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Symmetry properties of tetraammine platinum(II) with C_{2v} and C_{4v} point groups

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Abstract: Let G be a weighted graph with adjacency matrix $\boldsymbol{A}=[a_{ij}]$. An Euclidean graph associated with a molecule is defined by a weighted graph with adjacency matrix $\boldsymbol{D}=[d_{ij}]$, 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. Balasubramanian (1995) computed the Euclidean graphs and their automorphism groups for benzene, eclipsed and staggered forms of ethane and eclipsed and staggered forms of ferrocene. This paper describes a simple method, by means of which it is possible to calculate the automorphism group of weighted graphs. We apply this method to compute the symmetry of tetraammine platinum(II) with C_{2v} and C_{4v} point groups.

Key words: Weighted graph, Euclidean graph, Tetraammine platinum(II)
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INTRODUCTION

The simplicity and elegance of some of the applications of graph theory to chemistry can perhaps only be compared with the results from group theory dealing with symmetry as a basic quality of a system. In some problems connectivity and symmetry are combined and the question of determining symmetry properties of graph becomes important.

Given here are some definitions and notations. An automorphism of a graph G is a permutation g of the vertex set of G with the property that, for any vertices u and v, ug and vg are adjacent if and only if u is adjacent to v. The set of all automorphisms of a graph G, with the composition of permutations, is a permutation group on VG, denoted $Aut(G)$. By symmetry we mean the automorphism group symmetry of a graph. The symmetry of a graph, also called topological symmetry, accounts only for the bond relations between atoms, and does not fully determine molecular geometry. The symmetry of a graph need not be the same as (i.e. isomorphic to) the molecular point group symmetry. However, it does represent the maximal symmetry which the geometrical realization of a given topological structure may posses.

Randic (1974; 1976) showed that a graph can be depicted in different ways such that its point group symmetry or three dimensional perception may differ, but the underlying connectivity symmetry is still the same as characterized by the automorphism group of the graph. However, the molecular symmetry depends on the coordinates of the various nuclei which relate directly to its three dimensional geometry. Although the symmetry as perceived in graph theory by the automorphism group of the graph and the molecular group are quite different, Balasubramanian (1995) showed that the two symmetries are connected.

Automorphisms have other advantages such as in generating nuclear spin species, NMR spectra, nuclear spin statistics in molecular spectroscopy, chirality and chemical isomerism. There is also an-

other important applications of automorphism groups of weighted graphs to fullerenes. The reader is encouraged to consult the papers by Balasubramanian (1980; 1981; 1982; 1983; 1985; 1995; 2004a; 2004b; 2004c) for background material and basic computational techniques.

The perception of the symmetry of a graph through the automorphism group of the graph had been studied in considerable depth (Balasubramanian, 1980; 1981; 1982; 1983; 1985; 1995; 2004a; 2004b; 2004c; Randic and Davis, 1984; Ezra, 1982; Herndon, 1983; Trinajstic, 1992), but the connection between the graph automorphism problem and the symmetry of a molecule has not been explored as much. Longuet-Higgins (1963) showed that a more desirable representation of molecular symmetry is to use the nuclear permutation and inversion operations resulting in a group called Permutation-Inversion (PI) group. Balasubramanian (1995) showed that the automorphism group of Euclidean graphs of a molecule is the PI group of the molecule.

In (Ashrafi and Hamadanian, 2003; 2004; Hamadanian and Ashrafi, 2003a; 2003b), the full non-rigid group of trimethylamine with C_{3v} point group and tetraammine platinum(II) with C_{2v} and C_{4v} point groups are computed. In this paper we compute the symmetry of these molecules. Throughout this paper, all groups considered are assumed to be finite. Our notation is standard and taken mainly from (James and Liebeck, 1993).

EXPERIMENTAL DETAILS

A permutation of the vertices of a graph belongs to its automorphism group if it satisfies $\boldsymbol{P}^{\mathrm{T}}\boldsymbol{AP}=\boldsymbol{A}$, where $\boldsymbol{P}^{\mathrm{T}}$ is the transpose of permutation matrix $\boldsymbol{P}$ and $\boldsymbol{A}$ is the adjacency matrix of the graph under consideration. There are $n!$ possible permutation matrices for a graph with n vertices. However, all of them may not satisfy the above relation. For a given adjacency matrix $\boldsymbol{A}$, we can write a simple GAP program (Schönert *et al*., 1995) to calculate all the permutation matrices with $\boldsymbol{P}^{\mathrm{T}}\boldsymbol{AP}=\boldsymbol{A}$. To illustrate, let us consider the eclipsed and staggered conformations of ethane. Their point groups are well known to be $\boldsymbol{D}_{3h}$ and $\boldsymbol{D}_{3d}$, respectively. By (Balasubramanian, 1995), the matrix $\boldsymbol{A}$ is as follows:

$$\boldsymbol{A}=\begin{bmatrix}0&1&0&2&0&1\\1&0&1&0&2&0\\0&1&0&1&0&2\\2&0&1&0&1&2\\0&2&0&1&0&1\\1&0&2&0&1&0\end{bmatrix}$$

There is a typographic error in (Balasubramanian, 1995), for computing the automorphism group of the graph with the adjacency matrix $\boldsymbol{A}$. We now write a GAP program for calculating the symmetries of the eclipsed and staggered conformations of ethane:

```
P:=[[0,1,1,2,0,0], [1,0,1,0,2,0], [1,1,0,0,0,2], [2,0,0,0,
   1,1], [0,2,0,1,0,1], [0,0,2,1,1,0]];
n:=6; i:=0; H:=[];
t:=SymmetricGroup(n);
tt:=Elements(t);
for a in tt do
    x1:=PermutationMat(a, n);
    x:=TransposedMat(x1);
    y:=xPx1;
    if y=P then AddSet(H, a); fi;
od;
G:=Group(H);
```

Using this program, we can see that the symmetries of the eclipsed and staggered conformations of ethane is as follows:

G={(1)(2)(3)(4)(5)(6), (2,3)(5,6), (1,5,3,4,2,6), (1,2)(4,5), (1,2,3)(4,5,6), (1,3,2)(4,6,5), (1,3)(4,6), (1,4)(2,5)(3,6), (1,4)(2,6)(3,5), (1,5)(2,4)(3,6), (1,6,2,4,3,5), (1,6)(2,5)(3,4)}

Using several computations with computer algebra system GAP we conjecture that the automorphism group of a complete weighted graph must be trivial or has an even number of symmetries.

RESULTS AND DISCUSSION

The automorphism group of a graph depends only on the connectivity of the graph and does not depend on how the graph is represented in three di-

mensions. That is, a graph, in general, can be represented in different ways in three dimensions such that two representations could yield different three-dimensional symmetries and yet their automorphism groups are the same since the latter depends only on which vertices are connected in the graph. For this reason the symmetry of a graph was thought to be quite different from the point group symmetry and it is apparent that the two symmetries need not be related to each other.

In this section, we investigate the automorphism group of weighted graphs. By definition, a weighted graph is a graph whose edges and vertices are weighted with different weights. The adjacency matrix of a weighted graph is defined as: $\boldsymbol{A}_{ij}=\boldsymbol{w}_{ij}$, if $i\neq j$ and vertices i and j are connected by an edge with weight $\boldsymbol{w}_{ij}$; $\boldsymbol{A}_{ij}=\boldsymbol{v}_i$, if $i=j$ and the weight of the vertex i is $\boldsymbol{v}_i$, and, $\boldsymbol{A}_{ij}=0$, in the case that $i\neq j$ and i, j are not adjacent. Note that v_i can be taken as zero if all the nuclei are equivalent. Otherwise, one may introduce different weights for nuclei in different equivalence classes and the same weight for the nuclei in the same equivalence classes.

Consider the tetraammine platinum(II) (Fig.1) with C_{2v} and C_{4v} point groups to illustrate the Euclidean graphs (Figs.2 and 3) and their automorphism groups. It suffices to measure the Euclidean distances (Tables 1 and 2) in terms of the H–H bond lengths and then construct the Euclidean distance matrix $\boldsymbol{D}$. It should be mentioned that one does not have to work with exact Euclidean distances in that a mapping of weights into a set of integers would suffice as long as different weights are identified with different integers. In fact the automorphism group of the integer-weighted graph is identical to the automorphism group of the original Euclidean graph. To illustrate, let us map the Euclidean edge weighted for tetraammine platinum(II) with C_{2v} point group as 1.78→1, 4.00→2, 2.93→3, 4.15→4, 4.87→5, 5.18→6, 2.41→7, 3.80→8 and 4.81→9. Also, we map the Euclidean edge weighted for tetraammine platinum(II) with C_{4v} point group as 1.78→1, 3.44→2, 4.40→3, 3.27→4, 4.87→5, 5.18→6, 3.66→7, 2.18→8 and 4.70→9.

All 12! permutations of the vertices do not belong to the automorphism group of the weighted graph since the weights of all the edges are not the same. For example, the permutation (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12) does not belong to the automorphism group since the resulting graph shown in Fig.1 does not preserve connectivity.

We computed below the distance matrices $\boldsymbol{D}$ and $\boldsymbol{E}$ for tetraammine platinum(II) with C_{2v} and C_{4v} point groups, respectively.

$$\boldsymbol{D}=\begin{bmatrix}0&1&1&2&3&4&2&4&3&5&6&6\\1&0&1&3&7&8&4&9&8&6&6&5\\1&1&0&4&8&9&3&8&7&6&5&6\\2&3&4&0&1&1&5&6&6&2&4&3\\3&7&8&1&0&1&6&6&5&4&9&8\\4&8&9&1&1&0&6&5&6&3&8&7\\2&4&3&5&6&6&0&1&1&2&3&4\\4&9&8&6&6&5&1&0&1&3&7&8\\3&8&7&6&5&6&1&1&0&4&8&9\\5&6&6&2&4&3&2&3&4&0&1&1\\6&6&5&4&9&8&3&7&8&1&0&1\\6&5&6&3&8&7&4&8&9&1&1&0\end{bmatrix}$$

$$\boldsymbol{E}=\begin{bmatrix}0&1&1&2&3&4&2&4&3&5&6&6\\1&0&1&4&7&8&3&7&9&6&6&5\\1&1&0&3&9&7&4&8&7&6&5&6\\2&4&3&0&1&1&5&6&6&2&3&4\\3&7&9&1&0&1&6&6&5&4&7&8\\4&8&7&1&1&0&6&5&6&3&9&7\\2&3&4&5&6&6&0&1&1&2&4&3\\4&7&8&6&6&5&1&0&1&3&7&9\\3&9&7&6&5&6&1&1&0&4&8&7\\5&6&6&2&4&3&2&3&4&0&1&1\\6&6&5&3&7&9&4&7&8&1&0&1\\6&5&6&4&8&7&3&9&7&1&1&0\end{bmatrix}$$

Suppose G and H comprise the set of all permutations, which preserves the Euclidean connectivity for tetraammine platinum(II) with C_{2v} and C_{4v} point groups, respectively. Then using our GAP program, we have:

G={(1,10)(2,11)(3,12)(4,7)(5,8)(6,9), (1,7,10,4)(2,9,11,6)(3,8,12,5), (1,4)(2,5)(3,6)(7,10)(8,11)(9,12), (1,4,10,7)(2,6,11,9)(3,5,12,8), (1,7)(2,8)(3,9)(4,10)(5,11)(6,12), (2,3)(4,7)(5,9)(6,8)(11,12), (1,10)(2,12)(3,11)(5,6)(8,9), (1)(2)(3)(4)(5)(6)(7)(8)(9)(10)(11)(12)}

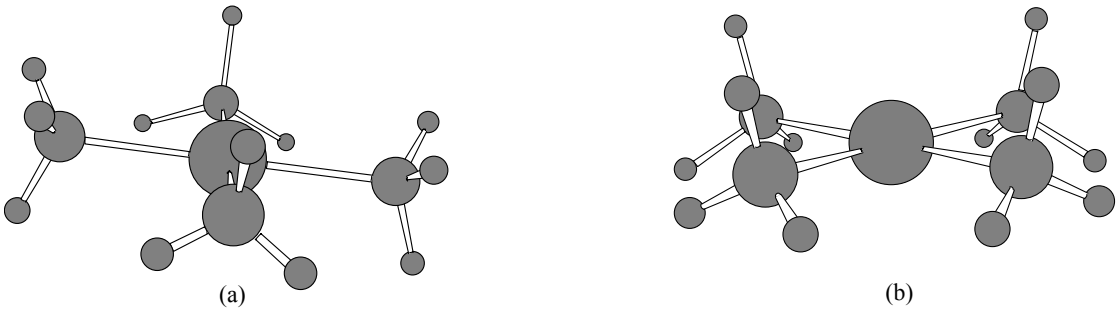

Fig.1 The structure of tetraamine platinum(II) (a) with C_{2v} point group; (b) with C_{4v} point group

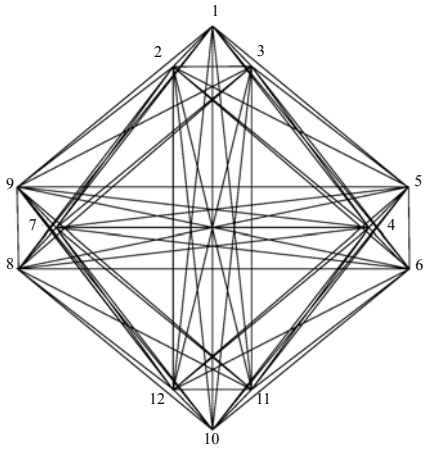

Fig.2 The Euclidean graph of tetraamine platinum(II) with C_{2v} point group

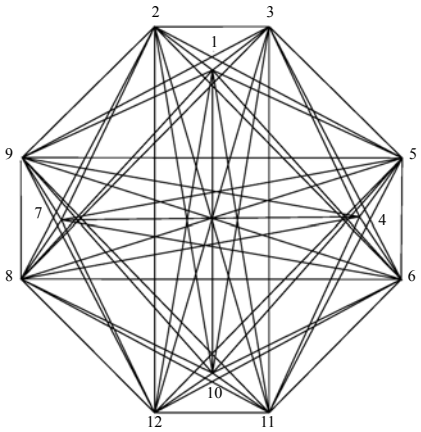

Fig.3 The Euclidean graph of tetraamine platinum(II) with C_{4v} point group

Table 1 Euclidean edges for tetraamine platinum(II) with C_{2v} point group

No.	1	2	3	4	5	6	7	8	9	10	11	12
1	0.00	1.78	1.78	4.00	2.93	4.15	4.00	4.15	2.93	4.87	5.18	5.18
2	1.78	0.00	1.78	2.93	2.41	3.80	4.15	4.81	3.80	5.18	5.18	4.87
3	1.78	1.78	0.00	4.15	3.80	4.81	2.93	3.80	2.41	5.18	4.87	5.18
4	4.00	2.93	4.15	0.00	1.78	1.78	4.87	5.18	5.18	4.00	4.15	2.93
5	2.93	2.41	3.80	1.78	0.00	1.78	5.18	5.18	4.87	4.15	4.81	3.80
6	4.15	3.80	4.81	1.78	1.78	0.00	5.18	4.87	5.18	2.93	3.80	2.41
7	4.00	4.15	2.93	4.87	5.18	5.18	0.00	1.78	1.78	4.00	2.93	4.15
8	4.15	4.81	3.80	5.18	5.18	4.87	1.78	0.00	1.78	2.93	2.41	3.80
9	2.93	3.80	2.41	5.18	4.87	5.18	1.78	1.78	0.00	4.15	3.80	4.81
10	4.87	5.18	5.18	4.00	4.15	2.93	4.00	2.93	4.15	0.00	1.78	1.78
11	5.18	5.18	4.87	4.15	4.81	3.80	2.93	2.41	3.80	1.78	0.00	1.78
12	5.18	4.87	5.18	2.93	3.80	2.41	4.15	3.80	4.81	1.78	1.78	0.00

Table 2 Euclidean edges for tetraamine platinum(II) with C_{4v} point group

No.	1	2	3	4	5	6	7	8	9	10	11	12
1	0.00	1.78	1.78	3.44	4.40	3.27	3.44	3.27	4.40	4.87	5.18	5.18
2	1.78	0.00	1.78	3.27	3.66	2.18	4.40	3.66	4.70	5.18	5.18	4.87
3	1.78	1.78	0.00	4.40	4.70	3.66	3.27	2.18	3.66	5.18	4.87	5.18
4	3.44	3.27	4.40	0.00	1.78	1.78	4.87	5.18	5.18	3.44	4.40	3.27
5	4.40	3.66	4.70	1.78	0.00	1.78	5.18	5.18	4.87	3.27	3.66	2.18
6	3.27	2.18	3.66	1.78	1.78	0.00	5.18	4.87	5.18	4.40	4.70	3.66
7	3.44	4.40	3.27	4.87	5.18	5.18	0.00	1.78	1.78	3.44	3.27	4.40
8	3.27	3.66	2.18	5.18	5.18	4.87	1.78	0.00	1.78	4.40	3.66	4.70
9	4.40	4.70	3.66	5.18	4.87	5.18	1.78	1.78	0.00	3.27	2.18	4.70
10	4.87	5.18	5.18	3.44	3.27	4.40	3.44	4.40	3.27	0.00	1.78	1.78
11	5.18	5.18	4.87	4.40	3.66	4.70	3.27	3.66	2.18	1.78	0.00	1.78
12	5.18	4.87	5.18	3.27	2.18	3.66	4.40	4.70	4.70	1.78	1.78	0.00

H={(1)(2)(3)(4)(5)(6)(7)(8)(9)(10), (2,3)(4,7)(5,9)(6,8)(11,12), (1,4,10,7)(2,5,11,8)(3,6,12,9), (1,4)(2,6)(3,5)(7,10)(8,12)(9,11), (1,7,10,4)(2,8,11,5)(3,9,12,6), (1,7)(2,9)(3,8)(4,10)(5,12)(6,11), (1,10)(2,11)(3,12)(4,7)(5,8)(6,9), (1,10)(2,12)(3,11)(5,6)(8,9)}

We can see that *G* and *H* are subgroups of a parent group *U* of order 16. This group has the following elements:

U={(4,7)(5,8)(6,9), (2,3)(5,6)(8,9)(11,12), (2,3)(4,7)(5,9)(6,8)(11,12), (1,4)(2,5)(3,6)(7,10)(8,11)(9,12), (1,4,10,7)(2,5,11,8)(3,6,12,9), (1,4)(2,6)(3,5)(7,10)(8,12)(9,11), (1,4,10,7)(2,6,11,9)(3,5,12,8), (1,7,10,4)(2,8,11,5)(3,9,12,6), (1,7)(2,8)(3,9)(4,10)(5,11)(6,12), (1,7,10,4)(2,9,11,6)(3,8,12,5), (1,7)(2,9)(3,8)(4,10)(5,12)(6,11), (1,10)(2,11)(3,12), (1,10)(2,11)(3,12)(4,7)(5,8)(6,9), (1,10)(2,12)(3,11)(5,6)(8,9), (1,10)(2,12)(3,11)(4,7)(5,9)(6,8), (1)(2)(3)(4)(5)(6)(7)(8)(9)(10)(11)(12)}

CONCLUDING REMARKS

We can use this method for computing with small groups. When the order of the symmetric group is large, the command "*Elements*(*t*)" is interrupted. In this situation, one can find all the conjugacy classes of symmetric groups and then compute the symmetries of the molecule under consideration in every conjugacy classes, separately. This method is usually very useful for calculating symmetries of the molecule, when the number of vertices are at most 30. In the case that the graph under consideration has a large number of vertices, it is better to find a subgroup of the full symmetric group containing automorphism group of our weighted graph. Then apply this subgroup and our GAP program to compute the automorphism group of the graph.

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