On the relation between Zenkevich and Wiener indices of alkanes

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Abstract: A relatively complicated relation was found to exist between the quantity U, recently introduced by Zenkevich (providing a measure of internal molecular energy), and the Wiener index W (measuring molecular surface area and intermolecular forces). We now report a detailed analysis of this relation and show that, in the case of alkanes, its main features are reproduced by the formula $U = -\alpha W + \beta + \gamma \nu_1$; where ν_1 is the number of methyl groups, and α, β and γ are constants, depending only on the number of carbon atoms. Thus, for isomeric alkanes with the same number of methyl groups, U and W are linearly correlated.

Keywords: Zenkevich index, Wiener index, alkanes.

INTRODUCTION

A few years ago Igor Zenkevich introduced a quantity U, which can easily be computed from the structural formula of an organic molecule (or, what is the same, from the respective molecular graph), and which provides a reliable estimate of the internal molecular energy.[1–6] The way in which U is related to the vibrational energy (and which approximations are used) is outlined in detail elsewhere.[7,8] In what follows we refer to U as the *Zenkevich index*.

For an alkane of the formula C_nH_{2n+2}, the Zenekvich index is given by

$$U = \sum \sqrt{\frac{(C+2H)n+2H}{[(C+2H)n_1+H][(C+2H)n_2+H]}} \qquad (1)$$

where the notation used is same as in a previous paper[8] – H and C stand, respectively, for the atomic masses of hydrogen and carbon ($H = 1.0$, $C = 12.0$), n_1 and n_2 are the number of carbon atoms on the two sides of a carbon–carbon bond ($n_1 + n_2 = n$), and the summation goes over all carbon–carbon bonds. The quantities n_1 and n_2 can be interpreted as the number of vertices lying on the two sides of an edge of the respective molecular graph,[9] in which case the summation goes over all edges of this molecular graph.

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In what follows, without loss of generality, it is assumed that $n_1 \leq n_2$.

From a physico-chemical point of view it is somewhat surprising that there exists any relation between the Zenkevich index (which represents an approximate measure of internal molecular energy) and the Wiener index W (a molecular-graph-based structure descriptor, known to be proportional to the molecular surface area and, consequently, to the magnitude of intermolecular van der Waals type interactions[10,11]). Such a relation can be anticipated by knowing that in the case of alkanes W obeys the relation[12]

$$W = \sum n_1 n_2 \tag{2}$$

where, again, the summation ranges over all edges of the molecular graph.

Initially[6,7] it was believed that the relation between U and W is linear. However, this (false) conclusion was based on the examination of alkanes with relatively small number of carbon atoms ($n \leq 7$). When the considerations were extended to larger alkane isomers[8] ($n \geq 9$), a much more complex pattern emerged. A typical example of this kind is shown in Fig. 1.
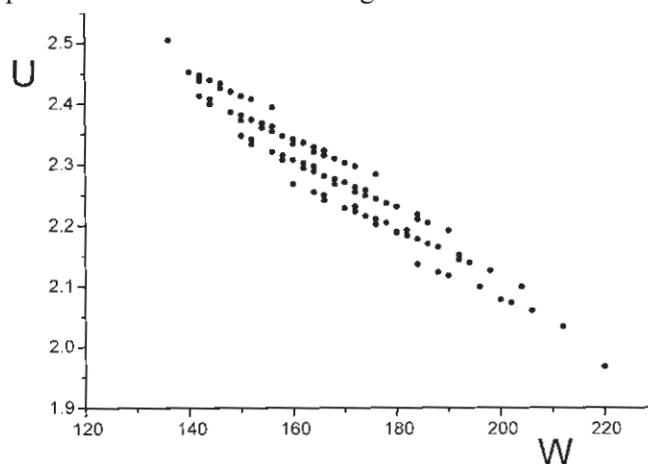

Fig. 1. The Zenkevich indices (U) of the 159 isomeric undecanes ($n = 11$) *vs.* the corresponding Wiener indices (W).

A REGULARITY FOR THE RELATION BETWEEN U AND W

As seen from Fig. 1, the (U, W)-points form several lines. These lines 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 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 by testing all alkanes with up to $n = 15$ carbon atoms. Not a single violation was detected. The results obtained for $7 \leq n \leq 12$ are collected in Table I.[13]

From Table I it can be seen that, for a fixed value of n, the slopes of the regression lines (a) are remarkably similar, implying that these lines are almost parallel. The respective intercepts (b) increase with increasing values of ν_1, but this is a much less accurate relationship, which hardly could be characterized as linear. Thus, analysis reveals that the claim that the (U, W)-lines are equidistant is acceptable only as a rough approximation.

TABLE I. The parameters of the lines $U = -aW + b$, drawn (by means of least–squares fitting) through the (U, W)-points corresponding to isomeric alkanes with n carbon atoms, $7 \le n \le 12$, and ν_1 methyl groups.[13] N and R are the number of data points and the corresponding correlation coefficient, respectively. Only the cases $N \ge 2$ were considered.

n	ν_1	N	a	b	R
7	3	3	0.0092	1.94	– 0.999996
7	4	4	0.0092	1.97	– 0.999996
8	3	4	0.0071	2.18	– 0.9997
8	4	8	0.0071	2.21	– 0.9997
8	5	4	0.0071	2.24	– 0.998
9	3	5	0.0056	2.40	– 0.9993
9	4	14	0.0057	2.44	– 0.9992
9	5	11	0.0056	2.47	– 0.998
9	6	4	0.0055	2.48	– 0.993
10	3	7	0.0045	2.61	– 0.998
10	4	23	0.0046	2.67	– 0.998
10	5	27	0.0046	2.70	– 0.997
10	6	15	0.0046	2.73	– 0.994
10	7	2	0.0038	2.68	– 1.0
11	3	8	0.0037	2.81	– 0.997
11	4	38	0.0038	2.88	– 0.997
11	5	57	0.0039	2.92	– 0.996
11	6	44	0.0038	2.96	– 0.984
11	7	12	0.0037	2.97	– 0.987
12	3	10	0.0031	3.01	– 0.996
12	4	54	0.0032	3.08	– 0.995
12	5	113	0.0033	3.14	– 0.994
12	6	117	0.0033	3.18	– 0.993
12	7	51	0.0032	3.21	– 0.991
12	8	9	0.0031	3.22	– 0.986

Anyway, the high values for the correlation coefficients, obtained in all cases, clearly confirm that it is justified to separately consider the data points for fixed values of n and ν_1, that within each such group of data points the Zenkevich and the Wiener index are linearly correlated, and that the number of methyl groups is the most important structural parameter which, in addition to n, influences the relation between U and W.

The above outlined, empirically established, regularities are corroborated by a mathematical analysis, based on Eqs. (1) and (2).

MATHEMATICAL ANALYSIS OF THE ZENKEVICH INDEX

In order to simplify our notation we use the abbreviations

$$A = \frac{\sqrt{(C+2H)n+2H}}{C+2H} \tag{3}$$

and

$$B = \frac{Hn}{C+2H} + \left(\frac{H}{C+2H}\right)^2 \tag{4}$$

by means of which Eq. (1) becomes

$$U = A \sum \frac{1}{\sqrt{n_1 n_2 + B}} . \tag{5}$$

The summation of the right-hand side of Eq. (5) goes over all edges of the respective molecular graph. Bearing in mind the empirical facts outlined in the previous section, this sum is now divided into two parts: the first pertaining to edges one endpoint of which is a vertex of degree one, and the other embracing all other edges. There are ν_1 edges one endpoint of which is a vertex of degree one, and for them $n_1 = 1$, $n_2 = n - 1$. Consequently,

$$U = \frac{A\nu_1}{\sqrt{n-1+B}} + A \sum_* \frac{1}{\sqrt{n_1 n_2 + B}} \tag{6}$$

where $\sum_*$ indicates summation over edges of the molecular graph connecting vertices the degrees of which are greater than one. There exist $n - 1 - \nu_1$ such edges. For these edges, $2 \leq n_1 \leq n/2$. Therefore the product $n_1 n_2 = n_1(n - n_1)$ assumes values from the interval $(2n - 4, n^2/4)$.

In view of Eqs. (5) and (6) we consider the function $1/\sqrt{x+B}$ and expand it into a power series around the point

$$\xi = \frac{1}{2}(2n - 4 + n^2/4). \tag{7}$$

Clearly, ξ is chosen to be the center of the above specified interval $(2n - 4, n^2/4)$. By direct calculation we get

$$\frac{1}{\sqrt{x + B}} = (\xi + B)^{-1/2} - \frac{1}{2}(\xi + B)^{-3/2}(x - \xi) + \text{higher order terms.}$$

Neglecting the higher order terms, proportional to $(x - \xi)^2$, $(x - \xi)^3$, *etc.* one arrives at

$$U \approx \frac{Av_1}{\sqrt{n - 1 + B}} + \frac{A}{2}\sum_{*}(3\xi + 2B)(\xi + B)^{-3/2} - \frac{A}{2}\sum_{*}(\xi + B)^{-3/2} n_1 n_2. \qquad (8)$$

The summand in the second term on the right-hand side of Eq. (8) is same for all edges, and therefore

$$\sum_{*}(3\xi + 2B)(\xi + B)^{-3/2} = (3\xi + 2B)(\xi + B)^{-3/2}(n - 1 - v_1).$$

Because of

$$\sum_{*} n_1 n_2 = \sum n_1 n_2 - (n - 1)v_1 = W - (n - 1)v_1$$

one obtains

$$\sum_{*}(\xi + B)^{-3/2} n_1 n_2 = (\xi + B)^{-3/2}[W - (n - 1)v_1].$$

TABLE II. The coefficients occurring in Eq. (9). Their values are in remarkably good agreement with the data given in Table I. In particular, $a \approx \alpha$ and $b \approx \beta + \gamma v_1$.

n	α	β	γ
7	0.0090	1.96	0.024
8	0.0069	2.17	0.029
9	0.0054	2.37	0.034
10	0.0044	2.56	0.038
11	0.0036	2.74	0.042
12	0.0030	2.92	0.046
13	0.0025	3.09	0.050
14	0.0022	3.26	0.053
15	0.0019	3.42	0.056

When all this is substituted back into Eq. (8), the final result is obtained:

$$U \approx -\alpha W + \beta + v_1 \gamma \qquad (9)$$

where

$$\alpha = \frac{A}{2}(\xi + B)^{-3/2}$$

$$\beta = \alpha(n-1)(3\xi + 2B)$$

$$\gamma = A/\sqrt{n-1+B} - \alpha(3\xi + 2B - n + 1)$$

and where A, B, and ξ are defined *via* Eqs. (3), (4), and (7), respectively. Although of a complicated algebraic form, the coefficients α, β, and γ in Eq. (9) depend only on the number n of carbon atoms in the alkane molecule considered. The numerical values of these coefficients are given in Table II.

DISCUSSION

Equation (9) explains all the main features of the relation between the Zenkevich and the Wiener index. The computed values of the coefficients α, β, and γ are in good quantitative agreement with what was found by direct calculation (*cf.* Tables I and II). This additionally cofirms that the approximations adopted in our mathematical analysis of the Zenkevich index were justified.

Formula (9) predicts that the (U, W)-points, pertaining to different values of ν_1, form separate lines, and that these lines are mutually parallel. This is in full agreement with our numerical testings. The other prediction, that these parallel lines are equidistant (with distance being equal to γ) agrees with empirical findings to a lesser extent.

Furthermore, we have observed that the quality of the linear correlation between the (U, W)-points is worsened as the number of carbon atoms increases. This indicates that in the case of very large alkane isomers, with $n \geq 15$ carbon atoms, structural details other than just the count of methyl groups need to be taken into account. The elucidation of these fine details of the correlation between the Zenkevich and the Wiener index remains a task for the future.

И З В О Д

О ОДНОСУ ИЗМЕЂУ ЗЕНКЕВИЧЕВОГ И ВИНЕРОВОГ ИНДЕКСА АЛКАНА

ИВАН ГУТМАН, БОРИС ФУРТУЛА, БИЉАНА АРСИЋ и ЖАРКО БОШКОВИЋ

Природно-математички факултет у Крагујевцу и Природно-математички факултет у Нишу

Раније је нађено да између величине U, коју је недавно увео Зенкевич (и која представља меру унутрашње молекулске енергије), и Винеровог индекса W (која мери површину молекула и међумолекулске силе) постоји релативно компликована релација. Детаљним испитивањем те релације установили смо да су, у случају алкана, њене најважније карактеристике описане формулом $U = -\alpha W + \beta + \gamma\nu_1$; где је ν_1 број метил-група, док су α, β и γ константе које зависе искључиво од броја угљеникових атома. У случају изомерних алкана са истим бројем метил- група, U и W су линеарно корелирани.

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13. Results analogous to those presented in Table I, for n = 13, 14, 15, are available from the authors (B. F.) upon request.