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Full Non-Rigid Group Theory and Symmetry of Melamine

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The non-rigid molecule group (NRG) theory in which the dynamic symmetry operations are defined as physical operations is a new field in chemistry. Smeyers, in a series of papers, applied this notion to determine the character table of restricted NRG of some molecules. For example, Smeyers and Villa computed the r-NRG of the triple equivalent methyl rotation in pyramidal trimethylamine with inversion and proved that the r-NRG of this molecule is a group of order 648, containing two subgroups of order 324 without inversion [5].

In this work, a simple method is described, through which it is possible to calculate character tables for the symmetry group of molecules. We study the full NRG of melamine, and prove that it is a groups of order 48, with 27 and 10 conjugacy classes. Also, we compute the symmetry of melamine and prove that it is a non-abelian groups of order 6. The method can be generalized to apply to other non-rigid molecules.

Keywords: Melamine, Character table, Full non-rigid group, Euclidean matrix

INTRODUCTION

The mathematical tools of group theory have been used extensively for the analysis of the symmetry properties of physical systems. The symmetry properties of rigid molecules are well known and so it is natural to investigate non-rigid molecules.

According to Y.G. Smeyers [1], the non-rigid molecule group (NRG) is strictly defined as the complete set of the molecular conversion operations, which commute with a given nuclear Hamiltonian operator, limited to large amplitude motions. In addition, these molecular conversation operations are expressed in terms of physical operations, such as rotations, internal rotations and inversions, similar to Altmann's theory, rather than in terms of permutations and permutation-inversions. This way of expressing the non-rigid operations is indeed more descriptive and flexible.

Longuet-Higgins investigated the symmetry groups of non-rigid molecules, where changes from one conformation to another can occur easily [2]. In many cases, these symmetry groups are not isomorphic with any of the familiar symmetry groups of rigid molecules, and their character tables are not known. It is therefore of some interest and importance to develop simple methods of calculating these character tables, which are needed for the classification of wave functions, determination of selection rules, and so on.

Lomont [3] has given two methods for calculating character tables. These are satisfactory for small groups, but both of them require a knowledge of the class constant and hence of the group multiplication table, thereby becoming very unwieldy as soon as the order of the group becomes even moderately large. For non-rigid molecules, whose symmetry

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groups may have several thousand elements, they are usually quite impracticable. The alternative approach is less mechanical, requiring a certain amount of thought, but it is nevertheless simpler in practice. This involves two steps: first, the decomposition of the group into classes, and second, the determination of sets of basic functions for certain representations, whose characters are then determined directly.

Stone described a method which is appropriate for molecules with a number of XH_3 groups attached to a rigid framework [4]. However, this method is not appropriate in cases where the framework is linear, as with ethane and dimethylacetylene.

Smeyers and Villa investigated the r-NRG of planar trimethylamine and proved that this is a group of order 324 [5]. Furthermore, they showed that this molecule has a pyramidal inversion and so the order of r-NRG of trimethylamine is 648.

Randic has shown 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 [6]. However, the molecular symmetry depends on the coordinates of the various nuclei which relate directly to their 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 has shown that the two symmetries are connected [7].

The character table of full non-rigid groups of trimethylamine, *cis*- and *trans*-dichloro diammine platinum(II) and tetraammine platinum(II) with C_{2v} and C_{4v} point groups was computed [8-10].

In this paper, we investigate the f-NRG and symmetry of melamine (2,4,6-triamino-1,3,5-triazine). We prove that the f-NRG of melamine has order 48 with 10 conjugacy classes.

Throughout this paper, the notation is standard [11,12] and all groups considered are assumed to be finite.

EXPERIMENTAL

Let us recall 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 operation of 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 a topological symmetry, accounts only for the bond relations between atoms, and does not fully determine molecular geometry. The symmetry of a graph does not need to be isomorphic to the molecular point group symmetry. However, it does represent the maximal symmetry possessed by the geometrical realization of a given topological structure.

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: $A_{ij} = w_{ij}$, if $i \neq j$ and vertices i and j are connected by an edge with weight w_{ij}; $A_{ij} = v_i$, if $i = j$ and the weight of the vertex i is v_i, and $A_{ij} = 0$. 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. The topic of perceiving the symmetry of a graph through the automorphism group of the graph has been studied in considerable depth [13]. However, the connection between the graph automorphism problem and the symmetry of a molecule has not been explored in as much detail. Longuet-Higgins has shown a more desirable representation of molecular symmetry using the nuclear permutation and inversion operations, resulting in a group called the Permutation-Inversion (PI) group [2]. Balasubramanian has shown that the automorphism group of the Euclidean graph of a molecule is the PI group of the molecule [7].

Our computations were carried out using the "Groups, Algorithms and Programming" (GAP) system [14]. GAP is a free and extensible software package for computation in discrete abstract algebra, in which you can write your own programs in the GAP language, and use them in the same way the programs which form part of the system are used. More information on the motivation and development of GAP to date can be found on the GAP web page (http://www.gap-system.org).

RESULTS AND DISCUSSION

Regarding the character table of the f-NRG of melamine and symmetry of this molecule, first of all we must consider the point group of this molecule in the rigid state. The point group of this molecule is D_{3h}, of order of 12. The process of enumerating the symmetry operations of this molecule and arranging them in classes entails the adoption of a numbering convention for the center of the molecule, central atom of every NH_2 group, and the center of other atoms, such as protons in the nuclei.

Character Table of Melamine

Using Fig. 1, we define the operations a = (10, 11), b = (12, 13) and c = (14, 15) for melamine which are rotations, in a positive sense, of each NH_2 group. We assume that all these operations are feasible.

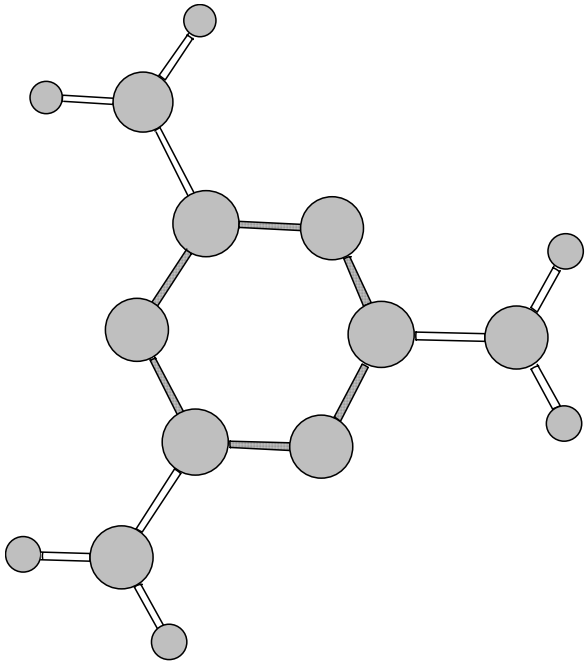
Let us first consider operations that leave the framework of the molecule unchanged. These operations are grouped according to their cycle structure; operations which rotate different numbers of NH_2 groups must belong to different conjugacy classes. If we now consider the operations which rotate one NH_2 group in melamine, we can see that they must all belong to the same class, since operations involving the rotation of the molecular framework will transform a into a^{-1}, b^{-1} or c^{-1}.

Consider next the operations that permute the nuclei of the framework; for this molecule, these fall into sets corresponding to the classes of D_{3h}. It is clear that the point group D_{3h} has exactly five different types of non-identity elements, *i.e*. C_2, C_3, S_3, σ_h and σ_v, which are related to rotation through the main axial, rotational reflection, reflection through horizontal and vertical planes. Now, we can consider different conjugacy classes of D_{3h} and fuse them to the non-rigid group. Assume that G denotes the non-rigid group of melamine.

$a_1 = (1,3,5)(2,4,6)(7,8,9)(10,12,14)(11,13,15)$,
$a_2 = (3,5)(2,6)(10,13)(8,7)(12,11)(15,14)$,
$a_3 = (2,6)(3,5)(7,8)(11,13)(10,12)$.

Then $|(a_1)^G| = 8$ and $|(a_2)^G| = |(a_3)^G| = 6$. The point group of melamine can be generated by the set $V_1 = \{a_1, a_2, a_3\}$, and if

(a)



(b)

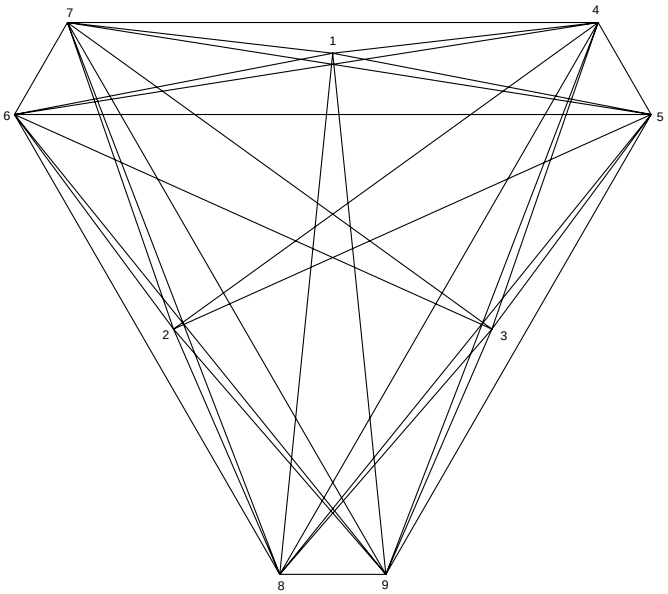


Fig. 1. (a) 2,4,6-triamino-1,3,5-triazine molecule (melamine) with D_{3h} point group. (b) The Euclidean graph of melamine.

$V_2 = \{\alpha, \beta, \gamma\}$ then $V_1 \cup V_2$ generates the non-rigid group of the molecule. Since, G is a permutation group, we can use the GAP system to find the conjugacy classes and character table of G. Thus G has order 48. Using the GAP System, we compute the character table of non-rigid group of melamine, as seen in Table 1.

Symmetry of Melamine

Symmetry operations on a graph are called graph automorphisms. They affect only the labels of vertices by permuting them so that the adjacency matrix of the graph remains unchanged. The graph symmetry is completely determined by all the automorphisms it has, *i.e*. by specifying all the permutations which leave the adjacency matrix intact.

We can associate a permutation matrix to every permutation a in S_n. A permutation of the vertices of a graph belongs to its automorphism group if it satisfies $P^tAP = A$, where P^t is the transpose of permutation matrix P and A is the adjacency matrix of graph under consideration. There are n! possible permutation matrices for a graph with n vertices. However, all of them may not satisfy the above relationship. For a given adjacency matrix A, we can write a simple GAP program to calculate all the permutation matrices with $P^tAP = A$.

Consider the Euclidean graph of melamine and its automorphism group. It suffices to measure the Euclidean distances in terms of the H-H bond lengths and then construct the Euclidean distance matrix D for melamine. 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 melamine as $2.322 \rightarrow 1$, $2.52 \rightarrow 2$, $3.22 \rightarrow 3$, $4.59 \rightarrow 4$, $1.75 \rightarrow 5$, $5.69 \rightarrow 6$, $4.61 \rightarrow 7$ and $6.36 \rightarrow 8$.

We assume that H is the automorphism group of the given weighted graph. We have written the following GAP program to compute the automorphism group Aut(H).

Table 1. Character Table of the f-NRG of Melamine

		1a	2a	2b	2c	2d	2e	4a	4b	3a	6a
	2p	1a	1a	1a	1a	1a	1a	2b	2b	3a	3a
	3p	1a	2a	2b	2c	2d	2e	4a	4b	1a	2c
	5p	1a	2a	2b	2c	2d	2e	4a	4b	3a	6a
χ_1		1	1	1	1	1	1	1	1	1	1
χ_2		1	1	1	1	-1	-1	-1	-1	1	1
χ_3		1	-1	1	-1	-1	1	1	-1	1	-1
χ_4		1	-1	1	-1	1	-1	-1	1	1	-1
χ_5		2	2	2	2	0	0	0	0	-1	-1
χ_6		2	-2	2	-2	0	0	0	0	-1	1
χ_7		3	-1	-1	3	-1	-1	1	1	0	0
χ_8		3	-1	-1	3	1	1	-1	-1	0	0
χ_9		3	1	-1	-3	-1	1	-1	1	0	0
χ_{10}		3	1	-1	-3	1	-1	1	-1	0	0

GAP Program for Finding Symmetry of Melamine

```
D := [[0,1,1,2,3,3,2,4,4],[1,0,1,4,4,2,3,2,3], [1,1,0,3,2,4,4,3,2],
     [2,4,3,0,5,6,7,8,6],[3,4,2,5,0,8,6,6,7],[3,2,4,6,8,0,5,7,6],
     [2,3,4,7,6,5,0,6,8],[4,2,3,8,6,7,6,0,5],[4,3,2,6,7,6,8,5,0]];
      n:=9; i:=0; H:=[];
      t := SymmetricGroup(n);
      tt:=Elements(t);
        for a in tt do
                x:=PermutationMat(a,n);
                y:=TransposedMat(x);
                z := y*D*x;
                if z = D then AddSet(H,a); fi;
        od;
G := Group(H);
```

In this program, the resulting distance matrix D for melamine is as follows:

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

Using our program, we can see that

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

which is isomorphic to S_3, the symmetric group on three symbols.

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