

Symmetry Properties of Some Chemical Graphs*

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Let G be a weighted graph with the adjacency matrix $A = [a_{ij}]$. A Euclidean graph associated with a molecule is defined by a weighted graph with the adjacency matrix $D = [d_{ij}]$, 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 to be zero if all the nuclei are equivalent. Otherwise, one may introduce different weights for different nuclei. Balasubramanian computed the Euclidean graphs and automorphism groups for benzene, eclipsed and staggered forms of ethane and eclipsed and staggered forms of ferrocene (see *Chem. Phys. Letters* **232** (1995) 415–423). The present work describes a simple computational method by means of which it is possible to calculate the automorphism group of weighted graphs. We have applied this method to compute the symmetry of trimethylamine and cubane.

INTRODUCTION

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

Let us recall some definitions and notations. An automorphism of a graph G is a permutation g of the vertex set VG of G with the property that, for any vertices u and v , $g(u)$ and $g(v)$ are adjacent if and only if u is adjacent to v . The set of all automorphisms of a graph G , with the operation of the composition of permutations, is a permutation group on VG , denoted $\text{Aut}(G)$. 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 that the geometrical realization of a given topological structure may possess.

In Refs. 1, 2, Randić 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 that 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, it was shown by Balasubramanian³ that the two symmetries are connected in some cases.

* Dedicated to Dr. Edward C. Kirby in happy celebration of his 70th birthday.

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The topic of perceiving the symmetry of a graph through the automorphism group of the graph has been studied in considerable depth,³⁻⁹ but the connection between the graph automorphism problem and the symmetry of a molecule has not been explored as much. Longuet-Higgins¹⁰ showed that a more desirable representation of molecular symmetry is to use the nuclear permutation and inversion operations resulting in a group called the Permutation-Inversion (PI) group. Balasubramanian³ noted that the automorphism group of the Euclidean graph of a molecule is sometimes the Permutation-Inversion group of the molecule.

In Ref. 11, the full non-rigid symmetry of trimethylamine with C_{3v} point group was computed. In this paper, we compute the symmetry of this molecule. Throughout the paper, all groups considered are assumed to be finite. Our notation is standard and taken mainly from Ref. 12.

EXPERIMENTAL

Computations of the symmetry properties of molecules were carried out using GAP.¹³ GAP is a free and extendable software package for computation in discrete abstract algebra. The term extendable means that you can write your own programs in the GAP language, and use them in just the same way as the programs which form part of the system (the »library«). More information on the motivation and development of GAP to date can be found on the GAP web page <http://www.gap-system.org>.

The method described in this paper appears to be quite general, and can be extended to solve several problems in computational chemistry. GAP contains a large library of functions. Here, we explain those which are important for the calculations in this paper. The function *Symmetric-Group*(n) returns the symmetric group S_n to n letters. It is a well-known fact that this group has order $n!$. We can associate a permutation matrix to every permutation $a \in S_n$. This permutation matrix can be calculated with the function *PermutationMat*(a, n). Also the function *TransposedMat*(A) returns the transpose matrix of matrix A .

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 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 A , we can write a simple GAP program to calculate all the permutation matrices with $P^tAP = A$.

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 dimensions. This means that 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 depend 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: $A_{ij} = w_{ij}$, 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 vertex i is v_i , and, $A_{ij} = 0$, otherwise. Note that A_{ii} 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 trimethylamine to illustrate the Euclidean graph 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 P . It should be noted that one does not have to work with exact Euclidean distances in that a mapping of weights into a set of integers suffices 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 use a Euclidean edge weighting for trimethylamine mapped from Euclidean distances as $1.78 \rightarrow 1$, $4.18 \rightarrow 2$, $3.63 \rightarrow 3$, $2.99 \rightarrow 4$, $2.40 \rightarrow 5$. The resulting distance matrix for this weighted Euclidean graph is:

$$\begin{bmatrix} 0 & 1 & 1 & 2 & 3 & 3 & 3 & 4 & 5 \\ 1 & 0 & 1 & 3 & 4 & 5 & 3 & 5 & 4 \\ 1 & 1 & 0 & 3 & 5 & 4 & 2 & 3 & 3 \\ 2 & 3 & 3 & 0 & 1 & 1 & 5 & 4 & 3 \\ 3 & 4 & 5 & 1 & 0 & 1 & 3 & 3 & 2 \\ 3 & 5 & 4 & 1 & 1 & 0 & 4 & 5 & 3 \\ 3 & 3 & 2 & 5 & 3 & 4 & 0 & 1 & 1 \\ 4 & 5 & 3 & 4 & 3 & 5 & 1 & 0 & 1 \\ 5 & 4 & 3 & 3 & 2 & 3 & 1 & 1 & 0 \end{bmatrix}$$

Not all $9!$ permutations of the vertices 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) does not belong to the automorphism group since the resulting graph shown in Figure 1 does not preserve connectivity. It has been computed by GAP that the set of permutations that preserves the Euclidean connectivity is:

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

Since there is a unique non-abelian group of order 6, *i.e.*, S_3 , G is isomorphic to the symmetric group on three symbols.

TABLE I. Euclidean edges of trimethylamine

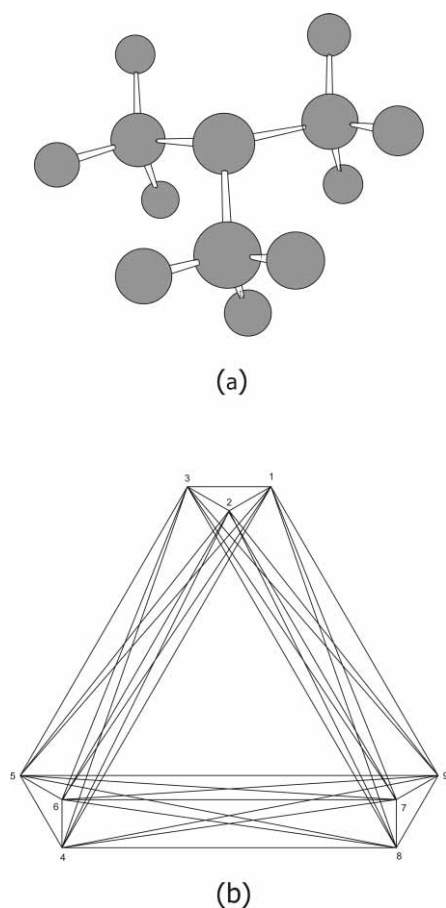
0.00	1.78	1.78	4.18	3.63	3.63	3.63	2.99	2.40
1.78	0.00	1.78	3.63	2.99	2.40	3.63	2.40	2.99
1.78	1.78	0.00	3.63	2.40	2.99	4.18	3.63	3.63
4.18	3.63	3.63	0.00	1.78	1.78	2.40	2.99	3.63
3.63	2.99	2.40	1.78	0.00	1.78	3.63	3.63	4.18
3.63	2.40	2.99	1.78	1.78	0.00	2.99	2.40	3.63
3.63	3.63	4.18	2.40	3.63	2.99	0.00	1.78	1.78
2.99	2.40	3.63	2.99	3.63	2.40	1.78	0.00	1.78
2.40	2.99	3.63	3.63	4.18	3.63	1.78	1.78	0.00

Below we write a GAP-program for computing the automorphism group of the Euclidean graph of trimethylamine. The program does not miss any permutation since it checks the candidate permutations of the given automorphism group in lexicographical order and saves them in a file named »H2.txt«. In our program, P denotes the integer matrix corresponding to the distance matrix of the molecule under consideration.

A GAP Program for Finding Symmetry of Trimethylamine

```
P:= [[0,1,1,2,3,3,3,4,5],[1,0,1,3,4,5,3,5,4],
[1,1,0,3,5,4,2,3,3],[2,3,3,0,1,1,5,4,3],
[3,4,5,1,0,1,3,3,2],[3,5,4,1,1,0,4,5,3],
[3,3,2,5,3,4,0,1,1],[4,5,3,4,3,5,1,0,1],
[5,4,3,3,2,3,1,1,0]];
n:=9;i:=0;H:=[];
t:=SymmetricGroup(n);
tt:=Elements(t);
for a in tt do
  x1:=PermutationMat(a,n);
  x:=TransposedMat(x1);
  y1:=x*P*x1;
  if y1 = P then AppendTo(»H2.txt«,a,»\n«);fi;
od;
G:=Group(H);
```

Using this program and a similar method we can calculate the automorphism group of cubane. To do this, we compute the Euclidean edges of this molecule in Table II. Again, since the automorphism group of the integer-weighted graph is identical to the automorphism group of the original Euclidean graph, it is enough to calculate the integer distance matrix E for cubane. The resulting weighted Euclidean graph for cubane is shown in Figure 2. Similarly to the case of trimethylamine, we

Figure 1. (a) Trimethylamine with C_{3v} point group; (b) The Euclidean graph of trimethylamine.

use Euclidean edge weighting for cubane mapped from Euclidean distances as $2.82 \rightarrow 1$, $3.99 \rightarrow 2$ and $4.89 \rightarrow 3$. The resulting Euclidean edges and the distance matrix for this weighted Euclidean graph are:

TABLE II. Euclidean edges and the integer matrix of cubane

0.00	2.82	3.99	2.82	2.82	3.99	4.89	3.99
2.82	0.00	2.82	3.99	3.99	2.82	3.99	4.89
3.99	2.82	0.00	2.82	4.89	3.99	2.82	3.99
2.82	3.99	2.82	0.00	3.99	4.89	3.99	2.82
2.82	3.99	4.89	3.99	0.00	2.82	3.99	2.82
3.99	2.82	3.99	4.89	2.82	0.00	2.82	3.99
4.89	3.99	2.82	3.99	3.99	2.82	0.00	2.82
3.99	4.89	3.99	2.82	2.82	3.99	2.82	0.00

$$E = \begin{bmatrix} 0 & 1 & 2 & 1 & 1 & 2 & 3 & 2 \\ 1 & 0 & 1 & 2 & 2 & 1 & 2 & 3 \\ 2 & 1 & 0 & 1 & 3 & 2 & 1 & 2 \\ 1 & 2 & 1 & 0 & 2 & 3 & 2 & 1 \\ 1 & 2 & 3 & 2 & 0 & 1 & 2 & 1 \\ 2 & 1 & 2 & 3 & 1 & 0 & 1 & 2 \\ 3 & 2 & 1 & 2 & 2 & 1 & 0 & 1 \\ 2 & 3 & 2 & 1 & 1 & 2 & 1 & 0 \end{bmatrix}$$

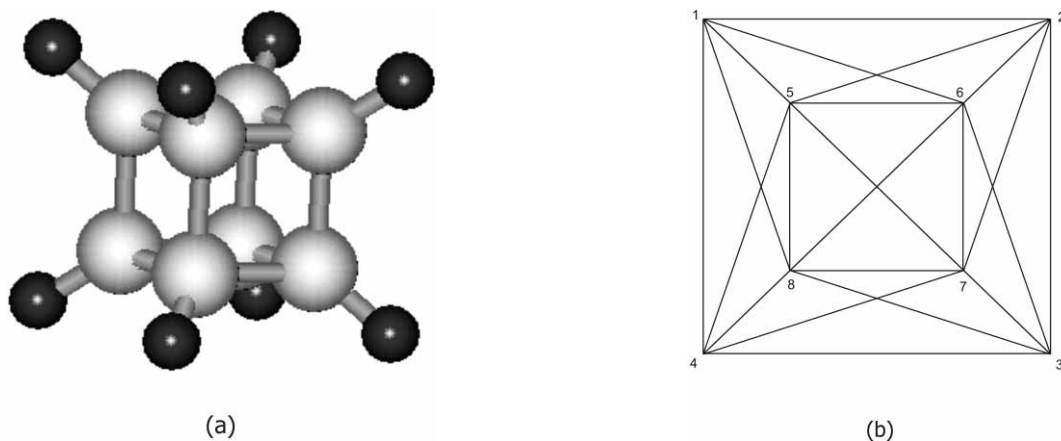


Figure 2. (a) Cubane with the O_h point group and its integer distance matrix; (b) The Euclidean graph of cubane.

In the end, we apply again our GAP program to compute the automorphism group of the Euclidean graph of cubane. Using this program, we have:

$$\mathbf{G} := \{ (), (2,4)(6,8), (1,6)(4,7), (3,6)(4,5), (1,3)(5,7), (2,5)(3,8), (1,8)(2,7), (1,8,3,6)(2,5,4,7), (1,5,6,7,3,4)(2,8), (2,4,5)(3,8,6), (1,2)(3,4)(5,6)(7,8), (1,5)(2,6)(3,7)(4,8), (1,3,8,6)(2,4,7,5), (1,2,6,7,8,4)(3,5), (1,6,8)(2,7,4), (1,4)(2,3)(5,8)(6,7), (1,3)(2,4)(5,7)(6,8), (1,4,8,5)(2,3,7,6), (1,4,8,7,6,2)(3,5), (1,3,8)(2,7,5), (1,7)(2,3)(4,6)(5,8), (1,2,3,7,8,5)(4,6), (1,6,8,3)(2,5,7,4), (1,5,8,7,3,2)(4,6), (1,6,3)(4,5,7), (1,7)(2,8)(3,5)(4,6), (1,7)(2,6)(3,5)(4,8), (1,5,6,2)(3,4,8,7), (1,7)(2,3,4,8,5,6), (1,8,6)(2,4,7), (1,7)(2,8)(3,4)(5,6), (1,6)(2,5)(3,8)(4,7), (1,8,6,3)(2,4,5,7), (1,4,3,7,6,5)(2,8), (1,3,6)(4,7,5), (1,4)(2,8)(3,5)(6,7), (1,8)(2,7)(3,6)(4,5), (1,2,6,5)(3,7,8,4), (1,7)(2,6,5,8,4,3), (1,8,3)(2,5,7), (1,2)(3,5)(4,6)(7,8), (1,5)(2,8)(3,7)(4,6), (1,5,8,4)(2,6,7,3), (1,3,6,8)(2,7,5,4), (2,5,4)(3,6,8), (1,4,3,2)(5,8,7,6), (1,6,3,8)(2,7,4,5), (1,2,3,4)(5,6,7,8) \}$$

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SAŽETAK

Simetrijska svojstva nekih kemijskih grafova

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Neka je G uteženi graf s matricom susjedstva $A = [a_{ij}]$. Euklidski graf pridružen molekuli definiran je kao uteženi graf s matricom susjedstva $D = [d_{ij}]$, gdje je d_{ij} euklidska udaljenost između čvorova i i j . U toj matrici dijagonalni elementi d_{ii} jednaki su nuli, ako su svi čvorovi grafa ekvivalentni. Ako nisu, tada se uvode težine za različite čvorove. Balasubramanian je izračunao euklidske grafove i grupe automorfizama benzena, otkrivene i zasjenjene konformacije etana i ferocena (vidi *Chem. Phys. Lett.* **232** (1995) 415–423). U ovome radu je prikazana jednostavna računaska metoda pomoću koje se mogu računati grupe automorfizama za utežene grafove. Metoda je ilustrirana na računanju simetrijskih svojstava grafova kojima su prikazani trimetilamin i kuban.