

Markaracter Table and *Q*-Conjugacy Character Table for the Non-Rigid Group 1,3,5-Trimethylbenzene

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The maturated and unmaturated groups were introduced by Shinsaku Fujita who used them in the markaracter table and the *Q*-conjugacy character table of a finite group. Then, he applied his results in this area of research to enumerate isomers of molecules. Using non-rigid group theory, it was shown that the full non-rigid (f-NRG) group of 1,3,5-trimethylbenzene (TMB) is isomorphic to wreath product of the cyclic group of order three and the symmetric group of order six on three letters (see *Int. J. Quantum Chem.* **2007**, *107*, 340). In this paper, we will show that this group has 13 dominant classes (similarly, *Q*-conjugacy characters) 9 of which are unmatured (similarly, *Q*-conjugacy characters such that they are the sum of two irreducible characters). Then Markaracter table and *Q*-conjugacy character table of the unmatured full non-rigid group TMB is derived.

In order to develop new methods of combinatorial enumeration of isomers, some relationship between character tables containing characters for irreducible representations and mark tables containing marks for coset representations have been clarified by Shinsaku Fujita who proposed not only markaracter tables, which enable us to discuss characters and marks on a common basis, but *Q*-conjugacy character tables, which are obtained for finite groups.[1–10]

The enumeration of chemical compounds has been accomplished by various methods but the Pólya-Redfield theorem has been a standard method for combinatorial enumerations of graphs and chemical compounds. A dominant class is defined as a disjoint union of conjugacy classes that corresponds to the same cyclic subgroup, which is selected as a representative of conjugate cyclic subgroups. Let G be a finite group and $h_1, h_2 \in G$. We say h_1 and h_2 are Q-conjugate and denote by $h_1 \approx_Q h_2$ if there exists $t \in G$ such that $t^{-1}\langle h_1\rangle t = \langle h_2\rangle$. The Q-conjugacy is an equivalence relation on G and generates equivalence classes which are called dominant classes, i.e. the group G is partitioned into dominant classes as follows: $G = K_1 + K_2 + \ldots + K_s$ in which K_i corresponds to the cyclic (dominant) subgroup G_i selected from a non-redundant set of cyclic subgroups of G denoted by *SCSG*.[3–16]

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 tunneling rearrangement. A non-rigid molecule typically possesses several potential valleys separated by relatively low energy barriers, and thus exhibits large amplitude tunneling dynamics among various potential minima. Because of this deformability, the non-rigid molecules exhibit some interesting properties of intramolecular dynamics, spectroscopy, dynamical NMR, and so, all of which can be interpreted 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 theories 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 in the literature.[17–22]

The molecular symmetry group of a non-rigid molecule was first defined by Longuet-Higgins[23] although there have been earlier works that suggested the need for such a framework by Hougen.[24] Bunker and Papoušek[25] 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 have been used together to treat the symmetry properties of molecules in electric and magnetic fields by Watson.[26]

The complete set of the molecular conversion operations that commute with the nuclear motion operator will contain overall rotation operations that describe a molecule rotating as a whole, and intramolecular motion operations that describe molecular moieties moving with respect to the rest of the molecule. These operations form a group which is called the full non-rigid molecule group (f-NRG) by Smeyers.[27] The notation we use is standard and the reader may consult references.[28,29] The non-rigid group theory also finds applications in the enumeration of isomers and substituted aromatics.[30,31]

The present study investigates the markaracter and *Q*-conjugacy character tables of TMB that the first author introduced its full non-rigid (f-NRG) group in[32] (see Figure 1). It is shown with the aid of GAP[33] that this is a group of order 162 with 13 dominant classes (similarly, *Q*-conjugacy characters) such that there are nine unmaturated (i.e. there are nine row column-reductions) in the character table of the f-NRG for TMB. TMB can be used as a dyestuff intermediate, solvent, paint thinner, or UV oxidation stabilizer for plastics.

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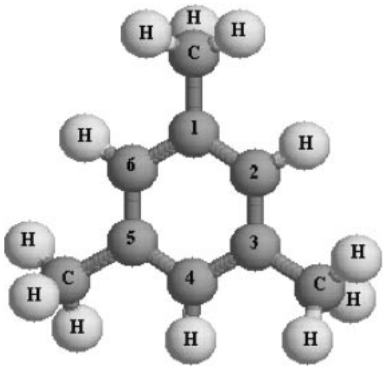

Figure 1. Structure of TMB.

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. A permutation representation P of a finite group G is obtained when the group G acts on a finite set $X = \{x_1, x_2, \ldots, x_t\}$ from the right, which means that we are given a mapping P: $X \times G \to X$ via $(x, g) \to xg$ such that holds the following: $(xg)g' = x(gg')$ and $x1 = x$, for each g, $g' \in G$ and $x \in X$.

Now let it be assumed that one is given an action P of G on X and a subgroup H of G. One considers the set of its right cosets H_{g_i} and the corresponding partition of G into these cosets: $G = H_{g_1} + H_{g_2} + \ldots + H_{g_m}$. If the cosets from the right are multiplied by a group element g, these cosets are permuted, in fact one obtains an action of G on the set X of cosets and, correspondingly, a permutation representation which is denoted by $G(/H)$, following Fujita's notation.[3,6]

If M is a normal subgroup of G and K is another subgroup of G such that $M \cap K = \{e\}$ and $G = MN = \langle M, N \rangle$, then G is called a semi direct product of N by M which is denoted by $N : M$. Let K and H be groups and suppose H acts on the set Γ. Then, the wreath product of K by H, denoted by $K \,_{\mathrm{wr}}\, H$ is defined to be the semi direct product $K^{\Gamma} : H$ such that $K^{\Gamma} = \{f | f : \Gamma \to K\}$.

Let C be a $u \times u$ matrix of character table of G. Then, C is transformed into a more concise form called the Q-conjugacy character table that we denote its $s \times s$ matrix by C^Q $(s \leq u)$ as follows: If $u = s$, then $C = C^Q$ i.e. G is a maturated group. Otherwise $s < u$, for each $G_i \in SCSG$ (the corresponding dominant class K_i) set $t_i = m(G_i)/\phi(|G_i|)$ where $m(G_i) = |N_G(G_i)|/|C_G(G_i)|$ (called the maturity discriminant), ϕ is the Euler function and finally $N_G(G_i)$ and $C_G(G_i)$ denote the normalizer and centralizer of G_i in G, respectively for $i = 1, \ldots, s$. If $t_i = 1$ then, K_i is exactly a conjugacy class so there is no reduction in row and column of C, but if $t_i > 1$ then K_i is a union of t_i-conjugacy classes of G (i.e. reduction in column) therefore the sum of t_i rows of irreducible characters via the same degree in C (reduction in rows) gives us a reducible character which is called the Q-conjugacy character which is integer-valued in both cases. See Ref. 34 for more details.

It is described in Ref. 32 that the f-NRG of TMB is the wreath product of the cyclic group of order three and the symmetric group of order six on three letters, i.e. $C_3 \,_{\mathrm{wr}}\, S_3$ which is a group of order 162.

Now set Tmb $= C_3 \,_{\mathrm{wr}}\, S_3$, the computations of the symmetry properties of molecules were carried out with the aid of GAP SYSTEM,[33] a group theory software package which is free and extendable. We run the following program at the GAP prompt to compute the character table and the set *SCSG* of the f-NRG of TMB as follows:

```
LogTo("Computations.txt");
      c3:=CyclicGroup(3);
   s3:=SymmetricGroup(3);
      Tmb:=WreathProduct(c3,s3);
         Char:=CharacterTable(Tmb);
         Order(Tmb);IsPermGroup(Tmb);
s:=ConjugacyClassesSubgroups(Tmb);
         Sort("s");
SCSG:=List(ConjugacyClassesSubgroups(Tmb),x->Elements(x));
  Len:=Length(SCSG); y:=[];
      for i in [1..Len]do
         if IsCyclic(SCSG[i][1])then Add(y,i);
           fi;
         od;
      Display(Char);
  Display(s);
      Print("Char", "\n");
Print("SCSG", "\n");
LogTo();
```

To denote the consecutive classes of elements of order n, for example if an element g has order n, then its class is denoted by nx, where x runs over the letters a, b, etc.

After running the program, we can see that Tmb has exactly 13 dominant (Q-conjugacy) classes as follow: $K_1 = 1\mathrm{a}$, $K_2 = 2\mathrm{a}$, $K_3 = 3\mathrm{a}$, $K_4 = 3\mathrm{b} \cup 3\mathrm{c}$, $K_5 = 3\mathrm{d} \cup 3\mathrm{f}$, $K_6 = 3\mathrm{e}$, $K_7 = 3\mathrm{g} \cup 3\mathrm{j}$, $K_8 = 3\mathrm{h} \cup 3\mathrm{i}$, $K_9 = 6\mathrm{a} \cup 6\mathrm{c}$, $K_{10} = 6\mathrm{b} \cup 6\mathrm{d}$, $K_{11} = 6\mathrm{e} \cup 6\mathrm{h}$, $K_{12} = 6\mathrm{f} \cup 6\mathrm{g}$, $K_{13} = 9\mathrm{a} \cup 9\mathrm{b}$. Here, just K_1, K_2, K_3, and K_6 are maturated dominant classes (similar discussion for Q-conjugacy characters). Besides, according to Refs. 4–10 since the dimensions of the Q-conjugacy character table of Tmb and the corresponding markaracter table of Tmb are equal so $|SCSG| = 13$ and a non-redundant set of cyclic subgroups of Tmb contains the following elements:

$G_1 = id$,
$G_2 = \langle (4,7)(5,8)(6,9) \rangle$,
$G_3 = \langle (1,2,3)(4,5,6)(7,8,9) \rangle$,
$G_4 = \langle (4,5,6)(7,8,9) \rangle$,
$G_5 = \langle (4,5,6)(7,9,8) \rangle$,
$G_6 = \langle (7,8,9) \rangle$,
$G_7 = \langle (1,2,3)(4,5,6)(7,9,8) \rangle$,
$G_8 = \langle (1,4,7)(2,5,8)(3,6,9) \rangle$,
$G_9 = \langle (4,5,6)(7,8,9), (4,7)(5,8)(6,9) \rangle$,
$G_{10} = \langle (4,7)(5,8)(6,9), (1,3,2)(4,5,6)(7,8,9) \rangle$,
$G_{11} = \langle (7,8,9), (1,4)(2,5)(3,6) \rangle$,
$G_{12} = \langle (4,7)(5,8)(6,9), (1,2,3)(4,5,6)(7,8,9) \rangle$,
$G_{13} = \langle (1,2,3)(4,5,6)(7,8,9), (1,4,7,2,5,8,3,6,9) \rangle$.

Therefore, by using the above calculations, we are able to calculate the Markaracter table (M^C) and the Q-conjugacy character table (C^Q) of group Tmb $= C_3 \,_{\mathrm{wr}}\, S_3$ which are stored in Table 1 and Table 2.

Table 1. Markaracter Table of the Non-Rigid TMB

M^C	G_1	G_2	G_3	G_4	G_5	G_6	G_7	G_8	G_9	G_{10}	G_{11}	G_{12}	G_{13}
Tmb($/G_1$)	162	0	0	0	0	0	0	0	0	0	0	0	0
Tmb($/G_2$)	81	9	0	0	0	0	0	0	0	0	0	0	0
Tmb($/G_3$)	54	0	54	0	0	0	0	0	0	0	0	0	0
Tmb($/G_4$)	54	0	0	18	0	0	0	0	0	0	0	0	0
Tmb($/G_5$)	54	0	0	0	18	0	0	0	0	0	0	0	0
Tmb($/G_6$)	54	0	0	0	0	18	0	0	0	0	0	0	0
Tmb($/G_7$)	54	0	0	0	0	0	18	0	0	0	0	0	0
Tmb($/G_8$)	54	0	0	0	0	0	0	6	0	0	0	0	0
Tmb($/G_9$)	27	3	0	9	0	0	0	0	3	0	0	0	0
Tmb($/G_{10}$)	27	3	0	0	0	0	9	0	0	3	0	0	0
Tmb($/G_{11}$)	27	3	0	0	0	9	0	0	0	0	3	0	0
Tmb($/G_{12}$)	27	3	27	0	0	0	0	0	0	0	0	3	0
Tmb($/G_{13}$)	18	0	18	0	0	0	0	0	0	0	0	0	3

Table 2. Q-Conjugacy Character Table of the Non-Rigid TMB

C^Q	K_1	K_2	K_3	K_4	K_5	K_6	K_7	K_8	K_9	K_{10}	K_{11}	K_{12}	K_{13}
ϕ_1	1	1	1	1	1	1	1	1	1	1	1	1	1
ϕ_2	1	−1	1	1	−1	−1	1	1	−1	1	−1	1	1
ϕ_3	2	−2	2	−1	1	1	−1	−1	1	2	−2	2	−1
ϕ_4	2	2	2	−1	−1	−1	−1	−1	−1	2	2	2	−1
ϕ_5	2	0	−1	2	0	0	−1	2	0	2	0	2	2
ϕ_6	4	0	−2	−2	0	0	1	−2	0	4	0	4	−2
ϕ_7	6	−2	0	3	−2	1	0	0	1	0	1	−3	−3
ϕ_8	6	−2	0	0	1	−2	0	−3	1	0	1	−3	3
ϕ_9	6	−2	0	−3	1	1	0	3	−2	0	1	−3	0
ϕ_{10}	6	2	0	3	2	−1	0	0	−1	0	−1	−3	−3
ϕ_{11}	6	2	0	0	−1	2	0	−3	−1	0	−1	−3	3
ϕ_{12}	6	2	0	−3	−1	−1	0	3	2	0	−1	−3	0
ϕ_{13}	6	0	0	0	0	0	0	0	0	−3	0	6	0

Conclusion

We considered the non-rigid 1,3,5-trimethylbenzene as a wreath product group $C_{3\,\mathrm{wr}}\,S_3$ of order 162, divided into thirteen dominant classes (similarly, thirteen Q-conjugacy characters). Such that just ϕ_1, ϕ_2, ϕ_5, and ϕ_{13} are just matured Q-conjugacy characters, ϕ_3, ϕ_4, ϕ_6, …, ϕ_{11}, and ϕ_{12} are the sum of two irreducible characters (i.e. $t = 2$).

The derived markaracter table and Q-conjugacy character table would also be valuable in other applications such as in the context of chemical applications of graph theory and aromatic compounds.[18–22]

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