

On the Stability of Fullerenes

M. B. AHMADI*, E. FARHADI, M. GHAVANLOO

Department of Mathematics, Faculty of Sciences, Shiraz University

ARTICLE INFO

Article History:

Received 3 October 2018

Accepted 5 January 2019

Published online 30 March 2019

Academic Editor: Tomislav Došlić

Keywords:

Fullerene graph

Stability

Optimization

ABSTRACT

Fullerenes have wide application in various fields including electronic and optic, medical science, biotechnology and have received a lot of recent chemists and mathematicians' attention. Due to many applications of fullerenes, the study of their stability is important. In this paper, we study the effective parameters that affect the fullerene's stability and then according to these parameters, we introduce a new function to examine the stability of every fullerene. By using this function, we determine the stable isometric of each fullerene in a unique way.

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1 INTRODUCTION

A fullerene is a polyhedral molecule consisting only of carbon atoms and exists only in pentagonal and hexagonal faces. Carbon atoms can form four chemical bonds. Three of these bonds are strong, and the other one is weak. A fullerene graph is planar, which contains 3-regular and 3-connected graph that has exactly 12 pentagonal faces and $m := n / 2 - 10$ hexagonal faces. Such graphs on n vertices exist for all even $n \geq 24$ and for $n = 20$ [15].

However, the notation C_n works as a unique identifier only for the three simplest fullerenes (those with n equal to 20, 24, or 26). For values other than those, the notation is ambiguous, as there are multiple C_n isomers, each one with a distinct fullerene graph. One popular solution to this problem involves ordering the isomers lexicographically using their smallest face spiral sequences [9,14]. For a given value of n , the notation for each isomer is combined with a number k (corresponding to its position in this order), resulting in $C_n:k$. For example, the

*Corresponding Author: (Email address: mbahmadi@shirazu.ac.ir)

DOI: 10.22052/ijmc.2019.151000.1397

Buckminster fullerene can be identified as C_{60} :1812 because its smallest face spiral is the last among the 1812 isomers.

In the graphical representation of a fullerene, we draw the three strong bonds by the edges in the graph. The fourth bond tends to occur as a double bond. A perfect matching of a graph is a set of edges that each vertex is encountered with exactly one edge. In a fullerene, the edges of a perfect matching graph correspond to the double bonds, and chemists call this matching a Kekulé structure.

Fullerenes have wide application in various fields including electronic, optic engineering [28], medical science [13], and biotechnology [6] and they have brought lots of recent chemists and mathematicians' attention [19, 30].

Due to many applications, the stability of these molecules and their isomers is very important. For instance, C_{60} molecule contains 1812 isomers that the most stable of them is Buckminster fullerene. Various methods were introduced to predict the stability of fullerene molecules. Some of these methods are IPR, HOMO LUMO gap and calculating the number of Kekulé structure, but each of these methods has pros and cons that we examine them later. For studying the stability, we can use another way that examines the Clar and Fries number of fullerenes. In the next section, we study the effective parameters that affects on fullerene stability and then according to these parameters, we introduce a new function to examine the stability of every fullerene and by using that, we determine the stable isometric of each fullerene in a unique way.

2. EFFECTIVE PARAMETERS RELATED TO STABILITY OF FULLERENES

The Clar and Fries numbers are two parameters that are related to the stability of fullerenes. The Fries number of a fullerene is the maximum number of hexagons contain three double bonds over all possible perfect matchings of a fullerene graph. The perfect matchings of fullerene graphs have been well studied [10, 11, 18, 22]. A set of hexagons contain three double bonds that attains the Fries number for a fullerene is called a Fries set. A set of disjoint hexagons of a perfect matching fullerene graph is called a sextet pattern if every hexagon in this set contains three double bonds. The Clar set is any sextet pattern with the maximum number of hexagons over all perfect matching of fullerene graph. The Clar number of a fullerene graph is the cardinality of a Clar set. In Clar theory, a fullerene is more stable if it has a larger Clar number [8, 17], but this criterion doesn't determine the stable isomer in a unique way. For example, among isomers the C_{66} fullerene has

fifteen isomers with the largest number of Clar that the Clar number of them is equal to each other and it doesn't clearly determine the stable isomer. In 1987, Kroto and colleagues suggested the Isolated Pentagon Rule (IPR) [21]. This rule can determine the most stable isomer of C_{60} and C_{70} fullerenes in a unique form, but this rule doesn't apply for molecules with more atoms. For instance, C_{84} fullerene has 24 isomers and C_{100} fullerene has 450 isomers that complies and follows the IPR rule [31].

In many cases, the N_p pentagon adjacency index is used for predicting the stability of C_n ($n \leq 70$) fullerene [5, 7]. N_p pentagon adjacency index based on neighboring pentagons is calculated with the following equation:

$$N_p = \frac{1}{2} \sum_k k p_k$$

where p_k counts the number of pentagons that includes exactly k pentagon with adjacent edge and $\sum_k p_k = 12$. As it can be seen, the N_p equals to the number of edges between adjacent pentagons.

According to the N_p minimum criterion, the fullerene contains the minimal N_p is more stable than the isomers that don't have this feature. For example, Buckminster fullerene has the highest stability among the isomers of C_{60} fullerene and it is the only isomer that the N_p has the zero minimum value [26].

It is worth mentioning that the N_p minimum criterion isn't enough for investigating the stability of molecules in a unique way, because some of the isomers of fullerene has the same N_p adjacent pentagon. For example, among the isomers of C_{66} fullerene there exist 3 isomers with the same lowest index of N_p . In addition, the C_{68} fullerene contains the eleven isomers with $N_p = 2$.

For predicting the stability of fullerene, Kekulé count method (perfect matchings of fullerene graph) is used, but the Kekulé count is not suitable for predicting the stability of fullerene. For example, Liu and colleagues noticed that some of the isomers of C_{60} fullerene have the bigger Kekulé count than the buckminsterfullerene [23, 24]. In addition, Austin and colleagues showed the configuration of the 20 different isomers of C_{60} fullerene that their Kekulé surpassed the buckminsterfullerene [4]. Therefore, the maximization of Kekulé for isomers of fullerene doesn't correspond to the stability.

3. A FUNCTION TO DETECT THE MOST STABLE ISOMER OF A FULLERENE

Heretofore, different approaches have been discussed for studying the stability of a fullerene. Each of them has the advantages and disadvantages. In fullerene

structure, existence of pentagons and hexagons in this set creates different attributes to these molecules. The arrangements of these shapes together are the reason that different isomers of fullerene molecule exist. For instance, the Kekulé count feature investigates the location of double bonds in this molecule and the pentagon adjacency index studies the manner of arrangements of pentagons. In addition, Clar and Fries numbers examine the manner of arrangements of hexagons. In Clar figure, the number of hexagons that belong to resonance set are very important (these hexagons are discrete) and to get the Fries number, we remove the distinction constraint from the definition of Clar number.

According to the preceding paragraphs, the aforementioned methods alone aren't enough for predicting the stability of fullerene molecule. Therefore, finding the method that allows us to test the stability of these molecules better is very necessary. Here, we use a combination of benchmarks.

It is known that increasing the Clar and Fries numbers are effective on stability of isomers. On the other hand, decreasing the N_p pentagon adjacency index and increasing the Kekulé count may also be effective on stability of an isomer.

According to these features and given that, the N_p pentagon adjacency index is zero for some of the isomers of C_n fullerene ($n \geq 70$), we define the following function:

$$\Delta = \begin{cases} \frac{N_p}{C \times K \times F} & n < 60 \\ \frac{N_p + 1}{C \times K \times F} & n \geq 60 \end{cases}$$

where C is the Clar number, K is the Kekulé number, F is the Fries number and N_p describes the pentagon adjacency index of fullerene graph.

Since the stability of an isomer has direct relation with parameters like Clar number, Fries number and Kekulé count and it has opposite relation with N_p parameter, so the Δ function can be considered as the stability parameter that its value for every isomer has opposite relation with the stability of that isomer. Therefore, the isomer that has the minimum value of Δ is considered as the most stable isomer. So if we consider \bar{C}_n as the set of all C_n isomers, then the most stable isomer can be obtained by solving the following minimization problem.

$$\begin{aligned} & \text{Minimize} && \Delta(I) \\ & \text{subject to} && I \in \bar{C}_n \end{aligned}$$

We extract the required parameters to compute Δ for C_n , $n \leq 80$ by the Fui Gui software [25] and for $n > 80$ by the mathematical models presented in [2,27].

4. NUMERICAL RESULTS

In this section, we compute the value of Δ for several different fullerenes. According to the results of this section, we can declare that Δ function is another suitable criterion for investigating the stability of fullerene. C_{34} fullerene has six different isomers that $C_{34}:4$ is the most stable isomer [3]. This isomer has the maximum value of Fries number ($F = 5$) and maximum value of Clar number ($C = 3$). For C_{34} fullerene, the value of Δ is calculated for the different isomers of fullerene. Investigating the Δ has shown that $C_{34}:4$ isomer has the minimum value of Δ that corresponds to the most stable one among C_{34} isomers. In Figure 1, the isomers are drawn based on Δ .

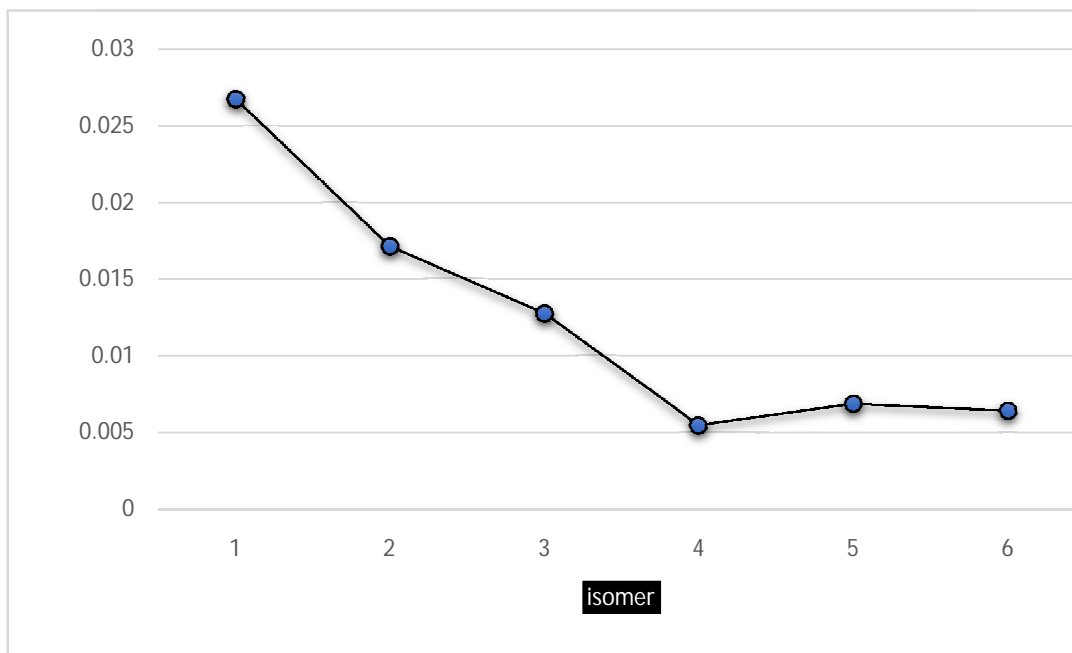


Figure 1: Graph of Δ function in terms of fullerene isomers C_{34} .

Fullerene C_{36} has fifteen isomers that among these isomers the $C_{36}:6$ is the most stable isomer [16]. According to Figure 2, this isomer has the maximum value of Fries number equals to 8 and has the maximum value of Clar number equals to 4. Investigating the Δ has shown that $C_{36}:6$ isomer has the minimum value of Δ that corresponds to the most stable one among C_{36} isomers. In Figure 2, the isomers are drawn based on Δ .

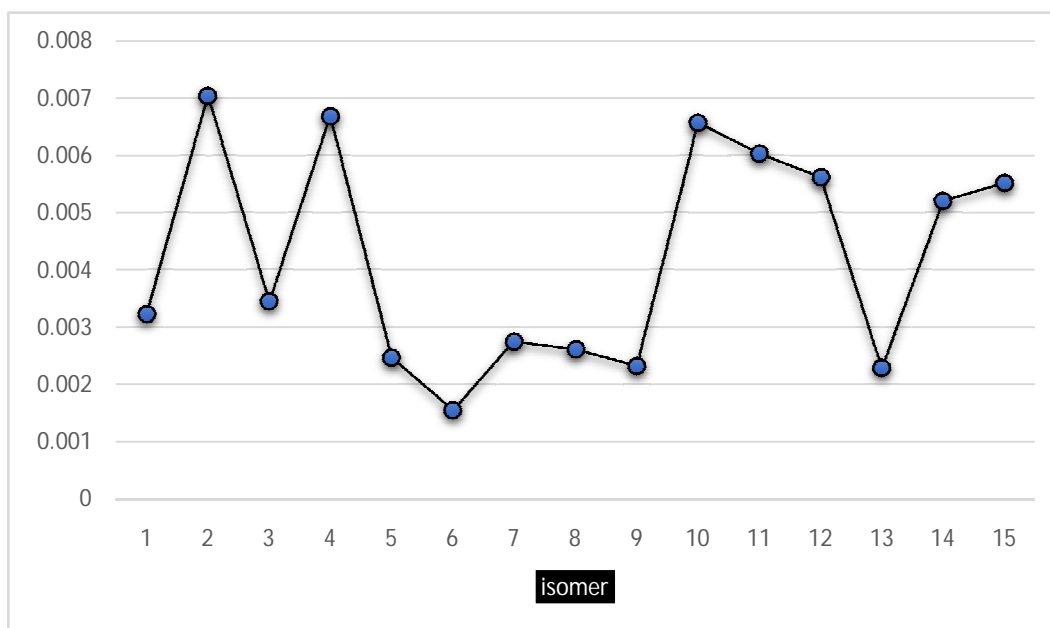


Figure 2: Graph of Δ function terms of fullerene isomers C_{36} .

Fullerene C_{38} has 17 isomers that $C_{38}:17(C_2)$ is the most stable isomer [1,3]. As shown in Figure 3, this isomer has the maximum value of Fries number that equals to 6 and maximum value of Clar number that equals to 3, although the Kekulé number of this isomer isn't the maximum value, the maximum of Clar and Fries numbers are adequate for the minimizing of Δ . By calculating of Δ (Figure 3), we noticed that the $C_{38}:17$ has the lowest value of Δ that corresponds to the most stable of C_{38} isomer.

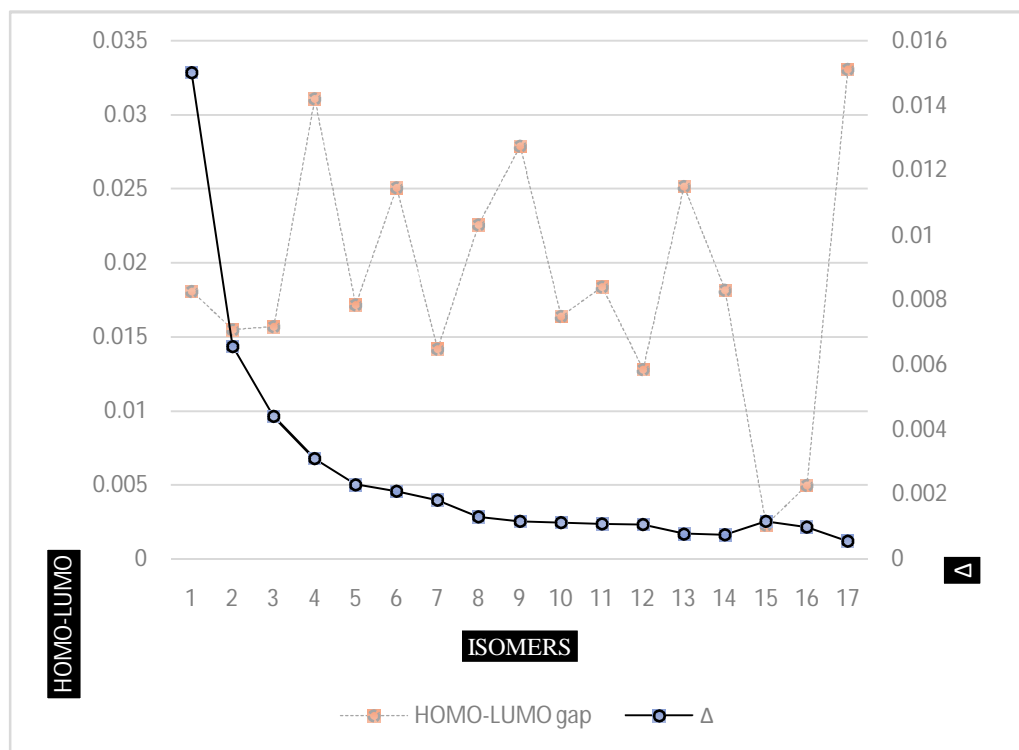


Figure 3: Graph of Δ and HOMO-LUMO gap in terms of fullerene isomers C_{38} .

Fullerene C_{40} has forty different isomers and from these isomers $C_{40}:39$ has the least HOMO-LUMO gap and is the most stable isomer [1]. This isomer has the maximum amount of Fries number ($F = 10$) and the maximum Clar number ($C = 4$). $C_{40}:38$ is the second stable isomer among C_{40} isomers that its only difference from 39 isomer is their Fries numbers. So based on the calculations in Figure 4, $C_{40}:39$ has the minimum value of Δ that corresponds to the most stable isomer of C_{40} .

Fullerene C_{42} has 45 different isomers that among of these isomers the $C_{45}:45$ has the minimum value of HOMO-LUMO gap and is the most stable isomer. By calculating Δ in Figure 5, we noticed that the lowest value of Δ is proportional to the lowest of HOMO-LUMO gap. This isomer has the 8 value of Fries number and the maximum of Clar number that equals to 5. The numbers related to this fullerene are presented in Figure 5.

As mentioned before, the Clar number doesn't determine the stable isomer in a unique way. For example, among isomers the C_{60} fullerene has eighteen isomers with the largest number of Clar that the Clar number of them is equal to

each other and it doesn't clearly determine the stable isomer. Hence, we obtained the value of Δ for these eighteen isomers and predicted the most stable isomer.

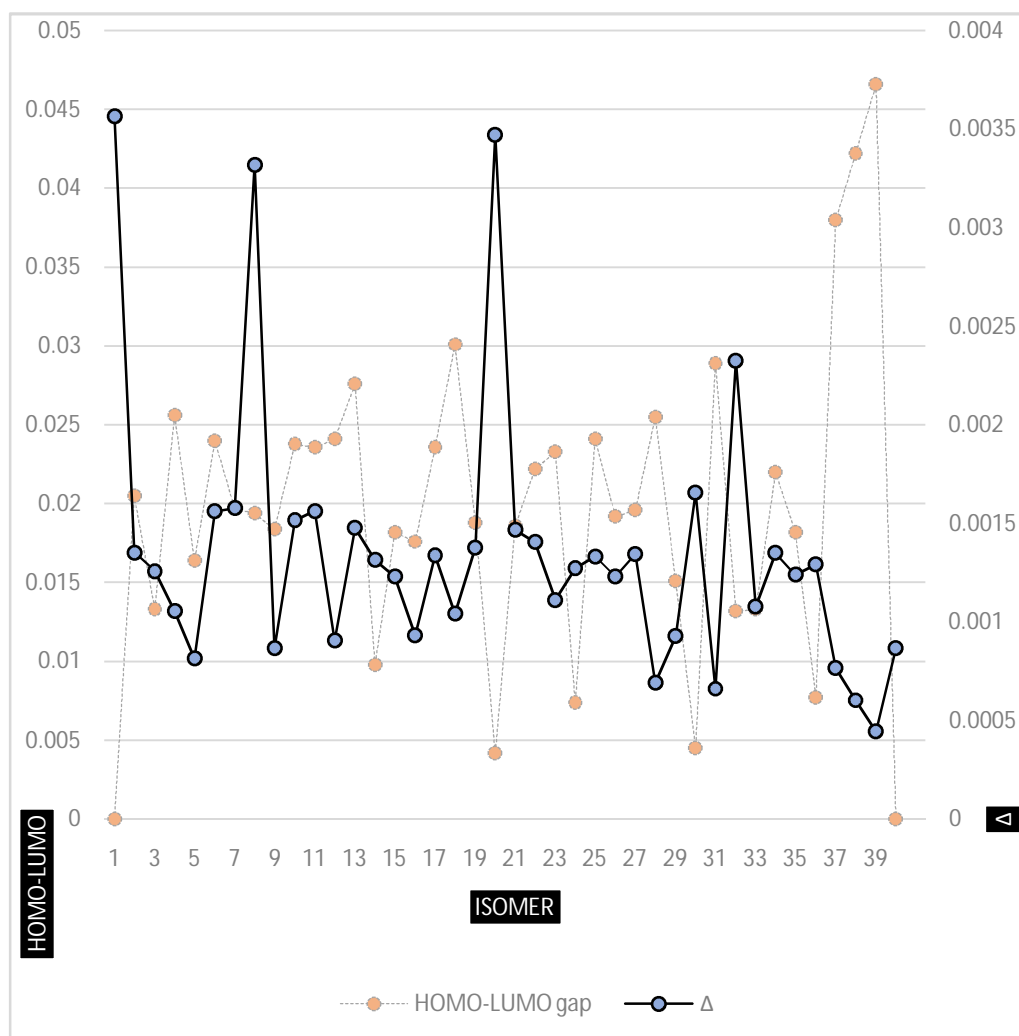


Figure 4: Graph of Δ and HOMO-LUMO gap in terms of fullerene isomers C_{40} .

According to Table 1, we noticed that the C_{60} :1812 isomer (buckminsterfullerene) has the maximum Clar number, Fries number, Kekulé count and the minimum value of N_p and the minimum value of Δ .

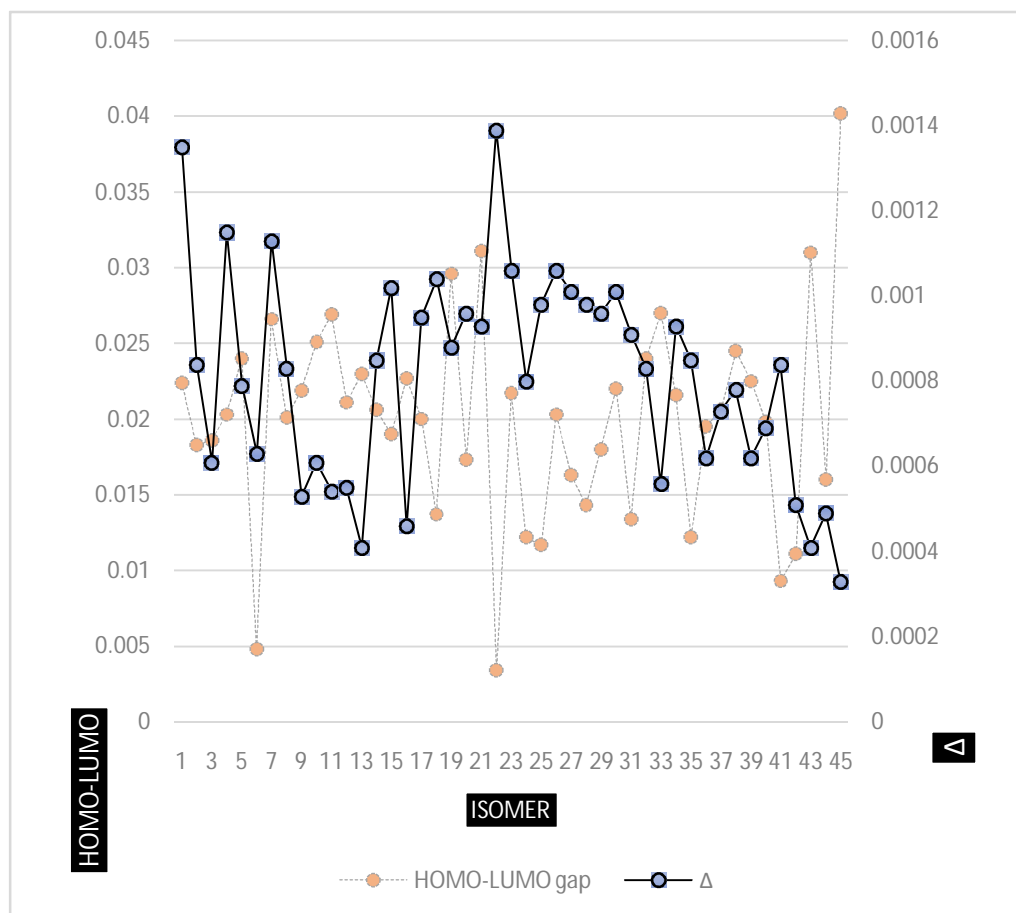


Figure 5: Graph of Δ and HOMO-LUMO gap in terms of fullerene isomers C_{42} .

For the set of C_{70} fullerene that has the maximum of Fries number, we can examine the above function. The most stable isomer of C_{70} is C_{70} : 8149[20, 28, 31] and according to the Table 2, it can be seen that the lowest value of Δ is related to the most stable isomer among the C_{70} isomers.

In [12] there is a list of isomers known to be stable: C_{60} : 1812, C_{70} : 8149, C_{76} : 19150, C_{78} : 24105, C_{78} : 24106, C_{78} : 24107, C_{84} : 51590, C_{84} : 51591. To evaluate the Δ as an stability criterion, we have calculated the Δ value for all C_{60} , C_{70} , C_{76} , C_{78} and C_{84} isomers and the results have been tabulated as follows. Table 3 is comprised of five columns: isomer, rank, Δ , Min, Max. They inform, respectively, the code identifying the isomer, rank of isomer based on the lower value of Δ , value of Δ , minimum value of Δ , maximum value of Δ .

<i>Isomer</i>	<i>Kekulé</i>	<i>Clar No.</i>	<i>Fries No.</i>	N_p	Δ
C_{60} : 43	11102	8	14	14	0.000120635
C_{60} : 44	11259	8	16	14	0.000104083
C_{60} : 1113	10370	8	16	6	5.27363E-05
C_{60} : 1114	10356	8	16	7	6.03515E-05
C_{60} : 1123	10386	8	16	6	5.2655E-05
C_{60} : 1124	10340	8	14	8	7.77148E-05
C_{60} : 1247	10538	8	14	10	9.32001E-05
C_{60} : 1251	10610	8	16	8	6.627E-05
C_{60} : 1279	10130	8	14	6	6.16979E-05
C_{60} : 1280	10258	8	14	6	6.09281E-05
C_{60} : 1283	10254	8	14	6	6.09518E-05
C_{60} : 1803	10250	8	14	3	3.48432E-05
C_{60} : 1804	10536	8	16	3	2.96602E-05
C_{60} : 1805	10476	8	16	4	3.72876E-05
C_{60} : 1808	10476	8	14	4	4.26144E-05
C_{60} : 1809	11230	8	18	2	1.85515E-05
C_{60} : 1810	10760	8	16	4	3.63034E-05
C_{60} : 1812	12500	8	20	0	0.000005

Table 1: Kekulé number, Clar number, Fries number, pentagon adjacency index N_p and value of Δ and related to C_{60} fullerene.

<i>Isomer</i>	<i>Kekulé</i>	<i>Clar No.</i>	<i>Fries No.</i>	N_p	Δ
C_{70} : 1940	49070	9	20	5	6.79302E-06
C_{70} : 5635	48440	9	20	3	4.58758E-06
C_{70} : 6503	47206	9	20	4	5.88437E-06
C_{70} : 7106	51068	9	20	2	3.26362E-06
C_{70} : 7716	53064	9	20	2	3.14086E-06
C_{70} : 8142	47594	8	20	2	3.93957E-06
C_{70} : 8144	49185	9	20	2	3.38857E-06
C_{70} : 8149	52168	9	20	0	1.06494E-06

Table 2: Kekulé number, Clar number, Fries number, pentagon adjacency index N_p and value of Δ and related to C_{70} fullerene.

<i>Isomer</i>	<i>rank</i>	Δ	<i>Min</i>	<i>Max</i>
C_{60} : 1812	1	0.000005	0.000005	0.000397703
C_{70} : 8149	1	1.06494E-06	1.06494E-06	5.16917E-05
C_{76} : 19150	1	4.01803E-07	4.01803E-07	1.62102E-05
C_{78} : 24105	3	2.77189E-07		
C_{78} : 24106	2	2.36323E-07	1.78437E-07	8.7726E-06
C_{78} : 24107	4	3.22732E-07		
C_{84} : 51590	11	9.54915E-08		
C_{84} : 51591	8	8.79168E-08	5.95963E-08	2.75186E-06

The value of Δ can also be calculated for C_n fullerenes with $n \geq 86$ and determined the most stable isomer in this way. But considering that calculating parameters like Clar number and Fries number is generally an NP-hard problem, using optimization techniques that has been mentioned in [2, 27], Δ can be calculated for $n \leq 300$ to determine the most stable isomer of C_n .

5. CONCLUSION

We showed that the parameters introduced to detect the stable isomer of fullerene, despite the advantages, are deficient. According to the numerical experiments, the function introduced by us has better performance for detecting the stability of a fullerene.

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