

Wiener-type indices and internal molecular energy*

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Abstract: In earlier studies it was established that internal molecular energies (E_{int}) of alkanes can be reproduced, in an approximate yet reliable manner, by means of a molecular-graph-based structure-descriptor U . It was also established that U is linearly correlated with the Wiener index W . We now show that the correlation between U and W is more complicated than earlier expected, and that it cannot be represented by a single line. We also show that a very good linear correlation exists between U and a modified version $W_m(\lambda)$ of the Wiener index, which is thus more suitable for modeling E_{int} than the ordinary Wiener index.

Keywords: Wiener index, modified Wiener index, internal molecular energy, alkanes.

INTRODUCTION

One of the present authors established recently a linear relation between gas chromatographic retention indices and internal molecular energies (E_{int}).^{1–6} Furthermore, correlations were found between retention indices, boiling points, E_{int} , and various topological indices (in particular, Wiener and Hosoya indices).⁶ For these reasons the knowledge of the actual value of E_{int} , at a chosen temperature, is of importance for the elucidation of structure-property relations of organic compounds.

The E_{int} -values can be obtained by means of pertinent computer-aided methods (described in detail below), but the calculations required are lengthy and difficult, and can be accomplished only for a limited number of molecules. In view of this it was desirable to find a shorter and easier procedure for gaining information about internal molecular energy. This was achieved by means of an auxiliary quantity U (whose definition is given below).^{3–6} At least in the case of alkanes, U can be directly computed from the molecular graph (*i.e.*, from the structural formula).

A mathematical analysis of U revealed⁷ that it is related to the Wiener index W . In this work, we continue these studies and show that the relation between U and W is more complicated than earlier believed, and that a more direct relation exists between U and a modi-

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fied version $W_m(\lambda)$ of the Wiener index. In this work we also correct some computational errors from our previous paper.⁷

COMPUTING THE INTERNAL MOLECULAR ENERGY

The general principles of computing the total internal molecular energy E_{int} are well known.⁸ The calculation of E_{int} at a chosen temperature requires the computer modeling of the intramolecular rotational and vibrational processes. For this the *HyperChem* software was employed.

Unfortunately, in order to obtain reliable E_{int} -values, very long computational times are needed. Another problem is that the molecule considered usually possesses several stable conformations (of different energies). In "unlucky" cases the geometry optimization converges to a stable, but not the most stable, conformation and then the entire analysis of molecular dynamics is done on a false object.

The intramolecular energies of all isomeric heptanes, are given in Table I at 400 K. The respective calculations were done by means of the *HyperChem 5.1* software, employing the following options:

- simulation temperature 400 K; (by using different values for this temperature the regularities observed remain the same);
- step size – 0.0005 ps;
- bath relaxation time – 0.1 ps;
- data collection period – 10 time steps;
- overall run time not to exceed 20 ps.
- The initial "heating" of the molecule to the chosen temperature may effect the accuracy of calculation. In order to prevent this, we interrupted the calculation after 1–1.5 ps and then resumed it with the option RESTART.

Note that, as usual in the data presentation in all versions of *HyperChem*, ps means picoseconds (10^{-12} s) of intramolecular vibrations and rotations in real molecular time.

TABLE I. Internal molecular energy (E_{int} , in kJ/mol) at 400 K, the auxiliary quantity U (defined via Eq. (1)) and the Wiener index W of the isomeric alkanes C_7H_{16} ; for details see text

Isomer	E_{int}	U	W
<i>n</i> -Heptane	259.0 ± 7.5	1.405	56
2-Methylhexane	265.3 ± 5.4	1.465	52
3-Methylhexane	266.9 ± 7.5	1.483	50
2,2-Dimethylpentane	273.6 ± 7.5	1.543	46
2,3-Dimethylpentane	277.8 ± 7.5	1.543	46
2,4-Dimethylpentane	275.7 ± 7.1	1.524	48
3,3-Dimethylpentane	279.9 ± 7.5	1.561	44
3-Ethylpentane	272.8 ± 7.1	1.501	48
2,2,3-Trimethylbutane	284.9 ± 7.5	1.602	42

The data given in Table I differ somewhat from those reported earlier.⁷ In particular, the earlier value for E_{int} of 2-methylhexane (namely 275.3 ± 7.1 kJ/mol) is now corrected to 265.3 ± 5.4 kJ/mol. The error committed before⁷ is, most probably, caused by an inappropriately determined conformation.

The correct U -values of 3-methylhexane, 2,2- and 2,3-dimethylpentane are 1.483, 1.543 and 1.543, respectively, and not 1.482, 1.546 and 1.546, as used in the earlier work.⁷

THE TOPOLOGICAL INDEX U AND ITS RELATION TO INTERNAL MOLECULAR ENERGY

In order to overcome the above specified computational difficulties, a drastic, yet reasonable, simplification was proposed.³⁻⁵ Its quality may be judged from Fig. 1.

The approximation is based on the assumption that the intramolecular rotational energy as well as a certain part of the intramolecular vibrational energy are (nearly) the same for all members of a group of isomers. Therefore the variable part of E_{int} comes only from certain vibrational modes, in particular from the stretching vibrations of the carbon-carbon bonds. This ultimately leads to the expression

$$U = \sum \sqrt{\frac{M}{M_1 M_2}} \quad (1)$$

which, multiplied by a pertinently chosen constant, is supposed to be equal to the variable (and thus the only interesting) part of E_{int} . The actual value of this constant is immaterial as far as correlations between U and other properties of the respective compounds are concerned.

In formula (1) M is the mass of the molecule considered (expressed in atomic mass units), whereas M_1 and M_2 are the masses of the fragments on the two sides of a vibrating carbon-carbon bond; $M_1 + M_2 = M$. The summation in (1) goes over all carbon-carbon bonds. More details on Eq. (1) can be found elsewhere.⁷

In the case of alkanes with n carbon atoms, formula (1) becomes

$$U = \sqrt{(C + 2H)n + 2H} \sum \{[(C + 2H)n_1 + H][(C + 2H)n_2 + H]\}^{-1/2} \quad (2)$$

where H and C stand for the relative atomic masses of hydrogen and carbon ($H = 1.0$, $C = 12.0$), and where n_1 and n_2 are the number of carbon atoms on the two sides of the vibrating carbon-carbon bond; $n_1 + n_2 = n$.

The correlation between E_{int} and U for the case of the heptane isomers ($n = 7$) is shown in Fig. 1. This correlation is linear and reasonably good, showing that for the purpose of quantitative structure-property relations (QSPR) U may be used instead of E_{int} .

In earlier works^{6,7} it was claimed that E_{int} , and therefore also U , are linearly correlated with the Wiener index W . As some of the previously reported⁷ data for E_{int} and U have been corrected, the plots of E_{int} vs. W and U vs. W for isomeric heptanes ($n = 7$) are shown again. Indeed, Fig. 3 gives the impression that the correlation between U and W is linear and of very good quality, implying that internal energy and Wiener index are simply and directly related.⁷

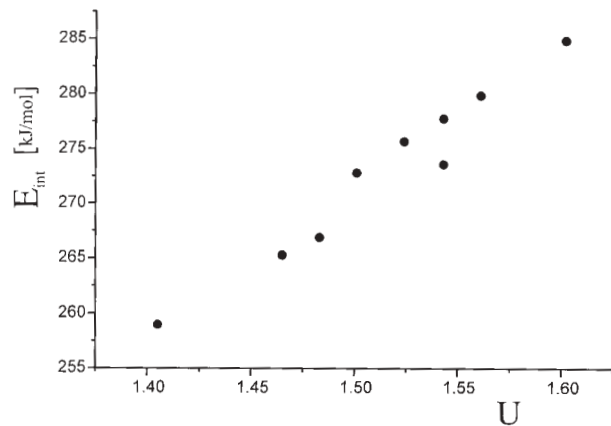


Fig. 1. Correlation between the internal energy (E_{int}) and its approximation U , Eqs. (1) and (2), in the case of isomeric heptanes ($n = 7$). Least-squares fitting yields $E_{\text{int}} = (134 \pm 11) U + (69 \pm 16)$ with correlation coefficient $R = 0.979$.

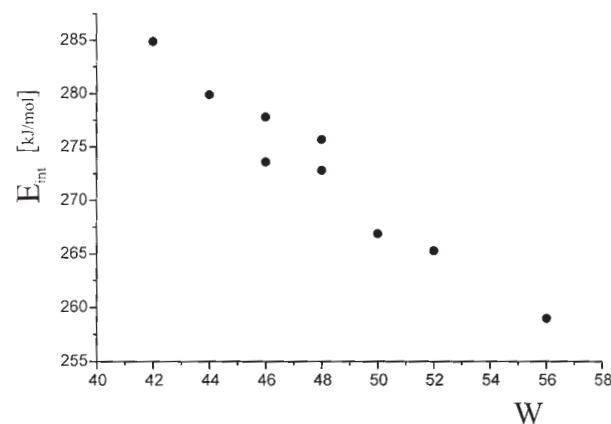


Fig. 2. Correlation between the internal energy (E_{int}) and the Wiener number W for isomeric heptanes. The respective regression line reads: $E_{\text{int}} = (-1.84 \pm 0.16) W + (361.1 \pm 7.6)$ with $R = -0.975$.

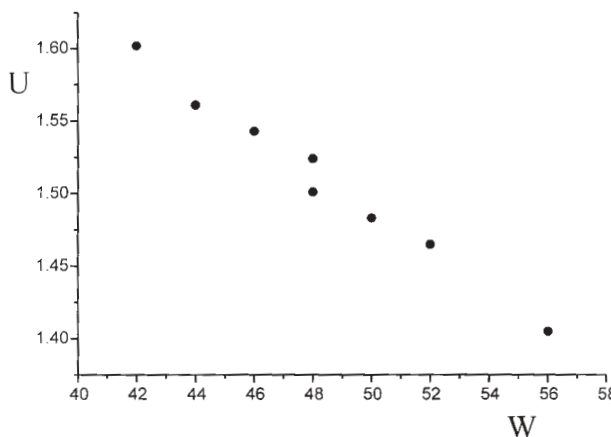


Fig. 3. Correlation between U and W in the case of isomeric heptanes ($n = 7$). The respective regression line reads: $U = (-0.0136 \pm 0.0006) W + (2.17 \pm 0.03)$ with $R = -0.992$. This very good linear correlation between U and W disappears for greater values of n , see Fig. 4.

Unfortunately, for larger values of n (or, more precisely, for all $n \geq 8$) the relation between U and W turns out to be much more complicated. This is illustrated in Fig. 4. Direct

checking revealed that the data points are clustered according to the number of methyl groups (*i.e.*, according to the number of pendant vertices in the molecular graph). Within each cluster, a linear correlation is noticed, but points pertaining to different clusters lie on different lines.

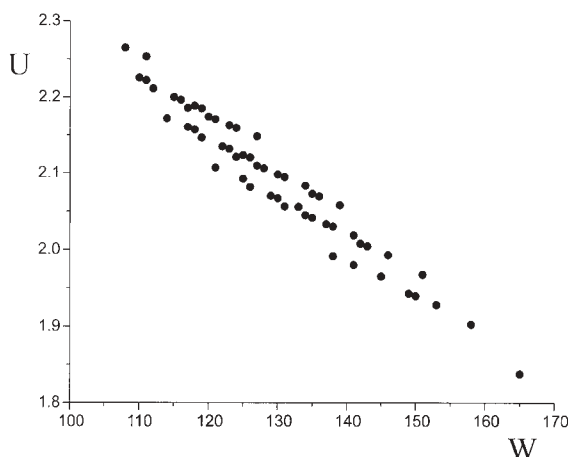


Fig. 4. The U -values of isomeric decanes ($n = 10$) plotted versus the respective W -values.

WIENER INDEX AND MODIFIED WIENER INDEX

Scores of papers in the chemical literature are concerned with the theory and physico-chemical applications of the Wiener index (W), the oldest graph-based molecular structure-descriptor. Interested readers are referred to the articles published in the special issues of *MATCH - Communications in Mathematical and Computer Chemistry* (No. 35 (1997)) and of *the Journal of the Serbian Chemical Society* (Vol. 62, No 3 (1997)), devoted to the 50th anniversary of W , as well as to some more recent works^{7,9-13} and the references quoted therein.

For the present considerations it suffices to recall that for all acyclic systems

$$W = \sum (n_1 \cdot n_2) \quad (3)$$

a result discovered by Wiener himself in 1947.¹⁴ The notation used in Eq. (3) is the same as in Eq. (2). However, the quantities n_1 and n_2 may be interpreted also in graph-theoretical terms:¹⁵ they count the vertices, lying on the two sides of an edge, and the summation in (3) goes over all edges of the respective (molecular) graph.

Recently, Eq. (3) was modified, as¹⁶

$$W_m = \sum (n_1 \cdot n_2)^{-1}$$

resulting in the so-called “modified Wiener index”. The logical next step in the same direction¹⁷⁻²¹ is to introduce a variable-exponent version of this quantity, namely

$$W_m(\lambda) = \sum (n_1 \cdot n_2)^\lambda \quad (4)$$

Clearly, for $\lambda = +1$ and $\lambda = -1$ the right-hand side of Eq. (4) reduces to the ordinary and the modified Wiener index, respectively.

THE MODIFIED WIENER INDEX AND ITS RELATION TO INTERNAL MOLECULAR ENERGY

The advantage of defining the variable-exponent modified Wiener index $W_m(\lambda)$ is seen from the following.

In formula (2) the term $H = 1$ is at least one order of magnitude smaller than $(C + 2H)n_1 = 14n_1$ and $(C + 2H)n_2 = 14n_2$, and can thus be neglected. Then, in view of Eq. (4), we arrive at

$$U \approx \frac{\sqrt{(C + 2H)n + 2H}}{C + 2H} W_m(-1/2) \quad (5)$$

or, more precisely, at the inequality $U < \sqrt{(C + 2H)n + 2H}/(C + 2H) W_m(-1/2)$.

The quality of the approximation (5) is extraordinarily good. This is seen from the data collected in Table II and the example shown in Fig. 5.

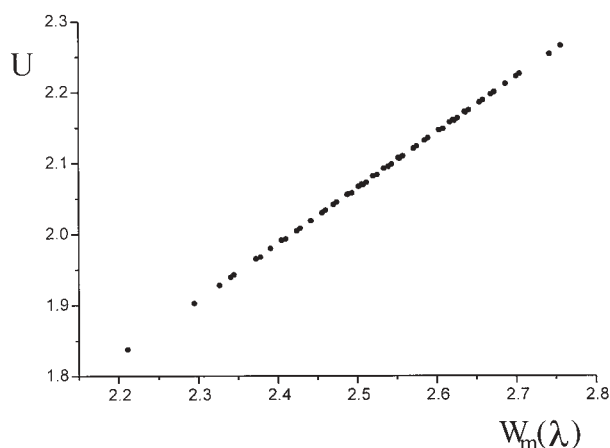


Fig. 5. Correlation between U and $W_m(\lambda)$, $\lambda = -1/2$ in the case of isomeric decanes. The respective regression line reads: $U = (0.7854 \pm 0.0008)W_m(\lambda) - (0.101 \pm 0.002)$ with $R = 0.99996$. This excellent linear correlation between U and the modified Wiener index should be compared with the correlation between U and the ordinary Wiener index shown in Fig. 4. Note that by setting $\lambda = \lambda_{\text{opt}} = -0.43$ the quality of the correlation between U and $W_m(\lambda)$ is further improved, *cf.* Table II.

TABLE II. Correlation coefficients (R) for the correlation between U and $W_m(\lambda)$ for the sets of all isomeric alkanes with n carbon atoms. The R -values are given for $\lambda = -1/2$ and for $\lambda = \lambda_{\text{opt}}$ for which R (considered as a function of λ) attains its maximum.

n	R for $\lambda = -0.5$	λ_{opt}	R for $\lambda = \lambda_{\text{opt}}$
6	0.999995	-0.41	0.99999994
7	0.99998	-0.42	0.99999996
8	0.99998	-0.42	0.99999994
9	0.99996	-0.43	0.99999993
10	0.99996	-0.43	0.99999995

The value $\lambda = -0.5$ is not optimal, as far as the quality of the correlation between U and $W_m(\lambda)$ is concerned. This correlation may be further improved by allowing the exponent λ to vary. In Fig. 6 is shown that the correlation coefficient R , viewed as a function of λ , has a well-pronounced maximum at $\lambda = \lambda_{\text{opt}} \approx -0.4$. The optimal values of the exponent λ and the corresponding correlation coefficients are given in Table II.

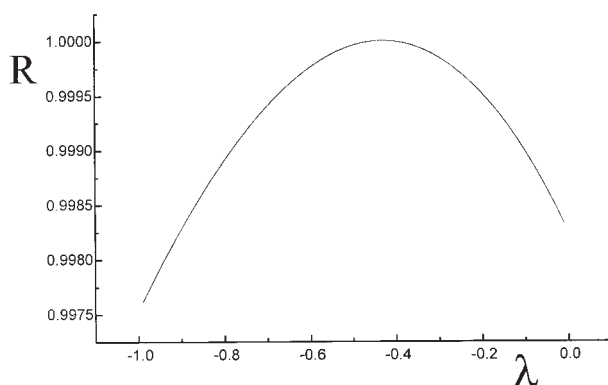


Fig. 6. The λ -dependence of the correlation coefficient R for the correlation between U and $W_m(\lambda)$ in the case of isomeric decanes ($n = 10$). Analogous curves are obtained also for other values of n , and they always possess a (unique) maximum near $\lambda = -0.5$. The exact value of $\lambda = \lambda_{\text{opt}}$ for which R is maximal is found in Table II.

Based on the above theoretical and computational result, we conclude that the modified Wiener index $W_m(\lambda)$ for $\lambda = -0.5$ (and even more for $\lambda \approx -0.4$) represents precisely the same properties of the underlying molecules as the earlier introduced quantity U . Consequently, $W_m(\lambda)$ may be used for the approximate evaluation of the internal molecular energy E_{int} , at least with the same success as U . In other words, the modified Wiener index contains information on the dynamics of organic molecules, in particular on their vibrational models.

ИЗВОД

ИНДЕКСИ ВИНЕРОВОГ ТИПА И УНУТРАШЊА МОЛЕКУЛСКА ЕНЕРГИЈА

ИВАН ГУТМАН, ДУШИЦА ВИДОВИЋ, БОРИС ФУРТУЛА И ИГОР Г. ЗЕНКЕВИЧ

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Ранија проучавања су показала да се унутрашња енергија (E_{int}) алкана може, као добра апроксимација, репродуковати помоћу структурног дескриптора U који се израчунава из молекулског графа. Такође је било установљено да је U линеарно корелиран са Винеровим индексом W . У овом раду показано је да је корелација између U и W компликованија него што се раније сматрало и да се не може приказати једном јединственом линијом. Такође показујемо да постоји веома добра линеарна корелација између U и једне модификације $W_m(\lambda)$ Винеровог индекса, који је због тога погоднија за моделовање E_{int} него оригинални Винеров индекс.

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