The Molecular Symmetry Group Theory for Trimethylamine-BH$_3$ Addend (BH$_3$ Free of Rotation)

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Abstract. A simple method is described, for calculation of character table for the symmetry group of molecules consisting of a number XH$_3$ groups attached to a rigid framework. For the full non-rigid group (f-NRG) of the trimethylamine-BH$_3$ addend (BH$_3$ free of rotation), with C_{3v} symmetry we prove that it is a group of order 648 with 14 conjugacy classes. The character tables of this group are calculated.

1 Introduction

The non-rigid molecule group theory (NRG) in which the dynamical symmetry operations are defined as physical operations is a new field of chemistry. Some authors in a series of papers applied this notation to determine the character table of restricted NRG of some molecules [1-7].

A molecule undergoing such large amplitude movements, between various possible configurations, is known as a non-rigid molecule. 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 [2; p.5].

The complete set of molecular conversion operations will contain overall rotation operations, describing the molecule rotating as a whole, and intramolecular motion operations, describing molecular moieties moving with

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respect to the rest of the molecule. Such a set forms a group, which we call the full non-rigid group (f-NRG).

Group theory for non-rigid molecules is becoming more and more relevant, and numerous application to large amplitude vibrational spectroscopy of small organic molecules are appearing in the literature [8-16].

In [17] Longuet-Higgins investigated the symmetry groups of non-rigid molecules, where changes from one conformation to another can occur easily. 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. It is therefore of some interest and importance to develop simple methods of calculating these character tables, which are needed for classification of wave functions, of selection rules, etc. [18,19].

The method as described here is appropriate for molecules which consist of a number XH_3 groups attached to a rigid framework. An example of such a molecule is the trimethylamine-BH_3 addend (BH_3 free of rotation) which is considered here in some detail. The method is not appropriate in the case where the framework is linear, as in ethane. However, Bunker [20] has shown how to deal with such molecules. In computing the character table of this molecule, we use [21,22], for the standard notation and terminology on character theory.

Lomont [23] has given two method for calculating character tables. These are a satisfactory for small group, but both of them require knowledge of the class structure and hence of the group multiplication table. These become inaccessible as soon as the order of the group becomes even moderately large. For a non-rigid molecule whose symmetry group may has several thousands of elements, they are usually quite impracticable.

The alternative approach is less mechanical and is simpler in practice. It involves two steps: decomposition of the group into classes, and determination of sets of basis functions for certain representations whose characters are then determined.

2   Theory

Throughout the present paper, the concepts of direct and semi-direct products will be used. For this purpose, let us consider two groups, I and G, which have no element in common except for the identity. If I and G are such that any element I_s commutes with any element G_r :

$$I_s G_r = G_r I_s$$

their product forms a group S which is the direct product of I and G :

$$I \times G = S$$

On the other hand, if I and G do not commute in detail but rather:

$$IG_r = G_r I$$

for all $G_r \in G$, then the group forms a set which is called the semi-direct product of I and G , and is expressed as:

$$I \wedge G = S$$

where the invariant subgroup I with respect to G is written on left side [2; p.15].

Trimethylamine-BH$_3$ addend (BH$_3$ free of rotation) occurs in its preferred conformation with three equivalent methyl groups in "staggered" configuration (see figure 1) [24].
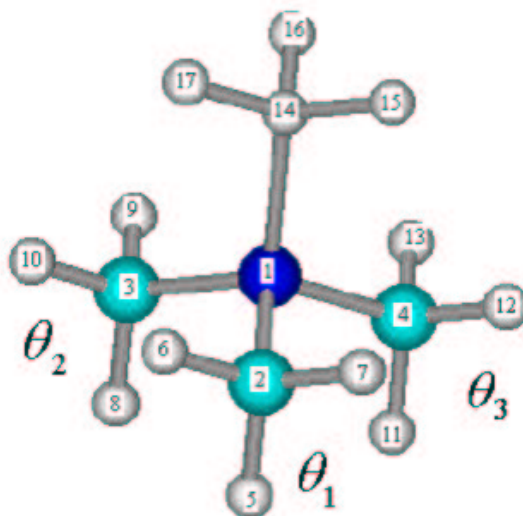
At first glance, the trimethylamine-BH$_3$ addend (BH$_3$ free of rotation) presents a type of large amplitude internal motion: the three rotations of the methyl groups. The variables which describe the three methyl rotations are the $\theta_1, \theta_2, \theta_3$, the three rotation axes being the N-CH$_3$ bonds.

The existence of the three equivalent methyl groups implies the existence of 27 isoenergetic conformations, described by three equivalent non-rigid subgroups. Notice that even when the methyl groups are distorted because of

environmental effects, the symmetry has to be respected since the hydrogen atoms are indistinguishable [25]:

$$C_{3_1}{}^I = [\hat{E} + \hat{C_{3_1}} + \hat{C_{3_1}}^2],$$
$$C_{3_2}{}^I = [\hat{E} + \hat{C_{3_2}} + \hat{C_{3_2}}^2],$$
$$C_{3_3}{}^I = [\hat{E} + \hat{C_{3_3}} + \hat{C_{3_3}}^2] \tag{1}$$

The direct product of these three subgroups contain 27 dynamical symmetry operations:

$$G_{27} = C_{3_1}{}^I \times C_{3_2}{}^I \times C_{3_3}{}^I \tag{2}$$

which describe 27 potential energy wells on the potential energy hypersurface.

In order to establish the remaining transformation operations let us consider the trimethylamine-BH3 addend (BH_3 free of rotation) in an arbitrary conformation in which $\theta_1 \neq \theta_2 \neq \theta_3$. Since the three equatorial methyl-groups are equivalent, the rotation angles may be interchanged by a 3-fold rotation without any energy variation,

$$\hat{W} f(\theta_1, \theta_2, \theta_3) \equiv f(\theta_3, \theta_1, \theta_2),$$
$$\hat{W}^2 f(\theta_1, \theta_2, \theta_3) \equiv f(\theta_2, \theta_3, \theta_1) \tag{3}$$

or by binary exchange (reflection) which induces an inversion of the rotation sense:

$$\hat{V} f(\theta_1, \theta_2, \theta_3) \equiv f(\theta_1, \theta_3, \theta_2) \tag{4}$$
$$\hat{U} f(\theta_1, \theta_2, \theta_3) \equiv f(\theta_2, \theta_1, \theta_3) \tag{5}$$
$$\hat{T} f(\theta_1, \theta_2, \theta_3) \equiv f(\theta_3, \theta_2, \theta_1) \tag{6}$$

$$W^I = [\hat{E} + \hat{W} + \hat{W}^2],$$
$$V^I = [\hat{E} + \hat{V}],$$
$$U^I = [\hat{E} + \hat{U}],$$
$$T^I = [\hat{E} + \hat{T}] \tag{7}$$

The semidirect product of these four subgroups forms another subgroup isomorphic with the C_{3v} symmetry point group:

$$G_{24} = [W^I \wedge V^I \wedge U^I \wedge T^I] \sim C_{3v} \tag{8}$$

which is the symmetry group of the trimethylamine-BH_3 addend (BH_3 free of rotation), skeleton with unstructured methyl groups.

As a result, the complete f-NRG of the trimethylamine-BH_3 addend (BH_3 free of rotation) may be written as

$$G_{648} = [W^I \wedge V^I \wedge U^I \wedge T^I] \wedge [C_{3_1}{}^I \times C_{3_2}{}^I \times C_{3_3}{}^I] \tag{9}$$

which is group of order 648.

3   Determination of classes and character table

We consider the point group of the trimethylamine-BH$_3$ addend (BH$_3$ free of rotation) in the case of a rigid framework. We consider the full non-rigid group G (f-NRG) of this molecule each equilibrium conformation of which has an ordinary point-group symmetry C_{3v} .

Since G is a permutation group, every two elements of this group with different cycle structure belong to different conjugacy classes. Using figure 1, we give the cycle structure of the representatives of the conjugacy classes of G , in Table 1. cc: stands for conjugacy classes,n is their number, and a permutation $\frac{(r_1,...,r_a)...(l_1,...l_a)}{b-number}$ $\frac{(t_1,...t_c)...(s_1,...s_c)}{d-number}$ is denoted by $a^b.c^d$ for $a, b, c, d \in N$

Table 1

cc	1	3^3	3	3^2	2.3	2.3^2	3^4	$3^2.9$	$2^3.4$	$2^3.3.4$	2^5	$2^3.6$
n	1	1	1	1	1	1	2	1	1	2	1	1

We need generators of G. For this purpose, we doing the following procedure:

Let us first consider the operations which leave the framework of the molecule unchanged. In this case, each methyl group can be left alone or rotated through 120° in either direction which commute with another equivalent methyl group;

We first obtain the following permutations:

a, b, c : The permutations obtained from the above rule (a obtained when the methyl group left alone, and b obtained when the methyl group rotated through 120° in left direction and c obtained when the methyl group rotated through 120° in right direction) when the symmetric element C_3 passes through the atoms: 1, 14.

d, e : The permutations obtained from the above rule (d obtained when the methyl group left alone and e obtained when the methyl group rotated through 120° in either direction) when the symmetric element σ_v passes through the atoms: 1, 4, 11, 14,15.

f, h : The permutations obtained from the above rule(f obtained when the methyl group left alone and h obtained when the methyl group rotated through 120° in either direction) when the symmetric element σ_v passes through the atoms: 1, 2, 5, 14, 16.

k, l : The permutations obtained from the above rule (k obtained when the methyl group left alone and l obtained when the methyl group rotated through 120° in either direction) when the symmetric element σ_v passes through the atoms: 1, 3, 8, 14, 17.

Therefore, we can write these relations as follows:

$$a:=(2,3,4)(5,8,11)(6,9,12)(7,10,13)(15,16,17);$$
$$b:=(2,3,4)(5,9,13,7,8,12,6,10,11)(15,16,17);$$
$$c:=(2,3,4)(5,10,12,6,8,13,7,9,11)(15,16,17);$$
$$d:=(2,3)(7,9)(5,10)(6,8)(12,13)(16,17);$$
$$e:=(2,3)(7,9,5,10,6,8)(12,13)(16,17);$$
$$f:=(3,4)(9,13)(10,12)(8,11)(6,7)(15,17);$$
$$h:=(3,4)(9,13,10,12,8,11)(6,7)(15,17);$$
$$k:=(2,4)(6,13)(5,12)(7,11)(9,10)(15,16);$$
$$l:=(2,4)(6,13,5,12,7,11)(9,10)(15,16);$$

By using the program of GAP [26] we can see that the permutation a, b, c, d, e, f, h, k, l are generators of G (any permutation in G can be written as a product of some a, b, c, d, e, f, h, k, l) . That is, $G =<a, b, c, d, e, f, h, k, l>$. Hence G is a group of order 648 and has 14 conjugacy classes which are listed in Table 2.

Table 2: The Representatives of conjugacy classes
of the Group G

No.	Representation	Size
1	*identity*	1
2	(5,6,7)(8,9,10)(11,12,13)	8
3	(11,12,13)	6
4	(5,7,6)(8,10,9)	12
5	(6,7)(12,13)	27
6	(5,6)(8,9,10)(11,12)	54
7	(2,3,4)(5,8,11)(6,9,12)(7,10,13)(15,16,17)	72
8	(2,3,4)(5,8,12,6,9,13,7,10,11)(15,16,17)	72
9	(2,3,4)(5,8,13,7,10,12,6,9,11)(15,16,17)	72
10	(3,4)(8,13,10,12)(9,11)(15,17)	54
11	(3,4)(5,6,7)(8,11,10,13)(9,12)(15,17)	54
12	(3,4)(5,7,6)(8,12,10,11)(9,13)(15,17)	54
13	(3,4)(6,7)(8,12)(9,11)(10,13)(15,17)	54
14	(3,4)(6,7)(8,13,10,11,9,12)(15,17)	108

We now calculate the character table of G by the following details in the environment of GAP:

```
gap>  G = < a, b, c, d, e, f, h, k, l >;
gap>  cc:= ConjugacyClasse(G);
gap>  n:=List(cc,x->Size(x));
gap>  tb:=CharacterTable(G);
gap>  Display(tb);
```

The character table of G is listed in Table 3;

Table 3: Character Table of G
$$A = \sqrt{3}$$

	1a	3a	3b	3c	2a	6a	3d	9a	9b	4a	12a	12b	2b	6b
χ_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
χ_2	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1
χ_3	2	2	2	2	2	2	-1	-1	-1	0	0	0	0	0
χ_4	3	3	3	3	-1	-1	0	0	0	1	1	1	-1	-1
χ_5	3	3	3	3	-1	-1	0	0	0	-1	-1	-1	1	1
χ_6	6	-3	3	0	2	-1	0	0	0	2	-1	-1	0	0
χ_7	6	-3	3	0	2	-1	0	0	0	-2	1	1	0	0
χ_8	6	-3	3	0	-2	1	0	0	0	0	A	-A	0	0
χ_9	6	-3	3	0	-2	1	0	0	0	0	-A	A	0	0
χ_{10}	8	-1	-4	2	0	0	2	-1	-1	0	0	0	0	0
χ_{11}	8	-1	-4	2	0	0	-1	-1	2	0	0	0	0	0
χ_{12}	8	-1	-4	2	0	0	-1	2	-1	0	0	0	0	0
χ_{13}	12	3	0	-3	0	0	0	0	0	0	0	0	-2	1
χ_{14}	12	3	0	-3	0	0	0	0	0	0	0	0	2	-1

4 Conclusions

The present character table for trimethylamine-BH_3 addend (BH_3 free of rotation) has been deduced from:

    − the structure of group:

$$G_{648} = [W^I \wedge V^I \wedge U^I \wedge T^I] \wedge [C_{3_1}{}^I \times C_{3_2}{}^I \times C_{3_3}{}^I]$$

    − the division of group in 14 classes, the sum of the square of the dimensions of which gives the order of the group:

$$2 \times (1)^2 + 1 \times (2)^2 + 2 \times (3)^2 + 4 \times (6)^2 + 3 \times (8)^2 + 2 \times (12)^2 = 648$$

    − the composition of the 14 classes in; 1, 8, 6, 12, 27, 54, 72, 72, 72, 54, 54, 54, 54 and 108 elements. The potential energy function for rotation five methyl groups will be described by a 27-fold well potential energy hypersurface. As a result, the spectrum of the trimethylamine-BH_3 addend (BH_3 Free of Rotation), is expected to prossess 27 substates.

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