Topological properties of four types of porphyrin dendrimers

Abdul Jalil M. Khalaf, Aisha Javed, Muhammad Kamran Jamil, Mehdi Alaeiyran, Mohammad Reza Farahani

Abstract:

A chemical compound can be represented as a chemical graph. A topological index of a (chemical) graph is a numeric value of a graph which characterize its topology and is usually graph invariant. The Zagreb indices, Randić index and sum-connectivity indices are useful in the study of anti-inflammatory activities, boiling point, molecular complexity heterosystems of certain chemical instances, and in elsewhere. In this paper, we calculate the mentioned topological indices of some infinite classes of porphyrin dendrimers.

Keywords: Dendrimers; Zagreb indices; Randić index; Sum-connectivity index.

MSC (2020): 05C10, 05C12, 05C15, 05C22, 05C31.

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1. Introduction

The properties of a molecule are tightly connected to its characteristics is one of the fundamental concepts in chemistry. In this connection, graph theory has been successfully applied [5, 11, 23].

Chemical graph theory is a branch of mathematical chemistry. It is concerned with handling chemical graphs that represent chemical systems. Hence, chemical graph theory deals with analyses of all consequences of connectivity in a chemical system. In other words, chemical graph theory is concerned with all aspects of the application of graph theory to chemistry area.

Chemists employ various types of designations and formulas when they want to communicate information about chemical compounds and their structures. In spite of this fact, most of the names and formulas have to direct, immediate or explicit mathematical meaning. It has been found to be a useful tool in QSAR (Quantitative Structure Activity Relationship) and QSPR (Quantitative Structure Property Relationship). A lot of studies have been done relating to the above mentioned fields by using what are called topological indices [7, 16, 24, 25].

A chemical structure can be represented by using graph theory, where vertices denote atoms and edges denotes molecular bonds. A topological index is a numeric number that indicates some useful information about the molecular structure. It is the numerical invariants of a molecular graph and is useful to correlate with their bioactivity and physiochemical properties. Researchers have found the topological index to be a powerful and useful tool in the description of molecular structure. Some applications related to topological indices of molecular graphs are included in the reference list [10, 15, 22, 26].

Dendrimers are among the most complex chemical and interesting structures and hyper-branched macromolecules, with a precise tailored architecture. Dendrimers have gained a wide range of application in supramolecular chemistry, particularly in host guest reactions and the self-assembly process [21]. The introduction of porphyrins into dendritic structures began in the early days of dendrimer chemistry, mainly as core entities, due to the morphological resemblance of these macrostructures to natural hemoproteins. Over
the years, porphyrin macrocycles have also been introduced as dendritic surface groups or within the dendritic branches [20].

Let \( G(V(G), E(G)) \) be a graph where \( V(G) \) is the vertex set and \( E(G) \) is the edge set of the graph \( G \). The degree, \( \text{deg}(v) \), of the vertex \( v \) in a graph \( G \) is the number of edges of \( G \) incident with \( v \) in \( G \). The length of the shortest path in a graph \( G \) between vertices \( u \) and \( v \) is the distance, \( d(u, v) \), between \( u \) and \( v \).

A graph can be represented by a polynomial, numerical value, or a matrix form. There are certain types of topological indices, which are mainly eccentric based, degree based and distance based. In this article, we deal with degree-based topological indices.

Zagreb index (\( M_1 \)) is one of the most oldest and important degree based topological indices. In 1972, Gutman and Trinajstić proposed this topological index [9]. After that, they introduced the second Zagreb index (\( M_2 \)) [8]. These indices are defined as follows

\[
M_1(G) = \sum_{v \in V(G)} d^2(G) = \sum_{uv \in E(G)} (d(u) + d(v))
\]

\[
M_2(G) = \sum_{uv \in E(G)} d(u)d(v)
\]

In 1975, M. Randić introduced the Randić index (\( R \)). This topological index has great importance in QSPR/QSAR. The Randić index of a graph \( G \) is defined as

\[
R(G) = \sum_{uv \in E(G)} \frac{1}{\sqrt{d(u)d(v)}}
\]

A closely related topological index named as sum-connectivity index was proposed by Zhou et. al. [27]. The sum-connectivity index of a graph \( G \) is obtained from Randić index by replacing the term \( d(u)d(v) \) by \( d(u) + d(v) \). In QSPR/QSAR, the sum connectivity index shows some better results in some aspects. It is defined as

\[
\chi(G) = \sum_{uv \in E(G)} \frac{1}{\sqrt{d(u) + d(v)}}
\]

The molecular graph of dendrimers structures is denoted by \( G_n \), where \( n \) is the growth stages and \( n \geq 0 \).

For detailed study computation of topological indices of molecular structures we refer [1, 2, 3, 4, 12, 13, 6, 18, 19].
2. Four Layered Prophyrin Core Dendrimers

The majority of porphyrin dendrimers reported to date possess a (metallo) porphyrin unit as the interior core moiety only. Pioneering work in the field of porphyrin dendrimers was performed in laboratories of Aida, Diederich and Suslick. The first example was described by Aida and co-workers in 1993 [14]. Figure 2.1 shows the Aida’s four layered porphyrin core dendrimer. In this section, we compute the certain topological indices of the four layered porphyrin core dendrimers.

The molecular graph shown in Figure 2.1 contain 136 · 2^n − 15 vertices (atom) and 152 · 2^n − 12 edges (bonds). There are four types of vertices based on the degree, vertices with degree 1, 2, 3 and 4. We partition the edge set of the molecular graph of Aida’s four layered prophyrin core dendrimer based on the degree of end vertices of each edge. Table 2.1 illustrate this partition.

<table>
<thead>
<tr>
<th>(d(u), d(v)), n ≥ 1</th>
<th>(2,2)</th>
<th>(2,3)</th>
<th>(1,3)</th>
<th>(3,3)</th>
<th>(3,4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of edges</td>
<td>32 · 2^n − 4</td>
<td>112 · 2^n − 32</td>
<td>8 · 2^n</td>
<td>20</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 2.1: Partition of the edge set of Aida’s four layered prophyrin core dendrimer based on the degree of end vertices of each edge.

Let $G_n$ be the molecular graph of the four layered prophyrin core dendrimer, then the Zagreb indices of $G_n$ is equal to

$$M_1(G_n) = 45 \cdot 2^{(n+4)} - 28$$

$$M_2(G_n) = 103 \cdot 2^{(n+3)} + 20$$

**Proof.** The graph $G_n$ contains the vertices of degrees 1, 2, 3 and 4. We found the edge partition of the form (2,2), (2,3), (1,3), (3,3) and (3,4) for $G_n$ based on the degree of end vertices of each edge. Table 2.1 explains such partition. By using the Table 2.1, we can compute the first and second Zagreb indices of $G_n$, as follows

$$M(G_n) = \sum_{uv \in E(G_n)} (d(u) + d(v))$$

$$= (32 \cdot 2^n - 4)(2 + 2) + (112 \cdot 2^n - 32)(2 + 3) + (8 \cdot 2^n)(1 + 3) + 20(3 + 3) + 4(3 + 4)$$

$$= 45 \cdot 2^{(n+4)} - 28$$
\[M_{(G_n)} = \sum_{uv \in E(G_n)} d(u)d(v)\]
\[= (32 \cdot 2^n - 4)(2 \cdot 2) + (112 \cdot 2^n - 32)(2 \cdot 3) + (8 \cdot 2^n)(1 \cdot 3) + 20(3 \cdot 3) + 4(3 \cdot 4)\]
\[= 103 \cdot 2^{n+3} + 20\]

\[\square\]

Let \(G_n\) be the molecular graph of the four layered prophyrin core dendrimer, then the Randić index of \(G_n\) is given as

\[R(G_n) = \frac{2}{3} \left( (6 + 3\sqrt{3} + 7\sqrt{6})2^{(n+2)} + 7 + \sqrt{3} - 8\sqrt{6} \right)\]

**Proof.** The edge partition of the graph \(G_n\) based on the degree of end vertices of each edge is shown in Table 2.1. Now we apply the formula of Randić index to obtain the result

\[R(G_n) = \sum_{uv \in E(G_n)} \frac{1}{\sqrt{d(u)d(v)}}\]
\[= (32 \cdot 2^n - 4)\frac{1}{\sqrt{2}^2} + (112 \cdot 2^n - 32)\frac{1}{\sqrt{2} \cdot 3} + (8 \cdot 2^n)\sqrt{1 \cdot 3} + 20\frac{1}{\sqrt{3} \cdot 3} + 4\frac{1}{\sqrt{3} \cdot 4}\]
\[= \frac{2}{3} \left( (6 + 3\sqrt{3} + 7\sqrt{6})2^{(n+2)} + 7 + \sqrt{3} - 8\sqrt{6} \right)\]

\[\square\]

Let \(G_n\) be the molecular graph of the four layered prophyrin core dendrimer, then the sum-connectivity index of \(G_n\) is

\[\chi(G_n) = (2 + 7\sqrt{5})2^{(n+4)} - 2 + 10\sqrt{\frac{7}{3} - \frac{32}{\sqrt{5}} + \frac{4}{\sqrt{7}}}\]

**Proof.** By using the definition of sum-connectivity index and the Table 2.1 we can obtain the required result. Since

\[\chi(G_n) = \sum_{uv \in E(G_n)} \frac{1}{\sqrt{d(u) + d(v)}}\]

this implies that

\[\chi(G_n) = (32 \cdot 2^n - 4)\frac{1}{\sqrt{2}^2 + 2} + (112 \cdot 2^n - 32)\frac{1}{\sqrt{2} \cdot 3 + 3} + (8 \cdot 2^n)\sqrt{1 + 3} + 20\frac{1}{\sqrt{3} \cdot 3 + 3} + 4\frac{1}{\sqrt{3} \cdot 4 + 4}\]
\[= (2 + 7\sqrt{5})2^{(n+4)} - 2 + 10\sqrt{\frac{7}{3} - \frac{32}{\sqrt{5}} + \frac{4}{\sqrt{7}}}\]

\[\square\]
Very recently, several dendritic porphyrins in which benzyl ether dendritic azides were clicked to an acetylene terminated Znporphyrin core through Cu-catalyzed cycloaddition reactions (52-90 to afford 1,2,3-triazole links were designed by Kimura et. al. [17]. A molecular graph of porphyrin-core dendrimer with \( n \) layers of internal triazole units is shown in Fig. 3.1.

From Figure 3.1 one can notice that the graph have \( 256 \cdot 2^n - 63 \) vertices (aotms) and \( 288 \cdot 2^n - 68 \) edges (bonds). There are vertices with degree 1, 2, 3 and 4. We partition the edge set of the molecular graph of porphyrin-core dendrimer with \( n \) layers of internal triazole units based on the degree of end vertices of each edge. Table 3.1 illustrate this partition.

<table>
<thead>
<tr>
<th>((d(u), d(v)), n \geq 1)</th>
<th>(2,2)</th>
<th>(2,3)</th>
<th>(1,3)</th>
<th>(3,3)</th>
<th>(3,4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of edges</td>
<td>48 \cdot 2^n - 12</td>
<td>208 \cdot 2^n - 80</td>
<td>24 \cdot 2^n</td>
<td>8 \cdot 2^n+20</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 3.1: Partition of the edge set of porphyrin-core dendrimer with \( N \) layers of internal triazole units based on the degree of end vertices of each edge.
Let $H_n$ be the molecular graph of the porphyrin-core dendrimer with $n$ layers of internal triazole units, then the Zagreb indices of $H_n$ is equal to

$$M_1(H_n) = 43 \cdot 2^{(n+5)} - 300$$
$$M_2(H_n) = 99 \cdot 2^{(n+4)} - 300$$

**Proof.** The graph $H_n$ contains the vertices of degrees 1, 2, 3 and 4. We found the edge partition of the form (2, 2), (2, 3), (1, 3), (3, 3) and (3, 4) for $H_n$ based on the degree of end vertices of each edge. Table 3.1 explains such partition. By using the Table 3.1, we can compute the first and second Zagreb indices of $H_n$, as follows

$$M_1(H_n) = \sum_{uv \in E(H_n)} (d(u) + d(v)) = (48 \cdot 2^n - 12)(2 + 2) + (208 \cdot 2^n - 80)(2 + 3) + (24 \cdot 2^n)(1 + 3) + (8 \cdot 2^n + 20)(3 + 3) + 4(3 + 4) = 43 \cdot 2^{(n+5)} - 300$$

$$M_2(H_n) = \sum_{uv \in E(H_n)} d(u)d(v) = (48 \cdot 2^n - 12)(2 \cdot 2) + (208 \cdot 2^n - 80)(2 \cdot 3) + (24 \cdot 2^n)(1 \cdot 3) + (8 \cdot 2^n + 20)(3 \cdot 3) + 4(3 \cdot 4) = 99 \cdot 2^{(n+4)} - 300$$

Figure 3.1: Porphyrin-core dendrimer with $n = 2$ layers of internal triazole units.
Let $H_n$ be the molecular graph of the porphyrin-core denrimer with $n$ Layers of internal triazole units, then the Randic index of $H_n$ is given as

$$R(H_n) = \frac{2}{3} \left( (10 + 3\sqrt{3} + 13\sqrt{6})2^{(n+2)} + 1 + \sqrt{3} - 20\sqrt{6} \right)$$

**Proof.** The edge partition of the graph $H_n$ based on the degree of end vertices of each edge is shown in Table 3.1. Now we apply the formula of Randic index to obtain the result

$$R(H_n) = \sum_{uv \in E(G_n)} \frac{1}{\sqrt{d(u)d(v)}} = (48 \cdot 2^n - 12) \frac{1}{\sqrt{2+2}} + (208 \cdot 2^n - 80) \frac{1}{\sqrt{2+3}} + (24 \cdot 2^n) \frac{1}{\sqrt{1+3}} +$$

$$(8 \cdot 2^n + 20) \frac{1}{\sqrt{3+3}} + 4 \frac{1}{\sqrt{3+4}}$$

$$= \frac{2}{3} \left( (10 + 3\sqrt{3} + 13\sqrt{6})2^{(n+2)} + 1 + \sqrt{3} - 20\sqrt{6} \right)$$

Let $H_n$ be the molecular graph of the porphyrin-core denrimer with $n$ Layers of internal triazole units, then the sum-connectivity index of $H_n$ is

$$\chi(H_n) = 9 \cdot 2^{(n+2)} - 6 + \frac{16(13 \cdot 2^n - 5)}{\sqrt{5}} + \frac{2^{(n+3)} + 20}{\sqrt{6}} + \frac{4}{\sqrt{7}}$$

**Proof.** By using the definition of sum-connectivity index and the Table 2.1 we can obtain the required result. Since

$$\chi(H_n) = \sum_{uv \in E(H_n)} \frac{1}{\sqrt{d(u) + d(v)}}$$

this implies that

$$\chi(H_n) = (48 \cdot 2^n - 12) \frac{1}{\sqrt{2+2}} + (208 \cdot 2^n - 80) \frac{1}{\sqrt{2+3}} + (24 \cdot 2^n) \frac{1}{\sqrt{1+3}} +$$

$$(8 \cdot 2^n + 20) \frac{1}{\sqrt{3+3}} + 4 \frac{1}{\sqrt{3+4}}$$

$$= 9 \cdot 2^{(n+2)} - 6 + \frac{16(13 \cdot 2^n - 5)}{\sqrt{5}} + \frac{2^{(n+3)} + 20}{\sqrt{6}} + \frac{4}{\sqrt{7}}$$

4. Proteo-dendrimers

In Proteo-dendrimers three hydrophobic Frchet dendrons with a hydrophilic polyether surface are combined with a poly(glutamic acid) dendron around a fluorescent Znporphyrin core. The molecular graph of Proteo-dendrimer is shown in Fig. 4.1.
The molecular graph of proteo-dendrimers have $154 \cdot 2^n - 62$ vertices (atoms) and $168 \cdot 2^n$ edges (bonds). There are vertices with degree 1, 2, 3 and 4. The partitioning of the edge set of the molecular graph of proteo-
dendrimers based on the degree of end vertices of each edge. Table 4.1 illustrate this partition.

<table>
<thead>
<tr>
<th>(d(u), d(v)), n ≥ 1</th>
<th>(2,1)</th>
<th>(2,2)</th>
<th>(2,3)</th>
<th>(1,3)</th>
<th>(3,3)</th>
<th>(3,4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of edges</td>
<td>$6 \cdot 2^n$</td>
<td>$56 \cdot 2^n - 1$</td>
<td>$98 \cdot 2^n - 22$</td>
<td>$6 \cdot 2^n - 1$</td>
<td>$2 \cdot 2^n + 20$</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 4.1: Partition of the edge set of proteo-dendrimers based on the degree of end vertices of each edge.

Let $I_n$ be the molecular graph of the Proteo-dendrimers, then the Zagreb indices of $I_n$ is equal to

$$M_1(I_n) = 6(2^{(n+7)} + 5)$$
$$M_2(I_n) = 215 \cdot 2^{(n+2)} + 89$$

**Proof.** The molecular graph of proteo-dendrimer contains the $154 \cdot 2^n - 62$ vertices of degrees one, two, three and four. Based on the end degrees of each edge the partition is shown in Table 4.1. Since

$$M_1(I_n) = \sum_{uv \in E(I_n)} (d(u) + d(v))$$
$$= (6 \cdot 2^n)(2 + 1) + (56 \cdot 2^n - 1)(2 + 2) + (98 \cdot 2^n - 22)(2 + 3) + (6 \cdot 2^n - 1)(1 + 3)$$
$$+(2 \cdot 2^n + 20)(3 + 3) + 4(3 + 4)$$
$$= 6(2^{(n+7)} + 5)$$

$$M_2(I_n) = \sum_{uv \in E(I_n)} d(u)d(v)$$
$$= (6 \cdot 2^n)(2 \cdot 1) + (56 \cdot 2^n - 1)(2 \cdot 2) + (98 \cdot 2^n - 22)(2 \cdot 3) + (6 \cdot 2^n - 1)(1 \cdot 3)$$
$$+(2 \cdot 2^n + 20)(3 \cdot 3) + 4(3 \cdot 4)$$
$$= 215 \cdot 2^{(n+2)} + 89$$

Let $I_n$ be the molecular graph of the Proteo-dendrimers, then the Randic index of $I_n$ is given as

$$R(I_n) = \frac{(6 \cdot 2^n)}{\sqrt{2}} + \frac{(172 \cdot 2^n + 37)}{6} + \frac{(98 \cdot 2^n - 22)}{\sqrt{6}} + \frac{(6 \cdot 2^n - 1)}{\sqrt{3}} + \frac{4}{\sqrt{12}}$$
Proof. By definition of Randić index and the Table 4.1, we have

\[
R(I_n) = \sum_{uv \in E(H_n)} \frac{1}{\sqrt{d(u)d(v)}} = \frac{(6 \cdot 2^n) - 1}{\sqrt{2}} + \frac{(56 \cdot 2^n - 22)}{\sqrt{6}} + \frac{(98 \cdot 2^n - 22)}{\sqrt{3}} + \frac{(6 \cdot 2^n - 1)}{\sqrt{3} + 3} + \frac{(2 \cdot 2^n + 20)}{\sqrt{6}} + \frac{4}{\sqrt{7}}
\]

Let \( I_n \) be the molecular graph of the Proteo-dendrimers, then the sum-connectivity index of \( I_n \) is

\[
\chi(I_n) = 31 \cdot 2^n - 2 + \frac{(6 \cdot 2^n)}{\sqrt{3}} + \frac{98 \cdot 2^n - 22}{\sqrt{5}} + \frac{(2 \cdot 2^n + 20)}{\sqrt{6}} + \frac{4}{\sqrt{7}}
\]

Proof. Result can be obtained by applying Table 4.1 in definition of sum-connectivity index as

\[
\chi(I_n) = \sum_{uv \in E(I_n)} \frac{1}{\sqrt{d(u)+d(v)}} = \frac{(6 \cdot 2^n)}{\sqrt{2} + 1} + \frac{(56 \cdot 2^n - 1)}{\sqrt{2} + 2} + \frac{(98 \cdot 2^n - 22)}{\sqrt{2} + 3} + \frac{(6 \cdot 2^n - 1)}{\sqrt{2} + 3} + \frac{(2 \cdot 2^n + 20)}{\sqrt{6} + 1} + \frac{4}{\sqrt{7}}
\]

\[
= 31 \cdot 2^n - 2 + \frac{(6 \cdot 2^n)}{\sqrt{3} + 1} + \frac{98 \cdot 2^n - 22}{\sqrt{5} + 1} + \frac{(2 \cdot 2^n + 20)}{\sqrt{6} + 1} + \frac{4}{\sqrt{7}}
\]

Figure 4.1: Molecular graph of Proteo-dendrimers.
5. Dendritic Iron (II) Porphyrins

The molecular graph of dendritic iron (II) porphyrins is shown in Fig. 5.1. This molecular structure has $168 \cdot 2^n - 4$ vertices (atoms) and $184 \cdot 2^n - 6$ edges (bonds). The vertices have degrees 1, 2, 3 and 4. Based on the degrees of the end vertices of each edge we partitioned the edge set. This partitioning is shown in Table 5.1.

\[
\begin{array}{|c|c|c|c|c|c|c|}
\hline
(d(u), d(v)), n \geq 1 & (1,2) & (2,2) & (2,3) & (1,3) & (3,3) & (3,4) \\
\hline
\text{number of edges} & 8 \cdot 2^n & 92 \cdot 2^n - 5 & 80 \cdot 2^n - 28 & 4 \cdot 2^n - 3 & 22 & 8 \\
\hline
\end{array}
\]

Table 5.1: Partition of the edge set of dendritic iron (II) porphyrin based on the degree of end vertices of each edge.

Let $J_n$ be the molecular graph of the Proteo-dendrimers, then the Zagreb indices of $J_n$ is

\[
M_1(J_n) = 8(101 \cdot 2^n + 2) \\
M_2(J_n) = 219 \cdot 2^{n+2} + 97
\]

Proof. The molecular graph of dendritic iron (II) porphyrin consist of $168 \cdot 2^n - 4$ vertices. Based on the end degrees of each edge the partition of edge set is illustrated in Table 5.1. Since
Let $J_n$ be the molecular graph of the dendritic iron (II) porphyrin, then
the Randić index of $I_n$ is equal to

$$R(J_n) = 2^n + 3 \sqrt{2} + \frac{(276 \cdot 2^n + 29)}{6} + \frac{(80 \cdot 2^n - 28)}{\sqrt{6}} + \frac{(4 \cdot 2^n + 1)}{\sqrt{3}}$$

**Proof.** From Table 5.1 and the definition of Randić index we have

$$R(J_n) = \sum_{uv \in E(J_n)} \sqrt{d(u) d(v)}$$

$$= \frac{(8 \cdot 2^n)}{\sqrt{2}} + \frac{(92 \cdot 2^n - 5)}{\sqrt{2} + 2} + \frac{(80 \cdot 2^n - 28)}{\sqrt{2} + 3} + \frac{(4 \cdot 2^n - 3)}{\sqrt{1 + 3}} + \frac{22}{\sqrt{3} + 3} + \frac{8}{\sqrt{4} + 4} \quad \Box$$

Let $J_n$ be the molecular graph of the dendritic iron (II) porphyrin, then
the sum-connectivity index of $I_n$ is given as

$$\chi(J_n) = 2^{n+3} \sqrt{3} + \frac{(96 \cdot 2^n - 8)}{2} + \frac{(80 \cdot 2^n - 28)}{\sqrt{5}} + \frac{22}{\sqrt{6}} + \frac{8}{\sqrt{7}}$$

**Proof.** Result is easily obtained from the definition and the Table 5.1 as

$$\chi(J_n) = \sum_{uv \in E(J_n)} \frac{1}{\sqrt{d(u) + d(v)}}$$

$$= \frac{(8 \cdot 2^n)}{\sqrt{2} + 2} + \frac{(92 \cdot 2^n - 5)}{\sqrt{2} + 2} + \frac{(80 \cdot 2^n - 28)}{\sqrt{2} + 3} + \frac{(4 \cdot 2^n - 3)}{\sqrt{1 + 3}} + \frac{22}{\sqrt{3} + 3} + \frac{8}{\sqrt{4} + 4} \quad \Box$$
References


