Central European Science Journals
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Central European Journal of Chemistry
Central European Science Journals
CEJC 3(4) 2005 647–657

New computer program to calculate the symmetry of molecules

Ali Reza Ashrafi*, Mohammad Reza Ahmadi

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

Received 16 March 2005; accepted 20 May 2005

Abstract: In this paper we present some MATLAB and GAP programs and use them to find the automorphism group of the Euclidean graph of the C_{80} fullerene with connectivity and geometry of I_h symmetry point group. It is proved that this group has order 120 and is isomorphic to $I_h \cong Z_2 \times A_5$, where Z_2 is a cyclic group of order 2 and A_5 is the alternating group on five symbols.

Keywords: Fullerene, Euclidean graph, symmetry

1 Introduction

Let G = (V,E) be 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 unweighted graph G can be regarded as a weighted graph in which for all edges e ∈ E(G), w(e) = 1. The Euclidean graph of a molecule is a complete weighted graph in which each edge is weighted by the Euclidean distance between its vertices.

An automorphism of a weighted graph G is a permutation g of the vertex set of G with the property that, (i) for any vertices u and v, g(u) and g(v) are adjacent if and only if u is adjacent to v; (ii) for every edge e, w(g(e)) = w(e). The set of all automorphisms of a weighted graph G, with the operation of composition of permutations, is a permutation group on V(G), denoted Aut(G).

By the symmetry of a system we mean the automorphism group symmetry of its graph. The symmetry of its graph, also called a topological symmetry, accounts only

* E-mail: ashrafi@kashanu.ac.ir

for the bond relations between the atoms in a molecule, and does not fully determine the molecular geometry. The symmetry of a graph does not need to be the same as (i.e. isomorphic to) the molecular point group symmetry. However, it does represent the maximal symmetry which the geometrical realization of a given topological structure may possess.

In Refs. [1,2], it was shown by Randić 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 which 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 Balasubramanian [3] that the two symmetries are connected.

In this paper we consider only weighted graphs. The motivation for this study is outlined in Refs [3-16] and the reader is encouraged to consult these papers for background material as well as for basic computational techniques. Our notation is standard and taken mainly from Refs. [17-19].

2 Computational details

In this section we first describe some notation, which will be kept throughout. Let G be a group and N be a subgroup of G. N is called a normal subgroup of G, if for any g∈G and x∈N, $g^{-1}xg$∈N. If H is another normal subgroup of G such that H∩N = {e} and G = HN = {xy | x∈H, y∈N}, then we say that G is a direct product of H and N denoted by H × N. A group with no proper non-trivial normal subgroup is called simple. Suppose X is a set. The set of all permutations on X, denoted by S_X, is a group which is called the symmetric group on X. In the case that, X = {1, 2,. . . , n}, we denote S_X by S_n or Sym(n).

The last years have seen a rapid spread of interest in the understanding, design and even implementation of group theoretical algorithms. These are gradually becoming accepted both as standard tools for a working group theoretician, as implemented, for example, in certain methods of proof, and as worthwhile objects of study, for example in exploring connections between notions expressed in theorems.

Our computations of the symmetry properties of molecules were carried out with the use of GAP [20]. GAP stands for Groups, Algorithms and Programming. The name was chosen to reflect the aim of the system, which is a group theoretical software for solving computational problems in computational group theory. This software was constructed by GAP's team in Aachen. GAP is a free and extendable software package. 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 GAP web page on http://www.gap-system.org. GAP contains a large library of functions,

which are important for the calculations of this paper.

GAP contains several functions for working with finite groups. For the sake of completeness, we describe some of these functions which are useful throughout. Let a_1, a_2, ..., a_r be permutations of {1,2,...,n}. The command "Group(a_1,a_2,...,a_r)" computes the group generated by permutations a_1, a_2, ..., a_r. For two groups A and B, the commands "Size(A)", "GeneratorsOfGroup(A)" and "Intersection(A,B)" compute the cardinality of the set A, a generator set for A and intersection of A and B, respectively. Finally the command "IsSimple(A)" determines whether or not A has a non-trivial proper normal subgroup. In this paper, we freely use these functions and the reader is encouraged to consult the GAP manual[20] and Refs. [14-16, 21].

Consider the equation $(P_\sigma)^t A P_\sigma = A$, where A is the adjacency matrix of the weighted graph G. Suppose Aut(G) = {σ_1, σ_2,..., σ_m}. The matrix $S_G = [s_{ij}]$, where $s_{ij} = \sigma_i(j)$ is called a solution matrix for G. Clearly, for computing the automorphism group of G, it is enough to calculate a solution matrix for G. In Ref. [16], one of us proved a result that is useful for computing symmetry of molecules. Using this result, Lemma 1 and its Corollary, we present a MATLAB program [22] for computing a solution matrix for the automorphism group of Euclidean graphs.

2.1 A MATLAB program for computing the symmetries of molecules

Our program needs the Cartesian coordinates of the atoms to determine the Euclidean distances in the molecule under consideration. If we calculate these distances using HyperChem, Gaussian 98 or similar software, then for computing the symmetry of molecule under consideration, the first eight lines of the program can be deleted and the distance matrix of the molecule directly loaded. A set of Cartesian coordinates for the C_{80} fullerene with I_h symmetry point group, calculated using Gaussian 98, are presented in Table 1.

```
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;
```

3 Results and discussion

In this section, we apply our program to compute the automorphism group of the Euclidean graph of the C_{80}-I_h molecule. The Cartesian coordinates of C_{80} were computed using HyperChem and Gaussian 98. It is important to note that in our program the accuracy is very important. Our calculations on the symmetry of some fullerenes show that, if we change the accuracy then the automorphism group will be changed. Hence in Table I, the Cartesian coordinates of C_{80}, were calculated to six digit accuracy.

We now calculate the symmetry of fullerene C_{80}. Fullerenes are molecules in the form of polyhedral closed cages made up entirely of n three-coordinate carbon atoms and having 12 pentagonal and (n/2 -10) hexagonal faces. Fullerene structures exist for all even numbers greater than or equal to 20, with the exception of n=22. Hence, the fullerene, C_{80}, (n = 80) has just 12 pentagonal faces and 30 hexagonal faces. Let G be the automorphism group of the Euclidean graph of the C_{80} fullerene with I_h symmetry point group. This molecule, Figure 1, will be used as an example to illustrate the Euclidean graphs and their automorphism group. It should be mentioned that one does not have to work with exact Euclidean distances since a mapping of weights into a set of integers suffices as long as different weights are identified with different integers. To illustrate let us use a Euclidean edge weighting for fullerenes C_{80} obtained from Table I and our program. Suppose A is the 80 × 80 matrix defined by Euclidean distances.

Not all 80! permutations of the vertices C_{80} belong to the automorphism group of its 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 does not preserve connectivity. Let X denote the set of all solutions of matrix equation $P^tAP = A$. Set $Y = \{\propto \in S_{80} | \ P_\propto \in X \}$. Then Y is the automorphism group of the Euclidean graph of C_{80}. We now apply our MATLAB program to find a solution matrix for this group. After running this program, we can see that G has order 120. Using the solution matrix of C_{80} and a simple GAP program, we can find the structure of the automorphism group G of Euclidean graph of C_{80}. We mention that this program is very fast and its running time is less than 0.01 s. Our GAP program is as follows:

3.1 A GAP Program for Computing the Structure of the Automorphism Group of the Euclidean Graphs of C_{80}

```
G := Group(X); Size(G);
R := NormalSubgroups(G);
I := Intersection(R[2],R[3]);
GeneratorsOfGroup(R[2]);
GeneratorsOfGroup(R[3]);
IsSimple(R[2]);
```

Using this GAP program two proper non-trivial normal subgroups N= R[2] and

M = R[3] are obtained which intersect trivially. Therefore, G is isomorphic to the direct product $Z_2 \times A_5$, where Z_2 is a cyclic group of order 2 and A_5 is the unique simple group of order 60. We now consider the following permutations:

A_1 = (2,3,4)(5,9,8)(6,10,7)(11,13,12)(14,19,17)(15,18,16)(20,26,23)
(21,27,24)(22,28,25)(29,37,33)(30,40,34)(31,39,35)(32,38,36)
(41,49,45)(42,52,46)(43,51,47)(44,50,48)(53,59,56)(54,60,57)
(55,61,58)(62,64,63)(65,70,68)(66,69,67)(71,75,74)(72,76,73)(77,78,79),

A_2 = (1,11,21,58,64,80,62,54,25,13)(2,20,30,70,75,77,53,42,19,9)
(3,5,29,48,76,78,71,41,36,10)(4,6,16,47,59,79,72,67,35,26)
(7,38,31,69,66,73,50,43,18,15)(8,14,17,46,49,74,65,68,34,37)
(12,28,22,57,60,63,61,55,24,27)(23,39,32,45,52,56,51,44,33,40),

B_1 =(1,80)(2,77)(3,78)(4,79)(5,71)(6,72)(7,73)(8,74)(9,75)(10,76)(11,62)
(12,63)(13,64)(14,65)(15,66)(16,67)(17,68)(18,69)(19,70)(20,53)(21,54)
(22,55)(23,56)(24,57)(25,58)(26,59)(27,60)(28,61)(29,41)(30,42)(31,43)
(32,44)(33,45)(34,46)(35,47)(36,48)(37,49)(38,50)(39,51)(40,52),

C_1 =(1,80)(2,77)(3,79)(4,78)(5,73)(6,74)(7,71)(8,72)(9,76)(10,75)(11,63)
(12,62)(13,64)(14,69)(15,70)(16,68)(17,67)(18,65)(19,66)(20,56)(21,55)
(22,54)(23,53)(24,61)(25,60)(26,59)(27,58)(28,57)(29,44)(30,43)(31,42)
(32,41)(33,50)(34,51)(35,52)(36,49)(37,48)(38,45)(39,46)(40,47),

C_2 =(1,60,54)(2,66,42)(3,49,67)(4,52,41)(5,75,43)(6,59,68)(7,65,36)
(8,51,35)(9,31,71)(10,32,53)(11,64,55)(12,61,25)(13,22,62)(14,48,73)
(15,30,77)(16,78,37)(17,72,26)(18,33,34)(19,23,50)(20,76,44)(21,80,27)
(28,58,63)(29,79,40)(38,70,56)(39,47,74)(45,46,69).

This program shows that $\{A_1,A_2\}$ is a generating set for G. Also, N = $<B_1>$ and M = $<C_1,C_2>$ are normal subgroups of G. Since M is a simple group of order 60 and A_5 is the unique simple group of this order, $M \cong A_5$. Therefore, the automorphism group of the Euclidean graph of fullerene C_{80} has order 120 and is isomorphic to $Z_2 \times A_5$.

4 Conclusions

Suppose T is a complete weighted graph and Supp(T) = $|\{w(e) \mid e \text{ is an edge of T}\}|$. If Supp(T) is large enough, for example greater than |V(T)|, then our algorithm and also our MATLAB program is very fast for computing the symmetry of the graph T. In particular, our program is suitable for computing the symmetry of fullerenes. We applied our programs for computing the symmetries of all molecules in Fullerene Gallery presented by Mitsuho Yoshida (for details see the web address http://www.cochem2.tutkie.tut.ac.jp/Fuller/higher/higherE.html) with running time less than 0.01 s for the GAP program and

less than 1 s for the MATLAB program running on parallel Pentium IV computers. The maximum running times were obtained for the case of fullerenes with I_h symmetry group.

We also mention that, our calculations with GAP and calculations done by Balasubramanian [3-9], Hao-Xu [10], Ivanov [11] and Ivanov-Schüürmann [12], suggest that the automorphism group of the Euclidean graph of every molecule is trivial or has an even number of elements.

Acknowledgment

We are greatly indebted to the referees, whose valuable criticisms and suggestions led us to rearrange the paper.

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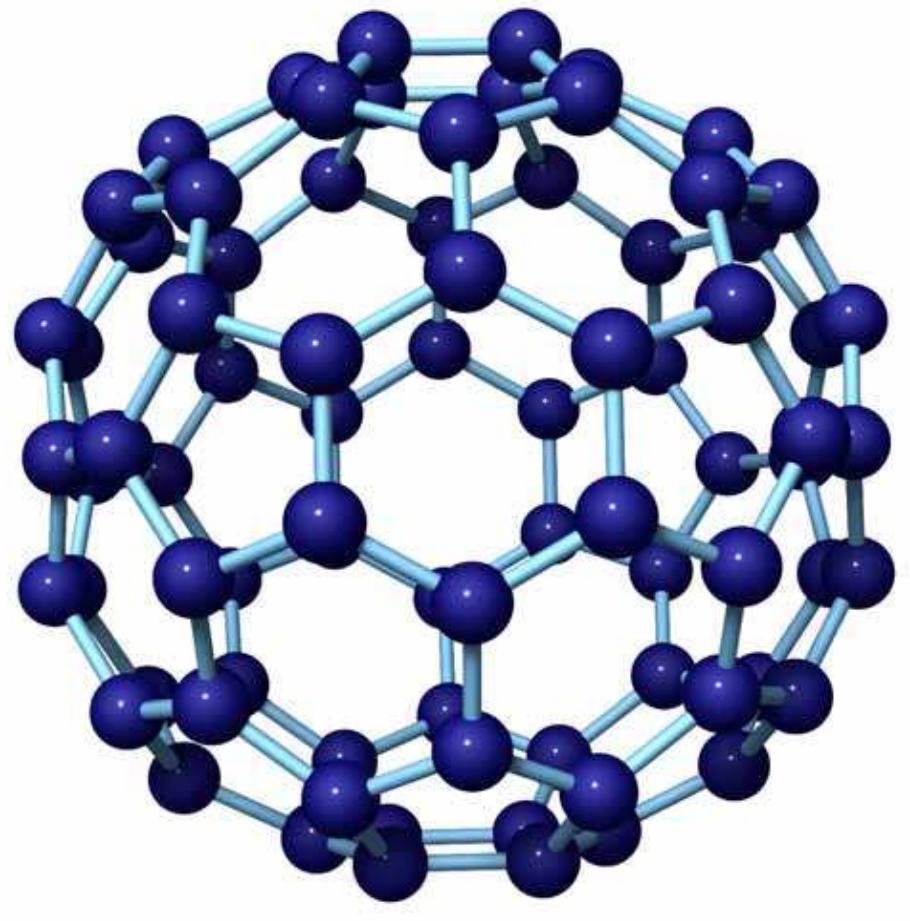

Fig. 1 The Fullerene C_{80}-I_h.

No.	Cartesian Coordinates	No.	Cartesian Coordinates
C(1)	(-1.408246,-0.234747,3.734826)	C(34)	(-3.497917,-1.579070,-1.174670)
C(2)	(-1.425582,1.154427,3.569457)	C(35)	(-2.758644,-2.750313,-0.969673)
C(3)	(-0.162489,-0.844639,3.919980)	C(36)	(-1.174199,-3.809160,0.474310)
C(4)	(-2.393305,-0.973526,3.071041)	C(37)	(0.940530,-3.685950,1.279230)
C(5)	(-0.238983,1.897231,3.528427)	C(38)	(3.073480,1.004397,2.378416)
C(6)	(1.024065,-0.101706,3.879941)	C(39)	(3.532814,-1.171676,1.502252)
C(7)	(-2.353758,1.774150,2.724498)	C(40)	(2.965856,-2.418377,1.210244)
C(8)	(-3.321435,-0.353931,2.225092)	C(41)	(-1.875657,-2.898698,-2.046089)
C(9)	(0.106700,-2.119051,3.406902)	C(42)	(-0.292211,-3.957559,-0.602151)
C(10)	(-2.124107,-2.248931,2.558092)	C(43)	(1.015019,-3.882087,-0.105101)
C(11)	(1.009633,1.278402,3.652287)	C(44)	(3.040391,-2.614642,-0.175078)
C(12)	(-3.299504,1.028367,2.011964)	C(45)	(3.957755,-0.597297,0.297962)
C(13)	(-0.859299,-2.832393,2.689232)	C(46)	(3.498375,1.578905,1.175116)
C(14)	(2.026729,-0.917566,3.340570)	C(47)	(2.758149,2.750005,0.969084)
C(15)	(1.459771,-2.164267,3.048561)	C(48)	(1.173704,3.808852,-0.474898)
C(16)	(-0.433729,2.975636,2.658166)	C(49)	(-0.941033,3.686634,-1.279947)
C(17)	(-1.740913,2.900035,2.160125)	C(50)	(-3.072976,-1.004690,-2.378961)
C(18)	(-3.626000,-1.245263,1.188670)	C(51)	(-3.533355,1.171497,-1.501851)
C(19)	(-2.885774,-2.416364,1.394702)	C(52)	(-2.966397,2.418198,-1.209842)
C(20)	(2.069816,1.820242,2.917743)	C(53)	(-2.070365,-1.819430,-2.917470)
C(21)	(0.613091,3.477989,1.876630)	C(54)	(-0.613594,-3.477305,-1.877348)
C(22)	(-2.050478,3.323037,0.862601)	C(55)	(2.049983,-3.323345,-0.863189)
C(23)	(-3.653731,1.488449,0.738862)	C(56)	(3.654189,-1.488614,-0.738416)
C(24)	(-3.919410,-0.787758,-0.100455)	C(57)	(3.919914,0.787464,0.099911)
C(25)	(-2.411613,-3.174201,0.318601)	C(58)	(2.411072,3.174021,-0.318199)
C(26)	(-0.412541,-3.640735,1.637571)	C(59)	(0.412038,3.641419,-1.638288)
C(27)	(1.897532,-2.925157,1.959053)	C(60)	(-1.898073,2.924978,-1.958651)
C(28)	(3.053305,-0.383763,2.554027)	C(61)	(-3.052847,0.383598,-2.553580)
C(29)	(1.876115,2.898533,2.046535)	C(62)	(-1.010174,-1.278581,-3.651885)
C(30)	(0.291670,3.957380,0.602553)	C(63)	(3.299962,-1.028532,-2.011518)
C(31)	(-1.015560,3.881907,0.105503)	C(64)	(0.859757,2.832228,-2.688785)
C(32)	(-3.040886,2.614334,0.174489)	C(65)	(-2.026272,0.917400,-3.340123)
C(33)	(-3.958296,0.597117,-0.297560)	C(66)	(-1.459313,2.164101,-3.048115)

Table 1 Cartesian coordinates of C_{80} molecule (angstroms).

No.	Cartesian Coordinates	No.	Cartesian Coordinates
C(67)	(0.434187,-2.975801,-2.657719)	C(74)	(3.321939,0.353638,-2.225636)
C(68)	(1.740418,-2.900343,-2.160714)	C(75)	(-0.106251,2.119878,-3.406584)
C(69)	(3.625505,1.244956,-1.189259)	C(76)	(2.124565,2.248765,-2.557646)
C(70)	(2.885233,2.416184,-1.394300)	C(77)	(1.426086,-1.154720,-3.570001)
C(71)	(0.239478,-1.896533,-3.529100)	C(78)	(0.162993,0.844345,-3.920524)
C(72)	(-1.023615,0.102533,-3.879624)	C(79)	(2.393755,0.974353,-3.070724)
C(73)	(2.354216,-1.774315,-2.724052)	C(80)	(1.408742,0.235445,-3.735499)

Table 1 (continued): Cartesian coordinates of C_{80} molecule (angstroms).