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B Roopa Sri[1] and Y Lakshmi Naidu[2*]

[1]Department of Mathematics and Computer Science, Sri Sathya Sai Institute of Higher Learning, Andhra Pradesh, India
[2]Centre for Excellence in Mathematical Biology, Sri Sathya Sai Institute of Higher Learning, Andhra Pradesh, India
*e-mail: ylakshminaidu@sssihl.edu.in

On Zagreb Connection Indices of γ Graphyne and its Zigzag Nanoribbon

Abstract. Chemical graph theory is a branch of Mathematical Chemistry that deals with chemical/molecular graphs to predict molecules' reactivity, stability, and topology through topological indices. γ graphyne is a carbon allotrope, a crystal lattice composed of one acetylene bond connecting two aromatic rings. Since there is no evidence of any economical method for its synthesis to date to study the physicochemical properties, reactivity, and stability, the in-silico methods can be of great help. In this paper, we have considered Zagreb connection indices, which haven't been explored in a wide range despite their correlation with the physicochemical properties being better than classical Zagreb Indices. Here, Zagreb connection indices of γ graphyne have been calculated using the edge partition technique and their trend in characteristics has been plotted. This might be beneficial to the fields of medicine, pharmacology, and nanotechnology in studying the reactivity and stability of this nanostructure without performing expensive experiments.
Key words: Chemical graph theory, γ graphyne, Zagreb connection indices.

Introduction

Carbon nanomaterials are nanomaterials that are built on carbon atoms. Based on their geometrical structure, they are classified as carbon allotropes (graphite and diamond) and nanostructures namely graphene single sheets, single and multiwalled nanotubes, carbon fibers, fullerenes, onions, and nanodiamonds are generated by carbon. Fullerenes are mostly produced through the vaporization of graphite electrodes using arc or plasma discharges or using laser ablation, pyrolysis of hydrocarbons and optimization of this process led to the mass production of the most widely studied fullerene C_{60} and other bigger fullerenes from C_{70} to C_{96} [1]. The arc discharge method is a well-established and broadly utilized technique for carbon nanotube synthesis. The resultant of the nanotube being single-walled or multi-walled depends on the selection of metal catalyst in the process. However, the laser ablation method gave a high yield of carbon nanotubes compared to other techniques but it is cost-consumable as it requires high energy power for vaporization of the target[2]. Various methods for Graphene synthesis are classified into top-down and bottom-up methods. For more information regarding the synthesis of carbon allotropes and nanomaterials, refer to [3] [4].

Most of these structural framework consists of either sp^2 or sp^3 hybridized carbon atoms. However, the presence of sp-hybridized carbons could affect the properties of the structures. Therefore, the great challenge for the researchers is to synthesize novel carbon isomers. One such challenge is synthesizing one of the carbon allotropes, graphyne, which consists of highly sp-hybridized carbon atoms. Mechanochemical synthesis, Sonogashira coupling, Castro–Stephens coupling, and alkyne metathesis are some of the developed methods for its synthesis but they have their advantages and limitations. This graphyne family has been proving its promising usage in the fields of medicine, photovoltaics, and the development of nanoscale devices.

Graphyne is a crystal lattice composed of acetylene bonds connecting the benzene rings. This can also be named graphyne-n depending on the number of acetylene molecules used for connecting the benzene rings. The most structurally stable families of graphyne are γ graphyne and γ graphdiyne as they contain benzene rings in their structure. In 1987, Baughman et al. [5] proposed this allotrope of carbon for the first time theoretically, and later in 2010, Li et al. [6] developed a successful methodology for graphdiyne films (benzene rings connected by diacetylene molecules) synthesis. Alkyne coupling reaction of hexaethynylbenzene (HEB) is the most

efficient method used to synthesize γ graphdiyne [7]. In 2019, Cui and co-workers proposed a technique for obtaining γ graphyne from benzene [8]. γ Graphyne is a graphyne family lattice comprising two aromatics rings connected by one acetylene molecule. But to date, there is no evidence of any economical method for the synthesis of this structure to study its molecular and topological properties. Hence, there is a need for in-silico methods. One such method is to calculate molecular descriptors for their quantitative structure-property and structure-activity relationship analysis.

A graph G is an ordered triple consisting of a set of vertices V(G) and a set of edges E(G), wherein each edge in E(G) is incident on a pair of vertices from V(G). A chemical graph or molecular graph is a simple connected graph of the chemical molecules in which atoms are taken as atoms and bonds between them as edges. The degree of the vertex, 'd(u)' is the number of edges incident on the vertex 'u'. The distance d(u,v) between two vertices 'u' and 'v' is the number of edges involved in the shortest path between 'u' and 'v'. Molecular descriptors are the quantitative representatives of molecular graphs that are used in physicochemical characteristics prediction and topological studies. These are categorized based on the dimensions of the molecular graphs. To study the properties and topology of 2-D graphs, the molecular descriptor considered is called the topological index. A topological index is a graph-invariant number obtained from a chemical graph and is formulated based on either the degree of the vertex or the distance between the vertices..

Materials and Methods

There is a branch of mathematics, known as chemical graph theory, in which the topological study of molecules takes place by considering their chemical graphs and calculating topological indices. Using these topological indices, structure-property and structure-activity analysis can be performed theoretically.

Literature Review

The first topological index, the Wiener index, is distance-based and was formulated by a Mathematician, named Wiener in the year 1947, and found that this index has a good correlation with the boiling points of paraffin [9]. To date, there are more than 3000 topological indices that are being under study by many researchers. These are being modified and reformulated to improve their accuracy in predicting the properties of chemical compounds. One such reformulation of degree-based topological indices, Zagreb Indices, using connection number instead of degree of the vertex, led to many open problems to be solved [10]. To study more on these, one can refer to [11, 12, 13].

A. Hakeem et al. have derived the mathematical closed-form expressions of different degree-based topological indices for γ graphyne and zig-zag graphyne nanoribbon through a graph-based edge partition technique [14]. They have explored the molecular descriptors of these structures for the first time. Motivated by this, we have extended their work by choosing Zagreb connection indices as a base and formulated the closed-form expressions with the help of these connection indices. One can refer to the above paper for the chemical structure of γ Graphyne.

Zagreb connection indices or leap Zagreb indices are formulated based on the connection number of the vertices. Connection number $\tau_G(u)$ of a vertex 'u' in graph G is the total number of vertices at a distance 2 from 'u'. These leap Zagreb indices were formulated in 1972 and were restudied by Akbar Ali and Nenad Trinajstic in 2018 [15] and they have shown that these indices can be generalized as Bond incident connection-number (BIC (G)) index:

$$BIC(G) = \sum_{0\le a\le b\le n-2} y_{a,b}(G) * \phi_{a,b} \qquad (1)$$

where $y_{a,b}(G)$ represents the number of edges in G incident on the vertices with connection numbers a and b and $\phi_{a,b}$ represents a non-negative real-valued function that depends on a and b.

Definition 1. For graph G, the first and the second Zagreb connection indices are defined as:

$$ZC_1(G) = \sum_{u\epsilon V(G)} \tau_G^2(u) \qquad (2)$$

$$ZC_2(G) = \sum_{uv\epsilon E(G)} \tau_G(u) * \tau_G(v) \qquad (3)$$

Definition 2. The modified first and second leap indices are given by Ali et al. [15]

$$ZC_1^*(G) = \sum_{uv\epsilon E(G)} \tau_G(u)+\tau_G(v) \qquad (4)$$

$$ZC_2^*(G) = \sum_{uv\epsilon E(G)} d_u\tau_G(u)+d_v\tau_G(v) \qquad (5)$$

Few works on these indices proved that there exists a strong correlation between the physical properties like entropy, standard enthalpy of vaporization, boiling point, and vapor infiltration of biochemical compounds and these indices compared to other indices. It has been proved that ZC_1 corresponds well with the entropy and acentric factors of octane isomers. These leap indices have also shown better results compared to the classical Zagreb indices [15]. References can be found in [15], [16], [17], and [18]. Despite their out-performance, these indices haven't been explored much in detail. Hence, in this paper, we have considered the least explored topological indices and chemical structure i.e., Zagreb connection indices of γ graphyne.

Results and Discussion

The chemical graphs of γ Graphyne, *G(m,n)* and its zig-zag nanoribbon, *G(n)* are depicted in Figures 1 and 2 by considering atoms of the structure as nodes and bonds between them as edges. Here $m \geq 1$ and $n \geq 1$ represent the number of rows and columns in the chemical graph. In this section, the mathematical closed-form expressions of above mentioned Zagreb connection indices are formulated for both structures. The trend in their characteristics can be inferred from the graphs plotted against each connection index.

γ Graphyne

In Figure 1, there are 36mn+12m+12n−6 vertices and 24mn+12m+12n−6 edges in each row. Using the edge partitioning method, we calculate the number of edges, |E|, incident on the vertices u and v with degrees d_u and d_v and connection numbers τ_u and τ_v respectively. From Figure 1, it is prominent that the vertices with degree 2 have the connection numbers 2, 3, or 5 and the vertices of degree 3 have 3, 5, or 6 as connection numbers.

Hence, in Table 1,

$$|E| = |\{uv \in E(G(m,n)): ((d_u, d_v), (\tau_u, \tau_v))\}|,$$

where τ_u is the connection number of vertex 'u' with degree d_u.

Theorem 1. For the graph *G(m,n)*

$$ZC_1(G(m,n)) = 864mn$$

$$ZC_2(G(m,n)) = 1296mn - 70m - 70n + 38$$

Table 1 – Edge-partition of γ graphyne

(d_u, d_v)	(τ_u, τ_v)	|E|
(2,2)	(2,2)	3; n=1 2; n≥2
	(3,2)	6; n=1 n+6; n≥2
(2,3)	(3,5)	2n+4
(3,3)	(5,5)	5n+1

Table 2 – Edge-partition of zig-zag γ graphyne nanoribbon

(d_u, d_v)	(τ_u, τ_v)	|E|
(2,2)	(3,2)	8m+8n-4
(2,3)	(3,5)	8m+8n-4
(3,3)	(5,5)	2m+2n+2
	(5,6)	12m+12n-12
	(6,6)	36mn-18m-18n+12

Table 3 – Zagreb connection indices of γ graphyne

n	ZC_1 (G(m, n))	ZC_2 (G(m, n))	ZC^*_1 (G(m, n))	ZC^*_2 (G(m, n))
1	864	1194	492	1356
2	3456	4942	1868	5324
3	7776	11282	4108	11884
4	13824	20241	7212	21036
5	21600	31738	11180	32780
6	31104	45854	16012	47116
7	42336	62562	21708	64044
8	55296	81862	28268	83564
9	69984	103754	35692	105676
10	86400	128238	43980	130380

Table 4 – Zagreb connection indices of zig-zag γ graphyne nanoribbon

n	ZC_1 (G(n))	ZC_2 (G(n))	ZC^*_1 (G(n))	ZC^*_2 (G(n))
1	228	288	150	378
2	346	451	222	578
3	464	612	293	776
4	582	773	364	974
5	700	934	435	1175
6	818	1095	506	1370
7	936	1256	577	1568
8	1054	1417	648	1766
9	1172	1578	719	1964
10	1290	1739	790	2162

Proof. Let *G(m,n)* be the graph of γ graphyne depicted in Figure 1. From eq.(2), we have

$$ZC_1(G(m,n)) = \sum_{u\epsilon V(G(m,n))} \tau_G^2(u)$$

This can also be written as

$$ZC_1(G(m,n)) = \sum_{u\epsilon V(G(m,n))} c_k k^2 \quad (6)$$

where 'k' is the connection number τ_u and c_k is the number of vertices with connection number 'k' in *G(m,n)*.

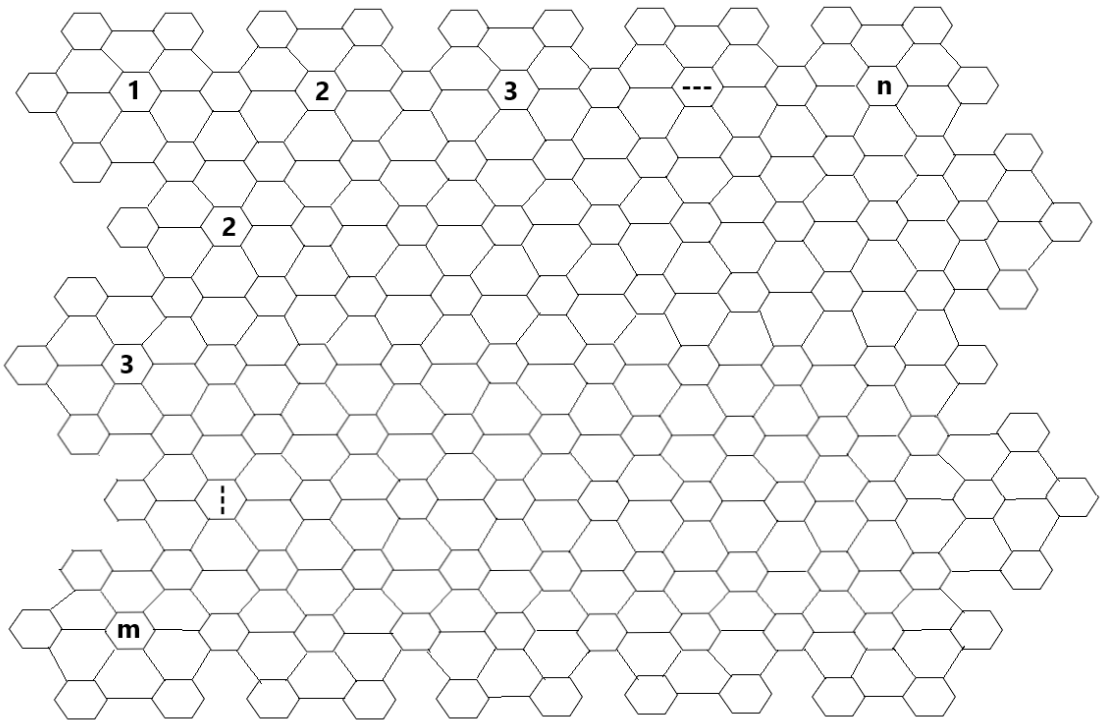

Figure 1 – Molecular graph of γ graphyne *G(m,n)*

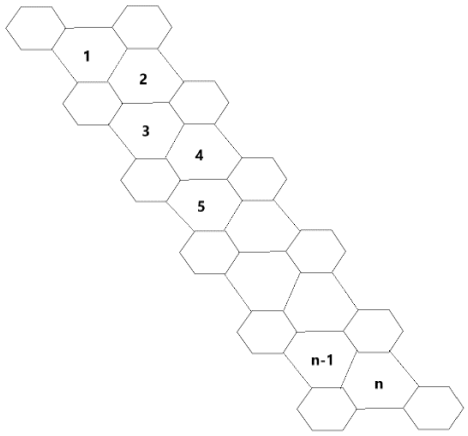

Figure 2 – Molecular graph of Zig-zag γ graphyne nanoribbon *G(n)*

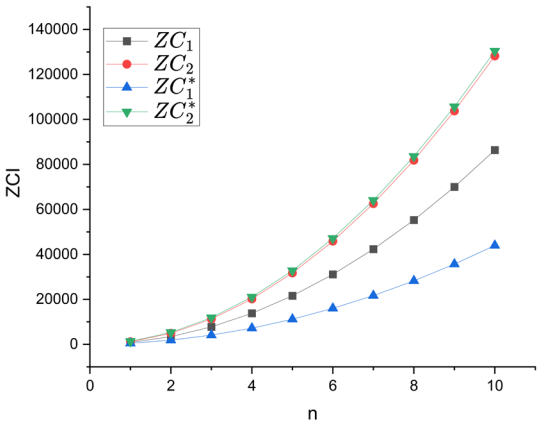

Figure 3 – Characteristics trend in γ graphyne

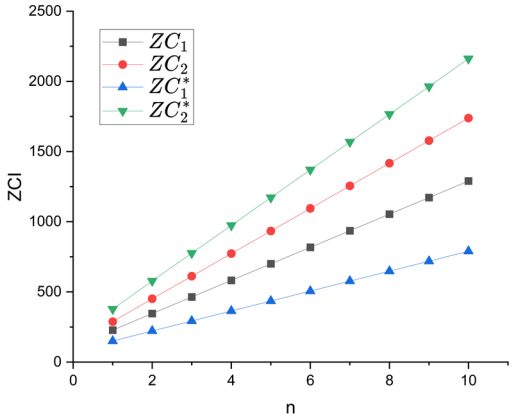

Figure 4 – Characteristics trend in zig-zag γ graphyne nanoribbon

The connection number, τ_u, obtained for every vertex 'u' in *G(m, n)* is either 2, 3, 5, or 6.

For k = 2 ,3, 5, & 6; c_k is found to be 8n − 2,16n − 4,16n −4, and 24mn − 16n + 4 respectively.

Hence, eq. (6) becomes

$ZC_1(G(m,n)) = (8n - 2)(4) + (16n - 4)(9) +$
$+ (16n - 4)(25) + (24mn - 16n + 4)(36) = 864mn$

Using Table 1, we have eq.(3)

$$ZC_2(G(m,n)) = \sum_{uv\epsilon E(G(m,n))} \tau_G(u) * \tau_G(v)$$
$= (6)(8m + 8n - 4) + (15)(8m + 8n - 4) +$
$+ (25)(2m + 2n + 2) + (30)(12m + 12n - 12) +$
$+ (36)(36mn - 18m - 18n + 12)$
$= 1296mn - 70m - 70n + 38$

Theorem 2. For the graph *G(m,n)*,

$ZC^*_1(G(m,n)) = 432nm + 40m + 40n - 20$

$ZC^*_2(G(m,n)) = 1296mn + 40m + 40n - 20$

Proof. Let *G(m, n)* be the graph of γ graphyne depicted in Figure 1. Now, eq.(4) can be written as

$$ZC^*_1(G(m,n)) = \sum_{uv\epsilon E(G(m,n))} \tau_G(u) + \tau_G(v)$$
$= (5)(8m + 8n - 4) + (8)(8m + 8n - 4) +$
$+ (10)(2m + 2n + 2) + (11)(12m + 12n - 12) +$
$+ (12)(36mn - 18m - 18n + 12)$
$= 432mn + 40m + 40n - 20$

Similarly, eq.(5) is

$$ZC^*_2(G(m,n)) = \sum_{uv\epsilon E(G(m,n))} d_u\tau_G(u) + d_v\tau_G(v)$$
$= (10)(8m + 8n - 4) + (19)(8m + 8n - 4) +$
$+ (30)(2m + 2n + 2) + (33)(12m + 12n - 12) +$
$+ (36)(36mn - 18m - 18n + 12)$
$= 1296mn + 40m + 40n - 20$

Zig-zag γ graphyne nanoribbon

In this graph, G(n), we shall consider a nanoribbon of zig-zag γ graphyne with n rows. Each row in Figure 2 consists of $5n + 1$ vertices and $6n$ edges. The connection number of vertices with degree 2 is 2 or 3 and those with degree 3 is 5 respectively. Different parameters in Table 2 can be inferred from Figure 2 as follows:

$$|E| = |\{uv \in E(G(n)) : ((d_u, d_v),(\tau_u, \tau_v))]|,$$

where τ_u is the connection number of vertex 'u' with degree d_u.

This is done using the edge-partition technique. But, here, |E| varies for different n.

Theorem 3. For the graph

$ZC_1(G(m,n)) = 118n + 110$
$ZC_2(G(m,n)) = 288;\ n=1$
$\quad = 161n + 129;\ n \geq 2$

Proof. Let G(n) be the graph of zig-zag γ graphyne nanoribbon depicted in Figure 2. From eq.(2), we have

$$ZC_1(G(n)) = \sum_{u\epsilon V(G(n))} \tau^2_G(u)$$

This can also be written as

$$ZC_1(G(n)) = \sum_{u \epsilon V(G(n))} c_k k^2 \quad (7)$$

where 'k' is the connection number τ_u and c_k is the number of vertices with connection number 'k' in G(n)

In G(n), τ_u for every vertex 'u', is found to be either 2 or 3, or 5. For k = 2,3, & 5; c_k is found to be 6,2n + 4, & 4n + 2 respectively. Hence, eq. (7) becomes

$$ZC_1(G(n)) = (6)4 + (2n + 4)9 + (4n + 2)25$$
$$= 118n + 110$$

Using Table 2 and eq.(3), we obtain two cases as follows.

$$ZC_2(G(n)) = \sum_{uv \epsilon E(G(n))} \tau_G(u) * \tau_G(v)$$

Case 1: For n = 1

$$ZC_2(G(n)) = 3(4) + 6(6) + 6(15) + 6(25) = 288$$

Case 2: For n ≥ 2

$$ZC_2(G(n)) = (2)4 + (n + 6)6 + (2n + 4)15 +$$
$$+ (5n + 1)25 = 161n + 129$$

Theorem 4. For the graph *G(n),*

$$ZC^*_1(G(n)) = 150 \quad ; n = 1$$
$$= 71n + 80; n \geq 2$$
$$ZC^*_2(G(n)) = 378; n = 1$$
$$= 198n + 182; n \geq 2$$

Proof. Let G(n) be the graph of zig-zag γ graphyne nanoribbon depicted in Figure 2.

From eq.(4), we have

$$ZC^*_1(G(n)) = \sum_{uv \epsilon E(G(n))} \tau_G(u) + \tau_G(v)$$

Case 1: For n = 1

$$ZC^*_1(G(n)) = (2)4 + (n + 6)6 + (2n + 4)15 +$$
$$+ (5n + 1)10 = (3)4 + (6)5 + (6)8 + (6)10 = 150$$

Case 2: For n ≥ 2

$$ZC^*_1(G(n)) = (2)4 + (n + 6)5 + (2n + 4)8 +$$
$$+ (5n + 1)10 = 71n + 80$$

Using Table 2 and eq.(5), the following two cases are obtained.

$$ZC^*_2(G(n)) = \sum_{uv \epsilon E(G(n))} d_u \tau_G(u) + d_v \tau_G(v)$$

Case 1: For n=1

$$ZC^*_2(G(n)) = 3(8) + 6(10) + 6(19) + 6(30)=378$$

Case 2: For n≥2

$$ZC^*_2(G(n)) =(2)8 + (n + 6)10 + (2n + 4)19 +$$
$$+ (5n + 1)30 =198n + 182$$

Using the closed-form mathematical expressions from the above Theorems 1, 2, 3, and 4, we calculated the four leap Zagreb indices such as the first Zagreb connection index, second Zagreb connection index, modified first Zagreb connection index, and modified second Zagreb connection index for different values of *m* and *n*. The leap Zagreb indices of γ graphyne and zig-zag γ graphyne nanoribbon were given in Tables 3 and 4 respectively. The graphical interpretation of the trend in these indices of G(m,n) and G(n) are depicted well in Figures 3 and 4.

Conclusion

We can observe from Figures 3 and 4 that the modified second Zagreb index, ZC^*_2, gave the highest values for both structures compared to other Zagreb connection indices.

According to the correlation between the Zagreb connection indices and various physicochemical properties, it can be concluded that this index can outperform other indices in predicting the physicochemical properties of these structures. The trend in the characteristics of these structures depends on the values *m* and *n*. It can also be observed that the trend in characteristics of these structures has a linear correlation with the connection indices. We could also observe that these connection indices have given better results when compared to the degree-based indices namely the Harmonic index, Randic index, sum connectivity index, Atom bond connectivity index, Geometric arithmetic index, and symmetric division degree index considered by A. Hakeem et al. in [14]. This once again proves that connection-based indices can be used in predicting various properties of molecules and molecular structures in place of other indices due to their better performance.

In the future, we will work on Zagreb connection indices of some other novel chemical structures. This might help the departments of medicine, bio-medicine, nanotechnology, and pharmaceutical sciences study the reactivity and stability of those structures without synthesizing and performing the required experiments.

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Information about authors:
B Roopa Sri – Department of Mathematics and Computer Science, Sri Sathya Sai Institute of Higher Learning (Andhra Pradesh, India) email: behararoopasri@sssihl.edu.in

Y Lakshmi Naidu (corresponding author) – Centre for Excellence in Mathematical Biology, Associate Professor, Department of Mathematics and Computer Science, Sri Sathya Sai Institute of Higher Learning (Andhra Pradesh, India) email: ylakshminaidu@ sssihl.edu.in

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