Enumeration of a class of IPR hetero-fullerenes

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Abstract: Hetero-fullerenes are fullerenes in which some of the carbon atoms are replaced by other atoms. This paper uses the Pólya theorem to count the number of their possible positional isomers and chiral isomers. To do this, the computer algebra system GAP was applied to compute this number for a class of IPR hetero-fullerenes with I_h point group symmetry. These fullerenes were constructed by means of the leapfrog principle.

Keywords: fullerene; hetero-fullerene; Pólya theorem; cycle index.

INTRODUCTION

Carbon exists in several forms in nature. One is the so-called fullerenes, which were discovered for the first time in 1985.[1] Fullerenes are carbon-cage molecules in which a large number of carbon atoms are bonded in a nearly spherically symmetric configuration. Let p, h, n and m be the number of pentagons, hexagons, carbon atoms and bonds between them, respectively, in a given fullerene F. Since each atom lies in exactly 3 faces and each edge lies in 2 faces, the number of atoms $n = (5p + 6h)/3$, the number of edges $m = (5p + 6h)/2 = 3n/2$ and the number of faces $f = p + h$. By the Euler formula, $n - m + f = 2$, it can be deduced that $(5p + 6h)/3 – (5p + 6h)/2 + p + h = 2$ and, therefore, $p = 12$, $v = 2h + 20$ and $e = 3h + 30$. This implies that such molecules made up entirely of n carbon atoms and having 12 pentagonal and $(n/2 - 10)$ hexagonal faces, where $n \neq 22$, is a natural number equal or greater than 20.[2] Hetero-fullerenes are fullerene molecules in which one or more carbon atoms are replaced by hetero-atoms, such as boron or nitrogen, the formation of which is a kind of "on-ball" doping of the fullerene cage.

Detecting symmetry of molecules is a well-studied problem with applications in a large number of areas. Randic,[3,4] and then Balasubramanian,[5–11] considered the Euclidean matrix of a chemical graph to find its symmetry. Here the Euclidean matrix of a molecular graph G is a matrix $\mathbf{D}(G) = [d_{ij}]$, where for $i \neq j$,

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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, different weights for different nuclei may be introduced.

Suppose σ is a permutation on n atoms of the molecule under consideration. Then the permutation matrix $\mathbf{P}_\sigma$ is defined as $\mathbf{P}_\sigma = [x_{ij}]$, where $x_{ij} = 1$ if $i = \sigma(j)$ and 0 otherwise. It is easy to see that $\mathbf{P}_\sigma\mathbf{P}_\tau = \mathbf{P}_{\sigma\tau}$, for any two permutations σ and τ on n objects, and hence 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 $\mathbf{P}_\sigma{}^t A \mathbf{P}_\sigma = \mathbf{A}$, where $\mathbf{A}$ is the adjacency matrix of $\mathbf{G}$. Thus, for computing the symmetry of a molecule, it is sufficient to solve the matrix equation $P^t E P = \mathbf{E}$, where $\mathbf{E}$ is the Euclidean matrix of the molecule under consideration and P varies on the set of all permutation matrices with the same dimension as $\mathbf{E}$.

A method[12,13] has been described on 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. If one starts with a C_n cluster with icosahedral symmetry, all the new clusters will be of the same symmetry, since this is the biggest symmetry group in 3-dimensional space. In the first step, an extra vertex has to be put into the centre of each face of C_n. Then, these new vertices have to be connected with all the vertices surrounding the corresponding face. Then, the dual polyhedron is again a fullerene having 3_n 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}. One just has to identify the vertices of C_n with the n new hexagonal faces of C_{3n}.[14] From Fig. 1, it can be seen that $Le(C_{20}) = C_{60}$.

(a)   (b)
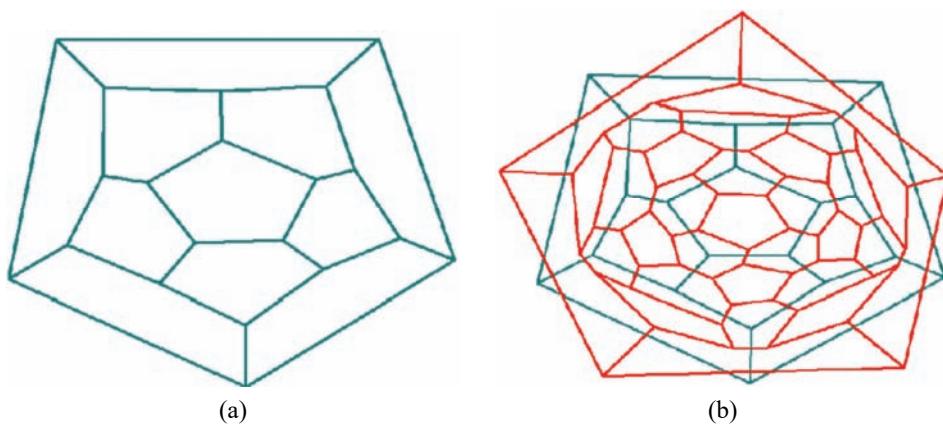
Fig. 1. The fullerene C_{20} (a) and $Le(C_{20})$ (b).

Balasubramanian[11] has re alized a lot o f work o n methods for isomer count-ing of hetero-fullerenes and of pol y-substituted full erenes, especially, using t he generalized character cycle index. Mathematically the isomer counting of poly -sub-stituted fullerene is essenti ally the sam e as that of hetero-fullerene. Shao and Ji -ang[15] discussed hy drogenated C_{60}. Furt hermore, Zhang[16] also studied fullerene cages. In this paper, the com pute nu mber of hetero-fullerenes, $C_{3^n \times 20}$, is co m-puted.

MAIN RESULT AND DISCUSSION

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 non-empty set. An ac-tion of G on X is denoted by G_X and X is called a G-set. It induces a group homo-morphism φ from G into the sy mmetric group S_X on X, where $\varphi(g)x = gx$ for al l $x \in X$. The orbit of x will b e denoted by Gx, which defines as a set all $\varphi(g)x$, $g \in G$. The set of al l G-orbits will be denoted by $G\backslash\backslash X := \{Gx \mid x \in X\}$. 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 $1^{\lambda_1}, 2^{\lambda_2}, ..., n^{\lambda_n}$.

Now, the no tion of a c ycle index is introduced. L et G be a perm utation group. The cy cle in dex of G acting on X is the pol ynomial $Z(G,X)$ over Q in terms of the indeterminates $x_1, x_2, …, x_t, t = |X|$, defined by:

$$Z(G,X) = \frac{1}{|G|} \sum_{p \in G} \prod_{i=1}^{t} x_i^{c_i(p)}$$

in which ($c_1(p), …, c_t(p)$) is the cy cle type of the perm utation $p \in G$. The gene-ralized character cycle index is defined as:

$$P_G^{\chi}(x_1, x_2, ..., x_t) = \frac{1}{|G|} \sum_{p \in G} \prod_{i=1}^{t} \chi(g) x_i^{c_i(p)}$$

where χ(g) is the linear character of the   irreducible r epresentation of G. In t his paper, two special cases are used: one is the anti-symmetric representation, that is:

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

and the other when χ is 1 for all g. Since, all ele ments of a conjugacy class of a permutation group have th e same cycle type, the cy cle index and the generalized character cycle index can be rephrased in the following way:

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

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$$P_G^{\chi}(x_1, x_2, ..., x_t) = \frac{1}{|G|} \sum_{C \in \text{Conj}(G)} |C| \prod_{i=1}^{t} \chi(g_C) x_i^{c_i(g_C)}$$

Enumeration of chemical compounds has been accomplished by various methods. The Pólya–Redfield theorem is a standard method for combinatorial enumerations of graphs, polyhedra, chemical compounds, *etc*. Combinatorial enumerations have found 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 $f : \{1, 2, ..., m\} \rightarrow \{x_1, x_2, ..., x_n\}$. The action of $p \in S_m$ *induced* on $C_{m,n}$ is defined by $\hat{p}(f) = f \circ p^{-1}$, $f \in C_{m,n}$. Treating the colors $x_1, x_2, ..., x_n$ that comprise the range of $f \in C_{m,n}$ as independent variables, the weight of f is:

$$W(f) = \prod_{i=1}^{m} f(i)$$

Evidently, $W(f)$ is a monomial of the (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 $p_1, p_2, ..., p_t$ be representatives of the distinct orbits of $\hat{G}$. The weight of p_i is the common value of $W(f)$, $f \in p_i$. The sum of the weights of the orbits is the pattern inventory:

$$W_G(x_1, x_2, ..., x_n) = \sum_{i=1}^{t} W(p_i)$$

Theorem 1 (the Pólya Theorem[17]). If G is a subgroup of S_m, the symmetry group on m symbols, then the pattern inventory for the orbits of the $C_{m,n}$ modula $\hat{G}$ is:

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

where $M_k = x_1^k + x_2^k + ... + x_n^k$ is the kth power sum of the *x*-es.

Theorem 2 (generalization of the Pólya Theorem[16]). Substituting M_i for x_i and in the generalized character cycle index, $i = 1, 2, ..., t$, one obtains the chiral generating function $CGF = P_G^{\chi}(M_1, ..., M_k)$.

To enumerate all possibilities of the hetero-fullerene structures, one has to consider the rotation group of the fullerene, and its whole automorphism group to enumerate the number of chiral isomers. Fripertinger[18] computed the symmetry of some fullerenes and then applied Symmetrica[19] 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.*[16] used the Pólya counting theorem for calculating the possibilities of different positional isomers. He also applied the generalization of the Pólya theorem to compute the number of chiral isomers.

Now is the time to enumerate the number of hetero-fullerenes in a series of fullerenes constructed by leapfrog. From the above discussion, the problem is reduced to the coloring of t he corresponding fulleren e graph with $3^n \times 20$ vertices. Consider the molecular graph of the fullerene $C_{3^n \times 20}$, Fig. 2. From the leapfrog principle, it can be seen that the sy mmetry group G of these fullerenes is isom orphic to the group $\mathbf{I}_h = \mathbf{Z}_2 \times \mathbf{A}_5$ of order 1 20 and t he cycle ty pes of e lements of G are as given:

Fullerene	Cycle type	No. of permutations
$C_{3^n \times 20}$	$1^{3^n \times 20}$	20
	$2^{3^n \times 10}$	
	$1^{3^{n-1} \times 4} 2^{3^{n-1} \times 28}$	
	$3^{3^{n-1} \times 20}$	
	$5^{3^n \times 4}$	
	$6^{3^{n-1} \times 10}$	
	$10^{3^n \times 2}$	
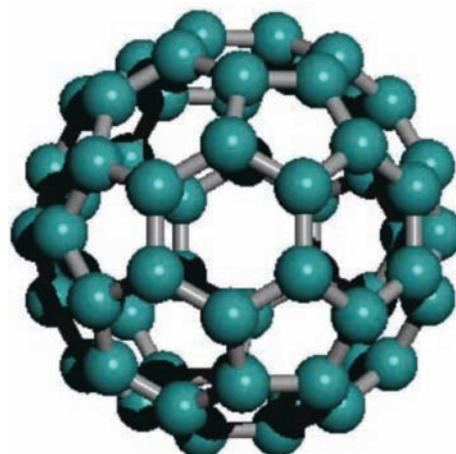
Fig. 2. The fullerene C_{60}.

Thus the cycle index of G is computed as:

$$Z(G,X) = x_1^{20 \times 3^n} + 20(x_3^{20 \times 3^{n-1}} + x_6^{10 \times 3^{n-1}}) + 24(x_5^{4 \times 3^n} + x_{10}^{2 \times 3^n}) +$$
$$+ 15 x_1^{4 \times 3^{n-1}} x_2^{28 \times 3^{n-1}} + 16 x_2^{20 \times 3^n}$$

However, from the cycle indices, the num ber of possible positional iso mers, the num ber of chiral isom ers and the num ber of orbits under the whole poin t

group I_h can be computed. For the number of orbits under the whole point group I_h, it should simply be noted that:

$$Z_{I_h} - P_{I_h}^{\chi} = P_{I_h}^{1}$$

In what follows, a GAP program is prepared to compute the number of hetero-fullerenes for $C_{3^n \times 20}$. It should be mentioned here that the present computations of the symmetry properties and cycle indices of the fullerenes were realized with the use of GAP. [20] This software was constructed by the GAP team in Aachen. In Table I, this program is applied to compute the number of hetero-fullerenes for the case of $n = 1$.

TABLE 1. The number of $C_{60-k}B_k$ molecules

$k,60-k$	Number of $C_{60-k}B_k$ molecules for		Number of orbits under whole point group I_h
	Rotational group	Symmetry group	
0,60	1	1	0
1,59	1	1	0
2,58	23	37	14
3,57	303	577	274
4,56	4190	8236	4046
5,55	45718	91030	45312
6,54	418470	835476	417006
7,53	3220218	6436782	3216564
8,52	21330558	42650532	21319974
9,51	123204921	246386091	123181170
10,50	628330629	1256602779	628272150
11,49	2855893755	5711668755	2855775000
12,48	11661527055	23322797475	11661270420
13,47	43057432740	86114390460	43056957720
14,46	144549869700	289098819780	144548950080
15,45	443284859624	886568158468	443283298844
16,44	1246738569480	2493474394140	1246735824660
17,43	3226849468425	6453694644705	3226845176280
18,42	7708584971055	15417163018725	7708578047670
19,41	17040023323785	34080036632565	17040013308780
20,40	34932048763560	69864082608210	34932033844650
21,39	66537224405790	133074428781570	66537204375780
22,38	117952355252550	235904682814710	117952327562160
23,37	194877787472550	389755540347810	194877752875260
24,36	300436595453640	600873146368170	300436550914530
25,35	432628675734195	865257299572455	432628623838260
26,34	582384767014701	1164769471671687	582384704656986
27,33	733373386161407	1466746704458899	733373318297492
28,32	864332935668892	1728665795116244	864332859447352
29,31	953746664302456	1907493251046152	953746586743696
30,30	985538239868528	1971076398255692	985538158387164

A gap program for counting the number of hetero-fullerene for $C_{3^n \times 20}$

```
f:=function(n)
local s,i,f,x,t,tt,g;
x:=Indeterminate(Rationals,"x");
f := ((1 + x)^(20*3^n) + 20*((1 + x^3)^(20*(3^(n − 
1)))) + 24*(( 1 + x^ 5)^(4*3^n) + (1 +   x^10)^(2*3^n)) + 15*( 1 +  x)^(4*(3^(n − 
1)))*(1 + x^2)^ (28*(3^(n − 1))) + 16*(1 + x^2)^(10*(3^n)))/120;
g := ((1 + x)^(20*3^      n) + 20*(1 + x^3)^(20*(3^(n        − 1))) + 15*(1 + 
x^2)^(10*(3^(n))) + 24*(1 + x^5)^(4*(3^n)))/60;
t := CoefficientsOfLaurentPolynomial(f);
tt := CoefficientsOfLaurentPolynomial(g);
Print("************************************************","\n");
Print("\n");
Print("THIS FULLERENE IS C_",3^n*20,"\n");
Print("\n");
Print("Number of Molecules for Symmetry Group =","\n");
for i in t[1] do
Print(i,"\n");
od;
Print("***********************************************","\n");
Print("Number of Molecules for Rotation Group=","\n");
for i in tt[1] do
Print(i,"\n");
od;
Print("*************************************************","\n");
Print("Number of Orbits underWhole Point Group Sn=","\n");
for i in [1..Length(t[1])] do
Print("[",i-1);Print(",",Length(t[1])-i);Print("]=");Print(tt[1][i]-t[1][i],"\n");
od;
Print("*****************************************","\n");
return;
end;
```

CONCLUSIONS

In this paper, an efficient method is presented which is useful for computing permutational isomers of hetero-fullerenes. The method was applied on a buck-minster fullerene and the number of such isomers was computed. From the cycle index of leap frog of a series of fullerenes with I_h point group symmetry, such numbers for all elements of the series can be computed. A GAP program for such calculations is also presented.

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И З В О Д

ПРЕБРОЈАВАЊЕ ЈЕДНЕ КЛАСЕ ХЕТЕРО-ФУЛЕРЕНА СА ИЗОЛОВАНИМ ПЕНТАГОНИМА

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Хетеро-фулерени су фулерени у којима су неки угљеникови атоми замењени другим атомима. У раду је примењена Појина (Pólya) теорема за пребројавање могућих како позиционих тако и хиралних изомера. Да би се то постигло, коришћена је компјутерска алгебра система GAP и он примењен за одређивање броја изомера за једну класу хетеро-фулерена са изолованим пентагонима (IPR), чије су групе симетрије $\mathbf{I}_h$. Ови фулерени су конструисани применом "липфрог" методе.

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