MATCH
Communications in Mathematical and in Computer Chemistry

MATCH Commun. Math. Comput. Chem. **56** (2006) 271-278

ISSN 0340 - 6253

Computation of the character table for p–Xylene

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(Received January 6, 2006)

Abstract

Using non-rigid group theory, it is shown that the full non-rigid(f-NRG) group of 1,4-dimethybenzene (p-xylene) is isomorphic to the group $C_2 \times G$ of order 36, where $G = C_3\ wr\ C_2$ and wr stands for wreath product. This group has 18 conjugacy classes and irreducible representations. Then the character table of the full non-rigid p-xylene is derived.

1 Introduction

A rigid molecule is defined as being such that the barriers between its versions are insuperable and there are no observable tunneling splittings. For non-rigid molecules, there are one or more contortional large amplitude vibrations such as inversion or internal rotation that give rise to tunneling splittings. Because of this deformability, the non-rigid molecules exhibit some interesting properties of intramolecular dynamics which can be studied more easily resorting to group theory.

Group theory is one of the most powerful mathematical tools in quantum chemistry and spectroscopy. It can predict, interpret and simplify complex

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theory and data. Group theory is the best formal method to describe the symmetry concept of molecular structures. Group theory for non-rigid molecules is becoming increasingly relevant and its numerous applications to large amplitude vibrational spectroscopy of small organic molecules are appearing in the literature [1-8].

The molecular symmetry group for non-rigid molecules, where changes from one conformation to another can occur easily, is first defined by Longuet-Higgins [9] although there have been earlier works that suggested the need for such a framework. When studying rigid molecules, the point group symmetry of minimum-energy geometries can be used to label electronic and vibration/rotation wave functions. In many cases, these symmetry groups are not isomorphic with any of the familiar symmetry groups of rigid molecules, and their character tables are not known. For non-rigid molecules, these point group symmetries are not useful. It is therefore of some interest and importance to develop simple methods of calculating these character tables, which are permit the labeling and classification of the energy levels and the vibrational functions and may also used to deduce selection rules for the infrared transitions.

Bunker and Papoušek [10] extended the definition of the molecular symmetry group to linear molecules using an extended molecular symmetry.

The operations of the molecular symmetry group and the three-dimensional rotation group are used together to treat the symmetry properties of molecules in electromagnetic fields by Watson [11].

The complete set of the molecular conversion operations that commute with the nuclear motion operator will contain overall rotation operations that describe the molecule rotating as a whole, and intramolecular motion operations that describe molecular moieties moving with respect to the rest of the molecule, forms a group which is called the full non-rigid molecule group (f-NRG) by Smeyers [12].

The method of computation of f-NRGs as described here is appropriate for molecules which consist of a number of methyl groups attached to a rigid framework. The methyl derivatives became the subject of our interest, since they are characterized by the high intensities of the CH3 torsional and C-CH3 wagging modes. Non-rigidity of methyl derivatives is due to torsion of methyl groups assuming that the barrier to rotation of the methyl groups is low. The present study investigates the f-NRG of 1,4-dimethylbenzene (p-xylene), which consists of two methyl groups attached to a benzene ring (Figure 1).

We show that the f-NRG of p-Xylene is of order 36 with 18 conjugacy classes and irreducible representations. Then we deduce it character table.

Computing the f-NRGs using wreath product formalism was first introduced by Balasubramanian [13]. The character theory of wreath product groups has been considered and discussed in [14,15]. Other applications of wreath product can be seen in [15-19]. Some of the previous approaches and the motivation of our study are outlined in references [20-27].

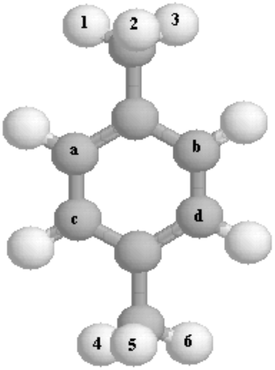

Figure 1: Geometry of p-Xylene

2 Computing the character table of p-Xylene

To justify the mean time dynamic symmetry of the molecule, we assume that the speed of rotations of the methyl groups sufficiently high. The description of the f-NRG of p-xylene is as follows. Note that each dynamic symmetry operation of this molecule, considering the symmetries of the methyl groups, is composed of two sequential physical operations. We first have a physical symmetry of the hexagonal framework and such operations are exactly the symmetry operations that change the carbon atoms among themselves. Let us number the carbon atoms of the hexagonal framework which are joined to one hydrogen atom by the letters a, b, c and d. Then the feasible symmetries of the framework in terms of permutations on the letters a, b, c and d are $\sigma = (a\ b)(c\ d)$ and $\tau = (a\ c)(b\ d)$.

It is easy to see that these permutations generate the Klein's fourgroup isomorphic to $C_2 \times C_2$. In fact the four permutations correspond to the following operations: identity, vertical reflection, horizontal reflection and a reflection through the center of the hexagon. After accomplishing the first framework symmetry operation, we have to map each of the two methyl groups to itself. The only feasible symmetry group of each methyl group is the cyclic group C_3 of order three. Now let us number the three hydrogen atoms in the upward direction of Figure 1 by 1, 2 and 3. Similarly those hydrogen atoms which are downward are numbered by 4, 5 and 6. Therefore the symmetry group of the methyl groups are $\{id., (1\ 2\ 3), (1\ 3\ 2)\}$ and $\{id., (4\ 5\ 6), (4\ 6\ 5)\}$.

Since the horizontal reflection changes the two methyl groups, therefore we may assume (1 4)(2 5)(3 6) is the permutation resulting the effect of the horizontal reflection. Therefore $G =< (1\ 2\ 3), (4\ 5\ 6), (1\ 4)(2\ 5)(3\ 6) >$ is the symmetry group as a result of the symmetries of the methyl groups and the horizontal reflection.

If we set $\alpha = (1\ 2\ 3)$, $\beta = (4\ 5\ 6)$ and $\gamma = (1\ 4)(2\ 5)(3\ 6)$, then $G = (< \alpha > \times < \beta >) :< \gamma >$ where : denotes the semi-direct product. As a matter of fact we have $G \cong C_3\ wr\ C_2$, where wr denotes wreath product. Now the effect of the vertical operation is to interchange the carbon atoms $\{a, c\}$ with $\{b, d\}$. In this event the methyl frameworks remain fixed and hence the f-NRG of the molecule is the direct product of G with a cyclic group of order two, namely $C_2 \times G$. If we calculate the character table of the group G, then using standard methods we can complete the character table of the group $C_2 \times G$. Note that the number of conjugacy classes, as well as the number of irreducible characters of the group $C_2 \times G$ is twice those of G. Therefore in the next section we give the details of computing the character table of the group G.

3 The Character table of the group G

In the previous section we mentioned that G has the following presentation $G = (< \alpha > \times < \beta >) :< \gamma >$, where $\alpha = (1\ 2\ 3)$, $\beta = (4\ 5\ 6)$ and $\gamma = (1\ 4)(2\ 5)(3\ 6)$. It is obvious that α and β are permutations of order three and γ is of order two, i.e. $\alpha^3 = \beta^3 = \gamma^2 = id$. Further calculations show that $\gamma^{-1}\alpha\gamma = \beta$. The group G has order 18 and its elements are either in the set $H = \{id., \alpha, \alpha^2, \beta, \beta^2, \alpha\beta, \alpha\beta^2, \alpha^2\beta^2\}$ or $H\gamma$.

Conjugacy classes of G are obtained by the action of $< \gamma >$, by conjugation, on H as well as the action of $< \alpha > \times < \beta >$ and $< \gamma >$ on $H\gamma$. Under the action of $< \gamma >$ on H we have the following conjugacy classes. $\{id.\}$ with size 1, $\{\alpha, \beta\}$ with size 2, $\{\beta^2, \alpha\}$ with size 2, $\{\alpha\beta\}$ with size 1, $\{\alpha^2\beta^2\}$ with size 1 and $\{\alpha^2\beta, \alpha\beta^2\}$ with size 2.

The conjugacy classes of G contained in $H\gamma$ are as follows: $\{\alpha, \alpha\beta^2\gamma, \alpha^2\beta\gamma\}$ with size 3, $\{\alpha\gamma, \beta\gamma, \alpha^2\beta^2\gamma\}$ with size 3 and $\{\alpha^2\gamma, \beta^2\gamma, \alpha\beta\gamma\}$ with size 3.

Therefore G has 9 conjugacy classes, hence 9 irreducible characters. An element of the form $x^{-1}y^{-1}xy$, where x and y belong to G, is called a commutator, and the subgroup of G generated by all the commutators is called the commutator subgroup of G and is denoted by G'. It is well-known that the number of irreducible characters of G with degree 1 is equal to the number of the elements in the abelian group G/G', see [28].

In the above group, it is easy to see that $G' =< \alpha^2\beta >$ is a group of order 3 and hence G has $|G/G'| = 6$ irreducible characters of degree 1. Since the sum of the square of the degrees of the irreducible characters of G must be equal to $|G| = 18$, therefore the remaining irreducible characters of G all have degree 2 and there ate three of them. Further calculations show that the center $Z(G)$ of G is the following $Z(G) = \{id., \alpha\beta, \alpha^2\beta^2\}$. Since G/G' is an abelian group, hence $G/G' \cong C_6$, the cyclic group of order 6, and since $G/Z(G)$ is non-abelian, hence $G/Z(G) \cong S_3$, the symmetric group of order 6. We use the above information to complete part of the character table of G by lifting the characters of the quotient groups C_6 and S_3. Note that if in general N is a normal subgroup of G and if $\chi : G/N \longrightarrow \mathbb{C}$ is a character of the quotient group G/N, then $\hat{\chi}$ defined by $\hat{\chi} : G \to \mathbb{C}$, $\hat{\chi}(g) = \chi(Ng), g \in G$, is a character of G. Moreover if χ is irreducible, then $\hat{\chi}$ is also irreducible. In this case we say that the character χ of G/N if lifted the character $\hat{\chi}$ of G.

From $G/G' =< \alpha\gamma G' >\cong C_6$ and by lifting the characters of the cyclic group of order 6 to G we obtain the values of all the characters of degree 1 in G. From $G/Z(G) =< \alpha Z(G), \gamma Z(G) >\cong S_3$ we are able to calculate the values of one of the irreducible characters of degree 2 of G by lifting the irreducible characters of degree 2 of S_3 to G. Next we use the orthogonality relation of rows and columns of the character table to compute the whole character table of G as follows. Note that in the following table we have $\omega = e^{\pi i/3}$ and $\bar{\omega}$ denotes complex conjugate of ω.

Table 1. The character table of the group G

Centralizer order	18	9	9	18	18	9	6	6	6
Class representative	*id.*	α	α^2	$\alpha\beta$	$\alpha^2\beta^2$	$\alpha^2\beta$	γ	$\alpha\gamma$	$\alpha^2\gamma$
χ_1	1	1	1	1	1	1	1	1	1
χ_2	1	$-\omega$	$\bar{\omega}$	$-\bar{\omega}$	$-\omega$	1	-1	ω	$\bar{\omega}$
χ_3	1	$-\bar{\omega}$	$-\omega$	$-\omega$	$-\bar{\omega}$	1	-1	$\bar{\omega}$	ω
χ_4	1	$-\bar{\omega}$	$-\omega$	$-\omega$	$-\bar{\omega}$	1	1	$-\bar{\omega}$	$-\omega$
χ_5	1	$-\omega$	$-\bar{\omega}$	$-\bar{\omega}$	$-\omega$	1	1	$-\omega$	$-\bar{\omega}$
χ_6	1	1	1	1	1	1	-1	-1	-1
χ_7	2	-1	-1	2	2	-1	0	0	0
χ_8	2	ω	$\bar{\omega}$	$-2\bar{\omega}$	-2ω	-1	0	0	0
χ_9	2	$\bar{\omega}$	ω	-2ω	$-2\bar{\omega}$	-1	0	0	0

As we mentioned earlier the full non-rigid group of p-Xylene is of the form $P = C_2 \times G$, where C_2 is isomorphic to the cyclic group of order 2. In fact if $z = (ab)(cd)$ corresponds to the vertical operation of the molecule framework, then $C_2 = \{id., z\}$ where $z^2 = id.$ The character table of the cyclic group of order 2 is

	id.	z
θ_1	1	1
θ_2	1	-1

The group P has 18 conjugacy classes and hence 18 irreducible characters which may be written as the product $\theta_j\chi_i$, $j = 1, 2$, $1 \leq i \leq 9$. The values of $\theta_j\chi_i$ on the whole of P can be calculated according to the following rules:

$$(\theta_j\chi_i)(id., u) = \chi_i(u)$$

$$(\theta_j\chi_i)(z, u) = \begin{cases} \chi_i(u), & \text{if } j = 1, \\ -\chi_i(u), & \text{if } j = 2. \end{cases}$$

where u is an arbitrary element of G, and χ_i is an irreducible character of G, where $1 \leq i \leq 9$. In this way the whole character table of the group P is obtained.

4 Conclusion

We have developed the group theory and character table of the non-rigid p-Xylene as a wreath product group and it consists of 36 operations divided into

18 conjugacy classes and irreducible representations. The derived character table would also be valuable in other applications such as in the context of chemical applications of graph theory [29] and aromatic compounds [30]. In the case of chemical applications of graph theory, applications can range from enumeration of isomers to the automorphism groups of chemical graphs. In other fields such as theory of quarks and generalized special unitary groups, such wreath products and their double groups find important applications.

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