possibilities have been considered:[7] the twisting may be caused by the interaction between the micelles through dispersion forces or the primary effect of the chiral compound may be to distort the micelles so that they themselves assume a chiral structure. Theoretical considerations show that disk-shaped micelles are distorted in first order with the concentration of a chiral compound while cylindrical micelles do not have a first-order effect.[13] The observation that the twisting power of BS is indeed stronger in the N_L phase is in agreement with this conclusion. We intend to verify the importance of the second mechanism by a more extensive study of the concentration dependence of the induced twist in the N_C phase.

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(13) Allender, D.; Saupe, A., to be published.

Self-Inverse and Non-Self-Inverse Degenerate Isomerizations

James G. Nourse

Contribution from the Department of Chemistry, Stanford University,
Stanford, California 94305.
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Abstract: All possible degenerate isomerizations of any chemical structure can be rigorously separated into two classes on the basis of an intrinsic group-theoretical symmetry property of the structure and its 3N-dimensional coordinate space. These classes are as follows: (1) self-inverse (SI) degenerate isomerizations for which there is a coordinate-space symmetry which exchanges reactants and products and (2) non-self-inverse (NSI) degenerate isomerizations for which there is no such coordinate-space symmetry. SI processes always have forward and reverse paths between reactant and product which "look alike". NSI processes do not generally have such "look alike" paths. Following others' earlier results on symmetry properties of saddle point transition states directly connecting reactant and product by paths of steepest descent, it is shown that SI processes can in principle proceed through such transition states with symmetries which exchange reactant and product. NSI processes can never proceed through such transition states with any more symmetry than that common to reactant and product. While NSI possibilities are statistically more abundant, SI processes tend to be favored for structures with any symmetry because of limitations on the kinds and orientations of symmetries possible in three-dimensional space, thus confirming empirical observations. The two classes could be conveniently differentiated experimentally in favorable cases by using two-dimensional NMR, and rules for predicting idealized spectra are given.

Degenerate isomerizations can be defined as those chemical reactions which lead to products differing from the reactants only by permutation of identical atoms and possible mirror-image reflection.[1] This definition encompasses cases in which both reactants and products include more than one molecule. While such reactions form a small subset of all possible reactions, they have been well studied in their own right.[1] It is the intention of the present work to show that degenerate isomerizations of structures with N atoms can be rigorously divided into two classes on the basis of an intrinsic symmetry property of the 3N-dimensional coordinate space describing all possible arrangements of the N atoms. The symmetry group of this coordinate space includes all the possible permutations of identical atoms in the set of N atoms along with the operation of overall coordinate inversion. It is this subgroup of the overall symmetry group of the coordinate space (which also includes spatial rotations and translations) that will be explicitly considered here. Operations in this symmetry group will permute the possible products and reactants of degenerate isomerizations.

The present work is divided into five principal sections. The first section describes the representations of symmetry operations and isomerizations necessary to visualize the later results. The second section presents the intrinsic symmetry property of the coordinate surface which allows the classification of degenerate isomerizations into two types and discusses the effect of the coordinate surface symmetry operations on the possible paths connecting the reactants and products of degenerate isomerizations. The third section discusses properties of intermediates and transition states for the two possible types. Here the potential energy surface is considered in addition to the coordinate space. The fourth section addresses the question of whether either type of degenerate isomerization is likely to be preferred (either statistically or energetically). The final section discusses experimental differentiation of the two types, primarily by two-dimensional NMR.

Table I. Correlation of Group-Theoretical Concepts and Their Chemical Representations

group-theoretical concept	chem representation
cosets	isomers based on atom numbering
right multiplicatn based on ref numbering	degenerate isomerizatns
left multiplicatn based on atom nos.	coordinate-space sym

1. Representation

It is necessary to choose a representation of the coordinate-space symmetry operations and isomerizations to work with and to aid visualization of the results of this work. McIver and Stanton have noted a difficulty with this visualization of permutation operations in their work on the symmetry properties of transition states.[2] It should be noted that other representations are possible but that the key result is intrinsic to the underlying group-theoretical structure and does not depend on the particular representation chosen. Three features of this representation must be described along with their correspondence to chemical concepts. These are summarized in Table I.

In any given structure all the atoms are numbered to distinguish them. In addition, one of the possible isomers (based on the atom numbers) of the structure being considered is chosen as a reference

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(1) Leone, R. E.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 860.

(2) Stanton, R. E.; McIver, J. W., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 3632.

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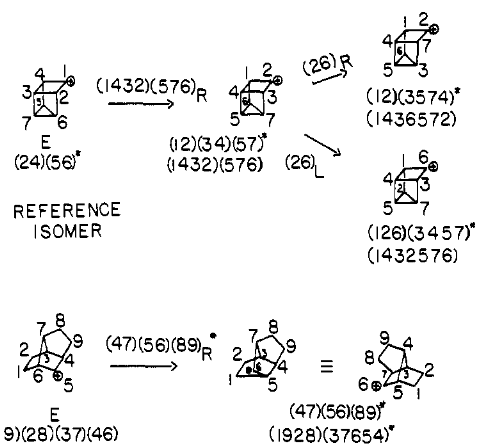

Figure 1. Degenerate isomerizations of the homoprismyl (top) and 2-brexyl (bottom) cations illustrate the operation and multiplication of permutations. The reference numbered isomer is on the left in each case and has its symmetry group listed underneath it. Under the other isomers are lists of the cosets of permutations which convert the reference isomer to that isomer.

structure (see Figure 1). For this structure only the atom numbers and reference numbers will coincide. For a given structure, which may undergo degenerate rearrangement, there are two permutation groups which are important. The first is the symmetry group, *P*, of the structure. This will generally be the point group for the structure but may be a nonrigid symmetry group as defined by Longuet-Higgins.[3] The notation of Longuet-Higgins is adopted here, and reflective operations are represented as permutation inversions which are atom permutations coupled with overall coordinate inversion (represented by an asterisk). This inversion operation acts on the spatial coordinates of the atoms in all structures including the reference structure. The second permutation group, *G*, is a symmetry group of the 3*N*-dimensional coordinate space. This group includes all the possible permutations of equivalent atoms and the overall coordinate inversion operation. All the possible isomers (based on the different atom numbers) of the structure correspond to the cosets of *P* in *G* (see Appendix A2).

Consider the structures shown in Figure 1. The reference-numbered structure is shown on the left in each case. Under each reference structure is the list of the permutations in its symmetry group, *G*. Under the other structures are the cosets of the symmetry group which include all the permutations that convert the reference structure to that structure. Isomerizations are expressed as permutations of atoms on the basis of the reference numbering and are independent of the atom numbering, and this must be taken into account when analyzing multistep isomerizations. Consider the isomerizations of the homoprismyl cation shown in Figure 1 (only the carbons are explicitly considered here). The second (hypothetical) isomerization, designated $(26)_R$, refers to the reference numbering (the leftmost structure) and not to the atom numbers. The first isomerization, designated $(1432)(576)_R$, acts on the reference structure so that the atom numbers and reference numbers coincide. Thus the problem of double labeling of atoms and reference structures can be largely avoided by analyzing one-step isomerizations with just the reference structure. This practice will be followed throughout the remainder of this work. The operation of permutations as isomerizations is referred to as the right action of the permutation, and the subscript R is used. The symmetry operations in the group *P* (usually the point group of the structure) are of this type also.

The desired visualization of the coordinate-space symmetry operations is achieved by another operation of the permutations. These permutations act on the atom numbers, are designated by the subscript L, and are referred to as the left action of the permutation. The effect of these permutations on structures is easily followed, and an example is shown in Figure 1. These permutations act by left multiplication on the cosets and in this way permute the possible isomeric structures (see Appendix A4 for details). On the coordinate space these permutations permute the three coordinate axes for each atom with the three axes for another atom.

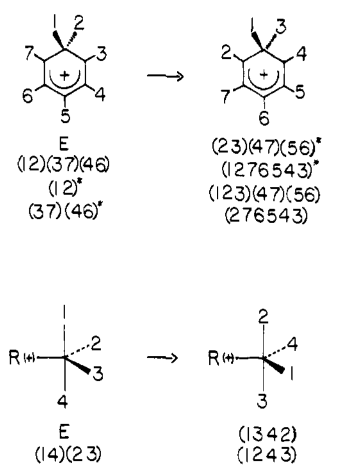

Figure 2. Two examples of self-inverse (SI) degenerate isomerizations. The reference numbered isomers are on the left and have their symmetry groups listed under them. The first example (top) is a methyl migration of a heptamethylcyclohexadienyl cation. The isomerization shown is effected by the permutation (276543). The other permutations in the list (coset) under the product (on right) would accomplish the same overall change. The second example (bottom) is a Berry pseudorotation of a trigonal-bipyramidal structure with a chiral ligand. The isomerization shown is effected by the permutation (1342).

Degenerate isomerizations of chiral structures are easily accommodated as shown by the example in Figure 1. Note that structures which have an enantiomeric skeleton (apart from atom numbers) to the reference structure will always be represented by a coset in which all permutations have a coordinate inversion (an asterisk) attached. Part of the reason for the choice of the permutation-inversion representation of Longuet-Higgins is the ease in dealing with chiral structures.[4]

2. Principal Symmetry Property

The principal symmetry property is the following. All possible degenerate isomerizations fall into two classes: (1) self-inverse (SI) degenerate isomerizations in which the reactant and product are exchanged by some symmetry operation of the coordinate space; (2) non-self-inverse (NSI) degenerate isomerizations in which the reactant and product are not exchanged by any symmetry operation of the coordinate space. There will be a symmetry operation of the coordinate space which takes reactant to product and another (its inverse) which takes product to reactant for a NSI isomerization but there will be none which actually exchanges the two. This seemingly trivial distinction is nevertheless the basis for the twofold classification and a number of interesting different properties of the two types of isomerizations. It should be emphasized that this is an intrinsic property of the structures of the two symmetry groups involved. Thus once the groups *P* and *G* are chosen, the self-inverse and non-self-inverse property is established and does not depend on further properties of the representation used or even the chemical system being studied.

Each possible pair of isomers is a self-inverse pair if a coordinate-space symmetry operation exchanges the members of the pair and a non-self-inverse pair if there is no such symmetry operation. The simplest method of determining whether a pair of isomers is a self-inverse pair is to use the coset representation developed above. If one of the pair is designated the reference isomer, the other is represented by a coset of the symmetry group of the reference isomer. If this coset contains a permutation of order 2 or a permutation of higher (only even) order and its inverse,

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[3] Longuet-Higgins, H. C. *Mol. Phys.* **1963**, *6*, 445.

[4] Nourse, J. G. In "The Permutation Group in Physics and Chemistry"; Springer-Verlag: New York, 1979; p 28.

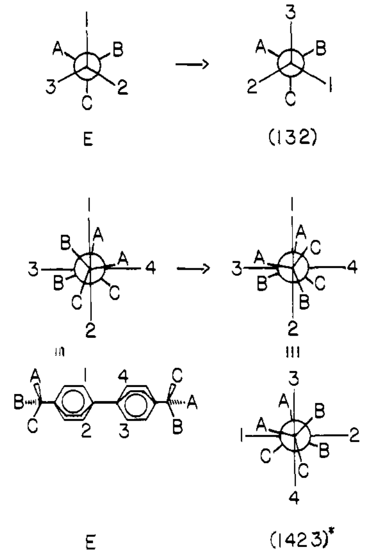
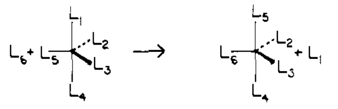


Figure 3. Two examples of a non-self-inverse (NSI) degenerate isomerization. The first example (top) is the internal methyl rotation of a chiral ethane derivative. The second example is the racemization of a meso-substituted biphenyl derivative by rotation of the front chiral ligand by 180°. The starting structure is shown in both an end-view and a side-view. The final structure is shown in two end-views. The enantiomeric relationship is emphasized by comparison of the end-view of the starting structure and the lower end-view of the final structure.

then the two isomers are a self-inverse pair and a degenerate isomerization taking one to the other is a self-inverse degenerate isomerization. The coordinate-space symmetry operation is represented by the left multiplication of the permutation of order 2 (or one of the inverse pair) on the cosets and will exchange them. Examples of SI isomerizations are shown in Figure 2. The heptamethylcyclohexadienyl cation migration shown is a SI process since the coset for the product has a permutation of order 2. The Berry pseudorotation of the chiral-substituted trigonal-bipyramidal structure is SI because the coset contains a permutation and its inverse. It is assumed that there is free rotation about the bond to the chiral ligand. A simple example of a NSI process is the rotation of a methyl group bonded to a carbon with three different substituents (Figure 3). A structure and its enantiomer (obtained by overall coordinate inversion) will always be a SI pair since the inversion operation is of order 2. However it does not follow that a structure and any enantiomeric structure will be a SI pair. An example of a NSI enantiomeric pair is shown in Figure 3 (last example) and is based on the classic *meso*-biphenyl compound discovered by Mislow.[5a]

A simple consequence of this coordinate-space symmetry condition is that there are forward and reverse reactions between SI pairs which "look alike" since paths between members of SI pairs are also exchanged by the coordinate-space symmetry operation. Thus for any path from A to B where A and B are a SI pair of isomers, there is a symmetrically equivalent reverse path from B to A. The forward and reverse paths may be the same path (i.e., the path is symmetric; see next section), but this need not be the case. The forward and reverse "look-alike" paths may also be enantiomeric as would be the case for a 1,2-methyl shift path for the hexamethylcyclohexadienyl cation migration shown in Figure 2. NSI pairs do not have this symmetry property so that there is not necessarily a reverse path symmetrically equivalent to a forward path connecting two members of a NSI pair and in general the reverse reaction will "look different" from the forward path. The difference may be subtle as in the case of the methyl group rotation in Figure 3. Clockwise rotation puts the hydrogen between atoms A and B closer to atom B. The reverse counterclockwise rotation puts it closer to atom A. Because atoms A and B are different, these slightly rotated structures are different and the forward and reverse reactions do not "look alike". If atoms A and B were identical, the forward and reverse rotations would be enantiomeric and the rotation would be self-inverse (SI). The difference is fairly obvious in the case of the NSI substitution reaction (eq 1) involving six equivalent ligands, which involves



1 2 (1)

equatorial replacement in the forward direction and axial replacement in the reverse direction.[6] There will often be forward and reverse paths between members of NSI pairs which "look alike" and go through other symmetrical intermediates (i.e., those with symmetry elements not present in either member of the NSI pair). These intermediates may be isomeric with the reactant and product. (See example in ref 6a, p 4573.) In such cases, each step of the multistep path will look like one reverse step but there will be no overall coordinate-space symmetry operation which exchanges the two ends of the path. (See example in section 4.)

The principal point here is that SI pairs of isomers will always have symmetrically related forward and reverse paths connecting them. This property has been made use of in some detailed studies of examples of SI degenerate isomerizations.[5b-d] NSI pairs of isomers will not in general have symmetrically related forward and reverse paths connecting them. Any forward path connecting a NSI pair will in general "look different" from any reverse path although the difference may be subtle.

3. Properties of Intermediates and Transition States

The available transition states for SI and NSI degenerate isomerizations differ in their symmetry properties on the basis of the rules of Stanton and McIver[2] and Pechukas.[7] These authors have established that only degenerate isomerizations can ever proceed through transition states with more symmetry than that common to reactants and products. Furthermore, the additional symmetry must exchange reactants and products. The assumptions of Pechukas[7] concerning saddle point transition states directly connected to reactant and product by paths of steepest descent will be adopted here. The term "transition state" will be used in this sense throughout this work. The possible symmetries of transition states are easily computed by using the present representation.

The existence of a coordinate-space symmetry operation which exchanges the members of a SI pair of isomers assures the existence of structures in the space which are fixed by this symmetry operation. These structures are available as transition states or intermediates for SI degenerate isomerizations. This is merely a statement of existence, and there is no assurance that these structures are energetically feasible or even chemically reasonable. By contrast, NSI degenerate isomerizations have no such symmetrical structures available. Thus only SI processes can in principle proceed through transition states which have symmetries that exchange reactants and products. The additional symmetry operations need not be of order 2 but must be of even order. In cases in which the transition state has this additional symmetry,

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(5) (a) Mislow, K.; Bolstad, R. *J. Am. Chem. Soc.* **1955**, *77*, 6712. (b) Burwell, R. L., Jr.; Pearson, R. G. *J. Phys. Chem.* **1966**, *70*, 300. (c) Wolfe, S.; Schlegel, H. B.; Csizmadia, I. G.; Bernardi, F. *J. Am. Chem. Soc.* **1975**, *97*, 2020. (d) Salem, L. *Acc. Chem. Res.* **1971**, *4*, 322.

(6) (a) Nourse, J. G.; Mislow, K. *J. Am. Chem. Soc.* **1975**, *97*, 4571. (b) A recently published example by Barltrop et al.[6c] may help the visualization of this distinction between SI and NSI isomerizations. They have given the 12 symmetry distinct permutation processes for a six-membered ring. With use of their nomenclature in their Figure 1, patterns P_5 and P_7 are NSI and the reverse of each other. In this case the forward and reverse reactions "look different" (i.e., if the forward reaction looks like P_5, the reverse looks like P_7). Similarly, P_6 and P_{10} are NSI and the reverse of each other. The remaining eight patterns are SI and for these forward and reverse "look alike". This result can be verified by noting that the twelve patterns correspond to the double cosets $D_6/S_6\backslash D_6$ and that eight of these are self-inverse and four are non-self-inverse (See Appendix A3, A5.) (c) Barltrop, J. A.; Barrett, J. C.; Carder, R. W.; Day, A. C.; Harding, J. R.; Long, W. E.; Samuel, C. J. *J. Am. Chem. Soc.* **1979**, *101*, 7510.

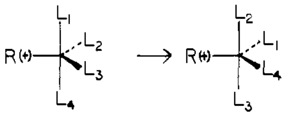
(7) Pechukas, P. *J. Chem. Phys.* **1976**, *64*, 1516.

Table II. Percentage of Possible Degenerate Isomerizations Which are Self-Inverse (SI) for N Atoms and Particular Symmetries

	N						
sym[a]	2	3	4	5	6	7	8
e	100	60	39	21	10	4.6	1.9
$2^{(n/2)}$	100	100	64	45	20	9.1	3.8
$2^{(n/2-1)}$		100	64	41	22	9.4	3.8
$3^{(n/3)}$		100	100	67	32	14	5.6

[a] Symmetry is expressed as a permutation cycle. For $N = 5$, $2^{(5/2)}$ means a single twofold symmetry operation of cycle type (12)(34); $2^{(5/2-1)} = 2^{(3/2)}$ means a single twofold operation of cycle type (12).

the potential surface will be symmetric with respect to these symmetry operations since the two sides of the barrier are also exchanged by the coordinate-space symmetry operation. The SI processes pictured in Figures 1 and 2 all have available intermediates or transition states which have symmetry that exchange reactants and products. This additional symmetry is easily computed by examination of the cosets representing the isomers of the SI pair (as long as one is the reference isomer). If the top permutation in the coset is of order 2 or is one of the permutations whose inverse is also in the coset (note that any permutation can be used to generate the coset and therefore be the top permutation; see Appendix A2), then the largest symmetry group available for the transition state is the set of order 2 elements and inverse pairs in the coset plus the permutations of the reference structure symmetry group which are next to them. (See Appendix A7 for an explanation of why this procedure works.) This procedure indicates that the carbonium ion isomerizations in Figures 1 and 2 can go through transition states with reflective symmetry (since the permutations which are recovered this way have an asterisk) and the Berry pseudorotation in Figure 2 has an available transition state with fourfold symmetry. By contrast the intramolecular SI isomerization (eq 2) does not have an easily accessible transition state with D_2 symmetry, the largest symmetry group available for a transition state and computed by the above method. (The bond to the chiral ligand R(+) would have to be broken and reformed.) NSI degenerate isomerizations cannot proceed through a transition state with any symmetry beyond that common to both the reactant and product since there are no available structures with symmetry which exchange reactant and product. Thus, NSI degenerate isomerizations have no more symmetry available to their potential transition states than do nondegenerate isomerizations.



(2)

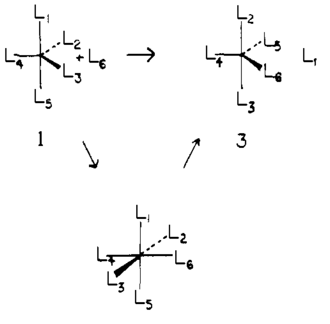
e (12)(34)
(14)(23) (13)(24)

4. Is Either Type Preferred?

Since degenerate isomerizations can be separated rigorously into two classes, it is interesting to investigate if one class either is preferred either statistically or energetically or is preferred for some other reason. While this particular symmetry property (of the coordinate space) does not lead to rigorous selection rules, some definite trends are apparent.

The question of statistical preference is easily answered. Table II gives the percentage of possible degenerate isomerizations which are SI for different numbers of atoms and some common skeletal symmetries. The combinatorial methods used are described in Appendix A5. It is apparent that NSI isomerizations predominate even for small structures (up to 8 atoms of the same type and hence available to be exchanged). This trend continues as the number of atoms increases. The percentage of possible SI isomerizations increases with increasing structural symmetry, and for smaller structures with a lot of symmetry, SI processes are statistically dominant. In spite of the overall dominance of NSI possibilities, SI examples seem to be disproportionately represented among known degenerate isomerizations.[8] Explanations for this trend are offered for both highly symmetric structures and structures with little or no symmetry.

Two reasons can be offered for the dominance of SI processes for highly symmetric structures. The first is the already noted trend toward statistical dominance of SI processes for symmetric structures (Table II). The second reason is that NSI processes are unlikely to be the lowest energy pathways which go through symmetrical stable intermediates (those with more symmetry than reactants or products) as there will often be a SI process which goes through the same intermediate. Such symmetrical structures have already been ruled out as transition states for NSI processes. Consider the hypothetical NSI substitution reaction (**1**–**3**). This



1 **3**

4

(3)

reaction might go through the octahedral intermediate, **4**. This octahedral structure could then expel any of the six equivalent ligands to reform the trigonal-bipyramidal structure. Expulsion of ligand L_4 would yield an overall SI process of equal energy to the NSI process (expulsion of ligand L_1). This situation (existence of an available SI process) will occur whenever the intermediate has an additional symmetry element of order 2 that is not present in both the reactant and product. It is relatively rare (although possible) for the symmetry of a structure to increase by adding only symmetry operations of order larger than 2.[9]

The overall NSI sequence in this example (expulsion of ligand L_1 of the octahedral intermediate **4**) provides an example in which forward and reverse paths connecting a NSI pair of isomers "look alike". This occurs because of the greater symmetry of the octahedral intermediate, **4**, in which all the ligands are equivalent. On the $3N$-dimensional coordinate surface there is a symmetry operation which fixes structure **4** and takes **1**–**3** and another symmetry operation (its inverse) which takes **3**–**1**. Since the paths go through this intermediate **4**, they are also permuted in the same manner.

Another reason for the apparent dominance of SI processes is based on the idea of least motion and the restriction on the possible geometric orientations of symmetry operations in three-dimensional space. The change that occurs during a degenerate isomerization is described by a permutation of atoms (the right action of the permutation described above). If this permutation is of order larger than 2 and the structure has no symmetry, then the isomerization will be NSI. A common situation, however, for degenerate isomerizations is for the structure to have one twofold element of symmetry (usually an axis or plane), and this case will be analyzed in more detail to illustrate factors which favor SI processes.

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[8] (a) Scott, L. T.; Jones, M., Jr. *Chem. Rev.* **1972**, *72*, 181. (b) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1970. (c) Reference 1. (d) Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26. All the examples of degenerate isomerizations discussed in these reviews are self-inverse (SI). While this was not an exhaustive search, the results are puzzling enough in comparison to the statistical dominance of NSI processes shown in Table II to warrant further investigation of the relative likelihood of the two types.

[9] In addition, any even order symmetry elements of order n which are added must when multiplied by themselves $n/2$ times give a symmetry element of order 2 which is common to the symmetry groups of both the reactant and product. An example which satisfies these conditions is the increase of symmetry from C_2 to C_6.

Table III. Self-Inverse (SI) and Non-Self-Inverse (NSI) Possibilities for a Degenerate Isomerization Expressed as a Sixfold Cyclic Permutation with Twofold Symmetry

sym operations	cycle type[a]	no. possible	SI or NSI
σ_v', C_2'	(1)(26)(35)(4)	3	SI
σ_v'', C_2''	(12)(34)(56)	3	SI
C_{2z}, i	(14)(25)(36)	1	NSI
σ_h	(1)(2)(3)(4)(5)(6)	1	NSI

[a] Atoms are numbered consecutively around the hexagon.

Consider a potential NSI process where the permutation describing the isomerization will include one or more cycles of length greater than 2. Consider one of these cycles of length N which can be expressed as $(12...N)$. The overall change of the isomerization is that the new environment of atom 1 is equivalent to the old environment of atom 2, etc. More importantly, the distance from 1 to 2 (as well as the type of bond if any) must become equal to the distance from 2 to 3, etc., the angle 1–2–3 must become equal to the old angle 2–3–4, etc. In principle these changes of structural parameters could occur for any initial orientation of the N atoms; however, in practice, this change will be more likely if the structural parameters which must become equivalent in the product are nearly equivalent in the reactant. This is a simple argument for least motion in the overall process; however, in the present context this restriction leads to interesting results. For a permutation cycle of length N, there are a limited number of orientations of the atoms which have the various structural parameters nearly equivalent. These correspond to perturbations of the possible orientations in which the structural parameters are exactly equivalent (i.e., symmetrical). For example, consider a cycle of length 6. There are three possible symmetric orientations which correspond to the C_6 rotation axis (e.g., benzene), the S_6 alternating axis (e.g., chair cyclohexane), and the S_3 alternating axis (e.g., prismane). Thus a structure undergoing a degenerate isomerization with a permutation cycle of length 6 and with minimal internal motion would have the 6 atoms in an orientation close to one of the three cases. Consider the case of the C_6 rotation. In the structure undergoing degenerate isomerization the 6 atoms would be nearly in a hexagonal orientation. Now the twofold symmetry operation must also have some effect on these 6 atoms. There are only four possibilities which only permute the 6 atoms among themselves, and they can be classified by their permutations of these 6 atoms (Table III). Having established the permutation cycle for the isomerizations and the skeletal symmetry, we determined the type of the degenerate isomerization (SI or NSI), and these are given in Table III also. These are the only possibilities, 75% give SI processes (based on the number possible given in Table III), and 25% give NSI processes. These percentages can be compared with those given in Table II for all possibilities in which NSI processes are more abundant. An example of the SI process with a plane of symmetry is the heptamethylcyclohexadienyl cation migration in Figure 2. An example of a NSI process with a C_{2z} axis would be the pseudorotation of all cis hexamethylcyclohexane in the twist conformation. For cycles with an odd number of atoms, all the possible orientations of twofold symmetry operations with respect to the ring of atoms give SI processes except when the entire ring is in a plane of symmetry. The principal point here is that the choice of permutations for the (minimal motion) degenerate isomerization and the symmetry operations of the structure are not independent on the basis of the limited number of relative orientations of the symmetry operations in three-dimensional space. In the case of cyclic orientations of several atoms with a twofold symmetry element (cases common among known degenerate isomerizations) SI possibilities are more numerous than NSI possibilities.

It is perhaps not surprising that many of the known structures which undergo degenerate isomerizations have some skeletal symmetry. This skeletal symmetry forces some of the structural parameters to be identical in both reactant and product, thus reducing the motion necessary to accomplish this during a degenerate isomerization. Degenerate isomerizations, which are expressed as permutations of order greater than 2 and which involve structures with no symmetry, will be NSI. A common example is the methyl group rotation in Figure 3. Many SI processes will become NSI by adding chiral ligands or some chiral environment to destroy any planes of symmetry. Thus there is no intrinsic difficulty with NSI processes for structures with no skeletal symmetry. The overwhelming statistical dominance of NSI processes in these cases (Table II) may still be misleading because the amount of motion necessary to exchange two atoms or atoms in pairs (a SI process) may often be less than that necessary to exchange larger sets (a NSI process), thus favoring SI processes.

5. Possible Experimental Observation

There is a particularly straightforward way of experimentally distinguishing between SI and NSI degenerate isomerizations in certain favorable cases using a two-dimensional NMR experiment recently described by Meier and Ernst.[10] The resulting spectrum in this type of experiment is a site-exchange matrix for the structure undergoing degenerate isomerization (in their example).

The predicted site-exchange matrix for a degenerate isomerization is easily computed by using any permutation which expresses the overall change of the isomerization.[11] The rows and columns of the matrix are the sets of symmetrically equivalent atoms. The entries are the number of atoms which go from one set of equivalent atoms to another in the isomerization. The sum of the entries is equal to the number of atoms involved. Thus matrix (I) is the site-exchange matrix for the heptamethylcyclohexadienyl cation migration in Figure 2 (also the example used by Meier and Ernst[10]).

$$\begin{array}{r|cccc|} 1,2 & 1 & 1 & 0 & 0 \\ 3,7 & 1 & 0 & 1 & 0 \\ 4,6 & 0 & 1 & 0 & 1 \\ 5 & 0 & 0 & 1 & 0 \end{array} \qquad \begin{array}{r|ccccc|} 1 & 0 & 1 & 0 & 0 & 0 \\ 2,4 & 1 & 0 & 1 & 0 & 0 \\ 3 & 0 & 1 & 0 & 0 & 0 \\ 5,6 & 0 & 0 & 0 & 1 & 1 \\ 7 & 0 & 0 & 0 & 1 & 0 \end{array}$$

I II

Matrix II is for the homoprismyl rearrangement in Figure 1. These matrices will always be symmetric across the principle diagonal for SI processes. If one further condition is satisfied, these matrices will not be symmetric across the principal diagonal for NSI processes. This further condition is that the property of being SI or NSI (for this purpose) is derived by using the symmetry group of the structure which includes all permutations of identical atoms not just those permutations which correspond to the usual point-group symmetry operations. This group will generally be larger than the point group.[14] If the coset of this group corresponding to another isomer contains no permutation of order 2 or any inverse pairs, then the pair of isomers will be NSI based on this additional criterion and the site-exchange matrix for the degenerate isomerization will not be symmetric across the principal diagonal. Matrix (III) is the site-exchange matrix for the methyl rotation in Figure 2, and matrix (IV) is for the hypothetical trigonal-bipyramid substitution reaction (**1**–**2**) shown above. The reverse reactions have site-exchange matrices which are the transposes of these.

$$\begin{array}{r|ccc|} 1 & 0 & 0 & 1 \\ 2 & 1 & 0 & 0 \\ 3 & 0 & 1 & 0 \end{array} \qquad \begin{array}{r|ccc|} 1,4 & 1 & 0 & 1 \\ 2,3,5 & 1 & 2 & 0 \\ 6 & 0 & 1 & 0 \end{array}$$

III IV

If this additional condition is satisfied then potential SI and NSI degenerate isomerizations can be distinguished by the 2D

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(10) (a) Meier, B. H.; Ernst, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 6442. (b) Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546.

(11) These matrices were first described by Frame.[12] They have been called double-coset symbols[13] and were used in the present context as site-exchange matrices by Klein and Cowley.[14]

(12) Frame, J. S. *Proc. Natl. Acad. Sci. U.S.A.* **1940**, *26*, 132.

(13) Kramer, P.; Seligman, T. H. *Nucl. Phys. A* **1969**, *136*, 545.

(14) Klein, D. J.; Cowley, A. H. *J. Am. Chem. Soc.* **1975**, *97*, 1633.

NMR method of Meier and Ernst.[10] If a NSI degenerate isomerization is being observed, then with the assumption that both the forward and reverse reactions occur, the observed spectrum will be the sum of the site-exchange matrices for the forward and reverse reactions. This will give a spectrum with twice as many peaks (doubly intense count twice) as the number of atoms involved. A SI degenerate isomerization will give a spectrum with as many peaks as atoms involved. This assumes that only one process is responsible for the exchange. Multiply occurring processes would give weighted sums of the site-exchange matrices for each process involved. These observed site-exchange matrices should be symmetric across the principal diagonal since forward and reverse reactions are expected to occur with equal probability. It would be very interesting if by choice of molecular system (e.g., with very unsymmetrical potential barriers) or experimental conditions[15] a nonsymmetric (across the principle diagonal) spectrum was observed. If a degenerate isomerization was used in such a study, only a NSI process could ever give a nonsymmetric spectrum.

It is also possible to make predictions about the site-exchange matrix spectra for nondegenerate isomerizations. Nothing has been said so far about nondegenerate isomerizations, and most of the considerations developed so far do not apply to these reactions. However, nondegenerate isomerizations can be formally considered as degenerate isomerizations of two molecules. The "isomerization" permutes atoms between the sites on the two molecules, and these can be classified as SI or NSI by using the product of the symmetry groups of both molecules. The same considerations about the number of peaks in the 2D NMR experiment apply to these cases also.[16]

6. Overview

To achieve an overview of the present work, consider the following situation: Given a degenerate isomerization of some structure, the questions may be asked whether there is a reverse isomerization which "looks like" the forward reaction and whether the isomerization could go through a symmetric transition state. There will always be a reverse path which looks like the forward path if the isomerization is self-inverse (SI), that is, there is a symmetry operation of the $3N$-dimensional coordinate space which exchanges the reactant and product. For these SI degenerate isomerizations there will also always be potential structures which are symmetric with respect to product and reactant (they have symmetry operations which exchange reactant and product), but there is no guarantee they will be energetically favorable as transition states or even chemically reasonable. There is another class of degenerate isomerizations called non-self-inverse (NSI) degenerate isomerizations for which there is no coordinate-space symmetry operation which exchanges reactant and product, and for these there is never a symmetric transition state (i.e., a saddle point directly connected to reactant and product by paths of steepest descent) and no guarantee of "look-alike" reverse paths. Examples of these two types are given in Figures 2 and 3. The rigorous separation of all possible degenerate isomerizations into two types (SI and NSI) is based on an intrinsic group-theoretical property of the symmetry groups of the chemical structure and of the coordinate space and is independent of the representation chosen and even the chemical details.[24] Having achieved this rigorous classification, we may ask two further questions: Is either type favored and how can they be experimentally distinguished? Even though NSI possibilities are statistically dominant, it is shown that for structures with any symmetry SI processes tend to be favored. The two types could be easily distinguished in favorable cases by the recently described two-dimensional NMR experiment of Meier and Ernst.[10]

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Appendix

This appendix summarizes some of the relevant group-theoretical properties used and gives proofs and clarifications of some of the assertions made in this paper.

A1. Permutations. Permutations written as $(123)_R$ or $(123)_L$ are read as follows: Those with subscript R act on the atom positions defined by a reference structure and are read as the atom which starts in reference position 1 goes to reference position 2, the atom in position 2 goes to position 3, the atom in position 3 goes to position 1. Those with subscript L act on the atom numbers in any structure and are read as atom number 1 goes to where atom number 2 starts, atom number 2 goes to where atom number 3 starts, etc. The order of a permutation is the number of times a permutation must be multiplied times itself to give the identity permutation (all atoms fixed). A cycle of a permutation is the set of numbers enclosed between a set of parentheses. The length of a cycle is the number of atoms in the cycle. The identity of a group (the permutation which leaves all atoms fixed) is expressed by the letter e.

A2. Cosets. Consider two groups, G and a subgroup P. G can be broken up into a union of cosets of P (eq 4) by taking elements

$$G = P \cup aP \cup bP \cup \ldots \tag{4}$$

a, b, ... not in P and multiplying by all the elements of P. This procedure gives a set of elements of G, called a coset of P, equal in size to the size of P. Any element of the coset can be used to generate the coset. Basic properties of cosets are summarized by Hall.[17]

A3. Double Cosets. G can also be broken up into a union of double cosets (eq 5) by multiplication of an element a, b, ... not

$$G = P \cup PaP \cup \mathrm{PbP} \cup \ldots \tag{5}$$

in P on both sides by all the elements of P. Each double coset is a collection of intact cosets. For the present purposes, there are two kinds of double cosets, those which contain all the inverses of each element in the double coset called a self-inverse double coset and those which contain no inverses called a non-self-inverse double coset. The cosets in a self-inverse double coset will contain at least one element of order two or a pair of inverse elements while a coset in a non-self-inverse double coset will contain no such elements. It is this simple property which has been chosen in the present work to distinguish these cases. These properties were first discovered by Frame,[18] and the choice of the terms self-inverse (SI) and non-self-inverse (NSI) for degenerate isomerizations was made to conform to Frame's original terminology. Double cosets have been the method of choice for defining symmetry distinct isomerization modes.[19]

A4. Right and Left Representation, Alternate Proof of Coordinate-Space Symmetry. Any element, p, of a group acts on the entire group by left multiplication, $px = x'$, and right multiplication, $xp = x''$. Each group element can be represented by a permutation matrix for the left multiplication and a (usually)

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(15) (a) Krupka, R. M.; Kaplan, H.; Laidler, K. J. *Trans. Faraday Soc.* **1966**, *62*, 2754. (b) Boyd, R. K. *Chem. Rev.* **1977**, *77*, 93.

(16) An alternative method for nondegenerate isomerizations is the following: Determine the overall degenerate isomerizations for one of the structures involved. This will be expressed as some permutation of the N atoms. If this permutation is in the same double-coset $P_r/S_n \backslash P_p$ as the identity where P_r is the symmetry group of the reactant and P_p is the symmetry group of the product, then there will be $2N$ entries in the site-exchange matrix. If not, there will be $4N$ entries.

(17) Hall, M., Jr. "The Theory of Groups"; MacMillan: New York, 1959.

(18) Frame, J. S. *Bull. Am. Math. Soc.* **1941**, *47*, 458.

(19) (a) Gielen, M.; Vanlautem, N. *Bull. Soc. Chim. Belg.* **1970**, *79*, 679. (b) Meakin, P.; Muetterties, E. L.; Tebbe, F. N.; Jesson, J. P. *J. Am. Chem. Soc.* **1971**, *93*, 4701. (c) Klemperer, W. G. *J. Chem. Phys.* **1972**, *56*, 5478. (d) Hasselbarth, W.; Ruch, E. *Theor. Chim. Acta*, **1973**, *29*, 259. (e) Brocas, J.; Willem, R.; Fastenkal, D.; Buschen, J. *Bull. Soc. Chim. Belg.* **1975**, *84*, 483. (f) Nourse, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 2063. See also ref 4, 6a, 14, and 19e for discussions about the possibilities of non-self-inverse double cosets.

(20) Burnside, W. "The Theory of Groups of Finite Order"; Dover: Toronto, **1955**; pp 22–24.

(21) Frame, J. S. *Bull. Am. Math. Soc.* **1943**, *49*, 81. Also ref 18.

(22) (a) Muetterties, E. L. *J. Am. Chem. Soc.* **1969**, *91*, 1636. (b) Klemperer, W. G. *Ibid.* **1972**, *94*, 6940.

(23) Ruch, E.; Hasselbarth, W.; Richter, B. *Theor. Chim. Acta* **1970**, *19*, 288.

(24) Nourse, J. G. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 2385.

different matrix for the right multiplication. The interesting property here is that all the left multiplication matrices commute with all the right multiplication matrices.[20] Now consider the action of the group elements on the cosets. The left multiplication permutes the cosets (see eq 6), but the right multiplication

$$gxH = x'H \tag{6}$$

(usually) breaks up the cosets (see eq 7). The left multiplication

$$xHg = \text{parts of several cosets} \tag{7}$$

on cosets can be represented by permutation matrices. The effect of the right multiplication on cosets is also represented by matrices called double-coset matrices. The left multiplication matrices commute with the double-coset matrices.[21] The double-coset matrices are the incidence matrices of "topological representations" which pictorially display isomer (coset) interconversion.[22] For the purposes here these topological representations can be considered as "nets" in the coordinate space in which the points are isomers and the edges symbolize paths between them. The key result is that the left multiplication matrices (permutation of identical atoms) commute with the topological representations and are therefore symmetries of the coordinate space. These double-coset matrices are symmetric across the principle diagonal if the double coset is self-inverse.[21]

A5. Combinatorics. Table II was constructed by using two previously published combinatorial formulas. Ruch[23] has given a formula for the total number of double cosets of a subgroup P in G. Frame[18] has given a formula for the number of self-inverse double cosets. The percentages in Table II for n larger than 5 were obtained by dividing the two numbers. This is only a good approximation for the number of possible SI and NSI processes since the sizes of double cosets vary. A formula which gives sizes of double cosets and does not need double-coset representatives is lacking. For n less than 5 the percentages are exact and were enumerated by generation of the various possibilities.

A6. Conjugation Invariance, Invariance to Choice of Reference Isomer and Atom Numbering. Changing the reference isomer or renumbering the atoms in a given problem has the effect of conjugation by the permutation, r, which expresses the change of numbering in eq 8. The operation of conjugation preserves

$$r^{-1}xr = x' \tag{8}$$

all the group-theoretical properties being used in the present work. These are the self-inverse property of cosets and double cosets, the size of double cosets, the cycle structure and order of a permutation, and the combinatorial results.

A7. Method for Computing the Largest Transition-State Symmetry Group. Consider a reference structure and another isomer. The symmetries common to both are the elements of the group intersection (eq 9) where P is the symmetry group of the

$$P \wedge x^{-1}Px \tag{9}$$

reference isomer, x is in the coset representing the other isomer, and $x^{-1}Px$ is the symmetry group of the other isomer. If x is an element of order 2 or a member of an inverse pair in the coset representing the nonreference isomer (and therefore exchanges the two isomers by left multiplication), then multiplication by any element, y, in the intersection group (which therefore fixes both isomers by left multiplication) will give another element which exchanges the two isomers. Repetition of this procedure for all members of the intersection group will give a group of size twice that of the intersection group and will include all the permutations which fix both isomers and all those which exchange them (there will be an equal number of each).

Structural Studies of Silicates by Solid-State High-Resolution ^{29}Si NMR

E. Lippmaa,* M. Mägi, A. Samoson,[1a] G. Engelhardt,[1b] and A.-R. Grimmer[1c]

Contribution from the Department of Physics, Institute of Cybernetics of the Estonian Academy of Sciences, Tallinn 200001, USSR, and the Central Institute of Physical Chemistry and the Central Institute of Inorganic Chemistry of the Academy of Sciences of the GDR, Berlin-Adlershof, East Germany. *Received December 27, 1979*

Abstract: The high-resolution ^{29}Si NMR spectra of solid silicates and aluminosilicates have been studied. High-speed magic angle sample spinning in combination with high-power proton decoupling and, wherever possible, polarization transfer was used to achieve high (1 ppm) resolution. Although ionization and cation influence are reflected on ^{29}Si chemical shifts, the isotropic ^{29}Si chemical shifts in solids and solutions are generally the same and depend mainly on the degree of condensation of silicon–oxygen tetrahedra. In solid aluminosilicates, additional paramagnetic shifts appear, which correlate well with the degree of silicon substitution by aluminum.

Introduction

We recently reported the results of preliminary experiments with solid-state high-resolution NMR spectroscopy of some representative groups of organic and inorganic compounds.[2] In this paper, we describe the results of further studies of solid silicates, which show that the very considerable possibilities of high-resolution NMR are not confined to liquids, solutions, and solid samples of predominantly organic compounds, but these techniques are perfectly well applicable to the study and analysis of solid, insoluble inorganic silicates and aluminosilicates.

High-resolution ^{29}Si NMR has proved to be an efficient method for structure elucidation of silicic acids and silicate anions in solution. Numerous studies of alkali-[3,4] and tetraalkylammonium silicates[5] as well as solutions of silicic acids[6,7] have established

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[1] (a) Institute of Cybernetics; (b) Institute of Physical Chemistry; (c) Institute of Inorganic Chemistry.

[2] E. T. Lippmaa, M. A. Alla, T. J. Pehk, and G. Engelhardt, *J. Am. Chem. Soc.*, **100**, 1929 (1978).

[3] G. Engelhardt, D. Zeigan, H. Jancke, D. Hoebbel, and W. Wieker, *Z. Anorg. Allg. Chem.*, **418**, 17 (1975).

[4] R. K. Harris and R. H. Newman, *J. Chem. Soc., Faraday Trans. 2*, **73**, 1204 (1977).

[5] D. D. Hoebbel, G. Garzó, G. Engelhardt, R. Ebert, E. Lippmaa, and M. Alla, *Z. Anorg. Allg. Chem.*, in press.

[6] D. Hoebbel, G. Garzó, G. Engelhardt, and A. Till, *Z. Anorg. Allg. Chem.*, **450**, 5 (1979).

[7] G. Engelhardt, W. Altenburg, D. Hoebbel, and W. Wieker, *Z. Anorg. Allg. Chem.*, **437**, 249 (1977).

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