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Enumeration of IPR hetero-fullerenes $C_{34\times 3^n}$ constructed by leapfrog principle

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Hetero-fullerenes are fullerene molecules in which one or more carbon atoms are replaced by hetero-atoms such as boron or nitrogen, whose formation is a kind of “on-ball” doping of the fullerene cage. In this paper by using the Pólya's theorem we compute the number of possible positional isomers and chiral isomers of the hetero-fullerenes.

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1. Introduction

A graph is a collection of points and lines connecting them. The points and lines of a graph are also called vertices and edges respectively. If e is an edge of G, connecting the vertices u and v, then we write e = uv and say "u and v are adjacent". A connected graph is a graph such that there exists a path between all pairs of vertices.

A molecular graph is a simple graph such that its vertices correspond to the atoms and the edges to the bonds. Note that hydrogen atoms are often omitted. According to the IUPAC terminology, a topological index is a numerical value associated with chemical constitution which can be then used for correlation of chemical structure with various physical and chemical properties, chemical reactivity and biological activity.

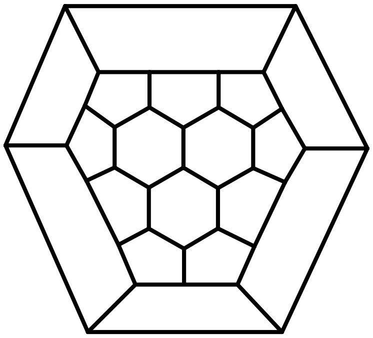
Fullerenes are carbon-cage molecules in which a large number of carbon (C) atoms are bonded in a nearly spherically symmetric configuration which was discovered for the first time in 1985.[1] By the Euler’s formula one can see that every fullerene graph with n vertices has exactly 12 pentagonal and (n/2 – 10) hexagonal faces, where $n \neq 22$ is a natural number equal or greater than 20.[2,3] Hetero-fullerenes are fullerene molecules in which one or more carbon atoms are replaced by hetero-atoms such as boron or nitrogen, whose formation is a kind of “on-ball” doping of the fullerene cage.

Stellation St of a graph consists of adding a new vertex in the center of its faces followed by connecting it with each boundary vertex. It is also called a capping operation or triangulation.[4,5]

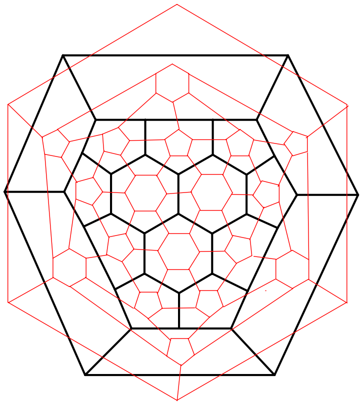
Dualization Du of a map can be achieved by locating a point in each of its faces. Two such points are joined if their corresponding faces share a common edge. The new edge is called the edge dual Du(e) and the transformed map, the dual Du(M). The vertices of Du(M) represent the faces of M and vice-versa. Leapfrog Le is a composite operation. It can be written as:

$$Le = Du(St(M))$$

In [6] and [7] a method is described how to construct a fullerene C_{3n} from a fullerene C_n having the same or even a bigger symmetry group as C_n. This method is called the Leapfrog principle. The Leapfrog fullerene has 3n vertices 12 pentagonal and (3n/2)-10 hexagonal faces. Knowing the 3-dimensional cycle index of $S(C_n)$ acting on the sets of vertices, edges and faces it is very easy to compute the cycle index for the induced action of $S(C_n)$ on the set of vertices of C_{3n}. We just have to identify the vertices of C_n with the n new hexagonal faces of C_{3n}.[7] From Fig. 1, one can see that $Le(C_{34}) = C_{102}$.



C_{34} Fullerene



$Le(C_{34}) = C_{102}$
Fig. 1. The Fullerene C_{34} and $Le(C_{102})$.

Detecting symmetry of molecules is a well-studied problem with applications in a large number of areas. Randic[8,9] and then Balasubramanian[10-16] considered the Euclidean matrix of a chemical graph to find its symmetry. Here the Euclidean matrix of a molecular graph G is a matrix D(G) = $[d_{ij}]$, where for $i \neq j$, d_{ij} is the Euclidean distance between the nuclei *i* and *j*. In this matrix d_{ii} can be taken as zero if all the nuclei are equivalent. Otherwise, one may introduce different weights for different nuclei.

Suppose σ is a permutation on *n* atoms of the molecule under consideration. Then the permutation matrix P_σ is defines as $P_\sigma = [x_{ij}]$, where $x_{ij} = 1$ if $i = \sigma(j)$ and 0 otherwise. It is easy to see that $P_\sigma P_\tau = P_{\sigma\tau}$, for any two permutations σ and τ on *n* objects, and so the set of all $n \times n$ permutation matrices is a group isomorphic to the symmetric group S_n on *n* symbols. It is a well-known fact that a permutation σ of the vertices of a graph G belongs to its automorphism group if it satisfies $P_\sigma{}^t A P_\sigma = A$, where A is the adjacency matrix of G. So, for computing the symmetry of a molecule, it is sufficient to solve the matrix equation $P^tEP = E$, where E is the Euclidean matrix of the molecule under consideration and P varies on the set of all permutation matrices with the same dimension as E.

Balasubramanian has done a lot of work on methods for isomer counting of hetero-fullerenes and of poly-substituted fullerenes, especially, using the generalized character cycle index. Mathematically the isomer counting of poly-substituted fullerene is essentially the same as that of hetero-fullerene. Shao and Jiang[17] discussed hydrogenated C_{60}. Furthermore, Zhang[18] also studied the fullerene cages. Ashrafi et al.[7] computed chiral isomers of a class of IPR hetero-fullerenes, namely $C_{3^n\times 20}$. In this paper we compute the number of hetero-fullerenes $C_{3^n\times 34}$.

2. Main results

Groups are often used to describe symmetries of objects. This is formalized by the notion of a group action. Let G be a group and X a nonempty set. An action of G on X is denoted by G_X and X is called a G-set. It induces a group homomorphism φ from G into the symmetric group S_X on X, where φ(g)x = gx for all x ∈ X. The orbit of x will be denoted by Gx and defines as the set of all φ(g)x, g ∈ G. The set of all G-orbits will be denoted by G\\X : = { Gx | x ∈ X}. Suppose g is a permutation of n symbols with exactly λ_1 orbits of size 1, λ_2 orbits of size 2, …, and λ_n orbits of size n. Then the cycle type of g is defined as $1^{\lambda_1}2^{\lambda_2}\ldots n^{\lambda_n}$.

We now introduce the notion of cycle index. Let G be a permutation group. The cycle index of G acting on X is the polynomial Z(G, X) over Q in terms of indeterminates $x_1, x_2, \ldots, x_t$, $t = |X|$, defined by $Z(G, X) = \frac{1}{|G|}\sum_{p\in G}\prod_{i=1}^{t} x_i^{c_i(p)}$, in which $(c_1(p), \cdots, c_t(p))$ is the cycle type of the permutation p ∈ G. The generalized character cycle index is defined as $P_G^{\chi}(x_1, x_2, \ldots, x_t) = \frac{1}{|G|}\sum_{p\in G}\prod_{i=1}^{t}\chi(p)x_i^{c_i(p)}$, where χ(*g*) is the linear character of the irreducible representation of *G*. In this paper we use two special cases: One is the anti-symmetric representation, that is

$$\chi(g) = \begin{cases} 1 & if\ \ g\ is\ a\ proper\ rotation, \\ -1 & if\ \ g\ is\ an\ improper\ rotation, \end{cases}$$

and the other when χ is 1 for all *g*. Since, all elements of a conjugacy class of a permutation group have the same cycle type, so the cycle index and the generalized character cycle index can be rephrased in the following way:

$$Z(G, x_1, \ldots, x_t) = \frac{1}{|G|}\sum_{C\in Conj(G)}|C|\prod_{i=1}^{t} x_i^{c_i(g_C)},$$

$$P_G^{\chi}(x_1, \ldots, x_t) = \frac{1}{|G|}\sum_{C\in Conj(G)}|C|\prod_{i=1}^{t}\chi(g_c)x_i^{c_i(g_C)}.$$

Enumeration of chemical compounds has been accomplished by various methods. The Polya-Redfield theorem has been a standard method for combinatorial enumerations of graphs, polyhedra, chemical compounds, and so forth. Combinatorial enumerations have found a wide-ranging application in chemistry, since chemical structural formulas can be regarded as graphs or three-dimensional objects.

Denote by $C_{m,n}$ the set of all functions f: {1, 2, …, m} → {$x_1, x_2, \ldots, x_n$}. The action of p ∈ S_m induced on $C_{m,n}$ is defined by $\hat{p}(f) = fop^{-1}$, f ∈ $C_{m,n}$. Treating the colors $x_1, x_2, \ldots, x_n$ that comprise the range of f ∈ $C_{m,n}$ as, independent variables the weight of f is $W(f) = \prod_{i=1}^{m} f(i)$. Evidently, W(f) is a monomial of (total) degree m. Suppose G is a permutation group of degree m, $\hat{G} = \{\hat{p} : p \in G\}$, $\hat{p}$ is as defined above. Let $p_1, p_2, \ldots, p_t$ be representatives of the distinct orbits of $\hat{G}$. The weight of p_i is the common value of W(f), f ∈ p_i. The sum of the weights of the orbits is the pattern inventory $W_G(x_1,x_2,\ldots,x_n) = \sum_{i=1}^{t} W(p_i)$.

Theorem.1 (Pólya's Theorem[19]**)** If G is a subgroup of S_m, the symmetry group on m symbols, then the pattern inventory for the orbits of $C_{m,n}$ modula $\hat{G}$ is

$$W_G(x_1,x_2,\ldots,x_n) = \frac{1}{|G|}\sum_{p\in G} M_1^{C_1(p)} M_2^{C_2(p)} \ldots M_m^{C_m(p)},$$

where $M_k = x_1^k + x_2^k + \ldots + x_n^k$ is the kth power sum of the x's.

Theorem.2 (Generalization of Pólya's Theorem**)** Substituting M_i for x_i and in the generalized character cycle index, *i* = 1, 2, **…**, t, we get the chiral generating function $CGF = P_G^{\chi}(M_1, \ldots, M_k)$.

To enumerate all possibilities of the hetero-fullerene structures, we have to consider the rotation group of the fullerene, and its whole automorphism group to enumerate the number of chiral isomers. Fripertinger[20] computed the symmetry of some fullerenes and then applied SYMMETRICA[21] to calculate the number of $C_{60}H_kCl_{60-k}$

molecules and Balasubramanian computed the number of $C_{60}H_{36}$ isomers. F. Zhang et al.[18] for calculating the possibilities of different positional isomers used the Pólya's counting theorem. He also applied the generalization of the Pólya's theorem to compute the number of chiral isomers.

We are now ready to enumerate the number of hetero-fullerenes in a series of fullerenes constructed by leapfrog. From the above discussion our problem is reduced to the coloring of the corresponding fullerene graph with $3^n \times 20$ vertices. Consider the molecular graph of the fullerene $C_{3^n \times 20}$, Fig. 2. From leapfrog principle, one can see that the symmetry group G of these fullerenes is isomorphic to the group S_3 of order 6 and the cycle types of elements of G are as in the following table:

Fullerene	Cycle type	#Permutations
$C_{3^n \times 20}$	$1^{3^n \times 34}$	1
	$1^{6n} 2^{17\times 3^n - 3n}$	3
	$3^{3^{n-1} \times 34}$	2

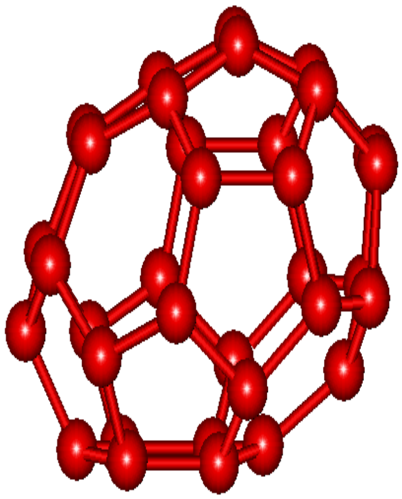


Fig. 2. The Fullerene C_{34}.

Thus the cycle index of G is computed as:

$$Z(G,X) = (x_1^{34\times 3^n} + 3x_1^{6n} x_2^{17\times 3^n - 3n} + 2x_3^{34\times 3^{n-1}})/6.$$

But from the cycle indices one can compute the number of possible positional isomers, the number of chiral isomers and the number of orbits under the whole point group I_h. For the number of orbits under the whole point group S_3, we simply note that $Z_{I_h} - P_{I_h}^{\chi} = P_{I_h}^{1}$.

We mention here that our computations of symmetry properties and cycle indices of fullerenes were carried out with the use of GAP[22]. This software was constructed by the GAP team in Aachen. In Table 1, we apply this software to compute the number of hetero- fullerenes for the case of $n = 1$.

Table 1. The number of $C_{34-k}B_k$ molecules.

k,34 -k	Number of $C_{34-k}B_k$ molecules for symmetry group
0,34	1
1,33	6
2,32	102
3,31	1001
4,30	7801
5,29	46376
6,28	224509
7,27	896621
8,26	3027224
9,25	8741931
10,24	21857839
11,23	47682960
12,22	91398638
13,21	154664070
14,20	232005664
15,19	309328074
16,18	367339214
17,17	388934370

3. Conclusions

In this paper an efficient method is presented which is useful for computing permutational isomers of hetero-fullerenes. We applied our method on C_{34} fullerene and compute the number of such isomers. From the cycle index of leapfrog of a series of fullerenes with S_3 point group symmetry, one can compute such numbers for all elements of the series.

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