Fischer projections are analyzed using the framework of group theory. It is shown that the rules and operations used to manipulate Fischer projections form the alternating group $A_4$ which is a normal subgroup of the permutation (symmetric) group $S_4$. 
Group Theory and Fischer Projections

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Abstract:

Fischer projections are analyzed using the framework of group theory. It is shown that the rules and operations which are used to manipulate Fischer projections form the alternating group $A_4$ which is a normal subgroup of the permutation (symmetric) group $S_4$.

Keywords:

Group theory/symmetry, Chirality/optical isomers
Introduction

The stereochemistry of organic molecules is an important part of every organic chemistry course, but its interpretation in terms of group theory is not given in the introductory textbooks or lectures on the subject. More advanced/specialized textbooks [1] do make the connection in a general way. Physical chemistry textbooks describe the general criterion for the chirality of a molecule as the absence of improper rotation axis ($S_n$) in the molecular point group [2]. This criterion is useful as the basis for checking chirality of molecules with any number of stereogenic carbons, but is not useful for description and manipulation of individual enantiomers and diastereomers as required in pedagogical practice. For example, the isomers of tartaric acid drawn in Scheme 1 can not be easily distinguished by this criterion without the use of models.

Scheme 1
The standard way around this difficulty is to use Fischer projections (FP). FP convention represents the molecule in the plane of the paper with the main C-C chain of the stereoisomer’s backbone drawn vertically and assumed to be below the plane of the paper. The side chains are drawn horizontally and presumed to project out of the paper plane. The rules for manipulating FP are given in many organic chemistry textbooks [3] and can be summarized as follows (Scheme 2):

**Rule 1.** Projections as single units may be rotated only in the plane of the paper and only by $180^\circ$.

![Scheme 2](image)

**Rule 2.** Any three groups may be rotated with the fourth remaining fixed in place.

![Scheme 2](image)

**Rule 3.** Rotation of the projection by $90^\circ$ or the exchange of any two groups gives the enantiomer of the original configuration (Scheme 3).
Rules 1 and 2 ensure that the result of FP manipulation is identical with the original molecule. FP serves to compare the stereochemistry of 3D structures and for assessing whether they are identical, enantiomeric or diastereomeric. Structures 1-4 can be represented using FP as shown below (Scheme 4)

FP representations allow one to readily observe that it is possible to draw only three rather than four distinct configurations, one of which (the rightmost) has a symmetry plane perpendicular to the plane of paper and thus can not be chiral. The rules regarding FP are given on “as is” basis and justified by their usefulness rather than being derived from general mathematical principles. To the best of the author’s knowledge, no standard chemistry text explicitly relates FP to group theory and we shall describe the relationship in this article.
Discussion

The analysis of algebraic structure of central molecular chirality (starting from FP) had been reported by Capozziello and Lattanzi [4]. The authors deduced matrix operators and showed how they constitute matrix representation of the orthogonal group $O(4)$.

The FP manipulations can be represented by permutation operations belonging to the symmetric (permutation) group $S_4$ which describes all possible permutations of four different objects (in our case the objects are four different substituents at the asymmetric carbon). There are 24 possible permutations in total which is consistent with the order of $S_4$ group being 24 [5]. Twelve of these permutations will generate identical absolute configuration while the remaining twelve will produce its mirror image (enantiomer). In this work we describe the algebraic structure of FP via permutation groups.

The application of Rules 1 and 2 generates identical configurations (not enantiomers) so the total number of acceptable permutations is reduced from 24 to 12. The permutation group describing Fischer projections is therefore the subgroup of $S_4$ and has the order 12. This subgroup is called the alternating group $A_4$ and contains only even permutations of the four objects out of the total of 24 in its parent group [6]. Those even permutations are described below.

There are three classes of symmetry operations in $A_4$ and they are: identity ($g_1$), the class of permutations of three objects ($g_2$) and the class of all transpositions on the two
pairs. The $g_1$, $g_2$ and $g_3$ classes comprise one, eight and three elements (operations), respectively.

Identity $g_1$ comprises one-cycle permutation labeled $(1)(2)(3)(4)$ and corresponds to the symbolic operation $1234 \Rightarrow 1234$.

Class $g_2$ comprises the following eight permutations:

\((123),(132),(124),(142),(134),(143),(234)\) and \((243)\). This class of operations is equivalent to the Rule 2 and correspond to the symbolic operation $1234 \Rightarrow 2314$.

Class $g_3$ comprises three permutations \((12)(34)\), \((13)(24)\) and \((14)(23)\). This class of operations is equivalent to the Rule 1 and corresponds to the symbolic operation $1234 \Rightarrow 2143$.

Textbooks and tutorial problems often do not discuss the fact that the configurations obtained by $90^0$ in-plane rotation, are different.

![Scheme 5](image)

The Rule 1 forbids such rotation, but does not explain why. Once again the symmetry argument provides a useful insight. Projection of the asymmetric carbon onto the plane of the paper makes the symmetry of FP higher (lowest symmetry being $C_s$ point group) than the symmetry of the original structure ($C_i$ point group in the example.
above). Subsequently, it is clear that the rotation of FP by $90^0$ (or any other angle) around the axis perpendicular to the paper plane leads to the identical structure. However, the effect is illusory because FP is not a faithful representation (congruent) in symmetry terms, of the original structure.

The extension of the permutation group approach can be made to provide for diastereomer generation, specification and enumeration. This approach introduces the configuration symmetry group which represents the topological symmetry of the graphs with special respect to the stereocenters. However, this powerful blend of graph theory and permutation groups is not suitable for undergraduate syllabus [5].

Our description of the relation between FP and group theory is useful for teaching stereoisomerism in physical organic chemistry classes and demonstrates how the group theory can be applied to describe symmetry operations other than the traditional ones (center of inversion, symmetry axis, symmetry plane). Many chiral molecules do not possess any standard symmetry elements and thus may not appear amenable to group theoretical description. Nonetheless, group theoretical analysis is of general nature and can involve symmetry operations other than inversion, rotation or reflection as illustrated in this note.
References and Notes:


