SOME TOPOLOGICAL INDICES DERIVED FROM THE $v^m d^n$ MATRIX. PART 2. THE "MEAN DEGREE OF VERTICES" SUMMATION-DERIVED INDICES OF THE BI_M-TYPE

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Abstract

The "mean degree of vertices" indices tested here form a group of summation-derived indices of the BI_M-type. One of them is the famous Randić index χ. They are good indices for indexing the influence of the increase of the size of molecule, but less good as branching indices. The Randić index χ ($\equiv RG_\Sigma(-\infty)$) is one of the best of them. Better than it are in many cases other indices RG_Σ, although the difference is not great in all instances. True but degenerated branching indices are the indices $A_\Sigma(-\infty)$, $G_\Sigma(0)$, $Ln_\Sigma(0)$, $Zg_\Sigma(0)$, $RA_\Sigma(0)$, $RG_\Sigma(0)$, $RLn_\Sigma(0)$, and $RZg_\Sigma(0)$.

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*. In other words, the Randić index χ is 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.

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, $N_{br} = 2$) 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*). 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.[4,5] As criteria regarding the degree of branching is used the intuition[6] as well as the *Methane based* definition and the *n-Alkane based* definition[7] 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[8] or from Lange's Handbook[9]. The data for the liquid molar volume (Vm), the intrinsic molar volume (V_i), the ratios Tc^2/Pc and Tc/Pc used instead of the van der Waals parameters a_0 and b_0, BP/Tc, and the molar refraction (MR) were calculated from data presented in the handbooks.

Results and discussion

The "mean degree of vertices" matrix and the indices derived from it by summation

The $v^{\mathbf{m}}d^{\mathbf{n}}$ 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 $v^{\mathbf{m}}d^{\mathbf{n}}$ 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 this group of indices is one of the

most useful indices, the Randić[2] index χ, having the exponents **a** = $-^1/_2$, **b** = $-^1/_2$, **c** = -∞, whereas its zero order variant, the index $^0\chi$, has the exponents **a** = $-^1/_2$, **b** = 0, **c** = -∞.

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 $\mathbf{g}_{ij}$ $(i \neq j) =$ ("mean(v_i,v_j)")$\times d_{ij}^{\mathbf{c}}$.

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_Σ(c),
- The geometric mean, $(v_i \times v_j)^{1/2}$, the indices being labelled as G_Σ or G_Σ(c),
- The logarithmic mean $(v_i-v_j)/(\ln v_i - \ln v_j)$, the indices being labelled as Ln_Σ or Ln_Σ(c).

For comparison, the Zagreb[10] 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_Σ(c). The indices were derived also using the reciprocal values of "mean(v_i,v_j)" and they were labelled as RA_Σ, RG_Σ, RLn_Σ, RZg_Σ or RA_Σ(c), RG_Σ(c), RLn_Σ(c), RZg_Σ(c), respectively.

On the other hand, the tested exponents **c** in $d_{ij}^{\mathbf{c}}$ were: -∞, -16, -12, -10, -8, -6, -4, -2, -1, 0, 1, 2, and 3.

The shorter labels, e.g. A_Σ, are used when speaking about that group of indices as a whole, whereas the forms as e.g. A_Σ(c), are used when speaking about that index at the value of exponent **c** specified in parentheses. The general label for all these indices is XY_Σ(c).

These indices are summation-derived as presented by Eq. 1:

$$XY_\Sigma(c) = ½ \sum(\text{"mean}(v_i,v_j)\text{"}) \times d_{ij}^{\mathbf{c}} \qquad (1)$$

They obey the *Methane-based* definition of branching,[7] therefore they belong to the BI_M-type of indices.

Characteristics of the "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 are the A_Σ and Zg_Σ indices when c = -∞ or an integer.

The degeneration of the "mean degree of vertices" indices

The number of degenerated data, i.e. of data having at least one equal counterpart among the "mean degree of vertices" indices of alkanes from propane through octanes, is presented in Table 1.

Table 1. The number of degenerated data of the "mean degree of vertices" indices of alkanes from propane through octanes. Maximum possible number is 38.

	c						
Index	**-∞**	**-∞ < c ≤ -2**	**-1**	**0**	**1**	**2**	**3**
$A_\Sigma(c)$	31			38	8	2	
$G_\Sigma(c)$, $Ln_\Sigma(c)$	4			24			
$Zg_\Sigma(c)$	4			26	4	2	
$RA_\Sigma(c)$	14		2	24	2		
$RG_\Sigma(c)$	4			22			
$RLn_\Sigma(c)$	4			24			
$RZg_\Sigma(c)$	16			24			

Table 2. The number of degenerated data of the "mean degree of vertices" indices of octanes. Maximum possible number is 18.

	c						
Index	**-∞**	**-∞ < c ≤ -2**	**-1**	**0**	**1**	**2**	**3**
A_Σ (c)	16			18	4	2	
$G_\Sigma(c)$, $Ln_\Sigma(c)$, $Zg_\Sigma(c)$	4			15			
$RA_\Sigma(c)$	8		2	15		2	
$RG_\Sigma(c)$, $RLn_\Sigma(c)$	4			15			
$RZg_\Sigma(c)$	2			15			

The degeneration causing exponents are **c** = -∞ and especially **c** = 0, whereas some degeneration is observed also at **c** = -1, 1 or 2. The most degenerated among tested indices is the index A_Σ, followed by RA_Σ, RZg_Σ, and Zg_Σ. The least degenerated are the RG_Σ indices, which include the Randić index χ. Among the data of the "mean degree of

vertices" indices of octanes, Table 2, the situation is similar. In this case, the index RZg_{Σ} is the least degenerated.

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

How the values of the "mean degree of vertices" indices of *n*-alkanes from propane through octanes increase with increasing carbon number is presented in Table 3 for all tested indices and in Fig. 1 for the index A_{Σ} as an example illustrating the situation among all of them.

Table 3. The schematic presentation of the shape of the increase of values of the "mean degree of vertices" indices of n-alkanes from C_3-C_8 and of the degree of the simplest polynomial having $r^2 > 0.9995$.

	c									
Index	**-∞**	**-∞ < c ≤ -8**	**-6**	**-4**	**-2**	**-1**	**0**	**1**	**2**	**3**
$A_{\Sigma}(c)$, $G_{\Sigma}(c)$, $Ln_{\Sigma}(c)$	/	*	*	*	⌋2	⌋2	⌋2	⌋3	⌋3	⌋4
$Zg_{\Sigma}(c)$	/	*	*	⌋2	⌋3	⌋3	⌋2	⌋3	⌋3	⌋4
$RA_{\Sigma}(c)$, $RG_{\Sigma}(c)$, $RLn_{\Sigma}(c)$	/	*	*	*	⌋2	⌋2	⌋2	⌋3	⌋3	⌋4
$RZg_{\Sigma}(c)$	/	*	⌋3	⌋4	⌋4	⌋3	⌋2	⌋2	⌋3	⌋3

/: Linear increase ⌋: Parabolic increase
*: Apparently linear; $r^2 > 0.9995$
The digits: The degree of the simplest polynomial having $r^2 > 0.9995$

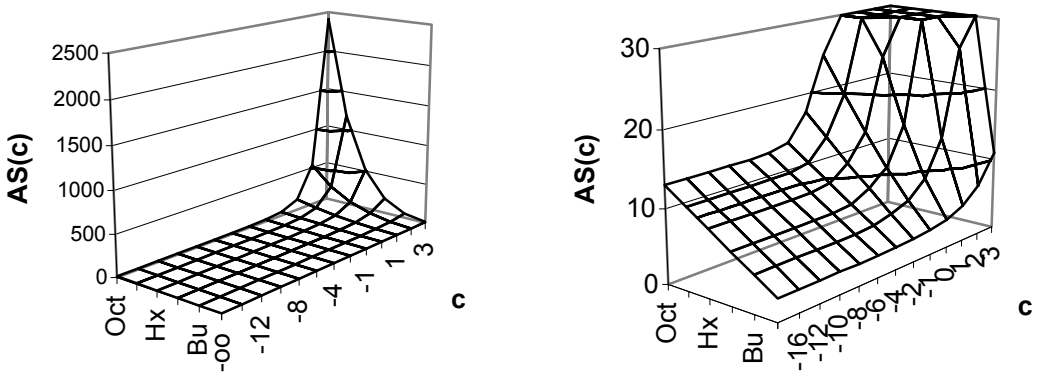

Fig. 1. The dependence of values of the index A_{Σ} on exponent **c** and on carbon number. Right: The enlarged view on the lower part of the left graph.

At **c** = -∞ they have a linear increase. At -∞ < **c** < -6 the increase is apparently but not truly linear. At **c** = 0 the increase is quadratic. In most other cases, the increase can

be described by a higher polynomial. The exponents $-\infty < \mathbf{c} < -6$ can be used to decrease or eliminate the degeneration of indices without affecting seriously their dependence on carbon number.

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

How the values of the "mean degree of vertices" indices of other 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.[5] 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.

Table 4. The increase of values of the "mean degree of vertices" indices on increase of the size of molecule.

	c						
Index	$-\infty \le \mathbf{c} \le -4$	**-2**	**-1**	**0**	**1**	**2**	**3**
$A_\Sigma(c)$	↓	↓	↓	=	↑	↑	↑
$G_\Sigma(c)$, $Ln_\Sigma(c)$	↓	↓	↑	↑	↑	↑	↑
$Zg_\Sigma(c)$	↓	↓	↓	↓	↑	↑	↑
$RA_\Sigma(c)$	↑	↑	↓	↓	↓	↓	↑
$RG_\Sigma(c)$, $RLn_\Sigma(c)$, $RZg_\Sigma(c)$	↑	↓	↓	↓	↓	↓	↑

=: The values increase equally among all isomers
↓: The values increase more among isomers having a less branched structure
↑: The values increase more among isomers having a more branched structure

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 all "mean degree of vertices" indices tested here. There is only one case, where the increase is equal among all isomers, Table 4. In other tested cases there is observed a higher increase of values of the "mean degree of vertices" indices either among less branched isomers or among more branched ones.

In Table 5 is presented, which structural feature has the highest influence on the increase of values of the "mean degree of vertices" indices on increase of the size of the

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 first situation is observed at the indices $G_\Sigma(0)$ and $Ln_\Sigma(0)$, the second at the indices $RA_\Sigma(0)$, $RG_\Sigma(0)$, $RLn_\Sigma(0)$, and $RZg_\Sigma(0)$, as well as at $A_\Sigma(-\infty)$. The last situation is observed at the index $A_\Sigma(c)$ when $-\infty < \mathbf{c} \leq -6$ as well as at the index $RZg_\Sigma(-2)$. Among all indices tested here, the distance between branches has the highest influence when $\mathbf{c} > 0$. This is the case also at the indices G_Σ, Ln_Σ, and Zg_Σ when $\mathbf{c} < 0$, as well as at the indices RA_Σ, RG_Σ, RLn_Σ, and RZg_Σ when $\mathbf{c} \leq -4$.

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

	c								
Index	**-∞**	**-∞ < c ≤ -6**	**-4**	**-2**	**-1**	**0**	**1**	**2**	**3**
$A_\Sigma(c)$	a1	BI	br↓	br↓	D↑	=	D↓	D↓	D↓
$G_\Sigma(c)$, $Ln_\Sigma(c)$	D↑	D↑	D↑	D↑	D↑	a	D↓	D↓	D↓
$Zg_\Sigma(c)$	D↑	D↑	D↑	D↑	D↑	a2	D↓	D↓	D↓
$RA_\Sigma(c)$, $RLn_\Sigma(c)$	D↑	D↑	D↑	D↑	br↓	a1	D↓	D↓	D↓
$RG_\Sigma(c)$	D↑	D↑	D↑	br↓	br↓	a1	D↓	D↓	D↓
$RZg_\Sigma(c)$	D↑	D↑	D↑	BI	br↓	a1	D↓	D↓	D↓

= : all values are equal
a: $0 < 1t < 2t < 2q < 2q1t$ a1: $0 > 1t > 2t > 2q > 2q1t$ a2: $2q > 0 > 1t > 2q1t > 2t$
BI: 0 > 2M > 3M > 3Et > 24M > 23M > 22M > 33M > 223M
br: The number of branches has the highest influence
↓ The higher the number of branches, the lower the value of the index
↑ The higher the number of branches, the higher the value of the index
D↓: 24M < 0 < ... < 223M < 33M, 22M, i.e the influence of $dist > N_{br}$
D↑: 33M, 22M < 0 < ... < 223M < 24M, i.e the influence of $dist > N_{br}$

The number of branches has the highest influence on the indices when the size of molecules increases, in the case of indices $A_\Sigma(-2)$, $A_\Sigma(-4)$, $RA_\Sigma(-1)$, $RG_\Sigma(-1)$, $RG_\Sigma(-2)$, $RLn_\Sigma(-1)$, and $RZg_\Sigma(-1)$.

Since the values of the "mean degree of vertices" indices increase with the size of molecule, they are the BI_M-type indices, i.e. they obey the *Methane-based* definition of branching.[7]

The dependence of the "mean degree of vertices" indices on branching

The increase or decrease with branching

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

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

	c						
Index	$-\infty \le$ **c** ≤ -4	**-2**	**-1**	**0**	**1**	**2**	**3**
$A_\Sigma(c)$	+	+	+	0	-	-	-
$G_\Sigma(c)$, $Ln_\Sigma(c)$	+	+	+	-	-	-	-
$Zg_\Sigma(c)$	+	+	+	+	±	-	-
$RA_\Sigma(c)$, $RG_\Sigma(c)$, $RLn_\Sigma(c)$	-	+	+	+	-	-	-
$RZg_\Sigma(c)$	±	+	+	+	+	±	±

+: 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 A_Σ, G_Σ, Ln_Σ, and Zg_Σ increase when **c** < 0, whereas most "reciprocal mean degree of vertices" indices decrease with branching when **c** < -2. Among the indices RZg_Σ the values for some isomers increase and the values for the others decrease with increasing branching.

The influence of structural features

Which structural feature influences most strongly the values of the tested "mean degree of vertices" indices is presented in Table 7. In majority of cases it is the number of branches (b).

The index $RA_\Sigma(-1)$ would be a candidate for a good branching index if it would not have a pair of degenerated values. The indices $G_\Sigma(0)$, $Ln_\Sigma(0)$, $Zg_\Sigma(0)$, $RA_\Sigma(0)$, $RG_\Sigma(0)$, $RLn_\Sigma(0)$, and $RZg_\Sigma(0)$ 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. The indices A_Σ, G_Σ, Ln_Σ, and Zg_Σ present also the information that when branches

are placed at or near the centre of molecule, then the structure seems to be more branched than if they are placed at the periphery of molecule.

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

	c							
Index	**-∞**	**-∞ < c ≤ -4**	**-2**	**-1**	**0**	**1**	**2**	**3**
A_Σ(c)	a2	b>e>c>s	b>e>c>s	b>e>c>s	0	b>e>c>s	b>e>c>s	b>e>c>s
G_Σ(c), Ln_Σ(c)	b>e=c>s	b>e>c>s	b>e>c>s	b>e>c>s	a1	b>e>c>s	b>e>c>s	b>e>c>s
Zg_Σ(c)	b>s>e=c	b>s>e>c	b>s>e>c	b>s>e>c	a	b>e>c>s	b>e>c>s	b>e>c>s
RA_Σ(c), RG_Σ(c), RLn_Σ(c)	b>e=c>s	b>e>c>s	b>e>c>s	b>e>c>s	a	b>e>c>s	b>e>c>s	b>e>c>s
RZg_Σ(c)	e=c>b>s	e>c>b>s	b>e>s>c	b>s>c>e	a	b>s>e>c	e>c>s>b	b>e>c>s

a: $0 < 1t < 2t < 2q < 3t < 2q1t < 4q$ a1: $0 > 1t > 2t > 2q > 3t > 2q1t > 4q$

a2: $0 < 1t < 2t < 2q = 3t < 2q1t < 4q$

b>e>c>s: The contribution of the number of branches (b) is higher than the contribution of ethyl (e) vs. methyl groups, followed by the position of branches (c: central) and the separation between branches (s)

The "mean degree of vertices" indices that might be good branching indices

Taking into account the information presented in Table 5 and 7 we can conclude that no one of the tested "mean degree of vertices" indices can be considered as a candidate for a good branching index. Namely, none of them has an ideal sequence of isomers when the size of molecule as well as when the branching increases.

Correlation of physicochemical properties with the "mean degree of vertices" indices

The correlation of the "mean degree of vertices" indices with the tested physicochemical properties assuming the linear relationship was derived using data of all alkanes from propane through octanes, as well as only for octanes. The former case is illustrated in Fig. 2 with help of the A_Σ index as a general example. The pattern observed testing the indices G_Σ and Ln_Σ is quite similar but not equal. The pattern observed on testing the index Zg_Σ is less similar, since at **c** < 0 the correlations are lower.

The pattern when testing the indices derived from the reciprocal values of the "mean(v_i,v_j)" is less similar; therefore it is illustrated in Fig. 3 with indices RG_Σ, RLn_Σ, and RZg_Σ. The pattern observed testing the index RA_Σ is similar to that of RG_Σ.

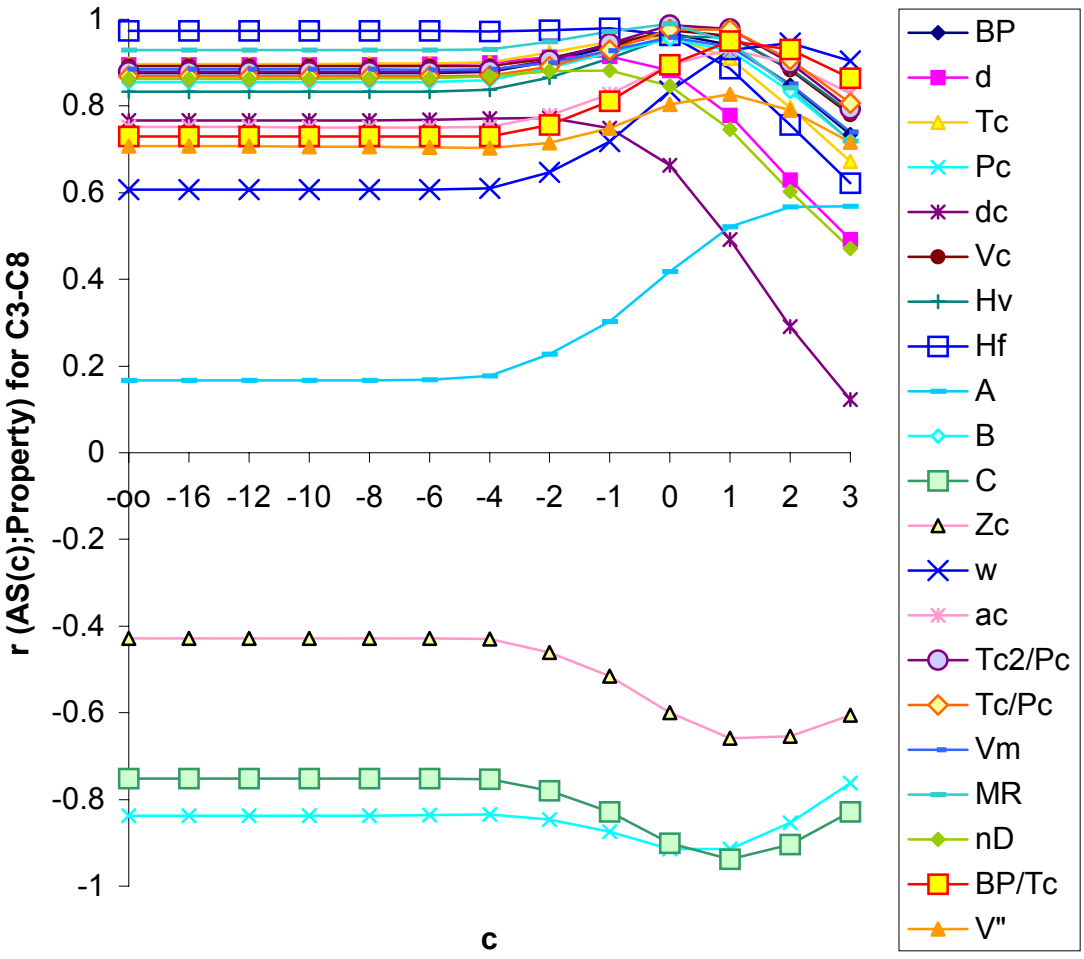

Fig. 2. Correlation coefficient of values of the index $A_\Sigma(c)$ with tested physicochemical properties for all alkanes from propane through octanes.

A quite different pattern is observed when only data of octanes are correlated. Two examples are presented here. One of them is the index A_Σ presented in Fig. 4, the other one is the index RG_Σ presented in Fig. 5.

In graphs of the indices A_Σ, G_Σ, Ln_Σ, and Zg_Σ the curves cross the abscissa only once; at $\mathbf{c} = 0$, $\mathbf{c} \approx -{}^1/_2$, $\mathbf{c} \approx -{}^1/_2$, and $0 < \mathbf{c} < 2$, respectively. In graphs of the indices RA_Σ, RG_Σ, $RLn_\Sigma(c)$, and RZg_Σ, on the other hand, the curves cross the abscissa twice, cf. Fig. 5; namely at $\mathbf{c} \approx -3$ and $\mathbf{c} \approx ½$, at $\mathbf{c} \approx -3$ and $\mathbf{c} \approx ½$, at $-16 < \mathbf{c} < -10$ and $-6 < \mathbf{c} < -4$, as well as at $-6 < \mathbf{c} < -2$ and $1 < \mathbf{c} < 3$, respectively.

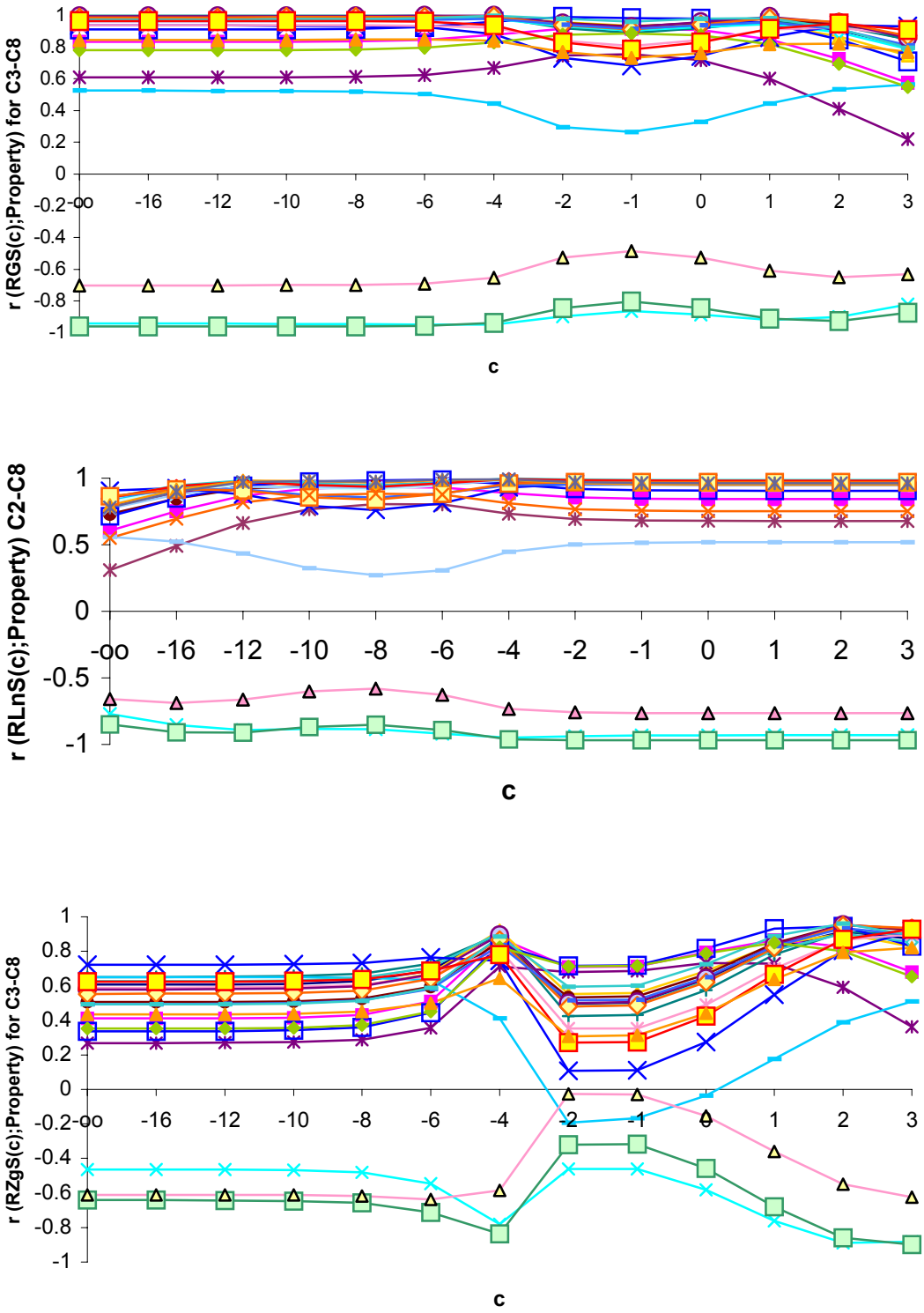

Fig. 3. Correlation coefficient of the values of the index $RG_{\Sigma}(c)$ and $RZg_{\Sigma}(c)$ with the tested physicochemical properties for all alkanes from propane through octanes. The symbols are the same as in Fig. 2.

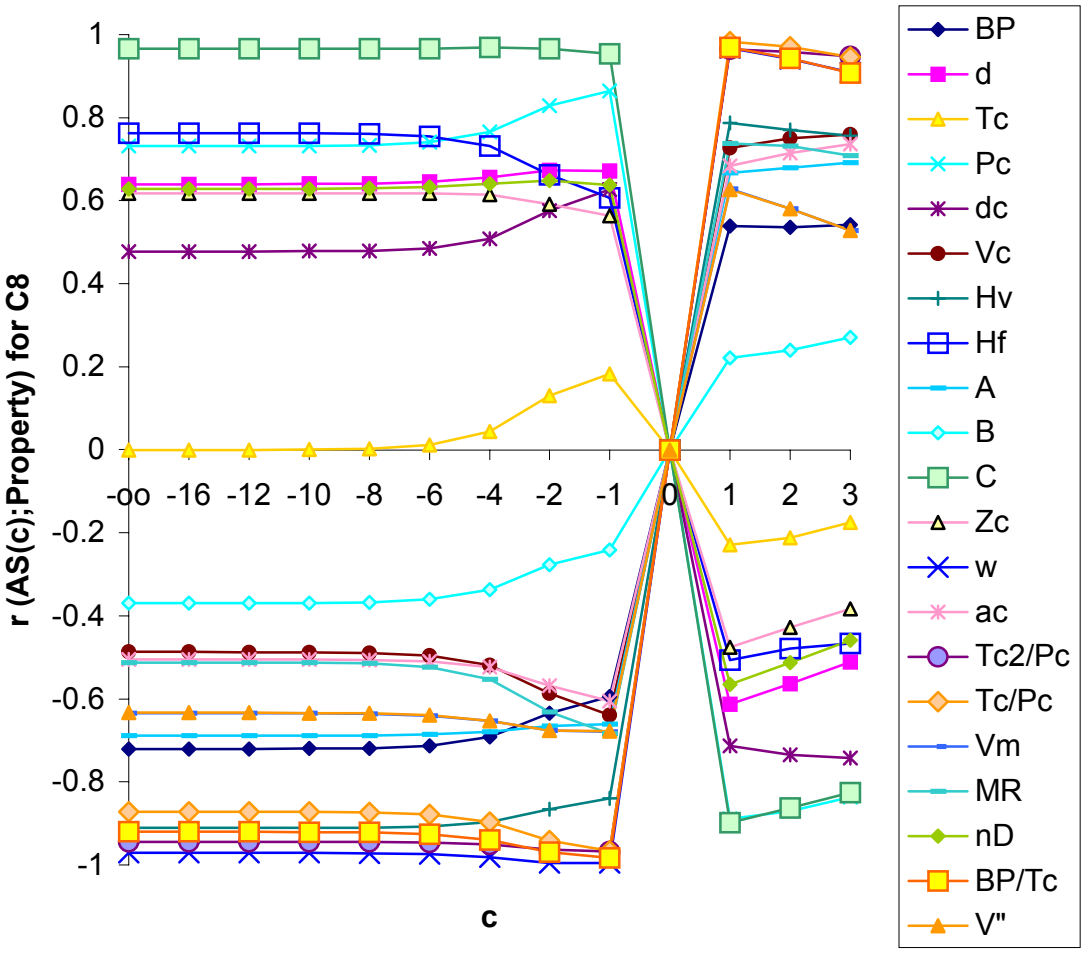

Fig. 4. Correlation coefficient of values of index $A_\Sigma(c)$ with tested physicochemical properties for octanes.

In Fig. 5 we can see that the values of the correlation coefficients differ from one physicochemical property to another, as well as from one tested index to another 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 give rise to the best correlation of the particular index and physicochemical property, when the data of alkanes from propane through octanes are considered. The "best" exponents differ widely. It is interesting that the Randić index χ ($\chi \equiv RG_\Sigma(-\infty)$) correlates best in five of 21 cases (with αc, Zc, BP/Tc, ω, and C). In the majority of other cases give rise to better correlations other negative exponents, e.g. **c** = -4.

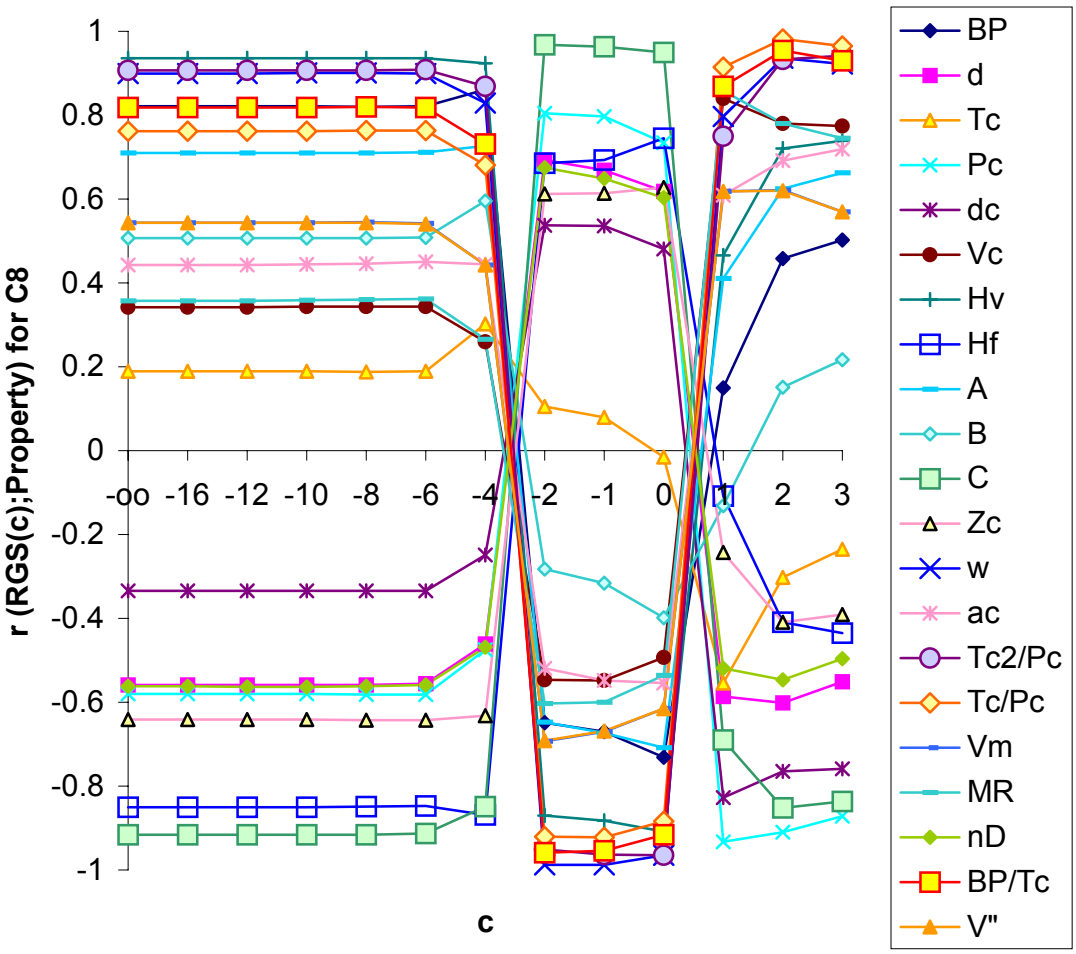

Fig. 5. Correlation coefficient of values of the index $RG_{\Sigma}(c)$ with tested physicochemical properties for all octanes.

As can be deduced from Fig. 2 and Table 8, these correlations are in many cases (BP, ΔHv, B, Tc^2/Pc, Tc/Pc, and V"; $\Delta r^2 < 0.01$) only marginally better than that of index χ and do not contribute a substantial improvement. In other cases, the differences in correlation are higher:

$0.01 < \Delta r^2 < 0.1$: Tc, Pc, Vc, Vm, A, MR
$\Delta r^2 > 0.1$: ΔHf°g, dc, d, n_D.

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. There is only one case in Table 9 where the Randić index χ has the best correlation (ΔHv; r = 0.997), which is quite high. In spite of that, the situation is not unfavourable for the Randić

index χ, since Fig. 5 shows that in several cases, there is not a substantial improvement of correlation on replacing the exponent **c** = -∞, observed at the index χ, for the "best" exponent:

$\Delta r^2 < 0.01$: Zc
$0.01 < \Delta r^2 < 0.1$: BP, ΔHf°g, A, and B

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

Physicochem.	**c**							
property	$A_\Sigma(c)$	$G_\Sigma(c)$	$Ln_\Sigma(c)$	$Zg_\Sigma(c)$	$RA_\Sigma(c)$	$RG_\Sigma(c)$	$RLn_\Sigma(c)$	$RZg_\Sigma(c)$
BP	0	0	0	1	-4	-4	-4	2
ΔHv	0	0	0	1	-4	-8	-4	2
ΔHf°g	-1	-∞	-∞	0	-2	-2	-2	2
Tc	0	-1	-1	0	-2	-4	-4	-4
Pc	1	0	0	1	-4	-4	-4	2
Vc	0	0	0	1	-2	-4	-4	2
dc	-2	-4	-4	-2	-1	-1	-1	0
αc	1	1	1	1	-4	-∞(χ)	-6	3
Zc	1	1	1	2	-∞	-∞(χ)	-∞	3
BP/Tc	1	1	1	1	-6	-∞(χ)	-8	3
Tc/Pc	0	0	0	1	-4	-4	-4	2
Tc^2/Pc	0	0	0	1	1	-4	-4	2
ω	2	2	2	2	-∞	-∞(χ)	-∞	3
d	-1	-2	-2	-1	-1	-2	-1	-4
Vm	0	0	0	1	-2	-4	-4	2
V"	1	1	1	1	-4	-6	-4	3
A	3	2	2	3	-∞	3	3	-∞
B	0	0	0	1	-4	-6	-4	-4
C	1	1	1	1	-4	-∞(χ)	-6	3
n_D	1	-2	-2	-1	-1	-1	-1	1
MR	0	-1	0	1	-2	-4	-4	2

In other cases, the differences in correlation are higher:

$\Delta r^2 > 0.1$: Vc, dc, Pc, αc, Tc, BP/Tc, Tc/Pc, Tc^2/Pc, ω, C, d, Vm, V", n_D, and MR.

In Table 10 are collected the cases of "best" correlations for data of all alkanes from propane 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.[7] When all tested alkanes are considered, in 17 out of 21 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 7 cases and $|r| > 0.99$ in 3 cases. Consequently, several of the tested "mean degree of vertices" indices are good indices of the influence of size of the molecules and only few of them indicate well also 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 ω, Tc/Pc, and BP/Tc, followed by Tc^2/Pc, C, Pc, and ΔHv. This is the case with the indices $A_\Sigma(-1)$, $G_\Sigma(-1)$, $G_\Sigma(-2)$, followed by $G_\Sigma(1)$, $RA_\Sigma(-1)$, $RZg_\Sigma(3)$, and $RA_\Sigma(-\infty)$, 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 "mean degree of vertices" index, $XY_\Sigma(c)$, among octanes.

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

None of the Ln_Σ indices belongs to the best indices of this group. Considering all 21 tested physicochemical properties, for indexing the influence of the size of molecules

are the best indices RLn_{Σ} (12 cases), RG_{Σ} (8 cases), followed by RA_{Σ} (2 cases), Zg_{Σ} (1 case). For indexing of branching are the best ones the indices from the group Zg_{Σ} (6 cases), followed by RZg_{Σ} (4 cases), RA_{Σ} (4 cases), G_{Σ} (3 cases), RLn_{Σ} (2 cases), A_{Σ} and RG_{Σ} (1 case each).

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

Physicochem.	C_3-C_8			C_8		
property	r_{best}	index	**c**	r_{best}	index	**c**
BP	0.**99**4	RG_{Σ}	-4	0.862	RG_{Σ}	-4
ΔHv	0.**99**7	RG_{Σ}	-8	0.**9**39	RA_{Σ}	-∞
ΔHf°g	0.**9**90	RLn_{Σ}	-2	-0.873	RZg_{Σ}	-∞
Tc	0.**9**86	RG_{Σ}	-4	-0.794	RZg_{Σ}	2
Pc	-0.**9**49	RG_{Σ}, RLn_{Σ}	-4	-0.**9**45	RZg_{Σ}	3
Vc	0.**9**86	RG_{Σ}, RLn_{Σ}	-4	0.845	RA_{Σ}	1
dc	0.805	RLn_{Σ}	-1	-0.832	RA_{Σ}	1
αc	0.**9**51	RLn_{Σ}	-6	0.720	RLn_{Σ}	3
Zc	-0.765	RLn_{Σ}	-∞	0.658	Zg_{Σ}	0
BP/Tc	0.**9**66	RA_{Σ}	-6	-0.**99**1	G_{Σ}	-2
Tc/Pc	0.**99**4	RLn_{Σ}	-4	-0.**99**4	G_{Σ}	-1
Tc^2/Pc	0.**99**7	RLn_{Σ}	-4	0.**9**77	G_{Σ}	1
ω	0.**9**70	RA_{Σ}	-∞	-0.**99**6	A_{Σ}	-1
d	0.**9**31	RLn_{Σ}	-1	0.836	Zg_{Σ}	-∞
Vm	0.**9**76	RG_{Σ}	-4	-0.846	Zg_{Σ}	-∞
V"	0.846	RG_{Σ}	-6	-0.845	Zg_{Σ}	-∞
A	0.560	RLn_{Σ}	3	0.724	RLn_{Σ}	-4
B	0.**9**84	RLn_{Σ}	-4	0.715	RZg_{Σ}	2
C	-0.**9**69	RLn_{Σ}	-6	0.**9**69	RA_{Σ}	-1
n_D	0.**9**09	Zg_{Σ}	-1	0.804	Zg_{Σ}	-∞
MR	0.**99**5	RG_{Σ}	-4	0.882	Zg_{Σ}	1

Conclusions

The "mean degree of vertices" indices tested here form a group of summation-derived indices of BI_M-type. 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 $XY_{\Sigma}(c)$ indices. One of them is the famous Randić[2] index χ, which is identical with the index $RG_{\Sigma}(-\infty)$.

The "mean degree of vertices" summation-derived indices, derived from the matrices having in their non-diagonal elements the exponent **c** = -∞, and especially those

having **c** = 0, are degenerated. To avoid degeneration without affecting seriously the properties of an index having **c** = -∞, i.e. being derived from the adjacency matrix, the exponent -∞ < **c** < -6 is to be used. To eliminate the degeneration in the case when **c** = 0, two measures are to be taken: using **c** slightly different from 0 and using the exponent on the degree of vertex slightly different from 1.

When **c** = -∞, the tested indices exhibit a linear increase with the size of molecule. At -∞ < **c** < -6 the increase is apparently linear, at **c** = 0 it is quadratic. In other cases it can be described by higher polynomials. The sequence of isomers on increasing the size of molecule is regular at the index $A_\Sigma(c)$ when -∞ < **c** ≤ -6, as well as at the index $RZg_\Sigma(-2)$. 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 $A_\Sigma(-\infty)$, $G_\Sigma(0)$, $Ln_\Sigma(0)$, $Zg_\Sigma(0)$, $RA_\Sigma(0)$, and $RG_\Sigma(0)$.

A regular sequence of isomers on increasing branching has none of tested indices. Only the information about the contribution of the number of branches and of the type of the branched structure to branching present the indices $A_\Sigma(-\infty)$, $G_\Sigma(0)$, $Ln_\Sigma(0)$, $Zg_\Sigma(0)$, $RA_\Sigma(0)$, $RG_\Sigma(0)$, $RLn_\Sigma(0)$, and $RZg_\Sigma(0)$. These indices are degenerated but true branching indices.

The "mean degree of vertices" indices are good indices for indexing the influence of the increase of the size of molecule, but less good as branching indices. The Randić index χ is one of the best of them. In many cases other indices RG_Σ are better than it, although the difference is not always great. If the best-known reference values[5] are taken as a criterion, then branching is indexed quite well also by the indices $A_\Sigma(-1)$, $G_\Sigma(-1)$, $G_\Sigma(-2)$, followed by $G_\Sigma(1)$, $RA_\Sigma(-1)$.

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Povzetek

Med indekse tipa BI_M spadajo tudi nekateri indeksi izvedeni z uporabo povprečnih valenc točk in potenciranih razdalj med njimi. Mednje spada tudi Randićev indeks χ, ki je identičen indeksu $RG_\Sigma(-\infty)$ in je eden najboljših v tej skupini. Boljši od njega so marsikdaj drugi indeks iz skupine RG_Σ. Ti indeksi dobro kažejo doprinos povečanja molekul, slabše pa doprinos razvejanja. Pravi, vendar degenerirani indeksi razvejanja iz te skupine so indeksi $A_\Sigma(-\infty)$, $G_\Sigma(0)$, $Ln_\Sigma(0)$, $Zg_\Sigma(0)$, $RA_\Sigma(0)$, $RG_\Sigma(0)$, $RLn_\Sigma(0)$ in $RZg_\Sigma(0)$.