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OMEGA POLYNOMIAL FOR NANOSTRUCTURES DESIGNED BY $(P_4)^k$Le OPERATIONS

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ABSTRACT. New cages are designed by repeating P_4 map operation and finalized by Le operation. The energy of some small non-classical fullerenes, tessellated according to above sequences of map operations was evaluated at the level of semiempirical method PM3. The topology of the networks is described in terms of Omega counting polynomial. Close formulas for this polynomial and the Cluj-Ilmenau index derived from it, as well as formulas to calculate the net parameters, are given.

Keywords: *Counting polynomial, CI index, non-classical fullerenes.*

INTRODUCTION

It is well established that covering/tessellation of fullerenes (nanostructures, in general) dictates the stability and reactivity of these molecules [1-3]. Covering and its modifications enables understanding of chemical reactions (their regioselectivity) occurring in nanostructures, particularly in carbon allotropes. In this respect, TOPO GROUP Cluj has developed some software programs [1], based on either well-known or original map operations [4-7]. A map M is a discretized (closed) surface [1].

We recall here the only two operations used in designing the proposed tessellation of the cages derived from the Platonic solids: tetrahedron T, octahedron Oct, Cube C, dodecahedron Do and icosahedron Ico.

Polygonal P_4 mapping is achieved by adding a new vertex in the center of each face and one point on the boundary edges; next, connecting the central point with one vertex on each edge, results in quadrilaterals covering [1,6].

Leapfrog Le is a composite operation, firstly described by Eberhard (1891) [8] and next by Fowler [9] and Diudea [6], that can be achieved as follows: add a point in the center of each face and join it with all the corners of a face, next truncate this point together with the edges incident in it (Figure 1). The original face will appear twisted by π/s, (s being the folding of the original face) and surrounded by polygons of 2d0 folding, where d0 is the degree of the parent vertices (in a regular graph).

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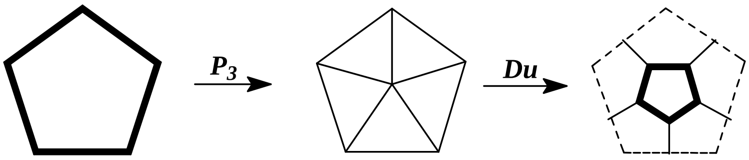


Figure 1. The Leapfrog *Le* operation on a pentagonal face

If the parent cage is a d_0 regular graph, the number of vertices in *Le*(M) is d_0 times larger than in the original map M, irrespective of the tessellation type. Note that in *Le*(M) the vertex degree is *always* 3, as a consequence of the involved triangulation P_3. In other words, the dual Du of a triangulation is a *cubic net* [2]. It is also true that truncation always provides a trivalent map. The leapfrog operation can be used to insulate the parent faces by surrounding (most often hexagonal) polygons.

CAGE BUILDING

Cages are built up, starting from the Platonic solids, by repeating the P_4 operation and finalized by Le operation; the sequence [10] of operations can be written as $Le(P_4(\mathrm{M}))^k)$. Due to dual pairs: Tetrahedron-Tetrahedron, T-T; Cube-Octahedron, C-Oct and Dodecahedron-Icosahedron, Do-Ico, there will be only three series of transformed cages (Figures 2 to 4, non-optimized). One can see that the central face/ring (in red) is twice the folding of parent face; similarly, the corner face (in blue) is twice the degree d_0 of parent vertices. These faces are distanced to each other by squares and octagons. The counting of faces/rings will be given below by the Ring polynomial [1].

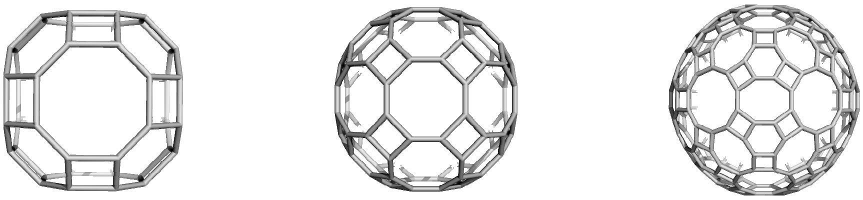
Figure 2. $Le(P_4(\mathrm{T}))^2)$; v=192 ; 3D-vue (left) and orthoscopic vue (right)

Figure 3. 3D-vue of $Le(P_4(\mathrm{C}))^2)$; v=192 ; (left) and $Le(P_4(\mathrm{Oct}))^2)$; v=192 ; (right)

Figure 4. 3D-vue of $Le(P_4(\mathrm{Do}))^2)$; v=960 ; (left) and $Le(P_4(\mathrm{Ico}))^2)$; v=960 ; (right)

ENERGETIC STABILITY

The calculations reported here were done at PM3 level of theory and serve only as arguments for the topological description of the interesting cages built up by $Le((P_4(M))^k)$ sequence of operations. Data, for the smallest representatives of this series (Figure 5) are listed in Table 1; for comparison, data for C_{60}, are also given.



Le(P_4(T)) Le(P_4(C)) Le(P_4(Do))

Figure 5. The smallest cages built up by $Le((P_4(M))^k)$.

It can be seen that the proposed cages show a moderate stability (by the values of heat of formation per number of atoms HF/N and HOMO-LUMO gap HLGAP), lower than that of C_{60}, the reference structure in nanoscience [1].

Regarding aromaticity, even C_{60} shows a low value of the geometry-based HOMA (harmonic oscillator model of aromaticity) index [11-13]; the new cages appear as anti-aromatic and this result is in agreement with the massive presence in structure of anti-aromatic faces f_4 and f_8, along with some aromatic f_6 and f_{10} (cf. Hückel theory) [14-16].

Table 1. Data for structures built up by $(P_4)^k$Le and C_{60}; heat of formation per number of atoms HF/N; HOMO-LUMO gap HLGAP; point group symmetry Sym

	Name	N atoms	HF/N (kcal/mol)	HLGAP (eV)	Sym.	HOMA	POAV1
1	Le(P_4(T))	48	24.386	5.948	O_h	-0.871	9.457
2	Le(P_4(C))	96	20.633	5.917	O_h	-0.868	4.831
3	Le(P_4(Do))	240	19.597	6.047	I_h	-0.879	2.067
4	C_{60}	60	13.514	6.596	I_h	0.169	8.257

The last column in Table 1 refers to the strain of cage covering, in terms of Haddon's theory [17-19]. Clearly, the larger cage is the most relaxed structure and this is supported by the lowest value of HF/N.

Computations were done by MOPAC2009 software package [20]. Calculations at a higher level of quantum chemistry are in progress in our lab.

OMEGA POLYNOMIAL

In a connected graph *G*(*V*,*E*), with the vertex set *V*(*G*) and edge set *E*(*G*), two edges *e = uv* and *f = xy* of *G* are called *codistant e co f* if they obey the relation [21]:

$$d(v,x)=d(v,y)+1=d(u,x)+1=d(u,y) \quad (1)$$

which is reflexive, that is, *e co e* holds for any edge *e* of *G*, and symmetric, if *e co f* then *f co e*. In general, relation *co* is not transitive; if "*co*" is also transitive, thus it is an equivalence relation, then *G* is called a *co-graph* and the set of edges $C(e) := \{ f \in E(G);\ f \ co\ e\}$ is called an *orthogonal cut oc* of *G*, *E*(*G*) being the union of disjoint orthogonal cuts: $E(G)=C_1 \cup C_2 \cup ... \cup C_k,\ C_i \cap C_j = \varnothing, i \neq j$. Klavžar [22] has shown that relation *co* is a theta Djoković-Winkler relation [23,24].

We say that edges *e* and *f* of a plane graph *G* are in relation *opposite, e op f,* if they are opposite edges of an inner face of *G*. Note that the relation *co* is defined in the whole graph while *op* is defined only in faces. Using the relation *op* we can partition the edge set of *G* into *opposite* edge *strips, ops.* An *ops* is a quasi-orthogonal cut *qoc*, since *ops* is not transitive.

Let *G* be a connected graph and $s_1, s_2, ..., s_k$ be the *ops* strips of *G*. Then the *ops* strips form a partition of *E(G)*. The length of *ops* is taken as maximum. It depends on the size of the maximum fold face/ring F_{max}/R_{max} considered, so that any result on Omega polynomial will have this specification.

Denote by *m*(*G*,*s*) the number of *ops* of length *s* and define the Omega polynomial as [25-33]:

$$\Omega(G,x)=\sum\nolimits_s m(G,s)\cdot x^s \quad (2)$$

Its first derivative (in *x*=1) equals the number of edges in the graph:

$$\Omega'(G,1)=\sum\nolimits_s m(G,s)\cdot s=e=\left|E(G)\right| \quad (3)$$

On Omega polynomial, the Cluj-Ilmenau index [21], *CI*=*CI*(*G*), was defined:

$$CI(G)=\left\{[\Omega'(G,1)]^2-[\Omega'(G,1)+\Omega''(G,1)]\right\} \quad (4)$$

RESULTS AND DISCUSSION

Cage parameters

Since the starting cages of this study are the graphs of Platonic solids, let's present the net parameters of these structures in Table 2, as $|p_0|$ parameters, p being vertices v (of degree d), edges e and faces f (of various folding s). By applying the sequence of operations $Le(P_4(M))^k)$, the transformed maps will show all the vertex degree d=3. Formulas for the value of the other parameters are given in Table 3. Observe, in the dual pair, the face of parent becomes the vertex of transform and this interchanging operates also on the corresponding parameters: s_0f_0 becomes d_0v_0, while the number of edges remains unchanged.

Table 2. Platonic solid graph parameters

Graph	Vertices $\|v_0\|$	Degree d_0	Edges $\|e_0\|$	Ring folding s_0	Faces $\|f_0\|$
T	4	3	6	3	4
C	8	3	12	4	6
Oct	6	4	12	3	8
Do	20	3	30	5	12
Ico	12	5	30	3	20

Table 3. Transforms of the Platonic solid graphs by *Le*(P_4(M))^k)

M	Vertices $\|v_0\|$	Edges $\|e_0\|$	Faces $\|f_0\|$
T	12×4^k	18×4^k	$6\times4^k+2$
C	24×4^k	36×4^k	$12\times4^k+2$
Do	60×4^k	90×4^k	$30\times4^k+2$
Formula	$\|v\|=4^k\times s_0f_0$	$\|e\|=3\times4^k\times e_0$	$\|f\|=4^k\times e_0+2$
Oct	24×4^k	36×4^k	$12\times4^k+2$
Ico	60×4^k	90×4^k	$30\times4^k+2$
Formula	$\|v\|=4^k\times d_0v_0$	$\|e\|=3\times4^k\times e_0$	$\|f\|=4^k\times e_0+2$

Ring polynomial

The ring polynomial for the graphs originating in trivalent Platonics is as follows:

$$R(Le((P_4(\mathrm{T}))^k),x)=\left(3\times4^a\right)x^4+8x^6+\left(3\times4^a-6\right)x^8 \tag{5}$$

$$R(Le((P_4(\mathrm{C}))^k),x)=\left(6\times4^a\right)x^4+8x^6+\left(6\times4^a-6\right)x^8 \tag{6}$$

$$R(Le((P_4(\mathrm{Do}))^k),x)=\left(15\times4^a\right)x^4+20\,x^6+\left(15\times4^a-30\right)x^8+12\,x^{10} \tag{7}$$

Generalizing, for the graphs transformed from the trivalent Platonics, the formula for ring polynomial is of the form:

$$\begin{aligned}R(Le((P_4(G(d_0:3)))^k),x)=&\left(s_0f_0\times2^{2(k-1)}\right)x^4+v_0x^6+\\&\left(s_0f_0\times2^{k-1}(2^{k-1}-1)+e_0(2^k-1)\right)x^8+f_0\;x^{2s_0}\end{aligned} \tag{8}$$

Now, considering the relation between the dual pairs, for the trigonal Platonics we have:

$$\begin{aligned}R(Le((P_4(G(f_0:3)))^k),x)=&\left(d_0v_0\times2^{2(k-1)}\right)x^4+f_0x^6+\\&\left(d_0v_0\times2^{k-1}(2^{k-1}-1)+e_0(2^k-1)\right)x^8+v_0\;x^{2d_0}\end{aligned} \tag{9}$$

Omega Polynomial

The Omega polynomial (calculated at R_{max}[8]) for the graphs transformed from the trivalent Platonics is as follows:

$$\Omega(Le((P_4(\mathrm{T}))^k),x)=\left(3(2^k-1)+6\right)x^{2^{k+2}}+4(2^{k-1}-1)\,x^{3\times 2^k} \quad (10)$$

$$\Omega(Le((P_4(\mathrm{C}))^k),x)=\left(4(2^k-1)+6\right)x^{3\times 2^{k+1}}+\left(6(2^{k-1}-1)+3\right)x^{2^{k+2}} \quad (11)$$

$$\Omega(Le((P_4(\mathrm{Do}))^k),x,R[8])=6(2^k-1)\,x^{5\times 2^{k+1}}+12(2^{k-1}-1)\,x^{5\times 2^k}+15\,x^{2^{k+3}} \quad (12)$$

Generalizing, we have:

$$\begin{aligned}\Omega(Le((P_4(\mathrm{G}))^k),x)=&\left(f_0(2^{k-1}-1)+3\frac{1+(-1)^{s_0}}{2}\right)x^{s_0\times 2^k}+\\ &\left(s_0+\left\lfloor\frac{s_0+1}{6}\right\rfloor\right)(2^k-1)\,x^{\left(s_0+\left\lfloor\frac{s_0+1}{6}\right\rfloor-1\right)\times 2^{k+1}}+\frac{e_0}{\left\lceil\frac{s_0}{3}\right\rceil}x^{(s_0-1)\times 2^{k+1}}\end{aligned} \quad (13)$$

And for *CI* we have:

$$CI\ (Le((P_4(\mathrm{T}))^k))=324\cdot 4^{2k}-6\cdot 4^k(11\cdot 2^k-1)-18\cdot 4^k \quad (14)$$

$$CI\ (Le((P_4(\mathrm{C}))^k))=1296\cdot 4^{2k}-12\cdot 4^k(16\cdot 2^k-1)-36\cdot 4^k \quad (15)$$

$$CI\ (Le((P_4(\mathrm{Do}))^k))=8100\cdot 4^{2k}-30\cdot 4^k(25\cdot 2^k-1)-90\cdot 4^k \quad (16)$$

The Omega polynomial, calculated at R_{max}=10, in case M=Do, is as follows.

$$\begin{aligned}\Omega(Le((P_4(\mathrm{Do}))^k),x,R[10])=&\,6(k^2-p-2)\cdot x^{5(k^2-p)}+15\cdot x^{2^k+3}+\\ &6(k^2-p-1)\cdot x^{10(k^2-p)}\end{aligned} \quad (17)$$

$$\Omega'(Le((P_4(\mathrm{Do}))^k),1,R[10])=120p-180k^2p+120\cdot 2^k-120k^2+90k^4+90p^2 \quad (18)$$

$$\begin{aligned}CI(Le((P_4(\mathrm{Do}))^k),R[10])=&\,2250k^4p-1800k^2p+900k^4-750k^6+\\ &900p^2+750p^3-2250k^2p^2-960\cdot 2^{2k}+(\Omega'(Le((P_4(\mathrm{Do}))^k),1,R[10]))^2\end{aligned} \quad (19)$$

Table 4 lists some examples for the formulas derived within this paper. Computations were made by Nano Studio software [34].

Table 4. Examples for the herein derived formulas

***Le*((P$_4$(M))^k)** **M ; k ; R$_{max}$**	**V**	**Omega polynomial**	**CI**	**Ring polynomial**
T; k=3 ; R[8]	768	$12x^{24}+27x^{32}$	1292544	$192x^{4}+8x^{6}+210x^{8}$
C; k=3 ; R[8]	1536	$21x^{32}+34x^{48}$	5208576	$384x\hat{\ }4+8x^{6}+402x^{8}$
Do; k=3;R[8]	3840	$30x^{8}+30x^{24}+36x^{40}+42x^{80}$	32832000	$960x^{4}+20x^{6}+930x^{8}+12x^{10}$
Do; k=3;R[10]		$36x^{40}+15x^{64}+42x^{80}$	32789760	
T; k=4; R[8]	3072	$28x^{48}+51x^{64}$	20960256	$768x^{4}+8x^{6}+786x^{8}$
C; k=4; R[8]	6144	$45x^{64}+66x^{96}$	84142080	$1536x^{4}+8x^{6}+1554x^{8}$
Do; k=4; R[8]	15360	$30x^{16}+30x^{48}+84x^{80}+90x^{160}$	527923200	$3840x^{4}+20x^{6}+3810x^{8}+12x^{10}$
Do; k=4; R[10]		$84x^{80}+15x^{128}+90x^{160}$	527754240	

CONCLUSIONS

In this article, new cages designed by $Le((P_4(M))^k)$ sequence of map operations are reported. The energy of some small non-classical fullerenes, tessellated according to the above map operations was evaluated at the level of semiempirical method PM3; it was shown that these non-classical fullerenes have a moderate stability, less than the reference C60 fullerene, a result pertinent for a tessellation with massive anti-aromatic faces R_4 and R_8. The topology of the networks was described in terms of Omega counting polynomial. Close formulas for this polynomial and the Cluj-Ilmenau index, as well as formulas to calculate the net parameters, were given.

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