Enumeration in hexagonal chains

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12 October 2018

Submitted in partial fulfillment of a structured masters degree at AIMS South Africa

Abstract

Hexagonal chains are simple models of benzenoid polymers which are common molecular structures in chemistry. These structures can be characterised using the Hosoya and Merrifield-Simmons indices such that their physicochemical properties can be predicted. This characterisation makes use of recursive relations and transfer matrices in order to determine the extremal values of the Hosoya and Merrifield-Simmons indices. We prove that the linear chain produces a maximum Hosoya index and a minimum Merrifield-Simmons index, and that the zig-zag chain produces a minimum Hosoya index and a maximum Merrifield-Simmons index.

Declaration

I, the undersigned, hereby declare that the work contained in this research project is my original work, and that any work done by others or by myself previously has been acknowledged and referenced accordingly.

Zakiena Hoossen, 12 October 2018

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1. Introduction

The Hosoya index was first introduced by Haruo Hosoya (Hosoya, 1971). In this paper, he introduced what is now known as the “Hosoya index” as a “topological index” (a term that is now used to refer to a variety of quantities). He showed the correlations between the Hosoya index and the boiling point of alkane isomers (saturated hydrocarbons). The correlation was based on data obtained in 1957 with respect to the boiling point of octane isomers as shown in Figure 1.1 (Hosoya, 2002b; Gutman and Polansky, 2012).

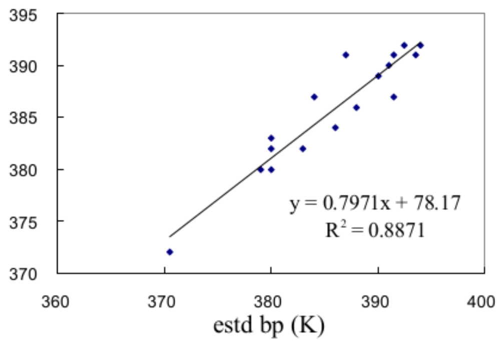


Figure 1.1: Observed and estimated boiling points of octane isomers (Hosoya, 2002b).

The correlation showed that the boiling point was related to the number of carbon atoms in the molecule. Thus, increasing the carbon atoms in a molecule would increase the boiling point. Since more than one isomer could exist an average boiling point value was taken for a given isomer. The boiling point values were estimated within a $\pm 4^o C$ range (Hosoya, 2002b).

The Merrifield-Simmons index was introduced by Merrifield and Simmons in order to describe molecular structures in terms of finite-set topology (Merrifield and Simmons, 1989). The Merrifield-Simmons index is the number of open sets of the finite topology and is equal to the number of independent sets of vertices of the graph corresponding to that topology (Huang et al., 2016).

Hexagonal chains are simple models of benzenoid polymers that are common molecular structures in chemistry. The molecular structure is the three-dimensional arrangement of the atoms that constitute a molecule. By understanding these structures one can understand why molecules of this form have certain physicochemical properties (Hosoya, 2002a). These properties are related to both physical and chemical properties, as well as the changes, and reactions according to physical chemistry such as the boiling point, absolute entropy and the heat of vaporization which have been established for alkane isomers (Gutman and Polansky, 2012).

1.0.1 Definition. (Dobrynin et al., 2002) Hexagonal chains are composed only of hexagons (six membered rings). The length of a chain is determined by the number of hexagons in the chain. These chains are defined such that hexagons can either be linked by a common edge with both hexagons sharing the vertices of the edge or by an edge where each vertex is part of a different hexagon. Only two hexagons can share a common edge. No branching (side chain) is allowed, which means that three hexagons cannot share a common vertex, all the hexagons except the terminal ones are adjacent (linked) to exactly two other hexagons.

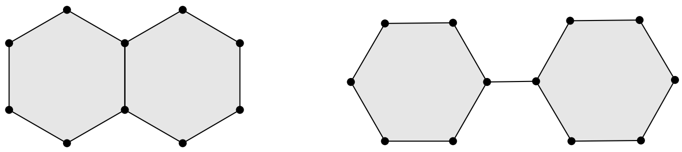


Figure 1.2: The hexagonal chains are linked either by a common edge with both hexagons sharing the vertices of the edge or by an edge, where each vertex is part of a different hexagon.

The hexagonal chains that will be covered in this paper are those where hexagons are connected by a common edge. For these hexagonal chains a hexagon can be added to a hexagonal chain in three different ways as shown in Figure 1.3. The type of addition is labelled 1, 2 and 3 respectively.

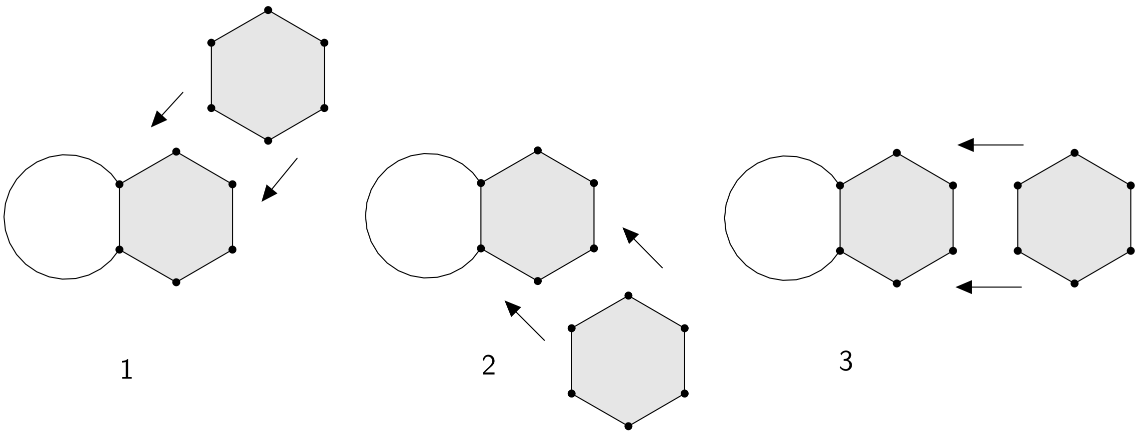
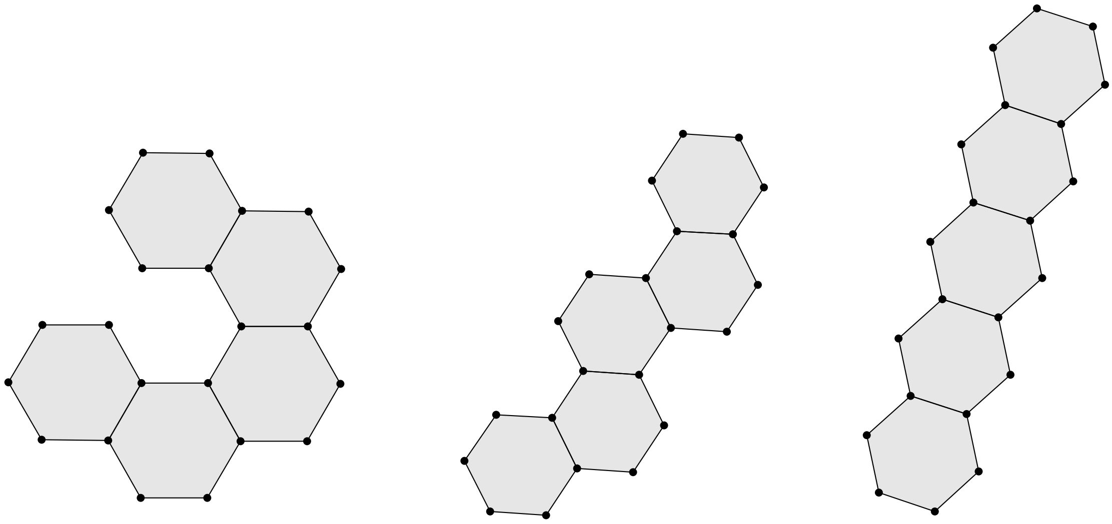


Figure 1.3: The three ways of attaching a hexagon to a chain.

1.0.2 Definition. A helical chain H_h is a chain of h hexagons formed when hexagons are always added to one another through type 1 addition (or always through a type 2 addition) addition as shown in Figure 1.4 (a).

1.0.3 Definition. A zig-zag chain S_h is a chain of h hexagons formed when hexagons are added to one another alternately through a type 1 and 2 addition as shown in Figure 1.4 (b). For the zig-zag chain the last hexagon is chosen to be a type 1 addition. Therefore, depending on the number of hexagons the chain starts with type 1 if h is even and with type 2 otherwise.

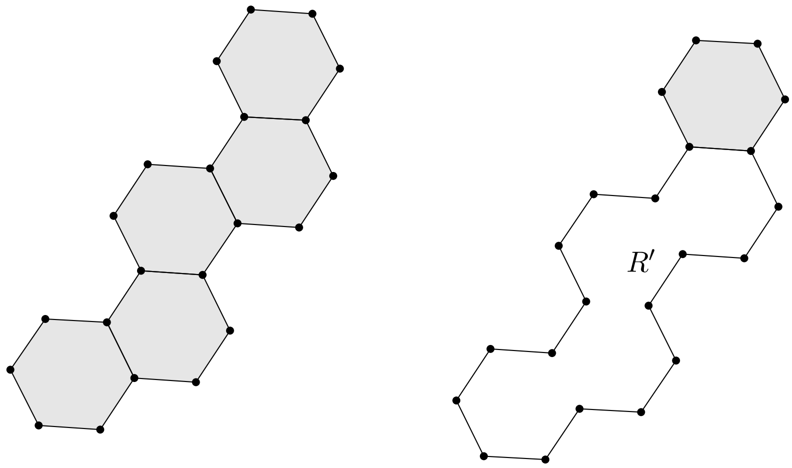
1.0.4 Definition. A linear chain L_h is a chain of h hexagons formed when hexagons are added only to one another through a type 3 addition as shown in Figure 1.4 (c).



(a) (b) (c)

Figure 1.4: The types of hexagonal chains shown are (a) helical, (b) zig-zag and (c) linear.

A chain of h hexagons can be considered as a shorter chain R' with an extra hexagon at the end. Here, R' is a hexagonal chain which contains $h-1$ hexagons.



(a) (b)

Figure 1.5: A R chain R is decomposed into the unshaded chain R' and an attached shaded hexagon.

1.0.5 Definition. We define certain auxiliary graphs associated with a hexagonal chain. These graphs are called derivatives of R' and shown in Figure 1.6. These graphs are produced by the removal of certain edges from the final hexagon added to the chain R'. If no further edges of the final hexagon are included, we obtain the graph $R_a = R'$; with one additional edge, we obtain the graphs R_b and R_c; with two additional edges the graph R_d. Later the Hosoya and the Merrifield-Simmons indices for hexagonal chains will be reduced to indices of these graphs using recursive relations associated with these indices.

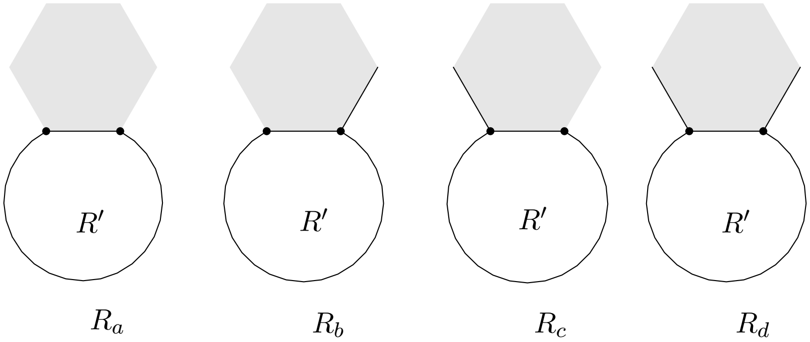


Figure 1.6: The different derivatives that are considered.

In this research project formulas for the Hosoya index and Merrifield-Simmons index of hexagonal chains are derived. An investigation into transfer matrices is made to enumerate matchings and independent sets in different families of hexagonal chains. An alternate method to that of Gutman and Zhang is used to determine the extremal values of these indices (Gutman, 1993; Lianzhu, 1998).

2. Recursive relations for the Hosoya and Merrifield-Simmons indices

In this chapter we derive recursive relations for the number of independent sets and matchings that are applied to vertices or edges of a graph.

2.0.1 Definition. A graph consists of a finite set of vertices V and a finite set of edges E. An edge connects two vertices to one another. For a vertex $v \in V$, $G - v$ is the graph induced by the vertices in $V - \{v\}$. The graph $G - e$ is the graph G without the edge e. The set of all vertices that share an edge to a specific vertex v is called the (open) neighbourhood of v and denoted by $N_G(v)$ (or just $N(v)$ for short). The set $N[v] = N(v) \cup v$ which also includes v itself is called the closed neighbourhood of v.

2.0.2 Definition. A matching is a set of independent edges (edges that do not share a common vertex). The Hosoya index $Z(G)$ of a graph G is the total number of matchings of G.

2.0.3 Definition. An independent set is a set of vertices that are not connected by an edge. The Merrifield-Simmons index $\sigma(G)$ of a graph G is the number of independent sets of G.

2.0.4 Example. In Figure 2.1 the capital letters refer to vertices and the lower case letters refer to edges. For example, $\{a\}$, $\{b\}$ and $\{c\}$ are three matchings containing only one edge, and $\{a, c\}$, $\{a, d\}$, $\{a, e\}$ are matchings containing two edges. Likewise, $\{A\}$, $\{B\}$ and $\{C\}$ are three independent sets containing only one vertex, and $\{A, C\}$, $\{A, D\}$, $\{A, E\}$ are three independent sets containing two vertices.

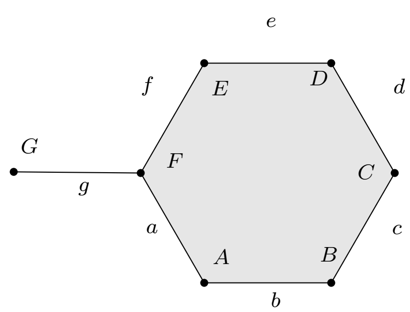


Figure 2.1: A graph used to describe matchings and independent sets.

2.0.5 Definition. An isolated vertex is a vertex that contains no edges connected to it.

2.0.6 Lemma. (Wagner and Wang, 2018) If edges are removed from a graph, then the Merrifield-Simmons index increases, while the Hosoya index decreases. If vertices are removed from a graph, then the Merrifield-Simmons index decreases. The Hosoya index does not increase, and decreases strictly if at least one of the vertices that are removed is not an isolated vertex.

Proof. If one removes an edge from the graph G, the Merrifield-Simmons index for that graph increases because the independent sets of the graph G are still independent sets in the graph $G - e$. In addition the graph $G - e$ also contains independent sets with the vertices that were connected to that particular edge. On the contrary, when an edge is removed from a graph, the matchings that contain that edge are also removed. Thus the Hosoya index decreases.

If a vertex v is removed from a graph then the independent sets which contained that vertex are removed. Thus the Merrifield-Simmons index for that graph $G-v$ decreases. When a vertex is removed any edge connected to that particular vertex is subsequently removed. Therefore, the matchings that contained those edges are also removed. Hence, the Hosoya index for that graph $G-v$ decreases. This implies that the Hosoya index strictly decreases if the vertex removed is not an isolated vertex. □

2.0.7 Definition. (Wikipedia) Connected components are maximal connected graphs (connected subgraphs that are not contained in a larger one). An example of three connected components that form a graph is shown in Figure 2.2.

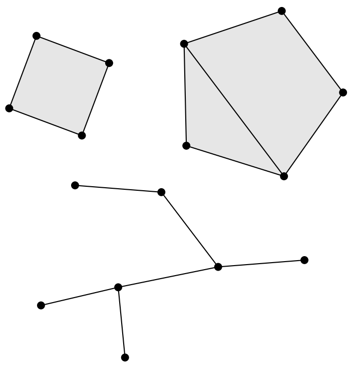


Figure 2.2: A graphical example of connected components.

2.0.8 Lemma. (Gutman, 1993) If G_1, G_2 , . . . , G_k are the connected components of a graph G, we have

$$\sigma(G) = \prod_{j=1}^{k} \sigma(G_j).$$

Proof. Every independent set of G can be decomposed uniquely into independent sets in G_1, G_2 , . . . , G_k. Thus, the total number of independent sets is the product of the number of independent sets of all the components. □

2.0.9 Lemma. (Gutman, 1993) For every vertex v of a graph G, we have

$$\sigma(G) = \sigma(G-v) + \sigma(G-N[v]).$$

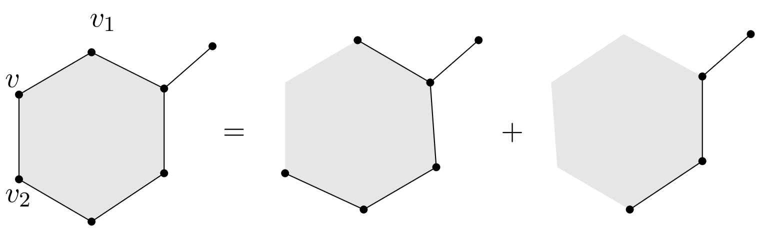


Figure 2.3: A graphical example of Lemma 2.0.9.

Proof. The number of independent sets of G without the vertex v is $\sigma(G-v)$. If v is contained in an independent set, then none of its neighbours is, and the remaining vertices form an independent set of $G-N[v]$. Thus the number of independent sets including v is $\sigma(G-N[v])$.

□

2.0.10 Lemma. (Gutman, 1993) For every edge e of graph G whose ends are vertices v and w, we have

$$\sigma(G) = \sigma(G-e) - \sigma(G-(N[v]\cup N[w])).$$

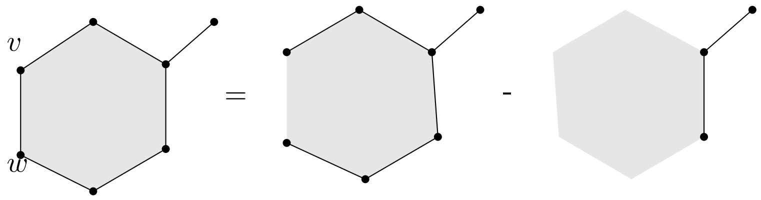


Figure 2.4: A graphical example of Lemma 2.0.10.

Proof. All independent sets of G are still independent sets of $G-e$ and $G-e$ has additional independent sets containing both v and w. The remaining vertices of such an independent set form an independent set in $G-(N[v]\cup N[w])$, thus the number of additional independent sets is $\sigma(G-(N[v]\cup N[w]))$.

□

2.0.11 Lemma. (Gutman, 1993) If G_1, G_2 , . . . , G_k are the connected components of a graph G, we have

$$Z(G) = \prod_{j=1}^{k} Z(G_j).$$

Proof. The proof is similar to the proof for independent sets. The matchings of G are uniquely decomposed into matchings of G_1, G_2 , . . . , G_k. Thus, the total number of matchings is the product of the number of matchings of all the components. □

2.0.12 Lemma. (Gutman, 1993) For every vertex v of G, we have

$$Z(G) = Z(G-v) + \sum_{w\in N(v)} Z(G-\{v,w\}).$$

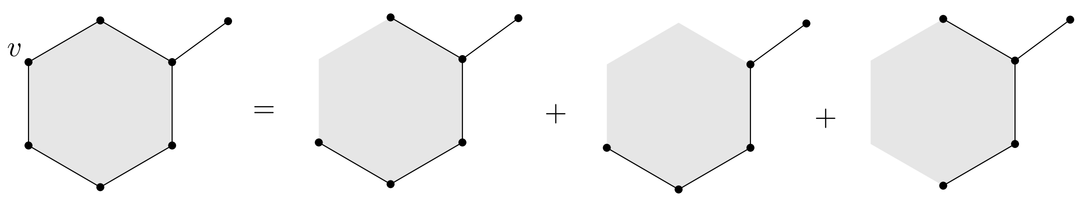


Figure 2.5: An example of the recursive relation for the number of matchings applied to a vertex v.

Proof. A matching contains either no edge incident with v or precisely one edge incident with v. The number of matchings of G that contain no edges connected to v is $Z(G - v)$ and the number of matchings that contains the edge between v and w is $Z(G - \{v, w\})$, since the remaining edges form a matching in $G - \{v, w\}$. The sum over all neighbours w of v counts the number of matchings containing an edge incident with v. □

2.0.13 Lemma. (Gutman, 1993) For every edge e of G whose ends are v and w, we have

$$Z(G) = Z(G - e) + Z(G - \{v, w\}).$$

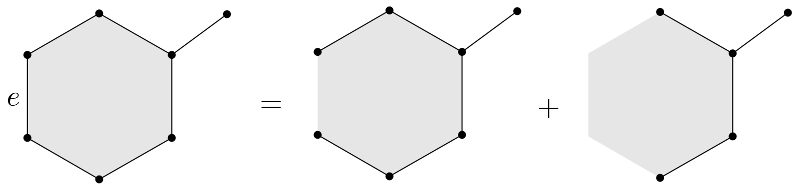


Figure 2.6: An example of the recursive relation for the number of matchings applied to an edge, e.

Proof. The number of matchings that exclude the edge e is $Z(G - e)$. The number of matchings that include e is $Z(G - \{v, w\})$ by the same argument as before.

□

3. Characterisation of the recursive relations using transfer matrices

In this chapter, recursive relations for the Hosoya and Merrifield-Simmons indices are derived, based on the auxiliary graphs (derivatives) as shown in Figure 1.6. The main aim is to characterise these recursive relations using transfer matrices. The transfer matrices represent the type of hexagon addition from a chain R' to a chain R. The transfer matrices are then later used to determine the extremal values of the indices.

3.1 Hosoya index

3.1.1 Definition. We denote the Hosoya index of R_a, R_b, R_c and R_d by $a(R)$, $b(R)$, $c(R)$ and $d(R)$ respectively. We define a vector $v(R) = (a(R), b(R), c(R), d(R))^T$ associated with the chain R.

We have $Z(R) = a(R)+b(R)+c(R)+2d(R)$ using essentially the same reasoning as in Example 3.1.4.

3.1.2 Definition. $R(i_1, i_2, \ldots, i_h)$ denotes a chain where h hexagons are added to an initial hexagon. For every j, $i_j \in \{1, 2, 3\}$ represents the type of the j-th addition, see Figure 1.3.

3.1.3 Theorem. *(Wagner, 2005) If R is constructed from R' as shown in Figure 1.5 by a type i addition for $i \in \{1, 2, 3\}$, then the vector $v(R)$ can be written in terms of $v(R')$ as*

$$v(R) = M_i v(R') \text{ for } i \in \{1, 2, 3\},$$

where M_1, M_2 and M_3 are transition matrices that are given by

$$M_1 = \begin{pmatrix} 1 & 1 & 1 & 2 \\ 2 & 1 & 3 & 2 \\ 1 & 2 & 1 & 3 \\ 3 & 2 & 4 & 3 \end{pmatrix}, \quad M_2 = \begin{pmatrix} 1 & 1 & 1 & 2 \\ 1 & 1 & 2 & 3 \\ 2 & 3 & 1 & 2 \\ 3 & 4 & 2 & 3 \end{pmatrix}, \quad M_3 = \begin{pmatrix} 1 & 1 & 1 & 2 \\ 1 & 2 & 1 & 3 \\ 1 & 1 & 2 & 3 \\ 1 & 2 & 2 & 5 \end{pmatrix}.$$

Note that the matrices M_1 and M_2 are similar to each other, because the hexagon addition is symmetric.

Proof. The recursive relations of Lemma 2.0.11, 2.0.12 and 2.0.13 for the Hosoya index are used to relate values associated with the chain R, to those associated with the chain R', i.e. $a(R)$, $b(R)$, $c(R)$ and $d(R)$ are expressed in terms of $a(R'), b(R'), c(R')$ and $d(R')$. An example of how a row of the transition matrices is obtained is given in Example 3.1.4, as the other cases are similar.

3.1.4 Example. We want to prove that

$$a(R) = Z(R') = a(R') + b(R') + c(R') + 2d(R').$$

If the recursive relation from Lemma 2.0.13 is used

$$Z(G) = Z(G - e) + Z(G - \{v, w\}),$$

then $a(R)$ is reduced to the number of matchings based on the derivatives of chain R'' (R' without the last hexagon) as follows. The recursive relation is applied to the edge e in Figure 3.1. The Hosoya index is thus the sum of $Z(R'-e)$ and $Z(R'-\{e,e_1,e_2\})=d(R')$ where e_1 and e_2 are the neighbours of e. The $Z(R'-e)$ is not one of the derivatives of $R''=R'$ as shown in Figure 1.6 and is therefore further reduced by applying the recursive relation to e_1 and subsequently to e_2. This results in a total of one $a(R')$, $b(R')$, $c(R')$ and two $d(R')$. This is the first row of the matrices M_1, M_2 and M_3. Since $a(R)$ is the same for all types of additions, if any of the three matrices are applied to $v(R')$, then $a(R)=Z(R')=a(R')+b(R')+c(R')+2d(R')$ is obtained in the first row.

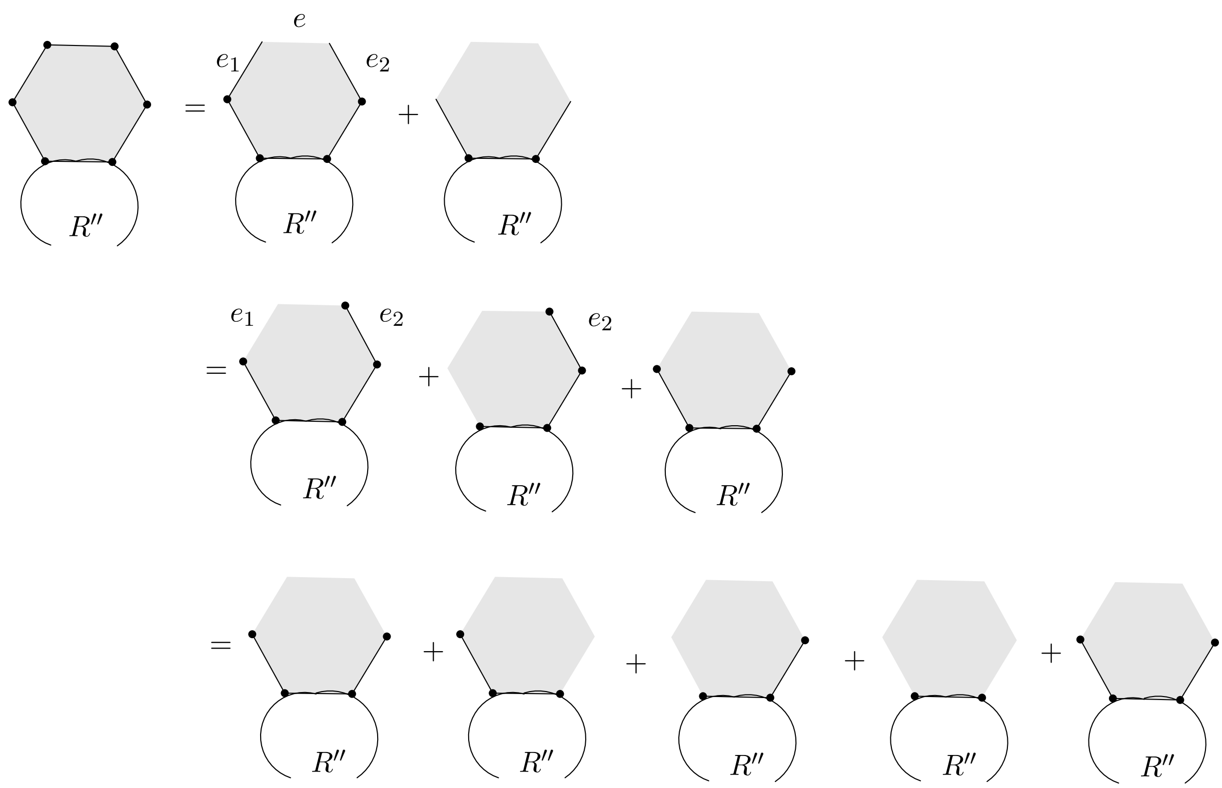


Figure 3.1: Reduction from a chain to a shorter chain.

The other rows of the matrices are determined by reducing the derivatives of the chain R' in a similar way.

The vector associated with a single hexagon is obtained directly by considering the graphs as shown in Figure 3.2. It is determined by direct inspection of these graphs that the vector for a single hexagon is $v(R)=(2,3,3,5)^T$.

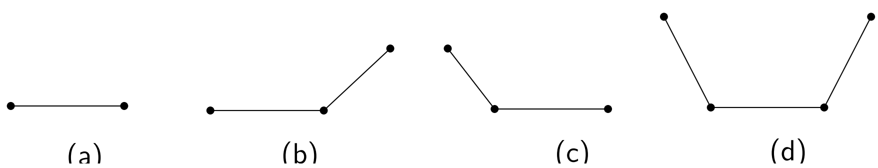


Figure 3.2: The entries of the vector v for a single hexagon are the Hosoya indices of these graphs.

The matrix of each additional hexagon added is subsequently multiplied by the previous chain's representation. Therefore, the full chain is represented by a product of matrices. The vector $v(R)$ can be written as

$$v(R) = M_{i_1} \cdot M_{i_2} \cdot M_{i_3} \dots M_{i_{h-1}} \cdot (2, 3, 3, 5)^T$$

where h is the number of hexagons and $i_1, i_2 \dots$ represent the types of addition.

3.1.5 Example. In Figure 3.3 (a) we start with one hexagon. The Hosoya index vector representation for this graph is

$$v(A_1) = (2, 3, 3, 5)^T.$$

In Figure 3.3 (a) an additional hexagon is added in order to produce (b). The additional hexagon by definition that is added to (a) to produce (b) is a type 1. We have

$$v(A_2) = M_1 \cdot (2, 3, 3, 5)^T = (18, 26, 26, 39)^T.$$

Then the type 1 hexagon addition is made to (b) to produce (c).

$$v(A_3) = M_1 \cdot M_1 \cdot (2, 3, 3, 5)^T = (148, 218, 213, 327)^T.$$

Finally a type 3 hexagon addition is made to (c) to produce (d).

$$v(A_4) = M_3 \cdot M_1 \cdot M_1 \cdot (2, 3, 3, 5)^T = (1233, 1778, 1773, 2645)^T.$$

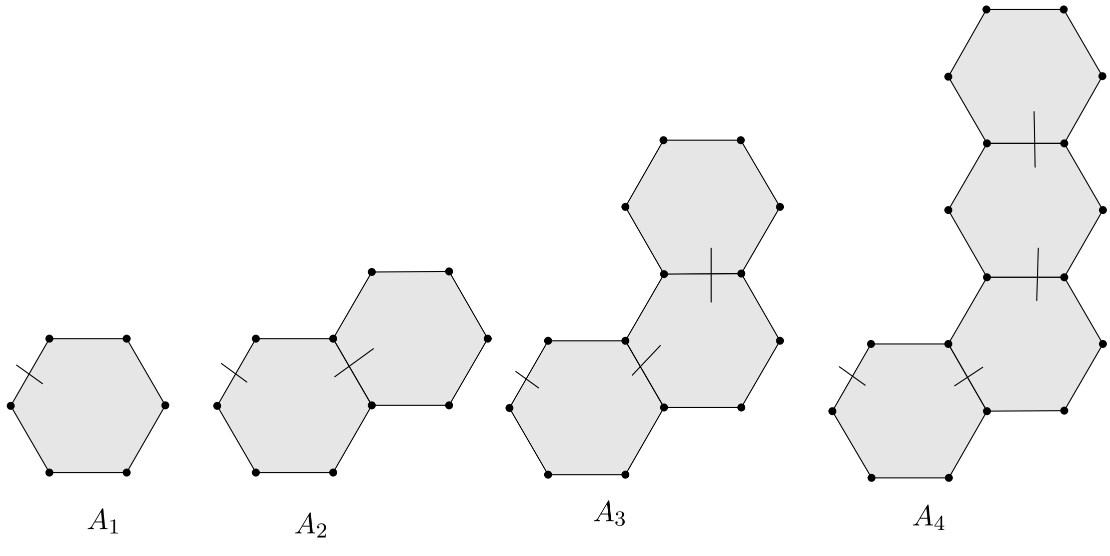


Figure 3.3: A sequence of hexagonal chains.

From these calculations, we also obtain that $Z(A_1) = 18$, $Z(A_2) = 148$, $Z(A_3) = 1233$ and $Z(A_4) = 10074$. □

3.2 The Merrifield-Simmons

3.2.1 Definition. We denote the Merrifield-Simmons index of R_a, R_b, R_c and R_d are $a'(R)$, $b'(R)$, $c'(R)$ and $d'(R)$ respectively. We define a vector $\rho(R) = (a'(R), b'(R), c'(R), d'(R))^T$ associated with the chain R.

We have $\rho(R) = b'(R) + c'(R) + d'(R)$ using essentially the same reasoning as in Example 3.2.3.

3.2.2 Theorem. *If R is constructed from R' as shown in Figure 1.5 by a type i addition for $i \in \{1, 2, 3\}$, then the vector $\rho(R)$ can be written in terms of $\rho(R')$ as*

$$\rho(R) = N_i \rho(R') \text{ for } i \in \{1, 2, 3\},$$

where N_1, N_2 and N_3 are transition matrices that are given by

$$N_1 = \begin{pmatrix} 0 & 1 & 1 & 1 \\ 0 & 1 & 2 & 2 \\ 1 & 3 & 1 & 1 \\ 2 & 4 & 2 & 2 \end{pmatrix}, \quad N_2 = \begin{pmatrix} 0 & 1 & 1 & 1 \\ 1 & 1 & 3 & 1 \\ 0 & 2 & 1 & 2 \\ 2 & 2 & 4 & 2 \end{pmatrix}, \quad N_3 = \begin{pmatrix} 0 & 1 & 1 & 1 \\ 0 & 2 & 1 & 2 \\ 0 & 1 & 2 & 2 \\ 0 & 2 & 2 & 4 \end{pmatrix}$$

Note that the matrices M_1 and M_2 are similar to each other, because the hexagon addition is symmetric.

Proof. The recursive relations of Lemma 2.0.8, 2.0.9 and 2.0.10 for the Merrifield-Simmons index are used to relate values associated with the chain R, to those associated with the chain R', i.e. $a'(R)$, $b'(R)$, $c'(R)$ and $d'(R)$ are expressed in terms of $a'(R'), b'(R'), c'(R')$ and $d'(R')$. An example of how a row of the transition matrices is obtained is given in Example 3.2.3, as the other cases are similar.

3.2.3 Example. We want to prove that

$$a'(R) = \sigma(R') = b'(R') + c'(R') + d'(R').$$

If the recursive relation from Lemma 2.0.9 is used

$$\sigma(G) = \sigma(G - v) + \sigma(G - N[v]),$$

then $a'(R)$ is reduced to the number of independent sets based on the derivatives of chain R'' (R' without the last hexagon) as follows. The recursive relation is applied to the vertex v in Figure 3.4. The Merrifield-Simmons index is thus the sum of $\sigma(R' - v)$ and $\sigma(R' - \{v, v_1, v_2\}) = b(R')$ where v_1 and v_2 are the neighbours of v. The $\sigma(R' - v)$ is not one of the derivatives of $R'' = R'$ as shown in Figure 3.4 and is therefore, further reduced by applying the recursive relation to v_1. This results in a total of one $b(R')$, $c(R')$ and $d(R')$ and zero $a(R')$. This is the first row of the matrices N_1, N_2 and N_3. Since $a(R)$ is the same for all types of additions, if any of the three matrices is applied to the $\rho(R'')$, then $a'(R) = \sigma(R') = b'(R') + c'(R') + d'(R')$ is obtained.

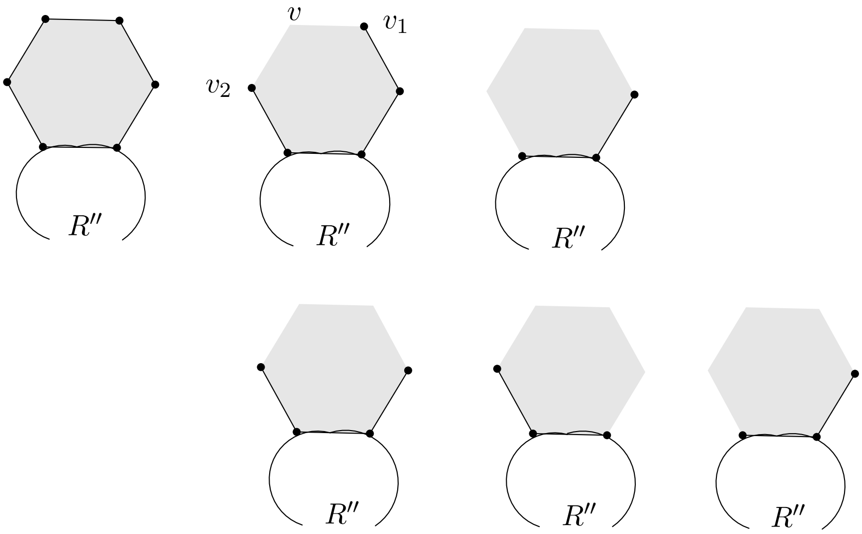


Figure 3.4: Reduction from a chain to a shorter chain.

The other rows of the matrices are determined by reducing the derivatives of the R' chain in a similar way.

The vector associated with a single hexagon is obtained directly by considering the graphs as shown in Figure 3.5. It is determined by direct inspection of these graphs that the vector for a single hexagon is $\rho(R) = (3, 5, 5, 8)^T$.

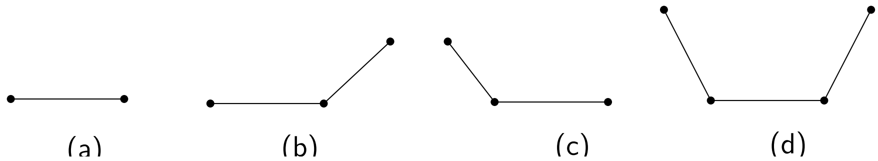


Figure 3.5: The entries of the vector ρ for a single hexagon are the Merrifield-Simmons indices of these graphs.

The matrix of each additional hexagon added is subsequently multiplied by the previous chain's representation. Therefore, the full chain is represented by a product of matrices. The vector $\rho(R)$ can be written as

$$\sigma(R) = N_{i_1} \cdot N_{i_2} \cdot N_{i_3} \dots N_{i_{h-1}} \cdot (3, 5, 5, 8)^T,$$

where h is the number of hexagons and $i_1, i_2 \dots$ represent the types of addition.

3.2.4 Example. In Figure 3.6 (a) we start with one hexagon. The Merrifield-Simmons index vector representation for this graph is

$$\rho(A_1) = (3, 5, 5, 8)^T.$$

In Figure 3.3 (a) an additional hexagon is added in order to produce (b). The additional hexagon by definition that is added to (a) to produce (b) was a type 1. We have

$$\rho(A_2) = N_1 \cdot (3, 5, 5, 8)^T = (18, 31, 31, 52)^T.$$

Then the type 1 hexagon addition is made to (b) to produce (c).

$$\rho(A_3) = N_1 \cdot N_1 \cdot (3, 5, 5, 8)^T = (114, 197, 194, 326)^T.$$

Finally a type 3 hexagon addition is made to (c) to produce (d).

$$\rho(A_4) = N_3 \cdot N_1 \cdot N_1 \cdot (3, 5, 5, 8)^T = (717, 1240, 1237, 2086)^T.$$

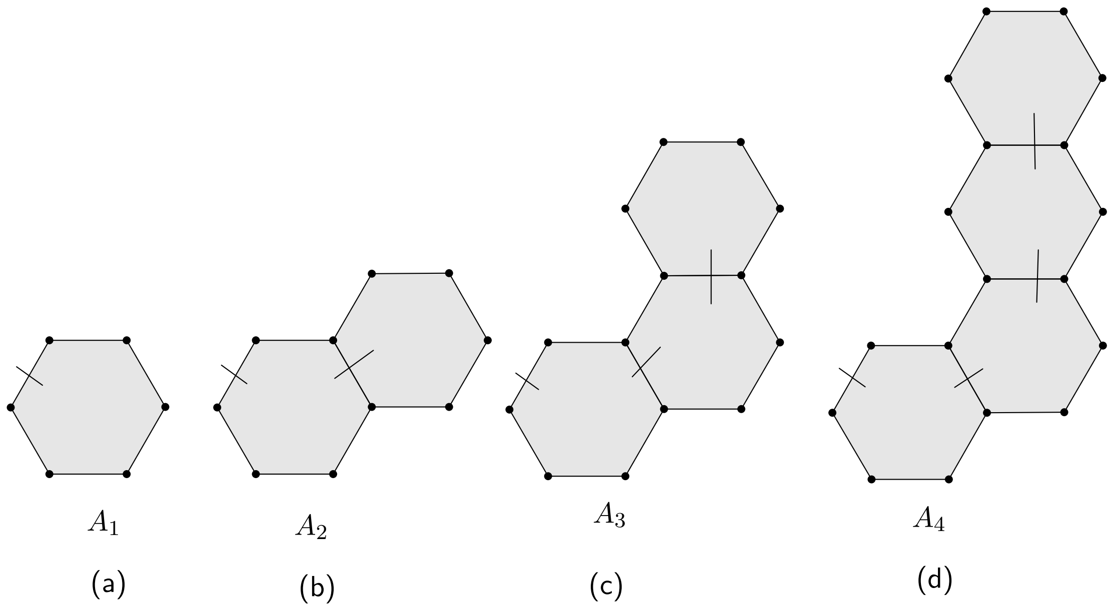


Figure 3.6: A sequence of hexagonal chains.

From these calculations, we also obtain that $\sigma(A_1) = 18$, $\sigma(A_2) = 114$, $\sigma(A_3) = 717$ and $\sigma(A_4) = 4563$. □

4. The extremal values of the Hosoya and Merrifield-Simmons indices

In this chapter the hexagonal chains with the maximal and minimal values for the Hosoya and Merrifield-Simmons indices are determined. The theorems 4.1.2 and 4.1.4 related to these extremal values have been proven before, but using a different approach to that done in this paper (Gutman, 1993; Lianzhu, 1998).

4.1 Hosoya index

4.1.1 Lemma. For all hexagonal chains R, $a(R) + c(R) \geq d(R)$ and $a(R) + b(R) \geq d(R)$.

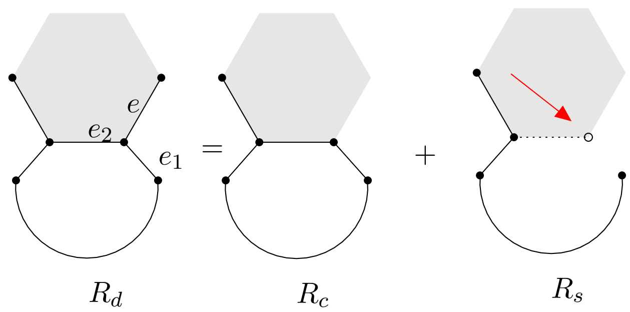


Figure 4.1: The graphs used for the first inequality $a(R) + c(R) \geq d(R)$.

Proof. Using Lemma 2.0.13, one can decompose $d(R) = Z(R_d)$ into $c(R)$ and $Z(R_s) = S(R)$. Since R_s has an edge less than R_a, we have $S(R) \leq a(R)$ and thus $d(R) = c(R) + S(R) \leq c(R) + a(R)$. Hence the first inequality holds. A similar proof is used for the second inequality. □

4.1.2 Theorem. *The minimal values of* $a(R), b(R), c(R)$ *and* $d(R)$ *(given the number* h *of hexagons) all occur for the linear chain* $R = L_h = R(3, 3, \ldots, 3)$*; in particular,* L_h *is the hexagonal chain of minimal Hosoya index, given the number of hexagons.*

Proof. (Proof by induction)

The initial case is a chain consisting of one hexagon as shown in Figure 4.2 (a). Since no hexagons are added together, there is only one configuration for this chain which can be considered a linear chain. Thus the minimal values for $a(R), b(R), c(R)$ and $d(R)$ are those of a linear chain.

The case of 2 hexagons is such that any type of addition still produces a linear chain as shown in Figure 4.2 (b). Thus only one configuration is formed which produces the minimal values of $a(R)$, $b(R)$, $c(R)$ and $d(R)$.

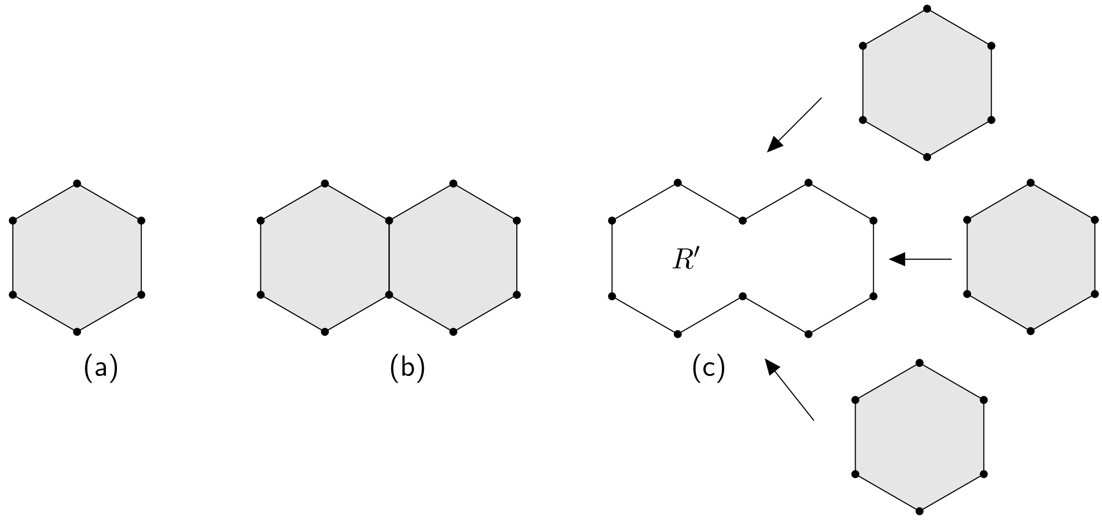


Figure 4.2: The first two cases (a) and (b) have only one possible configuration.

The induction hypothesis can be made that among all hexagonal chains consisting of $h-1$ hexagons, L_{h-1} has an associated vector $v(L_{h-1})$ which is componentwise minimal. This means that $a(L_{h-1})$, $b(L_{h-1})$, $c(L_{h-1})$ and $d(L_{h-1})$ are the minimal values, given the number of hexagons of a chain.

An arbitrary hexagonal chain R with h hexagons is considered as shown in Figure 4.2 (c), consisting of a chain R' and an additional hexagon. The additional hexagon can be added by a type 1, 2 or 3 addition such that

$$v(R) = M_i v(R') \text{ for } i \in \{1,2,3\}.$$

By the induction hypothesis, we have

$$v(R) = M_i v(R') \geq M_i v(L_{h-1}) \qquad \text{componentwise for } i \in \{1,2,3\}.$$

Since each type of addition is represented by a matrix, applying the three possible matrices to $v(L_{h-1}) = (a(L_{h-1}),\ b(L_{h-1}),\ c(L_{h-1}), d(L_{h-1}))^T$, one can determine which type of addition gives the componentwise minimal values for the resulting vector. For simplicity, we write a, b, c and d instead of $a(L_{h-1}), b(L_{h-1})$, $c(L_{h-1})$ and $d(L_{h-1})$.

In order to show that a linear chain produces the minimal values, it suffices to show that a type 3 addition produces the minimal values as follows:

$$M_1(a,b,c,d)^T \geq M_3(a,b,c,d)^T \text{ and}$$
$$M_2(a,b,c,d)^T \geq M_3(a,b,c,d)^T,$$

where " $\geq$ " means "componentwise $\geq$".

Since L_{h-1} is symmetric, we have $b=c$ and the two systems of inequalities are equivalent. Therefore, it suffices to only show that the system of inequalities for the type 1 addition using matrix M_1 relative to the type 3 addition using matrix M_3 are true:

$$\begin{aligned}
a+b+c+2d &\geq a+b+c+2d,\\
2a+b+3c+2d &\geq a+2b+c+3d,\\
a+2b+c+3d &\geq a+b+2c+3d,\\
3a+2b+4c+3d &\geq a+2b+2c+5d.
\end{aligned}$$

Placing $b=c$ reduces the inequalities to the following set of inequalities.

$$\begin{aligned}
a+2b+2d &\geq a+2b+2d,\\
2a+4b+2d &\geq a+3b+3d,\\
a+3b+3d &\geq a+3b+3d,\\
3a+6b+3d &\geq a+4b+5d.
\end{aligned}$$

The first and third inequalities are trivial. The second and fourth inequalities follow directly from Lemma 4.1.1. For example the second inequality is proven by using the fact that $a+b \geq d$.

$$\begin{aligned}
2a+b+3c+2d &= (a+c)+(a+b)+2c+2d\\
&\geq a+c+d+2c+2d && \text{(Lemma 4.1.1)}\\
&\geq a+2b+c+3d,
\end{aligned}$$

Thus the type of addition that produces the componentwise minimal $v(R)$ is a type 3 addition. Therefore,

$$v(R) = M_i v(R') \geq M_i v(L_{h-1}) \geq M_3 v(L_{h-1}) = v(L_h) \qquad \text{componentwise for } i=1,2,3.$$

The componentwise minimality of $v(R)$ implies minimality of $Z(R)$. We have

$$Z(R) = a(R)+b(R)+c(R)+2d(R),$$

and because $a(R)$, $b(R)$, $c(R)$ and $d(R)$ are minimal, the sum of $a(R)$, $b(R)$, $c(R)$ and $d(R)$ minimal.

□

4.1.3 Lemma. For the zig-zag chain, we have $b(S_h) \geq c(S_h)$.

Proof. (Proof by induction)

For the initial odd case, only 1 hexagon is considered. This corresponds to

$$v(S_1) = (2, 3, 3, 5)^T.$$

Here $b(S_1) = c(S_1)$.

For the initial even case, 2 hexagons are considered. This corresponds to

$$v(S_2) = M_1(2, 3, 3, 5)^T = (18, 26, 26, 39)^T.$$

Here $b(S_2) = c(S_2)$.

Assume that $b(S_{h-2}) \geq c(S_{h-2})$ for some zig-zag chain with $h-2$ hexagons. We write a, b, c and d for $a(S_{h-2}), b(S_{h-2}), c(S_{h-2})$ and $d(S_{h-2})$ respectively. Then add two hexagons such that a zig-zag chain is formed. This addition is represented by the vector associated with S_{h-2} being multiplied by $M_1 \cdot M_2$

$$v(S_h) = M_1 \cdot M_2 v(S_{h-2}) = M_1 \cdot M_2(a, b, c, d)^T.$$

The explicit set of equations for $v(S_h)$ is

$$\begin{aligned} a(S_h) &= 10a + 13b + 8c + 13d \\ b(S_h) &= 15a + 20b + 11c + 19d \\ c(S_h) &= 14a + 18b + 12c + 19d \\ d(S_h) &= 22a + 29b + 17c + 29d \end{aligned}$$

Since $b \geq c$ by the induction hypothesis, it follows that $b(S_h) \geq c(S_h)$ for a zig-zag chain of length h. □

4.1.4 Theorem. *The maximal values of $a(R), b(R), b(R) + c(R)$ and $d(R)$ (given the number h of hexagons) all occur for the zigzag chain $R = S_h = R(\ldots, 2, 1, 2, 1)$ (the sequence starts with 1 if h is odd and with 2 otherwise); in particular, S_h is the hexagonal chain of maximal Hosoya index, given the number of hexagons (note that $R(\ldots, 2, 1, 2, 1) \simeq R(\ldots, 1, 2, 1, 2)$, so there are two possible representations).*

The zig-zag chain in Figure 4.3 (a) is reduced by removing two hexagons producing the chain in Figure 4.3 (b). Removing two hexagons retains the orientation of the chain whereas removing one hexagon produces a mirror image of S_{h-1}. In order to use the induction hypothesis two hexagons need to be removed at a time.

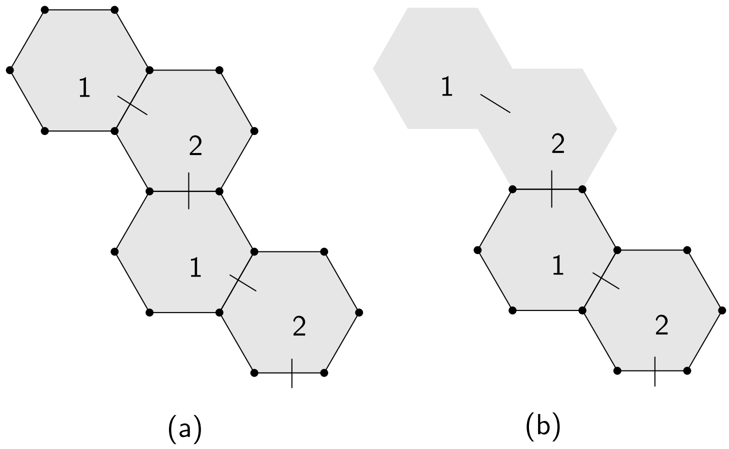


Figure 4.3: The zig-zag chain in (a) is reduced by removing two hexagons producing the chain in (b).

Proof. (Proof by induction)

In order for both odd and even h to be covered, an initial case for each value needs to be considered.

The initial odd case is a chain consisting of one hexagon. Since only one configuration exists, the maximal values of $a(R), b(R), b(R)+c(R)$ and $d(R)$ are obtained.

The initial even case is a chain consisting of two hexagons. Again, only one configuration exists, so the maximal values of $a(R), b(R), b(R)+c(R)$ and $d(R)$ are obtained.

An arbitrary hexagonal chain R with h hexagons is considered, consisting of a chain R' with $h-2$ hexagons and two additional hexagons. There are nine possible choices of adding the two hexagons. They are represented by the matrices M_1M_2, M_1^2, M_2^2, M_3^2, M_2M_1, M_3M_1, M_3M_2, M_1M_3 and M_2M_3 such that

$$v(R) = M_i \cdot M_j v(R') \text{ for } i \in \{1,2,3\} \text{ and } j \in \{1,2,3\}.$$

1. Symmetric cases

   We first show that $a(R)$, $b(R)+c(R)$ and $d(R)$ are maximal.

   Assume without loss of generality that $b(R') \geq c(R')$. Applying the inequalities $a(R)+c(R) \geq d(R)$ and $a(R)+b(R) \geq d(R)$ from Lemma 4.1.1, it can be shown that the M_1M_2 type of addition is always the optimal choice for $a(R)$, $b(R)+c(R)$ and $d(R)$.

   An example of the possible combinations of hexagon addition and their effect on $a(R)$, $b(R)+c(R)$ and $d(R)$ is shown.

   4.1.5 Example. The comparison between the M_1M_2 and M_1M_3 types of addition as shown in Figure 4.4 is done explicitly. We write a, b, c and d for $a(R'), b(R')$, $c(R')$ and $d(R')$ to simplify notation.

$$\begin{aligned} a(R) &: 10a+13b+8c+13d \geq 5a+8b+8c+18d, \\ b(R)+c(R) &: 29a+38b+23c+38d \geq 15a+23b+24c+52d, \\ d(R) &: 22a+29b+17c+29d \geq 12a+17b+19c+39d. \end{aligned}$$

All three inequalities follow from the fact that $a + b \geq d$ (Lemma 4.1.1) combined with the assumption $b \geq c$, for example

$$\begin{aligned}10a + 13b + 8c + 13d &= 5a + 8b + 8c + 13d + 5(a + b) \\ &\geq 5a + 8b + 8c + 18d \qquad \text{(Lemma 4.1.1)}\end{aligned}$$

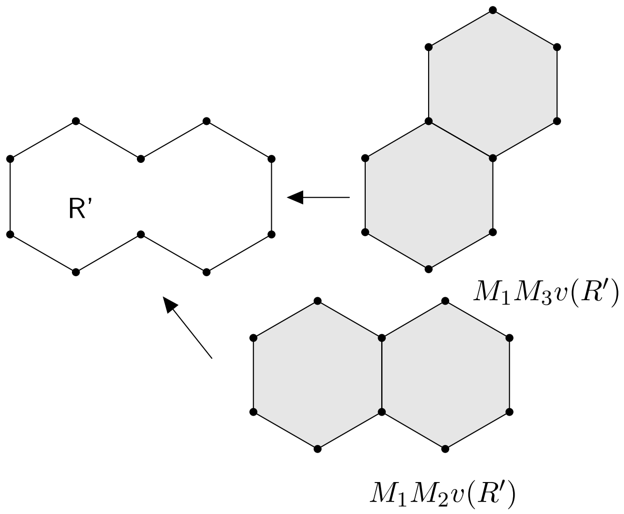


Figure 4.4: For the comparison between M_1M_2 and M_1M_3.

2. Non-symmetric case

   For the maximality of $b(R)$, we have to consider two possibilities.

   (a) $b(R') \geq c(R')$

   Here, it can be shown that the second entry of $(M_i \cdot M_j(a, b, c, d)^T)$ is less than or equal to the second entry of $(M_1 \cdot M_2(a, b, c, d)^T)$ for $i \in \{1, 2, 3\}$ and $j \in \{1, 2, 3\}$.

   4.1.6 Example. The comparison between the M_1M_2 and M_1M_3 types of addition as shown in Figure 4.4 is explicitly done with the use of Lemma 4.1.1. We write a, b, c and d for $a(R'), b(R')$, $c(R')$ and $d(R')$ to simplify notation.

$$\begin{aligned}15a + 20b + 11c + 19d &= 8a + 11b + 11c + 19d + 7(a + b) + 2b, \\ &\geq 8a + 11b + 13c + 26d.\end{aligned}$$

   (b) $b(R') \leq c(R')$

   Here it can be shown that M_1M_2 applied to the mirror image is better than any of the possible choices. The second entry of $(M_i \cdot M_j(a, b, c, d)^T)$ is less than or equal to the second entry of $(M_1 \cdot M_2(a, c, b, d)^T)$ for $i \in \{1, 2, 3\}$ and $j \in \{1, 2, 3\}$.

4.1.7 Example. The comparison between the M_1M_2 and M_1M_3 types of addition as shown in Figure 4.4 is done explicitly with the use of Lemma 4.1.1. We write a, b, c and d for $a(R'), b(R')$, $c(R')$ and $d(R')$ to simplify notation.

$$\begin{aligned}15a + 11b + 20c + 19d &= 8a + 11b + 13c + 19d + 7(a + c),\\ &\geq 8a + 11b + 13c + 26d.\end{aligned}$$

Thus a componentwise comparison of $a(R)$, $b(R)$, $b(R) + c(R)$ and $d(R)$ is made and the M_1M_2 type of addition is found to be maximal.

The induction hypothesis can be made that for some zig-zag chain consisting of $h-2$ hexagons, $a(S_{h-2})$, $b(S_{h-2})$, $b(S_{h-2}) + c(S_{h-2})$ and $d(S_{h-2})$ are the maximal values.

By the considerations above, the maximum values of $a(R), b(R), b(R) + c(R)$ and $d(R)$ are all attained for a chain R that results from a type M_1M_2 addition to a chain R'. Then we have

$$\begin{aligned}a(R) &= 10a(R') + 13b(R') + 8c(R') + 13d(R')\\ &= 10a(R') + 5b(R') + 8(b(R') + c(R')) + 13d(R')\end{aligned}$$

$$\begin{aligned}b(R) &= 15a(R') + 20b(R') + 11c(R') + 19d(R')\\ &= 15a(R') + 9b(R') + 11(b(R') + c(R')) + 19d(R')\end{aligned}$$

$$\begin{aligned}b(R) + c(R) &= 29a(R') + 38b(R') + 23c(R') + 38d(R')\\ &= 29a(R') + 15b(R') + 23(b(R') + c(R')) + 38d(R')\end{aligned}$$

$$\begin{aligned}d(R) &= 22a(R') + 29b(R') + 17c(R') + 29d(R')\\ &= 22a(R') + 12b(R') + 17(b(R') + c(R')) + 29d(R')\end{aligned}$$

Since $a(R')$, $b(R')$, $b(R') + c(R')$ and $d(R')$ are all maximal when $R' = S_{h-2}$, it follows that $a(R)$, $b(R)$, $b(R) + c(R)$ and $d(R)$ are also all maximal when $R' = S_{h-2}$ and thus $R = S_h$.

□

4.2 The Merrifield-Simmons index

4.2.1 Lemma. For all hexagonal chains R, we have $a'(R)+c'(R) \leq d'(R)$ and $a'(R)+b'(R) \leq d'(R)$.

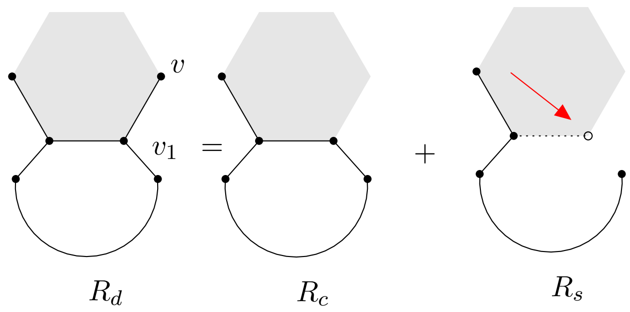


Figure 4.5: The graphs corresponding to the first inequality $a'(R) + c'(R) \leq d'(R)$.

Proof. Using Lemma 2.0.9, one can decompose $d'(R) = \sigma(R_d)$ into $c'(R)$ and $\sigma(R_s) = S'(R)$. Since R_s has an edge less than R_a, we have $S'(R) \geq a'(R)$ and $d'(R) = c'(R) + S'(R) \geq c'(R) + a'(R)$. Hence the first inequality holds. A similar proof is used for the second inequality. □

4.2.2 Theorem. *The maximal values of $a'(R), b'(R), c'(R)$ and $d'(R)$ (given the number h of hexagons) all occur for the linear chain $R = L_h = R(3, 3, \ldots, 3)$; in particular, L_h is the hexagonal chain of maximal Merrifield-Simmons index, given the number of hexagons.*

Proof. (Proof by induction)

The initial case is a chain consisting of one hexagon as shown in Figure 4.2 (a). Since no hexagons are added together, there is only one configuration for this chain which can be considered a linear chain. Thus the maximal values for $a'(R), b'(R), c'(R)$ and $d'(R)$ are those of a linear chain.

The case of two hexagons is such that any type of addition still produces a linear chain as shown in Figure 4.2 (b). Thus only one configuration is formed which produces the maximal values for the Merrifield-Simmons index.

The induction hypothesis can be made that among all hexagonal chains consisting of $h-1$ hexagons, L_{h-1} has an associated vector $\rho(L_{h-1})$ which is componentwise maximal. This means that $a'(L_{h-1})$, $b'(L_{h-1})$, $c'(L_{h-1})$ and $d'(L_{h-1})$ are the maximal values, given that the number of hexagons of a chain.

An arbitrary hexagonal chain R with h hexagons is considered as shown in Figure 4.2 (c), consisting of a chain R' and an additional hexagon. The additional hexagon can be added by a type 1, 2 or 3 addition such that

$$\rho(R) = N_i \rho(R') \text{ for } i \in \{1, 2, 3\}.$$

By the induction hypothesis, we have

$$\rho(R) = N_i \rho(R') \geq N_i \rho(L_{h-1}) \qquad \text{componentwise for } i \in \{1, 2, 3\}.$$

Since each type of addition is represented by a matrix, applying the three possible matrices to $\rho(L_{h-1}) = (a'(L_{h-1}), b'(L_{h-1}), c'(L_{h-1}), d'(L_{h-1}))^T$, one can determine which type of addition is optimal. For simplicity, we write a', b', c' and d' instead of $a'(L_{h-1}), b'(L_{h-1}), c'(L_{h-1})$ and $d'(L_{h-1})$.

In order to show that a linear chain produces the maximal values, it suffices to show that a type 3 addition produces the maximal values as follows:

$$N_1(a',b',c',d')^T \leq N_3(a',b',c',d')^T \text{ and}$$
$$N_2(a',b',c',d')^T \leq N_3(a',b',c',d')^T,$$

where " $\leq$ " means "componentwise $\leq$".

Since L_{h-1} is symmetric, we have $b' = c'$ and the two systems of inequalities are equivalent. Therefore, it suffices to only show that the system of inequalities for the type 1 addition using matrix N_1 relative to the type 3 addition using matrix N_3 are true:

$$\begin{aligned} b' + c' + d' &\leq b' + c' + d', \\ b' + 2c' + 2d' &\leq 2b' + c' + 2d', \\ a' + 3b' + c' + d' &\leq b' + 2c' + 2d', \\ 2a' + 4b' + 2c' + 2d' &\leq 2b' + 2c' + 4d'. \end{aligned}$$

Placing $b' = c'$ reduces the inequalities to the following set of inequalities.

$$\begin{aligned} 2b' + d' &\leq 2b' + d', \\ 3b' + 2d' &\leq 3b' + 2d', \\ a' + 4b' + d' &\leq 3b' + 2d', \\ 2a' + 6b' + 2d' &\leq 4b' + 4d'. \end{aligned}$$

The first and second inequalities are trivial. The third and fourth inequalities follow directly from Lemma 4.2.1. For example the third inequality is proven by using the fact that $a' + b' \leq d'$.

$$\begin{aligned} a' + 4b' + d' &= (a' + b') + 3b' + d' \\ &\leq d' + 3b' + d' && \text{(Lemma 4.2.1)} \\ &= 3b' + 2d', \end{aligned}$$

Thus the type of addition that produces the componentwise maximal $\rho(R)$ is a type 3 addition. Therefore,

$$\rho(R) = N_i\rho(R') \leq N_i\rho(L_{h-1}) \leq N_3\rho(L_{h-1}) = \rho(L_h) \qquad \text{componentwise for } i = 1, 2, 3.$$

The componentwise maximality of $\rho(R)$ implies maximality of $\sigma(R)$. We have

$$\sigma(R) = b'(R) + c'(R) + d'(R),$$

and because $a'(R)$, $b'(R)$, $c'(R)$ and $d'(R)$ are maximal, the sum of $a'(R)$, $b'(R)$, $c'(R)$ and $d'(R)$ is maximal.

□

4.2.3 Lemma. For the zig-zag chain, we have $b'(S_h) \geq c'(S_h)$.

Proof. (Proof by induction)

For the initial odd case, only 1 hexagon is considered. This corresponds to

$$\rho(S_1) = (3, 5, 5, 8)^T.$$

Here $b'(S_1) = c'(S_1)$.

For the initial even case, 2 hexagons are considered. This corresponds to

$$\rho(S_2) = N_1(3, 5, 5, 8)^T = (18, 31, 31, 52)^T.$$

Here $b'(S_2) = c'(S_2)$.

Assume that $b'(S_{h-2}) \geq c'(S_{h-2})$ for some zig-zag chain with $h-2$ hexagons. We write a', b', c' and d' for $a'(S_{h-2}), b'(S_{h-2}), c'(S_{h-2})$ and $d'(S_{h-2})$ respectively. Then add two hexagons such that a zig-zag chain is formed. This addition is represented by the vector associated with S_{h-2} being multiplied by $N_1 \cdot N_2$

$$\rho(S_h) = N_1 \cdot N_2 \rho(S_{h-2}) = N_1 \cdot N_2(a', b', c', d')^T.$$

The explicit set of equations for $\rho(S_h)$ is

$$\begin{aligned} a'(S_h) &= 3a' + 5b' + 8c' + 5d' \\ b'(S_h) &= 5a' + 9b' + 13c' + 9d' \\ c'(S_h) &= 5a' + 8b' + 15c' + 8d' \\ d'(S_h) &= 8a' + 14b' + 24c' + 14d' \end{aligned}$$

Since $b' \geq c'$ by the induction hypothesis, and $d' \geq c'$, it follows that

$$\begin{aligned} b'(S_h) &= 5a' + 9b' + 13c' + 9d' \\ &\geq 5a' + 8b' + 14c' + 9d' \\ &\geq 5a' + 8b' + 15c' + 8d' \\ &= c'(S_h) \end{aligned}$$

for a zig-zag chain of length h. □

4.2.4 Theorem. *The minimal values of $a'(R), b'(R), b'(R) + c'(R)$ and $d'(R)$ (given the number h of hexagons) all occur for the zigzag chain $R = S_h = R(\dots, 2, 1, 2, 1)$; in particular, S_h is the hexagonal chain of minimal the Merrifield-Simmons index, given the number of hexagons.*

The zig-zag chain in Figure 4.6 (a) is reduced by removing two hexagons producing the chain in Figure 4.6 (b). Removing two hexagons retains the orientation of the chain whereas removing one hexagon produces a mirror image of S_{h-1}. In order to use the induction hypothesis two hexagons need to be removed at a time.

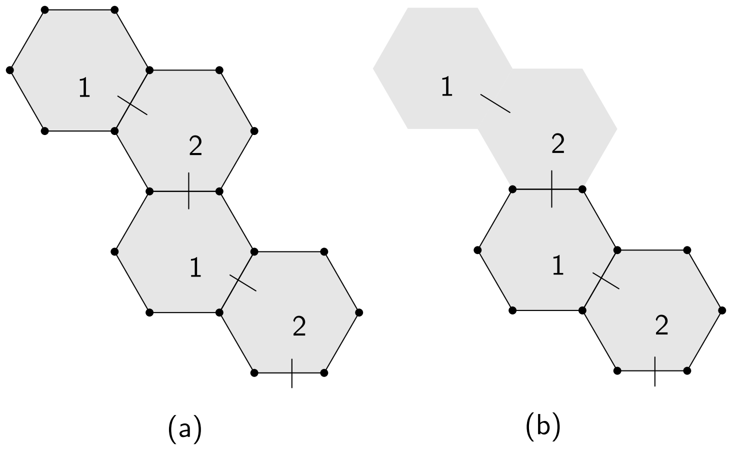


Figure 4.6: The zig-zag chain in (a) is reduced by removing two hexagons producing the chain in (b).

Proof. (Proof by induction)

In order for both odd and even h to be covered, an initial case for each value needs to be considered.

The initial odd case is a chain consisting of one hexagon. Since only one configuration exists, the minimal values of $a'(R), b'(R), b'(R)+c'(R)$ and $d'(R)$ are obtained.

The initial even case is a chain consisting of two hexagons. Again, only one configuration exists, so the minimal values of $a'(R), b'(R), b'(R)+c'(R)$ and $d'(R)$ are obtained.

An arbitrary hexagonal chain R with h hexagons is considered, consisting of a chain R' with $h-2$ hexagons and two additional hexagons. There are nine possible choices of adding the two hexagons. They are represented by the matrices N_1N_2, N_1^2, N_2^2, N_3^2, N_2N_1, N_3N_1, N_3N_2, N_1N_3 and N_2N_3 such that

$$\rho(R) = N_i \cdot N_j \rho(R') \text{ for } i \in \{1,2,3\} \text{ and } j \in \{1,2,3\}.$$

1. Symmetric cases

   We first show that $a'(R)$, $b'(R)+c'(R)$ and $d'(R)$ are minimal.

   Assume without loss of generality that $b'(R') \geq c'(R')$. Applying the inequalities $a'(R)+c'(R) \leq d'(R)$ and $a'(R)+b'(R) \leq d'(R)$ from Lemma 4.2.1, it can be shown that the N_1N_2 type of addition is always the minimal choice for $a'(R)$, $b'(R)+c'(R)$ and $d'(R)$.

   An example of the possible combinations of hexagon addition and their effect on $a'(R)$, $b'(R)+c'(R)$ and $d'(R)$ is shown.

   4.2.5 Example. The comparison between the N_1N_2 and N_1N_3 types of addition as shown in Figure 4.7 is done explicitly. We write a', b', c' and d' for $a'(R'), b'(R')$, $c'(R')$ and $d'(R')$ to simplify notation.

$$\begin{aligned} a'(R) &: 3a' + 5b' + 8c' + 5d' \leq 5b' + 5c' + 8d', \\ b'(R)+c'(R) &: 10a' + 17b' + 28c' + 17d' \leq 18b' + 17c' + 27d', \\ d'(R) &: 8a' + 14b' + 24c' + 14d' \leq 16b' + 14c' + 22d'. \end{aligned}$$

All three inequalities follow from the fact that $a' + b' \le d'$ (Lemma 4.2.1) combined with the assumption $b' \ge c'$, for example

$$\begin{aligned} 3a' + 5b' + 8c' + 5d' &= 3(a' + c') + 5b' + 5c' + 5d' \\ &\le 5b' + 5c' + 8d'. \qquad \text{(Lemma 4.2.1)} \end{aligned}$$

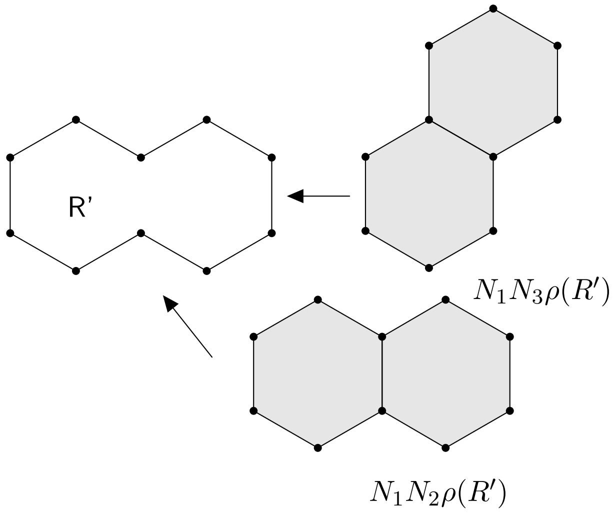


Figure 4.7: For the comparison between N_1N_2 and N_1N_3.

2. Non-symmetric case

   For the minimality of $b'(R)$, we have to consider two possibilities.

   (a) $b'(R') \ge c'(R')$

   Here, it can be shown that the third entry of $(N_i \cdot N_j(a', b', c', d')^T)$ is greater than or equal to the third entry of $(N_1 \cdot N_2(a', b', c', d')^T)$ for $i \in \{1, 2, 3\}$ and $j \in \{1, 2, 3\}$.

   4.2.6 Example. The comparison between the N_1N_2 and N_1N_3 types of addition as shown in Figure 4.7 is explicitly done with the use of Lemma 4.2.1. We write a', b', c' and d' for $a'(R'), b'(R')$, $c'(R')$ and $d'(R')$ to simplify notation.

$$\begin{aligned} 5a' + 8b' + 15c' + 8d' &= 5(a' + c') + 8b' + 2c' + 8c' + 8d', \\ &\le 10b' + 8c' + 13d', \end{aligned}$$

   (b) $b'(R') \le c'(R')$

   Here it can be shown that N_1N_2 applied to the mirror image is better than any of the possible choices. The third entry of $(N_i \cdot N_j(a', c', b', d')^T)$ is greater than or equal to the third entry of $(N_1 \cdot N_2(a', b', c', d')^T)$ for $i \in \{1, 2, 3\}$ and $j \in \{1, 2, 3\}$.

4.2.7 Example. The comparison between the following N_1N_2 and N_1N_3 types of addition as shown in Figure 4.7 is done explicitly with the use of Lemma 4.2.1. We write a', b', c' and d' for $a'(R'), b'(R')$, $c'(R')$ and $d'(R')$ to simplify notation.

$$\begin{aligned} 5a' + 15b' + 8c' + 8d' &= 5(a' + b') + 10b' + 8c' + 8d', \\ &\leq 10b' + 8c' + 13d', \end{aligned}$$

Thus a componentwise comparison of $a'(R)$, $b'(R)$, $b(R)+c'(R)$ and $d'(R)$ is made and the N_1N_2 type of addition is found to be minimal.

The induction hypothesis can be made that for some zig-zag chain consisting of $h-2$ hexagons, $a(S_{h-2})$, $b'(S_{h-2})$, $b'(S_{h-2}) + c'(S_{h-2})$ and $d'(S_{h-2})$ are the maximal values.

By the considerations above, the maximum values of $a'(R), b'(R), b'(R) + c'(R)$ and $d'(R)$ are all attained for a chain R that results from a type N_1N_2 addition to a chain R'. Then we have

$$\begin{aligned} a'(R) &= 3a'(R) + 5b'(R) + 8c'(R) + 5d'(R) \\ &= 3a'(R) + 5(b'(R) + c'(R)) + 3c'(R) + 5d'(R) \end{aligned}$$

$$\begin{aligned} c'(R) &= 5a'(R) + 8b'(R) + 15c'(R) + 8d'(R) \\ &= 5a'(R) + 8(b'(R) + c'(R)) + 7c'(R) + 8d'(R) \end{aligned}$$

$$\begin{aligned} b'(R) + c'(R) &= 10a'(R) + 17b'(R) + 28c'(R) + 17d'(R) \\ &= 10a'(R) + 17(b'(R) + c'(R)) + 11c'(R) + 17d'(R) \end{aligned}$$

$$\begin{aligned} d'(R) &= 8a'(R) + 14b'(R) + 24c'(R) + 14d'(R) \\ &= 8a'(R) + 14(b'(R) + c'(R)) + 10c'(R) + 14d'(R) \end{aligned}$$

Since $a'(R)$, $b'(R)$, $b'(R) + c'(R)$ and $d'(R)$ are all minimal when $R' = S_{h-2}$, it follows that $a'(R)$, $b'(R)$, $b'(R) + c'(R)$ and $d'(R)$ are also all minimal when $R' = S_{h-2}$ and thus $R = S_h$. □

5. Conclusion

The theorems about the Hosoya and Merrifield-Simmons indices for hexagonal chains in this paper have been proven using an alternative method to that of Gutman and Zhang but has been shown to be consistent with their findings. The linear chain produces a maximum Hosoya index and a minimum Merrifield-Simmons index. The zig-zag chain produces a minimum Hosoya index and a maximum Merrifield-Simmons index. (Gutman, 1993; Zhang and Zhang, 2000)

This method characterised the Hosoya and Merrifield-Simmons indices of hexagonal addition by means of transfer matrices M and N. Thus the vector associated with a chain can be written as a product of the transfer matrix with the vector of the previous chain.

$$v(R) = M_i v(R') \text{ for } i = 1, 2, 3,$$

$$\rho(R) = N_i \rho(R') \text{ for } i = 1, 2, 3,$$

The matrices can be used to give explicit formulas for $Z(S_h)$, $Z(L_h)$, $\sigma(S_h)$, $\sigma(L_h)$.

Further research can be done in terms of probability theory where each type of addition as shown in Figure 1.3 has a probability of occurring. The probabilities for each type of addition are p_1, p_2 and $q = 1 - p_1 - p_2$ for the first, second and third addition respectively. It can be shown that the maximal average Hosoya index and minimal average Merrifield-Simmons index are obtained for $p_1 = p_2 = \frac{1}{2}$ and that the minimial average Hosoya index and maximal average Merrifield-Simmons index are obtained for $p_1 = p_2 = 0$ which yields is the linear chain. (Dobrynin and Gutman, 1999)

Acknowledgements

I would like to thank Allah for granting me the opportunity to experience AIMS.

A special thanks to Prof Neil Turok, Prof. Barry Green, Prof. Jeff Sanders, Jan Groenewald, Igsaan Kamalie and all the AIMS staff for assisting me in furthering my education.

My appreciation and gratitude goes to my supervisor Prof. Stephan Wagner for his guidance and patience throughout my essay. I learnt a lot in a short period of time.

Last but certainly not least a warm felt thanks to my family Mummy Shamiela, Daddy Abdullah, M Hasan, Amina, Kauthar and all the others for their endless support and assistance. Many thanks to all my tutors and friends Kenneth, Taofikat, Mohamoud, Phillemon, Bathata, Ylaney, Daniel, Kelone and everyone else who made AIMS a home away from home.

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