MATCH
Communications in Mathematical and in Computer Chemistry

MATCH Commun. Math. Comput. Chem. **57** (2007) 171-182

ISSN 0340 - 6253

Some Non-Transitive Chemical Graphs and Their Symmetries

Ahmad Gholami

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

E-mail: gholami@kashanu.ac.ir

(Received August 29, 2005)

Abstract

An Euclidean graph associated with a molecule is defined by a weighed graph with adjacency matrix $M = [d_{ij}]$, 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 distinct nuclei. A.T. Balaban introduced some monster graphs and then M. Randic computed complexity indices of them. In this paper, we go on our studies describes a simple method, by means of which it is possible to calculate the automorphism group of weighted graphs. (see A.T. Balaban, Rev. Roum. Chim. **18**(1973) 841-853 and M. Randic, *Croat. Chem. Acta* **74**(3)(2001) 683-705).

INTRODUCTION

Graph theory is a branch of discrete mathematics concerned with relation, between objects. From the point of the graph theory, all organic molecular structures can be drawn as graphs in which atoms and bonds are represented by vertices and edges, respectively. Structural symmetry is related to the automorphism group of the vertices, which is a subgroup of the vertex permutation group.

Randic[1,2] showed that a graph can be depicted in different ways from its point group symmetry or three dimensional perception, 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, it was shown by Balasubramanian[3] that the two symmetries are connected.

Automorphisms have other advantages such as in generating of nuclear spin species, NMR spectra, nuclear spin statistics in molecular spectroscopy, chirality and

chemical isomerism. There is also another important application of the automorphism group of weighted graphs to fullerenes. The reader is encouraged to consult the leading papers by Balasubramanian[3-11] and Refs. 12-17, for background materials as well as basic computational techniques.

Longuet-Higgins[18] showed that a more desirable representation of molecular symmetry is to use nuclear permutation and inversion operations resulting in a group called Permutation-Inversion (PI) group. Balasubramanian[3] showed that the automorphism group of Euclidean graph of a molecule is the Permutation-Inversion group of the molecule.

Ashrafi[19] showed that for each finite group H, there exists a finite regular completed weighted graph G such that Aut(G) contains a copy of H. This shows that the order of Aut(G) can be arbitrarily large. He also proved an algorithm to compute the automorphism group of weighted graphs. In this paper, using this algorithm and a GAP program,[20,21] we calculate the automorphism group of some graphs of Balaban's paper.[12]

EXPERIMENTAL

A Euclidean graph associated with a molecule is defined by a weighted graph with adjacency matrix $M = [d_{ij}]$, 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 distinct nuclei.

A simple graph G is called a weighted graph if each edge e is assigned a non-negative number w(e), called the weight of e. An automorphism of a weighted graph G = (V,E) is a permutation g of V with the following properties: (i) for any u,v in V, g(u) and g(v) are adjacent if and only if u is adjacent to v. (ii) for each e in E, w(g(e)) = w(e). The set of all the automorphisms of a weighted graph G, with the operation of composition of permutations, is a permutation group on V(G), denoted Aut(G). A non-empty subset X of V(G) is called an orbit of G under the action of Aut(G), if there exists $x \in X$ such that $X = \{\alpha(x) \mid \alpha \in Aut(G)\}$. G is called vertex transitive or simply transitive, if it has a unique orbit.

A permutation of the vertices of a graph belongs to its automorphism group if it satisfies

$$P^t A P = A \qquad (1)$$

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 relation (1).

We would like to bring to attention of the spectroscopy community a free software package for group theory named GAP[21], which greatly facilitates the following calculations. For a given adjacency matrix A, we can write a simple GAP program to calculate all the permutation matrices with $P^tAP = A$. Using this program and a similar approach as in Refs. 22-26, in the next section, we calculate the automorphism group of three weighted graphs.

RESULTS AND DISSCUSSION

The adjacency matrix $A = [w_{ij}]$ 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, Aij=0, in the case that i≠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.

A.T. Balaban[12] introduced the monster graphs G_6, G_{12} and G_{18}, as shown in Figures 1, 2 and 3. We calculate automorphism groups and Euclidean distances of G_6, G_{12} and G_{18} .

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 weighed for G_6 as: 0.13 → 1, 0.60 → 2, 0.79 → 3, 0.92 → 4. We compute these values by HyperChem 97.

Also, we map the Euclidean edge weighed for G_{12} as: 0.10 → 1, 0.66 → 2, 0.80 → 3, 0.97 → 4,.

And the Euclidean edge weighed for G_{18} as: 0.10 → 1, 0.40 → 2, 0.58 → 3, 0.80 → 4, 0.86 → 5, 0.95 → 6.

Consider G_6 to illustrate a Euclidean graph and its automorphism group. It suffices to measure the Euclidean distances and then to construct the Euclidean distance matrix A. We now write a GAP program for calculating the symmetries of graph G_6.

```
P:=  [[0,1,0,0,0,0,0,0,0,0,0,0,0,0,0,0,2,0,0,0,0,1],
      [1,0,1,0,0,0,0,0,0,0,0,0,0,4,0,0,0,0,0,0,0,0],
      [0,1,0,1,0,0,0,0,2,0,0,0,0,0,0,0,0,0,0,0,0,0],
      [0,0,1,0,1,0,0,0,0,0,0,0,0,0,0,0,0,0,0,3,0,0],
      [0,0,0,1,0,1,0,0,0,0,0,3,0,0,0,0,0,0,0,0,0,0],
      [0,0,0,0,1,0,1,0,0,0,0,0,0,0,0,0,0,0,0,0,0,2],
      [0,0,0,0,0,1,0,1,0,0,0,0,0,0,0,0,4,0,0,0,0,0],
      [0,0,0,0,0,0,1,0,1,0,0,0,0,2,0,0,0,0,0,0,0,0],
      [0,0,2,0,0,0,0,1,0,1,0,0,0,0,0,0,0,0,0,0,0,0],
      [0,0,0,0,0,0,0,0,1,0,1,0,0,0,0,0,0,0,0,0,4,0],
      [0,0,0,0,0,0,0,0,0,1,0,1,0,0,0,0,2,0,0,0,0,0],
      [0,0,0,0,3,0,0,0,0,0,1,0,1,0,0,0,0,0,0,0,0,0],
      [0,0,0,0,0,0,0,0,0,0,0,1,0,1,0,0,0,0,3,0,0,0],
      [0,0,0,0,0,0,0,2,0,0,0,0,1,0,1,0,0,0,0,0,0,0],
      [0,4,0,0,0,0,0,0,0,0,0,0,1,0,1,0,0,0,0,0,0,0],
      [0,0,0,0,0,0,0,0,0,0,0,0,0,1,01,0,0,0,0,2,0,0],
      [0,0,0,0,0,0,0,0,2,0,0,0,0,0,0,1,0,1,0,0,0,0],
      [0,0,0,0,0,0,4,0,0,0,0,0,0,0,0,0,1,0,1,0,0,0],
      [2,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,1,0,1,0,0],
      [0,0,0,0,0,0,0,0,0,0,0,3,0,0,0,0,0,1,0,1,0,0],
      [0,0,0,3,0,0,0,0,0,0,0,0,0,0,0,0,0,0,1,0,1,0],
      [0,0,0,0,0,0,0,0,0,0,0,0,0,0,2,0,0,0,0,1,0,1],
      [0,0,0,0,0,0,0,0,0,2,0,0,0,0,0,0,0,0,0,0,1,0],
      [1,0,0,0,0,2,0,0,0,0,0,0,0,0,0,0,0,0,0,0,1,0]]

n:=24; 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 of the given automorphism group in lexicographic order. The output of this program is the automorphism group of the weighted graph G_6. After running this program for the weighted graphs G_6, we calculate automorphism group of G_6, $Aut(G_6)$, as follows:

$Aut(G_6)$={(1),
(1,2)(3,24)(4,23)(5,22)(6,21)(7,20)(8,19)(9,18)(10,17)
(11,16)(12,15)(13,14),
(1,19,13,7)(2,20,14,8)(3,21,15,9)(4,22,16,10)
(5,23,17,11)(6,24,18,12),
(1,8)(2,7)(3,6)(4,5)(9,24)(10,23)(11,22)(12,21)
(13,20)(14,19)(15,18)(16,17),
(1,13)(2,14)(3,15)(4,16)(5,17)(6,18)(7,19)(8,20)
(9,21)(10,22)(11,23)(12,24),
(1,14)(2,13)(3,12)(4,11)(5,10)(6,9)(7,8)(15,24)
(16,23)(17,22)(18,21)(19,20),
(1,7,13,19)(2,8,14,20)(3,9,15,21)(4,10,16,22)
(5,11,17,23)(6,12,18,24),
(1,20)(2,19)(3,18)(4,17)(5,16)(6,15)(7,14)(8,13)
(9,12)(10,11)(21,24)(22,23)}

Using these calculations, we can see that G_6, as the weighted graph, is not vertex transitive. In fact, G_6, have exactly 3 orbits. These orbits are as follows:

$$O_6(1)= \{1,2,7,8,13,14,19,20\},$$

$$O_6(3)= \{3,6,9,12,15,18,21,24\},$$

$$O_6(4)= \{4,5,10,11,16,17,22,23\}.$$

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

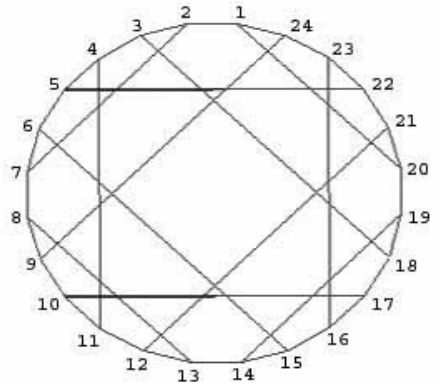


Figure 1 .Topoligical representation of isomerizations of G_6.

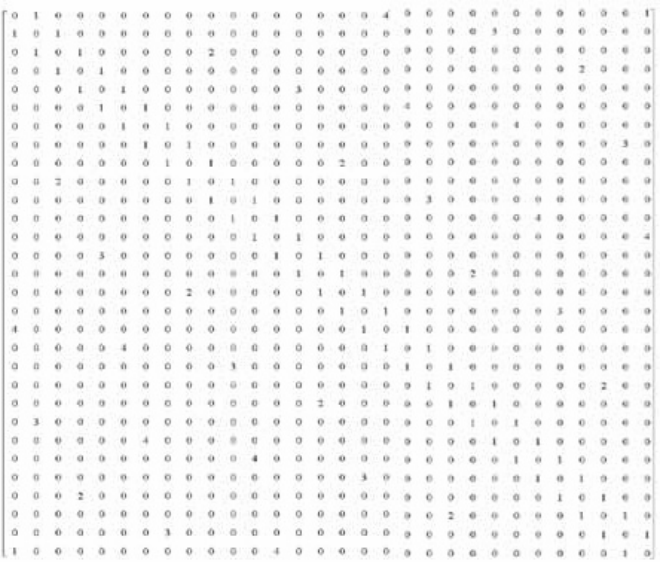
Now consider G_{12} to illustrate a Euclidean graph and its automorphism group. As before, it suffices to measure the Euclidean distances and then to construct the Euclidean distance matrix B. After running the GAP program as above with n=30, for the weighted graph G_{12}, we calculate $Aut(G_{12})$ as follows:

$Aut(G_{12})$ ={ (1),
(1,6)(2,5)(3,4)(7,30)(8,29)(9,28)(10,27)(11,26)(12,25)(13,24)(14,23)
(15,22)(16,21)(17,20)(18,19),
(1,25,19,13,7)(2,26,20,14,8)(3,27,21,15,9)(4,28,22,16,10)(5,29,23,17,11)
(6,30,24,18,12),
(1,12)(2,11)(3,10)(4,9)(5,8)(6,7)(13,30)(14,29)(15,28)(16,27)(17,26)
(18,25)(19,24)(20,23)(21,22),
(1,19,7,25,13)(2,20,8,26,14)(3,21,9,27,15)(4,22,10,28,16)(5,23,11,29,17)
(6,24,12,30,18),
(1,18)(2,17)(3,16)(4,15)(5,14)(6,13)(7,12)(8,11)(9,10)(19,30)(20,29)
(21,28)(22,27)(23,26)(24,25),
(1,13,25,7,19)(2,14,26,8,20)(3,15,27,9,21)(4,16,28,10,22)(5,17,29,11,23)
(6,18,30,12,24),
(1,24)(2,23)(3,22)(4,21)(5,20)(6,19)(7,18)(8,17)(9,16)(10,15)(11,14)
(12,13)(25,30)(26,29)(27,28),
(1,7,13,19,25)(2,8,14,20,26)(3,9,15,21,27)(4,10,16,22,28)(5,11,17,23,29)
(6,12,18,24,30),
(1,30)(2,29)(3,28)(4,27)(5,26)(6,25)(7,24)(8,23)(9,22)(10,21)(11,20)
(12,19)(13,18)(14,17)(15,16)}

Using these calculations, we can see that $G_{12,}$ as the weighted graph, is not vertex transitive. In fact, G_{12}, have exactly 3 orbits. These orbits are as follows:

$O_{12}(1)$= {1,6,7,12,13,18,19,24,25,30}
$O_{12}(2)$= {2,5,8,11,14,17,20,23,26,29}
$O_{12}(3)$= {3,4,9,10,15,16,21,22,27,28}

$$B =$$



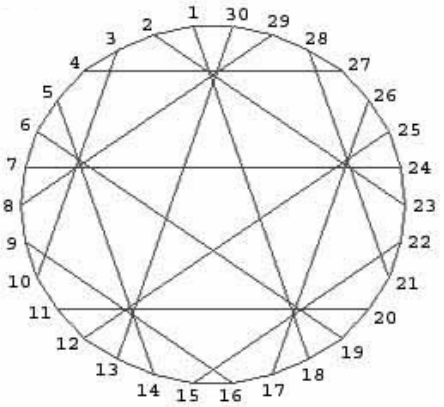


Figure 2. Topoligical representation of (G_{12})

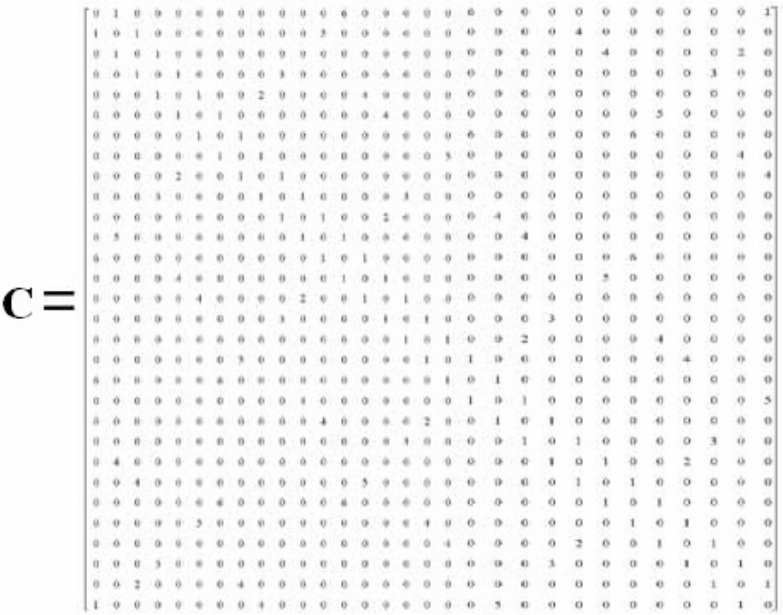
Now consider G_{18} to illustrate a Euclidean graph and its automorphism group. As before it suffices to measure the Euclidean distances and then to construct the Euclidean distance matrix C. After running the GAP program as above with n=30, for the weighted graph G_{18}, we calculate $Aut(G_{18})$ as follows:

$Aut(G_{18})$ = { (1),
(2,30)(3,29)(4,28)(5,27)(6,26)(7,25)(8,24)(9,23)(10,22)(11,21)(12,20)
(13,19)(14,18)(15,17),
(1,7)(2,6)(3,5)(8,30)(9,29)(10,28)(11,27)(12,26)(13,25)(14,24)(15,25)
(16,26)(17,27)(18,28)(19,29),
(1,25,19,13,7)(2,26,20,14,8)(3,27,21,15,9)(4,28,22,16,10)
(5,29,23,17,11)(6,30,24,18,12),
(1,13)(2,12)(3,11)(4,10)(5,9)(6,8)(14,30)(15,29)(16,28)(17,27)
(18,26)(19,25)(20,24)(21,23),
(1,19,7,25,13)(2,20,8,26,14)(3,21,9,27,15)(4,22,10,28,16)
(5,23,11,29,17)(6,24,12,30,18),
(1,19)(2,18)(3,17)(4,16)(5,15)(6,14)(7,13)(8,12)(9,11)(20,30)(21,29)
(22,28)(23,27)(24,26),
(1,13,25,7,19)(2,14,26,8,20)(3,15,27,9,21)(4,16,28,10,22)(5,17,29,11,23)
(6,18,30,12,24),
(1,25)(2,24)(3,23)(4,22)(5,21)(6,20)(7,19)(8,18)(9,17)(10,16)(11,15)
(12,14)(26,30)(27,29),
(1,7,13,19,25)(2,8,14,20,26)(3,9,15,21,27)(4,10,16,22,28)(5,11,17,23,29)
(6,12,18,24,30)}

Using these calculations, we can see that $G_{18,}$ as the weighted graph, is not vertex transitive. In fact, G_{18}, have exactly 4 orbits. These orbits are as follows:

$O_{18}(1)$= {1,7,13,19,25}
$O_{18}(2)$= {2,6,8,12,14,18,20,24,26,30}
$O_{18}(3)$= {3,5,9,11,15,17,21,23,27,29}
$O_{18}(4)$= {4,10,16,22,28}

$$C =$$



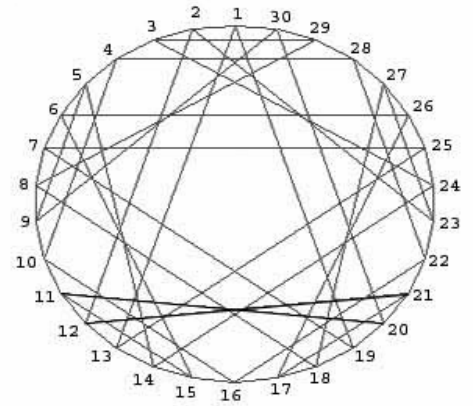


Figure 3. Topoligical representation of (G_{18})

REFERENCES

1. M. Randic, *Chem. Phys. Letters* **42**(2)(1976) 283-287.
2. M. Randic, *J. Chem. Phys*. **60**(1974) 3920-3928.
3. K. Balasubramanian, *Chem. Phys. Letters* **232**(1995) 415-423.
4. K. Balasubramanian, *J. Chem. Phys*. **72**(1980) 665-677.
5. K. Balasubramanian, *Intern. J. Quantum Chem.* **21**(1982) 411-418.
6. K. Balasubramanian, *Chem.Rev.* **85**(1985) 599-618.
7. K. Balasubramanian, *Studies Phys. Theor. Chem.* **23**(1983), 149-168.
8. K. Balasubramanian, *J. Chem. Phys.* **75**(1981), 4572-4585.
9. K. Balasubramanian, *J. Phys. Chem.* **108**(2004) 5527-5536.
10. K. Balasubramanian, *Chem. Phys. Letters* **391**(2004) 64-68.
11. K. Balasubramanian, *Chem. Phys. Letters* **391**(2004) 69-74.
12. A.T. Balaban, Rev. Roum. Chim. **18**(1973) 841-853.
13. M. Randic, *Croat. Chem. Acta* **74**(3)(2001) 683**-**705**.**
14. G. S. Ezra, "*Symmetry Properties of Molecules*", Lecture Notes in Chemistry 28, Springer, 1982.
15. W.C. Herndon, in: *Studies in Physical and Theoretical Chemistry*, Vol. 28.Chemical applications of graph theory and topology, ed. R.B. King (Elsevier, Amsterdam 1983) pp. 231-242.
16. N. Trinajstic, "*Chemical Graph Theory*", CRC Press, Boca Raton, FL. 1992.
17. G. James, M. Liebeck, "*Representations and Characters of Groups*", Cambridge University Press, 1993.
18. H. C. Longuet-Higgins, *Mol. Phys.* **6** (1963) 445-460.
19. A.R. Ashrafi, *Chem. Phys. Letters* **406** (2005) 75-80.
20. A.R. Ashrafi, *MATCH Commun. Math. Comput. Chem.* **53** (2005) 161-174.
21. M. Schonert et al., "*GAP*, *Groups, Algorithms and Programming*", Lehrstuhl D für Mathematik, RWTH, Aachen, 1992.
22. M. Ghorbani, A. Gholami, *MATCH Commun. Math. Comput. Chem.* **55** (2006) 65-7*2.*

23. M. Dabirian, A. Iranmanesh, *MATCH Commun. Math. Comput. Chem.* **54** (2005) 75-88.
24. M. Dabirian, A. Iranmanesh, *MATCH Commun. Math. Comput. Chem.* **54** (2005) 357-376.
25. A.R. Ashrafi, M. Hamadanian, accepted by *Croat. Chem. Acta*, 2004.
26. M. R. Darafsheh, Y. Farjami, A. R. Ashrafi, *MATCH Commun. Math. Comput. Chem.* **54** (2005) 53-74.