CROATICA CHEMICA ACTA
CCACAA **80** (2) 169–179 (2007)

ISSN-0011-1643
CCA-3157
Original Scientific Paper

A Graph Theoretical Method for Partial Ordering of Alkanes*

Damir Vukičević,[a,] Jelena Sedlar,[b] and Sarah Michele Rajtmajer[c]**

[a]*Faculty of Science, University of Split, Nikole Tesle 12, 21000 Split, Croatia*

[b]*Faculty of Civil Engineering and Architecture, University of Split, Matice hrvatske 15, 21000 Split, Croatia*

[c]*Ruđer Bošković Institute, P. O. Box 180, 10002 Zagreb, Croatia*

RECEIVED SEPTEMBER 15, 2006; REVISED FEBRUARY 12, 2007; ACCEPTED FEBRUARY 14, 2007

Keywords
Zagreb index M_1
modified Zagreb index ${}^{\lambda}M_1$
partial order

The topological Zagreb index M_1 introduces an ordering on the set of alkanes. Recently, modified Zagreb indices ${}^{\lambda}M_1$ have been proposed, and it is noted that they differently order alkanes. In this paper, the level of consistency between these orders is analyzed. A new partial order $\succ$ as the intersection of all partial orders ${}^{\lambda}M_1$ (where m is at least 2) is introduced and its properties are analyzed.

INTRODUCTION

Over 30 years ago, topological indices named Zagreb indices and denoted M_1 and M_2 were introduced.[1] Variants of these indices were introduced and studied as well. The most famous example is the descriptor for characterizing molecular branching, first introduced by Randić,[2] which was soon named the connectivity index and later generalized to connectivity indices of various orders.[3] The first-order connectivity index is similar to the Zagreb M_2 index.

Recently, it has been noticed that Zagreb indices in their basic form are not best suited for modeling the contributions of some parts of a molecule to its physical, chemical and biological properties. Hence, modified Zagreb indices denoted ${}^{m}M_1$ and ${}^{m}M_2$ were proposed and studied.[4,5] Another variant of Zagreb indices has also been introduced and researched recently, namely the Zagreb complexity indices.[4,6] Zagreb indices and their variants have been used to study molecular complexity,[6,7] chirality,[8] *ZE*-isomerism[9] and heterosystems.[10] Mathematical properties of Zagreb indices have been studied as well.[11]

In this paper, we will establish a graph theoretical method for partially ordering alkanes based on a variant of the Zagreb index M_1, and we will therefore use concepts and terminology from graph theory, like many authors before us who studied the Zagreb indices.

An alkane is a molecular compound represented by a simple, acyclic graph, *i.e.,* a graph with no loops, multiple edges, or cycles. Here, we will be analyzing kenographs,[12] *i.e.,* graphs in which vertices representing hydrogen atoms will be suppressed. In our paper, alkanes with n carbon atoms are partitioned into classes represented by 4-tuples (n_1, n_2, n_3, n_4) where n_i represents the number of vertices of degree i in the graph of an alkane.

${}^{\lambda}M_1$ is a variant of the Zagreb index M_1 with ${}^{2}M_1$ being precisely equal to M_1. Based on ${}^{\lambda}M_1$, we define a partial ordering of alkanes and investigate how the fraction of orderable pairs depends on the number of carbon atoms.

* Dedicated to Professor Haruo Hosoya in happy celebration of his 70th birthday.

** Author to whom correspondence should be addressed. (E-mail: vukicevi@pmfst.hr)

Many properties of this ordering are proven, and a table containing the number N of different classes of alkanes on n vertices, the number $\binom{N}{2}$ of all possible pairs of classes of alkanes, the number e of all orderable pairs of classes of alkanes, and finally the fraction $e/\binom{N}{2}$ of orderable pairs is presented for n = 5, K, 50. Asymptotic behavior is also studied. These results may represent a contribution to studies of partial orders in chemistry.

PRELIMINARIES

Let us choose an arbitrary integer $n \geq 1$ and then fix it. For a chosen n, consider all alkanes with n carbon atoms, *i.e.,* all simple connected acyclic graphs with n vertices. Furthermore, let (n_1, n_2, n_3, n_4) represent the class of alkanes, *i.e.,* simple connected acyclic graphs with n vertices containing n_1 vertices of degree 1, n_2 vertices of degree 2, n_3 vertices of degree 3, and n_4 vertices of degree 4. Note that $n = n_1 + n_2 + n_3 + n_4$. For the sake of simplicity, we say that (n_1, n_2, n_3, n_4) represents an alkane instead of the class of alkanes in further text. Let G be the graph of an alkane (n_1, n_2, n_3, n_4) with a set of vertices V(G) and a set of edges E(G). Note that $|V(G)| = n$ and let $e := |E(G)|$.

Futhermore, note that:

$$^{\lambda}M_1(n_1, n_2, n_3, n_4) := \sum_{v \in V(G)} d_G(v)^{\lambda}.$$

Therefore, $^{\lambda}M_1(n_1, n_2, n_3, n_4) = 1^{\lambda}n_1 + 2^{\lambda}n_2 + 3^{\lambda}n_3 + 4^{\lambda}n_4$.

Now let (a_1, a_2, a_3, a_4) and (b_1, b_2, b_3, b_4) represent two alkanes. We say that $(a_1, a_2, a_3, a_4) \succ (b_1, b_2, b_3, b_4)$ if and only if $^{\lambda}M_1(a_1, a_2, a_3, a_4) > {}^{\lambda}M_1(b_1, b_2, b_3, b_4)$ for every $\lambda \in [2, \infty)$ or $(a_1, a_2, a_3, a_4) = (b_1, b_2, b_3, b_4)$. Obviously, relation "$\succ$" is reflexive, transitive and antisymmetric. Therefore, relation "$\succ$" is a partial order relation. Also, if $(a_1, a_2, a_3, a_4) \succ (b_1, b_2, b_3, b_4)$, we also say $(b_1, b_2, b_3, b_4) \prec (a_1, a_2, a_3, a_4)$. Since the focus of our interest is on the pairs of different alkanes being related, in further text we will omit the relation of the alkane to itself.

We will show that n_1 and n_2 depend on n_3 and n_4. We have $2e = \sum_{v \in V(G)} d_G(v)$ from the handshaking lemma and $e = n - 1$ since G is acyclic. Combining these two facts we get:

$$2(n_1 + n_2 + n_3 + n_4 - 1) = n_1 + 2n_2 + 3n_3 + 4n_4$$

$$n_1 = n_3 + 2n_4 + 2 \qquad (1)$$

Hence,

$$n_2 = n - 2n_3 - 3n_4 - 2\,. \qquad (2)$$

Now that we have expressed n_1 and n_2 dependent on n_3 and n_4, there is no longer a need to represent alkanes with 4-tuples (n_1, n_2, n_3, n_4). Instead, we will represent them with ordered pairs (n_3, n_4), calculating n_1 and n_2 using (1) and (2). Also using (1) and (2), we show the following:

$$^{\lambda}M_1(n_1, n_2, n_3, n_4) = 1n_1 + 2^{\lambda}n_2 + 3^{\lambda}n_3 + 4^{\lambda}n_4 =$$

$$(n_3 + 2n_4 + 2) + 2^{\lambda}(n - 2n_3 - 3n_4 - 2) + 3^{\lambda}n_3 + 4^{\lambda}n_4.$$

Thus, $^{\lambda}M_1(n_1, n_2, n_3, n_4)$ depends only on n_3 and n_4 as well, and can therefore be denoted $^{\lambda}M_1(n_3, n_4)$. Consequently, our partial order relation "$\prec$" becomes:

$(a_3, a_4) \succ (b_3, b_4)$ iff

$$^{\lambda}M_1(a_3, a_4) > {}^{\lambda}M_1(b_3, b_4),\ \forall\, \lambda \in [2, \infty),$$

i.e.,

$(a_3, a_4) \succ (b_3, b_4)$ iff

$$[(a_3 + 2a_4 + 2) + 2^{\lambda}(a - 2a_3 - 3a_4 - 2) + 3^{\lambda}a_3 + 4^{\lambda}a_4] -$$

$$[(b_3 + 2b_4 + 2) + 2^{\lambda}(b - 2b_3 - 3b_4 - 2) + 3^{\lambda}b_3 + 4^{\lambda}b_4] > 0$$

for every $\lambda \in [2, \infty)$. To simplify the expression on the right side of this equivalence, it is helpful to let $x_3 := a_3 - b_3$ and $x_4 := a_4 - b_4$. It then becomes:

$$x_3\,(1 - 2 \cdot 2^{\lambda} + 3^{\lambda}) + x_4\,(2 - 3 \cdot 2^{\lambda} + 4^{\lambda}) > 0\,.$$

We have

$(a_3, a_4) \succ (b_3, b_4)$ iff

$$x_3(1 - 2 \cdot 2^{\lambda} + 3^{\lambda}) + x_4(2 - 3 \cdot 2^{\lambda} + 4^{\lambda}) > 0,\ \forall\, \lambda \in [2, \infty)\,.$$

Now we will establish the necessary and sufficient conditions on x_3 and x_4 such that $(a_3, a_4) \succ (b_3, b_4)$. In other words, we will establish the necessary and sufficient conditions on x_3 and x_4 such that $x_3(1 - 2 \cdot 2^{\lambda} + 3^{\lambda}) + x_4(2 - 3 \cdot 2^{\lambda} + 4^{\lambda}) > 0$ for every $\lambda \in [2, \infty)$.

Lemma 1. – If $x_3(1 - 2 \cdot 2^{\lambda} + 3^{\lambda}) + x_4(2 - 3 \cdot 2^{\lambda} + 4^{\lambda}) > 0$ for every $\lambda \in [2, \infty)$, then $x_4 \geq 0$.

Proof: Suppose the opposite, *i.e.*, $x_4 < 0$ and $(x_3 + 2x_4) + 2^{\lambda}(-2x_3 - 3x_4) + 3^{\lambda}x_3 + 4^{\lambda}x_4 > 0$ for each $\lambda \in [2, \infty)$. For large lambdas, the sign of the second expression depends only on x_4. Hence, it must be $x_4 \geq 0$, which is a contradiction. ■

Theorem 2. – $(a_3, a_4) \succ (b_3, b_4)$ if and only if $(a_4 = b_4, a_3 > b_3)$ or $\left(a_4 > b_4, \dfrac{a_3 - b_3}{a_4 - b_4} > -3\right)$.

Proof: From Lemma 1, it follows that we need only consider the cases where $x_4 \ge 0$ (*i.e.*, $a_4 - b_4 \ge 0$).

CASE I: $x_4 = 0$ (*i.e.*, $a_4 - b_4 = 0$).

Let us prove that in this case $x_3(1 - 2\cdot 2^\lambda + 3^\lambda) + x_4(2 - 3\cdot 2^\lambda + 4^\lambda) > 0$ for every $\lambda \in [2, \infty)$ if and only if $x_3 > 0$. It is sufficient to prove that $1 - 2\cdot 2^\lambda + 3^\lambda > 0$ for every $\lambda \in [2, \infty)$. Since $1 - 2\cdot 2^2 + 3^2 > 0$, it is sufficient to prove that the function $f(\lambda) = 1 - 2\cdot 2^\lambda + 3^\lambda$ is increasing, *i.e.*, that $f'(\lambda) = -2\cdot 2^\lambda \cdot \ln 2 + 3\cdot 3^\lambda \ln 3 > 0$, but this is obviously true.

CASE II: $x_4 > 0$ (*i.e.* $a_4 - b_4 > 0$).

Let us prove that in this case $(a_3, a_4) \succ (b_3, b_4)$ if and only if $\dfrac{x_3}{x_4} > -3$. Since $x_4 > 0$, we can divide inequality $x_3(1 - 2\cdot 2^\lambda + 3^\lambda) + x_4(2 - 3\cdot 2^\lambda + 4^\lambda) > 0$ by x_4 and thus we obtain:

$$\frac{x_3}{x_4}(1 - 2\cdot 2^\lambda + 3^\lambda) > -2 + 3\cdot 2^\lambda - 4^\lambda,$$

$$\frac{x_3}{x_4} > \frac{-2 + 3\cdot 2^\lambda - 4^\lambda}{1 - 2\cdot 2^\lambda + 3^\lambda}.$$

Thus, we conclude that $(a_3, a_4) \succ (b_3, b_4)$ if and only if $\dfrac{x_3}{x_4} > \dfrac{-2 + 3\cdot 2^\lambda - 4^\lambda}{1 - 2\cdot 2^\lambda + 3^\lambda}$ for every $\lambda \in [2, \infty)$. Let us define $M' := \max\left\{\dfrac{-2 + 3\cdot 2^\lambda - 4^\lambda}{1 - 2\cdot 2^\lambda + 3^\lambda} : \lambda \in [2, \infty)\right\}$. Then $\dfrac{x_3}{x_4} > \dfrac{-2 + 3\cdot 2^\lambda - 4^\lambda}{1 - 2\cdot 2^\lambda + 3^\lambda}$ for every $\lambda \in [2, \infty)$ if and only if $\dfrac{x_3}{x_4} > M'$. We claim that $M' = -3$. The proof of this claim is somewhat technical, so we omit it here and prove it in Lemma 3 following this theorem. Thus, in this case, $(a_3, a_4) \succ (b_3, b_4)$ if and only if $\dfrac{x_3}{x_4} > -3$, *i.e.* $\dfrac{a_3 - b_3}{a_4 - b_4} > -3$. ■

Lemma 3. – The inequality $\dfrac{-2 + 3\cdot 2^\lambda - 4^\lambda}{1 - 2\cdot 2^\lambda + 3^\lambda} \le -3$ holds for every $\lambda \in [2, \infty)$ and the inequality is sharp.

Proof: Note that this claim is equivalent to $\dfrac{4^\lambda - 3\cdot 2^\lambda + 2}{3^\lambda - 2\cdot 2^\lambda + 1} \ge 3$. Let us define $\mathrm{Num}(\lambda) = 4^\lambda - 3\cdot 2^\lambda + 2$ and $\mathrm{Den}(\lambda) = 3^\lambda - 2\cdot 2^\lambda + 1$. It is easily calculated that:

$$\mathrm{Num}'(\lambda) - \mathrm{Den}'(\lambda) =$$
$$(\ln 4)\cdot 4^\lambda - 3\cdot(\ln 2)\cdot 2^\lambda - (\ln 3)\cdot 3^\lambda + 2\cdot(\ln 2)\cdot 2^\lambda =$$

$$(\ln 2)\cdot\left(2\cdot 4^\lambda - 2^\lambda - \frac{\ln 3}{\ln 2}\cdot 3^\lambda\right) =$$

$$(\ln 2)\cdot\left(2 - \frac{2^\lambda}{4^\lambda} - \frac{\ln 3}{\ln 2}\cdot\frac{3^\lambda}{4^\lambda}\right)\cdot 4^\lambda.$$

Since clearly $\dfrac{2^\lambda}{4^\lambda} \le \dfrac{1}{4}$ and $\dfrac{3^\lambda}{4^\lambda} \le \dfrac{9}{16}$ for $\lambda \in [2, \infty)$, we conclude that:

$$\mathrm{Num}'(\lambda) - \mathrm{Den}'(\lambda) \ge$$
$$(\ln 2)\cdot\left(2 - \frac{1}{4} - \frac{\ln 3}{\ln 2}\cdot\frac{9}{16}\right)\cdot 4^\lambda \ge 0.58\cdot 4^\lambda > 0.$$

Thus, $\mathrm{Num}(\lambda)$ increases more rapidly than $\mathrm{Den}(\lambda)$ for $\lambda \in [2, \infty)$, and so the ratio $\mathrm{Num}(\lambda) / \mathrm{Den}(\lambda)$ always exceeds its value at $\lambda = 2$. Therefore:

$$\frac{4^\lambda - 3\cdot 2^\lambda + 2}{3^\lambda - 2\cdot 2^\lambda + 1} \ge \frac{4^2 - 3\cdot 2^2 + 2}{3^2 - 2\cdot 2^2 + 1} = 3.$$ ■

THE ORDERING

Recall that we have shown that $n_1 = n_3 + 2n_4 + 2$ is a necessary condition for 4-tuple (n_1, n_2, n_3, n_4) to represent an alkane. It can be shown that it is a sufficient condition too. More precisely, the following Lemma has been proven in Ref. 14:

Lemma 4. – The 4-tuple (n_1, n_2, n_3, n_4) of nonnegative integers represents an alkane if and only if $n_1 = n_3 + 2n_4 + 2$.

Since $n_1 = n_3 + 2n_4 + 2$ is equivalent to $n_2 = n - 2n_3 - 3n_4 - 2$, where $n = n_1 + n_2 + n_3 + n_4$, we can restate Lemma 4 as follows.

Lemma 5. – Let (n_1, n_2, n_3, n_4) be a 4-tuple of nonnegative integers such that $n_1 + n_2 + n_3 + n_4 = n$. Then (n_1, n_2, n_3, n_4) represents an alkane if and only if $n_1 = n_3 + 2n_4 + 2$ and $n_2 = n - 2n_3 - 3n_4 - 2$.

Now, we will show that the pair of conditions from Lemma 5 is equivalent to a pair of conditions more convenient to us.

Lemma 6. – Let n_3 and n_4 be non-negative integers. Then, there are non-negative integers n_1 and n_2 such that $n_1 + n_2 + n_3 + n_4 = n$, $n_1 = n_3 + 2n_4 + 2$, and $n_2 = n - 2n_3 - 3n_4 - 2$ if and only if $n_3 \le \dfrac{n-2}{2}$ and $n_4 \le \dfrac{n - 2n_3 - 2}{3}$.

Proof: Let us prove necessity first. Suppose $n_1 = n_3 + 2n_4 + 2$ and $n_2 = n - 2n_3 - 3n_4 - 2$. Since $n_2 \ge 0$, we have:

$$-2n_3 \ge -n + 3n_4 - 2.$$

Since $n_4 \geq 0$, it follows that:

$$-2n_3 \geq -n + 2\,,$$

$$n_3 \leq \frac{n-2}{2}\,.$$

From $n - 2n_3 - 3n_4 - 2 \geq 0$, it also follows that $n_4 \leq \frac{n-2n_3-2}{3}$. Now we have to prove sufficiency. Suppose $n_3 \leq \frac{n-2}{2}$ and $n_4 \leq \frac{n-2n_3-2}{3}$. From $n_4 \leq \frac{n-2n_3-2}{3}$, it follows that $n - 2n_3 - 3n_4 - 2 \geq 0$. So, we let $n_2 := n - 2n_3 - 3n_4 - 2$ and we put $n_1 = n_3 + 2n_4 + 2$. Since $n_3 \geq 0$ and $n_4 \geq 0$, it follows that $n_1 \geq 0$ too. It remains to show that $n_1 + n_2 + n_3 + n_4 = n$. We have:

$n_1 + n_2 + n_3 + n_4 =$
$(n_3 + 2n_4 + 2) + (n - 2n_3 - 3n_4 - 2) + n_3 + n_4 = n\,.$ ■

We define $V_{p0}(n) := \left\{ (n_3,n_4) : n_3 \leq \frac{n-2}{2}, n_4 \leq \frac{n-2n_3-2}{3} \right\}$.
There is obviously a one to one correspondence between elements of $V_{p0}(n)$ and classes of alkanes with n carbon atoms, *i.e.*, $V_{p0}(n)$ is the set of all ordered pairs (n_3, n_4) representing an alkane with n carbon atoms. Let $N := |V_{p0}|$. Thus, N is the number of ordered pairs that meet the criteria, *i.e.*, the number of different ordered pairs that represent an alkane.

Let $G_{p0}(n)$ be a directed graph with a set of vertices $V_{p0}(n)$ and a set of arcs:

$A_{p0}(n) :=$
$\{ ((a_3, a_4), (b_3, b_4)) \in V(p_0(n))^2 : (a_3, a_4) \succ (b_3, b_4)\}\,.$

From the above, follows Eq. (3).

We wish to calculate the ratio of the number of arcs in G_{p0} to the number of arcs in a graph on the set of vertices $V_{p0}(n)$ whose underlying undirected graph is complete, *i.e.*, $\frac{|A_{p0}(n)|}{\binom{N}{2}}$.

Cases n = 2, 3, 4 are trivial. In the first two cases, $G_{p0}(n)$ has only one vertex, and in the third case, $G_{p0}(n)$ has two vertices connected with an arc (*i.e.*, its underlying graph is complete) and so the considered ratio is one. Let us look at the case $n = 5$. In this case, $V_{p0}(n)$ consists of all pairs (n_3,n_4) such that $n_3 \leq \frac{5-2}{2} = \frac{3}{2}$ and $n_4 \leq \frac{5-2n_3-2}{3} = 1 - \frac{2n_3}{3}$. Obviously, $n_3 = 0,1$. If $n_3 = 0$, then $n_4 \leq 1$ and if $n_3 = 1$, then $n_4 = 0$. We conclude that $V_{p0}(5) = \{(0,0), (0,1), (1,0)\}$ and $N = |V_{p0}| = 3$. Checking which of these pairs are ordered, we get $(0,1) \succ (1,0)$, $(0,1) \succ (0,0)$ and $(1,0) \succ (0,0)$. Therefore, $|A_{p0}(5)| = 3$ and the underlying undirected graph of $G_{p0}(n)$ is complete

$$A_{p0}(n) = \left\{ \begin{array}{l} ((a_3,a_4),(b_3,b_4)) : a_3,a_4,b_3,b_4 \in N_0;\, a_3,b_3 \leq \frac{n-2}{2};\, a_4 \leq \frac{n-2a_3-2}{3}; \\ b_4 \leq \frac{n-2b_3-2}{3} \text{ and } \left[(a_4 = b_4, a_3 > b_3) \text{ or } \left(a_4 > b_4, \frac{a_3-b_3}{a_4-b_4} > -3\right) \right] \end{array} \right\} \quad (3)$$

TABLE I. Classes of octanes

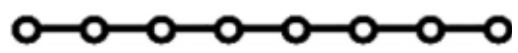
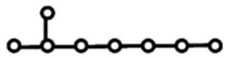
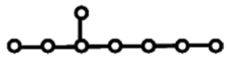
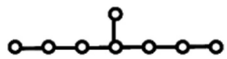
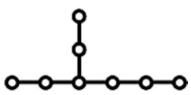
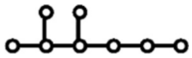
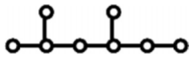
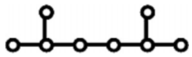
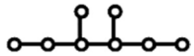
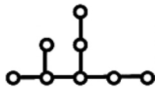
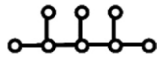
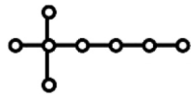
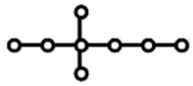
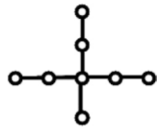
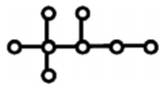
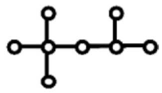
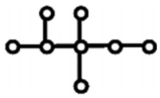
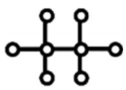
$V_{p0}(8)$	Corresponding 4-tuples	Octanes in the class	Images
(0,0)	(2,6,0,0)	Octane	
(1,0)	(3,4,1,0)	2-Methylheptane	
		3-Methylheptane	
		4-Methylheptane	
		3-Ethylhexane	

TABLE I. (cont.)

$V_{p0}(8)$	Corresponding 4-tuples	Octanes in the class	Images
(2,0)	(4,2,2,0)	2,3-Dimethylhexane	
		2,4-Dimethylhexane	
		2,5-Dimethylhexane	
		3,4-Dimethylhexane	
		3-Ethyl-2-methylpentane	
(3,0)	(5,0,3,0)	2,3,4-Trimethylpentane	
(0,1)	(4,3,0,1)	2,2-Dimethylhexane	
		3,3-Dimethylhexane	
		3-Ethyl-3-methylpentane	
(1,1)	(5,1,1,1)	2,2,3-Trimethylpentane	
		2,2,4-Trimethylpentane	
		2,3,3-Trimethylpentane	
(0,2)	(6,0,0,2)	2,2,3,3-Tetramethylbutane	

again. Thus, in cases n = 2, 3, 4, 5 the ordering "$\prec$" is complete.

Actually, the smallest n for which there are two pairs that cannot be ordered (*i.e.,* for which "$\prec$" is not complete) is n = 8. Note that in that case $V_{p0}(8) = \{(0,0), (0,1), (0,2), (1,0), (1,1), (2,0), (3,0)\}$. Two pairs that cannot be ordered are (0,1) and (3,0), since neither of the two criteria for $A_{p0}(8)$ is met.

The partial order of octanes, *i.e.*, the corresponding graph $G_{p0}(8)$, is shown in Figure 1.

Let us now compare the order presented in this paper with the orders induced by the Zagreb index M_1

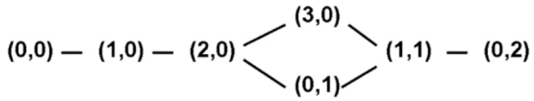


Figure 1. Graph $G_{p0}(8)$

TABLE II. Orders induced by M_1 and $^4M_1$ on a set of alkanes with $n = 12$

$V_{p0}(12)$	M_1	$^4M_1$
(0.0)	42	162
(0.1)	48	372
(0.2)	54	582
(0.3)	60	792
(1.0)	44	212
(1.1)	50	422
(1.2)	56	632
(2.0)	46	262
(2.1)	52	472
(2.2)	58	682
(3.0)	48	312
(3.1)	54	522
(4.0)	50	362
(5.0)	52	412

and the modified Zagreb index $^4M_1$ on the set of alkanes with $n = 12$. Values of the Zagreb index M_1 and the modified Zagreb index $^4M_1$ for the dodecanes are easily calculated, and the results are presented in Table II.

These values induce order on the set of alkanes with $n = 12$, *i.e.,* on set $V_{p0}(12)$. But, let us consider alkanes (0,1) and (4,0). Both orders, the one induced by M_1 and the one induced by $^4M_1$ order them, but they order them differently. Index M_1 orders them as (0,1) < (4,0), whereas index $^4M_1$ orders them as (4,0) < (0,1). Hence, both indices refine our partial order, but in an inconsistent manner.

Since we suspect that the occurrence of un-orderable pairs will increase with increasing n, we have established a table of some values of n and their corresponding $A(G_{p0})$. Using the definition of $V_{p0}(n)$ and $A_{p0}(n)$, the simple program based on 4 »four-loops« is constructed and the results are recorded in Table III.

This table contains the number N of different classes of alkanes on n vertices, the number $\binom{N}{2}$ of all possible pairs of classes of alkanes, the number $|A_{p0}(n)|$ of all orderable pairs of classes of alkanes, and finally the fraction $|A_{p0}(n)| / \binom{N}{2}$ of orderable pairs for $n = 5, K, 50$. The ratio $|A_{p0}(n)| / \binom{N}{2}$ may be considered as the measure of the »extent« of total ordering.

TABLE III. Analyses of graph $G_{p0}(n)$

n	N	$\lvert A_{p0}(n)\rvert$	$\lvert A_{p0}(n)\rvert / \binom{N}{2}$
5	3	3	1.000000
6	4	6	1.000000
7	5	10	1.000000
8	7	20	0.952381
9	8	27	0.964286
10	10	42	0.933333
11	12	62	0.939394
12	14	84	0.923077
13	16	111	0.925000
14	19	156	0.912281
15	21	192	0.914286
16	24	249	0.902174
17	27	318	0.905983
18	30	390	0.896552
19	33	474	0.897727
20	37	594	0.891892
21	40	696	0.892308
22	44	838	0.885835
23	48	1002	0.888298
24	52	1170	0.882353
25	56	1360	0.883117
26	61	1610	0.879781
27	65	1830	0.879808
28	70	2115	0.875776
29	75	2435	0.877477
30	80	2760	0.873418
31	85	3120	0.873950
32	91	3570	0.871795
33	96	3975	0.871711
34	102	4476	0.868957
35	108	5028	0.870197
36	114	5586	0.867257
37	120	6195	0.867647
38	127	6930	0.866142
39	133	7602	0.866029
40	140	8407	0.864029
41	147	9282	0.864971
42	154	10164	0.862745
43	161	11116	0.863043
44	169	12236	0.861933
45	176	13272	0.861818
46	184	14484	0.860299
47	192	15788	0.861038
48	200	17100	0.859296
49	208	18504	0.859532
50	217	20124	0.858679

LARGE GRAPHS

The question which remains is what happens with $\frac{|A_{p0}(n)|}{\binom{N}{2}}$ when n gets larger and larger? We are interested in calculating $\lim_{n\to\infty}\frac{|A_{p0}(n)|}{\binom{N}{2}} = \lim_{n\to\infty}\frac{\frac{|A_{p0}(n)|}{n^4}}{\frac{\binom{N}{2}}{n^4}}$, which is equal to $2\frac{\lim_{n\to\infty}\frac{|A_{p0}(n)|}{n^4}}{\left(\lim_{n\to\infty}\frac{N}{n^2}\right)^2}$ if the limit $\lim_{n\to\infty}\frac{N}{n^2}$ exists and is not zero. Recalling that $n_3 \le \frac{n-2}{2}$ and $n_4 \le \frac{n-2n_3-2}{3}$, we have:

$$\lim_{n\to\infty}\frac{N}{n^2} = \lim_{n\to\infty}\frac{\sum_{n_3=0}^{\left\lfloor\frac{n-2}{2}\right\rfloor}\left(1+\left\lfloor\frac{n-2n_3-2}{3}\right\rfloor\right)}{n^2} =$$

$$= \lim_{n\to\infty}\frac{\sum_{n_3=0}^{\left\lfloor\frac{n-2}{2}\right\rfloor}\frac{n-2n_3}{3}}{n^2} =$$

$$= \frac{1}{3}\cdot\lim_{n\to\infty}\frac{n\cdot\left\lfloor\frac{n-2}{2}\right\rfloor - 2\cdot\frac{\left\lfloor\frac{n-2}{2}\right\rfloor\cdot\left(\left\lfloor\frac{n-2}{2}\right\rfloor+1\right)}{2}}{n^2} =$$

$$= \frac{1}{3}\cdot\lim_{n\to\infty}\frac{\frac{n^2}{2}-\frac{n^2}{4}}{n^2} = \frac{1}{12}.$$

In order to calculate $\frac{|A_{p0}(n)|}{n^4}$, we would like to express n_3 in terms of n_4, and n_4 in terms only of n. Thus, from $n - 2n_3 - 3n_4 - 2 \ge 0$ (this we already established as (3)), we derive new inequalities: $n_3 \le \frac{n-3n_4-2}{2}$ and $n_4 \le \frac{n-2}{3}$.

Let $\frac{|A_{p0}(n)|}{n^4} = \frac{T_1}{n^4} + \frac{T_2}{n^4}$, where T_1 counts arcs between vertices (a_3, a_4) and (b_3, b_4) such that $a_4 = b_4$ and $a_3 > b_3$ and T_2 counts arcs between vertices (a_3, a_4) and (b_3, b_4) such that $a_4 > b_4$ and $\frac{a_3-b_3}{a_4-b_4} > -3$.

First, let us calculate $\lim_{n\to\infty}\frac{T_1}{n^4}$. Obviously, $\lim_{n\to\infty}\frac{T_1}{n^4} \ge 0$. From:

$$\lim_{n\to\infty}\frac{T_1}{n^4} = \lim_{n\to\infty}\frac{\sum_{a_4=0}^{\left\lfloor\frac{n-2}{3}\right\rfloor}\sum_{a_3=1}^{\left\lfloor\frac{n-3a_4-2}{2}\right\rfloor} a_3}{n^4} \le \lim_{n\to\infty}\frac{\sum_{a_4=0}^{n}\sum_{a_3=1}^{n} n}{n^4} =$$

$$= \lim_{n\to\infty}\frac{n^3+n^2}{n^4} = 0$$

it follows that $\lim_{n\to\infty}\frac{T_1}{n^4} = 0$.

Now, let us calculate $\lim_{n\to\infty}\frac{T_2}{n^4}$. Note that the numbers a_3, a_4, b_3 and b_4 have to fulfill the following conditions:

$$a_3 \le \frac{n-3a_4-2}{2}\ ;\ a_4 \le \frac{n-2}{3}\ ;\ b_3 \le \frac{n-3b_4-2}{2}\ ;$$
$$b_4 \le \frac{n-2}{3}\ ;\ a_3 > b_3 - 3a_4 + 3b_4.$$

Hence:

$$\lim_{n\to\infty}\frac{T_2}{n^4} = \lim_{n\to\infty}\frac{\sum_{a_4=1}^{\left\lfloor\frac{n-2}{3}\right\rfloor}\sum_{b_4=0}^{a_4-1}\sum_{b_3=0}^{\left\lfloor\frac{n-3b_4-2}{2}\right\rfloor}\sum_{a_3=\max\{b_3-3a_4+3b_4+1,0\}}^{\left\lfloor\frac{n-3a_4-2}{2}\right\rfloor} 1}{n^4} =$$

$$= \lim_{n\to\infty}\left[\frac{1}{n^4}\cdot\sum_{a_4=1}^{\left\lfloor\frac{n-2}{3}\right\rfloor}\sum_{b_4=0}^{a_4-1}\sum_{b_3=0}^{\left\lfloor\frac{n-3b_4-2}{2}\right\rfloor}\max\left\{0,\left\lfloor\frac{n-3a_4-2}{2}\right\rfloor-\max\{b_3-3a_4+3b_4+1,0\}+1\right\}\right] =$$

$$= \lim_{n\to\infty}\left[\frac{1}{n^4}\cdot\sum_{a_4=1}^{\left\lfloor\frac{n-2}{3}\right\rfloor}\sum_{b_4=0}^{a_4-1}\sum_{b_3=0}^{\left\lfloor\frac{n-3b_4-2}{2}\right\rfloor}\max\left\{0,\left\lfloor\frac{n-3a_4}{2}\right\rfloor-\max\{b_3-3a_4+3b_4+1,0\}\right\}\right] = \left\{\begin{matrix}\text{from properties}\\ \text{of } a_i, b_i\end{matrix}\right\} =$$

$$= \lim_{n\to\infty}\left[\frac{1}{n^4}\cdot\sum_{a_4=1}^{\left\lfloor\frac{n-2}{3}\right\rfloor}\sum_{b_4=0}^{a_4-1}\sum_{b_3=0}^{\left\lfloor\frac{n-3b_4-2}{2}\right\rfloor}\left(\left\lfloor\frac{n-3a_4}{2}\right\rfloor-\max\{b_3-3a_4+3b_4+1,0\}\right)\right]=$$

$$= \lim_{n\to\infty}\left[\frac{1}{n^4}\cdot\sum_{a_4=1}^{\left\lfloor\frac{n-2}{3}\right\rfloor}\sum_{b_4=0}^{a_4-1}\sum_{b_3=0}^{\left\lfloor\frac{n-3b_4-2}{2}\right\rfloor}\left\lfloor\frac{n-3a_4}{2}\right\rfloor\right]-\lim_{n\to\infty}\left[\frac{1}{n^4}\cdot\sum_{a_4=1}^{\left\lfloor\frac{n-2}{3}\right\rfloor}\sum_{b_4=0}^{a_4-1}\sum_{b_3=0}^{\left\lfloor\frac{n-3b_4-2}{2}\right\rfloor}\max\{b_3-3a_4+3b_4+1,0\}\right] .$$

Let us calculate the first of these two limits:

$$\lim_{n\to\infty}\left[\frac{1}{n^4}\cdot\sum_{a_4=1}^{\left\lfloor\frac{n-2}{3}\right\rfloor}\sum_{b_4=0}^{a_4-1}\sum_{b_3=0}^{\left\lfloor\frac{n-3b_4-2}{2}\right\rfloor}\frac{n-3a_4}{2}\right]=\lim_{n\to\infty}\left[\frac{1}{4n^4}\cdot\sum_{a_4=1}^{\left\lfloor\frac{n-2}{3}\right\rfloor}\sum_{b_4=0}^{a_4-1}\left[(n-3a_4)\cdot(n-3b_4)\right]\right]=$$

$$=\lim_{n\to\infty}\left[\frac{1}{4n^4}\cdot\sum_{a_4=1}^{\left\lfloor\frac{n-2}{3}\right\rfloor}\left[-\frac{9a_4^{\ 2}}{2}+\frac{9a_4^{\ 3}}{2}+\frac{3a_4n}{2}-\frac{9a_4^{\ 2}n}{2}+a_4n^2\right]\right]=$$

$$=\lim_{n\to\infty}\left[\frac{1}{4n^4}\cdot\sum_{a_4=1}^{\left\lfloor\frac{n-2}{3}\right\rfloor}\left[\frac{9a_4^{\ 3}}{2}-\frac{9a_4^{\ 2}n}{2}+a_4n^2\right]\right]=$$

$$=\lim_{q\to\infty}\left[\frac{1}{4\cdot(3q+2)^4}\cdot\sum_{a_4=1}^{q}\left[\frac{9a_4^{\ 3}}{2}-\frac{9a_4^{\ 2}(3q+2)}{2}+a_4(3q+2)^2\right]\right]=$$

$$=\lim_{q\to\infty}\left[\frac{1}{4\cdot81\cdot q^4}\cdot\sum_{a_4=1}^{q}\left[\frac{9a_4^{\ 3}}{2}-\frac{27a_4^{\ 2}q}{2}+9a_4q^2\right]\right]=$$

$$=\lim_{q\to\infty}\left[\frac{1}{4\cdot81\cdot q^4}\cdot\left(-\frac{9q^2}{8}+\frac{9q^4}{8}\right)\right]=\frac{1}{288} .$$

Now, let us calculate the second limit:

$$\lim_{n\to\infty}\left[\frac{1}{n^4}\cdot\sum_{a_4=1}^{\left\lfloor\frac{n}{3}\right\rfloor}\sum_{b_4=0}^{a_4}\sum_{b_3=0}^{\left\lfloor\frac{n-3b_4}{2}\right\rfloor}\max\{b_3-3a_4+3b_4,0\}\right]=$$

$$=\lim_{n\to\infty}\left[\frac{1}{n^4}\cdot\sum_{a_4=1}^{\left\lfloor\frac{n}{3}\right\rfloor}\sum_{b_4=0}^{a_4}\sum_{b_3=3a_4-3b_4}^{\left\lfloor\frac{n-3b_4}{2}\right\rfloor}(b_3-3a_4+3b_4)\right]=$$

$$=\lim_{n\to\infty}\left[\frac{1}{n^4}\cdot\sum_{a_4=1}^{\left\lfloor\frac{n}{3}\right\rfloor}\sum_{b_4=\max\left\{0,\left\lceil 2a_4-\frac{n}{3}\right\rceil\right\}}^{a_4}\sum_{b_3=3a_4-3b_4}^{\left\lfloor\frac{n-3b_4}{2}\right\rfloor}(b_3-3a_4+3b_4)\right]=$$

$$= \lim_{n\to\infty}\left[\frac{1}{n^4}\cdot\sum_{a_4=1}^{\left\lfloor\frac{n}{6}\right\rfloor}\sum_{b_4=0}^{a_4}\sum_{b_3=3a_4-3b_4}^{\left\lfloor\frac{n-3b_4}{2}\right\rfloor}\left(b_3-3a_4+3b_4\right)\right]+$$

$$+\lim_{n\to\infty}\left[\frac{1}{n^4}\cdot\sum_{a_4=\left\lfloor\frac{n}{6}\right\rfloor}^{\left\lfloor\frac{n}{3}\right\rfloor}\sum_{b_4=\left\lceil 2a_4-\frac{n}{3}\right\rceil}^{a_4}\sum_{b_3=3a_4-3b_4}^{\left\lfloor\frac{n-3b_4}{2}\right\rfloor}\left(b_3-3a_4+3b_4\right)\right].$$

Let us calculate the first of these two summands:

$$\lim_{n\to\infty}\left[\frac{1}{n^4}\cdot\sum_{a_4=1}^{\left\lfloor\frac{n}{6}\right\rfloor}\sum_{b_4=0}^{a_4}\sum_{b_3=3a_4-3b_4}^{\left\lfloor\frac{n-3b_4}{2}\right\rfloor}\left(b_3-3a_4+3b_4\right)\right]=$$

$$=\lim_{n\to\infty}\left[\frac{1}{2n^4}\cdot\sum_{a_4=1}^{\left\lfloor\frac{n}{6}\right\rfloor}\sum_{b_4=0}^{a_4}\sum_{b_3=6a_4-6b_4}^{n-3b_4}\left(\frac{b_3}{2}-3a_4+3b_4\right)\right]=$$

$$=\lim_{n\to\infty}\left[\frac{1}{8n^4}\cdot\sum_{a_4=1}^{\left\lfloor\frac{n}{6}\right\rfloor}\sum_{b_4=0}^{a_4}\left(36\cdot a_4^{\,2}-36a_4\cdot b_4+9b_4^{\,2}-12a_4\cdot n+6b_4\cdot n+n^2\right)\right]=$$

$$=\lim_{n\to\infty}\left[\frac{1}{8n^4}\cdot\sum_{a_4=1}^{\left\lfloor\frac{n}{6}\right\rfloor}\left(21\cdot a_4^{\,3}-9a_4^{\,2}\cdot n+a_4\cdot n^2\right)\right]=$$

$$=\lim_{n\to\infty}\left[\frac{1}{48n^4}\cdot\sum_{a_4=1}^{n}\left(21\cdot\left(\frac{a_4}{6}\right)^3-9\left(\frac{a_4}{6}\right)^2\cdot n+\left(\frac{a_4}{6}\right)\cdot n^2\right)\right]=$$

$$=\frac{1}{48n^4}\cdot\frac{7n^4}{288}=\frac{7}{13824}\ .$$

Let us calculate the second summand:

$$\lim_{n\to\infty}\left[\frac{1}{n^4}\cdot\sum_{a_4=\left\lfloor\frac{n}{6}\right\rfloor}^{\left\lfloor\frac{n}{3}\right\rfloor}\sum_{b_4=\left\lceil 2a_4-\frac{n}{3}\right\rceil}^{a_4}\sum_{b_3=3a_4-3b_4}^{\left\lfloor\frac{n-3b_4}{2}\right\rfloor}\left(b_3-3a_4+3b_4\right)\right]=$$

$$=\lim_{n\to\infty}\left[\frac{1}{8n^4}\cdot\sum_{a_4=\left\lfloor\frac{n}{6}\right\rfloor}^{\left\lfloor\frac{n}{3}\right\rfloor}\sum_{b_4=\left\lceil 2a_4-\frac{n}{3}\right\rceil}^{a_4}\left(36\cdot a_4^{\,2}-36a_4\cdot b_4+9b_4^{\,2}-12a_4\cdot n+6b_4\cdot n+n^2\right)\right]=$$

$$=\lim_{n\to\infty}\left[\frac{1}{24n^4}\cdot\sum_{a_4=\left\lfloor\frac{n}{6}\right\rfloor}^{\left\lfloor\frac{n}{3}\right\rfloor}\sum_{b_4=6a_4-n}^{3a_4}\left(36\cdot a_4^{\,2}-12a_4\cdot b_4+b_4^{\,2}-12a_4\cdot n+2b_4\cdot n+n^2\right)\right]=$$

$$= \lim_{n\to\infty}\left[\frac{1}{24n^4}\cdot\sum_{a_4=\left\lfloor\frac{n}{6}\right\rfloor}^{\left\lfloor\frac{n}{3}\right\rfloor}(-9a_4^3+9a_4^2\cdot n-3a_4\cdot n^2+\frac{n^3}{3})\right]=$$

$$= \lim_{n\to\infty}\left[\frac{1}{144n^4}\cdot\sum_{a_4=n}^{2n}(-9\left(\frac{a_4}{6}\right)^3+9\left(\frac{a_4}{6}\right)^2\cdot n-3\left(\frac{a_4}{6}\right)\cdot n^2+\frac{n^3}{3})\right]=$$

$$= \lim_{n\to\infty}\left[\frac{1}{144n^4}\cdot\frac{n^4}{96}\right]=\frac{1}{13824}\ .$$

Finally, we calculate:

$$\lim_{n\to\infty}\frac{\left|\mathrm{A}_{p0}(n)\right|}{\binom{N}{2}}=2\frac{\lim\limits_{n\to\infty}\frac{\left|\mathrm{A}_{p0}(n)\right|}{n^4}}{\left(\lim\limits_{n\to\infty}\frac{N}{n^2}\right)^2}=2\cdot\frac{\frac{1}{288}-\left(\frac{7}{13824}+\frac{1}{13824}\right)}{\left(\frac{1}{12}\right)^2}=\frac{5}{6}\ .$$

This is in accordance with the results presented in Table I.

CONCLUSIONS

In this paper, the consistency of partial orderings by ${}^{\lambda}M_1$, $\lambda \geq 2$ is discussed. It is shown that these indices show a great deal of consistency. More then 80 % of 4-tuples (n_1, n_2, n_3, n_4) are consistently ordered. However, there are some smaller differences in ordering between the various ${}^{\lambda}M_1$. This proves that it may be useful to adopt the original definitions of the Zagreb index for some specific problems. However, it seems that these modifications should be useful only as improved predictors of those properties which are already relatively well predicted by the original Zagreb M_1 index.

The new partial order $\prec$ proposed in this paper is an intersection of all of these partial orderings. Hence, the results obtained by this newly proposed partial order are in agreement with all ${}^{\lambda}M_1$, $\lambda \geq 2$, and therefore, each result obtained by this partial order is of great confidence. On the other hand, »the price« of this great confidence is the fact that many alkanes will be incomparable and no information will be extracted from the order $\prec$.

REFERENCES

1. I. Gutman and N. Trinajstić, *Chem. Phys. Lett.* **17** (1972) 535–538.
2. M. Randić, *J. Am. Chem. Soc.* **97** (1975) 6609–6615.
3. L. B. Kier, L. H. Hall, W. J. Murray, and M. Randić, *J. Pharm. Sci.* **65** (1976) 1226–1230.
4. S. Nikolić, G. Kovačević, A. Miličević, and N. Trinajstić, *Croat. Chem. Acta* **76** (2003) 113–124.
5. D. Bonchev, *J. Mol. Graphics Modelling* **20** (2001) 65–75.
6. S. Nikolić, N. Trinajstić, I. M. Tolić, G. Rücker, and C. Rücker, in: D. Bonchev and D. H. Rouvray (Eds.), *Complexity –Introduction and Fundamentals*, Francis & Taylor, London, 2003, pp. 29–89.
7. S. Nikolić, I. M. Tolić, N. Trinajstić, and I. Baučić, *Croat. Chem. Acta* **73** (2000) 909–921.
8. A. Golbraikh, D. Bonchev, and A. Tropsha, *J. Chem. Inf. Comput. Sci.* **41** (2001) 147–158.
9. A. Golbraikh, D. Bonchev, and A. Tropsha, *J. Chem. Inf. Comput. Sci.* **42** (2002) 769–787.
10. A. Miličević and S. Nikolić, *Croat. Chem. Acta* **77** (2004) 97–101.
11. D. Vukičević and N. Trinajstić, *Croat. Chem. Acta* **76** (2003) 183–187.
12. D. Vukičević, A. Miličević, S. Nikolić, J. Sedlar, and N. Trinajstić, *ARKIVOC* **10** (2005) 33–44.
13. R. Bruggemann and L. Carlsen (Eds.), *Partial Order in Environmental Sciences and Chemistry*, Springer-Verlag, New York, 2006.
14. D. Veljan and D. Vukičević, *Journal of Mathematical Chemistry*, to be published.

SAŽETAK

Metoda teorije grafova za parcijalni uređaj na alkanima

Damir Vukičević, Jelena Sedlar i Sarah Michele Rajtmajer

Zagrebačkim topološkim indeksom M_1 uvodi se uređaj na skupu alkana. Nedavno su predloženi modificirani zagrebački indeksi ${}^{\lambda}M_1$, te je uočeno da se uređaji koje oni uvode razlikuju. U ovom se radu istražuje razina konzistentnosti tih uređaja. Uvodi se novi parcijalni uređaj $\succ$ koji je presjek svih parcijalnih uređaja ${}^{\lambda}M_1$ (pri čemu je m barem 2), te se istražuju njegova svojstva.