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On the Multiplicative *Wiener* Index and Its Possible Chemical Applications

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Summary. The recently introduced multiplicative *Wiener* index π is a molecular structure descriptor equal to the product of the distances between all pairs of vertices of the underlying molecular graph. It was expected that π has a different structure dependency than the ordinary *Wiener* index W which is equal to the sum of vertex distances. We now show that this is not the case: for a variety of classes of isomeric alkanes, monocycloalkanes, bicycloalkanes, benzenoid hydrocarbons, and phenylenes a very good (either linear or slightly curvilinear) correlation between π and W is found. For homologous series, the relation between π and W happens to be somewhat less simple. For alkanes, $\ln\pi \sim CW^{2/3}$ approaches asymptotically $\ln W$, with C being a constant depending on the particular homologous series considered.

Keywords. Topological index; *Wiener* index; Multiplicative *Wiener* index; Chemical graph theory.

Introduction

One of the main directions of research in contemporary chemical graph theory [1] is the design and application of so-called topological indices – numerical structure descriptors that can be calculated from the molecular graph [1–3]. Of the almost countless topological indices put forward in the chemical literature, only a few found noteworthy chemical, physio-chemical, and/or pharmacologic applications (for a review, see Refs. [3–9]. The first such structure descriptor was invented in 1947 by *Harold Wiener* [10] and is nowadays called the *Wiener* index; it is still extensively used in quantitative structure-property and structure-activity studies (for some recent applications, see Refs. [11–14]. The *Wiener* index is defined as

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

where $d(u, v|G)$ denotes the distance of the vertices u and v in the molecular graph G and the summation embraces all pairs of vertices of G [1, 2]. Recall that if the vertices u and v are adjacent, $d(u, v|G) = 1$, whereas otherwise $d(u, v|G) > 1$.

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Recall also that if n is the number of vertices of the graph G, there are $\binom{n}{2} = \frac{1}{2}n(n-1)$ vertex pairs and, consequently, $\binom{n}{2}$ summands in Eq. (1).

In a recent work [15] the multiplicative version of the *Wiener* index was conceived:

$$\pi = \pi(G) = \prod_{u<v} d(u, v|G). \tag{2}$$

The mathematical arguments leading to Eq. (2) have been outlined in due detail in Ref. [15] and will not be repeated here. What deserves to be emphasized is the following.

In analogy to Eq. (1), the product on the right-hand side of Eq. (2) has $\binom{n}{2}$ factors. However, unit factors have no effect on the value of this product and may be disregarded. This, in turn, means that adjacent vertex pairs (which in the case of W have a non-negligible contribution) have no effect on the value of the π-index. In other words, in contrast to the *Wiener* index, the π-index reflects only long-distance structural features of a molecule. In view of this it may be expected that π and W depend on the structure of the underlying molecule in somewhat different manner.

In Ref. [15] it was shown that, surprisingly, in the case of alkanes there exists a very good correlation between π and W. The question whether this is also the case for cyclic molecules required further studies, the results of which are communicated in the subsequent action.

Results and Discussion

The π-index of isomeric cyclic molecules and its relation to the Wiener index

In order to envisage the regularities governing the structure dependency of the π-index of molecules containing cyclic moieties we computed if for several classes of isomeric molecules (for details, see Table 1). Based on these calculations we established the following.

Two molecules, possessing different carbon skeletons, usually have different values for π and W. However, it was found that there exist pairs of (structurally distinct) alkane isomers whose π-values or W-values or both are equal [15]. We can now extend these observations:

(*a*) There exist isomeric monocycloalkanes and bicycloalkanes with equal W- and π-indices. The smallest such pairs seem to be cyclopentane and 1,1-dimethylcyclopropane $(W = 15, \pi = 32)$ as well as bicyclo[1.1.1]pentane and spiropentane $(W = 14, \pi = 15)$.

(*b*) There exist isomeric monocycloalkanes and bicycloalkanes with equal *Wiener*- but different π-indices. The smallest such pairs seem to be 1,3-dimethylcyclobutane $(W = 28, \pi = 2304)$ and isopropyl-cyclopropane $(W = 28, \pi = 2592)$ as well as 1,3-dimethylbicyclo[1.1.1]pentane $(W = 38, \pi = 36864)$ and [3.1.1]bicycloheptane $(W = 38, \pi = 41472)$.

(*c*) Curiously, however, among almost one thousand cyclic molecules examined, we did not find a single pair with equal π-but different W-index. Finding of such a pair remains a challenge for scholars interested in computer-aided combinatorical searches. What we can claim already at this stage is that in the

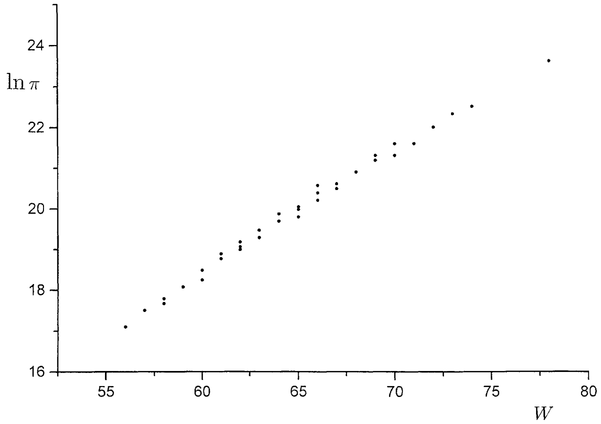

Fig. 1. A characteristic example: correlation between $\ln\pi$ and W in the case of monocycloalkanes C_8H_{16}; for this particular correlation a slight curvilinearity could be established; for details, see Table 1

case of cyclic molecules the isomer discriminating power of the π-index is superior to that of the *Wiener* index, a feature which usally is considered as an advantage [16].

The number of isomeric pairs of type (*a*) and (*b*) rapidly increases with increasing number of carbon atoms.

Within sets of isomeric molecules we have examined the correlation between $\ln\pi$ and W. Since this correlation is evidently not far from linear (see Fig. 1), we considered the linear model

$$\ln\pi \approx A_1 + B_1 W \tag{3}$$

and compared it with the simplest possible curvilinear model

$$\ln\pi \approx A_2 + B_2 W + C_2 W^2 \tag{4}$$

By means of an F-test (99% confidence level) we checked whether the curvilinearity of the correlation is statistically significant. The results obtained are given in Table 1. For the sake of completeness we included in Table 1 also the results for alkanes [15].

From the data given in Table 1 we may safely conclude that for all types of carbon-atom skeletons the ordinary and the multiplicative *Wiener* indices are highly correlated quantitites, thus being of nearly equal practical value for applications in quantitative structure-property and structure-activity studies. Furthermore, the correlation between $\ln\pi$ and W of cyclic molecules is essentially linear, with a slight curvilinearity observed in a few cases.

In the first paper by *Wiener* [10], the topological index W was used to calculate the boiling points of alkanes. Eventually, numerous other applications of W have been reported, pertaining to a variety of physio-chemical properties such as molar volumes, refractive indices, heats of vaporization, chromatographic retention times, molecular surface areas, and intermolecular forces, to mention just a few. Several studies in which W was used for predicting pharmacologic activities of different classes of compounds have appeared in the literature, for instance [11–13]. In

Table 1. Sets of hydrocarbons studied and the quality of the models Eq. (3) and (4); numerical values for the coefficients A_1, B_1, A_2, B_2, C_2 in Eqs. (3) and (4), obtained by least-squares fitting, are available upon request from *Ž. T.*; the results for alkanes were previously communicated [15]; mono- and bicycloalkanes are those examined in Ref. [17]; the catacondensed benzenoid hydrocarbons and [6]phenylenes are chosen by random among all possible isomers [18, 19]; the *F*-test is positive (+) if there is a statistically significant (at 99% confidence level) increase of accuracy of Eq. (4) relative to Eq. (3), implying that the correlation between lnπ and *W* is curvilinear; otherwise, the *F*-test is negative (−), implying linear correlation

Class of isomers	Formula	No. of cycles	Sample size	Correl. Coeff. Eq. (3)	Correl. coeff. Eq. (4)	*F*-test
Alkanes	C_5H_{12}	0	3	0.9990	1.0000	
Alkanes	C_6H_{14}	0	5	0.9985	0.9998	−
Alkanes	C_7H_{16}	0	9	0.9973	0.9992	−
Alkanes	C_8H_{18}	0	18	0.9967	0.9991	+
Alkanes	C_9H_{20}	0	35	0.9967	0.9986	+
Alkanes	$C_{10}H_{22}$	0	75	0.9961	0.9983	+
Monocycloalkanes	C_5H_{10}	1	4	1.0000	1.0000	
Monocycloalkanes	C_6H_{12}	1	13	0.9983	0.9988	−
Monocycloalkanes	C_7H_{14}	1	31	0.9975	0.9985	−
Monocycloalkanes	C_8H_{16}	1	73	0.9968	0.9982	+
Bicycloalkanes	C_5H_8	2	5	1.0000	1.0000	
Bicycloalkanes	C_6H_{10}	2	17	0.9984	0.9990	−
Bicycloalkanes	C_7H_{12}	2	57	0.9979	0.9986	−
Bicycloalkanes	C_8H_{14}	2	178	0.9968	0.9986	+
Benzenoids	$C_{26}H_{16}$	6	36	0.9937	0.9940	−
Benzenoids	$C_{38}H_{22}$	9	29	0.9984	0.9986	−
Phenylenes	$C_{36}H_{16}$	11	36	0.9987	0.9990	−

practically all cases, the physico-chemical or pharmacologic properties were modeled as linear functions of the parameter *W*. The best results were achieved by employing models consisting of linear combinations of *W* and other structure descriptors [5, 7, 9, 10].

Now, in view of the very good (linear) correlation established between *W* and the logarithm of the π-index, it is clear that the π-index could be used in the precisely same quantitative structure-property and structure-activity studies, with basically equal success. The above conclusions apply for classes of isomers (in which the number of carbon atoms is constant). In series of molecules with variable number of carbon atoms the situation is significantly different. This issue is considered in the subsequent section.

The π-index of homologous series and its relation to the Wiener index

The lnπ and *W* values of members of homologous series are also correlated, but this correlation is evidently non-linear. Two important (extremal) examples are depicted in Fig. 2.

We first focus our attention to normal alkanes $CH_3(CH_2)_{n-2}CH_3$ whose molecular graph [1, 2] is the path graph P_n, see Fig. 3.

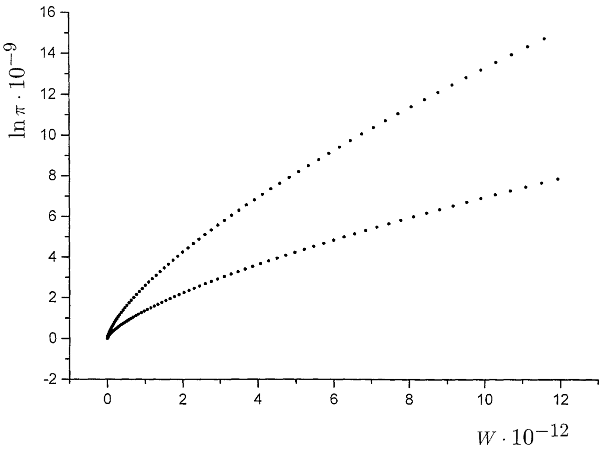

Fig. 2. The $\ln\pi$-values of two homologous series (P_n and R_n, see Fig. 3) plotted *versus* the respective W-values; upper curve: R_n, lower curve: P_n; the curves of all other homologous series of alkanes fall between these two extremes

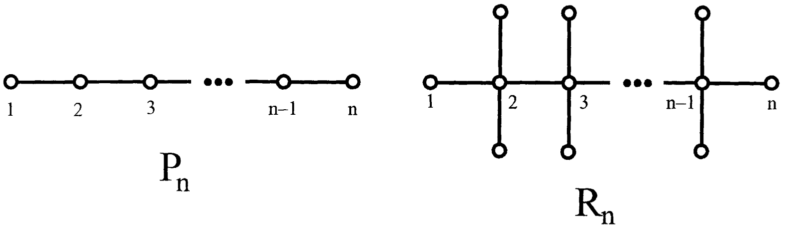

Fig. 3. The molecular graphs of the normal alkanes (P_n) and of a class of highly branched alkanes (R_n); these graphs have n and $3n - 4$ vertices, respectively

It is well known that

$$W(P_n) = \binom{n+1}{3} = \frac{n^3 - n}{6} \tag{5}$$

and it has been shown in Ref. [15] that

$$\pi(P_n) = \prod_{k=1}^{n-1} k!. \tag{6}$$

If $f_1(x)$ and $f_2(x)$ are two functions, and if

$$\lim_{x\to\infty} \frac{f_1(x)}{f_2(x)} = 1,$$

then we say that for $x \to \infty$ the functions $f_1(x)$ and $f_2(x)$ are asymptotically equal and denote this by $f_1(x) \sim f_2(x)$.

Suppose that the parameter n is sufficiently large and let us examine the asymptotic behaviour of $W(P_n)$ and $\ln\pi(P_n)$. From Eq. (5) immediately follows that $W(P_n) \sim n^3/6$, i.e.

$$n \sim \sqrt[3]{6W(P_n)}. \tag{7}$$

For the asymptotic behavior of the π-index, from Eq. (6) we get

$$\begin{aligned}\ln\pi(P_n) &= \sum_{k=1}^{n-1}\ln k! \sim \sum_{k=1}^{n-1}(k\ln k - k) \sim \sum_{k=1}^{n}(k\ln k - k)\\ &\sim \int_1^n (x\ln x - x)\mathrm{d}x = \frac{1}{2}x^2\ln x - \frac{3}{4}x^2\Big|_1^n \sim \frac{1}{2}n^2\ln n - \frac{3}{4}n^2\end{aligned}$$

which finally results in

$$\ln\pi(P_n) \sim \frac{1}{2}n^2\ln n. \tag{8}$$

Substituting Eq. (7) back into Eq. (8) we arrive at

$$\ln\pi(P_n) \sim \frac{1}{\sqrt[3]{6}}W(P_n)^{2/3}\ln W(P_n) \tag{9}$$

which reproduces the lower curve in Fig. 2 for large values of n. Recall that $1/^3\sqrt{6} \approx 0.55032$.

The molecular graph R_n (see Fig. 3) corresponds to the highly branched alkanes $CH_3(C(CH_3)_2)_{n-2}CH_3$. The analysis of their π-indices is much simplified by the identity

$$\pi(R_n) = 2^{-3(n-2)}(\pi(P_n))^9$$

which combined with Eq. (9) readily yields

$$\ln\pi(R_n) \sim \frac{9}{2}n^2\ln n. \tag{10}$$

Since, in addition [20],

$$W(R_n) = \frac{3}{2}n^3 - \frac{27}{2}n + 16 \sim \frac{3}{2}n^3,$$

we obtain

$$n \sim \sqrt[3]{2W(R_n)/3}. \tag{11}$$

From Eqs. (10) and (11) we obtain

$$\ln\pi(R_n) \sim \sqrt[3]{3/2W(R_n)^{2/3}}\ln W(R_n) \tag{12}$$

which reproduces the upper curve in Fig. 2 for large values of n. Recall that $\sqrt[3]{3/2} \approx 1.14471$.

Both Eq. (9) and (12) have the same mathematical form (Eq. 13)) and differ only in the value of the constant C. Because P_n and R_n are two extremal cases a completely unbranched and a maximally branched system, we conclude that Eq. (13) holds for other homologous series as well (at least for alkanes, but most probably also for systems containing cyclic elements).

$$\ln\pi = CW^{2/3}\ln W \tag{13}$$

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