MATCH
Communications in Mathematical and in Computer Chemistry

MATCH Commun. Math. Comput. Chem. **55** (2006) 65-72

ISSN 0340 - 6253

Symmetry of Pyrene and Triphenylmethane Molecules

Mojtaba Ghorbani and Ahmad Gholami*

Department of Mathematics, Faculty of Science, University of Kashan, Kashan, Iran

(Received May 4, 2005)

Abstract

An Euclidean graph associated with a molecule is defined by a weighted graph with adjacency matrix. 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 pyrene and triphenylmethane.

INTRODUCTION

By symmetry we mean the automorphism group symmetry of a graph. The symmetry of a graph does not need to be 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.

Although the symmetry as perceived in graph theory by the automorphism group of the graph and the molecular symmetry group are quite different we would like to show in this paper these two symmetries are connected for pyrene and triphenylmethane. This connection is established by generalizing the automorphism group of an ordinary graph to the automorphism group of a weighted graph which represents the Euclidean geometric distances between the nuclear centers. The resulting automorphism group of the edge-weighted graph is shown to be the permutation-inversion group proposed by Longuet-Higgins [1], and so graph theoritical perception of molecular symmetry could provide novel computational algorithms for the machine perception of molecular symmetry.

*Author to whom correspondence should be addressed. (E-mail: Gholami@kashanu.ac.ir)

In our work, graph theory provides an elegant and natural representation of molecular symmetry and the resulting group expressed in terms of permutations is isomorphic to the permutation-inversion group of Longuet-Higgins [1].

The symmetry of a graph through the automorphism group of the graph has been studied in Refs. [2-5]. As shown by Randic a graph can be depicted in different ways such that its point group symmetry or three dimensional preception may differ, but the underlying connectivity symmetry is still the same as characterised by the automorphism group of the graph which by definition comprises permutations of the vertices of the graph that leave the adjacency matrix invariant [6]. However, the molecular symmetry depends on the coordinates of the various nuclei which relate directly to their three dimensional geometry.

The 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 another important applications of automorphism groups of weighted graphs to fullerenes. The reader is encouraged to consult papers by Balasubramanian for background material and computational techniques on this topic [7-15].

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 and edge with weight w_{ij}; $A_{ij} = v_i$, if $i = j$ and weight of the vertex *i* is v_i, and, $A_{ij} = 0$, otherwise. 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.

Throughout this paper, all groups considered are assumed to be finite. Our notation is standard and taken mainly from Refs. [16-18].

RESULT AND DISCUSSION

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.

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. 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.

Balasubramanian[7] calculated the automorphism group of the Euclidean graph of benzene molecule. By his result, this is a group of order 12. We continue Balasubramanian's result to compute the automorphism group of the Euclidean graph of pyrene and triphenylmethane molecules.

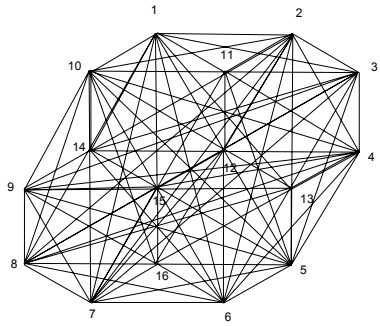

Figure 1: Euclidean graph of Pyrene

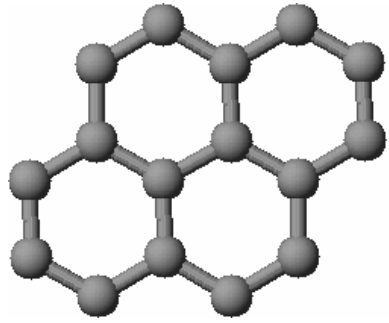

Figure 2: The Structure of Pyrene

A permutation of the vertices of the Euclidean graph under consideration belongs to the permutation representation of an operation in the point group if and only if the corresponding permutation matrix satisfies $M^tDM = D$, where M^t is the transpose of permutation matrix M and D is the adjacency matrix of the graph.. All such permutations of the nuclei which preserve the connectivity of the Euclidean graph of the molecule form a group which we call the Euclidean distance group.

Consider the Pyrene molecule to illustrate the Euclidean graph and its automorphism group. It suffices to measure the Euclidean distances and then construct the Euclidean distance matrix C. 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 suffices as long as different weights are identified with different integers. In fact the automorphism group of the integer-weighted graph, Figure 2, is identical to the automorphism group of the original

Euclidean graph. The resulting distance matrix is shown below. It is far from true that all 16! 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) does not belong to the automorphism group since the resulting graph shown in Fig. 1 does not preserve connectivity.

$$C = \begin{bmatrix}
0 & 1 & 1 & 2 & 2 & 3 & 3 & 2 & 2 & 1 & 4 & 5 & 5 & 2 & 3 & 2 \\
1 & 0 & 2 & 1 & 3 & 2 & 4 & 5 & 5 & 2 & 6 & 7 & 4 & 3 & 2 & 1 \\
1 & 2 & 0 & 3 & 1 & 2 & 2 & 1 & 3 & 2 & 6 & 4 & 7 & 5 & 4 & 5 \\
2 & 1 & 3 & 0 & 2 & 1 & 6 & 4 & 7 & 5 & 8 & 9 & 10 & 4 & 5 & 2 \\
2 & 3 & 1 & 2 & 0 & 1 & 5 & 2 & 4 & 5 & 8 & 10 & 9 & 7 & 6 & 4 \\
3 & 2 & 2 & 1 & 1 & 0 & 7 & 5 & 6 & 4 & 11 & 8 & 8 & 6 & 7 & 5 \\
3 & 4 & 2 & 6 & 5 & 7 & 0 & 1 & 1 & 2 & 5 & 2 & 4 & 5 & 7 & 6 \\
2 & 5 & 1 & 4 & 2 & 5 & 1 & 0 & 2 & 3 & 7 & 5 & 6 & 4 & 6 & 7 \\
2 & 5 & 3 & 7 & 4 & 6 & 1 & 2 & 0 & 1 & 2 & 1 & 3 & 2 & 5 & 4 \\
1 & 2 & 2 & 5 & 5 & 4 & 2 & 3 & 1 & 0 & 3 & 2 & 2 & 1 & 2 & 3 \\
4 & 6 & 6 & 8 & 8 & 11 & 5 & 7 & 2 & 3 & 0 & 1 & 1 & 2 & 5 & 7 \\
5 & 7 & 4 & 9 & 10 & 8 & 2 & 5 & 1 & 2 & 1 & 0 & 2 & 3 & 4 & 6 \\
5 & 4 & 7 & 10 & 9 & 8 & 4 & 6 & 3 & 2 & 1 & 2 & 0 & 1 & 2 & 5 \\
2 & 3 & 5 & 4 & 7 & 6 & 5 & 4 & 2 & 1 & 2 & 3 & 1 & 0 & 1 & 2 \\
3 & 2 & 4 & 5 & 6 & 7 & 7 & 6 & 5 & 2 & 5 & 4 & 2 & 1 & 0 & 1 \\
2 & 1 & 5 & 2 & 4 & 5 & 6 & 7 & 4 & 3 & 7 & 6 & 5 & 2 & 1 & 0
\end{bmatrix}$$

Suppose G is the set of all permutations which preserves the Euclidean connectivity. It is useful to mention that our calculations were done by a GAP program. Using such a program, we can recalculate all the examples of Balasubramanian[7]. For the sake of completeness we write below our GAP-program for computing the automorphism group of the Euclidean graph of the mentioned molecule.

A GAP Program for Computing the Symmetries of Pyrene

```
gap> a:=[[0,1,1,2,2,3,3,2,2,1,4,5,5,2,3,2], [1,0,2,1,3,2,4,5,5,2,6,7,4,3,2,1],
[1,2,0,3,1,2,2,1,3,2,6,4,7,5,4,5],[2,1,3,0,2,1,6,4,7,5,8,9,10,4,5,2],
[2,3,1,2,0,1,5,2,4,5,8,10,9,7,6,4],[3,2,2,1,1,0,7,5,6,4,11,8,8,6,7,5],
[3,4,2,6,5,7,0,1,1,2,5,2,4,5,7,6],[2,5,1,4,2,5,1,0,2,3,7,5,6,4,6,7],
[2,5,3,7,4,6,1,2,0,1,2,1,3,2,5,4],[1,2,2,5,5,4,2,3,1,0,3,2,2,1,2,3],
[4,6,6,8,8,11,5,7,2,3,0,1,1,2,5,7],[5,7,4,9,10,8,2,5,1,2,1,0,2,3,4,6],
```

```
[5,4,7,10,9,8,4,6,3,2,1,2,0,1,2,5],[2,3,5,4,7,6,5,4,2,1,2,3,1,0,1,2],
[3,2,4,5,6,7,7,6,5,2,5,4,2,1,0,1],[2,1,5,2,4,5,6,7,4,3,7,6,5,2,1,0]];
gap> f:=[a[1],a[10]];
gap> b:=[a[2],a[3],a[9],a[14]];
gap> c:=[a[4],a[5],a[12],a[13]];
gap> d:=[a[6],a[11]];
gap> e:=[a[7],a[8],a[15],a[16]];
gap> S:=[f,b,c,d,e];
gap> G:=[];n:=16;Q:=[];
gap> for k in[1..Length(S)] do
gap> for i in S[k] do
gap> for j in S[k] do
gap> AddSet(G,PermListList(i,j));od;od;
gap> od;
gap> Print("G:=",G,"\n");
gap> for i in G do
gap> x1:=PermutationMat(i,n);
gap> w:=i*(1,2);
gap> z1:=PermutationMat(w,n);
gap> x:=TransposedMat(x1);
gap> z:=TransposedMat(z1);
gap> y1:=x*a*x1;
gap> y2:=x*a*z1;
gap> if y1= a then AddSet(Q,i);
gap> fi;
gap> if y2= a then AddSet(Q,w);
gap> fi;
gap> od;
gap> Print("Automorphism Group: ",Q,"\n");
```

The program does not miss any permutation since it checks the candidate permutations of the given automorphism group in lexiographical order. By this program, we have:

Q = {(1),(2 3)(4 5)(7 15)(8 16)(9 14)(12 13), (1 10)(2 9)(3 14)(4 12)(5 13)(6 11)(7 16)(8 15),
(1 10)(2 14)(3 9)(4 13)(5 12)(6 11)(7 8)}.

We now consider the Triphenylmethane molecule to illustrate the Euclidean graph and its automorphism group, as shown in Figure 3. We can see again all 19! 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. Suppose E is the integer matrix and H is the automorphism group of weighted graph depicted in Figure 3. Then we have:

H={(1), (3,4)(5,6)(8,14)(9,16)(10,15)(11,18)(12,17)(13,19),
(2,14,8)(3,15,9)(4,16,10)(5,17,11)(6,18,12)(7,19,13),
(2,8)(3,10)(4,9)(5,12)(6,11)(7,13)(15,16)(17,18),
(2,8,14)(3,9,15)(4,10,16)(5,11,17)(6,12,18)(7,13,19),
(2,14)(3,16)(4,15)(5,18)(6,17)(7,19)(9,10)(11,12)}.

$$E=\begin{bmatrix}
0,1,2,2,3,3,4,1,2,2,3,3,4,1,2,2,3,3,4\\
1,0,5,5,6,6,7,8,10,9,11,12,13,8,9,10,12,11,13\\
2,5,0,6,5,7,6,9,12,8,13,10,11,10,12,11,14,2,1\\
2,5,6,0,7,5,6,10,11,12,2,14,1,9,8,12,10,13,11\\
3,6,5,7,0,6,5,12,14,10,1,11,2,11,13,2,1,3,15\\
3,6,7,5,6,0,5,11,2,13,3,1,15,12,10,14,11,1,2\\
4,7,6,6,5,5,0,13,1,11,15,2,3,13,11,1,2,15,3\\
1,8,9,10,12,11,13,0,5,5,6,6,7,8,10,9,11,12,13\\
2,10,12,11,14,2,1,5,0,6,5,7,6,9,12,8,13,10,11\\
2,9,8,12,10,13,11,5,6,0,7,5,6,10,11,12,2,14,1\\
3,11,13,2,1,3,15,6,5,7,0,6,5,12,14,10,1,11,2\\
3,12,10,14,11,1,2,6,7,5,6,0,5,11,2,13,3,1,15\\
4,13,11,1,2,15,3,7,6,6,5,5,0,13,1,11,15,2,3\\
1,8,10,9,11,12,13,8,9,10,12,11,13,0,5,5,6,6,7\\
2,9,12,8,13,10,11,10,12,11,14,2,1,5,0,6,5,7,6\\
2,10,11,12,2,14,1,9,8,12,10,13,11,5,6,0,7,5,6\\
3,12,14,10,1,11,2,11,13,2,1,3,15,6,5,7,0,6,5\\
3,11,2,13,3,1,15,12,10,14,11,1,2,6,7,5,6,0,5\\
4,13,1,11,15,2,3,13,11,1,2,15,3,7,6,6,5,5,0
\end{bmatrix}$$

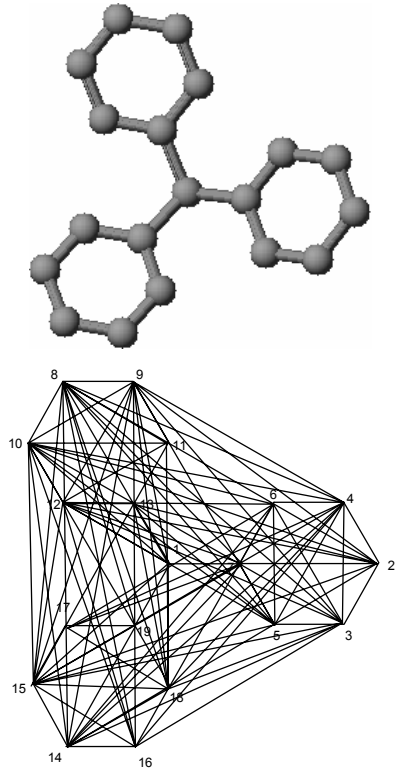

Figure 3: The Euclidean graph and Structure of Triphenylmethane

REFERENCES

1. H.C. Longuet-Higgins, *Mol. Phys*. **1963**, 6, 445.

2. P.R. Bunker, *Mol. Phys*. **1964**, 8, 81.

3. S.L. Altmann, "Induced Representation in Crystal & Molecules", Academic Press, London, 1977.

4. G.S. Ezra, "Symmetry Properties of Molecules", Lecture Notes in Chemistry 28, Springer, 1982.

5. P.R. Bunker, "Molecular Symmetry in Spectroscopy", Academic Press, 1979.

6. M. Randic, *Chem. Phys. Letters* **1976**, 42(2), 283.

7. K. Balasubramanian, *Chem. Phys. Letters* **1995**, 232, 415.

8. K. Balasubramanian, *J. Chem. Phys*. **1980**, 72, 665.

9. K. Balasubramanian, Intern*. J. Quantum Chem*. **1982**, 21, 411.

10. K. Balasubramanian, *Chem.Rev.* **1985**, 85, 599.

11. K. Balasubramanian, *Studies Phys. Theor. Chem*. **1983**, 23, 149.

12. K. Balasubramanian, *J. Chem. Phys*. **1981**, 75, 4572.

13. K. Balasubramanian, *J. Phys. Chem*. **2004**, 108, 5527.

14. K. Balasubramanian, *Chem. Phys. Letters* **2004**, 391, 64.

15. K. Balasubramanian, *Chem. Phys. Letters* **2004**, 391, 69.

16. A. R. Ashrafi, M. Hamadanian, accepted by *Croat. Chem. Acta*, **2005**.

17. A. R. Ashrafi, *MATCH Commun. Math. Comput. Chem*. **2005**, 53(1),161.

18. M.R. Darafsheh, Y. Farjami, A. R. Ashrafi, *MATCH Commun. Math. Comput. Chem*. **2005**, 54(1), 53.