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 objects1 that have captivated the attention of mankind from prehistoric times.2,5 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’t Hoff and Lé 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,7,8 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 us14,15 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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