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Character of the Representative Permutation as a Tool of Stereoisomers Counting: Application to the Permethrinic Acid

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Abstract

A combinatorial counting using the character of the representative permutation approach has been carried out on the permethrenic acid in order to determine the exact number of his chiral and achiral stereo isomers having the empirical formulae $C_3H_2X_2YZ$; where X, Y and Z, stand respectively for the methyl, the diclhorovinyl and the carboxyl groups. We have shown that permethrenic acid presents sixteen stereoisomers, divided into fourteen enantiomeric pairs or chiral forms of C_1 symmetry and two achiral forms belonging to C_s' point group.

Keywords: Character; Representative permutation; Permethrenic acid; Chiral; Achiral; Stereoisomers

Introduction

Permethrenic acid is known as one of the precursors of permethrin having weak insecticidal activity used in the agricultural and veterinary fields [1,2]. It is an organ chlorine compound derived from carboxylic cyclopropane [3,4].

Given the different positions that the methyl, dichlorovinyl and carboxyl groups may occupy on the cyclopropane skeleton, several stereoisomers of this compound can be generated and some of them already exist in nature. In order to evaluate the biological activity of this compound in relation to its structure, it is necessary to know the exact number and structure of its different stereoisomers.

Therefore, the character of permutations used in the combined formalism of Fowler and Shao can be used to enumerate the stereoisomers of this compound [5,6]. This formalism allows the examination of permutations of different substitution sites on the basic skeleton or parent molecule. The contributions of the different symmetry operations of the point group of the parent molecule are grouped into subgroups of permutations allowing to characterize the listed derivatives and to split them into chiral or achiral isomers.

Literature Review

Computational details

Symmetry of parent molecule: Let us consider the stereograph cyclopropane shown in Figure 1 as the parent building block.

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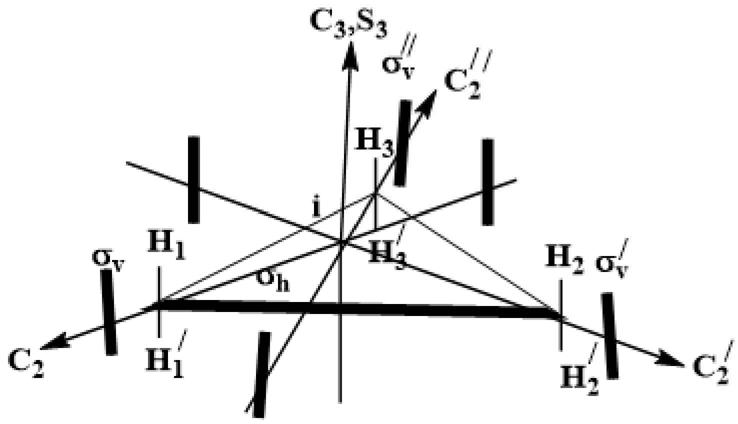

FIG. 1. **Stereograph of cyclopropane with its symmetry elements.**

This stereograph belongs to D_{3h} point group and exhibits 12 symmetry elements/operations listed in equation 1

$$\mathbf{D_{3h}} = \left\{E, C_3^1, C_3^2, C_2, C_2', C_2'', \sigma_h, S_3^1, S_3^2, \sigma_v, \sigma_v', \sigma_v''\right\} \quad (1)$$

These symmetry operations are partitioned into 6 equivalence classes given in equation 2 here after:

$E, 2C_3, 3C_2, \boldsymbol{\delta}_h, 2S_3, 3\boldsymbol{\delta}_v$ (2)

This latter gives rise to 10 non-redundant subgroups comprising 4 chiral subgroups and 6 achiral subgroups shown in Table 1.

TABLE 1. **Subgroups of D_{3h}.**

Subgroup	Symmetry operations	Chirality
C_1	E	Chiral
C_2	E,C_2	Chiral
C_s	E, σ_h	Achiral
C_s	E,σ_v	Achiral
C_3	$E,C^1{}_3,C^2{}_3$	Chiral
C_{2v}	E,C_2,σ_h,σ_v	Achiral
C_{3v}	$E,C^1{}_3,C^2{}_3,\sigma_v,\sigma'_v,\sigma''_v$	Achiral
C_{3h}	$E,C^1{}_3,C^2{}_3,\sigma_h,S^1{}_3,S^2{}_3$	Achiral
D_3	$E,C^1{}_3,C^2{}_3,C_2,C'_2,C''_2$	Chiral
D_{3h}	$E,C^1{}_3,C^2{}_3,C_2,C'_2,C''_2,\sigma_h,S^1{}_3,S^2{}_3, \sigma_v, \sigma'_v, \sigma''_v$	Achiral

Fowler's approach: The application of symmetry operations on a parent molecule generates permutations from which we can find representative permutation associated with the movements of atoms (Table 2).

Let us denote Γ_{σ} this representation and $\chi^{R}_{\Gamma_{\sigma}}$ the representative character under each operation R of the parent group. This latter represents the number of invariant points under the effect of this operation. The symmetric square character of the representation noted $\left[\Gamma^2_{\sigma}\right]$ is calculated by using the following equation 3.

$$\chi^{R}_{\left[\Gamma^2_{\sigma}\right]}(R)=\frac{1}{2}\left[\left(\chi^{R}_{\Gamma_{\sigma}}\right)^2+\chi^{R^2}_{\Gamma_{\sigma}}\right] \quad (3)$$

With $\left(\chi^{R}_{\Gamma_{\sigma}}\right)^2=\Gamma^2_{\sigma}$ et $\chi^{R^2}_{\Gamma_{\sigma}}=\Gamma_{\sigma}$

and the following table gives the permutations generated by the symmetry operations of D_{3h} on the hydrogen atom of cyclopropane and reducible representations $\Gamma_{\sigma,}\Gamma^2_{\sigma},\Gamma^3_{\sigma}$ and $\left[\Gamma^2_{\sigma}\right]$.

TABLE 2. **Generated permutations and reductible representation.**

Symmetry operation	Generated permutations	Γ_{σ}	Γ^2_{σ}	Γ^3_{σ}	$[\Gamma^2_{\sigma}]$
E	$(H_1)(H_2)(H_3)(H'_1)(H'_2)(H'_3)$	6	36	126	21
C^1_3	$(H_1H_3H_2)(H'_1H'_3H'_2)$	0	0	0	0
C^2_3	$(H_1H_2H_3)(H'_1H'_2H'_3)$	0	0	0	0
C_2	$(H_1H_1')(H_2H_2')(H_3H_3')$	0	0	0	0
C'_2	$(H_1H'_3)(H_2H'_2)(H_2H'_2)$	0	0	0	0
C''_2	$(H_1H'_2)(H_2H_1')(H_3H'_3)$	0	0	0	0
σ_h	$(H_1H'_1)(H_2H'_2)(H_3H'_3)$	0	0	0	0
S^1_3	$(H_1H'_3H_2H'_1H_3H'_2)$	0	0	0	0
S^2_3	$(H_1H'_2H_3H'_1H_2H'_3)$	0	0	0	0
σ_v	$(H_1)(H_2H_3)(H'_1)(H'_2H'_3)$	2	4	8	5
σ'_v	$(H_1H_3)(H_2H'_2)(H'_1H'_3)$	2	4	8	5
σ''_v	$(H_1H_2)(H_3)(H'_1H'_2)(H'_3)$	2	4	8	5

Reductible representation for quadruple replacement of type X_2YZ

According to Fowler, the reductible representation for isomer counting for quadruple replacement of type X_2YZ denoted by Γ_{X_2YZ} is given by equation 4.

$$\Gamma_{X_2YZ}=\Gamma^2_{\sigma}\times\left[\Gamma^2_{\sigma}\right]-3\Gamma^3_{\sigma}-\Gamma_{\sigma}\times\left[\Gamma^2_{\sigma}\right]+6\Gamma^2_{\sigma}-3\Gamma_{\sigma} \quad (4)$$

Γ_{X_2YZ} can be reduce using equation 5.

$$\Gamma_{X_2YZ}=\sum_i a_i\Gamma_i \quad (5)$$

Where Γ_i is the irreductible representation of the parent group and the coefficient a_i correspond to the number of containing in the initial set and given in equation 6.

$$a_i=\frac{1}{g}\sum_i n_t\chi_{\Gamma_{X_2YZ}}\chi^{(i)}\Gamma_i. \quad (6)$$

This reduction allows to find the number of stereoisomer having tological formulae $C_3H_2X_2YZ$

Coset representation

The designation of the global symmetry G in term of local one represented by its subgroup H is called Coset and denoted G/H. there are $|G|/|H|$ configurations corresponding to a single isomer.

The isomer permutation Γ can be expressed in term of the spaned representation of by $|G|/|H|$ configurations as follow:

$$\Gamma = \sum_{H} n_H \Gamma_{G/H} \quad (7)$$

Where n_H is the number of isomers with symmetry H.

In general Γ is given by the equation 8

$$\Gamma = \sum_{H} c_\gamma \Gamma_G^\gamma \quad (8)$$

Where c_γ and Γ_G^γ represent respectively the multiplicity and the γth irreducible representation of group G.

$\Gamma_{G/H}$ can take the form of eq.8 as follow:

$$\Gamma_{G/H} = \sum_{\gamma} a_{0,H}^\gamma \Gamma_G^\gamma \quad (9)$$

$a_{0,H}^\gamma$ is the multiplicity and is given by eq.10:

$$\Gamma_G^\gamma = \sum_{\eta} a_{\eta,H}^\gamma \Gamma_H^\eta = a_{0,H}^\gamma \Gamma_H^0 + a_{1,H}^\gamma \Gamma_H^1 + \dots \quad (10)$$

Where Γ_H^η is the ηth irreducible representation of subgroup H.

The combination of eq.7-eq.10 gives the following relation:

$$\sum_{H} n_H a_{0,H}^\gamma = c_\gamma \quad (11)$$

Results and Discussion

Characters of Γ_{X_2YZ}

The application of equation 4 allows us to obtain characters of the reducible representation Γ_{X_2YZ} under each class of equivalent symmetry operation shown in the following Table 3.

TABLE 3. **Characters of Γ_{X_2YZ}**

	E	**2*C*3**	**3*C*2**	**2*S*3**	**σh**	**3σv**
Γ_{X2YZ}	180	0	0	0	0	4

Γ_{X_2YZ} can be expressed as sum of irreducible representation of the parent group. Using equation 8, one can show that:

$$\Gamma_{X_2YZ} = 16A_1^{/} + 14A_2^{/} + 30E^{/} + 14A_1^{//} + 16A_2^{//} + 30E^{//}$$

The multiplicity of the totally symmetric irreducible representation of D_{3h} is the total number of stereoisomers of $C_3H_2X_2YZ$. In the present situation this number is equal to 16 because A'_1 is totally symmetric irreducible representation of D_{3h}.
From the correlation table of D3h point group one can show that:

$$\Gamma_{(D_{3h}/C_1)} = A_1' + A_2' + 2E' + A_1' + A_2' + 2E''$$

$$\Gamma_{(D_{3h}/C_2)} = A_1' + E' + A_1'' + E''$$

$$\Gamma_{(D_{3h}/C_3)} = A_1' + A_2' + A_1'' + A_2''$$

$$\Gamma_{(D_{3h}/C_S')} = A_1' + E' + A_2'' + E''$$

$$\Gamma_{(D_{3h}/C_S)} = A_1' + A_2' + E'$$

$$\Gamma_{(D_{3h}/C_{2V})} = A_1' + E'$$

$$\Gamma_{(D_{3h}/C_{3V})} = A_1' + A_2''$$

$$\Gamma_{(D_{3h}/C_{3h})} = A_1' + A_2'$$

$$\Gamma_{(D_{3h}/D_3)} = A_1' + A_1''$$

$$\Gamma_{(D_{3h}/D_{3h})} = A_1'$$

From equation 7 we deduce that:

$$\Gamma_{X_2YZ} = n_{C_1}\Gamma_{D_{3h}/C_1} + n_{C_2}\Gamma_{D_{3h}/C_2} + n_{C_S'}\Gamma_{D_{3h}/C_S'} + n_{C_S}\Gamma_{D_{3h}/C_S} + n_{C_{2V}}\Gamma_{D_{3h}/C_{2V}} + n_{C_{3V}}\Gamma_{D_{3h}/C_{3V}} + n_{C_3}\Gamma_{D_{3h}/C_3} + n_{C_{3h}}\Gamma_{D_{3h}/C_{3h}} + n_{D_3}\Gamma_{D_{3h}/D_3} + n_{D_{3h}}\Gamma_{D_{3h}/D_{3h}}$$

The corresponding linear system is given as follow:

$$\begin{cases} n_{C_1} + n_{C_2} + n_{C_S} + n_{C_S'} + n_{C_{2V}} + n_{C_3} + n_{C_{3V}} + n_{C_{3h}} + n_{D_3} + n_{D_{3h}} = 16 \\ n_{C_1} + n_{C_S} + n_{C_3} + n_{C_{3h}} = 14 \\ 2n_{C_1} + n_{C_2} + n_{C_S'} + n_{C_S} + n_{C_{2V}} = 30 \\ n_{C_1} + n_{C_2} + n_{C_3} + n_{D_3} = 14 \\ n_{C_1} + n_{C_S'} + n_{C_3} + n_{C_{3V}} = 16 \\ 2n_{C_1} + n_{C_2} + n_{C_S'} = 30 \end{cases}$$

Notice that it is not possible to find the exact solution of this linear system of 6 equations with 10 unknowns. Fortunately some of them can be predefine by the geometry of the molecule and the type of substitution [7,8].

For instance any heterosubstitution on the cyclopropane skeleton cancel the C_2, C_3 axis and σ_h symmetry elements. As a result all the subgroups containing these 3 elements plane consequently every subgroup containing these 3 elements namely C_S,C_2,C_{2V},C_3,C_{3V},C_{3h},D_3,D_{3h} will disappear.

Thus $n_{C_2} = n_{C_S} = n_{C_3} = n_{C_{2V}} = n_{C_{3V}} = n_{C_{3h}} = n_{D_3} = n_{D_{3h}} = 0$.

The linear system of 6 equations can be reduce as follow:

$$\begin{cases} n_{C_1} + n_{C'_S} = 16 \\ n_{C_1} = 14 \\ 2n_{C_1} + n_{C'_S} = 30 \\ n_{C_1} = 14 \\ n_{C_1} + n_{C'_S} = 16 \\ 2n_{C_1} + n_{C'_S} = 30 \end{cases}$$

The solution of this system is: $n_{C_1} = 14$ and $n_{C'_S} = 2$.

The permethrenic acid generates simultaneously 14 enatiomeric pairs or chiral form with the C_1 symmetry and 2 achiral forms belonging to C'_s group. The Figure 2 shows the molecular graph of the sixteen stereoisomers of permethrenic acid (Figure 2).

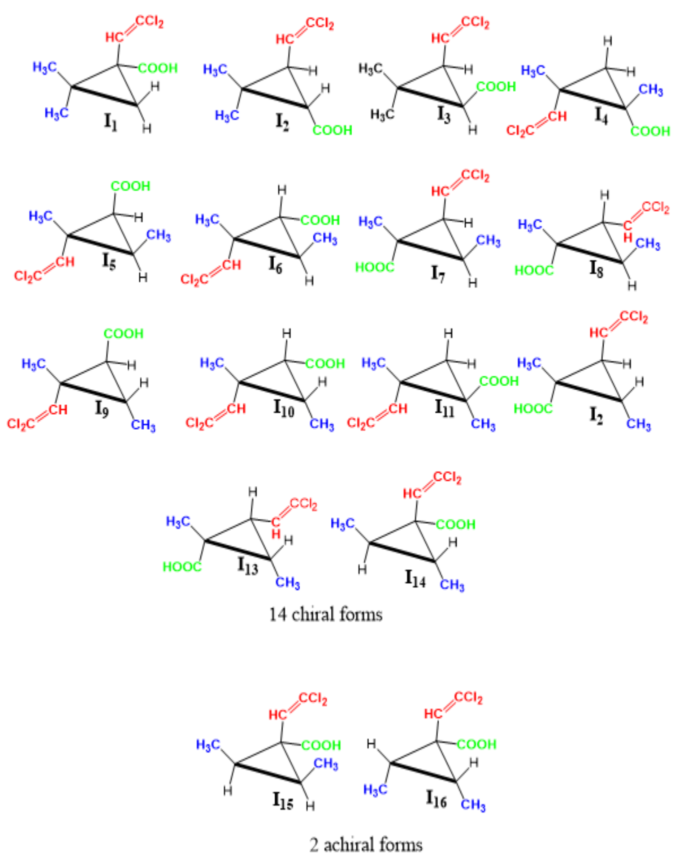

FIG. 2. **Molecular graph of permethrenic stereoisomers.**

Conclusion

The enumeration of stereoisomers of permethrenic acid symbolized by the empirical formula the empirical formulae $C_3H_2X_2YZ$; where X, Y and Z and symbolizes respectively the methyl, the dichlorovinyl and the carboxyl groups using character of the representation has been carried out. We have 14 chiral form which possess the C_1 symmetry and 2 achiral forms belonging to C'_S group. We can also notice that in this family of compound the chiral forms are predominant.

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