

On Structure Descriptors Related with Intramolecular Energy of Alkanes

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In an earlier work it was demonstrated that the Zenkevich index U provides a measure of the intramolecular energy of an organic molecule, and that – in the case of alkanes – it is related to the Wiener index. We now show that U is much closer related to the recently introduced variable Wiener index W_λ : Within sets of isomeric alkanes, the relation between U and W_λ is linear, the (U, W_λ) -points forming several, mutually parallel, lines. Each such line pertains to a group of isomers possessing a fixed number of methyl groups. There exists a critical value of the parameter λ for which all the (U, W_λ) -lines coalesce, in which case the relation between U and W_λ becomes independent of the number of methyl groups. Approximate analytical expressions for the (U, W_λ) -dependence are deduced.

Key words: Wiener Index; Variable Wiener Index; Zenkevich Index; Intramolecular Energy; Alkanes.

Introduction

In a recent paper [1] it was established that in the case of alkanes, the structure–descriptor U , introduced a short time ago by Zenkevich [2–6], and the classical Wiener index W [7–10] are mutually related. From a physico–chemical point of view this is a surprising finding, because U is conceived as a (rough) measure of the intramolecular energy, whereas W has been recognized as a (rough) measure of the molecular surface area [11] and intermolecular van der Waals forces [12]. The reason for the existence of a relation between U and W lies in the fact that both quantities depend on the same structural features of the underlying molecular graph [1]. More specifically, if T is the graph representing an alkane molecule C_nH_{2n+2} (in which case T necessarily is a tree [13]), then

$$W = \sum_e n_1(e|T) n_2(e|T) \quad (1)$$

and

$$U = \sum_e \sqrt{\frac{(C+2H)n+2H}{[(C+2H)n_1(e|T)+H][(C+2H)n_2(e|T)+H]}} \quad (2)$$

where n is the number of vertices of T , and where H and C stand for the atomic masses of hydrogen and carbon ($H = 1.0$, $C = 12.0$).

In (1) and (2), $n_1(e|T)$ and $n_2(e|T)$ denote the number of vertices lying on the two sides of an edge e of T , whereas the summations go over all edges of the molecular graph T . Recall that an n -vertex tree possesses $n - 1$ edges, and for each of these edges,

$$n_1(e|T) + n_2(e|T) = n. \quad (3)$$

A modification of the Wiener index was recently proposed [14–16], viz.,

$$W_\lambda = \sum_e [n_1(e|T) n_2(e|T)]^\lambda, \quad (4)$$

where λ is an adjustable parameter. The structure–descriptor W_λ was named [15] “variable Wiener index”. Clearly, for $\lambda = 1$ the variable Wiener index reduces to the ordinary Wiener index.

By comparing the right–hand sides of (1), (2), and (4), we may expect that for some values of the parameter λ , different from unity, the (approximate) relation between U and W_λ will become much more accurate than between U and W . As shown below, this indeed is the case.

The Methyl Group Rule

Initially it was believed [14] that the combination of (2) and (4) implies the existence of a linear correlation

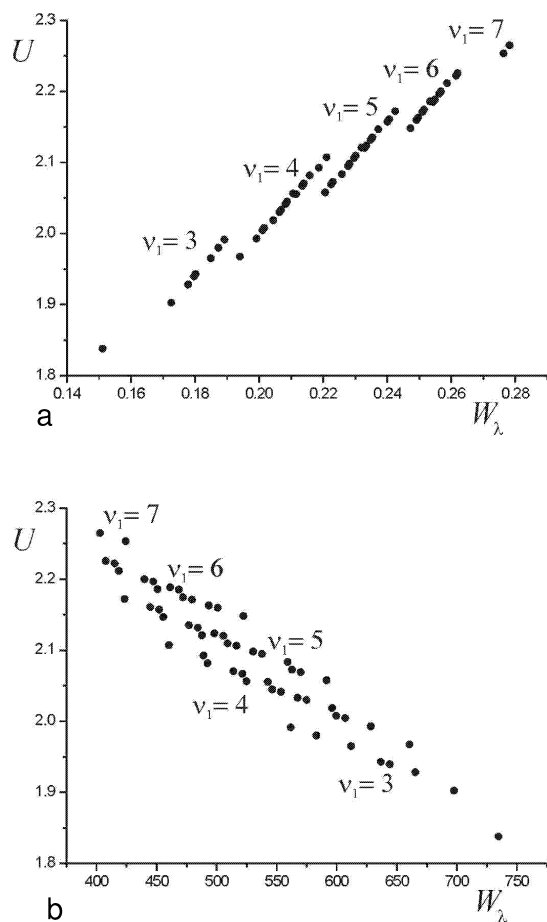


Fig. 1. The Zenkevich index (U) versus the variable Wiener index (W_λ) for isomeric decanes ($n = 10$), for (a) $\lambda = -1.5$ and (b) $\lambda = +1.5$. The data-points lie on several lines, each line corresponding to isomers with a fixed number (v) of methyl-groups; the “outlyer” is the data-point corresponding to n -decane, the only isomer with two methyl groups. Note that the ordering of these lines (with regard to v) in diagram (a) is opposite to that in diagram (b). This inversion pertains to the sign-change of the coefficient γ in (5).

between U and W_λ . However, the actual relation between U and W_λ is somewhat more complicated. If n is sufficiently large (say, $n \geq 10$), then the (U, W_λ) -points form a pattern illustrated in Figure 1.

As seen from Fig. 1, the (U, W_λ) -points form several lines. These are nearly parallel and nearly equidistant. The clue for rationalizing such a behavior was the observation that the points belonging to a line correspond to alkane isomers with the same number v of methyl groups. In other words, the respective molecular graphs have the same number of vertices of degree one.

That this is a generally applicable regularity was checked in the case of $\lambda = 1$ by testing all alkanes with up to $n = 15$ carbon atoms [17]. The analysis was then repeated for various values of λ in the interval $[-10, +10]$; as explained below, the case $\lambda = 0$ is exceptional and was therefore avoided. It was found that, for a fixed value of n , the slopes of the regression lines are remarkably similar, implying that these lines are almost parallel. Their distances vary with increasing values of v , and depend very much on λ . The analysis of the computed data reveals that the claim that the (U, W) -lines are equidistant is acceptable only as a plausible, but not very accurate approximation (cf. Fig. 1).

Anyway, the high correlation coefficients, obtained for all examined values of n and v , and for $-10 \leq \lambda \leq +10$, confirm that it is justified to separately consider the data points for fixed n and v , that within each of such group of data points, the Zenkevich and the variable Wiener index are linearly correlated, and that the number of methyl groups is the most important structural parameter that, in addition to n , influences the relation between U and W_λ .

By the above outlined empirical examination of the relations between the Zenkevich and the variable Wiener indices, the following regularity could be established, that we refer to as the

Methyl Group Rule: For a fixed value of $\lambda \neq 0$, the (U, W_λ) -points lying (approximately) on the same line pertain to isomeric alkanes with equal number of methyl groups; the (U, W_λ) -points corresponding to isomeric alkanes with different number of methyl groups lie on different lines.

The way in which the pattern shown in Fig. 1 changes with λ is essentially the following:

For $\lambda > 0$ the Zenkevich index is a decreasing function of W_λ . As λ decreases, the respective regression lines become steeper, and their slopes tend to $-\infty$ when $\lambda \rightarrow 0$. For $\lambda < 0$ the Zenkevich index is an increasing function of W_λ . As λ increases, the respective regression lines become steeper, and their slopes tend to $+\infty$ when $\lambda \rightarrow 0$. There exists a critical value of λ , denoted by λ_0 , at which the regression lines pertaining to various values of v coalesce. For $\lambda > \lambda_0$ the line for $v = k + 1$ lies above the line for $v = k$. For $\lambda < \lambda_0$ the line for $v = k + 1$ lies below the line for $v = k$.

This relatively complicated behavior of the relation between U and W_λ could be rationalized by a pertinent mathematical analysis of (2). As shown below,

the *Methyl Group Rule* and its dependence on λ are reasonably well reproduced by the approximation (5):

$$U \approx -\alpha W_\lambda + \beta + \gamma v, \quad (5)$$

where the coefficients α , β , and γ are functions of the variable λ , and, in addition, depend only on n .

According to (5), for a given value of n , the (U, W_λ) -points lie on several mutually parallel lines (all having the same slope $-\alpha$). The relative position of these lines depends on the sign of γ , as shown in Figure 1. The way in which α , β , and γ change with λ is seen from Figs. 2, 3, and 4, and is discussed in due detail below.

Analysis of the Relation between U and W_λ

Introduce first an auxiliary variable x

$$x(e) = [n_1(e|T)n_2(e|T)]^\lambda. \quad (6)$$

Then, bearing in mind (3), we can rewrite (2) as

$$U = A \sum_e (x(e)^{1/\lambda} + B)^{-1/2}, \quad (7)$$

where

$$A = \frac{\sqrt{(C+2H)n+2H}}{C+2H} \quad (8)$$

and

$$B = \frac{Hn}{C+2H} + \left(\frac{H}{C+2H}\right)^2. \quad (9)$$

Note that both A and B depend only on the number n of carbon atoms, and are independent of any other structural detail of the alkane molecule under consideration.

The summation on the right-hand side of (7) goes over all edges of the respective molecular graph, i. e., over all carbon-carbon bonds. Bearing in mind the *Methyl Group Rule* outlined in the previous section, this sum is now divided into two parts: one pertaining to the edges whose one endpoint is a vertex of degree one, and the other embracing all other edges. There are v edges whose one endpoint is a vertex of degree one. For these edges, $n_1 = 1$, $n_2 = n - 1$, and thus $x(e) = (n - 1)^\lambda$. Consequently

$$U = Av(n-1+B)^{-1/2} + A \sum_* (x(e)^{1/\lambda} + B)^{-1/2}, \quad (10)$$

where \sum_* indicates summation over edges of the molecular graph connecting vertices whose degrees are

greater than one. There exist $n - 1 - v$ such edges. For these edges, the product $n_1 n_2$ assumes values from the interval $[2n - 4, \lfloor n^2/4 \rfloor]$. Therefore the variable $x(e)$, defined by (6), belongs either to the interval $[(2n - 4)^\lambda, (\lfloor n^2/4 \rfloor)^\lambda]$ if $\lambda \geq 0$, or to the interval $[(\lfloor n^2/4 \rfloor)^\lambda, (2n - 4)^\lambda]$ if $\lambda \leq 0$. For any value of λ the center of this interval is at

$$\xi = \frac{1}{2} \left[(2n - 4)^\lambda + (\lfloor n^2/4 \rfloor)^\lambda \right]. \quad (11)$$

In view of (7) and (10), and taking into account (4), we consider the function $(x^{1/\lambda} + B)^{-1/2}$ and expand it into a power series in the variable x , around the point ξ . By direct calculation one gets

$$\begin{aligned} (x^{1/\lambda} + B)^{-1/2} = & (\xi^{1/\lambda} + B)^{-1/2} - \frac{1}{2\lambda} (\xi^{1/\lambda} + B)^{-3/2} \xi^{1/\lambda-1} (x - \xi) \\ & + \text{higher order terms.} \end{aligned}$$

Neglecting the higher order terms, proportional to $(x - \xi)^2$, $(x - \xi)^3$, etc, we arrive at

$$\begin{aligned} U \approx & Av(n-1+B)^{-1/2} \\ & + A \sum_* \left[(\xi^{1/\lambda} + B)^{-1/2} + \frac{1}{2\lambda} (\xi^{1/\lambda} + B)^{-3/2} \right. \\ & \quad \left. - \frac{1}{2\lambda} (\xi^{1/\lambda} + B)^{-3/2} \xi^{1/\lambda-1} x(e) \right] \\ = & Av(n-1+B)^{-1/2} + A(n-1-v) \\ & \cdot \left[(\xi^{1/\lambda} + B)^{-1/2} + \frac{1}{2\lambda} (\xi^{1/\lambda} + B)^{-3/2} \right] \\ & - \frac{A}{2\lambda} (\xi^{1/\lambda} + B)^{-3/2} \xi^{1/\lambda-1} \sum_* x(e). \end{aligned} \quad (12)$$

Because of

$$\sum_e x(e) = v(n-1)^\lambda + \sum_* x(e),$$

from (4) we get

$$\sum_* x(e) = W_\lambda - v(n-1)^\lambda.$$

When the latter relation is substituted back into (12), we obtain the following expressions for the coefficients occurring on the right-hand side of the Ansatz (5):

$$\alpha = \alpha(\lambda) = \frac{A \xi^{1/\lambda-1}}{2\lambda} (\xi^{1/\lambda} + B)^{-3/2}, \quad (13)$$

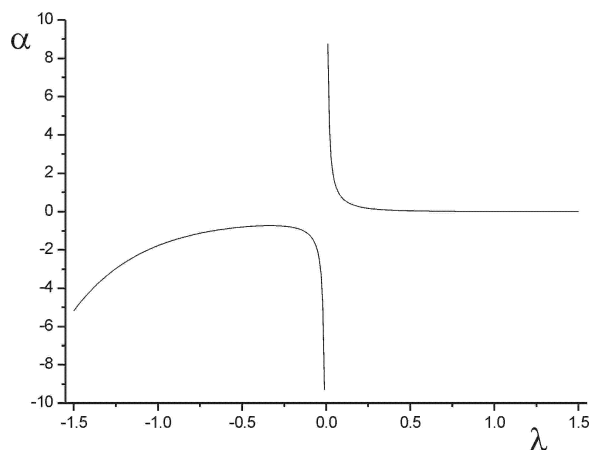


Fig. 2. Dependence of the coefficient α in (5) on the parameter λ , in the (typical) case of $n = 10$.

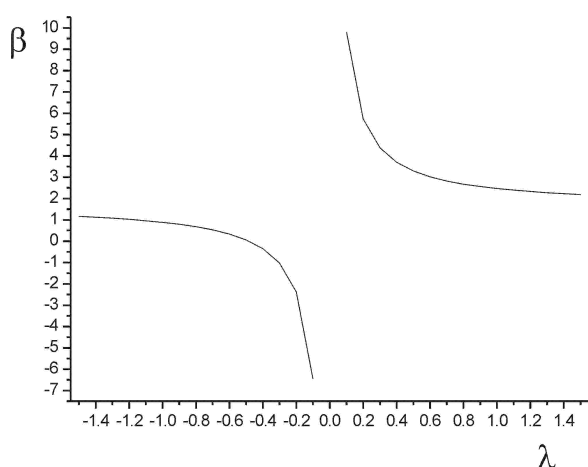


Fig. 3. Dependence of the coefficient β in (5) on the parameter λ , in the (typical) case of $n = 10$.

$$\beta = \beta(\lambda) = A(n-1) \left[\left(\xi^{\frac{1}{\lambda}} + B \right)^{-\frac{1}{2}} + \frac{\xi^{\frac{1}{\lambda}}}{2\lambda} \left(\xi^{\frac{1}{\lambda}} + B \right)^{-\frac{3}{2}} \right], \quad (14)$$

$$\gamma = \gamma(\lambda) = A \left\{ (n-1+B)^{-\frac{1}{2}} - \left(\xi^{\frac{1}{\lambda}} + B \right)^{-\frac{1}{2}} + \frac{\xi^{\frac{1}{\lambda}-1}}{2\lambda} \left(\xi^{\frac{1}{\lambda}} + B \right)^{-\frac{3}{2}} \left[(n-1)^\lambda - \xi \right] \right\}. \quad (15)$$

Recall that A , B , and ξ , defined via (8), (9), and (11), are constants, independent of λ and dependent only on the number n of carbon atoms in the alkane molecule considered. Therefore, the coefficients α , β , and γ in (5) can be viewed as functions (having a rather compli-

Table 1. The critical value of the parameter λ , denoted by λ_0 and obtained by solving the equation $\gamma(\lambda) = 0$, with $\gamma(\lambda)$ given by (15), as well as the coefficients α_0 and β_0 occurring in (16); for details see text.

n	λ_0	α_0	β_0
7	-0.419	-0.65615	-0.17681
8	-0.424	-0.69286	-0.18546
9	-0.428	-0.72798	-0.19426
10	-0.431	-0.76159	-0.20308
11	-0.433	-0.79384	-0.21187
12	-0.435	-0.82484	-0.22059
13	-0.437	-0.85471	-0.22926
14	-0.439	-0.88356	-0.23783
15	-0.440	-0.91146	-0.24635
16	-0.441	-0.93851	-0.25478
17	-0.442	-0.96478	-0.26309
18	-0.443	-0.99030	-0.27142
19	-0.444	-1.01517	-0.27962
20	-0.445	-1.03940	-0.28777
21	-0.446	-1.06305	-0.29589
22	-0.446	-1.08616	-0.30389
23	-0.447	-1.10875	-0.31190
24	-0.447	-1.13087	-0.31982
25	-0.448	-1.15253	-0.32769
26	-0.449	-1.17379	-0.33546
27	-0.449	-1.19462	-0.34326
28	-0.449	-1.21507	-0.35103
29	-0.450	-1.23517	-0.35870
30	-0.450	-1.25491	-0.36639

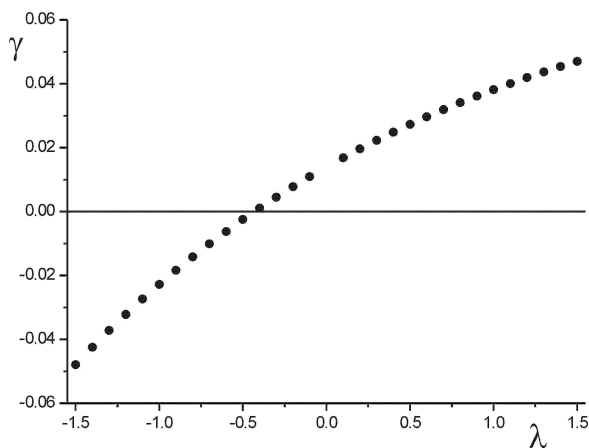


Fig. 4. Dependence of the coefficient γ in (5) on the parameter λ , in the (typical) case of $n = 10$. At $\lambda = -0.43$ this coefficient changes sign, resulting in the inversion shown in Fig. 1; for details see Table 1.

cated algebraic form) of the variable λ , dependent, in addition, on the parameter n . The λ -dependence of α , β , and γ is illustrated in Figs. 2, 3, and 4, for decanes ($n = 10$).

1. Discussion

In order to understand the λ -dependence of α and β in (5), one should note that for $\lambda = 0$ the variable Wiener index of all alkanes C_nH_{2n+2} is equal to $n - 1$. Therefore, when the Zenkevich index is plotted versus the variable Wiener index at $\lambda = 0$, a vertical line is obtained. In other words, the coefficients α and β , viewed as functions of λ , possess a singularity at $\lambda = 0$. This feature is well reproduced by the expressions (13) and (14), cf. Figs. 2 and 3.

As seen from the examples given in Fig. 1, the mutual position of the (U, W_λ) -lines (with regard to their v -values) differs for different values of λ . The type of the ordering of these lines depends on the sign of the coefficient γ in (5). As seen from Fig. 4, at a certain value of λ , the function $\gamma = \gamma(\lambda)$ changes sign, i. e., it is equal to zero. This "critical" value is denoted by λ_0 . For $\lambda \approx \lambda_0$, the relation between the Zenkevich and the variable Wiener indices becomes independent of the number of methyl groups. In other words, at $\lambda \approx \lambda_0$

the (U, W_λ) -lines, pertaining to different values of v , coalesce. Then (and only then) a simple linear correlation between U and W_λ can be observed [14].

Thus, our analysis reveals that the relation between the Zenkevich and the variable Wiener indices should be best considered when $\lambda = \lambda_0$. In that case this relation is simplified to:

$$U \approx -\alpha_0 W_{\lambda_0} + \beta_0, \quad (16)$$

where $\alpha_0 = \alpha(\lambda_0)$ and $\beta_0 = \beta(\lambda_0)$.

The values of λ_0 , α_0 , and β_0 for the chemically relevant values of n are given in Table 1.

The definition of the variable Wiener index, (4), is much simpler than that of the Zenkevich index, (2). Consequently, the dependence of W_λ on the molecular structure is easier to envisage than the analogous dependence of U . In view of this, (5) and, especially, (16) make the study of the intramolecular (mainly vibrational) energy of alkanes, and its dependence on the molecular structure, somewhat easier task.

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