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The Full Non-Rigid Group Theory for *cis*- and *trans*-Dichlorodiammine Platinum(II) and Trimethylamine

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The non-rigid molecule group theory (NRG), in which the dynamical symmetry operations are defined as physical operations, is a new field of chemistry. In a series of papers Smeyers applied this notion to determine the character table of restricted NRG (r-NRG) of some molecules. For example, Smeyers and Villa computed the r-NRG of the triple equivalent methyl rotation in pyramidal trimethylamine with inversion and proved that the r-NRG of this molecule is a group of order 648, containing two subgroups of order 324 without inversions (see *J. Math. Chem.* **28** (2000) 377–388). In this work, a simple method is described, by means of which it is possible to calculate character tables for the symmetry group of molecules consisting of a number of AH_3 groups attached to a rigid framework. We have studied the full non-rigid group (f-NRG) of *cis*- and *trans*-dichlorodiammine platinum(II) and trimethylamine and we have proven that they are groups of orders 36, 72 and 1296 with 9, 18 and 28 conjugacy classes, respectively. This shows that the full non-rigid group and the restricted non-rigid group of these molecules are not isomorphic. The method can be generalized to apply to other non-rigid molecules. The f-NRG molecule group theory is shown to be used advantageously to study the internal dynamics of such molecules.

Key words
character table
full non-rigid group
cis-dichlorodiammine platinum(II)
trans-dichlorodiammine platinum(II)
trimethylamine

INTRODUCTION

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] As it is well known, group theory for non-rigid molecules was essentially developed for two points of view:

i) The molecular symmetry group theory (MSG) of permutation inversion groups (PI) constructed by permutations and permutation-inversions of identical particles. The MSG group is then formed by all feasible permutations and permutation-inversions.[9,10]

In Ref. 9, 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, determination of selection rules, and so on.

Lomont[11] has proposed two methods for calculating character tables. These are satisfactory for small groups,

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but both of them require knowledge of the class structure and hence of the group multiplication table and they become very unwieldy as soon as the order of the group becomes even moderately large. They are usually quite impracticable for non-rigid molecules, whose symmetry groups may have several thousands of elements.

The alternative approach is less mechanical, requiring a certain amount of thought, but it is nevertheless simpler in practice. This involves two steps: first, the decomposition of the group into classes, and second, the determination of sets of basis functions for certain representations, whose characters are then determined directly.

In Ref. 12, Stone described a method appropriate for molecules with a number of XH_3 groups attached to a rigid framework. It is not appropriate in cases where the framework is linear, as it is in ethane and dimethylacetylene.

ii) The full and restricted non-rigid group theory (f- or r-NRG) built up with physical operations, expressed in terms of internal coordinates that transform one conformation into another iso-energetic one. The r-NRG is then formed by the complete set of physical operations which commute with the given restricted or Hamiltonian operators.[13,14]

In Ref. 15, Smeyers and Villa investigated the r-NRG of planer trimethylamine and proved that this is a group of order 324. Furthermore, they showed that this molecule has a pyramidal inversion and so the order of r-NRG of trimethylamine is 648.

The motivation for this study is outlined in Refs. 7, 8, 16, 17 and the reader is encouraged to consult these papers for background material as well as basic computational techniques.

In this paper, we investigate the f-NRG of *cis*-dichlorodiammine platinum(II), *trans*-dichlorodiammine platinum(II) and pyramidal trimethylamine. We prove that these are groups of orders 36, 72 and 1296, respectively.

We now recall some algebraic definitions that will be used in the paper. Suppose that T is a group and *x, y* are elements of T. The commutator element $[x, y]$ is defined by $x^{-1}y^{-1}xy$ and the subgroup of T generated by its commutators is called the commutator subgroup of T. This subgroup is denoted by D(T). According to the well-known fact in group theory, the number of linear characters of a finite group T is the order of factor group T modulus its derived subgroups, *i.e.,* D(T).[18]

Let T be a finite group and let N be a normal subgroup of T. If $|N| > 1$, then the factor group T/N is smaller than T. The characters of T/N should therefore be easier to find than the characters of T. In fact, we can use the characters of T/N to get some of the characters of T, by a process which is known as lifting. Thus, normal subgroups help us to find characters of T. To see this, we assume that χ is a character of T/N. Define the map ϕ: T$\rightarrow$C, C is the field of complex numbers, by $\phi(g) = \chi(g\mathrm{N})$, for $g \in$T. Then χ is a character of T and χ and ϕ have the same degree. The character ϕ of T is called the lift of χ to T. It is well known that χ is irreducible if and only if ϕ is irreducible (Ref. 19, p. 168).

Suppose that χ and ϕ are characters of group T. The inner product of these characters is denoted by (χ,ϕ) and defined by $(\chi,\phi) = |T|^{-1} \Sigma_{g\in T} \chi(g)\phi(g^{-1})$. If $\chi = \phi$, the inner product (χ,χ) is denoted by $\|\chi\|$.

Finally, for every element x of group T, the subgroup $C_T(x) = \{y \in T \mid xy = yx\}$ is called the centralizer of x in T. If T is finite, then by the well-known theorem in group theory $|C_T(x)| = |T| / |Cl_T(x)|$, in which $Cl_T(x)$ is the conjugacy class of x in T.[18,19] Also, $|C_T(x)|$ and $|Cl_T(x)|$ are called the centralizer order and conjugacy length of x in group T, respectively. To simplify our argument, we denote by *na*, *nb*, *nc* … the different conjugacy classes of the elements of order n in group T. The conjugacy vector of T is a vector of size k, k is the number of conjugacy classes of T, such that every array of this vector is a conjugacy length for T. Similarly, we can define the centralizer vector of T.

Throughout this paper, all groups considered are assumed to be finite. We denote a cyclic group of order n by Z_n and a symmetric group on n symbols by S_n. Also, Z(G) denotes the center of group G and for a prime p, a group of type $Z_p \times ... \times Z_p$ is called elementary abelian. Other notations are standard and taken mainly from Refs. 14, 18 and 19.

EXPERIMENTAL

First of all, we consider the point group of each molecule in the rigid state. The point groups of *cis*- and *trans*-dichlorodiammine platinum(II) are C_{2v} and the point group of pyramidal trimethylamine is C_{3v}. The process of enumerating the symmetry operations of these molecules and arranging them in classes entails the adoption of a numbering convention for the central atom of the molecule, central atom of every XH_3 group, and the other atoms, such as proton nuclei, as shown in Figure 1.

We define the operation $\alpha = (6,7,8)$, $\beta = (9,10,11)$, for *cis*- and *trans*-dichlorodiammine platinum(II), and $\alpha' = (5, 6,7)$, $\beta' = (8,9,10)$, $\gamma' = (11,12,13)$ for trimethylamine, which are rotations, in a positive sense, of each XH_3 group. We assume that all of these operations are feasible.

Let us first consider operations that leave the framework of the molecule unchanged. These operations are grouped according to their cycle structure; operations which rotate different numbers of XH_3 groups must belong to different conjugacy classes. If we now consider the operations that rotate one XH_3 group, we can see that they must all belong to the same class, since operations involving rotation of the molecular framework will transform α into α^{-1} or β^{-1} (or γ'^{-1} for trimethylamine), changing the sense of the rotation.

For a small group, the classes are conveniently found by conjugating a particular element with all other elements. The resulting set then forms one class, and repetition of this

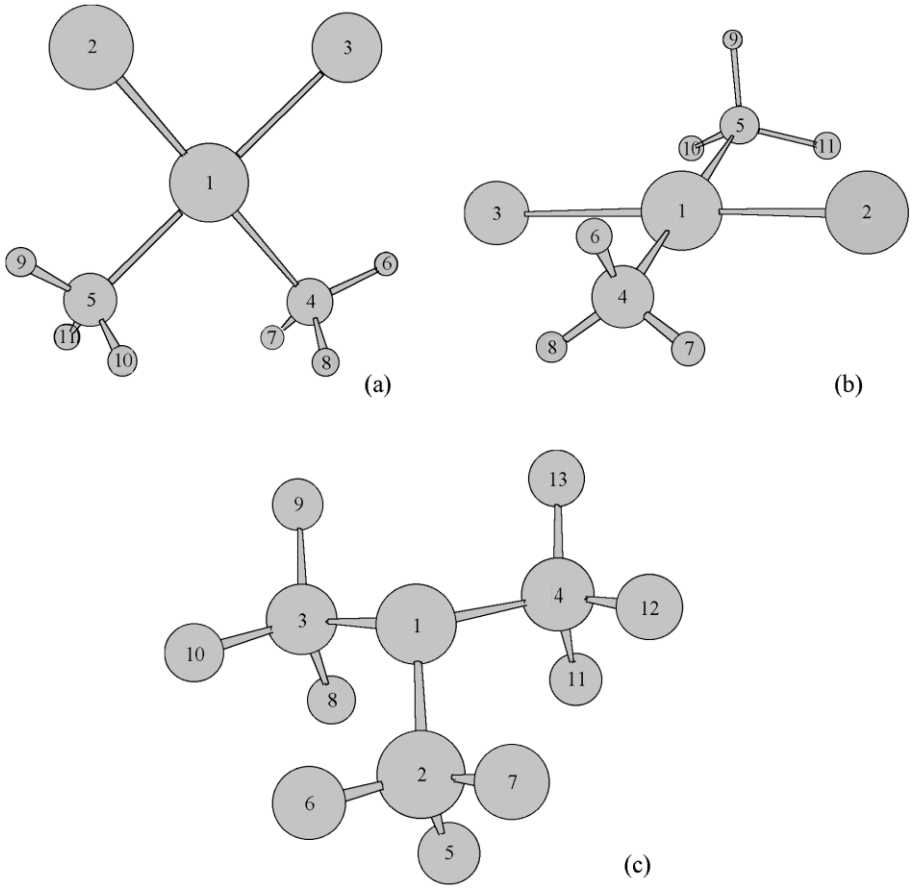

Figure 1. The structure of molecules: (a) *cis*-Dichlorodiammine platinum(II); (b) *trans*-Dichlorodiammine platinum(II); (c) Trimethylamine.

process eventually gives all the classes. This becomes impracticable for large groups. However, it is simpler to find the classes by inspection; they can be rigorously checked at a later stage.

RESULTS AND DISCUSSION

In this section, we investigate the conjugacy classes of each molecule introduced in the previous section separately. Then, we compute the whole irreducible character table for them.

Conjugacy Classes of cis-*Dichlorodiammine Platinum(II)*

Let us first consider operations that leave the framework of the molecule unchanged. Each XH_3 group can be left alone or rotated by 180° in either direction, so that there are $3^2 = 9$ such operations. These elements make four classes, the class numbers 1, 2, 4 and 5 of Table I. In this table, we calculate a representative for each class of the group. We continue our argument for finding conjugacy classes of H. First, we grouped the operations according to their cycle structures. The operations that rotate different numbers of XH_3 groups must belong to different conjugacy classes. We now consider the four operations that rotate one XH_3 group; it is easy to see that they must all belong to the same class, since operations involving rotation of the molecular framework will transform α into α^{-1}, or β^{-1}, changing the sense of the rotation. All operations that rotate two XH_3 groups constitute two conjugacy classes of the group.

TABLE I. Representatives of conjugacy classes of the full non-rigid group of *cis*-dichlorodiammine platinum(II)

No.	Representatives	Size	No.	Representatives	Size
1	()	1	6	(2,3)(4,5)(6,9)(7,10)(8,11)	3
2	(6,7,8)	4	7	(2,3)(4,5)(6,9,7,10,8,11)	6
3	(7,8)(10,11)	9	8	(2,3)(4,5)(6,9)(7,11)(8,10)	3
4	(6,7,8)(9,10,11)	2	9	(2,3)(4,5)(6,9,7,11,8,10)	6
5	(6,7,8)(9,11,10)	2			

Consider next the operations that permute the nuclei of the framework; these fall into sets corresponding to the classes of C_{2v}. It is clear that the point group C_{2v} has exactly two different types of non-identity elements of the group (C_2 and σ_v).

The unique C_2 operation of C_{2v} applied to the framework is the permutation (2,3)(4,5), but this is not feasible for the molecule as the whole, and the protons have to be permuted as well. Our main argument will consider two cases:

CASE 1. The protons of each XH_3 group do not rotate.

First, we suppose that

$$R_1 = (2,3)(4,5)(6,9)(7,11)(8,10).$$

But in this case, all of the permutations of cycle type $1^1 2^5$ are conjugate in the group. Thus, we obtain a conjugacy class of length 3.

CASE 2. The protons of each XH_3 group rotate.

In this case, we assume that:

$$R_2 = (2,3)(4,5)(6,9,7,10,8,11),$$

$$R_3 = (2,3)(4,5)(6,9,7,11,8,10).$$

Using a tedious calculation we can see that R_2 and R_3 are not conjugate in the group, but every permutation of this type is conjugate with R_2 or R_3. Hence, we obtain two more conjugacy classes of length 6.

Similar methods are applied to other operations of the point group (σ_v) to derive other sets of conjugacy classes of this molecule. If we define

$$\sigma_{v1} = (7,8)(10,11),$$

$$\sigma_{v2} = (2,3)(4,5)(6,9)(7,10)(8,11).$$

Then we obtain two conjugacy classes of lengths 9 and 3 with the representatives' σ_{v1} and σ_{v2}, respectively. Using similar arguments, we can calculate all 9 conjugacy classes of group H. In Table I, we give a representative for each conjugacy class of H.

The Character Table of cis-*Dichlorodiammine Platinum(II)*

From the conjugacy classes of group H, we can see that H is a group of order 36. First of all, we collect conjugacy class labels and the corresponding centralizer orders in two vectors:

$$\boldsymbol{A} = (1a,3a,2a,3b,3c,2b,6a,2c,6b),$$

$$\boldsymbol{B} = (36,9,4,18,18,12,6,12,6).$$

Since $H/D(H) \cong Z_2 \times Z_2$, where D(H) is the derived subgroup of H and $Z_2 \times Z_2$ is an elementary abelian group of order 4, we can obtain four linear characters of H, which are irreducible. We denote these irreducible characters by χ_1, χ_2, χ_3, and χ_4. We now assume that T_1 and T_2 are subgroups of H generated by classes 5 and 6 for T_1, and by classes 4 and 8 for T_2 of Table I.

$$T_1 = \langle (6,7,8)(9,11,10),(2,3)(4,5)(6,9)(7,10)(8,11) \rangle,$$

$$T_2 = \langle (6,7,8)(9,10,11),(2,3)(4,5)(6,9)(7,11)(8,10) \rangle.$$

TABLE II. The character table of group H and its power map

		1*a*	3*a*	2*a*	3*b*	3*c*	2*b*	6*a*	2*c*	6*b*
	2P	1*a*	3*a*	1*a*	3*b*	3*c*	1*a*	3*b*	1*a*	3*c*
	3P	1*a*	1*a*	2*a*	1*a*	1*a*	2*b*	2*b*	2*c*	2*c*
	5P	1*a*	3*a*	2*a*	3*b*	3*c*	2*b*	6*a*	2*c*	6*b*
χ_1		1	1	1	1	1	1	1	1	1
χ_2		1	1	1	1	1	–1	–1	–1	–1
χ_3		1	1	–1	1	1	–1	–1	1	1
χ_4		1	1	–1	1	1	1	1	–1	–1
χ_5		2	–1	0	2	–1	0	0	2	–1
χ_6		2	–1	0	2	–1	0	0	–2	1
χ_7		2	–1	0	–1	2	–2	1	0	0
χ_8		2	–1	0	–1	2	2	–1	0	0
χ_9		4	1	0	–2	2	0	0	0	0

Since these subgroups are the union of conjugacy classes of H, they are normal in H. The factor groups of H modulus T_1 and T_2 are not abelian: $H/T_1 \cong H/T_2 \cong S_3$, the symmetric group on three symbols. Now, we obtain two irreducible characters of degree 2 of H by lifting the irreducible characters of these factor groups. We denote these characters by χ_5 and χ_7, respectively.

$$\chi_5 = (2,-1,0,2,-1,0,0,2,-1),$$

$$\chi_7 = (2,-1,0,-1,2,-2,1,0,0).$$

We define $\chi_6 = \chi_5\chi_2$ and $\chi_8 = \chi_7\chi_3$. Finally, by using the orthogonality relations, we obtain an irreducible character of degree 4, which we denote by χ_9. This completes the character table of H (see Table II).

Conjugacy Classes of trans-*Dichlorodiammine Platinum(II)*

Our argument for computing the conjugacy classes and character table of *trans*-dichlorodiammine platinum(II) is similar to that for the *cis* form. We explain briefly our methods for this molecule.

First of all, we consider the operations that leave the framework of the molecule unchanged. Each XH_3 group can be left alone or rotated by 180° in either direction, so that there are $3^2 = 9$ such operations. These fall into four classes; the class numbers 1, 2, 4 and 5 of Table III, where we give a representative of each together with the number of elements in the class.

Consider next the operations that permute the nuclei of the framework. As before, we have two operations, C_2 and σ_v, for point group C_{2v}. The C_2 operation applied to the framework is the permutation (2,3)(4,5). We now consider permutations of protons, if the protons of each XH_3 group do not rotate. Suppose that

TABLE III. Representatives of conjugacy classes of the full non-rigid group of *trans*-dichlorodiammine platinum(II)

No.	Representatives	Size	No.	Representatives	Size
1	()	1	10	(2,3)	1
2	(6,7,8)	4	11	(2,3)(9,10,11)	4
3	(7,8)(10,11)	9	12	(2,3)(7,8)(10,11)	9
4	(6,7,8)(9,10,11)	2	13	(2,3)(6,7,8)(9,10,11)	2
5	(6,7,8)(9,11,10)	2	14	(2,3)(6,7,8)(9,11,10)	2
6	(4,5)(6,9)(7,10)(8,11)	3	15	(2,3)(4,5)(6,9)(7,10)(8,11)	3
7	(4,5)(6,9,7,10,8,11)	6	16	(2,3)(4,5)(6,9,7,10,8,11)	6
8	(4,5)(6,9)(7,11)(8,10)	3	17	(2,3)(4,5)(6,9)(7,11)(8,10)	3
9	(4,5)(6,9,7,11,8,10)	6	18	(2,3)(4,5)(6,9,7,11,8,10)	6

$$R'_1 = (2,3)(4,5)(6,9)(7,11)(8,10)\ .$$

But, all of the permutations of cycle type $1^1 2^5$ are conjugate in the group. Thus, we obtain a conjugacy class of length 3. Suppose the protons of each XH_3 group rotate and assume that:

$$R'_2 = (2,3)(4,5)(6,9,7,10,8,11),$$

$$R'_3 = (2,3)(4,5)(6,9,7,11,8,10).$$

We can see that R'_2 and R'_3 are not conjugate in the group, but every permutation of this type is conjugate with R'_2 or R'_3. Thus, we obtain two conjugacy classes of length 6.

We now consider the second operation of point group C_{2v} and define:

$$\sigma'_{v1} = (2,3)(7,8)(10,11),$$

$$\sigma'_{v2} = (4,5)(6,9)(7,10)(8,11),$$

$$\sigma'_{v3} = (4,5)(6,9,7,10,8,11).$$

Then we obtain three conjugacy classes of lengths 9, 3 and 6 with the representatives' σ'_{v1}, σ'_{v2} and σ'_{v3}, respectively. Using similar arguments, we can calculate all of the 18 conjugacy classes of group H'. In Table III, we give a representative for each conjugacy class of group H'.

The Character Table of trans*-Dichlorodiammine Platinum(II)*

From the conjugacy classes of group H', we can see that H' is a group of order 72. First of all, we list the conjugacy classes of H' and their corresponding centralizer orders in two vectors:

$$\boldsymbol{A} = (1a,3a,2a,3b,3c,2b,6a,2c,6b,2d,6c,2e,6d,6e,\ 2f,6f,2g,6g),$$

$$\boldsymbol{B} = (72,18,8,36,36,24,12,24,12,72,18,8,36,36,\ 24,12,24,12).$$

TABLE IV. The character table of group V

		1*a*	2*a*	3*a*	2*b*	3*b*	2*c*	6*a*	6*b*	3*c*
	2P	1*a*	1*a*	3*a*	1*a*	3*b*	1*a*	3*c*	3*b*	3*c*
	3P	1*a*	2*a*	1*a*	2*b*	1*a*	2*c*	2*b*	2*c*	1*a*
	5P	1*a*	2*a*	3*a*	2*b*	3*b*	2*c*	6*a*	6*b*	3*c*
χ_1		1	1	1	1	1	1	1	1	1
χ_2		1	1	1	–1	1	–1	–1	–1	1
χ_3		1	–1	1	1	1	–1	1	–1	1
χ_4		1	–1	1	–1	1	1	–1	1	1
χ_5		2	0	–1	0	–1	2	0	–1	2
χ_6		2	0	–1	0	–1	–2	0	1	2
χ_7		2	0	–1	–2	2	0	1	0	–1
χ_8		2	0	–1	2	2	0	–1	0	–1
χ_9		4	0	1	0	–2	0	0	0	–2

Since $H'/D(H') \cong Z_2 \times Z_2 \times Z_2$, where D(H') is the derived subgroup of H', we can obtain eight linear characters of H', which are irreducible. We denote these irreducible characters by χ_1, χ_2, ... χ_8. Next, we can see that H' has two normal subgroups T'_1 and T'_2 of order 12. The normal subgroup T'_1 is generated by classes 2, 5 and 15 in Table III. Also, classes 2, 4 and 16 of this table generate the normal subgroup T'_2. The factor groups of H' modulus T'_1 and T'_2 are not abelian: $H'/T'_1 \cong H'/T'_2 \cong S_3$. Now, we obtain two irreducible characters of H' of degree 2 by lifting irreducible characters of S_3. We denote these characters by χ_9 and χ_{13}.

$$\chi_9 = (2,–1,0,2,–1,0,0,–2,1,–2,1,0,–2,1,0,0,2,–1),$$

$$\chi_{13} = (2,–1,0,–1,2,–2,1,0,0,–2,1,0,1,–2,2,–1,0,0).$$

We calculate the Kronecker product of χ_9 and χ_{13} with eight linear irreducible characters of H' and obtain eight irreducible characters of degree 2. We denote these by χ_9, χ_{10}, ... χ_{16}. Consider the group $U = H'/Z(H')$. In Table IV, we compute the character table of U. Using this table and lifting its irreducible character of degree 4 to H', we obtain the irreducible character χ_{17} for H'. Finally, we can see that $\chi_{18} = \chi_2 \cdot \chi_{17}$ is an irreducible character of group H'. This completes the irreducible characters of H' (see Table V).

Conjugacy Classes of Trimethylamine

Suppose H'' is the full non-rigid group of trimethylamine without inversion and G'' is the f-NRG of this molecule. It is easy to see that G'' is isomorphic to $Z_2 \times H''$. We want to compute the conjugacy classes and the character table of H''. Since G'' is the direct product of two subgroups H'' and Z_2, it is well known that the classes and characters for G'' are just products of those for H'' and

TABLE V. The character table of group H' and its power map

		1*a*	3*a*	2*a*	3*b*	3*c*	2*b*	6*a*	2*c*	6*b*	2*d*	6*c*	2*e*	6*d*	6*e*	2*f*	6*f*	2*g*	6*g*
	2P	1*a*	3*a*	1*a*	3*b*	3*c*	1*a*	3*b*	1*a*	3*c*	1*a*	3*a*	1*a*	3*b*	3*b*	1*a*	3*b*	1*a*	3*c*
	3P	1*a*	1*a*	2*a*	1*a*	1*a*	2*b*	2*b*	2*c*	2*c*	2*d*	2*d*	2*e*	2*d*	2*d*	2*f*	2*f*	2*g*	2*g*
	5P	1*a*	3*a*	2*a*	3*b*	3*c*	2*b*	6*a*	2*c*	6*b*	2*d*	6*c*	2*e*	6*d*	6*e*	2*f*	6*f*	2*g*	6*g*
χ_1		1	1	1	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	–1	–1	–1	–1
χ_3		1	1	–1	1	1	–1	–1	1	1	1	1	–1	1	1	–1	–1	1	1
χ_4		1	1	–1	1	1	1	1	–1	–1	1	1	–1	1	1	1	1	–1	–1
χ_5		1	1	1	1	1	–1	–1	–1	–1	–1	–1	–1	–1	–1	1	1	1	1
χ_6		1	1	1	1	1	1	1	1	1	–1	–1	–1	–1	–1	–1	–1	–1	–1
χ_7		1	1	–1	1	1	1	1	–1	–1	–1	–1	1	–1	–1	–1	–1	1	1
χ_8		1	1	–1	1	1	–1	–1	1	1	–1	–1	1	–1	–1	1	1	–1	–1
χ_9		2	–1	0	2	–1	0	0	–2	1	–2	1	0	–2	1	0	0	2	–1
χ_{10}		2	–1	0	2	–1	0	0	–2	1	2	–1	0	2	–1	0	0	–2	1
χ_{11}		2	–1	0	2	–1	0	0	2	–1	–2	1	0	–2	1	0	0	–2	1
χ_{12}		2	–1	0	2	–1	0	0	2	–1	2	–1	0	2	–1	0	0	2	–1
χ_{13}		2	–1	0	–1	2	–2	1	0	0	–2	1	0	1	–2	2	–1	0	0
χ_{14}		2	–1	0	–1	2	–2	1	0	0	2	–1	0	–1	2	–2	1	0	0
χ_{15}		2	–1	0	–1	2	2	–1	0	0	–2	1	0	1	–2	–2	1	0	0
χ_{16}		2	–1	0	–1	2	2	–1	0	0	2	–1	0	–1	2	2	–1	0	0
χ_{17}		4	1	0	–2	–2	0	0	0	0	–4	–1	0	2	2	0	0	0	0
χ_{18}		4	1	0	–2	–2	0	0	0	0	4	1	0	–2	–2	0	0	0	0

Z_2. Thus, it is enough to investigate the conjugacy classes and the character table of H".

Consider next the operations that permute the nuclei of the framework; these fall into sets corresponding to the classes of C_{3v}. One of the C_3 operations of C_{3v} applied to the framework is the permutation (2, 3, 4); but this is not feasible for the molecule as a whole, and the protons have to be permuted as well. First presuming that the protons of each methyl group do not rotate, consider

$$R''_1 = (2,3,4)(5,8,11)(6,9,12)(7,10,13)\ .$$

Since all of the permutations of cycle type $1^1 3^4$ are conjugate in the group, we obtain a conjugacy class of length 72. Next, we assume that the protons of each methyl group rotate and define:

$$R''_2 = (2,3,4)(5,9,13,7,8,12,6,10,11),$$

$$R''_3 = (2,3,4)(5,10,12,6,8,13,7,9,11).$$

Using a tedious calculation we can see that R''_2 and R''_3 are not conjugate in the group, but every permutation of this type is conjugate with R''_2 or R''_3. Thus, we obtain two more conjugacy classes, each of length 72.

Similar methods are applied to the other class of C_{3v} to derive other sets of classes for trimethylamine. If we define

$$\sigma''_{v1} = (3,4)(6,7)(8,11)(9,13)(10,12),$$

$$\sigma''_{v2} = (3,4)(6,7)(8,12,10,13,9,11).$$

Then we obtain two conjugacy classes of lengths 54 and 108 with the representatives σ_{v1} and σ_{v2}, respectively. Using similar arguments, we can calculate all 14 conjugacy classes of group H". Since $G'' \cong Z_2 \times H''$, we can see that G" has exactly 28 conjugacy classes.

In Table VI, we give a representative for each conjugacy class of H". The conjugacy classes of group G" can be computed from this table.

Determination of the Character Table of Trimethylamine

From the conjugacy classes of group H", we can see that H" is a group of order 648. First of all, we collect the conjugacy class labels and the corresponding centralizer orders in two vectors:

$$\boldsymbol{A} = (1a,3a,3b,3c,2a,6a,3d,9a,9b,4a,12a,12b,6b,2b),$$

$$\boldsymbol{B} = (648,81,54,108,24,12,9,9,9,12,12,12,6,12).$$

Also, we can see that H" has a normal subgroup T of order 108. The factor group H" modulus T is not abelian: $H''/T \cong S_3$. Now, we obtain three irreducible characters

TABLE VI. Representatives of conjugacy classes of the full non-rigid group of trimethylamine

No.	Representatives	Size	No.	Representatives	Size
1	()	1	8	(2,3,4) (5,9,13,7,8,12,6,10,11)	72
2	(5,6,7)(8,9,10) (11,12,13)	8	9	(2,3,4) (5,10,12,6,8,13,7,9,11)	72
3	(5,6,7)(8,9,10)	12	10	(3,4)(9,13) (8,12,10,11)	54
4	(5,6,7)	6	11	(3,4)(5,7,6)(9,12) (8,11,10,13)	54
5	(5,7)(11,13)	27	12	(3,4)(5,6,7)(9,11) (8,13,10,12)	54
6	(5,7)(8,9,10) (11,13)	54	13	(3,4)(6,7) (8,13,9,12,10,11)	108
7	(2,3,4)(5,8,11) (6,9,12)(7,10,13)	72	14	(3,4)(6,7)(8,11) (9,13)(10,12)	54

of H" by lifting irreducible characters of S_3. We call these characters χ_1, χ_2 and χ_3, and we have:

$$\chi_1 = (1,1,1,1,1,1,1,1,1,1,1,1,1),$$

$$\chi_2 = (1,1,1,1,1,1,1,1,1,–1,–1,–1,–1,–1),$$

$$\chi_3 = (2,2,2,2,2,2,–1,–1,–1,0,0,0,0,0).$$

We now consider the action of H" on the set {2, 3, ..., 13}. If we denote by P the permutation character of this action, then we have:

$$P = (12,3,6,9,8,5,0,0,0,4,1,1,2,2).$$

Since $||P|| = 9$, $(P,\chi_1) = 2$ and $(P,\chi_3) = 2$, $P – 2\chi_1 – 2\chi_2$ is an irreducible character of H", which we denote by χ_6. Consider the symmetric and anti-symmetric parts χ_S and χ_A of χ_6.[12] We have:

$$\chi_S = (21,3,0,6,5,2,0,0,0,3,0,0,0,3),$$

$$\chi_A = (15,6,0,3,–1,–1,0,0,0,1,1,1,0,–3).$$

In addition, $||\chi_S|| = 4$ and $||\chi_A|| = 2$. Since $(\chi_S,\chi_1) = 1$, $(\chi_S,\chi_3) = 1$ and $(\chi_S,\chi_6) = 1$, hence $\chi_S – \chi_1 – \chi_3 – \chi_6$ is an irreducible character of H", which we denote by χ_{14}. On the other hand, $||\chi_A|| = 2$ and $(\chi_A,\chi_{14}) = 1$, so $\chi_A – \chi_{14}$ is an irreducible character of H, which is denoted by χ_4. Now we define $\chi_7 = \chi_6\chi_2$, $\chi_5 = \chi_4\chi_2$ and $\chi_{13} = \chi_{14}\chi_2$ and then we obtain three irreducible characters of H", which are different from χ_1, χ_2, χ_3, χ_6 and χ_{14}.

Finally, we consider the character $\psi = \chi_5\chi_6$. Then $||\psi|| = 3$ and $(\psi, \chi_7) = 1$. Thus, $\psi – \chi_7$ is a sum of two irreducible characters. Since the square of character degrees is the order of the group and the number of irreducible characters of degree $n \geq 3$ is even, $\psi – \chi_7 = \chi_8 + \chi_2\chi_8$, in which χ_8 is an irreducible character of H". Thus, we obtain two new irreducible characters χ_8 and $\chi_9 = \chi_2\chi_8$. Using orthogonality relations we have:

$$\chi_8 = (6,–3,0,3,–2,1,0,0,0,0,\sqrt{3},–\sqrt{3},0,0),$$

$$\chi_9 = (6,–3,0,3,–2,1,0,0,0,0,–\sqrt{3},\sqrt{3},0,0).$$

Using the character $\chi_6\chi_{14}$ and the powers of χ_2, we obtain other irreducible characters. Our calculations are summarized in Table VII, the character table of group H". As mentioned above, since $G" \cong Z_2 \times H"$, we can compute the character table of G" from Table VII.

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TABLE VII. The Character table of group H" and its power map

		1*a*	3*a*	3*b*	3*c*	2*a*	6*a*	3*d*	9*a*	9*b*	4*a*	12*a*	12*b*	6*b*	2*b*
	2P	1*a*	3*a*	3*b*	3*c*	1*a*	3*c*	3*d*	9*a*	9*b*	2*a*	6*a*	6*a*	3*b*	1*a*
	3P	1*a*	1*a*	1*a*	1*a*	2*a*	2*a*	1*a*	3*a*	3*a*	4*a*	4*a*	4*a*	2*b*	2*b*
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	0	3	2	–1	0	0	0	2	–1	–1	0	0
χ_7		6	–3	0	3	2	–1	0	0	0	–2	1	1	0	0
χ_8		6	–3	0	3	–2	1	0	0	0	0	$\sqrt{3}$	$-\sqrt{3}$	0	0
χ_9		6	–3	0	3	–2	1	0	0	0	0	$-\sqrt{3}$	$\sqrt{3}$	0	0
χ_{10}		8	–1	2	–4	0	0	–1	2	–1	0	0	0	0	0
χ_{11}		8	–1	2	–4	0	0	–1	–1	2	0	0	0	0	0
χ_{12}		8	–1	2	–4	0	0	2	–1	–1	0	0	0	0	0
χ_{13}		12	3	–3	0	0	0	0	0	0	0	0	0	–1	2
χ_{14}		12	3	–3	0	0	0	0	0	0	0	0	0	1	–2

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SAŽETAK

Teorija potpune GNK za *cis*- i *trans*-diklordiamminoplatinat (II) i trimetilamin

Masood Hamadanian i Ali Reza Ashrafi

Teorija grupa za gipke (non-rigid) molekule (GNK), gdje su operacije dinamičke simetrije definirane kao fizikalne operacije, predstavlja novo područje kemije. Ovo je područje započeo Smeyers koji je za niz gipkih molekula izračunao tablice karaktera pripadnih ograničenih GNK. Autori su opisali jednostavan postupak koji omogućava računanje tablica karaktera za grupe simetrije gipkih molekula u kojima je određen broj AH_3 skupina vazan na kruti skeleton. Posebice su proučene potpune GNK za *cis*- i *trans*-diklordiamminoplatinat(II) i trimetilamin. Pokazano je da ove grupe sadrže 36, 72 i 1296 elemenata, koji se respektivno dijele u 9, 18 i 28 klasa konjugiranih elemenata, što pokazuje da za ove molekule potpune i ograničene GNK nisu izomorfne. Opisani postupak potpunih GNK dade se poopćiti i primjeniti i na druge gipke molekule, i u odnosu na do sada rabljene metode daje bolji uvid u intramolekularnu dinamiku gipkih molekula.