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 $n = \frac{(5p + 6h)}{3}$, the number of edges $m = \frac{(5p + 6h)}{2} = 3n/2$ and the number of faces $f = p + h$. By the Euler formula, $n - m + f = 2$, it can be deduced that $\frac{(5p + 6h)}{3} - \frac{(5p + 6h)}{2} + p + h = 2$ 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. Randić,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 $D(G) = [d_{ij}]$, 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 $\sigma$ is a permutation on $n$ atoms of the molecule under consideration. Then the permutation matrix $P_\sigma$ is defined 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 $\sigma$ and $\tau$ 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 $\sigma$ of the vertices of a graph $G$ belongs to its automorphism group if it satisfies $P_\sigma A P_\sigma = A$, where $A$ is the adjacency matrix of $G$. Thus, for computing the symmetry of a molecule, it is sufficient to solve the matrix equation $P^t E P = E$, 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 $E$.

A method\textsuperscript{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 $3n$ 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 $C_{3n}$. One just has to identify the vertices of $C_n$ with the $n$ new hexagonal faces of $C_{3n}$\textsuperscript{14}. From Fig. 1, it can be seen that $\text{Le}(C_{20}) = C_{60}$.

Fig. 1. The fullerene $C_{20}$ (a) and $\text{Le}(C_{20})$ (b).
Balasubramanian\textsuperscript{11} has realized 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 Ji\textsuperscript{15} discussed hydrogenated C\textsubscript{60}. Furthermore, Zhang\textsuperscript{16} also studied fullerene cages. In this paper, the compute number of hetero-fullerenes, $C_{3^n \times 20}$, is computed.

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 action of $G$ on $X$ is denoted by $G \times X$ and $X$ is called a $G$-set. It induces a group homomorphism $\varphi$ from $G$ into the symmetric group $S_X$ on $X$, where $\varphi(g)x = gx$ for all $x \in X$. The orbit of $x$ will be denoted by $Gx$, which defines as a set all $\varphi(g)x$, $g \in G$.

The set of all $G$-orbits will be denoted by $G \backslash X = \{ Gx \mid x \in X \}$. Suppose $g$ is a permutation of $n$ symbols with exactly $\lambda_1$ orbits of size 1, $\lambda_2$ orbits of size 2,\ldots, and $\lambda_n$ orbits of size $n$. Then the cycle type of $g$ is defined as $\lambda_1, \lambda_2, \ldots, \lambda_n$.

Now, the notion of a cycle index is introduced. Let $G$ be a permutation group. The cycle index of $G$ acting on $X$ is the polynomial $Z(G,X)$ over $\mathbb{Q}$ in terms of the 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 $(c_1(p), \ldots, c_t(p))$ is the cycle type of the permutation $p \in G$. The generalized character cycle index is defined as:

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

where $\chi$ is the linear character of the irreducible representation of $G$. In this 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 $\chi$ is 1 for all $g$. Since, all elements of a conjugacy class of a permutation group have the same cycle type, the cycle index and the generalized character cycle index can be rephrased in the following way:

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

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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 $f: \{1,2,\ldots,m\} \to \{x_1,x_2,\ldots,x_n\}$. The action of $p \in S_m \text{ induced on } C_{m,n}$ is defined by $\hat{p}(f) = fop^{-1}, f \in C_{m,n}$. Treating the colors $x_1,x_2,\ldots,x_n$ 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 $p_1,p_2,\ldots,p_t$ be representatives of the distinct orbits of $\hat{G}$. The weight of $p_i$ is the common value of $W(f), f \in p_i$. 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 (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 $G$ is:

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

where $M_k = x_1^k + x_2^k + \ldots + x_n^k$ is the $k$th 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, $i = 1, 2, \ldots, t$, one obtains the chiral generating function $\text{CGF} = P_G^G(M_1,\ldots,M_k)$.

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 computed the symmetry of some fullerenes and then applied Symmetrica 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. 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.

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

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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 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 the leapfrog principle, it can be seen that the symmetry group $G$ of these fullerenes is isomorphic to the group $I_h = \mathbb{Z}_2 \times A_5$ of order 120 and the cycle types of elements of $G$ are as given:

<table>
<thead>
<tr>
<th>Fullerene</th>
<th>Cycle type</th>
<th>No. of permutations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{3^n \times 20}$</td>
<td>$1^{20}$</td>
<td>$20$</td>
</tr>
<tr>
<td></td>
<td>$2^{10}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$1^{3^n \times 4} 2^{3^n \times 28}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$3^{3^n \times 20}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$5^{3^n \times 4}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$6^{3^n \times 10}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$10^{3^n \times 2}$</td>
<td></td>
</tr>
</tbody>
</table>

Thus the cycle index of $G$ is computed as:

$$Z(G, X) = x_1^{20} x_3^{3^n} + 20(x_3^{20} x_3^{3^n-1} + x_6^{10} x_3^{3^n-1}) + 24(x_3^{4} x_3^{3^n} + x_{10}^{2} x_3^{3^n}) +$$

$$+ 15 x_1^{4} x_3^{3^n-1} x_2^{2} x_3^{3^n-1} + 16 x_2^{2} x_3^{3^n}$$

However, from the cycle indices, the number of possible positional isomers, the number of chiral isomers and the number of orbits under the whole point group is...
group $I_h$ can be computed. For the number of orbits under the whole point group $I_h$, it should simply be noted that:

$$Z_{I_h} - P_{I_h}^{\sigma} = P_{I_h}^l$$

In what follows, a GAP program is prepared to compute the number of hetero-fullerenes for $C_{60} \times n$. 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. 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>
<thead>
<tr>
<th>$k, 60-k$</th>
<th>Number of $C_{60-k}B_k$ molecules for Rotational group</th>
<th>Symmetry group</th>
<th>Number of orbits under whole point group $I_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,60</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>1,59</td>
<td>1</td>
<td>1</td>
<td>0</td>
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<tr>
<td>2,58</td>
<td>23</td>
<td>37</td>
<td>14</td>
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<tr>
<td>3,57</td>
<td>303</td>
<td>577</td>
<td>274</td>
</tr>
<tr>
<td>4,56</td>
<td>4190</td>
<td>8236</td>
<td>4046</td>
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<td>91030</td>
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<td>835476</td>
<td>417006</td>
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<td>7,53</td>
<td>3220218</td>
<td>6436782</td>
<td>3216564</td>
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<td>21319974</td>
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<td>123204921</td>
<td>246386991</td>
<td>123181170</td>
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<td>628272150</td>
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<td>43056957720</td>
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<td>389755540347810</td>
<td>194877752875260</td>
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<td>300436550914530</td>
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<td>1164769471671687</td>
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<td>73373318297492</td>
</tr>
<tr>
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<td>1728665795116244</td>
<td>864332859447352</td>
</tr>
<tr>
<td>29,31</td>
<td>953746664302456</td>
<td>1907493251046152</td>
<td>953746586743696</td>
</tr>
<tr>
<td>30,30</td>
<td>985538239868528</td>
<td>197107639255692</td>
<td>985538158387164</td>
</tr>
</tbody>
</table>
A gap program for counting the number of hetero-fullerene for $C_{3^n \times 20}$

\[ f := \text{function}(n) \]
\[ \text{local } s, i, f, x, t, tt, g; \]
\[ x := \text{Indeterminate(Rationals,"x");} \]
\[ f := ((1 + x)^{(20 \times 3^n)} + 20 \times ((1 + x^3)^{(20 \times (3^n - 1)})) + (1 + x^6)^{(10 \times (3^n - 1))}) + 24 \times ((1 + x^5)^{(4 \times 3^n)} + (1 + x^{10})^{(2 \times 3^n)}) + 15 \times (1 + x)^{(4 \times (3^n - 1))} \times (1 + x^2)^{(28 \times (3^n - 1))}) + 16 \times (1 + x^2)^{(10 \times (3^n))})/120; \]
\[ g := ((1 + x)^{(20 \times 3^n)} + 20 \times (1 + x^3)^{(20 \times (3^n - 1)}) + 15 \times (1 + x^2)^{(10 \times (3^n))}) + 24 \times (1 + x^5)^{(4 \times (3^n))})/60; \]
\[ t := \text{CoefficientsOfLaurentPolynomial}(f); \]
\[ tt := \text{CoefficientsOfLaurentPolynomial}(g); \]
\[ \text{Print("***************************************************", \\
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\]

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 buckminster 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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ИЗВОД
ПРЕБРОЈАВАЊЕ ЈЕДНЕ КЛАСЕ ХЕТЕРО-ФУЛЕРЕНА СА ИЗОЛОВАНИМ ПЕНТАГОНИМА

АЛИ РЕЗА АШРАФИ И МОДЖТАБА ГОРБАНІ
Институт за наносценауку и нанотехнологију, Универзитет у Кашану, Кашан 87317-51167, И. Р. Јран

Хетеро-фулерени су фулерени у којима су неки угљеникови атоми замењени другим атомима. У раду је примењена Појина (Пólya) теорема за пребројавање могућих позиционих тако и хирапских 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 \( I_6 \). Ови фулерени су конструисани применом "липфрог" методе.

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REFERENCES
20. The GAP Team : *GAP, Groups, Algorithms and Programming*, R WTH, Aachen, Germany, 1995

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