CROATICA CHEMICA ACTA CCACAA **68** (1) 105–129 (1995)

ISSN 0011-1643
CCA–2216

Author's Review

The Wiener Index: Development and Applications[*]

Sonja Nikolić[**] *and Nenad Trinajstić*

The Rugjer Bošković Institute, P.O.B. 1016, HR-41001 Zagreb, Croatia

and

Zlatko Mihalić

Faculty of Science, The University of Zagreb, HR-41001 Zagreb, Croatia

Received June 26, 1994; revised October 6, 1994; accepted October 10, 1994

> »The structure of a molecule is completely defined by the number and kind of atoms and the linkages between them«.
>
> Ernest L. Eliel (1962)[1]

The definitions and methods of computing the Wiener index are reviewed. It is pointed out that the Wiener index is a useful topological index in the structure-property relationship because it is a measure of the compactness of a molecule in terms of its structural chracteristics, such as branching and cyclicity. A comparative study between the Wiener index and several of the commonly used topological indices in the structure-boiling point relationship revealed that the Wiener index is, in this case, rather inferior to most indices, a result that has been observed by other authors as well. New developments, such as an extension of the Wiener index to its three-dimensional version are also mentioned.

INTRODUCTION

The Wiener index (often also called the Wiener number) W is the first topological (graph-theoretical) index to be used in chemistry.[2–4] It was introduced in 1947 by Harold Wiener* as the path number.[5] The path number was introduced for alkanes

---

[*] Reported in part at MATHC/CHEM/COMP 1994, an International Course and Conference on the Interfaces between Mathematics, Chemistry and Computer Science, Dubrovnik, Croatia: June 27 – July 1, 1994.

[**] Author to whom inquiries should be addressed.

and is equal to the number of the carbon-carbon bonds between all pairs of carbon atoms in an alkane. Wiener also introduced the second index, which he called the polarity number and which was denoted by the letter p. This number is equal to the count of carbon-atom pairs separated by three bonds. Although p is called the polarity number, it is really related to steric characteristics of an alkane.[6]

By using the structure-property relationship of the type shown below:[5]

$$\text{bp} = a\,W + b\,p + c \tag{1}$$

one obtains a reasonable prediction of boiling points (bp's) of alkanes. If one considers all alkanes from n-butane to decanes (methane, ethane and propane are not taken into account since for them p=0), then the statistical characteristics of Eq. (1) are: a = 0.6863 (± 0.0237), b = 4.766 (± 0.273), c = 24.94 (± 2.24), R = 0.975, s = 8.06 and F = 1367. A plot of the boiling point calculated by Eq. (1) against experimental boiling points of the alkanes considered is given in Figure 1.

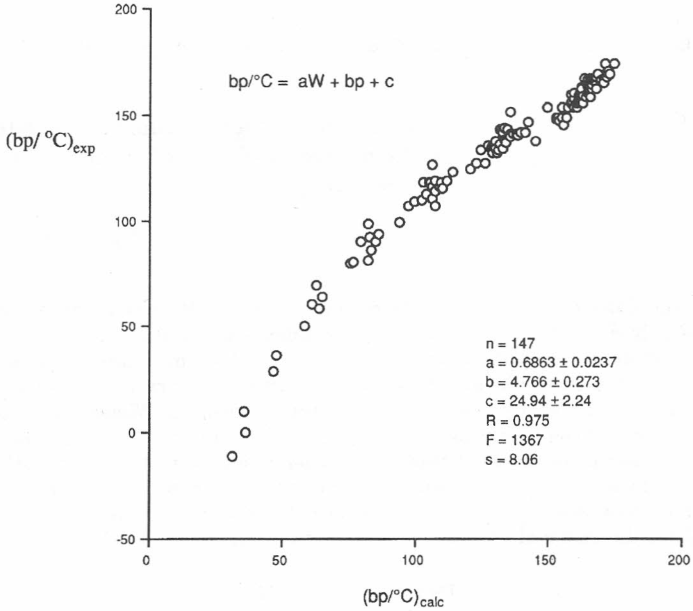


Figure 1. A plot of boiling points calculated by Eq. (1) against experimental boiling points of the lowest 147 alkanes. Methane, ethane and propane are not considered because in their case the polarity number is equal to zero.

---

* At that time Wiener was a chemistry student at Brooklyn College. After getting a degree in chemistry, he went on to medical school and left chemistry for good.

One can improve the above relationship by using:[7]

$$\mathrm{bp} = a\ W_r + b\ p + c \tag{2}$$

where

$$W_r = W/N^2\ . \tag{3}$$

In the above equation N is the number of carbon atoms in an alkane. The statistical characteristics of Eq. (2) for the lowest 147 alkanes are: $a = 117.51\ (\pm\ 1.77)$, $b = 7.061\ (\pm\ 0.108)$, $c = -64.62\ (\pm\ 2.01)$, $R = 0.995$, $s = 3.74$ and $F = 6606$. A plot of the boiling points calculated by Eq. (2) against experimental boiling points of the alkanes considered is given in Figure 2.

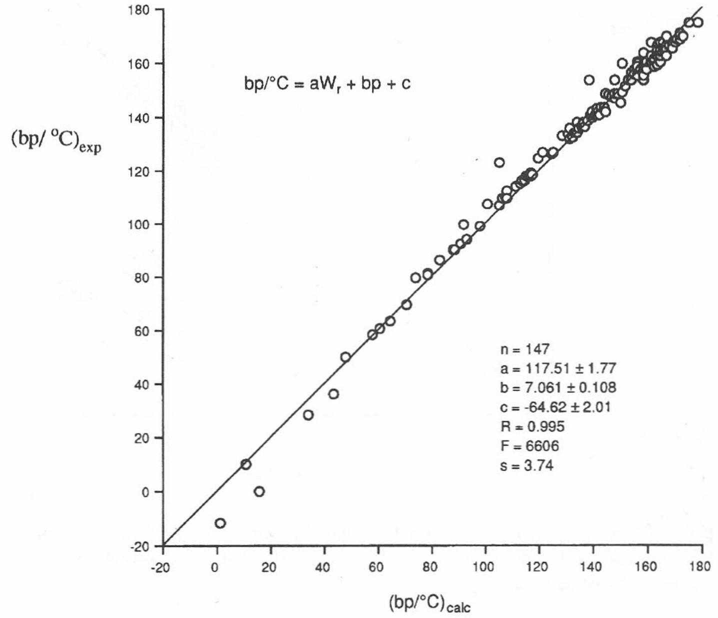


Figure 2. A plot of boiling points calculated by Eq. (2) against experimental boiling points of the lowest 147 alkanes. Methane, ethane and propane are not considered because in their case the polarity number is equal to zero.

In fact, in his initial work Wiener used the differences Δbp, ΔW_r, and Δp, respectively, between the boiling points, the path numbers and polarity numbers of linear alkanes and their branched isomers, that is, $\Delta \mathrm{bp} = (\mathrm{bp})_l - (\mathrm{bp})_b$, $\Delta W_r = (W_r)_l - (W_r)_b$ and $\Delta p = p_l - p_b$, where l denotes the linear and b the branched isomer. In this case, Eq. (2) becomes:

$$\Delta \mathrm{bp} = a\Delta W_{\mathrm{r}} + b\Delta \mathrm{p}\ . \tag{4}$$

The statistical characteristics of this relationship are: a = 86.87 (± 2.66), b = 5.420 (± 0.167), c = –1.799 (± 0.506), R = 0.943, s = 2.30 and F = 573. A plot of boiling points calculated by Eq. (4) against experimental boiling points of the alkanes considered is given in Figure 3. We note here that Eq. (4) gives the smallest value for the standard deviation although its correlation coefficient is the poorest of the three models tested.

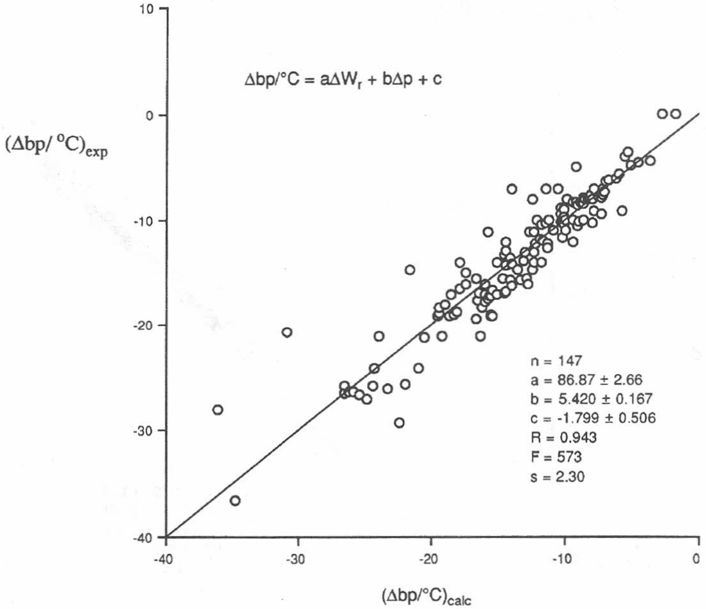


Figure 3. A plot of boiling points calculated by Eq. (4) against experimental boiling points of the lowest 147 alkanes. Methane, ethane and propane are not considered because in their case the polarity number is equal to zero.

In subsequent studies, Wiener has shown that Eq. (4) can also be used to predict other physical parameters of alkanes, such as heats of formation, heats of vaporization, molar volumes and molar refractions.[8–11]

Platt[6] was apparently the first to realize the significance of the Wiener approach and he tried to rationalize its origin. This is because one of Platt's interest was also the structure-property relationships for alkanes.[12] He also pointed out:[6] »The Wiener number (Platt was the first to use this term) is in fact a particular neighbor-sum (*J. Chem. Phys.* **15** (1947) 766),[9] but with the property that the coefficients of successive orders of neighbors, instead of approaching zero, increase linearly with increasing distance. This is another way of saying that it would correspond to long-range forces if it were an internal property.« After these initial efforts by Wiener and a little later by Platt, the Wiener index was hardly used or mentioned in the literature[13] until the revival of the interest in chemical applications of graph theory in the early seventies.[14] The advent of chemical graph theory stimulated, among many things, numerous studies on the Wiener index, its properties and the range of its applicability.[2–4,7,15–47]

We decided to prepare this report with the aim to review the important steps in the development of the Wiener index and to mention a few key applications of this index in the structure-property modelling. Let us also mention here that the structure-property model usually means the relationship between structure and property in a quantitative mathematical form suitable for further use.[48] Since the interest in the Wiener index and related topological indices is still very much present in the literature,[49–69] it has even been used to study the C_{76} fullerene isomers,[70] this report also appears to be timely. A novice will find that there a lot of work has been done on the formal theory and applications behind the simple term »the Wiener index or the Wiener number«. The most natural field for applications of the Wiener index is in the QSPR modelling. The acronym QSPR stands for the quantitative structure-property relationships.[21] Let us mention at this point that the Woodward rules[71] for the estimation of UV spectra of α,β-unsaturated ketones are a splendid example of an early structure-property scheme. There are also other fields of application,[44] but the contributions there are not so numerous as in the case of the QSPR research.

To simplify the presentation, we will use the graph-theoretical concepts and terminology throughout the article.[72] Molecules will be converted into hydrogen-depleted molecular graphs in the usual way.[24,40]

The article is structured as follows. In the next section, we give definitions of the Wiener index. The various methods for computing the Wiener index are reviewed in the third section. The fourth section contains a comparative study between the Wiener index and several commonly used topological indices in the structure-boiling point relationship. The selected new developments are briefly described in the fifth section. We end the article with our concluding remarks.

DEFINITIONS OF THE WIENER INDEX

Original definition of Wiener

In his first paper,[5] Wiener defined the path number W (which we now call the Wiener index or the Wiener number after him): »...as the sum of the distances between any two carbon atoms in the molecule, in terms of carbon-carbon bonds.«. Under the term »molecule« he meant »alkane«, because this definition is not valid in the case of (poly)cyclic systems. In the case of the latter molecules, one should use the term »shortest distances« in the above sentence.

Definition of Hosoya

Hosoya[14] was the first to define the Wiener index using the graph-theoretical approach. He pointed out that the Wiener index can be obtained from the distance matrix[40,73,74] of a molecular graph. The Wiener index $W = W(\mathrm{G})$ of a (molecular) graph G is defined as the half-sum of the elements of the distance matrix $\boldsymbol{D}$:

$$W = (1/2) \sum_{i=1}^{N} \sum_{j=1}^{N} (\boldsymbol{D})_{ij} \tag{5}$$

where $(\boldsymbol{D})_{ij}$ represents off-diagonal elements of $\boldsymbol{D}$.

The polarity number $p = p(\mathrm{G})$ of a (molecular) graph G is then given by:

$$p = (1/2) \sum_{i} (p_3)_i \tag{6}$$

where p_3 is the number of paths of length 3 or the number of off-diagonal elements of $\boldsymbol{D}$ with distance 3.

Definition based on the adjacency matrix

The Wiener index W of a (molecular) graph G can also be obtained from the adjacency matrix[40,73] of G. In this case, W is defined by means of the square of the adjacency matrix $\boldsymbol{A}$ of G:[75]

$$W = (1/2) \sum_{i=1}^{N} W_i \tag{7}$$

where

$$W_i = \sum_{l=1}^{l_{\max}} (\boldsymbol{A}_l^2)_{ii} \cdot l \ . \tag{8}$$

The matrix $\boldsymbol{A}_l$ is defined as:

$$(\boldsymbol{A}_l)_{ij} = \begin{cases} 1 & \text{if the vertx (atom) } v_j \text{ is the } l\text{–th neighbour of the vertex } v_i \\ 0 & \text{otherwise} \end{cases} \tag{9}$$

Note, that $l_{\max}$ in Eq. (8) is the length of the longest path in G.

Similarly, the polarity number p can also be defined in terms of the $\boldsymbol{A}_3$ matrix:

$$p = (1/2) \sum_{i=1}^{N} (\boldsymbol{A}_3^2)_{ii} \ . \tag{10}$$

Definition based on the adjacency matrix, the distance matrix and the degree row-matrix

In 1989, Schultz[76] introduced an index, named the molecular topological index MTI, for characterizing alkanes by an integer. This index was subsequently named the Schultz index.[40] The formal definition of the MTI was given by Müller *et al.*:[77]

$$\mathrm{MTI} = \sum_{i=1}^{N} e_i \tag{11}$$

where e_i ($i = 1,...N$) are the elements of the row ($1 \times N$) matrix:

$$e_i = \boldsymbol{v}(\boldsymbol{A} + \boldsymbol{D}) \tag{12}$$

where $\boldsymbol{v}$, $\boldsymbol{A}$ and $\boldsymbol{D}$ are, respectively, the degree row-matrix, the adjacency matrix and the distance matrix of an alkane tree.

The Wiener index can be given in terms of the MTI index as follows:[78,79]

$$W = [\mathrm{MTI} - 2p_2 + (N{-}1)(N{-}2]\,/4 \tag{13}$$

where p_2 is the number of paths of length 2 and N the number of vertices (atoms) in an alkane-tree. This formula is valid only for acyclic structures.

The Wiener index can also be expressed in terms of the MTI for [N]cycles depicting carbon skeletons of cycloalkanes or [N]annulenes. In this case, the formula connecting the Wiener index and the MTI index is rather simple:

$$W = (\mathrm{MTI}/4) - N\,. \tag{14}$$

Attempts to generalize the above formulae to include polycyclic structures and (poly)cyclic structures with branches have been unsuccessful so far.[80] However, it is worth noting that there is a strong correlation ($r = 0.996$) between the Wiener number and the MTI for 102 randomly selected (poly)cyclic graphs with branches. This indicates that a relationship between the Wiener number and the Schultz number may also exist for other classes of molecules, but perhaps not for an arbitrary case.

Definition based on the Laplacian eigenvalues

The Laplacian matrix $\boldsymbol{L} = \boldsymbol{L}(\mathrm{G})$ of a graph G is defined[81,82] as follows:

$$\boldsymbol{L} = \boldsymbol{V} - \boldsymbol{A} \tag{15}$$

where $\boldsymbol{A}$ is the adjacency matrix and $\boldsymbol{V}$ is the degree matrix, which is a diagonal matrix with entries:

$$(\boldsymbol{V})_{ii} = D(i) \tag{16}$$

The Laplacian matrix $\boldsymbol{L}$ is a real symmetric matrix. The diagonalization of the Laplacian matrix produces $\boldsymbol{N}$ real eigenvalues (called Laplacian eigenvalues): $0 = x_1 \le x_2 \le \ldots \le x_N$. The smallest Laplacian eigenvalue is always zero. This is the result of the special structure of the Laplacian matrix.

The Wiener index of a tree T can be defined in terms of its Laplacian eigenvalues:[81,83]

$$W = N \sum_{i=1}^{N} (1/x_i) \; . \tag{17}$$

METHODS FOR COMPUTING THE WIENER INDEX

Original method of Wiener

Wiener instructed the reader how to compute, in a simple way, the path number with the following words[5] »Multiply the number of carbon bonds on one side of any bond by those on the other side; W is the sum of these values for all bonds«. These words may be formalized as shown below. Let T be a tree (an alkane) with N vertices (atoms) and e one of its edges (bonds). Let also $N_1(e)$ and $N_2(e) = N - N_1(e)$ be the numbers of vertices of the two parts of T – e. Then:

$$W = \sum_{e} N_1(e)\, N_2(e) \tag{18}$$

where the summation is over all $N - 1$ edges of T. The use of formula (18) is illustrated in Figure 4.

Method based on the concept of branching vertices

This method is an extension of Wiener's method.[44] It is based on the concept of branching vertices in a tree. A branching vertex v_b is any vertex of a tree with the degree higher than two. If the numbers of vertices in the branches attached to v_b are denoted by $N_1, N_2, \ldots N_p$, then:

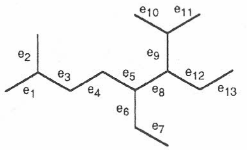
$$W = \binom{N+1}{3} - \sum_{v_\mathrm{b}} \sum_{i,j,k} N_i N_j N_k \; . \tag{19}$$

The first summation in Eq. (19) goes over all branched vertices v_b of a tree. This method is illustrated in Figure 5 also for a tree T representing 5-ethyl-6-isopropyl-2-methyloctane.

Method based on the distance matrix

This method was introduced by Hosoya[14] and it is illustrated in Figure 6 for the same tree that is used in Figures 4 and 5.

Unlike most of the others, this method is also applicable to polycyclic systems. In Figure 7, we also illustrate the use of the Hosoya method for a polycyclic case.



T

$$W = \sum_{e} N_1(e)N_2(e)$$

$N_1(e_1)N_2(e_2)$	1 × 13	13
$N_1(e_2)N_2(e_2)$	1 × 13	13
$N_1(e_3)N_2(e_3)$	3 × 11	33
$N_1(e_4)N_2(e_4)$	4 × 10	40
$N_1(e_5)N_2(e_5)$	5 × 9	45
$N_1(e_6)N_2(e_6)$	2 × 12	24
$N_1(e_7)N_2(e_7)$	1 × 13	13
$N_1(e_8)N_2(e_8)$	8 × 6	48
$N_1(e_9)N_2(e_9)$	3 × 11	33
$N_1(e_{10})N_2(e_{10})$	1 × 13	13
$N_1(e_{11})N_2(e_{11})$	1 × 13	13
$N_1(e_{12})N_2(e_{12})$	2 × 12	24
$N_1(e_{13})N_2(e_{13})$	1 × 13	13
		W = 325

Figure 4. Computation of the Wiener index for a tree T representing the carbon skeleton of 5-ethyl-6-isopropyl-2-methyloctane using Wiener's original method.

Method based on the adjacency matrix

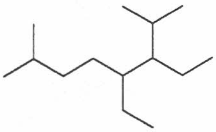
Unlike the one described above, this method is applicable to all kinds of acyclic and cyclic molecules. We will illustrate the method for a tree T representing the carbon skeleton of 2-methylbutane (see Figure 8).

Method based on the combination of the adjacency matrix, the distance matrix and the degree row-matrix

This is not as general a method as methods based on the distance matrix and the adjacency matrix, but is more general than the first two methods reported. It will be illustrated in Figure 9 and Figure 10, respectively, on the same tree as the methods shown in Figures 4–6 on a monocyclic graph with 11 vertices.

Method based on the Laplacian eigenvalues

This method is applicable only to acyclic structures. It will be illustrated in Figure 11 on the same branched tree as all the methods from above.

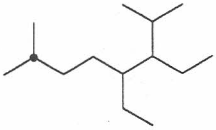


T

$$W = \binom{N+1}{3} - \sum_{v_b} \sum_{i,j,k} N_i N_j N_k$$

(i) $\binom{N+1}{3} = \binom{15}{3} = 455$

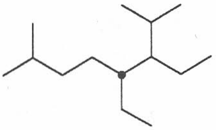
(ii)



$N_i = 1$; $N_j = 1$; $N_k = 11$

$N_i N_j N_k = 11$

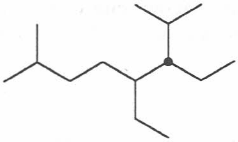
(iii)



$N_i = 5$; $N_j = 2$; $N_k = 6$

$N_i N_j N_k = 60$

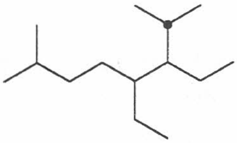
(iv)



$N_i = 8$; $N_j = 3$; $N_k = 2$

$N_i N_j N_k = 48$

(v)



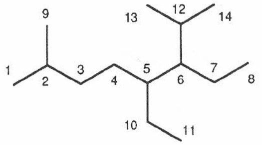
$N_i = 11$; $N_j = 1$; $N_k = 1$

$N_i N_j N_k = 11$

(vi)

$W = 455 - (11 + 60 + 48 + 11) = 325$

Figure 5. Computation of the Wiener index for the tree T from Figure 4 using the method based on excising the branching vertices from T.

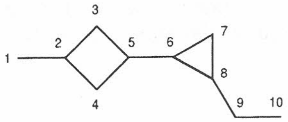


T

$$\mathbf{D} = \begin{bmatrix} 0 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 2 & 5 & 6 & 6 & 7 & 7 \\ 1 & 0 & 1 & 2 & 3 & 4 & 5 & 6 & 1 & 4 & 5 & 5 & 6 & 6 \\ 2 & 1 & 0 & 1 & 2 & 3 & 4 & 5 & 2 & 3 & 4 & 4 & 5 & 5 \\ 3 & 2 & 1 & 0 & 1 & 2 & 3 & 4 & 3 & 2 & 3 & 3 & 4 & 4 \\ 4 & 3 & 2 & 1 & 0 & 1 & 2 & 3 & 4 & 1 & 2 & 2 & 3 & 3 \\ 5 & 4 & 3 & 2 & 1 & 0 & 1 & 2 & 5 & 2 & 3 & 1 & 2 & 2 \\ 6 & 5 & 4 & 3 & 2 & 1 & 0 & 1 & 6 & 3 & 4 & 2 & 3 & 3 \\ 7 & 6 & 5 & 4 & 3 & 2 & 1 & 0 & 7 & 4 & 5 & 3 & 4 & 4 \\ 2 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 0 & 5 & 6 & 6 & 7 & 7 \\ 5 & 4 & 3 & 2 & 1 & 2 & 3 & 4 & 5 & 0 & 1 & 3 & 4 & 4 \\ 6 & 5 & 4 & 3 & 2 & 3 & 4 & 5 & 6 & 1 & 0 & 4 & 5 & 5 \\ 6 & 5 & 4 & 3 & 2 & 1 & 2 & 3 & 6 & 3 & 4 & 0 & 1 & 1 \\ 7 & 6 & 5 & 4 & 3 & 2 & 3 & 4 & 7 & 4 & 5 & 1 & 0 & 2 \\ 7 & 6 & 5 & 4 & 3 & 2 & 3 & 4 & 7 & 4 & 5 & 1 & 2 & 0 \end{bmatrix}$$

$W = 325$

Figure 6. Computation of the Wiener index for the tree T from Figure 4 using the method based on the distance matrix.

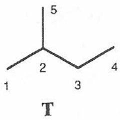


G

$$\mathbf{D} = \begin{bmatrix} 0 & 1 & 2 & 2 & 3 & 4 & 5 & 5 & 6 & 7 \\ 1 & 0 & 1 & 1 & 2 & 3 & 4 & 4 & 5 & 6 \\ 2 & 1 & 0 & 2 & 1 & 2 & 3 & 3 & 4 & 5 \\ 2 & 1 & 2 & 0 & 1 & 2 & 3 & 3 & 4 & 5 \\ 3 & 2 & 1 & 1 & 0 & 1 & 2 & 2 & 3 & 4 \\ 4 & 3 & 2 & 2 & 1 & 0 & 1 & 1 & 2 & 3 \\ 5 & 4 & 3 & 3 & 2 & 1 & 0 & 1 & 2 & 3 \\ 5 & 4 & 3 & 3 & 2 & 1 & 1 & 0 & 1 & 2 \\ 6 & 5 & 4 & 4 & 3 & 2 & 2 & 1 & 0 & 1 \\ 7 & 6 & 5 & 5 & 4 & 3 & 3 & 2 & 1 & 0 \end{bmatrix}$$

$W = 133$

Figure 7. Computation of the Wiener index for a polycyclic graph G with branches using the method based on the distance matrix.



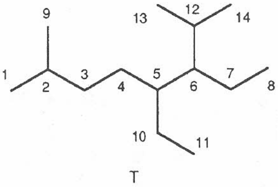
$$\mathbf{A} = \mathbf{A}_1 = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 1 \\ 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \end{bmatrix} \quad \mathbf{A}_1^2 = \begin{bmatrix} 1 & 0 & 1 & 0 & 1 \\ 0 & 3 & 0 & 1 & 0 \\ 1 & 0 & 2 & 0 & 1 \\ 0 & 1 & 0 & 1 & 0 \\ 1 & 0 & 1 & 0 & 1 \end{bmatrix} \quad W_1 = \sum_{i=1}^{5} (A_1^2)_{ii} \cdot 1 = 8$$

$$\mathbf{A}_2 = \begin{bmatrix} 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 \end{bmatrix} \quad \mathbf{A}_2^2 = \begin{bmatrix} 2 & 0 & 1 & 0 & 1 \\ 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 2 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 1 & 0 & 2 \end{bmatrix} \quad W_2 = \sum_{i=1}^{5} (A_2^2)_{ii} \cdot 2 = 16$$

$$\mathbf{A}_3 = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 \end{bmatrix} \quad \mathbf{A}_3^2 = \begin{bmatrix} 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 \\ 1 & 0 & 0 & 0 & 1 \end{bmatrix} \quad W_3 = \sum_{i=1}^{5} (A_3^2)_{ii} \cdot 3 = 12$$

$$W = \frac{1}{2} \sum_i W_i = 18$$

Figure 8. Computation of the Wiener index for a tree T depicting the carbon skeleton of 2-methylbutane using the method based on the adjacency matrix.



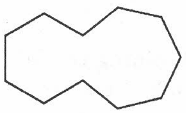
$$\mathbf{v} = [\,1\ 3\ 2\ 2\ 3\ 3\ 2\ 1\ 1\ 2\ 1\ 3\ 1\ 1\,]$$

$$\mathrm{MTI} = \sum_{j=1}^{N} \sum_{i=1}^{N} (\mathbf{v})_i \, [(\mathbf{A})_{ij} + (\mathbf{D})_{ij}] = 1176$$

$$2p_2 = 2 \times 16 = 32$$

$$W = [\,\mathrm{MTI} - 2p_2 + (N-1)(N-2)\,]/4 = 325$$

Figure 9. Computation of the Wiener index for the tree T from Figure 4 using the method based on the combination of the adjacency matrix, the distance matrix and the degree row-matrix.



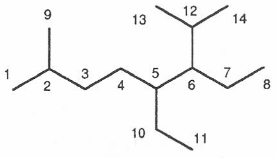
G

$$\mathbf{v} = [2\,2\,2\,2\,2\,2\,2\,2\,2\,2\,2]$$

$$\mathrm{MTI} = \sum_{j=1}^{N}\sum_{i=1}^{N} (\mathbf{v})_i\,[(\mathbf{A})_{ij} + (\mathbf{D})_{ij}] = 704$$

$$W = (\mathrm{MTI}/4) - 11 = 165$$

Figure 10. Computation of the Wiener index for a graph G representing the carbon skeleton of [11]annulene using the method based on the combination of the adjacency matrix, the distance matrix and the degree row-matrix.



T

$$\mathbf{L} = \begin{bmatrix} 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 3 & -1 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 2 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 2 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 3 & -1 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 3 & -1 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 2 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 2 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 3 & -1 & -1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 1 \end{bmatrix}$$

$$\{x_i\} = \{0.096, 0.246, 0.333, 0.788, 1, 1, 1.559,$$
$$2.146, 2.675, 3.100, 3.891, 4.231, 4.935\}$$

$$W = 14 \sum_{i=2}^{N} \left(\frac{1}{x_i}\right) = 325$$

Figure 11. Computation of the Wiener index for the tree T from Figure 4 using the method based on its Laplacian eigenvalues.

Computer methods

Computer methods for obtaining the Wiener number are usually concerned with the efficient ways of computing the distance matrix of a (molecular) graph. This is so because the construction of the distance matrix for large (often complex) graphs is a nontrivial task and, in order to be carried out, a computer must be used. Most commonly, the distance matrix of a graph G has been generated using powers of the corresponding adjacency matrix of G.[84–86] Here, we describe Hosoya's method for obtaining the distance matrix from the adjacency matrix.[85,87]

Hosoya's method can be outlined in the following way. Let us first define the adjacency matrix $\boldsymbol{A}_l$ as:

$$(\boldsymbol{A}_l)_{ij} = \begin{cases} 1 & \text{if the shortest distance between } i \text{ and } j \text{ is } l \\ 0 & \text{otherwise.} \end{cases} \tag{20}$$

Let us also define the adjacency matrix $\boldsymbol{B}_l$ as:

$$(\boldsymbol{B}_l)_{ij} = \begin{cases} 1 & \text{if the shortest distance between } i \text{ and } j \text{ is equal or less than } l \\ 0 & \text{otherwise.} \end{cases} \tag{21}$$

Matrices $\boldsymbol{A}_l$ and $\boldsymbol{B}_l$ are related in the following way:

$$\boldsymbol{B}_l = \boldsymbol{B}_{l-1} - \boldsymbol{A}_l \quad (l \geq 1)\ . \tag{22}$$

Note also that:

$$(\boldsymbol{A}_l)_{ij} = (\boldsymbol{B}_{l-1})_{ij}\, (\boldsymbol{A}_1^l)_{ij}\ . \tag{23}$$

Then, the distance matrix $\boldsymbol{D}$ is given in terms of matrices $\boldsymbol{B}_l$ as:

$$\boldsymbol{D} = \sum_{l=0}^{k-1} \boldsymbol{B}_l \tag{24}$$

where k is the largest distance in a graph G. Hosoya's method may be schematized as it is done in Figure 12. In a simple case, it is enough to use Eqs. (21) and (24). This is illustrated in Figure 13.

There are algorithms and computer programs available that are much faster than the matrix power method.[88–95] For example, Bersohn's method[89] is about thirty times faster than the method based on powers of the adjacancy matrix when used to construct the distance matrices for steroids on an IBM 3033 computer. The weak point of the matrix power method is the number of matrix multiplications required by the procedure, since computers multiply much more slowly than the store, fetch, add and substract. Bersohn's method does not require any multiplications at all. The

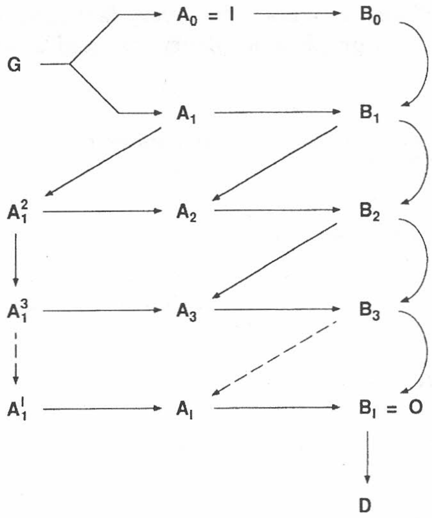
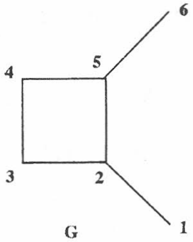


Figure 12. A schmetic presentation of Hosoya's method for the construction of the distance matrix.



$$\mathbf{B}_o = \begin{bmatrix} 0 & 1 & 1 & 1 & 1 & 1 \\ 1 & 0 & 1 & 1 & 1 & 1 \\ 1 & 1 & 0 & 1 & 1 & 1 \\ 1 & 1 & 1 & 0 & 1 & 1 \\ 1 & 1 & 1 & 1 & 0 & 1 \\ 1 & 1 & 1 & 1 & 1 & 0 \end{bmatrix} \qquad \mathbf{B}_1 = \begin{bmatrix} 0 & 0 & 1 & 1 & 1 & 1 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 0 & 1 & 1 \\ 1 & 1 & 0 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 1 & 1 & 1 & 1 & 0 & 0 \end{bmatrix}$$

$$\mathbf{B}_2 = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 \end{bmatrix} \qquad \mathbf{D} = \sum_{\ell=0}^{2} \mathbf{B}_\ell = \begin{bmatrix} 0 & 1 & 2 & 3 & 2 & 3 \\ 1 & 0 & 1 & 2 & 1 & 2 \\ 2 & 1 & 0 & 1 & 2 & 3 \\ 3 & 2 & 1 & 0 & 1 & 2 \\ 2 & 1 & 2 & 1 & 0 & 1 \\ 3 & 2 & 3 & 2 & 1 & 0 \end{bmatrix}$$

Figure 13. Computation of the distance matrix for a graph G using simplified Hosoya's method.

method of Müller *et al.* [92] also appears to be a very fast computer method for setting up the distance matrix for a graph of arbitrary size and complexity.[96]

Analytical formulae

For some classes of molecules, the Wiener index can be computed by analytical formulae.[4,15,24,29,38,40,44,59,97–101]

1. Linear alkanes with N carbon atoms

$$W = (N^3 - N)/6\ . \tag{25}$$

2. The star molecules with N carbon atoms

$$W = (N - 1)^2\ . \tag{26}$$

3. Comb-like branched alkanes with N carbon atoms

$$W = (N^3 + 6N^2 - 10N)/12\ . \tag{27}$$

4. Cycloalkanes or annulenes with N carbon atoms

$$W = \begin{cases} N^3/8 & N = \text{even} \\ N(N^2 - 1)/8 & N = \text{odd.} \end{cases} \tag{28}$$

5. [N]radialenes

$$W = \begin{cases} N^3/2 + 2N^2 - N & N = \text{even} \\ N^3/2 + 2N^2 - 3N/2 & N = \text{odd.} \end{cases} \tag{29}$$

$$W = (16H^3 + 36H^2 + 26H + 3)/3 \ . \tag{32}$$

9. Phenanthrenes and helicenes with H number of hexagons

$$W = (8H^3 + 72H^2 - 26H + 27)/3 \ . \tag{33}$$

10. Polymeric chains of singly-connected hexagons with N carbon atoms

$$W = (2N^3 + 9N)/18 \ . \tag{34}$$

11. Polymeric chains of doubly-connected naphthalene units with N carbon atoms

$$W = (2N^3 + 235N - 1080)/30 \ . \tag{35}$$

A COMPARATIVE STUDY OF THE WIENER INDEX AND SEVERAL MOST FREQUENTLY USED TOPOLOGICAL INDICES

The Wiener index is extensively used in the structure-property-activity studies. The reason for this is that this topological index appears to be a good measure of the compactness of a molecule.[7,15,102,103] The smaller the Wiener index, the larger the compactness of a structure in terms of its structural features such as branching and cyclicity. Therefore, it can be reliably used in the correlations with those physical and chemical properties which depend largely on the ratio betweeen the volume and the surface of a molecule. These are the properties of acyclic and cyclic, saturated, unsaturated and aromatic hydrocarbons, such as the heats of formation, the heats of atomization, the heats of isomerization, the heats of vaporization, densities, boiling points, critical pressures, refractive indices, surface tensions, viscosities, chromatographic retention times, *etc.*

We also point out that the Wiener index is not a particularly discriminating topological index. Already in the set of heptanes, two pairs of heptanes with the same Wiener index appear.[15] Bonchev *et al.*[104] defined the mean isomer degeneracy δ of the Wiener indices as:

$$\delta = n/t \tag{36}$$

where n is the number of isomers considered and t is the number of distinct values that the Wiener index assumes for these isomers. Obviously, when each isomer is associated with a distinct value of the Wiener index, then $\delta = 1$. In all other cases, δ is greater than one and shows how many isomers on average possess an identical value of W. Thus, δ appears to be a valuable criterion for the discriminating power of a topological index, because the larger the value of δ, the smaller the isomer-discriminating power of the index.

We decided to compare the Wiener index and the following topological indices (TIs), which are most frequently used in structure-property studies: The connectivity index χ,[105] the Harary index η,[106–108] the Balaban index J,[109] the Hosoya index Z,[14]

TABLE I

The Wiener indices (W), the connectivity indices (χ), the Harary indices (η), the Balaban indices (J), the Hosoya indices (Z), the connectivity ID numbers, the WID numbers, the Merrifield-Simmons indices (σ) and boiling points (b.p.) in °C for octanes.

ALKANE	W	χ	η	J	Z	ID	WID	σ	b.p./°C
2,2,3,3-tetramethylbutane	58	3.2500	16.0000	4.0204	17	14.0625	8.0230	80	106.5
2,2,3-trimethylpentane	63	3.4814	15.4167	3.6233	22	14.2751	8.0199	70	110
2,3,3-trimethylpentane	62	3.5040	15.5000	3.7083	23	14.2717	8.0205	68	114.7
2,2,4-trimethylpentane	66	3.4165	15.1667	3.3889	19	14.2791	8.0182	77	99.2
2,2-dimethylhexane	71	3.5607	14.7667	3.1118	23	14.4405	8.0163	69	106.8
3,3-dimethylhexane	67	3.6213	15.0333	3.3734	25	14.4311	8.0181	66	112
3-ethyl-3-methylpentane	64	3.6820	15.2500	3.5832	28	14.4301	8.0196	62	118.2
2,3,4-trimethylpentane	65	3.5534	15.1667	3.4642	24	14.3351	8.0186	66	113.4
2,3-dimethylhexane	70	3.6807	14.7333	3.1708	27	14.4960	8.0166	62	115.6
3-ethyl-2-methylpentane	67	3.7187	14.9167	3.3549	28	14.5011	8.0178	61	115.6
3,4-dimethylhexane	68	3.7187	14.8667	3.2925	29	14.4916	8.0174	60	117.7
2,4-dimethylhexane	71	3.6639	14.6500	3.0988	26	14.4966	8.0161	64	109.4
2,5-dimethylhexane	74	3.6259	14.4667	2.9278	25	14.5019	8.0150	65	109
2-methylheptane	79	3.7701	14.1000	2.7158	29	14.6660	8.0137	60	117.6
3-methylheptane	76	3.8081	14.2667	2.8621	31	14.6601	8.0146	58	118
4-methylheptane	75	3.8081	14.3167	2.9196	30	14.6585	8.0150	59	117.7
3-ethylhexane	72	3.8461	14.4833	3.0744	32	14.6659	8.0159	57	118.5
octane	84	3.9142	13.7429	2.5301	34	14.8311	8.0126	55	125.7

the connectivity ID number,[110] the WID number,[110] and the Merrifield-Simmons index σ.[112] They will be compared in an attempt to derive the best TI-boiling point relationships for octanes. K-parameter structure-property relationships will be derived in order to see, for each value of K, which of the considered TIs produces the best correlation. Octanes are used since they represent a sufficiently large and structurally diverse group of alkanes for the preliminary testing of TIs.[113] The above indices for octanes are reported in Table I.

We systematically studied the structure-property relationships[114] from one to five parameters. The study was done in this way, as recently suggested by Randić,[115] as a convenient strategy to search for the optimum topological index (or indices) and the best regression equation for predicting a given property. The following results have been obtained. Note, that we report in each case only the best K-parameter structure-property relationship.

i. 1-parameter relationship

$$bp = (1.21 \pm 0.11)\, Z + (82.01 \pm 4.24)$$
$$n = 18,\ r = 0.884,\ s = 2.93,\ F = 57.1$$

The symbols have the following meaning: r = the correlation coefficient, s = the standard deviation and F = F-test.

Close to the above relationship is the one based on the Merrifield-Simmons index σ, as expected, because the Z-index and the σ-index are closely related graph-theoretical indices:[116]

$$\text{bp} = (-0.8 \pm 0.11)\ \sigma + (165.46 \pm 7.08)$$
$$n = 18,\ r = 0.878,\ s = 2.99,\ F = 54.11$$

This 1-parameter relationship with the Wiener index is rather inferior to those above:

$$\text{bp} = (0.50 \pm 0.20)\ W + (78.90 \pm 13.90)$$
$$n = 18,\ r = 0.533,\ s = 5.3,\ F = 6.3$$

According to Randić's classification (based on r and s quantities)[115] of structure-property regressions, the former regressions are marginally fair, while the latter is useless.[113]

ii. 3-parameter relationship

$$\text{bp} = (4.25 \pm 0.68)\ Z - (82.86 \pm 18.23)\ \chi + 304.24$$
$$n = 18,\ r = 0.953,\ s = 1.96,\ F = 74.0$$

Following Randić's[115] the quality of this regression can be graded as very good.

iii. 2-parameter relationship

$$\text{bp} = (49.45 \pm 4.43)\ J + (2.58 \pm 0.26)\ W - (1.013 \pm 0.05)\ \sigma - 160.68$$
$$n = 18,\ r = 0.990,\ s = 0.96,\ F = 220.6$$

The quality of this regression can be graded as outstanding according to Randić's classification scheme.

iv. 4-parameter relationship

$$\text{bp} = (48.47 \pm 3.79)\ J + (2.85 \pm 0.24)\ W - (19.92 \pm 7.90)\ \text{ID} - (1.29 \pm 0.12)\ \sigma + 129.05$$
$$n = 18,\ r = 0.993,\ s = 0.82,\ F = 229.6$$

Similarly, the quality of this regression can also be graded as outstanding according to Randić's proposal. It is gratifying that in both 3-parameter and 4-parameter relationships the Wiener index appears. It should also be noted that, according to Randić[115] the boiling points are »difficult« molecular properties, because they are hard to represent successfully by a single-variable regression. Only the multivariate regressions can be successful in this case. Just to mention, the other difficult molecular properties are critical temperatures, critical pressures, critical volumes, *etc.* On the other hand, »easy« molecular properties (that is, it is easy to find a descriptor that will give a fair or better regression) are, for example, Pitzer acentric factor, heat of vaporization, octane number, *etc.*

We also point out that the topological indices employed in the above analysis are not strongly intercorrelated indices, except for the pair χ and W ($r = 0.98$).[34] Strongly intercorrelated pairs of indices are those with $r \geq 0.98$.[34,117]

Gao and Hosoya[118] studied the size-dependency of the correlation of the Wiener index (and several other topological indices) with 12 thermodynamic properties of alkanes. They have found that the correlation coefficients for some properties, *e.g.*, entropy, do not change with the increase of molecular size, while for others they do. For example, the correlation coefficient of structure-boiling point relationship does not change with size up to decane, but above undecane is size-dependent. In this paper, these authors also pointed out that the polarity number p is not a particularly good parameter to reflect the steric characteristics of alkanes, contrary to the opinion of Platt.[6]

NEW DEVELOPMENTS

In spite of some opinions occasionally expressed that there is nothing new to expect in this area, the research on the Wiener index and the Wiener index-like indices continues to thrive. Expecially exciting is the development of hyper-Wiener index,[61,69] the Wiener matrix[66] and the search for the formula for computing the Wiener index for dendritic molecules.[44] Here, we wish to review briefly the development of the concept of the 3-dimensional Wiener index.

The 3-D Wiener number ^3W is based on the $^3\boldsymbol{D}$ (geometric, topographic) distance matrix, much the same as the 2-D Wiener index ^2W (discussed above) is based on the $^2\boldsymbol{D}$ (graph-theoretical, topological) distance matrix. The $^3\boldsymbol{D}$ distance matrix of a molecule is a real $N \times N$ matrix, whose elements $(^3\boldsymbol{D})_{ij}$ represent the shortest Cartesian distance betweeen atoms i and j in the molecule. The 3-D Wiener number is then equal to the half-sum of the elements of $^3\boldsymbol{D}$ matrix:[74,119,120]

$$^3W = (1/2) \sum_{i=1}^{N} \sum_{j=1}^{N} (^3\boldsymbol{D})_{ij} \; . \tag{37}$$

This was first proposed by Mekenyan *et al.*[120] It appears that Dr. Ovanes Mekenyan from Burgas was the first person to suggest the 3-dimensional Wiener number in his D.Sc. Thesis in 1990.[121]

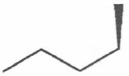
The $^3\boldsymbol{D}$ distance matrix can be constructed from the known geometry of a molecule. But, this is not always possible because for many molecules their geometries are unknown. One way to model the geometry of an unknown molecule is by the molecular mechanics approach.[122] In Figure 14, we give the $^3\boldsymbol{D}$ distance matrices and ^3W indices for four conformations of n-pentane.

The 3-D Wiener index possesses a different value for each different conformation of a molecule. The most extended conformation has the largest value of the ^3W index, while the most compact conformation has the smallest ^3W value. Evidently, the ^3W index decreases with increasing spheroidicity of a molecule. Thus, it appears that the 3-D Wiener index is a good measure of the shape of the molecule. However, the 3-D Wiener number was only slightly more successful than the 2-D Wiener number in the structure-boiling point relationships of 54 selected alkanes.[57] It should be also noted that, in the case of the ^3W index, the calculation was carried out for the whole molecule, *i.e.*, the carbon-hydrogen bonds were also included in the $^3\boldsymbol{D}$ distance matrix. For example, the following 3-parameter relationships with ^2W and ^3W indices, respectively, were obtained:

$$\text{bp} = (108.6 \pm 6.4)\,(^2W)^{0.228 \pm 0.008} - (178.0 \pm 7.9)$$
$$n = 54,\ r = 0.995,\ s = 8.39,\ F = 263$$

$$^{3}\mathbf{D} = \begin{bmatrix} 0 & 1.534 & 2.544 & 3.914 & 5.087 \\ 1.534 & 0 & 1.537 & 2.548 & 3.914 \\ 2.544 & 1.537 & 0 & 1.537 & 2.544 \\ 3.914 & 2.548 & 1.537 & 0 & 1.534 \\ 5.087 & 3.914 & 2.544 & 1.534 & 0 \end{bmatrix}$$

$^{3}W = 26.694$



$$^{3}\mathbf{D} = \begin{bmatrix} 0 & 1.534 & 2.571 & 3.155 & 4.581 \\ 1.534 & 0 & 1.538 & 2.574 & 3.929 \\ 2.571 & 1.538 & 0 & 1.537 & 2.543 \\ 3.155 & 2.574 & 1.537 & 0 & 1.535 \\ 4.581 & 3.929 & 2.543 & 1.535 & 0 \end{bmatrix}$$

$^{3}W = 25.497$

$$^{3}\mathbf{D} = \begin{bmatrix} 0 & 1.533 & 2.583 & 3.174 & 3.442 \\ 1.533 & 0 & 1.539 & 2.597 & 3.486 \\ 2.583 & 1.539 & 0 & 1.539 & 2.574 \\ 3.174 & 2.597 & 1.539 & 0 & 1.535 \\ 3.442 & 3.486 & 2.574 & 1.535 & 0 \end{bmatrix}$$

$^{3}W = 23.912$

$$^{3}\mathbf{D} = \begin{bmatrix} 0 & 1.534 & 2.570 & 3.135 & 3.757 \\ 1.534 & 0 & 1.538 & 2.601 & 3.135 \\ 2.570 & 1.538 & 0 & 1.538 & 2.570 \\ 3.135 & 2.601 & 1.538 & 0 & 1.534 \\ 3.757 & 3.135 & 2.570 & 1.534 & 0 \end{bmatrix}$$

$^{3}W = 24.001$

Figure 14. The diagrams, the $^{3}\boldsymbol{D}$ distance matrices and 3-*D* Wiener numbers $^{3}\boldsymbol{W}$ for four conformers of *n*-pentane.

$$\mathrm{bp} = (395.0 \pm 68)\,(^{3}W)^{0.099 \pm 0.010} - (682.0 \pm 79)$$
$$n = 54,\ r = 0.998,\ s = 5.84,\ F = 5402$$

This result is in a way disappointing, because it is much harder to compute the ^{3}W index than the ^{2}W index and the improvement obtained for the standard deviation is still unsatisfactory. On the other hand, we should remember that the boiling point is a difficult molecular property to predict.[115] Nevertheless, in spite of this initial frustration, we continue our work on the ^{3}W index with the aim of discerning the conformation of molecules responsible for the bulk property of the compounds under investigation. In this respect, the computer graphics modelling of molecules in bulk might be of some help. However, it should be pointed out that a series of structure-activity studies of the Burgas group, *e.g.*,[123] is rather encouraging: The 3-*D* Wiener index and its information-theoretic analogue I_{WG} strongly overperform the 2-*D* versions and are among the best molecular descriptors for correlating biological activities, *e.g.*, modelling the anticancer activity of a series of vitamin A analogs.

It is interesting to note that the ^{2}W index, computed only for carbon skeletons of alkanes, and the ^{3}W index, computed for carbon-hydrogen skeletons of alkanes, are closely intercorrelated indices. A linear relationship betweeen these two versions of the Wiener index is given by:

$$^{3}W = (0.085 \pm 0.001)\ ^{2}W - (13.005 \pm 0.941)$$
$$n = 150,\ r = 0.997,\ s = 3.66,\ F = 22995$$

The significance on the above result is that both ^{2}W and ^{3}W indices contain, to a great extent, similar structural information. Could it be that the topological features make a gross part of the structural characteristics of the molecule, while spatial features make only a minor part? It could be so, but then spatial characteristics of molecules, irrespective of how minor is their part in the structure of the molecule, are important for a number of molecular properties, especially biological ones. On the other hand, perhaps the success of the ^{2}W index in some applications can really be attributed to this similarity between the 2-*D* and 3-*D* versions of the Wiener index.

CONCLUDING REMARKS

In this report, we reviewed the definitions and the algorithms for computing the Wiener index, the oldest of graph-theoretical indices to be used in chemistry. We compared the original Wiener structure-boiling point model for the 147 lowest alkanes (methane, ethane and propane were not considered because the polarity number for them is equal to zero) with two more modern ones. The result is that the Wiener approach gives the lowest value of the standard deviation, but also the lowest value of the correlation coefficient. This is not surprising because Wiener devised his procedure with the aim of reproducing as well as possible the experimental boiling points of alkanes.

The Wiener index is interpreted as a measure of the compactness of a molecule in terms of its structural characteristics, such as branching and/or cyclicity. However, the Wiener index is not a very discriminating topological index. The meaning of this statement is that non-isomorphic structures with identical values of the topological index could appear. In the case of the Wiener index, this happens already in heptanes, where two pairs of heptane isomers with the same value of *W* appear.

A comparative study between the Wiener index and several topological indices commonly used in the structure-property correlations (the connectivity index, the Harary index, the Balaban index, the Hosoya index, the connectivity ID number, the WID number and the Merrifield-Simmons index) revealed that the Wiener index in the case of 1-parameter structure-boiling point relationships is inferior to almost all the mentioned indices, but to the Balaban index and the WID number. The best results have been obtained for the 3-parameter and 4-parameter structure-boiling point relationships, which in both cases included the Wiener index (other indices used were, in the former case, the Balaban index and the Merrifield-Simmons index and, in the latter case, besides these two indices, the ID number).

Finally, we mentioned recent developments related to the Wiener index, including the Wiener matrix and indices derived from it, the hyper-Wiener index and its three-dimensional version. The structure-property studies with ^{3}W are still in the initial stages and it is difficult to predict how useful they are going be in the QSPR and QSAR studies (although some other people reported considerably greater improvements in using ^{3}W over the use of ^{2}W) because, although they show some improvements over studies which use ^{2}W, the labor included in computing ^{3}W is much more involved. However, work in this area is still in progress with the aim to discern the conformation of molecules responsible for the bulk properties of compounds under study.

Acknowledgements. – This work was supported by the Ministry of Science and Technology of the Republic of Croatia through Grants Nos. 1–07–159 and 1–07–85. We are grateful to the referees for their constructive comments.

REFERENCES

1. E. L. Eliel, *Stereochemistry of Carbon Compounds,* McGraw-Hill, New York, 1962, p.1.
2. D. H. Rouvray, *Sci. Amer.* **254** (1986) 40.
3. P. J. Hansen and P. C. Jurs, *J. Chem. Educ.* **65** (1988) 574.
4. P. E. Polansky, in: MATH/CHEM/COMP 1988, A. Graovac (Ed.), Elsevier, Amsterdam, 1989, p. 167.
5. H. Wiener, *J. Amer. Chem. Soc.* **69** (1947) 17.
6. J. R. Platt, *J. Phys. Chem.* **56** (1952) 328.
7. P. G. Seybold, M. May, and U. A. Bagal, *J. Chem. Educ.* **64** (1987) 575.
8. H. Wiener, *J. Amer. Chem. Soc.* **69** (1947) 2636.
9. H. Wiener, *J. Chem. Phys.* **15** (1947) 766.
10. H. Wiener, *J. Phys. Chem.* **52** (1948) 425.
11. H. Wiener, *ibid.* **52** (19948) 1082.
12. J. R. Platt, *J. Chem. Phys.* **15** (1947) 419.
13. e.g., L. Stiel and G. Thodos, *J. Amer. Inst. Chem. Eng.* **8** (1962) 527.
14. H. Hosoya, *Bull. Chem. Soc. Japan* **44** (1971) 2332.
15. D. Bonchev and N. Trinajstić, *J. Chem. Phys.* **67** (1977) 4517.
16. D. Bonchev and N. Ttinajstić, *Int. J. Quantum Chem.: Quantum Chem. Symp.* **12** (1978) 293.
17. D. Bonchev, J. V. Knop, and N. Trinajstić, *Math. Chem. (Mülheim/Ruhr)* **6** (1979) 21.
18. O. Mekenyan, D. Bonchev, and N. Trinajstić, *ibid.* **6** (1979) 93.
19. D. Bonchev, O. Mekenyan, G. Protić, and N. Trinajstić, *J. Chromatogr.* **176** (1979) 149.
20. D. Bonchev, O. Mekenyan, and N. Trinajstić, *Int. J. Quantum Chem.* **17** (1980) 845.
21. A. Sabljić and N. Trinajstić, *Acta Pharm.* **31** (1981) 189.
22. O. Mekenyan, D. Bonchev, and N. Trinajstić, *Math. Chem. (Mülheim/Ruhr)* **11** (1981) 145.
23. O. Mekenyan, D. Bonchev, and N. Trinajstić, *Croat. Chem. Acta* **56** (1983) 237.
24. N. Trinajstić, *Chemical Graph Theory*, CRC Press, Boca Raton, FL. 1983, Vol. II, Chapter 4.
25. D. Bonchev, *Information Theoretic Indices for Characterization of Chemical Structures,* Research Studies Press, Letchworth, Herts., 1983, p. 71.
26. D. H. Rouvray, in: *Chemical Applications of Topology and Graph Theory*, R. B. King (Ed.), Elsevier, Amsterdam, 1983, p. 159.
27. A. T. Balaban, I. Motoc, D. Bonchev, and O. Mekenyan, *Topics Curr. Chem.* **114** (1983) 21.
28. D. H. Rouvray, in: *Mathematics and Computational Concepts in Organic Chemistry*, N. Trinajstić (Ed.), Horwood, Chichester, 1986, p. 295.
29. I. Gutman and O. E. Polansky, *Mathematical Concepts in Organic Chemistry*, Springer-Verlag, Berlin, 1986, Chapter 11.
30. D. H. Rouvray, in: *Graph Theory and Topology in Chemistry,* R. B. King and D. H. Rouvray (Eds.), Elsevier, Amsterdam, 1987, p. 177.
31. D. Bonchev, O. Mekenyan, and O. E. Polansky, in: *ibid.*, Elsevier, Amsterdam, 1987, p. 209.
32. E. Hladka and L. Matyska, *Chem. Listy* **82** (1988) 1009.
33. M. I. Stankevich, I. V. Stankevich, and N. S. Zefirov, *Russ. Chem. Rev.* **57** (1988) 191.
34. K. Kovačević, D. Plavšić, N. Trinajstić, and D. Horvat, in: MATH/CHEM/COMP 1988, A. Graovac (Ed.), Elsevier, Amsterdam, 1989, p. 213.
35. N. Adler, L. Kovačić-Beck, and N. Trinajstić, *ibid.* p. 225.
36. A. K. Mukherjee and K. K. Datta, *Indian J. Chem.* **29A** (1990) 613.
37. L. Benedetti, G. Battistuzzi Gavioli and C. Fontanesi, *J. Chem. Soc. Faraday Trans.* **86** (1990) 329.
38. N. Trinajstić, S. Nikolić, J. V. Knop, W. R. Müller, and K. Szymanski, *Computational Chemical Graph Theory: Characterization, Enumeration and Generation of Chemical Structures by Computer Methods*, Horwood, Chichester, 1991, Chapter 9.
39. K. Osmialowski and R. Kaliszan, *Quant. Struct. – Act. Relat.* **10** (1991) 125.
40. N. Trinajstić, *Chemical Graph Theory*, 2nd revised CRC Press, Boca Raton, FL., 1992.
41. L. Benedetti, G. Battistuzzi Gavioli, and C. Fontanesi, *J. Chem. Soc. Faraday Trans.* **88** (1992) 843.
42. Z. Mihalić, S. Nikolić, and N. Trinajstić, *J. Chem. Inf. Comput. Sci.* **32** (1992) 28.
43. Z. Mihalić and N. Trinajstić, *J. Chem. Educ.* **69** (1992) 701.

44. I. Gutman, Y. -N. Yeh, S. -L. Lee, and Y. -L. Luo, *Indian J. Chem.* **32A** (1993) 651.
45. (a) A. Voelkel, T. Kopczynski, and A. Gawalek, *J. Mol. Struct. (Theochem)* **279** (1993) 217.
    (b) T. Kopczynski and A. Voelkel, ibid. **284** (1993) 143.
46. M. Randić and N. Trinajstić, *J. Mol. Struct.* **300** (1993) 551.
47. (a) O. E. Polansky and D. Bonchev, *Math. Chem.* (Mülheim/Ruhr) **21** (1986) 133.
    (b) O. E. Polansky, in: *MATH/CHEM/COMP 1988*, A. Graovac (Ed.), Elsevier, Amsterdam, 1989, p. 167.
    (c) O. E. Polansky and D. Bonchev, *Math. Chem. (Mülheim/Ruhr)* **25** (1990) 3.
48. L. H. Hall and L. B. Kier, in: *Reviews in Computational Chemistry II,* K. B. Lipkowitz and D. B. Boyd, VCH, New York, 1991, p. 367.
49. N. Adler and L. Kovačić-Beck, in: *Graph Theory and Topology in Chemistry,* R. B. King and D. H. Rouvray (Eds.), Elsevier, Amsterdam, 1987, p. 194.
50. M. P. Hanson and D. H. Rouvray, in: *ibid.* 1987, p. 201.
51. I. Lukovits, *J. Chem. Soc. Perkin Trans. 2* (1988) 1667.
52. (a) I. Lukovits, *Reports Mol. Theory* **1** (1990) 127.
    (b) I. Lukovits, *Quant. Struct. – Act. Relat.* **9** (1990) 125.
53. (a) D. Bonchev, V. Kamenska, and O. Mekenyan, *Int. J. Quantum Chem.* **37** (1990) 135.
    (b) D. Bonchev, V. Kamenska, and O. Mekenyan, *J. Math. Chem.* **5** (1990) 43.
54. I. Gutman and D. H. Rouvray, *Comput. Chem.* **14** (1990) 29.
55. J. K. Labanowski, I. Motoc, and R. A. Dammkoehler, *ibid.* **15** (1991) 47.
56. N. Bošnjak, Z. Mihalić, and N. Trinajstić, *J. Chromatogr.* **540** (1991) 430.
57. Z. Mihalić and N. Trinajstić, *J. Mol. Struct. (Theochem)* **232** (1991) 65.
58. S. Nikolić, N. Trinajstić, Z. Mihalić, and S. Carter, *Chem. Phys. Lett.* **179** (1991) 21.
59. A. Graovac and T. Pisanski, *J. Math. Chem.* **8** (1991) 53.
60. I. Gutman and Z. Šoltés, *Z. Naturforsch.* **46a** (1991) 868.
61. I. Lukovits, *J. Chem. Inf. Comput. Sci.* **31** (1991) 503.
62. D. J. Klein, Z. Mihalić, D. Plavšić, and N. Trinajstić, *ibid.* **32** (1992) 304.
63. I. Lukovits, *Int. J. Quantum Chem.: Quantum Biol. Symp.* **19** (1992) 217.
64. D. Horvat, A. Graovac, D. Plavšić, N. Trinajstić, and M. Strunje, *ibid.* **26** (1992) 401.
65. M. Randić, *Chem. Phys. Lett.* **211** (1993) 478.
66. M. Randić, X. Guo, T. Oxley, and H. Krishnapriyan, *J. Chem. Inf. Comput. Sci.* **33** (1993) 709.
67. M. Randić and N. Trinajstić, *Croat. Chem. Acta* **66** (1993) 411.
68. N. Trinajstić, D. Babić, S. Nikolić, D. Plavšić, D. Amić, and Z. Mihalić, *J. Chem. Inf. Comput. Sci.* **34** (1994) 368.
69. I. Lukovits and W. Linert, *ibid.* **34** (1994) 899.
70. O. Ori and M. D'Mello, *Chem. Phys. Lett.* **197** (1992) 49.
71. R. B. Woodward, *J. Amer. Chem. Soc.* **63** (1941) 1123.
72. F. Harary, *Graph Theory*, 2nd printing, Addison-Wesley, Reading MA, 1971.
73. D. H. Rouvray, in: *Chemical Applications of Graph Theory,* A. T. Balaban (Ed.), Academic Press, London, 1976, p. 175.
74. Z. Mihalić, D. Veljan, D. Amić, S. Nikolić, D. Plavšić, and N. Trinajstić, *J. Math. Chem.* **11** (1992) 223.
75. M. Barysz, D. Plavšić, and N. Trinajstić, *Math. Chem. (Mülheim/Ruhr)* **19** (1986) 89.
76. H. P. Schultz, *J. Chem. Inf. Comput. Sci.* **29** (1989) 227.
77. W. R. Müller, K. Szymanski, J. V. Knop, and N. Trinajstić, *ibid.* **30** (1990) 160.
78. D. J. Klein, Z. Mihalić, D. Plavšić, and N. Trinajstić, *ibid.* **32** (1992) 304.
79. S. Nikolić, N. Trinajstić, and Z. Mihalić, *J. Math. Chem.* **12** (1993) 251.
80. D. Plavšić, S. Nikolić, N. Trinajstić, and D. J. Klein, *Croat. Chem. Acta* **66** (1003) 345.
81. B. Mohar, in: *MATH/CHEM/COMP 1988*, A. Graovac (Ed.), Elsevier, Amsterdam, 1989, p.1.
82. N. Trinajstić, D. Babić, S. Nikolić, D. Plavšić, D. Amić, and Z. Mihalić, *J. Chem. Inf. Comput. Sci.* **34** (1994) 368.
83. B. Mohar, D. Babić, and N. Trinajstić, *ibid.* **33** (1993) 153.
84. C. Berge, *Théorie des graphes et ses applications,* Dunod, Paris, 1958, 136.
85. H. Hosoya, in: *Proceedings of the Conference on Molecular Structure*, Tokyo, 1970, p. 291.
86. F. S. Roberts, *Discrete Mathematics Model,* Prentice-Hall, Englewood Cliffs, 1976, p. 58.
87. H. Hosoya, private communication to NT (June 17, 1991).

88. R. W. Floyd, *Comm. ACM* **5** (1962) 345.
89. M. Bersohn, *J. Comput. Chem.* **4** (1983) 110.
90. I. V. Peredunova, V. E. Kuzmin, and Y. P. Konovortskii, *Russ. J. Struct. Chem.* **24** (1983) 645.
91. N. Deo and C. Pang, *Networks* **14** (1984) 275.
92. W. R. Müller, K. Szymanski, J. V. Knop and N. Trinajstić, *J. Comput. Chem.* **8** (1987) 170.
93. P. Senn, *Comput. Chem.* **12** (1988) 267.
94. B. Mohar and T. Pisanski, *J. Math. Chem.* **2** (1988) 267.
95. K. Balasubramanian, *J. Comput. Chem.* **11** (1990) 829
96. S. S. Tratch, M. I. Stankevich, and N. S. Zefirov, *ibid.* **11** (1990) 899.
97. R. C. Entringer, D. E. Jackson, and D. A. Synder, *Czech. Math. J.* **26** (19756) 283.
98. D. Bonchev, O. Mekenyan, J. V. Knop, and N. Trinajstić, *Croat. Chem. Acta* **52** (1979) 361.
99. E. R. Canfield, W. R. Robinson, and D. H. Rouvray, *J. Comput. Chem.* **6** (1985) 598.
100. D. H. Rouvray, *ibid.* **8** (1987) 470.
101. I. Gutman, J. V. Kennedy, and L. V. Quintas, *Chem. Phys. Lett.* **173** (1990) 403.
102. P. G. Seybold, M. A. May, and M. L. Gargas, *Acta Pharm.* **36** (1986) 253.
103. D. E. Needham, I.-C. Wei, and P. G. Seybold, *J. Amer. Chem. Soc.* **110** (1988) 4186.
104. D. Bonchev, O. Mekenyan, and N. Trinajstić, *J. Comput. Chem.* **2** (1981) 127.
105. M. Randić, *J. Amer. Chem. Soc.* **97** (1975) 6609.
106. D. Plavšić, S. Nikolić, N. Trinajstić, and Z. Mihalić, *J. Math. Chem.* **12** (1993) 235.
107. O. Ivanciuc, T. -S. Balaban, and A. T. Balaban, *ibid.* **12** (1993) 309.
108. A. T. Balaban, *J. Chem. Inf. Comput. Sci.* **34** (1994) 398.
109. A. T. Balaban, *Chem. Phys. Lett.* **89** (1982) 399.
110. M. Randić, *J. Chem. Inf. Comput. Sci.* **24** (1984) 164.
111. K. Szymanski, W. R. Müller, J. V. Knop, and N. Trinajstić, *Int. J. Quantum Chem: Quantum Chem. Symp.* **20** (1986) 173.
112. R. E. Merrifield and H. E. Simmons, *Theoret. Chim. Acta* **55** (1980) 55.
113. M. Randić and N. Trinajstić, *J. Mol. Struct. (Theochem)* **300** (1993) 551.
114. M. Randić, Z. Mihalić, S. Nikolić, and N. Trinajstić, *Croat. Chem. Acta* **66** (1993) 411.
115. M. Randić, *ibid.* **66** (1993) 289.
116. N. Trinajstić, Report at *Pedagogical Symposium on Graph Theory in Chemistry – The Fourth Chemical Congress of North America*, New York, August 25–30, 1991.
117. I. Motoc, A. T. Balaban, O. Mekenyan, and D. Bonchev, *Math. Chem. (Müllheim/Ruhr)* **13** (1982) 369.
118. Y.-d. Gao and H. Hosoya, *Bull. Chem. Soc. Japan* **61** (1988) 3093.
119. (a) B. Bogdanov, S. Nikolić, and N. Trinajstić, *J. Math. Chem.* **3** (1989) 291.
    (b) B. Bogdanov, S. Nikolić, and N. Trinajstić, *ibid.* **5** (1990) 305.
120. O. Mekenyan, D. Peitchev, D. Bonchev, N. Trinajstić, and I. Bangov, *Drug Design* **36** (1986) 176.
121. O. Mekenyan, *Molecular Structure Description and Modelling of Structure-Activity Relationships*, D.Sc. Thesis, Burgas, 1990.
122. K. Burkert and N. L. Allinger, *Molecular Mechanics*, ACS, Washington, D.C., 1982.
123. D. Bonchev, C. F. Mountain, W. A. Seitz, and A. T. Balaban, *J. Med. Chem.* **36** (1993) 1562.

SAŽETAK

Wienerov broj – razvoj i primjene

Sonja Nikolić, Nenad Trinajstić i Zlatko Mihalić

Prikazane su definicije i metode računanja Wienerova broja. Istaknuto je da je Wienerov broj mjera kompaktnosti molekule, definirana njezinim strukturnim značajkama kao što su razgrananost i prstenastost. Usporedba Wienerova broja i nekih drugih često upotrebljavanih topologijskih indeksa u relacijama struktura-vrelište za oktane pokazale je da je Wienerov broj u ovom slučaju inferioran većini razmatranih indeksa. To je rezultat koji su opazili i drugi autori. Spomenuti su također i novi razvoji vezani uz Wienerov broj i indekse koji su mu vrlo slični. Također je prikazano i proširenje Wienerova broja u njegovu tro-dimenzionalnu inačicu.