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 + ·OH → R·, and the addition of oxygen onto R· are quite nonselective, the reactions which follow these steps are mainly intramolecular, slower and more selective. The rate of the intramolecular hydrogen abstraction ROO· → ·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 A4b.

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

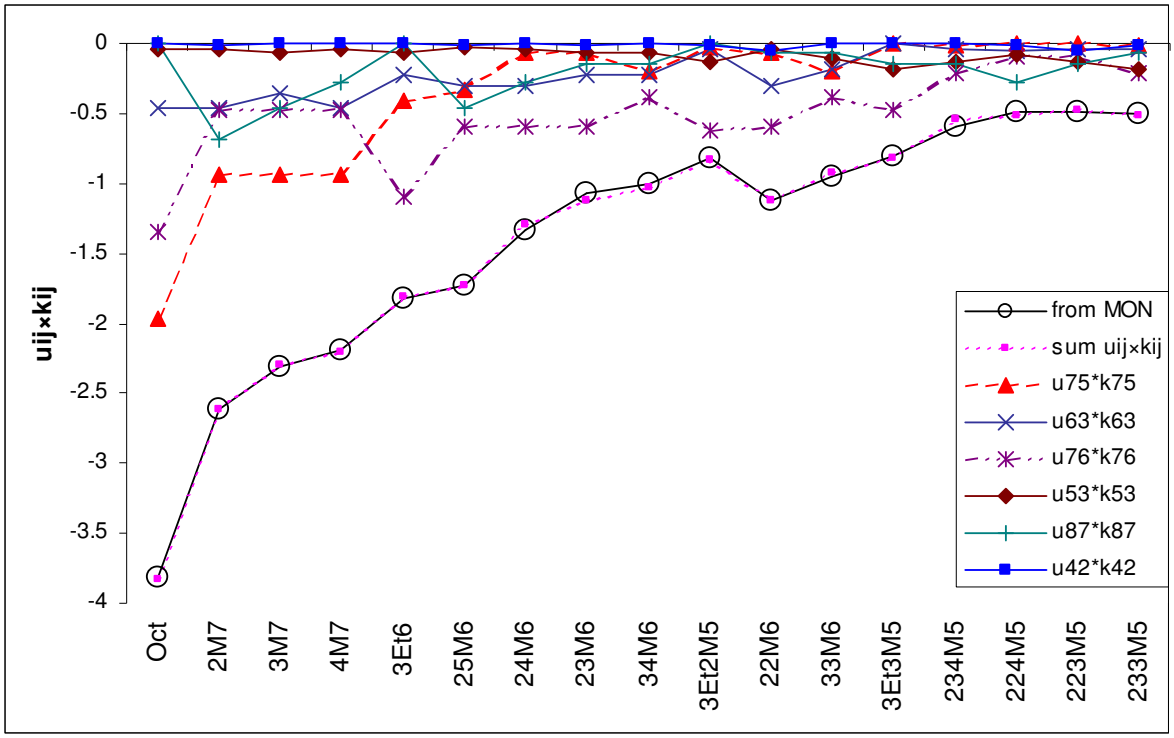

Figure A4. Contribution of particular matrix elements (u_{75}, u_{63}, u_{76}, u_{53}, u_{87}, and u_{42}) to the best observed optimized combined topological index derived from them in the case of MON.

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.