

# Study of the Band Gap Changes in Flat Acenes

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**Abstract** In the future molecular electronic is substitute the silicon electronic by the organic molecules. Due to p orbital's, upper and lower electron clouds, and resonance phenomenon, the aromatic hydrocarbon from the root of benzene can provide suitable environments for electron transition. A useful approach for this purpose is an appropriate pattern to predict electronic properties by topological indices method (TIM). Therefore, it is first tried to produce a relationship between the topological indices based on the number of rings; then F index values are measured for Circumacenes family. The gap energy changes in the family of  $C_{8(n+2)/3}H_{(2n+22)/3}$  was calculated using Gaussian 09 Software by Hartree–Fock method. The relationships described the gap energy changes in the Circumacenes family achieved by F index. Finally, some heavier members of Circumacenes family are exposed to TIM to predict of Gap energy.

**Keywords** Nanoelectronic, Circumacenes, HOMO-LUMO, Topological Indices Method

## 1. Introduction

Focusing on the molecular electronics is a considerable point which should attract attention because minifying the size of electronic components on Nano-scale confronts various limitations. The molecular electronics is a branch of science based on Nano-technology with multiple applications in electronic industry in which organic molecules are basic, and the electronic circuits and logic gates are designed out of the joining of these hydrocarbons [1- 4]. Aromatic hydrocarbon from the root of benzene can provide suitable environments for electron transition due to p orbital's, upper and lower electron clouds, and resonance

phenomenon. A family of organic molecules which is focused in molecular electronic is Circumacenes with the chemical formula  $C_{8(n+2)/3}H_{(2n+22)/3}$  [5, 6].

The chemical graph theory is a branch of mathematical chemistry which we would use it to solve molecular problems by the applications of graph theory. In general, a graph is used to represent a molecule by considering the atoms as the vertices of the graph and the molecular bonds as the edges. In graph-theoretical terms via the molecular graph a single number representing a chemical structure and it's called a topological descriptor. In addition if this descriptor was correlated with a property of molecule it is a topological index [7-12]. Topological indices are interesting since they capture some of the properties of a molecule in a single number. Hundreds of topological indices have been introduced and studied for modelling physical and chemical properties [13-21]. Because they are converted into optimal semiconductors by reducing band gap, the Circumacenes family are could replace to silicon semiconductors in electronic circuits in the nanoelectronics industry. Thereby, this leads to reducing the cost of manufacturing, and the size and weight of electronic circuits. For example: in field effect transistors, solar cells, sensors and etc [22, 23].

### 1.1. Definitions

Let  $G$  be a simple graph with  $n$  vertices and  $m$  edges, with vertex set  $V(G) = \{v_1, v_2, \dots, v_n\}$  and edge set  $E(G)$ . The edge connecting the vertices  $v_i$  and  $v_j$  will be denoted by  $ij$ . The degree of the vertex  $v_i$ , denoted by  $d_i$ , is the number of first neighbours of  $v_i$  in the graph. Followed by the first and second Zagreb indices, Furtula and Gutman were defined the forgotten topological index (or F-index) as below [24, 25]:

$$F = F(G) = \sum_{u \in V(G)} \deg(u)^3 = \sum_{uv \in E(G)} [\deg(u)^2 + \deg(v)^2] \quad (1)$$

where  $\deg(v)$  and  $\deg(u)$  are the degrees of vertices  $v$  and  $u$  in  $G$  for any  $v \in V(G)$ .

### 1.2. Hartree–Fock (HF) Method

The HF method is based on providing the wave function for many particles systems, which the basis is the wave functions of one atom [26, 27]. In this case, the interaction Hamiltonian of many-body systems as follows:

$$H = \sum_i^N \frac{P_i^2}{2m_i} + V_i + V_{ij} \quad (2)$$

Where  $\frac{P_i^2}{2m_i}$ ,  $V_i$  and  $V_{ij}$  are Kinetic energy, external interaction potential, and interaction of the electron – electron respectively. The external interaction potential is given by:

$$V_i = -\sum_{k=1}^N \frac{Z_k e^2}{(r_i - R_k)} \quad (3)$$

Where  $r_i$  is the coordinates of the  $i$ th electrons and  $Z_k$  is an atomic number of the nucleus which is in the coordinates of  $R_k$ . And the interaction of the electron – electron is given by:

$$V_{ij} = \sum_{i < j}^N \frac{1}{(r_i - r_j)} \quad (4)$$

## 2. Research Method

To present a simple model based on graph theory to predict electronic and optical properties of Circumacenes, it is first tried to produce a relationship between the topological indices based on the number of rings, and then  $F$  index values are calculate for some members of Circumacenes family. Figure 1 shows the simple graph of Circumacenes family ( $C(8n 16)/3H(2n 22)/3$ ) as.

*Theorem 1:* Suppose  $n$  is the number of dual rings in Circumacenes family; therefore  $F$  index equals to:

$$F = \frac{100n + 104}{3} \quad (5)$$

Proof: Consider a simple molecular graph which is divided into nine regions and shown in figure 2:

- I. All vertices and edges that are located between two L1 and L2 levels and it is called G1.
- II. All vertices and edges that are located between two L2 and L3 levels and it is called G2.
- III. All vertices and edges that are located between two L3 and L4 levels and it is called G3.
- IV. All vertices and edges that are located between two L4 and L5 levels and it is called G4.
- V. All vertices and edges that are located between two L5 and L6 levels and it is called G5.
- VI. All vertices and edges that are located between two L6 and L7 levels and it is called G6.
- VII. All vertices and edges that are located between two L7 and L8 levels and it is called G7.

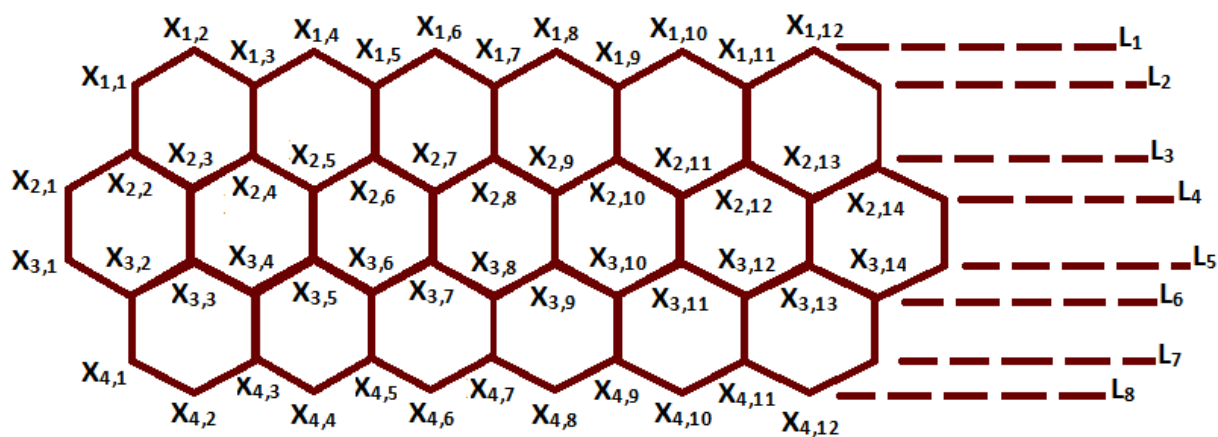


Figure 1. Simple molecular graph of Circumacenes ( $C_{(8n+16)/3}H_{(2n+22)/3}$ )

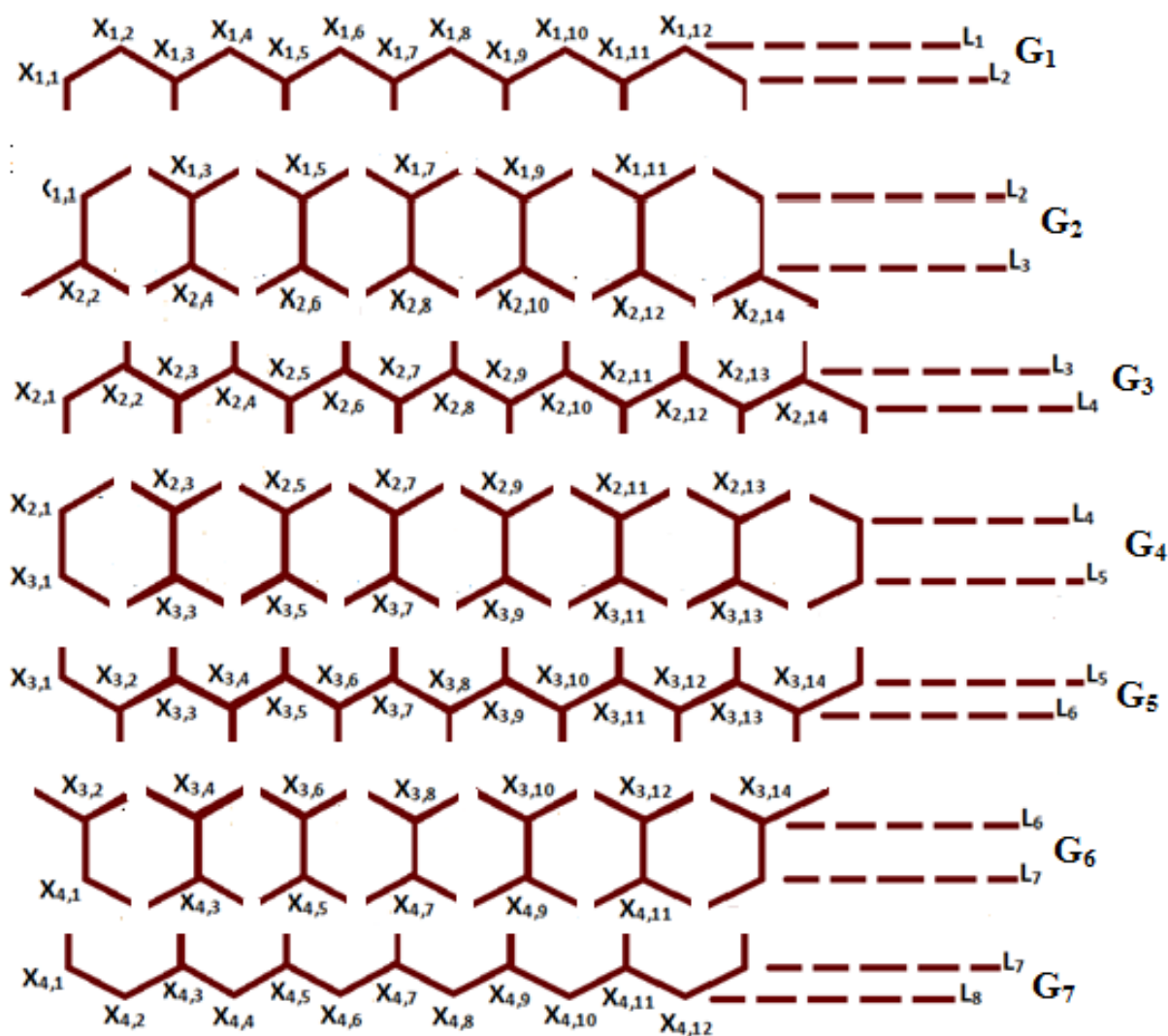


Figure 2. All vertices and edges that are located between two  $L_i$  and  $L_{i+1}$  ( $i=1, \dots, 7$ ) levels

For  $G_1$ , using equation 1, we have:

$$F(G_1) = \sum_{m=1}^{k-1} [(d_{1,m})^2 + (d_{1,m+1})^2] \quad (6)$$

The first and last terms are separated:

$$F(G_1) = (d_{1,1}^2 + d_{1,2}^2) + (d_{1,k-1}^2 + d_{1,k}^2) + \sum_{m=2}^{k-1} (d_{1,m}^2 + d_{1,m+1}^2) \quad (7)$$

And for the first two terms in equation 7 we have

$$(d_{1,1}^2 + d_{1,2}^2) = (d_{1,k-1}^2 + d_{1,k}^2) = 8 \quad (8)$$

And for  $m \neq 1$  and  $m \neq k$  we will have:

$$(d_{1,m}^2 + d_{1,m+1}^2) = 13 \quad (9)$$

And though equations 8 and 9, we can conclude:

$$F(G_1) = 8 + 8 + \sum_{m=2}^{k-2} 13 = 16 + 13(k-3) \quad (10)$$

And since  $k = \frac{2n+1}{3}$ , therefore:

$$F(G_1) = 16 + 13\left(\frac{2n-8}{3}\right) \quad (11)$$

In  $G_2$ , first we separate first and last terms:

$$F(G_2) = \sum_{m=1}^k (d_{1,m}^2 + d_{2,m}^2) = (d_{1,1}^2 + d_{2,1}^2) + (d_{1,k}^2 + d_{2,k}^2) + \sum_{m=2}^{k-1} (d_{1,m}^2 + d_{2,m}^2) \quad (12)$$

Equation 12 signifies for the first two terms as:

$$(d_{1,1}^2 + d_{2,1}^2) = (d_{1,k}^2 + d_{2,k}^2) = 13 \quad (13)$$

And for two terms of  $m \neq 1$  and  $m \neq k$ , we have:

$$(d_{1,m}^2 + d_{2,m}^2) = 8 \quad (14)$$

Equations 13 and 14 will lead to:

$$F(G_2) = 13 + 13 + \sum_{m=2}^{k-1} 8 = 26 + 8(k-2) \quad (15)$$

And  $k = \frac{n+2}{3}$ , so:

$$F(G_2) = 26 + 8\left(\frac{n-4}{3}\right) \quad (16)$$

In  $G_3$ , first we separate first and last terms:

$$F(G_3) = \sum_{m=1}^{k-1} (d_{2,m}^2 + d_{2,m+1}^2) = (d_{2,1}^2 + d_{2,2}^2) + (d_{2,k-1}^2 + d_{2,k}^2) + \sum_{m=2}^{k-2} (d_{2,m}^2 + d_{2,m+1}^2) \quad (17)$$

Equation 17 signifies for the first two terms as:

$$(d_{2,1}^2 + d_{2,2}^2) = (d_{2,k-1}^2 + d_{2,k}^2) = 13 \quad (18)$$

And for two terms of  $m \neq 1$  and  $m \neq k$ , we have:

$$(d_{2,m}^2 + d_{2,m+1}^2) = 8 \quad (19)$$

Equations 18 and 19 will lead to:

$$F(G_3) = 13 + 13 + \sum_{m=2}^{k-2} 8 = 26 + 8(k-3) \quad (20)$$

And  $k = \frac{2n+7}{3}$ , so:

$$F(G_3) = 26 + 8\left(\frac{2n-2}{3}\right) \quad (21)$$

For  $G_4$ , we can write:

$$F(G_4) = \sum_{m=1}^k (d_{2,m}^2 + d_{3,m}^2) \quad (22)$$

The first and last terms are separated:

$$F(G_4) = (d_{2,1}^2 + d_{3,1}^2) + (d_{2,k}^2 + d_{3,k}^2) + \sum_{m=2}^{k-1} (d_{2,m}^2 + d_{3,m}^2) \quad (23)$$

And for the first two terms in equation 23 we have

$$(d_{2,1}^2 + d_{3,1}^2) = (d_{2,k}^2 + d_{3,k}^2) = 1 \quad (24)$$

And for  $m \neq 1$  and  $m \neq k$  we will have:

$$(d_{2,m}^2 + d_{3,m}^2) = 8 \quad (25)$$

And though equations 24 and 25, we can conclude:

$$F(G_4) = 8 + 8 + 16 + 8(k-2) \quad (26)$$

And  $k = \frac{n+5}{3}$ , therefore:

$$F(G_4) = 2 + 8\left(\frac{n-1}{3}\right) \quad (27)$$

The calculation procedure of  $G_5, G_6$  and  $G_7$  are as the same as  $G_3, G_2$ , and  $G_1$  respectively and is given through equations 11, 16 and 21, Therefore:

$$F(G) = F(G_1) + F(G_2) + F(G_3) + F(G_4) + F(G_5) + F(G_6) + F(G_7) \quad (28)$$

So, equation 5 is achieved and the theorem is proved.

Then F index was calculated for some Circumacenes family members using equation 5 and the results are shown in Table 1.

**Table 1.** F index for the first five members of Circumacenes family

Chemical Formula	IUPAC Name	F Index
C <sub>24</sub> H <sub>12</sub>	coronene	268
C <sub>32</sub> H <sub>14</sub>	ovalene	368
C <sub>40</sub> H <sub>16</sub>	circumanthracene	468
C <sub>48</sub> H <sub>18</sub>	circumtetracene	568
C <sub>56</sub> H <sub>20</sub>	circumpentacene	668

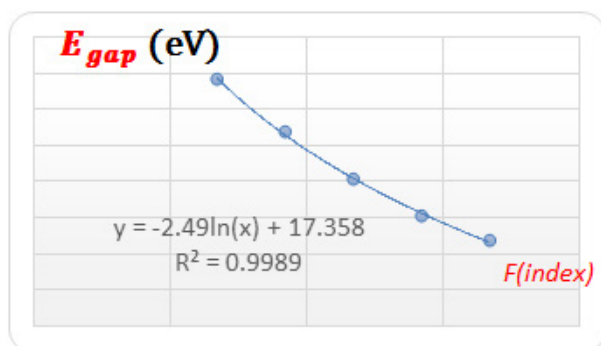
### 3. Results

The band gap energy ( $E_{gap}$ ) of Circumacenes family ( $C_{8(n+2)}H_{3(2n+2)}$ ) was calculated using Gaussian 09 Software and Hartree–Fock (HF) method. The results were compared to the experimental data and from the validated references [22, 23]. These results were given in Table 2.

**Table 2.** The band gap energy ( $E_{gap}$ ) of the first five members of Circumacenes family

Chemical Formula	$E_{gap}$ (eV)
C <sub>24</sub> H <sub>12</sub>	3.42
C <sub>32</sub> H <sub>14</sub>	2.69
C <sub>40</sub> H <sub>16</sub>	2.03
C <sub>48</sub> H <sub>18</sub>	1.54
C <sub>56</sub> H <sub>20</sub>	1.18

Figure 3 shows the band gap energy changes for Circumacenes family according to F index as the results of this work.



**Figure 3.** The band gap energy changes in Circumacenes family according to F index

Figure 3 shows that the band gap be calculated by the F index with a high level of precision ( $R^2=0.9989$ ), as below:

$$E_{gap} = -2.49 \ln(F) + 17.358 \quad (29)$$

### 4. Conclusions

For providing the validity of TIM method the band gap changes were calculated in five members of Circumacenes family using equation 26, and the results shows in Table 3. These results could be compared with the reference values (Table 2).

**Table 3.** Calculation the band gap of five members Circumacenes through TIM method

Chemical Formula	$E_{gap}$ (eV)
C <sub>24</sub> H <sub>12</sub>	3.4364
C <sub>32</sub> H <sub>14</sub>	2.6468
C <sub>40</sub> H <sub>16</sub>	2.0483
C <sub>48</sub> H <sub>18</sub>	1.5661
C <sub>56</sub> H <sub>20</sub>	1.1623

In heavier members of Circumacenes family which the experimental and other theoretical methods are too difficult and very expensive, the TIM method is an optimized method. So, the equation 26 was used to calculation the band gap in three heavier members of Circumacenes family and results shows in Table 4.

**Table 4.** Predicting Gap Energy through TIM method

Chemical Formula	F Index	$E_{gap}$ (eV)
C <sub>64</sub> H <sub>22</sub>	768	0.8149
C <sub>72</sub> H <sub>24</sub>	868	0.5101
C <sub>80</sub> H <sub>26</sub>	968	0.2386

With increasing the number of the atoms in the heavier members of this family, the energy levels of conduction bands and capacity also has increased. So, the highest occupied molecular orbital (HOMO) is shifted to up and also the lowest unoccupied molecular orbital (LUMO) shifted to down at the same time. As a result the band gap has decreased and the electron transition due to the p orbital's, upper and the lower electron clouds have increased in the heavier members of Circumacenes.

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