THE KNOT THEORY OF MOLECULES

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Abstract

Macromolecules (such as polymethylenes and DNA) are large and flexible, and can present themselves in 3-space in topologically interesting ways. The branch of topology known as knot theory is the mathematical study of flexible graphs in 3-space. Knot theory can be used to quantify and compare the various configurations of large molecules, and to study the various spatial isomers of molecules which have complicated molecular graphs.

1. Introduction

Topology is a branch of mathematics which studies those properties of objects which do not change when the object is elastically deformed. Topology allows stretching, shrinking, twisting — any kind of continuous deformation short of breaking and reassembling the object. For example, to a topologist, a coffee cup and a doughnut are one and the same — each can be deformed into the other — never mind the difference in taste! The basic idea in topology is to relax the rigid Euclidean notion of equivalence (congruence) and replace it with the more flexible notions of equivalence (homeomorphism, diffeomorphism, etc.). One can think of topology as a mathematical attempt to quantify "shape". A flexible molecule does not usually maintain a fixed three-dimensional configuration. Such a molecule can assume a variety of configurations, driven from one to the other by thermal motion, solvent effects, experimental manipulation, etc. From an initial configuration for a molecule, topology can help identify all of the possible attainable configurations of that molecule. For molecules which possess complicated molecular graphs, topology can also aid in the prediction and detection of various types of spatial isomers. As evidence for the utility of topology in chemistry and molecular biology, see the excellent survey articles by Walba [1], and Wasserman and Cozzarelli [2].

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2. What is knot theory?

Knot theory is the branch of topology which studies the properties of flexible graphs in 3-space. Although at present there are few introductions to knot theory written for non-mathematicians (see Neuwirth [3]), there are a number of excellent mathematical expositions (Crowell and Fox [4], Fox [5], Rolfsen [6], Burde and Zieschang [7]). For a given flexible graph, the phenomenon of knotting is defined to be the existence of three-dimensional configurations of that graph which are not superimposable through elastic deformation of space. That is, the given graph must admit two configurations, such that to change from one configuration to the other, one must either break and then reassemble the graph, or allow an elastic spatial deformation to pass edges of the graph through each other. Knots are relatively difficult to detect - one has to develop a fair amount of algebraic and geometric machinery in order to prove that there is no deformation whatsoever which will make a given configuration coincide with another. What follows is a short and simple description of knot theory, which attempts to convey the flavor and intuition of the subject, while suppressing the details. Throughout this discussion, we disallow chemically irrelevant, extreme topological pathology such as tying an infinite sequence of smaller and smaller knots converging to a point, and pulling a knot infinitely tight so as to make it disappear.

Knot theory is the study and quantization of configurations of graphs (1-complexes) in Euclidean 3-space ($\mathbb{R}^3$). We first think of graphs as abstract objects. As an abstract object, a graph consists of a finite number of vertices (points) and edges (line segments). Two graphs $\{G, H\}$ are isomorphic if there is a function

$$f: G \rightarrow H$$

such that $f$ is a homeomorphism ($f$ is 1-1, onto, and both $f$ and $f^{-1}$ are continuous) which takes vertices to vertices and edges to edges. Figure 1 shows the molecular graphs of three familiar compounds - ethane (a), $n$-butane (b), and isobutane (c). No pair of these graphs is isomorphic, but the graphs of ethane and $n$-butane are homeomorphic. The homeomorphism, however, forgets the chemically important information that the interior vertices of $n$-butane code the positions of carbon atoms, and regards them as just points in a (bent) line segment connecting the endpoints.