GEOMETRIC CHIRALITY PRODUCTS

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Abstract

Developed from Guye's "produit d'asymétrie" and formally similar to Ruch's chirality products, geometric chirality products are functions purely of molecular shape, without reference to chemical characteristics. In their normalized versions, geometric chirality products have all the attributes of a chirality measure, i.e. they are similarity invariant and dimensionless in the interval $[-1, 1]$. An application to Boys' model of the tetrahedron is presented, and a detailed study of the results for triangular domains in E^2 is reported. According to this measure, the most chiral triangle is infinitely flat and infinitely skewed. The analysis leads to the paradoxical conclusion that the most chiral triangle is infinitesimally close to an achiral one. The results are compared with those obtained for an overlap measure of chirality, and the relationship between molecular models and measures of chirality is briefly discussed.

1. Introduction

In 1890, 100 years ago at this writing and only 16 years after van 't Hoff's and LeBel's revolutionary proposals to extend the structural formulas of chemistry into three-dimensional space, Guye [1] introduced the first function designed to correlate a pseudoscalar property, i.e. optical rotation, with the molecular structure of a chiroid. Appropriately called "produit d'asymétrie", this was the first example of a chirality function in chemistry. It was also the first attempt to quantify a chirality property.

In this paper, we show that, starting from Guye's chirality product, a function can be derived that we call *geometric chirality product* and that expresses the shape of geometric chiroids. We go on to illustrate this new concept by an analysis of triangular shapes from which it emerges that, according to this measure, the most chiral triangle is one that is infinitely flat and skewed.

According to Guye [1], the chirality product P for a tetrahedral coordination skeleton, in which the angles subtended by the central carbon atom remain those of the regular tetrahedron (the "α-constraint", where α is the tetrahedral angle), is defined by eq. (1), where d_i is the perpendicular distance of the molecular center of mass to

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the ith of six planes defined by each of the six edges and the center of the tetrahedron. Thus, $P(d)$ is the product of six terms:

$$P(d) \equiv \prod_{i=1}^{6} d_i .$$ (1)

$P(d)$ may be expressed by eq. (2), where m_1, m_2, m_3, and m_4 are four masses at the vertices of the tetrahedron, separated by four distances l_1, l_2, l_3, and l_4 from the central carbon atom [2]. For the special case in which all four distances are the same (l), i.e. in which the coordination skeleton is a regular tetrahedron, eq. (2) reduces to eq. (3):

$$P(m,l) = \left(\frac{\sin \alpha/2}{\sum_{i=1}^{4} m_i} \right)^{6} \prod_{i>j}^{1...4} (m_i \, l_i - m_j \, l_j),$$ (2)

$$P(m) = \left(\frac{l \, \sin \alpha/2}{\sum_{i=1}^{4} m_i} \right)^{6} \prod_{i>j}^{1...4} (m_i - m_j).$$ (3)

In the course of their systematic development of a general theory of chirality products, Ruch and coworkers [3,4] defined a function $\chi(\lambda)$ with reference to a model in which a set of n ligands is partitioned among the n sites of an achiral permutation skeleton, such as a regular tetrahedron. In this definition (eq. (4)), λ is a transferable, ligand-specific, scalar parameter with a physical dimension, e.g. polarizability, or with geometrical properties:

$$\chi(\lambda_1, \lambda_2, \ldots, \lambda_n) \equiv \prod_{i>j}^{1...n} (\lambda_i - \lambda_j).$$ (4)

The formal resemblance between the product terms in eqs. (3) and (4) is obvious on inspection: in both cases, the chirality polynomial of lowest degree is an expansion of a determinant whose elements are $a_{ij} = m_i^{j-1}$ or λ_i^{j-1} ("Vandermonde" determinant [3(b)]). However, a crucial condition on any chirality function is that it must vanish identically if the model is achiral, and $P(m)$ fails to meet this test: as first pointed out by Walden [5] in a trenchant critique of Guye's chirality product, and as would be expected on grounds of symmetry alone, compounds such as dimethyl O-acetyl malate ($CH_3OOCCH(OCOCH_3)CH_2COOCH_3$) are optically active even though two of the ligands attached to the central carbon atom, $OCOCH_3$ and $COOCH_3$, have the same mass. The choice of $\lambda = m$ therefore seems particularly unfortunate, not only because Guye's model does not conform with modern theories

of optical activity [6] but also because the ligands are represented as point masses, so that $P(m)$ fails to take into account different distributions of masses within the ligands.

2. Geometric chirality products as expressions of shape

If the four point-masses in Guye's model are taken to be all the same, then eq. (2) reduces to eq. (5), where $c = (\sin \alpha/2)^6/4^6$:

$$P(l) = c \prod_{i>j}^{1...4} (l_i - l_j). \tag{5}$$

Now $P(l)$ is a function of symmetry alone and behaves properly: it vanishes in all cases but one, that of the asymmetric tetrahedron. Because of their purely geometric character, functions such as $P(l)$ will hereafter be called *geometric chirality products*.

Only five tetrahedral symmetries, T_d, C_{3v}, C_{2v}, C_s, and C_1, are possible for $P(l)$ under the α-constraint. These are the same five symmetries that result from different ligand partitions on a regular tetrahedral permutation skeleton [7]. This mapping finds its fullest expression in the following construct. Imagine a regular tetrahedron **t** with center-to-vertex distances r inscribed within a tetrahedron **T** modeled by $P(l)$, so that the center of **t** coincides with the central carbon atom of **T** and the r's of **t** are coextensive with the l's of **T**. Because **t** is inscribed within **T**, $l - r \geq 0$. The four line segments $l - r$ are therefore the geometric equivalents of ligands on a T_d permutation skeleton, and the chirality product for this construct is accordingly given by the formulation of eq. (5) as eq. (6):

$$P(l) = c \prod_{i>j}^{1...4} [(l_i - r) - (l_j - r)]. \tag{6}$$

Ruch [3(i)] has previously pointed out that the ligand parameters λ may describe a geometrical property of the ligands, which he has likened to the diameters of spheres centered at the vertices of achiral coordination skeletons. The present construct, with $\lambda = l - r$, evokes a similar image. In short, as a chirality product, $P(l)$ fully accords with Ruch's theory [3] even though there is no obvious correlation of $l - r$ with any pseudoscalar observable. Furthermore, most important of all for what is to follow, *chirality products such as $P(l)$ express the shapes of geometric chiroids.*

A geometric chirality product with significantly different scope may be constructed by taking the six edges of the tetrahedron as the variable parameters. Let e_{ij} denote the length of an edge, i.e. the shortest distance between the ith and jth vertices. There are $6(6 - 1)/2 = 15$ combinations of differences in edge lengths, 12 of which are differences in the lengths of adjacent edges, e.g. $(e_{ij} - e_{ik})$. The remaining three, which are differences in the lengths of the three pairs of non-adjacent edges, e.g. $(e_{ij} - e_{km})$,

are unsuitable as factors in a chirality product because all three would be zero under D_2 symmetry, and two of the three under C_2 symmetry, so that the chirality product would vanish for these chiral tetrahedra. These three differences must therefore be excluded. Because this chirality product $P(e)$ circumvents the α-constraint, it includes D_2 and C_2 symmetries, although it fails for C_1 tetrahedra with adjacent edges of equal length. $P(e)$ consists of twelve rather than six terms, although there are redundancies for D_2 and C_2 tetrahedra. Equation (7) shows three of the twelve terms, i.e. those for the triangular face ijk:

$$P(e) = (e_{ij} - e_{ik}) (e_{ji} - e_{jk}) (e_{ki} - e_{kj}) \ldots . \tag{7}$$

An alternative approach involves taking the length of each edge to be the sum of two vertex-specific segments $(e_{ij} = v_i + v_j)$ so that, for example, $e_{ik} - e_{jk} = e_{im} - e_{jm} = v_i - v_j$. In terms of this approach, tetrahedra with two adjacent edges of equal length have to be achiral, and C_1 tetrahedra with such edges are ipso facto excluded. However, the new chirality product (eq. (8)) can no longer accommodate D_2 and C_2 symmetries:

$$P(v) = \prod_{i>j}^{1\ldots4} (v_i - v_j)^2. \tag{8}$$

The first application of this type of chirality product to chemistry was provided more than 50 years ago by Boys [8], who used it as a measure of optical rotatory power. In Boys' model, four spheres are brought into mutual contact and their centers form the vertices of a tetrahedron. The length of each edge of the tetrahedron therefore equals the sum of the radii of two spheres. Clearly, the model is chiral only if the tetrahedron is asymmetric. The essentially geometric character of his chirality product was recognized by Boys, who remarked that the variables "were termed the radii of repulsion of the radicals, but rather than representing any exact physical quantity they must be regarded more as parameters used to express the shape of the molecule".

3.   Similarity invariance and bounds on geometric measures of chirality

As previously discussed [9], geometric measures of chirality should be similarity invariant: chirality is measured by shape and not by size, and similarity invariance eliminates the factor of size.

However, *none* of the chirality products $P(x)$ discussed so far meet the criterion of similarity invariance. Although these functions [3,4,8], which we call *chemical chirality products*, can be made similarity invariant in an *algebraic* sense, it is not clear whether such an approach is chemically meaningful. On the other hand, this problem is not beyond remedy for geometric chirality products.

Consider, for example, the chirality products given by eq. (8) for two similar but non-isometric tetrahedra T and T′. It is obvious by inspection that if the vertex-specific segments v and $v′$ in the two tetrahedra are related by a scaling factor μ,

so that $v' = \mu v$, then $P'(v') = \mu^{12}P(v)$. Division of each term in P and P' by $v_k = \max\{v_i, v_j\}$ and $v'_k = \mu v_k$, respectively, results in a chirality product $\chi(v)$ (eq. (9)) that is the *same* for T and T' and that has the proper attributes of a geometric chirality measure [9]: like $P(v)$, $\chi(v)$ vanishes identically for achiral tetrahedra ($v_i = v_j$) and is oppositely signed for enantiomorphous tetrahedra but, unlike $P(v)$, $\chi(v)$ is also similarity invariant, dimensionless, and bounded in the range $[-1, 1]$. The absolute value of $\chi(v)$ is therefore a suitable measure of the degree of chirality of tetrahedra [9] in terms of a vertex parameter v, such as the radii of four mutually touching spheres in Boys' model [8]:

$$\chi(v) = \prod_{i>j}^{1...4} \left(\frac{v_i - v_j}{\max\{v_i, v_j\}} \right)^2. \tag{9}$$

We next draw attention to an important feature of eq. (9): the bounds of the range of the normalized function $[-1, 1]$ are only approachable as a limit. That is, $\chi(v) = \pm 1$ only in the limit of $v_j/\max\{v_i - v_j\} = 0$, i.e. when the radii of the spheres in Boys' model [8] have shrunk to the vanishing point, along with the tetrahedron itself. This is consistent with the non-compactness of the space of similarity equivalent tetrahedra [9]. Accordingly, a "most chiral" object may not be attainable if the measure is a similarity invariant chirality product.

4. A chirality product for triangles

4.1. CHOICE OF A MEASURE

Whenever molecules are modeled by geometric objects, molecular shapes – a common theme in structural chemistry – are reflected in the shapes of the corresponding geometric representations. As we saw, geometric chirality products are expressions of chiral shapes, and a study of the corresponding polynomials is therefore of obvious relevance to problems in structural chemistry. A study of geometric chirality products such as $\chi(v)$ would be of particular interest, since the asymmetric tetrahedron has played a special role in organic chemistry that dates back to the days of van 't Hoff [7]. However, the complexity of the polynomials involved is certain to obscure basic features that are easily seen in the far more tractable third-order polynomials of chirality products for triangles. We therefore opted for a study of these two-dimensional counterparts of tetrahedra.

Chirality product $P(e)$ for triangles (eq. (10)), where a, b, and c are the lengths of the sides, is analogous to the chirality product for tetrahedra given by eq. (7). Like eq. (7), eq. (10) is not subject to the two-dimensional analog of an α-constraint, i.e. to the constraint that none of the internal angles in the triangle can exceed $2\pi/3$ radians:

$$P(e) = (a - b)(b - c)(c - a). \tag{10}$$

Division by abc transforms $P(e)$ into $\chi(e)$ (eq. (11)):

$$\chi(e) = (1 - b/a)(1 - c/b)(1 - a/c). \tag{11}$$

All the conditions for a measure of chirality [9] are met by this chirality product, which (a) is a continuous and real-valued function that vanishes identically if, and only if, any two sides of the triangle are equal, i.e. if, and only if, the triangle is achiral in E^2 (isosceles or equilateral), (b) gives values that are equal in magnitude but opposite in sign for enantiomorphous triangles, and (c) is similarity invariant, bounded, normalized, and dimensionless in the interval $[-1, 1]$. While the range of $\chi(e)$ is bounded, it is nonetheless open since the space of similarity equivalent ovals is not compact, and the bounds of any measures defined on this space may thus not be attainable. It follows that a most chiral triangle, corresponding to $\chi(e) = \pm 1$, may not exist, but may only be approached as a limit.

4.2. MAPPING TRIANGULAR SHAPES

A minimum of two independent parameters, for example two internal angles, is needed to define the shape of a triangle. These are the coordinates of a point in a two-dimensional "shape space". The shape space of our choice is an xy-coordinate system in which side c opposite vertex C of a triangle ABC coincides with the x-axis, and in which the center of c is fixed at the origin. Because $\chi(e)$ is similarity invariant and because our concern is with shape and not with size, we may therefore take $c = 1$ without loss of generality, so that the coordinates of A, B, and C are $(1/2, 0)$, $(-1/2, 0)$, and (x, y), respectively (fig. 1). Accordingly, the coordinates of C define
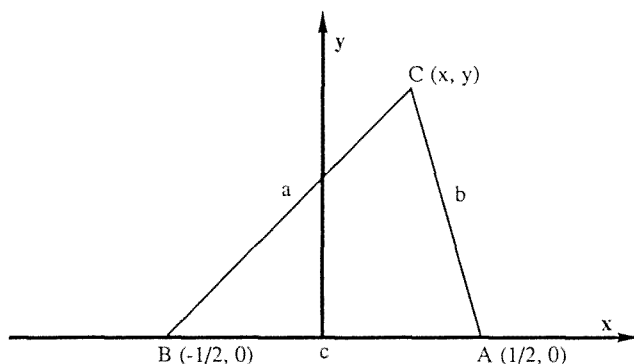

Fig. 1. Coordinate system and labeling convention for the space of triangles in which a, b, and c, in that order, are arranged in a clockwise manner.

the shape of the triangle. We shall adhere to the labeling convention in fig. 1 throughout the following discussion.

Points in the xy plane that represent isosceles triangles lie on one of three nodal curves, depending on whether $a = b$ (eq. (12)), $a = c$ (eq. (13)), or $b = c$ (eq. (14)):

$$x = 0, \qquad (12)$$

$$(x + 1/2)^2 + y^2 = 1, \qquad (13)$$

$$(x - 1/2)^2 + y^2 = 1. \qquad (14)$$

Figure 2 depicts the two nodal curves that correspond to eqs. (13) and (14) as semicircles with radius $c = 1$ centered at $(-1/2, 0)$ and $(1/2, 0)$, respectively. These curves intersect the third nodal curve, i.e. the y-axis (eq. (12)), at $(0, \sqrt{3}/2)$, the point that represents the equilateral triangle. The three nodal curves divide the xy plane into
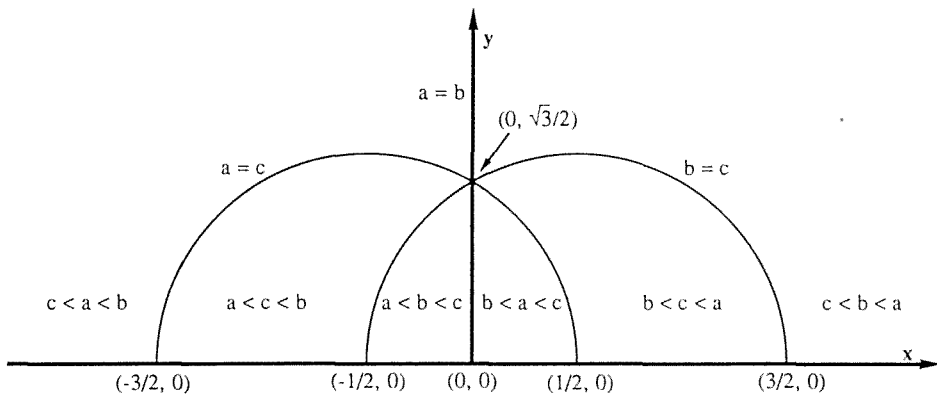

Fig. 2. The segments of shape space labeled according to the convention in fig. 1.

six segments, each of which represents all chiral (scalene) triangles that have in common a given inequality of sides, e.g. the triad $a < b < c$. A shown in fig. 2, each segment is characterized by one of six triads that result from the permutation of the three labels in the inequality. Under the labeling convention mentioned above, these six segments fall into two sets representing *enantiomorphous* triangles: $\{a < b < c,\ b < c < a,\ c < a < b\}$ and $\{a < c < b,\ b < a < c,\ c < b < a\}$. For example, a chiral triangle whose shape is defined by the two angles $\pi/2$ and $\pi/6$ is represented six times in fig. 2: by positions of vertex C at $(-1/2, \sqrt{3})$, $(-1/4, \sqrt{3}/4)$, and $(1/2, 1/\sqrt{3})$ in segments labeled $c < a < b$, $a < b < c$, and $b < c < a$, respectively, and at $(1/2, \sqrt{3})$, $(1/4, \sqrt{3}/4)$, and $(-1/2, 1/\sqrt{3})$ in segments labeled $c < b < a$, $b < a < c$, and $a < c < b$, respectively. The triangles in the first set are enantiomorphs of those in the second set; although the three triangles within each set differ in size, they have the same shape, i.e. they are not isometric but they *are* similar.

The six segments in fig. 2 may therefore be reduced to two, e.g. those in which c is taken to be the longest side. All triangular shapes are then accommodated, without redundancy, within two segments, $a < b < c$ and $b < a < c$. In fig. 2, these

segments are contained within a gothic arch whose apex is at $(0, \sqrt{3}/2)$ and which is bounded on two sides by arcs of length $\pi/3$ that belong to the two nodal semicircles and on the third by the x-axis. *This gothic arch is a unique representation of our shape space.* All isosceles triangles with $a = c$ or $b = c$ are represented by points on the two arcs, while those with $a = b$ are represented by points on the y-axis. All points that lie on the x-axis represent degenerate triangles, i.e. triangles whose three vertices are collinear, and are excluded from the set of triangles under consideration. The shape space within the gothic arch is therefore bounded on all three sides, but it is not closed at $y = 0$.

4.3.   CHIRALITY PRODUCTS AND TRIANGULAR SHAPES

The dependence of the chirality product $\chi(e)$ on triangular shape is conveniently explored by examining the behavior of $\chi(e)$ as x varies for a given value of y within the bounds of the two arcs, i.e. within the limits of $x = 1/2 - \sqrt{1 - y^2}$ and $x = -(1/2 - \sqrt{1 - y^2})$. Since $c = 1$, this corresponds to an examination of $\chi(e)$ as a function of triangular shape for all triangles with a given area $y/2$.

Figure 3 displays plots of $\chi(e)$ versus x, computed for selected values of the altitude y. For each of the two enantiomorphous sets of triangles $a < b < c$ and $b < a < c$, all values of $\chi(e)$ have the same sign, positive and negative, respectively, regardless of triangular shape. Within the conceptual framework developed by Ruch and coworkers [3], $\chi(e)$ may therefore be characterized as a homochirality function: the two sets are mutually heterochiral, all triangles within a given set are homochiral (i.e. chirally related), the boundary between and around the two sets is the set of achiral triangles, and the dimension of this boundary is $n - 1$, where n is the dimension of the space of the chiral triangles [4d].

We find that for each value of y, $\chi(e)$ assumes a maximum value χ_{max} which is the same in magnitude but oppositely signed for the two sets. It is obvious on inspection of fig. 3 that with decreasing values of y, χ_{max} increases in magnitude and at the same time the corresponding value of x is shifted in the direction of the bounds at $x = \pm 1/2$. In the limit of $y = 0$, $\chi(e)$ becomes the chirality product of a linear array in which c is made up of two segments a and b. Substitution of $a + b = c = 1$ in eq. (11) yields $\chi(e) = b - a$ and, if $a = 0.5 + x$ and $b = 0.5 - x$, it follows that $\chi(e) = -2x$ in the interval $(-1/2, 1/2)$. Thus, $\chi(e)$ in the limit of $y = 0$ becomes a measure of one-dimensional chirality.

As suggested in fig. 3, the magnitude of χ_{max} is negligible for values of y greater than 0.5 , becoming significant only for triangles that are both extremely flat, i.e. for values of y close to zero, and extremely skewed, i.e. for values of x close to $\pm 1/2$. Within this domain, as the triangle becomes more chiral, two of its sides become more and more similar to each other, and the vertex C representing the triangle with χ_{max} shifts towards the arched borders of the shape space. In the limit, the most chiral triangle is infinitely close to an achiral one. This paradox can be understood within the confines of the measure of chirality adopted here (see below). In the limit
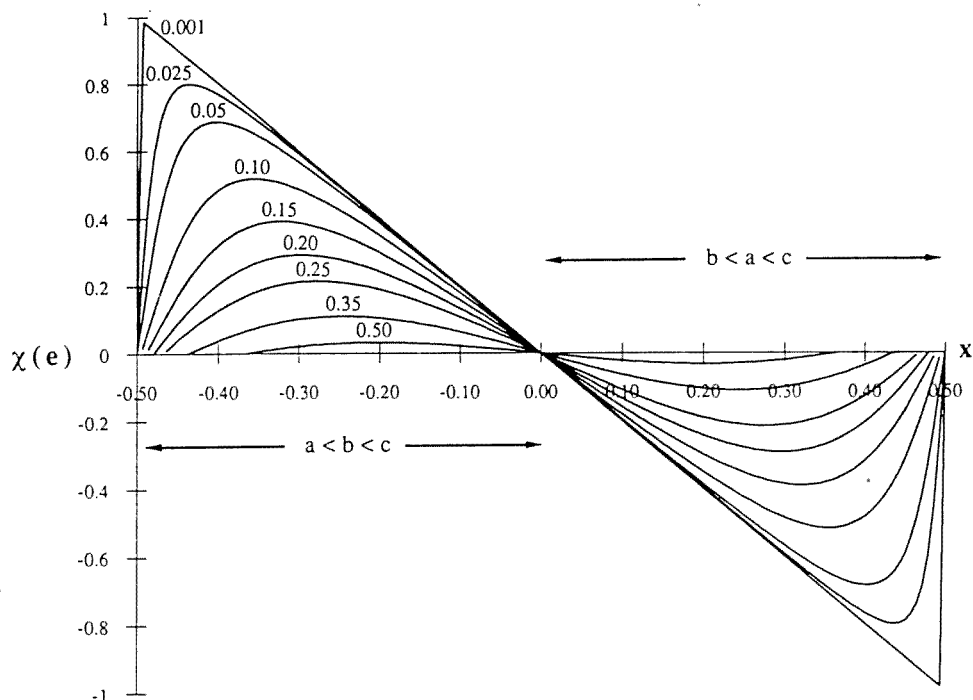
Fig. 3. Calculated plots of the chirality product $\chi(e)$ for triangles versus x for the unique segments $\{a < b < c, \; b < a < c\}$ as a function of x for selected values of the altitude y. The altitudes are indicated by the numbers above the curves.

of $x = \pm 1/2$ and $\chi_{max} = \mp 1$, vertex C coincides with A or B. The most chiral triangle is therefore one that is infinitely flat and skewed, with an altitude y that is arbitrarily close to zero, and for which $a/c \approx 1$ and $b/c \approx 0$, or $b/c \approx 1$ and $a/c \approx 0$.

5. Geometric chirality measures and molecular models

A result similar to the one above was recently obtained in a study [9,10] in which the chirality of triangular domains in the Euclidean plane E^2 was gauged by superimposing enantiomorphs T and T' in such a way that their intersection $T^* = T \cap T'$ was maximized. The chirality measure was defined as

$$\chi(T) = 1 - [T^*]/[T],$$

where $[T^*]$ and $[T]$ denote the areas of the corresponding triangular domains. In that study, it was found that the most chiral triangular domain is one with sides a, b, and c whose altitude h from side c is arbitrarily close to zero and for which $b/c = 1/\sqrt{2}$

and $a/c = 1 - 1/\sqrt{2}$ in the limit of $h = 0$. That is, according to this overlap measure the most chiral triangular domain is beyond reach and is arbitrarily close to a line segment. In contrast to the geometric chirality product, the overlap measure does not exhibit the paradox discussed in the previous section: in this limit, the line segment has $[T] = 0$ and $\chi(T)$ is thus undefined. Therefore, the ultimate (degenerate) triangle cannot be discussed within the confines of this overlap measure.

There are some other important differences in the results of the two studies. As we saw, although both measures lead to the conclusion that the most chiral general triangle is infinitely flat, the two measures give different relationships for the sides of that ultimate triangle. Equally telling are the differences in the results for the most chiral right triangle. Within the gothic arch, all right triangles are represented by points on a semicircle of radius 1/2 that is centered at $(0, 0)$. Consequently, the height of the right triangle is tied to its skewedness, and the maximum degree of chirality for the points on this locus occurs at $x \approx \pm 0.40$, $y \approx 0.30$, with $|\chi(e)| \approx 0.074$. By contrast, the overlap measure yields as the most chiral right triangle [9] one whose shape is given by $2\cos^3\alpha = 1$ and whose degree of chirality $(2^{1/3} - 1)/(2^{1/3} + 1)$ ≈ 0.115, while that of the most chiral general triangle is $(2^{1/2} - 1)/(2^{1/2} + 1) \approx 0.172$.

It should be emphasized that the overlap measure demands a triangle with a uniform and continuous distribution of points (triangular domain), whereas the chirality product measure requires only a set of three discrete points (vertices). Although the geometric chirality product can be applied both to triangular domains and to triangles defined as a set of three vertices, the overlap measure can only be used with the former. The distinction between these two approaches carries over to geometric models of molecules. Space-filling (CPK) models describe molecular shape by assigning van der Waals radii to each atom. The overlap measure of chirality requires an integration of the molecular volume and can therefore be applied to such models only on the assumption that the distribution of points inside the volume is uniform and continuous. Therefore, this method cannot be applied to molecular models that localize matter in discrete regions, and the geometric chirality product is consequently the more appropriate one for such models. As is evident from this discussion, *quantification of molecular chirality crucially depends on the model employed and on the measure of chirality associated with that model.*

Acknowledgement

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