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Omega Polynomial in Azulenic Dendrimers•

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Abstract

Azulene is a homoaromatic bicycle, isoelectronic with naphthalene. Azulenic patterns have been studied in Mathematical Chemistry in connection with ((5,7)3) coverings, eventually involved in the metallic character of some nanotubes. Dendrimers are hyper-branched nano-structures with rigorously tailored architecture. In this paper, dendrimers designed by monomeric units containing disjoint azulenic patterns are studied. Consequently, a precise topological description of such structures is needed and it is achieved in terms of Omega polynomial $\Omega(G,x)$. Formulas for counting the number of atoms and monomers in dendrimers grown at various generations are also given.

•This paper is dedicated to Edward C. Kirby, The Resource Use Institute, Pitlochry, Perthshire, Scotland, UK, for his bright contribution to the development of Chemical Graph Theory.

1. Introduction

A set of disjoint faces of a trivalent polyhedral map M, forming a 2-factor (*i.e.*, a regular 2-valent spanning subgraph built up on all vertices of a polyhedral map M), is called a perfect Clar PC structure.[1-3] It is complementary to a Fries structure,[4] which is a Kekulé structure having the maximum possible (v/3) number of benzenoid (alternating single-double edge) faces. A Kekulé structure is a set of pairwise disjoint edges/bonds of the molecule (over all its atoms) that coincides with a perfect matching and a 1-factor[5] in Graph Theory. A trivalent polyhedral graph, like that of fullerenes, has a PC structure if and only if it has a Fries structure.[1] Such structures represent *total resonant sextet* TRS benzenoid molecules and it is expected to be extremely stable, according to the VB theory.[6,7]

Figure 1 illustrates two PC structures embedded in the sphere (g=0) and the open tetrahedron (g=2). In the above, g is the genus of a surface, meaning the number of hollows to be added to the sphere to make it homeomorphic to a given surface; also, g is the number of simple tori on the given surface.

(a) $Le_{2,2}$(D); v = 240; g = 0
(as 2-factor (5,6))

(b) $Le_{2,2}$(Op(Ca(T))); v = 264; g = 2
(as 2-factor (6,7))

Figure 1. Disjoint faces embedded in the sphere (a) and (open) tetrahedron (b)

Patterns other than benzene: naphthalene, coronene, sumanene or azulene (*i.e.*, a pair of pentagonal-heptagonal carbon rings) have also been considered.[6,8,9] Disjoint faces can be embedded on the sphere (in surfaces of various genera, see Figure 1) by map operations,[10-14] as implemented in our original software CageVersatile.[15]

Dendrimers are hyper-branched macromolecules, with a rigorous, aesthetically appealing architecture.[16-22] They can be synthesized, in a controlled manner, either by divergent methods of by convergent ones. A self-assembly process would be expected for dendrimers (if any) obtainable by aggregation of vaporized graphite.

These rigorously tailored structures reach rather soon a spherical shape, thus stopping the raising process. The size of dendrimers is in the nanometer scale. The endgroups (*i.e.*, the groups reaching the outer periphery) can be functionalized, thus modifying their physico-chemical or biological properties. Dendrimers have gained a wide range of applications in supra-molecular chemistry, particularly in host-guest reactions and self-assembly processes but also biological applications, e.g., as gene transfer vectors.[23,24]

Studies on Molecular Topology of dendrimers include vertex and fragment enumeration[25] as well as calculation of some topological descriptors, such as topological indices or polynomials.[26,27]

The present work aims to describe a dendritic azulenic polymer in terms of Omega polynomial. The article is organized as follows: The second section introduces to the building and topology of azulenic monomers up to the dendrimer stage. The third section provides the definition of Omega polynomial while the forth one details the monomeric contributions to the global polynomial, in these hypothetical dendrimers. Conclusions and references will close the article.

2. Azulenic structures

Azulene[28-31] $C_{10}H_8$ is a 5,7 homoaromatic bicycle, isoelectronic with the naphthalene, to which can rearrange by heating, but it is blue in color, and its physico-chemical properties differ from those of naphthalene. Azulenic patters were extensively studied by Kirby.[32] A total resonant azulenoid structure was defined as a carbon network with at least one Kekulé structure equivalent to a set of azulene units all interconnected by essentially single bonds. It is the realization of a graph *G* that everywhere is locally planar and allows a 2-factor of disjoint 10-cycles, defined on every vertex.

The pattern generated by the sequence of map operations: *Op*(*Le*(*Op*(*Ca*(*M*)))) is a disjoint azulenoid, obeying the Kirby's definition. Figure 2 illustrates an azulenic Azu pattern and its complement (a tri-naphthylenic TNP pattern) embedded in the tetrahedron.

(a) *Op*(*Le*(*Op*(*Ca*(*T*)))) ; Azu
$v = 120$; $e = 174$; $f = 52$; $g = 2$

(b) *Op*(*Le*(*Op*(*Ca*(*T*)))); TNP

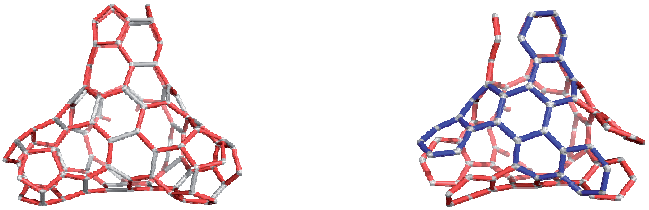

Figure 2. Azulenic pattern (a) and its tri-naphthylenic co-patern (b)

A unit like that in Figure 2a, can join itself to give either a linear structure (Figure 3a) or a supra-dodecahedron (Figure 3b), or can arrange in a dendritic tree, of progressive degree p=3 (Figure 4).

(a) Infinite Azu linear structure
$v = 600$

(b) Supra-dodecahedron by Azu units
$v = 2400$; $g = 21$

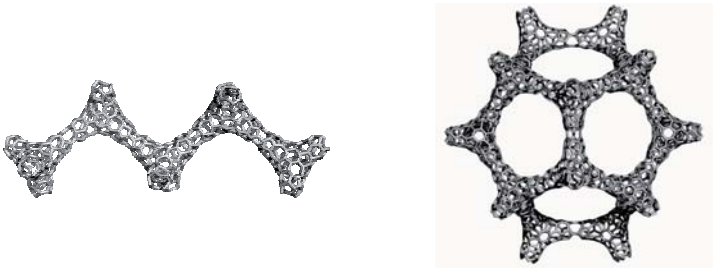

Figure 3. Two possible ways in evolution of the azulenic unit in Figure 2a.

(a) Monocentric Azu dendrimer; v=600; m=5 (b) Dicentric Azu dendrimer; v=960; m= 8

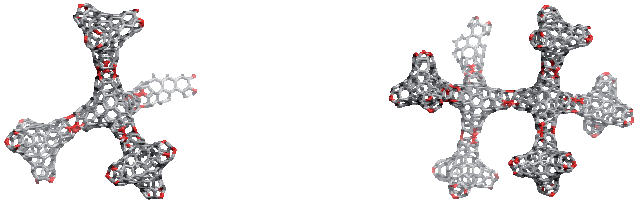

Figure 4. Monocentric (a) and dicentric (b) azulenic dendrimers, at the first generation stage.

3. Omega polynomial

Counting of monomeric units and their consisting substructures is the subject of Chemical Graph Theory. Several counting polynomials have been proposed for characterizing the topology of nanostructures, particularly of dendrimers.

Let $G(V,E)$ be a connected bipartite graph, with the vertex set $V(G)$ and edge set $E(G)$. Two edges $e = (x,y)$ and $f = (u,v)$ of G are called "opposite": e *op* f if they are topologically parallel:

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

A set of opposite edges $C(e) := \{f \in E(G); f \; op \; e\}$ within the same face/ring eventually forming a strip of adjacent faces/rings, is called an opposite edge strip *ops*. Under *ops* closure, $E(G)$ is the union of disjoint ops: $C_1 \cup C_2 \cup ... \cup C_k$ and $Ci \cap Cj = \emptyset$ for $i \neq j, i, j = 1,2,..,k$. The relation *ops* is not necessarily transitive.

Let $m(G,c)$ be the number of *ops* of length c; Omega polynomial[33] is defined as:

$$\Omega(G,x) = \sum_c m(G,c) \cdot x^c \quad (2)$$

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

$$\Omega'(G,1) = \sum_c m(G,c) \cdot c = e = |E(G)| \quad (3)$$

A topological index, called Cluj-Ilmenau,[34] CI=$CI(G)$, was defined on Omega polynomial:

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

It is easily seen that, for a single *ops*, one calculates the polynomial: $\Omega(G,x) = 1 \times x^c$ and the index $CI(G) = c^2 - (c + c(c-1)) = c^2 - c^2 = 0$.

In tree graphs, the Omega polynomial simply counts the non-opposite edges, being included in the term of exponent c=1. More about Omega polynomial the reader can find in refs.[35,36]

4. Omega polynomial in nano-dendrimers

The Omega polynomial strictly follows the polygonal covering of structure and consists of four terms. The term at the highest exponent c=6 counts the opposite edges between two joined tetrapodal units/monomers m (Figure 5), the number of such strips being 3; it follows that a_6=3(m-1). Next term, at c=3, counts naphthylenic units related to the trinaphthylenes (Figure 2b), six for each face of the tetrahedron and three shared between two faces, 6×4+3/2×4=30, while accounting for the bonded branches and cross-junction, a_3=5(5m+1).

The term at c=2, accounts for isolated opposite edges, being 2×3×4=24 in one monomer, to which 6 strips are added for each junction, to give a_2=6(5m-1). Finally, the non-opposite edges are counted: 3×3×4=36 per unit, and a_1=12(12m+1). Formulas are listed in Table.

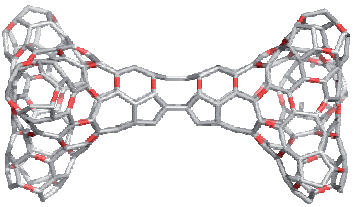

Figure 5. Dicentric azulenic *Azu* dendrimer,
at generation r=0; v=240; m=2; strip c=6

Table. Composition rules for Omega polynomial in Azu-dendrimers designed by *Op*(*Le*(*Op*(*Ca*(*T*)))) operations.

	Formulas
1	$\Omega(\mathrm{D}_{azu},x)=a_1X^1+a_2X2+a_3X^3+a_6X^6$
2	$CI(\mathrm{D}_{azu})=[\Omega'(\mathrm{D})]^2-[\Omega'(\mathrm{D})+\Omega''(\mathrm{D})]$
	Monocentric Dendrimer
3	$\Omega(\mathrm{D}_{\mathrm{azu}},m,x)=12(2m+1)X^1+6(5m-1)X^2+5(5m+1)X^3+3(m-1)X^6$
4	$\Omega'(\mathrm{D}_{\mathrm{azu}},1)=177m-3\,;\ \Omega''(\mathrm{D}_{\mathrm{azu}},1)=300m-72$
5	$CI(\mathrm{D}_{\mathrm{azu}})=31329m^2-1539m+84$
6	$v(\mathrm{D}_{\mathrm{azu}})=120m$
7	$R[6](\mathrm{D}_{\mathrm{azu}})=28m\,;\ R[5,7](\mathrm{D}_{\mathrm{azu}})=12m\,;\ R[8](\mathrm{D}_{\mathrm{azu}})=3(m-1)$
	Dicentric Dendrimer
8	$\Omega(\mathrm{D}_{\mathrm{azu}},m,x)=12(2m+1)X^1+6(5m-1)X^2+5(5m+1)X^3+3(m-1)X^6$ $\Omega(\mathrm{D}_{\mathrm{azu}},k,x)=12(2\cdot3^k-1)X^1+9(10\cdot3^{k-1}-4)X^2+5(15\cdot3^{k-1}-4)X^3+3(3^k-2)X^6$
	Number of monomers *m* at the stage/generation *r*
9	$m(\mathrm{D}(p,r))=1+(p+1)\sum_{i=1}^{r}p^{i-1}=\frac{2(p^{r+1}-1)}{p-1}-p^r$ $m(\mathrm{MD}_{\mathrm{azu}})=2\cdot3^r-1\,;\ m(\mathrm{DD}_{\mathrm{azu}})=3^{r+1}-1\,;\ p=3;r=k-1;k=1,2,3,...$

It can be seen that the Omega polynomial is calculated by the same formula for monocentric and dicentric azu-dendrimers, difference is made by the meaning of m, the number of monomer units is different, as given by the formulas in row 9. A formula function of integer *k* (related to the generations *r* in dendrimers) is given for the dicentric dendrimer (Table, row 8).

The reader in invited to consult our recent book[37] for a gallery of such junctions. Note worthy, these monomers, in the form of hydrogenated ends, show excellent stability (total energy, HOMO-LUMO gap, strain and aromaticity), originating in the coronene moiety/flower; their structure shows a perfect Clar PC structure and an associate Fries structure (see Figure 2), both predicting a particular stability for such dendrimers. These results, which could be attractive for synthesists, will be published in a future article. Numerical evaluation of Omega polynomial was made by our software program Omega counter.[38]

5. Conclusions

Dendrimers are highly ordered hyper-branched structures at the nano-dimensions. Complex nano-dendrimers can be designed by using sequences of map operations. Composition of the global polynomial function of monomeric contributions was derived for both mono- and di-centric dendrimers, according to their topology. Counting formulas for the number of monomers in dendrimers grown at various generations were also given.

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