

Symmetries of Weighted Complete Graphs of Tetranitrocubane and Octanitrocubane

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Abstract

An Euclidean graph associated to a molecule is defined by a weighted graph with the adjacency matrix $D = [d_{ij}]$, where d_{ij} is the Euclidean distance between the nuclei i and j . Balasubramanian computed the Euclidean graphs and its automorphism groups for benzene, eclipsed and staggered forms of ethane and eclipsed and staggered forms of ferrocene (see Chem. Phys. Letters 232(1995), 415-423). In this work using the D_4 geometry of octanitrocubane (ONC) and D_2 geometry of tetranitrocubane (TNC), which are essentially the same as the conformation found in crystal states, the distance matrices of ONC and TNC are computed. Then using GAP, the automorphism group of weighted graphs related to tetranitrocubane and octanitrocubane are calculated.

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1. DEFINITIONS AND TERMINOLOGY

Mathematical chemistry is becoming one of the most interesting areas of research in theoretical chemistry. However, most of its concepts are directly derived from mathematical formalisms such as graph theory and group theory. In some problems related to the applications of graph theory in chemistry connectivity and symmetry are combined and the question of determining symmetry properties of graph becomes important [1-4].

For real world chemical and spectroscopic applications one needs to utilize graphs which contain weights for edges, for example, to discriminate signals and double bonds. In the context of NMR and multiple NMR spectroscopy, the nuclear spin coupling can be represented by graphs called NMR graphs. In these examples, the vertices are the various nuclei in the molecule while the edges are either isotopic J -coupling constants or dipolar coupling constants. The nuclear coupling constants between the various nuclei in a molecule are often different as they depend on the Euclidean distances between the nuclei. Consequently, it is necessary to label the edges of the complete graph of a molecule with the appropriate nuclear spin-spin coupling constants. The same is true for hyperfine structure in the ESR spectra [3-7].

Let us recall some definitions and notations. A weighted graph $G = (V, E, \omega)$ is a combinatorial object consisting of an arbitrary set $V = V(G)$ of vertices, a set $E = E(G)$ of unordered pairs $\{x, y\} = xy$ of distinct vertices of G called edges, and weighting function $\omega: E(G) \rightarrow R$ assigns positive real numbers (weights) to edges. The weighted adjacency matrix $A(G)$, has the edge weights w_{ij} as elements. This differs from the ordinary adjacency matrix in that all weights of ordinary adjacency matrix are unities for connected vertex pairs and zero for not connected pairs. This important difference in the edge weights introduces a contrast in the automorphism of an edge weighted graph compared to an ordinary graph.

An Euclidean graph associated to a molecule is defined by a weighted graph with the adjacency matrix $D = [d_{ij}]$, where d_{ij} is the Euclidean distance between the nuclei i and j . Let $G = (V, E, \omega)$ be a weighted graph. An automorphism of 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 $e=uv$, $\omega(g(e)) = \omega(e)$, where $g(e):=g(u)g(v)$ is the permuted edge.

This can be generalized using the following precise mathematical definition. The automorphism group of an edge weighted graph consists of permutations g of the vertices whose permutation matrix P satisfy $P'DP = D$ [3-6].

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 symmetry we mean the automorphism group symmetry of a graph. The symmetry of a graph, also called a topological symmetry, accounts only for the bond relations between atoms, and does not fully determine 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 [3].

In [1, 2] it is shown by Randić that a graph can be depicted in different ways such that its point group symmetry or three-dimensional perceptions 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 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 showed by Balasubramanian [3] that the two symmetries are connected.

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 are also other important applications of automorphism groups of weighted graphs to fullerenes. The reader is encouraged to consult the references [3-19] for background material as well as basic computational techniques.

Longuet-Higgins [20] showed that a more desirable representation of molecular symmetry is to use the nuclear permutation and inversion operations resulting in a group called Permutation-Inversion (PI) group or Complete Nuclear Permutation Inversion group

(CNPI). Balasubramanian [3] showed that the automorphism group of Euclidean graph of a molecule is the Permutation-Inversion symmetry group of the molecule.

The successful synthesise of octanitrocubane(ONC) by Eaton's group [21] and [22] impressed the research area of explosive and highly energetic materials. The subsequent detailed molecular dynamic analysis of octanitrocubane in [22-25] motivated the present research.

The GAP package is a useful package for computing the character tables and even the group structure, which merits more attention from the chemical community [26]. In an early paper the present authors applied this package to compute the non-rigid group of ONC and TNC [27].

Throughout this paper, all groups considered are assumed to be finite. Our notation is standard and taken mainly from [26-29].

2. SYMMETRY OF TETRANITROCUBANE AND OCTANITROCUBANE

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. For this reason the symmetry of a graph was thought to be quite different from the point group symmetry and it is apparent that the two symmetries need not be related to each other.

We consider the Octanitrocubane (ONC) with D_4 point group to illustrate the Euclidean graphs and their automorphism group. This configuration of ONC is the same conformation found in crystal states [21-24]. Following Balasubramanian [3] it suffices to measure the Euclidean distances and then construct the Euclidean distance matrix $D=[d_{ij}]$. 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.

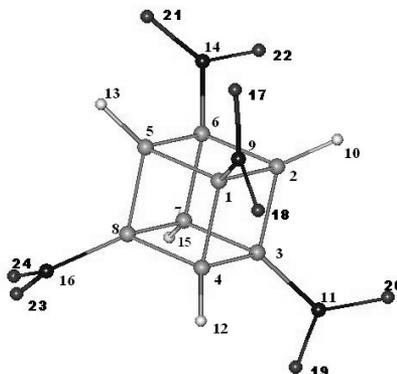
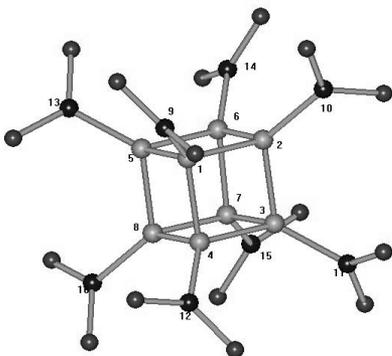


Figure 1: Labeling the atoms of Octanitrocubane. **Figure 2:** Labeling the atoms of Tetranitrocubane.

The solid geometry of ONC with D_4 symmetry can be described as follows. The regular cube frame consists of eight carbon atoms, C_i , $i=1, \dots, 8$, where the bond length of adjacent carbons is $a:=CC$. Each carbon C_i is connected to a nitrogen atom N_{i+8} , with the bond length $b:=CN$ in the direction of large diagonal of the cube passing through C_i . Connected to this nitrogen atom are two oxygen atoms $O_{(2i-1)+16}$ and O_{2i+16} with equal bond lengths $c:=ON$. The angle between the two bonds $N_{i+8}O_{(2i-1)+16}$ and $N_{i+8}O_{2i+16}$ is 125.7° as computed in [21-25]. At the corner i the body of NO_2 group characterize a plane V_i that also passes through the respective large body diagonal of the cube and includes C_i . Now we consider a plane W_i at the corner i which is perpendicular to the large body diagonal passing through this corner. The projection of the three CC bonds and V_i the NO_2 plane, at this corner to W_i shows that there are three angles α_i , β_i , γ_i between the three CC bonds and the projected V_i . The list of this angles using the results of [22-25], and noting that the antipodal NO_2 groups are perpendicular is as follows,

i	1	2	3	4	5	6	7	8
α_i	45°							
β_i	75°	165°	75°	165°	165°	75°	165°	75°
γ_i	165°	75°	165°	75°	75°	165°	75°	165°

Now using a Maple programming assuming $a:=CC=2$, $b:=CN=1$, $c:=NO=1$ the coordinates of all 32 atoms are computed and the distance matrix of this coordinates is calculated. The computed distance matrix is a 32×32 matrix that due to the suitable labeling has the following form,

	$C_j, 1 \leq j \leq 8$	$N_j, 9 \leq j \leq 16$	$O_j, 17 \leq j \leq 32$
$C_i, 1 \leq i \leq 8$	$d(C_i, C_j)$	$d(C_i, N_j)$	$d(C_i, O_j)$
$N_i, 9 \leq i \leq 16$	$d(N_i, C_j)$	$d(N_i, N_j)$	$d(N_i, O_j)$
$O_i, 17 \leq i \leq 32$	$d(O_i, C_j)$	$d(O_i, N_j)$	$d(O_i, O_j)$

where $d(A_i, B_j)$ means the distance between A_i and B_j . A similar argument applies for TNC. For the spatial configuration of the atoms in ONC and TNC molecules it is enough to only consider the $d(O_i, O_j)$ submatrix. For tetranitrocubane this submatrix is the 8×8 matrix E and for octanitrocubane the submatrix is the 16×16 matrix D given below, where the distances are represented up to two and three digits respectively.

$$E = \begin{bmatrix} 0 & 17 & 52 & 52 & 46 & 53 & 63 & 52 \\ 17 & 0 & 52 & 57 & 53 & 60 & 53 & 42 \\ 52 & 52 & 0 & 17 & 62 & 53 & 46 & 53 \\ 52 & 57 & 17 & 0 & 53 & 42 & 53 & 60 \\ 46 & 53 & 62 & 53 & 0 & 17 & 52 & 52 \\ 53 & 60 & 53 & 42 & 17 & 0 & 52 & 57 \\ 63 & 53 & 46 & 53 & 52 & 52 & 0 & 17 \\ 52 & 42 & 53 & 60 & 52 & 57 & 17 & 0 \end{bmatrix}$$

$$D = \begin{bmatrix} 0 & 177 & 487 & 375 & 523 & 522 & 329 & 301 & 329 & 471 & 465 & 530 & 649 & 649 & 621 & 539 \\ 177 & 0 & 375 & 293 & 522 & 573 & 471 & 428 & 301 & 428 & 530 & 606 & 649 & 649 & 539 & 423 \\ 487 & 375 & 0 & 177 & 329 & 471 & 621 & 539 & 523 & 522 & 649 & 649 & 465 & 530 & 329 & 301 \\ 375 & 293 & 177 & 0 & 301 & 428 & 539 & 423 & 522 & 573 & 649 & 649 & 530 & 606 & 471 & 428 \\ 523 & 522 & 329 & 301 & 0 & 177 & 487 & 375 & 649 & 649 & 621 & 539 & 329 & 471 & 465 & 530 \\ 522 & 573 & 471 & 428 & 177 & 0 & 375 & 293 & 649 & 649 & 539 & 423 & 301 & 428 & 530 & 606 \\ 329 & 471 & 621 & 539 & 487 & 375 & 0 & 177 & 465 & 530 & 329 & 301 & 523 & 522 & 649 & 649 \\ 301 & 428 & 539 & 423 & 375 & 293 & 177 & 0 & 530 & 606 & 471 & 428 & 522 & 573 & 649 & 649 \\ 329 & 301 & 523 & 522 & 649 & 649 & 465 & 530 & 0 & 177 & 329 & 471 & 621 & 539 & 487 & 375 \\ 471 & 428 & 522 & 573 & 649 & 649 & 530 & 606 & 177 & 0 & 301 & 428 & 539 & 423 & 375 & 293 \\ 465 & 530 & 649 & 649 & 621 & 539 & 329 & 471 & 329 & 301 & 0 & 177 & 487 & 375 & 523 & 522 \\ 530 & 606 & 649 & 649 & 539 & 423 & 301 & 428 & 471 & 428 & 177 & 0 & 375 & 293 & 522 & 573 \\ 649 & 649 & 465 & 530 & 329 & 301 & 523 & 522 & 621 & 539 & 487 & 375 & 0 & 177 & 329 & 471 \\ 649 & 649 & 530 & 606 & 471 & 428 & 522 & 573 & 539 & 423 & 375 & 293 & 177 & 0 & 301 & 428 \\ 621 & 539 & 329 & 471 & 465 & 530 & 649 & 649 & 487 & 375 & 523 & 522 & 329 & 301 & 0 & 177 \\ 539 & 423 & 301 & 428 & 530 & 606 & 649 & 649 & 375 & 293 & 522 & 573 & 471 & 428 & 177 & 0 \end{bmatrix}$$

All permutations of the vertices for octanitrocubane do not belong to the automorphism group of its weighted graph since the weights of all the edges are not the same. For example, the permutation $(1,2,\dots,32)$ does not belong to the automorphism group since the resulting graph of the molecule shown in Fig. 1 does not preserve connectivity. We have to search for permutations from the complete permutation inversion group of octanitrocubane $\mathbf{G}^{(ONC)}$ which is a direct product of permutation groups of identical nuclei, $\mathbf{G}^{(ONC)} \equiv \mathbf{S}_8^{(C)} \times \mathbf{S}_8^{(N)} \times \mathbf{S}_{16}^{(O)}$, which commute with the distance matrix of octanitrocubane, here, for example, $\mathbf{S}_n^{(C)}$ mean the permutation group on n carbon atoms. Let $P = (P_{(C)}, P_{(N)}, P_{(O)})$ be a permutation from $\mathbf{G}^{(ONC)}$. Due to the distance geometry of ONC, if $P_{(O)}$ is specified the $P_{(N)}$ and $P_{(C)}$ will be known. That is, if a permutation which preserves the distances between oxygen atoms also preserves all distances. Hence we have to find the permutations from $\mathbf{S}_{16}^{(O)}$ which commutes with the 16×16 matrix $D = [d(O_i, O_j)]$.

A permutation of the vertices of a weighted graph belongs to its automorphism group if it satisfies $P^t D P = D$, where P^t is the transpose of permutation matrix P and D is the weight 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 above relation. For a given adjacency matrix D , we can write a simple GAP program [26] to

$\mathbf{G} := \{ () , (1,3)(2,4)(5,9)(6,10)(7,15)(8,16)(11,13)(12,14) , (1,5)(2,6)(3,7)(4,8)(9,13)(10,14)(11,15)(12,16) , (1,7,11,9)(2,8,12,10)(3,5,13,15)(4,6,14,16) , (1,9,11,7)(2,10,12,8)(3,15,13,5)(4,16,14,6) , (1,11)(2,12)(3,13)(4,14)(5,15)(6,16)(7,9)(8,10) , (1,13)(2,14)(3,11)(4,12)(5,7)(6,8)(9,15)(10,16) , (1,15)(2,16)(3,9)(4,10)(5,11)(6,12)(7,13)(8,14) \}$.

In [21-24], the rigid symmetry group of octanitrocubane for an equilibrium crystal state is given to be \mathbf{D}_8 , which is a group of order 8. This is because that in the rigid case the substitution, of cubane hydrogen atoms for nitro groups, destroys the 3-fold axes that run along the body diagonals of the \mathbf{O}_h frame. Also, it is well-known that tetranitrocubane has a \mathbf{C}_{2v} point group of order 4. It should be mentioned here that the groups \mathbf{H} is isomorphic to $\mathbf{Z}_2 \times \mathbf{Z}_2$ and that the group \mathbf{G} is isomorphic to the dihedral group of order 8. The dihedral group of order 8 is isomorphic to the semi-direct product of \mathbf{Z}_2 with \mathbf{Z}_4 which is a non-abelian group.

Using several computations with computer algebra system GAP we conjecture that the automorphism group of a complete weighted graph must be trivial or has an even number of symmetries.

3. CONCLUDING REMARKS

We can use this method for computing with small groups. When the order of the symmetric group is large, the command “**Elements (t)**” is interrupted. In this situation, one can find all the conjugacy classes of symmetric groups and then compute the symmetries of the molecule under consideration in every conjugacy classes, separately. This method is usually very useful for calculating symmetries of the molecule, when the number of vertices is at most 30. In the case that the graph under consideration has a large number of vertices, it is better to find a subgroup of the full symmetric group containing automorphism group of our weighted graph. Then apply this subgroup and our GAP program to compute the automorphism group of the graph.

The Maple code and the GAP programs used in this paper are available upon the request from the authors.

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