The Enumeration of Chiral Isomers of Tetraammine Platinum(II)

Modjtaba Ghorbani*, Mahin Songhori

Department of Mathematics, Faculty of Science, Shahid Rajaee
Teacher Training University, Tehran, 16785-136, I. R. Iran

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Abstract

In this paper the problem of finding formulas of chiral isomers of tetraammine platinum (II) is considered. The procedure starts with the computing the point group of a given molecular structure and then we determine it's cycle index. Finally, by using a GAP program we enumerate all chiral isomers of tetraammine platinum (II).

1. Introduction

All graphs in this paper are connected simple graph. A graph is a collection of points and lines connecting them. The points and lines of a graph are also called vertices and edges respectively. If $e$ is an edge of $G$, connecting the vertices $u$ and $v$, then we write $e = uv$ and say "$u$ and $v$ are adjacent". A connected graph is a graph such that there exists a path between all pairs of vertices. A molecular graph is a simple graph such that its vertices correspond to the atoms and the edges to the bonds.

A coloring of a graph is the assignment of a color to each vertex of the graph so that no two adjacent vertices are assigned the same color. There is a close relationship between

* Author to whom correspondence should be addressed. (E-mail: mghorbani@srttu.edu)
graph coloring and counting number of the chiral isomers of a molecular graph. In other words, in this paper we enumerate all possible coloring of a graph on \( n \) vertices with \( k \) colors. We do this by using Polya's theorem. Here, our notation is standard and mainly taken from [1, 2].

2. Main Results and Discussion

The problem of enumerating structural isomers has fascinated mathematicians and chemists since the end of the nineteenth century. Enumeration of chiral isomers of substituted fullerene cages (\( C_{20}-C_{70} \)) is considered using the generalized character cycle index of the alternating representation of the point group of the parent cage.\(^1\)\(^2\). It is shown that there are no chiral isomers for the monosubstituted fullerenes \( C_{20}, C_{24}, C_{28}, C_{30}, C_{36}, \) and \( C_{60} \) but there are chiral isomers for other monosubstituted cages. Ghorbani\(^3\)-\(^7\) computed the number of chiral isomers of a series of fullerenes. The aim of this section is to compute the symmetry group of tetraammine platinum(II) and then finding it's cycle index. Finally, by using Polya's theorem we compute all it's chiral isomers.

2.1 The concept of symmetry group

Symmetry plays an central role in the analysis of the structure, bonding, and spectroscopy of molecules. Chemists classify molecules according to their symmetry. The molecular symmetry first defined by Longuet-Higgins.\(^8\) Detecting symmetry of molecules is a well-studied problem with applications in a large number of areas. Randić\(^9\),\(^10\) and then Balasubramanian\(^1\),\(^2\),\(^11\) 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.

There is a close relationship between groups and the notion of symmetry. For instance, a symmetry group present the symmetry features of a geometrical object. On the other hand, the collection of symmetry elements present in a molecule forms a group, typically called a point group. We name it as point group, since all the symmetry elements will intersect at a single point. The symmetry properties of molecules may be described in terms of the presence of certain symmetry elements and their associated symmetry operations. Symmetry elements
are properties which are related to the structure of the molecule including mirror planes, axes of rotation, centers of inversion and improper axes of rotation.

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

Basically, a group action is nothing more than seeing your abstract group as a group of permutations. Recall that $S_X$ is the set of all bijections of $X$, which are called permutations by another name, with the binary operation of function composition rendering this set a group. Hence, a permutation representation of $G$ on $X$ is a homomorphism from $G$ into $S_X$. Permutations are often written in cyclic form so that given the set $X = \{1, 2, 3, 4\}$, a permutation $f$ of $X$ with $f(1) = 2$, $f(2) = 4$, $f(4) = 1$ and $f(3) = 3$ will be written as $(1, 2, 4, 3)$ since 3 is left unchanged.

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 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 $\sigma$ 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 $G$. So, 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 $E$.

### 2.2 The concept of cycle index and Polya's enumeration theorem

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 $Z(G, X) = \frac{1}{|G|} \sum_{\sigma \in G} \prod_{i=1}^t x_i^{c_i(\sigma)}$, in which $(c_1(\sigma), \ldots, c_t(\sigma))$ is the cycle type of the permutation $\sigma \in G$. 
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.

A coloring of the vertices, edges or faces of a molecule with \( k \) colors can be interpreted as a function from the set of all vertices, edges or faces into the set of \( k \) colors. Two colorings are called different if and only if the corresponding functions lie in different or orbits of the symmetry group acting on the set of all these functions in a natural way. This means that the group is acting on the domain of these functions. From the cycle indices above one can compute the number of different colorings using \( k \) colors via Pólya - theory by replacing each variable \( x_i \) in the cycle index by \( k \).

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 \( p \in S_m \) induced on \( C_{m,n} \) is defined by \( \hat{p} (f) = f o p^{-1}, f \in C_{m,n} \). 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 \( W(f) = \prod_{i=1}^{n} f(i) \). Evidently, \( W(f) \) is a monomial of (total) degree \( m \).

To enumerate all possibilities of the heterostructures, we have to consider the rotation group of the tetraammine platinum(II) and its whole automorphism group to enumerate the number of chiral isomers. From the above discussion our problem is reduced to the coloring of the corresponding molecular graph.

Before computing the cycle index tetraammine platinum(II) we calculate the cycle index of IPR fullerene \( C_{80} \), see Figure 1. A fullerene graph is a cubic 3-connected planar graph
with exactly 12 pentagonal faces. For a fullerene with \( n \) vertices there are exactly \( n/2 \cdot 10 \) hexagonal faces.

We mention here that our computations of symmetry properties and cycle indices of fullerenes were carried out with the use of GAP.\(^{13}\) This software was constructed by the GAP team in Aachen.

**Theorem 2.**

\[
Z(C_{80}, X) = \left( x_1^{80} + 4x_2^{16} + 6x_2^{40} + 4x_2^{80} + 5x_1^4x_2^{38} \right)/20.
\]

**Proof.** By using concept of symmetry one can see that the generators of fullerene graph \( C_{80} \) are as follows:

\[

\[

By using GAP program one can see that \( X^2 = Y^2 = (XY)^{10} = 1 \) and \( X^{-1}(XY)X = (XY)^{-1} \) and so this symmetry group is isomorphic with a Dihedral group of order 20, namely \( D_{20} \). Now by using definition of the cycle index the proof is completed.

![Figure 2.3 - D graph of fullerene \( C_{80} \).](image)
Now we are ready to compute the cycle index of tetra ammine platinum (II). The full, non-rigid group and symmetry properties of tetraammine platinum(II) of order 5184 with $C_{2v}$ and $C_{4v}$ point groups were computed. Let $G$ be the symmetry group of tetraammine platinum(II) (see Figure 2), then by the following program in GAP:

```
gap> G:=Group((2,3,4,5)(6,9,12,15,7,10,13,16,8,11,14,17),(2,3,4,5)(6,9,12,15,7,10,13,17,8,11,14,16),(2,5)(3,4)(6,15)(7,17)(8,16)(9,12)(10,14)(11,13));
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one can compute it's cycle index.

![Figure 2. The structure of tetraammine platinum(II).](image)

However, by using GAP, one can see that the symmetry group $S$ is of order 5184 and the cycle types of elements of $S$ are as in the following table:

<table>
<thead>
<tr>
<th>Symmetry group</th>
<th>Cycle type</th>
<th>#Permutations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G$</td>
<td>$1^{17}$</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$1^{14}3$</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>$1^{13}2^2$</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>$1^{11}3^2$</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>$1^{10}2^23$</td>
<td>216</td>
</tr>
<tr>
<td></td>
<td>$1^{10}3^3$</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>$1^{9}2^4$</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>$1^{9}4^2$</td>
<td>12</td>
</tr>
</tbody>
</table>
Thus the cycle index of symmetry group $S$ is computed as:

$$Z(G, X) = \frac{1}{5184} \left( x_1^{17} + 8x_1^{14}x_3 + 54x_1^{13}x_2^2 + 24x_1^{11}x_2^2 + 216x_1^{10}x_2^2x_3 + 32x_1^8x_3^3 
+ 8x_1^9x_2^4 + 12x_1^9x_3^2 + 24x_1^9x_2x_6 + 216x_1^7x_2^2x_3^2 + 16x_1^7x_2^4 
+ 216x_1^7x_2x_4 + 48x_1^6x_2^2x_4 + 96x_1^6x_2x_3x_6 + 108x_1^5x_3^2 + 216x_1^5x_2^2x_6 
+ 432x_1^4x_2x_3x_4 + 48x_1^4x_2^2x_3^2 + 96x_1^4x_2x_3x_6 + 108x_1^3x_4^2 
+ 432x_1^3x_2x_6 + 972x_1^3x_2^2x_4 + 288x_1^3x_2x_2^2 + 432x_1^3x_2^2 + 864x_4^2 + 144x_4^2 \right).$$
3. Conclusions

In this paper an efficient method is presented which is useful for computing permutational isomers of hetero-molecules. We applied our method on tetraammine platinum(II) and compute the number of such isomers.

References


