Rules on chiral and achiral molecular transformations

Paul G. Mezey

Mathematical Chemistry Research Unit,
Department of Chemistry and Department of Mathematics and Statistics,
University of Saskatchewan, 110 Science Place, Saskatoon, SK, Canada S7N 5C9

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The properties of chiral and achiral transformations between mirror images of n-dimensional point sets are investigated. Several rules are proven, relevant to chirality-preserving and chirality-abandoning molecular transformations.

1. Introduction and preliminaries

Molecular transformations which interconvert chiral mirror images yet avoid achiral intermediate nuclear configurations have been reported long ago [1], but still are considered oddities by many chemists. In this study we shall consider this problem in a more general setting: the transformation of chiral point sets in an n-dimensional Euclidean space.

Chirality of point sets in various dimensions, specifically, chirality in the ordinary, three-dimensional space and two-dimensional chirality along planar surfaces are of importance in chemistry. In recent years the interest in mathematical-chemical aspects of chirality in general, n-dimensional spaces has increased. Detailed background information on several newer results can be found in refs. [2–43], whereas some of the earlier developments are reviewed in refs. [44,45].

In this study we are interested in various nuclear motions of molecules and their influence on molecular chirality. Usually, the chirality of nuclear arrangements is studied in a three-dimensional space; however, some motions can be restricted to two dimensions, for example, some molecular motions along surfaces of metallic catalysts can be approximated by motions along a plane. In rare instances, for example, within channels of zeolites or within nanotubes, one-dimensional chirality of chain molecules may be relevant. Chirality problems of dimensions higher than three also occur in studies of potential energy hypersurfaces and multidimensional configuration spaces [46]. In this study we shall investigate the problem of chirality preserving and violating properties of motions of point sets in a general, n-dimensional Euclidean space $E^n$. 

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Chirality will be considered in the following sense: a set $S$ embedded in an $n$-dimensional space $E^n$ is chiral, if no rigid motion of $S$ can bring it into superposition with its mirror image within $E^n$. Otherwise, $S$ is achiral. The definition of chirality is precise only if the space is specified. Chirality of point sets is dimension-dependent; a point set can be chiral when embedded in one Euclidean space, while the same point set embedded in a Euclidean space of different dimension can be achiral. In general, we use the terms $n$-chiral or $n$-achiral for a point set $S$ if it is chiral or achiral, respectively, when embedded in the $n$-dimensional Euclidean space $E^n$.

The following important restriction applies: any $n$-chiral object $S$ is $(n + 1)$-achiral. More precisely, the following restrictions hold:

**THEOREM 1**

An object $S$ that is chiral in $n$-dimensions is achiral in $(n + 1)$-dimensions and in any higher dimensions. Chirality may occur only in the lowest dimension where $S$ is embeddable.

A simple proof and some implications of this theorem have been given in refs. [31,45].

A similarly simple but important property is proven below. Consider an $n$-chiral arrangement $S$ of $m$ points in $E^n$, where $m$ is finite:

$$S = \{a_1, a_2, a_3, \ldots, a_n, a_{n+1}, \ldots, a_{m-1}, a_m\}. \quad (1)$$

**THEOREM 2**

For an $n$-chiral arrangement $S$ of $m$ points, each point $a_j \in S$ can be moved in any direction by some small enough distance without $S$ becoming $n$-achiral.

**Proof**

Take any point $a_j \in S$. Let $d(a_j, a_k)$ denote the distance between any two points $a_j, a_k$ of set $S$. Note that $d(a_j, a_k) \neq 0$ and positive for each $k \neq j$, since all points of $S$ are different. Let $\alpha(S, a_j)$ denote the set of all possible locations for a displaced point $a_j$ which turn the set $S$ into $n$-achiral. This set $\alpha(S, a_j)$ may be empty. Let $d(a_j, \alpha(S, a_j))$ denote the distance between point $a_j \in S$ and set $\alpha(S, a_j)$, that is, the nearest new position for $a_j$ that turns the set $S$ into $n$-achiral. If $\alpha(S, a_j)$ is empty, then set $d(a_j, \alpha(S, a_j)) = \infty$. Note that the distance $d(a_j, \alpha(S, a_j)) \neq 0$ and positive for each $a_j \in S$, since $S$ is an $n$-chiral set. Define a distance $d(a_j)$ as

$$d(a_j) = \frac{1}{2} \min\{d(a_j, a_k), d(a_j, \alpha(S, a_j))\}_{k=1, \ldots, m, k \neq j}. \quad (2)$$

Evidently, $d(a_j) > 0$ for each point $a_j \in S$, and each point $a_j$ can be moved in any direction by the distance $d(a_j)$ while the point set retains its $n$-chiral property. \qed

In other words, $n$-chiral configurations $S$ of finite point sets form an open set in the corresponding configuration space. This can be regarded as the consequence of