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Elements of an Universal Matrix as Topological Indices for Physicochemical Properties of Octanes

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Abstract

Some of the elements of the Universal matrix and their combinations are useful topological indices of physicochemical properties of octanes. Whereas some of the single elements of the Universal matrix give rise to $0.70 < |R| < 0.99$, mutually optimized combinations of only four to six out of 56 of them in the Universal matrix of octanes give rise to $R > 0.99$ and in the worst cases to $R > 0.98$. Also a new measure of goodness of correlation, the information content in the topological index, *IC* (%), is introduced. Structural interpretation of some of the physicochemical properties of octanes is demonstrated as well as of the contribution by the most useful elements of the Universal matrix.

Keywords: Information content; Goodness of topological indices; Universal matrix elements; Octanes; Structural interpretation of: Octane Number, van der Waals constant a_0, Boiling point, Refractive index, Critical temperature, Critical density, Vapor pressure

1. Introduction

Mathematical methods occupy an eminent place in the field of prediction of properties and activities of chemical compounds, and even materials. These methods, known under the acronym QSPR/QSAR (quantitative-structure-property or structure-activity relationship) use also graph-theoretical descriptors, where molecules are seen as chemical graphs, i.e. as a set of vertices attached to each other by a set of non-metrical connections.[1] These descriptors are proposed as topological indices. They are the simplest means of describing the structure of a molecule, characterizing it by a single number.[2]

There is known a plethora of topological indices.[3–9] After their compilations, a huge number of new ones has been described and new and new ones are being developed, cf. e.g.[10,11]

A substantial part of topological indices is derived from one or another matrix associated with molecular topology. Ivanciuc[12,13] presented the Dval matrix and its characteristics, and we have shown[14] that this matrix represents a step in unification of several matrices which had been used to derive topological indices, i.e. of the adjacency matrix, the distance matrix, the reciprocal distance matrix, etc, being thus an Universal matrix. The characteristics of some groups of topological indices derived by means of this generalized vertex-degree vertex-distance matrix have been studied and there was demonstrated the usefulness of some of those new topological indices.[14]

The well known topological indices W,[15] RW,[16] χ,[17] for example, are composed of the one half of the sum of all 56 matrix elements $\mathbf{u}_{ij}(a, b, c)$ of the Universal matrix, where at W:[15] (a, b, c) = (0, 0, 1); at RW:[16] (a, b, c) = (0, 0, –1); and at χ:[17] (a, b, c) = (–½, –½, –∞).

There arose the question whether particular elements of the Universal matrix as well as their combinations are good topological indices or not. It has been demonstrated that although particular elements of the Universal matrix are not invariant to molecular labelling, they are invariant regarding the structural features of octanes, and the topological indices, which are not invariant to molecular labelling give rise to better correlations than the topological indices, which are invariant to molecular labeling.[18]

For this reason, the elements of the Universal matrix and their mutually optimized combinations have been systematically studied and the results are presented here.

2. Data and Definitions

The origin of data of physicochemical properties (PCP), as well as the notations of octanes have been presented elsewhere.[14] The data are presented in Appendix 1. Correlation between physicochemical properties of octanes used in present study is presented in Appendix 2. Grouping of physicochemical properties of octanes by their intercorrelation in Appendix 2 and put into subgroups according to the correlation coefficient with the best topological indices (TI) based on grid values of exponents[14] in TI(a, b, c) are presented in Table 1.

For demonstration of usefulness of elements of the Universal matrix as well as of their combinations, there was chosen in Table 1 from subgroup 1a **MON** as a physicochemical property having the best correlations with previously tested topological indices. As a less good example was taken from the subgroup 1b $\mathbf{Tc^2/Pc}$ representing the van der Waals parameter a_0 with constants omitted. From the group 2, **BP** was chosen. From subgroup 2,3b, **Tc** was selected and from the subgroup 3a $\mathbf{n_D}$. As two of the worst cases were chosen from the group 4 **dc**, and from the group 5 **logVP**.

2. 1. Universal Matrix and its Elements

The Universal matrix[14] **U**(a, b, c) (first described by Ivanciuc[12,13] as the **Dval** matrix) has its elements defined here as follows: $\mathbf{u}_{ij}(a, b, c) = v_i^a * v_j^b * d_{ij}^c$, where v_i and v_j are the vertex degrees of vertices i and j, d_{ij} is the distance between them. Each element of the Universal matrix is a function of exponents on vertex degrees and vertex distances, $\mathbf{u}_{ij}(a, b, c) = f(a, b, c)$. For easier comparison, the Universal matrix relating to 2,3-dimethylhexane and used here is presented in Appendix 3. The relation between matrix elements from the left side of the Universal matrix and from its right side is simple, for example: $u_{52}(a, b, c) = u_{25}(b, a, c)$. The elements of the Universal matrix, which contain the factor 1^a or 1^b resp. 1^c are given in the form demonstrated here for $\mathbf{u}_{32}(a, b, c) \equiv \mathbf{u}_{32}(a, b, 1^c)$ to demonstrate that the factors 1^a or 1^b resp. 1^c do not influence the usefulness of the topological index.

2. 2. Exponent Values

The first step to assess the usefulness of elements of the Universal matrix is the goodness of their correlation with the physicochemical properties of octanes.

To assess where approximately the maxima in absolute values of correlation coefficient *R* are positioned in the space of exponents **a**, **b**, and **c**, a 3D grid of values of exponents was applied and the values of correlation coefficients at those combinations of values were derived. The exponent values –5, –4, –3, –2, –1, –0.5, –0.3, –0.2, –0.1, 0, 0.1, 0.2, 0.3, 0.5, 1, 2, 3, 4, and 5 were chosen as the grid points in all three dimensions of exponents.

The true maximum of the correlation coefficient can then be approached by exponent optimization using also two-digit and, if necessary, three-digit values of exponents besides the grid values. The values of exponents were limited to at most three decimals.

2. 3. Goodness of Topological Indices

To illustrate the potential goodness of topological indices, the correlation coefficient *R* and standard error *S*

Table 1. Tested physicochemical properties grouped by their intercorrelation and by the correlation coefficient (*R*) with the best topological indices of the type TI(a, b, c).[14]

Group No.	$\|R\|$	Physicochemical property, PCP
Group 1		
Subgroup 1a	$\|R\| > 0.99$	BON, RON, MON, BP/Tc, Tc/Pc, ω
Subgroup 1b	$0.99 > \|R\| > 0.95$	Tc^2/Pc, S, R^2, C
Subgroup 1c	$0.95 > \|R\| > 0.90$	αc
Between the group 1 and 2		
Subgroup 1,2a	$0.99 > \|R\| > 0.95$	ΔHv
Subgroup 1,2b	$0.95 > \|R\| > 0.90$	A
Between the group 1 and 3	$0.99 > \|R\| > 0.95$	Pc
Group 2	$0.99 > \|R\| > 0.95$	BP, ΔHf°g
Between the group 2 and 3		
Subgroup 2,3a	$0.95 > \|R\| > 0.90$	ST
Subgroup 2,3b	$\|R\| < 0.90$	B, CED, Sol.par., Tc
Group 3		
Subgroup 3a	$0.99 > \|R\| > 0.95$	n_D, d, Vm
Subgroup 3b	$0.95 > \|R\| > 0.90$	MR
Group 4	$\|R\| < 0.90$	dc, Vc
Group 5	$\|R\| << 0.90$	logVP, Zc

Acronyms for physicochemical properties are given in Appendix 1.

are generally used. Here is proposed also another quantity, the information content (*IC*) about the physicochemical property in question contained in the topological index (index combination) in question.

The information content (*IC*) in the topological index (index combination) in question about the physicochemical property (PCP) of octanes in question is defined as follows:

$$IC = 1 - [\sum(PCP_{exp} - PCP_{calc})^2 / \sum(PCP_{exp} - PCP_{av})^2]^{1/2}$$

where PCP_{exp} means experimental PCP data of octanes, PCP_{calc} those calculated from the topological index (index combination) values, and PCP_{av} is the average of PCP_{exp}.

To the experimental PCP data of octanes, PCP_{exp}, is ascribed the information content $IC = 1$, whereas to the average of PCP_{exp} data of octanes, PCP_{av}, is ascribed the information content $IC = 0$ since PCP_{av} does not contain any information about the contribution of branching in octanes to the value of PCP in question.

The value of *IC* contributed by particular matrix elements in the index combination is given normalized in such a way that the sum of all particular *IC* is equal to the value of *IC* of the topological index combination.

2. 4. Topological Index Combination

To assess the usefulness of the topological index combination (TI_{comb}) composed of two or several elements of the Universal matrix the approach:

$$TI_{comb} = \sum \mathbf{u}_{ij}(a_i, b_j, c_{ij}) \times k_{ij}$$

was used, where

$$\sum abs(k_{ij}) = 1 \text{ and } 0 < abs(k_{ij}) < 1$$

and the exponents a_i, b_j, c_{ij} as well as the smallest k_{ij} have two significant digits. The exponents a_i, b_j, c_{ij} as well as the factors k_{ij} are mutually optimized to reach the highest *R* value possible.

3. Results

As the first step to assess the usefulness of particular elements of the Universal matrix, $\mathbf{u}_{ij}(a, b, c)$, as topological indices is the goodness of their correlation with the physicochemical properties of octanes.

The best correlations between tested physicochemical properties (PCP) and $\mathbf{u}_{ij}(a, b, c)$ elements using grid values of exponents are presented in the form $|\boldsymbol{R}_{max\ grid}|$ (PCP, $\mathbf{u}_{ij}$) as follows: **0.99** > (MON, $\mathbf{u}_{75}$) > (RON, $\mathbf{u}_{75}$) > (Pc, $\mathbf{u}_{53}$) > (BON, $\mathbf{u}_{75}$) > **0.95** > (BP/Tc, $\mathbf{u}_{63}$) > (R^2, $\mathbf{u}_{75}$) > (Tc^2/Pc, $\mathbf{u}_{75}$) > (B, $\mathbf{u}_{63}$) > (n_D, $\mathbf{u}_{63}$) > (ω, $\mathbf{u}_{63}$) > (Tc/Pc, $\mathbf{u}_{65}$) > **0.90** > (Tc, $\mathbf{u}_{63}$) > (ST, $\mathbf{u}_{63}$) > (Vm, $\mathbf{u}_{63}$) > (d, $\mathbf{u}_{63}$) > (C, $\mathbf{u}_{65}$) > (A, $\mathbf{u}_{75}$) > (S, $\mathbf{u}_{32}$) > (BP, $\mathbf{u}_{72}$) > (CED, $\mathbf{u}_{52}$) > (ΔHf°g, $\mathbf{u}_{72}$) > (ΔHv, $\mathbf{u}_{76}$) > (Sol.par., $\mathbf{u}_{52}$) > (MR, $\mathbf{u}_{31}$) > (Vc, $\mathbf{u}_{63}$) > **0.85** > (dc, $\mathbf{u}_{63}$) > (ác, $\mathbf{u}_{65}$) > **0.80** > (logVP, $\mathbf{u}_{72}$) > (Zc, $\mathbf{u}_{84}$) > **0.70**.

Particular elements of the Universal matrix are thus quite good topological indices for some of the tested physicochemical properties. The topological index $\mathbf{u}_{63}(a, b, c)$ is the best one in 10 cases, $\mathbf{u}_{75}(a, b, c)$ in 6 cases, $\mathbf{u}_{65}(a, b, c)$ and $\mathbf{u}_{72}(a, b, c)$ in 3 cases, $\mathbf{u}_{52}(a, b, c)$ in two cases, $\mathbf{u}_{31}(a, b, c)$, $\mathbf{u}_{32}(a, b, c)$, $\mathbf{u}_{53}(a, b, c)$, $\mathbf{u}_{76}(a, b, c)$, and $\mathbf{u}_{84}(a, b, c)$ in one case each out of 29 cases.

The usefulness of particular elements of the Universal matrix increases on going from grid values of exponents to two-digit values of them as well as on using mutual optimization of combination of two or more matrix elements using two-digit values of exponents. This is demonstrated in the case of octanes in Tables 2, 3, and 4 for physicochemical properties MON, Tc^2/Pc, BP, n_D, Tc, dc, and logVP.

In Tables 2 through 4 can be seen that using only 4 out of 56 non-diagonal matrix elements of the Universal matrix, after optimization of their exponent values and their relative contribution, there can be achieved in the best tested case (MON) $R = 0.996$, $S = 3.10$, $IC = 96.1\%$ for the combination $TI_{comb} = -0.8349 \times u_{75}(0.52, 4.3, -3.7) - 0.0268 \times u_{76}(1.18, 4.3, 1.97) - 0.1335 \times u_{42}(0.25, 0.68, 0.147) - 0.0048 \times u_{63}(-1.70, -3.3, 3.6)$, whereas in the worst tested case (dc) $R = 0.944$, $S = 0.0028$, $IC = 67.0\%$ for the combination $TI_{comb} = -0.02874 \times$

Table 2. Best observed correlation coefficients (*R*) between the vertex-degree vertex-distance optimized matrix element (or their combination) and physicochemical property (PCP) of octanes.

No. of matrix elements	PCP						
	MON	**Tc^2/Pc**	**BP**	**n_D**	**Tc**	**dc**	**logVP**
one, grid*	–0.975	0.927	–0.871	–0.922	–0.897	–0.837	0.753
one, two digit*	–0.978	0.930	–0.872	–0.923	–0.901	–0.841	0.754
two	0.993	0.980	0.950	0.977	0.966	0.908	0.887
three	0.996	0.989	0.980	0.981	0.975	0.923	0.902
four	0.996	0.995	0.984	0.989	0.980	0.944	0.954
five	0.9994	0.998	0.990	0.993	0.983	0.964	0.973
six	0.9996	0.999	0.995	0.995	0.986	0.986	0.986

* grid resp. two-digit values of exponents

Table 3. Best observed standard errors of estimation (*S*) between the vertex-degree vertex-distance optimized matrix element (or their combination) and physicochemical property of octanes.

No. of matrix elements	MON	Tc^2/Pc	BP	PCP n_D	Tc	dc	logVP
one, grid	7.56	1623	3.10	0.00209	3.87	0.0047	0.117
one, two digit	7.11	1590	3.09	0.00208	3.81	0.0046	0.117
two	4.01	861	1.97	0.00114	2.27	0.0036	0.082
three	3.12	652	1.26	0.00103	1.94	0.0033	0.077
four	3.10	444	1.12	0.00079	1.75	0.0028	0.053
five	1.19	263	0.90	0.00064	1.59	0.0023	0.041
six	0.91	194	0.60	0.00054	1.45	0.0014	0.030

Table 4. Best observed information content (*IC*, %) contained in a matrix element (or their combination) about the physicochemical property of octanes.

No. of matrix elements	MON	Tc^2/Pc	BP	PCP n_D	Tc	dc	logVP
one, grid	90.5	62.5	50.9	61.3	55.8	45.3	34.2
one, two digit	91.1	63.3	51.0	61.5	56.5	45.9	34.4
two	95.0	80.1	68.8	78.9	74.0	58.1	53.9
three	96.1	85.0	80.1	80.8	77.8	61.5	56.8
four	96.1	89.7	82.3	85.3	80.0	67.0	70.2
five	96.5	93.9	85.8	88.2	81.9	73.2	76.7
six	97.3	95.5	90.5	89.9	83.4	83.1	83.3

$u_{64}(0.121, 0.55, -1.02) - 0.90395 \times u_{43}(-3.2, -3.0, 1^c) - 0.06696 \times u_{62}(0.93, 1.62, -3.2) + 0.00035 \times u_{85}(1^a, -3.7, 2.4)$.

Extrapolation of the best observed regression data to the structure of 2,2,3,3-tetramethylbutane indicates that its missing MON value would be around 98.5, and if 2,2,3,3-tetramethylbutane would exist at normal pressure and 20 °C in the liquid state, it would have n_D of around 1.429 and logVP of around 3.51.

The illustration, which elements of the Universal matrix, values of their exponents, and their relative contribution give rise to the values presented in Table 2 through 4 for BP of octanes is as follows:

One matrix element, grid values of exponents:

$\mathbf{u}_{72}(-0.2, 0.3, -0.1)$, $R = -0.871$, $S = 3.10$, $IC = 50.9\%$

One matrix element, two-digit values of exponents:

$\mathbf{u}_{72}(-0.170, 0.30, -0.104)$, $R = -0.872$, $S = 3.09$, $IC = 51.0\%$

Two matrix elements:

$-0.9979 \times \mathbf{u}_{63}(-3.1, -3.6, -2.0) + 0.0021 \times \mathbf{u}_{74}(0.91, 0.74, 0.85)$, $R = 0.950$, $S = 1.97$, $IC = 68.8\%$

Three matrix elements:

$-0.9952 \times \mathbf{u}_{63}(-3.9, -3.4, -1.74) + 0.0021 \times \mathbf{u}_{74}(1.26. -0.0190, 1.29) -0.0027 \times \mathbf{u}_{42}(-1.23, 4.2, -6.0)$, $R = 0.980$, $S = 1.26$, $IC = 80.1\%$

Four matrix elements:

$-0.995129 \times \mathbf{u}_{63}(-3.1, -3.9, -1.92) + 0.002096 \times \mathbf{u}_{74}(1.09, 0.0040, 1.12) - 0.002696 \times \mathbf{u}_{42}(-0.65, 4.2, -5.9) + 7.9E{-}05 \times \mathbf{u}_{72}(-0.91, 3.2, 0.25)$, $R = 0.984$, $S = 1.12$, $IC = 82.3\%$

Five matrix elements:

$-0.991771 \times \mathbf{u}_{63}(-1.69, -4.2, -1.21) + 0.001858 \times \mathbf{u}_{74}(1.11, 0.32, 1.29) - 0.005132 \times \mathbf{u}_{42}(0.020, 4.2, -5.9) + 0.000102 \times \mathbf{u}_{72}(-\infty, 3.2, -0.055) + 0.001137 \times \mathbf{u}_{32}(-0.59. 2.5, 1^c)$, $R = 0.990$, $S = 0.90$, $IC = 85.8\%$

Six matrix elements:

$-0.95898 \times \mathbf{u}_{63}(-0.98, -4.2, -0.94) + 0.002541 \times \mathbf{u}_{74}(1.21, -0.73, 1.20) - 0.005451 \times \mathbf{u}_{42}(0.21, 4.2, -5.9) + 0.000205 \times \mathbf{u}_{72}(-\infty, 3.2, -0.44) + 0.001426 \times \mathbf{u}_{32}(-1.39, 2.5, 1^c) + 0.031397 \times \mathbf{u}_{53}(-0.26, -0.64, 0.80)$, $R = 0.995$, $S = 0.60$, $IC = 90.5\%$

The sign of the factor k_{ij} defines the sign of the product $k_{ij} * u_{ij}(v_i^a \times v_j^b \times d_{ij}^c) \equiv k_{ij} * u_{ij}(a, b, c)$.

Contribution of particular matrix elements (u_{63}, u_{74}, u_{42}, u_{72}, u_{32}, u_{53}, and u_{43}) to the optimized combined topological index derived from them in the case of BP is presented in Figure 1.

Individual goodness of elements of the Universal matrix in their best combination presented in Figure 1 is presented in Table 5, whereas their goodness observed in

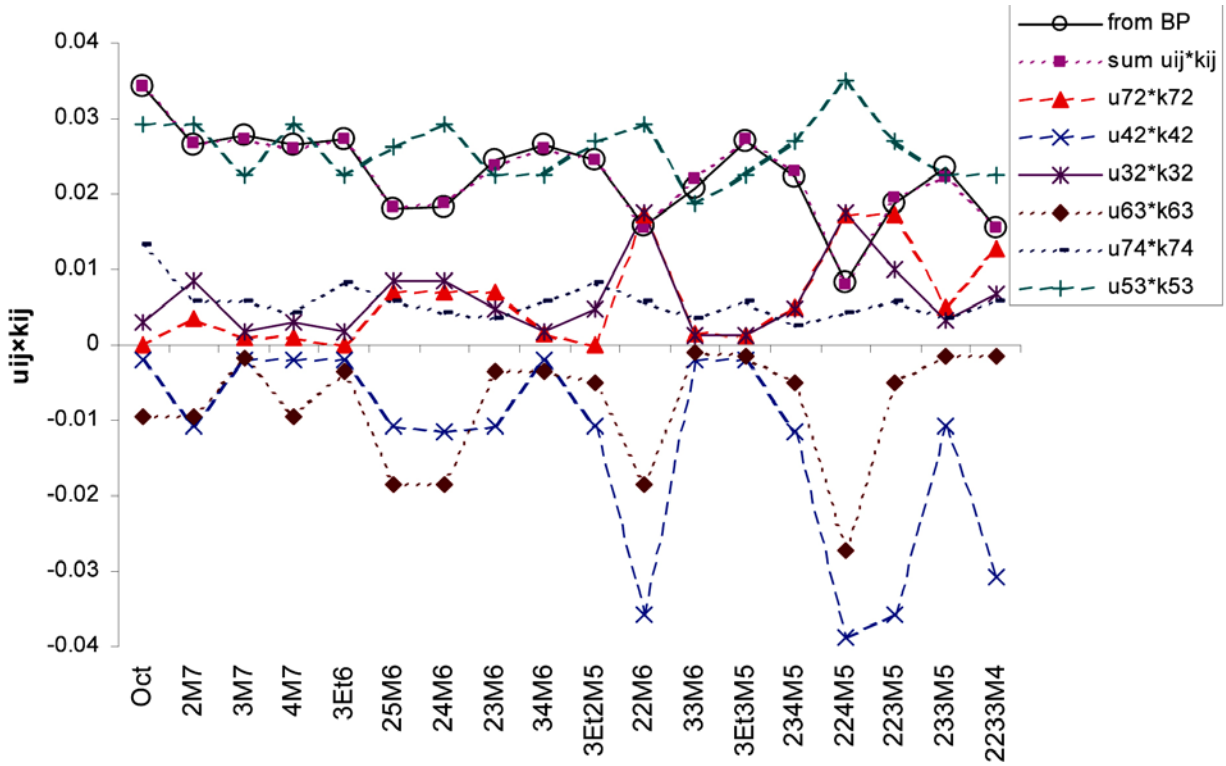

Figure 1. Contribution of particular matrix elements (u_{72}, u_{42}, u_{32}, u_{63}, u_{74}, and u_{53}) to the optimized combined topological index derived from them in the case of BP.

Table 5. Individual goodness of elements of the Universal matrix presented in Figure 1 for the case of BP.

u_{ij}	**a**	**b**	**c**	***R***	***S***	***IC* (%)**
u_{72}	–∞	3.2	–0.44	–0.834	3.48	25.0
u_{42}	0.21	4.2	–5.9	0.819	3.62	23.8
u_{32}	–1.39	2.5	1[c]	–0.775	3.99	20.5
u_{63}	–0.98	–4.2	–0.94	0.583	5.13	10.5
u_{74}	1.21	–0.73	1.20	0.499	5.47	7.4
u_{53}	–0.26	–0.64	0.80	–0.341	5.93	3.3

Their collective goodness is $R = 0.9958$, $S = 0.58$, $IC = 90.8\%$

Table 6. Goodness of elements of the Universal matrix observed in the case of their individual best two-digit exponents to index BP.

u_{ij}	**a**	**b**	**c**	***R***	***S***	***IC* (%)**
u_{72}	–0.170	0.30	–0.104	–0.872	3.09	51.0
u_{42}	0.54	2.9	–5.9	–0.839	3.43	45.6
u_{32}	–0.50	3.1	1[c]	–0.827	3.55	43.8
u_{63}	–∞	–2.1	–1.60	–0.832	3.50	44.6
u_{74}	3.7	–0.9	2.4	0.547	5.28	16.3
u_{53}	–∞	–4.3	0.80	–0.610	5.00	20.7

the case of their individual best two-digit exponents is presented in Table 6.

In Figure 1 can be seen that the individual contributions of particular matrix elements vary widely but their collective result is very good. In Table 5 and 6 can be seen that their goodness is better in the best individual cases than in their contribution to the collective result, but the collective goodness is decidingly better. Such a situation has been observed in all tested cases.

4. Discussion

Several well known indices, e.g. the Wiener index,[15] the Randić index,[17] etc, are in fact derived from the Universal matrix using the grid values of exponents.

It has been observed that the first digit in the exponent, e.g. 2, defines in most tested cases the first three decimals of the correlation coefficient. The second digit, e.g. 2.3, improves in most tested cases the value of the third to fifth decimal, depending on how far from the best value of the exponent is its one-digit grid value approximation. The third digit in the exponents **a**, **b**, and **c**, e.g. 2.31, improves the value of the fifth or higher decimal of the correlation coefficient.[19] In the space of exponents **a**, **b**, and **c**, there are observed several local maxima of correlation coefficient *R*.

For our purpose, in the first step of assessment three decimals in the correlation coefficient are sufficient, therefore in our first step we use one-digit grid value of exponents. For optimization, five decimals in the value of the correlation coefficient are considered sufficient, therefore

only two digits in the value of exponents **a**, **b**, **c** and factors k_{ij} are needed.

Some of the elements of the Universal matrix **U**(a, b, c), i.e. $\mathbf{u}_{ij}$(a, b, c), proved to be useful topological indices of some physicochemical properties of octanes. Already using grid values of exponents, there are $\mathbf{0.99} > |R_{max}| > \mathbf{0.95}$ at (MON, $\mathbf{u}_{75}$) > (RON, $\mathbf{u}_{75}$) > (Pc, $\mathbf{u}_{53}$) > (BON, $\mathbf{u}_{75}$). The improvements by using optimized two digit values of exponents, by combinations of particular matrix elements with mutually optimized two-digit values of exponents in the form $\sum k_{ij} \times u_{ij}(a_i, b_j, c_{ij})$ are demonstrated in Tables 2 through 4.

The improvement of the *R* in two of the worst cases tested, from 0.753 to 0.986 in the case of logVP, and from –0.837 to 0.986 in the case of dc, shows that the approach using elements of the Universal matrix as topological indices and especially the combinations of them by using mutually optimized two-digit values of exponents is a promising one.

The information content (*IC*) in the topological index (or index combination) in question about the physicochemical property (PCP) of octanes in question as defined under the heading Data and definitions proved to be linearly and negatively correlated with one of the important measures of goodness of correlation, *S*. The relation between *IC* and *S* is as follows:

$$IC = 1 - S(PCP_{exp}; PCP_{calc}) / S(PCP_{exp}; PCP_{av})$$

Having this relation, there arises the question, which of them is more useful, *S* or *IC*. Each of them has its own type of usefulness. *IC* is in some way more illustrative than *S* since it directly indicates the information content contained in the tested topological index (index combination). It is an easily comprehensible direct indication of goodness of the topological index (index combination).

S is an inverse measure. Inverse measures are in general less easily to comprehend. And, *S* can not be used for inter-PCP comparisons of goodness of topological indices.

On the other hand, the *IC* is not dependent on numerical values of PCP in question and can be used also for inter-PCP comparisons of goodness of topological indices. In this respect it is more similar to the usefulness of the correlation coefficient *R* and its use together with *R* is suggested. However, *R* is dependent on the number of regression parameters, and *IC* is not. Therefore *IC* is a better criterion for the goodness of model. In order not to mistake *IC* data for *R* data, it is suggested to express *IC* in %. This way we have three different indications of goodness of correlation, $-1 < R < 1$, then $0 < IC < 100$ (%), and *S*. The parallelism of values of *R* and *IC* is illustrated in Table 7. Thus, if $|R| = 0.99$ is considered as the lower limit of sufficient goodness of a topological index,[2] then such a lower limit would be also *IC* = 86%. One can, of course, put also a reverse consideration. For example, if one defines that *IC* = 90% or any other *IC* value is a proper criterion, then $|R| = 0.995$ or another $|R|$ value would result as an additional criterion.

Table 7. Parallel values of *R* and *IC*.

$\|R\|$	*IC* (%)
0.9996	97.3
0.999	95.5
0.995	90.0
0.990	85.9
0.980	80.0
0.970	75.5
0.950	68.7
0.900	56.0
0.866	50.0
0.800	40.0
0.714	30.0
0.600	20.0
0.436	10.0

The criterion, how to choose the upper reasonable limit of our demand for $|R|$ and *IC* is the uncertainty of the experimental data. For example, when the values of a physicochemical property are known to three significant digits as e.g. at dc, and when the uncertainty of the third digit is ±1, then due to uncertainties in the experimental data it is reasonable to demand $|R|$ of about 0.995 and *IC* of about 90%. If the uncertainty of the third digit is ±2, then due to uncertainties in the experimental data there would be reasonable to demand $|R|$ of about 0.98 and *IC* of about 80%.

Using *IC* there arises the question to which quantity to ascribe as not having any information about the differences in the physicochemical property in question among different compounds, for example among isomers of octane. Among octanes, one could suggest its average value as done above, but also the value at *n*-octane or even at *cyclo*octane, which graph contains no vertices of degree one. For practical reasons, since there may not be known the PCP value of a particular octane, it is suggested to ascribe the value of zero information to the average of available data. If we take a different basis for the value of zero information, the *IC* data will be slightly different, but all approaching the value of 1 as the correlation is improving.

As a rule of thumb can be concluded that if the correlation coefficient using optimized values of exponents in an element of the Universal matrix is sufficiently good, e.g. $|R| > 0.99$,[2] then such a topological index can be used as a predictor of values of that physicochemical property. If the correlation coefficient in such a case is not sufficiently good, then the combination of two or more elements of the Universal matrix representing the mutual contribution of graph vertices to the value of the topological index[20] should be tested, mutually optimizing their exponents and their relative contribution.

Let us look at the results from these points of view. If we present in Table 8 the *IC* data of individual matrix

Table 8. Information content about the physicochemical property of octanes (*IC*, %) contained in particular matrix elements in the best combination of six of them.

Matrix element	MON	Tc^2/Pc	PCP BP	n_D	Tc	dc	logVP
best	37.8	37.9	25.0	43.2	46.8	27.5	29.8
second best	26.5	28.2	23.8	25.0	20.1	15.4	28.1
third best	17.0	21.8	20.5	15.3	11.4	13.0	10.9
fourth best	11.3	6.2	10.5	6.0	4.0	12.9	5.7
fifth best	2.5	1.0	7.4	0.2	1.0	12.5	5.1
worst	2.1	0.4	3.3	0.1	0.1	1.8	3.7
$\sum IC$	97.3	95.5	90.5	89.9	83.4	83.1	83.3

elements in the best combinations of six of them, the results of which are presented in Table 4, we can see that most of information is contained in the mutually optimized combination of the best three or four matrix elements. In the worst case (dc) it is contained in five of them out of 56 matrix elements.

Here is the question how to continue the improvement. One possibility is to use the brute force optimization testing all possible combinations of matrix elements. Another possibility is to look in the graph of PCP vs. matrix elements combination, which isomers depart the most from the linear regression line. An example is given in Table 9 and 10 for the case of dc, which is one of the worst examples in Tables 2 through 4.

Table 9. The best combination of four matrix elements in the case of dc.

$\mathbf{u_{ij} \times k_{ij}}$	*R*	*IC* (%)
$u_{85}(1^a, -3.7, 2.4) \times 0.00035$	0.626	20.6
$u_{43}(-3.2, -3, 1^c) \times -0.90395$	0.592	18.2
$u_{62}(0.93, -1.62, -3.2) \times -0.06696$	–0.532	14.4
$u_{64}(0.121, 0.55, -1.02) \times -0.02874$	0.522	13.8
$\sum \mathbf{u}_{ij} \times k_{ij}$	0.944	67.0

Table 10. The largest differences $dc_{exp} - dc_{calc}$ for the case of the best four mutually optimized matrix elements.

Isomer	$\mathbf{dc_{exp} - dc_{calc}}$
33M6	0.0046
223M5	0.0045
234M5	0.0031
4M7	0.0019
22M6	0.0016
Oct	–0.0013
233M5	–0.0032
224M5	–0.0038
23M6	–0.0063

In Table 10 we can see that the largest difference is at the octane isomers branched at the vertices No. 2, 3, and 4. The matrix elements containing information about them are u_{32}, u_{42}, u_{43}, etc. The matrix element u_{43} has been already one of the four best ones. Therefore we start testing first u_{32} and u_{42}, and continue with other ones containing the information about said vertices. The result using the optimized best combination of six matrix elements gives rise to a correlation, Table 11, $R = 0.986$, which is close to $R = 0.99$.

Table 11. The best combination of six matrix elements in the case of dc.

$\mathbf{u_{ij} \times k_{ij}}$	*R*	*IC* (%)
$u_{83}(1^a, -2.7, -0.134) \times -0.3545$	0.758	27.5
$u_{54}(-2.9, -2.6, -1.39) \times 0.1933$	0.593	15.4
$u_{76}(0.65, 2.7, 0.88) \times -0.0052$	0.550	13.0
$u_{65}(-0.075, -3.1, -0.37) \times -0.0654$	–0.547	12.9
$u_{53}(-0.13, -0.38, 2^c) \times 0.3177$	–0.539	12.5
$u_{32}(0.67, -2.4, 1^c) \times 0.0639$	0.210	1.8
$\sum \mathbf{u}_{ij} \times k_{ij}$	0.986	83.1

So, the use of mutually optimized combination of elements of the Universal matrix is promising to reach good correlations.

There is also to distinguish, which matrix element contributes the most to good correlation, and which one contributes the most to the »numerical volume« of the combined index. At MON this is not expressed as evidently as at Tc^2/Pc, BP, nD, Tc, and especially at dc and logVP. In the case of dc, Table 11, there contributes the matrix element $u_{83}(1^a, -2.7, -0.134)$ the most to the observed correlation of the combined index, whereas the matrix element $u_{53}(-0.13, -0.38, 2^c)$ contributes the most to the »numerical volume« of the combined index presented in Table 11 as $\sum \mathbf{u}_{ij} \times k_{ij}$.

There arises also a principal question, whether the best combination of six matrix elements presented above is an overparametrized situation or not. Counting the number of factors k_{ij} and exponents a, b, c in $\sum \mathbf{u}_{ij}(a, b, c) \times k_{ij}$ being 24 in the case of 18 octanes seems to confirm the overparametrization. However, one must compare this situation from the same point of view, i.e. from the point of view of the Universal matrix, also with the situation in well known topological indices, e.g. the Wiener index.

Wiener index is felt as a single number (single parameter) for each isomer. From the point of view of the Universal matrix one observes that in Wiener index, which is one half of the sum of all (in the case of octanes 56) elements of the Universal matrix, there are contained in the case of octanes in derivation of Wiener index 225 parameters giving rise to a single number of the Wiener index value. This is about one order of magnitude more parameters than in the best combination of six matrix elements presented above. Also in the case of the best combination of six out of 56 matrix elements the result is a single number, as in the case of the Wiener index. The situation in the case of the best combination of six matrix elements presented above is thus, compared to the situation at the Wiener index, not overparametrized.

4. 1. Degeneracy of Elements of the Universal Matrix

A standard question about topological indices is the question of their degeneracy. Elements of the Universal matrix of octanes are quite degenerated. All of them are totally degenerated when a = b = c = 0, being $u_{ij}(a, b, c) = 1$, as well as when a = b = c = –∞, being $u_{ij}(a, b, c) = 0$. If a = b ≠ c, there are totally degenerated the following elements of the Universal matrix of octanes: $u_{21}(a, b, c)$, $u_{31}(a, b, c)$, $u_{32}(a, b, c)$, $u_{41}(a, b, c)$, $u_{42}(a, b, c)$, $u_{43}(a, b, c)$, and $u_{53}(a, b, c)$. If a = b = c ≠ 0 and a = b = c ≠ –∞, the elements of the Universal matrix of octanes are not totally degenerated. When a ≠ b ≠ c, then the degeneracy is (written in a shorthand way) u_{21}, $u_{31} > u_{41}$, u_{43}, $u_{87} > u_{42}$, u_{51}, u_{54}, u_{61}, u_{64}, u_{71}, u_{81}, u_{83}, u_{84}, $u_{85} > u_{32}$, u_{53}, u_{65}, u_{73}, u_{74}, $u_{76} > u_{63}$, u_{75}, $u_{86} > u_{52}$, $u_{82} > u_{62}$, u_{72}. Lower degeneracy parallels somewhat the higher usefulness of exponents of $u_{63} > u_{75} > u_{65} = u_{72} > u_{52} > u_{31} = u_{32} = u_{53} = u_{76} = u_{84}$ using grid values as presented above.

Degeneracy decreases, in several cases drastically, when mutually optimized exponents are used in combinations of matrix elements. For example, in one of the worst cases of tested physicochemical properties of octanes, dc, in the best observed combination of two of matrix elements, $u_{43}(–3.3, –3.1, 1^c)$ and $u_{64}(0.147, 0.72, –0.32)$, R = 0.908, S = 0.0036, IC = 58.1%, there are four pairs of isomers having equal value of the combined topological index. In the best observed combination of three matrix elements, $u_{83}(1^a, –0.49, 0.51)$, $u_{76}(–∞, 2.7, 1.17)$, and $u_{65}(0.20, –2.0, –1.20)$, R = 0.923, S = 0.0033, IC = 61.5%, there are two pairs of isomers having equal value of the combined topological index. In the best observed combinations of four matrix elements, in $u_{83}(1^a, –0.94, 0.70)$, $u_{76}(–0.43, 2.8, 1.12)$, $u_{65}(–1.38, –3.1, –0.38)$, and $u_{54}(–∞, –2.5, –2.1)$, R = 0.943, S = 0.0028, IC = 66.8%, there are two pairs of isomers having equal value of the combined topological index as well, whereas in the combination of $u_{43}(–3.2, –3.0, 1^c)$, $u_{64}(0.121, 0.55, –1.02)$, $u_{85}(1^a, –3.7, 2.4)$, and $u_{62}(0.93, –1.62, –3.2)$, R = 0.944, S = 0.0028, IC = 67.0%, there is observed no degeneracy. In the best observed combinations of five matrix elements, however, in $u_{83}(1^a, –1.97, 1.25)$, $u_{76}(0.043, 2.7, 1.01)$, $u_{65}(–0.31, –∞, –0.47)$, $u_{54}(–3.9, –2.6, –1.89)$, and $u_{32}(0.28, –2.4, 1^c)$, R = 0.964, S = 0.0023, IC = 73.2%, as well as in the combination of $u_{43}(–4.9, –3.0, 1^c)$, $u_{64}(0.113, –0.020, –1.14)$, $u_{85}(1^a, –2.4, 2.4)$, $u_{62}(0.23, –1.73, –3.5)$, and $u_{32}(–0.26, 0.124, 1^c)$, R = 0.960, S = 0.0024, IC = 72.1%, there is observed no degeneracy.

These data demonstrate that the degeneracy of topological indices is an important criterion of their goodness but not always decisive.

4. 2. Meaning of Exponent Values in Elements of the Universal Matrix

When exponent values for a, b and c in the equation $\mathbf{u}_{ij}(a, b, c) = v_i^a \times v_j^b \times d_{ij}^c$ are equal to 1 (one) it means that the values of vertex degrees resp. vertex distances contribute proportionally to their values. An exponent value of >1 means that the contribution of higher vertex degrees resp. vertex distances is exaggerated. An exponent value between 1 and 0 means that the contribution of vertex degrees resp. vertex distances is diminished, i.e. the contribution of higher vertex degrees resp. vertex distances is less than their original value would indicate. An exponent value of 0 (zero) means that different values of vertex degrees resp. vertex distances contribute equally. An exponent value of <0 means that the higher values of vertex degrees resp. vertex distances contribute less than the lower ones. An exponent value of –∞ means that vertex degrees resp. vertex distances higher than 1 do not contribute anything.

4. 3. Structural Interpretation of Some of the Physicochemical Properties of Octanes Based on Elements of the Universal Matrix

Next question is, whether the elements of the Universal matrix, which represent particular structural features, in our case of octanes, enable the structural interpretation of their physicochemical properties.

Structural interpretation of Octane Number, which is a PCP governed by a series of chemical reactions, has already been performed, cf. e.g.[21,22] Structural interpretation of the elements of the Universal matrix, which give rise to the best observed correlation with MON data is presented in Appendix 4.

The van der Waals constant a_0, represented here by Tc^2/Pc, is not a chemical reaction governed PCP but it is governed by the volume of the molecules, by intermolecular attractions and collisions. It decreases with increasing branching of octanes quite monotonously, Oct > 2M7 > 3M7 > 4M7 > 3Et6 > 25M6 > 23M6 > 34M6 > 24M6 > 22M6 > 3Et2M5 > 33M6 > 3Et3M5 > 234M5 >

233M5 > 223M5 > 224M5 > 2233M4. Above the general trend are positioned Oct and 233M5, below it 24M6, 224M5, and 2233M4. Structural interpretation of the elements of the Universal matrix, which give rise to the best observed correlation with Tc^2/Pc data is presented in Appendix 5.

The Boiling point (BP) is governed by the intermolecular attractions and collisions as well. It decreases with increasing branching that gives at octanes the sequence of BP: Oct > 3M7 > 3Et6 > 3Et3M5 > 34M6 > 4M7 > 2M7 > 3Et2M5 > 23M6 > 233M5 > 234M5 > 33M6 > 223M5 > 24M6 > 25M6 > 22M6 > 2233M4 > 224M5. It is presented in Figure 1. The above sequence of BP of octanes indicates a complex dependence of BP on branching. Obviously it depends on the number of branches, e.g. Oct > 3M7 > 34M6 > 234M5 > 2233M4. The sequence of number of branches is, however, modified by the position of branches, e.g. at octanes having one branch: 3M7 > 3Et6 > 4M7 > 2M7, at octanes having two branches: 3Et3M5 > 34M6 > 3Et2M5 > 23M6 > 33M6 > 24M6 > 25M6 > 22M6, at octanes having three branches: 233M5 > 234M5 > 223M5 > 224M5. These partial sequences indicate that a branch in position No. 3 gives rise to higher BP than those in positions No. 4 or No. 2; more centrally positioned branches give rise to higher BP than more peripheral positioned ones; more symmetrical branching gives rise to higher BP than the less symmetrical one. Structural interpretation of the elements of the Universal matrix, which give rise to the best observed correlation with BP data is presented in Appendix 6.

The Refractive index n_D is a volumetric PCP. The sequence of values of n_D is as follows: 3Et3M5 > 233M5 > 234M5 > 34M6 > 3Et2M5 > 223M5 > 3Et6 > 23M6 > 3M7 > 33M6 > 4M7 > Oct > 2M7 > 22M6 > 24M6 > 25M6 > 224M5. From this sequence follows that a higher number of branches on vertex No. 3 in the structure of octanes contributes to the value of n_D more than on vertices in other positions, especially if vertex No. 3 is in a more central position. The vertices bearing most of branching, i.e. vertices No. 2 and 3, are involved in the contribution to *IC*: vertex No. 2 together with vertex No. 5 to 43.2% , vertex No. 3 together with vertices No. 6 and 8 to 40.3%. Structural interpretation of the elements of the Universal matrix, which give rise to the best observed correlation with n_D data is presented in Appendix 7.

The sequence of values of Critical temperature, Tc, is 3Et3M5 > 233M5 > 34M6 > Oct > 2233M4 > 3Et2M5 > 234M5 > 3Et6 > 3M7 > 223M5 > 23M6 > 33M6 > 4M7 > 2M7 > 24M6 > 25M6 > 22M6 > 224M5. It is governed by similar rules as BP. Structural interpretation of the elements of the Universal matrix, which give rise to the best observed correlation with Tc data is presented in Appendix 8.

Several pairs of Critical density (dc) data are equal or apparently equal in value. The sequence of values of dc is 223M5 > 3Et2M5 ~ 33M6 > 3Et6 ~ 3Et3M5 ~ 233M5 > 234M5 ~ 2233M4 > 3M7 > 34M6 > 23M6 ~ 224M5 > 24M6 > 4M7 > 22M6 > 25M6 > 2M7 > Oct. It presents the contribution to dc of the branch Ethyl > Methyl; and at the methyl branches on vertices No.:

– one branch: 3 > 4 > 2 > none;
– two branches: 3 > 4 > 2 > 5;
– three branches: 3 > 4.

Thus, the sequence of structures having two branches is the most illustrative for dc. Structural interpretation of the elements of the Universal matrix, which give rise to the best observed correlation with dc data is presented in Appendix 9.

The sequence of the logVP values 24M6 > 224M5 > 33M6 > 223M5 > 25M6 ~ 22M6 > 3Et2M5 > 234M5 ~ 233M5 > 23M6 > 3M7 ~ 3Et3M5 > 34M6 > 3Et6 > 2M7 ~ 4M7 > Oct indicates some apparently conflicting conclusions. One of them is higher logVP at peripheral substitution than at central one at octanes having two or three branches. There are also exceptions, where the branch on the vertex No. 3 contributes to higher value of logVP at 3M7 vs. 2M7 and 4M7; at 33M6 vs. 22M6; as well as at 24M6 vs. 25M6, 23M6 and 34M6. Structural interpretation of the elements of the Universal matrix, which give rise to the best observed correlation with loVP data is presented in Appendix 10.

5. Conclusions

Particular elements of the Universal matrix and especially the mutually optimized combinations of few (four to six out of 56) of them can be used as good topological indices, correlating to tested physicochemical properties to $R > 0.985$ even in the worst tested cases.

Besides *R* and *S*, an additional quantity useful to illustrate the potential goodness of topological indices is proposed, the information content (*IC*). *IC* is linearly and negatively correlated to *S*. It is an easily comprehensible direct indication of goodness of the topological indices (index combination) and is not dependent on numerical values of PCP in question, so it can be used also for inter-PCP comparisons of goodness of topological indices.

Structural interpretations of MON, Tc^2/Pc, BP, n_D, Tc, dc, and logVP are presented, as well as interpretations of what contribute to it particular matrix elements, which are members of the best combined topological indices that are mutually optimized combinations of six matrix elements.

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Povzetek

Kot topološki indeksi za fizikokemijske lastnosti oktanov so uporabni tudi elementi Univerzalne matrike in kombinacije po nekaj od njih. Medtem ko nekateri posamezni elementi Univerzalne matrike dajo $0.70 < |R| < 0.99$, pa medsebojno optimirane kombinacije po 4 do 6 od 56 elementov Univerzalne matrike oktanov dajo $R > 0.99$ in v najslabših primerih $R > 0.98$. Uvedeno je tudi novo merilo za oceno, kako dobra je korelacija, to je vsebnost informacije v topološkem indeksu, *IC* (%). Narejena je tudi strukturna interpretacija nekaterih fizikalno-kemijskih lastnosti oktanov ter doprinosa posameznih elementov matrike.

Appendix 1.

Physicochemical properties of octanes.

MW: 114.232

To notate the isomers of octanes the IUPAC Nomenclature was applied. The structures of alkanes are presented in shorthand, e.g. Oct is *n*-octane, 223M5 is 2,2,3-trimethylpentane, 3Et2M5 is 3-ethyl-2-methylpentane, etc.

PCP \ Octane	Oct	2M7	3M7	4M7	3Et6	25M6	24M6	23M6	34M6	3Et2M5	22M6	33M6	3Et3M5	234M5	224M5	223M5	233M5	2233M4	Octane \ PCP
ST	21.76	20.6	21.17	21.17	21.51	19.73	20.05	20.99	21.64	21.52	19.6	20.63	21.99	21.14	18.77	20.67	21.56		ST
BON	-19	13	30	31	49	56	65	71	67	76	67	73	77	97	100	105	100		BON
RON	-19	21.7	26.8	26.7	33.5	55.5	65.2	71.3	76.3	87.3	72.5	75.5	80.8	102.7	100	109.6	106.1		RON
MON	-19	23.8	35	39	52.4	55.7	69.9	78.9	81.7	88.1	77.4	83.4	88.7	95.9	100	99.9	99.4		MON
S	111.67	109.84	111.26	109.23	109.43	105.72	106.98	108.02	106.59	106.06	103.42	104.74	101.48	102.39	104.09	101.31	102.06	93.06	S
R^2	2.0449	1.8913	1.7984	1.7673	1.7673	1.6449	1.6142	1.6464	1.523	1.5525	1.6744	1.7377	1.5214	1.3698	1.401	1.4306	1.4931	1.4612	R^2
MR	39.19	39.23	39.25	39.12	38.96	39.27	38.92	38.98	38.81	38.84	39.25	39.01	38.73	38.87	39.27	38.93	38.76	38.63	MR
n_D	1.3974	1.3949	1.4002	1.3979	1.4018	1.3925	1.3929	1.4011	1.4041	1.404	1.3935	1.4001	1.4078	1.4042	1.3915	1.403	1.4075	1.4695	n_D
BP/Tc	0.7012	0.6984	0.6957	0.6959	0.6927	0.6950	0.6913	0.6900	0.6872	0.6857	0.6911	0.6853	0.6789	0.6827	0.6847	0.6797	0.6764	0.6685	BP/Tc
Tc^2/Pc	129822	126113	124807	124162	122619	121677	119903	120827	119914	119112	119569	119049	118400	117553	115240	116312	116673	112333	Tc^2/Pc
Tc/Pc	228.20	225.32	221.41	221.01	216.83	221.19	216.59	214.42	210.78	210.04	217.44	211.79	205.34	207.51	211.84	206.41	203.40	197.84	Tc/Pc
CED	0.05058	0.04937	0.05005	0.04996	0.05016	0.04735	0.04776	0.04950	0.05011	0.04962	0.04693	0.04823	0.04992	0.04923	0.04488	0.04796	0.04914	0.05418	CED
Sol.par.	0.2249	0.2222	0.2237	0.2235	0.2240	0.2176	0.2185	0.2225	0.2238	0.2228	0.2166	0.2196	0.2234	0.2219	0.2119	0.2190	0.2217	0.2328	Sol.par.
ΔHv	8.225	8.08	8.1	8.1	8.03	7.8	7.79	7.94	7.95	7.88	7.71	7.76	7.84	7.82	7.41	7.65	7.73	7.51	ΔHv
ΔHf°g	49.82	51.5	50.82	50.69	50.38	53.21	52.44	51.13	50.91	50.48	53.71	52.61	51.38	51.97	53.57	52.61	51.73	53.99	ΔHf°g
ω	0.398	0.378	0.37	0.371	0.361	0.356	0.343	0.346	0.338	0.33	0.338	0.32	0.303	0.315	0.303	0.297	0.29	0.251	ω
BP	398.805	390.797	392.075	390.859	391.684	382.253	382.579	388.757	390.875	388.8	379.99	385.119	391.409	386.617	372.388	382.99	387.91	379.62	BP
d	0.7025	0.698	0.7058	0.7046	0.7136	0.6935	0.7004	0.7121	0.72	0.7193	0.6953	0.71	0.7274	0.7191	0.6919	0.7161	0.7262	0.8242	d
Vm	162.61	163.66	161.85	162.12	160.08	164.72	163.1	160.42	158.66	158.81	164.29	160.89	157.04	158.85	165.1	159.52	157.3	138.6	Vm
logVP	3.28	3.31	3.49	3.31	3.32	3.57	3.89	3.54	3.33	3.56	3.57	3.64	3.49	3.55	3.8	3.63	3.55		logVP
Tc	568.76	559.57	563.6	561.67	565.42	549.99	553.45	563.42	568.78	567.02	549.8	561.95	576.51	566.34	543.89	563.43	573.49	567.85	Tc
Pc	24.54	24.52	25.13	25.09	25.74	24.54	25.23	25.94	26.57	26.65	24.76	26.19	27.71	26.94	25.43	26.94	27.83	28.3	Pc
dc	0.232	0.234	0.246	0.24	0.251	0.237	0.242	0.244	0.245	0.258	0.239	0.258	0.251	0.248	0.244	0.262	0.251	0.248	dc
Vc	0.4924	0.4882	0.4644	0.476	0.4551	0.482	0.4721	0.4682	0.4663	0.4428	0.478	0.4428	0.4551	0.4606	0.4682	0.436	0.4551	0.4606	Vc
Zc	0.259	0.261	0.252	0.259	0.252	0.262	0.262	0.263	0.265	0.254	0.264	0.251	0.267	0.267	0.266	0.254	0.269	0.28	Zc
αc	7.76	7.68	7.58	7.58	7.58	7.5	7.47	7.47	7.4	7.47	7.49	7.48	7.32	7.35	7.37	7.25	7.28	7.65	αc
A	6.919	6.917	6.899	6.901	6.891	6.86	6.853	6.87	6.88	6.867	6.837	6.851	6.867	6.854	6.812	6.825	6.844	6.877	A
B	1351.99	1337.47	1331.53	1327.66	1327.88	1287.27	1287.88	1315.5	1330.04	1318.12	1273.59	1307.88	1347	1315.08	1257.84	1294.88	1328.05	1329.93	B
C	209.15	213.69	212.41	212.57	212.6	214.41	214.79	214.16	214.86	215.31	215.07	217.44	219.68	217.53	220.74	218.42	220.38	226.36	C
PCP \ Octane	Oct	2M7	3M7	4M7	3Et6	25M6	24M6	23M6	34M6	3Et2M5	22M6	33M6	3Et3M5	234M5	224M5	223M5	233M5	2233M4	Octane \ PCP

The data for the boiling point (BP), density (d), the critical data Tc, Pc, Vc, Zc, αc, and dc, 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[1] or from Lange's Handbook[2]. 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 (reduced BP), the molar refraction (MR), cohesive energy density (CED) and its square root, the solubility parameter (Sol. par.) were calculated from data presented in the handbooks. The data for Octane Numbers (BON, MON, RON) were taken from: Pogliani,[3] Balaban and Motoc,[4] Gutman et al.,[5] Warnatz et al.,[6] and Morley;[7] those for vapour pressure (logVP) from Goll and Jurs,[8] and those for the entropy (S) and quadratic mean radius (R^2) from Ren.[9] Surface tension (ST) data were taken from Li.[10]

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Appendix 2.

Correlations between physicochemical properties of octanes used in present study.

	BON	RON	MON	Tc^2/Pc	C	S	R^2	ω	αc	Tc/Pc	BP/Tc	A	ΔHv	BP	ΔHf°g	CED	Sol.par.	B	ST	Pc	Tc	d	V_m	n_D	MR	dc	Vc	logVP	Zc
BON	1																												
RON	**0.99**	1																											
MON	**0.98**	**0.98**	1																										
Tc^2/Pc	**-0.99**	**-0.98**	**-0.98**	1																									
C	*0.88*	*0.89*	*0.87*	**-0.91**	1																								
S	*-0.87*	*-0.89*	*-0.85*	*0.89*	*-0.89*	1																							
R^2	**-0.94**	**-0.94**	**-0.92**	**0.93**	*-0.83*	*0.83*	1																						
ω	**-0.95**	**-0.95**	**-0.93**	**0.96**	**-0.96**	**0.93**	*0.88*	1																					
αc	**-0.95**	**-0.95**	**-0.93**	**0.94**	-0.89	**0.90**	**0.94**	**0.95**	1																				
Tc/Pc	**-0.91**	**-0.91**	**-0.91**	*0.89*	*-0.85*	*0.85*	*0.87*	**0.95**	**0.94**	1																			
BP/Tc	**-0.90**	**-0.91**	*-0.89*	*0.90*	**-0.91**	*0.89*	*0.85*	**0.97**	**0.94**	**0.99**	1																		
A	*-0.89*	*-0.87*	*-0.85*	**0.91**	*-0.81*	*0.83*	0.80	*0.85*	*0.81*	0.68	0.72	1																	
ΔHv	*-0.85*	*-0.84*	*-0.81*	*0.89*	*-0.85*	*0.80*	0.78	*0.83*	0.76	0.63	0.69	**0.97**	1																
BP	-0.66	-0.63	-0.62	0.71	-0.61	0.56	0.60	0.55	0.50	0.31	0.36	*0.86*	**0.91**	1															
ΔHf°g	0.55	0.55	0.52	-0.60	0.57	-0.62	-0.47	-0.50	-0.46	-0.24	-0.31	-0.80	*-0.83*	**-0.91**	1														
CED	-0.49	-0.47	-0.45	0.56	-0.52	0.46	0.43	0.43	0.35	0.15	0.22	0.79	*0.86*	**0.97**	**-0.92**	1													
Sol.par.	-0.49	-0.47	-0.45	0.56	-0.52	0.46	0.43	0.43	0.35	0.15	0.22	0.79	*0.86*	**0.97**	**-0.91**	**1.00**	1												
B	-0.53	-0.50	-0.49	0.57	-0.40	0.41	0.46	0.38	0.35	0.15	0.18	0.79	*0.81*	**0.96**	*-0.87*	**0.94**	**0.94**	1											
ST	-0.24	-0.22	-0.20	0.30	-0.24	0.18	0.20	0.13	0.08	-0.16	-0.10	0.57	0.64	0.88	*-0.85*	**0.94**	**0.94**	**0.91**	1										
Pc	0.71	0.72	0.72	-0.67	0.70	-0.69	-0.68	*-0.80*	*-0.80*	**-0.93**	**-0.91**	-0.40	-0.34	0.04	-0.08	0.19	0.19	0.21	0.49	1									
Tc	-0.05	-0.02	-0.02	0.11	0.00	-0.04	0.03	-0.10	-0.13	-0.35	-0.32	0.38	0.46	0.77	-0.71	*0.83*	*0.83*	*0.85*	**0.96**	0.66	1								
d	0.40	0.42	0.43	-0.35	0.35	-0.39	-0.40	-0.49	-0.53	-0.73	-0.67	-0.03	0.06	0.42	-0.44	0.57	0.57	0.54	0.79	**0.91**	*0.89*	1							
V_m	-0.40	-0.41	-0.43	0.34	-0.34	0.38	0.39	0.48	0.52	0.72	0.67	0.02	-0.07	-0.43	0.44	-0.57	-0.57	-0.54	-0.79	**-0.91**	*-0.89*	**-1.00**	1						
n_D	0.33	0.35	0.36	-0.27	0.30	-0.33	-0.33	-0.43	-0.47	-0.67	-0.62	0.04	0.13	0.48	-0.48	0.61	0.62	0.60	*0.82*	*0.87*	**0.91**	**0.98**	**-0.99**	1					
MR	-0.51	-0.53	-0.55	0.48	-0.43	0.47	0.51	0.57	0.61	0.78	0.71	0.18	0.10	-0.23	0.28	-0.39	-0.39	-0.34	-0.62	*-0.89*	-0.72	**-0.91**	**0.91**	*-0.83*	1				
dc	0.68	0.66	0.68	-0.65	0.56	-0.54	-0.55	-0.70	-0.65	-0.78	-0.75	-0.48	-0.40	-0.14	0.04	0.01	0.01	-0.06	0.24	0.76	0.37	0.66	-0.66	0.64	-0.62	1			
Vc	-0.69	-0.67	-0.70	0.66	-0.57	0.55	0.56	0.71	0.66	0.79	0.76	0.49	0.41	0.15	-0.04	0.00	-0.01	0.06	-0.24	-0.77	-0.36	-0.66	0.67	-0.64	0.63	**-1.00**	1		
logVP	0.64	0.63	0.61	-0.68	0.58	-0.52	-0.57	-0.58	-0.53	-0.41	-0.44	*-0.81*	-0.80	-0.80	0.71	-0.76	-0.76	-0.77	-0.64	0.14	-0.51	-0.19	0.19	-0.28	-0.05	0.31	-0.31	1	
Zc	0.31	0.35	0.31	-0.33	0.43	-0.44	-0.45	-0.35	-0.40	-0.30	-0.32	-0.28	-0.33	-0.24	0.29	-0.23	-0.23	-0.12	-0.13	0.24	-0.02	0.08	-0.07	0.02	-0.20	-0.36	0.35	0.14	1
	BON	RON	MON	Tc^2/Pc	C	S	R^2	ω	αc	Tc/Pc	BP/Tc	A	ΔHv	BP	ΔHf°g	CED	Sol.par.	B	ST	Pc	Tc	d	V_m	n_D	MR	dc	Vc	logVP	Zc

Bold: R > 0.95
Bold: 0.95 > R > 0.90
Italics: 0.90 > R > 0.80
1.00: rounded to

Appendix 3.

Universal matrix[14] **U**(a, b, c) (**Dval**[12, 13] matrix) of 2,3-dimethylhexane.

0	$1^a3^b1^c$	$1^a3^b2^c$	$1^a2^b3^c$	$1^a2^b4^c$	$1^a1^b5^c$	$1^a1^b2^c$	$1^a1^b3^c$
$3^a1^b1^c$	0	$3^a3^b1^c$	$3^a2^b2^c$	$3^a2^b3^c$	$3^a1^b4^c$	$3^a1^b1^c$	$3^a1^b2^c$
$3^a1^b2^c$	$3^a3^b1^c$	0	$3^a2^b1^c$	$3^a2^b2^c$	$3^a1^b3^c$	$3^a1^b2^c$	$3^a1^b1^c$
$2^a1^b3^c$	$2^a3^b2^c$	$2^a3^b1^c$	0	$2^a2^b1^c$	$2^a1^b2^c$	$2^a1^b3^c$	$2^a1^b2^c$
$2^a1^b4^c$	$2^a3^b3^c$	$2^a3^b2^c$	$2^a2^b1^c$	0	$2^a1^b1^c$	$2^a1^b4^c$	$2^a1^b3^c$
$1^a1^b5^c$	$1^a3^b4^c$	$1^a3^b3^c$	$1^a2^b2^c$	$1^a2^b1^c$	0	$1^a1^b5^c$	$1^a1^b4^c$
$1^a1^b2^c$	$1^a3^b1^c$	$1^a3^b2^c$	$1^a2^b3^c$	$1^a2^b4^c$	$1^a1^b5^c$	0	$1^a1^b3^c$
$1^a1^b3^c$	$1^a3^b2^c$	$1^a3^b1^c$	$1^a2^b2^c$	$1^a2^b3^c$	$1^a1^b4^c$	$1^a1^b3^c$	0

Elements of the universal matrix defined here as topological indices.

No.	1	2	3	4	5	6	7	8
1	0	u_{12}	u_{13}	u_{14}	u_{15}	u_{16}	u_{17}	u_{18}
2	u_{21}	0	u_{23}	u_{24}	u_{25}	u_{26}	u_{27}	u_{28}
3	u_{31}	u_{32}	0	u_{34}	u_{35}	u_{36}	u_{37}	u_{38}
4	u_{41}	u_{42}	u_{43}	0	u_{45}	u_{46}	u_{47}	u_{48}
5	u_{51}	u_{52}	u_{53}	u_{54}	0	u_{56}	u_{57}	u_{58}
6	u_{61}	u_{62}	u_{63}	u_{64}	u_{65}	0	u_{67}	u_{68}
7	u_{71}	u_{72}	u_{73}	u_{74}	u_{75}	u_{76}	0	u_{78}
8	u_{81}	u_{82}	u_{83}	u_{84}	u_{85}	u_{86}	u_{87}	0

$\mathbf{u}_{21}$, for example, marks the matrix element $\mathbf{u}_{21}$(a, b, c).

Appendix 4.

Structural interpretation of contribution of matrix elements to the best observed combined topological index for Octane Number

The Octane Number of a fuel is a chemical reactions dependent physicochemical property. It depends mainly on the rates of reactions between the fuel and oxygen. Whereas the fastest initial reaction RH + $^{\cdot}$OH → R$^{\cdot}$, and the addition of oxygen onto R$^{\cdot}$ are quite nonselective, the reactions which follow these steps are mainly intramolecular, slower and more selective. The rate of the intramolecular hydrogen abstraction ROO$^{\cdot}$ → $^{\cdot}$ROOH is: from βCH_2 > from βCH_3 > from γCH > from αCH > from αCH_2, from γCH_2 > from αCH_3, from γCH_3 etc. [21,23] There take place also several other reactions determining the Octane Number values of alkanes.[22]

Let us look now at the elements of the Universal matrix, which contribute to the best-observed combined topological index for MON derived from them.

Table A4a shows that in combination with other matrix elements the matrix element u_{75}(1.06, 4.1, –3.9) contributes to the good correlation overall the most, followed by u_{63}, u_{76}, u_{53}, u_{87}, and u_{42}, whereas Table A4b shows that the best correlation to MON of individual matrix elements is at u_{75}(0.87, 2.9, –2.3). The best individual correlation of an element of the Universal matrix (Table A4b) is in all tested cases better than its correlation in the best combination with other matrix elements (Table A4a).

Table A4a. Best correlation to MON of octanes of the combination of six matrix elements and the contributions of individual matrix elements.

$u_{ij} \times k_{ij}$	*R*	*IC* (%)
u_{75}(1.06, 4.1, –3.9) × –0.8198	0.960	37.8
u_{63}(0.62, –0.68, 4.2) × –0.0048	0.868	26.5
u_{76}(1.52, 4.3, 2.0) × –0.0239	0.736	17.0
u_{53}(–0.89, 1.32, 1.66) × –0.0094	–0.619	11.3
u_{87}(1[a], –1.10, 2.2) × –0.0134	0.302	2.5
u_{42}(–5.0, 5.7, –7.7) × –0.1287	–0.283	2.1
$\sum u_{ij} \times k_{ij}$	0.9996	97.3

Table A4b. Best individual correlations of matrix elements presented in Table A4a.

Matrix element	*R*	*IC* (%)
u_{75}(0.87, 2.9, –2.3)	–0.978	79.0
u_{63}(0.27, –0.068, 0.22)	–0.910	58.5
u_{76}(1.04, 5.3, 2.0)	–0.910	58.4
u_{53}(–0.101, 0.079, 2[c])	0.666	25.4
u_{87}(1[a], 4.8, 1.99)	–0.690	27.6
u_{42}(0.110, 0.2, 2[c])	0.508	13.8

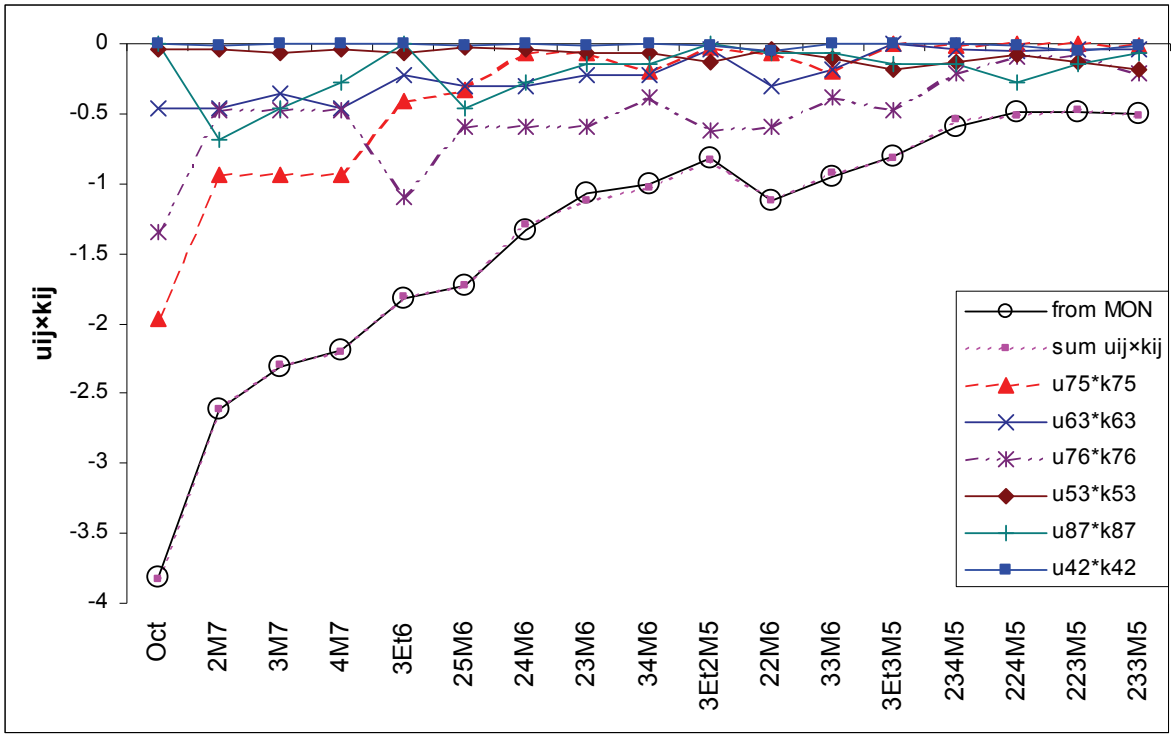

Figure A4. Contribution of particular matrix elements (u_{75}, u_{63}, u_{76}, u_{53}, u_{87}, and u_{42}) to the best observed optimized combined topological index derived from them in the case of MON.

Figure A4 presents the results using mutual optimization of contribution of the matrix elements u_{75}, u_{63}, u_{76}, u_{53}, u_{87}, and u_{42} to the MON values. The bottom curves present the index combination values as well as the experimental MON data recalculated into the index values using the function of the MON - combined index regression line. The calculated data differ from experimental ones by more than one octane number unit at isomers: 2 (units) > 234M5 > 23M6 > 24M6 > 224M5 > 1 > others.

Octane number, including MON, is a reactivity dependent property of alkanes. Looking from the point of view of branching, MON in general increases with branching. Looking from the point of view of reactivity of structural features of octanes, MON decreases with the reactivity of structural features in octanes and the reactivity influencing the MON values is in general higher at lower branching of octanes. Trying to perform the structural interpretation of influence of particular elements of the Universal matrix in Figure A4, the latter influence, i.e. the decrease in MON with the increasing reactivity of structural features is mainly observed.

Let us look first at the sequence of octane isomers according to their decreasing MON values: 224M5 > 223M5 > 233M5 > 234M5 > 3Et3M5 > 3Et2M5 > 33M6 > 34M6 > 23M6 > 22M6 > 24M6 > 25M6 > 3Et6 > 4M7 > 3M7 > 2M7 > Oct. It was already interpreted.[21]

Then, let us look at the contribution of particular matrix elements forming the best combination of six ones. All of them have negative values since all factors k_{ij} are negative. So a higher contribution to the combined topological index means a more negative value of it.

$u_{75}(1.06, 4.1, –3.9)$

The curves due to particular matrix elements in Figure A4 show that the highest contribution to the low values of combined index data of less substituted isomers (Oct, 2M7, 3M7, 4M7) has the matrix element $u_{75}(1.06, 4.1, –3.9)$ contributing to lowering of combined index value (from here on, the sign > means "contributing more than") at Oct (CH_2-β-CH_2) > 2M7, 3M7, 4M7 (CH_3-β-CH_2) >> 3Et6 (CH_2-γ-CH_2) > 25M6 (CH_3-δ-CH) > 34M6, 33M6 (CH_3-γ-CH_2) () >> 22M6, 23M6, 24M6 (CH_3-δ-CH_2) > 3Et2M5 (CH_2-γ-CH_3) > 233M5, 234M5 (CH_3-γ-CH_3) > 223M5, 224M5, 3Et3M5 (CH_3-δ-CH_3).

At *n*-octane the matrix element u_{75} presents the CH_2-β-CH_2 group, which is the most amenable to the fast intramolecular peroxidation reactions.[21,23] Besides it, there are present in Oct additional five CH_2-β-CH_2 groups as well as two CH_2-β-CH_3 groups.

At 2M7, 3M7, 4M7 the matrix element u_{75} represents the fast reacting -$CH_2OO^{\bullet}$ → β-CH_2 groups resp. the less fast reacting -$CHOO^{\bullet}$ → β-CH_3 groups. Besides these, there exist in these isomers also additional CH_2-β-CH_2 groups as well as the CH-β-CH_2 groups.

At the octane isomers 3Et6 > 25M6 > 34M6 > 33M6 the situation is as follows.

At 3E6 the matrix element u_{75} represents the CH_2-γ-CH_2 group and there are present also four additional βCH_2 groups.

At 25M6 the matrix element u_{75} represents the CH_3-δ-CH group, which is less amenable to intramolecular peroxidation reactions. However, there are present also four βCH_2 groups.

At 34M6 and 33M6 the matrix element u_{75} represents the quite reactive CH_3-γ-CH_2 group and there are present also the CH_3-β-CH_2 and CH-β-CH_2 groups.

Except in the case of *n*-octane, the degree of vertex No. 7 is equal to one and the exponent 1.06 reflects this fact.

The exponent of 4.1 to which the degree of vertex No. 5 is raised, indicates that the vertices of degree >1 are in the case of MON much more important than the vertices of degree one. This is in line with the reaction rates of these vertices.

The exponent of –3.9 to which the distance between the vertex No. 7 and No. 5 is raised, is in line with the decresing reaction rate as the distance between the two vertices increases.

The small deviations from the simplicity in these exponents indicate some subtleties in reactivity of this vertex pairs.

u_{63}(–1.70, –3.3, 3.6)

The matrix element u_{63}(–1.70, –3.3, 3.6) contributes to the value of the combined index less than the matrix element u_{75}(1.06, 4.1, –3.9). The contribution of the matrix element u_{63}(–1.70, –3.3, 3.6) is at Oct, 2M7, 4M7 (CH_2-γ-CH_2) > 3M7 (CH_2-γ-CH) > 22M6, 24M6, 25M6 (CH_3-γ-CH_2) > 34M6, 23M6, 3Et6 (CH_3-γ-CH) > 33M6 (CH_3-γ-Cq) > 224M5 (CH_3-β-CH_2) > 223M5, 234M5, 3Et2M5 (CH_3-β-CH) > 233M5 (CH_3-β-Cq) > 3Et3M5 (CH_2-α-Cq).

In this matrix element, vertex No. 6 contributes to Oct, 2M7, 4M7, 3M7, 3Et3M5 less than to other octane isomers. Vertex No. 3 contributes to Oct, 2M7, 4M7, 24M6, 25M6, 22M6, 224M5 > 3M7, 3Et6, 34M6, 23M6, 223M5, 234M5, 3Et2M5 > 33M6, 233M5, 3Et3M5. The distance between vertices No. 6 and No. 3 contributes to Oct, 2M7, 4M7, 3M7, 22M6, 24M6, 25M6, 34M6, 23M6, 3Et6, 33M6 > 224M5, 223M5, 234M5, 3Et2M5, 233M5 > 3Et3M5. The quaternary carbons in 33M6, 233M5 and 3Et3M5 are not involved in the initial peroxidation reactions, so the matrix element u_{63}(–1.70, –3.3, 3.6) contributes besides some information of the consequences of the initial reactions also some information about the consequeces of the reactions after disruptions of the original structure of octane isomers.

u_{76}(1.52, 4.3, 2.0)

The matrix element u_{76}(1.52, 4.3, 2.0) has the highest contribution at octane isomers Oct (CH_2-α-CH_2) > 3Et6 (CH_2-δ-CH_3) > 3Et2M5 (CH_2-γ-CH_3) > 22M6, 23M6, 24M6, 25M6 (CH_3-ε-CH_3) > 2M7, 3M7, 4M7, 3Et3M5 (CH_3-α-CH_2) > 34M6, 33M6 (CH_3-δ-CH_3) > 234M5, 233M5 (CH_3-γ-CH_3) > 224M5, 223M5 (CH_3-β-CH_3).

In this matrix element, vertex No. 7 contributes to Oct more than to other isomers since at Oct it represents the CH_2 group and at all the other ones the CH_3 group.

Vertex No. 6 contributes to Oct, 2M7, 3M7, 4M7, 3Et3M5 much more than to other isomers.

The distance between vertices No. 7 and 6 is also important in the matrix element u_{76}(1.52, 4.3, 2.0). It contributes to 22M6, 23M6, 24M6, 25M6 > 3Et6, 34M6, 33M6 > 3Et2M5,

234M5, 233M5 > 224M5, 223M5 > Oct, 2M7, 3M7, 4M7, and 3Et3M5. At the octane isomers 3Et6, 25M6, 33M6, 24M6, 23M6, 34M6, 22M6, and 3Et2M5, there is not seen any important direct contribution of the matrix element u_{76}(1.52, 4.3, 2.0), but only as a representative of the CH_2-α-CH_2 and the CH_3-α-CH_2 and CH_3-α-CH groups positioned elsewhere in the structure. At 3Et3M5 it represents the CH_3-α-CH_2 groups directly.

u_{53}(–0.89, 1.32, 1.66)

The matrix element u_{53}(–0.89, 1.32, 1.66) contributes little to the combined index of less branched octane isomers. It presents the series 233M5, 3Et3M5 (CH_3-β-Cq) > 3Et2M5, 234M5, 223M5 (CH_3-β-CH) > 33M6 (CH_2-β-Cq) > 224M5 (CH_3-β-CH_2) > 34M6, 23M6, 3Et6, 3M7 (CH_2-β-CH) > 22M6, 24M6, 4M7, 2M7, Oct (CH_2-β-CH_2) > 25M6 (CH-β-CH_2).

It differentiates the higher branched isomers, 233M5 (CH_3-β-Cq) > 223M5, 234M5 (CH_3-β-CH) > 224M5 (CH_3-β-CH_2), the ethyl substituted ones, 3Et3M5 (CH_3-β-Cq) > 3Et2M5 (CH_3-β-CH) > 3Et6 (CH_2-β-CH), the dimethyl substituted ones 33M6 (CH_2-β-Cq) > 34M6, 23M6 (CH_2-β-CH) > 22M6, 24M6 (CH_2-β-CH_2) > 25M6 (CH-β-CH_2) and the monosubstituted ones 3M7 (CH_2-β-CH) > 4M7, 2M7, Oct (CH_2-β-CH_2) adding the missing information of the contribution of quaternary carbons.

Vertex No. 5 contributes to 233M5, 234M5, 223M5, 224M5, 3Et3M5, 3Et2M5 > Oct, 2M7, 3M7, 4M7, 3Et6, 24M6, 23M6, 34M6, 22M6, 33M6 > 25M6.

Vertex No. 3 contributes to 233M5, 3Et3M5, 33M6 > 3Et2M5, 234M5, 223M5, 34M6, 23M6, 3Et6, 3M7 > Oct, 2M7, 4M7, 24M6, 22M6, 224M5, 25M6.

The distance between vertices No. 5 and 3 is constant and does not contribute to any differentiation among the octane isomers.

$u_{87}(1^a, -1.10, 2.2)$

The matrix element $u_{87}(1^a, -1.10, 2.2)$ differentiates between themselves the octane isomers 2M7 (CH_3-ζ-CH_3) > 3M7 (CH_3-ε-CH_3) > 4M7 (CH_3-δ-CH_3) as well as also 25M6 (CH_3-ε-CH_3) > 24M6 (CH_3-δ-CH_3) > 34M6, 23M6 (CH_3-γ-CH_3) > 33M6, 22M6 (CH_3-β-CH_3) and 224M5 (CH_3-δ-CH_3) >223M5, 234M5 (CH_3-γ-CH_3) > 233M5 (CH_3-β-CH_3). It contributes very little to the octane isomers Oct, 3Et6 and 3Et2M6. By far the main contribution of the matrix element $u_{87}(1^a, -1.10, 2.2)$ derives from the differences in distance between the vertices No. 8 and 7.

u_{42}(0.25, 0.68, 0.147)

The matrix element u_{42}(0.25, 0.68, 0.147) contributes to the best combined molecular desriptor derived from six elements of the Universal matrix very little. Itself it represents the β-CH_x groups.

The contribution of the matrix element u_{42}(0.25, 0.68, 0.147) is at 223M5, 22M6 (CH_2-β-Cq) > 233M5, 3Et2M5, 23M6, 25M6, 2M7 (CH_2-β-CH) > 224M5 (CH-β-Cq) > 234M5, 24M6 (CH-β-CH) > 3Et3M5, 33M6, 3Et6, 3M7, Oct (CH_2-β-CH_2) > 34M6, 4M7 (CH-β-CH_2).

In present combination of elements of the Universal matrix as the topological index for MON, the matrix element u_{42}(0.25, 0.68, 0.147) obviously does not indicate the consequences of starting reactions, since the quaternary carbons are not involved in them. It indicates the contributions after the scision of the quaternary structures as well as the influence of structural details of its vertices to their surrounding.

Appendix 5.

Structural interpretation of contribution of matrix elements to the best combined topological index for the van der Waals constant a_0 represented here by Tc^2/Pc.

The best observed topological index for Tc^2/Pc derived from six elements of the Universal matrix is presented in Table A5 and Figure A5.

Table A5. Best observed correlation to Tc^2/Pc of combination of six matrix elements and the contributions of individual matrix elements.

$u_{ij} \times k_{ij}$	*R*	*IC* (%)
$u_{64}(-3.2, -1.19, 1.10) \times -0.04619$	0.747	37.9
$u_{75}(0.35, -0.65, -2.8) \times 0.74585$	0.661	28.2
$u_{54}(-0.48, 0.27, -0.014) \times -0.109594$	0.591	21.8
$u_{72}(-1.19, -0.92, 0.28) \times -0.090734$	–0.326	6.2
$u_{52}(5.1, 2.2, -2.5) \times 6.2E{-}05$	0.133	1.0
$u_{32}(-3.2, 2.4, 1^c) \times -0.00757$	0.085	0.4
$\sum u_{ij} \times k_{ij}$	0.999	95.5

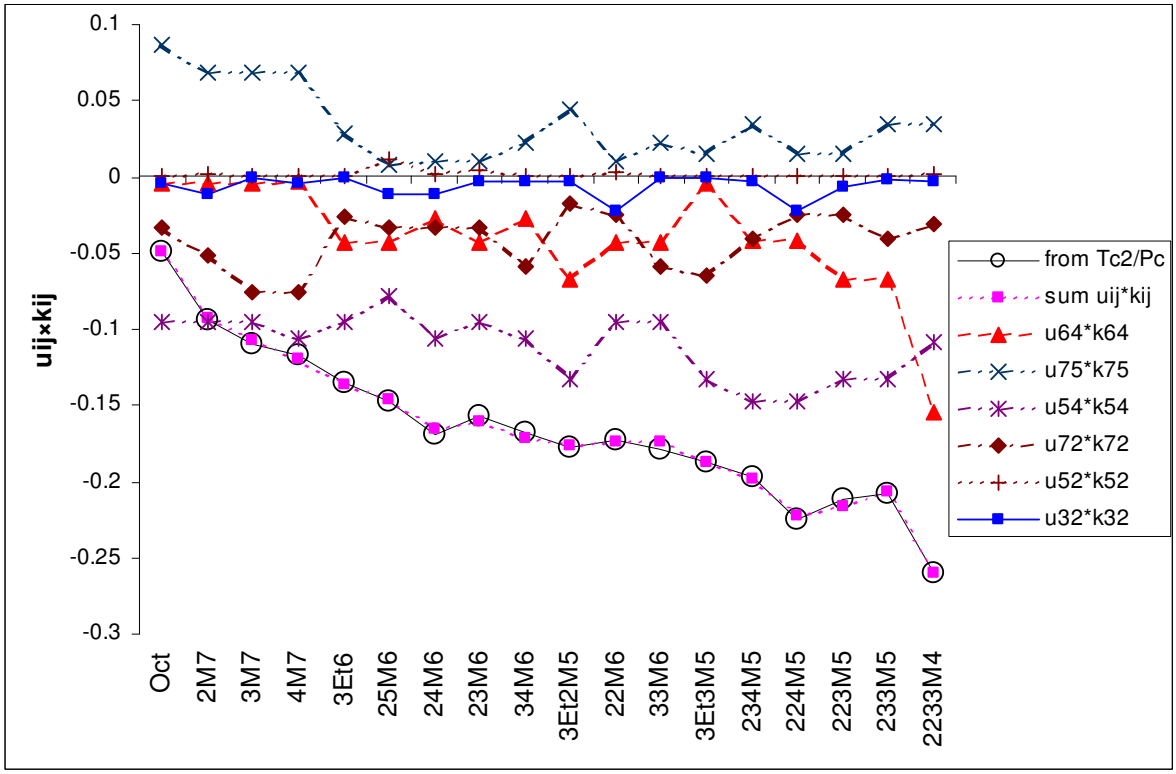

Figure A5. Contribution of particular matrix elements (u_{64}, u_{75}, u_{54}, u_{72}, u_{52}, and u_{32}) to the optimized combined topological index derived from them in the case of Tc^2/Pc.

Individual matrix elements in this combination contribute different contributions to the combined effect. Positive in value are the contributions of the matrix elements $u_{75}(0.35, -0.65, -2.8)*k_{75}$ and u_{52} $u_{52}(5.1, 2.2, -2.5)*k_{52}$, whereas negative in value are the contributions of u_{64} $u_{64}(-3.2, -1.19, 1.10)*k_{64}$, u_{54} $u_{54}(-0.48, 0.27, -0.014)*k_{54}$, u_{72} $u_{72}(-1.19, -0.92, 0.28)*k_{72}$, and u_{32} $u_{32}(-3.2, 2.4, 1^c)*k_{32}$. The sign of the contribution depends on the sign of factor k_{ij}.

$u_{64}(-3.2, -1.19, 1.10)$,

The matrix element $u_{64}(-3.2, -1.19, 1.10)$, which presents the most overall information to the combined index, presents the least to 4M7, little to Oct, 2M7, 3M7, and 3Et3M5, more to 24M7 and 34M6, additionally more to 224M5 and 234M5, followed by 3Et6, 25M6, 23M6, 33M6, 22M6, then by 233M5, 223M5, 3Et2M5 and the most to 2233M4. If we group the octane isomers by the substitution patterns, we observe that the contribution of the matrix element u_{64} to the best combined index for Tc^2/Pc is:

2233M4 (CH_3-γ-CH_3) > 233M5, 223M5, 3Et2M5 (CH_3-γ-CH_2) > 33M6, 22M6, 23M6, 25M6, 3Et6 (CH_3-β-CH_2) > 224M5, 234M5 (CH_3-γ-CH) > 34M6, 24M6 (CH_3-β-CH) > 3Et3M5, 3M7, 2M7, Oct (CH_2-β-CH_2) > 4M7 (CH_2-β-CH)

The exponent of –3.2 on the degree of vertex No. 6 indicates that the importance of its degree is high. However, the degree of vertex No. 6 is equal to 2 only at Oct, 2M7, 3M7, 4M7, and 3Et3M5, to which u_{64} contributes the least. In all other cases it is equal to one, so this exponent draws a distinction between the mentioned octane isomers and the other ones.

The exponent of –1.19 on the degree of vertex No. 4 indicates the importance of its degree. So, it causes 4M7 < Oct, 2M7, 3M7, 3Et6; and also 24M7, 34M6 < 25M6, 23M6, 33M6, 22M6; as well as 224M5, 234M5 < 233M5, 223M5.

The exponent of 1.10 on the distance values indicates that the importance of the distance between the vertex No. 6 and No. 4 is little higher than its original values. It draws a distinction between 2233M4, 233M, 223M5, 3Et2M5, 224M5, 234M5 and other octane isomers.

$u_{75}(0.35, -0.65, -2.8)$

The matrix element $u_{75}(0.35, -0.65, -2.8)$ contributes as in the case of MON the most to isomers Oct, 2M7, 3M7, and 4M7. At Tc^2/Pc they are followed by 3Et2M5 and some highly branched octane isomers, and it contributes little to other octanes having two branches:
Oct (CH_2-β-CH_2) > 2M7, 3M7, 4M7 (CH_3-β-CH_2) > 3Et2M5 (CH_2-γ-CH_3) > 2233M4, 233M5, 234M5 (CH_3-γ-CH_3) > 3Et6 (CH_2-γ-CH_2) > 34M6, 33M6 (CH_3-γ-CH_2) > 223M5, 224M5, 3Et3M5 (CH_3-δ-CH_3) > 22M6, 23M6, 24M6 (CH_3-δ-CH_2) > 25M6 (CH_3-δ-CH).

The exponent on the vertex No. 7 causes some contribution to Oct, 3Et6, 3Et2M6 and nothing to other isomers.

The exponent on the value of vertex No. 5 puts the octane isomers into three different groups: 3Et2M5, 3Et3M5, 223M5, 224M5, 233M5, 234M5, 2233M4 > Oct, 2M7, 3M7, 4M7, 3Et6, 23M6, 24M6, 34M6, 22M6, 33M6 > 25M6.

The exponent on the distance puts the octane isomers into three groups: Oct, 2M7, 3M7, 4M7 > 3Et2M5, 2233M4, 233M5, 234M5, 3Et6, 34M6, 33M6 > 223M5, 224M5, 3Et3M5, 22M6, 23M6, 24M6, 25M6.

$u_{54}(-0.48, 0.27, -0.014)$

The matrix element $u_{54}(-0.48, 0.27, -0.014)$ contributes the most to the "numerical volume" of the combined index, especially at higher branched isomers including 3Et2M5 and 3Et3M5:
234M5, 224M5 (CH_3-α-CH) > 3Et2M5, 3Et3M5, 223M5, 233M5 (CH_3-α-CH_2) > 2233M4 (CH_3-γ-CH_3) > 4M7, 24M6, 34M6 (CH_2-α-CH) > Oct, 2M7, 3M7, 3Et6, 22M6, 33M6, 23M6 (CH_2-α-CH_2) > 25M6 (CH-α-CH_2)

Among the isomers having equal number of branches, it contributes the most at isomers having a branch in position No. 4.

The exponent of –0.48 on the value of vertex No. 5 puts the octane isomers into three different groups: 3Et2M5, 3Et3M5, 223M5, 224M5, 233M5, 234M5, 2233M4 > Oct, 2M7, 3M7, 4M7, 3Et6, 23M6, 24M6, 34M6, 22M6, 33M6 > 25M6.
The exponent of 0.27 on the degree of vertex No. 4 indicates that the importance of its degree is not high but inspite of that it separates the octane isomers into three groups: 4M7, 24M7, 34M6, 224M5, 234M5 > Oct, 2M7, 3M7, 3Et3M5, 3Et6, 25M6, 23M6, 33M6, 22M6, 233M5, 223M5, 3Et2M5 > 2233M4.

The exponent of –0.014, to which the distance between vertices No. 5 and No. 4 is raised, causes a slightly higher contribution of (CH_3-α-CH) and (CH_3-α-CH_2) groups than of (CH_3-γ-CH_3) groups in the structure of octanes.

u_{72}(–1.19, –0.92, 0.28)

The matrix element u_{72}(–1.19, –0.92, 0.28) contributes some fine–tuning to the combination of matrix elements contributing to:
3M7, 4M7 (CH_3-ε-CH_2) > 3Et3M5 (CH_3-γ-CH_2) > 34M6, 33M6 (CH_3-β-CH_2) > 2M7 (CH_3-ε-CH) > 234M5, 233M5 (CH_3-β-CH) > 25M6, 24M6, 23M6 (CH_3-α-CH) > Oct (CH_2-ε-CH_2) > 2233M4 (CH_3-β-Cq) > 3Et6 (CH_2-β-CH_2) > 22M6, 224M5, 223M5 (CH_3-α-Cq) > 3Et2M5 (CH_2-β-CH)

Vertex No. 7 contributes to other octane isomers more than to Oct, 3Et6, and 3Et2M6. Vertex No. 2 contributes to Oct, 3M7, 4M7, 3Et6, 34M6, 33M6, 3Et3M6 > 2M7, 25M6, 24M6, 23M6, 3Et2M5, 234M5, 233M5 > 22M6, 224M6, 223M6, 2233M4.

The distance between vertices No. 7 and No. 2 contributes to Oct, 2M7, 3M7, 4M7 > 3Et3M5 > 3Et6, 3Et2M5, 34M6, 33M6, 234M5, 233M5, 2233M4 > 22M6, 25M6, 24M6, 23M6, 224M5, 223M5.

u_{52}(5.1, 2.2, –2.5)

The matrix element u_{52}(5.1, 2.2, –2.5) contributes some fine–tuning to the combination of matrix elements contributing to 25M6 (CH-γ-CH) > 23M6 (CH_2-γ-CH) > 22M6 (CH_2-γ-Cq) > 24M6, 2M7 (CH_2-γ-CH) > 2233M4 (CH_3-α-Cq) > 33M6, 34M6, 3Et6, 4M7, 3M7, Oct (CH_2-γ-CH_2) > 223M5, 224M5 (CH_2-γ-Cq) > 3Et2M5, 233M5, 234M5 (CH_3-γ-CH) > 3Et3M5 (CH_3-γ-CH_2), which results in 25M6 > 23M6 > 22M6 > 24M6, 2M7 > 2233M4 and very little to other octane isomers.

The exponent on the degree of vertex No. 5 puts the octane isomers in three different groups: Oct, 2M7, 3M7, 4M7, 3Et6, 23M6, 24M6, 34M6, 22M6, 33M6 >> 25M6 >> 3Et2M5, 3Et3M5, 223M5, 224M5, 233M5, 234M5, 2233M4.

The exponent on the degree of vertex No. 2 puts the octane isomers into three different groups: 22M6, 224M6, 223M6, 2233M4 > 2M7, 25M6, 24M6, 23M6, 3Et2M5, 234M5, 233M5 > Oct, 3M7, 4M7, 3Et6, 34M6, 33M6, 3Et3M6.

The exponent on the distance between vertices No. 5 and No. 2 puts the octane isomers into four different groups: 22M6, 25M6, 24M6, 23M6, 224M5, 223M5 > 3Et6, 3Et2M5, 34M6, 33M6, 234M5, 233M5, 2233M4 > 3Et3M5 > 3M7, 4M7, 2M7, Oct

u_{32}(–3.2, 2.4, 1^c)

The matrix element u_{32}(–3.2, 2.4, 1^c) adds some additional fine–tuning to the combination of matrix elements, contributing to 22M6, 224M5 (CH_2-α-Cq) > 2M7, 25M6, 24M6 (CH_2-α-CH) > 223M5 (CH-α-Cq) > Oct, 4M7 (CH_2-α-CH_2) > 23M6, 3Et2M, 234M5 (CH-α-CH) = 34M6 (CH-α-CH_2) > 2233M4 (Cq-α-Cq) > 233M5 (Cq-α-CH) > 3M7, 3Et6 (CH-α-CH_2) > 33M6, 3Et3M5 (Cq-α-CH_2) resulting in 22M6, 224M5 > 2M7, 25M6, 24M6 > 223M5, and much less to the index values for other isomers. Overall, it contributes the most at isomers having a branch in position No. 2 as a consequence of the fact that the vertex degree in

position No. 2 is raised to the exponent 2.4, whereas the vertex degree in position No. 3 is raised to the exponent –3.2. The distance between vertices No. 3 and No. 2 is in all cases equal to one, so it doesn't contribute anything.

Appendix 6.

Structural interpretation of contribution of matrix elements to the best observed combined topological index for BP.

The best observed topological index for BP of octanes composed of a combination of the six elements of the Universal matrix is presented in Table A6 and Figure A6.

Table A6. Best correlation to BP of octanes of the combination of six matrix elements and the contributions of individual matrix elements.

$u_{ij}\times k_{ij}$	*R*	*IC* (%)
$u_{72}(-\infty, 3.2, -0.44) \times 0.000205$	–0.834	25.0
$u_{42}(0.21, 4.2, -5.9) \times -0.005451$	0.819	23.8
$u_{32}(-1.39, 2.5, 1^c) \times 0.001426$	–0.775	20.5
$u_{63}(-0.98, -4.2, -0.94) \times -0.95898$	0.583	10.5
$u_{74}(1.21, -0.73, 1.20) \times 0.002541$	0.499	7.4
$u_{53}(-0.26, -0.64, 0.80) \times 0.031397$	–0.341	3.3
$\sum u_{ij}\times k_{ij}$	0.995	90.5

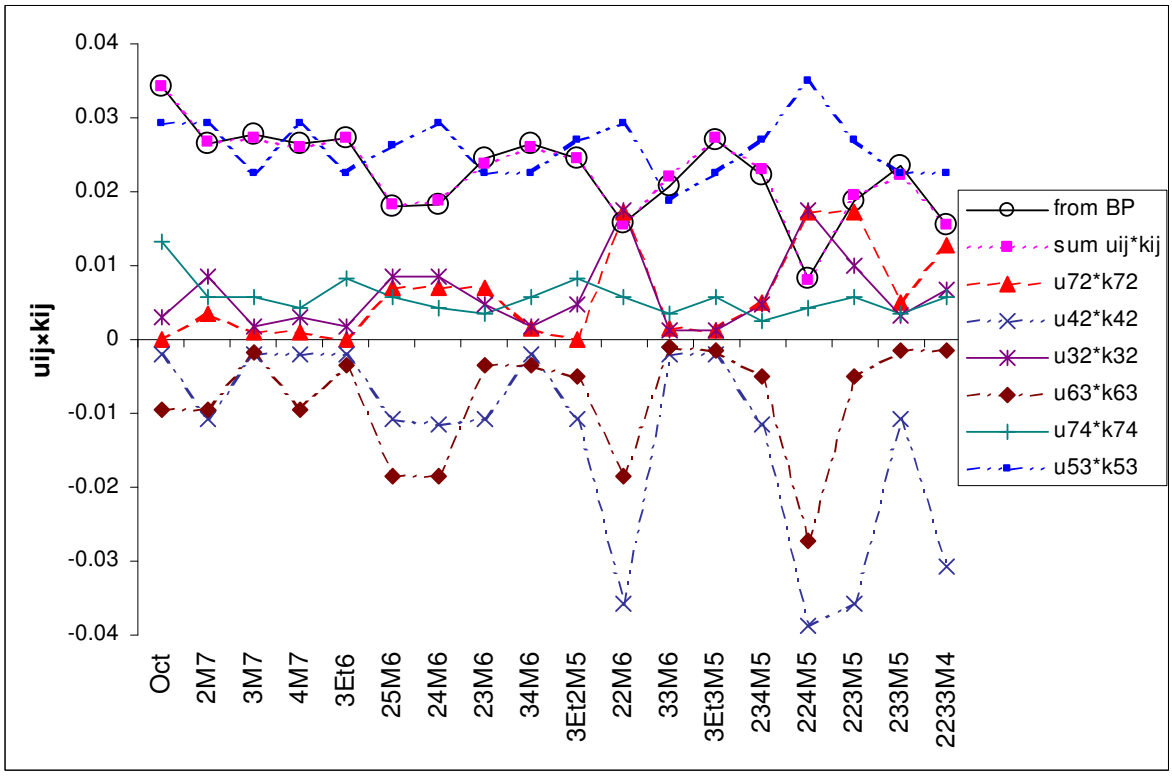

Figure A6. Contribution of particular matrix elements (u_{72}, u_{42}, u_{32}, u_{63}, u_{74}, and u_{53}) to the optimized combined topological index derived from them in the case of BP of octanes.

Positive in value are the contributions of $u_{72}(-\infty, 3.2, -0.44)*k_{72}$, $u_{32}(-1.39, 2.5, 1^c)*k_{32}$ $u_{74}(1.21, -0.73, 1.20)*k_{74}$, and $u_{53}(-0.26, -0.64, 0.80)*k_{53}$, whereas negative in value are the contributions of $u_{42}(0.21, 4.2, -5.9)*k_{42}$ and $u_{63}(-0.98, -4.2, -0.94)*k_{63}$.

According to Table A6 and Figure A6, at BP of octanes are of high importance the vertices No. 2, 3, and 4, i.e. the branching bearing vertices in the structure of octanes. They are involved in the contribution to *IC*: vertex No. 2 together with vertices No. 3, 4, and 7 to 69.3%, vertex No. 3 together with vertices No. 2, 5, and 6 to 34.3%, vertex No. 4 together with vertices No. 2 and 7 to 31.2%, whereas the vertices No. 5, 6, and 7 are involved in only

3.3, 10.5, and 7.4%, respectively. The mutual contribution of only the branches bearing vertices No. 2, 3, and 4 is 44.3%, i.e. almost one half of the total information content contained in this combination of elements of the Universal matrix.

The matrix element $u_{72}(-\infty, 3.2, -0.44)$ contributes to 22M6, 224M5, 223M5 > 2233M4 > 25M6, 24M6, 23M6 > 234M5, 233M5 > 2M7 > 34M6, 33M6 > 3Et3M5 > 3M7, 4M7 > 3Et2M5, 3Et6, Oct = 0. It stresses thus the importance of the substitution pattern 2,2- over 2- and over 3- and 4-.

The matrix element $u_{42}(0.21, 4.2, -5.9)$ subtracts at Oct, 3M7, 3Et6, 33M6, 3Et3M5 < 4M7, 34M6 < 2M7, 25M6, 23M6, 3Et2M5, 233M5 < 234M5, 24M6 < 2233M4 < 22M6, 223M5 < 224M5 i.e. counter the contribution of the matrix element $u_{72}(-\infty, 3.2, -0.44)$ but in different extents.

The matrix element $u_{32}(-1.39, 2.5, 1^c)$ contributes to 22M6, 224M5 > 223M5 > 2M7, 25M6, 24M6 > 2233M4 > 23M6, 3Et2M5, 234M5 > 233M5 > Oct, 4M7 > 3M7, 3Et6, 34M6 > 33M6, 3Et3M5, stressing the importance of the substitution pattern 2,2- over 2- and over 3- and 4- but in a different way than the matrix element $u_{72}(-\infty, 3.2, -0.44)$.

The matrix element $u_{63}(-0.98, -4.2, -0.94)$ subtracts at 33M6 < 3Et3M5 < 233M5, 2233M4 < 3M7 < 3Et6, 23M6, 34M6 < 3Et2M5, 234M5, 223M5 < Oct, 2M7, 4M7 < 25M6, 24M6, 22M6 < 224M5 i.e. counter the contribution of the matrix elements $u_{72}(-\infty, 3.2, -0.44)$ and $u_{32}(-1.39, 2.5, 1^c)$ but in different extents than the matrix element $u_{42}(0.21, 4.2, -5.9)$.

The matrix element $u_{74}(1.21, -0.73, 1.20)$ adds little to Oct > 3Et6, 3Et2M5 > 2233M4 > 2M7, 3M7, 25M6, 34M6, 22M6, 3Et3M5, 223M5 > 4M7, 24M6, 224M5 > 23M6, 33M6, 233M5 > 234M5 contributing some fine-tuning to the combined descriptor.

The matrix element $u_{53}(-0.26, -0.64, 0.80)$ contributes the main part of the "numerical volume" of the combined descriptor, and especially to 224M5 > Oct, 2M7, 4M7, 24M6, 22M6 > 3Et2M5, 234M5, 223M5 > 25M6 > 3M7, 3Et6, 23M6, 34M6 > 3Et3M5, 233M5, 2233M4 > 33M6 stressing thus the importance of vertices No. 2 and 4.

The exponent of $-\infty$ in $u_{72}(-\infty, 3.2, -0.44)$ shows that the vertex No. 7 as an interior vertex in *n*-octane does not contribute anything to the value of the combined index of *n*-octane. The values of exponents to which the degree of vertex No. 2 is raised in matrix elements presented in Table BP (3.2, 4.2, resp. 2.5) show the high contribution of this vertex to the value of the combined index for BP of octanes. The values of exponents to which the degree of vertex No. 3 is raised (–1.39, –0.42, resp.–0.64) resp. those at vertex No. 4 (0.21, 1.21) indicate a lower contribution of these vertices than that of vertex No. 2. The values of exponents to which the values of vertices No. 5, and especially 6 and 7 are raised indicate their importance as terminal vertices.

The distances between pairs of vertices in Table BP have the following influences on the value of the combined molecular descriptor:

The exponent on the distance between vertices No. 7 and No. 2 puts the octane isomers into four different groups: 22M6, 25M6, 24M6, 23M6, 224M5, 223M5 > 3Et6, 3Et2M5, 34M6, 33M6, 234M5, 233M5, 2233M4 > 3Et3M5 > 3M7, 4M7, 2M7, Oct

The distance between vertices No. 3 and No. 2, between vertices No. 4 and No. 2 as well as between vertices No. 5 and No. 3 is constant.

The exponent on the distance between vertices No. 6 and No. 3 puts the octane isomers into four different groups: 3Et3M5 > 224M5, 223M5, 234M5, 3Et2M5, 233M5 > Oct, 2M7, 4M7, 3M7, 22M6, 24M6, 25M6, 34M6, 23M6, 3Et6, 33M6.

The exponent on the distance between vertices No. 7 and No. 4 puts the octane isomers into two different groups: Oct, 2M7, 3M7, 4M7, 25M6, 224M6, 23M6, 22M6, 3Et3M5, 234M5, 224M5, 223M5 > 3Et6, 34M6, 3Et2M6, 33M6, 233M5, 2233M4

Appendix 7.

Structural interpretation of contribution of matrix elements to the best observed combined topological index for n_D.

Matrix elements, which give rise to the best-observed correlation with the refractive index (n_D) of octanes, not considering 2233M4, which is in solid state at room temperature, are presented in Table A7. Their values at particular octane isomers are presented in Figure A7.

In difference to the situation at BP, at n_D all vertex degrees in Table A7 are raised to negative values of exponents meaning that vertices of higher degrees contribute less than those of lower degrees.

Due to the sign of k_{ij}, the contribution of matrix elements $u_{52}(a, b, c)\times k_{52}$, $u_{75}(a, b, c)\times k_{75}$, $u_{74}(a, b, c)\times k_{74}$, and $u_{86}(a, b, c)\times k_{86}$ is positive in value, wheres the contribution of matrix elements $u_{63}(a, b, c)\times k_{63}$ and $u_{83}(a, b, c)\times k_{83}$ is negative in value. The "numerical volume" of the combined index as well as the highest information content about n_D is contributed by the matrix element $u_{52}(a, b, c)\times k_{52}$.

Table A7. Best correlation to n_D of the combination of six matrix elements and the contributions of individual matrix elements.

$u_{ij}\times k_{ij}$	*R*	*IC* (%)
$u_{52}(-0.48, -0.37, -0.53) \times 0.08195$	0.803	43.2
$u_{63}(-0.26, -3.5, -2.2) \times -0.9049$	0.642	25.0
$u_{83}(1^a, -0.25, -\infty) \times -0.00398$	–0.516	15.3
$u_{75}(-\infty, -\infty, 1.42) \times 0.00036$	0.330	6.0
$u_{74}(-0.32, -1.11, 0.73) \times 0.00552$	–0.062	0.2
$u_{86}(1^a, -\infty, -0.85) \times 0.00329$	–0.051	0.1
$\sum u_{ij}\times k_{ij}$	0.995	89.9

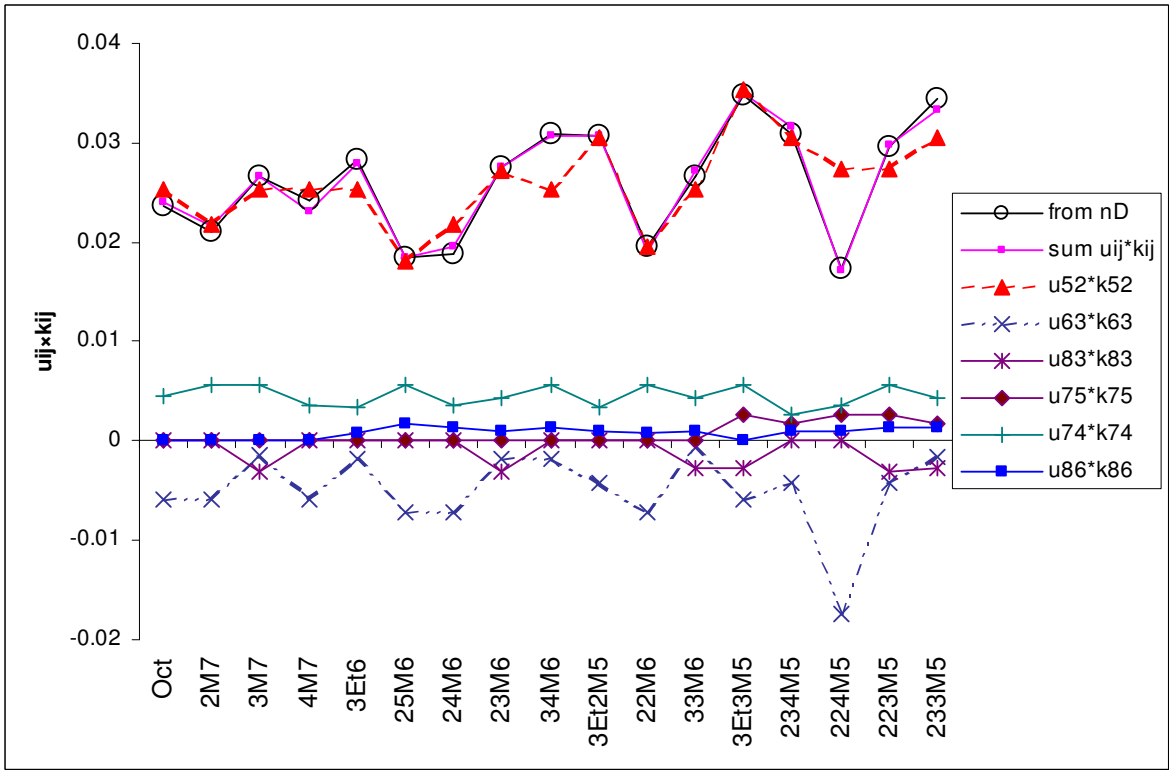

Figure A7. Contribution of particular matrix elements (u_{52}, u_{63}, u_{83}, u_{75}, u_{74}, and u_{86}) to the optimized combined topological index derived from them in the case of n_D.

u_{52}(–0.48, –0.37, –0.53)

The matrix element u_{52}(–0.48, –0.37, –0.53) follows the most closely the trend of n_D and it presents the following sequence of n_D values of octanes: 3Et3M5 > 3Et2M5, 234M5, 233M5 > 224M5, 223M5 > 23M6 > Oct > 3M7, 4M7, 3Et6, 34M6, 33M6 > 2M7, 24M6 > 22M6 > 25M6.

In it, the exponent on the degree of vertex No. 5 puts the octane isomers in three different groups: 3Et2M5, 3Et3M5, 223M5, 224M5, 233M5, 234M5 > Oct, 2M7, 3M7, 4M7, 3Et6, 23M6, 24M6, 34M6, 22M6, 33M6 > 25M6.

The exponent on the degree of vertex No. 2 puts the octane isomers into three different groups: Oct, 3M7, 4M7, 3Et6, 34M6, 33M6, 3Et3M6 > 2M7, 25M6, 24M6, 23M6, 3Et2M5, 234M5, 233M5 > 22M6, 224M6, 223M6.

The exponent on the distance between vertices No. 5 and No. 2 puts the octane isomers into four different groups: 22M6, 25M6, 24M6, 23M6, 224M5, 223M5 > 3Et6, 3Et2M5, 34M6, 33M6, 234M5, 233M5 > 3Et3M5 > 3M7, 4M7, 2M7, Oct.

u_{63}(–0.26, –3.5, –2.2)

The matrix element u_{63}(–0.26, –3.5, –2.2) contributes to the value of the combined index at 33M6 > 3M7 > 233M5 > 3Et6, 23M6, 34M6 > 3Et2M5, 234M5, 223M5 > 3Et3M5 > Oct, 2M7, 4M7 > 25M6, 24M6, 22M6 > 224M5, i.e. also in this case the vertices in position No. 3 contribute more than those in other positions.

This matrix element subtracts from the values contributed by the matrix element u_{52}(–0.48, –0.37, –0.53) at most at 224M5 followed by 25M6, 24M6, 22M6 > Oct, 2M7, 4M7 >3Et3M5 > 3Et2M5, 234M5, 223M5 > 3Et6, 23M6, 34M6 > 233M5 > 3M7 and here more than from 33M6.

In this matrix element, vertex No. 6 contributes to Oct, 2M7, 4M7, 3M7, 3Et3M5 less than to other octane isomers.

Vertex No. 3 contributes to Oct, 2M7, 4M7, 24M6, 25M6, 22M6, 224M5 > 3M7, 3Et6, 34M6, 23M6, 223M5, 234M5, 3Et2M5 > 33M6, 233M5, 3Et3M5.

The distance between vertices No. 6 and No. 3 contributes to 3Et3M5 > 224M5, 223M5, 234M5, 3Et2M5, 233M5 > Oct, 2M7, 4M7, 3M7, 22M6, 24M6, 25M6, 34M6, 23M6, 3Et6, 33M6.

u_{83}(1^a, –0.25, –∞)

The matrix element u_{83}(1^a, –0.25, –∞) subtracts from 3M7, 23M6, 223M5 more than from 33M6, 233M5, and 3Et3M5. From the values at other isomers it does not subtract anything.

Vertex No. 8 does not contribute any information since its degree is equal to one in all tested cases.

Vertex No. 3 contributes to Oct, 2M7, 4M7, 24M6, 25M6, 22M6, 224M5 > 3M7, 3Et6, 34M6, 23M6, 223M5, 234M5, 3Et2M5 > 33M6, 233M5, 3Et3M5.

Due to the exponent of –∞, the distance between vertices No. 8 and No. 3 contributes to 3M7, 23M6, 33M6, 3Et3M5, 223M5, and 233M5 only.

u_{75}(–∞, –∞, 1.42)

The matrix element u_{75}(–∞, –∞, 1.42) adds to 3Et3M5, 224M5, and 223M5 more than to 234M5 and 233M5. To other isomers it does not contribute anything.

Due to the exponent of –∞, vertex No. 7 eliminates the contribution of Oct, 3Et6, and 3Et2M5 to the matrix element $u_{75}(-\infty, -\infty, 1.42)$. Vertex No. 5 eliminates the contribution of Oct, 2M7, 3M7, 4M7, 3Et6, 24M6, 34M6, 23M6, 22M6, 33M6, and 25M6.

The distance between vertices No. 7 and No 5 contributes to Oct, 2M7, 4M7, 3M7 > 3Et6, 34M6, 3Et2M5, 33M6, 234M5, 233M5 > 25M6, 24M6, 23M6, 22M6, 3Et3M5, 224M5, 223M5.

$u_{74}(-0.32, -1.11, 0.73)$

The matrix element $u_{74}(-0.32, -1.11, 0.73)$ adds to 2M7, 3M7, 25M6, 34M6, 22M6, 3Et3M5, 223M5 > Oct > 23M6, 33M6, 233M5 > 4M7, 24M6, 224M5 > 3Et6, 3Et2M5 > 234M5.

In this matrix element, vertex No. 7 contributes to Oct, 2M7, 3M7, 4M7, 3Et3M5 less than to other octane isomers.

Vertex No. 4 contributes to Oct, 2M7, 3M7, 3Et6, 25M6, 23M6, 3Et2M5, 22M6, 33M6, 3Et3M5, 223M5, 233M5 > 4M7, 24M6, 34M6, 234M5, 224M5.

The distance between vertices No. 7 and No. 4 contributes to Oct, 2M7, 3M7, 4M7, 25M6, 24M6, 23M6, 22M6, 3Et3M5, 234M5, 224M5, 223M5 > 3Et6, 34M6, 3Et2M5, 33M6, 233M5.

$u_{86}(1^a, -\infty, -0.85)$

The matrix element $u_{86}(1^a, -\infty, -0.85)$ adds to 25M6 > 24M6>34M6>223M5>233M5 > 23M6>3Et2M5>33M6>234M5>224M5 > 3Et6, 22M6 whereas to Oct, 3Et3M5, 4M7, 3M7, 2M7 it does not contribute anything.

Vertex No. 8 does not contribute any information since its degree is equal to one in all tested cases.

Due to the exponent of –∞, vertex No. 6 contributes nothing at Oct, 2M7, 3M7, 4M7, and 3Et3M5, whereas it contributes an equal value of 1 at other isomers.

The distance between vertices No. 8 and No. 6 contributes to Oct, 25M6, 3Et3M5 > 4M7, 24M6, 34M6, 223M5, 233M5 > 3M7, 23M6, 3Et2M5, 33M6, 234M5, 224M5 > 2M7, 3Et6, 22M6.

Appendix 8.

Structural interpretation of contribution of matrix elements to the best observed combined topological index for Tc.

The best observed topological index for Tc of octanes composed of a combination of six elements of the Universal matrix is presented in Table A8 and Figure A8. Due to the sign of k_{ij}, the contribution of matrix elements $u_{52}(a, b, c)\times k_{52}$, $u_{86}(a, b, c)\times k_{86}$, $u_{62}(a, b, c)\times k_{62}$, and $u_{74}(a, b, c)\times k_{74}$ is positive in value, wheres the contribution of matrix elements $u_{63}(a, b, c)\times k_{63}$ and $u_{54}(a, b, c)\times k_{54}$ is negative in value.

Table A8. Best correlation to Tc of the combination of six matrix elements and the contributions of individual matrix elements.

$u_{ij}\times k_{ij}$	*R*	*IC* (%)
$u_{63}(-2.2, -4.3, -2.4) \times -0.96569987$	0.799	46.8
$u_{52}(-0.30, -0.23, -0.35) \times 0.01459994$	0.560	20.1
$u_{86}(1^{a}, 5.3, -5.5) \times 0.00309998$	0.430	11.4
$u_{62}(-1.49, -1.19, -0.63) \times 0.01149923$	0.259	4.0
$u_{74}(-0.092, -2.4, 7.4) \times 9.8E{-}07$	–0.131	1.0
$u_{54}(1.56, -4.5, -0.38) \times -0.0051$	–0.045	0.1
$\sum u_{ij}\times k_{ij}$	0.986	83.4

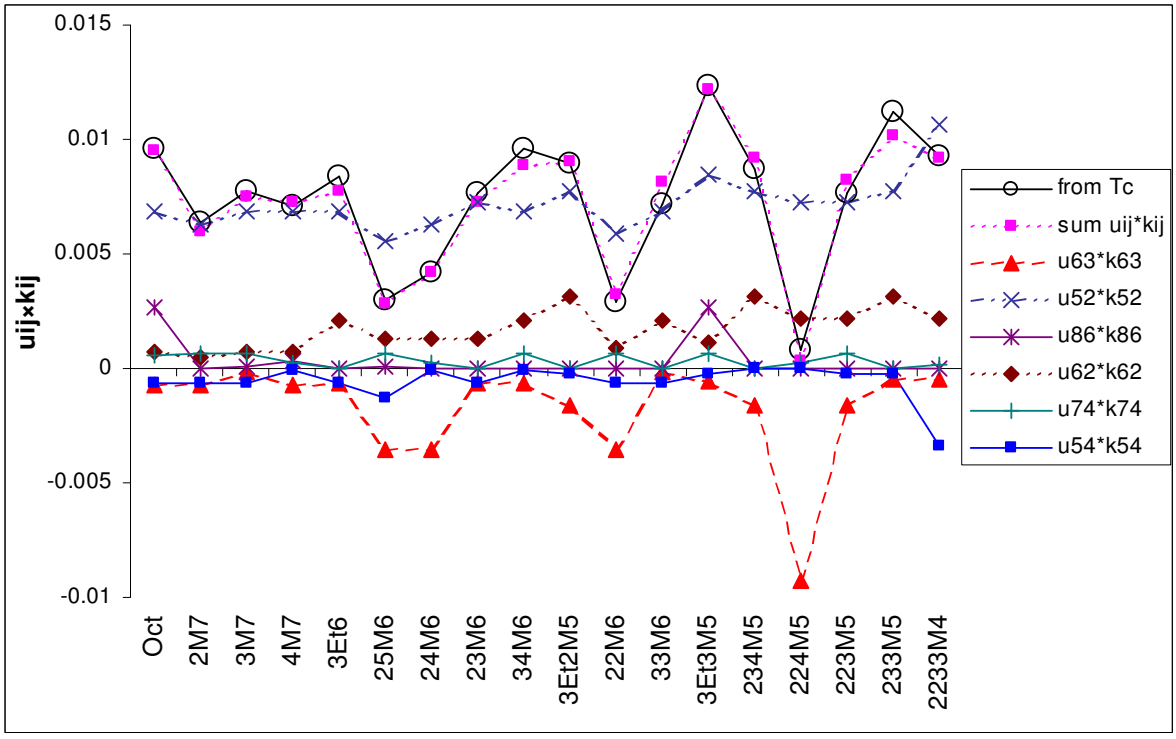

Figure A8. Contribution of particular matrix elements (u_{63}, u_{52}, u_{86}, u_{62}, u_{74}, and u_{54}) to the optimized combined topological index derived from them in the case of Tc.

The contribution of particular elements of the Universal matrix presented in Table Tc and Figure Tc is as follows.

$u_{52}(-0.30, -0.23, -0.35)$

The matrix element $u_{52}(-0.30, -0.23, -0.35)$ contributes the most to the "numerical volume" of the combined index and also the most of information about the contribution of branching to Tc of octanes. It adds the most at 2233M4 > 3Et3M5 > 3Et2M5, 234M5, 233M5 > 23M6 > 224M5, 223M5 > Oct, 3M7, 4M7, 3Et6, 34M6, 33M6 > 2M7, 24M6 > 22M6 > 25M6.

The exponent on the degree of vertex No. 5 puts the octane isomers into three different groups: 3Et2M5, 3Et3M5, 223M5, 224M5, 233M5, 234M5, 2233M4 > Oct, 2M7, 3M7, 4M7, 3Et6, 23M6, 24M6, 34M6, 22M6, 33M6 > 25M6.

The exponent on the degree of vertex No. 2 puts the octane isomers into other three groups: Oct, 3M7, 4M7, 3Et6, 34M6, 33M6, 3Et3M6 > 2M7, 25M6, 24M6, 23M6, 3Et2M5, 234M5, 233M5 > 22M6, 224M6, 223M6, 2233M4.

The exponent on the distance between vertices No. 5 and No. 2 puts the octane isomers into four different groups: 22M6, 25M6, 24M6, 23M6, 224M5, 223M5 > 3Et6, 3Et2M5, 34M6, 33M6, 234M5, 233M5, 2233M4 > 3Et3M5 > 3M7, 4M7, 2M7, Oct.

$u_{63}(-2.2, -4.3, -2.4)$

The matrix element $u_{63}(-2.2, -4.3, -2.4)$ subtracts due to k_{63} the most at 224M5 > 25M6, 24M6, 22M6 > 3Et2M5, 234M5, 223M5 > Oct, 2M7, 4M7 > 3Et6, 23M6, 34M6 > 3Et3M5 > 233M5 > 2233M4 > 33M6 > 3M7 where it subtractes at least.

Vertex No. 6 contributes to subtraction at Oct, 2M7, 4M7, 3M7, 3Et3M5 less than at other isomers.

Vertex No. 3 contributes to subtraction at Oct, 2M7, 4M7, 24M6, 25M6, 22M6, 224M5 > 3M7, 3Et6, 34M6, 23M6, 223M5, 234M5, 3Et2M5 > 33M6, 233M5, 3Et3M5.

The distance between vertices No. 6 and No. 3 contributes to subtraction at 3Et3M5 > 224M5, 223M5, 234M5, 3Et2M5, 233M5 > Oct, 2M7, 4M7, 3M7, 22M6, 24M6, 25M6, 34M6, 23M6, 3Et6, 33M6.

$u_{86}(1^a, 5.3, -5.5)$

The matrix element $u_{86}(1^a, 5.3, -5.5)$ adds the most at Oct, 3Et3M5 >> 4M7 >> 25M6 > 3M7 > 2M7 > 24M6, 34M6, 223M5, 233M5, 2233M4 > 23M6, 3Et2M5, 33M6, 234M5, 224M5 and very little at 3Et6 and 22M6.

Vertex No. 8 does not contribute anything.

Vertex No. 6 contributes at Oct, 2M7, 4M7, 3M7, 3Et3M5 and nothing at other isomers.

The distance between vertices No. 8 and No.6 contributes at Oct, 25M6 > 4M7, 24M6, 34M6, 3Et3M5, 223M5, 233M5, 2233M4 > 3M7, 23M6, 3Et2M5, 33M6, 234M5, 224M5 > 2M7, 3Et6, 22M6.

$u_{62}(-1.49, -1.19, -0.63)$

The matrix element $u_{62}(-1.49, -1.19, -0.63)$ adds the most at 3Et2M5, 234M5, 233M5 > 224M5, 223M5, 2233M4 > 3Et6, 34M6, 33M6 > 25M6, 24M6, 23M6 > 3Et3M5 > 22M6 > Oct, 3M7, 4M7 > 2M7.

Vertex No. 6 contributes at other isomers more than at Oct, 2M7, 4M7, 3M7, and 3Et3M5.

Vertex No. 2 contributes at Oct, 3M7, 4M7, 3Et6, 34M6, 33M6, 3Et3M5 > 2M7, 25M6, 24M6, 23M6, 3Et2M5 234M5, 233M5 > 22M6, 224M5, 223M5, 2233M4.

The distance between vertices No. 6 and No. 2 contributes at 3Et2M5, 234M5, 233M5, 224M5, 223M5, 2233M4 > 3Et3M5 > Oct, 3M7, 4M7, 2M7, 3Et6, 25M6, 24M6, 23M6, 34M6, 22M6, 33M6.

$u_{74}(-0.092, -2.4, 7.4)$

The matrix element $u_{74}(-0.092, -2.4, 7.4)$ adds very little at 2M7, 3M7, 25M6, 34M6, 22M6, 3Et3M5, 223M5 > Oct > 4M7, 24M6, 224M5 > 2233M4 > 23M6, 33M6, 233M5 > 3Et2M5, 3Et6 > 234M5.

Vertex No. 7 contributes to other octane isomers more than to Oct, 3Et6, and 3Et2M6.

Vertex No. 4 contributes to 2233M4 > Oct, 2M7, 3M7, 3Et3M5, 3Et6, 25M6, 23M6, 33M6, 22M6, 233M5, 223M5, 3Et2M5 > 4M7, 24M7, 34M6, 224M5, 234M5.

The distance between vertices No. 7 and No. 4 contributes at Oct, 2M7, 3M7, 4M7, 25M6, 24M7, 23M6, 22M6, 3Et3M5, 233M5, 223M5, and 224M5 much more than at 3Et6, 34M6, 3Et2M5, 33M6, 234M5, and 2233M4.

$u_{54}(1.56, -4.5, -0.38)$

Due to the sign of k_{54}, the matrix element $u_{54}(1.56, -4.5, -0.38)$ subtracts the most at 2233M5 > 25M6 > 33M6, Oct, 2M7, 3M7, 3Et6, 23M6, 22M6 > 3Et2M5, 3Et3M5, 223M5, 233M5 > 4M7, 24M6, 34M6 > and the least at 234M5 and 224M5.

The exponent on the degree of vertex No. 5 puts the octane isomers into three groups: 3Et2M5, 3Et3M5, 223M5, 224M5, 233M5, 234M5, 2233M4 > Oct, 2M7, 3M7, 4M7, 3Et6, 23M6, 24M6, 34M6, 22M6, 33M6 > 25M6.

The exponent on the degree of vertex No. 4 puts the octane isomers into other three groups: 2233M4 > Oct, 2M7, 3M7, 3Et3M5, 3Et6, 25M6, 23M6, 33M6, 22M6, 233M5, 223M5, 3Et2M5 > 4M7, 24M7, 34M6, 224M5, 234M5.

The distance between vertices No. 5 and No. 4 contributes at 2233M4 less than at other octane isomers.

Appendix 9.

Structural interpretation of contribution of matrix elements to the best observed combined topological index for critical density (dc) of octanes.

Matrix elements, which give rise to the best-observed correlation with critical density (dc), are presented in Table A9. Their values at particular octane isomers are presented in Figure A9. Due to the sign of k_{ij}, the contribution of matrix elements $u_{54}(a, b, c)\times k_{54}$, $u_{53}(a, b, c)\times k_{53}$, and $u_{32}(a, b, c)\times k_{32}$ is positive in value, wheres the contribution of matrix elements $u_{83}(a, b, c)\times k_{83}$, $u_{76}(a, b, c)\times k_{76}$, and $u_{65}(a, b, c)\times k_{65}$ is negative in value. The "numerical volume" of the combined index is contributed mainly by the matrix element $u_{53}(a, b, c)\times k_{53}$. It contributes less information about dc than four other matrix elements but anyway more than 10% of it. Each of the six matrix elements, which contribute to the best-observed combined index, has a low correlation with dc of octanes; only $u_{83}(1^a, -2.7, -0.134)$ correlates with $0.7 < R < 0.8$.

Table A9. Best correlation to dc of the combination of six matrix elements and the contributions of individual matrix elements.

$u_{ij}\times k_{ij}$	*R*	*IC* (%)
$u_{83}(1^a, -2.7, -0.134) \times -0.3545$	0.758	27.5
$u_{54}(-2.9, -2.6, -1.39) \times 0.1933$	0.593	15.4
$u_{76}(0.65, 2.7, 0.88) \times -0.0052$	0.550	13.0
$u_{65}(-0.075, -3.1, -0.37) \times -0.0654$	–0.547	12.9
$u_{53}(-0.13, -0.38, 2^c) \times 0.3177$	–0.539	12.5
$u_{32}(0.67, -2.4, 1^c) \times 0.0639$	0.210	1.8
$\sum u_{ij}\times k_{ij}$	0.986	83.1

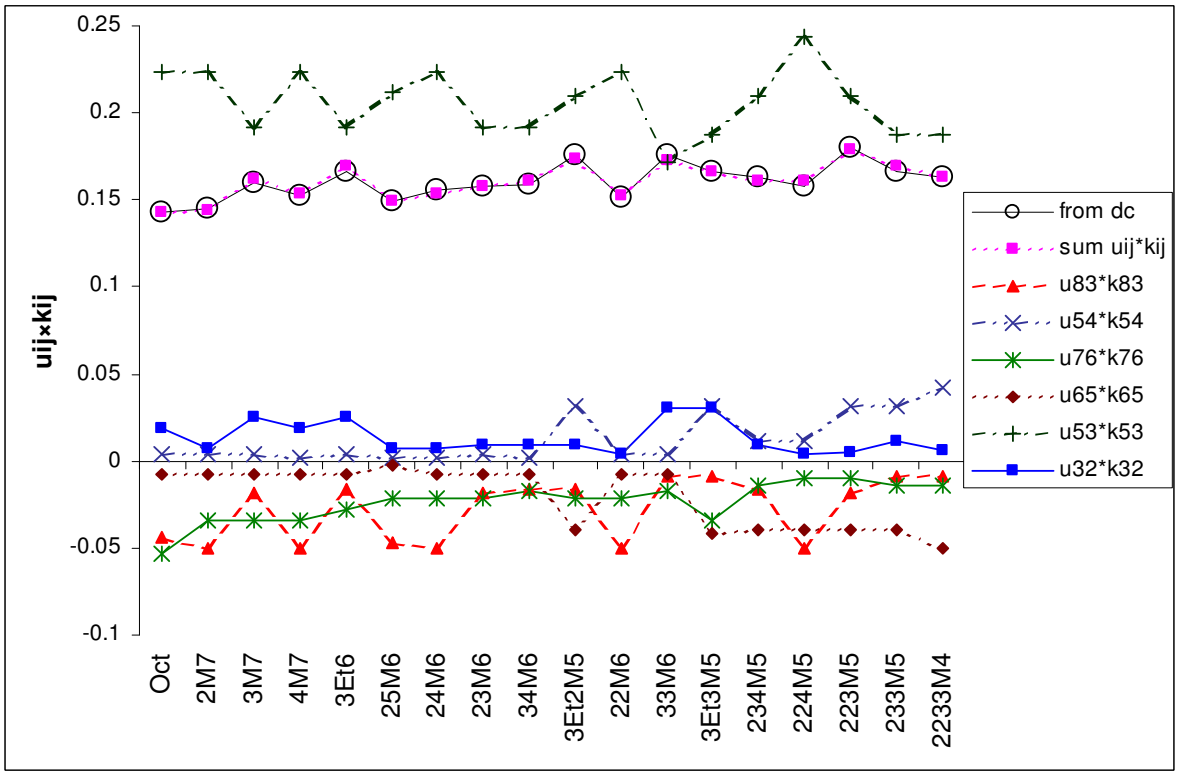

Figure A9. Contribution of particular matrix elements (u_{83}, u_{54}, u_{76}, u_{65}, u_{53}, and u_{32}) to the optimized combined topological index derived from them in the case of dc.

$u_{83}(1^a, -2.7, -0.134)$

The matrix element $u_{83}(1^a, -2.7, -0.134)$ contributes the most at 2M7, 4M7, 24M6, 22M6, 224M5 > 25M6 > Oct > 3M7, 23M6, 223M5 > 3Et6, 34M6, 3Et2M5, 234M5 > 33M6, 3Et3M5, 233M5, 2233M4.

The exponent on the degree of vertex No. 8 has no influence. The exponent on the degree of vertex No. 3 puts the octane isomers into three different groups: Oct, 2M7, 4M7, 24M6, 25M6, 22M6, 224M5 > 3M7, 3Et6, 34M6, 23M6, 223M5, 234M5, 3Et2M5 > 33M6, 233M5, 3Et3M5.

The exponent on the distance between vertices No. 8 and No. 3 puts the octane isomers into four different groups: 3M7, 23M6, 33M6, 3Et3M5, 233M5, 2233M4, 223M5 > 2M7, 4M7, 3Et6, 24M6, 34M6, 3Et2M5, 22M6, 234M5, 224M5 > 25M6 > Oct.

$u_{54}(-2.9, -2.6, -1.39)$

The matrix element $u_{54}(-2.9, -2.6, -1.39)$ contributes the most at 2233M4 > 3Et2M5, 3Et3M5, 223M5, 233M5 > 234M5, 224M5 > Oct > 2M7 > 3M7 > 3Et6 > 22M6 > 33M6 > 23M6 > 4M7, 24M6, 34M6 > 25M6.

The exponent on the degree of vertex No. 5 puts the octane isomers into three different groups: 3Et2M5, 3Et3M5, 223M5, 224M5, 233M5, 234M5, 2233M4 > Oct, 2M7, 3M7, 4M7, 3Et6, 23M6, 24M6, 34M6, 22M6, 33M6 > 25M6

The exponent on the degree of vertex No. 4 puts the octane isomers into three different groups: 2233M4 > Oct, 2M7, 3M7, 3Et3M5, 3Et6, 25M6, 23M6, 33M6, 22M6, 233M5, 223M5, 3Et2M5 > 4M7, 24M7, 34M6, 224M5, 234M5.

The exponent on the distance between vertices No. 5 and No. 4 puts the octane isomers into two groups: 234M5, 224M, 3Et2M5, 3Et3M5, 223M5, 233M5, 4M7, 24M6, 34M6, Oct, 2M7, 3M7, 3Et6, 22M6, 33M6, 23M6, 25M6 > 2233M4, i.e. it distinguishes only 2233M4 from the other octane isomers.

$u_{76}(0.65, 2.7, 0.88)$

The matrix element $u_{76}(0.65, 2.7, 0.88)$ contributes the most at Oct > 2M7, 3M7, 4M7, 3Et3M5 > 3Et2M5, 3Et6 > 25M6, 24M6, 23M6, 22M6 > 234M5, 233M5, 2233M4 > 34M6, 33M6 > 224M5, 223M5.

Vertex No. 7 as well as vertex No. 6 contribute to Oct, 3Et6, and 3Et2M6 more than to other octane isomers.

The distance between these vertices contributes to 22M6, 23M6, 24M6, 25M6 > 3Et6, 34M6, 33M6 > 3Et2M5, 234M5, 233M5 > 224M5, 223M5 > Oct, 2M7, 3M7, 4M7, 3Et3M5

$u_{65}(-0.075, -3.1, -0.37)$

The matrix element $u_{65}(-0.075, -3.1, -0.37)$ contributes the most at 2233M4 > 3Et3M5 > 3Et2M5, 234M5, 224M5, 223M5, 233M5 > 3Et6, 24M6, 23M6, 34M6, 22M6, 33M6 > Oct, 2M7, 3M7, 4M7 > 25M6.

The exponent on the value of vertex No. 6 puts the octane isomers in two groups: other ones > Oct, 2M7, 4M7, 3M7, 3Et3M5.

The exponent on the value of vertex No. 5 puts the octane isomers into three different groups: 3Et2M5, 3Et3M5, 223M5, 224M5, 233M5, 234M5, 2233M4 > Oct, 2M7, 3M7, 4M7, 3Et6, 23M6, 24M6, 34M6, 22M6, 33M6 > 25M6.

The distance from vertex No. 6 to the vertex No. 5 puts the octane isomers into four different groups: Oct, 2M7, 3M7, 4M7, 3Et6, 24M7, 34M6, 25M6, 23M6, 33M6, 22M6 > 2233M4 > 3Et3M5 > 3Et2M5, 224M5, 234M5, 233M5, 223M5.

$u_{53}(-0.13, -0.38, 2^c)$

The matrix element $u_{53}(-0.13, -0.38, 2^c)$ contributes the most at 224M5 > Oct, 2M7, 4M7, 24M6, 22M6 > 25M6 > 3Et2M5, 234M5, 223M5 > 3M7, 3Et6, 23M6, 34M6 > 3Et3M5, 233M5, 2233M4 > 33M6.

The exponent on the value of vertex No. 5 puts the octane isomers in three different groups: 1 = 3Et2M5, 3Et3M5, 223M5, 224M5, 233M5, 234M5, 2233M4 > 0.72 = Oct, 2M7, 3M7, 4M7, 3Et6, 23M6, 24M6, 34M6, 22M6, 33M6 > 0.59 = 25M6.

The exponent on the value of vertex No. 3 puts the octane isomers in three different groups as well: 0.91 = Oct, 2M7, 4M7, 24M6, 25M6, 22M6, 224M5 > 0.87= 3M7, 3Et6, 34M6, 23M6, 223M5, 234M5, 3Et2M5 > 0.84 = 33M6, 233M5, 3Et3M5.

The distance between vertices No. 5 and No. 3 is equal among all octane isomers and does not contribute any separation into groups.

$u_{32}(0.67, -2.4, 1^c)$

The matrix element $u_{32}(0.67, -2.4, 1^c)$ contributes the most at 33M6, 3Et3M5 > 3M7, 3Et6 > Oct, 4M7 > 233M5 > 23M6, 34M6, 3Et2M5, 234M5 > 2M7, 25M6, 24M6 > 2233M4 > 223M5 > 22M6, 224M5.

The exponent on the degree of vertex No. 3 puts the octane isomers into three different groups: 33M6, 233M5, 3Et3M5 > 3M7, 3Et6, 34M6, 23M6, 223M5, 234M5, 3Et2M5 > Oct, 2M7, 4M7, 24M6, 25M6, 22M6, 224M5.

The exponent on the degree of vertex No. 2 puts the octane isomers into three different groups: Oct, 3M7, 4M7, 3Et6, 34M6, 33M6, 3Et3M6 > 2M7, 25M6, 24M6, 23M6, 3Et2M5, 234M5, 233M5 > 22M6, 224M6, 223M6, 2233M4.

The distance between vertices No. 3 and No. 2 is equal among all octane isomers and does not contribute any separation into groups.

Appendix 10.

Structural interpretation of contribution of matrix elements to the best observed combined topological index for logVP of octanes.

Matrix elements, which give rise to the best-observed correlation with logVP, are presented in Table A10. Their values at particular octane isomers are presented in Figure A10.

Due to the sign of k_{ij}, the contribution of matrix elements $u_{63}(a, b, c)\times k_{63}$, $u_{72}(a, b, c)\times k_{72}$, and $u_{32}(a, b, c)\times k_{32}$ is positive in value, wheres the contribution of matrix elements $u_{64}(a, b, c)\times k_{64}$, $u_{62}(a, b, c)\times k_{62}$, and $u_{75}(a, b, c)\times k_{75}$ is negative in value. The "numerical volume" of the combined index is contributed mainly by the matrix element $u_{75}(a, b, c)\times k_{75}$, although it contributes little information content about logVP. In fact, each of the six matrix elements, which contribute to the best-observed combined index, has a low individual correlation with logVP of octanes. Let us see what contribute these matrix elements.

Table A10. Best correlation to logVP of octanes of the combination of six matrix elements and the contributions of individual matrix elements.

$u_{ij}\times k_{ij}$	*R*	*IC* (%)
$u_{63}(-\infty, -5.3, 1.05) \times 0.3558$	0.589	29.8
$u_{72}(-0.32, -2.1, -2.0) \times 0.5250$	0.573	28.1
$u_{64}(-1.08, 1.91, -1.05) \times -0.0046$	–0.368	10.9
$u_{62}(3.2, 1.10, -2.2) \times -0.0020$	–0.269	5.7
$u_{75}(0.039, 0.30, 0.36) \times -0.0899$	–0.253	5.1
$u_{32}(2.3, -5.8, 1^c) \times 0.0227$	–0.217	3.7
$\sum u_{ij}\times k_{ij}$	0.986	83.3

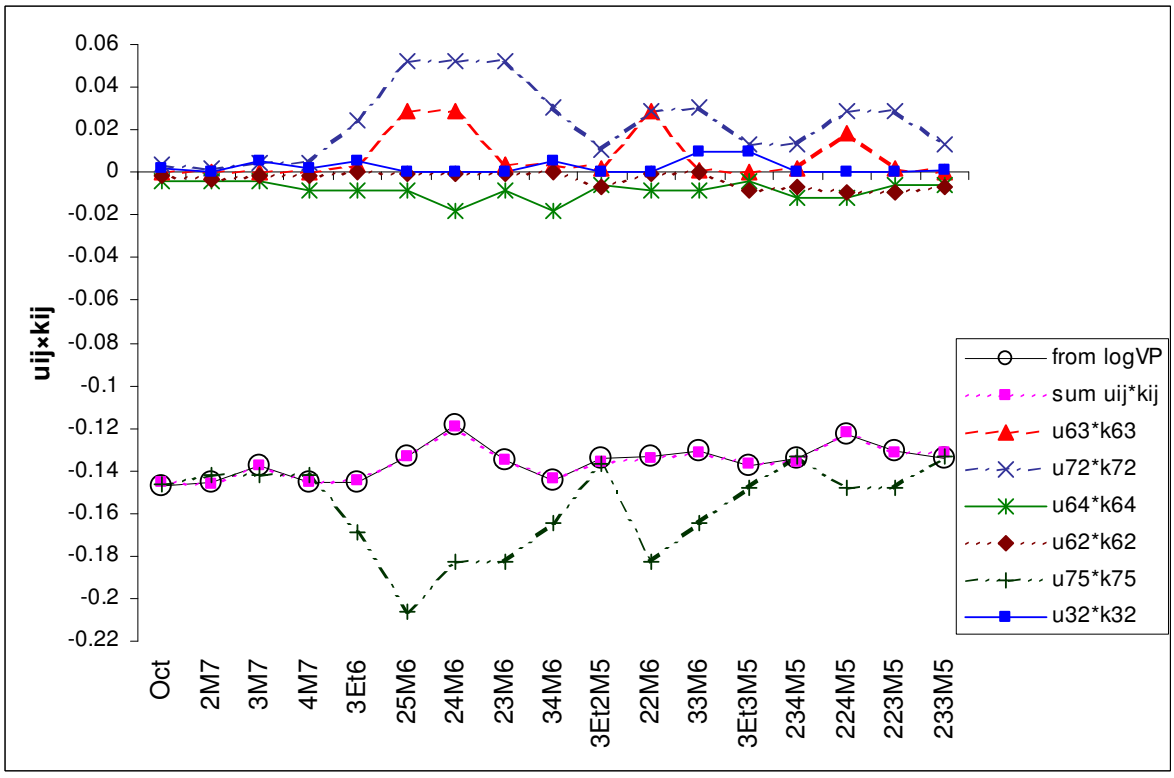

Figure A10. Contribution of particular matrix elements (u_{63}, u_{72}, u_{64}, u_{62}, u_{75}, and u_{32}) to the optimized combined topological index derived from them in the case of logVP of octanes.

$u_{63}(-\infty, -5.3, 1.05)$

The matrix element $u_{63}(-\infty, -5.3, 1.05)$ contributes the most at 25M6, 24M6, 22M6 > 224M5 > 3Et6, 23M6, 34M6 > 3Et2M5, 234M5, 223M5 > 33M6 > 233M5 > Oct, 2M7, 4M7, 3M7, 3Et3M5 = 0.

The exponent on the degree of vertex No. 6 puts the octane isomers into two different groups: 1 = other ones > Oct, 2M7, 4M7, 3M7, 3Et3M5 = 0.

The exponent on the degree of vertex No. 3 puts the octane isomers into three different groups: Oct, 2M7, 4M7, 24M6, 25M6, 22M6, 224M5 > 3M7, 3Et6, 34M6, 23M6, 223M5, 234M5, 3Et2M5 > 33M6, 233M5, 3Et3M5.

The exponent on the distance between vertex No. 6 and No. 3 puts the octane isomers into three different groups as well: Oct, 2M7, 4M7, 3M7, 22M6, 24M6, 25M6, 34M6, 23M6, 3Et6, 33M6 > 224M5, 223M5, 234M5, 3Et2M5, 233M5 > 3Et3M5.

$u_{72}(-0.32, -2.1, -2.0)$

The matrix element $u_{72}(-0.32, -2.1, -2.0)$ contributes the most at 25M6, 24M6, 23M6 > 34M6, 33M6 > 22M6, 224M5, 223M5 > 3Et6 > 3Et3M5 > 234M5, 233M5 > 3Et2M5 > 3M7, 4M7 > Oct > 2M7.

The exponent on the degree of vertex No. 7 contributes to other octane isomers more than to Oct, 3Et6, and 3Et2M6.

The exponent on the degree of vertex No. 2 puts the octane isomers into three groups: 22M6, 224M6, 223M6, 2233M4 > 2M7, 25M6, 24M6, 23M6, 3Et2M5, 234M5, 233M5 > Oct, 3M7, 4M7, 3Et6, 34M6, 33M6, 3Et3M6.

The exponent on the distance between vertex No. 7 and No. 2 puts the octane isomers into four groups: 22M6, 25M6, 24M6, 23M6, 224M5, 223M5 > 3Et6, 3Et2M5, 34M6, 33M6, 234M5, 233M5, 2233M4 > 3Et3M5 > 3M7, 4M7, 2M7, Oct.

$u_{64}(-1.08, 1.91, -1.05)$

The matrix element $u_{64}(-1.08, 1.91, -1.05)$ contributes the most at 24M6, 34M6 > 234M5, 224M5 > 4M7 > 22M6, 33M6 > 3Et6, 25M6, 23M6 > 3Et2M5, 223M5, 233M5 > Oct, 2M7, 3M7, 3Et3M5.

The exponent on the degree of vertex No. 6 contributes to other octane isomers more than to Oct, 3Et6, and 3Et2M6.

The exponent on the degree of vertex No. 4 puts the octane isomers into three groups: 4M7, 24M7, 34M6, 224M5, 234M5 > Oct, 2M7, 3M7, 3Et3M5, 3Et6, 25M6, 23M6, 33M6, 22M6, 233M5, 223M5, 3Et2M5 > 2233M4.

The exponent on the distance between vertex No. 6 and No. 4 puts the octane isomers into two groups: Oct, 2M7, 3M7, 4M7, 3Et6, 24M7, 34M6, 25M6, 23M6, 33M6, 22M6, 3Et3M5 > 3Et2M5, 224M5, 234M5, 233M5, 223M5, 2233M4.

$u_{62}(3.2, 1.1, -2.2)$

The matrix element $u_{62}(3.2, 1.1, -2.2)$ contributes the most at 224M5, 223M5 > 3Et3M5 > 3Et2M5, 234M5, 233M5 > 2M7 > Oct, 3M7, 4M7 > 22M6 > 25M6, 24M6, 23M6 > 3Et6, 34M6, 33M6.

The exponent on the degree of vertex No. 6 contributes to Oct, 3Et6, and 3Et2M6 more than to other octane isomers.

The exponent on the degree of vertex No. 2 puts the octane isomers into three different groups: 22M6, 224M6, 223M6, 2233M4 > 2M7, 25M6, 24M6, 23M6, 3Et2M5, 234M5, 233M5 > Oct, 3M7, 4M7, 3Et6, 34M6, 33M6, 3Et3M6.

The exponent on the distance between vertex No. 6 and No. 2 puts the octane isomers into three groups: 3Et2M5, 234M5, 233M5, 224M5, 223M5, 2233M4 > 3Et3M5 > Oct, 3M7, 4M7, 2M7, 3Et6, 25M6, 24M6, 23M6, 34M6, 22M6, 33M6.

$u_{75}(0.039, 0.30, 0.36)$

The matrix element $u_{75}(0.039, 0.30, 0.36)$ contributes the most at 25M6 > 24M6, 23M6, 22M6 > 3Et6 > 34M6, 33M6 > 3Et3M5, 224M5, 223M5 > Oct > 2M7, 3M7, 4M7 > 3Et2M5 > 234M5, 233M5.

The exponent on the degree of vertex No. 7 contributes to Oct, 3Et6, and 3Et2M6 more than to other octane isomers.

The exponent on the degree of vertex No. 5 puts the octane isomers into three different groups: 25M6 > Oct, 2M7, 3M7, 4M7, 3Et6, 23M6, 24M6, 34M6, 22M6, 33M6 > 3Et2M5, 3Et3M5, 223M5, 224M5, 233M5, 234M5, 2233M4.

The exponent on the distance between vertex No. 7 and No. 5 puts the octane isomers into three groups: 223M5, 224M5, 3Et3M5, 22M6 , 23M6, 24M6, 25M6 > 3Et2M5, 2233M4, 233M5, 234M5, 3Et6, 34M6, 33M6 > Oct, 2M7, 3M7, 4M7.

$u_{32}(2.3, -5.8, 1^c)$

The matrix element $u_{32}(2.3, -5.8, 1^c)$ contributes the most at 33M6, 3Et3M5 > 3M7, 3Et6, 34M6 > Oct, 4M7 > 233M5 > 23M6, 3Et2M5, 234M5 > 2M7, 25M6, 24M6 > 223M5 > 22M6, 224M5.

The exponent on the degree of vertex No. 3 puts the octane isomers into three different groups: 33M6, 233M5, 3Et3M5 > 3M7, 3Et6, 34M6, 23M6, 223M5, 234M5, 3Et2M5 > Oct, 2M7, 4M7, 24M6, 25M6, 22M6, 224M5.

The exponent on the degree of vertex No. 2 puts the octane isomers into three different groups: Oct, 3M7, 4M7, 3Et6, 34M6, 33M6, 3Et3M6 > 2M7, 25M6, 24M6, 23M6, 3Et2M5, 234M5, 233M5 > 22M6, 224M6, 223M6, 2233M4.

The distance between vertex No. 3 and No. 2 is equal to one at all octanes.