Randić ordering of chemical trees

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Abstract

We introduce a partial order on the collection of chemical trees based on tree transformations. This partial order is tightly related to the Randić connectivity index χ. Its analysis provides new structural information about the behavior of χ. As an illustration of the approach presented, we give a different and more structural view of some known results about the first values of χ on the collection of chemical trees.

1 Introduction

Let G be a simple graph (i.e. G does not have loops or multiple edges) with n vertices. The connectivity index of G, denoted by χ, is defined as follows

$$\chi(G) = \sum_{1 \leq i \leq j \leq n-1} \frac{m_{ij}(G)}{\sqrt{ij}} \tag{1}$$

where $m_{ij}(G)$ is the number of edges in G between vertices of degrees i and j.

Randić ([13]) introduced this index (known today as the Randić index) in the study of branching properties of alkanes, and it became one of the most useful graph-based molecular descriptors in applications to physical and chemical properties ([9, 10]).

Let T and S be two chemical trees with n vertices. Are there structural properties of T and S guaranteeing that $\chi(S) < \chi(T)$? More specifically, we are interested in the following problem. Suppose S can be obtained from T by some elementary transformation (performed on T), under which condition $\chi(S) < \chi(T)$? There are a number of transformations that can be naturally considered as elementary. First of all, the operation that consists on moving a pendent edge at a vertex x (i.e. an edge with one of its extreme being a pendent vertex) to a vertex y. This naturally leads to more general operations like moving an exterior path (i.e. a path starting from a pendent) or a maximal subtree (which will be defined later). Based only on these operations we will show that there are many χ-monotone chains of trees. More precisely, we will show how to construct chemical trees $T_0, T_1, T_2, \cdots, T_m$ such that T_{i+1} can be obtained from T_i by one of these transformations and $\chi(T_i) < \chi(T_{i+1})$. We will write $S \prec_{mso} T$ when such sequence exists with $T_0 = S$ and $T_m = T$ and, as usual, we will write $S \preceq_{mso} T$ when $S = T$ or $S \prec_{mso} T$. The relation $\preceq_{mso}$ is a partial order on the collection of all chemical trees with n vertices.

The main purpose of this paper is to study $\preceq_{mso}$ and show how to obtain, from the properties of $\preceq_{mso}$, structural information about the behavior of χ. As an illustration, we will deduce various known results about extremal trees. For instance, $T \preceq_{mso} L_n$ for every chemical tree T with n vertices. Notice that this claim is stronger than just saying that $\chi(T) \leq \chi(L_n)$, where L_n is the path tree with n vertices (see [1, 2]). We will also characterize the $\preceq_{mso}$-minimal chemical trees and, as a corollary of this, we will get some of the results from [1, 2, 5, 7, 8] about the first values of χ on the collection of chemical trees. On the other

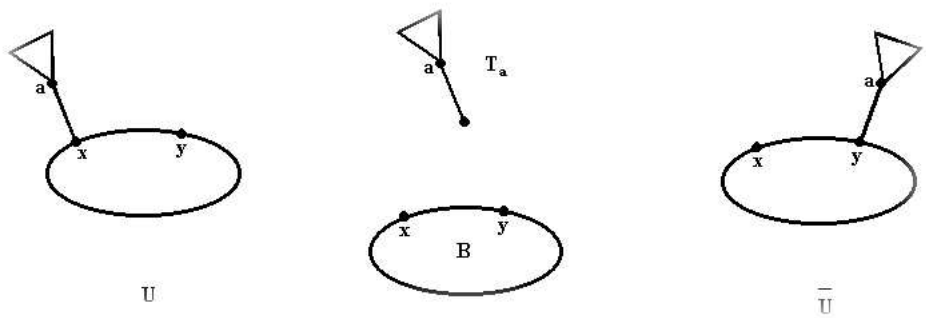

Figure 1:

hand, our analysis gives new structural information about χ. For example, we will show that there are chemical trees T such that $\chi(T)$ is second χ-minimal but they are $\preceq_{mso}$-minimal, that is to say, they cannot be transformed into a tree with minimal χ using one of the transformation considered in this paper (see Example 5.5). Something analogous happens with third χ-minimal trees. For example, for $n \equiv 1\ mod(3)$, if T and S are chemical trees with $\chi(T)$ second minimal and $\chi(S)$ third minimal, then $S \not\preceq_{mso} T$ (see Theorem 5.10). In particular, it is not possible to transform T using a maximal subtree operation into a tree with χ second minimal.

Our results reflect the non-linear nature of $\preceq_{mso}$ and therefore might also reflect more accurately the already recognized belief that "... branching is a subtle concept and it probably cannot (and should not) be quantified by a single number"[5].

The idea of considering graph transformations as a criteria for defining neighborhood structure has been successfully used for finding graphs with extremal properties. For instance, the Autographic System developed by Caporossi and Hansen [3] is based on the so called Variable Neighborhood Search (VNS). Roughly speaking, these neighborhoods are defined as follows. Let $\mathcal{T}$ be a collection of transformations on graphs. Define the neighborhood $N_{\mathcal{T}}(G)$, for a graph G, as the set of those graphs obtained as the result of applying to G a transformation belonging to $\mathcal{T}$. The use of different choices of $\mathcal{T}$ is a key ingredient of the VNS. Our approach fits very well in this context and, in fact, many of the results about χ obtained by the VNS heuristics served us for testing the scope of our approach. We have shown that for a particular choice of $\mathcal{T}$ (namely, what we call maximal subtree operations), the search algorithm based on it provides enough detailed information about the behavior of χ on the class of chemical trees. Moreover, the results presented suggest that this approach (of focusing on a particular family of transformations) can be used to unravel some structural properties of the connectivity index. In the last section we will comment more on this topic.

2 Maximal subtree operation on a tree

Let T be a tree (i.e. an acyclic connected graph) with set of vertices $V(T)$ and set of edges $E(T)$. If $v \in V(T)$ we denote by δ_v the degree of the vertex v and $\mathcal{N}_v$ denotes the set of vertices in T which are adjacent to v.

Assume that T is a tree and $v \in V(T)$. As in [11], consider the set $\mathcal{P}_v(T)$ consisting of all subtrees of T which have v as a pendent vertex. If $P, Q \in \mathcal{P}_v(T)$, then the relation $P \subseteq Q$, (i.e. P is a subtree of Q), is a partial order relation over $\mathcal{P}_v(T)$. Moreover, for each $w \in \mathcal{N}_v$, we denote by $T(v)_w$ the unique maximal subtree of $\mathcal{P}_v(T)$ which contains the vertex w. The set $\{T(v)_w\}_{w \in \mathcal{N}_v}$ is called the set of maximal subtrees of T at v.

Consider the situation described in Figure 1

The operation mentioned in the introduction is defined as follows.

Definition 2.1 *A maximal subtree operation (mso, for short) on U consists in "moving" the maximal subtree $T(x)_a$ of U at a vertex $x \in V(U)$ ($\delta_x \geq 2$) which contains the vertex $a \in \mathcal{N}_x$ to another vertex $y \in V(U)$ (see Figure 1). The new tree obtained in this way is denoted by $\mathcal{M}(U, x, a, y)$. We will say that $\overline{U}$ is obtained from U by a mso if there are x, a and y such that $\overline{U} = \mathcal{M}(U, x, a, y)$ and in this case we will write $\overline{U} = \mathcal{M}(U)$.*

We will constantly refer to the trees $U, \overline{U}$ and the vertices x, y and a above.

This informal description of a maximal subtree operation suffices for understanding the results presented in this paper. However, for the sake of precision, we can make it more formal as follows. Let us recall the definition of coalescence of two trees [4, p. 158]: given two trees T_1 and T_2 with $v_1 \in V(T_1)$ and $v_2 \in (T_2)$, the coalescence of T_1 and T_2 with respect to v_1 and v_2, is formed by identifying v_1 and v_2 and is denoted by $T_1(v_1) \bullet T_2(v_2)$. In other words, $V(T_1(v_1) \bullet T_2(v_2)) = V(T_1) \cup V(T_2) \cup \{v^*\} - \{v_1, v_2\}$, with two vertices in $T_1(v_1) \bullet T_2(v_2)$ adjacent if they are adjacent in T_1 or T_2, or if one is v^* and the other one is adjacent to v_1 or v_2 in T_1 or T_2.

Now a *mso* can be defined as follows. Let S be a maximal subtree of U at x, with pendent vertex x and $N_x = \{a\}$. Then $U = B(x) \bullet S(x)$, where $B := U - (S - \{x\})$ is the tree obtained from U by deleting the set of vertices $V(S) - \{x\}$. For every $y \in V(U)$ such that $y \notin S$, we have that $\mathcal{M}(U, x, a, y)$ is the tree $B(y) \bullet S(x)$.

We can estimate the variation of the Randić index when a *mso* is applied to a tree. In [11, Theorem 2.3] it was shown that if T is a tree and $v \in V(T)$ then

$$\chi(T) = \sum_{w \in \mathcal{N}_v} \chi(T_w) + \left(\frac{1}{\sqrt{\delta_v}} - 1\right) R_T(v), \tag{2}$$

where $R_T(v)$ is the Randić constant of T at v, defined as $R_T(v) = \sum_{w \in \mathcal{N}_v} \frac{1}{\sqrt{\delta_w}}$.

As a consequence of (2) we get the following crucial result.

Lemma 2.2 *Let U and $\overline{U} = \mathcal{M}(U, x, a, y)$. Then*

$$\begin{aligned} \chi(U) - \chi(\overline{U}) &= \left(\frac{1}{\sqrt{\delta_x^U}} - \frac{1}{\sqrt{\delta_x^U - 1}}\right) R_B(x) + \left(\frac{1}{\sqrt{\delta_y^U}} - \frac{1}{\sqrt{\delta_y^U + 1}}\right) R_B(y) \\ &\quad + \left(\frac{1}{\sqrt{\delta_x^U}} - \frac{1}{\sqrt{\delta_y^U + 1}}\right) \frac{1}{\sqrt{\delta_a^U}} \end{aligned}$$

where B is the tree obtained from U by deleting the set of vertices $V(T_a) - \{x\}$ and T_a is the maximal subtree of U at x that contains a.

Although Definition 2.1 and Lemma 2.2 hold for general trees, we are particularly interested in chemical trees, that is, trees for which every vertex has degree ≤ 4. Let $\mathcal{C}_n$ denote the set of chemical trees with n vertices. We next introduce a partial order on $\mathcal{C}_n$ which is the main object of study of this paper.

Definition 2.3 *Let S and T be trees in $\mathcal{C}_n$. We define a partial order relation on $\mathcal{C}_n$ as follows:*

$$S \preceq_{mso} T$$

if $S = T$ or there exists a sequence of trees $\{U_j\}_{j=0}^k \subseteq \mathcal{C}_n$, where $U_0 = S$, $U_k = T$, $U_j = \mathcal{M}(U_{j-1})$ and $\chi(U_{j-1}) < \chi(U_j)$ for each $1 \leq j \leq k$.

We will strongly rely on the variation formula given in Lemma 2.2 to study the order $\preceq_{mso}$ defined over $\mathcal{C}_n$. In spite of the numerous parameters appearing in this formula, we will find rather general structure

results that assures the increase or decrease of χ when a *mso* is applied to a tree. These results are based on the following ideas: if $U \in \mathcal{C}_n$ then we can classify a *mso* on U according to the degrees of the vertices x and y : if $\delta_x^U = k$ and $\delta_y^U = l$ then $\overline{U}$ is obtained from U by a (k,l)-*mso*. On the other hand, we can associate to $U \in \mathcal{C}_n$ the degree sequence

$$(n_1, n_2, n_3, n_4)$$

where n_i denotes the number of vertices of U with degree i $(1 \leq i \leq 4)$. In Table 1 we show all possible (k,l)-*mso* on $U \in \mathcal{C}_n$ such that $\overline{U} \in \mathcal{C}_n$, together with the transformations of the degree sequences:

(k,l)-*mso*	U	$\longrightarrow$	$\overline{U}$
$(4,3)$-	(n_1,n_2,n_3,n_4)		(n_1,n_2,n_3,n_4)
$(4,2)$-	(n_1,n_2,n_3,n_4)		(n_1,n_2-1,n_3+2,n_4-1)
$(4,1)$-	(n_1,n_2,n_3,n_4)		$(n_1-1,n_2+1,n_3+1,n_4-1)$
$(3,3)$-	(n_1,n_2,n_3,n_4)		(n_1,n_2+1,n_3-2,n_4+1)
$(3,2)$-	(n_1,n_2,n_3,n_4)		(n_1,n_2,n_3,n_4)
$(3,1)$-	(n_1,n_2,n_3,n_4)		(n_1-1,n_2+2,n_3-1,n_4)
$(2,3)$-	(n_1,n_2,n_3,n_4)		$(n_1+1,n_2-1,n_3-1,n_4+1)$
$(2,2)$-	(n_1,n_2,n_3,n_4)		(n_1+1,n_2-2,n_3+1,n_4)
$(2,1)$-	(n_1,n_2,n_3,n_4)		(n_1,n_2,n_3,n_4)

Table 1

Notice that some of these transformations are inverse of others. For instance, if $\overline{U}$ is obtained from U by a $(4,2)$-*mso*, then U can be obtained from $\overline{U}$ by a $(3,3)$-*mso*. However, as we shall see, this fact is rarely used due to the constrains on the degree of the vertices which guarantees the χ-monotony.

3 χ-increasing sequences of trees in $\mathcal{C}_n$

In this section we show that for every tree $U \in \mathcal{C}_n$, we can construct by means of maximal subtree operations, a χ-increasing sequence of trees in $\mathcal{C}_n$ which ends in L_n, the path tree with n vertices. That is to say, $U \preceq_{mso} L_n$ for every $U \in \mathcal{C}_n$.

Lemma 3.1 *Let $U \in \mathcal{C}_n$. If $\overline{U}$ is obtained from U by a $(4,1)$-mso then $\chi(U) < \chi(\overline{U})$.*

Proof. Assume that $\delta_x^U = 4$ and $\delta_y^U = 1$. It is easy to see that $R_B(x) \geq \frac{3}{2}$ and $\frac{1}{\sqrt{\delta_a^U}} \geq \frac{1}{2}$. On the other hand, $R_B(y) \leq \frac{1}{\sqrt{2}}$. It follows from Lemma 2.2 that

$$\begin{aligned}
\chi(U) - \chi(\overline{U}) &= \left(\frac{1}{2} - \frac{1}{\sqrt{3}}\right) R_B(x) + \left(1 - \frac{1}{\sqrt{2}}\right) R_B(y) \\
&\quad + \left(\frac{1}{2} - \frac{1}{\sqrt{2}}\right) \frac{1}{\sqrt{\delta_a^U}} \\
&\leq \left(\frac{1}{2} - \frac{1}{\sqrt{3}}\right) \frac{3}{2} + \left(1 - \frac{1}{\sqrt{2}}\right) \frac{1}{\sqrt{2}} + \left(\frac{1}{2} - \frac{1}{\sqrt{2}}\right) \frac{1}{2} < 0
\end{aligned}$$

■

Now we consider $(3,1)$-*mso* on a chemical tree. In general, these operations are not χ-increasing. However, under certain degree conditions we can assure that $\chi(U) < \chi(\overline{U})$ when $\overline{U}$ is obtained from a $(3,1)$-*mso* on U.

Lemma 3.2 *Let $U \in \mathcal{C}_n$ and assume that $\overline{U}$ is a tree obtained from U by a $(3,1)$-mso. If $n_2^U = 0$ or $n_4^U = 0$ then $\chi(U) < \chi(\overline{U})$.*

Proof. Assume that $\delta_x^U = 3$ and $\delta_y^U = 1$. By Lemma 2.2,

$$\chi(U) - \chi(\overline{U}) = \left(\frac{1}{\sqrt{3}} - \frac{1}{\sqrt{2}}\right)\left(R_B(x) + \frac{1}{\sqrt{\delta_a^U}}\right) + \left(1 - \frac{1}{\sqrt{2}}\right) R_B(y)$$

(i) If $n_4^U = 0$ then it is easy to see that $R_B(x) + \frac{1}{\sqrt{\delta_a^U}} \geq \frac{3}{\sqrt{3}}$. Also, $R_B(y) \leq \frac{1}{\sqrt{2}}$. Consequently,

$$\chi(U) - \chi(\overline{U}) \leq \left(\frac{1}{\sqrt{3}} - \frac{1}{\sqrt{2}}\right)\left(\frac{3}{\sqrt{3}}\right) + \left(1 - \frac{1}{\sqrt{2}}\right)\left(\frac{1}{\sqrt{2}}\right) < 0$$

(ii) If $n_2^U = 0$ then $R_B(x) + \frac{1}{\sqrt{\delta_a^U}} \geq \frac{3}{2}$ and $R_B(y) \leq \frac{1}{\sqrt{3}}$. Hence

$$\chi(U) - \chi(\overline{U}) \leq \left(\frac{1}{\sqrt{3}} - \frac{1}{\sqrt{2}}\right)\frac{3}{2} + \left(1 - \frac{1}{\sqrt{2}}\right)\left(\frac{1}{\sqrt{3}}\right) < 0$$

■

Lemmas 3.1 and 3.2 gives an algorithm to construct by means of maximal subtree operations, a χ-increasing sequence of trees ending in L_n, the path tree with n vertices.

Theorem 3.3 *For every $U \in \mathcal{C}_n$ with degree sequence (n_1, n_2, n_3, n_4) we can construct a χ-increasing sequence of trees $\{U_j\}_{j=0}^{n_1-2} \subseteq \mathcal{C}_n$, where $U_0 = U, U_{n_1-2} = L_n$ and $U_j = \mathcal{M}(U_{j-1})$ for each $1 \leq j \leq n_1 - 2$. In particular, $U \preceq_{mso} L_n$.*

Proof. By a repeated use of Lemma 3.1, we can construct a χ-increasing sequence of trees $\{U_j\}_{j=0}^{n_4} \subseteq \mathcal{C}_n$ such that $U_0 = U$ and the degree sequence of U_{n_4} is $(n_1 - n_4, n_2 + n_4, n_3 + n_4, 0)$. Since U_{n_4} has no vertices of degree 4 and a $(3,1)$-*mso* does not modify the number of vertices of degree 4 (see Table 1), we can apply Lemma 3.2 to obtain a χ-increasing sequence of trees $\{U_j\}_{j=n_4}^{n_3+2n_4} \subseteq \mathcal{C}_n$, where $U_{n_3+2n_4} = L_n$. The result follows from the fact that $n_1 = n_3 + 2n_4 + 2$. ■

Example 3.4 *Table 2 illustrates the algorithm given in Theorem 3.3 to construct a χ-increasing sequence $\{U_j\}_{j=0}^{7} \subseteq \mathcal{C}_{19}$ such that $U_i = \mathcal{M}(U_{i-1}, x, a, y)$, for each $1 \leq i \leq 7$.*

Table 2

4 χ-decreasing sequence of trees in $\mathcal{C}_n$

Now we turn our attention to the problem of constructing χ-decreasing sequences of chemical trees using maximal subtree operations.

Lemma 4.1 *Let $U \in \mathcal{C}_n$ with degree sequence (n_1, n_2, n_3, n_4) and assume that $n_2 \geq 2$. Then there exists $\overline{U} \in \mathcal{C}_n$, obtained by a $(2,2)$-mso on U, such that $\chi(U) > \chi(\overline{U})$.*

Proof. We can choose $x, y \in V(U)$ such that $\delta_x^U = \delta_y^U = 2$ and there are no vertices of degree 2 between them. By Lemma 2.2,

$$\chi(U) - \chi(\overline{U}) = \left(\frac{1}{\sqrt{2}} - 1\right) R_B(x) + \left(\frac{1}{\sqrt{2}} - \frac{1}{\sqrt{3}}\right)\left(R_B(y) + \frac{1}{\sqrt{\delta_a^U}}\right)$$

We distinguish two cases: (i) If $xy \in E(U)$ then $R_B(x) = \frac{1}{\sqrt{2}}$, $R_B(y) \geq 1 + \frac{1}{2}$ and $\frac{1}{\sqrt{\delta_a^U}} \geq \frac{1}{2}$. Therefore,

$$\chi(U) - \chi(\overline{U}) \geq \left(\frac{1}{\sqrt{2}} - 1\right)\frac{1}{\sqrt{2}} + \left(\frac{1}{\sqrt{2}} - \frac{1}{\sqrt{3}}\right) 2 > 0$$

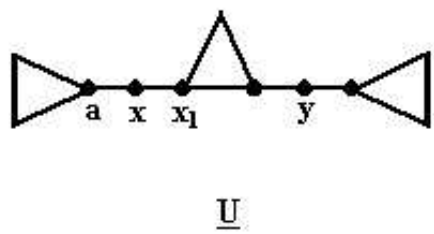

Figure 2:

(ii) Otherwise, we may choose x, y as in the Figure 2

Figure 2

where $\delta_{x_1}^U \geq 3$ since by our choice x_1 cannot be of degree 2. Notice that $x_1 = y_1$ is possible. Then $R_B(x) \leq \frac{1}{\sqrt{3}}$, $R_B(y) \geq 1$ and $\frac{1}{\sqrt{\delta_a^U}} \geq \frac{1}{2}$ and therefore

$$\chi(U) - \chi(\overline{U}) \geq \left(\frac{1}{\sqrt{2}} - 1\right)\left(\frac{1}{\sqrt{3}}\right) + \left(\frac{1}{\sqrt{2}} - \frac{1}{\sqrt{3}}\right)\left(\frac{3}{2}\right) > 0$$

■

Lemma 4.2 *Let $U \in \mathcal{C}_n$ with degree sequence $(n_1, 1, n_3, n_4)$. If $n_3 \geq 1$ then every $\overline{U} \in \mathcal{C}_n$ obtained by a $(2,3)$-mso on U satisfies $\chi(U) > \chi(\overline{U})$.*

Proof. Let $x, y \in V(U)$ such that $\delta_x^U = 2$ and $\delta_y^U = 3$. By Lemma 2.2,

$$\begin{aligned}\chi(U) - \chi(\overline{U}) &= \left(\frac{1}{\sqrt{2}} - 1\right) R_B(x) + \left(\frac{1}{\sqrt{3}} - \frac{1}{2}\right) R_B(y) + \\ &\quad \left(\frac{1}{\sqrt{2}} - \frac{1}{2}\right)\frac{1}{\sqrt{\delta_a^U}}\end{aligned}$$

Since $R_B(x) \leq \frac{1}{\sqrt{3}}$, $R_B(y) \geq \frac{3}{2}$ and $\frac{1}{\sqrt{\delta_a^U}} \geq \frac{1}{2}$ we deduce

$$\chi(U) - \chi(\overline{U}) \geq \left(\frac{1}{\sqrt{2}} - 1\right)\frac{1}{\sqrt{3}} + \left(\frac{1}{\sqrt{3}} - \frac{1}{2}\right)\frac{3}{2} + \left(\frac{1}{\sqrt{2}} - \frac{1}{2}\right)\frac{1}{2} > 0$$

■

By Lemma 4.1 and an inductive argument we can show that if $U \in \mathcal{C}_n$ has degree sequence (n_1, n_2, n_3, n_4) and $n_2 = 2l$ or $n_2 = 2l+1$, where l is a positive integer, we can construct a χ-decreasing sequence $\{U_j\}_{j=0}^{l} \subseteq \mathcal{C}_n$, where $U_0 = U$ and $U_j = \mathcal{M}(U_{j-1})$ for each $1 \leq j \leq l$. The degree sequence of U_l is

$$\begin{array}{lll}(n_1 + l, 0, n_3 + l, n_4) & \text{if} & n_2 = 2l \\ (n_1 + l, 1, n_3 + l, n_4) & \text{if} & n_2 = 2l + 1\end{array}$$

Now, by Lemma 4.2, if U_k has degree sequence $(n_1 + l, 1, n_3 + l, n_4)$ then we can construct a tree $U_{l+1} \in \mathcal{C}_n$ using a $(2,3)$-*mso* on U_l, such that $\chi(U_l) > \chi(U_{l+1})$, and U_{l+1} has degree sequence $(n_1 + l + 1, 0, n_3 + l - 1, n_4 + 1)$ (see Table 1). In this way we have shown the following result:

Theorem 4.3 *Let $U \in \mathcal{C}_n$ with degree sequence (n_1, n_2, n_3, n_4). Then there exists a χ-decreasing sequence $\{U_j\}_{j=0}^{l} \subseteq \mathcal{C}_n$, where $U = U_0$, $U_j = \mathcal{M}(U_{j-1})$ for each $1 \le j \le l$, and the following conditions hold:*

1. *If $n_2 \equiv 0 \bmod (2)$ then $l = \frac{n_2}{2}$ and U_l has degree sequence*
$$\left(n_1 + \frac{n_2}{2}, 0, n_3 + \frac{n_2}{2}, n_4\right)$$
2. *If $n_2 \equiv 1 \bmod (2)$ then $l = \frac{n_2+1}{2}$ and U_l has degree sequence*
$$\left(n_1 + \frac{n_2+1}{2}, 0, n_3 + \frac{n_2-3}{2}, n_4 + 1\right)$$

We have reduced the problem to chemical trees with no vertices of degree 2.

Lemma 4.4 *Let $U \in \mathcal{C}_n$ with degree sequence $(n_1, 0, n_3, n_4)$. If $n_3 \ge 2$ then there exists a tree $\overline{U} \in \mathcal{C}_n$ obtained by a $(3,3)$-mso on U, such that $\chi(U) > \chi(\overline{U})$.*

Proof. Let $x, y \in V(U)$ such that $\delta_x^U = \delta_y^U = 3$. By Lemma 2.2
$$\chi(U) - \chi(\overline{U}) = \left(\frac{1}{\sqrt{3}} - \frac{1}{\sqrt{2}}\right) R_B(x) + \left(\frac{1}{\sqrt{3}} - \frac{1}{2}\right)\left(R_B(y) + \frac{1}{\sqrt{\delta_a^U}}\right)$$
Assume first that $xy \in E(U)$ (see Figure 3).

Figure 3

If $\delta_c^U = \delta_d^U = 1$ then $R_B(x) \le \frac{1}{\sqrt{3}} + 1$, $R_B(y) = 2 + \frac{1}{\sqrt{2}}$ and $\frac{1}{\sqrt{\delta_a^U}} \ge \frac{1}{2}$. Hence
$$\chi(U) - \chi(\overline{U}) \ge \left(\frac{1}{\sqrt{3}} - \frac{1}{\sqrt{2}}\right)\left(\frac{1}{\sqrt{3}} + 1\right) + \left(\frac{1}{\sqrt{3}} - \frac{1}{2}\right)\left(\frac{5}{2} + \frac{1}{\sqrt{2}}\right) > 0$$
Without loosing generality, we can assume that $\delta_a^U = \min\{\delta_a^U, \delta_b^U, \delta_c^U, \delta_d^U\}$ and by our previous argument, δ_a^U and δ_b^U are not simultaneously equal to 1. In particular, $\delta_b^U \ge 2$. We consider two cases:

(i) Suppose $\delta_a^U = 1$. Since $R_B(x) \le \frac{1}{\sqrt{3}} + \frac{1}{\sqrt{2}}$ and $R_B(y) \ge \frac{1}{\sqrt{2}} + 1$, then
$$\chi(U) - \chi(\overline{U}) \ge \left(\frac{1}{\sqrt{3}} - \frac{1}{\sqrt{2}}\right)\left(\frac{1}{\sqrt{3}} + \frac{1}{\sqrt{2}}\right) + \left(\frac{1}{\sqrt{3}} - \frac{1}{2}\right)\left(\frac{1}{\sqrt{2}} + 2\right) > 0$$
(ii) Suppose $2 \le \delta_a^U \le 4$. Then $R_B(x) \le \frac{1}{\sqrt{3}} + \frac{1}{\sqrt{\delta_a^U}}$ since $\frac{1}{\sqrt{\delta_a^U}} \ge \frac{1}{\sqrt{\delta_b^U}}$. Also, $R_B(y) \ge \frac{1}{\sqrt{2}} + 1$ and $\frac{1}{\sqrt{\delta_a^U}} \le \frac{1}{\sqrt{2}}$. Consequently,
$$\begin{aligned}\chi(U) - \chi(\overline{U}) &\ge \left(\frac{1}{\sqrt{3}} - \frac{1}{\sqrt{2}}\right)\left(\frac{1}{\sqrt{3}} + \frac{1}{\sqrt{\delta_a^U}}\right) + \left(\frac{1}{\sqrt{3}} - \frac{1}{2}\right)\left(\frac{1}{\sqrt{2}} + \frac{3}{2}\right) \\ &\ge \left(\frac{1}{\sqrt{3}} - \frac{1}{\sqrt{2}}\right)\left(\frac{1}{\sqrt{3}} + \frac{1}{\sqrt{2}}\right) + \left(\frac{1}{\sqrt{3}} - \frac{1}{2}\right)\left(\frac{1}{\sqrt{2}} + \frac{3}{2}\right) > 0\end{aligned}$$
and we are done.

Now suppose that $xy \notin E(U)$. We may assume that U has the form

Figure 4

where $\delta_{x_1}^U = 4$ and $\delta_{y_1}^U = 4$ ($x_1 = y_1$ is possible). Then, an identical analysis as above proves the result. ■

Let $U \in \mathcal{C}_n$ with degree sequence $(n_1, 0, n_3, n_4)$. By Lemma 4.4 there exists $U_1 \in \mathcal{C}_n$ with degree sequence $(n_1, 1, n_3 - 2, n_4 + 1)$ and $\chi(U) > \chi(U_1)$. If $n_3 - 2 > 0$ then we can apply Lemma 4.2 to obtain a tree $U_2 \in \mathcal{C}_n$ with degree sequence $(n_1 + 1, 0, n_3 - 3, n_4 + 2)$ and $\chi(U_1) > \chi(U_2)$. If $n_3 - 3 > 0$ then we again apply Lemma 4.4 ... Continuing this (finite) process we arrive by a counting argument to our next result:

Theorem 4.5 *Let $U \in \mathcal{C}_n$ with degree sequence $(n_1, 0, n_3, n_4)$. Then there exists a χ-decreasing sequence $\{U_j\}_{j=0}^{l} \subseteq \mathcal{C}_n$, where $U = U_0$, $U_j = \mathcal{M}(U_{j-1})$ for each $1 \leq j \leq l$, and the following holds:*

1. *If $n_3 \equiv 0 \bmod (3)$ then $l = \frac{2n_3}{3}$ and U_l has degree sequence*

$$\left(n_1 + \frac{n_3}{3}, 0, 0, n_4 + \frac{2n_3}{3}\right)$$

2. *If $n_3 \equiv 1 \bmod (3)$ then $l = \frac{2n_3-2}{3}$ and U_l has degree sequence*

$$\left(n_1 + \frac{n_3-1}{3}, 0, 1, n_4 + \frac{2n_3-2}{3}\right)$$

3. *If $n_3 \equiv 2 \bmod (3)$ then $l = \frac{2n_3-1}{3}$ and U_l has degree sequence*

$$\left(n_1 + \frac{n_3-2}{3}, 1, 0, n_4 + \frac{2n_3-1}{3}\right)$$

From Theorems 4.3 and 4.5 we obtain an algorithm to construct, using maximal subtree operations, a χ-decreasing sequence of chemical trees ending in a tree which belongs to one of the sets $\mathcal{C}_{00}$, $\mathcal{C}_{01}$ or $\mathcal{C}_{10}$ defined as

$$\begin{aligned}
\mathcal{C}_{00} &= \left\{U \in \mathcal{C}_n : n_2^U = 0 \text{ and } n_3^U = 0\right\}; \\
\mathcal{C}_{01} &= \left\{U \in \mathcal{C}_n : n_2^U = 0 \text{ and } n_3^U = 1\right\} \text{ and} \\
\mathcal{C}_{10} &= \left\{U \in \mathcal{C}_n : n_2^U = 1 \text{ and } n_3^U = 0\right\}.
\end{aligned}$$

We recall the well-known relations verified by a tree $U \in \mathcal{C}_n$ with degree sequence (n_1, n_2, n_3, n_4)

$$\begin{aligned}
n_1 + n_2 + n_3 + n_4 &= n \\
n_3 + 2n_4 + 2 &= n_1
\end{aligned} \tag{3}$$

which implies

$$n = 2 + n_2 + 2n_3 + 3n_4. \tag{4}$$

From this relations we get that, depending on the value of n *mod*(3), only one of these sets is not empty. Thus we have shown the following result.

Theorem 4.6 *Let $U \in \mathcal{C}_n$.*

1. *If $n \equiv 0 \bmod (3)$ then there exists $V \in \mathcal{C}_{10}$ such that $V \preceq_{mso} U$.*
2. *If $n \equiv 1 \bmod (3)$ then there exists $V \in \mathcal{C}_{01}$ such that $V \preceq_{mso} U$.*
3. *If $n \equiv 2 \bmod (3)$ then there exists $V \in \mathcal{C}_{00}$ such that $V \preceq_{mso} U$.*

Example 4.7 *Table 3 illustrates the algorithm given by Theorems 4.3 and 4.5 to construct a χ-decreasing sequence $\{U_j\}_{j=0}^{5} \subseteq \mathcal{C}_{20}$ such that $U_i = \mathcal{M}(U_{i-1}, x, a, y)$, for each $1 \leq i \leq 5$. Note that $U_5 \in \mathcal{C}_{00}$ which is consistent with Theorem 4.6 since $20 \equiv 2 \bmod (3)$.*

Table 3

5 Extremal elements in $\mathcal{C}_n$ with respect to $\preceq_{mso}$

In this section we will determine the maximal and minimal elements of $\mathcal{C}_n$ with respect to $\preceq_{mso}$. It follows from Theorem 3.3 that $U \preceq_{mso} L_n$, for every $U \in \mathcal{C}_n$. In other words, L_n is the unique maximal element in $\mathcal{C}_n$ with respect to the order $\preceq_{mso}$. By Theorem 4.6, the question about the minimal elements is reduced to determine the minimal elements of $\mathcal{C}_{00}$, $\mathcal{C}_{01}$ and $\mathcal{C}_{10}$.

The following identity will be useful [6]: if G is a graph with n vertices (non-isolated vertices) then

$$\chi(G) = \frac{n}{2} - \frac{1}{2} \sum_{1 \le i < j \le n-1} \left(\frac{1}{\sqrt{j}} - \frac{1}{\sqrt{i}} \right)^2 m_{ij} \tag{5}$$

where m_{ij} denotes the number of edges connecting a vertex of degree i to a vertex of degree j.

Theorem 5.1 *Suppose $n \equiv 2 \bmod (3)$. Then $\mathcal{C}_{00}$ is the set of minimal elements of $\mathcal{C}_n$ with respect to $\preceq_{mso}$.*

Proof. By Theorem 4.6 it suffices to show that χ is constant on $\mathcal{C}_{00}$. If $T \in \mathcal{C}_{00}$ then

$$\begin{array}{lll} m_{12} = 0 & m_{13} = 0 & m_{14} = n_1 \\ m_{23} = 0 & m_{24} = 0 & m_{34} = 0 \end{array}$$

Hence by (5)

$$\chi(T) = \frac{n}{2} - \frac{1}{2} \left(\frac{1}{2} - 1 \right)^2 n_1$$

From relations (3) we deduce that $n_1 = \frac{2(n+1)}{3}$ which implies $\chi(T) = \frac{5n-1}{12}$. Since $\chi(T)$ depends only on n we conclude that χ is constant on $\mathcal{C}_{00}$. ■

We now turn our attention to the set $\mathcal{C}_{01}$. Let us assume that $n \ge 13$ (which implies $n_4 \ge 3$ by equation (4)). Then we can decompose $\mathcal{C}_{01}$ as a disjoint union

$$\mathcal{C}_{01} = \mathcal{P}_0 \cup \mathcal{P}_1 \cup \mathcal{P}_2$$

where $\mathcal{P}_i = \{P \in \mathcal{C}_{01} : m_{13} = i\}$ for $0 \le i \le 2$ (see Figure 5).

Figure 5

Lemma 5.2 *If $P_0 \in \mathcal{P}_0$, $P_1 \in \mathcal{P}_1$ and $P_2 \in \mathcal{P}_2$, then $\chi(P_0) = \frac{5n-11}{12} + \frac{3}{2\sqrt{3}}$, $\chi(P_1) = \frac{5n-14}{12} + \frac{2}{\sqrt{3}}$ and $\chi(P_2) = \frac{5n-17}{12} + \frac{5}{2\sqrt{3}}$. In particular, the Randić function χ is constant on each of the sets $\mathcal{P}_i$, where $i = 0, 1, 2$. Moreover, $\chi(P_0) < \chi(P_1) < \chi(P_2)$.*

Proof. If $P_1 \in \mathcal{P}_1$ then

$$\begin{array}{lll} m_{12} = 0 & m_{13} = 1 & m_{14} = n_1 - 1 \\ m_{23} = 0 & m_{24} = 0 & m_{34} = 2 \end{array}$$

It follows from (5) that

$$\begin{aligned} \chi(P_1) &= \frac{n}{2} - \frac{1}{2} \left[\left(\frac{1}{\sqrt{3}} - 1 \right)^2 + (n_1 - 1) \left(\frac{1}{2} - 1 \right)^2 + 2 \left(\frac{1}{2} - \frac{1}{\sqrt{3}} \right)^2 \right] \\ &= \frac{n}{2} - \frac{n_1 + 9}{8} + \frac{2}{\sqrt{3}} \end{aligned}$$

From relations (3)

$$\begin{aligned} n_1 + 1 + n_4 &= n \\ n_1 &= 3 + 2n_4 \end{aligned}$$

we obtain $n_1 = \frac{1}{3}(2n+1)$ and so $\chi(P_1) = \frac{5n-14}{12} + \frac{2}{\sqrt{3}}$. Note that $\chi(P_1)$ only depends on n, which implies that χ is constant on the set $\mathcal{P}_1$. The rest of the proof is similar. ■

We will need the following notation for describing the minimal elements of $\mathcal{C}_{01}$.

Notation 5.3 *If $P \in \mathcal{C}_n$ and $x \in V(P)$, then we denote by $n_1(x)$ the cardinality of the set*

$$\{y \in \mathcal{N}_x : \delta_y = 1\}$$

Theorem 5.4 *Suppose $n \equiv 1 \bmod(3)$ and $n \geq 13$. Then the set of minimal elements of $\mathcal{C}_n$ with respect to $\preceq_{mso}$ is*

$$\mathcal{P}_0 \cup \{P \in \mathcal{P}_1 : \ n_1(x) \geq 2 \text{ for every } x \in V(P) \text{ such that } \delta_x = 4.\}$$

Proof. It is clear from Theorem 4.6 and Lemma 5.2 that every $P \in \mathcal{P}_0$ is minimal. On the other hand, we note that in $\mathcal{C}_{01}$, the only possible maximal subtree operations are of the type $(4,3)$-, $(4,1)$- and $(3,1)$- (see Table 1). However, by Lemmas 3.2 and 3.1 every $(4,1)$-*mso* and $(3,1)$-*mso* in $\mathcal{C}_{01}$ is χ-increasing, so we only need to consider $(4,3)$-*mso* on $\mathcal{C}_{01}$. The rest of the proof is a consequence of the following facts.

(i) Let $P \in \mathcal{P}_1$. Then P is minimal if and only if $n_1(x) \geq 2$ for every $x \in V(P)$ such that $\delta_x = 4$. In fact, assume that $n_1(x) \geq 2$ for every $x \in V(P)$ such that $\delta_x = 4$. If $\overline{P}$ is obtained from P by a $(4,3)$-*mso*, then it is easy to see that $\overline{P} \in \mathcal{P}_1 \cup \mathcal{P}_2$ which implies by Lemma 5.2 that $\chi(P) \leq \chi(\overline{P})$. Hence, P is minimal. On the other hand, if $n_1(x) = 0$ or 1, then there exists a $\overline{P} \in \mathcal{P}_0$ obtained from P by a $(4,3)$-*mso*. By Lemma 5.2, $\chi(\overline{P}) < \chi(P)$ and so P is not minimal.

(ii) No $P \in \mathcal{P}_2$ is minimal. In fact, let $P \in \mathcal{P}_2$. If $n \geq 13$ then there exist a $x \in V(P)$ such that $\delta_x = 4$ and $n_1(x) \leq 2$. It follows easily that there exists $\overline{P} \in \mathcal{P}_0 \cup \mathcal{P}_1$ which is obtained by a $(4,3)$-*mso* on P. Consequently, $\chi(\overline{P}) < \chi(P)$ and so P is not minimal. ■

Example 5.5 *Consider the tree P shown in Figure 6. Then P is minimal with respect to the relation $\preceq_{mso}$.*

Figure 6

Finally consider the set $\mathcal{C}_{10}$. For $i = 0, 1$, let $\mathcal{Q}_i = \{P \in \mathcal{C}_{10} : m_{12} = i\}$ (see Figure 7).

Figure 7

Assume that $n \geq 9$, which implies by equation (4) that $n_4 \geq 2$. Then $\mathcal{C}_{10}$ is the disjoint union

$$\mathcal{C}_{10} = \mathcal{Q}_0 \cup \mathcal{Q}_1$$

Lemma 5.6 *If $Q_0 \in \mathcal{Q}_0$ and $Q_1 \in \mathcal{Q}_1$ then $\chi(Q_0) = \frac{5n-9}{12} + \frac{1}{\sqrt{2}}$ and $\chi(Q_1) = \frac{5n-12}{12} + \frac{3}{2\sqrt{2}}$. In particular, the Randić function χ is constant on each of the sets $\mathcal{Q}_i$, where $i = 0, 1$. Moreover, $\chi(Q_0) < \chi(Q_1)$.*

Proof. Let $Q_1 \in \mathcal{Q}_1$. Then

$$\begin{array}{ccc} m_{12} = 1 & m_{13} = 0 & m_{14} = n_1 - 1 \\ m_{23} = 0 & m_{24} = 1 & m_{34} = 0 \end{array}$$

It follows from (5) that

$$\begin{aligned} \chi(Q_1) &= \frac{n}{2} - \frac{1}{2}\left[\left(\frac{1}{\sqrt{2}} - 1\right)^2 + (n_1 - 1)\left(\frac{1}{2} - 1\right)^2 + 2\left(\frac{1}{2} - \frac{1}{\sqrt{2}}\right)^2\right] \\ &= \frac{n}{2} - \frac{1}{2}\left[2 - \frac{3}{\sqrt{2}} + \frac{n_1}{4}\right] \end{aligned}$$

From relations (3) we get that $n_1 + 1 + n_4 = n$ and $n_1 = 2 + 2n_4$. Thus $n_1 = \frac{2n}{3}$ and so $\chi(Q_1) = \frac{5n-12}{12} + \frac{3}{2\sqrt{2}}$. Similarly in the case $Q_0 \in \mathcal{Q}_0$. ■

From Theorem 4.6 and the previous result we immediately deduce that every $U \in \mathcal{Q}_0$ is necessarily $\preceq_{mso}$-minimal in $\mathcal{C}_{10}$ (and thus in $\mathcal{C}_n$). To fully describe all minimal elements of $\mathcal{C}_{10}$ we need to introduce some notation. For each $U \in \mathcal{Q}_1$, we denote by $y_0^U \in V(U)$ the unique vertex of degree 2 and x_0^U the neighbor vertex of y_0^U of degree 4.

Theorem 5.7 *Suppose $n \equiv 0 \bmod (3)$ and $n \geq 9$. Then the set of minimal elements of $\mathcal{C}_n$ with respect to $\preceq_{mso}$ is*

$$\mathcal{Q}_0 \cup \{U \in \mathcal{Q}_1 : \ n_1(x_0^U) \geq 1 \text{ and } n_1(z) \geq 2 \text{ for all } z \in V(U) \text{ such that } \delta_z^U = 4,\ z \neq x_0^U\}$$

Proof. We have already argued that every $U \in \mathcal{Q}_0$ is minimal. Notice that in $\mathcal{C}_{10}$ the only maximal subtree operations possible (see Table 1) are of the form $(4,2)$-, $(4,1)$- and $(2,1)$-. Again, by Lemma 3.1 every $(4,1)$-*mso* is χ-increasing. On the other hand, if $\overline{Q}$ is obtained from $Q \in \mathcal{Q}_1$ by a $(2,1)$-*mso* then clearly $\overline{Q} \in \mathcal{Q}_1$ which implies by Lemma 5.6 that $\chi(Q) = \chi(\overline{Q})$. So we only need to consider $(4,2)$-*mso* on $\mathcal{Q}_1$.

Now let $U \in \mathcal{Q}_1$. We will write y_0 and x_0 in place of y_0^U and x_0^U. We consider first the case where there exists $z \in V(U)$ such that $\delta_z^U = 4$, $z \neq x_0$ and $n_1(z) \leq 1$. We return to the notation U and $\overline{U}$ in Figure 1. By Lemma 2.2

$$\chi(U) - \chi(\overline{U}) = \left(\frac{1}{2} - \frac{1}{\sqrt{3}}\right)\left(R_B(x) + \frac{1}{\sqrt{\delta_a^U}}\right) + \left(\frac{1}{\sqrt{2}} - \frac{1}{\sqrt{3}}\right) R_B(y_0) \tag{6}$$

If $n_1(z) = 1$ then let $x = z$ and a the unique neighbor of z of degree 1. Then $R_B(x) = \frac{3}{2}$, $\delta_a^U = 1$ and $R_B(y_0) = \frac{3}{2}$. On the other hand, if $n_1(z) = 0$ then again let $x = z$ and a any neighbor of z. Then $R_B(x) = \frac{3}{2}$, $\delta_a^U = 4$ and $R_B(y_0) = \frac{3}{2}$. In any case, from (6) we get $\chi(U) - \chi(\overline{U}) > 0$ which implies that U is not minimal.

Let us consider now the case where $n_1(x_0) = 0$. Let $x = x_0$ and a any neighbor of x_0 of degree 4. In this case $R_B(x_0) = 1 + \frac{1}{\sqrt{2}}$ and $R_B(y_0) = 1 + \frac{1}{\sqrt{3}}$. Thus from (6) we get $\chi(U) - \chi(\overline{U}) > 0$ which implies that U is not minimal.

Suppose now that $U \in \mathcal{Q}_1$, $n_1(x_0^U) \geq 1$ and $n_1(z) \geq 2$ for all $z \in V(U)$ such that $\delta_z^U = 4$, $z \neq x_0^U$. To see that U is minimal is suffices to show that $\chi(U) - \chi(\overline{U}) < 0$ for any choice of x and any neighbor a of x. To simplify the argument, notice that $R_B(x) + \frac{1}{\sqrt{\delta_a^U}} = R_U(x)$. We consider two cases:

(i) Suppose $x \neq x_0$. Since $n_1(x) \geq 2$, $R_U(x) = 3$ and $R_B(y_0) = \frac{3}{2}$.

(ii) Suppose $x = x_0$. Then $R_B(y_0) = 1 + \frac{1}{\sqrt{3}}$. If $n_1(x_0) = 2$, then $R_U(x_0) = 5/2 + 1/\sqrt{2}$ and if $n_1(x_0) = 1$, then $R_U(x_0) = 2 + 1/\sqrt{2}$. Note that $n_1(x_0) \neq 3$ since $n \geq 9$.

In every case, we have that $R_U(x) \geq 2 + 1/\sqrt{2}$ and $R_B(y_0) \leq 1 + 1/\sqrt{3}$. Therefore from (6) we get that $\chi(U) - \chi(\overline{U}) < 0$. Consequently, U is minimal. ■

Example 5.8 *Consider the tree U shown in Figure 8.*

Figure 8

We end this section by illustrating a novel approach, based on the properties of $\preceq_{mso}$, for establishing bounds for χ. We will give an alternative method to that found in [5] for determining the minimal, second minimal and third minimal value of χ on $\mathcal{C}_n$. We will work the particular case when $n \equiv 1$ *mod*(3). The idea is roughly speaking as follows. Let T be a chemical tree. By Theorem 4.6 there is a descending $\preceq_{mso}$-chain $\{T_i\}_{i=0}^k$, such that $T_0 = T$, $T_{i+1} \prec_{mso} T_i$ and $T_k \in \mathcal{C}_{01}$ (here is where we need that $n \equiv 1$ *mod*(3)) but $T_{k-1} \notin \mathcal{C}_{01}$. The way this chain is constructed gives enough information to estimate $\chi(T_{k-1})$ and from this we will determine the first values of χ on $\mathcal{C}_n$. More precisely, we have the following key fact.

Lemma 5.9 *For $n \equiv 1$ mod(3), $\chi(U) \geq \frac{5n-11}{12} + \sqrt{2} - 1/2$ for every $U \in \mathcal{C}_n \setminus (\mathcal{P}_0 \cup \mathcal{P}_1)$.*

Proof. Let $U \in \mathcal{C}_n \setminus (\mathcal{P}_0 \cup \mathcal{P}_1)$. From Lemma 5.2 we know that the result is valid if $U \in \mathcal{P}_2$, therefore we assume that $U \notin \mathcal{C}_{01} = \mathcal{P}_0 \cup \mathcal{P}_1 \cup \mathcal{P}_2$. By Theorem 4.6 there is a descending $\preceq_{mso}$-chain $\{T_i\}_{i=0}^k$ such that $T_0 = U$, $T_{i+1} \prec_{mso} T_i$ and T_k is in $\mathcal{C}_{01}$ but T_{k-1} is not in $\mathcal{C}_{01}$. We will denote T_k by S and T_{k-1} by T. Since $S \in \mathcal{C}_{01}$, then by Lemma 5.2 $\chi(S) \geq \frac{5n-11}{12} + \frac{3}{2\sqrt{3}}$. On the other hand, as $\chi(U) \geq \chi(T)$, it suffices to show that $\chi(T) - \chi(S) \geq \sqrt{2} - 1/2 - \frac{3}{2\sqrt{3}}$.

Since the algorithm used in the course of the proof of Theorem 4.6 uses either a $(2,3)$-mso, or a $(3,3)$-mso or a $(2,2)$-mso, then we know that S was obtained from T by one of these operations. However, by considering the degree sequence given by Table 1 we conclude that using a $(3,3)$-mso it is impossible to get to a tree in $\mathcal{C}_{01}$. So there are only two possible cases to consider.

(i) S was obtained from T by a $(2,3)$-mso. As in the proof of Lemma 4.2 we know that $\chi(T)-\chi(S) \geq (\frac{1}{\sqrt{2}}-1)\frac{1}{\sqrt{3}} + (\frac{1}{\sqrt{3}}-\frac{1}{2})\frac{3}{2} + (\frac{1}{\sqrt{2}}-\frac{1}{2})\frac{1}{2}$ and the result follows.

(ii) S was obtained from T by a $(2,2)$-mso. As in the proof of Lemma 4.1 there are two possibilities which need to be considered separately since they provide different lower bounds for $\chi(T)-\chi(S)$.

The first case considered in the proof of Lemma 4.1 gives that $\chi(T)-\chi(S) \geq (\frac{1}{\sqrt{2}}-1)\frac{1}{\sqrt{2}} + (\frac{1}{\sqrt{2}}-\frac{1}{\sqrt{3}})2$ and the result follows. The second case considered in the proof of Lemma 4.1 can be improved, since now we know that n_3^T is necessarily equal to zero (see Table 1) as $n_3^S = 1$. Following the proof of Lemma 4.1 but now using the fact that $R_B(x) = 1/\sqrt{4}$, we get $\chi(T)-\chi(S) \geq (\frac{1}{\sqrt{2}}-1)(\frac{1}{\sqrt{4}}) + (\frac{1}{\sqrt{2}}-\frac{1}{\sqrt{3}})\frac{3}{2}$. From this it follows that $\chi(T) \geq \frac{5n-11}{12} + \sqrt{2} - 1/2$. Notice that this is the only case where we obtain exactly the same bound as in the statement of the Lemma. ■

Theorem 5.10 *Let $n \equiv 1$ mod(3).*

1. *The minimal value of χ in $\mathcal{C}_n$ is $\frac{5n-11}{12} + \frac{3}{2\sqrt{3}}$ and it is attained exactly by the elements of $\mathcal{P}_0$.*
2. *The second minimal value of χ in $\mathcal{C}_n$ is $\frac{5n-14}{12} + \frac{2}{\sqrt{3}}$ and it is attained exactly by the elements of $\mathcal{P}_1$.*
3. *The third minimal value of χ in $\mathcal{C}_n$ is $\frac{5n-11}{12} + \sqrt{2} - 1/2$ and it is attained exactly by those trees such that $n_2 = 2$, $n_3 = 0$ and the two vertices of degree 2 are adjacent to two vertices of degree four.*

Proof. 1 follows from Lemma 5.2 and Theorem 5.4.

To show 2, we know from Lemma 5.2 that χ is constant in $\mathcal{P}_1$ with value $\frac{5n-14}{12} + \frac{2}{\sqrt{3}}$. It is also clear from Theorem 5.4 and Lemma 5.2 that every tree with χ equal to $\frac{5n-14}{12} + \frac{2}{\sqrt{3}}$ is necessarily in $\mathcal{P}_1$. From this and Lemma 5.9 the result follows.

Finally, notice that every tree as described in 3 has χ equal to $\frac{5n-11}{12} + \sqrt{2} - 1/2$ and from the proof of Lemma 5.9 it follows that they are the only trees with exactly this value of χ. Now the result follows from Lemma 5.2 and Lemma 5.9. ■

6 A general approach for ordering $\mathcal{C}_n$

In this section we will give a more precise formulation of the general approach outlined in the introduction.

By a tree transformation we will understand a binary relation $t(\cdot,\cdot)$ on $\mathcal{C}_n$. The motivating example is the relation $t(U,\overline{U})$ if $\overline{U} = \mathcal{M}(U)$, as defined in 2.1. Let $\mathcal{T}$ be a collection of transformations on $\mathcal{C}_n$. We associate to $\mathcal{T}$ a partial order as follows: $S \prec_{\mathcal{T}} T$ iff there is $t \in \mathcal{T}$ such that $t(S,T)$ and $\chi(S) < \chi(T)$. And define $\preceq_{\mathcal{T}}$ as usual. For instance, if $\mathcal{T}$ consists of all *mso*, then $\preceq_{\mathcal{T}} = \preceq_{mso}$.

The order $\preceq_{\mathcal{T}}$depends heavily on the choice of $\mathcal{T}$. Consider, for example, the subfamily $\mathcal{T}_l$ of *mso* consisting on all *mso* that moves a leave. That is to say, in definition 2.1 we restrict to those *mso* where $\delta_a = 1$. We will denote the corresponding order $\preceq_{\mathcal{T}_l}$ by just $\preceq_{leave}$. Analogously, let $\preceq_{path}$ be the corresponding order for the subfamily of *mso* that moves a exterior path (i.e. in definition 2.1 we restrict to those *mso* where the maximal subtree at x containing a is a path).

To see the difference between these partial orders, consider the tree U depicted in Figure 9

Figure 9

It is routine to verify that every tree obtained from U by moving a pendent vertex will have smaller connectivity index. In other words, U is $\preceq_{leave}$-maximal. It is also routine to verify that by moving any path of U

to a pendent vertex we get a tree with larger χ. That is to say, U is not $\preceq_{path}$-maximal. Consider now the tree W shown in Figure 10.

Figure 10

Let k be the length of longest $\preceq_{mso}$-chain from W to L_n and let l be the length of longest analogous $\preceq_{path}$-chain. It is routine (but a bit tedious) to verify that $k > l$. In other words, by using maximal subtrees instead of just paths we get, as expected, a more detailed picture of the behavior of χ. More subtle properties of $\preceq_{mso}$ will be apparent when dealing with the problem of computing extremal elements of some special subclasses of $\mathcal{C}_n$. This problem will be treated in a forthcoming paper [12].

One gets a different family of transformations by considering the relation $t(S, T)$ if the symmetric difference between S and T has cardinality at most 2. It is not difficult to show that this is the case if S is the result of applying a *mso* to T. These transformations were used in [3, 2] to define the heuristic routine for finding extremal graphs. It is an interesting topic for future research to study the corresponding partial order. And more generally, to study partial orders on $\mathcal{C}_n$ which are included in the total pre-order induced by χ.

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