Bulletin of the Chemists and Technologists of Macedonia, Vol. **25**, No. 1, pp. 23–27 (2006)
GHTMDD – 479 ISSN 0350 – 0136
Received: October 10, 2005 UDC: 547.53
Accepted: May 16, 2006

Short communication

SYMMETRY OF BENZENOID CHAINS

Ahmad Gholami*, Ali Reza Ashrafi, M. Ghorbani

Department of Mathematics, Faculty of Science, University of Kashan, Kashan, Iran
*gholami@kashanu.ac.ir

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. In this paper, using the group theory package GAP, we compute the automorphism group of the Euclidean graph of benzenoid chains.

Key words: symmetry group; benzenoid chains; Euclidean graph

СИМЕТРИЈА НА БЕНЗЕНОИДНИ НИЗИ

Теоријата на графови дава елегантна и природна репрезентација (претстава) на молекулската симетрија и соодветната група прикажана преку пермутации е изоморфна на пермутационо-инверзионата група на Longuet-Higgins. Во овој труд, со помош на програмскиот пакет од теоријата на групите *GAP*, е пресметан автоморфизмот на групата на Евклидовиот граф на бензеноидните низи.

Клучни зборови: симетрија на групи; бензеноидни низи; Евклидов граф

INTRODUCTION

By definition, a weighted graph is a graph whose edges and vertices are weighted with different weights [1]. 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.

The symmetry of a graph through the automorphism group of the graph has been studied in Refs [2, 3, 4, 5]. As shown by Randić [7, 8], 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, which by definition comprises permutations of the vertices of the graph that leave the adjacency matrix invariant. However, the molecular symmetry depends on the coordinates of the various nuclei which relate directly to their three dimensional geometry.

Throughout this paper, all groups considered are assumed to be finite. Our notation is standard and taken mainly from [16–21]. For further study on applications of group theory in chemistry, we refer the interested readers to consult the papers by Fujita and Iliev [22–24].

RESULT AND DISCUSSION

Symmetry operations on a graph are called graph autumorphisms. 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.

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 P satisfies $P^tDP = D$, where P^t is the transpose of permutation matrix P, 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.

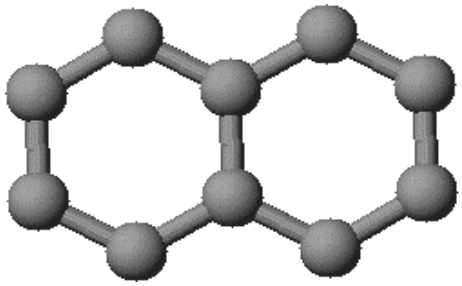

Fig. 1. The structure of naphthalene

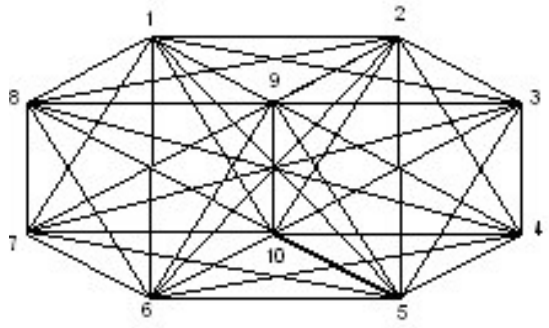

Fig. 2. Euclidean graph of naphthalene

Consider the naphthalene molecule to illustrate the Euclidean graph and its automorphism group. It suffices to measure the Euclidean distances and then construct the Euclidean distance matrix 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 (Fig. 1) 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 10! 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. 2 does not preserve connectivity.

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

Suppose G is the set of all permutations which preserves the Euclidean connectivity. It is important to mention that our calculations were performed by a GAP program. Using such a program, we can recalculate all the examples of Balasubramanian [8]. For the sake of completeness, presented below is our GAP-program for computing the automorphism group of the Euclidean graph of the mentioned molecule.

A GAP program for computing the symmetries of naphthalene

```
P:= [[0,1,1,2,2,3,4,5,6,7], [1,0,2,1,3,2,6,7,4,5], [1,2,0,3,1,2,5,7,7,2],
    [2,1,3,0,2,1,7,2,5,7], [2,3,1,2,0,1,3,2,2,1], [3,2,2,1,1,0,2,1,3,2],
    [4,6,5,7,3,2,0,1,1,2], [5,7,7,2,2,1,1,0,2,3], [6,4,7,5,2,3,1,2,0,1],
    [7,5,2,7,1,2,2,3,1,0]];
n: = 10; i:=0; H: = [];
t: = SymmetricGroup(n);
tt: =Elements(t);
for a in tt do
```

```
    x1: =PermutationMat(a,n);
     x: =TransposedMat(x1);
     y: =x*P*x1;
if y = P then AddSet(H,a);fi;
od;
G: = Group(H);
```

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

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

(1,7)(2,9)(3,8)(4,10)(5,6),(1,9)(2,7)(3,10)(4,8)}.

Let's consider the anthracene molecule to illustrate the Euclidean graph and its automorphism group, as shown in Fig. 3.

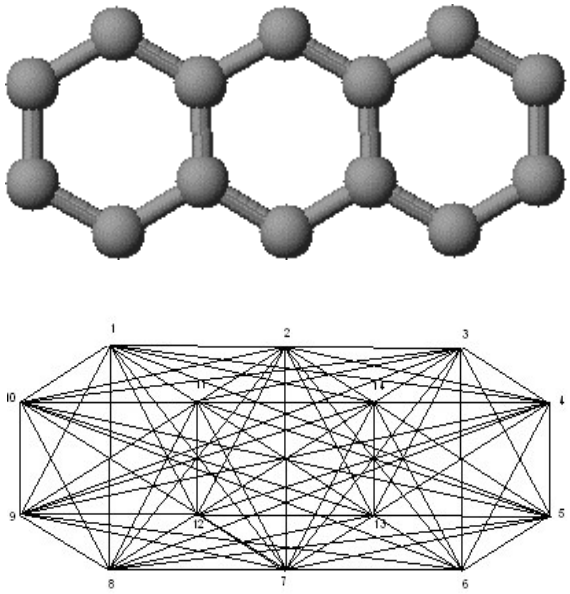

Fig. 3. The structure and Euclidean graph of anthracene

We can see again that all 14! 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. If we suppose that E is the integer matrix and H is the automorphism group of weighted graph depicted in Fig. 3, then:

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

$$E = \begin{bmatrix} 0 & 1 & 1 & 2 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 \\ 1 & 0 & 2 & 1 & 3 & 2 & 6 & 7 & 4 & 5 & 10 & 11 & 8 & 9 \\ 1 & 2 & 0 & 3 & 1 & 2 & 5 & 7 & 7 & 2 & 9 & 17 & 11 & 6 \\ 2 & 1 & 3 & 0 & 2 & 1 & 7 & 2 & 5 & 7 & 11 & 6 & 9 & 17 \\ 2 & 3 & 1 & 2 & 0 & 1 & 3 & 2 & 2 & 1 & 4 & 5 & 6 & 7 \\ 3 & 2 & 2 & 1 & 1 & 0 & 2 & 1 & 3 & 2 & 6 & 7 & 4 & 5 \\ 4 & 6 & 5 & 7 & 3 & 2 & 0 & 1 & 1 & 2 & 2 & 1 & 3 & 2 \\ 5 & 7 & 7 & 2 & 2 & 1 & 1 & 0 & 2 & 3 & 7 & 2 & 5 & 7 \\ 6 & 4 & 7 & 5 & 2 & 3 & 1 & 2 & 0 & 1 & 3 & 2 & 2 & 1 \\ 7 & 5 & 2 & 7 & 1 & 2 & 2 & 3 & 1 & 0 & 5 & 7 & 7 & 2 \\ 8 & 10 & 9 & 11 & 4 & 6 & 2 & 7 & 3 & 5 & 0 & 1 & 1 & 2 \\ 9 & 11 & 17 & 6 & 5 & 7 & 1 & 2 & 2 & 7 & 1 & 0 & 2 & 3 \\ 10 & 8 & 11 & 9 & 6 & 4 & 3 & 5 & 2 & 7 & 1 & 2 & 0 & 1 \\ 11 & 9 & 6 & 17 & 7 & 5 & 2 & 7 & 1 & 2 & 2 & 3 & 1 & 0 \end{bmatrix}$$

Finally, we consider the naphtacene molecule (Fig. 4) to illustrate the Euclidean graph and its automorphism group. We first compute the integer matrix F for calculating the automorphism graph:

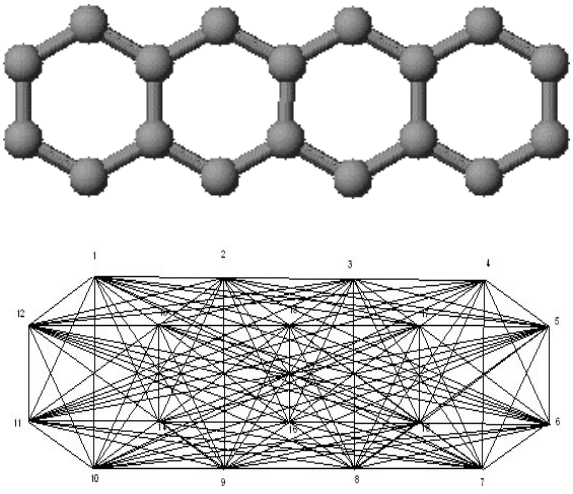

Fig. 4. The structure and Euclidean graph of naphtacene

$$\mathbf{F} = \begin{bmatrix}
0 & 1 & 1 & 2 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 & 14 & 13 & 15 \\
1 & 0 & 2 & 1 & 3 & 2 & 6 & 7 & 4 & 5 & 10 & 11 & 8 & 9 & 13 & 15 & 12 & 14 \\
1 & 2 & 0 & 3 & 1 & 2 & 5 & 7 & 7 & 2 & 9 & 17 & 11 & 6 & 14 & 16 & 15 & 10 \\
2 & 1 & 3 & 0 & 2 & 1 & 7 & 2 & 5 & 7 & 11 & 6 & 9 & 17 & 15 & 10 & 14 & 16 \\
2 & 3 & 1 & 2 & 0 & 1 & 3 & 2 & 2 & 1 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 \\
3 & 2 & 2 & 1 & 1 & 0 & 2 & 1 & 3 & 2 & 6 & 7 & 4 & 5 & 10 & 11 & 8 & 9 \\
4 & 6 & 5 & 7 & 3 & 2 & 0 & 1 & 1 & 2 & 2 & 1 & 3 & 2 & 6 & 7 & 4 & 5 \\
5 & 7 & 7 & 2 & 2 & 1 & 1 & 0 & 2 & 3 & 7 & 2 & 5 & 7 & 11 & 6 & 9 & 17 \\
6 & 4 & 7 & 5 & 2 & 3 & 1 & 2 & 0 & 1 & 3 & 2 & 2 & 1 & 4 & 5 & 6 & 7 \\
7 & 5 & 2 & 7 & 1 & 2 & 2 & 3 & 1 & 0 & 5 & 7 & 7 & 2 & 9 & 17 & 11 & 6 \\
8 & 10 & 9 & 11 & 4 & 6 & 2 & 7 & 3 & 5 & 0 & 1 & 1 & 2 & 2 & 1 & 3 & 2 \\
9 & 11 & 17 & 6 & 5 & 7 & 1 & 2 & 2 & 7 & 1 & 0 & 2 & 3 & 7 & 2 & 5 & 7 \\
10 & 8 & 11 & 9 & 6 & 4 & 3 & 5 & 2 & 7 & 1 & 2 & 0 & 1 & 3 & 2 & 2 & 1 \\
11 & 9 & 6 & 17 & 7 & 5 & 2 & 7 & 1 & 2 & 2 & 3 & 1 & 0 & 5 & 7 & 7 & 2 \\
12 & 13 & 14 & 15 & 8 & 10 & 6 & 11 & 4 & 9 & 2 & 7 & 3 & 5 & 0 & 1 & 1 & 2 \\
14 & 15 & 16 & 10 & 9 & 11 & 7 & 6 & 5 & 17 & 1 & 2 & 2 & 7 & 1 & 0 & 2 & 3 \\
13 & 12 & 15 & 14 & 10 & 8 & 4 & 9 & 6 & 11 & 3 & 5 & 2 & 7 & 1 & 2 & 0 & 1 \\
15 & 14 & 10 & 16 & 11 & 9 & 5 & 17 & 7 & 6 & 2 & 7 & 1 & 2 & 2 & 3 & 1 & 0
\end{bmatrix}$$

If we suppose that K denotes the automorphism group of Euclidean graph of naphtacene, by using our program the following can be obtained:

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

CONCLUDING REMARKS

We proved that the automorphism graph of naphtalene, anthracene and naphtacene have an order of four, and we also found their automorphism groups. If we consider a benzenoid chain T with n rings, and assume that P is the automorphism group of Euclidean graph of T, then it is easy to see that T has exactly $4n+2$ vertices, and our calculations show that the group P has order 4, with its elements as follows:

P: = {(1)(2)….(4n+1)(4n+2), (1,2)(3,4)(5,6)…

(2n+1,2n+3)(2n+2,2n+4)…(4n,4n+2)}.

REFERENCES

[1] N. Trinajstić, *Chemical Graph Theory*, CRC, Boca Raton, FL,1992.

[2] P. R. Bunker, The rotational-torsional wavefunctions of molecules that have two identical co-axial rotors *Mol. Phys*., **8** (1), 81–91 (1964).

[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] H. C. Longuet-Higgins, The symmetry groups of non-rigid molecules, *Mol. Phys*., **6** (5), 445–460 (1963).

[6] P. R. Bunker, *Molecular Symmetry in Spectroscopy*, Academic Press, 1979.

[7] M. Randić, *Croat. Chem, Acta*, **49**, 643 (1977).

[8] M. Randić, On discerning symmetry properties of graphs, *Chem. Phys. Letters*, **42** (2), 283–287 (1976).

[9] K. Balasubramanian, Graph theoretical perception of molecular symmetry, *Chem. Phys. Letters*, **232**, 415–423 (1995).

[10] K. Balasubramanian, Applications of combinatorics and graph theory to spectroscopy and quantum chemistry, *Chem. Rev.*, **85**, 599–618 (1985).

[11] K. Balasubramanian, *Studies Phys. Theor. Chem.*, **23**, 149–168 (1983).

[12] K. Balasubramanian, Generating functions for the nuclear spin statistics of nonrigid molecules, *J. Chem. Phys*., **75**, 4572–4585 (1981).

[13] K. Balasubramanian, Nonrigid group theory, tunneling splittings, and nuclear spin statistics of water pentamer: $(H_2O)_5$, *J. Phys. Chem*., **108**, 5527–5536 (2004).

[14] K. Balasubramanian, Group theoretical analysis of vibrational modes and rovibronic levels of extended aromatic C48N12 azafullerene, *Chem. Phys. Letters*, **391**, 64–68 (2004).

[15] K. Balasubramanian, Nuclear spin statistics of extended aromatic C48N12 azafullerene, *Chem. Phys. Letters*, **391**, 69–74 (2004).

[16] A. R. Ashrafi, M. Hamadanian, Symmetry Properties of Some Chemical Graphs, *Croat. Chem. Acta*, **78**, 159–163 (2005).

[17] A. R. Ashrafi, On Non-Rigid Group Theory for Some Molecules, *MATCH Commun. Math. Comput. Chem*., **53** (1), 161–174 (2005).

[18] R. Darafsheh, Y. Farjami, A. R. Ashrafi, Computing the Full Non-Rigid Group of Tetranitrocubane and Octanitrocubane Using Wreath Product, *MATCH Commun. Math. Comput. Chem*., **54** (1), 53 (2005).

[19] M. Dabirian, A. Iranmanesh, The Full Non-Rigid Group Theory for Trimethylamine-BH3 Complex, *MATCH Commun. Math. Comput. Chem.,* **54** (1), 75–88 (2005).

[20] M. Schonert et al., *GAP*, *Groups, Algorithms and Programming*. *Lehrstuhl für Mathematik*, RWTH, Aachen, 1992.

[21] M. Ghorbani, A. Gholami, Symmetry of Pyrene and Triphenylmethane Molecules, *MATCH Commun. Math. Comput. Chem.,* **55** (1), 65–72 (2006).

[22] S. Fujita, A Proof for the Existence of Five Stereogenicity Types on the Basis of the Existence of Five Types of Subgroups of RS-Stereoisomeric Groups. Hierarchy of Groups for Restructuring Stereochemistry (Part 3), *MATCH Commun. Math. Comput. Chem.,* **54** (1), 39–52 (2005).

[23] S. Fujita, Orbits Among Molecules. A Novel Way of Stereochemistry Through the Concepts of Coset Representations and Sphericities (Part 2), *MATCH Commun. Math. Comput. Chem.,* **55** (1), 5–38 (2006).

[24] V. V. Iliev, The Genetic Reactions of Ethane, *MATCH Commun. Math. Comput. Chem.* **56** (1), 21–95 (2006).