SOME TOPOLOGICAL INDICES DERIVED FROM THE $v^m d^n$ MATRIX. PART 3. THE LARGEST EIGENVALUES OF THE $v^m d^n$ MATRIX AS TOPOLOGICAL INDICES OF THE BI_M-TYPE

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Abstract

The L(m,n) indices are the largest eigenvalues of the $v^m d^n$ matrix. Their properties are in many cases similar to properties of W(m,n) indices. The values of most, but not all tested L(m,n) indices increase with the size of the molecule. The increase is in general non-linear. Other structural features, e.g. the distance between the branches, the number of branches, and the type of branched structure have a substantial influence on the value of L(m,n) indices when the size of the molecule increases. The indices L(-∞,-∞) and L(-1,-∞) present no information about the properties of alkanes. The index L(0,0) presents only the information about the size of molecules. The index L(-∞,0) is a simple, primitive and degenerated, but a true branching index linking the BI_M indices obeying the *Methane based* definition of branching with the BI_A indices obeying the *n-Alkane-based* definition of branching. Several L(m,0) indices suggest that a branch on a quaternary carbon (i.e. on a vertex of degree four) contributes more to branching (complexity) than a branch on a tertiary carbon (i.e. on a vertex of degree three). The contrary is presented by the index L(2,0) and few other L(m,n) indices. The majority of other tested L(m,n) indices indicates that the isomers having branches closer to the centre of molecule are more branched, whereas those having a larger distance between branches are less branched. The L(m,n) indices are worse branching indices than the W(m,n) indices.

Introduction

Several hundred topological indices have been developed and tested for their performance as branching indices or indices of substances' properties.[1,2] The 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 indices[3] and combinations of them are to be used.[4] In spite of that, interest in topological indices has grown remarkably during the recent years. Therefore, the study of those topological indices that might be good branching indices remains an important area of research.

A substantial part of topological indices is derived from one or another matrix. Ivanciuc[5] mentions 14 different types of matrices as sources of topological indices. That these types of matrices are different has been considered also by other authors.[6] There have been developed the matrices that enable the derivation of an infinite number of indices.[6,7] Using the so-called $\mathbf{v^m d^n}$ matrix, 225 out of an infinite number of possible Wiener[8]-like[9] indices of BI_M-type labelled as W(m,n) indices and obeying the *Methane based* definition of branching, were derived and tested.[7] In present paper we test a set of 225 indices which are the largest eigenvalues of the $\mathbf{v^m d^n}$ matrices and we label them as L(m,n) indices.

Data

The structures of alkanes are presented in shorthand, e.g. Hp is *n*-heptane, Oct is *n*-octane, 223M5 is 2,2,3-trimethylpentane, 3Et2M5 is 3-ethyl-2-methylpentane, etc. The other terms are explained on 2,2-, 2,3- and 2,5-dimethyl hexane (22M6, 23M6 and 25M6) as examples. The two branches (the number of branches, $N_{br} = 2$) in 22M6 are positioned on a quaternary carbon (2*q*) placed on the periphery (*per*) of the molecule. The two branches in 23M6 and 25M6 are positioned on tertiary carbons (2*t*). In 23M6 the branches are adjacent (*adj*) and those in 25M6 are distant (*dist*). The branches on carbons No. 2 and 5 are placed on the periphery of the molecule, and the one on carbon No. 3 is placed near the centre (*ctr*) of the molecule. 25M6 is symmetric, whereas 22M6 and 23M6 are not. Since we only consider alkanes, we use the words "vertex" and "carbon" as synonyms that reflect different contexts. The use of "vertex" implies the graph-theoretical consideration, whereas the use of "carbon" implies the chemical consideration of the same thing. Their number is given as N_C or N_v, respectively.

The susceptibility for the increase in carbon number, $S_{i,i+1}$, and the susceptibility for branching, $S_{n,i}$, is defined as the normalised difference of the indices' or properties' values.[7,10] Which one is more branched is concluded by intuition as presented in ref.[11] as well as by the *Methane based* definition and the *n-Alkane based* definition[12] of branching. The indices obeying the *Methane based* definition of branching are labelled as the BI_M-type indices.

The physicochemical properties

The data for the boiling point (BP), density (d), the critical data Tc, Pc, Vc, Zc, αc, and dc, as well as the standard enthalpy of formation for the ideal gas (ΔHf°g), the enthalpy of vaporisation (ΔHv), the Antoine constants A, B, and C, as well as the

Pitzer's acentric factor (ω) and the refractive index (n_D) were taken from the CRC Handbook[13] or from Lange's Handbook[14]. The data for the liquid molar volume (Vm), the intrinsic molar volume (V_i), the ratios Tc^2/Pc and Tc/Pc used instead of the van der Waals parameters a_0 and b_0, BP/Tc, and the molar refraction (MR) were calculated from data presented in the handbooks.

Results and discussion

The L(m,n) *indices*

The L(m,n) indices are the largest eigenvalues of the $v^m d^n$ matrix. The $v^m d^n$ matrix is a matrix having the main (backslash) diagonal elements, $\mathbf{g}_{ii} = 0$, and all the others, $\mathbf{g}_{ij}$ $(i \neq j) = v_j^{\mathbf{m}} \times d_{ij}^{\mathbf{n}}$, where v_j is the degree of vertex *j* (in alkanes it is the number of the C-C bonds which the carbon in question is involved in) and d_{ij} is the shortest distance from vertex *i* to vertex *j* (in alkanes it is the lowest number of bonds between the carbons in question).[7] One of the L(m,n) indices is the index λ_1, the largest eigenvalue of the adjacency matrix[15]: $\lambda_1 \equiv L(0,-\infty)$.

Characteristics of* L(m,n) *indices

The indices L(m,n) of methane are equal to zero since $\mathbf{g}_{ii} = 0$ by definition. The L(m,n) indices of ethane are in any case equal to 1 since $1^{\mathbf{m}} = 1^{\mathbf{n}} = 1$. Four of 225 tested L(m,n) indices are integers: L(-∞,-∞), L(-1,-∞), L(-∞,0), and L(0,0). All the others are real numbers. Compared to W(m,n) indices,[7] a lower number of L(m,n) indices are integers.

The degeneration of L(m,n) *indices*

How many data of the tested L(m,n) indices is degenerated, i.e. equal to at least one more, is presented in Fig. 1 for all alkanes from propane through octanes. Highly degenerated are the indices L(m,0), and some degeneration is observed also among some of the indices of the groups L(m,-∞), L(-∞,-1), L(-∞,1/2), L(-∞,1), and L(-∞,2). The "degeneration causing" exponents are **m** = -∞, and **n** = -∞, -1, **0**, ½, 1, and 2. The unconditionally degeneration causing exponent is presented in bold.

m	-∞	-6	-4	-2	-1	-1/2	-1/3	-1/4	0	1/4	1/3	1/2	1	2	3
3									24*						
2									24*						
1									24*						
1/2									24*						
1/3									24*						
1/4									24*						
0	18♦								37■						
-1/4									24*						
-1/3									24*						
-1/2									24*						
-1	38■								24*						
-2	13#								24*						
-4									24*						
-6									24*						
-∞	38■				4				37□			2	6	4	

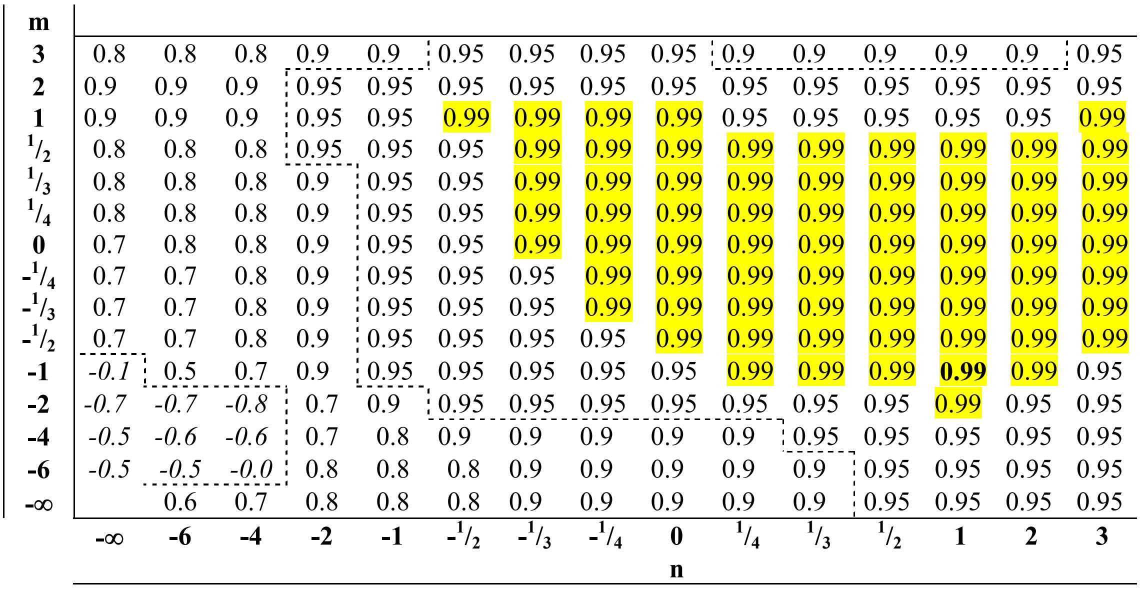
n

Fig. 1. Degenerated data of L(m,n) indices of alkanes from propane through octanes, in the plane of exponents **m** and **n**. The symbols indicate the number of degenerated data among octanes: ■: 18 □: 16 *: 15 #: 4 ♦: 2.

A substantial part of degeneration is observed among alkanes of different carbon number, which contrasts the situation among the W(m,n) indices.[7] The exceptions are L(-1,-∞), L(-∞,-∞), and L(0,0) where each isomer has at least one equal counterpart, as well as the other L(m,0) indices where the degeneration is substantial but not so severe. If we compare the data presented in Fig. 1 and that in Fig. 5 of ref.[7], we can conclude that the L(m,n) indices are less degenerated than the W(m,n) indices and for this reason at least some of them should be preferably used. The suggestion regarding the use of index D ≡ L(0,1) instead of index W ≡ W(0,1) in ref .[16] is thus to be applied generally.

The correlation between the L(m,n) *and* W(m,n) *indices*

The correlation between the L(m,n) and W(m,n) indices assuming a linear relationship is indicated in Fig. 2 for indices of alkanes from propane through octanes and in Fig. 3 for the case when only octanes are considered. A substantial number of L(m,n) and W(m,n) indices correlate quite well. Thus, several of them may be redundant. The highest is the correlation between the indices W(-1,1) and L(-1,1) and from this point the correlation decreases in all directions. In Fig. 2 is especially low the correlation between the indices W(-6,-4) and L(-6,-4), as well as W(-1,-∞) and L(-1,-∞).



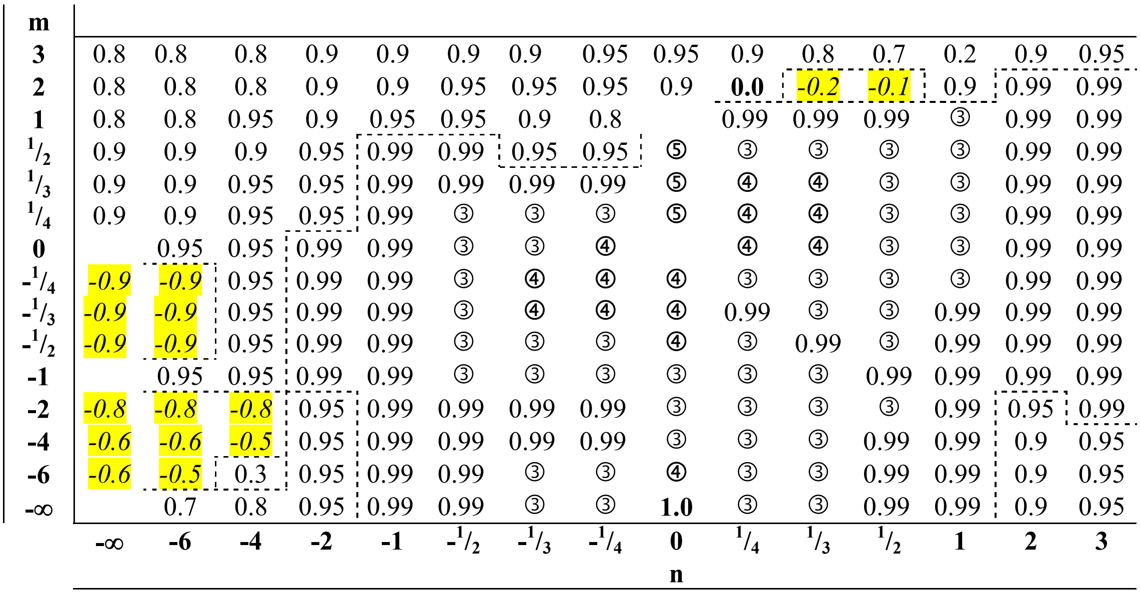
m \ n	-∞	-6	-4	-2	-1	$-^1/_2$	$-^1/_3$	$-^1/_4$	0	$^1/_4$	$^1/_3$	$^1/_2$	1	2	3
3	0.8	0.8	0.8	0.9	0.9	0.95	0.95	0.95	0.95	0.9	0.9	0.9	0.9	0.9	0.95
2	0.9	0.9	0.9	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95
1	0.9	0.9	0.9	0.95	0.95	0.99	0.99	0.99	0.99	0.95	0.95	0.95	0.95	0.95	0.99
$^1/_2$	0.8	0.8	0.8	0.95	0.95	0.95	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
$^1/_3$	0.8	0.8	0.8	0.9	0.95	0.95	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
$^1/_4$	0.8	0.8	0.8	0.9	0.95	0.95	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
0	0.7	0.8	0.8	0.9	0.95	0.95	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
$-^1/_4$	0.7	0.7	0.8	0.9	0.95	0.95	0.95	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
$-^1/_3$	0.7	0.7	0.8	0.9	0.95	0.95	0.95	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
$-^1/_2$	0.7	0.7	0.8	0.9	0.95	0.95	0.95	0.95	0.99	0.99	0.99	0.99	0.99	0.99	0.99
-1	*-0.1*	0.5	0.7	0.9	0.95	0.95	0.95	0.95	0.95	0.99	0.99	0.99	**0.99**	0.99	0.95
-2	*-0.7*	*-0.7*	*-0.8*	0.7	0.9	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.99	0.95	0.95
-4	*-0.5*	*-0.6*	*-0.6*	0.7	0.8	0.9	0.9	0.9	0.9	0.9	0.95	0.95	0.95	0.95	0.95
-6	*-0.5*	*-0.5*	*-0.0*	0.8	0.8	0.8	0.9	0.9	0.9	0.9	0.9	0.95	0.95	0.95	0.95
-∞		0.6	0.7	0.8	0.8	0.8	0.9	0.9	0.9	0.9	0.9	0.95	0.95	0.95	0.95

Fig. 2. Correlation coefficients between W(m,n) and L(m,n) indices for data of alkanes from propane through octanes, in the plane of exponents **m** and **n**.

0.99: $0.99 < r < 0.999$ 0.95: $0.95 < r < 0.99$ 0.9: $0.9 < r < 0.95$
0.8: $0.8 < r < 0.9$ 0.7: $0.7 < r < 0.8$, etc.
-0.0: $0 > r > -0.1$ *-0.1*: $-0.1 > r > -0.2$ *-0.5*: $-0.5 > r > -0.6$ *-0.6*: $-0.6 > r > -0.7$
-0.7: $-0.7 > r > -0.8$ *-0.8*: $-0.8 > r > -0.9$

The correlation between the indices of octanes is more differentiated than if all alkanes from propane through octanes are taken into account. The correlation among the L(m,n) and W(m,n) indices of octanes is caused only by the similarity in their dependence on branching. The differences in correlation observed comparing Fig. 2 and Fig. 3 are thus caused by the different dependence of L(m,n) and W(m,n) indices on the size of molecule. The similarity of dependence on the size of molecules is presented in Fig. 4 with help of correlation of this type of dependence of L(m,n) and W(m,n) indices of *n*-alkanes. The data in Figs. 3 and 4 indicate that the size of molecule influences the indices in a different way than branching and these effects are to be studied separately.

Among octanes (Fig. 3), several L(m,n) and W(m,n) indices correlate very well whereas only a low number of them correlate to a low or very low extent. For the well correlating cases, which are grouped around **m** = 0 and **n** = 0, there may be no need to study the L(m,n) indices separately. It may suffice to take into account the conclusions regarding the W(m,n) indices presented in ref.[7] In Fig. 3 there are two regions of low correlation. One of them is observed at **m** ≥ 2 and ¼ ≤ **n** ≤ 1, the other one at **m** < 0 and **n** ≤ -4.



m															
3	0.8	0.8	0.8	0.9	0.9	0.9	0.9	0.95	0.95	0.9	0.8	0.7	0.2	0.9	0.95
2	0.8	0.8	0.8	0.9	0.9	0.95	0.95	0.95	0.9	**0.0**	*-0.2*	*-0.1*	0.9	0.99	0.99
1	0.8	0.8	0.95	0.9	0.95	0.95	0.9	0.8		0.99	0.99	0.99	③	0.99	0.99
$^1/_2$	0.9	0.9	0.9	0.95	0.99	0.99	0.95	0.95	⑤	③	③	③	③	0.99	0.99
$^1/_3$	0.9	0.9	0.95	0.95	0.99	0.99	0.99	0.99	⑤	④	④	③	③	0.99	0.99
$^1/_4$	0.9	0.9	0.95	0.95	0.99	③	③	③	⑤	④	④	③	③	0.99	0.99
0		0.95	0.95	0.99	0.99	③	③	④		④	④	③	③	0.99	0.99
$-^1/_4$	*-0.9*	*-0.9*	0.95	0.99	0.99	③	④	④	④	③	③	③	③	0.99	0.99
$-^1/_3$	*-0.9*	*-0.9*	0.95	0.99	0.99	③	④	④	④	0.99	③	③	0.99	0.99	0.99
$-^1/_2$	*-0.9*	*-0.9*	0.95	0.99	0.99	③	③	③	④	③	0.99	③	0.99	0.99	0.99
-1		0.95	0.95	0.99	0.99	③	③	③	③	③	③	0.99	0.99	0.99	0.99
-2	*-0.8*	*-0.8*	*-0.8*	0.95	0.99	0.99	0.99	0.99	③	③	③	③	0.99	0.95	0.99
-4	*-0.6*	*-0.6*	*-0.5*	0.95	0.99	0.99	0.99	0.99	③	③	③	0.99	0.99	0.9	0.95
-6	*-0.6*	*-0.5*	0.3	0.95	0.99	0.99	③	③	④	③	③	0.99	0.99	0.9	0.95
-∞		0.7	0.8	0.95	0.99	0.99	③	③	**1.0**	③	③	0.99	0.99	0.9	0.95
	-∞	**-6**	**-4**	**-2**	**-1**	**$-^1/_2$**	**$-^1/_3$**	**$-^1/_4$**	**0**	**$^1/_4$**	**$^1/_3$**	**$^1/_2$**	**1**	**2**	**3**
									n						

Fig. 3. Correlation coefficients between W(m,n) and L(m,n) indices for data of octanes, in the plane of exponents **m** and **n**.

1.0: r = 1.0000 ⑤: r > 0.99999 ④: 0.9999 < r < 0.99999
③: 0.999 < r < 0.9999;
0.99: 0.99 < r < 0.999 0.9: 0.9 < r < 0.99 0.8: 0.8 < r < 0.9
0.7: 0.7 < r < 0.8 0.3: 0.3 < r < 0.4 0.2: 0.2 < r < 0.3 **0.0**: 0 < r < 0.1
-0.1: -0.1 > r > -0.2, etc. in this way.

The reason for the non-perfect correlations presented in Fig. 4 is the fact that the L(m,n) indices increase with carbon number less intensively than the W(m,n) indices. The difference in the increase of values of indices increases with carbon number and with the decrease of exponent **n**. The reasons for low or negative correlations are given below discussing Fig. 5. Furthermore, it seems quite probable that L(m,n) indices correlating with W(m,n) indices very well (r>0.99), have similar properties and a similar information content. There may be no need to study them separately, except for fine details.

m															
3	0.8	0.8	0.8	0.8	0.9	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.99	0.99	0.99
2	0.8	0.8	0.8	0.9	0.9	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.99	0.99	0.99
1	0.8	0.8	0.8	0.9	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.99	0.99	0.99
$^{1}/_{2}$	0.8	0.8	0.8	0.9	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.99	0.99
$^{1}/_{3}$	0.8	0.8	0.8	0.9	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.99	0.99
$^{1}/_{4}$	0.8	0.8	0.8	0.9	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.99	0.99
0	0.8	0.8	0.8	0.9	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.99	0.99
-$^{1}/_{4}$	0.8	0.8	0.8	0.9	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.99	0.99
-$^{1}/_{3}$	0.8	0.8	0.8	0.9	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.99	0.99
-$^{1}/_{2}$	0.8	0.8	0.8	0.9	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.99	0.99
-1	0.2	0.8	0.8	0.9	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.99	0.99
-2	*-0.7*	*-0.7*	*-0.7*	*-0.6*	0.9	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.99	0.99
-4	*-0.5*	*-0.6*	*-0.6*	*-0.8*	*-0.8*	0.8	0.99	**0.999**	0.99	0.95	0.95	0.95	0.95	0.99	0.99
-6	*-0.5*	*-0.5*	*-0.6*	*-0.8*	*-0.9*	*-0.8*	*-0.8*	*-0.6*	0.99	0.95	0.95	0.95	0.95	0.99	0.99
-∞		**-0.99**	*-0.95*	*-0.95*	*-0.95*	*-0.95*	*-0.95*	*-0.95*		0.95	0.95	0.95	0.95	0.99	0.99
	-∞	**-6**	**-4**	**-2**	**-1**	**-$^{1}/_{2}$**	**-$^{1}/_{3}$**	**-$^{1}/_{4}$**	**0**	**$^{1}/_{4}$**	**$^{1}/_{3}$**	**$^{1}/_{2}$**	**1**	**2**	**3**
									n						

Fig. 4. Correlation coefficients between W(m,n) and L(m,n) indices for data of *n*-alkanes from C_3 to C_{15}, in the plane of exponents **m** and **n**.

0.999: $0.999 < r < 0.9999$ 0.99: $0.99 < r < 0.999$ 0.95: $0.95 < r < 0.99$
0.9: $0.9 < r < 0.95$ 0.8: $0.8 < r < 0.9$ 0.2: $0.2 < r < 0.3$
-0.5: $-0.5 > r > -0.6$ *-0.6*: $-0.6 > r > -0.7$ *-0.7*: $-0.7 > r > -0.8$ *-0.8*: $-0.8 > r > -0.9$, etc. in this way.

The change of values of L(m,n) *indices of n-alkanes due to the increase of size of the molecule*

The values of most tested L(m,n) indices of *n*-alkanes (the $L(m,n)_n$ indices) depend on the size of molecule and consequently also on *n*-alkanes' carbon numbers. The indices $L(-\infty,-\infty)_n$, $L(-1,-\infty)_n$, and $L(-\infty,0)_n$ do not depend on the size of molecule. A linear increase with the size of molecule have the indices $L(0,0)_n$ and $L(-\infty,1)_n = N_C - 1$. There exists also a simple relation: $L(-\infty,n)_n = (N_C - 1)^{\mathbf{n}}$. At the $L(m,-\infty)$ indices the situation is less simple. $L(m,-\infty)_{\mathrm{Pr}} = 2^{(m+1)/2}$, $L(m,-\infty)_{\mathrm{Bu}} = 2^{m-1}(1+(2^{2-m}+1)^{1/2})$, $L(m,-\infty)_{\mathrm{Pe}} = 2^{m/2}(2^{m+1}+1)^{1/2}$. For the odd values of N_C, the following relation is valid for the index $\lambda_1 \equiv L(0,-\infty)$: $L(0,-\infty)_{2N_C+1} = (L(0,-\infty)_{N_C} + 2)^{1/2}$.

The shape of dependence of indices L(m,n) on the size of molecule is schematically presented in Fig 5. When **n** < 0, the shape of the dependence of $L(m,n)_n$ indices on carbon number seems to be composed of the contribution of the hyperbole inherent to the L(-∞,n)$_n$ indices and indicated by the symbol \\ , as well as of the contribution of the hyperbole inherent to L(m,n)$_n$ indices with **m** > -1 and indicated by the symbol (. The combination of these contributions seems to give rise to all other observed shapes, i.e. the trough-shape indicated by the symbol ∪, the sigmoid shape indicated by the symbol ∫, and the combination thereof indicated by the symbol ∪∫. It could be reasonably expected that some L(m,n)$_n$ indices seeming to give rise to the hyperbolic shape presented here as \\ are in fact of a combined shape presented by the symbol ∪∫ but this effect would be observed at higher carbon numbers than those tested here.

m	-∞	-6	-4	-2	-1	-1/2	-1/3	-1/4	0	1/4	1/3	1/2	1	2	3
3	(	(	(	(	(	(	(	(	)	)	)	)	)	)	)
2	(	(	(	(	(	(	(	(	)	)	)	)	)	)	)
1	(	(	(	(	(	(	(	(	)	)	)	)	)	)	)
1/2	(	(	(	(	(	(	(	(	)	)	)	)	)	)	)
1/3	(	(	(	(	(	(	(	(	)	)	)	)	)	)	)
1/4	(	(	(	(	(	(	(	(	)	)	)	)	)	)	)
0	(	(	(	(	(	(	(	(	/	)	)	)	)	)	)
-1/4	(	(	(	(	(	(	(	(	(	)	)	)	)	)	)
-1/3	(	(	(	(	(	(	(	(	(	)	)	)	)	)	)
-1/2	(	(	(	(	(	(	(	(	(	)	)	)	)	)	)
-1	—	(	(	(	(	(	(	(	(	)	)	)	)	)	)
-2	\\	\\	\\	∪	(	(	(	(	(	)	)	)	)	)	)
-4	\\	\\	\\	\\	∪	∪	∪∫	∫	(	(	(	(	)	)	)
-6	\\	\\	\\	\\	\\	\\	∪	∪	(	(	(	(	)	)	)
-∞	—	\\	\\	\\	\\	\\	\\	\\	—	(	(	(	/	)	)

n

Fig. 5. The schematic presentation of the shape of the change of values of L(m,n) indices of *n*-alkanes (C_3-C_{15}) with carbon number.
— : No change on increasing the carbon number
/ : Linear increase with carbon number, L(m,n)$n = N_C - 1$
\\ : Hyperbolic decrease
∪: Trough-like shape
∫ : Sigmoid shape
∪∫ : Combined shape: a through-like shape that converts into the sigmoid one
(: Hyperbolic increase
) : Parabolic increase

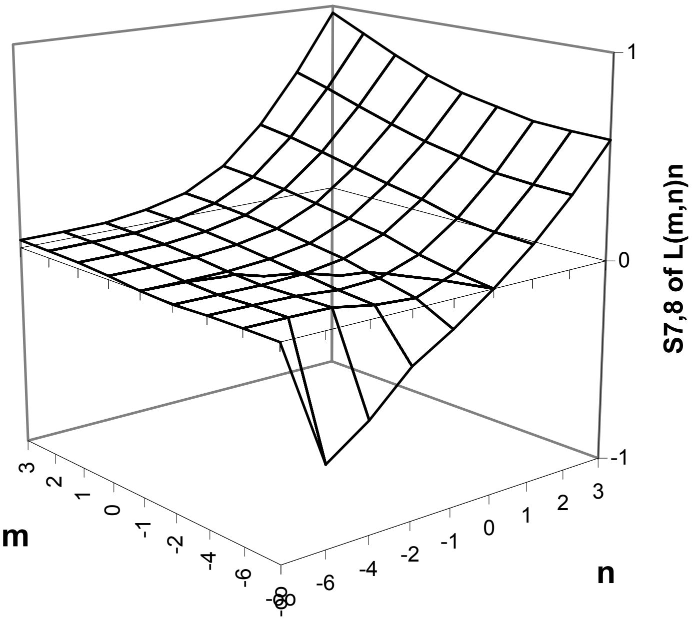


Fig. 6. The dependence of susceptibility for the increase in carbon number from 7 to 8 of L(m,n) indices of *n*-alkanes on exponents **m** and **n**.

Another possibility of presenting the influence of exponents **m** and **n** on the dependence of L(m,n) indices of *n*-alkanes due to the increase in carbon number is to use the susceptibility for the increase of carbon number by one, $S_{i,i+1}$, cf. ref.[16] This possibility is presented in Fig. 6 with $S_{7,8}$, i.e. for the increase of carbon number from 7 to 8. The highest increase with carbon number has the index $L(3,3)_n$, like the index $W(3,3)_n$ among the W(m,n)[7] indices. There is also an important difference in the dependence of L(m,n) and W(m,n) indices on the increase in carbon number. At low **m** and low **n**, i.e. when **m** < 0 and **n** < 0, and especially when **m** < -6, there is $S_{7,8}$ of $L(m,n)_n$ indices negative because the values of these indices decrease with increasing carbon number. This is reflected also in negative correlation with $W(m,n)_n$ indices which is presented in Fig. 4. All the $W(m,n)_n$ indices, except $W(-\infty,-\infty)_n$, increase with carbon number,[7] whereas the mentioned $L(m,n)_n$ indices do decrease. These $L(m,n)_n$ indices do not obey the *Methane based* definition of branching and for this reason they can not be expected to be candidates for good branching indices. In spite of that, some of them may be good indices of some compounds' properties that decrease with the size of molecule in a hyperbolic fashion.

The change of values of L(m,n) *indices due to the increase of the size of molecules of other alkane isomers*

How the values of L(m,n) indices of other isomers change when the size of a molecule increases, is the most easily presented by the susceptibility of typical structural types for the increase in carbon number by one, $S_{i,i+1}$, cf. ref.[7] We consider here $S_{7,8}$. The following transitions were considered:

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

In these transitions the main chain of the alkane is elongated by insertion of a methylene group, so that the branched structure is preserved as much as possible although it is shifted to the periphery of the molecule. In Fig. 7 is presented the sign of changes of L(m,n) indices. It indicates that in most cases the values of L(m,n) indices increase on increasing size of molecule among all isomers.

m															
3	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
2	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
$^{1}/_{2}$	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
$^{1}/_{3}$	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
$^{1}/_{4}$	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
0	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
$-^{1}/_{4}$	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
$-^{1}/_{3}$	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
$-^{1}/_{2}$	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
-1	0	±	±	+	+	+	+	+	+	+	+	+	+	+	+
-2	±	±	±	-	±	+	+	+	+	+	+	+	+	+	+
-4	±	±	±	-	-	±	±	±	+	+	+	+	+	+	+
-6	±	±	±	-	-	-	-	-	+	+	+	+	+	+	+
$-\infty$		-	-	-	-	-	-	-	0	+	+	+	+	+	+
	$-\infty$	**-6**	**-4**	**-2**	**-1**	**$-^{1}/_{2}$**	**$-^{1}/_{3}$**	**$-^{1}/_{4}$**	**0**	**$^{1}/_{4}$**	**$^{1}/_{3}$**	**$^{1}/_{2}$**	**1**	**2**	**3**

n

Fig. 7. The schematic presentation of the dependence of values of L(m,n) indices on the increase of carbon number of alkanes from 7 to 8.

+ : The value of all isomers increases on increasing the carbon number of alkane

- : The value of all isomers decreases on increasing the carbon number of alkane

± : The value of some isomers increases whereas the value of other isomers decreases on increasing the carbon number of alkane

m															
3	D↑	D↑	D↑	D↑	D↑	D↑	D↑	C↑	t↓q ↑	D↓	D↓	D↓	D↓	D↓	D↓
2	D↑	D↑	D↑	D↑	D↑	D↑	D↑	d	°	D↓	D↓	D↓	D↓	D↓	D↓
1	D↑	D↑	D↑	D↑	D↑	D↑	D↑	d	°	D↓	D↓	D↓	D↓	D↓	D↓
$^1/_2$	D↑	D↑	D↑	D↑	D↑	D↑	D↑	D↑	°	D↓	D↓	D↓	D↓	D↓	D↓
$^1/_3$	D↑	D↑	D↑	D↑	D↑	D↑	D↑	D↑	°	D↓	D↓	D↓	D↓	D↓	D↓
$^1/_4$	D↑	D↑	D↑	D↑	D↑	D↑	D↑	D↑	°	D↓	D↓	D↓	D↓	D↓	D↓
0	D↑	D↑	D↑	D↑	D↑	D↑	D↑	D↑	=	D↓	D↓	D↓	D↓	D↓	D↓
$-^1/_4$	D↑	D↑	D↑	D↑	D↑	D↑	D↑	D↑	#	D↓	D↓	D↓	D↓	D↓	D↓
$-^1/_3$	D↑	D↑	D↑	D↑	D↑	D↑	D↑	D↑	#	D↓	D↓	D↓	D↓	D↓	D↓
$-^1/_2$	D↑	D↑	D↑	D↑	D↑	D↑	D↑	D↑	#	d	D↓	D↓	D↓	D↓	D↓
-1	0	d	d	D↑	D↑	d	d	d	#	d	d	d	D↓	D↓	D↓
-2	D↑	d	d	D↑	d	d	d	d	#	d	d	d	D↓	D↓	D↓
-4	D↑	D↑	D↑	C↓	D↓	d	d	d	#	c	c	d	D↓	D↓	D↓
-6	D↑	D↑	D↑	D↓	D↓	D↓	D↓	d	#	d	c	c	D↓	D↓	D↓
-∞	0	d	d	D↓	D↓	D↓	D↓	D↓	0	D↑	c	c	D↓	D↓	D↓
	-∞	**-6**	**-4**	**-2**	**-1**	$-^1/_2$	$-^1/_3$	$-^1/_4$	**0**	$^1/_4$	$^1/_3$	$^1/_2$	**1**	**2**	**3**
									n						

Fig. 8. Which structural feature has the prevailing influence on values of L(m,n) indices when the carbon number of alkanes increases from 7 to 8.

C - The position of branches has the highest influence

c - The position of branches has the highest influence next to their number

D - The distance between branches has the highest influence

d - The distance between branches has the highest influence next to their number

t,q - The tertiary and quaternary structure has the highest influence

↑- A higher value of the structural feature causes a higher increase with carbon number and vice versa

↓ - A higher value of the structural feature causes a lower increase with carbon number or even a decrease and vice versa

° - a higher number of branches causes a higher increase of L(m,n) values on increasing carbon number; if the structure is quaternary, an additional increase is observed

- a higher number of branches causes a lower increase of L(m,n) values on increasing carbon number; if the structure is quaternary, an additionally lower increase is observed

There are several cases at negative exponents **m** and **n**, when the values of L(m,n) indices of all isomers decrease on increasing size of molecules. In vicinity of them there are several cases when the values of L(m,n) indices of some isomers increase whereas the values of the others decrease on increasing size of molecules.

Which structural feature has the highest contribution to these changes is presented in Fig. 8. In the majority of tested cases, the distance between branches has the highest influence on the changes of values of L(m,n) indices when the size of molecule increases, especially at positive **m** and/or positive **n**. The influence of the number of branches prevails at negative values of **m**, especially close to **n** = 0. There are noticed only two cases where on increase of size of the molecule, the influence of the position of branches prevails.

The dependence of L(m,n) *indices on branching*

How the values of the L(m,n) indices change when the structure gets more branched is presented in Fig. 9. The values of the majority of tested L(m,n) indices increase with increasing branching. There are two regions, one at positive **n**, the other one at **n** < -4 and **m** < -1, where the values of L(m,n) indices decrease with increasing branching.

m															
3	+	+	+	+	+	+	+	+	+	+	+	±	±	-	-
2	+	+	+	+	+	+	+	+	+	±	±	-	-	-	-
1	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-
$^1/_2$	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-
$^1/_3$	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-
$^1/_4$	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-
0	+	+	+	+	+	+	+	+	0	-	-	-	-	-	-
$-^1/_4$	+	+	+	+	+	+	+	+	+	-	-	-	-	-	-
$-^1/_3$	+	+	+	+	+	+	+	+	+	±	±	-	-	-	-
$-^1/_2$	+	+	+	+	+	+	+	+	+	+	±	±	-	-	-
-1	0	+	+	+	+	+	+	+	+	+	+	+	±	-	-
-2	-	-	±	+	+	+	+	+	+	+	+	+	+	-	-
-4	-	-	±	+	+	+	+	+	+	+	+	+	+	±	-
-6	-	±	±	+	+	+	+	+	+	+	+	+	+	±	-
-∞		+	+	+	+	+	+	+	+	+	+	+	+	±	-
	-∞	**-6**	**-4**	**-2**	**-1**	**$-^1/_2$**	**$-^1/_3$**	**$-^1/_4$**	**0**	**$^1/_4$**	**$^1/_3$**	**$^1/_2$**	**1**	**2**	**3**

n

Fig. 9. The schematic presentation of the change of values of L(m,n) indices of octanes on increasing branching.

+ : The value of all isomers increases on increasing branching

- : The value of all isomers decreases on increasing branching

± : The value of some isomers increases whereas the value of other isomers decreases on increasing branching

0 : The values of the L(m,n) index do not change with branching

+: L(-∞,0) = 1 + N_{br} ; cf. W(-∞,-∞) = 1 + $N_{br}/2$, ref.[7]

Between them there are the transition regions where the values of the L(m,n) indices either do not change with branching or they change in different directions. Which structural feature has the highest influence on the values of L(m,n) indices when the structure gets more branched, is schematically presented in Fig. 10.

m															
3	c4	c4	c4	c4	c	c	c	c	2q	p	p11	**P1**	**C1**	c6	c5
2	c4	c4	c4	c4	c	c	c	c	2t	**C2**	**C3**	c6	c5	c1	c1
1	c4	c5	c5	c4	c	c4	c4	C2	2q	c1	c1	c1	c1	c1	c1
$^{1}/_{2}$	c4	c4	c4	c	c	c4	C1	C3	2q	c1	c1	c1	c1	c1	c1
$^{1}/_{3}$	c4	c4	c3	c	c	c4	c4	C1	2q	c1	c1	c1	c1	c1	c1
$^{1}/_{4}$	c3	c4	c3	c	c	c4	c4	c7	2q	c1	c1	c1	c1	c1	c1
0	c3	c4	c3	c	c	c	c	c	0	c1	c1	c1	c1	c1	c1
$-^{1}/_{4}$	c3	c4	c3	c	c	c	c	c	2q	C4	c7	c2	c1	c1	c1
$-^{1}/_{3}$	c3	c4	c3	c	c	c	c*	c*	2q	**P2**	**C4**	c5	c1	c1	c1
$-^{1}/_{2}$	c3	c4	c3	c	c*	c*	c*	c*	2q	p2	**P3**	**C3**	c2	c1	c1
-1	0	c4	c3	c*	c*	c*	c*	c*	2q	p2	p2	p2	C1	c1	c1
-2	xx	p1	P2	x3	x3	x4	x4	c*	2q	p2	p2	p2	P1	c5	c1
-4	xt	xx	**P4**	x11	x2	x21	x21	x21	2q	xy	xy	xy	p2	C2	c1
-6	xt	P1	X	x1	x	x21	x21	x21	2q	xz	xz	xz	p2	C1	c1
-∞	0	x	x	x	x	x21	x21	x21	N_{br}	xz	xz	xz	p2	C1	c1
	-∞	**-6**	**-4**	**-2**	**-1**	**$-^{1}/_{2}$**	**$-^{1}/_{3}$**	**$-^{1}/_{4}$**	**0**	**$^{1}/_{4}$**	**$^{1}/_{3}$**	**$^{1}/_{2}$**	**1**	**2**	**3**
									n						

Fig. 10. The influence of the type of the branched structure and of the position of branches on the L(m,n) indices. The labels used in Fig. 10 are presented in Table 1.

The conclusions are based on the supposition that all L(m,n) indices present that 2233M4 is more branched than *n*-octane. In the majority of tested cases, i.e. those marked in Fig. 10 with lowercase letters, the number of branches has the highest contribution to the values of L(m,n) indices. The shape of this contribution is presented in Fig. 11 and it is saddle-like but different from that among the W(m,n) indices.[7] The lowercase letters used as symbols in Fig. 10 indicate which structural feature influences the L(m,n) index next to the number of branches. The uppercase letters indicate the cases when the central position or the peripheral position of branches has a higher influence than the number of branches.

There are three small regions where a peripheral position of branches has a higher influence than a central position.

Table 1. The labels of Fig. 10.

c*: The sequence of isomers is: **Oct**<2M7<3M7<4M7<3Et6<25M6<24M6<23M6< 34M6<3Et2M5<22M6<33M6<3Et<3M5<234M5<224M5<223M5<233M5<**2233M4**
2t: 2*t*>2*q*
2q: 2*q*>2*t*
C1: 25M6>2M7>...>**Oct**>...>**2233M4**>...>233M5>3Et3M5
C2: 25M6>224M5>...>**Oct**>...>**2233M4**>...>3Et6>3Et3M5
C3: 25M6>2M7>**Oct**>...>**2233M4**>233M5>3Et3M5
C4: 2M7>**Oct**>...>**2233M4**>...>233M5>3Et3M5
C1: 3Et3M5>233M5>**2233M4**>...>25M6>2M7>**Oct**
C3: 3Et3M5>3Et2M5>233M5>...>**2233M4**>...>25M6>2M7>**Oct**
C4: 3Et3M5<233M5<**2233M4**<...<25M6<2M7<**Oct**
C2: 3Et3M5>233M5> ...>**2233M4**>...>25M6>2M7>**Oct**
C̲1: **2233M4**<3Et3M5<233M5<...<**Oct**<2M7<25M6
C̲2: **2233M4**<233M5<3Et3M5<...<**Oct**<25M6<2M7
c: **Oct**<2M7<...<233M5<**2233M4**
c1: **Oct** >2M7>...>233M5>**2233M4**
c2: **Oct** >2M7>...>3E3M5>233M5>**2233M4**
c3: **Oct** <2M7<...<233M5<**2233M4**
c4: **Oct** <2M7<25M6<...<233M5<**2233M4**
c5: **Oct**>2M7>25M6>...>3Et3M5>233M5>**2233M4**
c6: **Oct** >2M7>25M6>...>233M5>3Et3M5>**2233M4**
c7: **Oct** <2M7<25M6<...<233M5<3Et3M5<**2233M4**
P1: 3Et6<3Et3M5<**Oct**<...<**2233M4**<224M5
P2: 3Et3M5<3Et6<...<**Oct**<...<**2233M4**<...<224M5<25M6
P3: 3Et6<3Et3M5<...<**Oct**<...<**2233M4**<224M5
P4: 3Et3M5>3Et6>...>**Oct**>...>**2233M4**>...>224M5>25M6
P̲1: **Oct**<3Et6<4M7<3Et3M5<...<**2233M4**<234M5<25M6<224M5
P1: 3Et6>**Oct**>...>224M5>**2233M4**
P2: 3Et6>**Oct**>3Et3M5>...>224M5>**2233M4**
p1: **Oct**>3Et6>4M7>...>224M5>**2233M4**
p2: **Oct**<3Et6<4M7<...<224M5<**2233M4**
x: **Oct**<3Et6<4M7<...<224M5<223M5<**2233M4**
x1: **Oct**<4M7<3Et6<...<224M5<223M5<**2233M4**
x11: **Oct**<4M7<3M7<...<224M5<223M5<**2233M4**
x2: **Oct**<4M7<3Et6<...<233M5<223M5<**2233M4**
x21: **Oct**<3Et6<4M7<...<233M5<223M5<**2233M4**
x3: **Oct**<2M7<4M7<...<233M5<223M5<**2233M4**
x4: **Oct**<2M7<3M7<...<233M5<223M5<**2233M4**
X̲: 25M6<234M5<2M7<...<**Oct**<...<233M5<3Et3M5<223M5<**2233M4**
xx: **Oct**>2M7>...>224M5>**2233M4**
xy: **Oct**<2M7<...<224M5<**2233M4**
xt: **Oct**>2M7>...>224M5>234M5>**2233M4**
xz: **Oct**<2M7<...<224M5<234M5<**2233M4**

One of them is at **m** = 3 and 0 < **n** < 1; in a triangle between **m** < -1/3, **n** = 1/4, **m** = -2, **n** = ¼ and 1; at -∞ ≤ **m** ≤-2 and **n** = 1; as well as in some cases in the square at -6 ≤ **m** ≤ -2, -4 ≤ **n** ≤ -6. At **m** < -1 there are several cases of curious sequences of isomers labelled by the letter x. The distance between branches seems to have a higher influence than the position of branches only at L(-2,-∞) and L(-4,-6), label xx. In all tested cases has the contribution of distance between branches to the value of the L(m,n) indices on increasing branching the same sign as the exponent **n**.

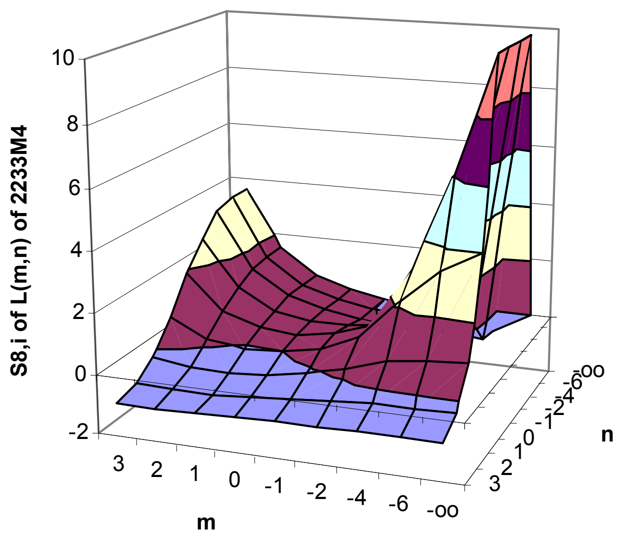


Fig. 11. The shape of contribution of the number of branches to the values of L(m,n) indices presented in the plane of exponents **m** and **n**.

The L(m,n) *indices that might be good branching indices.*

Which L(m,n) indices might be good branching indices is presented in Fig. 12. Twelve of tested L(m,n) indices have the ideal sequence of isomers among octanes. None of tested L(m,n) indices has an ideal sequence of isomers when the size of molecules increases. Therefore, none of tested L(m,n) indices is an ideal branching index of the BI_M[10] type, whereas eight of them could be a good source of branching indices of BI_A type.[17]

The information about branching and the complexity in the L(m,n) *indices*

Two of tested L(m,n) indices present no information about the properties of alkanes. They are L(-∞,-∞) and L(-1,-∞).

The size of the molecule

Among the tested L(m,n) indices presents the information about the size of molecule as the sole information only the index L(0,0) = N_C -1. Linearly increasing with the size of molecule is also the index L(-∞,1) which contains also the information about branching.

m															
3									°						
2									°						
1									°						
1/2									°						
1/3									°						
1/4									°						
0									0						
-1/4									°						
-1/3							8	8	°						
-1/2					8	8	8	8	°						
-1	0	a3Et	a3Et	8	8	8	a,8	a,8	°						
-2		b	b			b	a	a,8	°						
-4						b			°		b				
-6									°			b			
-∞									•						
	-∞	**-6**	**-4**	**-2**	**-1**	**-1/2**	**-1/3**	**-1/4**	**0**	**1/4**	**1/3**	**1/2**	**1**	**2**	**3**

n

Fig. 12. L(m,n) indices that might be good branching indices.

8: The sequence of isomers among octanes is ideal: Oct < 2M7 < 3M7< < 4M7 < 3Et6 < 25M6 < 24M6 < 23M6 < 34M6 < 3Et2M5 < 22M6 < 33M6 < 3Et3M5 < 234M5 < 224M5 < 223M5 < 233M5 < 2233M4

a : In the sequence of $S_{7,8}$ data, the position of one isomer (3Et or 24M) is not ideal.

b : In the sequence of $S_{7,8}$ data, the positions of two isomers (22M and 24M at **m** = -2 and **n** = $-^1/_2$; 22M and 33M in other cases) are not ideal.

• : Presents only the influence of the number of branches.

°: Presents the influence of the number of branches and of the type of branched structure.

Number of branches

The information about the number of branches as the sole information presents the index L(-∞,0) = 1 + N_{br}. Its importance is the same as that of the index W(-∞,-∞).[7] The other L(m,n) indices not mentioned above present also additional information.

The type of the branched structure

The indices L(m,0), with exception of L(-∞,0) and L(0,0) mentioned above, present besides the information about the size of molecule and the number of branches also the information about the type of the branched structure, i.e. whether the branch bearing carbon is tertiary or quaternary. The influence of the type of branched structure is as follows, $0 < 1t < 2t < 2q < 3t < 2q1t < 4q$, except at L(2,0) where it is $0 < 1t < 2q < 2t < 2q1t < 3t < 4q$, where 0 means no branch, *t* stands for branches in tertiary structures, *q* for branches in quaternary structures, and the digits present the number of branches of these types in octanes.

Position of branches

The majority of tested L(m,n) indices presents the isomers having the branches closer to the centre of molecule as more branched, Fig. 10.

Distance between branches

When **n** > 0, then a greater distance between branches has a positive contribution to the value of the L(m,n) index. The reverse is true when **n** < 0.

m	**-∞**	**-6**	**-4**	**-2**	**-1**	**-$^1/_2$**	**-$^1/_3$**	**-$^1/_4$**	**0**	**$^1/_4$**	**$^1/_3$**	**$^1/_2$**	**1**	**2**	**3**
3								n_D							
2						d									
1			dc					Tc	B				Zc		
$^1/_2$									BP		Hv		*		
$^1/_3$											Pc				
$^1/_4$											**		⊕		
0										Vm		#			
-$^1/_4$										MR		Vc			
-$^1/_3$															
-$^1/_2$								Hf						ω	
-1															
-2															
-4															
-6															
-∞		A												V"	

n

Fig. 13. The positions of 21 physicochemical properties determined by the highest correlation coefficient (data in parentheses, see below) for data of alkanes from propane through octanes, in the plane of exponents **m** and **n**.

Single standing ones (r): n_D (0.**9**06), d (0.**9**31) , dc (0.855), Tc (0.**98**5), B (0.**97**5), Zc (-0.699), BP (**0.99**1), ΔHv (0.**99**0), Pc (-0.**95**8), Vm (0.**98**0), MR (**0.999**), Vc (0.**99**2), **ΔHf°g** (**0.99**2), ω (0.**97**3), A (-0.614), V" (0.864)
*: **BP/Tc** (0.**98**0)
** : Tc^2/Pc (**0.999**),
⊕: C (-0.**96**1), αc (0.**94**8)
#: **Tc/Pc** (**0.99**8)

Correlation of physicochemical properties with L(m,n) *indices*

The positions of 21 physicochemical properties in the plane of exponents **m** and **n** determined by the highest correlation coefficient for data of alkanes from propane through octanes with indices L(m,n), Fig. 13, are different from positions observed when the indices W(m,n)[7] are considered. The best correlation coefficients of 21 physicochemical properties with L(m,n) indices are slightly better than with W(m,n) indices, except at BP, Vm, and ΔHf°g.

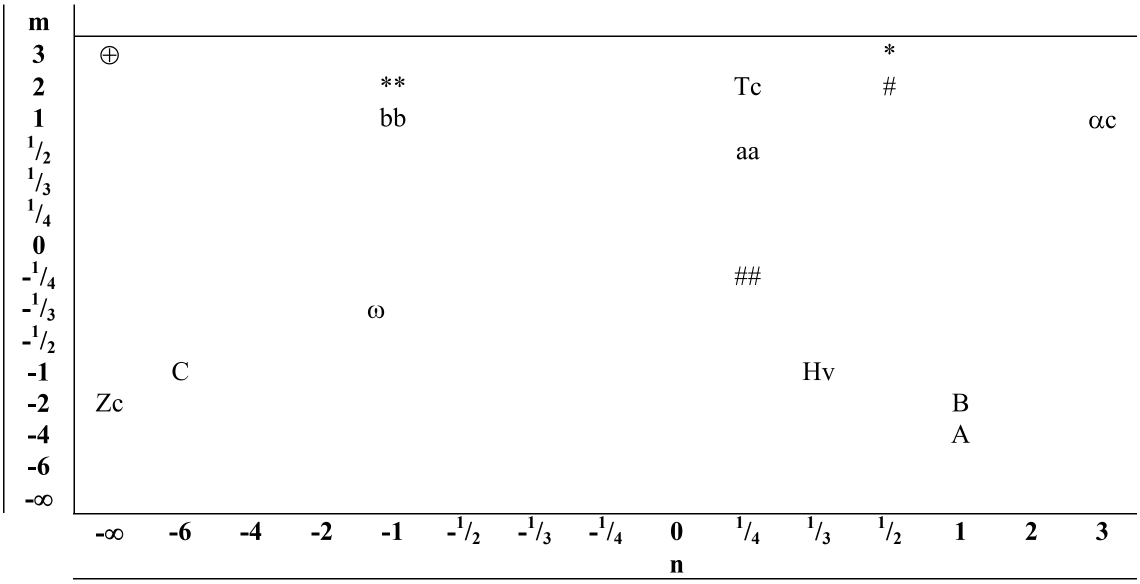


Fig. 14. The positions of 21 physicochemical properties determined by the highest correlation coefficient (data in parentheses, see below) for data of octanes, in the plane of exponents **m** and **n**.

Single standing ones (r): Tc (-0.800), ΔHv (0.**9**23), A (-0.775), B (-0.738), C (0.**9**67), Zc (-0.728), ω (**-0.995**), αc (0.740)
aa: Tc^2/Pc (**0.98**2) bb: **Tc/Pc** (**0.99**6) #: Pc (-0.**9**64), MR (0.877)
##: dc (-0.829), Vc (0.841) *: BP (-0.867), **ΔHf°g** (0.880) ** : **BP/Tc** (**-0.99**1),
⊕: d (0.835), Vm (-0.847), V" (-0.847), n_D (0.801)

Considering only octanes, Fig. 14, the positions in the plane of exponents **m** and **n** of 21 physicochemical properties determined by the highest correlation coefficient with indices L(m,n) are different from positions observed when the indices W(m,n)[7] are considered, too. The best correlation coefficients of following physicochemical properties of octanes with L(m,n) indices are slightly better than those with W(m,n) indices: n_D, A, d, BP/Tc, αc, Zc , Tc/Pc, Tc, V", and Pc. Almost equal are those of BP, dc, B, Tc^2/Pc, and Vm. Slightly better than with L(m,n) indices are those with W(m,n) indices in the case of Vc, ΔHf°g, ΔHv, C, ω, and MR.

In Fig. 15 are presented five best positions of L(m,n) indices regarding the correlation with one of the six physicochemical properties considered the best candidates for primary reference values for branching indices,[12] (Tc/Pc, Tc^2/Pc, BP/Tc, ΔHf°g, ω, and C) and with two next good ones, BP and ΔHv. We can see that the positions as well as their patterns differ substantially.

m															
3											**f3**	**f1**			
2	*pp5*	*pp4*	*pp3*	*pp2*	*pp1*										
1				bb2	bb1				C3						
$^1/_2$					bb3				*v3*	aa1	aa3				
$^1/_3$									*v4*	aa2	aa5				
$^1/_4$						bb4			*v5*	aa4					
0															
-$^1/_4$					ω3	ω5									
-$^1/_3$					ω1										
-$^1/_2$				ω4	ω2					**f2**	**f5**				
-1		C1	C2	C4						*v2*	*v1*	BP4			
-2													BP5		
-4	**f4**														
-6															
-∞															
	-∞	**-6**	**-4**	**-2**	**-1**	**-$^1/_2$**	**-$^1/_3$**	**-$^1/_4$**	**0**	**$^1/_4$**	**$^1/_3$**	**$^1/_2$**	**1**	**2**	**3**
									n						

Fig. 15. The positions in the plane of exponents **m** and **n** of the L(m,n) indices having the five highest correlation coefficients (data in parentheses, see below) with some physicochemical properties of octanes.

Tc^2/Pc: aa1-aa3 (0.982), aa4,5: (0.981)

Tc/Pc: bb1 (-0.996), bb2 (-0.995), bb3 (-0.994), bb4 (-0.993), *pp1*(-0.993)

BP/Tc: *pp1,2* (-0.991), *pp3* (-0.988), *pp4* (-0.987), *pp5* (-0.986)

ΔHf°g : **f1** (0.880), **f2** (0.875), **f3** (0.867), **f4** (0.857), **f5** (0.856)

ω: ω1 (-0.995), ω2,3,4,5 (-0.994)

C: C1 (0.967), C2 (0.965), C3 (-0.965), C4 (0.964), *v3* (-0.956)

BP: **f1** (-0.867), **f2** (-0.856), **f3** (0.852), bp4 (-0.851), bp5 (-0.849)

ΔHv: *v1* (-0.923), *v2* (-0.920), *v3,4,5* (0.914)

Conclusions

The L(m,n) indices are the largest eigenvalues of the $\mathbf{v^m d^n}$ matrix. Their properties are in many cases similar to properties of W(m,n) indices. This is reflected in high correlation between many L(m,n) and W(m,n) indices. There are also some differences indicating that in spite of many similarities they are two different sets of indices.

Seven of the 225 L(m,n) indices tested here correlate with a particular out of the 21 tested physicochemical properties of alkanes from propane through octanes with $r \geq 0.99$. Additional ten cases have $r \geq 0.90$. To a substantial extent this is due to the mutual dependence on the size of the molecule. If only octanes are considered, in three case $|r| \geq 0.99$ and in four additional cases $|r| \geq 0.90$.

The values of most, but not all tested L(m,n) indices increase with the size of the molecule. The increase is in general non-linear. Other structural features, e.g. the distance between the branches, the number of branches, and the type of branched structure have a substantial influence on the value of L(m,n) indices when the size of the molecule increases. Depending on the value of exponents **m** and **n**, these structural features can enhance or diminish the increase of L(m,n) indices due to the increase of the size of the molecule.

In the case of alkanes with the same carbon number, i.e. of alkane isomers, the structural features can have a crucial influence on the values of L(m,n) indices as well. The exponents **m** and **n** significantly influence the values of L(m,n) indices. The combination of exponents decides whether a L(m,n) index increases or decreases with branching, as well as to what extent. The dependence is in general saddle-like.

The indices L(-∞,-∞) and L(-1,-∞) present no information about the properties of alkanes. The index L(0,0) presents only the information about the size of molecules. The indices L(0,0) and L(-∞,1) are linear measures of the size. The index L(-∞,0) is a simple, primitive and degenerated, but a true branching index linking the BI_M indices obeying the *Methane based* definition of branching with the BI_A indices obeying the *n-Alkane-based* definition of branching. The information contained in it seems to be: the presence and the number of branches is of the highest importance in the branching (complexity) of molecules. The indices L(m,0) with exception of those mentioned above and the index L(2,0) suggest that a branch on a quaternary carbon (i.e. on a vertex of degree four) contributes more to branching (complexity) than a branch on a tertiary carbon (i.e. on a vertex of degree three). The contrary is presented by the index L(2,0) and few other L(m,n) indices. The majority of other tested L(m,n) indices indicates that the isomers having branches closer to the centre of molecule are more branched, whereas those having a larger distance between branches are less branched. Some L(m,n) indices indicate that the position of branches is more important than their number. The extreme cases are $L(-{}^{1}/_{3},{}^{1}/_{4})$ and $L(2,{}^{1}/_{4})$. The L(m,n) indices are worse branching indices than the W(m,n) indices.

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Povzetek

Indeksi vrste L(m,n) so največje lastne vrednosti matrik $\mathbf{v^m d^n}$. Po lastnostih so v marsičem podobni indeksom W(m,n). Večina vrednosti indeksov L(m,n), vendar ne vsi, se povečuje z večanjem velikosti molekul. To naraščanje je v splošnem nelinearno. Druge strukturne značilnosti, npr. razdalja med vejami, število vej, vrsta razvejane strukture, precej vplivajo na vrednosti indeksov pri večanju molekul. Indeksa L(-∞,-∞) in L(-1,-∞) ne vsebujeta nikakršnih podatkov o lastnostih alkanov. Indeks L(0,0) vsebuje le podatek o velikosti molekule. Indeks L(-∞,0) povezuje indekse tipa BI_M z indeksi tipa BI_A, ki ustrezajo *n*-alkanskemu pravilu. To je enostaven in degeneriran, vendar pravi indeks razvejanja, ki pove, da je prisotnost in število metilnih skupin (točk valence ena) najpomembnejši podatek v zvezi z razvejanostjo (kompleksnostjo) molekul. Številni indeksi vrste L(m,0) kažejo, da

veja na kvarternem ogljiku (točki valence štiri) prispeva k stopnji razvejanosti molekule (kompleksnosti) več kot veja na terciarnem ogljiku (točki valence tri). Nasprotno kaže indeks L(2,0) in še nekateri drugi. Večina preizkušenih indeksov vrste L(m,n) kaže, da so molekule, ki imajo veje bližje sredini molekule, bolj razvejane in tiste, kjer je razdalja med vejami večja, manj razvejane. Indeksi vrste L(m,n) so slabši indeksi razvejanja kot indeksi vrste W(m,n).