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Prediction of the electronic transitions of Benzene using the character table and the conjugacy classes of the direct product of pair of dihedral groups

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Abstract: Benzene is a colourless volatile organic chemical compound with the molecular formula C_6H_6 present in coal tar and petroleum, and used in chemical synthesis. A considerable number of scholars in recent times have carried out studies on the electronic transitions of benzene using concepts in group theory. The Studies were consistent on the fact that benzene belong to the dihedral point group $D_{6\ h}$ with symmetry elements and operations as rotation axes, mirror plane and inversion centre. The group algorithm programming (GAP) was used to obtain the character table and the conjugacy classes of benzene which helped in revealing its π-electron molecular orbitals. Group theory concepts namely isomorphism and symmetry operations were applied to predict the allowed and forbidden electronic transitions based on symmetry arguments. Clearly, insights into the electronic transitions of benzene were provided and usefulness of group theory in predicting the electronic properties of molecules demonstrated.

Key words: Electronic Transmission, Benzene, Molecules, Group Theory, Point Group Symmetry, Dihedral Groups, Character Table, Conjugacy Classes, Symmetry Operations

1. Introduction

Mathematical theory for symmetry and group theory are of great importance in the applied sciences as they prove to be a great tool in solving physics and chemistry problems. As clearly demonstrated in [10],[11],[12],[17] and [18], Group theory concepts have been applied to electronic transitions in molecules of physical as well as chemical algebraic structures. For example these concepts can be applied when it comes to analyzing the electronic spectrum of benzene and predict the energy levels of its π-electrons.

Benzene, a cyclic aromatic hydrocarbon consists of six each of carbon and hydrogen atoms. It has a planar structure with alternating single and double bonds between the carbon atoms. The molecular orbitals of benzene are formed by the linear combination of the atomic orbitals of the carbon atoms. The molecular orbitals can be classified into two types: bonding and antibonding. Bonding orbitals are lower in energy and more stable than antibonding orbitals. Antibonding orbitals are higher in energy and less stable than bonding orbitals. Benzene exists as a chemical compound with molecular formula as C_6H_6. The electronic transitions of benzene are the changes in the occupancy of the molecular orbitals due to the absorption or emission of photons. The electronic transitions of benzene can be predicted by using the character table and the conjugacy classes.

Full rigid molecules' symmetry properties are well known and so investigating them is a natural thing

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to do, though study in this research area is new in chemistry. [14] presented a number of papers on the determination of character tables of restricted f-NRG of some chemical molecules. For example, Computation of the r-NRG of the triple equivalent methyl rotation in pyramidal trimethylamine with inversion was done by [15]. The authors proved that the r-NRG of this molecule is a group has 648 elements, consists two subgroups of order 324 without inversion. We also have in [4] and [5] where computation of full non-rigid group of some other molecules were carried out. In the same vein, [1] computed full non-rigid group of tetra-ammine platinum (II), trimethylamine, tetraammine platinum (II), etc which are all examples of C2v and C4v point groups. Authors such as [2] and [7] proved that molecular structure tetra-amine platinum (II) is isomorphic to the Wreath Product of certain degree. [8] worked on hexamethylbenzene while [9] and [3] studied melamine.

2. MATERIALS AND METHODS

Dihedral groups, the groups of symmetries of a regular polygon, which consist of rotations and reflections according to Cameron (2013) are good examples of finite permutation groups and have series of applications especially in natural sciences and engineering. There are two notable notations for dihedral groups associated with a polygon with n regular sides or degree namely D_{n} and $D_{2\mathrm{n}}$. In this work, we shall stick to D_{n} which symbolizes the symmetry of a regular polygon with n sides (that is, the dihedral group of degree n).

Conventionally, we write $D_{\mathrm{n}} = \langle r, f \mid r^n = f^2 = 1, fr = r^{n-1}f = r^{-1}f \rangle$ and we say that D_{n} is the group generated by the elements r and f subject to the conditions.

The direct product of a pair of dihedral groups is a mathematical concept that arises in group theory. Specifically, the dihedral group of order $2n$, denoted by D_n, can be expressed as a direct product $\mathrm{G} \times \mathrm{H}$ of two nontrivial groups if and only if $\mathrm{n} = 2$. In general, the direct product of two groups G and H is a new group that consists of all possible pairs of elements (g, h), where g is an element of G and h is an element of H, with the group operation defined componentwise. The direct product of two dihedral groups can be calculated using the rules for direct products of irreducible representations, which are necessary for working through transition moment integrals in chemistry.

In this paper, we employ group theory concepts to simplify the analysis of the electronic spectrum of benzene by predicting the allowed and forbidden electronic transitions, as well as the selection rules for these transitions. Then, on the bases of the structure of the group, a useful computational group theory, namely, "Groups, Algorithms and Programming" (GAP) is used to compute the conjugacy classes and the character table. The use of this computational group theory package (GAP) is capable of revealing many properties of a group according to [11] and [13]. We calculate the order of the point group of benzene from the character table.

3. RESULT AND DISCUSSION

Benzene molecules belong to the $\mathrm{D_{6\ h}}$ point group since it has a principal axis of rotation of $\mathrm{C_6}$, and contains two $\mathrm{C_3}$ axes. However, the $\mathrm{C_3}$ axis lies along the $\mathrm{C_6}$ axis, and both run through the center of the ring perpendicular to the plane of the molecule. This axis is also a $\mathrm{C_2}$ axis.

Figure 1: Benzene Structure.

Figure 2: Benzene Geometry.

Where:

Figure 1= Structure of Benzene

Figure 2= Geometry of Benzene

From figure 1 we have a $\mathrm{C_6}$ principal axis, and six additional $\mathrm{C_2}$ axes, but no other symmetry element.

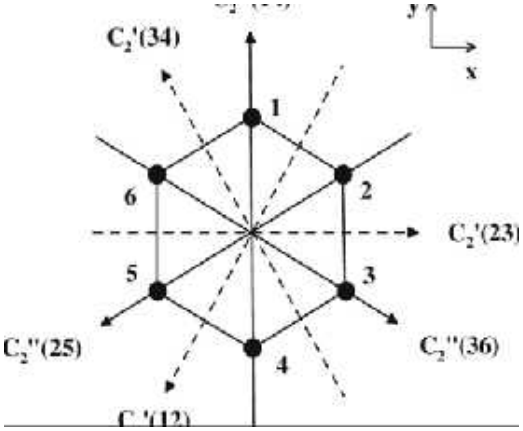

Figure 1. Benzene Structure

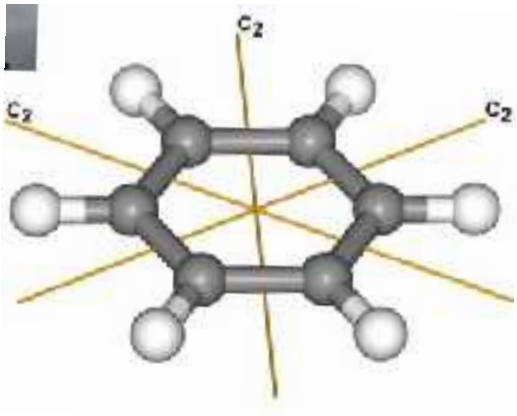

Figure 2. Benzene Geometry

The C_6 axis stands perpendicular to the paper plane, and the six C_2 axes are in the paper plane. Therefore the symmetry of C_6H_6 has a hexagonal shape which is a dihedral group of degree 6 . The C_6 axis goes through the centre of the atom of the C molecules, and the three C_2 axes go through the six H atoms. The C_6H_6 symmetry elements, namely C_6 and C_2 axes, are denoted by $C_3 := \langle(1,2,3,4,5,6)\rangle$ and $C_2 := \langle(7,8)\rangle$ respectively. Therefore the full symmetry of Benzene as can be viewed clearly from figure 2 , is: D_6 and D_2, which we can write in terms of direct product as $D_6 \times D_2$. We used GAP package to get the group as follows:

$gap >$
$gap > c6 := DihedralGroup(IsGroup, 12);$
$Group([(1,2,3,4,5,6),(2,6)(3,5)])$
$gap > c2 := DihedralGroup(IsGroup, 2);$
$Group([(1,2)])$
$gap > DG := DirectProduct(c2, c6);$
$Group([(1,2),(3,4,5,6,7,8),(4,8)(5,7)])$
$gap >$
$gap > Order(DG);$

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$gap >$
$gap > CC := ConjugacyClasses(DG);$
$[()^G, (4,8)(5,7)^G, (3,4)(5,8)(6,7)^G, (3,4,5,6,7,8)^G, (3,5,7)(4,6,8)^G, (3,6)(4,7)(5,8)^G]$
$gap >$
$gap > List(CC, x- > Order(Representative(x)));$
$[1,2,2,6,3,6]$
$gap >$
$gap > Display(CharacterTable(DG));;$
$gap >$
$gap >$

Table 1: The Representatives of Conjugacy Classes for Benzene

S/N	Representatives	Size	Name
1.	(1)	1	e
2.	(1, 2)	2	C_2
3.	(4, 8)(5, 7)	2	σ_h
4.	(3, 5, 7)(4, 6, 8)	2	C_3
5.	(3, 6)(4, 7)(5, 8)	2	σ_v
6.	(1, 2)(3, 5, 7)(4, 6, 8)	6	C_6

Table 2: Character Table for Benzene

	e	C_2	σ_h	C_6	C_3	σ_v
2P	e	e	e	C_3	3a	e
3P	e	C_2	σ_h	σ_v	e	σ_v
5P	e	C_2	σ_h	C_6	C_3	σ_v
X.1	1	1	1	1	1	1
X.2	1	-1	-1	1	1	1
X.3	1	-1	-1	1	1	1
X.4	1	-1	1	-1	1	-1
X.5	1	-1	1	-1	1	-1
X.6	1	1	-1	-1	1	-1

The character table of benzene is a tool that summarizes the symmetry properties of the molecule and its molecular orbitals. The character table has four columns: the symmetry operations, the classes, the characters, and the irreducible representations. The symmetry operations are the ways to transform the molecule into itself, such as rotations, reflections, and inversions. The classes are the groups of symmetry operations that have the same effect on the molecule. The characters are the numerical values that indicate how the molecular orbitals change under each symmetry operation. The irreducible representations are the labels that identify the symmetry types of the molecular orbitals.

The conjugacy classes of benzene are the subsets of the molecular orbitals that have the same symmetry type and energy. The conjugacy classes of benzene are Class containing the identity element (E) : The identity

element represents the absence of any symmetry operation; Class of rotations (C_6) : Elements in this class are the rotations of benzene by multiples of $60°$. There are six distinct rotations in this class; Class of reflections in the horizontal mirror plane (σ_h) : Elements in this class are reflections of benzene in the horizontal mirror plane; Class of reflections in the vertical mirror planes (σ_v) : Elements in this class are reflections of benzene in the six vertical mirror planes; Class of 2-fold rotations (C_2) : Elements in this class are the 180degree rotations; and Class of 3-fold rotations (C_3) : Elements in this class are the 120-degree rotations. The C_2 and C_3 classes are non-degenerate, meaning they have only one orbital each. The σ_h and σ_v classes are also non-degenerate, but they have different energies than the E and C_6 classes. The E and C_6 classes are degenerate, meaning they have two orbitals each with the same energy.

The transition from the E to the C_6 class is allowed, because the total symmetry is the same (E), the change in the number of nodes is even (2), and the change in the energy matches the energy of the photon. However, the transition from the σ_h to the C_3 class is forbidden, because the total symmetry is different (C_2 and σ_v), the change in the number of nodes is odd (1), and the change in the energy does not match the energy of the photon.

4. CONCLUSIONS

In this work, the symmetry operations of the Benzene molecule were studied. The conjugacy classes and the irreducible character tables of the molecules were computed as seen in table 1 and 2 using computational group theory. We found that the group is isomorphic to the

Direct Product of $D_6 \times D_2$. and has order 24 and 9 conjugacy classes. We used GAP 4.11.1 for our calculations. Clearly, understanding the electronic transitions of benzene can provide insights into its electronic properties, which are important for many chemical and physical processes. Thus, symmetry can be applied in the prediction electronic transitions of benzene. Note, only orbitals that have the same irreducible representation have the correct symmetry to overlap and form a molecular orbital. It is natural to extend these methodologies to other aromatic molecules.

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