SOME TOPOLOGICAL INDICES DERIVED FROM THE $v^m d^n$ MATRIX. PART 4. THE LARGEST EIGENVALUES OF THE "MEAN DEGREE OF VERTICES " MATRICES AS TOPOLOGICAL INDICES OF THE BI_M-TYPE

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Abstract

The largest eigenvalues of the "mean degree of vertices" matrices form a group of the BI_M type indices. They are good indices for indexing the influence of the size of molecule, but less good as branching indices. True but degenerated branching indices are the indices $A_\lambda(0)$, $G_\lambda(0)$, $Ln_\lambda(0)$, $RA_\lambda(0)$, $RG_\lambda(0)$, $RLn_\lambda(0)$, and $RZg_\lambda(0)$. Regular sequences of isomers on increasing branching have only the indices $RA_\lambda(-1)$, $RG_\lambda(-1; -2)$, and $RLn_\lambda(-1)$.

Introduction

One of the most useful topological indices besides the Wiener[1] index W is the Randić index χ.[2,3] In view of the formalism of the $v^m d^n$ type of matrix,[4] the Wiener index W is derived by summation of the elements of the matrix having the nondiagonal elements $\mathbf{g}_{ij} = (v_i \times v_j)^0 \times d_{ij}^1$, whereas the Randić index χ is derived by summation of the elements of the matrix having the nondiagonal elements $\mathbf{g}_{ij} = (v_i \times v_j)^{-1/2} \times d_{ij}^{-\infty}$, where v is the degree of vertex and d_{ij} is the shortest distance from vertex *i* to vertex *j*.

Randić index χ can be considered also as a "reciprocal geometric mean of the degree of adjacent vertices" type of summation-derived indices. Looking at the index χ from this point of view, there arises the question whether there exist also some other good indices of the "mean degree of vertices" type having d_{ij} raised to other values of exponent. In a previous paper[5] we considered the summation-derived "mean degree of vertices" type indices. In present paper we consider the indices, which are the largest eigenvalues of the same matrices.

Data and methods

The structures of alkanes are presented in shorthand, e.g. Hp is *n*-heptane, Oct is *n*-octane, 223M5 is 2,2,3-trimethylpentane, 3Et2M5 is 3-ethyl-2-methylpentane, etc. The other terms are explained on 2,2-, 2,3- and 2,5-dimethyl hexane (22M6, 23M6 and 25M6) as examples. The two branches (the number of branches, *Nbr* = 2) in 22M6 are

positioned on a quaternary carbon (2*q*) placed on the periphery (*per*) of the molecule. The two branches in 23M6 and 25M6 are positioned on tertiary carbons (2*t*). Regarding the separation between branches (*s*), in 23M6 the branches are adjacent (*adj*) and those in 25M6 are distant (*dist*). The branches on carbons No. 2 and 5 are placed on the periphery of the molecule, and the one on carbon No. 3 is placed near the centre (*ctr*) of the molecule. 25M6 is symmetric, whereas 22M6 and 23M6 are not.

Since we only consider alkanes, we use the words "vertex" and "carbon" as synonyms that reflect different contexts. The use of "vertex" implies the graph-theoretical consideration, whereas the use of "carbon" implies the chemical consideration of the same thing. Their number is given as N_C or N_v, respectively.

The susceptibility for the increase in carbon number, $S_{i,i+1}$, and the susceptibility for branching, $S_{n,i}$, is defined as the normalised difference of the indices' or properties' values.[4,6] As criteria regarding the degree of branching is used the intuition[7] as well as the *Methane based* definition and the *n-Alkane based* definition[8] of branching.

The physicochemical properties

The data for the boiling point (BP), density (d), the critical data Tc, Pc, Vc, Zc, αc, and dc, as well as the standard enthalpy of formation for the ideal gas (ΔHf°g), the enthalpy of vaporisation (ΔHv), the Antoine constants A, B, and C, as well as the Pitzer's acentric factor (ω) and the refractive index (n_D) were taken from the CRC Handbook[9] or from Lange's Handbook[10]. The data for the liquid molar volume (Vm), the ratios Tc^2/Pc and Tc/Pc used instead of the van der Waals parameters a_0 and b_0, the ratio BP/Tc (reduced BP), and the molar refraction (MR) were calculated from data presented in the handbooks. The data for Motor Octane Numbers (MON) was taken from Pogliani[11] and Ren,[12] those for vapour pressure (logVP) from Goll and Jurs,[13] and those for the entropy (S) and quadratic mean radius (R^2) from Ren.[12]

Results and discussion

The "mean degree of vertices" matrix and its largest eigenvalue as a topological index

The $v^m d^n$ matrix[4] is a matrix having the main diagonal elements, $\mathbf{g_{ii}} = 0$, and all the others, $\mathbf{g_{ij}}$ $(i \neq j) = v_j^{\mathbf{m}} \times d_{ij}^{\mathbf{n}}$, where v_j is the degree of vertex j (in alkanes it is the number of the C-C bonds which the carbon in question is involved in) and d_{ij} is the shortest distance from vertex i to vertex j (in alkanes it is the lowest number of bonds between the carbons in question). A more general type of the $v^m d^n$ matrix is the matrix having the elements $\mathbf{g_{ij}}$ $(i \neq j) = v_i^{\mathbf{a}} \times v_j^{\mathbf{b}} \times d_{ij}^{\mathbf{c}}$. A representative of the indices, summation-derived from this matrix, is one of the most useful indices, the Randić[2] index χ, having the exponents $\mathbf{a} = -{}^1/_2$, $\mathbf{b} = -{}^1/_2$, $\mathbf{c} = -\infty$, whereas its zero order variant, the index ${}^0\chi$, has the exponents $\mathbf{a} = -{}^1/_2$, $\mathbf{b} = 0$, $\mathbf{c} = -\infty$.

The Randić[2] index χ is thus a "reciprocal geometric mean of the degree of adjacent vertices" index,[4] derived from the matrix having the non-diagonal elements $\mathbf{g_{ij}}$ $(i \neq j) = (v_i \times v_j)^{-1/2} \times d_{ij}^{-\infty}$. Due to the great success of this index, it seemed plausible to test also other indices derived by using other types of the "mean of the degree of vertices", denoted also as "mean(v_i,v_j)", where $\mathbf{g_{ij}}$ $(i \neq j) = (\text{"mean}(v_i,v_j)\text{"}) \times d_{ij}^{\mathbf{c}}$.

On the one hand, the indices were derived using as the "mean(v_i,v_j)":

- The arithmetic mean (average) of the degrees of vertices, $(v_i+v_j)/2$, the indices being labelled as A_Σ or $A_\Sigma(c)$,
- The geometric mean, $(v_i \times v_j)^{1/2}$, the indices being labelled as G_Σ or $G_\Sigma(c)$,
- The logarithmic mean $(v_i-v_j)/(\ln v_i - \ln v_j)$, the indices being labelled as Ln_Σ or $Ln_\Sigma(c)$.

For comparison, the Zagreb[14] product $(v_i \times v_j)^2$ was included as a "mean(v_i,v_j)" and the indices derived using it were labelled as Zg_Σ or $Zg_\Sigma(c)$. The indices were derived also using the reciprocal values of "mean(v_i,v_j)"; so they were labelled as RA_Σ, RG_Σ, RLn_Σ, RZg_Σ or $RA_\Sigma(c)$, $RG_\Sigma(c)$, $RLn_\Sigma(c)$, $RZg_\Sigma(c)$, respectively. On the other hand, the tested exponents **c** in $d_{ij}^{\mathbf{c}}$ were: $-\infty$, -16, -12, -10, -8, -6, -4, -2, -1, 0, 1, 2, and 3. The shorter labels, e.g. A_Σ, were used when speaking about that group of indices as a whole, whereas the forms as e.g. $A_\Sigma(c)$, were used when speaking about that index at the value of exponent **c** specified in parentheses. The general label for all these indices was $XY_\Sigma(c)$.

In present paper we consider the indices $A_\lambda(c)$, $G_\lambda(c)$, $Ln_\lambda(c)$, $Zg_\lambda(c)$, $RA_\lambda(c)$, $RG_\lambda(c)$, $RLn_\lambda(c)$, and $RZg_\lambda(c)$, which are the largest eigenvalues of the same matrices. A common label for these indices is $XY_\lambda(c)$.

Characteristics of the largest eigenvalues as "mean degree of vertices" indices

The values of the "mean degree of vertices" indices of methane are equal to zero and those of ethane are equal to 1. Integers, i.e. all equal to 1, are the values of $RG_\lambda(-\infty)$.

The degeneration of the largest eigenvalues as the "mean degree of vertices" indices

The number of degenerated data, i.e. of data having at least one equal counterpart among all tested $XY_\lambda(0)$ indices of alkanes from propane through octanes is equal to 24, whereas among octanes it is equal to 15. The index $RG_\lambda(-\infty)$ is totally degenerated.

Correlation between the largest eigenvalues and the summation-derived "mean degree of vertices" indices derived from the same matrices

The correlation coefficient between the data of the largest eigenvalues and the data of the summation-derived "mean degree of vertices" indices derived from the same matrices of alkanes from propane through octanes and assuming the linear relationship, is presented in Table 1, whereas for octanes it is presented in Table 2.

Table 1. Correlation between the largest eigenvalues and of summation-derived "mean degree of vertices" indices derived from the same matrices of alkanes from propane through octanes.

	Index							
c	$A_\lambda(c)$	$G_\lambda(c)$	$Ln_\lambda(c)$	$Zg_\lambda(c)$	$RA_\lambda(c)$	$RG_\lambda(c)$	$RLn_\lambda(c)$	$RZg_\lambda(c)$
3	0.9931	0.9934	0.9933	0.9839	0.9898	0.9895	0.9896	0.9562
2	0.9918	0.9920	0.9919	0.9695	0.9912	0.9905	0.9908	0.9600
1	0.9914	0.9909	0.9911	0.9515	0.9914	0.9915	0.9915	0.9866
0	0.9857	0.9875	0.9870	0.9316	0.9806	0.9824	0.9819	0.9737
-1	0.9643	0.9722	0.9697	0.9382	0.9654	0.9575	0.9607	0.8875
-2	0.9409	0.9504	0.9472	0.9499	0.9682	0.8973	0.9245	0.5341
-4	0.9149	0.9214	0.9191	0.9596	0.5489	0.6892	0.9563	0.2227
-6	0.9065	0.9116	0.9098	0.9617	0.3290	0.5595	0.3510	0.5056
-8	0.9043	0.9091	0.9073	0.9621	0.3056	0.5097	0.2054	0.5380
-10	0.9037	0.9084	0.9067	0.9622	0.3016	0.4911	0.1799	0.5442
-12	0.9036	0.9082	0.9066	0.9622	0.3008	0.4839	0.1742	0.5457
-16	0.9035	0.9082	0.9065	0.9623	0.3005	0.4797	0.1725	0.5461
-∞	0.9035	0.9082	0.9065	0.9623	0.3005		0.1724	0.5461

Among the indices of the groups $A_\lambda(c)$, $G_\lambda(c)$, $Ln_\lambda(c)$, $RA_\lambda(c)$, $RG_\lambda(c)$, and $RLn_\lambda(c)$, the correlations presented in Table 1 are quite good when **c** ≥ 0 and at increasingly negative values of exponent **c** they decrease to a limiting value. Among the indices of the groups $Zg_\lambda(c)$ and $RZg_\lambda(c)$ the correlations are not as good. The reason for this difference may be in the fact that the overall dimension in the degree of vertex is in the former group v^1 or v^{-1}, whereas in the latter group it is v^4 or v^{-4}. Some aspects of the influence of the exponent in $v^{\mathbf{m}}$ were described elsewhere.[4] If only octanes are considered, several correlation coefficients are higher, indicating that several largest eigenvalues of tested matrices contain the information very similar to that of the summation-derived indices of this type.

Table 2. Correlation between the largest eigenvalues and of summation-derived "mean degree of vertices" indices derived from the same matrices of octanes.

	Index							
c	$A_\lambda(c)$	$G_\lambda(c)$	$Ln_\lambda(c)$	$Zg_\lambda(c)$	$RA_\lambda(c)$	$RG_\lambda(c)$	$RLn_\lambda(c)$	$RZg_\lambda(c)$
3	0.9989	0.9989	0.9989	0.9701	0.9976	0.9972	0.9974	0.9415
2	0.9996	0.9996	0.9996	0.9011	0.9973	0.9970	0.9971	0.4633
1	0.9989	0.9996	0.9995	0.5688	0.9734	0.9899	0.9872	0.9639
0		0.9961	0.9927	0.9897	0.9995	0.9998	0.9997	0.9940
-1	0.9976	0.9990	0.9995	0.9854	0.9996	0.9998	0.9998	0.9969
-2	0.9860	0.9924	0.9887	0.9869	0.9946	0.9991	0.9986	0.9937
-4	0.9603	0.9706	0.9632	0.9886	0.9921	-0.8854	0.4522	0.6517
-6	0.9498	0.9616	0.9525	0.9891	0.9867	-0.9575	0.9957	0.7682
-8	0.9470	0.9592	0.9497	0.9892	0.9833	-0.9653	0.9960	0.7678
-10	0.9464	0.9587	0.9490	0.9892	0.9823	-0.9684	0.9956	0.7674
-12	0.9462	0.9586	0.9488	0.9892	0.9821	-0.9699	0.9955	0.7673
-16	0.9461	0.9585	0.9488	0.9892	0.9820	-0.9708	0.9955	0.7673
-∞	0.9461	0.9585	0.9488	0.9892	0.9820		0.9955	0.7673

The increase of values of the largest eigenvalues of the "mean degree of vertices" matrices of n-alkanes due to the increase of size of the molecule

How the values of the largest eigenvalues of the "mean degree of vertices" matrices of *n*-alkanes from propane through octanes increase with increasing carbon number is presented in Table 3 for all tested indices.

Whereas the tested $XY_\Sigma(c)$ indices[5] have at **c** = -∞ a linear increase with carbon number, and at -∞ < **c** < -6 the increase is apparently but not truly linear, the tested $XY_\lambda(c)$ indices have a declining increase of values, with $RZg_\lambda(c)$ which decreases with

carbon number, as an exception. At **c** = 0, the increase of the tested $XY_{\Sigma}(c)$ indices is quadratic, whereas most $XY_{\lambda}(c)$ indices are increasing either slightly more or slightly less than linearly. These differences are the main cause for lower correlation coefficients, Table 1, when **c** < 0. At **c** > 0, the increase can be described by a higher polynomial. Among the $XY_{\lambda}(c)$ indices it is in several instances of lower degree than among the $XY_{\Sigma}(c)$ indices.

Table 3. Schematic presentation of the shape of the increase of values of the "mean degree of vertices" $XY_{\lambda}(c)$ indices of *n*-alkanes from C_3-C_8 as well as of the degree of the simplest polynomial having $r^2 > 0.9995$.

	c				
Index	$-\infty \le$ **c** ≤ -1	**0**	**1**	**2**	**3**
$A_{\lambda}(c)$, $G_{\lambda}(c)$, $Ln_{\lambda}(c)$	⟋	⟋	⟋2	⟋3	⟋3
$Zg_{\lambda}(c)$	⟋	⟋	⟋2	⟋3	⟋4
*$RA_{\lambda}(c)$, $RG_{\lambda}(c)$, *$RLn_{\lambda}(c)$	⟋	⟋	⟋2	⟋3	⟋3
$RZg_{\lambda}(c)$	⟍	⟋	⟋2	⟋2	⟋3

* The values drop from C_2 to C_3

The increase of values of the largest eigenvalues of the "mean degree of vertices" matrices due to the increase of the size of molecules of other alkane isomers

How the values of the largest eigenvalues of the "mean degree of vertices" matrices of other alkane isomers increase with the size of a molecule is the most easily presented by the susceptibility of typical structural types for the increase in carbon number by one, $S_{i,i+1}$, cf. ref.[6] We consider here $S_{7,8}$:

Hp → Oct, 2M6 → 2M7, 3M6 → 3M7, 3Et5 → 3Et6, 24M5 → 24M6, 23M5 → 23M6, 22M5 → 22M6, 33M5 → 33M6, and 223M4 → 223M5.

In these transitions the main chain of the alkane is elongated by insertion of a methylene group, so that the branched structure is preserved as much as possible although it is shifted to the periphery of the molecule. On increase of the size of molecule increase also the values of most of largest eigenvalues of the "mean degree of vertices" matrices tested here, Table 4. The exceptions are the indices $RG_{\lambda}(c)$ when $-\infty \le$ **c** ≤ -4 and $RZg_{\lambda}(c)$ when **c** < -2, where some values of indices increase and the others

decrease. At $RZg_\lambda(-2)$ and $RZg_\lambda(-1)$ all values decrease on increasing size of the molecule.

Table 4. The increase of values of the largest eigenvalues of the "mean degree of vertices" matrices on increase of the size of molecule.

	c			
Index	**-∞**	**-∞ < c ≤ -4**	**-2 ≤ c ≤ -1**	**0 ≤ c**
$A_\lambda(c)$, $G_\lambda(c)$, $Ln_\lambda(c)$, $Zg_\lambda(c)$, $RA_\lambda(c)$, $RLn_\lambda(c)$	+	+	+	+
$RG_\lambda(c)$	0	±	+	+
$RZg_\lambda(c)$	±	±	-	+

0: The values do not change
+: The values increase with increasing size of molecule
-: The values decrease with increasing size of molecule
±: The values of index of some isomers increase with increasing size of molecule, the values of the others decrease

Table 5. The influence of structural features on change of values of the largest eigenvalues of the "mean degree of vertices" matrices due to the increase of the size of molecule.

	c									
Index	**-∞**	**-16 ≤ c ≤ -8**	**-6**	**-4**	**-2**	**-1**	**0**	**1**	**2**	**3**
$A_\lambda(c)$	*S*>*e*	*S*>*e*	*S*>*e*	*S*>*e*	*S*>*e*	*S*>*e*	a1	*s*	*s*	*s*
$G_\lambda(c)$	*S*>*e*	*S*>*e*	*S*>*e*	*S*>*e*	*S*>*e*	*S*>*e*	a	*S*	*S*>*e*	*S*
$Ln_\lambda(c)$	*S*>*e*	*S*>*e*	*S*>*e*	*S*>*e*	*S*>*e*	*S*>*e*	a	*S*>*e*	*S*	*S*
$Zg_\lambda(c)$	*S*>*e*	*S*>*e*	*S*>*e*	*S*>*e*	*S*>*e*	*S*	a2	*S*	*S*	*S*
$RA_\lambda(c)$	*s*	*s*	*s*	*S*	*S*>*e*	*s*	a1	*S*>*e*	*S*	*S*
$RG_\lambda(c)$	=	**BI**	*s*	*s*	*s*	*s*	a1	*S*>*e*	*S*>*e*	*S*
$RLn_\lambda(c)$	*S*	*S*	*S*	*S*	*S*	*s*	a1	*S*>*e*	*S*>*e*	*S*
$RZg_\lambda(c)$	*S*	*S*	*S*	*S*	*l*	*s*	a1	*S*>*e*	*S*>*e*	*S*

= : no change
a: $0 < 1t < 2t < 2q < 2q1t$ a1: $0 > 1t > 2t > 2q > 2q1t$
a2: $2q > 0 > 1t > 2t > 2q1t$
BI: 0 > 2M > 3M > 3E > 24M > 23M > 22M > 33M > 223M
Symbols for structural features:
e: ethyl vs. methyl *l*: position of branches (*ctr*) *s*: separation between branches
Uppercase symbols: That structural feature has the highest influence
Lowercase symbols: That structural feature has the highest influence (next to the number of branches, if not shown explicitly otherwise)

In Table 5 is presented, which structural feature has the highest influence on the increase of values of the largest eigenvalues of the "mean degree of vertices" matrices on increase of the size of molecule. In cases marked "a", "a1" or "BI" the sequence of

isomers seems regular as it would be expected for a good branching index. The former situation is observed when the exponent **c** = 0 at the indices G_λ and Ln_λ, the next one at the indices A_λ, RA_λ, RG_λ, RLn_λ, and RZg_λ. In these cases only the number of branches and the type of the branched structure influence the values of the indices. The last situation is observed at the index $RG_\lambda(c)$ when $-\infty < \mathbf{c} < -6$.

There are also given some qualitative conclusions which structural feature has a higher influence on the change of the index value. When $\mathbf{c} > 0$, then at the index A_λ the highest influence has the number of branches followed by the separation between them. Similar situation is among the indices RA_λ when $\mathbf{c} = -1$ or $-\infty \leq \mathbf{c} \leq -6$, RG_λ when $-\infty < \mathbf{c} < 0$, at $RLn_\lambda(-1)$ and $RZg_\lambda(-1)$. At $RZg_\lambda(-2)$, the number of branches has the highest influence, followed by the position of branches.

The dependence of the largest eigenvalues of the "mean degree of vertices" matrices on branching

The increase or decrease with branching

Whether the largest eigenvalues of the "mean degree of vertices" matrices increase or decrease with branching is presented in Table 6.

Table 6. The values of the largest eigenvalues of the "mean degree of vertices" matrices increase or decrease with branching

	c								
Index	**-∞**	**-16 ≤ c ≤ -6**	**-4**	**-2**	**-1**	**0**	**1**	**2**	**3**
$A_\lambda(c)$	+	+	+	+	+	+	-	-	-
$G_\lambda(c)$, $Ln_\lambda(c)$	+	+	+	+	+	-	-	-	-
$Zg_\lambda(c)$	+	+	+	+	+	+	±	±	-
$RA_\lambda(c)$	-	-	-	+	+	+	±	-	-
$RG_\lambda(c)$	=	+	+	+	+	+	±	-	-
$RLn_\lambda(c)$	-	-	±	+	+	+	±	-	-
$RZg_\lambda(c)$	-	-	±	+	+	+	+	±	-

+: The values increase on increasing branching
-: The values decrease on increasing branching
±: Some values increase whereas the other ones decrease when the branching increases

Most of them decrease when **c** > 0. The indices $RA_\lambda(c)$, $RLn_\lambda(c)$, and $RZg_\lambda(c)$ decrease also when **c** < -2 or -4, respectively. The values of the indices $A_\lambda(c)$, $G_\lambda(c)$, $Ln_\lambda(c)$, $Zg_\lambda(c)$, and $RG_\lambda(c)$ increase with branching when **c** < 0.

The influence of structural features

Which structural feature influences the value of the tested "mean degree of vertices" indices most strongly is presented in Table 7. In majority of cases it is the number of branches (a, a1, **BI** and lowercase symbols in Table 7) followed by either the type of branches (ethyl vs. methyl) or the separation between branches. The position of branches seems to have in most cases a lower influence than the other structural features.

Table 7. Which structural feature influences the values of the "mean degree of vertices" indices the most strongly.

						c		
Index	**-∞**	**-16 ≤ c ≤ -6**	**-4**	**-2**	**-1**	**0**	**1**	**c ≥ 2**
$A_\lambda(c)$	*s*	*s*	*s*	*e*	*e*	a	*e*	*e*
$G_\lambda(c)$, $Ln_\lambda(c)$	*s*	*s*	*s*	*e*	*e*	a1	*e*	*e*
$Zg_\lambda(c)$	*s*	*s*	*s*	*s*	*s*	a	*E>l*	*e*
$RA_\lambda(c)$	*s*	*s*	*e*	*e*	**BI**	a	*s*	*s*
$RG_\lambda(c)$	0	*s*	*s*	**BI**	**BI**	a	*e*	*e*
$RLn_\lambda(c)$	*e*	*e*	*E>l*	*e*	**BI**	a	*e*	*e*
$RZg_\lambda(c)$	*S>l*	*S>l*	*s*	*s*	*l*	a	*s*	*e*

a: 0 < 1*t* < 2*t* < 2*q* < 3*t* < 2*q*1*t* < 4*q* a1: 0 > 1*t* > 2*t* > 2*q* > 3*t* > 2*q*1*t* > 4*q*

BI: Oct < 2M7 < 3M7 < 4M7 < 3Et6 < 25M6 < 24M6 < 23M6 < 34M6 < 3Et2M5 < 22M6 < 33M6 < 3Et3M5 < 234M5 < 224M5 < 223M5 < 233M5 < 2233M4

Symbols for structural features:

e: ethyl vs. methyl *l*: position of branches (*ctr*) *s*: separation between branches

Uppercase symbols: That structural feature has the highest influence

Lowercase symbols: That structural feature has the highest influence (next to the number of branches, if not shown explicitly otherwise)

The largest eigenvalues of the "mean degree of vertices" matrices that might be good branching indices

Taking into account the information presented in Table 5 ($RG_\lambda(-16 \le c \le -8)$) and Table 7 ($RG_\lambda$(-2 and -1) can be concluded that none of tested largest eigenvalues of the "mean degree of vertices" matrices has an ideal full sequence of isomers on increasing

the size of molecule and on increase of branching, so none is a perspective candidate for an ideal branching index of BI_M^8 type. On the other hand, the indices $RA_\lambda(-1)$, $RG_\lambda(-1)$, $RG_\lambda(-2)$, and $RLn_\lambda(-1)$ have an ideal full sequence of isomers on increase of branching making them candidates for a good branching index of BI_A^8 type. The indices $A_\lambda(0)$, $G_\lambda(0)$, $Ln_\lambda(0)$, $Zg_\lambda(0)$, $RA_\lambda(0)$, $RG_\lambda(0)$, $RLn_\lambda(0)$, and $RZg_\lambda(0)$ have an ideal sequence of isomers presenting the information that the number of branches has the highest contribution and the quaternary structures contribute more than the tertiary ones. No other information is contained in them.

Correlation of physicochemical properties with the largest eigenvalues of the "mean degree of vertices" matrices

The correlation of the largest eigenvalues of the "mean degree of vertices" matrices with the tested physicochemical properties assuming the linear relationship was derived using data of all alkanes from ethane through octanes, as well as only for octanes. The patterns are similar to those observed at the indices XY_Σ.[5] The differences are as follows.

Data from ethane through octanes: At $\mathbf{c} < -4$ are the correlations lower among the indices Zg_λ, RA_λ, RLn_λ, and RZg_λ. At RA_λ, RLn_λ, and RZg_λ some curves cross the abscissa at **c** around or below -4.

When only data of octanes is correlated, we observe two patterns. Abscissa is crossed once at the indices A_λ, G_λ, Ln_λ, RG_λ, and Zg_λ at $0 < \mathbf{c} < 1$, $-1 < \mathbf{c} < 0$, $-1 < \mathbf{c} < 0$, $0 < \mathbf{c} < 1$, $0 < \mathbf{c} < 3$, respectively. Abscissa is crossed twice at the indices RA_λ, RLn_λ, and RZg_λ at $-4 < \mathbf{c} < -2$ and $0 < \mathbf{c} < 2$, at $-6 < \mathbf{c} < -2$ and $0 < \mathbf{c} < 2$, as well as at $-6 < \mathbf{c} < -2$ and $1 < \mathbf{c} < 2$, respectively.

The values of correlation coefficients differ from one physicochemical property to another, as well as from one tested index to the other one. Usually we are interested in the best correlation coefficients. This type of data is collected in Table 8-10. In Table 8 are presented the values of the exponent **c**, which gives rise to the best correlation of the particular index and physicochemical property, when the data of alkanes from ethane through octanes is considered. The "best" exponents are in most cases $0 \leq \mathbf{c} \leq 2$, in other cases they are mostly close to these values.

Table 8: The value of exponent **c** where the tested physicochemical property has the best correlation coefficient (r_{best}) with the particular tested largest eigenvalue of the "mean degree of vertices" matrices for alkanes, $XY_\lambda(c)$, from ethane through octanes.

Physicochem.	**c**							
property	$A_\lambda(c)$	$G_\lambda(c)$	$Ln_\lambda(c)$	$Zg_\lambda(c)$	$RA_\lambda(c)$	$RG_\lambda(c)$	$RLn_\lambda(c)$	$RZg_\lambda(c)$
BP	0	0	0	1	1	1	-4	2
ΔHv	1	0	0	1	1	1	1	2
ΔHf°g	0	-1	0	1	0	0	0	1
Tc	0	0	0	1	1	1	-4	2
Pc	0	0	0	1	1	1	1	2
Vc	0	0	0	1	1	1	1	2
dc	-2	-4	-2	0	-2	-1	-2	1
αc	1	1	1	1	1	1	1	2
Zc	1	1	1	2	2	2	2	2
BP/Tc	1	1	1	2	2	2	2	2
Tc/Pc	0	0	0	1	1	1	1	2
Tc^2/Pc	0	0	0	1	1	1	1	2
ω	1	1	1	2	2	2	2	3
d	0	-1	-1	0	0	0	0	1
Vm	0	0	0	1	1	1	1	2
A	3	2	2	3	-4	3	-6	3
B	0	0	0	1	1	1	1	2
C	1	1	1	2	1	1	1	2
n_D	-1	-1	-1	0	-2	0	0	1
MR	0	0	0	1	1	1	1	2
MON	3	3	3	3	3	3	3	3
logVP	0	0	0	1	1	1	1	2
Mw	0	0	0	1	1	1	1	2

In Table 9 are presented the results for the case when only data of octanes is considered. The "best" exponents differ more widely than in Table 8 and it could be reasonably expected that some correlations might be still better at **c** > 3.

In Table 10 are collected the cases of "best" correlations for data of all alkanes from ethane through octanes as well as when only octanes are considered. In bold are presented those physicochemical properties that are considered to be the best references for branching.[6] When all tested alkanes are considered, in 18 out of 23 cases $|r| > 0.9$ and in five cases even $|r| > 0.99$. When only data of octanes is considered, then $|r| > 0.9$ is observed in 10 out of 24 cases and $|r| > 0.99$ in two cases. Consequently, several of the tested indices, which are the largest eigenvalues of the "mean degree of vertices" matrices, are good indices of the influence of size of the molecules and only

few of them also indicate well branching. Branching is indicated well only in connection with the physicochemical properties that are considered to be the best references for branching, i.e. with Tc/Pc, ω, and BP/Tc, followed by Tc^2/Pc, MON, C, S, Pc, ΔHv, and R^2. This is the case with the indices $G_\lambda(-1)$, $RLn_\lambda(-2)$, $Ln_\lambda(-2)$, $G_\lambda(1)$, etc, respectively. The influence of branching on the values of ΔHf°g is not indexed as well by these indices.

Table 9. The value of exponent **c** where the tested physicochemical property has the best correlation coefficient (r_{best}) with the particular tested largest eigenvalue of the "mean degree of vertices" matrices for alkanes, $XY_\lambda(c)$, among octanes.

Physicochem.	**c**							
property	$A_\lambda(c)$	$G_\lambda(c)$	$Ln_\lambda(c)$	$Zg_\lambda(c)$	$RA_\lambda(c)$	$RG_\lambda(c)$	$RLn_\lambda(c)$	$RZg_\lambda(c)$
BP	0	0	0	1	-4	-4	-6	1
ΔHv	0	0	0	0	-4	-16	-6	-1
ΔHf°g	0	0	0	1	-4	-16	-6	-2
Tc	1	-∞	-4	1	1	1	-4	2
Pc	1	-1	-1	3	1	1	1	2
Vc	3	-1	3	3	1	1	1	3
dc	2	-1	3	3	1	1	1	2
αc	3	3	3	3	3	3	3	3
Zc	0	0	0	0	-∞	0	-∞	-1
BP/Tc	-1	-2	-2	-1	-2	2	-2	3
Tc/Pc	1	-1	-1	-2	2	2	2	3
Tc^2/Pc	2	1	1	0	3	0	0	0
ω	-1	0	-1	-1	-1	-2	-2	-1
d	-1	-∞	-2	-∞	-2	-2	-2	2
Vm	-1	-∞	-4	-∞	-2	-2	-2	2
A	0	3	3	0	3	3	0	1
B	0	0	0	1	-4	0	-4	1
C	0	0	0	0	-1	-6	-1	-1
n_D	-1	-∞	0	-∞	-2	-2	-2	-2
MR	1	-1	-1	2	1	1	1	2
MON	3	3	3	0	3	3	3	3
logVP	0	0	0	0	0	0	-6	1
S	0	0	0	0	-1	-6	-1	-2
R^2	3	3	3	0	3	3	3	1

Considering 23 tested physicochemical properties, for indexing the influence of the size of molecules are the best indices G_λ (15 cases), Ln_λ (5 cases), and A_λ (3 cases), followed by Zg_λ, RA_λ, RG_λ, and RLn_λ (1 case). For indexing of branching are the best ones the indices from the group Zg_λ (8 cases), followed by RLn_λ (6 cases), G_λ (5 cases), RA_λ and RZg_λ (2 cases), and Ln_λ (1 case). For indexing the size of molecules are the best exponents **c** = 0 (15 cases), **c** = 1 (8 cases), **c** = -4 (2 cases), **c** = 3 and -1 (one case each). For indexing of branching are the best exponents **c** = 3 (5 cases), **c** = -6 (4 cases), **c** = -∞, -1 or 1 (3 cases each), **c** = -2 or 2 (2 cases each), and **c** = -4 or 0 (one case each).

Table 10. The cases of the best correlation coefficients (r_{best}) between tested physicochemical properties and the largest eigenvalues of the "mean degree of vertices" matrices, $XY_\lambda(c)$, among alkanes from ethane through octanes as well as only among octanes.

Physicochem.	C_2-C_8			C_8		
property	r_{best}	index	**c**	r_{best}	index	**c**
BP	0.**9**89	G_λ	0	0.824	RLn_λ	-6
ΔHv	0.**9**86	G_λ	0	0.**9**35	RLn_λ	-6
ΔHf°g	0.**9**89	A_λ	0	-0.860	RLn_λ	-6
Tc	0.**9**81	Ln_λ, G_λ	0	0.831	RLn_λ	-4
Pc	-0.**9**50	G_λ	0	-0.**9**55	RZg_λ	2
Vc	0.**99**1	G_λ	0	0.841	Zg_λ	3
dc	0.899	G_λ	-4	-0.824	Zg_λ	3
αc	0.**9**51	A_λ	1	0.740	G_λ	3
Zc	-0.744	G_λ	1	0.686	Zg_λ	0
BP/Tc	0.**9**65	Ln_λ	1	-0.**9**89	Ln_λ	-2
Tc/Pc	0.**99**3	G_λ, RG_λ, RLn_λ	0, 1, 1	-0.**99**6	G_λ	-1
Tc^2/Pc	0.**99**7	G_λ	0	0.**9**85	G_λ	1
ω	0.**9**71	G_λ	1	-0.**99**3	RLn_λ	-2
d	0.**9**29	G_λ	-1	0.884	Zg_λ	-∞
Vm	0.**9**80	G_λ	0	-0.890	Zg_λ	-∞
A	0.716	RA_λ	-4	-0.775	RZg_λ	1
B	0.**9**79	G_λ	0	-0.723	Zg_λ	1
C	-0.**9**54	A_λ, Ln_λ	1	0.**9**68	RA_λ	-1
n_D	0.886	Zg_λ	0	0.860	Zg_λ	-∞
MR	0.**99**8	Ln_λ	0	0.891	Zg_λ	2
MON	-0.804	G_λ	3	-0.**9**84	G_λ	3
logVP	-0.**9**86	G_λ	0	-0.727	RLN_λ	-6
S				-0.**9**61	RA_λ	-1
R^2				0.**9**17	G_λ	3
Mw	0.**999**	Ln_λ	0			

Correlation between the largest eigenvalues of tested "mean degree of vertices" matrices

In Tables 3-10 can be seen that the largest eigenvalues of tested "mean degree of vertices" matrices share many similar characteristics. To test this observation they were correlated between themselves. The results are presented in Table 11 for all data from propane through octanes and in Table 12 for octanes.

Table 11. Correlation coefficients between the values of the largest eigenvalues of tested "mean degree of vertices" matrices for propane through octanes.

A_λ	1							
G_λ	0.99994	1						
Ln_λ	0.99997	0.999993	1					
Zg_λ	0.96	0.95	0.95	1				
RA_λ	0.993	0.993	0.993	0.94	1			
RG_λ*	0.994	0.994	0.994	0.94	0.999987	1		
RLn_λ	0.994	0.993	0.993	0.94	0.999994	0.999998	1	
RZg_λ	0.98	0.98	0.98	0.93	0.998	0.998	0.998	1

* In correlations with RG_λ the values obtained with the exponent **c** = -∞ were not included since $RG_\lambda(-\infty) = 1$.

Table 12. Correlation coefficients between the values of the largest eigenvalues of tested "mean degree of vertices" matrices for octanes.

A_λ	1							
G_λ	0.99994	1						
Ln_λ	0.99997	0.999993	1					
Zg_λ	0.96	0.96	0.96	1				
RA_λ	0.994	0.993	0.994	0.95	1			
RG_λ*	0.994	0.9945	0.994	0.95	0.999987	1		
RLn_λ	0.994	0.994	0.994	0.95	0.999994	0.999999	1	
RZg_λ	0.985	0.985	0.98	0.948	0.998	0.998	0.998	1

* In correlations with RG_λ the values obtained with the exponent **c** = -∞ were not included since $RG_\lambda(-\infty) = 1$.

The values for ethane were excluded since they are all equal to 1. For the same reason the data of $RG_\lambda(-\infty)$ was excluded. In both tables are evident high correlations between the true "mean degree of vertices" indices, on the one hand between A_λ, G_λ, and Ln_λ, and on the other hand between RA_λ, RG_λ, and RLn_λ. Therefore, when testing the usefulness of the "mean degree of vertices" indices, only one of the three can be taken since they are mutually related. For example, according to the contents of Table 10, the indices of the group G_λ should be taken when the size of molecules is important,

whereas the indices of the group RLn_λ should be taken when only the contribution of branching is important.

Conclusions

The largest eigenvalues of the "mean degree of vertices" matrices tested here form a group of BI_M type indices. They are derived from the matrix having the non-diagonal elements $\mathbf{g}_{ij}$ ($i \neq j$) = ("mean(v_i,v_j)")×$d_{ij}^{\mathbf{c}}$ and presented here as XY_λ(c) indices.

The largest eigenvalues of the "mean degree of vertices" matrices, derived from the matrices having in their non-diagonal elements the exponent **c** = 0, are degenerated. The index $RG_\lambda(-\infty)$ is completely degenerated.

When **c** < 0, the XY_λ(c) indices of *n*-alkanes have a declining increase of values with carbon number, with RZg_λ(c), which decreases with carbon number, as an exception. At c = 0, most tested XY_λ(c) indices are increasing either slightly more or slightly less than linearly. At **c** > 0, the increase can be described by higher polynomials. Among other isomers, on increase of the size of molecule also increase the values of most XY_λ(c) indices tested here. The exceptions are the indices RG_λ(c) when $-\infty < \mathbf{c} \leq -2$ and RZg_λ(c) when c < -2, where the values of indices for some isomers increase and for the others decrease. At RZg_λ(-2 and -1) all values decrease on increasing the size of the molecule.

The sequence of isomers on increasing the size of molecule is regular at the index RG_λ(c) when $-16 \leq \mathbf{c} \leq -8$. A regular sequence of isomers presenting only the information about the contribution of the number of branches and of the type of the branched structure have the indices A_λ(0), G_λ(0), Ln_λ(0), RA_λ(0), RG_λ(0), RLn_λ(c), and RZg_λ(0). Among most of tested XY_λ(c) indices the highest influence on the values of indices when the size of molecule increases, has the separation between branches. Lower than the influence of the separation between branches is in most cases the influence of the type of branches or of their number.

Regular sequences of isomers of increasing branching have only the indices RA_λ(-1), RG_λ(-1 or -2), and RLn_λ(-1). The XY_λ(0) indices present only the information about the contribution of the number of branches and of the type of the branched structure. These indices are degenerated but true branching indices.

The largest eigenvalues of the "mean degree of vertices" matrices perform in general better as indices for indexing the influence of the size of molecule, and less well as branching indices. To index the influence of the size of molecule the use of the indices $G_\lambda(c)$ is recommended, and to index the influence of branching the indices $RLn_\lambda(c)$.

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Povzetek

Med indekse tipa BI_M spadajo tudi lastne vrednosti matrik, katerih elementi vsebujejo povprečne valence točk in potencirane razdalje med njimi. Ti indeksi dobro kažejo doprinos povečanja molekul, slabše pa doprinos razvejanja. Pravi, vendar degenerirani indeksi razvejanja iz te skupine so indeksi $A_\lambda(0)$, $G_\lambda(0)$, $Ln_\lambda(0)$, $RA_\lambda(0)$, $RG_\lambda(0)$, $RLn_\lambda(0)$ in $RZg_\Sigma(0)$. Regularno zaporedje izomer pri razvejanju imajo indeksi $RA_\lambda(-1)$, $RG_\lambda(-1$ in $-2)$ in $RLn_\lambda(-1)$.