STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LIV, 2, 2009

COUNTING NUMBERS OF PERMUTATIONAL ISOMERS OF AN INFINITE FAMILY OF FULLERENES

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ABSTRACT. 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, the numbers of all $C_{40n-k}X_k$ hetero-fullerenes are computed, where C_{40n} 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_{80} fullerene with D_{20} point group symmetry.

Keywords: *Fullerene, Hetero-fullerene, Cycle Index, Permutation Group.*

INTRODUCTION

Carbon exists in several allotropic forms in nature. Fullerenes are zero-dimensional nanostructures, discovered experimentally in 1985 [1]. Fullerenes are carbon-cage molecules in which a number of carbon atoms are bonded in a nearly spherical 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 therefore p = 12, n = 2h + 20 and m = 3h + 30. This implies that such molecules, made entirely of n carbon atoms, have 12 pentagonal and (n/2 – 10) hexagonal faces, while $n \neq 22$ 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 heteroatoms such as boron or nitrogen, whose formation is a kind of "on-ball" doping of the fullerene cage.

Enumerating molecules is a mind-boggling problem that has fascinated chemists and mathematicians alike for more than a century. Some of the solutions developed were not only valuable to chemists but to mathematicians as well. Indeed, while trying to solve the problem of counting the isomers of

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substituted aromatic compounds, important concepts in graph theory and combinatorics were developed. The terms graph and tree were even coined in a chemistry context. Historically, molecular enumeration has brought a fertile ground of research between Chemistry, Mathematics, and Computer Science. Still today, new concepts and techniques are being developed at the interface of these fields [3].

Detecting symmetry of molecules is a well-studied problem with applications in a large number of areas. Randić [4] and then Balasubramanian [5-7] considered the Euclidean matrix of a chemical graph to find its symmetry. Here the Euclidean matrix of a molecular graph G is a matrix $D(G) = [d_{i,j}]$, where for $i \neq j$, d_{ij} is the Euclidean distance between the nuclei i and j; in this matrix d_{ii} are zero.

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 a well-known fact that 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.

Ashrafi et al. [8-12] introduced some algorithms for computing the symmetry of molecules and applied them to compute the symmetry of some big fullerenes. We note that, to compute the number of isomers of a given fullerene, we need an efficient method for computing symmetry of fullerenes. Fripertinger [13] computed the symmetry of some fullerenes and then applied SYMMETRICA [14] to calculate the number of $C_{60}H_kCl_{60-k}$ molecules.

In this paper we extend our investigation on isomerism of hetero-fullerenes to $C_{40n-k}X_k$ [15]. Throughout this paper, the notation is standard and taken mainly from the standard books of Graph Theory.

RESULTS AND DISCUSSION

Groups are often used to describe the symmetry 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

defined as the set of all φ (g)x, g ∈ G. The set of all G-orbits will be denoted by G\\X := {x^G | x ∈ 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 cyclic type of g is defined as $1^{\lambda 1}\ 2^{\lambda 2}\ldots\ n^{\lambda n}$.

Enumeration of chemical isomers can be accomplished by various methods. The Polya-Redfield theorem[16] is a standard method for combinatorial enumeration of graphs, polyhedra, chemical isomers, etc.

Denote by $C_{m,n}$ the set of all functions $f:\{1,2,..,m\}\to\{x_1,x_2,..,x_n\}$. 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 $x_1,x_2,..,x_n$ that comprise the range of $f\in C_{m,n}$ as independent variables, the weight of *f* is $W(f)=\prod_i f(i)$. Evidently, $W(f)$ is a monomial of (total) degree *m*. Suppose *G* is a permutation group of degree *m*, $\hat{G}$ ={ $\hat{p}$:p∈ G}, $\hat{p}$ being as 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[16]**)** If G is a subgroup of S_m then the pattern inventory for the orbits of $C_{m,n}$ modulo $\hat{G}$ 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 is the sum of 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, …, 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 ∈ C.

The dihedral group D_n is the symmetry group of an n-sided regular polygon, of n > 1. These groups are one of the most important classes of finite groups currently applicable in chemistry. One group presentation for D_n is: <x,y | $x^n = y^2 = e$, $yxy = x^{-1}$>. This means that D_n is generated by a two elements set {x,y} with the condition $x^n = y^2 = e$ and $yxy = x^{-1}$.

In this section, an infinite class $C_{40n}(n \geq 2)$ of fullerene molecules with exactly 40n carbon atoms and symmetry group D_{20} is constructed, as shown in Figure 1. To compute the number of isomers of these fullerenes, we first compute a permutation representation for their symmetry group.

Consider the graph of fullerene C_{40n} (Figure 1). One can see that the generators of this group are as follows:

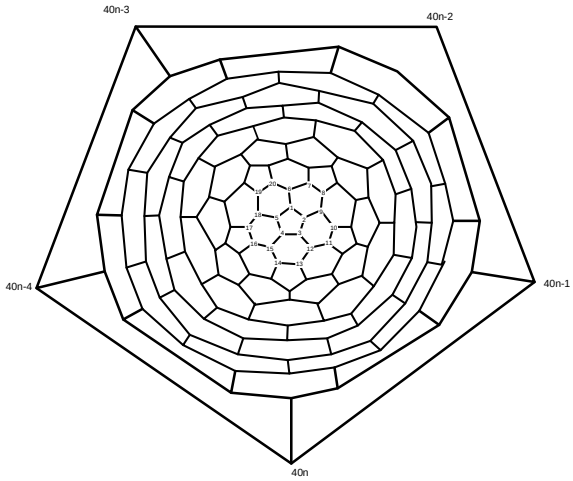

Figure 1. The Schlegel diagram of C_{40n}.

σ=(2,5)(3,4)(7,10)...(10n-10,10n-7)(10n-4,10n-2)(10n-1,10n),

τ=(1,10n-4,3,10n-1,5,10n-3,2,10n,4,10n-2)...(10n-44,10n-36,10n-41,10n-38,10n-43, 10n-39,10n-40,10n-37,10n-42,10n-32).

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.

Table 1. Cycle Types of Elements of C_{40n}.

Fullerene	Cycle type	#Permutations
C_{40n}	1^{40n}	1
	$1^{4n}2^{18n}$	5
	2^{20n}	6
	10^{4n}	4
	5^{8n}	4

Thus the cycle index of G is computed as $Z(G,X) = (x_1^{40n} + 5x_1^{4n}x_2^{18n} + 6x_2^{20n} + 4x_{10}^{4n} + 4x_5^{8n})/20$. From the cycle index one can compute the number of different colourings using k colours via Pólya's theorem by replacing each variable x_i in the cycle index by $1 + x^i$.

In what follows we present a GAP program [17] to compute the number of hetero-fullerenes for $C_{40n-k}X_k$, n ≥ .

A Gap Program for Counting the Number of Hetero fullerenes for C_{40n} (n≥2)

```
f:=function(n)
        local s,i,f,x,t,tt,g;
          Print("Number of vertices is: ",40*n,"\n");
           x:=Indeterminate(Rationals,"x");
f:=((1+x)^(40*n)+5*((1+x)^(4*n))*((1+x^2)^(18*n))+6*((1+x^2)^(20*
                        n))+4*((1+x^(10 ))^(4*n))+4*((1+x^5)^(8*n)))/20;
g:=((1+x)^(40*n)+4*((1+x^5)^(8*n))+5*((1+x^2)^(20*n)))/10;
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;
```

For first, we apply this program to compute the number of hetero-fullerenes for the case n=2 (Table 2).

To investigate the efficiency of this program, we consider the fullerene C_{80}, Figure 2.

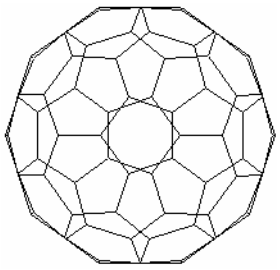

Figure 2. The Fullerene C_{80}

Table 2. Number of $C_{80-k}X_k$ molecules.

k,80-k	Number of $C_{80-k}X_k$ molecules For Symmetry Group	Number of $C_{80-k}X_k$ molecules For Rotational Group
0,80	1	1
1,79	6	8
2,78	186	336
3,77	4194	8216
4,76	79740	158548
5,75	1203782	2404008
6,74	15034806	30054960
7,73	158859426	317671640
8,72	1449480258	2898799410
9,71	11595241522	23190029720
10,70	82325438886	164649540064
11,69	523885533094	1047767706440
12,68	3012337514396	6024666231220
13,67	15756824366962	31513628709080
14,66	75407639879882	150815232429520
15,65	331793540197286	663586981674280
16,64	1347911182335707	2695822151503195
17,63	5074488888801112	10148977366779680
18,62	17760710869067496	35521420920448320
19,61	57956003064041544	115912004662694240
20,60	176765808675933576	353531614645048424
21,59	505045165439887512	1010090326346335520
22,58	1354439305721598168	2708878603630164160
23,57	3415542591867172296	6831085171456838240
24,56	8111913652414445976	16223827285003417560
25,55	18170686570736722680	36341373112150381184
26,54	38437990816963861368	76875981589411644864
27,53	76875981614459748280	153751963166790066848
28,52	145515250904543680112	291030501720170377168
29,51	260923898142211496104	521847796167085497824
30,50	443570626831407097544	887141253504158022032
31,49	715436494844336235640	1430872989490395719840
32,48	1095512132721165787070	2191024265188594496830
33,47	1593472192991913171700	3186944385683154103280
34,46	2202740972661988424780	4405481944959314508640
35,45	2895030992577728759340	5790061984745360652720
36,44	3618788740730127897800	7237577480988390941080
37,43	4303424448373513070740	8606848896243103666160
38,42	4869664507392977231060	9739329014235469036960
39,41	5244254084832211801660	10488508169105968435280
40,40	537536043690996540520	1075072087340254091572 0

We now apply the above presented cycle index to compute the number of permutational isomers of fullerenes under consideration (Table 3).

Table 3: Number of $C_{120-k}X_k$ molecules.

k,120-k	Number of $C_{120-k}X_k$ molecules For Symmetry Group	Number of $C_{120-k}X_k$ molecules For Rotational Group
0,120	1	1
1,119	9	12
2,118	405	744
3,117	14259	28084
4,116	412632	822342
5,115	9536367	19057812
6,114	182684265	365291656
7,113	2974542453	5948756892
8,112	42013919853	84026434917
9,111	522832240566	1045659267016
10,110	5803419985974	11606820594744
11,109	58034121398226	116068178638776
12,108	527143096685568	1054285981000812
13,107	4379341982282658	8758683326510712
14,106	33470683765816230	66941365617149616
15,105	236526160473589102	473052315663260312
16,104	1552202918686129347	3104405822819450907
17,103	9495829590389193519	18991659143539682964
18,102	54337247045227281915	108674493995424201624
19, 101	29170522081825316910 9	58341044140943833 1052
20,100	1473111364848094865916	2946222729155360589846
21,99	7014816022315509542745	1402963204341744558006 0
22,98	3156667209913163541 6019	6313334419554985517292 0
23,97	1345014724191133024615 95	2690029448324823261220 20
24,96	5436101176887145757715 45	1087220235365315747498985
25,95	2087462851912205617786356	4174925703800125701430752
26,94	7627268112737303829404844	1525453622542611964841788 8
27,93	2655419268874640663167782 8	5310838537740045942111793 6
28,92	8819785428756052864184332 8	1763957085749459131694666 16
29,91	2798000894638524398887107 24	5596001789273871069052771 68
30,90	8487269380401707292072894 84	1697453876079767487990657608
31,89	2464045949148508100000172492	4928091898296021941456150544
32,88	6853127796068800101072021819	1370625559213588582886284596 3
33,87	1827500745618250179426929928 9	3655001491236216273246644986 8
34,86	4676251907905403005037439659 7	9352503815810337472038584522 4
35,85	1149021897371019137348737352 91	2298043794741963878691715484 52
36,84	2712968368792657339706896734 32	5425936737585197116503264774 94
37,83	6159171431853551310799752847 59	1231834286370692349388801702308
38,82	1345292707483796525793076573689	2690585414967565890802955326728
39,81	2828564154196690639872133979477	5657128308393341518178262068764
40,80	5727842412248828296445487967359	1145568482449651867023323388 6183
41,79	1117627787755761792454298656751 4	2235255575511515429133849890584 8
42,78	2102204648397740661872180043445 8	4204409296795469896879813442337 6
43,77	3813301455233107986875661011695 8	7626602910466200484121142317709 6
44,76	6673277546657936223586474186598 4	1334655509331585155492600652964 68
45,75	1127042430102228769176769436470 06	2254084860204454809751359845797 52
46,74	1837569179514503034961855546443 30	3675138359029002524129966192224 80
47,73	2893194027320706255089864080332 90	5786388054641408045383925585175 60
48,72	4400065916550240254820271596085 35	8800131833100474915949990904983 35
49,71	6465402979420760345972779583732 55	1293080595884151389733754799136180
50,70	9180872230777479102734843628734 43	1836174446155494999379650802722024
51,69	1260119717949849972898410419576157	2520239435899698983128141706551692
52,68	1672081933433454711928110241702728	3344163866866908301016963593337634
53,67	2145312669310847447636010877139601	4290625338621693624396676664419644
54,66	2661776830441236597146467544097383	5323553660882471763161240697200632
55,65	3194132196529483813659635751641043	6388264393058966062990607479134372
56,64	3707474870971722252390899898299397	7414949741943442803545499299939301
57,63	4162778802494565249939680394539240	8325557604989128703646906989049312
58,62	4521639044088924319727997397894440	9043278088177846752565403398800192
59,61	4751552893788361090371095093480184	9503105787576720256120636674233376
60,60	4830745442018167136321641186395224	9661490884036332319521604735649640

CONCLUSIONS

Hetero-fullerenes or fullerene molecules in which one or more carbon atoms are replaced by hetero-atoms such as boron or nitrogen, can be enumerated by applying the Polya's theorem. In this paper, the numbers of all $C_{40n-k}X_k$ hetero-fullerenes were computed, C_{40n} being an infinite family of fullerenes. In this respect, we applied the computer algebra system GAP to compute the number of permutational isomers of hetero-fullerenes of the C_{80} fullerene with D_{20} point group symmetry.

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