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Non-Rigid Group of *Tris*[(3-Methyl thioazin)benzen]

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The non-rigid molecule group theory in which the dynamical symmetry operations are defined as physical operations is applied to deduce the character table of the full non-rigid molecule group (f-NRG) of *tris*[(3-methyl thioazin)-benzen]. The f-NRG of the Euclidean graph of this molecule are seen to be of order 81. Using GAP SYSTEM, we find the complex character table of these groups.

Key Words: *Tris*[(3-methyl thioazin)benzen], Non-rigid group.

INTRODUCTION

A molecule is said to be non-rigid if there are several local minima on the potential-energy surface easily surmountable by the molecular system *via* a tunnelling rearrangement. A non-rigid molecule typically possesses several potential valleys separated by relatively low energy barriers and thus exhibits large amplitude tunnelling dynamics among various potential minima. Because of this deformability, the non-rigid molecules exhibit some interesting properties of intermolecular dynamics, spectroscopy, dynamical NMR and so all of which can be interpreted resorting to group theory[1-4].

Group theory is one of the most powerful mathematical tools in quantum chemistry and spectroscopy. It can predict, interpret and simplify complex 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[5,6].

The molecular symmetry group of a non-rigid molecule was first defined by Longuet-Higgins[7]. Although there have been earlier works that suggested the need for such a framework by Hougen[8]. Bunker and Papoušek[9] extended the definition of the molecular symmetry group to linear molecules using an extended molecular symmetry. The operations of the molecular

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symmetry group and the three-dimensional rotation group are used together to treat the symmetry properties of molecules in electromagnetic fields by Watson[10].

Following Smeyers[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 intermolecular motion operations that describe molecular moieties moving with respect to the rest of the molecule. Together these operations form a group, which is called the full non-rigid molecule group (f-NRG).

The present study investigates the f-NRG of *tris*[(3-methyl thioazin)-benzen] (TMTB) (Fig. 1). We prove that this group is of order 81 and has 17 conjugacy classes and irreducible representations. The character table of this group is derived with the aid of GAP[12], a group theory package and this was done by characterizing the algebraic structure of f-NRG as the wreath product of known groups.

Calculating the f-NRGs using wreath product formalism was first introduced by Balasubramanian[13-23]. Some of the previous approaches has been applied to some molecules in the references[24-29]. The notation used is standard and the reader may consult references[30-32].

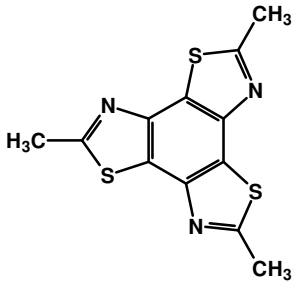

Fig. 1. Geometry of *tris*[(3-methyl thioazin)-benzen] (TMTB) molecule

RESULTS AND DISCUSSION

In this section, we first describe some notation which will be kept throughout. 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). Also, for a group G and a subset A of G, <A> is the subgroup of G generated by A.

Let H be a permutation group on X, a subgroup of SX and let G be a group. The set of all mappings $X \to G$ is denoted by G^X, *i.e.* $G^X = \{f \mid f: X \to G\}$. It is clear that $|G^X| = |G|^{|X|}$. We put $G\sim H = G^X \times H = \{(f; \pi) \mid f \in G^X, \pi \in H\}$. For $f \in G^X$ and $\pi \in H$, we define $f\pi \in G^X$ by $f\pi = fo\pi^{-1}$, where "o" denotes the composition of functions. It is easy to check that the composition: $(f; \pi)(f'; \pi') = (ff'\pi; \pi\pi')$, makes G~H into a group. This group is called the wreath product of G by H.

We now consider the non-rigid group G of TMTB molecule (Fig. 1). This group is computed using wreath product formalism. Before going into the details of the computations, we considered the speed of rotations of methyl groups sufficiently high so that the mean time dynamical symmetry of the molecules makes sense. In order to characterize the NRG of TMTB, we first note that each dynamic symmetry operation of TMTB, considering the rotations of CH_3 groups, is composed of two sequential physical operations. We first have a physical symmetry of the framework (as we have to map the CH_3 groups on CH_3 groups which are on vertices of the framework). Such operations form the group H of order 3, which as is well known, is isomorphic to the cyclic group C_3. After accomplishing the first framework symmetry operation we have to map each of the three CH_3 group on itself which forms the three elements group C_3. The number of all such operations is $3^3 \times 3 = 81$.

Let's use numbers {1,2,3} to indicate the central nitrogen atoms. Then H = {(), (1,2,3), (1,3,2)} is the symmetry group of rigid framework and the NRG group of TMTB is of the form G = C_3~H, which is a group of order 81. It is shown by Balasubramanian[7] that the conjugacy classes of such a group 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, Tables 1 and 2. To do this we need only the following simple program:

TABLE-1
REPRESENTATIVES OF THE G-CONJUGACY CLASSES AND THEIR LENGTHS

No	Representatives	# Conjugacy Class
1	(e,e,e,())	1
2	(e,e,e,(1,2,3))	9
3	(e,e,e,(1,3,2))	9
4	(e,e,f,())	3
5	(e,e,f,(1,2,3))	9
6	(e,e,f,(1,3,2))	9
7	(e,e,f^2,())	3
8	(e,e,f^2,(1,2,3))	9
9	(e,e,f^2,(1,3,2))	9
10	(e,f,f,())	3
11	(e,f,f^2,())	3
12	(e,f^2,f,())	3
13	(e,f^2,f^2,())	3
14	(f,f,f,())	1
15	(f,f,f^2,())	3
16	(f,f^2,f^2,())	3
17	(f^2,f^2,f^2,())	1

TABLE-2
CHARACTER TABLE OF THE GROUP G

		1a	3a	3b	3c	9a	9b	3d	9c	9d	3e	3f	3g	3h	3i	3j	3k	3l
	2P	1a	3b	3a	3d	9d	9c	3c	9b	9a	3h	3g	3f	3e	3l	3k	3j	3i
	3P	1a	1a	1a	1a	3i	3i	1a	3l	3l	1a	1a	1a	1a	1a	1a	1a	1a
	5P	1a	3b	3a	3d	9d	9c	3c	9b	9a	3h	3g	3f	3e	3l	3k	3j	3i
	7P	1a	3a	3b	3c	9a	9b	3d	9c	9d	3e	3f	3g	3h	3i	3j	3k	3l
χ_1		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
χ_2		1	1	1	A	A	A	W	W	W	W	1	1	A	1	A	W	1
χ_3		1	1	1	W	W	W	A	A	A	A	1	1	W	1	W	A	1
χ_4		1	A	W	1	A	W	1	A	W	1	1	1	1	1	1	1	1
χ_5		1	W	A	1	W	A	1	W	A	1	1	1	1	1	1	1	1
χ_6		1	A	W	A	W	1	W	1	A	W	1	1	A	1	A	W	1
χ_7		1	W	A	W	A	1	A	1	W	A	1	1	W	1	W	A	1
χ_8		1	A	W	W	1	A	A	W	1	A	1	1	W	1	W	A	1
χ_9		1	W	A	A	1	W	W	A	1	W	1	1	A	1	A	W	1
χ_{10}		3	0	0	0	0	0	0	0	0	0	D	Z	0	3	0	0	3
χ_{11}		3	0	0	0	0	0	0	0	0	0	Z	D	0	3	0	0	3
χ_{12}		3	0	0	B	0	0	X	0	0	-C	-C	0	C	D	-X	-B	Z
χ_{13}		3	0	0	X	0	0	B	0	0	C	0	0	–C	Z	-B	-X	D
χ_{14}		3	0	0	C	0	0	-C	0	0	-B	0	0	-X	D	B	X	Z
χ_{15}		3	0	0	-C	0	0	C	0	0	-X	0	0	–B	Z	X	B	D
χ_{16}		3	0	0	-X	0	0	-B	0	0	X	0	0	B	D	C	-C	Z
χ_{17}		3	0	0	-B	0	0	-X	0	0	B	0	0	X	Z	-C	C	D

In this table, $A = e^{4\pi i/3}$, $B = A + 2$, $C = -1 - 2A = i\sqrt{3}$, $D = 3A$, $W = \overline{A}$, $X = \overline{B}$ and $Z = \overline{D}$

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H := Group((1,2,3));
A:= CyclicGroup(3);
G:= WreathProduct(H,A);
T:= CharacterTable(G);
ConjugacyClasses(T);
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Concluding remarks: The small group library of GAP contains the structure and character table of all groups with order ≤ 2000 except from 1024, groups of order 5^5, 7^4 and groups of orders p^2q and pqr, where p, q and r are primes. Thus GAP is very useful for research and also education in chemistry.

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