

Stability Prediction in C_{40} Fullerenes

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ABSTRACT. The well-known "isolated pentagon rule" IPR is described in quantitative terms provided by the layer matrix of valences, constructed on the dual of the associate molecular graph of fullerenes. The derived pentagon valence pv parameter correlates well (it describes more than 90% of variance) with the PM3 heat of formation of small fullerenes C_{40} . The equivalence classes of their vertices, edges and faces are also deducible from some layer matrix invariants. They are important in simulating the ^{13}C NMR spectrum and/or in predicting the products of addition reactions of fullerenes.

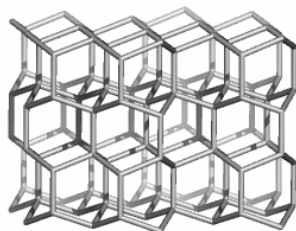
1. INTRODUCTION

The experimentally known allotropes of carbon can be classified into the following five categories:

(1) *Diamond* - infinite 3D lattice of covalently bonded sp^3 carbon atoms (Figure 1a); the interlocking C_6 rings are similar to those in cyclohexane or adamantane.

(2) *Nanosponges* - infinite 3D lattice of covalently bonded sp^2 carbon atoms (an example is given in Figure 1b); such structures are embedded on surfaces of genus higher than zero (see below) and include rings larger than C_6 , needed for inducing the negative curvature of such surfaces [1-3].

(a)



(b)

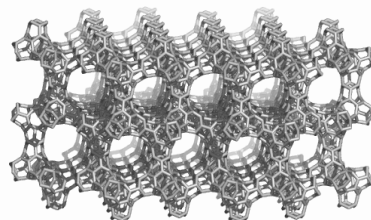


Figure 1. 3D Lattice of classical sp^3 (a) and porous sp^2 (b) diamond.

(3) *Graphite* - infinite 2D planar layers of hexagons of sp^2 carbon atoms (Figure 2a).

(4) *Nanotubes* - infinite 1D tubes, constructed from hexagons of sp^2 carbon atoms (Figure 2b) [4, 5].

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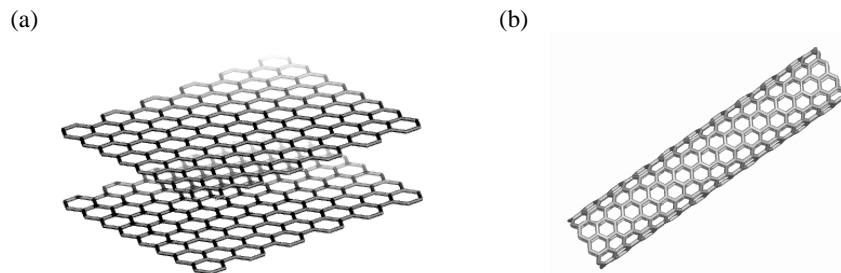


Figure 2. 2D Lattice of the graphite (a) and nanotubes (b); they are tessellated only by hexagons.

(5) Fullerenes - finite 0D molecular cages of sp^2 carbon atoms containing only C_6 and C_5 rings [6]. The three last sp^2 carbon structures are held together by van der Waals forces. The sp^2 carbon 3D, 1D and 0D structures have been theoretically predicted and experimentally discovered in the soot of vaporized graphite. The study of these novel carbon allotropes forms the modern realm of Nanoscience and Nanotechnology.

Resuming to the zero-dimensional sp^2 carbon structures, a fullerene is, according to a classical definition, a carbon cage consisting entirely of pentagons (exactly 12) and hexagons ($N/2-10$) [6]. Its associate graph is a (convex) polyhedron, obeying the Euler [7] theorem:

$$v - e + f = 2(1 - g) \quad (1)$$

with v , e , f , and g being the number of vertices, edges, faces and genus, respectively; g is the number of holes to be performed in the sphere to make it isomorphic to a given surface ($g = 0$, for sphere and plane; 1 for the torus and open tube and >1 for the surfaces of negative curvature).

The most representative, and first isolated, fullerene is C_{60} (Figure 3).

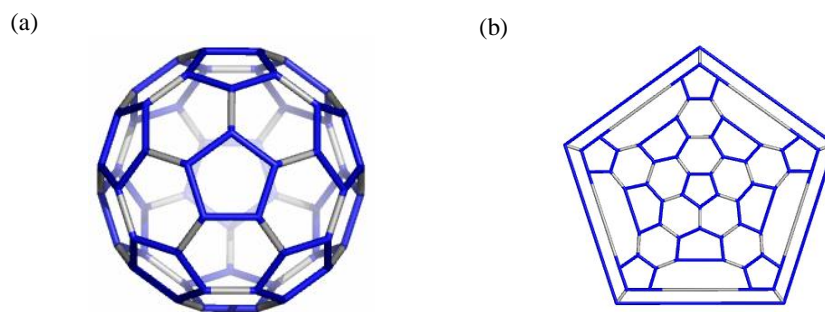


Figure 3. Fullerene C_{60} , embedded in the sphere (a) and in the plane (Schlegel projection - (b)).

It can be seen that all the pentagons are isolated from each other. This simple rule of construction was postulated as a condition for the thermodynamic stability of

fullerenes, known as the “isolated pentagon rule” IPR. All the isolated fullerenes (CN, N = 60, 70, 76, 78, 82, 84, etc) have IPR structures [8]. Another condition for the “preferable” fullerenes (i.e., real fullerenes) is to avoid (strained) triangular and (antiaromatic) 4n-fold rings.

2. CLASSES OF EQUIVALENCE IN FULLERENES BY LAYER MATRIX OF VALENCES

A study of topological symmetry in fullerenes will provide, in others, the classes of equivalence of the subgraphs included in the Euler formula: vertices, edges and faces. The knowledge of equivalence classes is important in simulating the ¹³C NMR spectrum and/or in predicting the addition reaction products of the fullerenes.

The equivalence classes are derivable on the ground of information provided by layer matrices built up on the parent fullerene (for vertices), on medial (for edges) and dual (for faces) derivatives of fullerenes.

2.1. LAYER MATRICES LM

A layer of vertices located at distance k to the vertex i is defined as [9-11]:

$$G(i)_k = \{v \mid v \in V(G); d_{iv} = k\} \quad (2)$$

Define the partition of G with respect to i as:

$$G(i) = \{G(i)_k ; k \in [0,1,\dots, ecc_i]\} \quad (3)$$

with ecc_i being the eccentricity of i (i.e., the largest distance from i to the other vertices of G). The entries in the layer matrix (of vertex property) LM, is defined as:

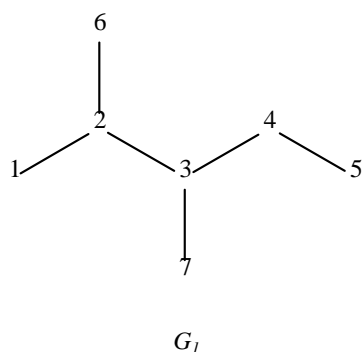
$$[\mathbf{LM}]_{i,k} = \sum_{v|d_{i,v}=k} p_v \quad (4)$$

with the most used operation being the summation. The zero column is just the column of vertex properties $[\mathbf{LM}]_{i,0} = p_i$. Any atomic/vertex property can be considered as p_i . More over, any square matrix M can be taken as info matrix, i.e., the matrix supplying local/vertex properties as row sum RS, column sum CS or diagonal entries given by the Walk matrix [10,11] (see below).

Layer matrix is a collection of the above defined entries:

$$\mathbf{LM} = \{[\mathbf{LM}]_{i,k} ; i \in V(G); k \in [0,1,\dots, d(G)]\} \quad (5)$$

with $d(G)$ being the diameter of the graph (i.e., the largest distance in G). Figure 4 illustrates the LV matrix (i.e., the matrix having the column $k = 0$ the vertex valences) of the graph G1. The numbers at the bottom of LV represent local or global invariants, eventually extended by distance (k) or reciprocal distance (1/k).



		LV (G_I)				
<i>i \ k</i>	0	1	2	3	4	<i>RS</i>
1	1	3	4	3	1	12
2	3	5	3	1	0	12
3	3	6	3	0	0	12
4	2	4	4	2	0	12
5	1	2	3	4	2	12
6	1	3	4	3	1	12
7	1	3	5	3	0	12
<i>CS</i>	12	26	26	16	4	
<i>CS·k</i>		26	52	48	16	142
<i>CS·1/k</i>		26	13	5.33	1	45.33

Figure 4. Layer matrix of valences **LV**

Layer matrices are used to derive two topological indices: (i) indices of centrality $C(LM)$ and (ii) indices of centrocomplexity $X(LM)$.

2.2. INDICES OF CENTRALITY

Indices of centrality $C(LM)$ look for the center of a graph and are defined as:

$$C(LM)_i = \left[\sum_{k=1}^{ecc} \left([LM]_{ik}^{2k} \right)^{1/(ecc)^2} \right]^{-1} \quad (6)$$

$$C(LM) = w \sum_i C(LM)_i \quad (7)$$

where ecc is the maximal distance in G (i.e., $\max_{i,k} d(i,k)$) and w is a weighting factor.

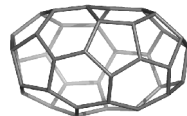
2.3. CLASSES OF EQUIVALENCE IN SMALL FULLERENES

The classes of equivalence in the set of fullerenes C₄₀ (Figure 5) have been obtained by calculating the C_i index on the LDS (Layer of Distance Sum) matrix. The resulted classes of equivalence are listed in Tables 1.

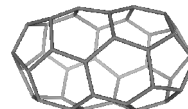
The structures of Figure 5 are listed in Table 1 in decreasing order of their point group symmetry. The ordering was stated by imposing the following hierarchy: vertices > edges > faces and, within each subgraph, the cardinality of class > no. classes.



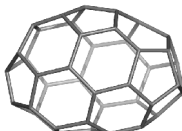
C₄₀:1



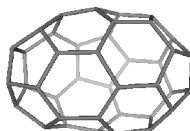
C₄₀:2



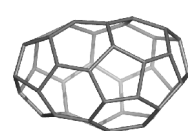
C₄₀:3



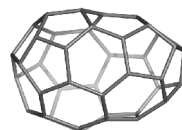
C₄₀:4



C₄₀:5



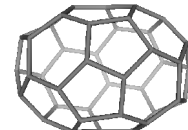
C₄₀:6



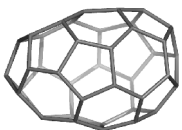
C₄₀:7



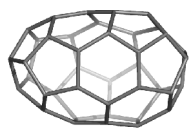
C₄₀:8



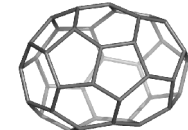
C₄₀:9



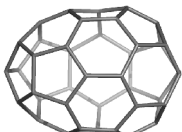
C₄₀:10



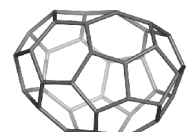
C₄₀:11



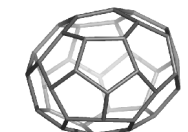
C₄₀:12



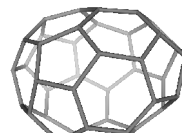
C₄₀:13



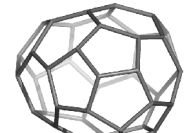
C₄₀:14



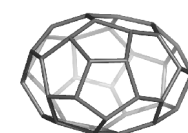
C₄₀:15



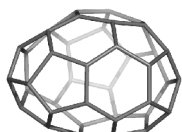
C₄₀:16



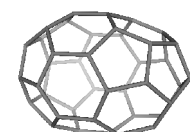
C₄₀:17



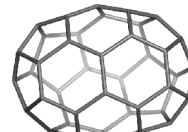
C₄₀:18



C₄₀:19



C₄₀:20



C₄₀:21

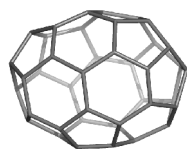
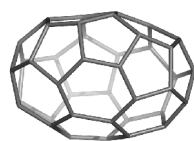
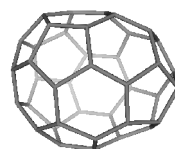
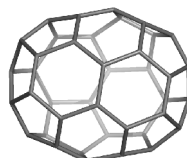
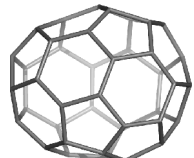
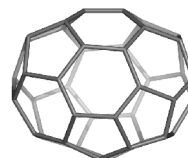
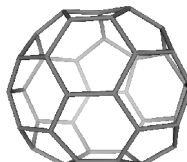
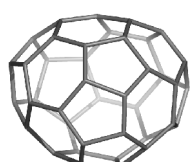
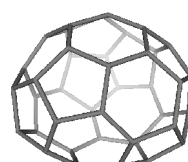
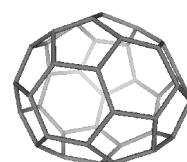
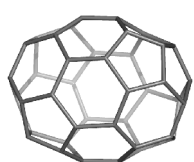
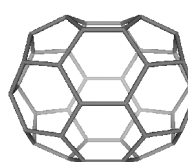
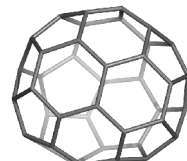
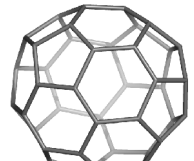
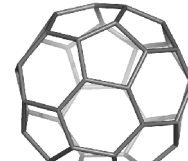
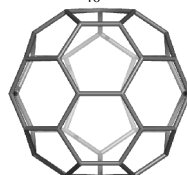
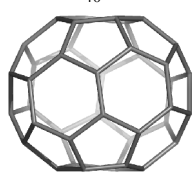
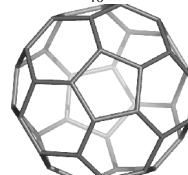
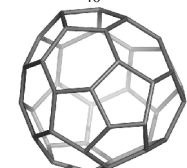
 $C_{40}:22$  $C_{40}:23$  $C_{40}:24$  $C_{40}:25$  $C_{40}:26$  $C_{40}:27$  $C_{40}:28$  $C_{40}:29$  $C_{40}:30$  $C_{40}:31$  $C_{40}:32$  $C_{40}:33$  $C_{40}:34$  $C_{40}:35$  $C_{40}:36$  $C_{40}:37$  $C_{40}:38$  $C_{40}:39$  $C_{40}:40$

Table 1. Classes of equivalence in the set of C_{40} fullerenes.

C_{40}	V(40)	E(60)	F(22)
40- T_d	$1 \times \{24\}; 1 \times \{12\}; 1 \times \{4\}$	$1 \times \{24\}; 3 \times \{12\}$	$1 \times \{12\}; 1 \times \{6\}; 1 \times \{4\}$
39- D_{5d}	$1 \times \{20\}; 2 \times \{10\}$	$1 \times \{20\}; 4 \times \{10\}$	$2 \times \{10\}; 1 \times \{2\}$
1- D_{5d}	$4 \times \{10\}$	$1 \times \{20\}; 4 \times \{10\}$	$2 \times \{10\}; 1 \times \{2\}$
33- D_{2h}	$3 \times \{8\}; 4 \times \{4\}$	$6 \times \{8\}; 2 \times \{4\}; 2 \times \{2\}$	$1 \times \{8\}; 3 \times \{4\}; 1 \times \{2\}$
38- D_2	$10 \times \{4\}$	$14 \times \{4\}; 2 \times \{2\}$	$1 \times \{6\}; 4 \times \{4\}$
3- D_2	$10 \times \{4\}$	$14 \times \{4\}; 2 \times \{2\}$	$5 \times \{4\}; 1 \times \{2\}$
32- D_2			
20- C_{3v}	$4 \times \{6\}; 5 \times \{3\}; 1 \times \{1\}$	$7 \times \{6\}; 6 \times \{3\}$	$1 \times \{6\}; 5 \times \{3\}; 1 \times \{1\}$
8- C_{2v}	$7 \times \{4\}; 6 \times \{2\}$	$13 \times \{4\}; 3 \times \{2\}; 2 \times \{1\}$	$1 \times \{6\}; 2 \times \{4\}; 4 \times \{2\}$
37- C_{2v}	$7 \times \{4\}; 6 \times \{2\}$	$13 \times \{4\}; 3 \times \{2\}; 2 \times \{1\}$	$4 \times \{4\}; 3 \times \{2\}$
30- C_3	$13 \times \{3\}; 1 \times \{1\}$	$20 \times \{3\}$	$7 \times \{3\}; 1 \times \{1\}$
19- C_2	$20 \times \{2\}$	$29 \times \{2\}; 2 \times \{1\}$	$2 \times \{4\}; 7 \times \{2\}$
27- C_2			
35- C_2	$20 \times \{2\}$	$29 \times \{2\}; 2 \times \{1\}$	$1 \times \{4\}; 9 \times \{2\}$
2- C_2	$20 \times \{2\}$	$29 \times \{2\}; 2 \times \{1\}$	$11 \times \{2\}$
15- C_2			
16- C_2			
18- C_2			
21- C_2			
23- C_2			
25- C_2			
29- C_2			
36- C_2			
28- C_s	$19 \times \{2\}; 2 \times \{1\}$	$27 \times \{2\}; 6 \times \{1\}$	$1 \times \{4\}; 6 \times \{2\}; 6 \times \{1\}$
31- C_s			
7- C_s	$18 \times \{2\}; 4 \times \{1\}$	$27 \times \{2\}; 6 \times \{1\}$	$9 \times \{2\}; 4 \times \{1\}$
24- C_s			
5- C_s	$17 \times \{2\}; 6 \times \{1\}$	$27 \times \{2\}; 6 \times \{1\}$	$8 \times \{2\}; 6 \times \{1\}$
13- C_s			
14- C_s			
4- C_1	$40 \times \{1\}$	$60 \times \{1\}$	$22 \times \{1\}$
6- C_1			
10- C_1			
12- C_1			
17- C_1			
22- C_1			
26- C_1			
34- C_1			

Note the consensus between the point group hierarchy and topological classes of equivalence; structures with identical equivalence classes of vertices and edges, are discriminated by the face symmetry. Point group refers to the maximal three-dimensional point symmetry group compatible with the polyhedron vertex adjacencies, assuming idealized values for all lengths and angles. This is just the so-called topological symmetry [12]. Physical realization of a polyhedron as a chemical species may lead to Jahn-Teller distortion or other symmetry-lowering effects that could cause a departure from this ideal [13]. This is the main reason that the heat of formation HF (a measure of thermodynamic molecular stability) of the fullerenes does not strictly follow the ordering in Table 1 (see below).

Vertex equivalence is important in calculating the ideal ¹³C NMR spectrum: the cardinality of a class gives the intensity of the NMR signal while the class frequency indicates the number of signals (at different chemical shift). The equivalence of edges/bonds and faces may be important in predicting the products of addition reactions of fullerenes.

3. ENERGETICS of C₄₀ FULLERENE ISOMERS

Semiempirical calculations have been performed on a 2x1GHz Pentium III PC by using the PM3 Hamiltonian, in standard parametrization supplied by HyperChem software (optimization by Polak-Ribiere conjugate-gradient method, at RMS gradient <0.01 kcal/(Å·mol)). The HF per atom and HOMO-LUMO gap (a rough measure of kinetic stability) for the set of C40 isomers are listed in Table 2.

The ordering of fullerene graphs, in Table 2, is that resulting from their spiral codes [6].

Pentagon fusion is a major destabilizing factor in the classical fullerenes. To account for this, Albertazzi et al. [14] have proposed the number *np*, of pentagon-adjacency: *np* ≤ 30 for any fullerene and varies from 20 to 10 within the C40 set. The maximum value occurs for the hemidodecahedral capped isomer 40:1, and the minimum for the two isomers 40: 38 and 40: 39.

We propose here a different descriptor for pentagon adjacency, namely the pentagon valence *pvk* parameter (Table 2, column 3). It is calculated as:

$$pv_k = (1/2) \sum_{p_i} [\mathbf{LV}(Du(\mathbf{M}))]_{i,k} \quad (8)$$

with summation running over all entries, in the layer matrix of valences *LV*, corresponding to pentavalent vertices in the dual of molecular graph. The *pvk* parameter means the sum of faces size at the *k*th shell around each pentagon, in the original graph. In case *k* = 1, (the subscript *k* omitted), it varies between 150 (in C20) and 180 (in IPR fullerenes), and from 160 to 170 within the set of C40 isomers (see Table 2). Our parameter is related to *np* as:

$$n_p = 180 - pv \quad (9)$$

with *np* = 0 in IPR fullerenes, as expected. In larger structures, *pvk* is naturally extended to *k* > 1, proving the usefulness of layer matrices in describing the covering structure of fullerenes [15]. The parameter *pv* was plotted against HF of C40 isomers (Table 2), as shown in Figure 6; it explains more than 90 % of HF variance.

Table 2. Topological and quantum chemical parameters of C₄₀ isomers.

C _{40:i}	n_p^{14}	pv	PM3 HF/atom (kcal/mol)	HL-GAP (eV)
1- <i>D</i> _{5d}	20	160	26.053	4.876
2- <i>C</i> ₂	16	164	24.057	5.443
3- <i>D</i> ₂	18	162	24.809	4.985
4- <i>C</i> ₁	15	165	23.542	5.628
5- <i>C</i> _s	14	166	23.008	5.548
6- <i>C</i> ₁	14	166	22.960	5.254
7- <i>C</i> _s	15	165	23.811	5.051
8- <i>C</i> _{2v}	15	165	23.589	4.908
9- <i>C</i> ₂	13	167	22.847	4.762
10- <i>C</i> ₁	13	167	22.588	5.269
11- <i>C</i> ₂	15	165	24.081	5.261
12- <i>C</i> ₁	13	167	22.304	5.397
13- <i>C</i> _s	13	167	22.692	4.716
14- <i>C</i> _s	12	168	21.982	5.005
15- <i>C</i> ₂	12	168	22.520	4.975
16- <i>C</i> ₂	13	167	22.469	5.524
17- <i>C</i> ₁	13	167	22.395	5.347
18- <i>C</i> ₂	14	166	23.151	5.542
19- <i>C</i> ₂	13	167	22.903	4.012
20- <i>C</i> _{3v}	12	168	22.721	4.218
21- <i>C</i> ₂	12	168	22.325	4.833
22- <i>C</i> ₁	12	168	21.991	5.165
23- <i>C</i> ₂	13	167	23.235	4.055
24- <i>C</i> _s	11	169	21.638	4.277
25- <i>C</i> ₂	12	168	22.134	5.322
26- <i>C</i> ₁	11	169	21.444	5.046
27- <i>C</i> ₂	12	168	21.967	5.181
28- <i>C</i> _s	12	168	21.927	5.609
29- <i>C</i> ₂	11	169	21.328	5.309
30- <i>C</i> ₃	12	168	22.272	3.963
31- <i>C</i> _s	11	169	20.972	5.743
32- <i>D</i> ₂	14	166	23.425	4.604
33- <i>D</i> _{2h}	14	166	24.922	4.137
34- <i>C</i> ₁	12	168	22.113	5.203
35- <i>C</i> ₂	11	169	22.192	4.551
36- <i>C</i> ₂	11	169	22.042	3.868
37- <i>C</i> _{2v}	11	169	21.231	5.904
38-<i>D</i>₂	10	170	20.408	5.955
39-<i>D</i>_{5d}	10	170	20.629	6.259
40- <i>T</i> _d	12	168	21.569	5.546

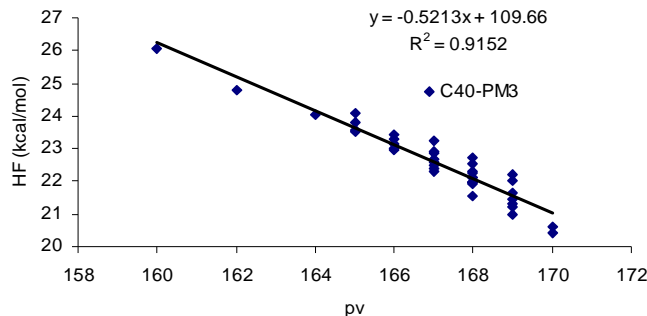


Figure 6. The plot HF vs. pv in the set of C₄₀ isomers.

Essentially the same result was reported by Albertazzi et al. [14], with some difference in HF values. The isomer 40: 38 (D_2) (with the pentagons arranged in two crescents of six) was the most thermodynamically stable, followed by 40: 39 (D_{5d}) (with an equatorial belt of 10 pentagons and the two remaining pentagons isolated at each pole). Note that the HOMO-LUMO gap energy of 40: 39 is higher than to that of 40: 38, suggesting a higher kinetic stability. The balance of the two main parameters of molecular stability remains as a debate. The third in energy was the isomer 40: 31 (C_s , with two pentagon triples!).

Clearly, a high symmetry is not directly correlated with a high stability! Some other subtle factors must infer in the overall molecular stability. At the end, note the high correlation ($R^2 = 0.976$) of our PM3 HFs with those supplied by the SCF Hartree-Fock (6-31G* basis set) calculations [14]. The estimated correlation of SCF HF by pv was 0.959.

CONCLUSIONS

The stability of fullerenes, as postulated by “isolated pentagon rule” IPR, was quantitatively expressed in terms of a layer matrix of valences LV invariant, calculated on the dual of the original molecular graph.

The equivalence classes of their vertices, edges and faces were found by using local invariants derived on the layer matrix of distance sum LDS, calculated on molecular graph, and its medial and dual, respectively. The equivalence of edges/bonds and faces may be important in predicting the products of addition reactions of fullerenes while that of vertices/atoms in simulating the ¹³C NMR spectra.

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