SOME TOPOLOGICAL INDICES DERIVED FROM THE $v^m d^n$ MATRIX. PART 5. SUMMATION-DERIVED SUSCEPTIBILITIES FOR BRANCHING AS BI_A TYPE INDICES

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Abstract

The ${}^SW_A(m,n)$ indices derived from the $v^m d^n$ matrix raise expectations that at least two groups of them might be good branching indices of BI_A type. The indices of one of these groups indicate that a peripherally substituted alkane is more branched than a centrally substituted one, whereas the indices of the other group indicate the reverse. Some of the ${}^SW_A(m,n)$ indices correlate well, having $|r| > 0.99$, with physicochemical properties ω and Tc/Pc. Several ones have $|r| > 0.9$ with BP/Tc, Tc2/Pc, C, ΔHf°g, Pc, and ΔHv.

Introduction

Several hundred topological indices have been developed and tested for their performance as branching indices or indices of substances' properties.[1,2] A substantial part of them is derived from one or another matrix associated with molecular structure. Several authors considered, for example, the adjacency matrix, the distance matrix, and the reciprocal distance matrix to be different types of matrices. Ivanciuc[3] mentions even 14 different types of matrices as sources of topological indices. Estrada[4] developed a matrix that enables the derivation of an infinite number of indices. We[5] presented some types of matrices that enable the derivation of an infinite number of indices and we have shown that these matrices represent a step in unification of several matrices used to derive topological indices, i.e. of the adjacency matrix, the distance matrix, the reciprocal distance matrix, etc.

Topological indices have been correlated with several physical, chemical, and biological properties of molecules. However, even several properties of alkanes still cannot be well described with particular available indices[6] and combinations of them are to be used.[7] In spite of that, interest in topological indices has grown remarkably during recent years. Therefore, the study of those topological indices that might be good branching indices remains an important area of research.

In previous papers[8-10] the suitability of 13 topological indices as branching indices, as well as of 25 physicochemical properties as reference properties for branching of alkanes was studied. The properties were divided into intrinsic and interaction-dependent ones and it was explained why most of the latter ones are not suitable as primary references for branching. The best reference properties to assess branching indices were found to be ΔHf°g, BP/Tc, and Tc/Pc. Two definitions of branching were presented, the *Methane based* definition as a general definition and the *n-Alkane based* definition as its subdefinition, more familiar to chemists working in this field. The indices obeying these definitions were labelled BI_M and BI_A indices, respectively. The search for true branching indices that would not necessarily fit particular properties but would only index branching has been encouraged. In the present paper are evaluated the BIA indices derived from a generalized distance matrix,[5] the $\mathbf{v^m d^n}$ matrix. This generalized matrix allows the derivation of an infinite number of indices and we present here the properties of two sets of 225 indices derived from it.

Data and notations

The structures of alkanes are presented in shorthand, e.g. Hp is *n*-heptane, Oct is *n*-octane, 223M5 is 2,2,3-trimethylpentane, 3E2M5 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 (i.e. the number of branches, *Nbr* = 2) in 22M6 are positioned on a quaternary carbon (2*q*) placed on the periphery (*per*) of the molecule. The two branches in 23M6 and 25 M6 are positioned on tertiary carbons (2*t*). In 23M6 the branches are adjacent (*adj*) and those in 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.

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 refractivity index (n_D) were taken from the CRC Handbook[11] or from Lange's Handbook.[12] The data for the liquid molar volume (Vm), the ratios Tc^2/Pc and Tc/Pc used instead of the van der Waals parameters a_0 and b_0, the ratio BP/Tc (i.e. reduced BP), and the molar refraction (MR) were calculated from data presented in the handbooks.

Methods

The susceptibility for branching

The susceptibility for branching is defined as the normalised difference of the indices' or properties' values,[9] Eq. 1,

$$S_{n,i} = X_i/X_n - 1 \qquad (1)$$

where $S_{n,i}$ is the susceptibility for branching, X is an index or a property, the subscript n referers to the n-alkane of a particular carbon number and the subscript i refers to any alkane of the same carbon number. For example, in $S_{8,i}$ the digit 8 refers to *n*-octane and *i* to any octane. In $S_{8,2M7}$, 2M7 refers to 2-methyl heptane.

Results and discussion

The $v^{\mathbf{m}}d^{\mathbf{n}}$ matrix is in general nonsymmetric. It has been shown that $\mathbf{m} = 0$ and $\mathbf{n} = -\infty$ give the adjacency matrix, the case $\mathbf{m} = 0$, $\mathbf{n} = 1$ gives the distance matrix, the case $\mathbf{m} = 0$, $\mathbf{n} = -1$ gives the reciprocal distance matrix, etc.[5] It has the main diagonal elements $\mathbf{g_{ii}} = 0$ and the nondiagonal elements $\mathbf{g_{ij}}$ $(i \neq j) = v_j^{\mathbf{m}} \times d_{ij}^{\mathbf{n}}$, where v_j is the degree of vertex j (in alkanes it is the number of C-C bonds the carbon in question is involved in) and d_{ij} is the shortest distance from vertex i to vertex j (in alkanes it is the smallest number of bonds between the carbons in question). The indices can be derived from the generalized matrices introduced above e.g. by summation of its elements, like the Wiener[13] index or by calculating the leading eigenvalues of the matrices. In present paper we consider the indices derived from the $v^{\mathbf{m}}d^{\mathbf{n}}$ matrix presented above by summation of its elements.

In a previous paper[5] we studied the W(m,n) indices, which were derived from the $v^{\mathbf{m}}d^{\mathbf{n}}$ matrix by summation of its elements. They are the BI_M type of indices, i.e. they obey the *Methane based* definition of branching. To derive the BI_A type of W(m,n) indices, i.e. the indices obeying the *n-Alkane based* definition of branching and labelled here as W_A(m,n) indices, we can use the susceptibility for branching[14] of the W(m,n) indices.[5] We label this type of BI_A indices, which are derived from the $v^{\mathbf{m}}d^{\mathbf{n}}$ matrix by summation of its elements followed by deriving their susceptibilities for branching, the $^{S}W_A$(m,n) indices.

The properties of $^{S}W_A$(m,n) *indices*

The $^{S}W_A$(m,n) indices of *n*-alkanes are equal to zero by definition. Some of the $^{S}W_A$(m,n) indices are negative and their absolute values seem an attractive possibility to be used. Later shall be shown that in several cases there are the properties of the abs($^{S}W_A$(m,n)) indices different from the genuine $^{S}W_A$(m,n) indices and they present an additional set of the BI_A type indices.

How the values of $^{S}W_A$(m,n) *indices depend on exponents* **m** *and* **n**

Fig. 1 serves as an illustration that the dependence of values of the $^{S}W_A$(m,n) indices on exponents **m** and **n** is saddle-like.

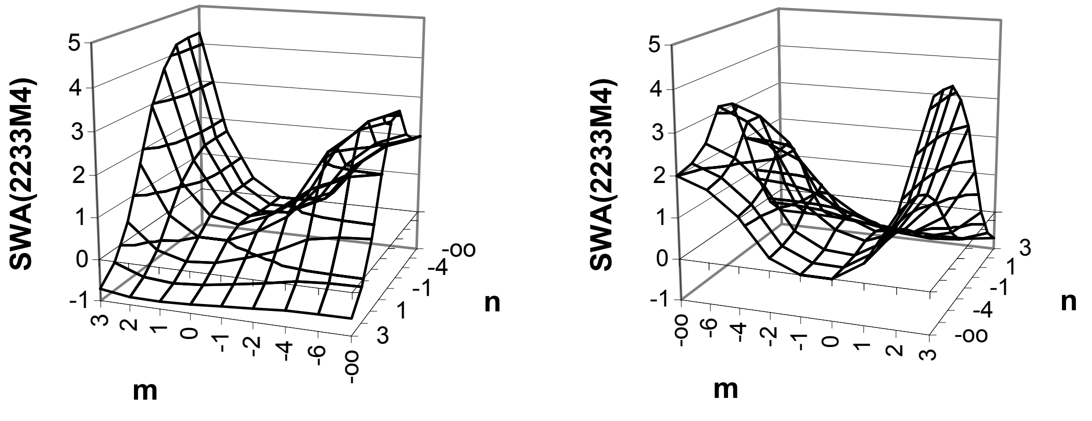


Fig. 1. Two views of the values of $^{S}W_A$(m,n) indices of 2,2,3,3-tetramethyl butane in the plain of exponents **m** and **n**.

The values of ${}^{S}W_A(m,n)$ indices are higher at 2233M4 than at 234M5, especially when **n** < 2 and **m** > 0 or **m** < -1. At **m** > 0 the effect is caused i.a. by the higher contribution of quaternary than tertiary structures.

${}^{S}W_A(m,n)$ *indices which are integers*

Few ${}^{S}W_A(m,n)$ indices are integers. ${}^{S}W_A(m,n) = 0$ when **m** = 0 and **n** = -∞ or 0, as well as when **m** = -1 and **n** = -∞, and when **m** = 1 and **n** = 0, as it was observed among the W(m,n) indices of BI_M type,[5] from which the ${}^{S}W_A(m,n)$ are derived. The ${}^{S}W_A(m,n)$ indices are in general not integers.

Degenerated ${}^{S}W_A(m,n)$ *indices*

The ${}^{S}W_A(m,n)$ indices, Table 1, are highly degenerated when **n** = -∞ or 0 as well in some cases when n = -1 or 1 or 2 and **m** = -∞ or -1 or 0 or 1 or 2.

m									
3	15				15				
2	15				16		4	2	
1	16				18		4	2	
$^1/_2 \le$ **m** $\le {}^1/_4$	15				15				
0	18		2		18		4		
$-^1/_4 \le$ **m** $\le -^1/_2$	15				15				
-1	18				15		4	2	
-2 ≤ **m** ≤ -6	15				15				
-∞	16		2		16		6	4	
	-∞	-∞ < **n** < -1	**-1**	-1 < **n** < 0	**0**	0 < **n** < 1	**1**	**2**	**3**
					n				

Table 1. Degeneration of the ${}^{S}W_A(m,n)$ indices among octanes expressed as the number of data having at least one equal counterpart among 18 possible ones.

How the structural features influence the ${}^{S}W_A(m,n)$ *indices*

When we studied the physicochemical properties of alkanes we have shown that they are influenced by several structural features, e.g. by the size of molecule, by the number of branches, by the type of the branched structure, by the position of branches, by the separation between branches, etc.[8] By definition (see Eq. 1) all ${}^{S}W_A(m,n)$ indices of n-alkanes are equal to zero. Thus the direct influence of the size of molecule is excluded. A qualitative presentation of the influence of particular structural features on the $^{S}W_{A}(m,n)$ indices, based on sequences of isomers, is presented in Tables 2-5.

Number of branches

The influence of the number of branches is presented in Table 2. In Table 2 there are two regions where the values of the $^{S}W_{A}(m,n)$ indices of octanes decrease with the number of branches. The values of these indices are negative. One region is observed at high **n**, the other at low **n** and they are observed especially but not exclusively at -1 < **m** < 1. Between them is the region where the values of $^{S}W_{A}(m,n)$ indices of octanes increase with the number of branches and they are positive. On the boundaries of these regions there is an intermediate region where the values of the $^{S}W_{A}(m,n)$ indices are either equal to 0 or seem to depend on the number of branches in an irregular way.

m											
3	↑	↑	↑	↑	↑	↑	↑	↑	1-	4+ 3-	↓
2	↑	↑	↑	↑	↑	↑	↑	4-	2+	↓	↓
1	↑	↑	↑	↑	0	↓	↓	↓	↓	↓	↓
$^{1}/_{2}$	↑	↑	↑	2+	↓	↓	↓	↓	↓	↓	↓
$^{1}/_{3}$	↑	↑	↑	1+	↓	↓	↓	↓	↓	↓	↓
$^{1}/_{4}$	↑	↑	↑	↑	↓	↓	↓	↓	↓	↓	↓
0	0	↑	↑	↑	0	↓	↓	↓	↓	↓	↓
-$^{1}/_{4}$	↓	↓	↑	↑	↑	3+	↓	↓	↓	↓	↓
-$^{1}/_{3}$	↓	↓	↑	↑	↑	4+ 11-	3+	↓	↓	↓	↓
-$^{1}/_{2}$	↓	↓	↑	↑	↑	↑	1+ 5-	2+ 2-	↓	↓	↓
-1	0	↑	↑	↑	↑	↑	↑	↑	1+ 2-	↓	↓
-2	↑	↑	↑	↑	↑	↑	↑	↑	2+	↓	↓
-4	↑	↑	↑	↑	↑	↑	↑	↑	↑	1+ 2-	↓
-6	↑	↑	↑	↑	↑	↑	↑	↑	↑	1+ 6-	↓
-∞	↑	↑	↑	↑	↑	↑	↑	↑	↑	1+ 8-	↓
	-∞	**-6**	-4 ≤**n**≤-$^{1}/_{3}$	**-$^{1}/_{4}$**	**0**	**$^{1}/_{4}$**	**$^{1}/_{3}$**	**$^{1}/_{2}$**	**1**	**2**	**3**
					n						

Table 2. The dependence of the $^{S}W_{A}(m,n)$ indices of octanes on the number of branches.

↓ The value of $^{S}W_{A}(m,n)$ decreases with the number of branches; it is negative

↑ The value of $^{S}W_{A}(m,n)$ increases with the number of branches; it is positive

4+ 3- Four of 18 octane isomers are presented by that $^{S}W_{A}(m,n)$ index as more branched than 2233M4, whereas three of them are presented as less branched than *n*-octane

0 $^{S}W_{A}(m,n) = 0$ for all isomers

Dotted lines - the intermediate region

m															
3	***q>t***	c>p	c>p	c>p	c>p	c>p	c>p	c>p	***q>t***	p>c	p>c	p>c	p>c	**c>p**	c>p
2	***q>t***	c>p	c>p	c>p	c>p	c>p	c>p	c>p	*q>t*	p>c	p>c	p>c	c>p	c>p	c>p
1	*q>t*	c>p	c>p	c>p	c>p	c>p	c>p	c>p	0	c>p	c>p	c>p	c>p	c>p	c>p
$^{1}/_{2}$	*q>t*	c>p	c>p	c>p	c>p	c>p	c>p	c>p	*q>t*	c>p	c>p	c>p	c>p	c>p	c>p
$^{1}/_{3}$	*q>t*	c>p	c>p	c>p	c>p	c>p	c>p	c>p	*q>t*	c>p	c>p	c>p	c>p	c>p	c>p
$^{1}/_{4}$	*q>t*	c>p	c>p	c>p	c>p	c>p	c>p	c>p	*q>t*	c>p	c>p	c>p	c>p	c>p	c>p
0	0	c>p	c>p	c>p	c>p	c>p	c>p	c>p	0	c>p	c>p	c>p	c>p	c>p	c>p
$-^{1}/_{4}$	*q>t*	c>p	c>p	c>p	c>p	c>p	c>p	c>p	*q>t*	c>p	c>p	c>p	c>p	c>p	c>p
$-^{1}/_{3}$	*q>t*	c>p		c>p	c>p	c>p	c>p	c>p	*q>t*	**p>c**	c>p	c>p	c>p	c>p	c>p
$-^{1}/_{2}$	*q>t*	c>p	p>c	c>p	c>p	c>p	c>p	c>p	*q>t*	p>c	**p>c**	**c>p**	c>p	c>p	c>p
-1	0	p>c	p>c	c>p	c>p	c>p	c>p	c>p	*q>t*	p>c	p>c	p>c	**c>p**	c>p	c>p
-2	*q>t*	p>c	p>c		c>p	c>p	c>p	c>p	*q>t*	p>c	p>c	p>c	c>p	c>p	c>p
-4	*q>t*	p>c	p>c			c>p	c>p	c>p	*q>t*	p>c	p>c	p>c	p>c	**c>p**	c>p
-6	*q>t*	p>c	p>c			c>p	c>p	c>p	*q>t*	p>c	p>c	p>c	p>c	**c>p**	c>p
-∞	*q=t*	p>c				c>p	c>p	c>p	*q=t*	p>c	p>c	p>c	p>c	**c>p**	c>p
	-∞	**-6**	**-4**	**-2**	**-1**	**$-^{1}/_{2}$**	**$-^{1}/_{3}$**	**$-^{1}/_{4}$**	**0**	**$^{1}/_{4}$**	**$^{1}/_{3}$**	**$^{1}/_{2}$**	**1**	**2**	**3**
									n						

Table 3. The ${}^{S}W_{A}(m,n)$ indices of octanes indicate which position of branches seems to contribute more to the degree of branching. The contribution of the position of branches is superimposed to the direction of the contribution of the number of branches, Table 2.

q>t	The contribution of two branches in a quaternary (*q*) structure is *higher than* the contribution of three branches in tertiary structures ($2q>3t$)
q>t	The contribution of two branches in a quaternary structure is *equal to* that of three branches in tertiary structures ($2q=3t$)
q>t	The contribution of two branches in a quaternary structure is higher than in tertiary structures ($2t<2q<3t$)
q=t	The contribution of two branches in a quaternary structure is equal to that in tertiary structures ($2q=2t$)
0	The position of branches has no influence

Empty space: The position of branches seems to have little influence

c>p: *ctr*>2233>...>Oct>*per*
c>p: 2233>*ctr*>...>Oct>*per*
c>p: *ctr*>2233>...>*per*>Oct
c>p: 2233>*ctr*>...>*per*>Oct

p>c: *per*>2233>...>Oct>*ctr*
p>c: *per*>2233>...>Oct>*ctr*
p>c: *per*>2233>...>Oct>*ctr*
p>c: *per*>2233>...>Oct>*ctr*

Example for **c>p** (at ${}^{S}W_{A}(-^{1}/_{2},^{1}/_{2})$: 3E3M5 < 233M5 < **2233M4** < 3E2M5 < 33M6 < 223M5 < 3E6 < 34M6< 234M5 < 23M6 < 4M7 < 24M6 < 224M5< 3M7 < 22M6 < **Oct** (= 0) < 25M6 < 2M7

This is the consequence of the saddle-like dependence of their values on the exponents **m** and **n**, cf. ref.[5] If absolute values of ${}^{S}W_{A}(m,n)$ indices are taken, then the correlations with indices in the intermediate regions alter their values whereas those in regular regions may change only the sign. Absolute values of the ${}^{S}W_{A}(m,n)$ indices in the intermediate regions of Table 2 present thus a second group of BI_A type indices that should be also tested for their possible usefulness.

From this point on we do not consider any more whether the values of an index are positive or negative, or, more positive or more negative, but only whether a structural feature causes that an index presents the octane having that structural feature as more branched or less branched than the other octanes. What holds true for octanes, holds true also for lower alkanes if not explicitly indicated otherwise.

Position of branches

Regarding the influence of the position of branches is the situation among the $^{S}W_A(m,n)$ indices quite complex, Table 3. There are two regions where the position of branches has no influence on the $^{S}W_A(m,n)$ indices: $^{S}W_A(m,-\infty)$ and $^{S}W_A(m,0)$. There are three triangle-like regions where the $^{S}W_A(m,n)$ indices indicate that an octane having the branch(es) near the periphery of molecule is more branched than that having the branch(es) near the centre of molecule. One region is, roughly speaking, at $\mathbf{m} > 1$ and $0 < \mathbf{n} < 2$, another is at $\mathbf{m} < -{}^{1}/_{3}$ and $-\infty < \mathbf{n} < -1$ or -2, and the third one is in a triangle at $\mathbf{m} < -{}^{1}/_{4}$ and $0 < \mathbf{n} < 2$. The majority of tested $^{S}W_A(m,n)$ indices indicates that an octane having the branch(es) near the centre of molecule is more branched than that having the branch(es) near the periphery. The positions in the plane of exponents **m** and **n**, where the influence of the position of branches is higher than the influence of their number are presented in boldface.

Separation between branches

The contribution of the separation between branches is presented schematically in Table 4. The values of the indices $^{S}W_A(m,-\infty)$ and $^{S}W_A(m,0)$ do not depend on the separation between branches. The situation is otherwise to some extent similar to that in Table 3: at low **m** and **n** values, i.e. at $\mathbf{m} < -{}^{1}/_{2}$ and $\mathbf{n} < -2$, as well as at $\mathbf{m} < -{}^{1}/_{4}$ or $\mathbf{m} > 1$ and $0 < \mathbf{n} < 2$ or 1, respectively, the values of $^{S}W_A(m,n)$ indices indicate that the larger the separation between branches the more branched seems an octane isomer. In other cases, the values of $^{S}W_A(m,n)$ indices indicate that an octane isomer is the less branched the larger is the separation between branches.

m											
3	0	↓	↓	↓	0	↑	↑	↑	↓	↓	↓
2	0	↓	↓	↓	0	↑	↑	↓	↓	↓	↓
$-{}^1/_4 \le$ **m** ≤ 1	0	↓	↓	↓	0	↓	↓	↓	↓	↓	↓
$-{}^1/_3$	0	↓	↓	↓	0	↑	↓	↓	↓	↓	↓
$-{}^1/_2$	0	↓		↓	0	↑	↓	↓	↓	↓	↓
-1	0	↑		↓	0	↑	↑	↑	↓	↓	↓
-2	0	↑	↑	↓	0	↑	↑	↑	↑	↓	↓
-4	0	↑	↑	↓	0	↑	↑	↑	↑	↓	↓
-6	0	↑	↑	↓	0	↑	↑	↑	↑	↓	↓
-∞	0	↑	↑	↓	0	↑	↑	↑	↑	↓	↓
	-∞	**-6**	**-4**	$-2 \le$ **n** $\le -{}^1/_4$	**0**	**$^1/_4$**	**$^1/_3$**	**$^1/_2$**	**1**	**2**	**3**
					n						

Table 4. The contribution of the separation between branches to the $^SW_A(m,n)$ index.

↑ A higher separation between branches is represented by that $^SW_A(m,n)$ index as contributing more to branching than a lower separation.

↓ A higher separation between branches is represented by that $^SW_A(m,n)$ index as contributing less to branching than a lower separation.

Empty space: little influence, unclear.

m											
3	=	>	>	>	>	>	=	<	<	<	>
2	=	>	>	>	>	>	=	<	<	>	>
$-{}^1/_3 \le$ **m** ≤ 1	=	>	>	>	>	>	=	>	>	>	>
$-{}^1/_2$	=	>	<	>	>	>	=	<	>	>	>
-1	=	<	<	>	>	>	=	<	<	>	>
-2	=	<	<	<	>	>	=	<	<	<	>
-4	=	<	<	<	<	>	=	<	<	<	>
-6	=	<	<	<	<	>	=	<	<	<	>
-∞	=	<	<	<	<	>	=	<	<	<	>
	-∞	**-6**	**-4**	**-2**	**-1**	$-{}^1/_2 \le$ **n** $\le -{}^1/_4$	**0**	$0 <$ **n** $< {}^1/_3$	**$^1/_2$**	**1**	**n** ≥ 2
							n				

Table 5. The contribution of the type of branches to the values of $^SW_A(m,n)$ indices.

> The ethyl substituted octane is represented by that $^SW_A(m,n)$ index as more branched than the methyl substituted one.

< The ethyl substituted octane is represented by that $^SW_A(m,n)$ index as less branched than the methyl substituted one.

= The index does not distinguish between the ethyl and methyl substituent, important is only the number of them.

Type of branches

There are also some differences when the branches are of different type, i.e. whether a branch is methyl or ethyl, Table 5. The values of ${}^{S}W_A(m,-\infty)$ and ${}^{S}W_A(m,0)$ indices do not depend on the type of branches. At low **m** and **n** values, i.e. at $\mathbf{m} < -{}^{1}/_{2}$ and $\mathbf{n} < -1$, as well as at $\mathbf{m} < -{}^{1}/_{3}$ or $\mathbf{m} > 1$ and $0 < \mathbf{n} < 2$, the values of ${}^{S}W_A(m,n)$ indices indicate that the structure containing branches in form of ethyl groups are less branched than those containing methyl groups. In other cases, the values of ${}^{S}W_A(m,n)$ indices indicate that an octane isomer is more branched if it contains an ethyl group as a branch. This situation is to some extent similar to that in Table 4.

Which ${}^{S}W_A(m,n)$ *indices could be good branching indices?*

There do not exist agreed criteria what characteristics should have a good branching index. Consequently, there exist several definitions of branching. One of the definitions is, for example, based on the Wiener[13] number,[15] some other ones are based on the leading eigenvalue of adjacency matrix,[16] or the leading eigenvalue of path matrix.[17] We presented the *Methane based* definition of branching as well as the *n-Alkane based* one[8] and evaluated a set of 13 most frequently used topological indices by a number of criteria, including partial sequences of isomers having equal number and type of branches.[10] By intuition, the next step in evaluation of indices would be the assumption that a good branching index should have a regular sequence of all isomers. What would be a regular sequence? Studying 21 physicochemical properties of alkanes,[8] we came to the conclusion that in a regular sequence of isomers the influence of the number of branches should be higher than that of the position of branches, followed by the separation between branches and the type of the branched structure. *Consequently, branching should not be defined by topological indices but by structural features of molecules*. Taking this conclusion as a guide, we can extend the principle of a regular sequence to all isomers in order to construct some "ideal" sequences of octanes of increasing branching, e.g.,

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

which indicates that a centrally substituted alkane is more branched than a peripherally substituted one, or, Oct < 3E6 < 4M7< 3M7 < 2M7 < 3E2M5 < 34M6 < 23M6 < 24M6 < 25M6 < 3E3M5 < 33M6 < 22M6 < 234M5 < 233M5 < 223M5 < 224M5 < 2233M4,

which indicates that a peripherally substituted alkane is more branched than a centrally substituted one. The sign can be either < as above, or >.

The Wiener[13] number, identical with W(0,1),[5] from which the index $^{S}W_A(0,1)$ is derived and on which is based the approach of Bonchev and Trinajstić,[15] has the sequence:

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

The leading eigenvalue of adjacency matrix, λ_1,[16] has the sequence:

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

The leading eigenvalue of path matrix[17] has the sequence:

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

Neither the Wiener[13] number, nor the leading eigenvalue of adjacency matrix[16] and the leading eigenvalue of path matrix[17] has an "ideal" sequence of octane isomers. Therefore these indices are not good bases to define branching.

The physicochemical properties, found to be the most appropriate references to assess branching[9] have the following sequences of isomers:

ω: Oct < 2M7 < 4M7 < 3M7 < 3E6 < 25M6 < 23M6 < 24M6 < 34M6 = 22M6 < 3E2M5 < 33M6 < 234M5 < 3E3M5 = 224M5 < 223M5 < 233M5 < 2233M4
Tc/Pc: Oct < 2M7 < 3M7 < 25M6 < 4M7 < 22M6 < 3E6 < 24M6 < 23M6 < 33M6 < 34M6 < 224M5 < 3E2M5 < 234M5 < 223M5 < 3E3M5 < 233M5 < 2233M4
BP/Tc: Oct < 2M7 < 4M7 < 3M7 < 25M6 < 3E6 < 24M6 < 22M6 < 23M6 < 34M6 < 3E2M5 < 33M6 < 224M5 < 234M5 < 223M5 < 3E3M5 < 233M5 < 2233M4
Tc^2/Pc: Oct < 2M7 < 3M7 < 4M7 < 3E6 < 25M6 < 23M6 < 22M6 < 34M6 < 24M6 < 3E2M5 < 33M6 < 3E3M5 < 234M5 < 233M5 < 223M5 < 224M5 < 2233M4
C: Oct < 3M7 < 4M7 = 3E6 < 2M7 < 23M6 < 25M6 < 24M6 < 34M6 < 22M6 < 3E2M5 < 33M6 < 234M5 < 223M5 < 3E3M5 < 233M5 < 224M5 < 2233M4
ΔHf°g: Oct < 3E6 < 3E2M5 < 4M7 < 3M7 < 34M6 < 23M6 < 3E3M5 < 2M7 < 233M5 < 234M5 < 24M6 < 33M6 = 223M5 < 25M6 < 224M5 < 22M6 < 2233M4
whereas
ΔHv: Oct < 3M7 = 4M7 < 2M7 < 3E6 < 34M6 < 23M6 < 3E2M5 < 3E3M5 < 234M5 < 25M6 < 24M6 < 33M6 < 233M5 < 22M6 < 223M5 < 2233M4 < 224M5
BP: Oct < 3M7 < 3E6 < 3E3M5 < 34M6 < 4M7 < 2M7 < 3E2M5 < 23M6 < 233M5 < 234M5 < 33M6 < 223M5 < 24M6 < 25M6 < 22M6 < 2233M4 < 224M5

ctr > *per*: ω, Tc/Pc, BP/Tc *per* > *ctr*: ΔHf°g, ΔHv, BP

None of them has a regular or “ideal” sequence. Among all of them in some instances the influence of the position of branches overrides the influence of the number of branches. The physicochemical properties ω, Tc/Pc, and BP/Tc indicate that a centrally substituted alkane is more branched than a peripherally substituted one, whereas ΔHf°g, ΔHv, and BP indicate that a peripherally substituted alkane is more branched than a centrally substituted one. The situation is not as clear at Tc^2/Pc and C.

m															
3	$2q>3t$	⊗	⊗	⊗		⊗	⊗	⊗	$2q>3t$	**	**	**			
2	$2q>3t$	⊗	⊗						$2q=3t$						
1	$2q=3t$								0						
$^1/_2$	$q>t$	#	#						$q>t$						
$^1/_3$	$q>t$	#	#						$q>t$						
$^1/_4$	$q>t$	#	#						$q>t$						
0	0								0						
$-^1/_4$	$q>t$								$q>t$						
$-^1/_3$	$q>t$		⊗					#	$q>t$						
$-^1/_2$	$q>t$	#		#	#	#	#	#	$q>t$						
-1	0		*		#	#	#	#	$q>t$						
-2	$q>t$	*	*						$q>t$						
-4	$q>t$		*						$q>t$						
-6	$q>t$								$q>t$						
-∞	*Nbr*								*Nbr*						
	-∞	**-6**	**-4**	**-2**	**-1**	**$-^1/_2$**	**$-^1/_3$**	**$-^1/_4$**	**0**	**$^1/_4$**	**$^1/_3$**	**$^1/_2$**	**1**	**2**	**3**

n

Fig. 2. The position of $^{S}W_A(m,n)$ indices considered as the best candidates for good branching indices. The sequences of isomers and the meaning of labels *, **, #, and ⊗ are presented in the text.

Nbr: The index depends only on the number of branches

q>t: The number of branches and the type of the branched structure influence these indices. Two branches on a quaternary carbon have a higher contribution than two branches on tertiary carbons, in fact $2q>2t$.

The question, whether some $^{S}W_A(m,n)$ indices have the “ideal” sequence of octane isomers is answered in Fig. 2, where the position of the $^{S}W_A(m,n)$ indices, candidates for good branching indices, is presented in the plane of exponents **m** and **n**. There is a number of tested $^{S}W_A(m,n)$ indices having one or another “ideal” sequence of isomers.

Four of them, namely $^{S}W_{A}(-1,-4)$, $^{S}W_{A}(-2,-4)$, $^{S}W_{A}(-4,-4)$, and $^{S}W_{A}(-2,-6)$ have the sequence:

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

indicating that a peripherally substituted alkane is more branched than a centrally substituted one.

The indices $^{S}W_{A}(3,{}^{1}/_{2})$, $^{S}W_{A}(3,{}^{1}/_{3})$, and $^{S}W_{A}(3,{}^{1}/_{4})$ have the sequence:

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

indicating also that the structure 3*t* is felt less branched than the structure 2*q*.

Seventeen $^{S}W_{A}(m,n)$ indices, namely $^{S}W_{A}(-{}^{1}/_{3},-{}^{1}/_{4})$, $^{S}W_{A}(-{}^{1}/_{2},-{}^{1}/_{4})$, $^{S}W_{A}(-1,-{}^{1}/_{4})$, $^{S}W_{A}(-{}^{1}/_{2},-{}^{1}/_{3})$, $^{S}W_{A}(-1,-{}^{1}/_{3})$, $^{S}W_{A}(-{}^{1}/_{2},-{}^{1}/_{2})$, $^{S}W_{A}(-1,-{}^{1}/_{2})$, $^{S}W_{A}(-{}^{1}/_{2},-1)$, $^{S}W_{A}(-1,-1)$, $^{S}W_{A}(-{}^{1}/_{2},-2)$, $^{S}W_{A}({}^{1}/_{2},-4)$, $^{S}W_{A}({}^{1}/_{3},-4)$, $^{S}W_{A}({}^{1}/_{4},-4)$, $^{S}W_{A}({}^{1}/_{2},-6)$, $^{S}W_{A}({}^{1}/_{3},-6)$, $^{S}W_{A}({}^{1}/_{4},-6)$, and $^{S}W_{A}(-{}^{1}/_{2},-6)$ have the sequence:

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

indicating that a centrally substituted alkane is more branched than a peripherally substituted one.

Nine tested indices: $^{S}W_{A}(3,-6)$, $^{S}W_{A}(2,-6)$, $^{S}W_{A}(3,-4)$, $^{S}W_{A}(2,-4)$, $^{S}W_{A}(-{}^{1}/_{3},-4)$, $^{S}W_{A}(3,-2)$, $^{S}W_{A}(3,-{}^{1}/_{2})$, $^{S}W_{A}(3,-{}^{1}/_{4})$, and $^{S}W_{A}(3,-{}^{1}/_{3})$ have the sequence:

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

Most of $^{S}W_{A}(m,n)$ indices, candidates for good branching indices, have **n** < 0.

Among physicochemical properties of alkanes as well as among topological indices associated with their molecular structure we do not observe the same direction of dependence on the structural features. There do not increase all physicochemical properties with the size of molecule or with increasing degree of branching, be it expressed as the number of branches, their position, the separation between branches, their type, etc. Therefore, there is not to be expected that only one branching index or only one set of them should exist. The results presented above indicate that at least two (independent) sets of branching indices should be sought for. One set of branching indices should indicate that a centrally substituted alkane is more branched than a peripherally substituted one, whereas another set of them should indicate that a peripherally substituted alkane is more branched than a centrally substituted one.

Correlation between the $^{S}W_A(m,n)$ *indices and physicochemical properties*

The correlation between the $^{S}W_A(m,n)$ indices and 20 physicochemical properties, assuming the linear relationship, is presented in Fig. 3 and 4. The indices $^{S}W_A(1,0)$, $^{S}W_A(0,0)$, $^{S}W_A(0,-\infty)$, and $^{S}W_A(-1,-\infty)$ do not index branching.

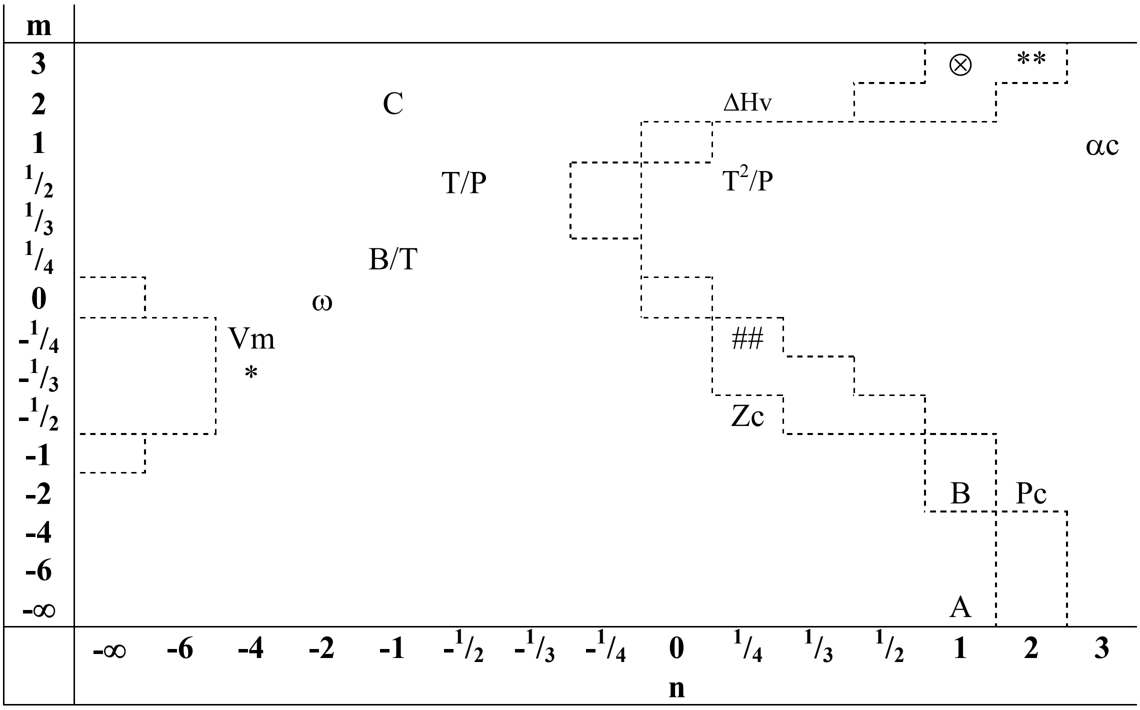


Figure 3. The position of 20 physicochemical properties determined by the highest correlation coefficient (r; data in parentheses) for data of abs(($^{S}W_A(m,n)$) indices of octanes, in the plane of exponents **m** and **n**.

Single standing ones: **C** (0.**97**), ΔHv (-0.**93**), αc (-0.74), ω (-0.**996**), Vm (-0.69), Zc (0.64), B (-0.74), Pc (0.**95**), A (-0.77), T/P: **Tc/Pc** (-0.**99**), B/T: **BP/Tc** (-0.**99**), T^2/P: Tc^2/Pc (-0.**98**),
##: dc (0.83), Vc (-0.84), ⊗: **ΔHf°g** (0.**94**), BP (-0.88), *: d (0.70), n_D (0.68), **: Tc (0.70), MR (-0.89),

In Fig. 3 the positions of the best correlation coefficients between the 20 tested physicochemical properties and abs($^{S}W_A(m,n)$) indices of octanes are presented in the plane of exponents **m** and **n**. Some of them, i.e. those of the properties ΔHf°g (0.94), BP (-0.88), Tc (0.70), MR (-0.89), dc (0.83), Vc (-0.84), and B (-0.74) are placed in the transition region marked with dotted lines, whereas most of them are positioned outside the transition region.

In Fig. 4 the positions of the best correlation coefficients between 20 tested physicochemical properties and $^{S}W_{A}(m,n)$ indices of octanes are presented in the plane of exponents **m** and **n**. In this case, the best correlation coefficients of the following properties, ΔHf°g (0.95), BP (-0.87), MR (0.89), B (-0.74), and Tc (-0.75) are placed in the transition region. Markedly different is the position of Tc, dc, and Vc.

The differences in the absolute values of their correlation coefficients relative to those with abs($^{S}W_{A}(m,n)$) indices are marginal. Thus both sets of indices are nearly equivalent if we neglect the difference in the sign of the correlation coefficients. The best correlation coefficients, r ($^{S}W_{A}(m,n)$, Property), were observed among the pairs: $^{S}W_{A}(0,-2)$ and ω (-0.996); $^{S}W_{A}(^1/_2,-^1/_2)$ and Tc/Pc (-0.994), $^{S}W_{A}(^1/_4,-1)$ and BP/Tc (-0.987), $^{S}W_{A}(^1/_2,^1/_4)$ and Tc^2/Pc (-0.981), $^{S}W_{A}(2,-1)$ and C (0.97), $^{S}W_{A}(3,1)$ and ΔHf°g (0.94), as well as $^{S}W_{A}(2,^1/_4)$ and ΔHv (-0.93).

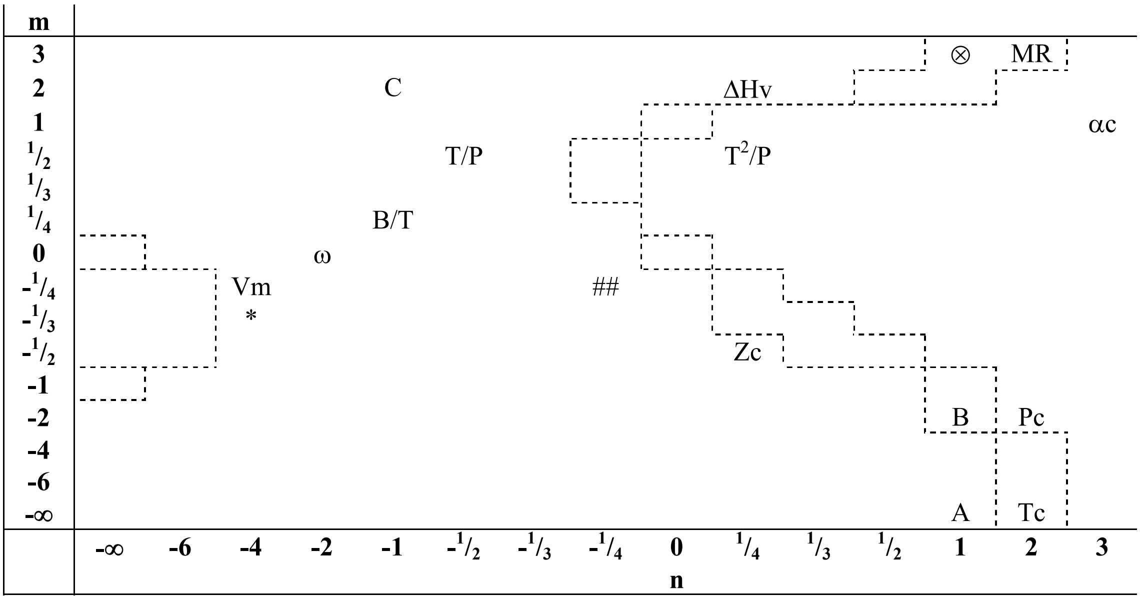
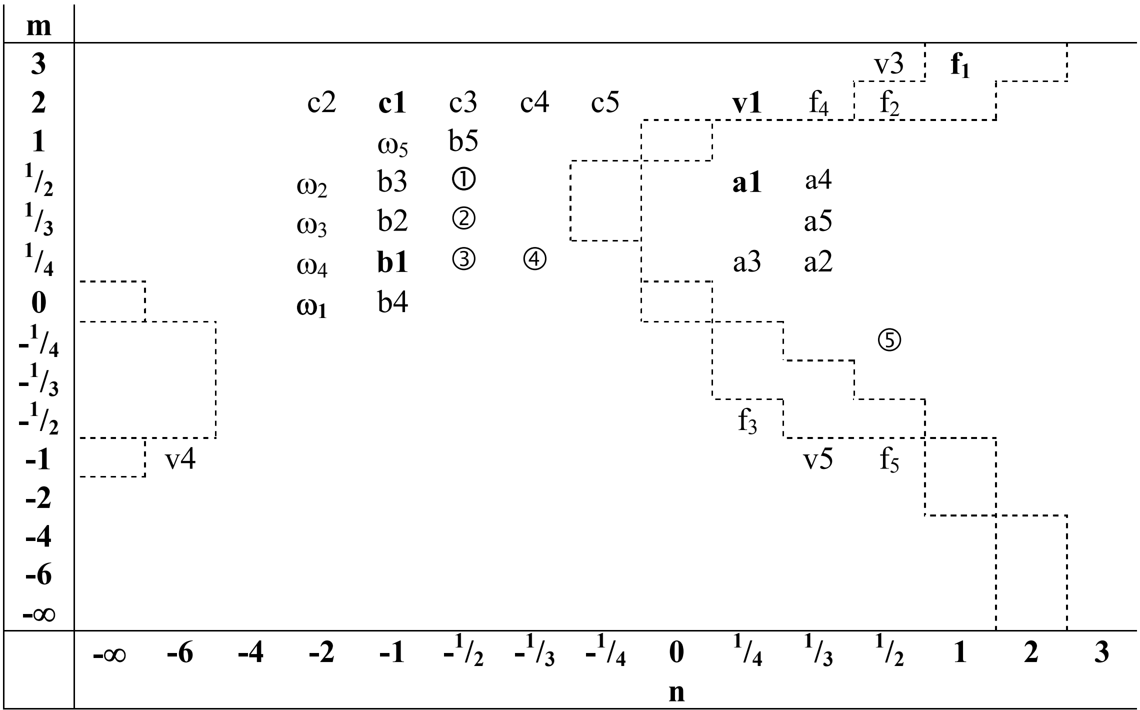


Figure 4. The position of 20 physicochemical properties determined by the highest correlation coefficient (r; data in parentheses) for data of $^{S}W_{A}(m,n)$ indices of octanes, in the plane of exponents **m** and **n**.

Single standing ones: MR (0.89), **C** (0.**97**), ΔHv (-0.**93**), αc (0.74), **ω** (-0.**996**),
Vm (-0.69), Zc (0.64), B (-0.74), Pc (0.**95**), A (-0.77), Tc (-0.75), T/P: **Tc/Pc** (-0.**99**),
B/T: **BP/Tc** (-0.**99**), T^2/P: Tc^2/Pc (0.**98**),
##: dc (-0.83), Vc (0.84), ⊗: **ΔHf°g** (0.**95**), BP (-0.87), *: d (0.70), n_D (0.68),

Fig. 5 illustrates how different ${}^{S}W_{A}(m,n)$ indices have similar correlation coefficients with a physicochemical property. This is represented by seven physicochemical properties having the best correlations. The positions of the five best correlations are grouped in particular areas (ω, BP/Tc, Tc^2/Pc, C) or spread (Tc/Pc, ΔHf°g, ΔHv) in the plane of exponents **m** and **n**. In several cases there is no great difference in the quality of the correlation among two or more possible indices, so several of them may be useful.



m															
3												v3	**f1**		
2				c2	**c1**	c3	c4	c5		**v1**	f4	f2			
1					ω5	b5									
1/2				ω2	b3	①				**a1**	a4				
1/3				ω3	b2	②					a5				
1/4				ω4	**b1**	③	④			a3	a2				
0				ω1	b4										
-1/4												⑤			
-1/3															
-1/2										f3					
-1		v4									v5	f5			
-2															
-4															
-6															
-∞															
	-∞	**-6**	**-4**	**-2**	**-1**	**-1/2**	**-1/3**	**-1/4**	**0**	**1/4**	**1/3**	**1/2**	**1**	**2**	**3**
								n							

Figure 5. ${}^{S}W_{A}(m,n)$ indices of octanes having the highest correlation coefficient (r) for data of physicochemical properties.

ω: ω1 (-0.9964), ω2 (-0.9962), ω3, ω4 (-0.9959), ω5 (-0.9958)
Tc/Pc: ① (-0.9935), ② (-0.9934), ③ (-0.9928), ④ (-0.9911), ⑤ (-0.9897)
BP/Tc: **b1**,b2 (-0.9871), b3 (-0.9870), b4 (-0.9852), b5 (-0.9844)
Tc^2/Pc: **a1** (0.9815), a2 (0.9813), a3, a4 (0.9805), a5 (0.9800)
C: **c1** (0.9706), c2 (0.9704), c3 (0.9703), c4 (0.9700), c5 (0.9696)
ΔHf°g: **f1** (0.9479), f2 (0.9338), f3 (0.8833), f4 (0.8772), f5 (0.8667)
ΔHv: **v1** (-0.9317), f4 (-0.9313), v3 (-0.9294), v4 (-0.9244), v5 (-0.9237)

Conclusions

Some of the $^{S}W_{A}(m,n)$ indices correlate well, having $|r| > 0.99$, with the physicochemical properties ω and Tc/Pc. Several ones have $|r| > 0.9$ with BP/Tc, Tc^2/Pc, C, ΔHf°g, Pc, and ΔHv.

The $^{S}W_{A}(m,n)$ indices derived from the $v^{\mathbf{m}}d^{\mathbf{n}}$ matrix raise expectations that some of them, especially those having the combination of exponents (m,n): (-2,-6), (-1,-4), (-2,-4), and (-4,-4), as well as $(-^1/_2,-6)$, $(^1/_2,-6)$, $(^1/_3,-6)$, $(^1/_4,-6)$, $(^1/_2,-4)$, $(^1/_3,-4)$, $(^1/_4,-4)$, $(-^1/_2,-2)$, $(-^1/_2,-1)$, (-1,-1), $(-^1/_2,-^1/_2)$, $(-1,-^1/_2)$, $(-^1/_2,-^1/_3)$, $(-1,-^1/_3)$, $(-^1/_3,-^1/_4)$, $(-^1/_2,-^1/_4)$, and $(-1,-^1/_4)$ might be good branching indices of BI_A type. The indices of the former group indicate that a peripherally substituted alkane is more branched than a centrally substituted one, whereas the latter group of indices indicates the reverse.

Such a dualism is also observed among some physicochemical properties of alkanes: ω, Tc/Pc, and BP/Tc indicate that a centrally substituted alkane is more branched than a peripherally substituted one, whereas ΔHf°g, ΔHv, and BP indicate the reverse. These facts do not indicate that a molecule has more than one branching, one described with one set of indices and another with another set of indices, or alternatively, one defined by one set of properties and the other by another set of properties. A molecule has only one branching, but this one branching is reflected differently in different physicochemical properties as well as it is evaluated differently by different topological indices. Therefore, branching should not be defined by a topological index or by a physicochemical property. A better choice to define branching seems to be the use of structural features of a molecule.

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Povzetek

Indeksi vrste $^{S}W_A(m,n)$, izvedeni iz matrik $v^m d^n$, obetajo, da bi vsaj dve skupini njih lahko bili dobri predstavniki indeksov razvejanja tipa BIA. Indeksi ene od teh skupin nakazujejo, da so bolj razvejani tisti alkani, ki imajo veje pri koncu verige, indeksi druge skupine pa, da so bolj razvejani tisti, ki imajo veje blizu sredine verige. Nekateri indeksi vrste $^{S}W_A(m,n)$ dobro korelirajo ($|r| > 0.99$) s fizikokemijskima lastnostma ω in Tc/Pc, drugi pa tudi ($|r| > 0.9$) z BP/Tc, Tc2/Pc, C, ΔHf°g, Pc in ΔHv.