Harmonic Index of Chemical Trees with Given Number of Vertices of Maximum Degree

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Dedicated with heartfelt love and gratitude to my loving parents.

Abstract

Graph theory is a major mathematical discipline that provides a powerful framework to solve complex problems that can be modeled in the form of graphs. Its applications are diversified into a number of scientific fields. It is widely used in analyzing the structure of molecules and predicting their physicochemical properties. One of the major concepts used to quantify these properties is topological indices. A topological index is a graph invariant that can be utilized to scrutinize the structure and topology of molecules under different conditions. One of such topological indices is the Harmonic index which has received a lot of attention in recent years. In this thesis, we will determine the extremal values of Harmonic index of chemical trees with given number of vertices of maximum degree.

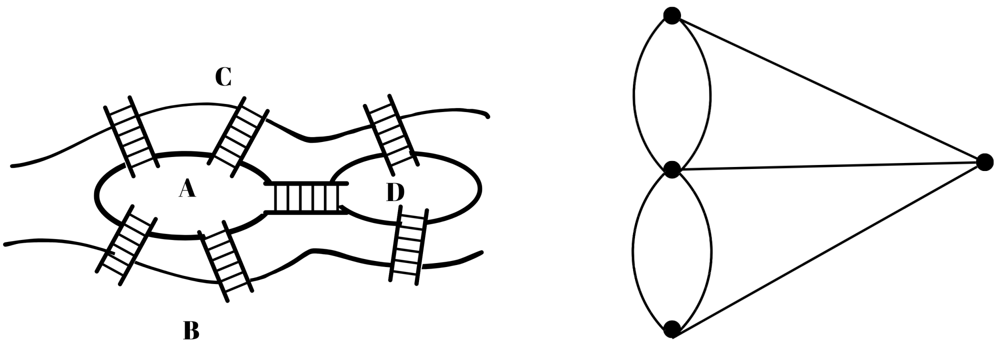
Contents

Chapter 1

Introduction to Graph Theory

Modeling real-life problems mathematically is a common practice that humans have engaged in for centuries. Converting a real-world problem into a mathematical form makes it easier to analyze and solve it using mathematical techniques.

The emergence of graph theory, a branch of mathematics, can also be attributed to such modeling of a real-world problem known as ”The Seven Bridges of Königsberg”. Königsberg was a city situated on the banks of Pregel River. The river consisted of two islands as well. There were seven bridges which connected islands to each other and to the city. The problem was to figure out a walk through the city of Königsberg such that each bridge is traversed only once, with the starting and ending point being the same. In 1735, a mathematician, named Leonhard Euler, proved that it is impossible for such a path to exist. He proved that such a path could exist only if the landmasses would have even number of bridges connected to them which was not the case in Königsberg problem. It is important to note that Euler did not make any mention of modern graph theory terms like graph, vertex or edge. However, the basic structure of his argument shares some similarities with the modern graph theory. The diagram he used to illustrate the problem is given in Fig. 1.1



(a) Geographic Map (b) Graphic Representation

Figure 1.1: The Königsberg Bridges

The Euler's solution to Königsberg bridge problem opened avenues for other mathematicians to explore further concepts in graph theory. However, this was not until 19th century. In 1847, Gustav Kirchoff, a German physicist, made some significant research in electrical networks which then laid the foundation of some new concepts regarding trees in graphs. He gave the famous Kirchoff's Theorem which is useful in finding the number of spanning trees in a connected undirected graph. After 10 years, Arthur Cayley, worked on trees that were generated from the enumeration of molecular isomers. On the way to finding out the isomers of saturated hydrocarbons, he found out that these isomers can be diagrammatically expressed in the form of trees.

Around the same time period, two significant problems gained the popularity. One of them was four-color conjecture and the other one was a puzzle formulated by William Rowan Hamilton. The four-color conjecture was that any map can be colored using only four colors such that no two regions sharing a boundary would have the same color. This conjecture was published by Arthur Cayley in 1879 and has been famous since forever. The Hamiltonian puzzle invented by Sir William Hamilton in 1859 involved finding a route on a dodecahedron (a polyhedron with 12 faces) that traverses through each vertex and ends on the starting vertex. These two problems grabbed attention of many mathematicians which resulted in concepts like Hamiltonian cycles, Hamiltonian paths etc. However, there were no important achievements made throughout the next half-century. Then, early 20th century witnessed a reawakening in interest in graph theory.

In the last 30 years, the field of graph theory has experienced exponential growth and has expanded into numerous branches. Consequently, graph theory has become an area of interest not only for mathematicians, but also for researchers in fields such as chemistry, physics, transportation, and social network analysis, and many more to list.

1.1 Graph Terminologies

Graph theory is the field of study within mathematics that provides a way to model and analyze complex systems and relationships using graphs. A graph is a mathematical entity consisting of nodes and edges. The nodes represent the objects and the edges represent the pairwise relationships among these objects. Graphs aid in analyzing these relationships and deducing results theoretically that would be a very tedious task, otherwise.

A graph G is a collection of three elements: two sets $V(G)$ and $E(G)$ and a function F_G:
1. $V(G)$ is a set of vertices in graph G.
2. $E(G)$ is a set of edges in G.
3. F_G represents a function that assigns each element of $E(G)$ an unordered pair of elements in $V(G)$.

Diagrammatically, vertices are represented by points and edges are represented by lines or arcs.

Let $V(G) = \{x_1, x_2, x_3, x_4, x_5, x_6\}$, $E(G) = \{m_1, m_2, m_3, m_4, m_5, m_6\}$, $F_G(m_1) = \{x_1, x_2\}$, $F_G(m_2) = \{x_1, x_3\}$, $F_G(m_3) = \{x_2, x_3\}$, $F_G(m_4) = \{x_3, x_4\}$, $F_G(m_5) = \{x_4, x_5\}$ and $F_G(m_6) = \{x_4, x_6\}$. Then G is a graph as shown in Fig. 1.2

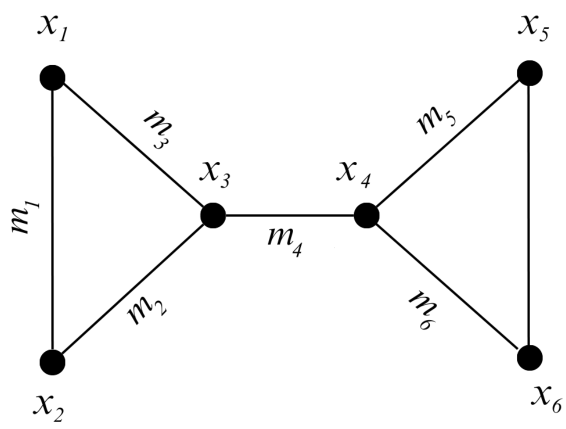


Figure 1.2: The Graph G

If $F_G(e) = \{u, v\}$, then we write $e = uv$ or vu. If $e = uv$, then u and v are known as endpoints of e and e is said to be incident with u and v. The cardinal number of the vertex set of G is called the order of G. The cardinal number of the edge set of G is called the size of graph G. A set of edges such that each edge joins the same pair of vertices is called multiple edges. An edge with endpoints being the same is known as loop. A vertex u is called the neighbor of vertex v in G if an edge e exists such that $e = uv$. The notation $N_G(u)$ is used to represent the collection of all neighbors of u. The degree of a vertex v is the number of vertices that share an edge with v. The notation $deg_G(v)$ is used to represent the degree of v. If there is a loop at vertex v, v will be counted twice. Two adjacent vertices have an edge joining them. A vertex of degree 0 is called an isolated vertex. A vertex of degree 1 is called a pendant vertex. The non-increasing sequence of degrees of vertices of a graph is called the sequence of the graph. An independent set of vertices is the subset of $V(G)$ such that no two vertices in the set are adjacent to each other.

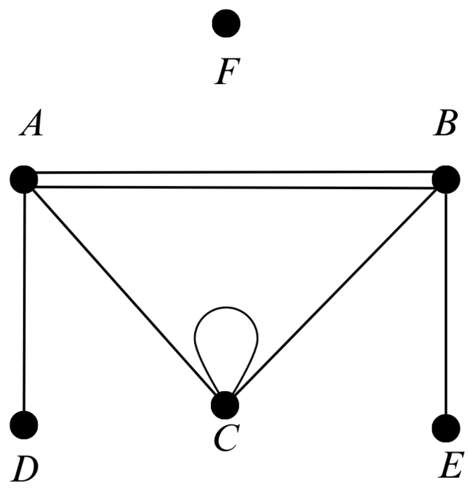


Figure 1.3: Graph G'

A walk in a graph is an alternating sequence of a finite number of vertices and edges such that both vertices and edges can be repeated. The number of edges in the walk while counting repeated edges each time as they appear is called length. Fig. 1.4 shows a graph containing a walk with sequence $v_0, e_1, v_2, e_2, v_1, e_3, v_3, e_4, v_2, e_5, v_4, e_6, v_3, e_3, v_1, e_0, v_0$. It is a closed walk as the starting and ending points are same.

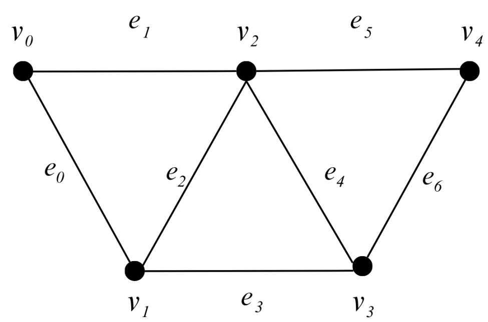


Figure 1.4: A walk

A trail in a graph can be described as a walk in which no edge appears twice. Fig. 1.5 shows a trail with sequence $v_0, e_0, v_1, e_1, v_2, e_2, v_0, e_3, v_3, e_4, v_2$.

It is an open trail as the starting and ending points are not the same.

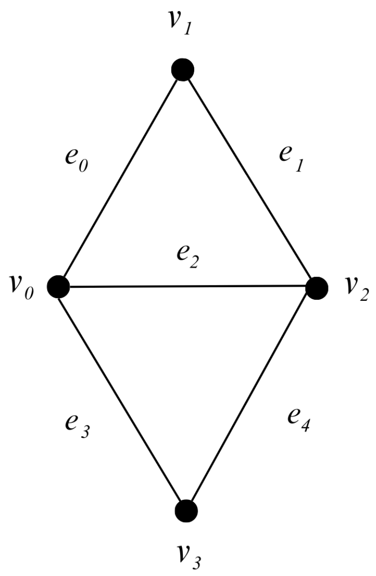


Figure 1.5: A Trail

A walk with distinct vertices and edges is called a path. The length of a path is the count of edges it consists. A path of length n is denoted by P_n. Fig. 1.6 shows a path of length 5.

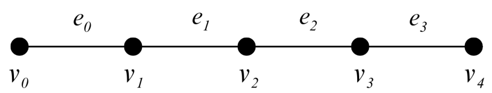


Figure 1.6: Path P_5

A cycle is a trail in which only starting and the ending vertices are repeated. A cycle of length n is denoted by C_n. Fig. 1.7 depicts a cycle of cycle of length 6. The length of the shortest cycle is called girth.

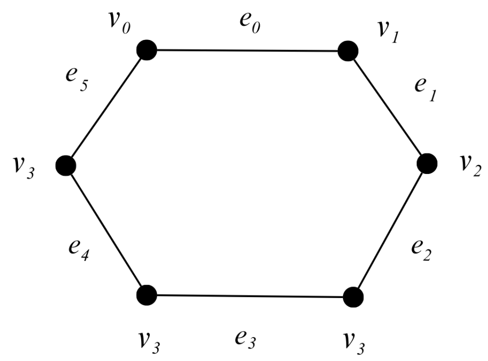


Figure 1.7: Cycle C_6

Two vertices u and v in a graph G are at a distance equal to the length of the shortest path connecting them and is represented by the notation $d_G(u, v)$. The distance between most distant vertices is termed as the diameter of the graph G and is represented by the notation $diam(G)$. The notation $e(v)$ is used to represent eccentricity of v that is described as the distance between v and the vertex that is farthest away from it.

A graph G is said to be isomorphic to graph H if there exists a bijective map from the vertex set of G to that of H that maps every edge in G to an edge in H. Fig. 1.8 shows two isomorphic graphs.

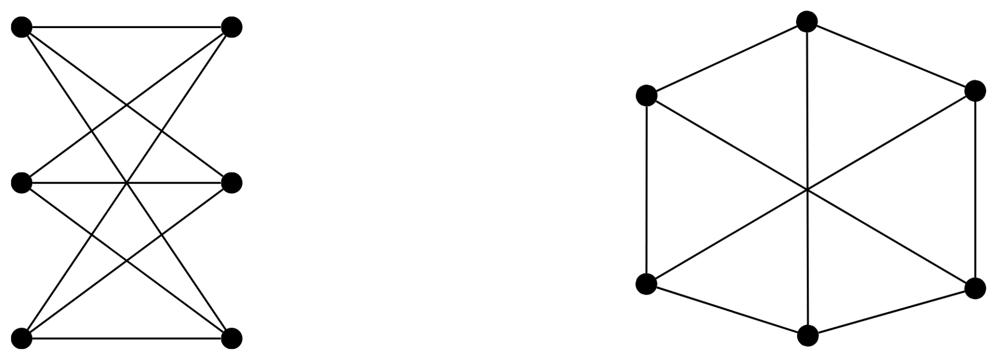


Figure 1.8: Isomorphic Graphs

1.2 Graph Representation in Data Structures

In order to use graphs in computer programming, they are represented using matrices. Adjacency matrix and incidence matrix are two most common ways to represent graphs using matrices. Let G be a graph of order n. The adjacency matrix of G is a matrix of order $n \times n$ where the ij^{th} entry is the number of edges joining the vertices i and j. The adjacency matrix of graph given in Fig. 1.3 is

$$A = \begin{bmatrix} 0 & 2 & 1 & 1 & 0 & 0 \\ 2 & 0 & 1 & 0 & 1 & 0 \\ 1 & 1 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}.$$

The incidence matrix of G is matrix of order $n \times m$ where n and m are the order and the size of the graph G and the ij^{th} entry is 1 if i^{th} vertex is incident to j^{th} edge and 0 otherwise. The incidence matrix of graph G' given in Fig. 1.3 is given by

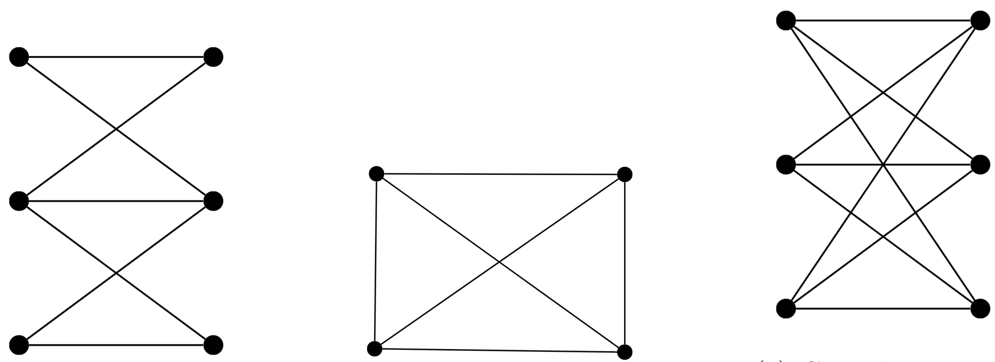
$$I = \begin{bmatrix} 1 & 1 & 1 & 1 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 1 & 1 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}.$$

1.3 Classification of Graphs

Graphs can be classified into different categories according to their structure. A graph that neither have any edge with the same endpoints nor two or more edges that share the same pair of vertices is called a simple graph. A graph G is said to be a null graph if $|V(G)| = |E(G)| = 0$. A graph G is said to be an empty graph if $|V(G)| \neq 0$ and $|E(G)| = 0$.

A directed graph is a graph in which each edge has a direction represented by an arrowhead. An undirected graph has its edges without any directions.

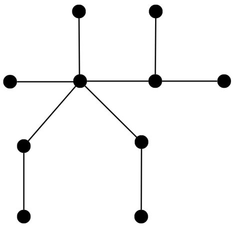
A graph with all vertices having equal degrees is called a regular graph. A graph with every vertex of degree k is called a k-regular graph. If the vertex set of a graph can be decomposed into two independent subsets then such a graph is called a bipartite graph. If the vertex set of a graph can be decomposed into k-independent subsets, then it is called a k-partite graph. A graph is called a complete graph if each vertex of the graph is connected to all other vertices. A complete bipartite graph is a bipartite graph such that each vertex of one independent set is adjacent to every other vertex of the other independent set. A connected graph is a graph such that there exists at least one path between each pair of vertices.



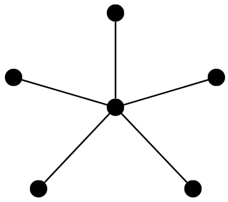
(a) Bipartite Graph (b) Complete Graph K_4 (c) Complete Bipartite Graph

Figure 1.9: Different types of Graphs

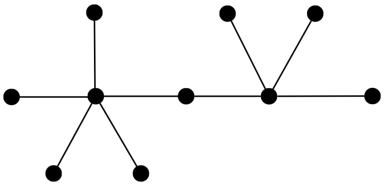
A connected graph with no cycle is called a tree. A caterpillar is a tree such that removing all pendant vertices results into a path. A caterpillar with exactly one non-pendant vertex is called a star. A broom is a tree consisting of a path and pendant vertices attached to one end of the path. A tree with maximum degree 4 is called a chemical tree.



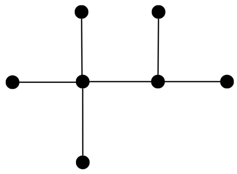
(a) A Tree



(b) A Star



(c) A Caterpillar



(d) A Chemical Tree

Figure 1.10: Trees

1.4 Some Basic Results in Graph Theory

We will mention some results that will be used later.

Theorem 1.4.1. [1] *The total sum of degrees of vertices of a graph is equal to twice of number of edges.*

Theorem 1.4.2. [1] *Let H be a graph with $|V(H)| = p$. Then, following statements are equivalent*
(a) H has no cycle and has $p-1$ edges.
(b) H has $p-1$ edges and is connected.
(c) H is connected and has no cycle.

Theorem 1.4.3. [1] *In a tree, there exists exactly one path between each pair of vertices.*

Theorem 1.4.4. [1] *Let T be a tree of order $n \geq 2$. Then T has at least two pendant vertices.*

1.5 Applications of Graph Theory

There is a multitude of fields where graph theory serves as a gateway to many complex problems. Its applications are not confined to network problems. The circumference of its applicability extends from analyzing molecular structures to interpreting the patterns in cosmic constellations. We will discuss the applications of graph theory in detail.

Network analysis: Graph theory plays a pivotal role in network analysis by detangling the complexities of the connections among different entities in the networks by implementing the concepts of centrality, transitivity and connectivity.

Internet and web algorithms: Graph theory is employed in page ranking algorithms in search engines which basically depend upon the importance of the web pages. The internet is a collection of web pages that are interlinked. Thus, it can be represented by a graph with directions such that the web pages are represented with vertices and their links with directed edges. Thus, a vertex with most edges is more likely to be the most important page and thus would be on the top of the list in the search results.

Operations research and optimization: Graph theory aids in finding solutions to many problems in optimization and operation research. Famous problems like traveling salesman problem, routing and schedulin problems and the maximum flow problem are solved by incorporating theoretical graph concepts.

Computer science and algorithms: Graph theory is extensively used in designing computer algorithms. Data structures like trees can be represented using graphs.

Social network analysis: Graph theory enables the study of social relationships and interactions in social networks. It helps identify influential individuals (e.g., key opinion leaders), analyze information diffusion, detect communities or clusters, and study the spread of influence or diseases through networks.

Bioinformatics and systems biology: Graph theory is extensively used in analyzing biological data and modeling biological systems. Graph-based algorithms help identify functional modules, predict protein functions, and analyze genetic relationships.

Image segmentation and computer vision: Graph theory is applied in image processing. Graph-based segmentation algorithms divide an image into meaningful regions based on pixel similarities and connectivity.

Chemistry and molecular modeling: As mentioned earlier, chemical graph theory is utilized in analyzing molecular structures, predicting properties, and designing drugs. Graph theory enables the representation of molecules as graphs and the application of graph algorithms to study their properties and interactions.

Transportation and logistics: Graph theory is applied to optimize transportation networks, route planning, and vehicle scheduling. It aids in finding the shortest or most efficient routes, minimizing costs, and improving logistics operations.

Graph theory is enormously used in transportation networks for the problems of route planning, vehicle scheduling, finding the most efficient paths, reducing logistics costs and improving logistics operations.

Linguistics and natural language processing: In linguistics, graph theory is used to analyze language structures, such as syntax trees and semantic networks. Graph-based algorithms are applied in natural language processing for tasks like text summarisation, sentiment analysis, and information extraction.

These are just a few instances of how graph theory is applied frequently. It is an invaluable tool in many scientific, technological, and practical fields due to its adaptability and application.

Chapter 2

Topological Indices

In this chapter, we explore the realm of chemical graph theory along with discussing its evolution over the years. We also discuss the emergence of topological indices and their applications in chemical graph theory. We also give a brief overview of the previous research on these indices. We also focus on one of the most important topological indices, that is, the Harmonic index.

2.1 Chemical Graph Theory

Chemical graph theory is one of the most common branches of graph theory. It primarily focuses on the modelling of the structure of molecules in the form of graphs. The vertices are used to represent atoms, the degrees represent the valency of the atom and the edges represent the covalent bonds. The analysis of such graphs gives information about the properties of the molecules, thus avoiding expensive and time-taking laboratory techniques.

If one looks at the developmental graph of chemical graph theory, one may notice that its journey was episodic and fluctuating in nature. While for a decade or two, it saw an explosive growth followed by sheer negligence in the next. At the outset of chemical graph theory, the chemists used graphs to enumerate the isomers of small alkanols and alkanes. Nowadays, the reason of C_5H_{12}, C_3H_8 and C_4H_{10} having 3, 1 and 2 isomers, respectively is stated that only that many graphic representations of their molecules are possible.[2]

In the 1950s and 1960s, the field of chemical graph theory gained significant momentum with the advent of computers and the development of efficient algorithms for graph analysis. Pioneering work was done by chemists such as Alexander Balaban, Haruo Hosoya, and Ivan Gutman, who contributed to the development of various graph invariants and algorithms for chemical structure analysis.

Chemical graph theory has been applied in various forms for more than two centuries and is highly suitable for the study of chemical phenomena. Its earliest application in the 18th century involved representing chemical interactions. In the 19th century, graphs were used to solve practical problems like enumerating chemical isomers. Throughout the 20th century, the applications of graph theory in chemistry expanded significantly, becoming so extensive and advanced that it would require a comprehensive treatise to review them all.

The popularity of chemical graph theory has grown substantially in recent years, as evidenced by the increasing number of research papers published in the field. The future of graph theory in chemistry appears promising, and further growth in the field is expected. It is possible that graph theory will prove to be one of the most powerful mathematical tools available to chemists.

2.2 Topological Indices

In chemical graph theory, there are numerical parameters known as topological indices which are used to study the graphs representing the chemical structure of the molecules.

With the inception of structure theory, many chemists tried to analyze and estimate the properties of the synthetic products before they were manufactured. Then, a few of these products were synthesized and the accuracy of the predictions was analyzed.

The pharmaceutical industry requires to bring changes to the formulas of the medicines in order to combat the problem of reduction in effectiveness of these medicines. They also need to deal with the infections that keep being discovered with time. The traditional way to solve these problems was to go for the products expected to give desired results regardless of the fact that they were natural or synthetic, and then to process the main components of those products to reduce the negative or unwanted results and hence increase their positive effects. The cost of this method increased as after the cell-based experimentation, there was a need to test these products on animals. After animal testing, the drug was made available in the market by the permission of FDA. As a result, the manufacturing cost of a drug that made it to the market was about millions of dollars. This made it essential for the drug companies to collect the revenue back within a very short period of time in order to invest more in research. Consequently, the need to analyze huge number of molecular structures rapidly emerged. At this point, quantum-chemistry calculations were executed to expedite the process. However, these calculations are very complex and can be very costly, and might not be able to scrutinize millions of structures simultaneously. This scenario set the scene for the emergence of topological indices which are simpler to calculate and deal with [3].

The topological indices are used to analyze the topology of a molecule in order to determine its physicochemical properties. They are defined in such a way that they remain unchanged under graph isomorphisms. They are based on different structural properties of the graph like degree, distance and eccentricity. The two most commonly used topological indices are degree-based indices and distance-based vertices.

Harry Wiener invented the first ever topological index in 1947, known as Wiener index, to study the boiling points of alkanes [4]. Wiener index sparked the interest of the researchers and hence, an extensive research was carried out on this index. As Wiener index turned out to be very useful in the chemical analysis of molecules, more topological indices were defined. There is Hosoya index, which is calculated by enumerating the vertices which are not adjacent. The Estrada index is calculated on the basis of spectrum of the graph. Randić, Zagreb and Sombor indices are calculated on the basis of degree of vertices of the graph. The list of famous indices and their formulas is given in Table 2.1.

There has been immense work done on the chemical trees in relation with different topological indices. Extremal chemical trees with respect to Wiener, atomic bond connectivity, Estrada, Sombor, Harmonic and Randić index and many other indices have been determined in [5–10]. Extremal chemical trees with perfect matching with respect to Sombor index are obtained in [11]. The extremal Randić index for chemical trees with k pendant vertices are also found in [12].

Topological Index	Notation	Formula
Randić Index	$R(H)$	$\sum_{rs\in E(H)} \frac{1}{\sqrt{deg_H(r)deg_H(s)}}$
First Zagreb Index	$M_1(H)$	$\sum_{rs\in E(H)} deg_H(r) + deg_H(s)$
Second Zagreb Index	$M_2(H)$	$\sum_{rs\in E(H)} deg_H(r)deg_H(s)$
Atom Bond Connectivity Index	$ABC(H)$	$\sum_{rs\in E(H)} \sqrt{\frac{deg_H(r) + deg_H(s) - 2}{deg_H(r)deg_H(s)}}$
Sum-Connectivity Index	$\mathcal{X}_\alpha$	$\sum_{rs\in E(H)} (deg_H(r) + deg_H(s))^\alpha$
Hyper Zagreb Index	$HM(H)$	$\sum_{rs\in E(H)} (deg_H(r) + deg_H(s))^2$
Redefined First Zagreb Index	$ReZH_1(H)$	$\sum_{rs\in E(H)} \frac{deg_H(r) + deg_H(s)}{deg_H(r)deg_H(s)}$
Redefined Second Zagreb Index	$ReZH_2(H)$	$\sum_{rs\in E(H)} \frac{deg_H(r)deg_H(s)}{deg_H(r) + deg_H(s)}$
Geometric-Arithmetic Index	$HA(H)$	$\sum_{rs\in E(H)} \frac{2\sqrt{deg_H(r)deg_H(s)}}{deg_H(r) + deg_H(s)}$
Sombor Index	$SO(H)$	$\sum_{rs\in E(H)} \sqrt{deg_H(r)^2 + deg_H(s)^2}$
Narumi-Katayama Index	$NK(H)$	${}_{r\in V(H)} deg_H(r)$
Sigma Index	$\sigma(H)$	$\sum_{rs\in E(H)} (deg_H(r) - d(s))^2$
Forgotten Index	$F(H)$	$\sum_{r\in V(H)} deg_H(r)^3$

Table 2.1: Topological Indices

2.3 Harmonic Index

Among the various topological indices in chemical graph theory, one that holds particular significance is the harmonic index which is defined as

$$H(G) = \sum_{uv \in E(G)} \frac{2}{deg_G(u) + deg_G(v)},$$

where uv is an edge joining vertex u and vertex v of graph G with edge set $E(G)$. Harmonic index is a degree-based index and was first introduced in 1987 [13]. There has been extensive work done on this index. Lv [14] worked on the Harmonic index of the graphs with exactly one cycle and matching number a. Zhong [15] studied the extremal values of Harmonic index with girth l. In [16], the lower bounds are determined in the class of graphs with exactly one cycle and diameter d. The authors of [17] characterized the extremal graphs in the class of total graphs. Sun [18] determined the maximum and minimum values of Harmonic index among the class of quasi-trees and two-trees. Liu [19] determined the chemical trees with the smallest Harmonic index and k vertices having degree 1. In [20] and [21], authors studied how Harmonic index is related with other topological indices. Hu [22] analyzed the relationship between the domination number and Harmonic index. Deng [23] worked on smallest four values of Harmonic index among trees. In [24], the author did his research on triangle-free graphs with extremal values of Harmonic index. In [25], the unicyclic graphs with girth l are studied and the maximum and minimum values of Harmonic index are obtained.

2.4 Harmonic Index of Some Basic Graphs

In this section, we give some results on the values of Harmonic index of some basic graphs.

Theorem 2.4.1. [26] *Let K be a simple connected graph such that* $|V(K)| \geq$

3. *Then*

$$H(K) \geq \frac{(2n-2)}{n}.$$

Theorem 2.4.2. [27] *Let T be a tree with n vertices and maximum degree Δ and $n \equiv a (mod\ \Delta - 1)$. Then*

$$H(T) \geq \begin{cases} \dfrac{2n^2-4n+2}{n(2+\Delta)+4-4\Delta} & \text{if } a = 0 \\[2ex] \dfrac{2n^2-4n+2}{n(2+\Delta)-3\Delta} & \text{if } a = 1 \\[2ex] \dfrac{2n^2-4n+2}{n(2+\Delta)0-2-2\Delta} & \text{if } a = 2 \\[2ex] \dfrac{2n^2-4n+2}{4+n(2+\Delta)-3-2\Delta+r(r-2)} & \text{if } a \geq 3. \end{cases}$$

Theorem 2.4.3. [27] *Let T be a tree with maximum degree Δ and $|V(T)| = k$. Then*

$$H(T) \leqslant \begin{cases} 2\left(\dfrac{k-1-\Delta}{2+\Delta} + \dfrac{2\Delta+1-k}{1+\Delta} + \dfrac{k-\Delta-1}{3}\right) & \text{if } \Delta > \dfrac{k-1}{2} \\[2ex] 2\left(\dfrac{\Delta}{3} + \dfrac{\Delta}{\Delta+2} + \dfrac{k-2\Delta-1}{4}\right) & \text{if } \Delta \leq \dfrac{k-1}{2}. \end{cases}$$

Theorem 2.4.4. [19] *Let T be a tree such that $\Delta \leq 4$ and $|V(T)| = p$. Then*

$$H(T) \geq \begin{cases} \dfrac{7n}{20} - \dfrac{1}{12} & p \equiv 0 (mod\ 3) \\[2ex] \dfrac{7n}{20} - \dfrac{13}{140} & p \equiv 1 (mod\ 3) \\[2ex] \dfrac{7n}{20} - \dfrac{3}{20} & p \equiv 2 (mod\ 3). \end{cases}$$

Theorem 2.4.5. [26] *Let T be a tree such that $\Delta \leq 4$ and $|V(T)| \geq 5$. Then*

$$H(T) \leq \frac{3n-1}{6}.$$

Chapter 3

Maximum Harmonic Index for Chemical Trees with Given Vertices of Maximum Degree

In the realm of chemical graph theory, the theory of topological indices centers around some key and extensively explored problems. These problems revolve around identifying structures that achieve the most extreme values of a particular topological index while adhering to specific constraints and establishing the most accurate lower and upper limits for a given topological index. In this chapter, we determine the largest values of the Harmonic index for chemical trees with k vertices of degree 4.

3.1 Preliminaries

Let

$$S = \{(u, v) \in \mathbb{N} \times \mathbb{N} \backslash (1, 1) \mid 1 \leq u \leq v \leq 4\},$$

where $\mathbb{N}$ is the set of natural numbers. Harmonic index for chemical trees can also be expressed as

$$H(T) = \sum_{(u,v)\in S} \frac{2}{u+v} m_{uv}. \tag{3.1.1}$$

In [28], following relations are given:

$$2m_{11} + m_{12} + m_{13} + m_{14} = n_1 \tag{3.1.2a}$$
$$m_{12} + 2m_{22} + m_{23} + m_{24} = 2n_2 \tag{3.1.2b}$$
$$m_{13} + m_{23} + 2m_{33} + m_{34} = 3n_3 \tag{3.1.2c}$$
$$m_{14} + m_{24} + m_{34} + 2m_{44} = 4n_4 \tag{3.1.2d}$$

where m_{ij} is the number of edges connecting vertices of degree i to vertices of degree j and n_i is the number of vertices with degree i. Clearly,

$$n = n_1 + n_2 + n_3 + n_4. \tag{3.1.3}$$

By Handshaking lemma,

$$2(n-1) = n_1 + 2n_2 + 3n_3 + 4n_4. \tag{3.1.4}$$

Lemma 3.1.1. *Let* $f(x) = \frac{2}{(a-b)+x} - \frac{2}{a+x}$ *, where* $a > b > 0$ *and* $x > 0$*. Then* f *is a strictly decreasing function.*

Proof. We see that

$$\frac{df}{dx} = \frac{2}{(a+x)^2} - \frac{2}{((a-b)+x)^2} < 0.$$

Thus $f(x)$ is a strictly decreasing function. □

Let $\mathcal{CT}(n,k)$ be the class of chemical trees of order n with exactly k vertices of degree 4, where $k \geq 1$. It is important to know that for a tree of order n with k vertices of degree 4 to be graphically feasible, $n \geq 3k+2$. In this chapter, we will determine the largest values of the Harmonic index for chemical trees with k vertices of degree 4.

Lemma 3.1.2. *Let $T \in \mathcal{CT}(n,k)$ has the maximum Harmonic index among the trees in $\mathcal{CT}(n,k)$. Then*

(i) $n_3 = 0$.

(ii) $n_1 = 2k+2$ *and* $n_2 = n-3k-2$.

Proof. (i). On the contrary, assume that there is a vertex p of degree 3 in T. Let p_1, p_2 and p_3 be the neighbors of p. We discuss two cases:

Case 1. When at most one neighbor of p has degree 4.

As there is at most one neighbor of p with degree 4, we can assume without loss of generality that $1 \le deg_T(p_1), deg_T(p_2) \le 3$ and $1 \le deg_T(p_3) \le 4$. Let $s \notin N_T(p)$ be the pendant vertex of T and let P be a p,s-path. Without loss of generality, assume that p_1 does not lie on P. Let $N_T(s) = \{s'\}$. Clearly, $2 \le deg_T(s') \le 4$. Let

$$T' = T - p_1p + p_1s.$$

Clearly, $deg_{T'}(p) = deg_T(p) - 1 = 2$, $deg_{T'}(s) = deg_T(s) + 1 = 2$ and $deg_{T'}(w) = deg_T(w)$ for all $w \in V(T)\backslash\{p,s\}$. Obviously, $T' \in \mathcal{CT}(n,k)$. Now, we show $H(T') - H(T) > 0$ to obtain a contradiction.

$$\begin{aligned}
H(T') - H(T) \quad &= \frac{2}{deg_T(p_1) + deg_T(s) + 1} + \frac{2}{deg_T(s) + 1 + deg_T(s')} \\
&+ \frac{2}{deg_T(p) - 1 + deg_T(p_2)} + \frac{2}{deg_T(p) - 1 + deg_T(p_3)} \\
&- \frac{2}{deg_T(p_1) + deg_T(p)} - \frac{2}{deg_T(s) + deg_T(s')} \\
&- \frac{2}{deg_T(p) + deg_T(p_2)} - \frac{2}{deg_T(p) + deg_T(p_3)} \\
&= \frac{2}{deg_T(p_1) + 2} + \frac{2}{2 + deg_T(s')} + \frac{2}{2 + deg_T(p_2)} \\
&+ \frac{2}{2 + deg_T(p_3)} - \frac{2}{deg_T(p_1) + 3} - \frac{2}{1 + deg_T(s')}
\end{aligned}$$

$$
\begin{aligned}
&-\frac{2}{3+deg_T(p_2)}-\frac{2}{3+deg_T(p_3)}\\
&=\frac{2}{2+deg_T(p_1)}-\frac{2}{3+deg_T(p_1)}+\frac{2}{2+deg_T(s')}\\
&-\frac{2}{1+deg_T(s')}+\frac{2}{2+deg_T(p_2)}-\frac{2}{3+deg_T(p_2)}\\
&+\frac{2}{2+deg_T(p_3)}-\frac{2}{3+deg_T(p_3)}.
\end{aligned}
$$

Now, by using the inequalities $1 \leq deg_T(p_1), deg_T(p_2) \leq 3$, $1 \leq deg_T(p_3) \leq 4$ and $2 \leq deg_T(s') \leq 4$ along with Lemma 3.1.1, we obtain

$$
\begin{aligned}
H(T') - H(T) \quad &\geq \frac{2}{2+3}-\frac{2}{3+3}+\frac{2}{2+2}-\frac{2}{3+3}+\frac{2}{2+3}-\frac{2}{1+2}+\frac{2}{2+4}\\
&-\frac{2}{3+4}\\
&= 0.014 > 0.
\end{aligned}
$$

Case 2. When at least two neighbors of p have degree 4.

As there are at least two neighbors of p with degree 4, we can assume without loss of generality that $deg_T(p_2) = deg_T(p_3) = 4$ and $1 \leq deg_T(p_1) \leq 4$. Let s be a pendant vertex and P be a p,s-path containing the edge p_3. Let $N_T(s) = \{s'\}$. Clearly, $2 \leq deg_T(s') \leq 4$. Let

$$T'' = T - p_2p - p_3p + ps + p_2p_3.$$

Clearly, $deg_{T''}(p) = deg_T(p) - 1 = 2$, $deg_{T''}(s) = deg_T(s) + 1 = 2$ and $deg_{T''}(w) = deg_T(w)$ for all $w \in V(T)\backslash\{p, s\}$. Obviously, $T'' \in \mathcal{CT}(n, k)$. Now, we show $H(T'') - H(T) > 0$ to obtain a contradiction.

$$
\begin{aligned}
H(T'') - H(T) \quad &= \frac{2}{deg_T(p_2)+deg_T(p_3)}+\frac{2}{deg_T(s)+1+deg_T(s')}\\
&+\frac{2}{deg_T(p)-1+deg_T(p_1)}+\frac{2}{deg_T(p)-1+deg_T(s)+1}\\
&-\frac{2}{deg_T(p)+deg_T(p_1)}-\frac{2}{deg_T(p)+deg_T(p_2)}
\end{aligned}
$$

$$
\begin{aligned}
&-\frac{2}{deg_T(p)+deg_T(p_3)}-\frac{2}{deg_T(s)+deg_T(s')}\\
&=\frac{2}{4+4}+\frac{2}{2+deg_T(s')}+\frac{2}{2+deg_T(p_1)}+\frac{2}{2+2}\\
&-\frac{2}{3+deg_T(p_1)}-\frac{2}{3+4}-\frac{2}{3+4}-\frac{2}{1+deg_T(s')}\\
&=\frac{2}{2+deg_T(s')}-\frac{2}{1+deg_T(s')}+\frac{2}{2+deg_T(p_1)}\\
&-\frac{2}{3+deg_T(p_1)}+\frac{2}{4+4}+\frac{2}{2+2}-\frac{2}{3+4}-\frac{2}{3+4}.
\end{aligned}
$$

Now, by using $1 \leq deg_T(p_1) \leq 4$ and $2 \leq deg_T(s') \leq 4$ along with Lemma 3.1.1, we obtain

$$
\begin{aligned}
H(T'')-H(T) \quad &\geq \frac{2}{2+2}-\frac{2}{1+2}+\frac{2}{2+4}-\frac{2}{3+4}+\frac{2}{4+4}+\frac{2}{2+2}\\
&-\frac{2}{3+4}-\frac{2}{3+4}\\
&=0.059>0,
\end{aligned}
$$

which contradicts the fact that T has maximum Harmonic index. Therefore, T has no vertex of degree 3, that is, $n_3 = 0$ in T.
(ii) Using Equations (3.1.4) and (3.1.3) and the fact that $n_3 = 0$ by Lemma 3.1.2(i), we get

$$
\begin{aligned}
n_1 + 2n_2 &= 2n - 2 - 4k,\\
n_1 + n_2 &= n - k.
\end{aligned} \tag{3.1.5}
$$

The solution of system (3.1.5) is $n_1 = 2k + 2$ and $n_2 = n - 3k - 2$. This completes the proof. □

Lemma 3.1.3. *Let $T \in \mathcal{CT}(n,k)$ has maximum Harmonic index among the trees in $\mathcal{CT}(n,k)$. Let s, $r \in V(T)$ such that $deg_T(s) = deg_T(r) = 4$. Let z be an internal vertex on s,r-path. Then $deg_T(z) = 4$.*

Proof. On the contrary, assume that $deg_T(z) \neq 4$. Clearly, $deg_T(z) \neq 1$. By Lemma 3.1.2(i), $deg_T(z) \neq 3$. Therefore, we only need to prove that $deg_T(z) \neq 2$. On the contrary, we assume $deg_T(z) = 2$. Obviously, there exist two vertices p and q of degree 4 on s,r-path such that p,q-path contains z and all its internal vertices have degree 2. Now, we will consider two cases.

Case 1. When $d_T(p,q) = 2$.

Clearly, $d_T(p,q) = 2$ implies that $N_T(z) = \{p,q\}$. Let t be a pendant vertex in T and t' be its neighbor. Without loss of generality, assume that zt- path contains q. Let

$$T' = T - pz - qz + pq + zt.$$

Clearly, $deg_{T'}(t) = deg_T(t) + 1 = 2$, $deg_{T'}(z) = deg_T(z) - 1 = 1$ and $deg_{T'}(w) = deg_T(w)$ for all $w \in V(T)\backslash\{t,z\}$. Obviously, $T' \in \mathcal{CT}(n,k)$. Now, we show $H(T') - H(T) > 0$ using Lemma 3.1.1 to obtain a contradiction.

$$\begin{aligned} H(T') - H(T) \quad &= \frac{2}{deg_T(p) + deg_T(q)} + \frac{2}{deg_T(t) + 1 + deg_T(z) - 1} \\ &+ \frac{2}{deg_T(t) + 1 + deg_T(t')} - \frac{2}{deg_T(t) + deg_T(t')} \\ &- \frac{2}{deg_T(z) + deg_T(p)} - \frac{2}{deg_T(z) + deg_T(q)} \\ &\geq \frac{2}{4+4} + \frac{2}{2+1} + \frac{2}{2+2} - \frac{2}{1+2} - \frac{2}{2+4} - \frac{2}{2+4} \\ &= 0.083 > 0. \end{aligned}$$

This contradicts the fact that T has largest Harmonic index.

Case 2. When $d_T(p,q) \geq 3$.

Let p_1 and q_1 be the neighbors of p and q, respectively lying on p,q-path. Let q_1' be the neighbor of q_1 other than q. Let t be a pendant vertex in T and t' be its neighbor. Clearly, $2 \leq deg_T(t') \leq 4$. Let

$$T'' = T - qq_1 - pp_1 + pq + p_1t.$$

Clearly, $deg_{T''}(t) = deg_T(t) + 1 = 2$, $deg_{T''}(q_1) = deg_T(q_1) - 1 = 1$ and $deg_{T''}(w) = deg_T(w)$ for all $w \in V(T)\backslash\{t,q_1\}$. Obviously, $T'' \in \mathcal{CT}(n,k)$.

Now, we show $H(T'') - H(T) > 0$ using Lemma 3.1.1 to obtain a contradiction.

$$\begin{aligned} H(T'') - H(T) &= \frac{2}{deg_T(p) + deg_T(q)} + \frac{2}{deg_T(t) + 1 + deg_T(p_1)} \\ &+ \frac{2}{deg_T(q_1) - 1 + deg_T(q_1')} + \frac{2}{deg_T(t) + 1 + deg_T(t')} \\ &- \frac{2}{deg_T(q_1) + deg_T(q)} - \frac{2}{deg_T(q_1) + deg_T(q_1')} \\ &- \frac{2}{deg_T(t) + deg_T(t')} \\ &- \frac{2}{deg_T(p) + deg_T(p_1)} \\ &= \frac{2}{4+4} + \frac{2}{2+2} + \frac{2}{1+2} + \frac{2}{2+2} - \frac{2}{2+4} - \frac{2}{2+2} \\ &- \frac{2}{1+2} - \frac{2}{4+2} \\ &= 0.083 > 0, \end{aligned}$$

which is a contradiction to the fact that T has maximum Harmonic index. Hence, $d(z) = 4$ in T. □

Lemma 3.1.4. *Let $T \in \mathcal{CT}(n, k)$ with $3k + 2 \leq n \leq 5k + 4$ has maximum Harmonic index among the trees in $\mathcal{CT}(n, k)$. Then*

(i) $m_{13} = m_{23} = m_{33} = m_{34} = 0$.

(ii) $m_{44} = k - 1$.

(iii) $m_{22} = 0$.

(iv) $m_{12} = n - 3k - 2$, $m_{24} = n - 3k - 2$, $m_{14} = 5k + 4 - n$.

Proof. (i). This result is a direct consequence of Lemma 3.1.2(i).
(ii). This result is a direct consequence of Lemma 3.1.3.
(iii). On the contrary, assume that T has an edge $e = pq$ with $deg_T(p) = deg_T(q) = 2$. We first show that there must exist an edge $e' = st$ with $deg_T(s) = 1$ and $deg_T(t) = 4$. To prove this using contradiction, assume that

there is no such edge, that is, $m_{14} = 0$. Now, by using Lemmas 3.1.2, 3.1.4(i) and 3.1.4(ii) to solve the system in Equations (3.1.2a) - (3.1.2d), we obtain $m_{22} = n - 5k - 4$. This implies $m_{22} \leq 0$ if $3k + 2 \leq n \leq 5k + 4$ and hence, a contradiction. Therefore, $e' = st \in E(T)$ with $deg_T(s) = 1$ and $deg_T(t) = 4$. Let p_1 and q_1 be the neighbors of p and q other than q and p respectively. Without loss of generality, let P be a p, s-path containing the vertex q. Let

$$T' = T - pp_1 + p_1 s.$$

Clearly, $deg_{T'}(p) = deg_T(p) - 1 = 1$, $deg_{T'}(s) = deg_T(s) + 1 = 2$ and $deg_{T'}(w) = deg_T(w)$ for all $w \in V(T) \backslash \{p, s\}$. Obviously, $T' \in \mathcal{CT}(n, k)$. Now, we show $H(T') - H(T) > 0$ to obtain a contradiction.

$$\begin{aligned}
H(T') - H(T) &= \frac{2}{deg_T(p_1) + deg_T(s) + 1} + \frac{2}{deg_T(p) - 1 + deg_T(q)} \\
&+ \frac{2}{deg_T(s) + 1 + deg_T(t)} - \frac{2}{deg_T(p) + deg_T(p_1)} \\
&- \frac{2}{deg_T(p) + deg_T(q)} - \frac{2}{deg_T(s) + deg_T(t)} \\
&= \frac{2}{deg_T(p_1) + 2} + \frac{2}{1+2} + \frac{2}{2+4} - \frac{2}{2 + deg_T(p_1)} - \frac{2}{2+2} \\
&- \frac{2}{2+4} \\
&= 0.1 > 0,
\end{aligned}$$

which is a contradiction since T has maximum Harmonic index. Hence, $m_{22} = 0$ in T for $3k + 2 \leq n \leq 5k + 4$.

(iv). Solving the system in Equations (3.1.2a) - (3.1.2d) for unknowns m_{14}, m_{24} and m_{12} by using the values of n_1, n_2 and n_3 from Lemma 3.1.2 and the values of m_{13}, m_{23}, m_{33}, m_{34}, m_{44} and m_{22} we obtain

$$m_{12} = n - 3k - 2,$$

$$m_{24} = n - 3k - 2,$$

$$m_{14} = 5k + 4 - n.$$

This finishes the proof. □

Lemma 3.1.5. *Let $T \in \mathcal{CT}(n,k)$ with $n > 5k+4$ has maximum Harmonic index among the trees in $\mathcal{CT}(n,k)$. Then*

(i) $m_{13} = m_{23} = m_{33} = m_{34} = 0$.

(ii) $m_{44} = k-1$.

(iii) $m_{14} = 0$.

(iv) $m_{12} = 2k+2$, $m_{24} = 2k+2$, $m_{22} = n-5k-4$.

Proof. (i). This result is a direct consequence of Lemma 3.1.2(i).
(ii). This result is a direct consequence of Lemma 3.1.3.
(iii). On the contrary, assume that T has an edge $e = st$ with $deg_T(s) = 1, deg_T(t) = 4$. We first show that $e' = pq \in E(T)$ with $deg_T(p) = deg_T(q) = 2$. To prove this using contradiction, assume that $m_{22} = 0$. Now, by using Lemmas 3.1.2, 3.1.5(i) and 3.1.5(ii) to solve the system in Equations (3.1.2a) - (3.1.2d), we obtain, $m_{14} = 5k+4-n$. This implies $m_{14} < 0$ for $n > 5k+4$ and hence, a contradiction. Now, by using the same argument and transformation as in Lemma 3.1.4(iii), we can conclude that $m_{14} = 0$ in T for $n > 5k+4$.
(iv). Solving the system in Equations (3.1.2a) - (3.1.2d) for unknowns m_{22}, m_{24} and m_{12} by using the values of n_1, n_2 and n_3 from Lemma 3.1.2 and the values of m_{13}, m_{23}, m_{33}, m_{34}, m_{44} and m_{14} we obtain

$$\begin{aligned} m_{12} &= 2k+2, \\ m_{24} &= 2k+2, \\ m_{22} &= n-5k-4. \end{aligned}$$

This completes the proof. □

3.2 Main Results

In this section, we obtain the values of Harmonic index maximum trees in $\mathcal{CT}(n,k)$ and provide the minimum trees that attain these upper bounds.

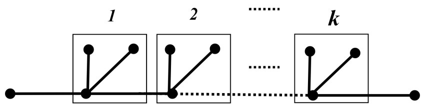
Theorem 3.2.1. *Let $T \in \mathcal{CT}(n,k)$ has maximum Harmonic index among the trees in $\mathcal{CT}(n,k)$. Then*

$$H(T) = \begin{cases} \frac{3}{5}n - \frac{3}{4}k - \frac{13}{20} & 3k+2 < n \leq 5k+4, \\ \frac{1}{2}n - \frac{1}{4}k - \frac{1}{4} & n > 5k+4, \end{cases}$$

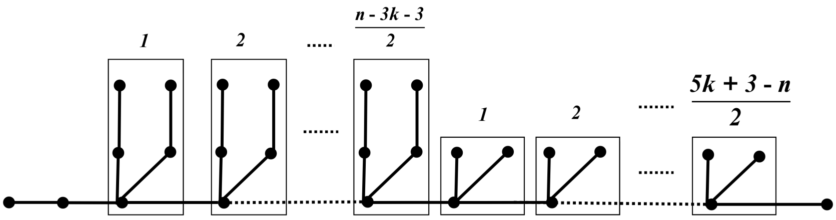
Proof. **Case 1.** When $3k+2 \leq n \leq 5k+4$.
The Harmonic index of T can be obtained by using the values of m_{uv} for $(u,v) \in S$ from Lemma 3.1.4 in Equation (3.1.1) as follows:

$$H(T) = \frac{3}{5}n - \frac{3}{4}k - \frac{13}{20}.$$

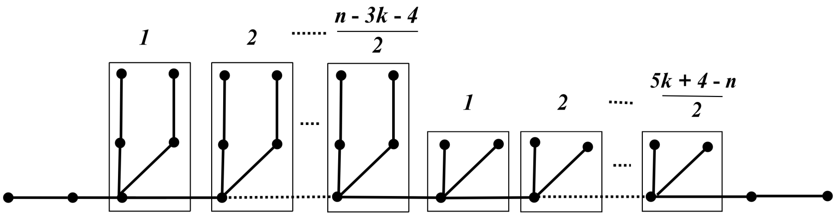
This value of $H(T)$ will be obtained if $T \cong T^1(n,k)$ where $T^1(n,k)$ is a tree as shown in Fig. 3.1.



(a) If $n = 3k + 2$.



(b) If $n - 3k - 2$ is odd.



(c) If $n - 3k - 2$ is even.

Figure 3.1: $T^1(n, k)$

Case 2. When $n > 5k + 4$.
The Harmonic index of T can be obtained by using the values of m_{uv} for $(u, v) \in S$ from Lemma 3.1.5 in Equation (3.1.1) as follows:

$$H(T) = \frac{1}{2}n - \frac{1}{4}k - \frac{1}{4}.$$

This value of $H(T)$ will be obtained if $T \cong T^2(n, k)$ where $T^2(n, k)$ is a tree as shown in Fig. 3.2.

□

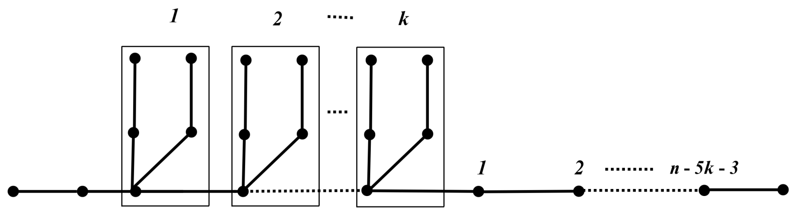


Figure 3.2: $T^2(n,k)$

Chapter 4

Minimum Harmonic Index for Chemical Trees with Given Vertices of Maximum Degree

In the domain of chemical graph theory, topological indices theory addresses crucial problems: identifying structures with extreme values while adhering to constraints and determining precise bounds for a given index. In this chapter, we determine the smallest values of the Harmonic index for chemical trees with k vertices of degree 4.

4.1 Preliminaries

Consider the following subsets of $\mathcal{CT}(n,k)$:

$$\begin{aligned}
\mathcal{CT}_1(n,k) \quad &= \{T \in \mathcal{CT}(n,k) \mid 3k+2 \le n \le 4k, k \ge 2\} \cup \{T \in \mathcal{CT}(n,k) \\
&\mid n \in \{3k+2\}, k = 1\}, \\
\mathcal{CT}_2(n,k) \quad &= \{T \in \mathcal{CT}(n,k) \mid \\
&4k < n < 5k-2, k \ge 4\} \cup \{T \in \mathcal{CT}(n,k) \mid n = 4k+1, k = 2\}, \\
\mathcal{CT}_3(n,k) \quad &= \{T \in \mathcal{CT}(n,k) \mid n \ge 5k-2, k \ge 3\} \cup \{T \in \mathcal{CT}(n,k)
\end{aligned}$$

$| \ n \geq 3k+4, k \in \{1,2\}.$

Lemma 4.1.1. *Let* $T \in \mathcal{CT}(n,k)$ *has the smallest Harmonic index among the trees in* $\mathcal{CT}(n,k)$*. Then* $n_2 \leq 1$.

Proof. On the contrary, assume that $n_2 > 1$. Let p and q be two vertices with $deg_T(p) = deg_T(q) = 2$. We consider two cases:

Case 1. When p and q are adjacent.

Let p_1 be the neighbor of p other than q and q_1 be the neighbor of q other than p. Let

$$T' = T - pp_1 + qp_1.$$

Clearly, $deg_{T'}(p) = deg_T(p) - 1 = 1$, $deg_{T'}(q) = deg_T(q) + 1 = 3$ and $deg_{T'}(w) = deg_T(w)$ for all $w \in V(T)\backslash\{p,q\}$. Obviously, $T' \in \mathcal{CT}(n,k)$. Now, we show that $H(T') - H(T) > 0$ by using Lemma 3.1.1 to obtain a contradiction.

$$\begin{aligned}
H(T') - H(T) \quad &= \frac{2}{deg_T(p_1) + deg_T(q) + 1} + \frac{2}{deg_T(q) + 1 + deg_T(p) - 1} \\
&+ \frac{2}{(deg_T(q) + 1) + deg_T(q_1)} - \frac{2}{deg_T(p_1) + deg_T(p)} \\
&- \frac{2}{deg_T(p) + deg_T(q)} - \frac{2}{deg_T(q) + deg_T(q_1)} \\
&= \frac{2}{deg_T(p_1) + 3} + \frac{2}{3+1} + \frac{2}{3 + deg_T(q_1)} - \frac{2}{deg_T(p_1) + 2} \\
&- \frac{2}{2+2} - \frac{2}{2 + deg_T(q_1)} \\
&\leq \frac{2}{4+3} + \frac{2}{3+1} + \frac{2}{3+4} - \frac{2}{4+2} - \frac{2}{2+2} - \frac{2}{2+4} \\
&= -0.095 < 0.
\end{aligned}$$

This contradicts our assumption and hence, there cannot be two adjacent vertices of degree 2 in T.

Case 2. When p and q are non-adjacent.

Let $deg_T(p) = deg_T(q) = 2$. Let p_1 and p_2 be the neighbors of p and q_1 and q_2 be the neighbors of q. Without loss of generality, assume that there exists a path P starting from p to q with p_1 and q_1 lying on it. By Case 1, degrees of p_1, p_2, q_1 and q_2 cannot be equal to 2. Let

$$T'' = T - pp_2 + qp_2.$$

Clearly, $deg_{T''}(p) = deg_T(p) - 1 = 1$, $deg_{T''}(q) = deg_T(q) + 1 = 3$ and $deg_{T''}(w) = deg_T(w)$ for all $w \in V(T) \backslash \{p, q\}$. Obviously, $T'' \in \mathcal{CT}(n, k)$. Now, we show that $H(T'') - H(T) < 0$ by using Lemma 3.1.1 to obtain a contradiction.

$$\begin{aligned}
H(T'') - H(T) \quad &= \frac{2}{deg_T(p_2) + deg_T(q) + 1} + \frac{2}{deg_T(q_1) + (deg_T(q) + 1)} \\
&+ \frac{2}{deg_T(q_2) + (deg_T(q) + 1)} + \frac{2}{(deg_T(p) - 1) + deg_T(p_1)} \\
&- \frac{2}{deg_T(p_2) + deg_T(p)} - \frac{2}{deg_T(q_1) + deg_T(q)} \\
&- \frac{2}{deg_T(q_2) + deg_T(q)} - \frac{2}{deg_T(p) + deg_T(p_1)} \\
&= \frac{2}{deg_T(p_2) + 3} + \frac{2}{deg_T(q_1) + 3} + \frac{2}{deg_T(q_2) + 3} \\
&+ \frac{2}{1 + deg_T(p_1)} - \frac{2}{deg_T(p_2) + 2} - \frac{2}{deg_T(q_1) + 2} \\
&- \frac{2}{deg_T(q_2) + 2} - \frac{2}{2 + deg_T(p_1)} \\
&= \frac{2}{deg_T(p_2) + 3} - \frac{2}{deg_T(p_2) + 2} + \frac{2}{deg_T(q_1) + 3} \\
&- \frac{2}{deg_T(q_1) + 2} + \frac{2}{deg_T(q_2) + 3} - \frac{2}{deg_T(q_2) + 2} \\
&+ \frac{2}{1 + deg_T(p_1)} - \frac{2}{2 + deg_T(p_1)}.
\end{aligned}$$

We know that $3 \leq deg_T(p_1) \leq 4$. Hence, by Lemma 3.1.1, we obtain

$$H(T'') - H(T) \quad \leq \frac{2}{4+3} - \frac{2}{4+2} + \frac{2}{4+3} - \frac{2}{4+2} + \frac{2}{4+3} - \frac{2}{4+2}$$

$$+\frac{2}{1+3}-\frac{2}{2+3}$$
$$= -0.0043 < 0.$$

This completes the proof. □

Lemma 4.1.2. *Assume that $T \in \mathcal{CT}(n,k)$ is a minimum chemical tree among the trees in $\mathcal{CT}(n,k)$ such that $n-k$ is even. Then*

(i) $n_2 = 0$.

(ii) $n_1 = \frac{n}{2} + \frac{k}{2} + 1$, $n_3 = \frac{n}{2} - \frac{3k}{2} - 1$.

Proof. (i). By Lemma 4.1.1, let $n_2 = 1$. Then $n - k \equiv 0 \pmod 2$ implies that $n - k = 2t$, $t \geq 1$. By Equation (3.1.3), we get $n_1 + n_3 = 2t - 1$. Since there are no vertices of odd degrees other than vertices of degree 1 and 3, $n_1 + n_3$ must be even. This gives us a contradiction. Hence $n_2 = 0$.
(ii). Using Equations (3.1.3), (3.1.4) and $n_2 = 0$, we get

$$\begin{aligned} n &= n_1 + n_3 + k, \\ n_1 + 3n_3 &= 2n - 2 - 4k. \end{aligned} \tag{4.1.1}$$

The solution of the system (4.1.1) is $n_1 = \frac{n}{2} + \frac{k}{2} + 1$ and $n_3 = \frac{n}{2} - \frac{3k}{2} - 1$ which completes the proof. □

Lemma 4.1.3. *Assume that $T \in \mathcal{CT}(n,k)$ is a minimum chemical tree among the trees in $\mathcal{CT}(n,k)$ such that $n-k$ is odd. Then*

(i) $n_2 = 1$.

(ii) $n_1 = \frac{n+k+1}{2}, n_3 = \frac{n-3k-3}{2}$.

Proof. (i). By Lemma 4.1.1, let $n_2 = 0$. Then $n - k \equiv 1 \pmod 2$ implies that $n - k = 2t + 1$, $t \geq 1$. By Equation (3.1.3), we get $n_1 + n_3 = 2t + 1$. Since there are no vertices of odd degrees other than vertices of degree 1 and

3, $n_1 + n_3$ must be even. This gives us a contradiction. Hence $n_2 = 1$.
(ii). Using Equations (3.1.3), (3.1.4) and $n_2 = 1$, we get

$$\begin{aligned} n &= n_1 + n_3 + 1 + k, \\ n_1 + 3n_3 &= 2n - 3 - 4k. \end{aligned} \tag{4.1.2}$$

The solution of the system (4.1.2) is $n_1 = \frac{n+k+1}{2}$ and $n_3 = \frac{n-3k-3}{2}$ which completes the proof. □

Lemma 4.1.4. *Assume that $T \in \mathcal{CT}_1(n,k)$ is a minimum tree such that $n-k$ is even. Then*

(i) $m_{44} \neq 0$ *when* $k \geq 2$.

(ii) $m_{22} = m_{12} = m_{23} = m_{24} = 0$.

(iii) $m_{13} = 0$.

(iv) $m_{33} = 0$.

(v) $m_{34} = \frac{3n}{2} - \frac{9k}{2} - 3$, $m_{14} = \frac{n}{2} + \frac{k}{2} + 1$, $m_{44} = 4k - n + 1$.

Proof. (i). On the contrary, assume that $m_{44} = 0$ when $k \geq 2$. Then Equation (3.1.2d) implies that

$$m_{14} + m_{24} + m_{34} = 4k. \tag{4.1.3}$$

Now, consider Equation (3.1.2a). It is easy to see that $m_{14} \leq n_1$ since m_{11}, m_{12}, $m_{13} \geq 0$. Also, by Lemma 4.1.2(i), we have $m_{24} = 0$. Then, Equation (4.1.3) becomes

$$\begin{aligned} m_{34} &= 4k - m_{14} \\ &\geq 4k - (\frac{n}{2} + \frac{k}{2} + 1) && \text{(Using Lemma 4.1.2(ii))} \\ &\geq 4k - (\frac{4k}{2} + \frac{k}{2} + 1) && \text{(Since } T \in \mathcal{CT}_1(n,k)\text{)} \\ &= \frac{3k}{2} - 1. \end{aligned} \tag{4.1.4}$$

Now, consider Equation (3.1.2c). It is easy to see that $m_{34} \leq 3n_3$ since m_{13}, m_{23}, $m_{33} \geq 0$. As $T \in \mathcal{CT}_1(n,k)$, by using $n \leq 4k$ and the value of n_3 from Lemma 4.1.2 in Equation (3.1.2c), we obtain $m_{34} \leq \frac{3k}{2} - 3$ which contradicts Equation (4.1.4). Hence, $m_{44} \neq 0$ in T.
(ii). This result is a direct consequence of Lemma 4.1.2(i).
(iii). On the contrary, assume that $e = pq \in E(T)$ such that $deg_T(p) = 1$ and $deg_T(q) = 3$. Let $N_T(q) \backslash \{p\} = \{q_1, q_2\}$. By Lemma 4.1.4(i), $e' = st \in E(T)$ such that $deg_T(s) = deg_T(t) = 4$. Without loss of generality, assume a path P exists connecting q and s and containing the edge qq_1. Clearly, $deg_T(q_1) \geq 3$ since $n_2 = 0$ by Lemma 4.1.2. Let

$$T' = T - pq - qq_1 - st + pq_1 + sq + qt.$$

Clearly, $deg_{T'}(w) = deg_T(w)$ for all $w \in V(T)$. Obviously, $T' \in \mathcal{CT}_1(n,k)$. Now, by showing $H(T') - H(T) < 0$ by using Lemma 3.1.1, we obtain a contradiction.

$$\begin{aligned}
H(T') - H(T) \quad &= \frac{2}{deg_T(s) + deg_T(q)} + \frac{2}{deg_T(q) + deg_T(t)} \\
&+ \frac{2}{deg_T(p) + deg_T(q_1)} - \frac{2}{deg_T(p) + deg_T(q)} \\
&- \frac{2}{deg_T(s) + deg_T(t)} - \frac{2}{deg_T(q) + deg_T(q_1)} \\
&= \frac{2}{4+3} + \frac{2}{3+4} + \frac{2}{1 + deg_T(q_1)} - \frac{2}{1+3} - \frac{2}{4+4} \\
&- \frac{2}{3 + deg_T(q_1)} \\
&= \frac{2}{4+3} + \frac{2}{3+4} - \frac{2}{1+3} - \frac{2}{4+4} + \frac{2}{1 + deg_T(q_1)} \\
&- \frac{2}{3 + deg_T(q_1)} \\
&\leq \frac{2}{4+3} + \frac{2}{3+4} - \frac{2}{1+3} - \frac{2}{4+4} + \frac{2}{1+3} - \frac{2}{3+3} \\
&= -0.011 < 0,
\end{aligned}$$

which is a contradiction since T has smallest Harmonic index. Hence, $m_{13} = 0$ in T.

(iv). On the contrary, assume that $e = pq \in E(T)$ such that $deg_T(p) = 3$ and $deg_T(q) = 3$. Let $N_T(q)\backslash\{p\} = \{q_1, q_2\}$. By Lemma 4.1.4(i), $e' = st \in E(T)$ such that $deg_T(s) = deg_T(t) = 4$. Without loss of generality, assume there exists a path P connecting q and s and containing the edge qq_1. Let

$$T' = T - pq - qq_1 - st + pq_1 + sq + qt.$$

Clearly, $deg_{T'}(w) = deg_T(w)$ for all $w \in V(T)$. Obviously, $T' \in \mathcal{CT}_1(n, k)$. Now, we show that $H(T') - H(T) < 0$ to obtain a contradiction.

$$\begin{aligned} H(T') - H(T) &= \frac{2}{deg_T(s) + deg_T(q)} + \frac{2}{deg_T(q) + deg_T(t)} \\ &+ \frac{2}{deg_T(p) + deg_T(q_1)} - \frac{2}{deg_T(p) + deg_T(q)} \\ &- \frac{2}{deg_T(s) + deg_T(t)} - \frac{2}{deg_T(q) + deg_T(q_1)} \\ &= \frac{2}{4+3} + \frac{2}{3+4} + \frac{2}{3 + deg_T(q_1)} - \frac{2}{3+3} - \frac{2}{4+4} \\ &- \frac{2}{3 + deg_T(q_1)} \\ &= -0.011 < 0, \end{aligned}$$

which is a contradiction since T has smallest Harmonic index. Hence, $m_{33} = 0$.

(v). Solving the system in Equations (3.1.2a) - (3.1.2d) for unknowns m_{34}, m_{14} and m_{44} by using the values of n_1, n_2 and n_3 from Lemma 4.1.2 and the values of m_{33}, m_{13}, m_{23}, m_{22}, m_{12} and m_{24} from Lemma 4.1.4, we obtain

$$\begin{aligned} m_{34} &= \frac{3n}{2} - \frac{9k}{2} - 3, \\ m_{14} &= \frac{n}{2} + \frac{k}{2} + 1, \\ m_{44} &= 4k - n + 1. \end{aligned}$$

This finishes the proof.

□

Lemma 4.1.5. *Assume that $T \in \mathcal{CT}_1(n,k)$ is a minimum tree such that $n-k$ is odd. Then*

(i) $m_{44} \neq 0$ *when* $k \geq 2$.

(ii) $m_{22} = 0$.

(iii) $m_{12} = 0$.

(iv) $m_{23} = 0$.

(v) $m_{13} = 0$.

(vi) $m_{33} = 0$.

(vii) $m_{34} = \frac{3n-9k-9}{2}$, $m_{14} = \frac{n+k+1}{2}$, $m_{24} = 2$ *and* $m_{44} = 4k-n+1$.

Proof. (i). On the contrary, assume that $m_{44} = 0$. This implies that

$$m_{14} + m_{24} + m_{34} = 4k. \tag{4.1.5}$$

We know that $m_{14} \leq n_1$ since m_{11}, m_{12}, $m_{13} \geq 0$. Also, by Lemma 4.1.3(i), $n_2 = 1$ which implies $m_{24} \leq 2$. This implies

$$\begin{aligned} m_{34} &= 4k - m_{14} - m_{24} \\ &\geq 4k - \frac{n+k+1}{2} - 2 && \text{(Using Lemma 4.1.3(ii))} \\ &\geq 4k - \frac{4k+k+1}{2} - 2k && \text{(Since } T \in \mathcal{CT}_1(n,k)\text{)} \\ &= \frac{3k}{2} - \frac{3}{2}. \end{aligned} \tag{4.1.6}$$

On the other hand, we know that $m_{34} \leq 3n_3$ since m_{13}, m_{23}, $m_{33} \geq 0$. As $T \in \mathcal{CT}_1(n,k)$, by using $n \leq 4k$ and the value of n_3 from Lemma 4.1.2, we obtain $m_{34} \leq \frac{3k}{2} - \frac{9}{2}$ but this contradicts Equation (4.1.6). Hence, $m_{44} \neq 0$.

(ii). This result is a direct consequence of Lemma 4.1.3(ii).
(iii). On the contrary, assume that $e = pq \in E(T)$ such that $deg_T(p) = 1$ and $deg_T(q) = 2$. Let $N_T(q)\backslash\{p\} = \{q_1\}$. Clearly, $deg_T(q_1) \geq 3$ since $n_2 = 1$ by Lemma 4.1.3. By Lemma 4.1.4(i), $e' = st \in E(T)$ such that $deg_T(s) = deg_T(t) = 4$. Let

$$T' = T - pq - qq_1 - st + pq_1 + sq + qt.$$

Clearly, $deg_{T'}(w) = deg_T(w)$ for all $w \in V(T)$. Obviously, $T' \in \mathcal{CT}_1(n, k)$. Now, we show that $H(T') - H(T) > 0$ by using Lemma 3.1.1 to obtain a contradiction.

$$\begin{aligned} H(T') - H(T) &= \frac{2}{deg_T(s) + deg_T(q)} + \frac{2}{deg_T(q) + deg_T(t)} \\ &+ \frac{2}{deg_T(p) + deg_T(q_1)} - \frac{2}{deg_T(p) + deg_T(q)} \\ &- \frac{2}{deg_T(s) + deg_T(t)} - \frac{2}{deg_T(q) + deg_T(q_1)} \\ &= \frac{2}{4+2} + \frac{2}{2+4} + \frac{2}{1 + deg_T(q_1)} - \frac{2}{1+2} - \frac{2}{4+4} \\ &- \frac{2}{2 + deg_T(q_1)} \\ &= \frac{2}{4+2} + \frac{2}{2+4} - \frac{2}{1+2} - \frac{2}{4+4} + \frac{2}{1 + deg_T(q_1)} \\ &- \frac{2}{2 + deg_T(q_1)} \\ &\leq \frac{2}{4+2} + \frac{2}{2+4} - \frac{2}{1+2} - \frac{2}{4+4} + \frac{2}{1+3} - \frac{2}{2+3} \\ &= -0.15 < 0, \end{aligned}$$

which is a contradiction since T has smallest Harmonic index. Hence, $m_{12} = 0$.
(iv). On the contrary, assume that $e = pq \in E(T)$ such that $deg_T(p) = 3$ and $deg_T(q) = 2$. Let $N_T(q)\backslash\{p\} = \{q_1\}$. By Lemma 4.1.5, $e' = st \in E(T)$

such that $deg_T(s) = deg_T(t) = 4$. Let

$$T' = T - pq - qq_1 - st + pq_1 + sq + qt.$$

Clearly, $deg_{T'}(w) = deg_T(w)$ for all $w \in V(T)$. Obviously, $T' \in \mathcal{CT}_1(n,k)$. Now, by showing $H(T') - H(T) < 0$ by using Lemma 3.1.1, we obtain a contradiction.

$$\begin{aligned}
H(T') - H(T) \quad &= \frac{2}{deg_T(s) + deg_T(q)} + \frac{2}{deg_T(q) + deg_T(t)} \\
&+ \frac{2}{deg_T(p) + deg_T(q_1)} - \frac{2}{deg_T(p) + deg_T(q)} \\
&- \frac{2}{deg_T(s) + deg_T(t)} - \frac{2}{deg_T(q) + deg_T(q_1)} \\
&= \frac{2}{4+2} + \frac{2}{2+4} - \frac{2}{3+2} - \frac{2}{4+4} + \frac{2}{3 + deg_T(q_1)} \\
&- \frac{2}{2 + deg_T(q_1)} \\
&\leq \frac{2}{4+2} + \frac{2}{2+4} - \frac{2}{3+2} - \frac{2}{4+4} + \frac{2}{3+4} - \frac{2}{2+4} \\
&= -0.03 < 0,
\end{aligned}$$

which is a contradiction since T has smallest Harmonic index. Hence, $m_{23} = 0$.

(v). The proof of this case is similar to Lemma 4.1.4(iii).

(vi). The proof of this case is similar to Lemma 4.1.4(iv).

(vii). Solving the system in Equations (3.1.2a) - (3.1.2d) for unknowns m_{34}, m_{14}, m_{24} and m_{44} by using the values of n_1, n_2 and n_3 from Lemma 4.1.3 and the values of m_{33}, m_{13}, m_{23}, m_{22} and m_{12} from Lemma 4.1.5, we obtain

$$\begin{aligned}
m_{34} \quad &= \frac{3n - 9k - 9}{2}, \\
m_{14} \quad &= \frac{n + k + 1}{2}, \\
m_{24} \quad &= 2, \\
m_{44} \quad &= 4k - n + 1.
\end{aligned}$$

This completes the proof. □

Lemma 4.1.6. *Assume that* $T \in \mathcal{CT}_2(n,k)$ *is a minimum tree such that* $n-k$ *is even. Then*

(i) $m_{22} = m_{12} = m_{23} = m_{24} = 0$.

(ii) $m_{44} = 0$.

(iii) $m_{13} = 0$.

(iv) $m_{34} = \frac{7k}{2} - \frac{n}{2} - 1$, $m_{14} = \frac{n}{2} + \frac{k}{2} + 1$, $m_{33} = n - 4k - 1$.

Proof. (i). This result is a direct consequence of Lemma 4.1.2(i).
(ii). On the contrary, assume that $m_{44} \neq 0$. Then m_{13} and m_{33} must not both be 0. To prove this, assume that both m_{13} and m_{33} are zero. Equations (3.1.2a) - (3.1.2d) along with Lemma 4.1.6(i) imply $m_{14} = n_1$ and $m_{34} = 3n_3$ and $m_{44} = 4k - n_1 - 3n_3$. By using values of n_1 and n_2 from Lemma 4.1.2, m_{44} becomes $8k+2-2n$ which further implies that $m_{44} \leq 0$ for $n \geq 4k+1$ which is a contradiction as $T \in \mathcal{CT}_2(n,k)$. Hence, when $m_{13} \neq 0$ or $m_{33} \neq 0$, then by using the argument and the transformation similar to those in Lemma 4.1.4(iii) or 4.1.4(iv), respectively, we can conclude that $m_{44} = 0$.
(iii). On the contrary, assume that $m_{13} \neq 0$, that is, $e = st \in E(T)$ such that $deg_T(s) = 1$ and $deg_T(t) = 3$. This implies that

$$
\begin{aligned}
m_{14} &< n_1 \\
&= \frac{n}{2} + \frac{k}{2} + 1 && \text{(Using Lemma 4.1.2(ii))} \\
&< \frac{5k-2}{2} + \frac{k}{2} + 1 && \text{(Since } T \in \mathcal{CT}_2(n,k)\text{)} \\
&= 3k.
\end{aligned}
$$

This implies that there exists a vertex p with degree $deg_T(p) = 4$ with at most 2 pendent vertices. Let p_1 and p_2 be the non-pendant neighbors of p. Let t_1 and t_2 be the neighbors of t other than s. Without loss of generality, let P be the path joining t and p containing the edges tt_1 and p_1p. By Lemma

4.1.2(i), $n_2 = 0$ which implies that $deg_T(p_2) \neq 2$. Also, Lemma 4.1.6(ii), we have $m_{44} = 0$ which implies $deg_T(p_2) \neq 4$. Hence, $deg_T(p_2) = 3$. Let r and z be the neighbors of p_2 other than p. Let

$$T' = T - p_2r - p_2z + sr + tr.$$

Clearly, $deg_{T'}(p_2) = deg_T(p_2) - 2$, $deg_{T'}(s) = deg_T(s) + 2$ and $deg_{T'}(w) = deg_T(w)$ for all $w \in V(T)\backslash\{p_2, s\}$. Obviously, $T' \in \mathcal{CT}_2(n,k)$. Now, we show that $H(T') - H(T) < 0$ to obtain a contradiction.

$$\begin{aligned}
H(T') - H(T) \quad &= \frac{2}{deg_T(q) + deg_T(s) + 2} + \frac{2}{deg_T(z) + deg_T(s) + 2} \\
&+ \frac{2}{deg_T(s) + 2 + deg_T(t)} + \frac{2}{deg_T(p) + deg_T(p_2) - 2} \\
&- \frac{2}{deg_T(p) + deg_T(p_2)} - \frac{2}{deg_T(p_2) + deg_T(r)} \\
&- \frac{2}{deg_T(p_2) + deg_T(z)} - \frac{2}{deg_T(s) + deg_T(t)} \\
&= \frac{2}{deg_T(r) + 3} + \frac{2}{deg_T(z) + 3} + \frac{2}{3+3} + \frac{2}{4+1} - \frac{2}{4+3} \\
&- \frac{2}{3 + deg_T(r)} - \frac{2}{3 + deg_T(z)} - \frac{2}{1+3} \\
&= -0.05 < 0,
\end{aligned}$$

which is a contradiction since T has the smallest Harmonic index. Hence, $m_{13} = 0$.

(iv). Solving the system in Equations (3.1.2a) - (3.1.2d) for unknowns m_{34}, m_{14} and m_{33} by using the values of n_1, n_2 and n_3 from Lemma 4.1.2 and the values of m_{12}, m_{24}, m_{22}, m_{23}, m_{13} and m_{44} from Lemma 4.1.6, we obtain

$$\begin{aligned}
m_{34} \quad &= \frac{7k}{2} - \frac{n}{2} - 1, \\
m_{14} \quad &= \frac{n}{2} + \frac{k}{2} + 1, \\
m_{33} \quad &= n - 4k - 1.
\end{aligned}$$

This finishes the proof. □

Lemma 4.1.7. *Assume that $T \in \mathcal{CT}_2(n,k)$ is a minimum tree such that $n-k$ is odd. Then*

(i) $m_{22} = 0$.

(ii) $m_{12} = 0$.

(iii) $m_{44} = 0$.

(iv) $m_{13} = 0$.

(v) $m_{24} = 2$ *and* $m_{23} = 0$.

(vi) $m_{34} = \frac{7k-n-5}{2}$, $m_{14} = \frac{n+k+1}{2}$, $m_{33} = n - 4k - 1$.

Proof. (i). This result is a direct consequence of Lemma 4.1.3(i).
(ii). On the contrary assume that $m_{12} \neq 0$, that is, $e = st \in E(T)$ such that $deg_T(s) = 1$ and $deg_T(t) = 2$. Let t_1 be the other neighbor of t. Let p be a vertex of degree 4. Let $N_T(p) = \{p_1, p_2, p_3, p_4\}$. Let P be the path connecting p and t and containing the edges tt_1 and pp_4. Let

$$T' = T - pp_1 - pp_2 - pp_3 + sp_1 + sp_2 + sp_3.$$

Clearly, $deg_{T'}(p) = deg_T(p) - 3$, $deg_{T'}(s) = deg_T(s) + 3$ and $deg_{T'}(w) = deg_T(w)$ for all $w \in V(T)\backslash\{p, s\}$. Obviously, $T' \in \mathcal{CT}_2(n,k)$. Now, by showing $H(T') - H(T) < 0$ using Lemma 3.1.1, we obtain a contradiction.

$$\begin{aligned} H(T') - H(T) \quad &= \frac{2}{deg_T(p_1) + deg_T(s) + 3} + \frac{2}{deg_T(p_2) + deg_T(s) + 3} \\ &+ \frac{2}{deg_T(p_3) + deg_T(s) + 3} + \frac{2}{deg_T(s) + 3 + deg_T(t)} \\ &+ \frac{2}{deg_T(p_4) + deg_T(p) - 3} - \frac{2}{deg_T(p) + deg_T(p_4)} \\ &- \frac{2}{deg_T(p) + deg_T(p_1)} - \frac{2}{deg_T(p) + deg_T(p_2)} \end{aligned}$$

$$
\begin{aligned}
&-\frac{2}{deg_T(p)+deg_T(p_3)}-\frac{2}{deg_T(s)+deg_T(t)}\\
&=\frac{2}{deg_T(p_1)+4}+\frac{2}{deg_T(p_2)+4}+\frac{2}{deg_T(p_3)+4}+\frac{2}{4+2}\\
&+\frac{2}{deg_T(p_4)+1}-\frac{2}{4+deg_T(p_4)}-\frac{2}{deg_T(p_1)+4}\\
&-\frac{2}{deg_T(p_2)+4}-\frac{2}{deg_T(p_3)+4}-\frac{2}{1+2}\\
&=\frac{2}{4+2}-\frac{2}{1+2}+\frac{2}{deg_T(p_4)+1}-\frac{2}{4+deg_T(p_4)}\\
&\le\frac{2}{4+2}-\frac{2}{1+2}+\frac{2}{3+1}-\frac{2}{4+3}=-0.11<0,
\end{aligned}
$$

which is a contradiction since T has the smallest Harmonic index. Hence, $m_{12}=0$.

(iii). On the contrary, assume that $m_{44}\neq 0$, that is, $e=st\in E(T)$ with $deg_T(s)=deg_T(t)=4$. Then m_{13}, m_{23} and m_{33} must not all be 0. To prove this, assume that all of m_{13}, m_{23} and m_{33} are equal to zero. Equations (3.1.2a) - (3.1.2d) along with Lemmas 4.1.7(i) and 4.1.7(ii) imply $m_{14}=n_1$, $m_{24}=2n_2$ and $m_{34}=3n_3$ and $m_{44}=4k-n_1-3n_3-2n_2$. By using values of n_1, n_2 and n_3 from Lemma 4.1.3, m_{44} becomes $8k-1-2n$ which further implies that $m_{44}>0$ if $n<4k-\frac{1}{2}$ which is a contradiction as $T\in\mathcal{CT}_2(n,k)$. Hence, when $m_{13}\neq 0$, $m_{33}\neq 0$ or $m_{23}\neq 0$, then by using the argument and the transformation similar to those in Lemmas 4.1.4(iii), 4.1.4(iv) or 4.1.5(iv), we can conclude that $m_{44}=0$.

(iv). On the contrary, assume that $m_{13}\neq 0$, that is, $e=st\in E(T)$ such that $deg_T(s)=1$ and $deg_T(t)=3$. This implies that

$$
\begin{aligned}
m_{14}&<n_1\\
&=\frac{n+k+1}{2} && \text{(Using Lemma 4.1.3(ii))}\\
&<\frac{5k-1+k+1}{2}+\frac{6k}{2k} && \text{(Since } T\in\mathcal{CT}_2(n,k))\\
&=3k.
\end{aligned}
$$

This implies that there exists a vertex p with degree $deg_T(p) = 4$ with at most 2 pendent vertices. Let p_1 and p_2 be the non-pendant neighbors of p. Let t_1 and t_2 be the neighbors of t other than s. Without loss of generality, let P be the path joining t and p containing the edges tt_1 and p_1p. By Lemma 4.1.7(iii), $m_{44} = 0$ which implies $deg_T(p_2) \neq 4$. Hence, $deg_T(p_2) \in \{2, 3\}$. The case when $deg_T(p_2) = 3$ proceeds in a similar way as in Lemma 4.1.6(iii). For the case when $deg_T(p_2) = 2$, let r be the neighbor of p_2 other than p. Let

$$T' = T - p_2r + sr.$$

Clearly, $deg_{T'}(p_2) = deg_T(p_2) - 1$, $deg_{T'}(s) = deg_T(s) + 1$ and $deg_{T'}(w) = deg_T(w)$ for all $w \in V(T)\backslash\{p_2, s\}$. Obviously, $T' \in \mathcal{CT}_2(n, k)$. Now, we show that $H(T') - H(T) < 0$ to obtain a contradiction.

$$\begin{aligned} H(T') - H(T) \quad &= \frac{2}{deg_T(r) + deg_T(s) + 1} + \frac{2}{deg_T(s) + 1 + deg_T(t)} \\ &+ \frac{2}{deg_T(p) + deg_T(p_2) - 1} - \frac{2}{deg_T(p) + deg_T(p_2)} \\ &- \frac{2}{deg_T(p_2) + deg_T(r)} - \frac{2}{deg_T(s) + deg_T(t)} \\ &= \frac{2}{deg_T(r) + 2} + \frac{2}{2+3} + \frac{2}{4+1} - \frac{2}{4+2} - \frac{2}{2 + deg_T(r)} \\ &- \frac{2}{1+3} \\ &= -0.03 < 0, \end{aligned}$$

which is a contradiction since T has the smallest Harmonic index. Hence, $m_{13} = 0$.

(v). On the contrary assume that $m_{24} \neq 2$. Clearly, $m_{24} \not> 2$ as $n_2 = 1$ by Lemma 4.1.3. Let p be the vertex with $deg_T(p) = 2$. Let p_1 and p_2 be its neighbors. Next, we consider the following cases.

Case 1: When $deg_T(p_1) = deg_T(p_2) = 3$

Let s be any vertex with degree 4. Let s' be the non-pendant neighbor of s.

Clearly, $deg_T(s') = 3$ by Lemma 4.1.7(iii). Let

$$T' = T - pp_1 - pp_2 - ss' + sp + s'p + p_1p_2.$$

Clearly, $deg_{T'}(w) = deg_T(w)$ for all $w \in V(T)$. Obviously, $T' \in \mathcal{CT}_2(n,k)$. Now, by showing $H(T') - H(T) < 0$ by using Lemma 3.1.1, we obtain a contradiction.

$$\begin{aligned} H(T') - H(T) &= \frac{2}{deg_T(s) + deg_T(p)} + \frac{2}{deg_T(s') + deg_T(p)} \\ &+ \frac{2}{deg_T(p_1) + deg_T(p_2)} - \frac{2}{deg_T(p) + deg_T(p_1)} \\ &- \frac{2}{deg_T(p_2) + deg_T(p)} - \frac{2}{deg_T(s) + deg_T(s')} \\ &= \frac{2}{4+2} + \frac{2}{3+2} + \frac{2}{3+3} - \frac{2}{2+3} - \frac{2}{3+2} - \frac{2}{4+3} \\ &= -0.019 < 0 \end{aligned}$$

which is a contradiction since T has minimum Harmonic index.

Case 2. When $deg_T(p_1) = 4$ and $deg_T(p_2) = 3$

By Lemma 4.1.3, $n_1 = \frac{n+k+1}{2}$. It can easily be seen that for $4k < n < 5k-2$, $\frac{5k-1}{2} < n_1 < \frac{6k-1}{2}$ or $2k < n_1 < 3k$. This implies that there exists a vertex with degree 4 and with exactly 3 pendant neighbors and there exists another vertex with degree 4 and at most 2 pendant neighbors.

Subcase 1: When p_1 has three pendant neighbors.

Let t be another vertex of degree 4 with at most 2 pendant neighbors. Let t_1 and t_2 be the non-pendant neighbors of t. As $m_{44} = 0$ by Lemma 4.1.7(iii), so $deg_T(t_1) = deg_T(t_2) = 3$. Let P be the path connecting p_1 and t and containing the edges p_1p and t_2t. Let

$$T'' = T - tt_1 - tt_2 + pt + p_2t.$$

Clearly, $deg_{T''}(w) = deg_T(w)$ for all $w \in V(T)$. Obviously, $T'' \in \mathcal{CT}_2(n,k)$.

Now, we show that $H(T'') - H(T) < 0$ to obtain a contradiction.

$$\begin{aligned} H(T'') - H(T) &= \frac{2}{deg_T(t) + deg_T(p)} + \frac{2}{deg_T(p_2) + deg_T(t)} \\ &+ \frac{2}{deg_T(t_1) + deg_T(t_2)} - \frac{2}{deg_T(t) + deg_T(t_1)} \\ &- \frac{2}{deg_T(t_2) + deg_T(t)} - \frac{2}{deg_T(p) + deg_T(p_2)} \\ &= \frac{2}{4+2} + \frac{2}{4+3} + \frac{2}{3+3} - \frac{2}{2+3} - \frac{2}{4+3} - \frac{2}{4+3} \\ &= -0.019 < 0, \end{aligned}$$

which is a contradiction since T has minimum Harmonic index.

Subcase 2: When p_1 has at most 2 pendant neighbors.

Let p_1' be the non-pendant neighbor of p_1 other than p. Let P be the maximal path that starts from p_1, contains p_1u and ends at a vertex, say q. It is clear that q is a pendant vertex. Let s be the neighbor of q. By Lemmas 4.1.7(ii) and 4.1.7(iv), $deg_T(s) = 4$. The maximality of path P also implies that s has 3 pendant vertices. Let s' be the non-pendant neighbor of s. Obviously, $deg_T(s') = deg_T(p_1') = 3$ as $m_{44} = 0$ by Lemma 4.1.7(iii). Let

$$\hat{T} = T - p_1'p_1 - pp_2 - s's + ps + p_1s' + p_1'p_2.$$

Clearly, $deg_{\hat{T}}(w) = deg_T(w)$ for all $w \in V(T)$. Obviously, $\hat{T} \in \mathcal{CT}_2(n, k)$. Now, we show that $H(\hat{T}) - H(T) < 0$ to obtain a contradiction.

$$\begin{aligned} H(\hat{T}) - H(T) &= \frac{2}{deg_T(s) + deg_T(p)} + \frac{2}{deg_T(p_1') + deg_T(p_2)} \\ &+ \frac{2}{deg_T(p_1) + deg_T(s')} - \frac{2}{deg_T(p_1') + deg_T(p_1)} \\ &- \frac{2}{deg_T(p_2) + deg_T(p)} - \frac{2}{deg_T(s') + deg_T(s)} \\ &= \frac{2}{4+2} + \frac{2}{3+4} + \frac{2}{3+3} - \frac{2}{3+4} - \frac{2}{2+3} - \frac{2}{4+3} \\ &= -0.019 < 0, \end{aligned}$$

which is a contradiction since T has minimum Harmonic index. Therefore $m_{24} = 2$. This further implies $m_{23} = 0$.
(vi). Solving the system in Equations (3.1.2a) - (3.1.2d) for unknowns m_{34}, m_{14} and m_{33} by using the values of n_1, n_2, n_3 from Lemma 4.1.3 and the values of m_{12}, m_{22}, m_{24}, m_{23}, m_{13} and m_{44} from Lemma 4.1.7, we obtain

$$\begin{aligned} m_{34} &= \frac{7k-n-5}{2}, \\ m_{14} &= \frac{n+k+1}{2}, \\ m_{33} &= n-4k-1. \end{aligned}$$

This completes the proof. □

Lemma 4.1.8. *Assume that $T \in \mathcal{CT}_3(n,k)$ is a minimum tree such that $n-k$ is even. Then*

(i) $m_{12} = m_{22} = m_{23} = m_{24} = 0$.

(ii) $m_{44} = 0$.

(iii) $m_{14} = 3k$.

(iv) $m_{34} = k$, $m_{13} = \frac{n}{2} - \frac{5k}{2} + 1$, $m_{33} = \frac{n}{2} - \frac{3k}{2} - 2$.

Proof. (i). This result is a direct consequence of Lemma 4.1.2(i).
(ii). The proof of this case is the same as that of Lemma 4.1.6(iii).
(iii). On the contrary assume that $m_{14} \neq 3k$. Clearly, $m_{14} \not> 3k$ because that would imply the existence of a vertex of degree 4 with 4 pendant neighbors. So, we consider the case when $m_{14} < 3k$. If $m_{14} < 3k$ then $m_{13} > 0$. Assume that $m_{13} = 0$ to prove this using contradiction. As $m_{12} = 0$ by Lemma 4.1.8(i), therefore Equation (3.1.2a) becomes $m_{14} = n_1$ which implies $n_1 < 3k$. By using the value of n_1 from Lemma 4.1.2(ii), we obtain $\frac{n}{2} + \frac{k}{2} + 1 < 3k$ which further implies that $n < 5k - 2$ which is a contradiction as $T \in \mathcal{CT}_3(n,k)$. Hence $m_{13} \neq 0$. This implies $e = st \in E(T)$ such that $deg_T(s) = 1$ and $deg_T(t) = 3$. Moreover, $m_{14} < 3k$ implies that there exists

a vertex p with degree $deg_T(p) = 4$ with at most 2 pendent vertices. Let p_1 and p_2 be the non-pendant neighbors of p. Let t_1 and t_2 be the neighbors of t other than s. Without loss of generality, let P be the path joining t and p containing the edges tt_1 and p_1p. As by Lemma 4.1.8(ii), $m_{44} = 0$, it implies that $deg_T(p_2) \neq 4$. Also, by Lemma 4.1.2, $n_2 = 0$, it implies that $deg_T(p_2) \neq 2$. Hence, $deg_T(p_2) = 3$. Let r and z be the neighbors of p_2 other than p. Let

$$T' = T - p_2r - p_2z + sr + zs.$$

Clearly, $deg_{T'}(p_2) = deg_T(p_2) - 2$, $deg_{T'}(s) = deg_T(s) + 2$ and $deg_{T'}(w) = deg_T(w)$ for all $w \in V(T)\backslash\{p_2, s\}$. Obviously, $T' \in \mathcal{CT}_3(n, k)$. Now, we show that $H(T') - H(T) < 0$ to obtain a contradiction.

$$\begin{aligned}
H(T') - H(T) \quad &= \frac{2}{deg_T(r) + deg_T(s) + 2} + \frac{2}{deg_T(z) + deg_T(s) + 2} \\
&+ \frac{2}{deg_T(s) + 2 + deg_T(t)} + \frac{2}{deg_T(p) + deg_T(p_2) - 2} \\
&- \frac{2}{deg_T(p) + deg_T(p_2)} - \frac{2}{deg_T(p_2) + deg_T(r)} \\
&- \frac{2}{deg_T(p_2) + deg_T(z)} - \frac{2}{deg_T(s) + deg_T(t)} \\
&= \frac{2}{deg_T(r) + 3} + \frac{2}{deg_T(z) + 3} + \frac{2}{3 + 3} + \frac{2}{4 + 1} - \frac{2}{4 + 3} \\
&- \frac{2}{3 + deg_T(r)} - \frac{2}{3 + deg_T(z)} - \frac{2}{1 + 3} \\
&= -0.05 < 0,
\end{aligned}$$

which is a contradiction since T has the smallest Harmonic index. Hence, $m_{14} = 3k$.

(iv). Solving the system in Equations (3.1.2a) - (3.1.2d) for unknowns m_{34}, m_{13} and m_{33} by using the values of n_1, n_2 and n_3 from Lemma 4.1.2 and the values of m_{12}, m_{22}, m_{23}, m_{24}, m_{14} and m_{44} from Lemma 4.1.8, we obtain

$$m_{34} \quad = k,$$

$$m_{13} = \frac{n}{2} - \frac{5k}{2} + 1,$$
$$m_{33} = \frac{n}{2} - \frac{3k}{2} - 2.$$

This finishes the proof. □

Lemma 4.1.9. *Assume that $T \in \mathcal{CT}_3(n, k)$ is a minimum chemical tree such that $n - k$ is odd. Then*

(i) $m_{22} = 0$.

(ii) $m_{12} = 0$.

(iii) $m_{44} = 0$.

(iv) $m_{23} = 1$.

(v) $m_{14} = 3k$.

(vi) $m_{24} = 1$, $m_{13} = \frac{n-5k+1}{2}$, $m_{33} = \frac{n-3k-5}{2}$, $m_{34} = k - 1$.

Proof. (i). This result is a direct consequence of Lemma 4.1.3(i).
(ii). The proof of this case is similar to that of Lemma 4.1.7(ii).
(iii). The proof of this case is same as that of Lemma 4.1.7(iii).
(iv). On the contrary assume that $m_{23} \neq 1$. Let p be the vertex with degree 2 and let p_1 and p_2 be its neighbors. It can easily be seen that m_{23} cannot be more than 2 as $n_2 = 1$ by Lemma 4.1.3. This leaves us with 2 cases:

Case 1. When $deg_T(p_1) = deg_T(p_2) = 3$.
This case is similar to Case 1 of Lemma 4.1.7(iv).

Case 2. When $deg_T(p_1) = deg_T(p_2) = 4$.
If $m_{24} = 2$, then m_{13} cannot be 0. To prove this, assume that $m_{13} = 0$. By Equation (3.1.2a), this implies

$$\begin{aligned} m_{14} &= n_1 \\ &= \frac{n+k+1}{2} && \text{(Using Lemma 4.1.3(ii))} \end{aligned}$$

$$> \frac{5k-3+k+1}{2} \qquad \text{(Since } T \in \mathcal{CT}_3(n,k)\text{)}$$
$$= 3k-1.$$

However, it is clear that $m_{14} < 3k$ for $k \geq 2$ and $n \geq 10$ as $m_{24} = 2$ and hence, a contradiction. Let $e = st \in E(T)$ such that $deg_T(s) = 3$ and $deg_T(t) = 1$. Without loss of generality, assume that p_1 does not lie on the path connecting p and s. Let

$$T' = T - pp_1 + tp_1.$$

Clearly, $deg_{T'}(p) = deg_T(p) - 1$, $deg_{T'}(t) = deg_T(t) + 1$ and $deg_{T'}(w) = deg_T(w)$ for all $w \in V(T)\backslash\{p,t\}$. Obviously, $T' \in \mathcal{CT}_3(n,k)$. Now, we show that $H(T') - H(T) < 0$ to obtain a contradiction.

$$\begin{aligned} H(T') - H(T) &= \frac{2}{deg_T(t)+1+deg_T(p_1)} + \frac{2}{deg_T(p)-1+deg_T(p_2)} \\ &+ \frac{2}{deg_T(t)+1+deg_T(s)} - \frac{2}{deg_T(p)+deg_T(p_1)} \\ &- \frac{2}{deg_T(p)+deg_T(p_2)} - \frac{2}{deg_T(t)+deg_T(s)} \\ &= \frac{2}{2+4} + \frac{2}{1+4} + \frac{2}{2+3} - \frac{2}{2+4} - \frac{2}{2+4} - \frac{2}{3+1} \\ &= -0.030 < 0. \end{aligned}$$

This contradicts our assumption that T is the tree with the minimum Harmonic index.

(v). On the contrary assume that $m_{14} \neq 3k$. Clearly, $m_{14} \not> 3k$ because that would imply the existence of a vertex of degree 4 with 4 pendant neighbors. So, we consider the case when $m_{14} < 3k$. If $m_{14} < 3k$, then $m_{13} > 0$. Assume that $m_{13} = 0$ to prove this using contradiction. As $m_{12} = 0$ by Lemma 4.1.9(ii), therefore Equation (3.1.2a) becomes $m_{14} = n_1$ which implies $n_1 < 3k$. By using the value of n_1 from Lemma 4.1.3(ii), we obtain $\frac{n+k+1}{2} < 3k$ which further implies that $n < 5k-1$ which is a contradiction as $T \in \mathcal{CT}_3(n,k)$. Hence $m_{13} \neq 0$. Moreover, $m_{14} < 3k$ implies that there exists a vertex p with $deg_T(p) = 4$ with at most 2 pendent vertices. Let p_1 and p_2 be the non-pendant neighbors of p. Let t_1 and t_2 be the neighbors of t other than s. Without loss of generality, let P be the path joining t and p containing the edges tt_1 and p_1p. As by Lemma 4.1.9(iii), we have $m_{44} = 0$, it implies that $deg_T(p_2) \neq 4$. Therefore, $deg_T(p_2) \in \{2, 3\}$. The case when $deg_T(p_2) = 3$ proceeds in a similar way as in Lemma 4.1.8. For the case when $deg_T(p_2) = 2$, let r be the neighbor of p_2 other than p. Let

$$T' = T - p_2r + sr.$$

Clearly, $deg_{T'}(p_2) = deg_T(p_2) - 1$, $deg_{T'}(s) = deg_T(s) + 1$ and $deg_{T'}(w) = deg_T(w)$ for all $w \in V(T)\backslash\{p_2, s\}$. Obviously, $T' \in \mathcal{CT}_3(n,k)$. Now, we show that $H(T') - H(T) < 0$ to obtain a contradiction.

$$\begin{aligned} H(T') - H(T) \quad &= \frac{2}{deg_T(r) + deg_T(s) + 1} + \frac{2}{deg_T(s) + 1 + deg_T(t)} \\ &+ \frac{2}{deg_T(p) + deg_T(p_2) - 1} - \frac{2}{deg_T(p) + deg_T(p_2)} \\ &- \frac{2}{deg_T(p_2) + deg_T(r)} - \frac{2}{deg_T(s) + deg_T(t)} \\ &= \frac{2}{deg_T(r) + 2} + \frac{2}{2+3} + \frac{2}{4+1} - \frac{2}{4+2} \\ &- \frac{2}{-} \frac{2}{1+3} \\ &= -0.03 < 0, \end{aligned}$$

which is a contradiction since T has the smallest Harmonic index. Hence, $m_{13} = 0$.

(vi). Solving the system in Equations (3.1.2a) - (3.1.2d) for unknowns m_{34}, m_{13}, m_{24} and m_{33} by using the values of n_1, n_2 and n_3 from Lemma 4.1.3, and the values of m_{12}, m_{22}, m_{23}, m_{14} and m_{44} from Lemma 4.1.9, we obtain

$$m_{24} \quad = 1,$$

$$\begin{aligned} m_{13} &= \frac{n-5k+1}{2}, \\ m_{33} &= \frac{n-3k-5}{2}, \\ m_{34} &= k-1. \end{aligned}$$

This completes the proof. □

4.2 Main Results

In this section, we obtain the values of the Harmonic index of minimum trees in $\mathcal{CT}(n,k)$ and provide the minimum trees that attain these lower bounds.

Theorem 4.2.1. *Let $T \in \mathcal{CT}(n,k)$ and has minimum Harmonic index. Then*

$$H(T) = \begin{cases} \frac{11}{5} & T \in \mathcal{CT}_(n,k) \text{ with } n=6 \text{ and } k=1, \\ \frac{53n-12k-29}{140} & T \in \mathcal{CT}_1(n,k) \text{ and n-k is even}, \\ \frac{159n-39k-71}{420} & T \in \mathcal{CT}_1(n,k) \text{ and n-k is odd}, \\ \frac{41n-14k-23}{105} & T \in \mathcal{CT}_2(n,k) \text{ and n-k is even}, \\ \frac{41n-7k-19}{105} & T \in \mathcal{CT}_2(n,k) \text{ and n-k is odd}, \\ \frac{5}{12}n - \frac{37}{140}k - \frac{1}{6} & T \in \mathcal{CT}_3(n,k) \text{ and n-k is even}, \\ \frac{5}{12}n - \frac{41}{28}k - \frac{19}{140} & T \in \mathcal{CT}_3(n,k) \text{ and n-k is odd}. \end{cases}$$

Proof. **Case 1.** When $T \in \mathcal{CT}(n,k)$ with $n=6$ and $j=1$.
When $n=6$ and $j=1$, $n_3=0$, $n_1=4$ and $n_2=1$ by Lemma 4.1.3. Using these values in Equations (3.1.2a) - (3.1.2d), we obtain $m_{22}=m_{23}=m_{13}=m_{33}=m_{33}=0$, $m_{24}=1$, $m_{12}=1$ and $m_{14}=3$. Using these values in Equations 2.1, we obtain

$$H(T) = \frac{11}{5}.$$

This value of $H(T)$ will be obtained if $T \cong T_0(6,1)$ where $T_0(6,1)$ is a tree as shown in Fig. 4.1.

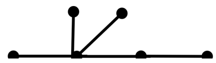


Figure 4.1: $T_0(n,k)$

Case 2. When $T \in \mathcal{CT}_1(n,k)$ and $n-k$ is even.
Using the values of m_{uv} for $(u,v) \in S$ from Lemma 4.1.4 in Equation (3.1.1), we obtain

$$H(T) = \frac{53n - 12k - 29}{140}.$$

This value of $H(T)$ will be obtained if $T \cong T_1(n,k)$ where $T_1(n,k)$ is a tree as shown in Fig. 4.2.

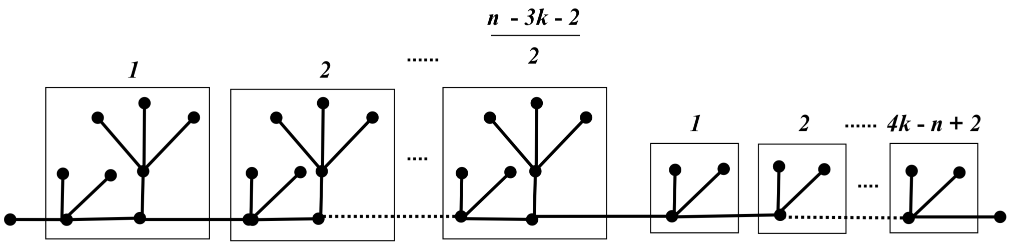


Figure 4.2: $T_1(n,k)$

Case 3. When $T \in \mathcal{CT}_1(n,k)$ and $n-k$ is odd.
Using the values of m_{uv} for $(u,v) \in S$ from Lemma 4.1.5 in Equation (3.1.1), we obtain

$$H(T) = \frac{159n - 39k - 71}{420}.$$

This value of $H(T)$ will be obtained if $T \cong T_2(n,k)$ where $T_2(n,k)$ is a tree as shown in Fig. 4.3.

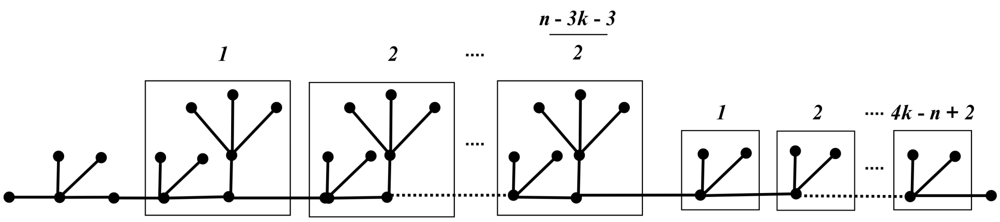


Figure 4.3: $CT_2(n,k)$

Case 4. When $T \in \mathcal{T}_2(n,k)$ and $n-k$ is even

Using the values of m_{uv} for $(u, v) \in S$ from Lemma 4.1.6 in Equation (3.1.1), we obtain

$$H(T) = \frac{41n - 14k - 23}{105}.$$

This value of $H(T)$ will be obtained if $T \cong T_3(n, k)$ where $T_3(n, k)$ is a tree as shown in Fig. 4.4.

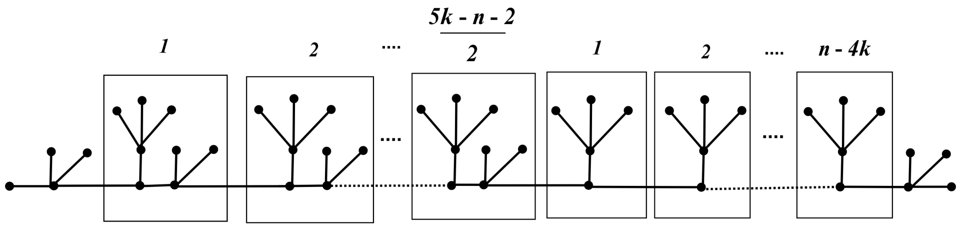
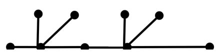


Figure 4.4: $CT_3(n, k)$

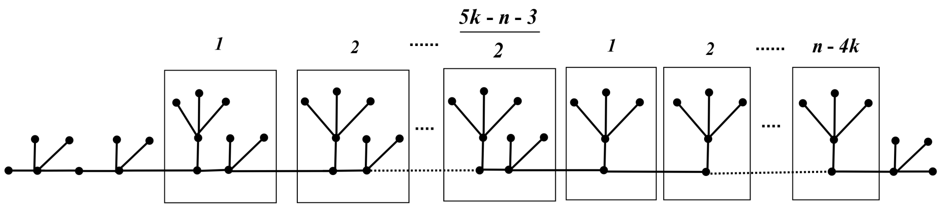
Case 5. When $T \in \mathcal{CT}_2(n, k)$ and $n - k$ is odd.
Using the values of m_{uv} for $(u, v) \in S$ from Lemma 4.1.7 in Equation (3.1.1), we obtain

$$H(T) = \frac{41n - 7k - 19}{105}.$$

This value of $H(T)$ will be obtained if $T \cong T_4(n, k)$ where $T_4(n, k)$ is a tree as shown in Fig. 4.5.



(a) If $k = 2$



(b) If $k \geq 3$

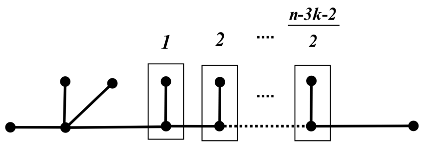
Figure 4.5: $T_4(n, k)$

Case 6. When $T \in \mathcal{CT}_3(n, k)$ and $n - k$ is even.
Using the values of m_{uv} for $(u, v) \in S$ from Lemma 4.1.8 in Equation (3.1.1),

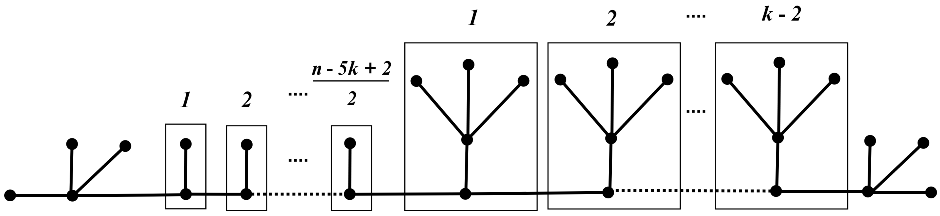
we obtain

$$H(T) = \frac{5}{12}n - \frac{37}{140}k - \frac{1}{6}.$$

This value of $H(T)$ will be obtained if $T \cong T_5(n,k)$ where $T_5(n,k)$ is a tree as shown in Fig. 4.6.



(a) If $k = 1$



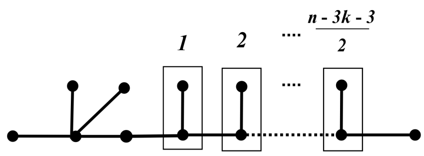
(b) If $k \geq 2$

Figure 4.6: $T_5(n,k)$

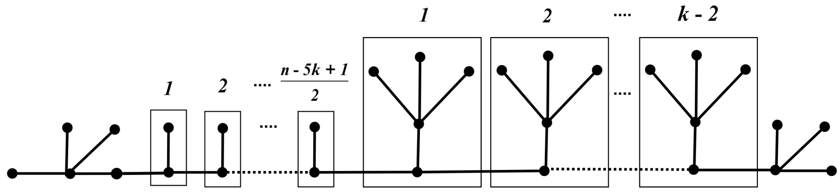
Case 7. When $T \in \mathcal{CT}_3(n,k)$ and $n-k$ is odd.
Using the values of m_{uv} for $(u,v) \in S$ from Lemma 4.1.9 in Equation (3.1.1), we obtain

$$H(T) = \frac{5}{12}n - \frac{41}{28}k - \frac{19}{140}.$$

This value of $H(T)$ will be obtained if $T \cong T_6(n,k)$ where $T_6(n,k)$ is a tree as shown in Fig. 4.7.



(a) If $k = 1$



(b) If $k \geq 2$

Figure 4.7: $T_6(n, k)$

□

4.3 Summary

In conclusion, this thesis aimed to explore the application of graph theory and chemical graph theory in analyzing chemical structures through the lens of topological indices. The first chapter provided a comprehensive overview of the basics of graph theory, establishing a foundation for understanding subsequent discussions.

The second chapter delved into the realm of chemical graph theory, focusing specifically on topological indices. The study of topological indices allows for the quantification of structural properties of chemical compounds, aiding in their characterization and prediction of various chemical properties. The Harmonic Index was highlighted as a specific topological index, mentioning its extremal values for various graphs.

The third and fourth chapters of this thesis were dedicated to finding the maximum and minimum values of Harmonic index of chemical trees with given order and a specified number of vertices of maximum degree.

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