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Chiral or Achiral Paths of Steepest Descent and Transition States: A Permutational Approach

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Abstract: Previous work has shown that the permutations describing degenerate isomerizations may be classified according to two important criteria: (1) their behavior with respect to reflection symmetry; (2) their self-inverse or non-self-inverse character. By analysis of the relationship between these two points of view, it is shown that, for degenerate isomerizations, it is possible to predict whether achiral paths of steepest descent and transition states are allowed on the basis of group theoretical properties of the permutations describing the molecular symmetry and the considered isomerization. Examples of chemical interest are discussed.

1. Introduction

The development of mathematical tools relevant to static and dynamic stereochemistry was initiated 10 years ago.[1-8] In these approaches, chemical concepts such as reaction paths, molecular configurations, and indistinguishable rearrangements or reactions have been related to mathematical objects such as permutations, cosets, and double cosets. This theoretical approach provides a general scheme based on symmetry and applicable in principle to any chemical system. However, as has often been pointed out, permutations describe merely the result of a chemical transformation and do not give direct information about the reaction path itself.

In spite of this restriction, the permutational approach has played an important role in dynamic stereochemistry. For instance, the interpretation of NMR line shape results concerning nonrigid molecules of high symmetry has been improved by the systematic use of permutational analysis.[9,10] Moreover, it is clear that the structure of the groups involved in the description of stereochemical transformations is related to important concepts such as stereochemical correspondence[11,12] and residual stereoisomerism.[13,14]

Five years ago, Stanton and McIver[15] derived very elegant group theoretical properties of reaction paths. These "selection rules for the transition states of chemical reactions" allow information to be obtained about the symmetry of transition states (TS) if the symmetry of the reactant and the permutation describing the reaction are known. Almost simultaneously, Pechukas[16] showed that the conservation of nuclear symmetry along paths of steepest descent (PSD) implies that "a transition state cannot have symmetries not shared by the reactants and products of the transformation it mediates" and that for degenerate reactions extra symmetries (interchanging reactant and product) of the TS are possible.

More recently, Nourse[17] has analyzed self-inverse (SI) vs. non-self-inverse (NSI) degenerate isomerizations: only SI degenerate isomerizations can traverse a transition state with symmetries that exchange reactant and product.

Even if permutations do not tell us how a reaction proceeds, this overview shows that many important properties of potential surfaces, reaction paths, and transition states are related to group theoretical properties. In the present paper, we derive some results that are in the same spirit. We first (section 2) discuss the relation between two important criteria that have been used to classify permutational rearrangements. The first of these criteria, which is related to chirality, has been formulated by Ruch[2] and Klemperer[6] and distinguishes between rotation and reflection symmetry of steric courses. The second one is the SI or NSI character introduced by Nourse.[17] We show that these two criteria, although apparently independent, are in fact related to each other. By combining them, we show that five different types of permutational rearrangements are possible.

From the permutational properties related to the above two criteria, we show that it is possible to predict whether achiral PSD and/or TS are allowed for any given permutational or polytopal rearrangement. This is done in section 3, where examples of chemical interest are discussed.

2. General Discussion

The classification theory of[2,6] permutational rearrangements has led to the definition of sets of permutations describing rearrangements that are equivalent to a rearrangement represented by a given permutation, x. A mode of rearrangements

$$M(x) = (AxA) \cup (A\sigma x\sigma^{-1}A) \qquad (1)$$

is, more precisely, the set of permutations representing rearrangements that are indistinguishable from the rearrangement represented by x because (a) they generate the same final configuration as x from the same initial one and/or (b) they must occur with the same probability as x, because of their symmetry equivalence.

In the above formula, A is the permutational representation of the group of proper symmetry operations of the molecule whose molecular point group (proper and improper operations) may be written

$$G = A \cup A\sigma \qquad (2)$$

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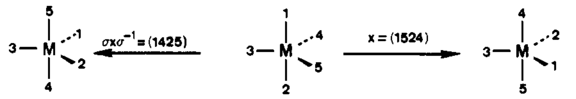

Figure 1. Permutations x and $\sigma x \sigma^{-1}$ lead to the same configuration ($\sigma = (12)$).

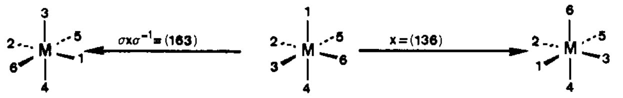

Figure 2. Permutations x and $\sigma x \sigma^{-1}$ lead to different configurations, for any σ; here $\sigma = (25)(36)$.

where σ is any improper operation and $\bigcup$ means "union".

The set $F(x) = AxA$ has been defined[6] as the set of nondifferentiable permutational isomerizations in a chiral environment. In achiral environment, $M(x)$ should be used instead of $F(x)$ (see eq 1 and eq 8 below). It is seen that $M(x)$ is the union of two such sets that are constructed with x and $\bar{x} = \sigma x \sigma^{-1}$ as generators. It has been shown[2,6] that if x leads from an ordered molecule[1] (OM) O_i to O_j, then $\bar{x}$ transforms $\bar{O}_i$ into $\bar{O}_j$, where $\bar{O}_i$ stands for the enantiomeric OM of O_i. If it is possible to describe a given reaction path by x, then the mirror image path can be described by $\sigma x \sigma^{-1}$, a permutation that is symmetry equivalent to x by an improper symmetry operation.

From a mathematical point of view, only two situations are possible: either $F(x)$ and $F(\bar{x})$ have a common permutation or they do not. In the former case they are identical:

$$\text{type I:} \quad AxA = A\sigma x \sigma^{-1}A \tag{3}$$

and in the latter case their intersection ($\bigcap$) is empty (ϕ):

$$\text{type II:} \quad (AxA) \bigcap (A\sigma x \sigma^{-1}A) = \phi \tag{4}$$

When eq 3 is satisfied, it is possible, for any given x, to find an improper operation σ such that $\sigma x \sigma^{-1}$ leads to the same configuration as x, starting from a fixed given one. When eq 4 is satisfied, there exists no such σ, i.e., x and $\sigma x \sigma^{-1}$ must lead to different configurations. These situations are illustrated in Figures 1 and 2, respectively, where the permutations act by "right multiplication",[17] a convention that will be used to describe isomerizations whereas "left multiplication"[17] will be used (see section 3) to compare the symmetries of reactants and products.

Klemperer has proposed the terms achiral or chiral[6] reactions on a mathematical basis, i.e., according to whether eq 3 or eq 4 are respectively satisfied. This is the first criterion. The implications of eq 3 and 4 concerning the chiral or achiral character of a PSD and of a TS will be discussed below.

The second criterion has been introduced more recently by Nourse.[17] In this formulation, the proper and improper symmetry operations are represented in the Hougen group[18]

$$R = A \bigcup A\sigma J \tag{5}$$

where J is the overall inversion about the center of mass. A configuration reached by the permutational rearrangement represented by x is associated to Rx. According to Nourse, the permutational rearrangement is SI if and only if Rx contains at least either a SI element or a pair of mutually inverse elements. Stated in these terms, there is apparently no relation between the two criteria (type I achiral vs. type II chiral and SI vs. NSI).

In fact, we now show that there are three different classes of SI rearrangements, each having a different behavior as far as chirality of PSD and TS is concerned.

Indeed the coset Rx may be split into two cosets relative to the group A of proper symmetry operations:

$$Rx = Ax \bigcup A\sigma Jx$$

and the SI character of the permutational rearrangment may be realized in three distinct ways since the SI element or the pair of mutually inverse elements may appear (a) in Ax only, (b) in $A\sigma Jx$ only, or (c) in both Ax and $A\sigma Jx$. In case a there exists at least one y such that $y = a_i x$ and $y^{-1} = a_k x$ (a_i and $a_k \in A$), which implies

$$Ay = Ay^{-1} \tag{6}$$

or equivalently

$$AxA = Ax^{-1}A \tag{6'}$$

In case b there exists at least one z such that $z = a_i \sigma x J$ and $z^{-1} = a_k \sigma x J$, which implies

$$z = \sigma y J$$

$$A(\sigma y) = A(\sigma y)^{-1} \tag{7}$$

$$A\sigma x \sigma^{-1}A = Ax^{-1}A$$

since type J commutes with any permutation and where y is defined as in eq 6. From eq 6 and 7 it is clear that in case c eq 3 is always obeyed (type I). Conversely, when eq 3 is satisfied, cases a and b are excluded. Therefore, cases a and b are automatically of type II, and SI rearrangements refer to three distinct situations: Ic, IIa, and IIb. Since two situations (types I and II) are possible for NSI rearrangements, five distinct situations have to be considered. These five situations are in direct connection to the structure of the extended modes of rearrangements[5,19,20] defined by

$$M_{\text{ext}}(x) = (AxA) \bigcup (A\sigma x \sigma^{-1}A) \bigcup (Ax^{-1}A) \bigcup (A\sigma x^{-1}\sigma^{-1}A) \tag{8}$$

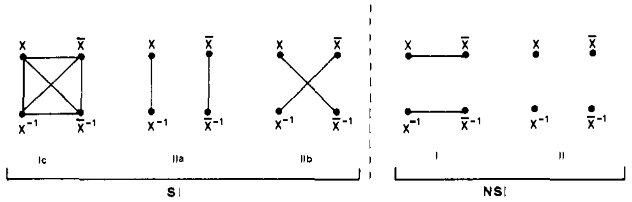

Figure 3. Structure of the extended modes of rearrangements.

This is represented in Figure 3, where the dots x, $\bar{x}$, x^{-1}, and $\bar{x}^{-1}$ stand respectively for each of the double cosets of eq 8 ($\bar{x} = \sigma x \sigma^{-1}$) and where a link between two dots means the equality of the corresponding double cosets. Hence the four double cosets in eq 8 may be all distinct, all identical, or pairwise identical.

3. Chirality or Achirality of the Paths of Steepest Descent and the Transition States

Using previous results[16,17] and the classification of Figure 3, we can now construct A_T, the largest group of proper symmetry operations of the TS, and R_T, its largest point group. We assume as in previous work,[16] that the transition state is a simple saddle point directly linked to reactants and products by paths of steepest descent. It is interesting to find out that different structures of A_T and R_T result from the five possible situations of Figure 3. Indeed, let $\tilde{A}$ denote the group of proper symmetry operations common to the starting (S) reactant and final (F) product configurations:

$$\tilde{A} = A_S \bigcap A_F = A \bigcap (x^{-1}Ax) \tag{9}$$

where the permutations of $\tilde{A}$ act by "left multiplication".[17] A similar definition may be adopted for $\tilde{R}$:

$$\tilde{R} = [A \bigcap (x^{-1}Ax)] \bigcup J[(A\sigma) \bigcap (x^{-1}A\sigma x)] \tag{10}$$

According to Pechukas[16] $\tilde{A}$ ($\tilde{R}$) is the largest group of proper symmetry operations (point group) of any nonstationary configuration on the PSD. For rearrangements of type II, there are no improper symmetry operations common to S and F. The second

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Table I. Largest TS Symmetry Groups (Achiral Molecules)

	$\tilde{R}$ (PSD)	A_T (TS)	R_T (TS)
NSI I	$\tilde{A} \cup \tilde{A}\tilde{\sigma}J$	$\tilde{A}$	$\tilde{A} \cup \tilde{A}\tilde{\sigma}J$
II	$\tilde{A}$	$\tilde{A}$	$\tilde{A}$
SI Ic	$\tilde{A} \cup \tilde{A}\tilde{\sigma}J$	$\tilde{A} \cup \tilde{A}y$	$\tilde{A} \cup \tilde{A}y \cup \tilde{A}\tilde{\sigma}J \cup \tilde{A}\tilde{\sigma}yJ$
IIa	$\tilde{A}$	$\tilde{A} \cup \tilde{A}y$	$\tilde{A} \cup \tilde{A}y$
IIb	$\tilde{A}$	$\tilde{A}$	$\tilde{A} \cup \tilde{A}\tilde{\sigma}yJ$

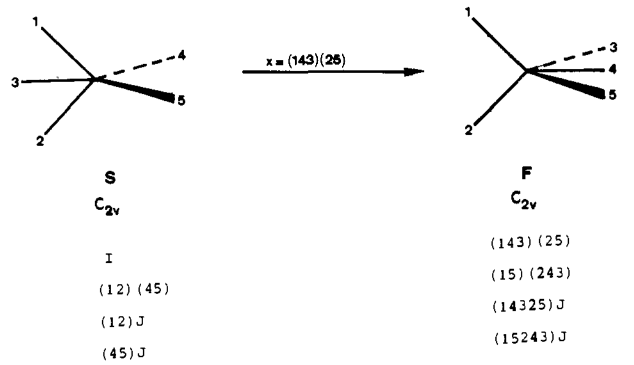

Figure 4. NSI permutational rearrangement of type I (achiral molecule).

term of eq 10 is then absent. Hence for SI rearrangements of types IIa and IIb and for NSI rearrangements of type II:

$$\tilde{R} = \tilde{A} \tag{11}$$

whereas for rearrangements of types Ic (SI) and I (NSI):

$$\tilde{R} = \tilde{A} \cup \tilde{A}\tilde{\sigma}J \tag{12}$$

where $\tilde{\sigma}$ is an improper operation common to S and F, i.e., belonging to the second term in eq 10.

The groups A_T and R_T are now easily obtained.[17] In case a $R_T = \tilde{A} \cup \tilde{A}y$, whereas in case b $R_T = \tilde{A} \cup \tilde{A}z = \tilde{A} \cup \tilde{A}\tilde{\sigma}yJ$ from the relation between y and z (see eq 7). The group A_T is easily obtained from R_T. For NSI rearrangements A_T (and R_T) coincides with $\tilde{A}$ (and $\tilde{R}$). In Table I, the structure of the groups A_T and R_T are shown for each of the five possible situations of Figure 3. This table deserve several comments in view of a comparison with previous work.

(A) For NSI rearrangements, Table I distinguishes between type I and type II rearrangements. It should be noted that the terms "achiral" and "chiral" have been used by Klemperer[6] to distinguish steric courses where eq 3 is satisfied from those where eq 4 is obeyed. For NSI rearrangements, this terminology applies as well to PSD as to simple saddle points (TS). Indeed, when eq 3 is obeyed (type I) both PSD and TS appear to be possibly achiral in Table I. Both must be chiral when eq 4 is obeyed (type II) as shown in this table. We now describe some examples of NSI rearrangements.

An example of type I is shown in Figure 4, where we consider an hypothetical C_{2v} pentacoordinate structure. Such a geometry has been discussed in a MO study of the role of BH_5 in the hydrolysis of BH_4^-.[21] The mechanism assumed in Figure 4 consists of a migration of hydrogen 3 from an equatorial position on the C_2 axis in S toward an equatorial position out of the C_2 axis in F. As a result, hydrogens 1 and 2, which are axial in S, become equatorial in F. As shown by the coset Rx describing F, this stereochemical change is NSI. The PSD and TS can only have symmetry operations common to both S and F, i.e., the plane containing B and hydrogens 3–5 expressed by $(12)J$. Hence the PSD and TS could be achiral as shown by Figure 4. Realistic NSI rearrangements of type I seem, however, to be rather uncommon.

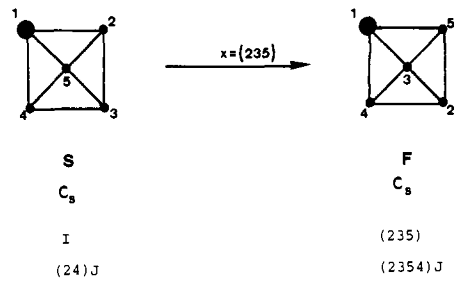

Figure 5. NSI rearrangement of type II (achiral molecule).

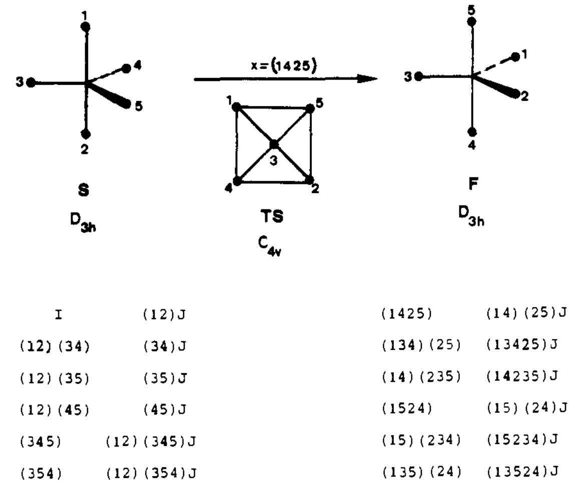

Figure 6. Berry mechanism, a SI rearrangement of type Ic (achiral molecule).

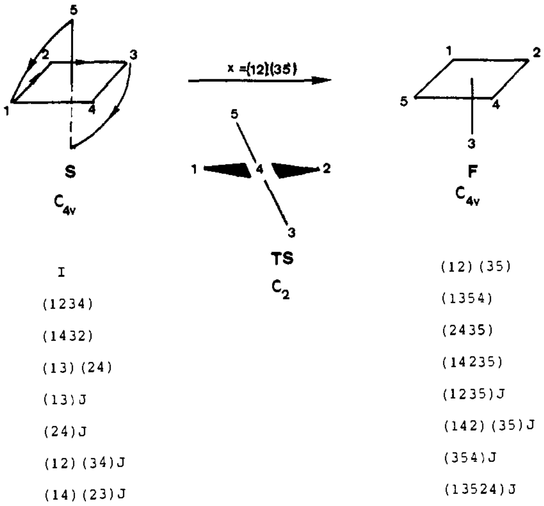

Figure 7. SI rearrangement of type IIa (achiral molecule).

In Figure 5 we show a NSI permutational rearrangement of type II. This figure consists of an axial view of a tetragonal pyramid with four ligands A and one ligand B (the large dot) in basal position, a situation that could occur if B is more electronegative than A.[22] Since the rearrangement is NSI and since there are no improper symmetry operations common to S and F, the PSD and TS *must* be chiral.

(B) For SI rearrangements, Table I shows that the order of R_T is twice the order of $\tilde{R}$, as shown by Nourse.[17] Note, however, that the order of A_T is not always twice the order of $\tilde{A}$. The distinction between cases IIa, IIb, and Ic provides interesting informations about the chirality of SI rearrangements. Case Ic is "achiral" according to Klemperer[6] since eq 3 is obeyed. In this case indeed as shown by Table I both PSD and TS might display improper symmetry operations. Cases IIa and IIb are "chiral" since eq 4 is obeyed. The PSD *must* indeed be chiral ($\tilde{R} = \tilde{A}$ for these cases). For case IIa the TS *must* also be chiral (R_T has

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Table II. Largest TS Symmetry Groups (Chiral Molecules)

	A_T	R_T
NSI enantiomerization	$\tilde{A}$	$\tilde{A}$
no enantiomerization	$\tilde{A}$	$\tilde{A}$
SI enantiomerization	$\tilde{A}$	$\tilde{A} \cup \tilde{A}yJ$
no enantiomerization	$\tilde{A} \cup Ay$	$\tilde{A} \cup \tilde{A}y$

no improper operations), whereas for case IIb, achiral TS are allowed due to the presence of SI improper elements $\tilde{\sigma}yJ$ in R_T. We now briefly discuss examples of SI rearrangements.

The Berry mechanism[23] is an example of SI rearrangement of type Ic. As may be seen on the coset of configuration F in Figure 6, SI elements appear in both Ax and $A\sigma xJ$ (respectively (1425), (1524), (14)(25)J, and (15)(24)J). The C_{4v} TS proposed for this mechanism has improper symmetry operations that are (i) common to both S and F, i.e., (12)J and (45)J and are (ii) of SI origin, i.e., (14)(25)J and (15)(24)J. The isomerization of cyclopropane[24,25] and the inversion of ammonia are other examples of type Ic.

For SI rearrangements of type IIa as for NSI rearrangements of type I it seems difficult to find a realistic example. In Figure 7 we show a hypothetical rearrangement of this type. There are no symmetry elements common to S and F. It is also seen that the only SI element is (12)(35), which belongs to Ax. Hence for the most symmetrical TS compatible with this steric course, one has $A_T = R_T = \{I,(12)(35)\}$. A mechanism that looks plausible (on symmetry basis at least) is proposed in Figure 7. Achiral PSD and/or TS are of course excluded.

It is very easy to find examples of chemical interest for SI rearrangements of type IIb. For instance, the isomerizations of homoprismyl and of heptamethylcyclohexadienyl cations discussed by Nourse,[17] the Bailar[5,26] twist for hexacoordinate complexes (see Figure 2), and the internal rotation of ethane[16] are of this type. In all these cases, the S and F configurations have no common improper symmetry operations, which excludes an achiral PSD, but an achiral TS is allowed because of the SI character of these rearrangements.

So far, we did consider only achiral molecules. The above discussion is, however, easy to apply to chiral molecules. Indeed, in such a case $R = G = A$ (see eq 2 and 5) and the distinction between type I and II becomes meaningless. Hence, if x is a permutation, the coset representing the product is either Ax or AxJ. The latter expression refers to the situation where S and F are enantiomers (labels *not* included). For SI transformations, a self-inverse element will therefore either be noted y or yJ. The various possibilities are shown in Table II. It is seen that the transformations of chiral molecules proceeding without enantiomerisation cannot traverse achiral transition states ($R_T = A_T$). Achiral transition states for chiral molecules are only allowed for SI enantiomerizations.

Examples for each of the cases listed in Table II are now given. The internal rotation of a chiral ethane derivative discussed previously[17] is a NSI rearrangement without enantiomerization, whereas the classic example of the mesobiphenyl compound[27] is a NSI enantiomerization when steric hindrance prevents the phenyl rings from being coplanar. Achiral TS are excluded for these two examples. In the absence of steric hindrance, the enantiomerization of mesobiphenyl might proceed through an achiral transition state (coplanar phenyl rings). It is easy to verify that this steric course is SI. The enantiomerization of the 2-brexyl cation[17] and the internal rotation of hydrazine are both SI enantiomerizations of chiral molecules. In Figure 8, the achiral TS has $A_T = \{I,(14)(23)\}$ and $R_T = \{I,(14)(23),(13)(24)J,(12)(34)J\}$. The improper symmetry operations are due to the SI character of this enantiomerisation. Examples of the same type have been discussed in detail in previous work.[28] The interconversion of the chiral structures **1** and **1′** in ref 28 might proceed through the achiral TS **2**. This is a SI enantiomerization. Note that **3** and **3′** in this reference have lower symmetry (C_1) than that predicted by the largest TS symmetry group (C_s). Such lower symmetry reaction path and TS are of course conceivable for any of the examples discussed above. The interconversion of chiral boat conformations of 6,6-dimethyl-1,3-dioxacyclooctane is another SI enantiomerization[25] (Figure 12 (I) of ref 25). A last example, the Berry pseudorotation of a trigonal bipyramid with a chiral equatorial ligand, is a SI rearrangement without enantiomerization.[17]

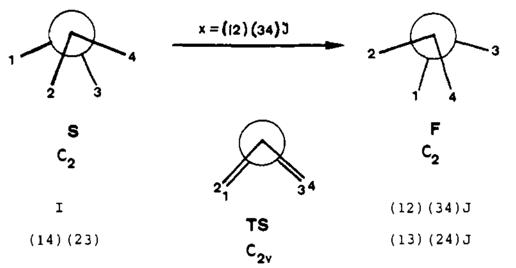

Figure 8. Internal rotation of hydrazine: a SI enantiomerization.

Finally, we discuss briefly polytopal[6] rearrangements, which are characterized by the fact that S and F have different geometries and energies, whereas for degenerate rearrangements S and F have by definition identical geometries and energies. Hence, as shown previously[16] for polytopal rearrangements, the only symmetry operations for the PSD and TS are those common to S and F. In particular, only polytopal rearrangements of type I, i.e., satisfying a relation similar to eq 3, have improper symmetry operations common to S and F and might possess achiral PSD and traverse achiral TS.

4. Conclusions

When using permutations to describe the steric course of a rearrangement, one merely compares the initial and final positions of the nuclei on a molecular skeleton. In principle, no information about the trajectory of these nuclei is available from these permutations. However, if one assumes a movement along a path of steepest descent and through a transition state directly connecting reactant to product, then the permutations describing the rearrangement determine very important symmetry properties of the trajectory.[16,17]

From previous work, it is known that the permutation describing a steric course is involved in two important criteria. The first one is related to its behavior with respect to reflection symmetry.[1-8] The second one is the SI or NSI character of the rearrangement.[17] We have shown that these two criteria are interrelated in spite of their apparent independence. By combining them, we are led to consider five different types of permutational rearrangements. For each of these types, we show that it is possible to predict whether achiral PSD and TS are allowed on the basis of purely permutational properties.

Of course, the description of a reaction path in terms of PSD is not the only possible one.[29] It might be interesting to examine whether other descriptions could lead to similar informations about the symmetry of the reaction path.

To conclude, we think that this work is another example of the physical relevance of the permutational analysis of steric courses and reaction paths.[30]

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