Scientific paper

Vertex Degree Weighted Path Indices

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Abstract

Vertex degree weighted path indices $P_N(a, b, ...)$, for example $P_1(a, b)$, $P_2(a, b, c)$, $P_3(a, b, c, d)$, and $P_4(a, b, c, d, e)$, are good topological indices for some of the physicochemical properties of octanes with $|R|_{max}$ up to 0.999. Mutually optimized combinations of them are even better, $R (P_1..P_4)$ is in the worst tested case > 0.9. The best results are obtained in mutually optimized combinations of some of them with some of the elements of the Universal matrix, in the worst tested case $R = 0.994$. Some of the vertex degree weighted path one indices give rise to a »regular« sequence of octane isomers of increasing branching.

Keywords: Connectivity indices; Octanes; Boiling point; Critical temperature; Critical density; Vapor pressure

1. Introduction

Path indices[1,2] are an eminent group of topological indices and together with the connectivity indices[3–6] they are frequently used, starting by Wiener[7,8] and followed by several other authors.

In a private discussion about topological indices, Prof. M. Randić suggested to study the path indices in a similar way as there were studied the indices derived from the Universal matrix $U(a, b, c)$,[9] and there should be tested also the combinations of them. The results of this approach are presented below.

2. Physicochemical Properties of Octanes

Notations and physicochemical properties (PCP) of octanes are presented elsewhere.[10] The data for all 18 octane isomers were used, except at the Octane Numbers (BON, MON, RON) and vapor pressure (logVP), where data for 2,2,3,3-tetramethylbutane are not available, as well as at the surface tension (ST) and refractive index (n_D), because 2,2,3,3-tetramethylbutane is not in the liquid state at the room temperature.

3. Goodness of Topological Indices

To illustrate the potential goodness of topological indices, the linear correlation between them and the physicochemical properties data is used and the goodness of correlation is expressed as the correlation coefficient R and standard error S. Besides them, also the information content[10] (IC) in the topological index (index combination) is used.

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:[10]

$$IC\ (\%) = 100 \times \{1 - [\Sigma(PCP_{exp} - PCP_{calc})^2 / \Sigma(PCP_{exp} - PCP_{av})^2]^{1/2}\} = 100 \times \{1 - S(PCP_{exp}; PCP_{calc}) / S(PCP_{exp}; PCP_{av})\}$$

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}, whereas $S(PCP_{exp}; PCP_{calc})$ and $S(PCP_{exp}; PCP_{av})$ are the respective standard errors.

To the experimental PCP data of octanes, PCP_{exp}, is ascribed the information content $IC = 100\%$, 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 indices 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.

4. Derivation of Indices

4. 1. Path Indices

If we present the path indices[1,2] in the way used to derive a variety of indices from the Universal matrix $\mathbf{U}$(a, b, c),[9,11] we see that they can be presented in the following way:

$$p_1 = \sum v_i^0 \times v_j^0 \times 1^0$$
$$p_2 = \sum v_i^0 \times v_j^0 \times v_k^0 \times 2^0$$
$$p_3 = \sum v_i^0 \times v_j^0 \times v_k^0 \times v_l^0 \times 3^0$$
$$p_4 = \sum v_i^0 \times v_j^0 \times v_k^0 \times v_l^0 \times v_m^0 \times 4^0$$
$$p_5 = \sum v_i^0 \times v_j^0 \times v_k^0 \times v_l^0 \times v_m^0 \times v_n^0 \times 5^0$$
etc.

4. 2. Vertex Degree Weighted Path Indices

Let us define the vertex degree weighted path of length N indices P_N(a, b, ...) in the following way:

$P_N(a, b, ...) = \sum v_i^a \times v_j^b \times ... \times d_N^n$, where v_i, v_j, etc. are the vertex degrees, whereas d_N is the distance between the starting and the target vertex in question.

The factor d_N^n is equal among all vertex degree weighted path indices of the same path length. It is thus a constant, which can be omitted. So the calculation of the vertex degree weighted path indices of the same path length can be simplified into $P_N(a, b, ...) = \sum v_i^a \times v_j^b \times ...$ with d_N = const.

The vertex degree weighted path indices would be thus:

$$P_1(a, b) = \sum v_i^a \times v_j^b$$
$$P_2(a, b, c) = \sum v_i^a \times v_j^b \times v_k^c$$
$$P_3(a, b, c, d) = \sum v_i^a \times v_j^b \times v_k^c \times v_l^d$$
$$P_4(a, b, c, d, e) = \sum v_i^a \times v_j^b \times v_k^c \times v_l^d \times v_m^e$$
etc.

The path indices[1,2] are thus the P_N(0, 0, ...) indices. And, all the path indices are in fact the constant distance indices.

For the purpose of keeping the »dimension«, the products shoud be raised to $1/(d_N+1)$ and not to $^1/_2$ only. Writing it explicitly, the vertex degree weighted path indices kept for the »dimension« should be used in the form:

$$^dP_1(a, b) = \sum (v_i^a \times v_j^b)^{1/2}$$
$$^dP_2(a, b, c) = \sum (v_i^a \times v_j^b \times v_k^c)^{1/3}$$
$$^dP_3(a, b, c, d) = \sum (v_i^a \times v_j^b \times v_k^c \times v_l^d)^{1/4}$$
$$^dP_4(a, b, c, d, e) = \sum (v_i^a \times v_j^b \times v_k^c \times v_l^d \times v_m^e)^{1/5}$$
etc.

However, during the optimization procedure the exponents get automatically corrected for this. It is only to

be remembered that the values of optimized exponents are in fact $a_{opt} = a/(d_N+1)$, etc.

There could be defined also the starting-and-target vertex weighted path indices. They would be:

$$P_{1st}(a, b) = P_1(a, b) = \sum (v_i^a \times v_j^b)^{1/2}$$
$$P_{2st}(a, b, c) = \sum (v_i^a \times v_j^0 \times v_k^b)^{1/3}$$
$$P_{3st}(a, b, c, d) = \sum (v_i^a \times v_j^0 \times v_k^0 \times v_l^d)^{1/4}$$
$$P_{4st}(a, b, c, d, e) = \sum (v_i^a \times v_j^0 \times v_k^0 \times v_l^0 \times v_m^e)^{1/5}$$

If good, they are automatically generated during the optimization procedure, therefore they do not need to be considered separately, except when applying the grid values of exponents, where they may indicate the usefulness of the vertex degree weighted path indices.

The connectivity indices[3–6] $^N\chi^v$ are members of the vertex degree weighted path indices, as well:

$$^1\chi^v \equiv P_1(-^1/_2, -^1/_2)$$
$$^2\chi^v \equiv P_2(-^1/_2, -^1/_2, -^1/_2)$$
etc.

If there would be the intention to keep the »dimension« in the connectivity indices, then their form would be as follows:

$$^1\chi^{«d»} \equiv P_1(-^1/_2, -^1/_2)$$
$$^2\chi^{«d»} \equiv P_2(-^1/_3, -^1/_3, -^1/_3)$$
etc., and in general, $^N\chi^{«d»} \equiv P_N(-^1/_{(N+1)}, ...)$.

The vertex degree weighted path length one index can be derived from the right side of the Universal[11] $\mathbf{U}$(a, b, c) (**Dval**[12,13]) matrix by summing the matrix elements containing the factor 1^c, which is usually not written, cf. Appendix 1. Other starting-and-target vertex degree weighted path indices can be derived from the right side of the Universal[11] $\mathbf{U}$(a, b, c) (**Dval**[12,13]) matrix by summing the matrix elements containing the factor 2^c, 3^c, 4^c, etc, respectively.

The Universal matrix[11] $\mathbf{U}$(a, b, c) (**Dval**[12,13]) presented in Appendix 1, from which the path one indices P_1(a, b) can be derived, is planar, i.e. its dimensionality is equal to 2. Higher vertex degree weighted path indices, i.e. P_2(a, b, c), P_3(a, b, c, d), P_4(a, b, c, d, e), etc, can be derived from matrices of higher dimensions. The dimensionality of the general Universal matrix, from which the path N indices $P_N(a, b, ...) = \sum v_i^a \times v_j^b \times ... \times d_N^n$ can be derived, is equal to N+1.

4. 3. Usefulness of Vertex Degree Weighted Path Indices

Whereas the original path one index p_1 is degenerated, the P_1(a, b) indices are in general not. Among octanes only their values for 3M7 and 4M7 are degenerated at all exponent values.

How useful are the indices belonging to these groups we test in relation to the physicochemical properties of octanes. The first step to assess the usefulness of the vertex degree weighted path indices is the goodness of their correlation with the physicochemical properties of octanes.

To assess where approximately are positioned the maxima in absolute values of correlation coefficient *R* in the space of exponents a, b, ..., a multidimensional grid of values of exponents was applied in the way presented earlier[9,11] and the values of correlation coefficients at those combinations of exponent 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 dimensions of exponents. In several cases, there is indicated by the grid values of exponents more than one local maximum and in such a case more than one is to be tested by the optimization procedure to find the global maximum of the correlation coefficient.

The true maximum of the correlation coefficient can be approached then by exponent optimization using also two-digit and, if necessary, three-digit values of exponents besides the grid values. In present study, the values of exponents were limited to at most three decimals. It has been observed that the first digit in the value of exponent, e.g. in 0.2, defines in most tested cases the first three decimals of the correlation coefficient. The second digit, e.g. in 0.23, improves in most tested cases the value of the third to the 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, ..., e.g. in 0.231, improves the value of the fifth or higher decimal of the correlation coefficient.[9] 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 values 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, ... are needed. For the optimization the Simplex method has been used.

To optimize the combination of indices, the approach $TI_{comb} = \sum P_N(a, b, ...) \times k_N$ has been used, where $\sum abs(k_N) = 1$ and $0 < abs(k_N) < 1$, and the exponents a, b, ... as well as the smallest k_N have two significant digits. The exponents a, b, ... as well as the factors k_N are mutually optimized to reach the highest *R* value possible.

5. Results

The correlations between the vertex degree weighted path indices and physicochemical properties of octanes have several local maxima in the space of exponents a, b, ... They can be located using the multidimensional grid of values of exponents. One has to be aware, however, that a global maximum observed using grid values of exponents presented above may not remain a global maximum after optimization of exponent values or after mutual optimization of exponent values and factors k_N in $\sum P_N(a, b, ...) \times k_N$ used to optimize the combination of two or more indices.

Vertex degree weighted path one indices $P_1(a, b)$

The results obtained using vertex degree weighted path one indices $P_1(a, b)$ using optimized two-digit values of exponents in them and presenting their correlation with physicochemical properties of octanes in form of $|R|_{max}$, are as follows: **0.996** > ω > BP/Tc > Tc/Pc > RON > **0.990** > BON > **0.98** > Pc > Tc^2/Pc > n_D > C > **0.97** > MON > S > d > R^2 > ΔHv > **0.95** > Vm > ΔHf°g > MR > ST > BP > **0.90** > Tc > αc > **0.80** > Vc > B > dc > A > logVP > **0.70** > Zc > CED > Sol.par. > **0.60**.

The $p_1 \equiv P_1(0, 0)$ index is degenerated.

The $P_1(-1/2, -1/2)$ ($\equiv {}^I\chi^v$) index gives rise to $|R|_{max}$ as follows: **0.95** > ΔHv > C > Tc^2/Pc > S > ω > **0.90** > RON > BON > ΔHf°g > BP > BP/Tc > MON > **0.80** > R^2 > Tc/Pc > logVP > A > **0.70** > Zc > ST > Pc > n_D > d > Vm > **0.50** > B > αc > MR > Vc > dc > Tc > Sol.par. > CED > **0.08**.

Among the vertex degree weighted path one indices a local maximum other than the best grid values one gives rise to a better correlation after optimization of two digit values of exponent in three cases: C, ST, and A.

Vertex degree weighted path two indices $P_2(a, b, c)$

The results obtained using vertex degree weighted path two indices $P_2(a, b, c)$ using optimized two-digit values of exponents in them and presenting their correlation with physicochemical properties of octanes as $|R|_{max}$, are as follows: **0.999** > ω > Tc/Pc > BP/Tc > **0.99** > RON > Pc > **0.98** > C > n_D > BON > Tc^2/Pc > d > **0.97** > Vm > MON > S > **0.96** > **0.95** > ΔHv > ST > R^2 > ΔHf°g > BP > MR > **0.90** > A > Vc > dc > Sol.par. > CED > αc > B > Tc > **0.80** > logVP > Zc > **0.70**.

The $p_2 \equiv P_2(0, 0, 0)$ index gives rise to $|R|_{max}$ as follows: **0.98** > ω > **0.97** > C > S > **0.95** > Tc^2/Pc > RON > BON > n_D > BP/Tc > ΔHv > **0.90** > MON > Tc/Pc > **0.80** > R^2 > ΔHf°g > Pc > BP > **0.70** > A > logVP > d > Vm > Zc > MR > αc > **0.50** > Vc > dc > ST > B > CED > Sol.par. > Tc > **0**.

The connectivity index $P_2(-1/2, -1/2, -1/2)$ ($\equiv {}^2\chi^v$) gives rise to $|R|_{max}$ as follows: **0.95** > ΔHv > ΔHf°g > **0.90** > BP > C > S > Tc^2/Pc > ω > **0.80** > ST > RON > BON > logVP > **0.70** > A > BP/Tc > MON > R^2 > Tc/Pc > Zc > B > **0.50** > n_D > d > Vm > Pc > Tc > αc > Vc > dc > Sol.par. > MR > CED > **0.10**.

The connectivity index kept for the »dimension«, $P_2(-1/3, -1/3, -1/3)$ ($\equiv {}^2\chi^{«d»}$), gives rise to $|R|_{max}$ as follows: **0.95** > ΔHv > C > **0.90** > S > ΔHf°g > Tc^2/Pc > ω > BP > RON > BON > **0.80** > BP/Tc > MON > logVP > R^2 > Tc/Pc > A > **0.70** > ST > Zc > n_D > d > B > Vm > Pc > **0.50** > αc > Vc > dc > MR > Tc > Sol.par. > CED > **0.10**.

Among the vertex degree weighted path two indices, a local maximum other than the best grid values one, gives rise to a better correlation after optimization of two digit values of exponent in RON, Vc, and dc, as well as slightly in ω, C, S, ΔHv, and A.

Vertex degree weighted path three indices P_3(a, b, c, d)

The results obtained using vertex degree weighted path three indices P_3(a, b, c, d) using optimized two-digit values of exponents in them and presenting their correlation with physicochemical properties of octanes as $|R|_{max}$, are as follows: **0.991** > RON > **0.99** > Tc/Pc > Pc > BP/Tc > MON > BON > ω > n_D > **0.98** > Tc^2/Pc > d > **0.97** > Vm > ST > C > R^2 > S > **0.96** > ΔHv > Tc > BP > **0.95** > MR > ΔHf$°$g > B > **0.90** > Sol.par. > CED > Vc > αc > dc > A > Zc > **0.80** > logVP > **0.70**.

The $p_3 \equiv P_3$(0, 0, 0, 0) index gives rise to $|R|_{max}$ as follows: **0.96** > Pc > **0.95** > MR > **0.90** > Tc/Pc > BP/Tc > **0.80** > Vc > Tc > dc > Vm > ω > **0.70** > d > n_D > Tc^2/Pc > ST > MON > S > RON > R^2 > BON > C > CED > Sol.par. > **0.50** > αc > B > ΔHv > Zc > A > BP > ΔHf$°$g > logVP > **0**.

The connectivity index P_3(–½, –½, –½, –½) ($\equiv$$^3\chi^v$) gives rise to $|R|_{max}$ as follows: **0.93** > MR > Pc > **0.90** > Tc/Pc > **0.80** > Tc > BP/Tc > **0.70** > Vm > Vc > ST > dc > d > ω > n_D > Sol.par. > CED > S > Tc^2/Pc > MON > RON > R^2 > C > BON > **0.50** > αc > B > Zc > BP > ΔHv > ΔHf$°$g > A > logVP > **0**.

The connectivity index kept for the »dimension«, P_3(–¼, –¼, –¼, –¼) ($\equiv$$^3\chi^{«d»}$) gives rise to $|R|_{max}$ as follows: **0.90** > MR > Pc > Tc > **0.80** > ST > Tc/Pc > **0.70** > BP/Tc > Vm > Vc > dc > d > Sol.par. > CED > ω > n_D > B > **0.50** > S > MON > RON > R^2 > Tc^2/Pc > C > αc > BON > BP > Zc > ΔHf$°$g > logVP > ΔHv > A > **0**.

Using best observed grid values of exponents on vertex degree values in vertex degree weighted path three index P_3(a, b, c, d) gives rise to some good correlations, whereas the optimization using two-digit values of exponents gives rise to slight additional improvement of correlation coefficients.

Among the vertex degree weighted path three indices, a local maximum other than the best grid-values one, gives rise to a better correlation after optimization of two digit values of exponents in B, as well as slightly in n_D, Vm, Tc, and Zc.

Vertex degree weighted path four indices P_4(a, b, c, d, e)

The results obtained using vertex degree weighted path four indices P_4(a, b, c, d, e) using optimized two-digit values of exponents in them and presenting their correlation with physicochemical properties of octanes as $|R|_{max}$, are as follows: **0.996** > RON > Tc/Pc > Pc > MON > **0.99** > BP/Tc > BON > ω > **0.98** > Tc^2/Pc > R^2 > **0.97** > ST >

Tc > S > **0.96** > **0.95** > αc > B > C > MR > Sol.par. > CED > Vm > d > n_D > **0.90** > ΔHv > Zc > A > Vc > ΔHf$°$g > dc > **0.80** > BP > logVP > **0.70**.

The $p_4 \equiv P_4$(0, 0, 0, 0, 0) index gives rise to $|R|_{max}$ as follows: **0.90** > d > n_D > ΔHv > **0.80** > Tc > BP/Tc > **0.70** > ω > A > CED > MR > Tc/Pc > Pc > Tc^2/Pc > S > αc > **0.50** > R^2 > Vm > ST > Sol.par. > C > BON > Vc > BP > logVP > MON > B > Zc > RON > ΔHf$°$g > dc > **0**.

The connectivity index P_4(–½, –½, –½, –½, –½) ($\equiv$$^4\chi^v$) gives rise to $|R|_{max}$ as follows: **0.80** > Vm > d > n_D > **0.70** > S > BP/Tc > Zc > C > ω > Pc > Tc/Pc > CED > Sol.par. > **0.50** > MR > Tc^2/Pc > ΔHf$°$g > Tc > ΔHv > RON > R^2 > ST > B > BON > MON > Vc > dc > BP > A > αc > logVP > **0**.

The connectivity index kept for the »dimension«, P_4(–⅕, –⅕, –⅕, –⅕, –⅕) ($\equiv$$^4\chi^{«d»}$) gives rise to $|R|_{max}$ as follows: **0.90** > Vm > d > n_D > **0.80** > S > **0.70** > BP/Tc > Pc > CED > Sol.par. > C > ω > Tc/Pc > Zc > MR > **0.50** > Tc > Tc^2/Pc > ST > B > ΔHf$°$g > ΔHv > RON > R^2 > Vc > dc > BON > MON > logVP > BP > αc > A > **0**.

Also in vertex degree weighted path four index P_4(a, b, c, d, e) the use of best observed grid values of exponents on vertex degree values, compared to those having equal values of exponents, improves the correlations substantially, whereas the optimization using two-digit values of exponents gives rise to slight additional improvement of correlation coefficients.

Among the vertex degree weighted path four indices, a local maximum other than the best grid values one, gives rise to a better correlation after optimization of two digit values of exponents in ST, BON, RON, MON, CED, Sol.par., dc, Vc, Zc, and B, as well as slightly in logVP, S, R^2, Tc^2/Pc, Tc/Pc, ΔHv, ΔHf$°$g, BP, Tc, and C.

The best results obtained by using two-digit values of exponents in vertex degree weighted path indices are summarized in Table 1. There can be seen that in ten cases the vertex degree weighted path indices give rise to $|R|_{max}$ > 0.99. Six physicochemical properties of octanes are involved in these cases.

5. 1. Synergism Between Path Indices – Mutually Optimized Two-digit Values of Exponents

To demonstrate the synergism between vertex degree weighted path indices we have chosen seven physi-

Table 1. The best correlations ($|R|_{max}$ > 0.99) using two-digit values of exponents in vertex degree weighted path indices.

PCP	*R*	P_N	*R*	P_N	*R*	P_N
ω	–0.998	P_2(a, b, c)	–0.995	P_1(a, b)		
Tc/Pc	–0.997	P_2(a, b, c)	–0.995	P_1(a, b)	0.992	P_4(a, b, c, d, e)
BP/Tc	–0.997	P_2(a, b, c)	–0.995	P_1(a, b)		
RON	0.995	P_4(a, b, c, d, e)	0.992	P_1(a, b)	–0.990	P_3(a, b, c, d)
MON	–0.992	P_4(a, b, c, d, e)				
Pc	–0.992	P_4(a, b, c, d, e)				

cochemical properties of octanes: MON, Tc^2/Pc, n_D, BP, Tc, dc and logVP, cf.[10] For the sake of comparison are presented in Table 2 the best results using two-digit values of exponents in the best observed individual vertex degree weighted path index.

The best observed correlations between values of physicochemical properties (PCP) and mutually optimi-
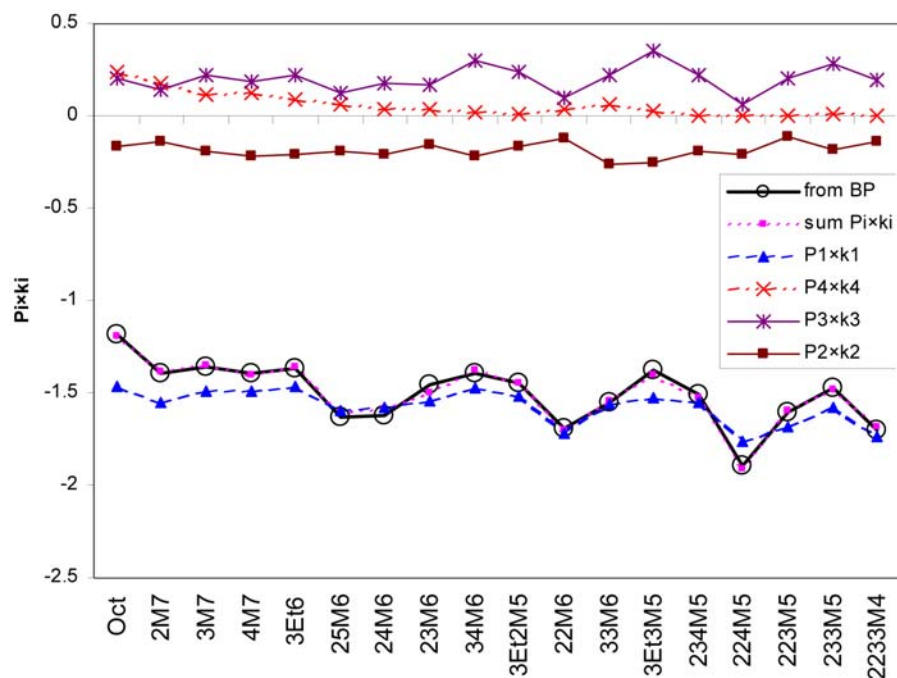
zed combinations of vertex degree weighted path indices using two-digit values of exponents and factors k_N in $\sum P_N(a, b, ...) \times k_N$ are illustrated in Table 3 and Figure 1 for the boiling point of octanes (BP). The results for physicochemical properties MON, Tc^2/Pc, n_D, BP, Tc, dc and logVP are presented in Appendix 2.

5. 2. Ordering of Structures Using Vertex Degree Weighted Path Indices

Ordering of structures was introduced by Randić and Wilkins.[4] They discovered that an ordering based on paths of length two (p_2) and paths of length three (p_3) indicates possible trends and behavior for many molecular properties. By considering a grid graph derived by attributing to each isomer coordinates (p_2, p_3) and connecting points along the coordinate axis, they obtained simple presentations useful for isomer structural interrelations.

Table 3. The best-observed mutually optimized combinations of vertex degree weighted path indices using two-digit values of exponents and factors k_N in the case of boiling point of octanes (BP).

$P_N(a, b, ...)$	k_N	R	IC (%)
$P_1(-0.40, 1.68)$	−0.0911	0.906	49.8
$P_4(1.04, -2.3, 0.44, -4.1, 2.7)$	0.4223	0.648	20.6
$P_3(-2.0, -1.43, -0.82, 0.020)$	0.4816	0.592	16.8
$P_2(0.63, -0.71, 2.9)$	−0.0050	−0.163	1.1
$\sum P_N(a, b, ...) \times k_N$		0.993	88.3

Figure 1. Contribution of particular vertex degree weighted path indices to the optimized combined topological index derived from them in the case of BP of octanes using two-digit values of exponents and factors k_N.

Table 2. The best correlations using the best two-digit values of exponents in individual vertex degree weighted path indices at MON, Tc^2/Pc, n_D, BP, Tc, dc and logVP.

PCP	P_N	a	b	c	d	e	R	S	IC (%)[10]
MON	P_4	0.65	−1.65	−0.40	−1.77	1.86	−0.992	4.389	87.0
Tc^2/Pc	P_3	−0.26	−2.3	−2.3	0.135		0.977	915	78.9
n_D	P_4	0.95	0.88	−1.96	2.4	1.84	−0.976	0.00117	78.3
BP	P_3	−0.98	−1.33	−1.67	−0.197		0.943	2.093	66.8
Tc	P_4	1.09	0.97	−1.30	2.4	0.165	−0.962	2.379	72.8
dc	P_3	0.97	2.4	−0.39	1.44		0.860	0.004338	49.0
logVP	P_2	−0.80	−1.48	−7.9			0.760	0.116	35.0

A similar procedure can be applied also to the vertex degree weighted path indices and the results are compared to those by Randić and Wilkins.[4] In order to make such a comparison, one has to recall that $p_1 = P_1(0, 0)$, $p_2 = P_2(0, 0, 0)$, $p_3 = P_3(0, 0, 0, 0)$, and $p_4 = P_4(0, 0, 0, 0, 0)$.

Randić and Wilkins[4] used in their study only paths of length two, p_2, and paths of length three, p_3, whereas here are considered the vertex degree weighted path indices P_1 through P_4, because members of all of them contribute in correlation seeking procedures. The results are presented in Appendix 3.

Within the indices of the same path length, the $P_N(1, 1, ...)$ vs. $P_N(0, 0 ...)$ indices are presented in Figure A3a through A3c. In Appendix 3 is given also the graph having coordinates p_2 and p_4 [i.e. $P_2(0, 0, 0)$ and $P_4(0, 0, 0, 0, 0)$], Figure A3d.

There is given in Figure A3e also the illustration that the graph of $P_1(-1, -1)$ vs. $P_1(1, 1)$ gives the resolution of most octane isomers. In Figure A3f, on the other hand, is given the demonstration of values of $P_2(3.5, -6.1, 3.0)$ and $P_4(0.65, 1.06, 0.063, 0.97, -0.154)$, which contribute together 54.9% of information about Tc of octanes.

6. Discussion

Vertex degree weighted path indices presented here, i.e. $P_1(a, b)$, $P_2(a, b, c)$, etc., are a generalized form of path indices, which includes besides the original[1,2] path indices p_1, p_2, etc. also the connectivity indices $^N\chi^v$.[3–6] The relations between them are:

$p_1 \equiv P_1(0, 0)$
$p_2 \equiv P_2(0, 0, 0)$
etc.

as well as
$^1\chi^v \equiv P_1(-1/2, -1/2)$
$^2\chi^v \equiv P_2(-1/2, -1/2, -1/2)$
etc.

If there would be the intention to keep in the connectivity indices the »dimension« of the vertex degree, then their form would be as follows:

$^1\chi^{«d»} \equiv P_1(-1/2, -1/2)$
$^2\chi^{«d»} \equiv P_2(-1/3, -1/3, -1/3)$
etc., and in general, $^N\chi^{«d»} \equiv P_N(-1/(N+1), ...)$.

The path indices and the connectivity indices are in fact the constant distance indices.

The usefulness of vertex degree weighted path indices as well as of vertex degree weighted connectivity indices is presented above, where in the text there are presented the physicochemical properties of octanes sorted by the decreasing absolute value of the correlation coefficient between them and said indices. For comparison there are presented also the values of the correlation coefficients ($|R|_{max}$) using:

– original path index characterized here by the exponents equal to 0 (zero),

– followed by the respective connectivity index characterized by the exponent value of $-1/2$,

– as well as by the respective connectivity index kept for the »dimension« of the vertex degree (characterized by the exponent value of $-1/2$, $-1/3$, $-1/4$, or $-1/5$, respectively).

Among the vertex degree weighted path one indices, a local maximum other than the best grid values one, gives rise to a better correlation after optimization of two digit values of exponent in the case of ST, and slightly at C and A.

Among the vertex degree weighted path two indices, such a situation is observed in the case of RON, Vc, and dc, as well as slightly at ω, C, S, ΔHv, and A.

Among the vertex degree weighted path three indices, such a situation is observed in the case of B, as well as slightly in n_D, Vm, Tc, and Zc.

Among the vertex degree weighted path four indices, such a situation is observed in the case of ST, BON, RON, MON, CED, Sol.par., dc, Vc, Zc, and B, as well as slightly at logVP, S, R^2, Tc^2/Pc, Tc/Pc, ΔHv, ΔHf°g, BP, Tc, and C.

The best cases having $|R|_{max} > 0.99$ are presented in Table 1. There can be seen that members of all tested vertex degree weighted path indices are involved there, as well as six physicochemical properties of octanes (ω, Tc/Pc, BP/Tc, RON, MON, and Pc).

If we compare the results using optimized two digit values of exponents to results using grid values of exponents, to results using exponents to keep the »dimension« of the vertex degree, to results using original path indices, to results using original connectivity indices, as well as to results using connectivity indices kept for the »dimension« of the vertex degree, we observe as a general rule that the correlation coefficients are the highest when using optimized two digit values of exponents. They are followed by the correlation coefficients using grid values of exponents. Using tested combinations of equal values of exponents mentioned above gives rise to lower results. For this reason, the use of optimized two digit values of exponents is to be preferred.

There is also the question of what do index the indices $P_3(a, b, c, d)$ and $P_4(a, b, c, d, e)$ in octanes. The answer to this question can be looked for from two different points of view. One point of view is from the reactivity of the structural elements represented by them. This is relevant for the Octane Number of octanes. Another point of view is from the consequences of the intermolecular attractions and collisions relevant in the case of several other physicochemical properties of octanes.

Let us look first from the point of view of the reactivity of structural elements represented by indices $P_3(a, b, c, d)$ and $P_4(a, b, c, d, e)$. The index $P_4(a, b, c, d, e)$ is derived from structural elements of the general form ... ⌒⌒ ..., where the degrees of vertices in them are in general different. The formation of hydroperoxides can proceed the fastest when a CH_2 group in β position is invol-

ved in it.[14,15] In a path of length four there are possible from none up to five CH_2 groups in one or another β position. The real structural features, part of which are these paths of length four, modify the number of CH_2 groups in β positions and other characteristics influencing the rate of reactions. This is reflected in value of the index P_4(a, b, c, d, e), which gives the best correlation with the Octane Number of octanes. The index P_3(a, b, c, d) represents shorter structural elements with a lower possible number of CH_2 groups in β position than in the case of P_4(a, b, c, d, e).

In the case of other physicochemical properties of octanes, a possible explanation would be that the indices P_3(a, b, c, d) and P_4(a, b, c, d, e) are i.a. two different measures of the flexibility resp. elasticity of molecules. However, this question deserves a separate study.

6. 1. Synergism Between Path Indices

The synergism between vertex degree weighted path indices is demonstrated using seven physicochemical properties of octanes: MON, Tc^2/Pc, n_D, BP, Tc, dc and logVP. The results are presented in Appendix 2, for BP of octanes also in Table 3 and Figure 1, and for the other ones also in Table 5. The results presented in Appendix 2 and Table 4 show that the correlation coefficient of the best observed correlation between $\sum P_N$(a, b, ...)×k_N and MON, Tc^2/Pc, n_D, BP, Tc, dc and logVP, is $|R|$ ($P_1..P_4$, PCP) = 0.9995 > MON > Tc^2/Pc > Tc > BP > n_D > 0.99 > 0.94 > logVP > dc > 0.90. The »numerical volume« of the combined in-

dex is presented mainly by P_1, the most of information is contributed by P_4 at MON, Tc^2/Pc, n_D, and Tc, by P_3 at dc, and by P_1 at BP and logVP, Table 4.

6. 2. Comparison of Results Obtained With Combinations of Path Indices to Those of Combinations of Matrix Elements

The best results enabling the comparison are given in Table 5 in form of correlation coefficients *R*. There is the question, which situations to compare – equal number of indices in combinations of them or equal number of vertices and distances, which are not constants. In the case of MON we can see the difference between the two approaches. In the case of equal number of indices in the index combination, R ($P_1..P_4$) > R (four u_{ij}). In the case of equal number of vertices and distances, which are not constants, R (five u_{ij}) > R ($P_1..P_4$). In the case of Tc^2/Pc, R ($P_1..P_4$) ~ R (five u_{ij}), in the case of BP and Tc, R ($P_1..P_4$) > R (five u_{ij}), in the case of n_D, logVP, and dc, R (five u_{ij}) > R ($P_1..P_4$). The situation depends thus on the physicochemical property in question.

6. 3. Combinations of Vertex Degree Weighted Path Indices With Combinations of Elements of the Universal Matrix

In the worst of the tested cases in Table 5, dc, where the best results were R (six u_{ij}) = 0.986,[10] and R ($P_1..P_4$) = 0.904, the mutually optimized combination of the best six elements of the Universal matrix[10] (u_{83}, u_{54}, u_{76}, u_{65}, u_{53}, and u_{32}), and of P_2(a, b, c) gives rise to R = 0.994, S = 0.000912, and IC = 89.3%, Table 6, which is much better that the result given in Table 5. The vertex degree weighted path two index P_2(a, b, c) gives better results than other vertex degree weighted path indices.

In the case of logVP, the mutually optimized combination of the best six elements of the Universal matrix[10] (u_{63}, u_{72}, u_{64}, u_{62}, u_{75}, and u_{32}), and of P_2(a, b, c) gives rise to R = 0.994, S = 0.0196, and IC = 89.0%, Table 7, which is again much better that the results given in

Table 4. Contribution of vertex degree weighted path indices to the best combination of them.

PCP	$|R|$ and *IC*	»Num.vol.«
MON	$P_4 > P_3 > P_2 >>> P_1$	P_1
Tc^2/Pc	$P_4 > P_1 > P_2 > P_3$	P_1
n_D	$P_4 > P_3 > P_1 > P_2$	
BP	$P_1 > P_4 > P_3 >> P_2$	P_1
Tc	$P_4 > P_2 > P_3 > P_1$	P_1
dc	$P_3 > P_1 > P_4 >>> P_2$	P_1, P_2
logVP	$P_1 > P_2 > P_3 > P_4$	P_2

Table 5. Goodness of best combinations of vertex degree weighted path indices vs. that of best combinations of elements[10] of the Universal matrix.

PCP	R ($P_1..P_4$) [14]	R (four u_{ij})	R (five u_{ij})	R (six u_{ij})
MON	0.9993	0.996 [12]	0.9994 [14]	0.9996 [17]
Tc^2/Pc	0.998	0.995 [12]	0.998 [15]	0.999 [17]
BP	0.993	0.984 [11]	0.990 [14]	0.995 [17]
n_D	0.992	0.989 [11]	0.993 [14]	0.995 [16]
Tc	0.995	0.980 [11]	0.983 [14]	0.986 [17]
logVP	0.936	0.954 [12]	0.973 [14]	0.986 [17]
dc	0.904	0.944 [11]	0.964 [13]	0.986 [15]

In square brackets: number of vertices and distances between them, contributing to this value since their degrees (values) are not constants (not equal among all isomers).

Table 6. Best correlation to dc of the combination of six elements of the Universal matrix and of the vertex degree weighted path two index P_2(a, b, c) as well as the contributions of individual matrix elements.

dc	k_{ij}	R	IC (%)
u_{83}(1^a, –2.7, –0.25)	–0.3581	0.737	28.0
u_{53}(–0.126, –0.39, 2^c)	0.3168	–0.556	14.6
u_{54}(–3.0, –2.6, –1.20)	0.1851	0.550	14.2
u_{76}(0.68, 2.7, 0.90)	–0.0052	0.548	14.1
u_{65}(–0.055, –3.0, –0.37)	–0.0649	–0.547	14.0
u_{32}(0.94, –2.3, 1^c)	0.0588	0.286	3.6
P_2(–0.67, –0.60, 0.87)	–0.0111	–0.130	0.7
Sum of them		0.994	89.3

Table 5. Also in this case, the vertex degree weighted path two index P_2(a, b, c) gives rise to better results than other vertex degree weighted path indices.

Extrapolation to 2233M4 presents the value of logVP = 3.45.

Table 7. Best correlation to logVP of the combination of six elements of the Universal matrix and of the vertex degree weighted path two index P_2(a, b, c) as well as the contributions of individual matrix elements.

u_{ij}	k_{ij}	R	IC (%)
u_{63}(–, –5.3, 1.06)	0.3361	0.588	29.3
u_{72}(–0.29, –2.1, –2.0)	0.4984	0.571	27.4
u_{64}(–1.19, 1.90, –1.18)	–0.0047	–0.367	10.7
P_2(–0.44, –1.97, –1.30)	0.0439	0.299	7.0
u_{62}(3.0, 0.96, –2.2)	–0.0022	–0.280	6.2
u_{75}(0.047, 0.30, 0.36)	–0.0849	–0.247	4.8
u_{32}(2.3, –5.7, 1^c)	0.0298	–0.217	3.6
Sum of them		0.994	89.0

6. 4. Ordering of Structures

Randić and Wilkins[4] introduced and discussed the significance of the results of ordering of alkane isomers based on paths of length two (p_2) and paths of length three (p_3) as well as their conceptual value.

Whereas the path of length one index, p_1, is totally degenerated, its value being among octanes equal to 7, other p_N indices are degenerated to some extent only. The degeneration of p_2 and p_3, as well as their integer values enabled Randić and Wilkins[4] to form rectangular grid graphs in form of coordinate systems similar to Mendeleev's periodic system of elements.

Similar forms are obtained also using the P_N(1, 1, ...) vs. P_N(0, 0 ...) indices within the indices of the same path length, cf. Figures A3a through A3c in Appendix 3.

In Figure A3a, the index P_2(0, 0, 0) distributes the octane isomers according to the number of branches. It separates also those having only tertiary carbons from those

having quaternary carbons grouping 234M5 among those having two branches on a quaternary carbon. The index P_2(1, 1, 1), on the other hand, separates the centrally substituted isomers from the peripherally substituted ones. 3Et2M5 is not separated from 34M6.

In Figure A3b, the index P_3(0, 0, 0, 0) separates the centrally substituted isomers from the peripherally substituted ones, whereas the index P_3(1, 1, 1, 1) separates the groups of isomers according to the number of branches.

In Figure A3c the separation is not that straightforward. The indices P_4(0, 0, 0, 0, 0) and P_4(1, 1, 1, 1, 1) separate the octane isomers by some other not yet resolved criteria.

There is given also the graph having coordinates p_2 and p_4 [i.e. P_2(0, 0, 0) and P_4(0, 0, 0, 0, 0)], Figure A3d, which did not serve well to the purpose of Randić and Wilkins.[4]

While $p_1 = P_1$(0, 0) is not useful due to its total degeneration, the graph of P_1(–1, –1) vs. P_1(1, 1), Figure A3e, gives the resolution of most octane isomers. There is evident the separation according to the number of branches, the position of branches, the separation between branches, and type of branches (Et or M). Although the shape of the grid is not rectangular, the separations are clearly visible with exception of two pairs of isomers, of 3M7 and 4M7 as well as 34M6 and 3Et2M5, which are not separated.

In mutually optimized combinations of the vertex degree weighted path indices, the appearence of the distribution of octane isomers may be quite complicated. This is demonstrated in Figure A3f in Appendix 3 for the values of P_2(3.5, –6.1, 3.0) and P_4(0.65, 1.06, 0.063, 0.97, –0.154), which contribute together 54.9% of information about Tc of octanes.

Bonchev and Trinajstić[16] formulated several general rules for branching based on Wiener[7] index that were improved later.[17] Randić[18] reminded that branching was in fact attempted to be defined using few topological indices, either the Wiener index[7] or the largest eigenvalue of the adjacency matrix[19,20] and he provided the largest eigenvalue of the path matrix as a new basis for the definition of branching.[18] Randić and Wilkins[4] followed with the ordering of structures based on path indices. Later[21] were presented »regular«, in part intuitively derived sequences of octane isomers of increasing branching, one of them being Oct < 2M7 < 3M7 < 4M7 < 3Et6 < 25M6 < 24M6 < 23M6 < 34M6 < 3Et2M5 < 22M6 < 33M6 < 3Et3M5 < 234M5 < 224M5 < 223M5 < 233M5 < 2233M4, as well as the indices derived from a simplified version of the Universal matrix giving rise to such »regular« sequences of octane isomers. Such a »regular« sequence is observed among some of the indices[10,11,22] V(a, b, c) ≡ V_{wm}(a, b, c) and V_L(a, b, c). The graphs presenting the values of exponents at V_L(a, b, c), V_{wm}(a, b, c) and P_1(a, b) giving rise to such a »regular« sequence of octane isomers are presented in Appendix 4. The relations between the exponents a, b,

and c in V_L(a, b, c), and V_{wm}(a, b, c) giving rise to the »regular« sequence of octane isomers presented above are quite complex, see Appendix 4, Figure A4a through A4e. Among the path indices, such a »regular« sequence of octane isomers is observed only at P_1(a, b). The graph presenting the values of exponents at P_1(a, b) giving rise to a »regular« sequence of octane isomers is presented in Appendix 4, Figure A4f, within the a, b plane marked by dots. In Appendix 3, Figure A3g, is presented such a sequence based on P_1(–0.05, –1) and P_1(0.5, 0.2).

The best observed two digit values of exponents in P_1(a, b) itself as well as in the mutually optimized exponents a, b and factor k_N in the combination of path one through path four indices, Appendix 2, in correlation with MON, Tc^2/Pc, BP, n_D, Tc, dc, and logVP are outside the plane marked by dots in Appendix 4, Figure A4f. Thus, as a rule, the values of exponents giving rise to a »regular« sequence of octane isomers do not give rise to good correlations with tested physicochemical properties of octanes.

Path indices P_2(a, b, c), P_3(a, b, c, d), and P_4(a, b, c, d, e) do not give rise to such a »regular« sequence of octane isomers. Their usefulness in fitting correlation procedures obviously derives from this fact, where they contribute information about physicochemical properties of octanes, which is not contained in the »regular« sequences of octane isomers.

7. Conclusions

The vertex degree weighted path of length N indices P_N(a, b, ...) are defined in the following way: P_N(a, b, ...) = $\sum v_i^a \times v_j^b \times ... \times d_N^n$, where v_i, v_j, etc. are the vertex degrees, whereas d_N is the distance between the starting and the target vertex in question. These vertex degree weighted path indices were found to be promising topological indices for several physicochemical properties of octanes with $|R|_{max}$ up to 0.999. The mutually optimized combinations of them are even better than individual vertex degree weighted path indices with the worst tested case R (P_1..P_4) > 0.9. The best results are obtained in mutually optimized combinations of some of them with some of the elements of the Universal matrix, in the worst tested case R = 0.994.
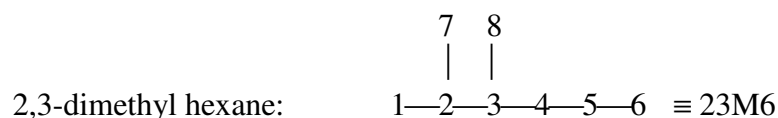
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Povzetek

Indeksi poti z uteženimi vrednostmi njihovih točk P_N(a, b, ...), na primer P_1(a, b), P_2(a, b, c), P_3(a, b, c, d) in P_4(a, b, c, d, e), so dobri topološki indeksi za nekatere fizikalno-kemijske lastnosti oktanov z $|R|_{max}$ do 0.999. Njihove medsebojno optimirane kombinacije so še precej boljše, R (P_1..P_4) je v najslabšem preizkušenem primeru > 0,9. Najboljše rezultate dobimo, če jih optimiramo z nekaterimi elementi Univerzalne matrike, kar da v najslabšem preizkušenem primeru R = 0,994. Nekateri indeksi poti dolžine ena z uteženimi vrednostmi njihovih točk razvrstijo izomere oktanov v »pravilno« zaporedje po naraščajoči razvejanosti.

Appendix 1

2,3-Dimethyl hexane: its formula, its label, its simple distance matrix composed of distances d_{ij}, its vectors of degrees of vertices, v_i and v_j, as well as the $\mathbf{U}(a, b, c)$ matrix derived from them. The matrix elements belonging to the vertex-degree-weighted path one index $P_1(a, b)$ are presented on the right side of the matrix in bold underlined, whereas on the left side in italics. The relation between them is: $P_{1\text{right}}(a, b) = P_{1\text{left}}(b, a)$.

$$
\begin{array}{c}
7 \quad 8 \\
| \quad | \\
\end{array}
$$

2,3-dimethyl hexane: $\quad$ 1—2—3—4—5—6 $\equiv$ 23M6

v_i $\qquad$ distance matrix

1	0	1	2	3	4	5	2	3
3	1	0	1	2	3	4	1	2
3	2	1	0	1	2	3	2	1
2	3	2	1	0	1	2	3	2
2	4	3	2	1	0	1	4	3
1	5	4	3	2	1	0	5	4
1	2	1	2	3	4	5	0	3
1	3	2	1	2	3	4	3	0

v_j $\quad$ 1 $\quad$ 3 $\quad$ 3 $\quad$ 2 $\quad$ 2 $\quad$ 1 $\quad$ 1 $\quad$ 1

$\mathbf{U}(a, b, c)$ matrix of 2,3-dimethyl hexane

0	$\underline{\mathbf{1^a3^b1^c}}$	$1^a3^b2^c$	$1^a2^b3^c$	$1^a2^b4^c$	$1^a1^b5^c$	$1^a1^b2^c$	$1^a1^b3^c$
$3^a1^b1^c$	0	$\underline{\mathbf{3^a3^b1^c}}$	$3^a2^b2^c$	$3^a2^b3^c$	$3^a1^b4^c$	$\underline{\mathbf{3^a1^b1^c}}$	$3^a1^b2^c$
$3^a1^b2^c$	$3^a3^b1^c$	0	$\underline{\mathbf{3^a2^b1^c}}$	$3^a2^b2^c$	$3^a1^b3^c$	$3^a1^b2^c$	$\underline{\mathbf{3^a1^b1^c}}$
$2^a1^b3^c$	$2^a3^b2^c$	$2^a3^b1^c$	0	$\underline{\mathbf{2^a2^b1^c}}$	$2^a1^b2^c$	$2^a1^b3^c$	$2^a1^b2^c$
$2^a1^b4^c$	$2^a3^b3^c$	$2^a3^b2^c$	$2^a2^b1^c$	0	$\underline{\mathbf{2^a1^b1^c}}$	$2^a1^b4^c$	$2^a1^b3^c$
$1^a1^b5^c$	$1^a3^b4^c$	$1^a3^b3^c$	$1^a2^b2^c$	$1^a2^b1^c$	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

Appendix 2.

The best observed correlations between values of physicochemical properties (PCP) and mutually optimized combinations of vertex degree weighted path indices using two-digit values of exponents and factors k_N in $\sum P_N$ (a, b, ...)$\times k_N$ for physicochemical properties MON, Tc^2/Pc, n_D, BP, Tc, dc and logVP.

MON

Table MON. The best-observed mutually optimized combinations of vertex degree weighted path indices using two-digit values of exponents and factors k_N in the case of MON.

| P_N(a, b, ...)	k_N	R	IC (%)
P_4(0.71, –1.08, 0.22, –3.4, 2.2)	–0.021	0.983	36.8
P_3(–1.12, –2.7, –3.2, –0.030)	–0.459	0.961	32.5
P_2(–1.33, –6.0, –0.83)	0.204	–0.909	26.3
P_1(0.040, 0.132)	0.316	–0.158	0.5
$\sum P_N$(a, b, ...)$\times k_N$		0.9993	96.2
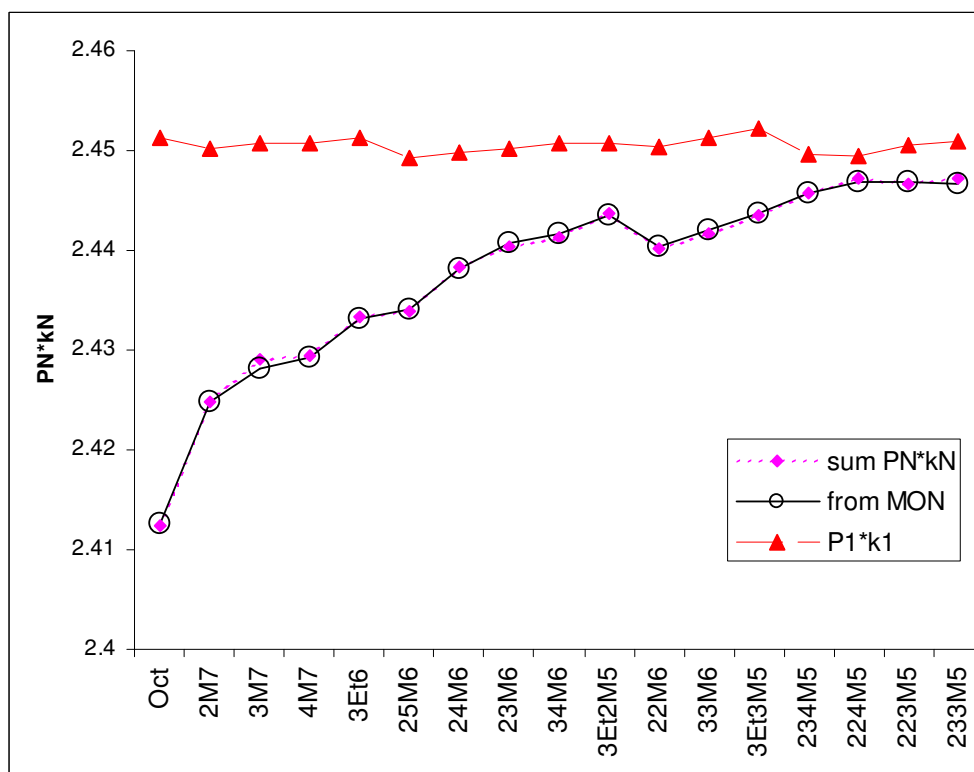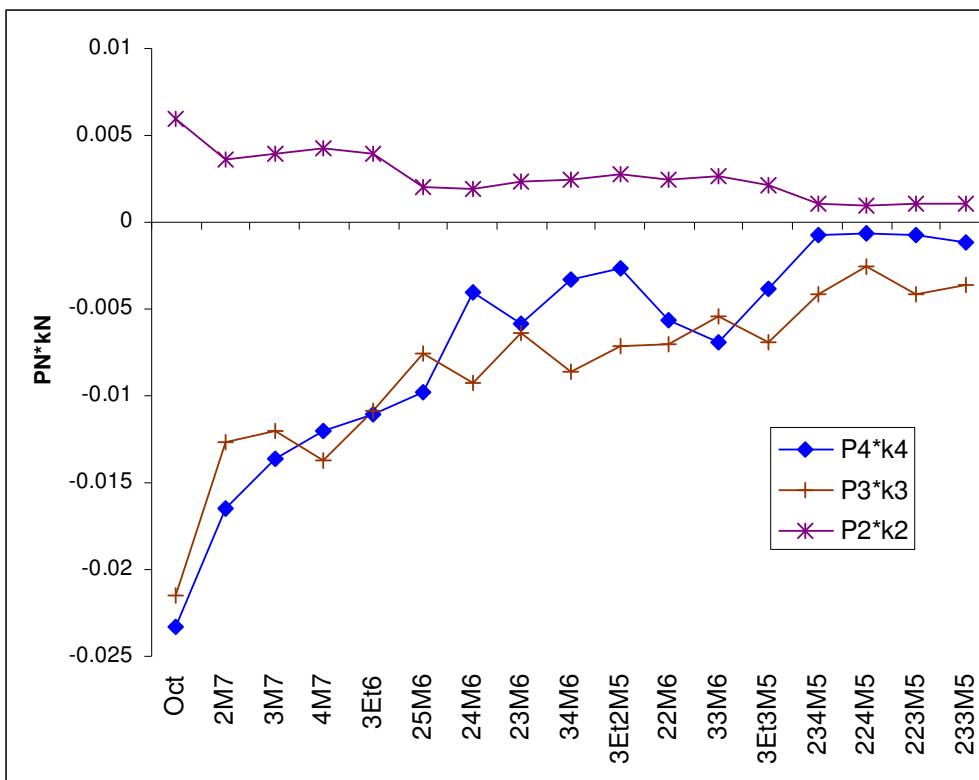
Figure MON. Contribution of particular vertex degree weighted path indices to the optimized combined topological index derived from them in the case of MON of octanes using two-digit values of exponents and factors k_N.

Table Tc^2/Pc. The best-observed mutually optimized combinations of vertex degree weighted path indices using two-digit values of exponents and factors k_N in the case of Tc^2/Pc.

| $P_N(a, b, ...)$	k_N	R	IC (%)
$P_4(1.01, -0.62, 0.28, -2.3, 2.0)$	0.025	0.963	41.8
$P_1(-0.165, -0.047)$	0.138	0.961	41.4
$P_2(-0.92, -2.7, -1.64)$	0.152	0.555	9.6
$P_3(-\infty, -1.53, -3.1, -1.38)$	0.685	-0.209	1.3
$\sum P_N(a, b, ...) \times k_N$		0.998	94.1
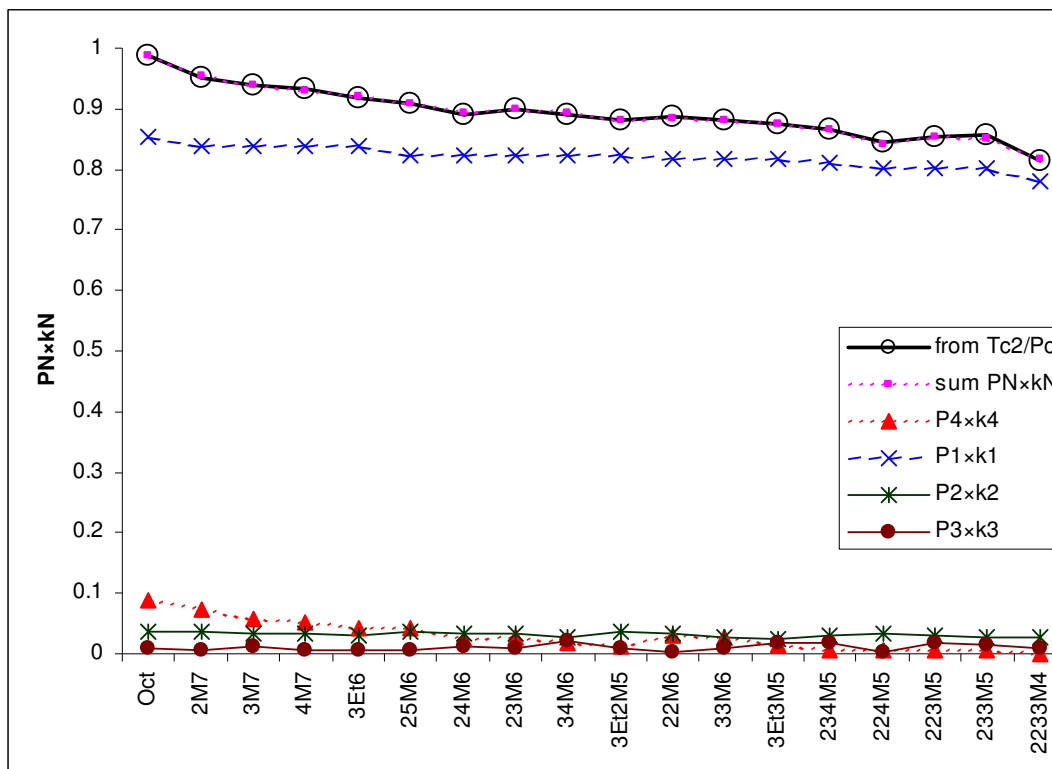
Figure Tc^2/Pc. Contribution of particular vertex degree weighted path indices to the optimized combined topological index derived from them in the case of Tc^2/Pc of octanes using two-digit values of exponents and factors k_N.

Table BP. The best-observed mutually optimized combinations of vertex degree weighted path indices using two-digit values of exponents and factors k_N in the case of BP.

| $P_N(a, b, ...)$	k_N	R	IC (%)
$P_1(-0.40, 1.68)$	-0.0911	0.906	49.8
$P_4(1.04, -2.3, 0.44, -4.1, 2.7)$	0.4223	0.648	20.6
$P_3(-2.0, -1.43, -0.82, 0.020)$	0.4816	0.592	16.8
$P_2(0.63, -0.71, 2.9)$	-0.0050	-0.163	1.1
$\sum P_N(a, b, ...) \times k_N$		0.993	88.3
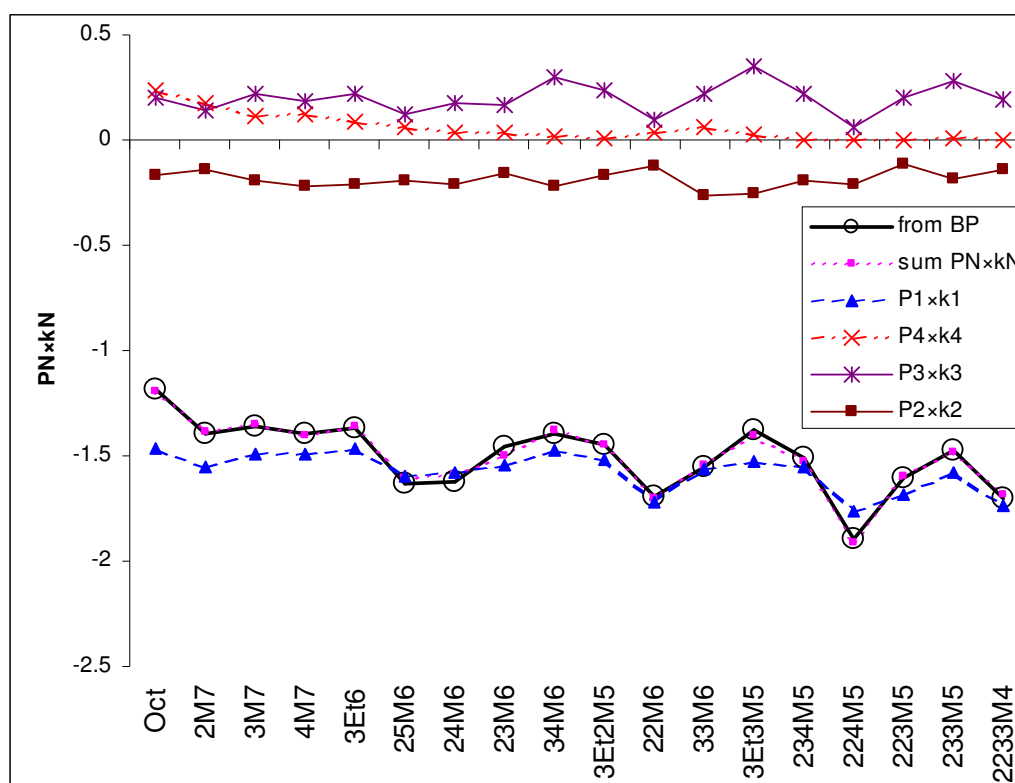
Figure BP. Contribution of particular vertex degree weighted path indices to the optimized combined topological index derived from them in the case of BP of octanes using two-digit values of exponents and factors k_N.

Table n_D. The best-observed mutually optimized combinations of vertex degree weighted path indices using two-digit values of exponents and factors k_N in the case of n_D.

| $P_N(a, b, ...)$	k_N	R	IC (%)
$P_4(0.63, 0.69, -4.0, 2.6, 2.0)$	-0.052	0.965	44.9
$P_3(-0.174, -0.13, -0.63, 0.091)$	0.400	0.923	37.5
$P_1(-\infty, 0.86)$	-0.414	0.358	4.0
$P_2(-4.2, 0.24, 0.65)$	0.134	-0.168	0.9
$\sum P_N(a, b, ...) \times k_N$		0.992	87.4
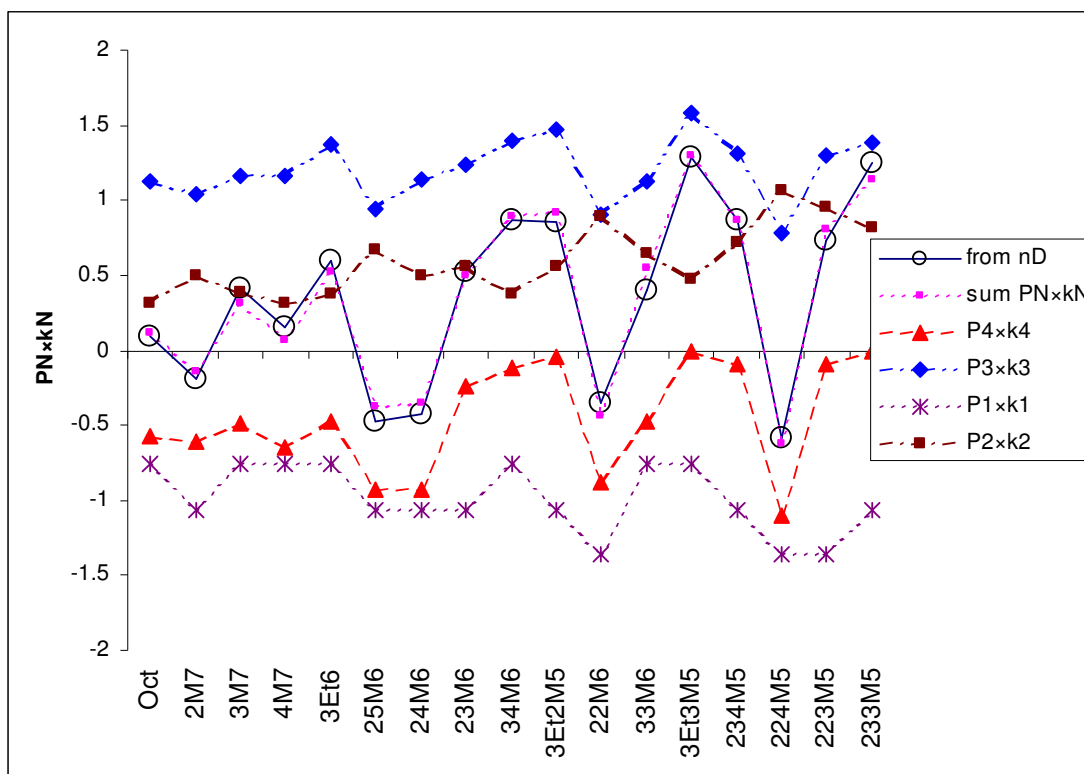
Figure n_D. Contribution of particular vertex degree weighted path indices to the optimized combined topological index derived from them in the case of n_D of octanes using two-digit values of exponents and factors k_N.

Table Tc. The best-observed mutually optimized combinations of vertex degree weighted path indices using two-digit values of exponents and factors k_N in the case of Tc.

$P_N(a, b, ...)$	k_N	R	IC (%)
$P_4(0.65, 1.06, 0.063, 0.97, -0.154)$	-0.018751	0.851	31.0
$P_2(3.5, -6.1, 3.0)$	0.004864	-0.773	23.9
$P_3(3.8, 1.34, 1.79, 1.51)$	7.6E–05	-0.729	20.7
$P_1(-0.115, 1.23)$	-0.976309	0.628	14.5
$\sum P_N(a, b, ...) \times k_N$		0.995	90.1
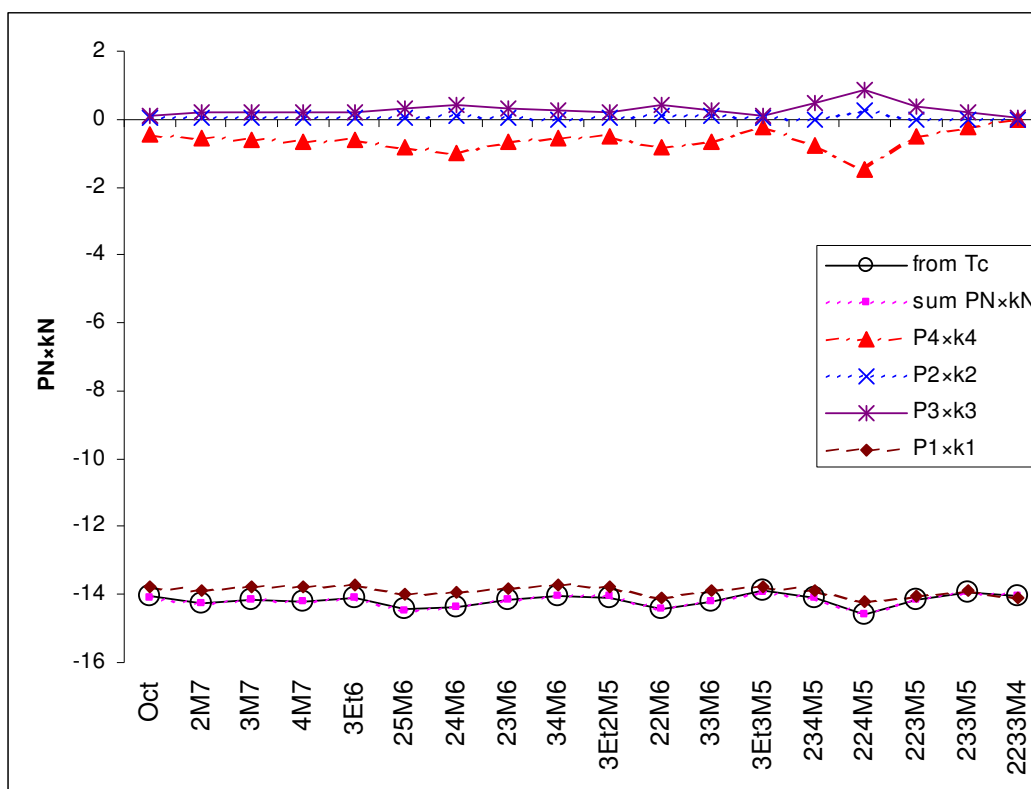
Figure Tc. Contribution of particular vertex degree weighted path indices to the optimized combined topological index derived from them in the case of Tc of octanes using two-digit values of exponents and factors k_N.

Table dc. The best-observed mutually optimized combinations of vertex degree weighted path indices using two-digit values of exponents and factors k_N in the case of dc.

$P_N(a, b, ...)$	k_N	R	IC (%)
P_3(1.16, 2.4, 0.072, 1.47)	0.00363	0.840	31.5
P_1(–0.55, –2.1)	–0.49733	–0.689	19.0
P_4(4.1, –3.9, 3.9, –2.1, 0.14)	0.00113	–0.430	6.7
P_2(–0.19, –0.78, 0.30)	0.49791	0.029	0.028
$\sum P_N(a, b, ...) \times k_N$		0.904	57.2
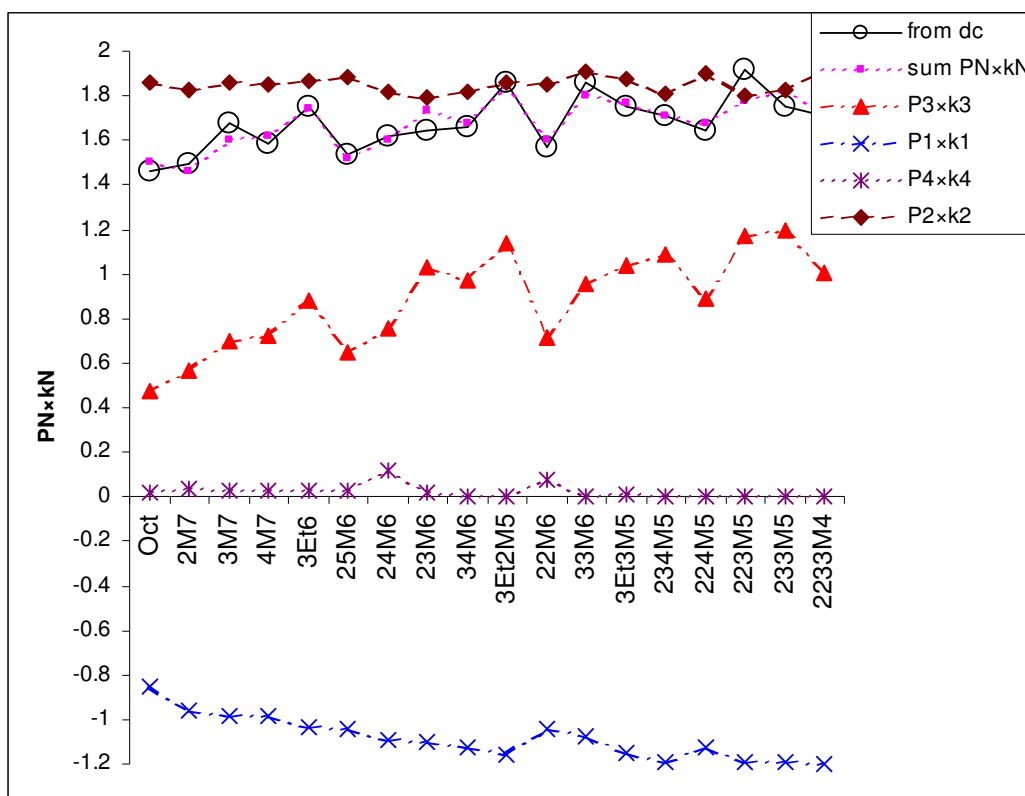
Figure dc. Contribution of particular vertex degree weighted path indices to the optimized combined topological index derived from them in the case of dc of octanes using two-digit values of exponents and factors k_N.

Table logVP. The best-observed mutually optimized combinations of vertex degree weighted path indices using two-digit values of exponents and factors k_N in the case of logVP.

$P_N(a, b, ...)$	k_N	R	IC (%)
$P_1(-3.6, -1.24)$	0.603	−0.682	31.2
$P_2(0.50, -1.31, -\infty)$	0.352	0.462	13.2
$P_3(-\infty, -8.6, 1.62, 6.0)$	−0.021	0.449	12.4
$P_4(0.98, 2.3, -3.5, 0.71, 1.29)$	0.024	0.364	8.0
$\sum P_N(a, b, ...) \times k_N$		0.936	64.8
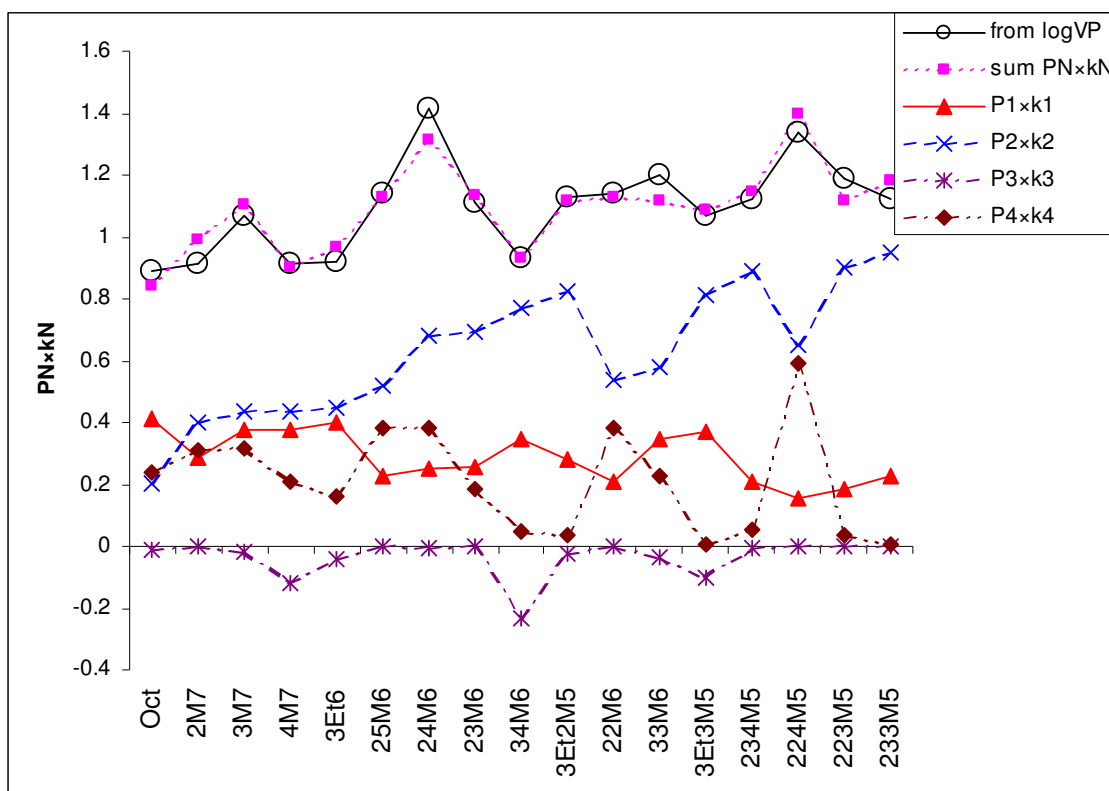
Figure logVP. Contribution of particular vertex degree weighted path indices to the optimized combined topological index derived from them in the case of logVP of octanes using two-digit values of exponents and factors k_N.

Ordering of octane isomers based on vertex degree weighted path indices $P_N(a, b, ...)$
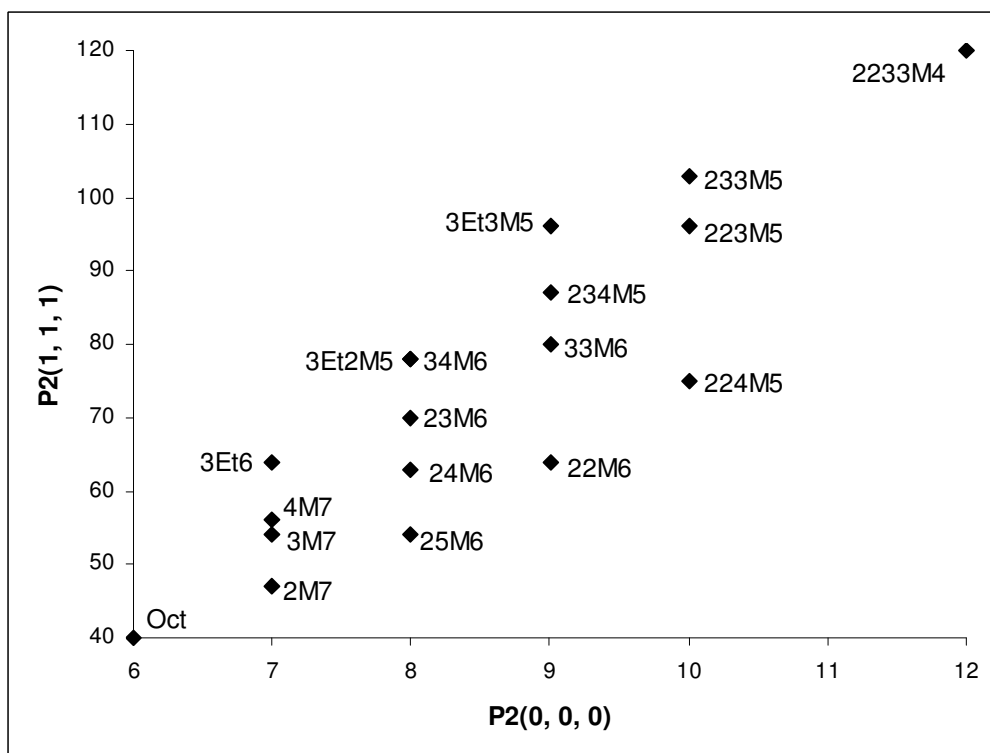
Figure A3a. Ordering of octane isomers based on vertex degree weighted path indices $P_2(0, 0, 0)$ and $P_2(1, 1, 1)$.
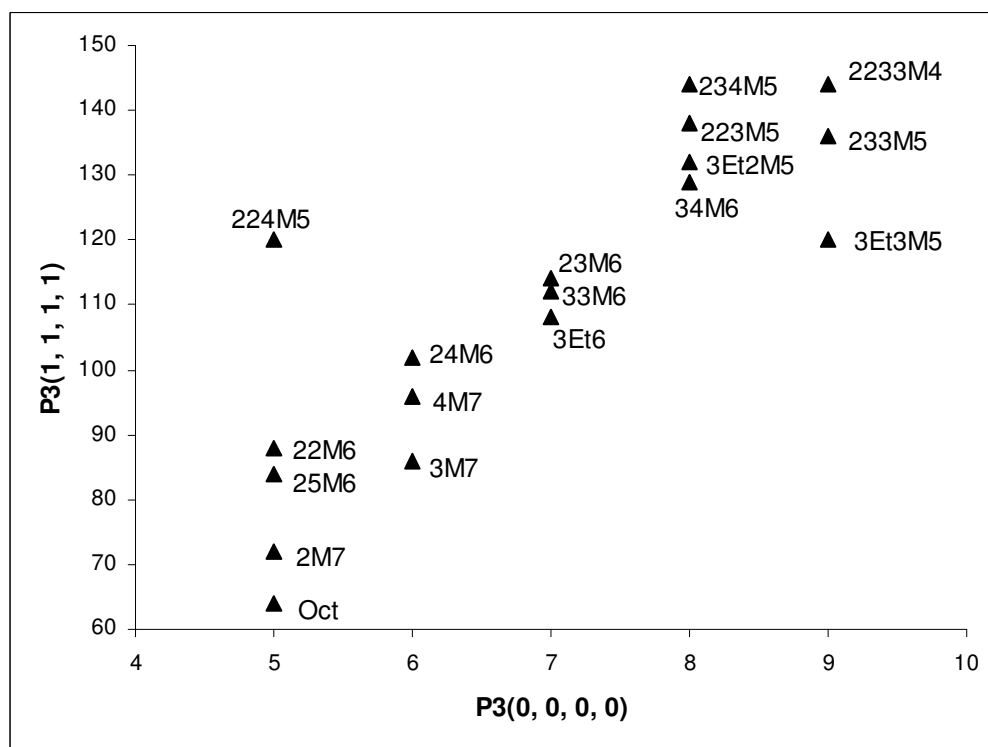
Figure A3b. Ordering of octane isomers based on vertex degree weighted path indices $P_3(0, 0, 0, 0)$ and $P_3(1, 1, 1, 1)$.
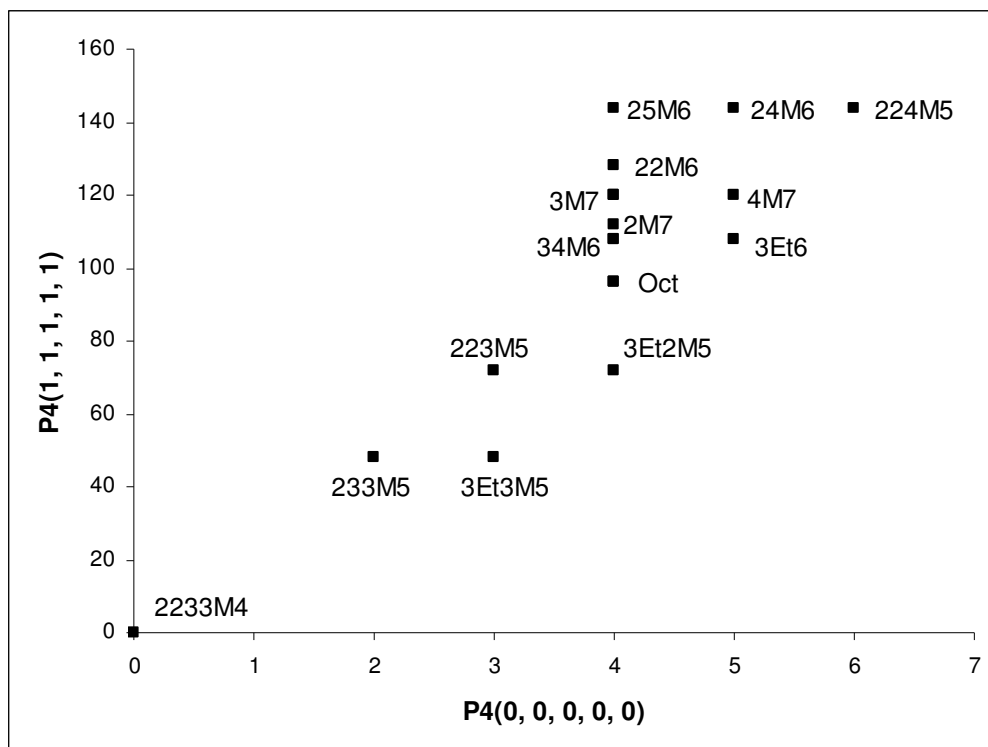
Figure A3c. Ordering of octane isomers based on vertex degree weighted path indices $P_4(0, 0, 0, 0, 0)$ and $P_4(1, 1, 1, 1, 1)$.
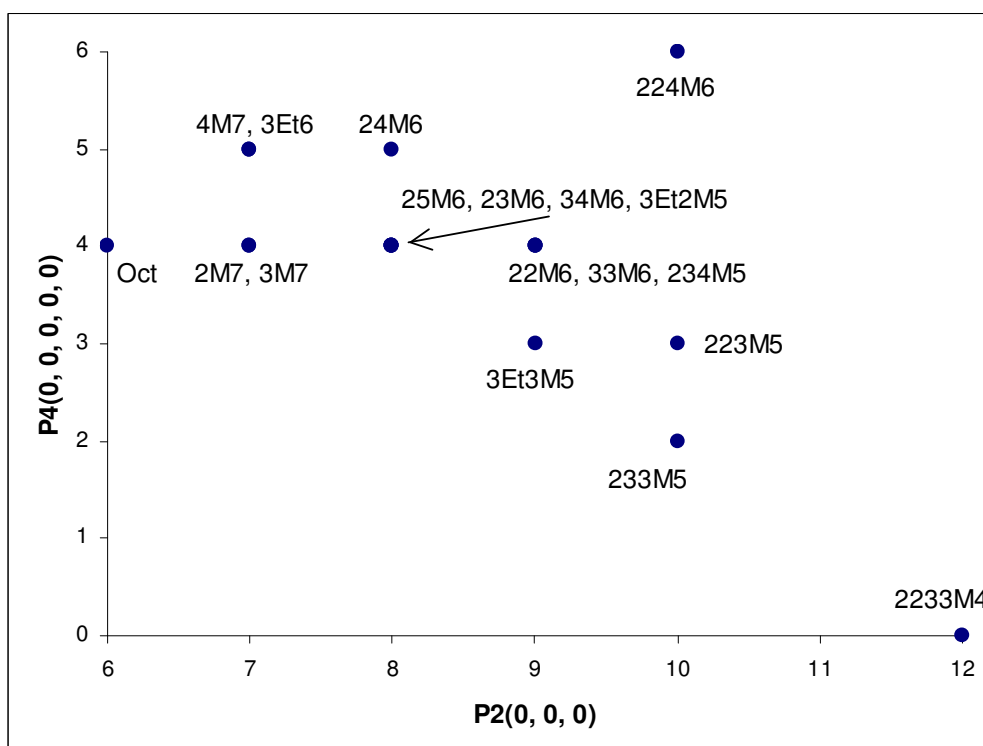
Figure A3d. Ordering of octane isomers based on vertex degree weighted path indices $P_2(0, 0, 0)$ and $P_4(0, 0, 0, 0, 0)$.
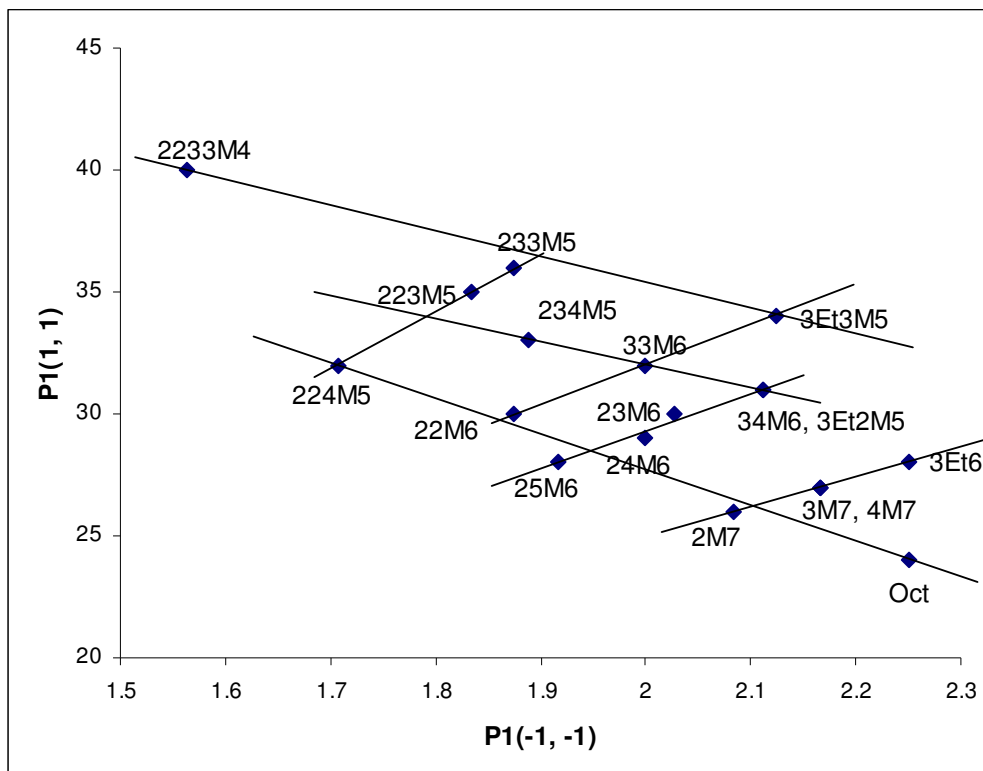
Figure A3e. Ordering of octane isomers based on vertex degree weighted path indices $P_1(-1, -1)$ and $P_1(1, 1)$.
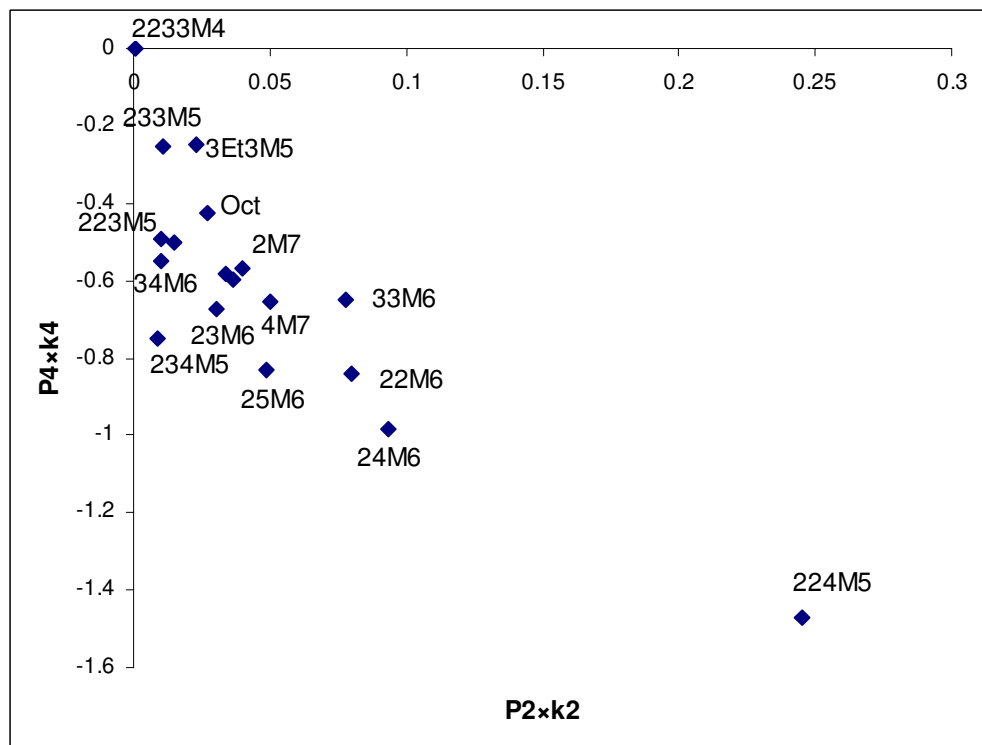
Figure A3f. Ordering of octane isomers based on vertex degree weighted path indices $P_2(3.5, -6.1, 3.0)$ and $P_4(0.65, 1.06, 0.063, 0.97, -0.154)$, which contribute together 54.9% of information about Tc of octanes.
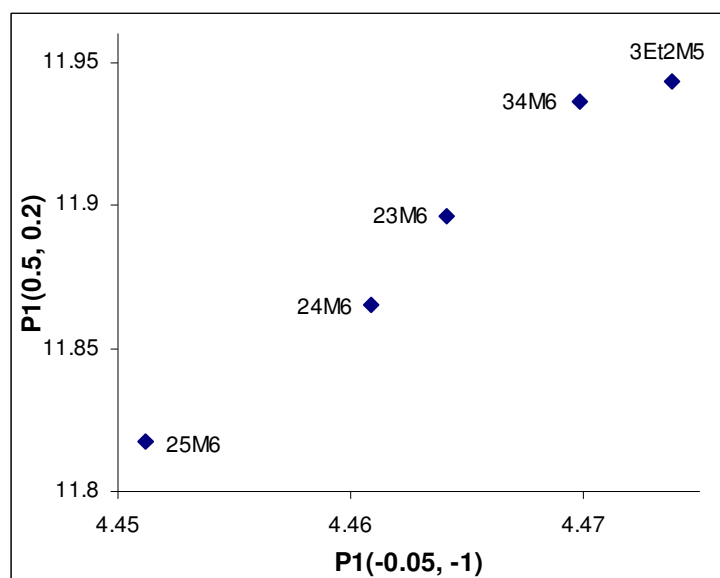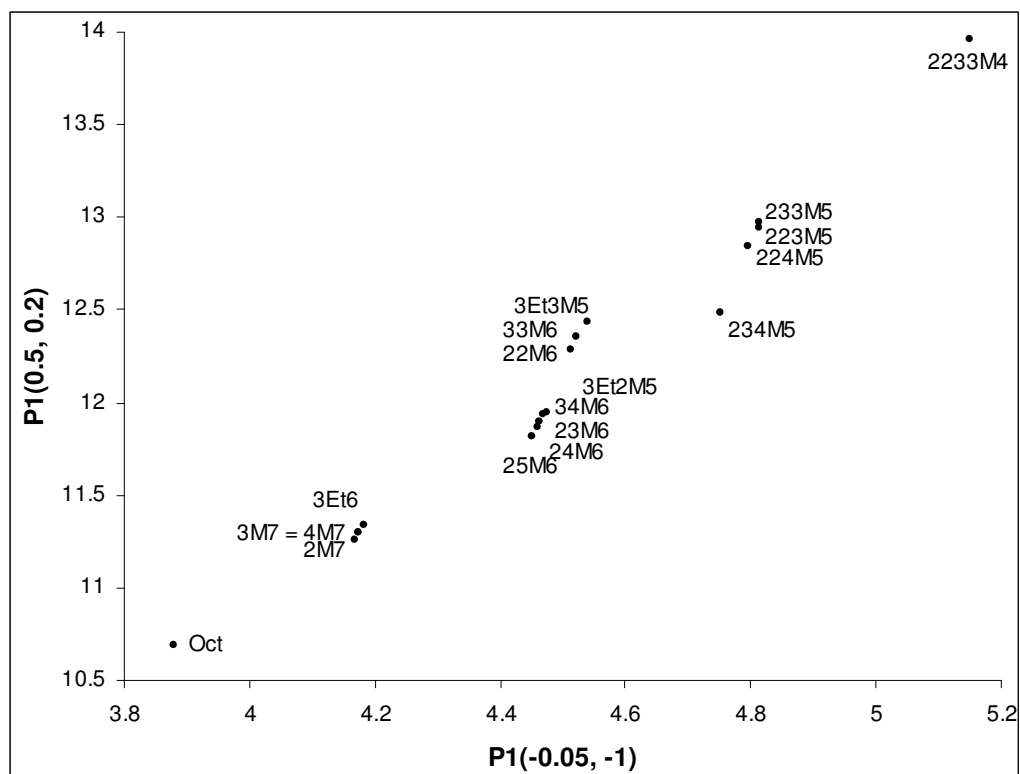
Figure A3g. Ordering of octane isomers based on vertex degree weighted path index $P_1(-0.05, -1)$ and $P_1(0.5, 0.2)$, presenting the "regular" sequence of octane isomers based on this index.

Appendix 4

Values of exponents, which give rise to the following sequence of octane isomers of increasing branching: Oct < 2M7 < 3M7 < 4M7 < 3Et6 < 25M6 < 24M6 < 23M6 < 34M6 < 3Et2M5 < 22M6 < 33M6 < 3Et3M5 < 234M5 < 224M5 < 223M5 < 233M5 < 2233M4.
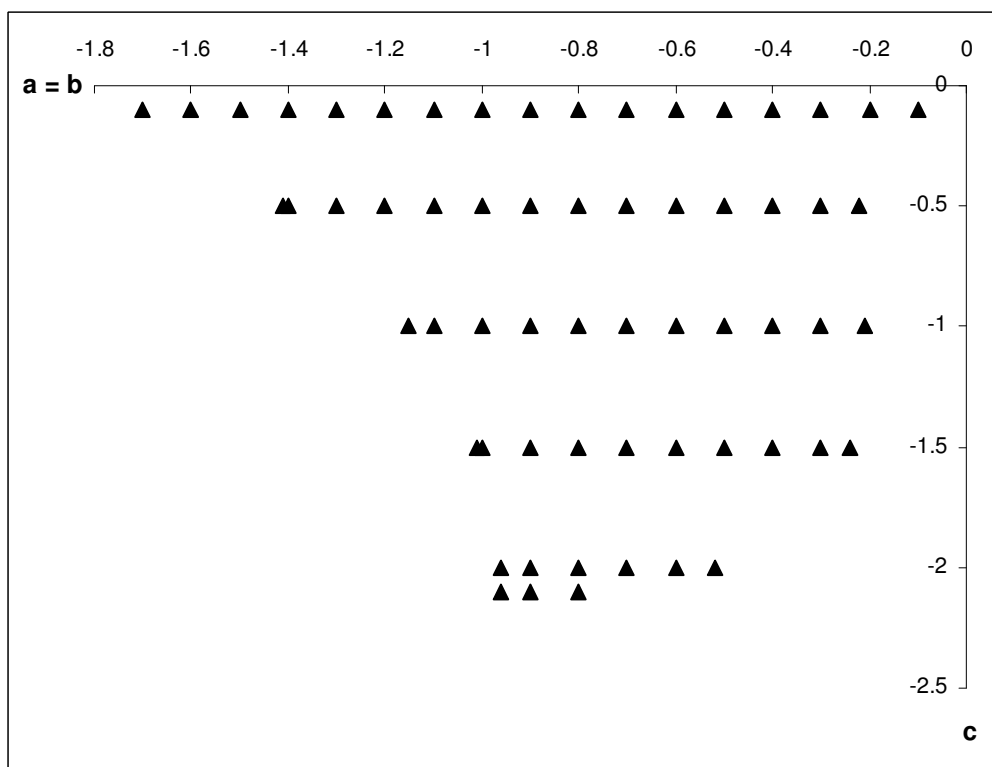
Figure A4a. Values of exponents, which give rise to the above sequence of octane isomers of increasing branching at the index $V_L(a, b, c)$ in the case of a = b vs. c.
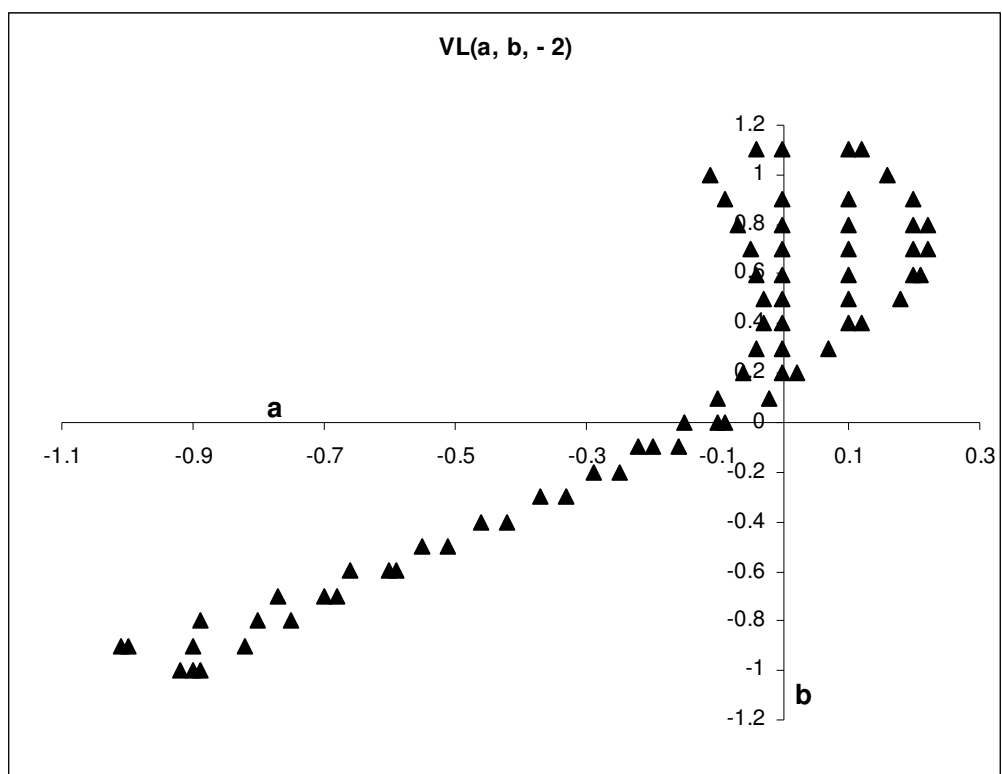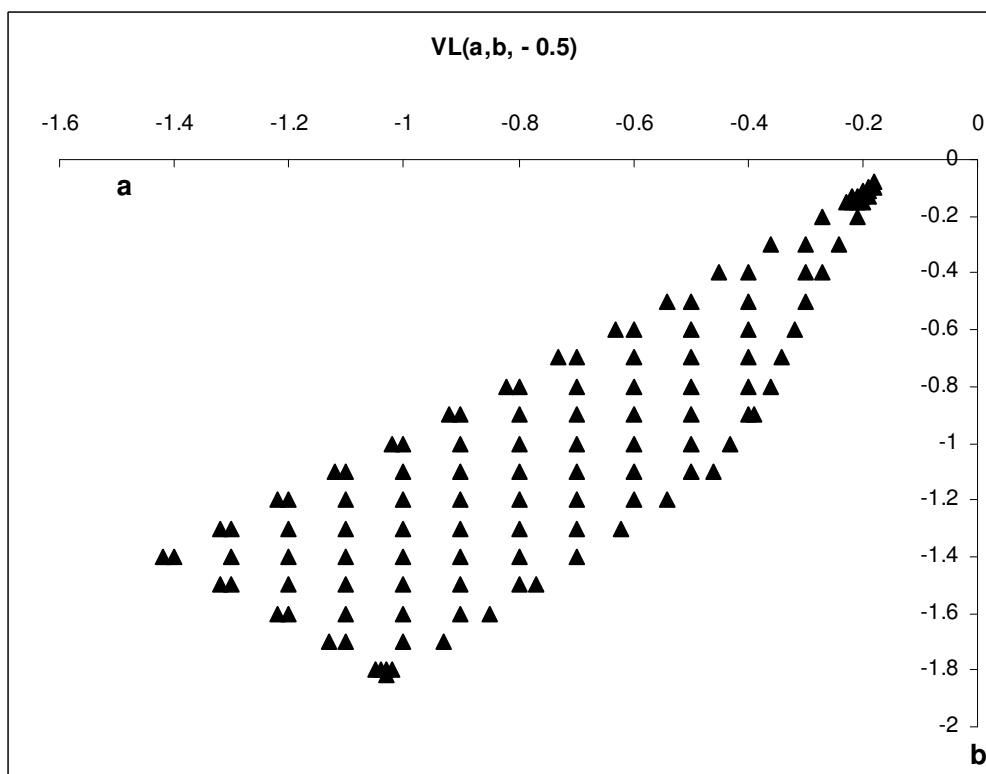
Figure A4b. Values of exponents, which give rise to the above sequence of octane isomers of increasing branching at the index $V_L(a, b, c)$ in the case of a vs. b at $c = -0.5$ resp. at $c = -2$.
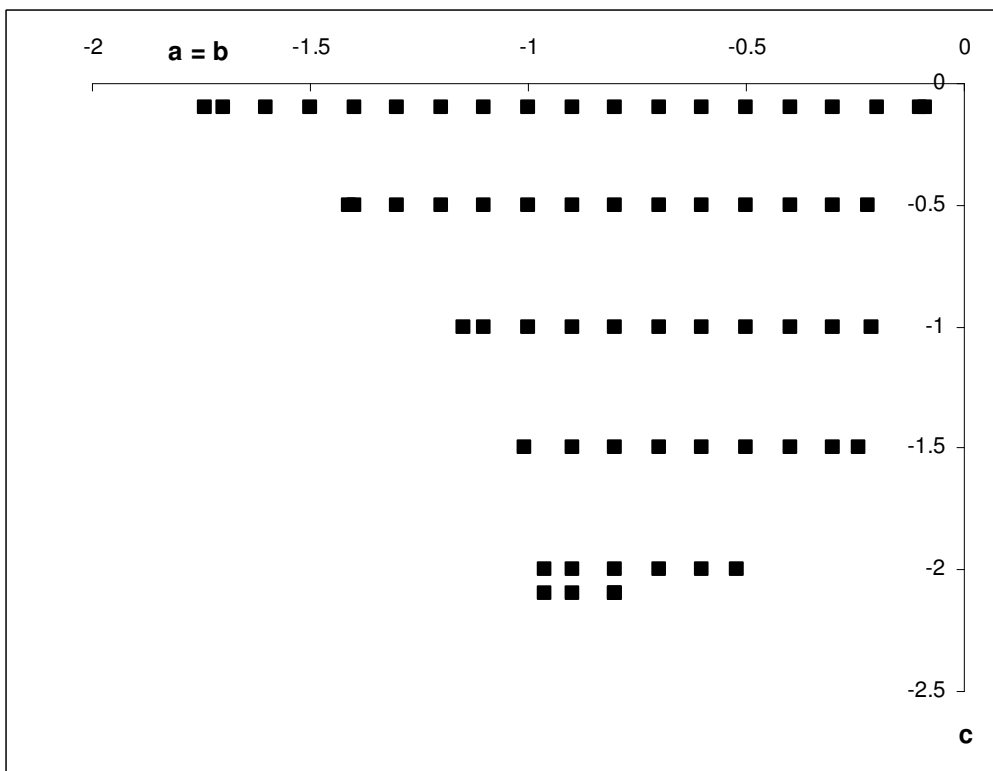
Figure A4c. Values of exponents, which give rise to the above sequence of octane isomers of increasing branching at the index $V_{wm}(a, b, c)$ for the case $a = b$ vs. c.
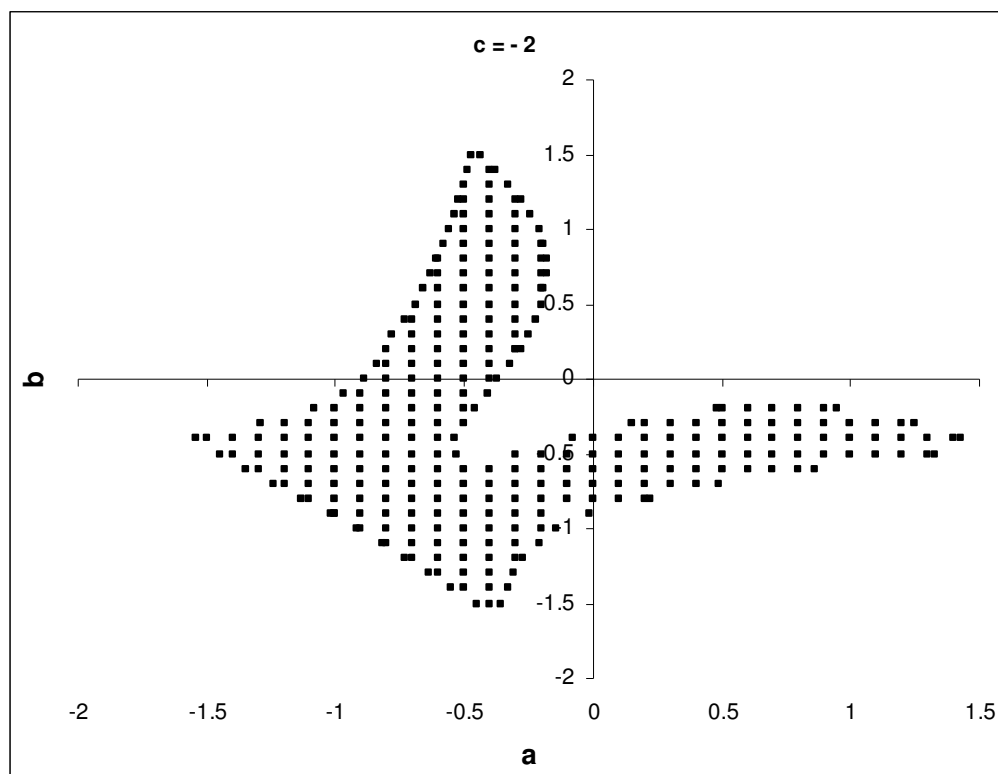

Figure A4d. Values of exponents, which give rise to the above sequence of octane isomers of increasing branching at the index $V_{wm}(a, b, c)$ in the case of a vs. b at $c = –2$.
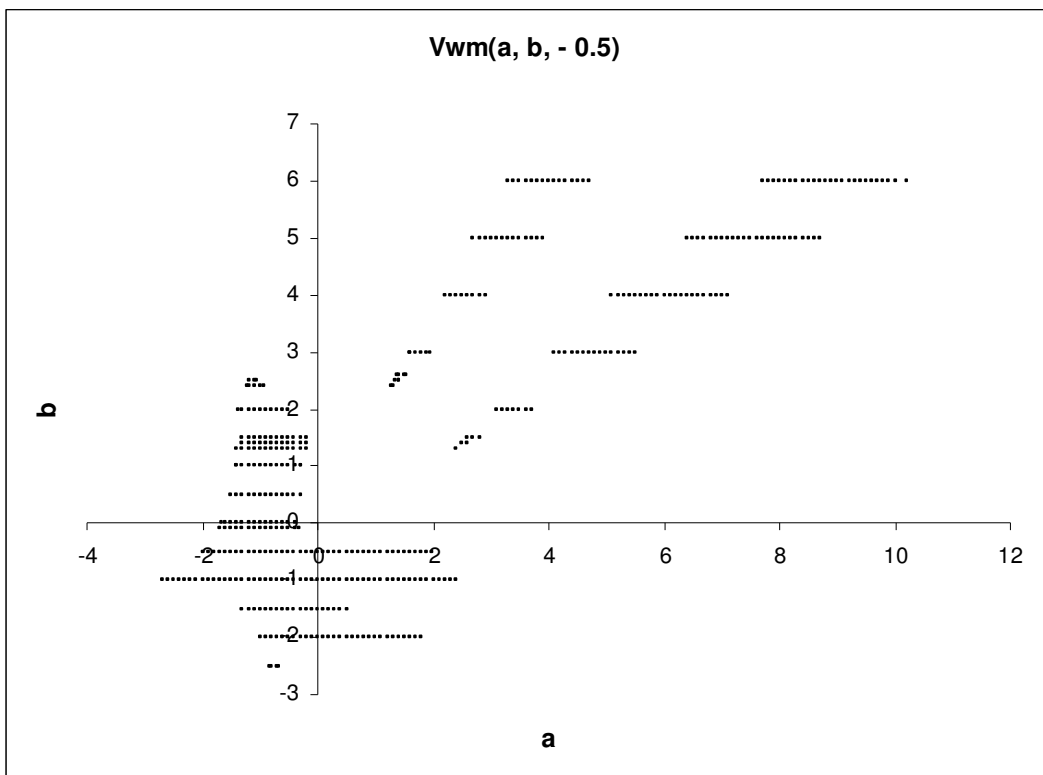
Figure A4e. Values of exponents, which give rise to the above sequence of octane isomers of increasing branching at the index $V_{wm}(a, b, c)$ in the case of a vs. b at c = –0.5.
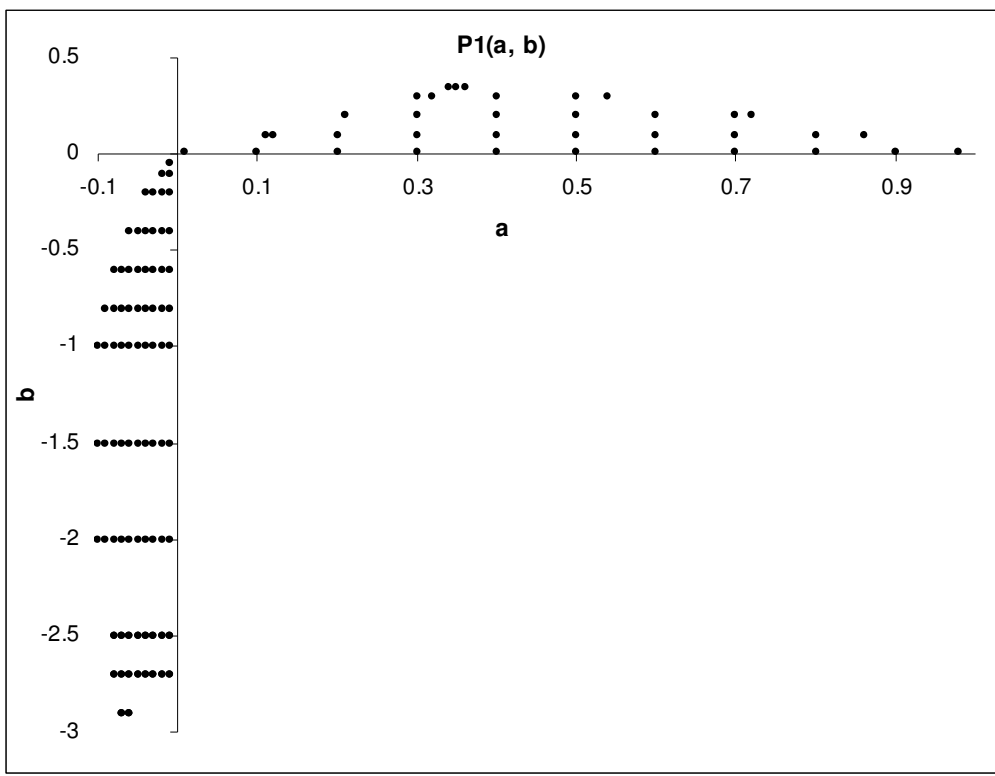
Figure A4f. Values of exponents, which give rise to the above sequence of octane isomers of increasing branching at the vertex degree weighted path one index $P_1(a, b)$. In all cases, $P_1(a, b)$ of 3M7 = $P_1(a, b)$ of 4M7.