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COUNTING NUMBERS OF PERMUTATIONAL ISOMERS OF HETERO FULLERENES

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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 C60-kBk molecules, where B is a hetero-atom such as Si. (see H. Fripertinger, MATCH Commun. Math. Comput. Chem. 33, 121 (1996)) In this paper, the numbers of all $C_{12n-k}B_k$ hetero-fullerenes are computed, where C_{12n} 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 Ih point group symmetry.

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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. Fullerenes are molecules in the form of cage-like polyhedra, consisting solely of carbon atoms. Fullerenes C_n can be drawn for $n = 20$ and for all even $n \geq 24$. They have n carbon atoms, $3n/2$ bonds, 12 pentagonal and $n/2$-10 hexagonal faces. The most important member of the family of fullerenes is C_{60}.[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 $P\sigma$ 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 $P_\sigma\ {}^tAP_\sigma = A$, 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

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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.

Ashrafi and his co autors[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 GX 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 indicated as x^G and defines as the set of all φ (g)x, g ∈ G. The set of all G-orbits will be denoted by G\\X := $\{x^G \mid x \in X\}$. Suppose g is a permutation of n symbols with exactly λ1 orbits of size 1, λ2 orbits of size 2, …, and λn orbits of size n. Then the cycle type of g is defined as $1^{\lambda 1}\, 2^{\lambda 2} \ldots\, n^{\lambda n}$.

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 Cm,n the set of all functions f: {1, 2, …, m} →{x_1, x_2, ..., x_n}.The action of p∈ Sm induced on Cm,n is defined by $\hat{p}(f) = fop^{-1}, f \in C_{m,n}$. Treating the colors x_1, x_2, …, x_n that comprise the range of f ∈ Cm,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 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[18]**)** If G is a subgroup of S_m 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 $M_k=x_1^k+x_2^k+\ldots+x_n^k$, the k^{th} power sum of the x_i'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 cycleindex of G acting on X is the polynomial Z(G, X) over Q in terms of in determinates x_1, x_2, …, x_t, t = |X|, defined by $Z(G, X)=\frac{1}{|G|}\sum_{C\in Conj(G)} |C| \prod_{i=1}^{t} x_i^{C_i(g_c)}$, 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_{12n} of fullerene molecules with exactly 12n carbon atoms and symmetry group D_{24} 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_{12n}, Figure 1. From Figure 1, one can see that the generators of this group are as follows:

σ=(1,12n-5)(2,12n-4)(3,12n-3)...(12n-24,12n-18)(12n-22,12n-19)(12n-21,12n-20),

τ=(1,12n-5,2,12n,3,12n-1,4,12n-2,5,12n-3,6,12n-4)...(12n-29,12n-25,12n-26,12n-18,12n-20,12n-19,

12n-22,12n-21,12n-24,12n-23,12n-28,12n-27).

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 24. In Table 1, the cycle types of elements of G are computed. Thus the cycle index of G is computed as $Z(G,X) = (x_1^{12n} + 6x_1^{2n} x_2^{5n} + 2x_6^{2n} + 2x_3^{4n} + 7x_2^{6n} + 4x_{12}^{n} + 2x_4^{3n}) / 24$. 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 $1 + x^i$.

In what follows we prepare a GAP program to compute the number of hetero fullerenes for C_{12n}. 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 3, we apply this program to compute the number of hetero fullerenes for the case of n = 3.

Table 1. Cycle Types of Elements of G.

Fullerene	Cycle type	#Permutations
C_{12n}	1^{20n}	1
	$1^{2n}2^{9n}$	5
	2^{10n}	6
	10^{2n}	4
	5^{4n}	4

We now present a GAP program to compute the numbers of different fullerene molecules $C_{12n-k}B_k$, for large n.
Program: A Gap Program for Counting the Number of Hetero Fullerene for C_{12n}

```
f:=function(n)
  local s,i,f,x,t,tt,g;
    Print("Number of vertices is: ",10*n,"\n");
     x:=Indeterminate(Rationals,"x");
f:=((1+x)^(12*n)+6*((1+x)^(2*n))*((1+x^2)^(5*n))+2*((1+x^6)^(2*n))+2*((1+x^3)^
(4*n))+7*((1+x^2)^(6*n))+4*((1+x^(12))^n)+2*((1+x^4)^(3*n)))/24;
g:=((1+x)^(12*n)+2*((1+x^6)^(2*n))+2*((1+x^3)^(4*n))+7*((1+x^2)^(6*n)))/12;
    t:=CoefficientsOfLaurentPolynomial(f);
     tt:=CoefficientsOfLaurentPolynomial(g);
        Print("\n");
          Print("\n");
            Print("Number of Molecules for Symmetry Group =","\n");
              for i in t[1] do
                 Print(i,"\n");
              od;
```

```
        Print("Number of  Molecules for Rotation Group=","\n");
          for i in tt[1] do
            Print(i,"\n");
          od;
    return;
end;
```

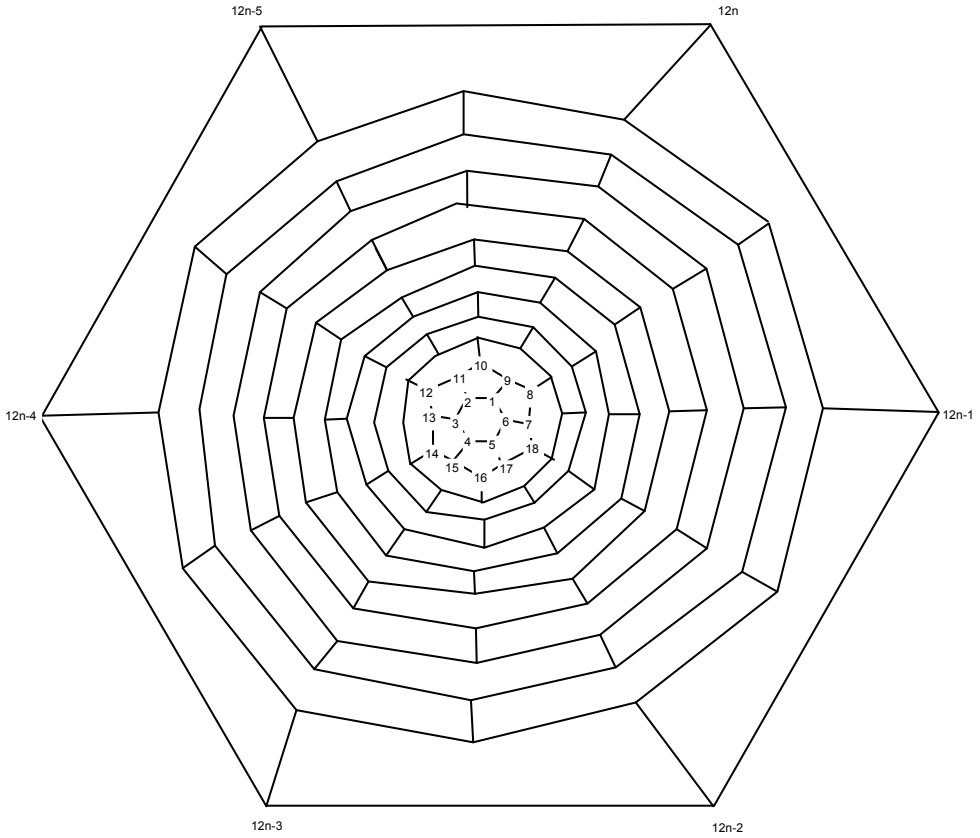

Fig. 1. The Schlegel diagram of C_{12n}.

To investigate the efficiency of this program, we consider the Buckminster fullerene C_{24}, 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:

$$Z(G,R) = \frac{1}{12}\,(2x_6^{\,4} + 2x_3^{\,8} + 4x_2^{\,12} + x_1^{\,24}),$$

$$Z(G,S) = \frac{1}{2}Z(G,R) + \frac{1}{24}\,(4x_{12}^{\,2} + 2x_4^{\,6} + 6x_1^{\,4}x_2^{\,10}).$$

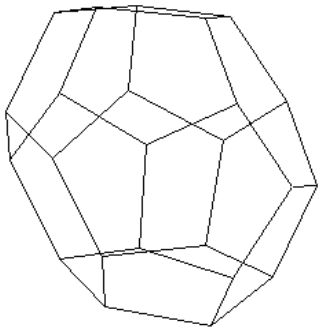

Fig 2. The Fullerene C_{24}

We apply these cycle indices program to compute the number of permutational isomers of this fullerene. Our calculations are given in Table 2. Fripertinger in the mentioned paper computed these cycle indices and one can see that our calculations have the same results.

Table 2. Number of $C_{24-k}B_k$ molecules.

k	Number of $C_{24-k}B_k$ molecules For Symmetry Group	Number of $C_{24-k}B_k$ molecules For Rotational Group
0,24	1	1
1,23	2	2
2,22	19	30
3,21	96	170
4,20	489	924
5,19	1826	3542
6,18	5775	11350
7,17	14586	28842
8,16	31034	61578
9,15	54814	108968
10,14	82358	163900
11,13	104468	208012
12,12	113434	225898

Table 3. Number of $C_{36-k}B_k$ molecules.

k	Number of $C_{36-k}B_k$ molecules For Symmetry Group	Number of $C_{36-k}B_k$ molecules For Rotational Group
0,36	1	1
1,35	3	3
2,34	39	63
3,33	326	597
4,32	2586	4998
5,31	15942	31416
6,30	81966	162804
7,29	349050	695640
8,28	1264188	2523480
9,27	3927135	7845310
10,26	10601220	21187236
11,25	25045566	50067108
12,24	52176447	104317389
13,23	96307470	192565800
14,22	158220312	316376664
15,21	232035188	463992012
16,20	304552704	609014868
17,19	358278360	716458050
18,18	378195662	756289794

k	Number of $C_{120-k}B_k$ molecules For Symmetry Group	Number of $C_{120-k}B_k$ molecules For Rotational Group
0,120	1	1
1,119	10	10
2,118	375	630

k	Number of $C_{120-k}B_k$ molecules For Symmetry Group	Number of $C_{120-k}B_k$ molecules For Rotational Group
3,117	12240	23410
4,116	346685	685580
5,115	7965002	15881502
6,114	152341115	304415550
7,113	2479309010	4957297410
8,112	35014043570	70022110370
9,111	435703858670	871382724160
10,110	4836224403394	9672351405780
11,109	48361919180380	96723482198980
12,108	439286444004870	878571659193250
13,107	3649453395393660	7298902772092260
14,106	27892241959149490	55784471411992500
15,105	197105150105626846	394210263052825920
16,104	1293502479242206510	2587004852775979230
17,103	7913191454130806070	15826382619616402470
18,102	45281039545077849185	90562078331984665050
19, 101	243087684880272228510	486175367841198609210
20,100	1227592806166512104239	2455185607642032825924
21,99	5845680023633471951780	11691360036181207757310
22,98	2630556009419056246552 5	5261112016301532933165 0
23,97	1120845603750011293675 50	2241691206937352717683 50
24,96	4530084314628985764521 85	9060168628046630288749 05
25,95	1739552376710063098311576	3479104753166771417844792
26,94	6356056760852287808676420	1271211352118929418425284 0
27,93	2212849390776016914653208 0	4425698781450038289650476 0
28,92	7349821190721212078121754 0	1469964238124578186243304 80
29,91	2331667412215922453799249 20	4663334824394892557543976 40
30,90	7072724483699605727133249 00	1414544896733148439148314 600
31,89	2053371624296066328287559960	4106743248580018284546792120
32,88	5710939830067211214797599070	1142187966011326312544834 7390
33,87	1522917288016895452637570 5490	3045834576030180227744067 5130
34,86	3896876589923988384873302 8535	7793753179841954347060131 8070
35,85	9575182478096427637693403 9586	1915036495618303232243095 08342
36,84	2260806973994616603500350 58325	4521613947987665805477975 03460
37,83	5132642859879108621619378 84970	1026528571975576957824001 418590
38,82	1121077256236673061514483 529395	2242154512472971916469495 764590
39,81	2357136795164172436988256 836250	4714273590327784598483890 594450
40,80	4773202010207294018481937 229034	9546404020413766257168445 627578
41,79	9313564897965238184159555 569620	1862712979592929524278208 2421540
42,78	1751837206998195720554413 7225070	3503674413996225047141326 7411340
43,77	3177751212694365111156059 4292740	6355502425388500403434285 2647580
44,76	5561064622215093901152573 3045270	1112212924442987653167634 12659240
45,75	9392020250852101795191115 2509564	1878404050170379008126200 24271468
46,74	1531307649595444682963089 59721150	3062615299190835475750525 86163500
47,73	2410995022767287807694080 85318900	4821990045534506704486604 65431300
48,72	3666721597125241149122298 12496220	7333443194250395823379076 31148620
49,71	5387835816184017377508464 54890950	1077567163236792824778128 999280150
50,70	7650726858981293592134614 92059233	1530145371796245841468948 664002650
51,69	1050099764958215551766088 716711890	2100199529916415819273466 210856210
52,68	1393401611194554037375002 296809615	2786803222389090262495164 078431940
53,67	1787760557759049201897170 212061430	3575521115518078020330563 887016370
54,66	2218147358701041361871100 597953965	4436294717402059817301853 188434610
55,65	2661776830441248499917190 861332718	5323553660882471719158839 565113262

k	Number of $C_{120-k}B_k$ molecules For Symmetry Group	Number of $C_{120-k}B_k$ molecules For Rotational Group
56,64	308956239247644821159102250960669O	617912478495286902024124033755517O
57,63	346898233541215154713002392174254O	693796467082427391970577770460916O
58,62	376803253674078474421096178084300O	753606507348153897954610200946168O
59,61	395962741149031577584204970236072O	791925482298060021343386389519448O
60,60	402562120168182095280559809555318O	805124240336361028597879051406914O

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