readily yields

$$W_\lambda(G) \approx \sum_{u<v} [1 + \lambda \ln d(u,v|G)] = \binom{n}{2} + \lambda \sum_{u<v} \ln d(u,v|G)$$

i.e.,

$$W_\lambda(G) \approx \binom{n}{2} + \lambda \ln \prod_{u<v} d(u,v|G) \tag{3}$$

NOVEL DISTANCE-BASED TOPOLOGICAL INDEX

Formula 3 suggests a novel distance-based topological index, which in fact is the product-form version of the Wiener

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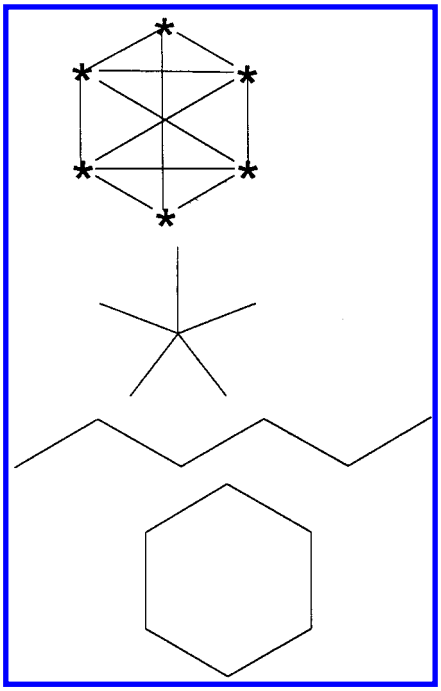

Figure 1. Some special graphs containing six vertexes: a complete graph (K_6), a star (S_6), a path (P_6), and a cycle (C_6). The vertexes of the complete graph have been marked.

index:

$$\pi = \pi(G) = \prod_{u<v} d(u,v|G) \qquad (4)$$

Notice the full formal analogy between eqs 1 and 4.

In our opinion, the π index is not just one more among the few dozen of distance-based structure descriptors.[4] In contrast to practically all currently used topological indexes,[16] π is a product-form topological index—a graph invariant obtained by multiplying the numerical characteristics of simple structural features.

The most remarkable difference between W and π is that vertex pairs at distance 1, i.e., adjacent vertexes, do not at all contribute to π (whereas their contribution to W is not negligible). Therefore, whereas the Wiener index consists of contributions coming from both short- and long-range interactions (although with long-range interactions dominating), in the case of the π-index, the effect of short-range interactions is completely disregarded.

EXAMPLES

1. Let K_n be the n-vertex complete graph (Figure 1). Any two vertexes of K_n are adjacent. Therefore, for all values of n, $\pi(K_n) = 1$. This simple result illustrates the earlier mentioned fact that the π index is insensitive to adjacent vertex pairs.

2. All vertex pairs in the star S_n (Figure 1) with n vertexes are at distance 1 or 2. There are $n - 1$ pairs of adjacent vertexes and, therefore, $n(n-1)2 - (n-1) = (n-1)(n-2)/2$ pairs at distance 2. Consequently,

$$\pi(S_n) = 2^{(n-1)(n-2)/2}$$

3. A proper generalization of the latter formula is

$$\pi(K_{a,b}) = 2^{a(a-1)/2+b(b-1)/2}$$

where $K_{a,b}$ denotes the complete bipartite graph with a vertexes in one class and b vertexes in the other class. Recall that $S_n = K_{1,n-1}$.

Recall that the factorial $n!$ is defined recursively as

$$1! = 1 \qquad 2! = 2 \qquad n! = n(n-1)!$$

for $n > 2$. In analogy to this, we now define the "double factorial" $n!!$ as

$$1!! = 1 \qquad 2!! = 2 \qquad n!! = n!(n-1)!!$$

for $n > 2$.

4. Let P_n be the n-vertex path (Figure 1). Then, $\pi(P_n) = (n-1)!!$.

5. Let C_n be the cycle with n vertexes. If n is odd, $n = 2k + 1$, $k = 1, 2, 3, ...$; then,

$$\pi(C_n) = (k!)^n$$

If n is even, $n = 2k$, $k = 2, 3, 4, ...$; then,

$$\pi(C_n) = k^k(k!)^n$$

SOME FUNDAMENTAL PROPERTIES OF THE π INDEX

A tree is a connected acyclic graph. Any tree with n vertexes possesses $n - 1$ edges, and this is the minimal number of edges in connected n-vertex graphs. Recall that the star S_n and the path P_n, mentioned in the preceding section, are n-vertex trees.

Theorem 1. Let T_n be any n-vertex tree, different from S_n and P_n. Then,

$$\pi(S_n) < \pi(T_n) < \pi(P_n)$$

The proof of theorem 1 is essentially the same as what earlier has been reported[17] for the analogous inequality involving the hyper-Wiener index and will therefore not be reproduced here.

Theorem 2. Let G_n be any connected n-vertex graph, different from K_n and P_n. Then,

$$\pi(K_n) < \pi(G_n) < \pi(P_n)$$

Proof. Because $\pi(K_n) < \pi(G_n)$ should be obvious, because whenever a graph has at least one vertex pair at a distance greater than unity, then, its π index is greater than unity. On the other hand, K_n is the only graph having no vertex pairs at a distance greater than unity.

Let G be a connected graph and e an edge of G. Let $G - e$ be the subgraph obtained by deleting the edge e from G but not deleting the end points of e. Assume that $G - e$ is also a connected graph. By deleting an edge from G (and keeping it connected), the distance between any two vertexes either remains the same or increases. Further, the distance between at least two vertexes (those which are the endpoints of the edge e) is strictly greater in $G - e$ than in G. Consequently, $\pi(G - e) > \pi(G)$.

Thus, by deleting edges from a connected graph so that it remains connected, the π index will necessarily increase. Thus, the n-vertex graph with maximal π index must be a

connected graph with a minimal number ($=n-1$) of edges, i.e., a tree. On the other hand, from theorem 1, we know that the tree with maximal π is the path.

Corollary 2.1. If G_n is a connected n-vertex graph, then,

$$1 \le \pi(G_n) \le (n-1)!!$$

Note that $(n-1)!!$, which in turn is just the π index of the n-vertex path P_n, is a very rapidly increasing function of n:

n	$\pi(P_n) = (n-1)!!$
2	1
3	2
4	12
5	288
6	34 560
7	24 883 200
8	125 411 328 000
9	5056 584 744 960 000

Therefore, in many practical applications of the π index, it is reasonable to use its logarithm.

Denote by $d(G,k)$ the number of vertex pairs of the graph G that are at distance k. Then,

$$\pi(G) = \prod_{k>1} k^{d(G,k)} \tag{5a}$$

i.e.,

$$\ln \pi(G) = \sum_{k>1} d(G,k) \ln k \tag{5b}$$

The polynomial

$$H(G,x) = \sum_{k\ge 0} d(G,k) x^k$$

is called the Hosoya polynomial (see ref 18 and the references quoted therein). Bearing in mind eq 5a or eq 5b, we see that the π index is fully determined by the Hosoya polynomial. (The reverse is not true, as shown in the subsequent section). In particular, whenever two graphs pertain to identical Hosoya polynomials, then also their π indexes coincide. It has been demonstrated[18] that molecular graphs with identical Hosoya polynomials are encountered quite frequently.

π INDEX OF ALKANES

To gain some numerical experience with the π index, we computed it for all alkanes C_nH_{2n+2} with n up to 10. We found the following:

(a) There exist isomeric alkanes with equal Wiener indexes but different π indexes. The smallest pairs of this kind are found at $n = 7$. There are two such pairs: 2,2-dimethylpentane ($W = 46$, $\pi = 1327\ 104$) and 2,3-dimethylpentane ($W = 46$, $\pi = 1492\ 992$), and 2,4-dimethylpentane ($W = 48$, $\pi = 2654\ 208$) and 3-ethylpentane ($W = 48$, $\pi = 2985\ 984$).

(b) There exist isomeric alkanes with equal π indexes but with different Wiener indexes. The smallest pair of this kind is found at $n = 9$ and is unique: 4-ethylheptane ($W = 102$, $\pi = 103\ 195\ 607\ 040\ 000$) and 2,2-dimethylheptane ($W = 104$, $\pi = 103\ 195\ 607\ 040\ 000$).

(c) There exist isomeric alkanes with equal π indexes and with equal Wiener indexes (and identical Hosoya polynomials). The smallest pair of this kind is found at $n = 9$ and is unique: 3-methyl-3-ethylhexane and 2,3,4-trimethylhexane ($W = 92$, $\pi = 6191\ 736\ 422\ 400$).

There are several examples of types b and c at $n = 10$, and evidently, their number rapidly increases with n, $n > 10$.

From what has been said above, one could expect that the topological indexes π and W have quite dissimilar structure dependencies. Whereas this may happen for some cycle-containing molecules, in the case of alkanes, a remarkably good correlation is found between π and W. This is illustrated in Figure 2.

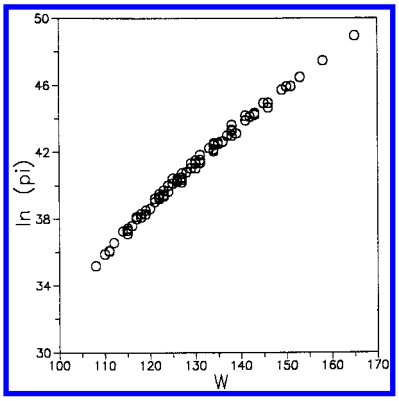

Figure 2. Logarithm of the π index of the 75 isomeric decanes, $C_{10}H_{22}$, plotted versus the respective W values; the correlation is slightly curvilinear; for details see text.

Table 1. Coefficients A, B, and C in eq 6 for the Isomeric Alkanes C_nH_{2n+2}[a]

n	A	B	C	R	R'
5	0.9060	6.569	0.014 72	1	0.9990
6	0.8048	8.416	0.007 60	0.9998	0.9985
7	0.6889	9.095	−0.003 98	0.9992	0.9973
8	0.6117	9.542	0.002 39	0.9991	0.9967
9	0.5481	8.653	0.001 46	0.9986	0.9967
10	0.5183	8.527	0.001 04	0.9983	0.9961

[a] R and R' are the correlation coefficients pertaining to eqs 6 and 7, respectively; since there are only three isomeric pentanes, the value of R for $n = 5$ is exactly 1.

In Table 1, some results of the statistical analysis are given. By means of the F-test, it was found that the quadratic regression

$$\ln \pi = AW + B + CW^2 \tag{6}$$

is significantly more accurate than the linear regression

$$\ln \pi = A'W + B' \tag{7}$$

where A, B, C, A', and B' are coefficients determined by least-squares fitting, separately for each set of isomers (for each n, $5 \le n \le 10$). For $n = 6$ and 7, the improvement of the accuracy of (6) relative to (7) is significant at the 95% (but not at the 99%) confidence level, whereas for $n > 7$ the improvement is significant at the 99% confidence level. Thus, in the case of alkanes, the correlation between $\ln \pi$ and W possesses a slight, but statistically significant, curvilinearity.

PHYSICOCHEMICAL APPLICATION: OCTANE NUMBERS

The aim of this work was not to elaborate QSPR and QSAR applications of the π index but to point out that π is

Table 2. Heptanes and Octanes: Octane Numbers and Values of the π Index

molecule	ln π	res octane no.[20]
n-C7	17.0297	0
2-Me-C6	15.9311	42.5
3-Me-C6	15.4203	52.0
2,2-Me_2-C5	14.0985	93.0
2,3-Me_2-C5	14.2163	91.1
2,4-Me_2-C5	14.7917	83.1
3,3-Me_2-C5	13.5231	80.8
2,2,3-Me_3-C4	12.8300	112.0
n-C8	25.5549	−19.0
2-Me-C7	24.3021	21.7
3-Me-C7	23.6090	26.8
2,2-Me_2-C6	22.1049	72.5
2,3-Me_2-C6	21.9995	71.3
2,4-Me_2-C6	22.2872	65.0
2,5-Me_2-C6	23.0212	55.0
3,4-Me_2-C6	21.4887	76.3
3-Et-2-Me-C5	21.2655	87.3
3-Et-C6	22.6927	33.5
2,2,3-Me_3-C5	19.8793	109.5
2,2,4-Me_3-C5	20.7423	100.0
2,3,3-Me_3-C5	19.5916	106.0
2,3,4-Me_3-C5	20.5724	102.5

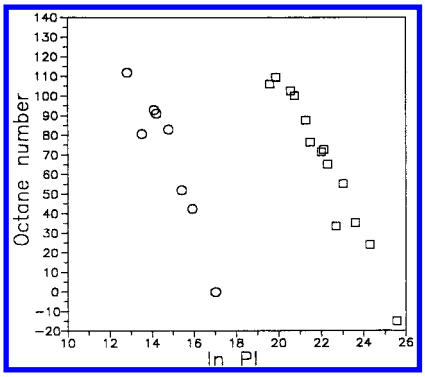

Figure 3. In π versus octane numbers of heptanes (○) and octanes (□) (octane number of heptanes $= -25.02\pi + 437.91$, $r = -0.949$; octane number of octanes $= -21.8\pi + 547.46$, $r = -0.975$).

a member of the W_λ family of topological indexes, eq 3. Nevertheless, we conclude our paper with an example, indicating that π has potential chemical applications.

Octane numbers[19] are related to the ability of alkanes to form radicals by cracking at high pressures and temperatures. The actual data were collected from the literature;[20] we consider here data pertaining to the "research octane number" only. The heptane and octane isomers along with their respective ln π and octane numbers are listed in Table 2. The correlation between these parameters is shown in Figure 3. The correlation coefficient between the octane numbers related to heptanes and the corresponding values of ln π was equal to $r = -0.949$, while the correlation related to the octanes was equal to $r = -0.975$. Both correlations are significant at the 99% confidence level. With increasing values of ln π, octane numbers decrease, meaning that decreasing compactness is favorable. Similar results were reported by Balaban et al.[21,22]

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