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Rules on chiral and achiral molecular transformations. II

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The properties of chiral and achiral transformations between mirror images of labeled, partially labeled and unlabeled n-dimensional point sets are investigated. Mislow's Label Paradox of three-dimensional chirality-preserving and chirality-abandoning molecular transformations of tetrahedra is generalized to simplexes of all higher dimensions n, and a sufficient and necessary partial labeling condition is given for fully chiral interconversion paths of mirror images of chiral n-dimensional simplexes.

1. Introduction

In this contribution the same notations and definitions are used as those specified in part I [1] of this study. In particular, a point set S is *n-chiral* or *n-achiral* if it is chiral or achiral, respectively, when embedded in the n-dimensional Euclidean space E^n.

In part I of this study [1], the general, n-dimensional problem of interconversion paths of chiral arrangements of finite sets S of m points to their mirror images, has been discussed. The following default convention has been used: the points of set S are considered to have distinct labels as specified by their serial numbers, unless two or more points are interrelated by a point symmetry operation or a permutation operation, in which case the points so interrelated are considered equivalent. If the serial indices are regarded as labels, a symmetry relation or permutation assignment of two points to one another renders these labels equivalent. Simple proofs have been given for several elementary results on n-chirality preserving and abandoning motions, that is, for deformations of finite point sets preserving or abandoning chirality in n dimensions. In particular, two properties proven in part I are of relevance to the present contribution:

(i) For n-chiral simplexes of $n+1$ different points $a_1, a_2, a_3, \dots a_n, a_{n+1}$, that is, for $n+1$ points all having distinct labels, the following holds:

No n-chiral simplex $S = \{a_1, a_2, a_3, \ldots a_n, a_{n+1}\}$ can be deformed continuously within E^n into its mirror image $S^\diamond = \{a_1^\diamond, a_2^\diamond, a_3^\diamond, \ldots a_n^\diamond, a_{n+1}^\diamond\}$ without passing through an n-achiral intermediate (theorem 3, part I [1]).

(ii) For every n-chiral point set a_1, a_2, a_3, $\ldots a_n$, a_{n+1}, $\ldots a_{m-1}$, a_m, of $m \geqslant n+2$ points where some points may be related by symmetry or by permutational assignment, that is, where not necessarily all points are required to have distinct labels, the following holds:
Any n-chiral point set $S = \{a_1, a_2, a_3, \ldots a_n,\ a_{n+1},\ \ldots a_{m-1},\ a_m\}$ of $m \geqslant n+2$ points can be transformed continuously within E^n, $n \geqslant 2$, into its mirror image $S^\diamond = \{a_1^\diamond, a_2^\diamond, a_3^\diamond, \ldots a_n^\diamond,\ a_{n+1}^\diamond,\ \ldots a_{m-1}^\diamond,\ a_m^\diamond\}$ without passing through any n-achiral arrangement (theorem 10, part I [1]).

For the special case of unlabeled three-dimensional simplexes, that is, for unlabeled tetrahedra, Mislow, Buda, and Poggi-Corradini [2,3] have presented an elegant approach and proof of the existence of fully chiral paths interconverting mirror images, that is, of the existence of motions of the vertices of any unlabeled chiral tetrahedron which convert the tetrahedron into its mirror image without encountering any achiral arrangement. Mislow has presented a result [4], independently of the general result for the n-dimensional case [1,5], demonstrating that for fully labeled, three-dimensional simplexes, that is, for fully labeled tetrahedra, no path interconverting chiral mirror images can preserve chirality. In general, the equivalence of labels increases the chances that a motion of a chiral point set converts the set into an achiral set, whereas distinct labels of points increase the chances of obtaining chiral arrangements. Consequently, it appears somewhat counterintuitive that unlabeled tetrahedra (i.e., tetrahedra with equivalent labels) can get converted into their mirror images without encountering achiral arrangements, whereas fully labeled chiral tetrahedra must become achiral in any rearrangement turning them into their mirror images. This counterintuitive behavior of labeled and unlabeled chiral tetrahedra, noted by Mislow [4], will be referred to as Mislow's Label Paradox.

In this contribution, Mislow's Label Paradox is generalized to the n-dimensional case of n-chiral simplexes of $n+1$ points; a sufficient and necessary partial labeling condition is given, and a relevant theorem is proven for the maximal labeling of n-dimensional chiral simplexes that still allows chirality preserving interconversion paths between mirror images. A simple explanation of the generalized, n-dimensional label paradox is presented.

2. An n-dimensional generalization of Mislow's Label Paradox

The seemingly paradoxical role of vertex labeling of chiral tetrahedra in allowing or preventing three-dimensional interconversion paths between mirror images to preserve chirality is in fact general for all n-chiral simplexes embedded in an n-dimensional Euclidean space E^n. In ref. [1] a simple proof has been given for the fully labeled case of n-dimensional simplexes necessarily becoming achiral in any interconversion process between n-chiral mirror images (theorem 3, part I [1]). As it will be proven below, by a minimal relaxation of the labeling constraint, that is, by allowing just two labels to become equivalent and preserving uniqueness for all other labels, chirality preserving interconversion paths between mirror images become possible for all arrangements of an n-chiral simplex. That is, Mislow's Label Paradox is generalized to any finite dimension n, $n \geqslant 3$. Since the unique label restriction is removed for the minimum number of points, that is, for two points, the proof presented below also provides a sufficient and necessary label relaxation condition (or, a maximal labeling condition) for the possibility of interconversion of mirror images of n-chiral simplexes by chirality preserving paths.

3. A sufficient and necessary maximal labeling condition for the existence of chirality preserving interconversion paths of mirror images of an n-chiral simplex

Consider an n-chiral simplex that is the convex hull of the point set

$$S = \{a_1, a_2, a_3, \ldots, a_{n-1}, a_n, a_{n+1}\}, \tag{1}$$

where each point a_i is distinctly labeled by its serial index i, except for the last two points a_n and a_{n+1} where the serial indices n and $n+1$, as distinguishing labels, are regarded as equivalent. Equivalently, one may regard the serial index as the distinguishing label for all points except a_{n+1}, which is assumed to carry the same distinguishing label n as a_n.

Since all point pairs are distinguishable by their labels except the pair a_n and a_{n+1}, this labeling corresponds to a *minimal relaxation of the unique labeling constraint*; alternatively, one may say that this labeling is *maximal* among all labelings short of the complete unique labeling. In what follows, a simple proof is given demonstrating that this minimal labeling relaxation is sufficient for the existence of chirality preserving paths. The necessity of a minimal relaxation has been already proven for the general, n-dimensional case; according to theorem 3, part I [1], less than this minimal relaxation, that is, no label relaxation, that is, a complete unique labeling, does not allow any chirality preserving path between n-chiral mirror images of simplexes.

Figure 1 illustrates the main ideas of the proof of the following theorem. The two diagrams correspond to a nondegenerate and a degenerate distance condition. Note that line Q represents an $(n-2)$-dimensional hyperplane, used as a rotation axis in n-dimensions, rotating the $(n-1)$-dimensional hyperplane A by angle α, turning A into the $(n-1)$-dimensional hyperplane A'. The $(n-1)$-dimensional

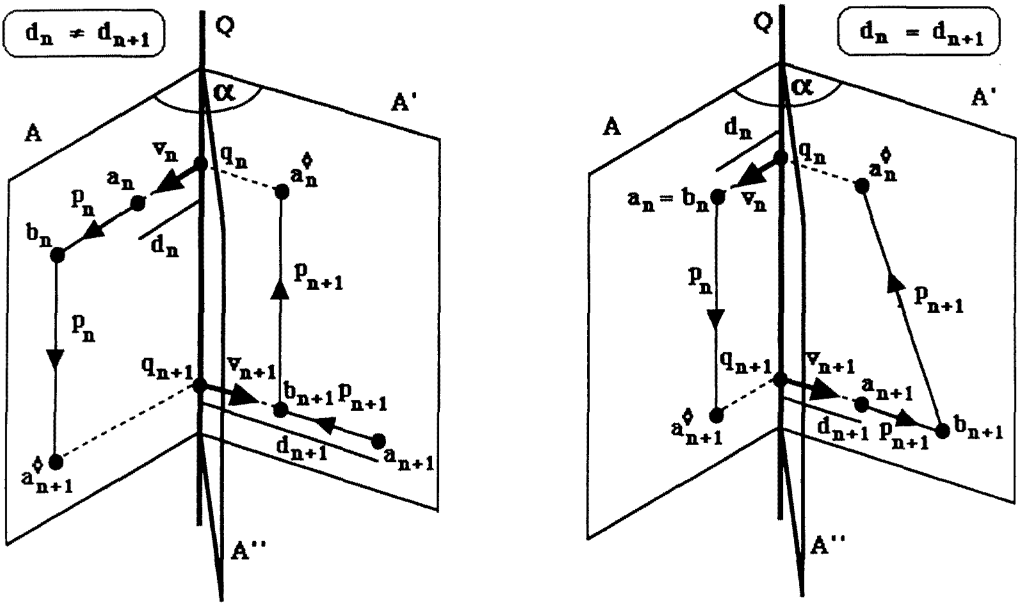

Fig. 1. An illustration of the proof of theorem 1. See text for details.

hyperplane A'' is the reflection plane that reflects the n-chiral simplex S into the actual mirror image $S^\diamond$.

THEOREM 1

Any n-chiral simplex $S = \{a_1, a_2, a_3, \ldots, a_{n-1}, a_n, a_{n+1}\}$, where each point a_i, $i = 1, \ldots, n-1$, is uniquely labeled by its serial index i, and the two points a_n and a_{n+1} both carry the same label n and are regarded equivalent, can be deformed continuously into its mirror image $S^\diamond = \{a_1^\diamond, a_2^\diamond, a_3^\diamond, \ldots, a_{n-1}^\diamond, a_n^\diamond, a_{n+1}^\diamond\}$ without passing through an n-achiral intermediate.

Proof

Since S is an n-chiral simplex in E^n, any collection of k vertices of S define a unique $(k-1)$-dimensional hyperplane that contains these k points. In particular, consider the $(n-2)$-dimensional, unique hyperplane Q that contains the first $n-1$, uniquely labeled vertices, and the maximum achiral subset A of S, where A is the unique $(n-1)$-dimensional hyperplane that contains the first n vertices of S. Clearly, $A \supset Q$. Hyperplane Q can be taken as an $(n-2)$-dimensional rotation axis in the n-dimensional space E^n, and the plane A can be rotated along this axis into a new position A', where point a_{n+1} falls within the rotated hyperplane A'. Denote the angle of this rotation by α. Carry out a rotation of the original hyperplane A along the axis Q by $\alpha/2$ in the same sense as in the previous rotation. The resulting new hyperplane A'' contains the first $n-1$ vertices of the simplex S, but it contains neither of the vertices a_n and a_{n+1}. The distances of points a_n and a_{n+1} from any given point of the hyperplane A'' are different, otherwise S could not be n-chiral, since then A'' could serve as a reflection hyperplane that reflects S onto itself, with a_n and a_{n+1} assigned to each other. Consider the particular reflected image

$$S^{\diamond} = \{a_1^{\diamond}, a_2^{\diamond}, a_3^{\diamond}, \ldots, a_{n-1}^{\diamond}, a_n^{\diamond}, a_{n+1}^{\diamond}\} \tag{2}$$

obtained when A'' is taken as reflection plane. Clearly, A'' reflects Q onto itself, hence

$$a_i^{\diamond} = a_i\,, \quad i = 1, \ldots, n-1\,, \tag{3}$$

for the first $n-1$ uniquely labeled points, whereas the point

$$a_n^{\diamond} \in A'\,, \tag{4}$$

and point

$$a_{n+1}^{\diamond} \in A \tag{5}$$

are not elements of the vertex set S.

From the set of all points of Q, take the unique point $q_n \in Q$ that has the shortest distance to point $a_n \in A$, and the unique point $q_{n+1} \in Q$ that has the shortest distance to point $a_{n+1} \in A'$. Denote these distances by d_n and d_{n+1}, respectively. Since set S is n-chiral, neither d_n nor d_{n+1} can be zero, that is, $d_n > 0$, and $d_{n+1} > 0$. Note that by virtue of reflection by A'', q_n and q_{n+1} are also the unique points of set Q which have the shortest distances, d_n and d_{n+1}, from $a_n^{\diamond} \in A'$, and $a_{n+1}^{\diamond} \in A$, respectively.

Define two unit vectors, $\boldsymbol{v}_n$ and $\boldsymbol{v}_{n+1}$, pointing from q_n to a_n, and from q_{n+1} to a_{n+1}, respectively. Select two points as

$$b_n = q_n + d_{n+1}\boldsymbol{v}_n \tag{6}$$

and

$$b_{n+1} = q_{n+1} + w d_n \boldsymbol{v}_{n+1}\,, \tag{7}$$

where $w = 2$ if $d_n = d_{n+1}$, and $w = 1$ otherwise. As it will become evident below, this choice of weight factor w, special for the case of $d_n = d_{n+1}$, ensures that in the course of the actual motions of points a_n and a_{n+1} of equivalent labels, at no intermediate locations along their paths will the two moving points a_n and a_{n+1} become A''-reflected mirror images of each other. By construction, $b_n \in A$, and $b_{n+1} \in A'$, respectively; furthermore, b_n, a_{n+1}, and $a_{n+1}^{\diamond}$ are at the same d_{n+1} distance from set Q, whereas b_{n+1}, a_n, and $a_n^{\diamond}$ are at the same d_n distance from set Q, except in the special case of $w = 2$, when b_{n+1} has the distance $2d_n$ from Q.

Construct a geometrical path p_n within A from the two straight line segments $[a_n, b_n]$ and $[b_n, a_{n+1}^{\diamond}]$, where $[a_n, b_n]$ is the degenerate, single point segment if $d_n = d_{n+1}$, and another geometrical path p_{n+1} within A' from the two straight line segments $[a_{n+1}, b_{n+1}]$ and $[b_{n+1}, a_n^{\diamond}]$. Parametrize these paths continuously as

$$p_n(u): \quad [0,1] \to A\,, \quad \text{where} \quad p_n(0) = a_n\,, \quad p_n(1) = a_{n+1}^{\diamond}\,, \tag{8}$$

and

$$p_{n+1}(u): \quad [0,1] \to A'\,, \quad \text{where} \quad p_{n+1}(0) = a_{n+1}\,, \quad p_{n+1}(1) = a_n^{\diamond}\,, \tag{9}$$

respectively, where for each path the parameter u is chosen proportionally to the arc length in E^n. If hyperplane A'' is used as reflection plane, the reflected image of the endpoint $p_n(0) = a_n$ is $p_{n+1}(1) = a_n^{\diamond}$, and the mirror image of $p_n(1) = a_{n+1}^{\diamond}$ is $p_{n+1}(0) = a_{n+1}$, however, the A''-reflected mirror images within each pair belong to different values of the parameter u. No other point of either path is an A''-reflected image of any point of the other path.

Carry out the deformation of point set S into its mirror image $S^{\diamond}$ by the concerted motion of simultaneously moving points a_n and a_{n+1} along paths p_n and p_{n+1} to their new locations $a_n^{\diamond}$ and $a_{n+1}^{\diamond}$, respectively, by varying the parameter value u as a common parameter for both paths $p_n(u)$ and $p_{n+1}(u)$. The n-chirality of the point set is preserved throughout the entire deformation of the n-dimensional simplex S into its mirror image $S^{\diamond}$. □

The deformation described in the proof of theorem 1 is an n-chirality preserving path in the $(3n-6)$-dimensional configuration space of the n points defining the simplex S.

4. An explanation of the n-dimensional Generalized Label Paradox

In the above proof an actual transformation is constructed that converts an n-chiral simplex S into its mirror image $S^{\diamond}$ while preserving chirality throughout the deformation. Note that after the completion of the deformation, the displaced point a_{n+1} becomes the mirror image of point a_n, and similarly, the displaced point a_n becomes the mirror image of point a_{n+1}. Such a role change is possible only because the two points a_n and a_{n+1} are declared equivalent, having the same formal label, denoted by n. Note, in particular, that if one restores the nonequivalence of points a_n and a_{n+1}, then the final arrangement obtained after completing the deformation described in the proof is not a mirror image of the original arrangement of S.

These observations provide the key to an explanation of the Generalized Label Paradox [5]. Whereas abandoning unique labeling allows fewer point configurations to be chiral, hence, it enhances the occurrence of achiral arrangements, nevertheless, by allowing an exchange of roles between points of equivalent labels, an abandoning of the unique labeling also provides additional chances for a deformed point set to become the mirror image of its original n-chiral arrangement. In particular, the role switching of points a_n and a_{n+1} allows the construction of a mirror image of the original simplex S without either a_n or a_{n+1} passing through the reflection plane A''. The equivalence of the labels of just two points is sufficient to exploit a role switch and the resulting new possibilities of reaching a mirror image configuration. A single role switch is sufficient, hence there is no need to modify the unique labels of $n - 1$ points. The chance of role switch has a more important influence on the family of chirality preserving deformations than the limitations implied by having additional achiral configurations.

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