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Computer Application of GAP to the Evaluation of Numbers of Permutational Isomers of Hetero Fullerenes

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Abstract

Hetero fullerenes are fullerenes where some of the carbon atoms are replaced by other atoms. Fripertinger applied SYMMETRICA to write some codes for computing the number of $C_{60-k}B_k$ molecules, where B is a hetero-atom such as S_i (see H. Fripertinger, MATCH Commun. Math. Comput. Chem. **1996**, 33, 121.). In this paper, the numbers of all $C_{10n-k}B_k$ hetero-fullerenes are computed, where C_{10n} is an infinite family of fullerenes. We apply the computer algebra system GAP to compute the number of permutational isomers of hetero fullerenes of the C_{60} fullerene with I_h point group symmetry.

1. Introduction

Carbon exists in several forms in nature. One is the so-called fullerene which was discovered for the first time in 1985.[1] Fullerenes are carbon-cage molecules in which a large number of carbon (C) 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, in a given fullerene F. Since each atom lies in exactly 3 faces and each edge lies in 2 faces, the number of atoms is n = (5p+6h)/3, the number of edges is m = (5p+6h)/2 = 3/2n and the number of faces is f = p + h. By the Euler's formula n − m + f = 2, one can deduce that (5p+6h)/3 – (5p+6h)/2 + p + h = 2, and

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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] Heterofullerenes are fullerene molecules in which one or more carbon atoms are replaced by heteroatoms such as boron or nitrogen, whose formation 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 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. On the other hand, it is well-known fact that 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.

The first author of this paper[12-15] introduced some algorithms for computing the symmetry of molecules and applied them to compute the symmetry of some big fullerenes. We notice that for computing the number of isomers of a given fullerene molecule, we need to an efficient method for computing symmetry of fullerenes. Fripertinger[16] computed the symmetry of some fullerenes and then applied SYMMETRICA[17] to calculate the number of $C_{60}H_kCl_{60-k}$ molecules and Balasubramanian[11] computed the number of $C_{60}H_{36}$ isomers.

Throughout this paper, our notation is standard and taken mainly from the standard book of the theory of graphs.

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 $\varphi(g)x = gx$ for all $x \in X$. The orbit of x will be indicated as x_G and defines as the set of all φ(g)x, $g \in G$. The set of all G-orbits will be denoted by $G\backslash\backslash X := \{x_G \mid x \in X\}$. 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 $1^{\lambda_1}2^{\lambda_2}...n^{\lambda_n}$.

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 $f: \{1, 2, \ldots, m\} \rightarrow \{x_1, x_2, ..., x_n\}$. The action of $p \in S_m$ induced on $C_{m,n}$ is defined by $\hat{p}(f) = fop^{-1}$, $f \in C_{m,n}$. 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 (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 (Pólya's Theorem[18]**)** 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

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

where $M_k = x_1^k + x_2^k + \ldots + x_n^k$, the k^{th} power sum of the x's, and $(C_1(p),\ldots,C_m(p))$ is the cycle type of the permutation p.

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 $p \in G$. All elements of a conjugacy class of a group have the same cycle type, so the cycle index can be rephrased in the following way:

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

where Conj(G) is the set of all conjugacy classes C of G with representatives $g_C \in C$.

The dihedral group D_n is the symmetry group of an n-sided regular polygon for $n > 1$. These groups are one of the most important classes of finite groups currently applicable in chemistry. For example D_3, D_4, D_5 and D_6 point groups are dihedral groups. One group presentation for D_n is $\langle x,y \mid x^n = y^2 = e, yxy = x^{-1}\rangle$. This means that D_n is generated by a two elements set {x,y} with the condition $x^n = y^2 = 1$ and $yxy = x^{-1}$. In this section, an infinite class C_{10n} of fullerene molecules with exactly 10n carbon atoms and symmetry group D_{20} is constructed, Figure 1. To compute the number of isomers of these fullerenes, we first compute a permutation representation for the symmetry group of these fullerenes.

Consider the Graph of Fullerene C_{10n}, Figure 1. From Figure 1, one can see that the generators of this group are as follows:

$$\boldsymbol{\sigma = (2,5)(3,4)(6,10)(7,9)(11,15)(12,14)...(10n-4,10n)(10n-3,10n-1),}$$

$$\boldsymbol{\tau = (1,10n-4,2,10n-3,3,10n-2,4,10n-1,5,10n)\ ...}$$
$$\boldsymbol{(7,10n-6,9,10n-14,11,10n-12,13,10n-10,15,10n-8),}$$

where σ fixes elements 1, 8, 19, 30, …, 11i-3, 11i+2, …, 10n-2 , i=1,2,…,n-1, and τ does not have fixed points. Since $\sigma^2 = \tau^{10}$ = identity and $\sigma^{-1}\tau\sigma = \tau^{-1}$, the symmetry group G of these fullerenes is isomorphic to the dihedral group of order 20. In Table 1, the cycle types of elements of G are computed.

Thus the cycle index of G is computed as $Z(G,X) = (x_1^{10n} + 5x_1^{2n}x_2^{4n} + 4_5^{2n} + 6x_2^{5n} + 4x_{10}^{n})/20$. But from the cycle indices one can compute the number of different colourings using k colours via Pólya-theory by replacing each variable x_i in the cycle index by $1 + x^i$.

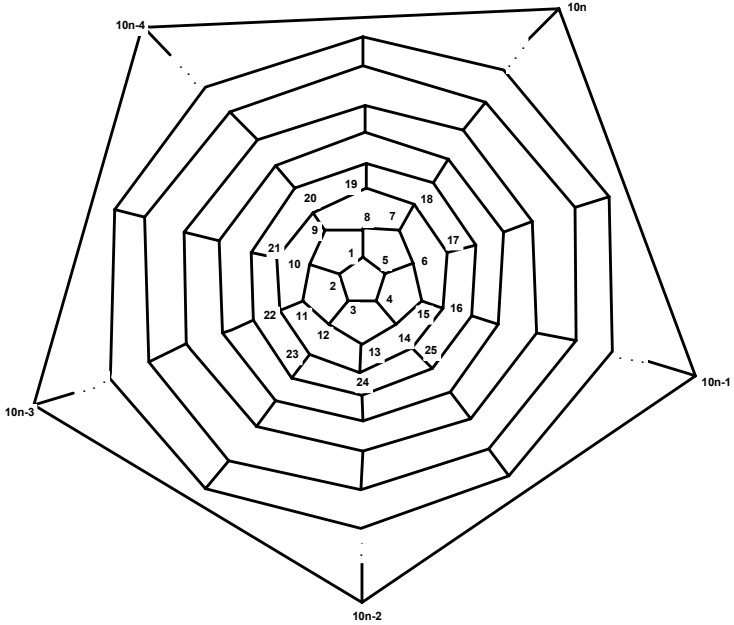

Figure 1. The Schlegel diagram of C_{10n}.

In what follows we prepare a GAP program to compute the number of hetero fullerenes for C_{10n}. We mention here that our computations of symmetry properties and cycle indices of fullerenes were carried out with the use of GAP[19,20]. This software was constructed by the GAP team in Aachen. In Table 2, we apply this program to compute the number of hetero fullerenes for the case of n = 30.

Table 1. Cycle Types of Elements of G.

Fullerene	Cycle type	#Permutations
C_{10n}	1^{10n}	1
	$1^{2n}2^{4n}$	5
	5^{2n}	4
	2^{5n}	6
	10^{n}	4

Program 1: A Gap Program for Counting the Number of Hetero Fullerene for C_{10n}

```
f:=function(n)
local s,i,f,x,t;
        Print("Number of vertices is: ",10*n,"\n");
        x:=Indeterminate(Rationals,"x");
        f:=(5*((1 + x)^(2*n))*((1 + x^2)^(4*n)) + 4*((1 + x^5)^(2*n)) +
        6*((1+x^2)^(5*n)) + 4*((1 + x^(10))^n) + (1 + x)^(10*n))/20;
        t := CoefficientsOfLaurentPolynomial(f);
                for i in t[1] do
                        Print(i,"\n");
                od;
        return;
end;
```

Table 2. Number of $C_{30-k}B_k$ molecules.

K	Number of $C_{30-k}B_k$ Molecules
0,30	1
1,29	3
2,28	33
3,27	226
4,26	1467
5,25	7287
6,24	30173
7,23	102468
8,22	294255
9,21	717299
10,20	1506051
11,19	2735358
12,18	4331275
13,17	5994081
14,16	7279821
15,15	7762876

We now present another GAP program to compute the numbers of different fullerene molecules $C_{n-k}B_k$, for large n.

Program 2: A GAP Program for Enumerating the Hetero Fullerenes

```
h:=function(f,g)
local t,i,tt;
Print("Coefficients Of f are:","\n");
t:=CoefficientsOfLaurentPolynomial(f);
for i in t[1] do
        Print(i,"\n");
od;
        Print("Coefficients Of g are:","\n");
        tt:=CoefficientsOfLaurentPolynomial(g);
        for i in tt[1] do
                Print(i,"\n");
        od;
return();
end;
```

To investigate the efficiency of the second program, we consider the Buckminster fullerene C_{60}, Figure 2. Fripertinger[16] computed the cycle indices for the actions of the rotational group R and symmetry group S on the set of all vertices as follows:

$$Z(G,R)=\frac{1}{60}\left(24x_5^{12}+20x_3^{20}+15x_2^{30}+x_1^{60}\right),$$

$$Z(G,S)=\frac{1}{120}\left(24x_{10}^{6}+20x_6^{10}+24x_5^{12}+20x_3^{20}+16x_2^{30}+15x_1^{4}x_2^{28}+x_1^{60}\right).$$

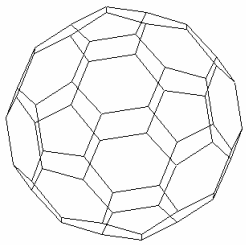

Figure 2. The Buckminster Fullerene C_{60}.

We apply these cycle indices and our second program to compute the number of permutational isomers of this fullerene. Our calculations are given in Table 3. Fripertinger in the mentioned paper computed these numbers for $1 \leq k \leq 10$ and one can see that our calculations have the same results.

Table 3. Number of $C_{60-k}B_k$ Molecules

k	Number of $C_{60-k}B_k$ molecules for Rotational Group	Number of $C_{60-k}B_k$ molecules for Symmetry Group
0,60	1	1
1,59	1	1
2,58	37	23
3,57	577	303
4,56	8236	4190
5,55	91030	45718
6,54	835476	418470
7,53	6436782	3220218
8,52	42650532	21330558
9,51	246386091	123204921
10,50	1256602779	628330629
11,49	5711668755	2855893755
12,48	23322797475	11661527055
13,47	86114390460	43057432740
14,46	289098819780	144549869700
15,45	886568158468	443284859624
16,44	2493474394140	1246738569480
17,43	6453694644705	3226849468425
18,42	15417163018725	7708584971055
19,41	34080036632565	17040023323785
20,40	69864082608210	34932048763560
21,39	133074428781570	66537224405790
22,38	235904682814710	117952355252550
23,37	389755540347810	194877787472550
24,36	600873146368170	300436595453640
25,35	865257299572455	432628675734195
26,34	1164769471671687	582384767014701
27,33	1466746704458899	733373386161407
28,32	1728665795116244	864332935668892
29,31	1907493251046152	953746664302456
30,30	1971076398255692	985538239868528

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