

SOME TOPOLOGICAL INDICES DERIVED FROM THE $v^m d^n$ MATRIX.PART 8. THE $L_{ij}(m,n)$ INDICES

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Abstract

The best correlation between some $L_{ij}(m,n)$ indices and physicochemical properties of alkanes, using data from propane to all octanes inclusive is observed at the pairs $L_{ij}(0,0)$ and Mw ($r = 1$), $L_{ij}(1/4,1/4)$ and Tc^2/Pc ($r = 0.9995$), $L_{ij}(0,0)$ and MR ($r = 0.998$), $L_{ij}(0,1/2)$ and Tc/Pc ($r = 0.998$), $L_{ij}(-1/3,0)$ and $\Delta H_f^\circ g$ ($r = 0.994$), $L_{ij}(0,1/3)$ and Vc ($r = 0.991$), and $L_{ij}(1/3,0)$ and BP ($r = 0.991$). The best correlation using only data of octanes is observed at the pairs $L_{ij}(1/2,-1)$ and Tc/Pc ($r = -0.996$), $L_{ij}(-1/4,-1)$ and ω ($r = -0.994$), $L_{ij}(1,-1)$ and BP/Tc ($r = -0.991$), $L_{ij}(1/4,3)$ and MON ($r = -0.984$), $L_{ij}(1/4,1/4)$ and Tc^2/Pc ($r = 0.982$), $L_{ij}(-1/2,-6)$ and C ($r = 0.967$), $L_{ij}(-1,-2)$ and S ($r = -0.961$), as well as at $L_{ij}(1,1/2)$ and Pc ($r = -0.961$). Thirteen $L_{ij}(m,n)$ indices having $-1 < m < 0$ and $-2 \leq n < 0$ have a regular sequence of isomers. These $L_{ij}(m,n)$ indices seem to be good sources of the susceptibility for branching derived BI_A type branching indices.

Introduction

A number of topological indices have been developed and tested for their performance as branching indices or indices of substances' properties.^{1,2} 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 indices³ and combinations of them have to be used.⁴ In spite of that, interest in topological indices has grown remarkably during recent years.

A substantial part of topological indices is derived from one or another matrix associated with molecular structure. Estrada⁵ developed a matrix that enables the derivation of an infinite number of indices. We⁶ 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. The characteristics of some groups of indices derived with help of the generalized vertex-degree, vertex distance matrices have been studied:

- the summation derived $W(m,n)$ indices⁶ which include besides the Wiener index⁷ W also some Ivanciuc indices,⁸
- the summation derived "mean degree of vertices" indices,⁹ which include the Randić index χ ,¹⁰
- the summation derived $V_{ij}(m,n)$ indices,¹¹ which include besides the Wiener index⁷ and several Ivanciuc indices^{8,12-16} also the Randić index χ ,¹⁰
- the susceptibilities for branching of the $W(m,n)$ indices,¹⁷ and the difference derived indices.¹⁸

In present paper are studied the $L_{ij}(m,n)$ indices, which are the largest eigenvalues of the matrices from which the $V_{ij}(m,n)$ indices¹¹ have been derived. One index of this group has a long tradition, namely λ_1 .^{19,20} It is also a member of the indices,^{21,22} which are the largest eigenvalues of the matrices from which the $W(m,n)$ indices⁶ or the "mean degree of vertices" indices⁹ are derived.

The approach used here is in some aspects similar to the search of novel drugs. Searching for novel drugs by combinatorial chemistry methods, several hundred compounds are synthesized and tested in order to find among them one or few compounds, which show some activity. In present study we tested 225 indices from the infinite family of the $L_{ij}(m,n)$ indices. All of them were tested for their characteristics in order to see the dependence of their values on the values of exponents **m** and **n**, on the structural features of alkanes (to perform also the structural interpretation of indices has been suggested recently^{23,24}), as well as to discover some of them, which either correlate well with physico-chemical properties or seem to be good candidates for branching indices.

Data

Notations

The structures of alkanes are presented in shorthand. The notation of *n*-alkanes is deliberately different from the branched ones in order to distinguish them easily, e.g. Hp is *n*-heptane, Oct is *n*-octane, etc, 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, i.e. eight vertices in the graph ($N = 8$), as well as four primary carbons, i.e. four vertices of degree

one ($Np = 4$). The two branches (i.e. the number of branches, $Nbr = 2$) in 22M6 are positioned on a quaternary carbon (q), i.e. on a vertex of degree four, which is placed on the periphery (per) of the main chain of the molecule. The two branches in 23M6 and 25M6 are positioned on tertiary carbons (t), i.e. on vertices of degree three. In 23M6 the branches are adjacent and those in 25M6 are distant, i.e. the separation between branches (s) in 25M6 is larger than in 23M6. On the other hand, in 23M6 is the branch in position 2 closer to the periphery of the main chain, whereas the branch in position 3 is closer to its centre (ctr).

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 Handbook²⁵ or from Lange's Handbook.²⁶ 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 Pogliani²⁷ and Gutman et al.,²⁸ those for vapour pressure ($\log VP$) from Goll and Jurs,²⁹ and those for the entropy (S) and quadratic mean radius (R^2) from Ren.³⁰

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

The $L_{ij}(m,n)$ indices are the largest eigenvalues of the matrix $\mathbf{G}(m,n)$ having the main diagonal elements \mathbf{g}_{ii} , which are equal to zero, and the nondiagonal elements \mathbf{g}_{ij} , which are equal to $v_i^m \times v_j^m \times d_{ij}^n$, where v_i and v_j is the degree of vertex i and j , respectively, 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.⁶ The label $L_{ij}(m,n)$ indicates that the degree of vertex v_i as well as that of vertex v_j is raised to the exponent \mathbf{m} , whereas the distance between them is raised to the exponent \mathbf{n} . Tested values of exponents \mathbf{m} resp. \mathbf{n} are: $-\infty$, -6 , -4 , -2 , -1 , $-1/2$, $-1/3$, $-1/4$, 0 , $1/4$, $1/3$, $1/2$, 1 , 2 , and 3 .

Methods

The one-spot estimation of the relative contribution of structural features to the value of an index is performed using the susceptibility for the increase of the size of the molecule or the susceptibility for branching.¹¹ The susceptibility³¹ is defined as the normalised difference of the indices' or properties' values, $S_{a,b} = X_b/X_a - 1$, where $S_{a,b}$ is the susceptibility, X is an index or a property, subscript a refers to the smaller in size or to the less branched structure and subscript b refers to the larger in size or to the more branched structure, as appropriate. Which structure is more branched is concluded by intuition as presented in ref.³² as well as by the *Methane based* definition and the *n-Alkane based* definition.³³ Two groups of susceptibilities are used.³¹

In the susceptibility for the increase of the size of the molecule, derived as $S_{a,a+1}$, the subscript a refers 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) is used, etc.

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

The one-spot estimation of 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 (b) is estimated by $b = S_{33\text{M}5,33\text{M}6} - S_{3\text{M}7,3\text{M}6}$. The contribution of the (central) position of branches (c) is estimated by $c = 1/2(S_{33\text{M}5,33\text{M}6} - S_{22\text{M}5,22\text{M}6})$. The contribution of the separation between branches (s) is estimated by $s = S_{24\text{M}5,24\text{M}6} - S_{23\text{M}5,23\text{M}6}$. The contribution of the change of the substituent from methyl to ethyl (e) is estimated by $e = S_{3\text{E}5,3\text{E}6} - S_{3\text{M}6,3\text{M}7}$.

The one-spot estimation of the relative contribution of a structural feature to the value of the index when branching of the molecule increases, is estimated as follows.

The contribution of the number of branches (b) is estimated by $b = S_{\text{Oct},33\text{M}6} - S_{\text{Oct},3\text{M}6}$. The contribution of the (central) position of branches (c) is estimated by $c = S_{\text{Oct},34\text{M}6} - S_{\text{Oct},23\text{M}6}$. The contribution of the separation between branches (s) is estimated by $s = S_{\text{Oct},24\text{M}6} - S_{\text{Oct},23\text{M}6}$. The contribution of the change of the substituent from methyl to ethyl (e) is estimated by $e = S_{\text{Oct},3\text{E}2\text{M}5} - S_{\text{Oct},23\text{M}6}$. An uppercase form of any of these labels is used to label the structural feature having the highest contribution to the value of the index in question. The results of estimations of the relative contribution of structural features are checked by the sequences of isomers obtained by sorting the values of indices corresponding to the isomers in question.

Results and discussion

The $L_{ij}(m,n)$ indices of methane are equal to zero since $\mathbf{g}_{ii} = 0$ by definition. The $L_{ij}(m,n)$ indices of ethane are equal to 1. The values of the index $L_{ij}(-\infty,-\infty)$ of other alkanes are equal to zero. The values of the index $L_{ij}(-1/2,-\infty)$ are equal to 1.

Long tradition has the index $\lambda_1^{19,20}$: $\lambda_1 \equiv L_{ij}(0,-\infty)$

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

Among the tested $L_{ij}(m,n)$ indices there are integers $L_{ij}(-\infty,-\infty)$, $L_{ij}(-1/2,-\infty)$, $L_{ij}(-\infty,0)$, and $L_{ij}(0,0)$.

Degeneration of $L_{ij}(m,n)$ indices

Among the tested indices, considering the structures of all 38 alkanes from propane to octanes inclusive, the indices $L_{ij}(0,-\infty)$, $L_{ij}(-1/2,-\infty)$, $L_{ij}(-1,-\infty)$, $L_{ij}(-4,-\infty)$, $L_{ij}(-6,-\infty)$, $L_{ij}(-\infty,-\infty)$, as well as the $L_{ij}(m,0)$ indices are highly degenerated. Some degeneration is observed also among the indices $L_{ij}(-1,-1)$, $L_{ij}(-2,-1)$, $L_{ij}(-\infty,-1)$, $L_{ij}(-\infty,1/2)$, $L_{ij}(-\infty,1)$, and $L_{ij}(-\infty,2)$. Among octanes are degenerated the indices $L_{ij}(0,-\infty)$, $L_{ij}(-1/2,-\infty)$, $L_{ij}(-1,-\infty)$, $L_{ij}(-6,-\infty)$, $L_{ij}(-\infty,-\infty)$, as well as the $L_{ij}(m,0)$ indices.

Correlation of $L_{ij}(m,n)$ indices with $V_{ij}(m,n)$ and $L(m,n)$ indices

When the structures of all 38 alkanes from propane to octanes inclusive are

considered, the correlation between the $L_{ij}(m,n)$ indices and $V_{ij}(m,n)$ indices,¹¹ assuming the linear relationship of the type: $y = ax + b$, is good at $n > 0$ when $-1 < m < 2$. It is most varying when $m < 0$ and $n < -1$. $L_{ij}(-\infty, -\infty) = V_{ij}(-\infty, -\infty) = 0$. If only octanes are considered, the best correlations are observed when $m \approx n$. There are several m, n combinations where the correlation is low. The $L_{ij}(m,n)$ and $L(m,n)$ indices²¹ are equal when $m = 0$ or $-\infty$. When the structures of all 38 alkanes from propane to octanes inclusive are considered, then the lowest correlation is observed around $m = -1$ and when $m > 1$. Among octanes, the situation is more differentiated. Low correlation is observed when $0 > m > -2$ and $m \approx -n$; in the region where $-\infty < m < -1/2$ and $-\infty < n < -2$, as well as in the region where $m > 1/2$ and $n > -1/3$.

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

Table 1 indicates whether the $L_{ij}(m,n)_n$ indices, i.e. the $L_{ij}(m,n)$ indices of n -alkanes increase or decrease with the increasing size of the molecule. We can see that in majority of tested cases they increase, except in the region represented roughly by $-\infty \leq m < -1/2$ and $-\infty \leq n < 0$. Within the latter region the values of $L_{ij}(m,n)$ indices of ethane are greater than at least those of propane and in several cases even greater than the $L_{ij}(m,n)$ indices of other higher n -alkanes. There are also indicated the shapes of the dependence of values of $L_{ij}(m,n)$ indices of n -alkanes on the size of the molecule. At $m < -1/2$ or $m < -1$ and $n < 0$, the values of $L_{ij}(m,n)$ indices of n -alkanes decrease on the increase of the size of the molecule. There exist also two intermediate domains. In the domain labelled C_{10} , C_{14} , Pe, Bu, and Pr, on increasing the size of the molecule the values of $L_{ij}(m,n)$ indices of n -alkanes decrease to a minimum at the specified n -alkane and beyond that minimum the values start to increase; i.e. there exists the combination of the decrease of values of $L_{ij}(m,n)$ indices at lower n -alkanes and of the increase at higher ones. In the domain labelled * there exists the combination of the shapes of increasing values of n -alkanes. Outside these domains, the values of $L_{ij}(m,n)$ indices of n -alkanes increase with the size of the molecule, resembling either a logarithmic-like increase, i.e. when $n < 0$ at $m > 0$ or at $n < 1$ at lower m , or an exponential increase in other cases.

Table 1. The changes of values of $L_{ij}(m,n)$ indices of n -alkanes on increasing carbon number. Tested were the carbon numbers from C_2 to C_{15} .

M															
m > 0	+	+	+	+	+	+	+	+	+	++	++	++	++	++	++
0	+	+	+	+	+	+	+	+	+	/	++	++	++	++	++
-1/4	+	+	+	+	+	+	+	+	+	+	++	++	++	++	++
-1/3	+	+	+	+	+	+	+	+	+	+	++	++	++	++	++
-1/2	—	+	+	+	+	+	+	+	+	+	++	++	++	++	++
-1	-	-	-	-	C ₁₀ =+	+	+	+	+	+	*	++	++	++	++
-2	-	-	-	-	C ₁₄	Pe	Bu	Pr	+	+	+	*	++	++	++
-4	-	-	-	-	-	-	-	-	+	+	+	+	++	++	++
-6	-	-	-	-	-	-	-	-	/	+	+	+	++	++	++
-∞	0	-	-	-	-	-	-	-	—	+	+	+	/	++	++
	-∞	-6	-4	-2	-1	-1/2	-1/3	-1/4	0	1/4	1/3	1/2	1	n > 1	
	n														

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

— The values of index do not change with the size of the molecule

/ The value of $L_{ij}(m,n)$ increases linearly with the size of the molecule

- The value of $L_{ij}(m,n)$ decreases hyperbolically with the size of the molecule

++ The value of $L_{ij}(m,n)$ increases exponentially with the size of the molecule

+ The value of $L_{ij}(m,n)$ increases with the size of the molecule resembling the shape of $\log(\text{size})$ or $\text{root}(\text{size})$

* The combination of shape + at low alkanes and shape ++ at higher ones

Pr (Bu, Pe, C₁₀, C₁₄): At the size of the molecule corresponding to propane (n -butane, n -pentane, n -decane, n -tetradecane, resp.) is observed the lowest $L_{ij}(m,n)_n$ value; beyond that size the values are increasing

= $L_{ij}(m,n)_{Et} = L_{ij}(m,n)_{Pr}$

Dashed lines indicate the intermediate domains between different types of dependence

The values of the indices $L_{ij}(-\infty,n)$ of n -alkanes can be expressed simply:
 $L_{ij}(-\infty,n)_n = (N-1)^n$, where N is the number of carbon atoms.

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

How the values of $L_{ij}(m,n)$ indices of other alkanes change on increasing the size of the molecule when the main chain of the alkane is elongated preserving the branched structure, is estimated using the susceptibility for the increase of the size of the molecule (S_{7,8}) and indicated in Table 2. In most cases the values of $L_{ij}(m,n)$ indices of all alkane isomers increase with increasing size of the molecule, except in some cases when $m \leq -1/2$ and $n < 0$. In the latter case, there is an intermediate domain, where the values of the $L_{ij}(m,n)$ indices of some isomers increase with the size of the molecule, whereas those of

other isomers decrease, as well as a domain at low values of exponent m , where the values of $L_{ij}(m,n)$ indices of all isomers decrease with the size of the molecule. Also in this respect the $L_{ij}(m,n)$ indices differ from the $V_{ij}(m,n)$ ¹¹ and $L(m,n)$ ²² indices in several cases.

Table 2. The changes of values of $L_{ij}(m,n)$ indices of other alkane isomers on increasing the size of the molecule expressed using the sign of $S_{7,8}$.

m										
$m > 0$	+	+	+	+	+	+	+	+	+	+
0	+	+	+	+	+	+	+	+	ES	+
$-1/4$	+	+	+	+	+	+	+	+	+	+
$-1/3$	+	+	+	+	+	+	+	+	+	+
$-1/2$	—	5-	3-	+	+	+	+	+	+	+
-1	1-	4-	6-	-	1-	+	+	+	+	+
-2	1-	1-	6-	-	-	8-	5-	4-	+	+
-4	1-	6-	-	-	-	-	-	-	+	+
-6	1-	-	-	-	-	-	-	-	+	+
$-\infty$	0	-	-	-	-	-	-	-	NS	+
	$-\infty$	-6	-4	-2	-1	$-1/2$	$-1/3$	$-1/4$	0	$n > 0$
	n									

- 0 The values of $L_{ij}(m,n)$ are equal to zero, except for ethane
 — The values of $L_{ij}(m,n)$ do not change with the size of the molecule
 + The value of $L_{ij}(m,n)$ increases with the size of the molecule among all isomers
 - The value of $L_{ij}(m,n)$ decreases with the size of the molecule among all isomers
 1- The value of $L_{ij}(m,n)$ of one isomer decreases and that of other isomers increase with the size of the molecule
 NS The values of index do not depend on the size of the molecule
 ES All isomers increase equally; the index measures only the size of the molecule
 Dashed lines indicate the transition domains between different types of dependence

How the structural features of alkanes influence the values of $L_{ij}(m,n)$ indices when the size of the molecule increases

The comparison of values of $L_{ij}(m,n)$ indices when the carbon number of alkanes in question increases by one, i.e from heptanes to octanes, allows some conclusions about the contribution of particular structural features. This comparison is based on the one-spot estimation of the relative contribution of a structural feature to the value of the index, see Methods.

Table 3. Structural features of alkanes having the highest influence on values of $L_{ij}(m,n)$ indices when the size of molecules increases.

m															
3	Se	Se	Se	Se	Sb	Sb	Sb	Bs	B	B-s	-Sb	-Sb	-Sb	-Sb	-Sb
2	Se	Se	Se	Se	Sb	Sb	Sb	Sb	B	B-s	-Sb	-Sb	-Sb	-Sb	-Sb
1	Se	Se	Se	Se	Sb	Sb	Sb	Sb	B	-Sb	-Sb	-Sb	-Sb	-Sb	-Sb
$\frac{1}{2}$	Se	Se	Se	Se	Se	Sb	Sb	Sb	B	-Sb	-Sb	-Sb	-Sb	-Sb	-Sb
$\frac{1}{3}$	Se	Se	Se	Se	Se	Se	Sb	Sb	B	-Sb	-Sb	-Sb	-S-e	-Sb	-Sb
$\frac{1}{4}$	Se	Se	Se	Se	Se	Se	Sb	Sb	B	-Sb	-Sb	-S-e	-S-e	-Sb	-Sb
0	Se	Se	Se	Se	Se	Se	Se	Se	NB	-S-e	-S-e	-S-e	-S-e	-Sb	-Sb
$-\frac{1}{4}$	S-b	S-b	S-b	Se	Se	S-b	S-b	-Bs	-B	-S-b	-S-b	-S-e	-S-e	-Sb	-Sb
$-\frac{1}{3}$	-Bs	-Bs	-Bs	Se	Se	S-b	-Bs	-Bs	-B	-B-s	-B-s	-S-b	-S-e	-Sb	-Sb
$-\frac{1}{2}$	0	-Bs	-Bs	-Bs	-Bs	-Bs	-Bs	-Bs	-B	-B-s	-B-s	-S-b	-S-e	-Sb	-Sb
-1	Bs	Bs	Sb	-Bs	-Bs	-Bs	-Bs	-Bs	-B	-B-s	-B-s	-B-s	-S-e	-Sb	-Sb
-2	Sb	Sb	S-b	-Bc	-B-s	-B-s	-B-s	-B-s	-B	-Bs	-Bc	-B-s	-S-e	-Sb	-Sb
-4	Sb	S-b	-Bc	-S-e	-S-e	-S-e	-S-e	-S-e	-B	Se	Se	-Ec	-S-e	-Sb	-Sb
-6	Sb	-Bc	-S-e	-S-e	-S-e	-S-e	-S-e	-S-e	-B	Se	Se	Ec	-S-e	-Sb	-Sb
$-\infty$	0	-E-s	-E-s	-S-e	-S-e	-S-e	-S-e	-S-e	NS	Se	Se	Ec	Sb	-Sb	-Sb
	$-\infty$	-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 or b - the influence of the number of branches

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

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

S or s - the influence of separation between branches

The most influential structural feature is presented with the uppercase letter

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

Meaning of combinations of labels:

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

Ec: $e>c>..$ -Ec: $-e>c>..$ -E-s: $-e>-s>..$

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

This contribution is superimposed to the contribution of the increase of the size of the molecule observed at n -alkanes. In Table 3 is presented the situation when the size of the molecule increases from a heptane to an octane by elongation of the main chain retaining the branched structure. There can be seen that depending on the combination of exponents **m** and **n**, the highest contribution has either the number of branches (indicated by label B) or the separation between branches (indicated by label S), and in few cases also the type of branches, i.e. if a methyl group is replaced by an ethyl one (indicated by label E). A higher value of the structural feature contributes either to a higher increase of

the value of the index (no sign before the label) or to a higher decrease of the value of the index (the - sign before the label). 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.

Regarding the influence of structural features, several $L_{ij}(m,n)$ indices differ from the $V_{ij}(m,n)$ indices¹¹ and this can be the reason for the cases of low correlation between these indices noticed above.

Table 4. Structural features of alkanes having the lowest influence on values of $L_{ij}(m,n)$ indices when the size of the molecules increases. Abbreviations as in Table 3.

m															
3	bc	bc	bc	bc	ec	ec	ec	ec	-e-c	-e-c	-e-c	-e-c	c-e	c-e	
2	bc	bc	bc	bc	ec	ec	ec	ec	-e-c	-e-c	-e-c	-e-c	-e-c	-e-c	
1	bc	bc	bc	bc	ec	ec	ec	ec	-e-c	-e-c	-e-c	-e-c	-e-c	-e-c	
$\frac{1}{2}$	bc	bc	bc	cb	bc	ec	ec	ec	-e-c	-e-c	-e-c	-e-c	-e-c	-e-c	
$\frac{1}{3}$	cb	cb	cb	cb	cb	bc	ec	ec	-e-c	-e-c	-e-c	b-c	-e-c	-e-c	
$\frac{1}{4}$	cb	cb	cb	cb	cb	bc	ec	ec	-e-c	-e-c	b-c	b-c	-e-c	-e-c	
0	c-b	c-b	cb	cb	cb	cb	cb	cb	-cb	-cb	-cb	-cb	-e-c	-e-c	
$-\frac{1}{4}$	ec	ec	ec	c-b	c-b	ec	ec	ec	-e-c	-c-e	-b-c	-c-b	-e-c	-e-c	
$-\frac{1}{3}$	ec	ec	ec	-bc	-bc	ec	ec	ec	-e-c	-e-c	-c-e	-c-b	-e-c	-e-c	
$-\frac{1}{2}$		-ce	-e-c	ec	ec	ec	ec	ec	-e-c	-e-c	-c-e	-c-b	-e-c	-e-c	
-1	c	c-e	-e-c	-c-e	ec	-e-c	ec	ec	-e-c	-e-c	-e-c	-c-b	-e-c	-e-c	
-2	ce	ce	-c-e	-s-e	-c-e	-c-e	-c-e	-c-e	ce	se	c-e	-c-b	-e-c	-e-c	
-4	ec	-c-e	-s-e	-c-b	-cb	-c-b	-c-b	-c-b	c-b	c-b	sb	-cb	-e-c	-e-c	
-6	ec	-s-e	-c-e	-cb	-cb	-cb	-cb	-cb	c-b	c-b	sb	b-c	-e-c	-e-c	
$-\infty$		b-c	-cb	-cb	-cb	-c-b	-cb	-cb	c-b	c-b	sb	-e-c	-e-c	-e-c	
	$-\infty$	-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														

Meaning of combinations of labels:

bc: ..>b>c b-c: ..>b>-c -bc: ..>-b>c -b-c: ..>-b>-c
 cb: ..>c>b c-b: ..>c>-b -c-b: ..>-c>-b -cb: ..>-c>b ce: ..>c>e c-e: ..>c>-e
 -ce: ..>-c>e -c-e: ..>-c>-e
 ec: ..>e>c -e-c: ..>-e>-c
 sb: ..>s>b se: ..>s>e -s-e: ..>-s>-e

In Table 4 are presented for comparison the structural features that have a lower contribution than those presented in Table 3. In Table 4 can be seen a higher variability with exponents m and n than in Table 3.

Dependence of $L_{ij}(m,n)$ indices on branching

Increase or decrease with branching

Whether the values of the $L_{ij}(m,n)$ indices increase or decrease with branching is presented for octanes in Table 5.

Table 5. Schematic presentation of the change of values of $L_{ij}(m,n)$ indices of octanes on increasing branching.

m												
3	+	+	+	+	+	+	+	+	+	+	6+	3+
2	+	+	+	+	+	+	+	+	+	11+	3+	-
1	+	+	+	+	+	6+	2+	-	-	-	-	-
$0 < m < 1$	+	+	+	+	-	-	-	-	-	-	-	-
0	+	+	+	+	NB	-	-	-	-	-	-	-
$-1/4$	+	+	+	+	+	+	12+	1+	-	-	-	-
$-1/3$	+	+	+	+	+	+	+	10+	-	-	-	-
$-1/2$	0	+	+	+	+	+	+	+	1+	-	-	-
-1	-	-	1+	+	+	+	+	+	+	-	-	-
-2	-	-	4+	+	+	+	+	+	+	1+	-	-
-4	-	5+	+	+	+	+	+	+	+	2+	-	-
-6	-	+	+	+	+	+	+	+	+	2+	-	-
$-\infty$	0	+	+	+	+	+	+	+	+	2+	-	-
	$-\infty$	-6	-4	$-2 \leq n < 0$	0	$1/4$	$1/3$	$1/2$	1	2	3	
	n											

+ : The value of the $L_{ij}(m,n)$ indices of all isomers increases on increasing branching

- : The value of the $L_{ij}(m,n)$ indices of all isomers decreases on increasing branching

1+ : The value of the $L_{ij}(m,n)$ index of one isomer is higher than the value of the $L_{ij}(m,n)$ index of n -octane, whereas the values of $L_{ij}(m,n)$ indices of other isomers are lower

0 : The value of the $L_{ij}(m,n)$ index is equal to zero

NB : The $L_{ij}(m,n)$ index does not index branching

Dashed lines indicate the transition domains between different types of dependence

The situation in Table 5 is similar to, but not equal to that observed among the $L(m,n)$ indices.²² In both cases we can observe in the plane of exponents m and n two domains where the values of indices decrease with increasing branching. They are separated from the domain, where the values of indices increase with increasing branching, by intermediate domains. In the intermediate domains, 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 domains among the $L(m,n)$ indices²² and $V_{ij}(m,n)$

indices¹¹ compared to those among the $L_{ij}(m,n)$ indices seem to be responsible for low correlations between them, which are mentioned above.

Influence of structural features

The comparison of values of the $L_{ij}(m,n)$ indices when branching increases, allows some conclusions about the contribution of particular structural features. In Table 6 can be seen that depending on the combination of exponents **m** and **n**, the highest contribution to the value of $L_{ij}(m,n)$ indices due to branching has either the number of branches (indicated by label B) or the presence of ethyl groups (indicated by the label E) or even the separation between branches (indicated by label S).

Table 6. Structural features having the highest contribution to the value of a $L_{ij}(m,n)$ 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	Sb	S-e	-E-c	
2	B-s	B-s	B-s	B-s	B-s	B-s	B-s	B-s	B	Bs	Bs	Bs	S-e	-B-e	-B-e	
1	B-s	B-s	B-s	B-s	Be	Be	Be	Be	B	-E-b	-B-e	-B-e	-B-e	-B-e	-B-e	
$\frac{1}{2}$	B-s	B-s	B-s	Be	Be	Be	Be	Be	B	-B-e	-B-e	-B-e	-B-e	-B-e	-B-e	
$\frac{1}{3}$	B-s	B-s	B-s	Be	Be	Be	Be	Be	B	-B-e	-B-e	-B-e	-B-e	-B-e	-B-e	
$\frac{1}{4}$	B-s	B-s	B-s	Be	Be	Be	Be	Be	B	-B-e	-B-e	-B-e	-B-e	-B-e	-B-e	
0	B-s	B-s	B-s	Be	Be	Be	Be	Be		-B-e	-B-e	-B-e	-B-e	-B-e	-B-e	
$-\frac{1}{4}$	B-s	B-s	B-s	Be	Be	Be	Be	Be	B	B-e	-E-c	-B-e	-B-e	-B-e	-B-e	
$-\frac{1}{3}$	B-s	B-s	B-s	Be	Be	Be	Be	Be	B	B-e	B-e	-E-c	-B-e	-B-e	-B-e	
$-\frac{1}{2}$		B-s	B-s	Be	B-s	Be	Be	Be	B	B-e	B-e	B-e	-B-e	-B-e	-B-e	
-1	-S-c	-S-b	-Se	Be	B-s	B-s	B-s	B-s	B	B-e	Bs	Bs	-Es	-B-e	-B-e	
-2	-S-c	-S-c	-Sb	B-s	Be	B-s	B-s	B-s	B	Bs	Bs	Bs	Bs	-B-e	-B-e	
-4	-S-c	-S-e	B-c	B-c	B-c	B-c	B-s	B-s	B	Bs	Bs	Bs	Bs	-B-e	-B-e	
-6	-S-c	B-c	B-c	B-c	B-c	B-c	B-s	B-s	B	Bs	Bs	Bs	Bs	-B-e	-B-e	
$-\infty$		B-c	B-c	B-c	B-c	B-c	B-s	B-s		Bs	Bs	Bs	Bs	-B-e	-B-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															

Labels: The label has four elements, e.g. $b>c>e>s$. In Table 6 are presented the former two in the form, e.g. Bc meaning $b>c>..$, whereas in Table 7 are presented the latter two, e.g. in the form es meaning $..>e>s$. Meaning of combinations of labels:

B-c: $b>-c>..$ Be: $b>e>..$ B-e: $b>-e>..$ -B-e: $-b>-e>..$ Bs: $b>s>..$ B-s: $b>-s>..$
 -E-b: $-e>-b>..$ -E-c: $-e>-c>..$ -Es: $-e>s>..$
 Sb: $s>b>..$ -Sb: $-s>b>..$ -S-b: $-s>-b>..$ -S-c: $-s>-c>..$ S-e: $s>-e>..$ -Se: $-s>e>..$
 -S-e: $-s>-e>..$

The contribution of ethyl groups or of the separation between branches is higher than that of the number of branches mainly among the $L_{ij}(m,n)$ indices positioned in the intermediate domains observed in Table 5. A higher value of the structural feature contributes either to a higher increase of the value of the index (no sign before the label) or to a higher decrease of the value of the index (the - sign before the label). 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 the $L_{ij}(m,n)$ index. Table 7 presents structural features that have a lower contribution than those presented in Table 6. Indices $L_{ij}(-\infty,-\infty)$ and $L_{ij}(-1/2,-\infty)$ do not index any contribution of structural features.

Table 7. Two structural features having the lowest contribution to the value of a $L_{ij}(m,n)$ index due to the increase of branching.

m															
3	ec	ec	ec	ce	ec	ec	ec	ec	-e-c	-e-c	-e-c	-e-c	-c-b	-bs	
2	ec	ec	ec	ec	ec	ec	ec	ec	-e-c	-e-c	-e-c	-c-b	-cs	-cs	
1	ec	ec	ec	ec	-sc	c-s	c-s	c-s	-cs	-cs	-cs	-cs	-cs	-cs	
$1/2$	ec	ec	ec	-sc	c-s	c-s	c-s	c-s	-cs	-cs	-cs	-cs	-cs	-cs	
$1/3$	ec	ec	ec	-sc	c-s	c-s	c-s	c-s	-cs	-cs	-cs	-cs	-cs	-cs	
$1/4$	ec	ec	ec	c-s	c-s	c-s	c-s	c-s	-cs	-cs	-cs	-cs	-cs	-cs	
0	ec	ec	ec	c-s	c-s	c-s	c-s	c-s	-cs	-cs	-cs	-cs	-cs	-cs	
$-1/4$	ec	ec	ec	-sc	c-s	c-s	c-s	c-s	-cs	s-b	-cs	-cs	-cs	-cs	
$-1/3$	ec	ec	ec	-sc	-sc	c-s	c-s	c-s	-cs	-cs	s-b	-cs	-cs	-cs	
$-1/2$		ec	ec	-sc	ec	-sc	-sc	-sc	-cs	-cs	-cs	-cs	-cs	-cs	
-1	-b-e	-c-e	-bc	-sc	ec	ec	ec	ec	-cs	-e-c	-e-c	-cb	-cs	-cs	
-2	-e-b	-e-b	-ce	-ce	-se	-c-e	-c-e	-c-e	ce	ce	c-e	-e-c	-cs	-cs	
-4	-e-b	-cb	-se	-se	-se	-se	-c-e	-c-e	ce	ce	ce	-e-c	-cs	-cs	
-6	-e-b	-se	-se	-se	-se	-se	-c-e	-c-e	ce	ce	ce	-e-c	-cs	-cs	
$-\infty$		-se	-se	-se	-se	-se	-c-e	-c-e	ce	ce	ce	-e-c	-cs	-cs	
	$-\infty$	-6	-4	-2	-1	$-1/2$	$-1/3$	$-1/4$	0	$1/4$	$1/3$	$1/2$	1	2	3
	n														

Meaning of combinations of labels:

-bc: $..>.b>c$ -bs: $..>.b>s$ -b-e: $..>.b>e$
-cb: $..>.c>b$ -c-b: $..>.c>b$ ce: $..>.c>e$ -ce: $..>.c>e$ -c-e: $..>.c>e$ c-s: $..>.c>s$
-cs: $..>.c>s$ ec: $..>.e>c$ -e-c: $..>.e>c$
s-b: $..>.s>b$ -sc: $..>.s>c$ -se: $..>.s>e$

Size of the molecule

Index $L_{ij}(0,0)$ indexes only the size of the molecule: $L_{ij}(0,0) = N-1$, where N is the

number of carbon atoms. Other $L_{ij}(m,n)$ indices except $L_{ij}(-\infty,0)$ index the size of the molecule and also the influence of other structural features. In majority of cases, except in some cases when $m < -1/2$ and $n < 0$, cf. Table 2, the contribution of the size of the molecule to the value of a $L_{ij}(m,n)$ index is greater than the contribution of structural features indicating branching. This fact will not be mentioned again below unless considered necessary.

Number of branches

The index $L_{ij}(-\infty,0)$ indexes only the number of branches. The contribution of the number of branches to the value of other $L_{ij}(m,n)$ indices is in most cases the major one, Table 6.

Type of the branched structure

$L_{ij}(m,0)$ indices, which are not mentioned above in the text, index the size of the 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. They indicate that the structure having a quaternary carbon is more branched than that having two tertiary carbons.

Type of branches

The label E in Table 6 indicates that at some combinations of exponents m and n , in the $L_{ij}(m,n)$ 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

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

Separation between branches

The separation between branches contributes to the value of indices $L_{ij}(3,1)$, $L_{ij}(3,2)$, $L_{ij}(2,1)$, $L_{ij}(-6 \text{ to } -1, -\infty)$, $L_{ij}(-4 \text{ to } -1, -6)$, $L_{ij}(-2, -4)$, and $L_{ij}(-1, -4)$ more than any other structural feature contributing to branching. It has the second greatest contribution to the values of several indices in the arc of the m,n plane extending from $(-\infty, 1)$ over $(0, -\infty)$ to $(3, 1/2)$.

The pattern of Fig. 1 here is, on the one hand, different from that of Fig. 1 in ref.¹¹ relating to the $V_{ij}(m,n)$ indices. The reason is obvious; the pattern reflects in both cases the vicinity of indices having a linear or nearly linear increase with carbon number.

Here, the pattern in Fig. 1 is, on the other hand, quite different from that in Fig. 3. In Fig. 1, there is a functional relationship between the molecular weight (M_w) and the index $L_{ij}(0,0)$, which indicates only the size of the molecule and increases linearly with carbon number. The majority of other tested physicochemical properties correlate best with other indices, derived using exponents m and n not very different from zero. They indicate that a nearly linear increase with carbon number is an important characteristic of an index to index the dependence of many physicochemical properties on the size of the molecule. Most of mentioned indices have a low but positive value of exponent m . The best correlations with data of physicochemical properties of alkanes from propane to octanes inclusive are observed at M_w ($r = 1$), T_c^2/P_c ($r = 0.9995$), MR ($r = 0.998$), T_c/P_c ($r = 0.998$), $\Delta H_f^\circ g$ ($r = 0.992$), V_c ($r = 0.991$), BP ($r = 0.991$), and ΔH_v ($r = 0.990$).

Figure 2. Positions in the plane of exponents m and n of best observed correlation coefficients of physicochemical property T_c^2/P_c (and the van der Waals parameter a_0) and $L_{ij}(m,n)$ indices for data of alkanes from propane to octanes inclusive.

m															
3															
2															
1								◇	□	□	□	◆			
$1/2$						◇	◇	◇	□	●	□	□	◇		
$1/3$						◇	◇	◇	□	○	□	□	◇		
$1/4$						◇	◇	◇	□	●	○	□	◇		
0						◇	◇	◇	◇	□	□	●	◇		
$-1/4$									◇	◇	◇	□	□		
$-1/3$									◇	◇	◇	◇	■		
$-1/2$											◇	◇	□		
-1													◇	◇	
-2														◇	
-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														

Open symbols: ○: $r > 0.999$, □: $0.99 < r < 0.999$, ◇: $0.95 < r < 0.99$, no symbol: $r < 0.95$

Closed symbol: local maximum

by exponents $\mathbf{m} = \mathbf{n}$ or $\mathbf{m} = -\mathbf{n}$. The best correlation is observed at Tc/Pc ($r = -0.996$), ω ($r = -0.994$), BP/Tc ($r = -0.991$), MON ($r = -0.985$), Tc²/Pc ($r = 0.982$), C ($r = 0.967$), S ($r = -0.961$), and Pc ($r = -0.961$).

Figure 4. Positions of best five correlations of eight physicochemical properties of octanes with $L_{ij}(m,n)$ indices in the plane of exponents \mathbf{m} and \mathbf{n} .

m															
3															
2															
1	P5	P3	P4	$\beta 2$	b5									P1	
$1/2$				b2	b1				C3	$\omega 4$					M4
$1/3$					b3					a3	a4			M5	M2
$1/4$					b4					a1	a2	a5			M1
0	(λ_1)													(D_1)	M3
$-1/4$				$\omega 2$	$\omega 1$										
$-1/3$				$\omega 3$	$\omega 5$										
$-1/2$		C1	C2	C4	S5										
-1				C5											
-2														P2	
-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														

*PCP L1: $L_{ij}(m,n)$ ($r(\text{PCP};L_{ij}(m,n))$)

MON M1: $L_{ij}(1/4,3)$ (-0.98420) M2: $L_{ij}(1/3,3)$ (-0.98413) M3: $L_{ij}(0,3)$ (-0.98344)

M4: $L_{ij}(1/2,3)$ (-0.98340) M5: $L_{ij}(1/3,2)$ (-0.98276)

Pc P1: $L_{ij}(1,1/2)$ (-0.96136) P2: $L_{ij}(-2,2)$ (-0.95502) P3: $L_{ij}(1,-6)$ (0.94988)

P4: $L_{ij}(1,-4)$ (0.94988) P5: $L_{ij}(1,-\infty)$ (0.94978)

C C1: $L_{ij}(-1/2,-6)$ (0.96729) C2: $L_{ij}(-1/2,-4)$ (0.96523) C3: $L_{ij}(1/2,0)$ (-0.96473)

C4: $L_{ij}(-1/2,-2)$ (0.96401) C5: $L_{ij}(-1,-2)$ (0.96356)

ω $\omega 1$: $L_{ij}(-1/4,-1)$ (-0.99425) $\omega 2$: $L_{ij}(-1/4,-2)$ (-0.99391) $\omega 3$: $L_{ij}(-1/3,-2)$ (-0.99270)

$\omega 4$: $L_{ij}(1/2,1/4)$ (0.99211) $\omega 5$: $L_{ij}(-1/3,-1)$ (-0.99211)

Tc/Pc b1: $L_{ij}(1/2,-1)$ (-0.99644) b2: $L_{ij}(1/2,-2)$ (-0.99491) b3: $L_{ij}(1/3,-1)$ (-0.99470)

b4: $L_{ij}(1/4,-1)$ (-0.99376) b5: $L_{ij}(1,-1)$ (-0.99258)

BP/Tc b5: $L_{ij}(1,-1)$ (-0.99106) $\beta 2$: $L_{ij}(1,-2)$ (-0.99077) P4: $L_{ij}(1,-4)$ (-0.98782)

P3: $L_{ij}(1,-6)$ (-0.98679) P5: $L_{ij}(1,-\infty)$ (-0.98644)

S C5: $L_{ij}(-1,-2)$ (-0.96148) C1: $L_{ij}(-1/2,-6)$ (-0.95777) C2: $L_{ij}(-1/2,-4)$ (-0.95723)

C4: $L_{ij}(-1/2,-2)$ (-0.95617) S5: $L_{ij}(-1/2,-1)$ (-0.95383)

Tc2/Pc a1: $L_{ij}(1/4,1/4)$ (0.98249) a2: $L_{ij}(1/4,1/3)$ (0.98187) a3: $L_{ij}(1/3,1/4)$ (0.98185)

a4: $L_{ij}(1/3,1/3)$ (0.98134) a5: $L_{ij}(1/4,1/2)$ (0.98036)

* Labelling system:

Physicochemical property (PCP) label in Fig. 4: $L_{ij}(m,n)$ ($r(\text{PCP};L_{ij}(m,n))$)

(λ_1) : largest eigenvalue of the \mathbf{A} (djacency matrix)^{19,20}

(D_1) : largest eigenvalue of the \mathbf{D} (istance matrix)

The comparison of Fig. 3 here with Fig. 2 in ref.¹¹ shows that there is a different pattern of positions of best correlation coefficients in the two groups of indices and physicochemical properties in the plane of exponents m and n . The best correlation coefficients are in most cases slightly higher for the $V_{ij}(m,n)$ indices than for the $L_{ij}(m,n)$ indices. The situation comparing the $V_{ij}(m,n)$ indices¹¹ with $L_{ij}(m,n)$ indices is similar to that when comparing the $W(m,n)$ indices⁶ with $L(m,n)$ indices²¹: The largest eigenvalues of the $v^m d^n$ matrices are mostly slightly better indices of the size of the molecules, whereas the summation-derived indices are mostly slightly better branching indices.

Figure 5. Positions in the plane of exponents m and n of best observed correlation coefficients of the physicochemical property T_c/P_c (and of the van der Waals parameter b_0) and $L_{ij}(m,n)$ indices for data of octanes.

m	$r < 0$ ←								→ $r > 0$						
3															
2															
1	◇	◇	◇	□	□	◇	◇	◇				◇	◆	◇	
1/2	◇	◇	□	□	■	□	◇			◇	◇	◇	◇	◇	
1/3	◇	◇	◇	□	□	◇				◇	◇	◇	◇	◇	
1/4	◇	◇	◇	□	□	◇				◇	◇	◇	◇	◇	
0	◇	◇	◇	◇	◇	◇	◇	◆		◆	◇	◇	◇	◇	
-1/4				◇	◇								■	◇	◇
-1/3													◇	◇	◇
-1/2														◇	◇
-1													■		◇
-2														◇	◇
-4															◇
-6															◇
-∞															◆
	-∞	-6	-4	-2	-1	-1/2	-1/3	-1/4	0	1/4	1/3	1/2	1	2	3
	n														

Open symbol: □: $0.99 < \text{abs}(r) < 0.999$, ◇: $0.95 < \text{abs}(r) < 0.99$, no symbol: $\text{abs}(r) < 0.95$
 Closed symbol: local maximum

In Fig. 4, five positions of best correlations of eight physicochemical properties of octanes correlating best with tested $L_{ij}(m,n)$ indices are given. They indicate different dependence of best correlation coefficients of physicochemical properties with tested $L_{ij}(m,n)$ indices on the combination of exponents m and n . The positions of five best

correlations corresponding to Pc, C, and ω indicate that there is more than one maximum of correlation coefficients in the plane of exponents \mathbf{m} and \mathbf{n} . The situation is illustrated in Fig. 5 for the best correlating physicochemical property, Tc/Pc. Inspection of all correlations of tested data shows that the occurrence of several local maxima is a general fact.

If we compare the contribution of structural features to the values of Tc/Pc of octanes with the contribution to indices in the highest local correlation maxima in Fig. 5, i.e. to $L_{ij}(\frac{1}{2}, -1)$, $L_{ij}(-\frac{1}{4}, 1)$, and $L_{ij}(-1, 1)$, the sequence of contribution of structural features is $-b>-e>-c>s$, $b>e>c>-s$, $-b>-e>-c>s$, and $-e>s>-c>b$, respectively. Thus, the indices $L_{ij}(\frac{1}{2}, -1)$ and $L_{ij}(-\frac{1}{4}, 1)$ have the same sequence as Tc/Pc, though the former one with opposite sign, which reflects also in the sign of the correlation coefficient. The index $L_{ij}(-1, 1)$, on the other hand, has a quite different sequence of contributions of structural features and in spite of that a quite good correlation. If we compare the relative values of these contributions, Table 8, we can see that they are quite different. It seems that several combinations of these contributions enable a good correlation.

Table 8. Relative contribution of structural features to the value of Tc/Pc and to three indices in local maxima in Fig. 5.

	Tc/Pc	$L_{ij}(\frac{1}{2}, -1)$	$L_{ij}(-\frac{1}{4}, 1)$	$L_{ij}(-1, 1)$
r (Tc/Pc; index)		-0.9964	0.9917	0.9915
sequence	$-b>-e>-c>s$	$b>e>c>-s$	$-b>-e>-c>s$	$-e>s>-c>b$
relative contribution of				
b	-1	1	-1	1
c	-0.38	0.28	-0.28	-1.10
s	0.23	-0.22	0.14	1.21
e	-0.46	0.38	-0.40	-1.34

Labels see Table 3.

$L_{ij}(\mathbf{m}, \mathbf{n})$ indices that might be good branching indices.

In Fig. 6, the $L_{ij}(\mathbf{m}, \mathbf{n})$ indices that may be good branching indices are presented in the plane of exponents \mathbf{m} and \mathbf{n} . The index $L_{ij}(-\infty, 0)$ indexes only the number of branches, i.e. $L_{ij}(-\infty, 0) = Np - 1 = Nbr + 1$, where Np is the number of vertices of degree one and Nbr is the number of branches. 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 $L_{ij}(m,0)$, $m \neq -\infty$ and $m \neq 0$, 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 $L_{ij}(-\infty,0)$.

The index $L_{ij}(-\infty,1)$ is interesting since it indexes quite distinctively the size of the molecule, the number of branches, as well as the separation between branches, followed by lower contributions of the type of branches and their position. From the sequence of octanes: Oct < 3Et6 < 4M7 < 3M7 < 2M7 < 3Et3M5 < 33M6 < 22M6 < 3Et2M5 < 34M6 < 23M6 < 24M6 < 25M6 < 233M5 < 223M5 < 234M5 < 224M5 < 2233M4 can be deduced the following rule: $n-$ ($Nbr = 0$) < $1t$ ($Nbr = 1$; $ctr < per$) < $2q$ ($Nbr = 2$; $s = 0$; $ctr < per$) < $2t$ ($Nbr = 2$; $s = 1$; $ctr < per$) < $2t$ ($Nbr = 2$; $s = 2$) < $2t$ ($Nbr = 2$; $s = 3$) < $2q1t$ ($Nbr = 3$; $s = 1$; $ctr < per$) < $3t$ ($Nbr = 3$) < $2q1t$ ($Nbr = 3$; $s = 2$) < $4q$ ($Nbr = 4$), where $n-$ stands for n -alkane, Nbr is the number of branches, t indicates that the branch is positioned on a tertiary carbon, q indicates that the branch is positioned on a quaternary carbon, ctr indicates the position of branch(es) closer to the centre of the main chain of the octane, per indicates the position of branch(es) closer to the end of the main chain of the octane, s is the separation between branches. The relative contribution of structural features is $b > s > e > c$. It indicates that a quaternary structure can be presented as a structure having the separation between branches equal to zero. Thus, whereas the index $L_{ij}(-\infty,1)$ distinguishes clearly the values of the separation between branches, the indices $V_{ij}(m,0)$, $n \neq -\infty$ and $n \neq 0$, distinguish only whether the separation between branches equals to zero or it is larger than zero.

There are also 13 $L_{ij}(m,n)$ indices having a "regular" sequence of isomers: Oct < 2M7 < 3M7 < 4M7 < 3E6 < 25M6 < 24M6 < 23M6 < 34M6 < 3E2M5 < 22M6 < 33M6 < 3E3M5 < 234M5 < 224M5 < 223M5 < 233M5 < 2233M4. They are grouped in a plane characterized by the values of exponents in the $v^m d^n$ matrix of $-1 < m < 0$ and $-2 \leq n < 0$. It is interesting that although they have the same sequence of isomers, this sequence is caused by three different sequences of contributions of structural features. These $L_{ij}(m,n)$ indices seem to be good sources of the susceptibility for branching derived¹⁷ BI_A type³³ branching indices.

Figure 6. $L_{ij}(m,n)$ indices that might be a source of good branching indices of BI_A group as well as other indices with interesting characteristics.

m																
3									$t < q$							
2									$t < q$							
1									$t < q$							
$1/2$									$t > q$							
$1/3$									$t > q$							
$1/4$									$t > q$							
0	(λ_1)								$N-1$						(D_1)	
$-1/4$					Ba	Ba	Ba	Ba	$t < q$							
$-1/3$					Bb	Ba	Ba	Ba	$t < q$							
$-1/2$	1			Bb	Bc	Bb	Bb	Bb	$t < q$							
-1									$t < q$							
-2									$t < q$							
-4									$t < q$						*	
-6									$t < q$						*	
$-\infty$	0								$Np-1$						*	
	$-\infty$	-6	-4	-2	-1	$-1/2$	$-1/3$	$-1/4$	0	$1/4$	$1/3$	$1/2$	1	2	3	
	n															

0 or 1: Measures neither size nor branching

Ba, Bb, Bc: The sequence of isomers is Oct < 2M7 < 3M7 < 4M7 < 3E6 < 25M6 < 24M6 < 23M6 < 34M6 < 3E2M5 < 22M6 < 33M6 < 3E3M5 < 234M5 < 224M5 < 223M5 < 233M5 < 2233M4, but the relative contribution of structural features is at Ba: b>e>c>-s, at Bb: b>e>-s>c, and at Bc: b>-s>e>c

$t < q$: The index indicates the number of branches as well as the fact that the vertices of degree three contribute less than the vertices of degree four

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

$Np-1$: $L_{ij}(-\infty, 0) = Np-1 = Nbr + 1$ $N-1$: $L_{ij}(0, 0) = N-1$

(λ_1) : largest eigenvalue of the **A**(djacency matrix)^{19,20}

(D_1) : largest eigenvalue of the **D**(istance matrix)

Comparing Fig. 3 with Fig. 6 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.

Conclusions

The $L_{ij}(m,n)$ indices are the largest eigenvalues of the generalized type of the vertex-degree, vertex-distance matrix. One index of this group has a long tradition:^{19,20}

$$\lambda_1 \equiv L_{ij}(0, -\infty).$$

Characteristics of the $L_{ij}(m,n)$ indices are as follows:

- a) The indices $L_{ij}(-\infty,-\infty)$ and $L_{ij}(\frac{1}{2},-\infty)$ are useless.
- b) Index $L_{ij}(0,0)$ indexes only the size of the molecule: $L_{ij}(0,0) = N-1$.
- c) Index $L_{ij}(-\infty,0)$ indexes only the number of branches: $L_{ij}(-\infty,0) = Np-1 = Nbr+1$.
- d) $L_{ij}(m,0)$ indices not mentioned above, index the size of the 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.
- e) All other $L_{ij}(m,n)$ indices index the size of the molecule, the number of branches, the type of branches, the separation between branches, and the position of branches. The type of the branched structure, i.e. whether the branch bearing carbon is tertiary or quaternary is presented by the separation between branches: on quaternary carbons the separation between branches is equal to zero, whereas on tertiary ones it is always greater than zero.
- f) The best correlation of $L_{ij}(m,n)$ indices with data of physicochemical properties of alkanes from propane to all octanes inclusive, assuming a linear relationship, is observed at the following pairs: $L_{ij}(0,0)$ and Mw ($r = 1$), $L_{ij}(\frac{1}{4},\frac{1}{4})$ and Tc^2/Pc ($r = 0.9995$), $L_{ij}(0,0)$ and MR ($r = 0.998$), $L_{ij}(0,\frac{1}{2})$ and Tc/Pc ($r = 0.998$), $L_{ij}(-\frac{1}{3},0)$ and ΔH_f° ($r = 0.994$), $L_{ij}(0,\frac{1}{3})$ and Vc ($r = 0.991$), and $L_{ij}(\frac{1}{3},0)$ and BP ($r = 0.991$). The best correlation with data of physicochemical properties of octanes is observed at the following pairs: $L_{ij}(\frac{1}{2},-1)$ and Tc/Pc ($r = -0.996$), $L_{ij}(-\frac{1}{4},-1)$ and ω ($r = -0.994$), $L_{ij}(1,-1)$ and BP/Tc ($r = -0.991$), $L_{ij}(\frac{1}{4},3)$ and MON ($r = -0.984$), $L_{ij}(\frac{1}{4},\frac{1}{4})$ and Tc^2/Pc ($r = 0.982$), $L_{ij}(-\frac{1}{2},-6)$ and C ($r = 0.967$), $L_{ij}(-1,-2)$ and S ($r = -0.961$), as well as at $L_{ij}(1,\frac{1}{2})$ and Pc ($r = -0.961$).
- g) Thirteen tested $L_{ij}(m,n)$ indices having $-1 < m < 0$ and $-2 \leq n < 0$, have a "regular" sequence of isomers: Oct < 2M7 < 3M7 < 4M7 < 3E6 < 25M6 < 24M6 < 23M6 < 34M6 < 3E2M5 < 22M6 < 33M6 < 3E3M5 < 234M5 < 224M5 < 223M5 < 233M5 < 2233M4. This sequence indicates that if the branch(es) is(are) positioned closer to the centre of the main chain of the molecule, then the isomer seems to be more branched than the isomer, which has the branch(es) positioned closer to the periphery of the main chain of the molecule. It is interesting that although these $L_{ij}(m,n)$ indices have the same sequence of isomers, this sequence is caused by three different sequences of

contributions of structural features. These $L_{ij}(m,n)$ indices seem to be good sources of the susceptibility for branching derived¹⁷ BI_A type³³ branching indices.

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Povzetek

Če uporabimo podatke za alkane od propana do vključno oktanov, indeksi $L_{ij}(m,n)$ najboljše korelirajo s fizikokemijskimi lastnostmi v naslednjih primerih: $L_{ij}(0,0)$ in Mw ($r = 1$), $L_{ij}(1/4, 1/4)$ in Tc^2/Pc ($r = 0.9995$), $L_{ij}(0,0)$ in MR ($r = 0.998$), $L_{ij}(0, 1/2)$ in Tc/Pc ($r = 0.998$), $L_{ij}(-1/3, 0)$ in $\Delta H_f^\circ g$ ($r = 0.994$), $L_{ij}(0, 1/3)$ in Vc ($r = 0.991$), ter $L_{ij}(1/3, 0)$ in BP ($r = 0.991$). Če uporabimo le podatke za oktane, pa $L_{ij}(1/2, -1)$ in Tc/Pc ($r = -0.996$), $L_{ij}(-1/4, -1)$ in ω ($r = -0.994$), $L_{ij}(1, -1)$ in BP/Tc ($r = -0.991$), $L_{ij}(1/4, 3)$ in MON ($r = -0.984$), $L_{ij}(1/4, 1/4)$ in Tc^2/Pc ($r = 0.982$), $L_{ij}(-1/2, -6)$ in C ($r = 0.967$), $L_{ij}(-1, -2)$ in S ($r = -0.961$), ter $L_{ij}(1, 1/2)$ in Pc ($r = -0.961$). Trinajst indeksov $L_{ij}(m,n)$, ki imajo $-1 < m < 0$ in $-2 \leq n < 0$, ima regularno zaporedje izomer pri večanju razvejanosti. Videti so dobra podlaga za pripravo indeksov razvejanja vrste BI_A .