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GEOMETRIC THEORY OF CHIRALITY. THE SENSE OF ELEMENTS OF CHIRALITY

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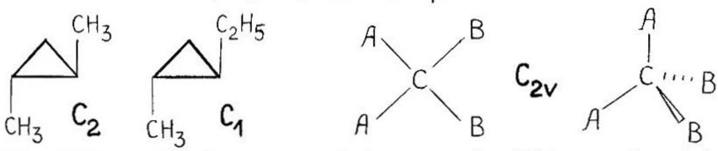
Summary. An isotropic n-dimensional space can be filled with the (n-1)-dimensional chiral figure in a chiral way. The whole system formed requires the presence of a singular achiral (n-2)-dimensional figure. The elements of chirality which are a centre, an axis, a plane can be considered as inherent singular achiral parts of the structures which are chiral in higher dimensions. Therefore they are the traces of those chiral structures whose reduction to these elements is demonstrated.

Introduction

Chirality is one of the fundamentals of a modern stereochemistry along with configuration and conformation[1]. While two latter notions are not well-defined and have been re-considered recently[1-3], the concept of chirality in 3-dimensional space was defined unambiguously from the very beginning, being based on the operation of the reflection about a plane mirror[4]. Similarly, chirality in 2-dimensional space[5] (i.e. on plane) takes into account the reflection about a straight line. This concept can be easily extended for the n-dimensional space wherein chirality can be determined using the reflection about (n-1)-dimensional space. In particular, on the straight line (1-dimensional space) the reflection should be made about a point (0-dimensional). Clearly, the introduction of chirality means the introduction of an element of metrics, namely, the distinction between equal distances (that corresponds achirality) and unequal distances (that corresponds chirality). For 1-dimensional non-linear systems, curves, one can build "the mirror image" taking into account the arc length only.

Now let us go from point to figures, and, first of all, it is worth to note two different approaches which are used in chiral stereochemistry. The first one is based on the point group symmetry, the second one deals with the elements of chirality. Despite the group symmetry approach looks more strict, it has the important defect in practical use because quite similar molecules should very often belong to different chiral subclasses as shown below. Trans-1,2-dimethylcyclopropane, C_2, and trans-1-methyl-2-ethylcyclopropane, C_1, can serve as example.



On the other hand, the same point group should be assigned to some isomers which are better to be distinguished like tetrahedral and planar-square CX_2Y_2 molecules which both belong to C_{2v}. This had been recognised by Pople who then derived the more complicated group symmetry notation which is a unique characteristic of a molecule[6].

The important shortage of another approach is the lack of a clear definition of the elements of chirality, the idea about which being mainly intuitive. This classification emerged on the structural grounds, and four types of chirality are to be distinguished: central, axial, planar, helical to which the following elements of chirality correspond: centre (point), axis (straight line), plane (plane), helicoide (surface).

In this communication the elements of chirality are treated as the essential achiral components of more complicated chiral structures in higher dimensions.

Finite and infinite molecules

Stereochemistry deals chiefly with the chirality of finite molecules, but it also knows large enough macromolecules which may be coiled into chiral helices and other structures, though. The conditions for chirality in finite figures, molecular polyhedra in 3-dimensional Euclidean space R^3 are well known, see for example[1]. So are known the infinite and chiral mathematical objects such as helical lines and helical surfaces as well as a limited surface Möbius band. Here the general problem is posed: how to determine chiral structures in isotropic continua R^n, in other words, the general ways to chiralize the straight line R^1, plane R^2, space R^3, hyperspaces R^n are sought. This pathway is supposed to permit the better understanding the real sense of the elements of chirality.

Chiralization of isotropic continua R^n

The existence of the chiral helicenes molecules which represent the fragments of the helicoide surface in molecular material suggests the possible way to chiralize R^3 space. Parametrical equations for helicoide are

$$x = a \cos \varphi , \quad y = a \sin \varphi , \quad z = F(a) + h\varphi, \ -\infty < a < +\infty$$

If a straight line, arbitrarily chosen and perpendicular to a fixed axis, will glide along it following the above-mentioned law with $h \to 0$ and $a \to \infty$, so space R^3 will turn out to be filled in with the resulted helicoidal surface in a chiral fashion, the sense of chirality being determined by the direction of gliding, that is, by sign of $\underset{\sim}{h}$.

Similarly, plane R^2 is chirally filled in with Archimedean spiral whose parametrical equations are:

$$x = a\varphi \cos\varphi, \qquad y = a\varphi \sin\varphi$$

It is evident that the distance between the neighbour coils of a spiral will grow infinitely small when $a \to 0$. One should note the continuity of both helicoide surface and Archimedean spiral. This is not the case with the filling of an infinite straight line R^1 with the chiral point set according to the law:

$$r = a\varphi \sin\varphi$$

It is interesting that another coördinate which is present in the equation for Archimedean spiral, $r = a\varphi \cos\varphi$, will result on R^1 in the achiral point set* which has a centre of inversion at $r = -1/2$ (Fig.1). This suggests that it is sinusoidal coördinate which is responsible for a chiral filling of R^n spaces with the figures of (n-1)-dimensionality, at least for $n = 1,2,3$. It looks possible that similar pattern will be maintained for $n > 3$ provided that one sinusoidal coördinate is kept.

Let us emphasize now the important feature of the chiral filling of isotropic spaces. This is that the n-dimensional isotropic space R^n is filled in with a (n-1)-dimensional chiral figure, and this process requires the obligatory presence of a singular (n-2)-dimensional achiral figure around which the filling figure is whirling. So, cylinderic helicoide fills in R^3 having a straight line as a base <u>axis</u>, and Archimedean spiral does R^2 with a point as a <u>centre</u>. Moreover, the filling in R^1 with points in the above-mentioned manner requires similarly the presence of a central, zero point whose singularity is in its multiplicity. It is likely that the chiral filling of hyperspace R^4 with a chiral (helical) 3-dimensional space should require 2-dimensional <u>plane</u> as a peculiar, singular element of the whole system. Of course, all these singular figures are achiral. These relationships are summarized in the TABLE. **

<u>Real sense of the elements of chirality</u>

This remarkable role played by the achiral singular figures of lower dimensionality in the chiral systems of higher dimensions suggests that "the elements of chirality" in stereochemistry (which are in themselves achiral and therefore look as semantic nonsense) represent, in reality, the essential part of the chiral systems of higher dimensions in accordance with the TABLE. In part, the plane of chirality is an achiral element of a chiral structure in hyperspace R^4. According to this concept, the epithet "chiral" as applied to a centre, an axis, a plane is used as a sign which designates the persistent relationship with the real chiral structures whose essential parts they are.

Let us now consider the transitions between chiral structures in spaces of different dimensions. If abscisse and ordinate

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* If the multiplicity of zero point may be discarded

**Very recently the concept derived has been applied[7] to the design of chiral helicoidal carbon

TABLE

Relationships between the dimensions of the isotropic space, of the chiral filling figure and of the achiral singular figure

Isotropic space to be filled (its dim)	Chiral filling figure (its dim)	Achiral singular figure (its dim)
straight line (1)	sinusoidal succession of points (0)	multiple zero point (less than zero *)
plane (2)	Archimedean spiral (1)	point (centre) (0)
space (3)	Helicoidal surface (2)	straight line (axis) (1)
hyperspace (4)	helicoidal space (3)	plane (plane) (2)
. . . (N)	. . . (N-1)	. . . (N-2)

* assigned because of the multiplicity of zero point

of a cylinderic helix is multiplied by factor φ , the applicate being unchanged, the equations for a conical helix will result which is going along the surface of the straight cone and therefore owns both chiral axis and chiral centre:

$$x = a\varphi\cos\varphi, \quad y = a\varphi\sin\varphi, \quad z = h\varphi$$

The projection of a conical helix on the plane orthogonal to the axis of the cone affords Archimedean spiral which, in its turn, being projected on the ordinate axis, results in the straight line filled in a chiral manner according to the law above discussed. Since this procedure can be reversed, in principle, the reconstitution of the n-dimensional picture starting from the (n-1)-dimensional one can be also made. Thus, in order to move from Archimedean spiral to a conical helix it is necessary to add the third coördinate which is linear applicate going through the centre, and the axis of applicate is now the axis of symmetry. One can think that similar operation will permit to go from a cylinderical helical surface to a helical space in a 4--dimensional hyperspace.

Unlike the conical helix, the cylinderical one when projected on the plane orthogonal to the axis of cylinder, gives rise to an infinitely-fold circle (Fig.2a, $h \to 0$). The similar procedure applied to a helicoidal surface will give the infinitely--fold plane σ. The related but different process, $h \to \infty$, affords the infinite set of planes σ' which all contain the axis of cylinder and are orthogonal to plane σ (Fig.2b).

Simultaneous realization of the operation $a \to 0$ pulling on σ to axis will result in a single point. This process can be regarded as a successive reduction of a chiralized space to the "plane of chirality", then to the "axis of chirality", and, finally, to the "centre of chirality". In other words, the elements of chirality should be considered as the traces of the successive steps in the rolling up of a chiral space.

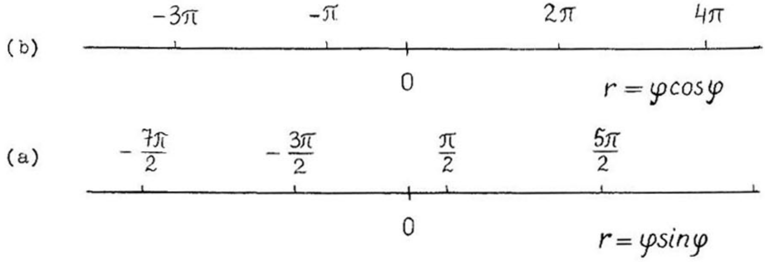

FIGURE 1. Chiral (a) and achiral (b) point successions on a straight line

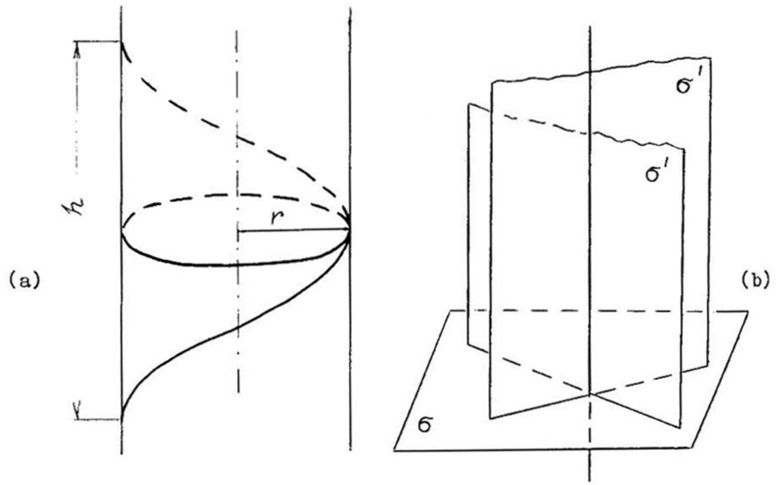

FIGURE 2. (a) Reduction of a helical line to an infinitely-fold circle ($h \rightarrow 0$) and to a straight line ($h \rightarrow \infty$)
(b) The result of the reduction of a helicoidal surface to an infinitely-fold plane σ ($h \rightarrow 0$) and to a set of orthogonal planes σ' ($h \rightarrow \infty$)

R E F E R E N C E S

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