On the Combinatorial Characterization of Fullerene Graphs

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Abstract: In order to characterize and classify quantitatively the local topological structure of traditional fullerene graphs a new method has been developed. The concept is based on the introduction of a finite set of novel topological invarians called pentagon arm indices. The definition of pentagon arm indices is similar to that of well known pentagon adjacency indices, and their common features is that both of them characterize the local topological neighborhood of pentagons included in traditional fullerenes. It will be demonstrated that pentagon adjacency indices and pentagon arm indices together can be successfully applicable for preselecting the stable candidates of lower fullerene isomers C_n with $n \leq 70$.

Keywords: graph invariant, pentagon-neighbor signature, prediction of fullerene stability

1   Introduction

Fullerenes are defined as 3-valent (3-regular) polyhedral graphs having only pentagonal and hexagonal faces.

Methods for topological characterization of fullerene isomers have made a steady progress over the past decade and many calculations of stabilities of traditional and non-traditional fullerenes have been reported [1-14]. A promising trend in fullerene science is the employment of graph theoretical invariants for the characterization of combinatorial structure and prediction of their stabilities.

Several topological descriptors have been proposed to evaluate and classify the topological structure of fullerene isomers: the pentagon adjacency index N_P [1-4], the Wiener index W_I [5], the resistance distance R_T [5], the Kekulé structure count [6], the graph independence number [7], the number of spanning trees [8], the combinatorial curvature [9], the bipartivity measure of fullerene graphs [10], the occurrence number of different structural motifs in fullerenes [12-14].

In the majority of cases, for the stability prediction of lower fullerene isomers C_n with n≤70 the pentagon adjacency index N_P (the so-called minimal-N_P criterion) is used [1, 3, 4]. Determination of the pentagon adjacency index N_P is based on the pentagon-neighbor signature $\{p_0, p_1, p_2, p_3, p_4, p_5\}$, where each entry p_k (k=0,1,2,…5) counts those pentagons that have exactly k pentagonal edge-neighbors. From these data the pentagon adjacency index N_P can be simply computed:

$$N_P = \frac{1}{2}\sum_k kp_k \tag{1}$$

where $\sum p_k = 12$. It is obvious that N_P is also equal to the number of edges between adjacent pentagons, in other words N_P is identical to the total number of fused pentagon pairs in an isomer.

According to the minimal-N_P rule it is supposed that fullerenes which minimize N_P are more likely to be stable than those that do not [3-5]. Consequently, it is believed that the buckminsterfullerene is the most stable C_{60} fullerene, because this is the only one for which N_P has a minimum value (N_P=0).

However in some cases the discriminating power (i.e. the efficiency of prediction) of N_P index is limited. (The minimal-N_P criterion does not suffice to uniquely characterize the structure of fullerene graphs with identical pentagon adjacency indices.) Even some lower fullerene isomers C_n with n≤70 are characterized by the same pentagon adjacency index N_P. In such cases, using N_P, the accuracy of stability prediction is problematic. For example, among C_{66} fullerenes there are three isomers with the same lowest pentagon adjacency index (N_P=2), moreover, among C_{68} fullerenes there exist 11 isomers with N_P=2.

In order to improve the efficiency of stability prediction, a novel three-variable topological descriptor denoted by Ψ has been constructed. This includes the N_P index, and additionally two other independent topological graph invariants as well. The construction of this novel descriptor Ψ is based on the introduction of the so-called pentagon arm signature vector, whose components can be simply computed from Schlegel diagrams of fullerenes.

2 Pentagon Arm Indices as Graph Invariants

In a fullerene a pentagonal face F_P has 5 vertices, and each vertex is incident to an edge not belonging to the pentagon under consideration. An edge E incident to a vertex of F_P is called an arm of F_P if i) both end-vertices of edge E are incident to pentagons, and ii) E shares two neighbor hexagons. This definition implies that any pentagonal face may have q=0, 1,2,…5 arms. Let us denote by n_q the number of pentagons having q arms in a fullerene. It follows that each fullerene can be characterized by a pentagon arm signature vector $\{n_0, n_1, n_2, n_3, n_4, n_5\}$, where each entry n_q (k=0,1,2,…5) counts those pentagons that have exactly q arms. Starting with this concept, for an arbitrary fullerene we define a pentagon arm index N_A as follows:

$$N_A = \frac{1}{2}\sum_q qn_q \tag{2}$$

where $\sum n_q = 12$.

From this concept it follows that parameter N_A is identical to the total number of edges whose end-vertices are incident to pentagons, and share two neighbor hexagons, exactly. It can be verified that for topological invariant N_{PA} defined as

$$N_{PA} = N_P + N_A \tag{3}$$

the inequality $0 \leq N_{PA} \leq 30$ holds [15]. Concerning the upper bound, it follows that for fullerene C_{20} (represented by the dodecahedron) N_{PA}=30+0=30, and for the buckminsterfullerene N_{PA}=0+30=30 holds. It is conjectured that for any other fullerenes the inequality $0 \leq N_{PA} \leq 25$ is valid. (For fullerene isomers C_{30} : 1(D_{5h}) and C_{50} : 271 (D_{5h}) we have $N_{PA}=N_P + N_A$= 25).

In order to construct the topological descriptor Ψ and classify the fullerene isomers into disjoint subsets, we used the first and second moments (M_1 and M_2) of pentagon arm signatures $\{n_0, n_1, n_2, n_3, n_4, n_5\}$:

$$M_k = \frac{1}{12}\sum_{q=0}^{5} q^k n_q \tag{4}$$

where k=1 and k=2, respectively. From the previous consideration it follows that $M_1=N_A/6$. By means of moments M_1 and M_2, the variance of q can be calculated as VAR=M_2− M_1*M_1. It is easy to see that VAR =0 if and only if there exists a positive integer $0 \leq q \leq 5$ among the components of pentagon arm signature vector for which n_q =12 holds. Starting with this concept, a fullerene is called balanced (more exactly q-balanced) if there exists a non-negative integer q for which n_q =12 valid. This means that a fullerene is balanced if and only if, VAR=0 holds. In Fig. 1 some examples are given for balanced fullerenes.
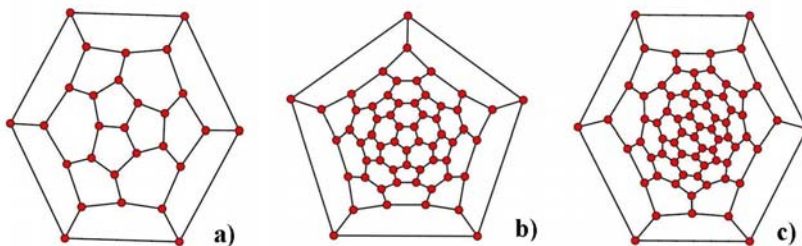
Figure 1
Schlegel diagrams of balanced fullerenes: a) 0-balanced C_{28} (T_d) isomer, b) 5-balanced C_{60} (I_h) isomer
(buckminsterfullerene) and c) 4-balanced C_{72} (D_{6d}) isomer

The 5-balanced and 4-balanced isomers illustrated in Fig. 1 belong to the family of IPR (isolated-pentagon rule) fullerenes. It is known that the number of IPR fullerenes (fullerenes with $N_P=0$) is infinite. Fullerenes with $N_{PA}= N_P + N_A=0$ are called strongly isolated fullerenes. This definition implies that strongly isolated fullerenes represent a subset of IPR fullerenes. The number of strongly isolated fullerenes is also infinite. In Fig. 2 the Schlegel diagram of a strongly isolated fullerene is shown.
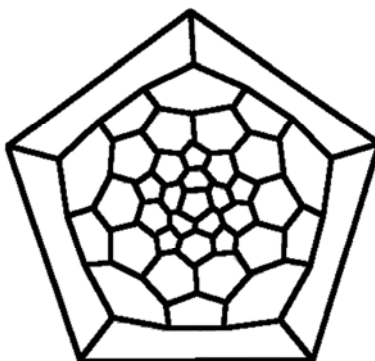

Figure 2
Schlegel diagram of the strongly isolated fullerene isomer C_{80} (I_h)

It can be verified that C_{80} (I_h) with vertex number 80 is the smallest strongly isolated fullerene. (See Fig. 2)

3   A Novel Graph-Theoretic Invariant for the Characterization of Fullerene Structures

In order to characterize the local combinatorial structure of fullerenes more efficiently, we defined the topological descriptor Ψ as follows

$$\Psi = \frac{30 + 6M_1}{1 + 4.5N_P + C(M_1, M_2)} = \frac{30 + N_A}{1 + 4.5N_P + C(M_1, M_2)} \tag{5}$$

where

$$C(M_1, M_2) = \frac{\sqrt{\dfrac{120M_2}{1 + 7M_1}}}{1 + 0.9(M_2 - M_1^2)^{1/5}} = \frac{\sqrt{\dfrac{120(VAR + M_1^2)}{1 + 7M_1}}}{1 + 0.9VAR^{1/5}} \tag{6}$$

For balanced fullerenes, (where VAR=0), coefficient $C(M_1,M_2)$ can be rewritten it the following simplified form:

$$C(M_1, M_2) = M_1\sqrt{\frac{120}{1 + 7M_1}} = N_A\sqrt{\frac{20}{6 + 7N_A}} \tag{7}$$

As can be seen, Ψ is defined as a function of 3 algebraically independent graph invariants: the pentagon neighbor index N_P and the moments M_1 and M_2. It follows that for strongly isolated fullerenes $N_P = N_A = C(M_1,M_2) = 0$, consequently in this case $\Psi = 30$. The constants included in Eqs. (6 and 7) were estimated using numerical methods, as a result of analyzing the possible combinatorial structures and the energetic parameters of C_{40} isomers. This choice is explained by the fact that several topological descriptors have been already calculated for C_{40} fullerene isomers.

As it is known isomer C40:38 is predicted to be the C_{40} fullerene of lowest energy by many methods [3-5], this is followed by C40:39 and C40:31 isomers. It has been also shown that C40:38 fullerene has the lowest resistance-distance in the set ($R_T = 920,27$). Two C_{40} isomers (C40:38 and C40:39) have the smallest pentagon adjacency indices ($N_P = 10$). Among the 40 isomers of C_{40}, fullerene C40:1 is the least stable isomer having the highest pentagon adjacency index ($N_P = 20$) and the highest resistance distance ($R_T = 955.15$). In Table 1 we summarized the computed values of pentagon arm signatures $\{n_0, n_1, n_2, n_3, n_4, n_5\}$, the pentagon adjacency indices N_P and the topological descriptors Ψ, for the forty C_{40} isomers. (Each of isomers is labeled according Fowler and Manolopoulos [1]). Simultaneously, using Density Functional Tight-Binding (DFTB) method [16] we calculated the total energy values Q_C characterizing the relative stability of isomers.

Table 1

Topological parameters and relative energies of the forty C_{40} isomers

Isomer	Topological parameters								Energy, Q_C
	n_0	n_1	n_2	n_3	n_4	n_5	N_P	Ψ	(eV)
C40:38	0	8	0	4	0	0	10	0.8140	-342,031
C40:39	0	10	0	0	0	2	10	0.8106	-341,631
C40:31	1	3	5	3	0	0	11	0.7631	-341,438
C40:29	2	2	4	4	0	0	11	0.7628	-341,345
C40:26	2	6	2	2	0	0	11	0.7108	-341,094
C40:24	3	4	3	2	0	0	11	0.7102	-341,022
C40:37	4	6	0	2	0	0	11	0.6744	-340,636
C40:40	0	0	12	0	0	0	12	0.6924	-340,580
C40:14	3	2	5	2	0	0	12	0.6715	-340,476
C40:36	4	6	2	0	0	0	11	0.6597	-340,431
C40:30	3	3	3	3	0	0	12	0.6711	-340,304
C40:25	4	4	2	2	0	0	12	0.6382	-340,277
C40:22	5	3	3	1	0	0	12	0.6219	-340,230
C40:35	4	6	2	0	0	0	11	0.6597	-340,196
C40:21	6	2	0	4	0	0	12	0.6358	-340,151
C40:27	4	6	0	2	0	0	12	0.6219	-340,126
C40:15	2	8	2	0	0	0	12	0.6250	-339,943
C40:17	2	6	4	0	0	0	13	0.5943	-339,884
C40:34	5	6	1	0	0	0	12	0.5923	-339,827
C40:28	4	5	2	0	0	1	12	0.6358	-339,777
C40:16	2	6	4	0	0	0	13	0.5943	-339,645
C40:20	6	6	0	0	0	0	12	0.5772	-339,627
C40:9	4	2	4	2	0	0	13	0.6075	-339,614
C40:10	6	2	4	0	0	0	13	0.5622	-339,558
C40:12	4	6	2	0	0	0	13	0.5641	-339,370
C40:13	7	2	3	0	0	0	13	0.5467	-339,347
C40:19	4	2	6	0	0	0	13	0.5933	-339,292
C40:23	8	2	2	0	0	0	13	0.5313	-338,690
C40:6	7	4	1	0	0	0	14	0.4970	-338,624
C40:18	6	6	0	0	0	0	14	0.4987	-338,341
C40:5	6	1	4	0	0	1	14	0.5497	-338,332
C40:32	8	4	0	0	0	0	14	0.4843	-338,270
C40:8	6	4	2	0	0	0	15	0.4785	-338,113
C40:33	4	8	0	0	0	0	14	0.5132	-337,922
C40:4	7	4	1	0	0	0	15	0.4654	-337,348
C40:7	6	6	0	0	0	0	15	0.4670	-337,330
C40:11	10	2	0	0	0	0	15	0.4404	-336,642
C40:2	8	4	0	0	0	0	16	0.4262	-336,489
C40:3	12	0	0	0	0	0	18	0.3659	-335,193
C40:1	12	0	0	0	0	0	20	0.3297	-333,806

These energies are also given in Table 1. As shown in Table 1, using the topological descriptor Ψ we get the following trends of relative stability: C40:38 > C40:39 > C40:31> C40:29. This corresponds to the theoretical results based on ab initio calculations [3-5]. This finding confirms that topological descriptor Ψ correlates highly with the computed total energy value Q_C. Moreover, from Table 1 it can be seen that in the set of C_{40} fullerenes, there are three balanced isomers: C40:40 is 2-balanced, while C40:1 and C40:3 are 0-balanced isomers.

4 Comparative Tests Performed on a Set of C_{66} Isomers

In order to test the discriminating power of topological descriptor Ψ, we used the sets of C_{66} isomers. The number of topologically different C_{66} isomers is 4478. All of them were generated and sorted in terms of the calculated total energy values. Among C_{66} fullerenes there are 3 isomers with lowest pentagon adjacency index 2, and 26 isomers with $N_P = 3$.

Table 2

Topological parameters and relative energies of the forty lowest energy C_{66} isomers

Isomer	Topological parameters								Energy,Q_C
	n_0	n_1	n_2	n_3	n_4	n_5	N_P	Ψ	(eV)
C66:4169	2	1	0	3	4	2	2	3.4756	-583.0067
C66:4348	0	4	0	4	2	2	2	3.4214	-582.8916
C66:4466	2	0	2	2	6	0	2	3.4214	-582.7047
C66:4007	2	2	2	3	2	1	3	2.4369	-582.3229
C66:3764	2	1	5	3	1	0	3	2.3537	-582.3027
C66:4456	2	2	2	6	0	0	3	2.3537	-582.1878
C66:4462	1	2	5	4	0	0	3	2.3557	-582.1816
C66:4060	2	3	2	3	2	0	3	2.3479	-582.1267
C66:4141	1	3	2	3	3	0	3	2.4423	-582.1118
C66:4312	0	3	2	6	0	1	3	2.4871	-582.0754
C66:4439	1	3	5	3	0	0	3	2.3126	-582.0316
C66:3765	2	1	5	1	3	0	3	2.3954	-582.0278
C66:3538	2	1	4	4	0	1	3	2.3954	-582.022
C66:4447	2	1	3	5	1	0	3	2.3982	-581.9169
C66:4458	2	2	3	2	3	0	3	2.3937	-5819087
C66:4331	0	4	4	2	2	0	3	2.3995	-581.8906
C66:4454	1	4	7	0	0	0	3	2.2279	-581.8632
C66:3824	3	1	1	2	4	1	3	2.4783	-581.8594
C66:4434	2	2	3	2	3	0	3	2.3937	-581.8251
C66:4369	2	3	2	3	2	0	3	2.3479	-581.8133
C66:4388	2	1	2	3	4	0	3	2.4862	-581.8098
C66:4410	1	6	3	2	0	0	3	2.2254	-581.8034
C66:4444	1	2	6	2	1	0	3	2.3558	-581.7878
C66:4398	3	4	2	2	1	0	3	2.2054	-581.7731
C66:4409	2	3	3	3	1	0	3	2.3056	-581.7640
C66:4455	2	1	5	3	1	0	3	2.3537	-581.6897
C66:3473	0	4	0	5	2	1	3	2.5324	-581.5661
C66:4449	2	0	5	2	3	0	3	2.4423	-581.5501
C66:4433	3	5	1	3	0	0	4	1.7236	-581.4675
C66:3961	1	6	3	2	0	0	4	1.7707	-581.4670
C66:4441	2	0	4	4	2	0	3	2.4430	-581.4669
C66:4316	2	0	4	6	0	0	4	1.9179	-581.4382
C66:4297	2	3	4	3	0	0	4	1.8054	-581.3990
C66:4346	0	7	1	3	1	0	4	1.8429	-581.3902
C66:4244	3	3	5	1	0	0	4	1.7303	-581.3872
C66:4313	0	4	6	2	0	0	4	1.8427	-581.3737
C66:4430	4	2	4	2	0	0	4	1.7236	-581.3698
C66:4381	1	7	3	1	0	0	4	1.7358	-581.3404
C66:4008	2	3	2	5	0	0	4	1.8415	-581.3177
C66:4349	0	6	6	0	0	0	4	1.7698	-581.2652

Table 2 shows the pentagon arm index signature, the pentagon adjacency index N_P, the topological descriptor Ψ, and the calculated total energy values Q_C for the 40 lowest-energy isomers. According to our results, and considering the computed values of Ψ, the most stable isomer is C66:4169, while the next two isomers with minimal energies are C66:4348 and C66:4466.

In these two latter cases the topological descriptor Ψ is identical ($\Psi=3.4214$). The calculated energies of top 5 isomers are in agreement with the results published in Refs. [17, 18].

In ranking the isomers, due to the larger amount of information included in Ψ it was reasonable to expect that Ψ performs better than N_P. According to experiments the discriminating ability of Ψ is more efficient than that of N_P.

Summary and Conclusions

In order to characterize and classify quantitatively the local topological structure of lower fullerenes C_n with n $\leq$70 a simple method has been suggested. The concept is based on the computation of a finite set of topological invarians called pentagon arm indices.

For stability prediction purposes, a novel three-variable topological descriptor (Ψ) has been defined. This includes not only the N_P index, but additionally two other independent topological graph invariants (M_1 and M_2) derived from the components of the pentagon arm signature vector.

To test and evaluate the discriminating power of Ψ the sets of C_{40} and C_{66} fullerene isomers have been chosen. It was demonstrated that the proposed topological descriptor Ψ is able not only to characterize the combinatorial structure of different fullerene isomers, but also to rank them in the order of decreasing stability.

Acknowledgements

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