On Symmetry of Some Non-transitive Chemical Graphs*

Gorban Ali Moghani[a] and Ali Reza Ashrafi[b,**]

[a]*Iran Research Color Center, Tehran, Iran*

[b]*Department of Mathematics, University of Kashan, Kashan, Iran*

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The automorphism group of a chemical graph has to be generated for computer-aided structure elucidation. 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. T. Balaban introduced some monster graphs and then M. Randić computed complexity indices for them. This paper describes a simple method, by means of which it is possible to calculate the automorphism group of weighted graphs.

INTRODUCTION

Chemists have paid much attention to molecular symmetry because it has an important impact on the properties of compounds. To elucidate some experimentally derived information, *e.g.,* X-ray diffraction patterns or IR spectra, molecular symmetry must be considered, in which the group theory is an effective tool. For a molecule, the first step is to decide to which group it belongs, and the next step is to define its properties. This method has been widely applied in quantum chemistry for many years. The shortcomings of this method are that symmetry cannot be determined without knowing to which group a structure belongs, and that it requires a large amount of calculation.

Graph theory is a branch of discrete mathematics concerned with relations between objects. From the viewpoint of graph theory, all organic molecular structures can be drawn as graphs in which atoms and bonds are represented by vertices and edges, respectively. By symmetry we mean the automorphism group symmetry of a graph, which is a subgroup of its vertex permutation group. The symmetry of a graph, also called topological symmetry, need not be isomorphic to the molecular point group symmetry. However, it does represent the maximal symmetry of its topological structure.

Randić[1,2] showed that a graph can be depicted in different ways so 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, molecular symmetry depends on the coordinates of the various nuclei, which relate directly to its three dimensional geometry. Although the symmetry as characterized 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, *e.g.,* in generation 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.

Data presented in Ref. 19 provided a result useful for computing the symmetry of molecules. Using this results, Lemma 1 and its Corollary, we present a MATLAB program for computing a solution matrix for the automorphism group of Euclidean graphs. Finally, we use GAP[20,21] to compute the full automorphism group of some graphs, as defined by Balaban.[12]

EXPERIMENTAL

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 automorphisms of a weighted graph G, with the operation of composition of permutations, makes a permutation group on V(G), which is 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∈X such that X = { α(x) | α∈Aut(G)}. G is called vertex transitive or simply transitive, if it has a unique orbit.

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

$$P^{T}AP = A \qquad (1)$$

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 relation (1).

We would like to bring to the 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 $P^{T}AP = A$. Using this program and a similar approach as in Ref. 22, in the next section we calculate the automorphism group of two 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, $A_{ij} = 0$, in case that $i \neq j$ 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 monster graphs G_{15} and G_{17} (Figures 1 and 2). We calculate Euclidean edges of G_{15} and G_{17} (Tables I and II) using a simple MAPLE
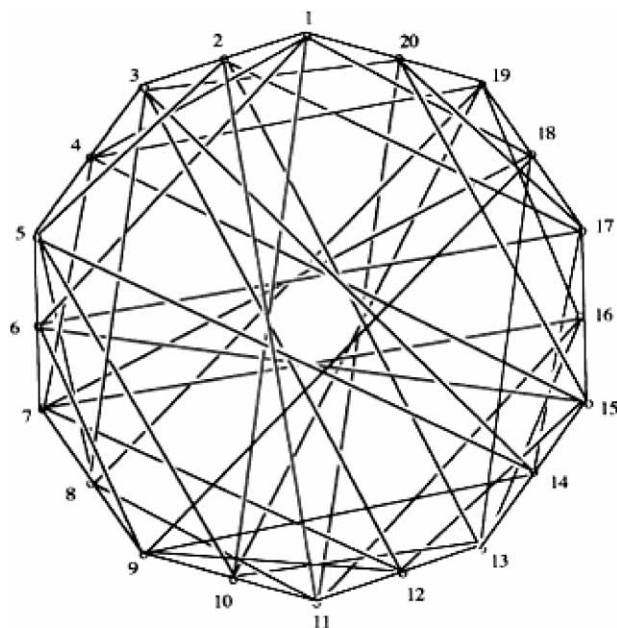

Figure 1. Topological representation of the rearrangement mode M2(6) of intramolecular isomerizations of a trigonal bipyramidal structure.

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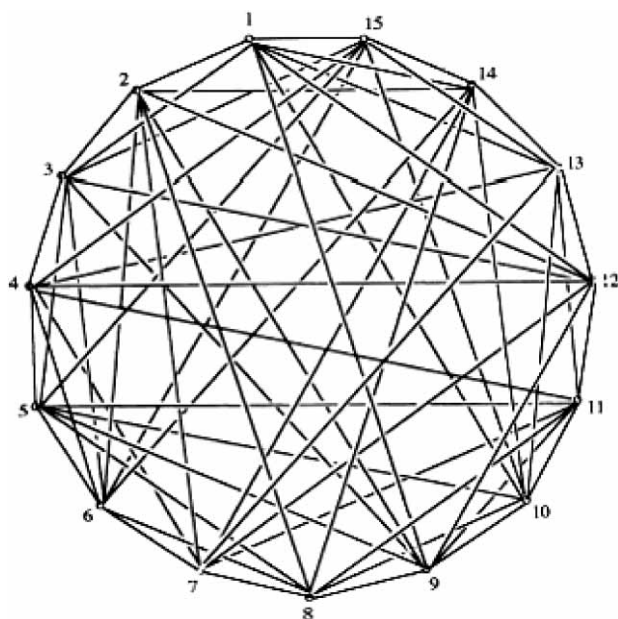\end{bmatrix}$$

Figure 2. Graph representing isomerization of octahedral complexes via the rhombic test mode.

program. It should be mentioned that one does not have to work with exact Euclidean distances and 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. As an illustration, let us map the Euclidean edge weighted for G_{15} as: $0.16 \rightarrow 1$, $0.45 \rightarrow 2$, $0.71 \rightarrow 3$ and $0.99 \rightarrow 4$. Also, we map the Euclidean edge weighted for G_{17} as: $0.21 \rightarrow 1$, $0.41 \rightarrow 2$, $0.59 \rightarrow 3$, $0.74 \rightarrow 4$, $0.87 \rightarrow 5$, $0.95 \rightarrow 6$ and $0.99 \rightarrow 7$.

Thus we got the distance matrices A and B for G_{15} and G_{17}, respectively. We now write our MATLAB pro-gram for calculating the symmetries of graph G_{15} as fol-lows:

A MATLAB Program for Computing the Symmetries of Molecules

```
n=length(a);
  for i=1:n–1
    for j=i+1:n
      b(i,j)=norm(a(i,:)-a(j,:));
    end
  end
b(n,n)=0;
b=b+b';

function y=halat(s,a)
  t=1:length(a);
  m=length(s);
  t(s)=[];
  j=0;
    for i=t
      if min(min(a(1:m+1,1:m+1)==a([s,i],[s,i])))==1
        j=j+1;
        y(j)=i;
      end
    end

function s=hazf(s)
  m=size(s);
    for i=m(1):–1:1
      if min(s(i,:))==0
        s(i,:)=[];
      end
    end

function s=jaigasht(a)
  m=length(a);
    for i=1:m
      s(i,1)=i;
    end
    for j=2:m
      n=size(s);
      k=0;
        for i=1:n(1)
          y=[halat(s(i,:),a)];
            for r=1:length(y)
              b(r+k,1:n(2)+1)=[s(i,:),y(r)];
            end
          k=k+length(y);
        end
      s=b;
      s=hazf(s);
    end
  b=0;
  n=size(s);
    for i=1:n(1)
      for j=1:n(2)
        b(i,s(i,j))=j;
      end
    end
  s=b;
```

Our program requires the Cartesian coordinates of the vertices to determine the Euclidean distances in the graph under consideration. If we calculate these distances by

TABLE I. Euclidean edge weights for G_{15}

0	0.16	0	0.45	0	0.71	0	0	0	0.99	0	0	0	0	0	0	0	0.45	0	0.16
0.16	0	0.16	0	0.45	0	0	0	0	0	0.99	0	0.99	0	0	0	0.71	0	0	0
0	0.16	0	0.16	0	0	0	0	0	0	0.99	0	0.99	0	0	0	0	0	0	0.45
0.46	0	0.16	0	0.16	0	0.45	0	0	0	0	0	0	0.99	0	0	0	0	0.71	0
0	0.45	0	0.16	0	0.16	0	0.45	0	0.71	0	0	0	0.99	0	0	0	0	0	0
0.71	0	0	0	0.16	0	0.16	0	0.45	0	0	0	0	0.99	0	0.99	0	0	0	0
0	0	0	0.45	0	0.16	0	0.16	0	0	0	0.71	0	0	0.99	0	0.99	0	0	0
0	0	0	0	0.45	0	0.16	0	0.16	0	0.45	0	0.71	0	0	0	0	0.99	0	0
0.99	0	0	0	0	0.71	0	0	0.16	0	0.16	0	0.45	0	0	0	0	0	0.99	0
0	0.99	0	0	0	0	0.45	0	0.16	0	0.16	0	0.16	0	0	0	0.71	0	0	0.99
0	0.99	0	0	0	0	0	0.45	0	0.16	0	0.16	0	0.16	0	0.45	0	0.71	0	0
0	0	0.99	0	0.99	0	0	0	0.71	0	0.16	0	0.16	0	0.45	0	0	0	0	0
0	0	0.99	0	0.99	0	0	0	0	0.45	0	0.16	0	0.16	0	0.16	0	0	0	0.71
0	0	0	0.99	0	0.99	0	0	0	0	0.45	0	0.16	0	0.16	0	0.16	0	0.45	0
0	0	0	0	0.99	0	0.99	0	0	0	0	0.71	0	0.16	0	0.45	0	0.16	0	0
0	0	0	0	0	0.99	0	0	0	0	0.45	0	0.16	0	0.16	0	0.45	0	0	0.71
0	0.71	0	0	0	0	0.99	0	0	0.71	0	0	0	0.16	0	0.16	0	0	0	0.45
0.45	0	0	0	0	0	0	0.99	0	0	0.71	0	0	0	0.45	0	0.16	0	0.16	0
0	0	0	0.71	0	0	0	0	0.99	0	0	0	0	0.45	0	0.16	0	0.16	0	0.16
0.16	0	0.45	0	0	0	0	0	0	0.99	0	0	0	0.71	0	0.45	0	0.16	0	0

TABLE II. Euclidean edge weights for G_{17}

0	0.21	0.41	0	0	0	0	0	1.00	0.95	0	0.74	0.59	0.41	0.21
0.21	0	0.21	0	0	0.74	0.87	0.95	1.00	0	0	0.87	0	0.59	0
0.41	0.21	0	0.21	0.41	0.59	0	0	0.95	0	0	0	0	0	0.59
0	0	0.21	0	0.21	0.41	0.59	0	0	0	1.00	1.00	0.95	0	0.74
0	0	0.41	0.21	0	0.21	0	0.59	0.74	0.87	0.95	0	0	0	0.87
0	0.74	0.59	0.41	0	0.21	0	0.21	0	0	0.74	0.87	0.95	1.00	0
0	0.87	0	0.59	0.41	0.21	0	0.21	0.41	0.59	0	0	0.95	0	0
1.00	1.00	0.95	0	0.74	0	0.21	0	0.21	0.41	0.59	0	0	0.95	0
0.95	0	0	0	0.87	0	0	0.41	0.21	0	0.21	0	0.59	0.74	0.87
0	0	0	1.00	0.95	0	0.74	0.59	0.41	0.21	0	0.21	0.41	0	0
0.74	0.87	0.95	1.00	0	0	0.87	0	0.59	0	0	0.21	0	0.21	0
0.59	0	0	0.95	0	0	0.95	0	0	0.59	0.41	0.21	0	0.21	0.41
0.41	0.59	0	0	0	1.00	1.00	0.95	0	0.74	0	0	0.21	0	0.21
0.21	0	0.59	0.74	0.87	0.95	0	0	0	0.87	0	0	0.41	0.21	0

HyperChem, Gaussian 98 or some other software, then to compute the symmetry of the molecule under consideration, it suffices to delete the first eight lines of the program and load the distance matrix of the molecule. It is useful to mention that our program takes only some seconds to compute the symmetry of these graphs.

The program does not miss any permutation since it checks the candidate of the given automorphism group in lexicographical order. The output of this program is the matrix whose rows represent the automorphisms of the graph. To complete our calculation, we can load this matrix into GAP and compute the automorphism group of the weighted graph G_{15}. After running this program for the weighted graphs G_{15} and G_{17}, we calculate $\mathrm{Aut}(G_{15})$ and $\mathrm{Aut}(G_{17})$ as follows:

$\mathrm{Aut}(G_{17})$ = { (), (1,11,6)(2,12,7)(3,13,8)(4,14,9)(5,15,10), (1,6,11)(2,7,12)(3,8,13)(4,9,14)(5,10,15)}.

$\mathrm{Aut}(G_{15})$={ (),
(1,17,13,9,5)(2,18,14,10,6)(3,19,15,11,7)(4,20,16,12,8),
(1,13,5,17,9)(2,14,6,18,10)(3,15,7,19,11)(4,16,8,20,12),
(1,9,17,5,13)(2,10,18,6,14)(3,11,19,7,15)(4,12,20,8,16),
(1,5,9,13,17)(2,6,10,14,18)(3,7,11,15,19)(4,8,12,16,20),
(1,4)(2,3)(5,20)(6,19)(7,18)(8,17)(9,16)(10,15)(11,14)(12,13),
(1,8)(2,7)(3,6)(4,5)(9,20)(10,19)(11,18)(12,17)(13,16)(14,15),
(1,12)(2,11)(3,10)(4,9)(5,8)(6,7)(13,20)(14,19)(15,18)(16,17),
(1,16)(2,15)(3,14)(4,13)(5,12)(6,11)(7,10)(8,9)(17,20)(18,19),
(1,20)(2,19)(3,18)(4,17)(5,16)(6,15)(7,14)(8,13)(9,12)(10,11)}.

Using these calculations, we can see that G_{15} and G_{17}, as weighted graphs, are not vertex transitive. In fact, G_{15}

and G_{17} have exactly two and five orbits, respectively. These orbits are:

$$\Delta_{G_{15}}(1) = \{1,4,5,8,9,12,13,16,17,20\},$$

$$\Delta_{G_{15}}(2) = \{2,3,6,7,10,11,14,15,18,19\},$$

$$\Delta_{G_{17}}(1) = \{1,6,11\},$$

$$\Delta_{G_{17}}(2) = \{2,7,12\},$$

$$\Delta_{G_{17}}(3) = \{3,8,13\},$$

$$\Delta_{G_{17}}(4) = \{4,9,14\},$$

$$\Delta_{G_{17}}(5) = \{5,10,15\}.$$

We end this paper with the following question:

Question: Under which conditions, both the simple graph and Euclidean weighted graph of a molecule are vertex transitive?

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SAŽETAK

O simetriji nekih netranzitivnih kemijskih grafova

Gorban Ali Moghani i Ali Reza Ashrafi

U računalno podržanom određivanju kemijskih struktura nužno je generirati grupe automorfizama pripadnih kemijskih grafova. U radu se definira Euklidov graf molekule kao uteženi graf čija je matrica susjedstva $M = [d_{ij}]$, gdje je d_{ij} za $i \neq j$ jednak euklidskoj udaljenosti između jezgri i i j. Ukoliko je $i = j$, tada se za d_{ii} može uzeti nula, ali isto tako i vrijednost koja će različito utežavati raznovrsne jezgre. Balaban je razmatrao razne čudovišne grafove, a Randić je za njih računao pripadne indekse kompleksnosti. U radu je opisan jednostavni postupak koji omogućava određivanje grupe automorfizama uteženih grafova.