

## Minimal Distortion Pathways in Polyhedral Rearrangements

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**Abstract:** A definition of minimum distortion paths between two polyhedra in terms of continuous shape measures (CShM) is presented. A general analytical expression deduced for such pathways makes use of one parameter, the minimum distortion constant, that can be easily obtained through the CShM methodology and is herein tabulated for pairs of polyhedra having four to eight vertexes. The work presented here also allows us to obtain representative model molecular structures along the interconversion pathways. Several commonly used polytopal rearrangement pathways are shown to be in fact minimum distortion pathways: the spread path leading from the tetrahedron to the square, the Berry pseudorotation that interconverts a square pyramid and a trigonal bipyramid, and the Bailar twist for the interconversion of the octahedron and the trigonal prism. Examples of applications to the analysis of the stereochemistries of several families of metal complexes are presented.

The regular Platonic polyhedra, semiregular Archimedean polyhedra, and the planar regular polygons are fascinating geometrical objects<sup>1–4</sup> that have captivated the attention of mankind from prehistoric times.<sup>5,6</sup> Polyhedral models found in Scotland have been dated in 2000 B.C.; in ancient Greece, Archimedes, Plato, Euclid, and others studied in detail the polyhedra; during the Renaissance, artists and polymaths such as Dürer, Pacioli (with drawings from Leonardo), and Kepler made extensive use of polyhedra, and their study was spread to China and Japan in the early XVIIth century. In Chemistry, these geometrical entities provide a simple and powerful way to represent the spatial arrangement of groups of atoms as, e.g., those directly bonded to a central atom, starting from the introduction of the tetrahedron by Van'Hoff and Le Bel to describe the stereochemistry of organic molecules and of the octahedron by Werner to explain the enantiomerism of metal coordination compounds. We can find nowadays examples of different kinds of molecules whose structures correspond to a

variety of polyhedra,<sup>7–13</sup> from boranes to purely organic molecules, fullerenes, coordination complexes, metal clusters, or supramolecular arrangements. Yet many molecules show in solution a dynamic behavior, undergoing a fast interconversion between two polyhedral structures (polytopal rearrangement) at room temperature, while many others exhibit in the solid state structures that are intermediate between two of the highly symmetric polyhedral shapes. A key question then is can we define a general polytopal rearrangement pathway between two symmetric geometries that occurs with the minimal loss of shape or symmetry?

### Shape and Symmetry Measures

To decide whether the loss of shape or symmetry is minimized along a rearrangement path, we need to consider them as continuous properties, in such a way that the loss of shape or symmetry can be quantitatively evaluated. The continuous symmetry and shape measures (CSM or CShM, respectively) proposed by one of us<sup>14,15</sup> comply with this requirement, providing us with quantitative estimates of the degree of distortion of a particular set of atoms from a

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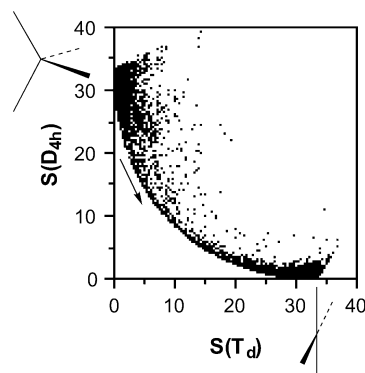
predetermined structure, such as an ideal polyhedron. It seems therefore adequate to try to describe the interconversion path between two ideal polyhedra in terms of the corresponding shape or symmetry measures.

At this point, it is important to clarify the subtle difference between symmetry and shape measures when we evaluate distortions from a polyhedron. Strictly speaking, a symmetry measure (CSM) calibrates how far a structure is (see below for a more detailed explanation) from a geometry that possesses the symmetry operations of a certain symmetry group, whereas a shape measure (CShM) tells the *distance* to a specific shape. It must be noted, though, that when the reference shape is a regular polyhedron (tetrahedron, octahedron, cube, icosahedron, or dodecahedron), shape and symmetry are equivalent. This can be exemplified by the cube, since all cubes are identical except for differences in size and orientation in space, all cubes have the  $O_h$  symmetry. When other polyhedra, such as bipyramids or prisms, are considered, there are infinite shapes with the same symmetry, and shape measures are different than symmetry measures. As an example, consider the trigonal bipyramid. We can build a variety of trigonal bipyramids by changing the ratio between axial and equatorial distances to the center of the bipyramid, all of them having the same symmetry ( $D_{3h}$ ). However, each of these bipyramids has a different shape, since they cannot be superimposed by the combined effect of a translation, a rotation, and an isotropic expansion or contraction. In summary, shape is a more restrictive criterion than symmetry, and we will use from here on shape measures rather than symmetry measures, even if in some cases the two may be equivalent.

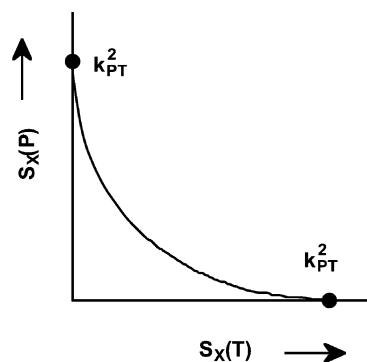
The calculation of the continuous shape measure of the coordination sphere of a given atom,  $AB_{N-1}$  (referred from here on as polyhedron Q), relative to an ideal polyhedron P requires the knowledge of the  $N$  vectors  $\vec{q}_i$  containing the  $3N$  Cartesian coordinates  $q_k$ , as well as the corresponding vectors containing the coordinates  $p_k$  of the ideal polyhedron. The ideal shape is then rotated, translated, and scaled in such a way as to minimize the distance function in eq 1 (more details on the minimization procedure are given below), which then gives the *shape measure* of the investigated structure Q relative to the ideal shape P,  $S_Q(P)$ . In eq 1,  $\vec{q}_0$  is the position vector of the geometric center of Q.

$$S_Q(P) = \min \left[ \frac{\sum_{i=1}^N |\vec{q}_i - \vec{p}_i|^2}{\sum_{i=1}^N |\vec{q}_i - \vec{q}_0|^2} \right] \times 100 \quad (1)$$

By considering several alternative geometries with  $N - 1$  vertexes, the coordination sphere Q can then be characterized by its shape measures relative to a variety of reference polyhedra with the same number of vertexes. As an example, for a tetracoordinated atom, we can use the values of  $S_Q(T_d)$ ,  $S_Q(D_{4h})$ , and  $S_Q(\text{sawhorse})$ , relative to the tetrahedron, square planar, and sawhorse geometries, respectively. Focusing on only two shape



**Figure 1.** Positions of the structures of tetracoordinate transition metal complexes in a shape map. The arrow indicates the path from the perfect tetrahedron (shape measures 0 and 33.3) to the perfect square (shape measures 33.3 and 0).



**Figure 2.** Generalized interconversion pathway between two polyhedra P and T in the shape map referred to their ideal structures P and T.

measures, we can represent in a scatterplot, e.g.,  $S_Q(D_{4h})$  as a function of  $S_Q(T_d)$  for molecular models, experimentally determined structures or theoretically optimized ones. We call such scatterplots *shape* (or *symmetry*) *maps* and have shown that they provide a highly useful means of identifying structural trends in tetra-,<sup>16</sup> hexa-,<sup>17</sup> or heptacoordinate<sup>18</sup> transition metal compounds. A shape map for tetracoordinate transition metal compounds<sup>16</sup> including more than 13 000 structural data is shown in Figure 1 as an example. There, the perfect tetrahedron corresponds to the (0, 33.33) point and the perfect square to the (33.33, 0) point. Distortions from the tetrahedron toward the square seem to have a lower limit that corresponds to an increase in square symmetry (i.e., a decrease in  $S_Q(D_{4h})$ ) accompanied with the minimal possible distortion of the tetrahedron (minimal value of  $S_Q(T_d)$ ).

Typical pathways for the interconversion of two ideal polyhedra P and T, such as the spread distortion from tetrahedral to square molecules (1), the Berry pseudorotation of pentacoordinate complexes (2), or the Bailar twist between the octahedron and the trigonal prism (3), have been seen to appear in the shape maps as curves of the type shown in Figure 2, representing a lower limit for the shape measures of experimental structures. In general, we consider the path for the interconversion of two arbitrary polyhedra P and T with the same number of vertexes, proceeding through a series of intermediate structures X that

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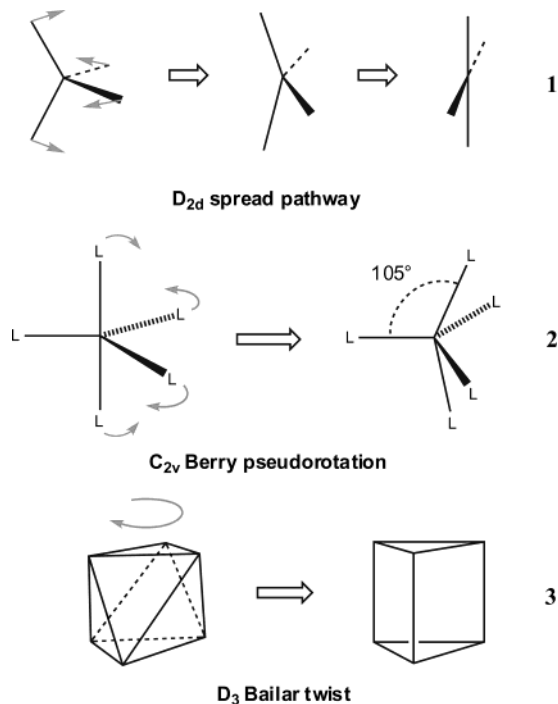
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are characterized by their shape measures  $S_X(P)$  and  $S_X(T)$ . We then define the *minimum distortion path* between P and T as the one that has the minimum value of  $S_X(T)$  for a given value of  $S_X(P)$  within the interval  $0 \leq S_X(P) \leq S_T(P)$ .



The curves representing minimum distortion paths in shape maps have the following properties, regardless of the number of vertexes of the polyhedra under study: (i) The shape measures of two structures relative to each other are identical and can be related to a constant  $k_{PT}$  associated to those two specific shapes (eq 2). (ii) The (0, 0) point is by definition unreachable, since it would correspond to a structure that has at the same time two different shapes, e.g., both perfect tetrahedral and square planar. (iii) There is only one allowed point at each coordinate axis, because the distance from a perfect polyhedron (i.e., a zero value for one shape measure) to the alternative one (i.e., the second shape measure) has a unique value. These common features of such different paths as those shown in 1–3 will allow us in a later section to put them in the same scale, thus offering a quite general description of polyhedral rearrangement pathways.

$$k_{PT} = \sqrt{S_P(T)} = \sqrt{S_T(P)} \quad (2)$$

In what follows, we will first review briefly the procedure used to obtain the shape measures defined in eq 1, since the meaning and nomenclature of the different parameters used will be needed for the subsequent sections. We will then show that all polyhedra with  $N - 1$  vertexes and the same size can be described as points on the surface of a hypersphere of fixed radius. The path between two polyhedra can therefore be described making use of a section of that hypersphere, and a simple formula can be deduced that expresses the minimum distortion pathway in terms of a constant that is characteristic of the pair of polyhedra considered (the *minimum distortion angle* or the related *minimum distortion constant*). The analytical expression deduced will be shown to be in excellent agreement

with molecular models for the three most characteristic paths (1–3). Furthermore, we will show that the determination of the shape measure of a polyhedron relative to another one provides a simple and efficient means of building molecular structures along their interconversion path. In the same spirit with which the shape measures provide information on the distance of a given structure to a reference shape, we will then define a deviation function relative to a given pathway that measures how close a structure is from a given pathway, regardless of the distance to the two extreme shapes. Finally, applications to the analysis of experimental structural data of the deviation functions will be shown. In addition, we provide as appendices two additional interesting aspects of the minimal distortion pathways: in Appendix 1, we will show under which circumstances a sum rule used earlier<sup>17</sup> represents a reasonable approximation to the analytical expression deduced, whereas, in Appendix 2, we will discuss two cases in which the minimal distortion angle in the shape hypersphere can be associated to bond angles in the interconverted structures.

### Calculation of Continuous Shape Measures

To deduce the minimum distortion paths for polytopal rearrangements in terms of continuous shape measures it is convenient first to briefly recall the procedure used to calculate shape measures, while a more detailed description of the algorithms can be found in the literature.<sup>19</sup> The goal of the computational procedure is to obtain the coordinates  $p_k$  of an ideal polyhedron  $P^0$  that is closest to a particular distorted polyhedron Q with vertexes at the positions defined by the  $\vec{q}_i$  vectors, in order to calculate the shape measures from eq 1. Such a process requires transformation of the ideal polyhedron  $P^0$  to a related polyhedron P with the same shape but whose size and orientation in space are adjusted in such a way as to minimize its distance (in the sense of eq 1) to the distorted polyhedron.

The algorithm for calculating the CShM's consists of the following steps:

(1) Both the original polyhedron and the reference one are placed with their geometric centers at the origin of coordinates (i.e., the coordinates of the origin in eq 1 are  $\vec{q}_o = \vec{0}$ ).<sup>19</sup> Their orientation and vertex labeling are either arbitrary or selected for convenience of computation (but see below). It can be demonstrated that once the problem and reference molecules have been placed at the origin, no further translation is required to minimize the distances between their vertexes.<sup>19</sup>

(2) Since the shape measures should be independent of size, we size-normalize the two objects  $P^0$  and Q as follows:

$$\sum_{k=1}^{3N} q_k^2 = \sum_{k=1}^{3N} (p_k^o)^2 = N \quad (3)$$

(3) The reference polyhedron undergoes a rigid rotation to minimize the distances between its vertexes and those of the investigated molecule, giving a new set of coordinates  $\vec{p}'_i = \mathbf{R} \vec{p}_i^o$ , where  $\mathbf{R}$  is a  $(3 \times 3)$  unitary transformation matrix that minimizes the distances between the two shapes.<sup>20</sup> Note that  $P'$  is also normalized as in eq 3.

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(4) At this point, we can define a distance function

$$d^2 = \sum_{k=1}^{3N} (q_k - p'_k)^2 \quad (4)$$

(5) An isotropic scaling factor,  $A_{QP}$ , is applied to the  $p'_k$  coordinates of the reference polyhedron,  $p_k = A_{QP}p'_k$ , that minimizes the new distance function

$$\sigma^2 = \sum_{k=1}^{3N} (q_k - p_k)^2 \quad (5)$$

(6) The process is repeated for all possible pairings between the vertices of the reference and the distorted polyhedron (i.e., the B atoms in an  $AB_{N-1}$  molecule), and the one that gives the minimal distance functions  $d$  and  $\sigma$  provides us with the closest ideal polyhedron P to our problem polyhedron Q. Such a minimal distance,  $\sigma_Q(P)$ , gives the shape measure of Q relative to P,  $S_Q(P)$ , through eq 6, where the denominator results from eq 1 when the normalization condition (eq 3) is taken into account. The shape measure  $S_Q(P)$  is adimensional and can adopt values between 0 and 100, in contrast with  $\sigma_Q(P)$  that has units of distance and can vary between 0 and  $\sqrt{N}$ .

$$S_Q(P) = \frac{\sigma_Q^2(P)}{N} 100 \quad (6)$$

For the calculation of the shape measures reported in this paper, we have used the program SHAPE<sup>21</sup> that can be obtained from the authors upon request.

### Shape Hypersphere and Minimum Distortion Pathway

Before dealing with the minimum distortion pathway between two polyhedra, we need to establish the framework in which it will be defined. By comparing eq 3 with the equation of a sphere ( $x^2 + y^2 + z^2 = r^2$ ), one realizes that a figure P' (e.g., a regular

square, with coordinates  $p'_k$ ) can be viewed as a point on a hypersphere of radius  $\sqrt{N}$  in  $3N$ -dimensional space. Other size-normalized figures with the same shape are related to P' through rigid rotations and correspond to other points on the hypersphere. If we search for the figure with another ideal shape (e.g., a tetrahedron) that is closest to P' in the CShM sense, let us say T', it will occupy another point on the surface of the hypersphere, with coordinates  $q_k$ . By definition of the CShM, all other structures with the same shape, related to T' by rotation, are farther away from P' than T'. Therefore, the shortest path between these two figures, T' and P', composed of all intermediate size-normalized figures X (see 4) corresponds to the circular section of our hypersphere.

Let us first consider the two extreme shapes P' and T' only (5). The distance between these two size-normalized structures,  $d_T(P)$ , is thus the base of an isosceles triangle with an angle  $\theta$ . Since the scaling factor applied to P' in order to minimize the distance between polyhedra P and T,  $A_{PT}$ , is isotropic, when applied to all the  $p'_k$  coordinates, it takes us radially to point P and the OPT' angle must be  $90^\circ$  in order to make  $\sigma_T(P)$  minimum. Several important conclusions arise: (a) The separation between structures T' and P' in the hypersphere is given by a constant angle  $\theta_{PT}$  independently of whether the scaling factor has been introduced or not, and we will refer to it as the *minimum distortion angle* for the interconversion of polyhedra P and T. (b) The scaling factor  $A_{PT}$  must always be less than or equal to one. (c) Since  $\sin(\theta_{PT})$  and  $\sigma$  are related by eq 7 and  $\sigma_T(P) \leq \sqrt{N}$ , the angle  $\theta$  must be in the range  $0 \leq \sin(\theta_{PT}) \leq 1$ , and we need only consider in what follows angles between  $0$  and  $90^\circ$ . (d) From 5, it can be deduced that the scaled and unscaled minimum distances are related by the simple expression in eq 8.

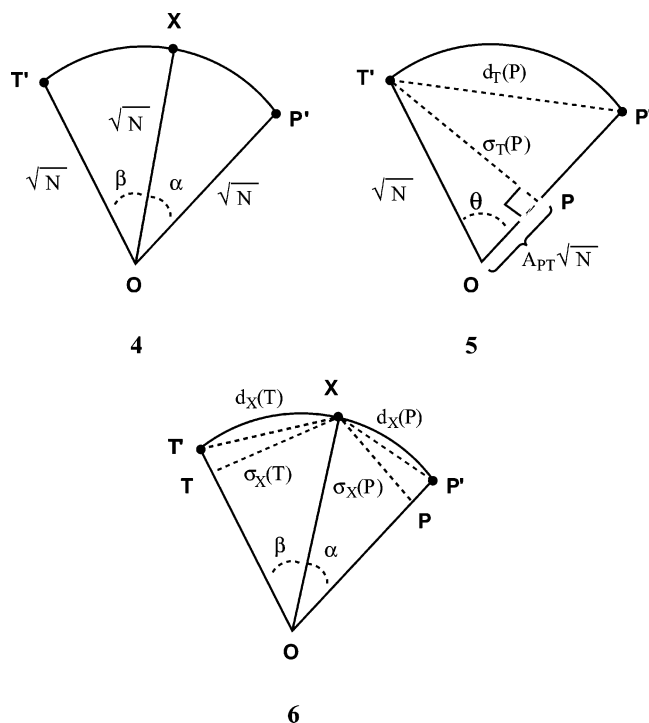
$$\sin \theta_{PT} = \frac{\sigma_T(P)}{\sqrt{N}} \quad (7)$$

$$d_T^2(P) = 2N \left( 1 - \sqrt{1 - \frac{\sigma_T^2(P)}{N}} \right) \quad (8)$$

If we wish to derive the analytical expression of the interconversion pathway in terms of shape measures, we need only to find a general expression for the position of the general point X in terms of the distance functions  $\sigma_X(T)$  and  $\sigma_X(P)$ . Since the scaling factor that is applied to the reference polyhedra when calculating the shape measure of each point X along the path is different, it is much simpler to use the angles  $\alpha$  and  $\beta$  to define the position of X relative to P and T, and these must obey eq 9. The different distances involved ( $d_X(P)$ ,  $d_X(T)$ ,  $d_T(P)$ ,  $d_P(T)$ , and the corresponding scaled distances  $\sigma$ ), as well as the shape measures  $S_T(P)$ ,  $S_P(T)$ ,  $S_X(P)$ , and  $S_X(T)$ , are fully determined by the angles  $\alpha$ ,  $\beta$ , and  $\theta_{PT}$ .

$$\alpha + \beta = \theta_{PT} \quad (9)$$

The trigonometric relationships between  $\sigma_X(P)$  and  $\alpha$  and between  $\sigma_X(T)$  and  $\beta$  deduced from 6 (remember the radius of



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the hypersphere is  $\sqrt{N}$  allow us to establish the following general expression for the least distortive pathway between polyhedra P and T

$$\arcsin \frac{\sigma_X(T)}{\sqrt{N}} + \arcsin \frac{\sigma_X(P)}{\sqrt{N}} = \theta_{PT} \quad (10)$$

which, taking into account eq 6, can be expressed in terms of shape measures, resulting in the following analytical expression for the minimum distortion path:

$$\arcsin \frac{\sqrt{S_X(P)}}{10} + \arcsin \frac{\sqrt{S_X(T)}}{10} = \theta_{PT} \quad (11)$$

It must be noted that there is a simple relationship between the shape constant  $k_{PT}$  defined earlier (eq 2)<sup>17</sup> and the minimum distortion angle  $\theta_{PT}$ :

$$k_{PT} = \sqrt{S_P(T)} = \sqrt{S_T(P)} = 10 \sin \theta_{PT} \quad (12)$$

It is now straightforward to generate the shape constants (eq 2) and minimum distortion angles (eq 12) for a variety of polyhedral rearrangements. In Table 1, we present the corresponding shape constants  $k_{PT}$  (upper entries of each table) and minimum distortion angles  $\theta_{PT}$  (lower entries of each table) for polyhedra having between four and eight vertexes and a central atom. For those cases in which the central atom is at the geometric center of the polyhedron, these constants apply also to polyhedra without a central atom. It might be useful in some instances to analyze the interconversion between, e.g., a cyclic and a chain structure, and we have therefore included in Table 2 the constants related to the interconversion of equally spaced linear chains and the two- (polygonal) and tridimensional (polyhedral) structures with the same number of atoms.

For some high-symmetry polyhedra,  $\theta_{PT}$  can be determined analytically from geometric parameters, as for the interconversion of the square and the tetrahedron. Such geometrical relationships also explain why the same value of the symmetry constant ( $k_{PT} = 5.7735$ ) appears for the tetrahedron-square and octahedron-hexagon interconversion paths (Table 1). For the interested reader, these aspects are discussed in Appendix 2.

We must recall at this point that in some cases a reference polyhedron is uniquely determined by symmetry, but in other cases there is some degree of arbitrariness. Among the geometries considered here, the ones that are univocally defined are the tetrahedron, the octahedron, the cube, all regular polygons, and all prisms and antiprisms, since we consider the latter as semiregular solids with all faces formed by regular polygons. For the reference bipyramids, we impose only the restriction that all vertexes are at the same distance from the center, whereas, for the pyramids, we further impose the central atom to be in the center of the base. For those polyhedra that can be derived from the octahedron by removal of one or two vertexes (the five vertex square pyramid of  $C_{4v}$  symmetry and the four vertex sawhorse structure of  $C_{2v}$  symmetry), we have retained the right angles of the octahedron. However, for some purposes it will be useful to consider as a reference square pyramid one with axial-equatorial angles of  $105^\circ$ , corresponding to the midpoint of the Berry pseudorotation pathway 2. The choice of a reference polyhedron for a few other cases has more degrees of freedom (the capped trigonal prism, the capped

**Table 1.** Minimum Distortion Constants  $k_{PT}$  (Upper Entries) and Angles  $\theta_{PT}$  (Lower Entries, in Degrees) for Several Combinations of Polyhedra with  $V$  Vertexes (IUPAC-Recommended Nomenclature for Polyhedra Is Used When Available) and a Central Atom<sup>a</sup>

$V=4$	T-4	SW-4	SP-4			
T-4		3.129	5.774			
SW-4	18.234		4.365			
SP-4	35.264	25.878				
$V=5$	VOC-5	SPY-5	TBPY-5	PP-5		
VOC-5		1.319	2.710	5.677		
SPY-5	7.582		2.320	5.770		
TBPY-5	15.722	13.417		6.088		
PP-5	34.588	35.243	37.506			
$V=6$	OC-6	TPR-6	PPY-6	HP-6		
OC-6		4.091	5.517	5.774		
TPR-6	24.149		4.125	5.803		
PPY-6	33.484	24.362		5.352		
HP-6	35.264	35.472	32.359			
$V=7$	OCF-7	TPRS-7	PBPY-7	HPY-7	HP-7	
OCF-7		1.236	2.899	4.130	6.146	
TPRS-7	7.099		2.577	4.467	5.989	
PBPY-7	16.852	14.934		5.166	5.934	
HPY-7	24.393	26.530	31.105		5.047	
HP-7	37.924	36.794	36.399	30.309		
$V=8$	CU-8	DD-8	SAPR-8	HBPY-8	HPY-8	OP-8
CU-8		2.820	3.315	2.897	5.533	6.190
DD-8	16.379		1.688	3.960	4.979	5.669
SAPR-8	19.360	9.716		4.296	4.953	5.111
HBPY-8	16.842	23.326	25.444		4.865	5.694
HPY-8	33.592	29.863	29.691	29.109		4.776
OP-8	38.240	34.533	30.736	34.708	28.528	

<sup>a</sup> T-4 = tetrahedron, SW-4 = sawhorse, SP-4 = square planar. PP-5 = planar regular pentagon, VOC-5 = vacant octahedron (square pyramid with  $90^\circ$  angles), SPY-5 = square pyramid ( $105^\circ$  angles), TBPY-5 = trigonal bipyramid. OC-6 = octahedron, TPR-6 = trigonal prism, PPY-6 = pentagonal pyramid, HP-6 = planar regular hexagon. OCF-7 = capped octahedron, TPRS-7 = capped trigonal prism, PBPY-7 = pentagonal bipyramid; HPY-7 = hexagonal pyramid; HP-7 = regular heptagon. CU-8 = cube; DD-8 = triangular dodecahedron; SAPR-8 = square antiprism; HBPY-8 = hexagonal bipyramid; HPY-8 = heptagonal pyramid; OP-8 = regular octagon.

**Table 2.** Minimum Distortion Constants  $k_{PT}$  between a Linear Chain and Two- or Three-Dimensional Arrangements of  $N$  Atoms

$N$	$k(N\text{-gon})$	polyhedron	abbreviation	$k(\text{polyhedron})$
4	7.071	tetrahedron	T-4	8.165
		sawhorse	SW-4	6.761
5	7.100	vacant octahedron	VOC-5	7.638
		trigonal bipyramid	TBPY-5	7.874
		Berry square pyramid	SPY-5	7.906
6	7.105	octahedron	OC-6	8.165
		trigonal prism	TPR-6	7.772
		pentagonal pyramid	PPY-6	7.608
7	7.110	capped octahedron	OCF-7	8.137
		capped trigonal prism	TPRS-7	8.141
		pentagonal bipyramid	PBPY-7	8.052
		hexagonal pyramid	HPY-7	7.500
8	7.113	cube	CU-8	8.165
		dodecahedron	DD-8	7.908
		square antiprism	SAPR-8	7.968
		hexagonal bipyramid	HBPY-8	7.924
		heptagonal pyramid	HPY-8	7.487

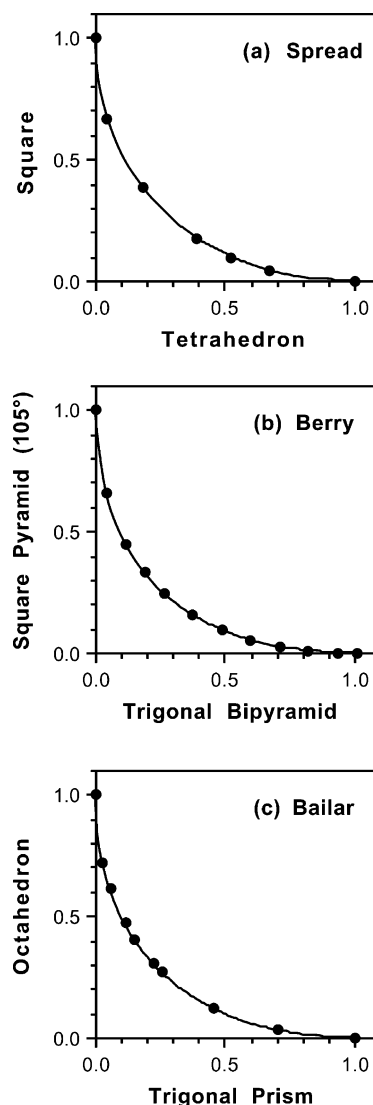
octahedron and the trigonal dodecahedron), and their definition as well as the justification for their choice are discussed in our work devoted to penta-,<sup>22</sup> hexa-,<sup>17</sup> hepta-,<sup>18</sup> and octacoordination.<sup>23</sup>

### Spread, Berry, and Bailar Pathways: Molecular Models and Experimental Data

In this section, we wish to look at the geometrical models for three of the most frequently used polytopal rearrangement mechanisms, defined in terms of angular distortions, and see if they actually correspond to minimum distortion paths as defined in eq 11. In addition, we wish to show the similar behavior of those paths and, most importantly, to check whether they represent correctly the experimental structures of various families of compounds. These are the spread pathway (1) for the interconversion of the tetrahedron and the square, the Berry pseudorotation (2) that takes the trigonal bipyramid to a square pyramid and viceversa, and the Bailar twist (3) for the interconversion of the octahedron and the trigonal prism. For each of these paths, we have obtained the shape measures corresponding to the least distortive paths by applying eq 11 with the minimum distortion angles of Table 1 and plotted them in Figure 3 (continuous lines) in *normalized shape maps*, in which the shape measures are divided by  $k_{PT}^2$ . In such normalized maps, the two ideal polyhedra correspond to the (1, 0) and (0, 1) points connected through the same path, regardless of the number of vertexes and shape distance between the two reference polyhedra. We also show in Figure 3 the values obtained from molecular models of these rearrangements used in our previous works (circles). There it can be seen that there is a perfect match between the analytical minimum distortion paths and those obtained from molecular models. Least-squares fitting of the molecular model data to an expression of the type shown in eq 11 gives values of  $\theta_{PT}$  of 35.264(3)°, 13.407°, and 24.19(4)° for the spread, Berry, and Bailar paths, to be compared with the analytical values of 35.264°, 13.417°, and 24.149°, respectively.

Having analytical expressions for minimum distortion paths in terms of shape measures is useful for the stereochemical analysis of families of compounds. However, it would be even more interesting if we could obtain molecular structures (i.e., atomic coordinates) along those paths. In the CShM procedure, once we have found the ideal polyhedron P that is closest to polyhedron Q, each atom of P is associated to its closest atom in Q, so that we can find the displacement vectors  $\vec{q}_i - \vec{p}_i$  (eq 5). The minimum distortion path corresponds precisely to those vectors, and we can obtain the atomic coordinates for as many steps along the interconversion path as we wish by scaling the vectors by a factor between 0 and 1. As examples, we show in Figure 4 several structures obtained in such a way that represent snapshots along the paths between the cube and the hexagonal bipyramid and between the square and the tetrahedron.

To illustrate the chemical relevance of the minimum distortion paths described by eq 11, as well as its applicability to any polyhedral rearrangement, we present in Figure 5 the three pathways analyzed here (spread for tetracoordinate, Berry for pentacoordinate, and Bailar for hexacoordinate complexes) in normalized shape maps. Together with the minimum distortion path, we show in Figure 5 the shape measures for the first coordination sphere of several families of coordination compounds, which appear nicely distributed along the interconversion pathways, thus suggesting that minimum distortion and low

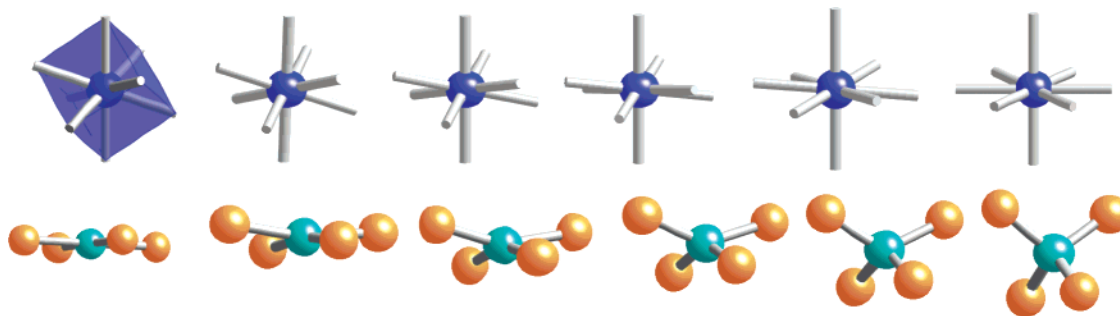


**Figure 3.** Normalized shape maps showing the analytical minimum distortion paths (eq 11, continuous lines) and paths calculated with molecular models (circles) for (a) the spread interconversion 1 of tetrahedron and square, (b) the Berry pseudorotation 2 for interconversion of the trigonal bipyramid and the square pyramid, and (c) the Bailar interconversion 3 of trigonal prism and octahedron.

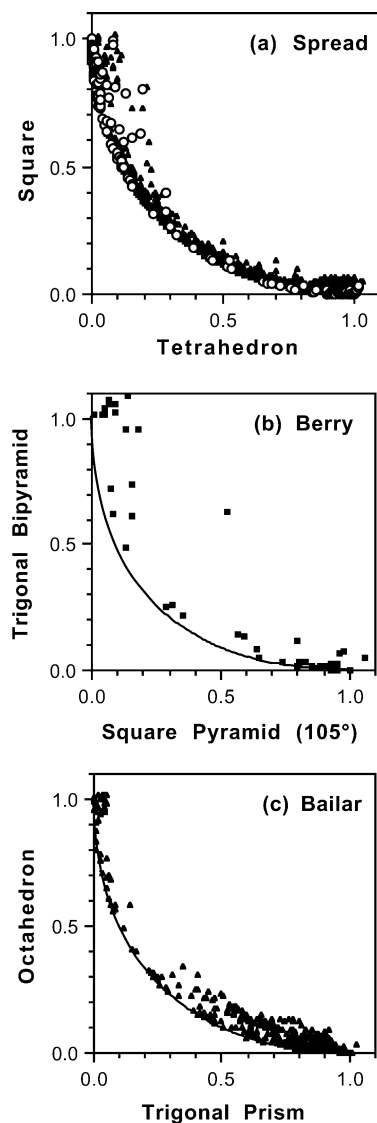
energy paths proposed by the structure correlation principle<sup>24–26</sup> (“...if a correlation can be found between two or more independent parameters describing the structure of a given fragment in a variety of environments, then the correlation function maps a minimum energy path in the corresponding parameter space”) are coincident. Furthermore, in Figure 5a we have included the shape measures of both the coordination spheres of d<sup>9</sup> complexes and the supramolecular architectures having four Cu atoms, to show how the spread pathway allows us to describe structures of polyhedra so diverse in size and molecular structure, using the minimum distortion path as a unifying feature.

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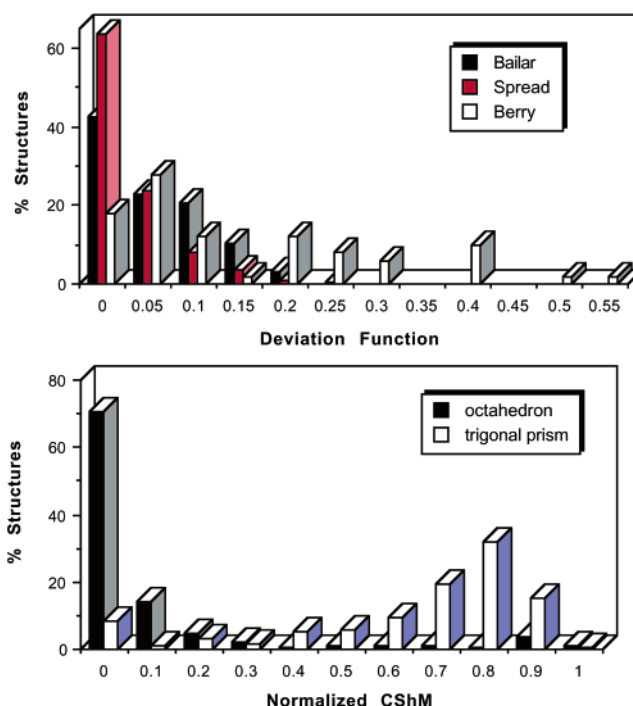
**Figure 4.** Snapshots along the minimum distortion paths between the cube and the hexagonal pyramid (top) and between the square and the tetrahedron (bottom), obtained from the calculation of the shape measures.



**Figure 5.** Analytical minimum distortion paths (eq 11) in normalized shape maps for three polytopal rearrangements, together with experimental data: (a) spread pathway and data for tetracoordinate complexes of  $d^9$  metal ions<sup>15</sup> (black triangles) and tetranuclear Cu compounds (white circles), (b) Berry pathway for homoleptic pentacoordinate complexes,<sup>20</sup> and (c) Bailar pathway for hexakis(alkyl), hexakis(thiolato), tris(bidentate), and encapsulated hexacoordinate complexes.<sup>17,28</sup>

### Evaluation of the Deviation of a Structure from a Path

In some instances, we may be interested in knowing not only how far a structure is from a reference polyhedron  $P$  but also how close it is from the rearrangement path to another



**Figure 6.** Distribution of the deviations (eq 13) from the spread, Berry, and Bailar interconversion paths (top) of the structures described in Figure 4, compared to that of the normalized shape measures of the hexacoordinate complexes relative to the octahedron and the trigonal prism (bottom).

polyhedron  $T$ . For this purpose, we consider a minimum distortion path given by eq 11 and define a deviation function  $\Delta(P,T)$  (eq 13). By definition of the minimum distortion path, the deviation function must always be zero (for structures that fall along the interconversion path) or positive. The inclusion of  $\theta_{PT}$  in the denominator puts the deviation functions for all pairs of polyhedra in the same scale

$$\Delta(P,T) \equiv \frac{1}{\theta_{PT}} \left[ \arcsin \frac{\sqrt{S_X(P)}}{10} + \arcsin \frac{\sqrt{S_X(T)}}{10} \right] - 1 \quad (13)$$

As examples of application of the deviation function, we have calculated such a parameter for the families of compounds analyzed above (Figure 5) with respect to the spread, Berry and Bailar interconversion pathways, respectively (1–3). The results, presented as a histogram in Figure 6 (top), clearly show that most of the tetra- and hexacoordinate structures are concentrated along the spread and Bailar paths, respectively, while the studied pentacoordinate complexes do not represent so well the Berry pseudorotation. For the case of the Bailar trigonal twist, we

present also the deviations from the ideal polyhedra, the octahedron, and the trigonal prism (Figure 6, bottom). Comparison of the two histograms clearly shows that a large number of molecules cannot be adequately described as either an octahedron or a trigonal prism, whereas all of them fall along the Bailar path within a good approximation.

## Conclusions

According to the CShM approach, the geometries of two size-normalized isomeric shapes (P and T), fully determine the minimum distortion pathway for their interconversion. The only parameter needed is the minimum distortion angle  $\theta_{PT}$  (or, alternatively, the related minimum distortion constant  $k_{PT}$ ), which is obtained by calculating the continuous shape measure of one shape relative to the other. Those parameters are reported here for the different pairs of polyhedra with four to eight vertexes.

A general expression has been derived that describes the minimum distortion path for the interconversion of any pair of polyhedra with the same number of vertexes. Such an expression is fully coincident with the paradigmatic pathways in coordination chemistry: the spread path for tetracoordination, the Berry pseudorotation for pentacoordinate, and the Bailar twist for hexacoordinate complexes. However, even in those cases in which a simple geometrical path for the interconversion of two polyhedra is not available, the general expression given here allows one to fully describe the minimum distortion path in terms of shape measures and to generate molecular models along the path. The use of normalized shape maps allows us to compare in the same scale the different interconversion pathways, describing a universal behavior that applies to polyhedra with different numbers of vertexes, and representing equally well, e.g., the structures of the coordination spheres of transition metal complexes and the spatial arrangement of metal atoms in polynuclear supramolecular architectures.

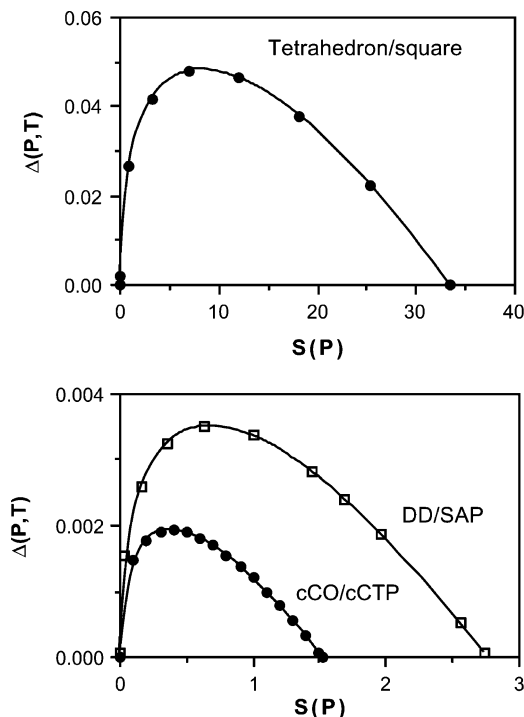
In addition to the assignment of a particular ideal polyhedron to a given molecular structure, which is so often problematic, we propose that the deviation from an appropriate minimum distortion path offers a useful stereochemical description. This has been shown to be of use for several families of transition metal compounds, such as the tetracoordinate  $d^9$  complexes. Among more than 2000 structures of such compounds, 80% can be classified as square planar, 7%, as tetrahedral, and the remaining 13% that are severely distorted can be unequivocally classified as being along the spread interconversion pathway according to the corresponding path deviation function.<sup>15</sup>

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## Appendix 1: The Sum Rule as an Approximation

Some pathways studied so far in terms of shape measures were earlier fitted to either an exponential<sup>27,28</sup> or a square root sum (eq 14), with the latter giving a better agreement with molecular models and experimental structures.<sup>16–18</sup>

$$\sqrt{S_X(P)} + \sqrt{S_X(T)} = k_{PT} \quad (14)$$



**Figure 7.** Relative deviation (eq 13) of the sum rule (eq 16) for several polytopal rearrangement paths, relative to the minimum distortion paths (eq 11): spread pathway between tetrahedron and square (top), conventional capped octahedron and conventional capped trigonal prism (bottom, black circles), and triangular dodecahedron and square antiprism.

We had already noticed that for geometries approximately midway between the two extreme polyhedra along the path, shape measures predicted by eq 14 are always slightly smaller than experimental structures or molecular models. Although a least-squares fitting of a model pathway to a square root sum can be obtained, the resulting expression does not correctly reproduce the points of intersection of the two axes ( $k_{PT} = \sqrt{S_P(T)} = \sqrt{S_P(T)}$ ). Let us then see under which circumstances the sum rule used previously for interconversion pathways (eq 14) is a valid approximation.

If  $\theta_{PT}$  is small, both  $\alpha$  and  $\beta$  are perforce small and eq 9 can be approximately expressed as,

$$\sin \theta_{PT} \approx \sin \alpha + \sin \beta \quad (15)$$

and from eqs 8 and 13, we obtain

$$\sqrt{S_X(P)} + \sqrt{S_X(T)} \approx k_{PT} \quad (16)$$

as empirically found in previous work from molecular models and experimental data.<sup>17,18</sup> In short, the sum rule of eq 16 should be expected to be a good approximation to the minimum distortion pathway for those pairs of polyhedra characterized by small minimum distortion angles  $\theta_{PT}$ . It can also be seen from eq 15 that the sum rule is a good approximation when either  $\alpha$  or  $\beta$  is small (i.e., for small distortions from either of the ideal polyhedra).

The agreement between the shape measures calculated from the sum rule (eq 14) and those from the analytical path defined in the shape hypersphere (eq 11) can be evaluated by means of

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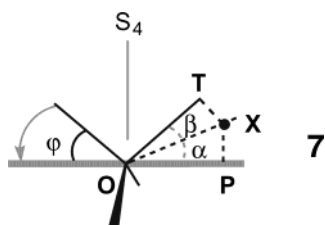
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the deviation function defined above (eq 13). We show in Figure 7 the deviation function for three pairs of polyhedra P and T. For the tetrahedron/square pair, characterized by a large angle ( $\theta_{PT} = 35.26^\circ$ ), deviations of up to 0.05 are obtained by using the sum rule for intermediate structures. In contrast, the capped octahedron/capped trigonal prism and triangular dodecahedron/square antiprism pairs of polyhedra, with seven and eight vertexes, respectively, characterized by small values of  $\theta_{PT}$  (see Table 1), give rather small deviation functions throughout the pathways (less than 0.004). These results confirm that the deviations of the sum rule from the analytical expression are much smaller for a path characterized by a smaller minimum distortion angle.

## Appendix 2: Geometrical Interconversion Paths

The shape measures for the spread interconversion pathway between the tetrahedron and the square (1) can be defined analytically in terms of geometrical parameters through a rather simple expression. Consider, e.g., the tetrahedron and the square superimposed in such a way that the improper  $S_4$  axis of the former is coincident with the  $C_4$  axis of the latter, as schematically depicted in 7, where the square is represented in a side view (thick line) and the closest tetrahedron is superimposed (black continuous lines). The perfect tetrahedron is defined by



$\varphi = \arcsin[1/\sqrt{3}]$ . Any structure X along the spread pathway that retains the  $D_{2d}$  symmetry can be defined by the deviation of the four ligands from the  $xy$  plane by an angle  $\alpha$  (positive values for two ligands, negative for the other two;  $\alpha = \varphi$  for the tetrahedron,  $\alpha = 0^\circ$  for the square). Prior to scaling, the distances of all vertexes to the center are assumed to be normalized in the sense of eq 3. Since the shape measure of structure X is given by the sum of the squares of the distances of its vertexes to those of the reference structure ( $D_{4h}$  or  $T_d$ ), scaled to minimize that distance, OPX and OTX angles must be right angles. Therefore, for each ligand,

$$\sigma_X(D_{4h}) = \sqrt{N} \sin \alpha \quad (17)$$

$$\sigma_X(T_d) = \sqrt{N} \sin \beta \quad (18)$$

and the shape measures can be expressed as

$$S_X(D_{4h}) = 100 \sin^2 \alpha \quad (19)$$

$$S_X(T_d) = 100 \sin^2 \beta \quad (20)$$

Since, by definition of the spread pathway,  $\alpha + \beta = \varphi$ , it follows that

$$\arcsin \frac{\sqrt{S_X(D_{4h})}}{10} + \arcsin \frac{\sqrt{S_X(T_d)}}{10} = \varphi \quad (21)$$

Comparison with eq 11 indicates that the spread distortion is a minimum distortive pathway between the tetrahedron and the square and that the minimum distortion angle is in this case  $\varphi$ , as found by computation (Table 1).

The pathway for the planarization of an octahedron to a hexagon can be described in analogous terms, aligning the  $S_6$  and  $C_6$  axes of the two reference figures. In this case, the angle between each M–L bond in the hexagonal structure and the closest M–L bond in the octahedral structure is again  $\varphi$ , and the path is defined in terms of the shape measures relative to the octahedron ( $O_h$ ) and the hexagon ( $D_{6h}$ ) by the general expression of eq 11 in which the minimum distortion angle is again  $\varphi$ .

$$\arcsin \frac{\sqrt{S_X(O_h)}}{10} + \arcsin \frac{\sqrt{S_X(D_{6h})}}{10} = \varphi \quad (22)$$

Thus, the analytical expressions for these two interconversion paths provide a geometrical meaning for the corresponding minimum distortion angles and explain why they adopt the same value in the tetrahedron-square and octahedron-hexagon cases (Table 1). An important conclusion is that only for those polyhedral rearrangements in which the vertexes of the two shapes can be related by means of a single angular parameter is there a clear correspondence between that parameter and the minimum distortion angle  $\theta_{PT}$  of the corresponding  $3N$ -dimensional shape hypersphere.

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