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Full Non-Rigid Group of 1,3,5-Trimethyl-2,4,6-trinitrobenzene Using Wreath Product

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Using non-rigid group theory, it is shown that the full non-rigid (f-NRG) group of 1,3,5-trimethyl-2,4,6-trinitrobenzene is isomorphic to the group $(C_2 \times C_3) \sim S_3$ of order 1296, where ~ stands for wreath product, C_2 and C_3 are cyclic groups of order 2 and 3, respectively and S_3 is the symmetric group of order 6 on 3 letters. This group has 98 conjugacy classes and irreducible representations. Then the character table of the full non-rigid 1,3,5-trimethyl-2,4,6-trinitrobenzene is derived for the first time.

Key Words: Full non-rigid group, Character table, 1,3,5-Trimethyl-2,4,6-trinitrobenzene.

INTRODUCTION

A rigid molecule is defined as 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 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 is first defined by Longuet-Higgins[9] although there have been earlier works that suggested the need for such a framework. 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 3-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

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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)[12].

The method as described here is appropriate for molecules which consist of a number of CH_3 or NO_2 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 CH_3 torsional and C-CH_3 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 1,3,5-trimethyl-2,4,6-trinitrobenzene (TNM), which consists of 3 nitro groups and 3 methyl groups attached to a benzene ring (Fig. 1). General interest on TNM is due to its potential as a high energy material[13-15]. The crystal structure of TNM is investigated by Hardy *et al.*[16]. We prove that the f-NRG group of TNM is of order 1296 with 98 conjugacy classes and irreducible representations. The character table of this group is derived with the aid of GAP[17], a group theory package and this was done by characterizing the algebraic structure of f-NRG as the wrath product of known groups.

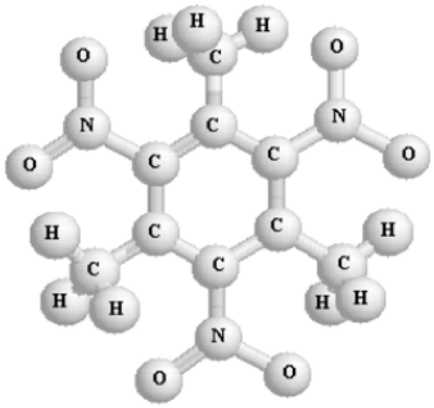

Fig. 1. Geometry of 1,3,5-trimethyl-2,4,6-trinitrobenzene (TNM)

Computing the f-NRGs using wreath product formalism was first introduced by Balasubramanian[18]. The character theory of wreath product groups has been considered and discussed in previous reports[19,20]. Other applications of wreath product can be seen in reported works[20-33]. Some of the previous approaches have been applied to some molecules in references[30-37]. The notation used is standard and the reader may consult the reference[38].

RESULTS AND DISCUSSION

Since the symmetry group of the molecule under consideration involves certain structures in group called the wreath product, hence we will explain this notion in the sequel. Suppose X = {1,2,…,n} is a set consisting of the numbers 1,2,…,n. The

set of all permutations of X under the composition of permutations is a group which is called the symmetric group of X and is denoted by the symbol S_n. Let H be a subgroup of S_n, *i.e.* a set consisting some permutations from S_n which is closed under the composition of permutations. Let G be any group. The set of all the mappings $X \rightarrow G$ is denoted by G^X, *i.e.* $G^X = \{f \mid f: X \rightarrow G\}$. The number of all the mappings from X into G is equal to $|G|^{|X|}$, where |G| denotes the order of G and $n = |X|$ is the number of elements in X.

Next we form the Cartesian product $G^X \times H$ which makes it into a group. If π is an element of H, then π is a permutation on X, *i.e.* a one-to-one correspondent $\pi : X \rightarrow X$. If f is an element of G^X, then f is a mapping $f : X \rightarrow G$ and hence we can form $f\circ\pi^{-1} : X \rightarrow G$, where π^{-1} is the inverse of π. We set $f_\pi = f\circ\pi^{-1}$ and remark that for every $x \in X$ we have $f_\pi(x) = (f\circ\pi^{-1})(x) = f(\pi^{-1}(x))$.

Now for (f,π) and (f',π') in $G^X \times H$ we define the composition law $(f,\pi)(f',\pi') = (ff'_\pi, \pi\pi')$ where ff'_π is defined by $(ff'_\pi)(x) = f(x)f'_\pi(x)$ for all $x \in X$. The set $G^X \times H$ under the above law is a group which is called the wreath product of G with H and is denoted by G~H or H[G]. The order of this group is equal to $|G|^n \times |H|$. Obviously the identity element of G~H is $(e, 1_H)$, where 1_H is the identity element of H and $e: X \rightarrow G$ is the mapping which assigns to every element of X the identity element 1_G of G. The inverse of (f,π) is (f',π^{-1}) where π^{-1} is the inverse of π in H and $f': X \rightarrow G$ is defined by $f'(x) = [f(\pi(x))]^{-1}$ for all x in X.

Before going into the details of the computations of TNM, we should mention that we consider the speed of rotations of methyl and nitro groups sufficiently high so that the mean time dynamical symmetry of the molecules makes sense.

We describe the f-NRG of TNM as follows: Note that each dynamic symmetry operation of this molecule, considering the symmetries of the CH_3 and NO_2 groups, is composed of two sequential physical operations. We first have a physical symmetry of the hexagon framework and such operations are exactly the symmetry operations that change the carbon atoms among them selves, as well as the nitrogen atoms. Evidently these operations form the symmetric group of order 6 on 3 letters denoted by S_3. After accomplishing the first framework symmetry operation, we have to map each of the 3 methyl group on itself, as well as nitro group. The feasible symmetry group of each methyl group is the cyclic group C_3 and that of each nitro group is the cyclic group C_2. Therefore the f-NRG of TNM is of the form $G = (C_2\times C_3)\sim S_3$ and is a group of order 1296. It is shown by Balasubramanian[19] that the conjugacy classes of the group G can be obtained by the matrix types and its character table can also be generated using the matrix generator. We now apply GAP to obtain the conjugacy classes and character table of the group G (Table-1). Table-1 shows the conjugacy classes, a representative from each class and the order of the conjugacy class. Since the character table of the group is very large in size, it is deposited as a supplementary material to this letter. In supplementary Table, we have the following conventions:

TABLE-1
THE REPRESENTATIVES OF THE CONJUGACY CLASSES OF THE GROUP $(C_2 \times C_3) \sim S_3$, THE NON-RIGID GROUP OF 1,3,5-TRIMETHYL-2,4,6-TRINITROBENZENE CONTAINING 1296 OPERATIONS

No.	Representatives	Size	No.	Representatives	Size
1	(e,e,e,())	1	50	(a,ab,ab^2,())	6
2	(e,ab^2,ab,(1,3))	18	51	(e,b^2,b,())	6
3	(b^2,ab,a,(1,3))	18	52	(ab,ab^2,ab,())	3
4	(ab,b,ab,())	3	53	(ab^2,ab,ab^2,())	3
5	(ab^2,b^2,ab^2,())	3	54	(b,ab,b,())	3
6	(b^2,b^2,b^2,())	1	55	(b^2,ab^2,b^2,())	3
7	(b,b,b,())	1	56	e,ab^2,ab,(1,3,2))	72
8	(a,e,a,())	3	57	(ab^2,a,b,())	6
9	(ab,a,b^2,(1,3))	18	58	(ab,a,b^2,())	6
10	(b^2,ab,b^2,())	3	59	(b^2,ab,e,())	6
11	(b,ab^2,b,())	3	60	(b,ab^2,e,())	6
12	(b,b^2,b,())	3	61	(b^2,b,ab^2,())	6
13	(b^2,b,b^2,())	3	62	(b,b^2,ab,())	6
14	(e,a,e,())	3	63	(a,ab^2,e,())	6
15	(e,b,e,())	3	64	(a,ab,e,())	6
16	(e,b^2,e,())	3	65	(ab,e,e,())	3
17	(b,b,b,(1,3))	18	66	(ab^2,e,e,())	3
18	(b^2,b^2,b^2,(1,3))	18	67	(a,b^2,b^2,())	3
19	(e,e,e,(1,3))	18	68	(a,b,b,())	3
20	(b,a,ab,(1,3))	18	69	(a,a,ab^2,(1,3))	18
21	(b^2,a,ab^2,(1,3))	18	70	(ab,a,a,(1,3))	18
22	(ab^2,e,ab^2,())	3	71	ab^2,a,ab,(1,3))	18
23	(ab,e,ab,())	3	72	(b^2,ab,b,(1,3))	18
24	(b,e,b,())	3	73	b^2,ab^2,b,(1,3))	18
25	(b^2,e,b^2,())	3	74	(b,e,b,(1,3))	18
26	(a,ab,a,())	3	75	(b^2,e,b^2,(1,3))	18
27	(a,ab^2,a,())	3	76	(a,ab,ab,(1,3))	18
28	(a,a,a,())	1	77	ab^2,ab^2,a,(1,3))	18
29	(ab^2,e,b^2,(1,3))	18	78	(b,b,b^2,(1,3))	18
30	(ab,e,b,(1,3))	18	79	(b,b^2,b^2,(1,3))	18
31	(e,e,a,(1,3))	18	80	(a,b^2,e,())	6
32	(a,ab^2,e,(1,3))	18	81	(a,b,e,())	6
33	(a,ab,e,(1,3))	18	82	(b^2,ab,ab^2,())	6
34	(a,b,a,())	3	83	(b,ab^2,ab,())	6
35	(a,b^2,a,())	3	84	(a,ab,b,())	6
36	(ab^2,b,b^2,(1,3))	18	85	(a,ab^2,b^2,())	6
37	(ab,b^2,b,(1,3))	18	86	(ab,ab^2,e,())	6
38	(ab,b^2,ab,())	3	87	(b,b,e,(1,3))	18
39	(ab^2,b,ab^2,())	3	88	(e,b^2,b^2,(1,3))	18
40	(e,b,b,(1,3,2))	72	89	(b^2,b,a,())	6
41	(b,b,b^2,(1,2,3))	72	90	ab^2,ab,a,(1,3))	18
42	ab^2,ab^2,a,(1,2,3))	72	91	a,ab^2,ab,(1,3))	18
43	(ab^2,a,a,(1,3,2))	72	92	b^2,b^2,ab^2,(1,3))	18
44	(ab,ab,ab,())	1	93	(b,b,ab,(1,3))	18
45	(ab^2,ab^2,ab^2,())	1	94	(ab,a,ab,())	3
46	(ab^2,ab,b^2,(1,3))	18	95	(ab^2,a,ab^2,())	3
47	(ab,ab^2,b,(1,3))	18	96	b,ab^2,e,(1,2,3))	72
48	(b,ab,e,())	6	97	(e,b^2,a,(1,3))	18
49	(b^2,ab^2,e,())	6	98	(e,b,a,(1,3))	18

$A = e^{2\pi i/3}$, $B = 3A^2$, $C = -2A^2$, $D = 6A$, $E = -3A-2A^2$, $F = -2A+A^2$, $G = -A-3A^2$, $H = -2A-A^2$, $I = -A+A^2$, $J = 4A^2$, $K = -4A-2A^2$ and $L = 2A-2A^2$. And /X stand for the complex conjugate of X.

Conclusion

We have developed the group theory and character table of the non-rigid 1,3,5-trimethyl-2,4,6-trinitrobenzene (TNM) for the first time as a wreath product group $(C_2 \times C_3)\sim S_3$ and it consists of 1296 operations divided into 98 conjugacy classes and irreducible representations. The derived character tables would also be valuable in other applications such as in the context of chemical applications of graph theory[39] and aromatic compounds[40]. 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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