

On functionalized fullerenes $C_{60}X_n$

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Abstract Optimal configurations of functionalized fullerenes $C_{60}X_n$ for $n = 2, 4, 6, 8$ have been determined by application of three topological stability measures. It has been found that the optimal configurations with higher n contain optimal configurations with lower values of n . Two stability measures prefer configurations in which functional groups X s are crowded while the third one points to configurations with isolated pairs of X s.

Keywords Buckminsterfullerene · Functionalized fullerenes · Aromaticity

1 Introduction

Fullerenes can be functionalized in a variety of ways. Here, we restrict our attention to derivatives of the most important fullerene—Buckminsterfullerene C_{60} [1,2]. Each functional group attached to a carbon atom of C_{60} introduces a break in π -electron conjugation at that site. We are interested in properties of π -electron network of fullerene derivatives like their aromaticity [3–5] and we assume a simplified mathematical model in which an introduction of a functional group equals a deletion of the corresponding atom from π -electron network.

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2 Results

Here we study $C_{60}X_n$ where X is an arbitrary functional group and n is number from 1 to 60. If n is an odd number, the fullerene would be not aromatic since remaining odd number of unfunctionalized carbon atoms can not be paired by π -electrons. Therefore, we study the cases where n is an even number. Further, in this note we restrict our attention to four cases: $n = 2, 4, 6$ and 8 . For each case we search for the most favorable configuration, i.e. the most stable (up to symmetry equivalence) arrangement of X s upon the network of C_{60} . We use three measures of the favorability of a configuration [3,6]:

- (1) number of its Kekulé structures;
- (2) number of conjugated hexagons summed up for all Kekulé structures;
- (3) average number of conjugated hexagons.

Let us describe mathematical model we use. Let G be a graph of the Buckminsterfullerene C_{60} and let $n \in \{2, 4, 6, 8\}$. We search for over all sets $S \subseteq V(G)$, where $V(G)$ is set of vertices of G , such that $|S| = n$ and try to find *stability measure 1* as:

$$k(G - S) = \max_{\substack{S' \subseteq V(G) \\ |S'|=n}} \{k(G - S')\},$$

where $k(H)$ is the number of Kekulé structures (perfect matchings) of graph H . Further, we search over all sets $S \subseteq V(G)$ such that $|S| = n$ and try to find *stability measure 2* as:

$$ch(G - S) = \max_{\substack{S' \subseteq V(G) \\ |S'|=n}} \{ch(G - S')\},$$

where $ch(H)$ is the number of conjugated hexagons summed up for all Kekulé structures of H . Further, we search over all sets $S \subseteq V(G)$ such that $|S| = n$ and try to find *stability measure 3* as:

$$ach(G - S) = \max_{\substack{S' \subseteq V(G) \\ |S'|=n}} \{ach(G - S')\},$$

where $ach(H)$ is the average number of conjugated hexagons of H .

Since these three stability measures are graph theoretical invariants, we are interested only to find the above sets S , i.e. configurations up to symmetry equivalence.

In order to do that, we use backtracking algorithm. First, we need to derive all possible configurations on n vertices (up to symmetry equivalence).

The labeling of carbon atoms of C_{60} is given below (Fig. 1):

We assume that configurations are ordered in the ascending order. Now, we choose for each configuration the smallest (according to the lexicographical order) symmetrical configuration to that one. Such a configuration we call certificate of configuration. Let us remind that lexicographical order on sequences of length n is defined by:

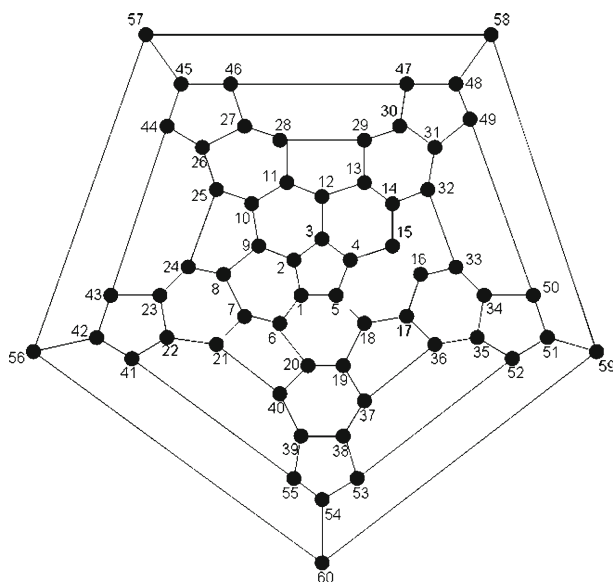


Fig. 1 Labeling of vertices of C_{60}

$a_1 a_2 \dots a_n < b_1 b_2 \dots b_n$ if and only if ($a_1 < b_1$ or there is $k \in \{2, \dots, n\}$ such that $a_i = b_i$, for all $i = 1, \dots, k - 1$ and $a_k < b_k$)

Naturally, only configurations equal to their certificate are of interest. For, the sake of simplicity, in order to find all these configurations, we just observe all configurations that contain vertex 1 and eliminate those that are not equal to their certificate. The corresponding program is not time-consuming; hence we did not use more complex and efficient algorithms.

After all configurations (up to symmetry equivalence) are found, each of them is analyzed via three above stability measures. All Kekulé structures are found by back-tracking algorithm. In each step the vertex with minimal number of uncovered neighbors (neighboring atoms not already covered by double bond) is analyzed in order to reduce the branching of the algorithm. After that for each Kekulé structure the number of conjugated cycles is calculated. All these values are summed up for all Kekulé structures that correspond to a given configuration and the total number of conjugated cycles is found. By dividing the total number of conjugated cycles with the number of Kekulé structures the average number of conjugated cycles is obtained.

Analysis of fullerene derivatives $C_{60}X_2$ gives consistent results. Namely, all three stability measures single out the same most stable configuration depicted below where white circles denote atoms which are to be functionalized (Fig. 2).

When functionalized fullerenes $C_{60}X_4$ are observed three stability measures lead to different results. Namely, the greatest number of Kekulé structures and conjugated cycles is realized by the left configuration and the greatest average number of conjugated cycles by the right configuration shown below (Fig. 3):

Similar situation occurs, when one observes fullerene derivatives $C_{60}X_6$. Again, the greatest number of Kekulé structures and conjugated cycles is realized by the

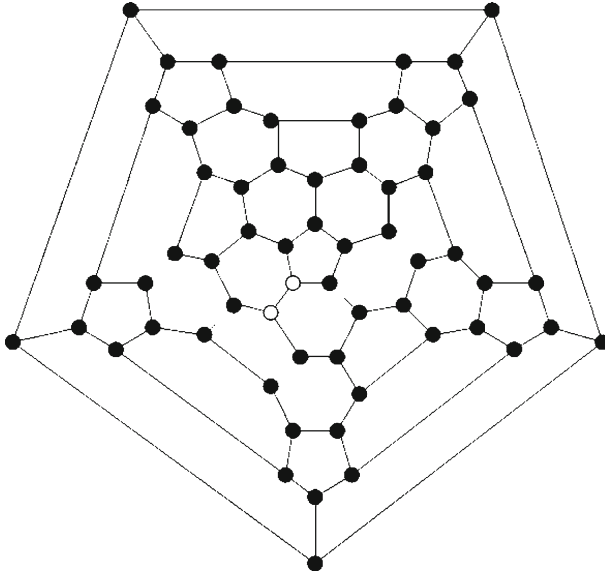


Fig. 2 The most favorable configuration of $C_{60}X_2$ according to all three stability measures

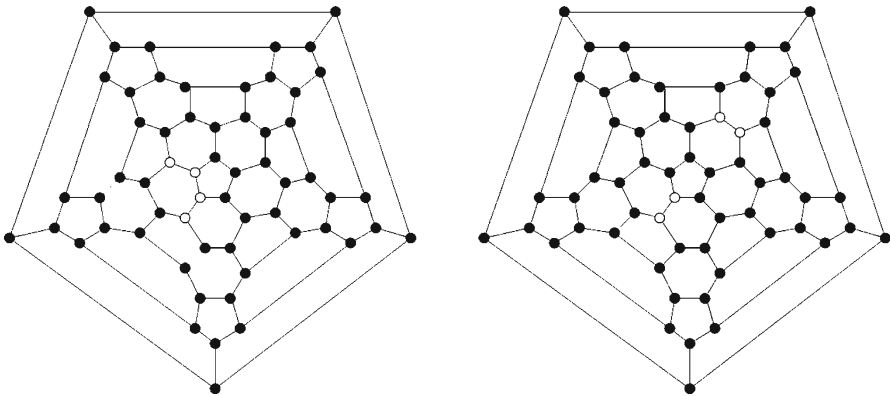


Fig. 3 Left configuration of $C_{60}X_4$ is the most favorable according to stability measures 1 and 2 while right one according to stability measure 3

left configuration and the greatest average number of conjugated cycles by the right configuration shown below (Fig. 4):

When one observes fullerene derivatives $C_{60}X_8$, we met the similar situation. Again, the greatest number of Kekulé structures and conjugated cycles is realized by the left configuration and the greatest average number of conjugated cycles by the right configuration shown below (Fig. 5):

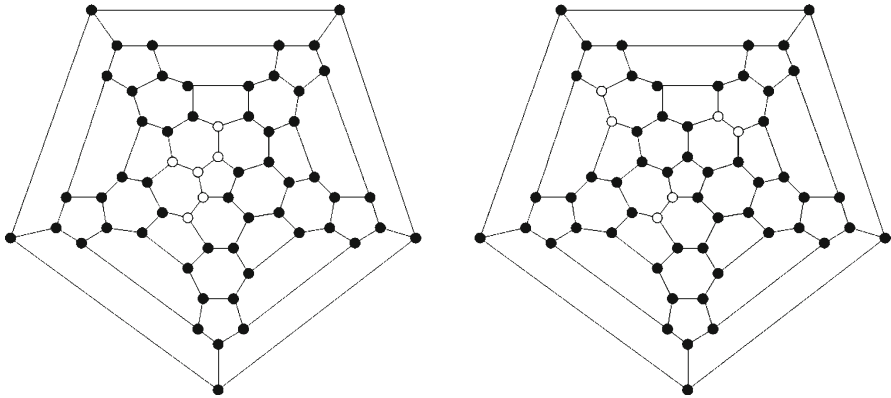


Fig. 4 Left configuration of $C_{60}X_6$ is the most favorable according to stability measures 1 and 2 while right one according to stability measure 3

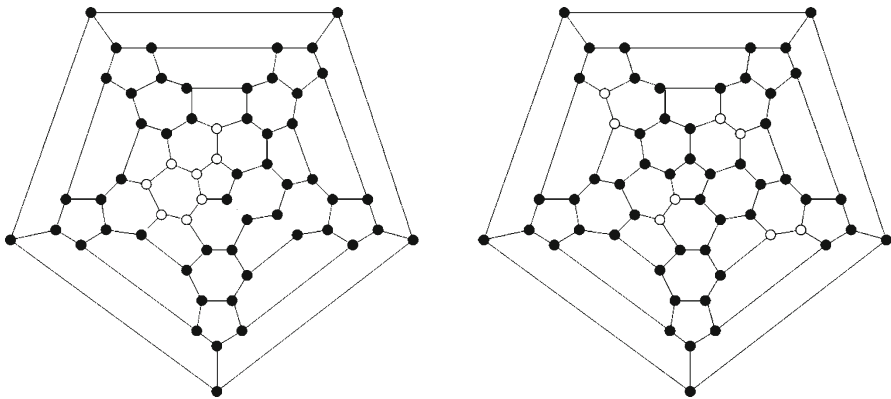


Fig. 5 Left configuration of $C_{60}X_8$ is the most favorable according to stability measures 1 and 2 while right one according to stability measure 3

3 Conclusions

All three stability measures agree that the optimal configurations of derivatives $C_{60}X_2$ is one with two functionalized carbon atoms being neighbors on the border of two hexagons. When derivatives $C_{60}X_n$ for $n = 4, 6$ and 8 are considered one notes an interesting regularity that the optimal configuration for higher n contains the optimal configuration for lower n and this is true for each of the stability measures used. However, the first and second stability measures lead to the optimal configurations with crowded X s and each new carbon atoms are neighbors to some of previous functionalized ones. On the other hand, the third stability measure leads to quite different configurations with less crowded X s where each newly formed pair of functionalized carbon atoms is fully separated from previously functionalized ones.

Which of three introduced measures is to be used for reliable predictions, and if any of them at all, will be studied in a continuation of this note [7].

As a part of these future studies we give here also the results for fullerene derivatives where we relax the strain by requiring that no two neighboring atoms in a given pentagon can be functionalized. Then for $C_{60}X_2$ all three stability measures predict that by functionalizations of atoms 1 and 6 the most favorable configurations are obtained. Here and in what follows the numbering of atoms is as in Fig. 1, and the results are given up to isomorphism. For $C_{60}X_4$ measures 1 and 2 predict functionalization of atoms 1, 6, 27 and 28 and measure 3 of atoms 1, 6, 13 and 14. For $C_{60}X_6$ measure 1 predicts functionalization of atoms 1, 6, 27, 28, 33 and 34 and measures 2 and 3 of atoms 1, 6, 13, 14, 25 and 26. It is interesting that the most favorable configurations for $C_{60}X_8$ are again the same for all three measures with atoms to be functionalized being 1, 6, 13, 14, 25, 26, 35 and 36. The measure 1 also predicts that choice of atoms 1, 6, 13, 14, 41, 48, 55 and 58 leads to equally favorable isomer.

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