

**SOME TOPOLOGICAL INDICES DERIVED FROM THE $v^m d^n$ MATRIX.
PART 7. THE $V_{ij}(m,n)$ INDICES****Anton Perdih,* Branislav Perdih***Mala vas 12, SI-1000 Ljubljana, Slovenia**Received 20-05-2002***Abstract**

The best correlations of some $V_{ij}(m,n)$ indices using data from propane through all octanes are observed at Mw ($r = 1$), MR ($r = 0.998$), Tc^2/Pc ($r = 0.998$), ΔH_v ($r = 0.997$), BP ($r = 0.994$), Tc/Pc ($r = 0.994$), ΔH_f° ($r = 0.991$), and logVP ($r = -0.990$). The best correlations using only data of octanes are observed at Tc/Pc ($r = -0.998$), ω ($r = -0.996$), BP/Tc ($r = -0.995$), MON ($r = -0.987$), Tc^2/Pc ($r = 0.984$), C ($r = 0.969$), S ($r = -0.961$), and Pc ($r = 0.950$). The index $V_{ij}(-2,-2)$ has a regular sequence of isomers due to the increase of the size of the molecule. The indices $V_{ij}(-1/4,-6)$, $V_{ij}(-1,1/4)$, $V_{ij}(-2,1/4)$, $V_{ij}(-2,1/3)$, $V_{ij}(3,-1/4)$ as well as a group of $V_{ij}(m,n)$ indices having $-1 \leq m \leq -1/4$ and $-1 \leq n \leq -1/4$ have a regular sequence of isomers due to increasing branching. These indices seem to be good sources of the susceptibility for branching derived BI_A type branching indices.

Introduction

Several hundred topological indices have been developed and tested for their performance as branching indices or indices of substances' properties.^{1,2} A substantial part of them is derived from one or another matrix associated with molecular structure. Estrada³ developed a matrix that enables the derivation of an infinite number of indices. We⁴ presented some types of matrices that enable the derivation of an infinite number of indices, too, and we have shown that these matrices represent a step in unification of several matrices used to derive topological indices, i.e. of the adjacency matrix, the distance matrix, the reciprocal distance matrix, etc.

Topological indices have been correlated with several physical, chemical, and biological properties of molecules. However, even several properties of alkanes still cannot be well described with particular available indices⁵ and combinations of them are to be used.⁶ In spite of that, interest in topological indices has grown remarkably during recent years. Therefore, the study of those topological indices that might be good branching indices remains an important area of research.

In recent papers^{4,7-11} we studied the characteristics of some groups of indices derived with help of the generalized vertex-degree, vertex distance matrices: the

summation derived $W(m,n)$ indices⁴ and the "mean degree of vertices" indices,⁷ the largest eigenvalues of the same matrices,^{8,9} the susceptibilities for branching of the $W(m,n)$ indices,¹⁰ as well as the difference derived indices.¹¹ In present paper are studied the summation derived $V_{ij}(m,n)$ indices.

Data and notations

The structures of alkanes are presented in shorthand. *n*-Alkanes are presented in a different way than branched ones, e.g. Hp is *n*-heptane, Oct is *n*-octane, whereas 223M5 is 2,2,3-trimethylpentane, 3E2M5 is 3-ethyl-2-methylpentane, etc. Other terms are explained on 2,2-, 2,3- and 2,5-dimethyl hexane (22M6, 23M6 and 25M6) as examples. All of them have eight carbons ($N = 8$) and four of them are primary carbons ($N_p = 4$). The two branches (i.e. the number of branches, $N_{br} = 2$) in 22M6 are positioned on a quaternary carbon (q) placed on the periphery (per) of the molecule. The two branches in 23M6 and 25M6 are positioned on tertiary carbons (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.

The physicochemical properties

The data for the boiling point (BP), density (d), the critical data T_c , P_c , V_c , Z_c , α_c , and d_c , as well as the standard enthalpy of formation for the ideal gas (ΔH_f°), the enthalpy of vaporisation (ΔH_v), 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 Handbook¹² or from Lange's Handbook¹³. The data for the liquid molar volume (V_m), the ratios T_c^2/P_c and T_c/P_c used instead of the van der Waals parameters a_0 and b_0 , the ratio BP/ T_c (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 Pogliani¹⁴ and Gutman et al.,¹⁵ those for vapour pressure ($\log VP$) from Goll and Jurs,¹⁶ and those for the entropy (S) and quadratic mean radius (R^2) from Ren.¹⁷

Methods

Susceptibility for the increase in carbon number; Susceptibility for branching

The susceptibility¹⁸ is defined as the normalised difference of the indices' or properties' values, Eq. 1,

$$S_{a,b} = X_b/X_a - 1 \quad (1)$$

where $S_{a,b}$ is the susceptibility, X is an index or a property, subscript a refers to the less branched structure and subscript b refers to the more branched structure. Which one is more branched is concluded by intuition as presented in ref.¹⁹ as well as by the *Methane based* definition and the *n-Alkane based* definition.²⁰ Two groups of susceptibilities are used. In the susceptibility for the increase in carbon number, denoted as $S_{a,a+1}$, subscript a refers mostly to the structure having the same number and type of branches if not explicitly shown otherwise. In these cases, the two alkanes taken into account differ in carbon number by one. For example, in $S_{7,8}$ the digit 8 means any octane having the same number and type of branches as a heptane which is represented by the digit 7. In $S_{\text{Hp,Oct}}$ the data of *n*-heptane (Hp) and *n*-octane (Oct) is used. In $S_{2\text{M}6,2\text{M}7}$ the data of 2-methyl hexane (2M6) and 2-methyl heptane (2M7) is used, in $S_{2\text{M}6,3\text{M}7}$ the data of 2-methyl hexane (2M6) and 3-methyl heptane (3M7), etc.

In the susceptibility for branching, $S_{n,b}$, the subscript n refers to the *n*-alkane and the subscript b refers to any alkane of the same carbon number. For example, in $S_{\text{Hp},b}$ Hp refers to *n*-heptane and b to any heptane. In $S_{\text{Hp},2\text{M}6}$, 2M6 refers to 2-methyl hexane.

Contribution of structural features

The relative contribution of structural features to the value of the index is estimated using the susceptibilities. The relative contribution of a structural feature to the value of the index when the size of the molecule increases, is estimated as follows. The contribution of the number of branches is estimated by $S_{33\text{M}5,33\text{M}6} - S_{3\text{M}7,3\text{M}6}$. The contribution of the position of branches is estimated by $1/2(S_{33\text{M}5,33\text{M}6} - S_{22\text{M}5,22\text{M}6})$. The contribution of the separation between branches is estimated by $S_{24\text{M}5,24\text{M}6} - S_{23\text{M}5,23\text{M}6}$. The contribution of the change of the substituent from methyl to ethyl is estimated by $S_{3\text{E}5,3\text{E}6} - S_{3\text{M}6,3\text{M}7}$.

The relative contribution of a structural feature to the value of the index when the branching of the molecule increases is estimated as follows. The contribution of the number of branches is estimated by $S_{\text{Oct},33\text{M}6} - S_{\text{Oct},3\text{M}6}$. The contribution of the position of branches is estimated by $S_{\text{Oct},34\text{M}6} - S_{\text{Oct},23\text{M}6}$. The contribution of the separation between branches is estimated by $S_{\text{Oct},24\text{M}6} - S_{\text{Oct},23\text{M}6}$. The contribution of the change of the substituent from methyl to ethyl is estimated by $S_{\text{Oct},3\text{E}2\text{M}5} - S_{\text{Oct},23\text{M}6}$. The contributions are labelled with letters b, c, s, and e, respectively. The uppercase letter is used to label the structural feature having the highest contribution to the value of index in question. The results of estimations of the relative contribution of structural features are checked by the sequences of isomers obtained by sorting $S_{7,8}$ or $S_{8,b}$.

Results and discussion

The $V_{ij}(m,n)$ indices and the source matrix

The $V_{ij}(m,n)$ indices are derived by summation of all elements of the matrix having the main diagonal elements $\mathbf{g}_{ii} = 0$ and the nondiagonal elements $\mathbf{g}_{ij} (i \neq j) = v_i^m \times v_j^m \times d_{ij}^n$, where v_i and v_j is the degree of vertex i and j , respectively, (in alkanes it is the number of C-C bonds 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 smallest number of bonds between the carbons in question), cf. ref.⁴

The $V_{ij}(m,n)$ indices of methane are equal to zero since $\mathbf{g}_{ii} = 0$ by definition. The $V_{ij}(m,n)$ indices of ethane are equal to 2 since $1^m \times 1^m \times 1^n + 1^m \times 1^m \times 1^n$ is in any case equal to 2. The values of the index $V_{ij}(-\infty, -\infty)$ of other alkanes are equal to zero.

Several indices of this group have a long tradition, e.g. the Wiener index,²¹ $W = 1/2 V_{ij}(0,1)$, the reciprocal Wiener index,²² $RW = 1/2 V_{ij}(0,-1)$, the Harary index,²³ $H = 1/2 V_{ij}(0,-2)$, the Zagreb index,²⁴ $M = 1/2 V_{ij}(2,-\infty)$, the Randić index,²⁵ $\chi = 1/2 V_{ij}(-1/2, -\infty)$, etc.

The $V_{ij}(m,n)$ indices which are integers

The tested $V_{ij}(m,n)$ indices are integers when the exponents \mathbf{m} and \mathbf{n} form any combination of values $-\infty, 0, 1, 2, \text{ or } 3$.

The degeneracy of $V_{ij}(m,n)$ indices

How much data of the tested $V_{ij}(m,n)$ indices is degenerated, i.e. equal to at least one more, is presented in Table 1 for all alkanes from propane through all octanes and in Table 2 for octanes. Highly degenerated are the indices $V_{ij}(m,-\infty)$ and $V_{ij}(m,0)$, and some degeneration is observed also among some other $V_{ij}(m,n)$ indices. The "degeneration causing" exponents are $m = -\infty, 0, 1$, and 2 , as well as $n = -\infty, -2, -1, 0, 1$, and 2 . The unconditionally degeneration causing exponents are presented in bold. A substantial part of degeneration is observed among isomers.

Table 1. Degeneracy of $V_{ij}(m,n)$ indices for 38 alkanes from propane through all octanes expressed as the number of data equal to at least one more. Empty space: no degeneration.

m									
3	4					24			
2	6					24		4	2
1	22			2		25		8	
$0 < m < 1$	4					24			
0	37			2		37		8	
$-1 < m < 0$	4					24			
-1	25					24			
-2	18					24			
$-\infty < m < -2$	4					24			
$-\infty$	38			2	6	37		24	8 3
	$-\infty$	$-\infty < n < -2$	-2	-1	$-1 < n < 0$	0	$0 < n < 1$	1	2 3
	n								

Table 2. Degeneracy of $V_{ij}(m,n)$ indices among 18 octanes expressed as the number of data equal to at least one more. Empty space: no degeneration.

m									
3	4					15			
2	4					15			2
1	8			2		16		4	
$0 < m < 1$	4					15			
0	18			2		18		4	
$-1 < m < 0$	4					15			
-1	10					15			
$-\infty < m < -1$	4					15			
$-\infty$	18			4		17		14	4
	$-\infty$	$-\infty < n < -1$	-1	$-1 < n < 0$	0	$0 < n < 1$	1	2 3	
	n								

Correlation of $V_{ij}(m,n)$ indices with $V_j(m,n)$ and $W(m,n)$ indices

The correlation coefficients between the $V_{ij}(m,n)$ indices tested here and the $V_j(m,n)$ indices as well as $W(m,n)$ indices⁴ ($V_j(m,n) = 2*W(m,n)$) are presented in Table 3 for all alkanes from propane through octanes and in Table 4 only for octanes. In Table 3 we can see a perfect correlation when $m = 0$, since $V_{ij}(0,n) = V_j(0,n) = 2*W(0,n)$. Some high correlation coefficients are observed when $n = -2$. The worst correlations are observed when $m < -1$ and $n < -2$.

Table 3. Correlation coefficients between $W(m,n)$ and $V_{ij}(m,n)$ indices for data of alkanes from propane through octanes, in the plane of exponents m and n .

m																
3	0.8	0.8	0.8	0.8	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	
2	0.9	0.9	0.9	0.9	0.9	②	②	②	②	②	②	②	②	②	②	
1	②	②	②	②	②	②	②	②	②	②	②	②	②	②	②	
$1/2$	②	②	②	③	③	③	③	③	③	③	③	③	②	②	③	③
$1/3$	②	③	③	③	③	③	③	③	③	③	③	③	③	③	③	③
$1/4$	③	③	③	④	③	③	③	③	③	③	③	③	③	③	③	③
0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$-1/4$	②	②	②	⑤	③	③	③	③	③	③	③	③	③	③	③	③
$-1/3$	②	②	②	④	③	②	②	②	②	②	②	②	②	②	③	③
$-1/2$	0.9	0.9	②	④	②	②	②	②	②	②	②	②	②	②	②	③
-1	0.8	0.8	0.9	②	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	②
-2	0.2	0.3	0.7	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
-4	-0.4	-0.1	0.8	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
-6	-0.5	0.7	0.8	0.8	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.8	0.8	0.9	0.9
$-\infty$	X	0.7	0.8	0.8	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.8	0.8	0.8	0.8	0.9
	$-\infty$	-6	-4	-2	-1	$-1/2$	$-1/3$	$-1/4$	0	$1/4$	$1/3$	$1/2$	1	2	3	
	n															

0.9: $0.9 < r < 0.99$ ②: $0.99 < r < 0.999$ ③: $0.999 < r < 0.9999$ ④: $0.9999 < r < 0.99999$ ⑤: $0.99999 < r < 1$ -0.4: $-0.4 > r > -0.5$ X: Division by zero

Among octanes, when $m = 0$, $V_{ij}(0,n) = V_j(0,n) = 2*W(0,n)$, too, but when $n = -\infty$ or 0, then the values of indices are equal for all octanes. On the other hand, $V_{ij}(1,1) = 2V_j(1,1) - 98$. Low correlation coefficients are observed in part near the diagonal $m = -n$, at $n = 2$ and $m < -1$, at $n = -4$ and $-4 < m < 0$, as well as at $n < -4$ and $m < -1$.

Table 4. Correlation coefficients between $W(m,n)$ and $V_{ij}(m,n)$ indices for data of octanes, in the plane of exponents m and n .

m																
3	0.8	0.8	0.8	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	
2	0.8	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	②	②	
1	0.9	0.9	0.9	0.9	0.9	0.9	0.8	0.7	X	②	②	③	1	③	③	
$1/2$	0.9	0.9	0.9	②	0.9	0.8	0.3	-0.0	④	②	②	③	③	③	③	
$1/3$	②	②	②	②	②	0.9	0.6	0.1	④	②	②	③	③	③	④	
$1/4$	②	②	②	②	②	0.9	0.8	0.4	④	②	②	③	③	③	④	
0	X	1	1	1	1	1	1	1	X	1	1	1	1	1	1	
$-1/4$	②	0.9	-0.7	③	②	②	②	②	④	-0.0	0.3	0.9	②	③	③	
$-1/3$	0.9	0.9	-0.8	③	②	②	②	②	③	0.4	-0.0	0.5	②	③	③	
$-1/2$	0.9	0.9	-0.8	③	②	②	②	②	③	0.9	0.7	-0.0	0.9	②	③	
-1	X	-0.9	-0.8	②	②	②	②	②	②	②	②	0.9	-0.0	0.9	②	
-2	-0.7	-0.7	-0.0	0.9	②	②	②	②	②	②	②	②	②	0.8	0.4	0.9
-4	-0.6	-0.3	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.0	0.7
-6	-0.6	0.7	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.1	0.7
-∞	X	0.8	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.1	0.6
	-∞	-6	-4	-2	-1	$-1/2$	$-1/3$	$-1/4$	0	$1/4$	$1/3$	$1/2$	1	2	3	
	n															

Abbreviations as in Table 3.

Table 5. The changes of values of $V_{ij}(m,n)$ indices of n -alkanes on increasing carbon number. Tested were the carbon numbers from C_2 to C_{15} .

m											
m > -1	/))))))))))
-1	=/))))))))))
-2	*/	*)	*)	*)	=/))))))
-4	*/	*∪Bu	*∪Pe	*∪Hp	*∪Hp	*∪Bu	*)	*))))
-6	*/	*∪Pe	*∪C ₈	*∪	*∪	*∪	*∪C ₁₁	*∪C ₈)))
-∞	*0	*∪	*∪	*∪	*∪	*∪	*∪	*∪	—))
	-∞	-6	-4	-2	-1	$-1/2$	$-1/3$	$-1/4$	0	n > 0	
	n										

/ The value of $V_{ij}(m,n)$ increases linearly with carbon number) The value of $V_{ij}(m,n)$ increases progressively with carbon number∪ The value of $V_{ij}(m,n)$ decreases hyperbolically with carbon number∪Pe n -Pentane has the lowest $V_{ij}(m,n)_n$ value; beyond it the values are increasing* $V_{ij}(m,n)_{Et} > V_{ij}(m,n)_{Pr}$ = $V_{ij}(m,n)_{Et} = V_{ij}(m,n)_{Pr}$

0 The values of index are equal to zero, except for ethane

— The values of index do not change with carbon number

Dependence of values of $V_{ij}(m,n)$ indices of n -alkanes on the increase of size of the molecule

Table 5 indicates whether the $V_{ij}(m,n)_n$ indices, i.e. the $V_{ij}(m,n)$ indices of n -alkanes increase or decrease with the increasing size of molecule. We can see that in majority of tested cases they increase, except in the region represented by $-6 \leq n \leq -1/4$ and $-\infty \leq m \leq -4$. Within and near the latter region the values of $V_{ij}(m,n)$ indices of ethane are greater than at least those of propane and in several cases even greater than the $V_{ij}(m,n)$ indices of other higher n -alkanes. There are also schematically indicated shapes of the increase or decrease. At $n = -\infty$ and $m > -\infty$, the increase is linear with the slope of 2^{2m+1} . Among the $W(m,-\infty)$ indices⁴ the slope is equal to 2^m . The increase of the $V_{ij}(m,0)$ indices can be described by a quadratic equation:

$$V_{ij}(m,0) = 2^{2m} * N^2 + (2^{(m+2)} - 2^{2m}) * N + 2,$$

where N is the number of vertices in the graph of the n -alkane (i.e. its carbon number).

Open remains the question whether there exists or not at each (m,n) combination, which indicates a decrease of the values of $V_{ij}(m,n)_n$ indices, a higher but finite carbon number where the $V_{ij}(m,n)_n$ index has its minimum.

Changes of values of $V_{ij}(m,n)$ indices due to the increase of the size of molecules of other alkane isomers

Table 6. The changes of values of $V_{ij}(m,n)$ indices of other alkanes on increasing carbon number

m						
-2 ≤ n ≤ 3	+	+	+	+	+	+
-4	+	+	+/-	+	+	+
-6	+	+/-	-	-	+	+
-∞		-	-	-	0	+
n	-∞	-6	-4 ≤ n ≤ -1/3	-1/4	0	1/4 ≤ n ≤ 3

- + The value of $V_{ij}(m,n)$ increases with carbon number
- The value of $V_{ij}(m,n)$ decreases with carbon number
- +/- The value of $V_{ij}(m,n)$ of some isomers increases and that of other isomers decreases with carbon number

How the values of $V_{ij}(m,n)$ indices of other alkanes change on increasing the size of molecule when the main chain of the alkane is elongated preserving the branched

structure, is presented in Table 6. In most cases the values of $V_{ij}(m,n)$ indices increase with increasing size of molecule, except in some cases when $-\infty < m \leq -4$ and $-\infty < n < 0$.

The contribution of structural features of alkanes to the values of $V_{ij}(m,n)$ indices on increase of the size of the molecule

The comparison of values of $V_{ij}(m,n)$ indices when the carbon number increases by one allows some conclusions about the contribution of particular structural features. This contribution is superimposed to the contribution of the increase of the size of molecule observed at n -alkanes.

Table 7. Two structural features, which have the highest influence on the values of $V_{ij}(m,n)$ indices when the size of molecules increases.

m															
3	S-b	S-b	S-b	S-b	Sb	Sb	Sb	Sb	B	B-s	-Sb	-Sb	-Sb	-Sb	-Sb
2	S-b	S-b	S-b	S-b	Se	Sb	Sb	Sb	B	B-s	-Sb	-Sb	-Sb	-Sb	-Sb
1	S-b	S-b	S-b	S-b	Se	Sb	Sb	Sb	B	B-s	-Sb	-Sb	-Sb	-Sb	-Sb
$\frac{1}{2}$	S-b	S-b	S-b	S-b	Se	Sb	Sb	Sb	B	B-s	-Sb	-Sb	-S-e	-S-e	-S-e
$\frac{1}{3}$	-Bs	-Bs	S-b	S-b	Se	Se	Sb	Sb	B	-Sb	-Sb	-S-e	-S-e	-S-e	-S-e
$\frac{1}{4}$	-Bs	-Bs	-Bs	S-b	Se	Se	Sb	Sb	B	-Sb	-Sb	-S-e	-S-e	-S-e	-S-e
0	NB	-Bs	-Bs	S-b	Se	Se	Se	Se	NB	-S-e	-S-e	-S-e	-S-e	-S-e	-S-e
$-\frac{1}{4}$	Bs	Bs	Sb	S-b	S-b	S-b	S-b	-Bs	-B	-S-b	-S-b	-S-e	-S-e	-S-e	-S-e
$-\frac{1}{3}$	Bs	Bs	Sb	S-b	S-b	S-b	-Bs	-Bs	-B	-B-s	-S-b	-S-e	-S-e	-S-e	-S-e
$-\frac{1}{2}$	Sb	Sb	Sb	-Bs	-Bs	-Bs	-Bs	-Bs	-B	-B-s	-B-s	-S-e	-S-e	-S-e	-S-e
-1	Sb	Sb	Sb	-Bs	-Bs	-Bs	-Bs	-Bs	-B	-B-s	-B-s	-B-s	-S-b	-S-e	-S-e
-2	S-c	S-c	S-b	-B-c	-S-b	-B-s	-Be	-Be	-B	-B-s	-B-s	-B-s	-S-b	-S-e	-S-e
-4	S-c	S-b	-Bs	-S-b	-S-b	-B-s	-B-s	-B-s	-B	-Bs	-Bs	-Bc	-S-b	-S-e	-S-e
-6	S-c	-Bs	-S-b	-S-e	-S-e	-S-e	-S-b	-S-b	-B	-Bs	-Bs	-Be	-S-b	-S-e	-S-e
$-\infty$	0	-S-e	-S-e	-S-e	-S-e	-S-e	-S-e	-S-b	NS	-Bs	-Bs	-Be	-S	-S-e	-S-e
	$-\infty$	-6	-4	-2	-1	$-\frac{1}{2}$	$-\frac{1}{3}$	$-\frac{1}{4}$	0	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{1}{2}$	1	2	3
	n														

b - the influence of the number of branches

c - the influence of the central position compared to the peripheral position of branches

e - the influence of the ethyl vs. the methyl group

s - the influence of separation between branches

- sign: The increase of that structural feature causes a decrease in the value of the index

The most influential structural feature is presented with the uppercase letter. Labels:

-Bc: $-b > c > ..$ -B-c: $-b > -c > ..$ -Be: $-b > e > ..$ Bs: $b > s > ..$

B-s: $b > -s > ..$ -Bs: $-b > s > ..$ -B-s: $-b > -s > ..$

Sb: $s > b > ..$ S-b: $s > -b > ..$ -Sb: $-s > b > ..$ -S-b: $-s > -b > ..$

S-c: $s > -c > ..$ Se: $s > e > ..$ -S-e: $-s > -e > ..$

0: The value of index is equal to zero

NB: Does not index branching

NS: Does not index the size of the molecule

Table 8. Structural features, which have the lowest influence on the values of $V_{ij}(m,n)$ indices when the size of the molecules increases. Labels as in Table 7.

m															
3	-e-c	-e-c	-e-c	ce	ec	ec	ec	ec		-e-c	-e-c	-e-c	-e-c	-e-c	-e-c
2	-e-c	-e-c	-e-c	ec	cb	ec	ec	ec		-e-c	-e-c	-e-c	-e-c	-e-c	-e-c
1	-e-c	-e-c	-e-c	ec	cb	ec	ec	ec		-e-c	-e-c	-e-c	-e-c	-e-c	-e-c
$\frac{1}{2}$	-e-c	-e-c	-e-c	ec	cb	ec	ec	ec		-e-c	-e-c	-e-c	b-c	b-c	b-c
$\frac{1}{3}$	-e-c	-e-c	-e-c	ec	cb	bc	ec	ec		-e-c	-e-c	b-c	b-c	b-c	b-c
$\frac{1}{4}$	-e-c	-e-c	-c-e	ec	cb	bc	ec	ec		-e-c	-e-c	b-c	-cb	b-c	b-c
0	NB	-ce	ec	ec	-c-b	-c-b	-c-b	-c-b	NB	-cb	-cb	-cb	-cb	-cb	b-c
$-\frac{1}{4}$	-e-c	-e-c	-e-c	ec	ec	ec	ec	ec		-e-b	-e-b	-b-c	-c-b	-cb	b-c
$-\frac{1}{3}$	-e-c	-e-c	-e-c	ec	ec	ec	ec	ec		-e-c	-e-b	-b-c	-c-b	-cb	b-c
$-\frac{1}{2}$	-e-c	-e-c	-e-c	ec	ec	ec	ec	ec		-e-c	-e-c	-b-c	-b-c	-cb	b-c
-1	-c-e	-e-c	-e-c	-c-e	ec	ec	ec	ec		-e-c	-e-c	-e-c	-e-b	-cb	-cb
-2	-e-b	-e-b	-e-c	s-e	-c-e	-ce	-c-s	sc		-e-c	-e-c	-e-c	-e-b	-cb	-cb
-4	-e-b	-c-e	-c-e	-c-e	-c-e	-e-c	-e-c	-e-c		ce	ce	es	-e-b	-cb	-cb
-6	-e-b	-ce	-c-e	-c-b	-c-b	-c-b	-e-b	-e-b		ec	ec	sc	-e-b	-cb	-cb
$-\infty$	0	-cb	-cb	-cb	-cb	-cb	-cb	-e-b	NS	ec	ec	sc		-cb	-cb
	$-\infty$	-6	-4	-2	-1	$-\frac{1}{2}$	$-\frac{1}{3}$	$-\frac{1}{4}$	0	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{1}{2}$	1	2	3
	n														

bc: ..>b>c b-c: ..>b>-c -b-c: ..>-b>-c
cb: ..>c>b -c-b: ..>-c>-b -cb: ..>-c>b
ce: ..>c>e -ce: ..>-c>e -c-e: ..>-c>-e -c-s: ..>-c>-s
ec: ..>e>c -e-c: ..>-e>-c -e-b: ..>-e>-b es: ..>e>s
sc: ..>s>c s-e: ..>s>-e>..

In Table 7 is presented the situation when the size of the molecule increases from heptane to octane by elongation of the main chain retaining the branched structure. There can be seen that the highest contribution has either the number of branches (indicated by letter B) or the separation between branches (indicated by letter S). A higher value of the structural feature contributes either to a higher increase of the value of the index (no sign before the letter) or to a higher decrease of the value of the index (the - sign before the letter). At $n = 0$, only the number of branches and the type of the branched structure (i.e. whether the branch bearing carbon is tertiary or quaternary) influence the value of index. The index $V_{ij}(-\infty,1)$, on the other hand, is influenced only by the separation between branches. The higher the separation between branches the lower is the value of this index.

In Table 8 are presented for comparison the structural features that have a lower contribution than those presented in Table 7. In Table 8 can be seen a higher variability with exponents m and n than in Table 7.

The dependence of $V_{ij}(m,n)$ indices on branching

The increase or decrease with branching

Whether the values of $V_{ij}(m,n)$ indices increase or decrease with branching is presented for octanes in Table 9.

Table 9. Schematic presentation of the change of values of $V_{ij}(m,n)$ indices of octanes on increasing branching.

m																
3	+	+	+	+	+	+	+	+	+	+	+	+	+	1-	4+	2+
2	+	+	+	+	+	+	+	+	+	+	+	+	4-	2+	-	-
1	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-
$1/2$	+	+	+	+	+	+	+	5-	5+	-	-	-	-	-	-	-
$1/3$	+	+	+	+	+	+	+	4-	6+	-	-	-	-	-	-	-
$1/4$	+	+	+	+	+	+	+	+	5-	-	-	-	-	-	-	-
0	NB	+	+	+	+	+	+	+	+	NB	-	-	-	-	-	-
$-1/4$	-	-	-	+	+	+	+	+	+	+	1-	9-	-	-	-	-
$-1/3$	-	-	-	+	+	+	+	+	+	+	+	1-	4+	-	-	-
$-1/2$	-	-	-	+	+	+	+	+	+	+	+	+	1-	-	-	-
-1	-, 0	1+	1+	+	+	+	+	+	+	+	+	+	+	+	-	-
-2	2+	2+	7-	+	+	+	+	+	+	+	+	+	+	+	2-	1+
-4	6+	7+	+	+	+	+	+	+	+	+	+	+	+	+	+	5+
-6	6+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	8+
$-\infty$	0	+	+	+	+	+	+	+	+	+	+	+	+	+	+	8-
	$-\infty$	-6	-4	-2	-1	$-1/2$	$-1/3$	$-1/4$	0	$1/4$	$1/3$	$1/2$	1	2	3	
	n															

+: The value of all isomers increases on increasing branching

-: The value of all isomers decreases on increasing branching

1+: The value of one isomer increases whereas the value of other isomers decreases on increasing branching

0: The value of index is equal to zero

NB: Does not index branching

Dotted lines: Intermediate region

The situation in Table 9 is similar but not equal to that observed among the $W(m,n)$ indices.⁴ In both cases we can observe in the plane of exponents m and n two regions

where the values of indices decrease with increasing branching. They are separated from the region, where the values of indices increase with increasing branching, by intermediate regions. In the intermediate regions the values of indices either do not depend on branching or the values of indices of some isomers increase with branching whereas the values of indices of other isomers decrease with branching. The different positions of the intermediate regions among the $W(m,n)$ indices⁴ compared to those among the $V_{ij}(m,n)$ indices seem to be responsible for low correlations presented in Table 4.

The influence of structural features

The comparison of values of $V_{ij}(m,n)$ indices when the branching increases allows some conclusions about the contribution of particular structural features. In Table 10 can be seen that the highest contribution to the value of $V_{ij}(m,n)$ indices due to branching has either the number of branches (indicated by letter B) or the presence of ethyl groups (indicated by the letter E) or even the separation between branches (indicated by letter S). The contribution of ethyl groups or of the separation between branches is higher than that of the number of branches mainly among the $V_{ij}(m,n)$ indices positioned in the intermediate region of Table 9. A higher value of the structural feature contributes either to a higher increase of the value of the index (no sign before the letter) or to a higher decrease of the value of the index (the - sign before the letter). At $n = 0$, only the number of branches and the type of the branched structure (i.e. whether the branch bearing carbon is tertiary or quaternary) influence the value of index.

In Table 11 are presented for comparison the structural features that have a lower contribution than those presented in Table 10.

The size of the molecule

Only the size of molecule index the indices $V_{ij}(0,0)$ and $V_{ij}(0,-\infty)$. Other $V_{ij}(m,n)$ indices except $V_{ij}(-\infty,0)$ index besides the size of molecule also the influence of other structural features and in majority of cases, except in some cases when $-\infty < m \leq -4$ and $-\infty < n < 0$, cf. Table 6, the contribution of the size of molecule to the value of index is

greater than the contribution of structural features indicating branching. This fact will be kept in mind and not be mentioned again below unless considered necessary.

Table 10. Two structural features having the highest contribution to the value of a $V_{ij}(m,n)$ index due to the increase of branching.

m															
3	B-s	B-s	B-s	B-s	B-s	B-s	B-s	B-s	B	Bs	Bs	Bs	S-e	Eb	Be
2	B-s	B-s	B-s	B-s	B-s	Be	Be	Be	B	B-e	Bs	-Es	Be	Be	Be
1	^{B-sce}	Be	Be	Be	Be	Be	Be	Eb	B	Be	Be	Be	Be	Be	Be
^{1/2}	Bce	Be	Be	Be	Be	Be	-E-c	-Eb	B	Be	Be	Be	Be	Be	Be
^{1/3}	Bce	Be	Be	Be	Be	Be	Ec	-E-c	B	Be	Be	Be	Be	Be	Be
^{1/4}	Bce	Be	Be	Be	Be	Be	Be	-E-c	B	Be	Be	Be	Be	Be	Be
0	NB	Be	Be	Be	Be	Be	Be	Be	NB	Be	Be	Be	Be	Be	Be
^{-1/4}	^{B-c-e}	B-e	B-e	Be	Be	Be	Be	Be	B	-Eb	-E-c	Be	Be	Be	Be
^{-1/3}	^{B-c-e}	B-e	B-e	Be	Be	Be	Be	Be	B	B-e	B-e	Ec	Be	Be	Be
^{-1/2}	^{B-c-e}	B-e	B-e	Be	Be	Be	Be	Be	B	B-e	B-e	B-e	Be	Be	Be
-1	^{B-c-e}	B-e	-E-c	Be	B-s	B-s	B-s	B-s	B	B-e	B-e	B-e	-Eb	Be	Be
-2	^{B-c-e}	-E-c	Ec	Be	B-s	B-s	B-s	B-s	B	Bs	Bs	Bs	Bs	-E-c	Be
-4	^{B-c-e}	-E-c	Be	B-c	B-c	B-s	B-s	B-s	B	Bs	Bs	Bs	Bs	Sb	Be
-6	^{B-c-e}	Be	B-c	B-c	B-c	B-s	B-s	B-s	B	Bs	Bs	Bs	Bs	Bs	Be
-∞	0	B-c	B-c	B-c	B-c	B-s	B-s	B-s	B	Bs	Bs	Bs	Bs	Bs	Be
	-∞	-6	-4	-2	-1	^{-1/2}	^{-1/3}	^{-1/4}	0	^{1/4}	^{1/3}	^{1/2}	1	2	3
	n														

Labels: The label has four elements, e.g. $b>c>e>s$. In Table 11 are presented the former two in the form, e.g. Bc meaning $b>c>..$, whereas in Table 12 are presented the latter two, e.g. in the form es meaning $..>e>s$

B : b ($c = e = s = 0$) Bce : $b>c = e..$ $B-c-e$: $b>-c = -e..$ $B-sce$: $b>-s = c = e$

$B-c$: $b>-c>..$ Be : $b>e>..$ $B-e$: $b>-e>..$

Bs : $b>s>..$ $B-s$: $b>-s>..$

Eb : $e>b>..$ $-Eb$: $e>b>..$ Ec : $e>c>..$ $-E-c$: $-e>-c>..$ $-Es$: $-e>s>..$

Sb : $s>b>..$ $S-e$: $s>-e>..$

0 : The value of index is equal to zero

NB : Does not index branching

Number of branches

Only the number of branches indexes the index $V_{ij}(-\infty,0)$. The contribution of the number of branches to the value of other $V_{ij}(m,n)$ indices is in most cases the major one, Table 10.

Table 11. Two structural features having the lowest contribution to the value of a $V_{ij}(m,n)$ index due to the increase of branching.

m																
3	c=e	ec	ec	ec	ec	ec	ec	ec			-e-c	-e-c	-e-c	-cb	c-s	c-s
2	c=e	ec	ec	ec	ec	-sc	-sc	-sc			-cs	-e-c	-cb	c-s	c-s	c-s
1		c-s	c-s	c-s	c-s	c-s	c-s	c-s			c-s	c-s	c-s	c-s	c-s	c-s
$\frac{1}{2}$	-s	c-s	c-s	c-s	c-s	c-s	s-b	-cs			c-s	c-s	c-s	c-s	c-s	c-s
$\frac{1}{3}$	-s	c-s	c-s	c-s	c-s	c-s	b-s	sb			c-s	c-s	c-s	c-s	c-s	c-s
$\frac{1}{4}$	-s	c-s	c-s	c-s	c-s	c-s	c-s	s-b			c-s	c-s	c-s	c-s	c-s	c-s
0	NB	c-s	c-s	c-s	c-s	c-s	c-s	c-s	NB		c-s	c-s	c-s	c-s	c-s	c-s
$-\frac{1}{4}$	s	-cs	-cs	c-s	c-s	c-s	c-s	c-s			-cs	s-b	c-s	c-s	c-s	c-s
$-\frac{1}{3}$	s	-cs	-cs	c-s	c-s	c-s	c-s	c-s			-cs	-cs	b-s	c-s	c-s	c-s
$-\frac{1}{2}$	s	-cs	-cs	c-s	c-s	c-s	c-s	c-s			-cs	-cs	-cs	c-s	c-s	c-s
-1	s	-cs	bs	-sc	ec	ec	ec	ec			s-c	s-c	-cs	-cs	c-s	c-s
-2	s	bs	b-s	-s-c	-c-e	-c-e	-c-e	-c-e			-e-c	-e-c	-e-c	-e-c	s-b	c-s
-4	s	-bs	-s-c	-s-e	-s-e	-c-e	-c-e	-c-e			ce	ce	ce	-e-c	-e-c	c-s
-6	s	-s-c	-s-e	-s-e	-s-e	-c-e	-c-e	-c-e			ce	ce	ce	-e-c	-e-c	c-s
$-\infty$	0	-e-s	-e-s	-e-s	-s-e	-c-e	-c-e	-c-e			ce	ce	ce		-c=e	c-s
	$-\infty$	-6	-4	-2	-1	$-\frac{1}{2}$	$-\frac{1}{3}$	$-\frac{1}{4}$	0	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{1}{2}$	1	2	3	
	n															

bs: ..>b>s b-s: ..>b>-s -bs: ..>-b>s
 -cb: ..>-c>b ce: ..>c>e c-e: ..>c>-e -c-e: ..>-c>-e -cs: ..>-c>s c-s: ..>c>-s
 ec: ..>e>c -e-c: ..>-e>-c -e-s: ..>-e>-s
 s: ...>s -s: ...>-s sb: ..>s>b s-b: ..>s>-b s-c: ..>s>-c -sc: ..>-s>c
 -s-c: ..>-s>-c -se: ..>-s>e -s-e: ..>-s>-e
 0: The value of index is equal to zero NB: Does not index branching

The type of the branched structure

The size of molecule, the number of branches as well as the type of the branched structure, i.e. whether the branch bearing carbon is tertiary or quaternary index the $V_{ij}(m,0)$ indices, which are not mentioned above. They indicate that the structure having a quaternary carbon is more branched than that having two tertiary carbons. The index $V_{ij}(2,0)$ indicates that the structure having three tertiary carbons is equally branched as that having one quaternary carbon.

The type of branches

The label E in Table 10 indicates that at some combinations of exponents **m** and **n** in the $V_{ij}(m,n)$ indices the exchange of a methyl group for an ethyl group in the

structure of an octane contributes to the value of index more than any other structural feature, whereas in several cases (label e) it is the second greatest contribution.

Position of branches

Position of branches contributes to the value of a $V_{ij}(m,n)$ index in most cases less than the number of branches and the type of branches.

Separation between branches

The separation between branches contributes to the value of the indices $V_{ij}(3,1)$ and $V_{ij}(-4,2)$ more than any other structural feature contributing to branching. It has the second greatest contribution to the values of several indices when $m \leq -1$ and $-1 \leq n \leq 2$.

Correlation of physicochemical properties with $V_{ij}(m,n)$ indices

The values of tested $V_{ij}(m,n)$ indices were correlated with values of 23 or 24 physicochemical properties, as applicable, assuming a linear relationship between them. The results are presented in Fig. 1 for data of propane through octanes and in Fig. 2 for data of octanes. The data of 2,2,3,3-tetramethyl butane are lacking at MON and logVP. In these cases, 2,2,3,3-tetramethyl butane is not considered in correlation.

The pattern in Fig. 1 is quite different from that in Fig. 2. As presented by Fig. 1, molecular weight correlates perfectly with the index $V_{ij}(0,-\infty)$ which indicates only the size of molecule and increases linearly with carbon number. Eleven other physicochemical properties correlate best with other $V_{ij}(m,-\infty)$ indices increasing linearly with carbon number with the slope of 2^{2m+1} . Four of them correlate best with the index $V_{ij}(-1/2,-\infty) \equiv 2\chi$. Additional five physicochemical properties correlate best with $V_{ij}(m,-6)$ indices that do not deviate much from the linear increase with carbon number. Most of mentioned indices have a negative value of exponent m . The best correlations with $V_{ij}(m,n)$ indices having a positive value of the exponent n have only the MON and ω . The best correlations are observed at M_w ($r = 1$) > MR ($r = 0.998$), T_c^2/P_c ($r = 0.998$) > ΔH_v ($r = 0.997$) > BP ($r = 0.994$), T_c/P_c ($r = 0.994$) > ΔH_f° ($r = 0.991$), logVP ($r = -0.990$). Most of them are slightly higher than with the $W(m,n)$ indices.⁴

The pattern of Fig. 2 is different from that of Fig. 1. Evidently, the pattern of Fig. 1 is governed mainly by the dependence of the values of physicochemical properties on the size of the molecule. The pattern in Fig. 2, on the other hand, is governed only by branching since the influence of the size of the molecule is excluded. Surprising is the emptiness of the lower central part of the figure. The best correlations are observed at Tc/Pc ($r = -0.998$), ω ($r = -0.996$), BP/Tc ($r = -0.995$), MON ($r = -0.987$), Tc²/Pc ($r = 0.984$), C ($r = 0.969$), S ($r = -0.961$), and Pc ($r = 0.950$).

m															
3															
2						n_D									
1															
$1/2$				d											MON
$1/3$	ΔH_f°														
$1/4$														ω	
0	M														
$-1/4$	P	V													
$-1/3$	BP	T ² /P													
$-1/2$	α	VP	Tc												
-1	Zc	dc	B												
-2	A														
-4															
-6															
$-\infty$															
	$-\infty$	-6	-4	-2	-1	$-1/2$	$-1/3$	$-1/4$	0	$1/4$	$1/3$	$1/2$	1	2	3
	n														

Figure 1. The positions of 23 physicochemical properties determined by the highest correlation coefficient r (data in parentheses, see below) for data of alkanes from propane through octanes, in the plane of exponents m and n .

Single standing: n_D (0.910), d (0.926), MON (-0.756), ΔH_f° (0.991), ω (0.948), BP (0.994), Tc²/Pc (0.998), logVP (-0.990), Tc (0.986), Zc (-0.732), dc (0.802), B (0.981), A (0.651)

M : Mw (1), MR (0.998) P : Tc/Pc (0.994), Pc (-0.957) V : Vc (0.988), Vm (0.979) α : α_c (0.936), BP/Tc (0.963), C (-0.959), ΔH_v (0.997)

The comparison of Fig. 2 here with Fig. 3 in ref.⁴ shows that there are some similarities but also several differences in positions of best correlations between the two groups of indices and physicochemical properties. The best correlation coefficients are higher for $V_{ij}(m,n)$ indices and the following physicochemical properties of octanes: Zc,

Tc, BP, ΔH_v , BP/Tc, d, Vm, and nD; they are higher for W(m,n) indices and the following physicochemical properties of octanes: A, B, MR, and ΔH_f° . For other physicochemical properties the correlations are very similar at both groups of indices.

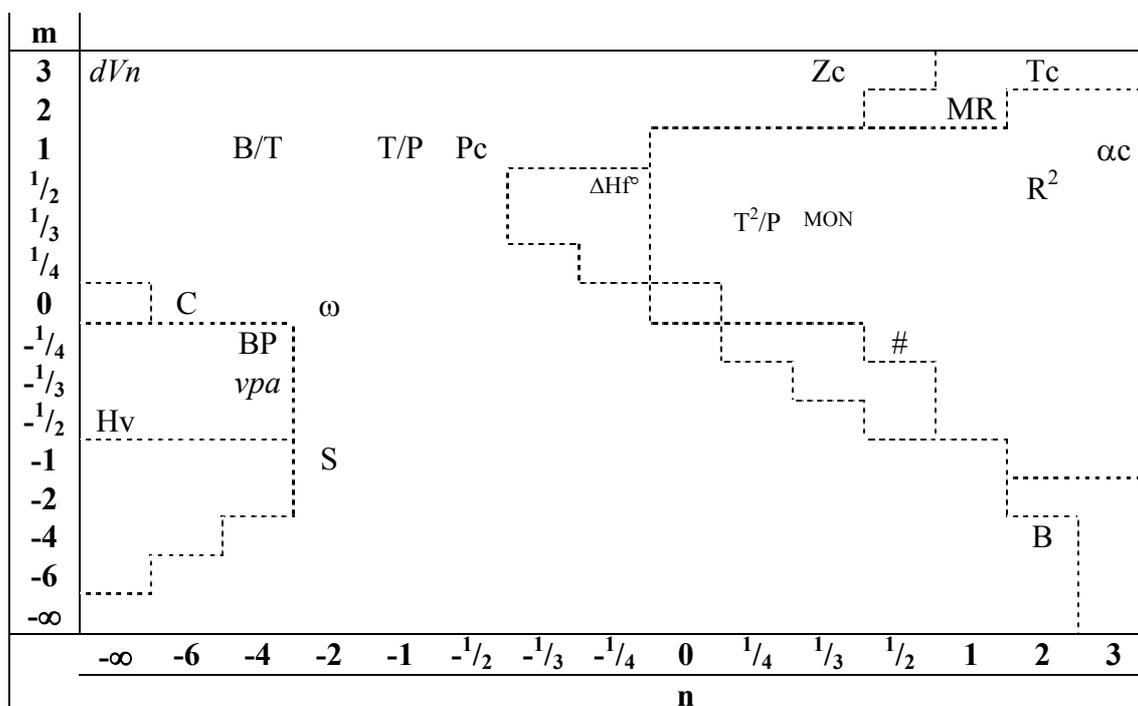


Figure 2. The positions of 24 physicochemical properties determined by the highest correlation coefficient r (data in parentheses, see below) for data of octanes, in the plane of exponents m and n .

Single standing: Zc (0.694), Tc (-0.830), MR (0.882), Pc (0.950), α_c (0.740), ΔH_f° (-0.904), R² (0.907), MON (-0.987), C (0.969), ω (-0.996), BP (0.885), ΔH_v (0.936), S (-0.961), B (-0.697)

B/T: BP/Tc (-0.995) T/P: Tc/Pc (-0.998) T²/P: Tc²/Pc (0.984)

dVn: d (0.915), Vm (-0.918), nD (0.899) vpa: logVP (-0.738), A (0.743)

#: Vc (0.844), dc (-0.831)

Dotted lines: Intermediate domains from Table 9.

The Vij(m,n) indices that might be good branching indices

In Fig. 3 are presented some interesting characteristics of the Vij(m,n) indices in the plane of exponents m and n . The index Vij(-∞,0) indexes only the number of branches, $V_{ij}(-\infty,0) = 2\sum(Np-1) = 2\sum(1+Nbr)$. It is a simple, primitive and degenerated, but a true branching index presenting the most important information about branching - the number of branches (the number of vertices of degree one).

The indices $V_{ij}(m,0)$, $n \neq -\infty$ and $n \neq 0$, index the size of the molecule, the number of branches and in addition they indicate that a quaternary structure is more branched than a tertiary one. They are degenerated branching indices, less simple than $V_{ij}(-\infty,0)$.

m																
3	=									BI	$t < q$					
2	=(M)										$t < q$					
1	=										$3t=2q$					
$1/2$	=										$t < q$					
$1/3$	=										$t < q$					
$1/4$	=										$t < q$					
0	NB			(H)	(RW)						NB		(W)			
$-1/4$	=	BI				BI	BI	BI	BI	BI	$t < q$					
$-1/3$	=					BI	BI	BI	BI	BI	$t < q$					
$-1/2$	=(X)					BI	BI	BI	BI	BI	$t < q$					
-1	=					BI	BI	BI	BI	BI	$t < q$	BI				
-2	=			#							$t < q$	BI	BI			
-4	=										$t < q$		□*			
-6	=										$t < q$	△	◇	*		
-∞	0									Nbr	◇	◇	◇	□		
		-∞	-6	-4	-2	-1	$-1/2$	$-1/3$	$-1/4$	0	$1/4$	$1/3$	$1/2$	1	2	3
		n														

Figure 3. $V_{ij}(m,n)$ indices that might be good branching indices (BI) and other indices with interesting characteristics. In parentheses: some traditional indices.

0 Does not measure branching

= $V_{ij}(m,-\infty)_{3M7} = V_{ij}(m,-\infty)_{4M7}$; $V_{ij}(m,-\infty)_{34M6} = V_{ij}(m,-\infty)_{3E2M5}$

BI Oct < 2M7 < 3M7 < 4M7 < 3E6 < 25M6 < 24M6 < 23M6 < 34M6 < 3E2M5 < 22M6 < 33M6 < 3E3M5 < 234M5 < 224M5 < 223M5 < 233M5 < 2233M4

BI Oct < 3E6 < 4M7 < 3M7 < 2M7 < 3E2M5 < 34M6 < 23M6 < 24M6 < 25M6 < 3E3M5 < 33M6 < 22M6 < 234M5 < 233M5 < 223M5 < 224M5 < 2233M4

$t < q$ $2t < 2q$

$S_{7,8}: n- > 2M > 3M > 3E > 24M > 23M > 22M > 33M > 223M$

□ $S_{7,8}: n- > 2M > 3M > 3E > 22M > 33M > 23M > 24M > 223M$

* Oct < 3E6 < 4M7 < 3M7 < 2M7 < 3E3M5 < 33M6 < 22M6 < 3E2M5 < 34M6 < 23M6 < 24M6 < 25M6 < 233M5 < 223M5 < 234M5 < 224M5 < 2233M4

◇ Oct < 2M7 < 3M7 < 4M7 < 3E6 < 22M6 < 33M6 < 3E3M5 < 23M6 < 3E2M5 < 34M6 < 24M6 < 25M6 < 223M5 < 233M5 < 224M5 < 234M5 < 2233M4

△ Oct < 2M7 < 3M7 < 4M7 < 3E6 < 22M6 < 33M6 < 3E3M5 < 23M6 < 3E2M5 < 34M6 < 24M6 < 25M6 < 223M5 < 233M5 < 234M5 < 224M5 < 2233M4

□ $n- < 1t < 2q$ (sep. = 0) < $2t$ (sep. = 1) < $2t$ (sep. = 2) < $2t$ (sep. = 3) < $2q1t$ (sep. = 1) < $2q1t=3t$ (sep. = 2) < $4q$ (sep. = 1). Thus, the influence is $B > s$, cf. Table 10 and 11; the position of branches is not important

Nbr Only the number of branches influences the value of this index

0: The value of index is equal to zero

NB: Does not index branching

The index $V_{ij}(-\infty,1)$ indexes the size of the molecule, the number of branches, as well as the separation between branches. It is also a degenerated branching index, less simple than $V_{ij}(-\infty,0)$. It indicates that a quaternary structure can be presented as a structure having the separation between branches equal to zero. Thus, whereas the index $V_{ij}(-\infty,1)$ distinguishes the values of the separation between branches, the indices $V_{ij}(m,0)$, $m \neq -\infty$ and $m \neq 0$, distinguish only whether the separation between branches equals to zero or it is larger than zero.

There are also several $V_{ij}(m,n)$ indices having some sort of a regular sequence of isomers. The index $V_{ij}(-2,-2)$, for example, has a regular sequence of isomers due to the increase of the size of the molecule. At the index $V_{ij}(-4,1)$, on the other hand, the contribution of the separation between branches prevails over the contribution of the position of branches when the size of the molecule increases as well as when branching increases. The following groups of $V_{ij}(m,n)$ indices have a regular sequence of isomers indicated by the label BI or *BI* in Fig. 3 and therefore they are candidates for true branching indices. The indices labelled *BI*, i.e. $V_{ij}(-1/4,-6)$, $V_{ij}(-1,1/4)$, $V_{ij}(-2,1/4)$, and $V_{ij}(-2,1/3)$ have a regular sequence of isomers indicating that a peripherally substituted alkane is more branched than a centrally substituted one. The reverse indicates the index $V_{ij}(3,-1/4)$ as well as a group of $V_{ij}(m,n)$ indices having $-1 \leq m \leq -1/4$ and $-1 \leq n \leq -1/4$, which are labelled BI. These $V_{ij}(m,n)$ indices seem to be good sources of the susceptibility for branching derived¹⁰ BI_A type²⁰ branching indices.

Comparing Fig. 2 with Fig. 3 we notice that the indices considered here as potentially good branching indices are not the best indices of tested 24 physicochemical properties of alkanes. This is understandable since none of the 24 tested physicochemical properties of alkanes has a regular sequence of isomers.¹⁰

Conclusions

Several traditional indices belong to the $V_{ij}(m,n)$ indices but they are not the best among them: neither regarding the correlation with the physicochemical properties nor as potential branching indices. An exception is the Randić index χ , which is a good measure for the influence of the size of the molecule on the values of several physicochemical properties; it is also a good index to present branching of ΔH_v , but cf.

also ref.⁷ indicating that other negative exponents may be better than $n = -\infty$ of the Randić index. The index $V_{ij}(-2,-2)$ has a regular sequence of isomers due to the increase of the size of the molecule. The indices $V_{ij}(-1/4,-6)$, $V_{ij}(-1,1/4)$, $V_{ij}(-2,1/4)$, and $V_{ij}(-2,1/3)$ have a regular sequence of isomers due to increasing branching, indicating that a peripherally substituted alkane is more branched than a centrally substituted one. The index $V_{ij}(3,-1/4)$ as well as a group of $V_{ij}(m,n)$ indices having $-1 \leq m \leq -1/4$ and $-1 \leq n \leq -1/4$ indicate that a centrally substituted alkane is more branched than a peripherally substituted one. These $V_{ij}(m,n)$ indices seem to be good sources of the susceptibility for branching derived¹⁰ BI_A type²⁰ branching indices.

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Povzetek

Najboljše korelacije z nekaterimi $V_{ij}(m,n)$ indeksi, če uporabimo podatke za alkane od propana do vključno oktanov, imajo fizikokemijske lastnosti M_w ($r = 1$), MR ($r = 0.998$), Tc^2/Pc ($r = 0.998$), ΔH_v ($r = 0.997$), BP ($r = 0.994$), Tc/Pc ($r = 0.994$), ΔH_f^o ($r = 0.991$) in $\log VP$ ($r = -0.990$). Če uporabimo le podatke za oktane, pa so to Tc/Pc ($r = -0.998$), ω ($r = -0.996$), BP/Tc ($r = -0.995$), MON ($r = -0.987$), Tc^2/Pc ($r = 0.984$), C ($r = 0.969$), S ($r = -0.961$) in Pc ($r = 0.950$). Indeks $V_{ij}(-2,-2)$ ima regularno zaporedje izomer pri večanju velikosti molekule. Indeksi $V_{ij}(-1/4,-6)$, $V_{ij}(-1,1/4)$, $V_{ij}(-2,1/4)$, $V_{ij}(-2,1/3)$, $V_{ij}(3,-1/4)$, kot tudi indeksi $V_{ij}(m,n)$ z $-1 \leq m \leq -1/4$ in $-1 \leq n \leq -1/4$ imajo regularno zaporedje izomer pri večanju razvejanosti. Videti so dobra podlaga za pripravo indeksov razvejanja vrste BI_A .