Topology inspires Möbius strip, other molecules

Molecular topology underlies certain chemical properties, such as unusual chirality of newly synthesized organic Möbius strip molecule

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Some molecules are interesting simply by virtue of their shape. That shape need not be real; sometimes the semi-imaginary shape assigned by chemical notation systems can do the trick. Now a recently synthesized chemical, called the "first molecular Möbius strip" by its makers, can lay claim to that virtue.

The new molecule, tris(tetrahydroxymethylethylene) or tris (THYME) for short, joins ranks with a rather odd collection of molecules that are studied more for their topologic curiosity than for any other intrinsically chemical property. To be sure, some topologically interesting molecules, such as DNA, have interesting chemical properties that are dictated in key ways by shape. And, ultimately, shape can affect all kinds of chemical behavior, giving ample long-term justification of what often can seem a purely esthetic branch of science.

The synthetic Möbius strip is the topologic brainchild of David M. Walba, a synthetic organic chemist interested in crown ethers, crystallographer R. Curtis Haltiwanger, and graduate student Rodney M. Richards, all at the University of Colorado, Boulder. Their work, which has received support from the Petroleum Research Fund of the American Chemical Society, the National Science Foundation, and Monsanto, has the long-term goal of producing compact, totally synthetic catalytic units. Meanwhile, the short-term accomplishments are "novel and esthetically pleasing," according to Walba.

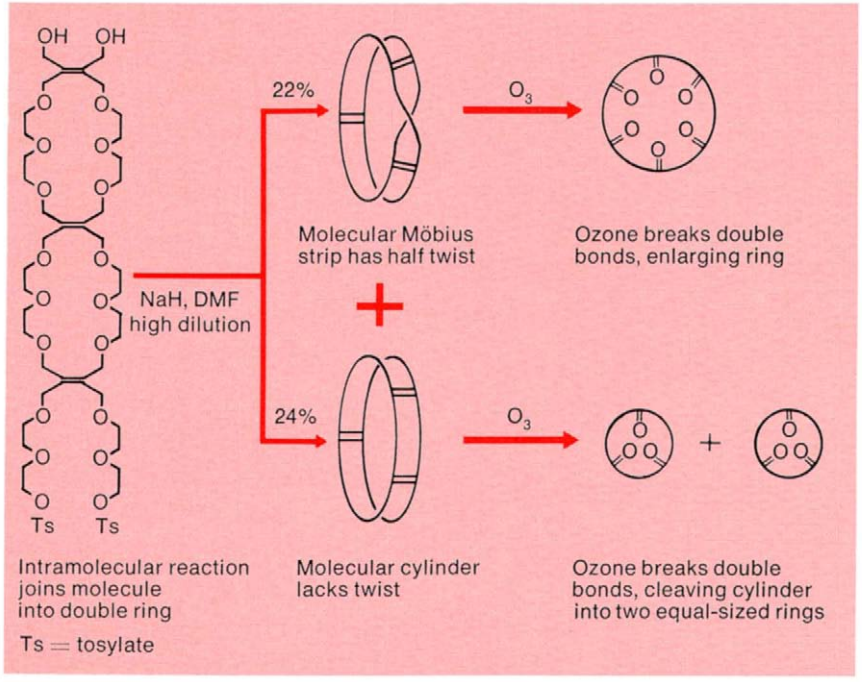
A Möbius strip usually is visualized as a ribbon that has been joined into a continuous loop containing a half twist. That half twist imparts a unique property to the strip, namely, a single or continuous edge. Thus when such a ribbon is sliced in half along its length, it opens up into a double-sized loop, which contains a full twist and thus is no longer a Möbius strip. A second cutting of the enlarged loop, incidentally, results in two rings linked together, or catenated. Had the original ribbon lacked a half twist, cutting it merely would produce two equal-sized loops.

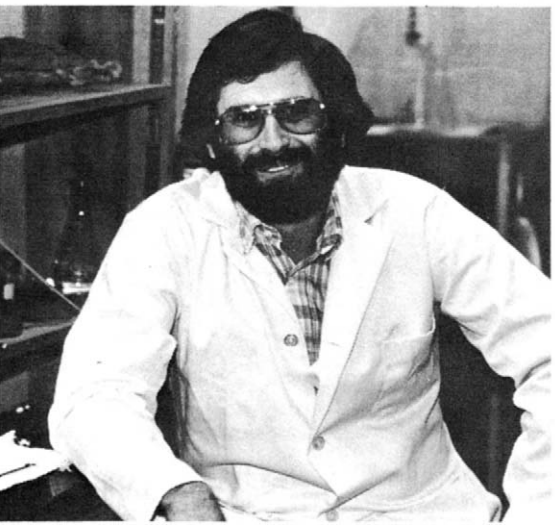
All of these manipulations (except the second cutting of the enlarged loop) have been carried out chemically by the research group at Colorado. Walba and his associates used tris(THYME) diol ditosylate as their "open" ribbon. The two alcohol groups at one end and the two tosylate groups at the other end of this molecule can join (intramolecularly) in two ways. If joined "in parallel," they form a closed ribbon in the shape of a simple cylinder lacking any twists. However, if joined in "crisscross" to close the ribbon, the molecule contains a half twist, thus making the Möbius strip. Built into these two types of molecules are useful chemical constraints, particularly three carbon-carbon double bonds that serve to hold the original polyether chains of the open ribbon together.

Those three carbon-carbon double bonds later can be cleaved easily from the "closed" molecules by treating them with ozone—the chemical equivalent of slicing a looped ribbon down the middle. The results are striking, according to Walba. So treated, the Möbius strip molecule seems "bigger," as judged by gel permeation chromatography. The results point to a closed circular molecule twice its original size. And, as expected, the compound formed after ozone treatment from the untwisted cylindrical version of tris(THYME) is correspondingly smaller. Other properties, including proton and carbon nuclear magnetic resonance data, corroborate this topologic interpretation, Walba says, adding: "We really need mass spec analysis to nail the clipping down."

That "nailing down" really is worrying over a fine point inasmuch as most of the data indicate that the tris(THYME) Möbius molecule obeys the expected topologic rules. It also has other properties expected of a Möbius strip. Walba says the mol-

Large ring molecule can form into Möbius strip





Walba: topology strange to chemists

ecule is "topologically chiral," meaning that it cannot be converted from one enantiomer (mirror image) to the other. "No molecular rigidity is required to make them [the enantiomers] distinct," he adds. "This is fairly rare."

At least one other synthetic organic molecule shares this rare and peculiar property. It is a trioxa derivative of hexaquinane, and procedures for its synthesis were published simultaneously in 1981 by Howard E. Simmons III and John E. Maggio at Harvard University and by Leo A. Paquette and Michel Vazeux at Ohio State University.

Simmons, who now is at Du Pont, calls this hexaquinane derivative "the first topologically nonplanar molecule." That property represents "a new kind of isomerism," he says. "It's not Earth shattering; we see no chemical consequences as of yet."

This unusual isomerism is, in part, a matter of how chemicals are depicted. By custom and convention, chemists draw molecules as two-dimensional graphs. Typically, an organic molecule is represented by dots and lines, with the dots representing the nuclei of carbon, oxygen, hydrogen, and other atoms, and the lines representing the bonds between such atoms. This simple notation system works remarkably well most of the time. But for a special class of molecules it fails.

For a graph to be "planar," it must be drawn so that no two edges intercept one another, Simmons explains. In trying to depict the hexaquinane derivative, there's no way to bend it to fit that rule. "No matter how it's drawn," Simmons says, "you will have at least two edges intersecting."

"For most chemists, topology is pretty strange," says Walba. Chemists are accustomed to thinking in terms of Euclidean geometry for which the emphasis is considerably different from topology. A useful aid for making the transition from one frame of thought to the other is "to pretend that chemical bonds are rubber threads," he says.

Take the problem of mirror-image isomers of an ordinary chiral organic molecule. If the bonds are turned into make-believe rubber threads, then the atoms can be squashed into a plane, thereby eliminating the image of chirality. Put in other terms, ordinary chirality is a three-dimensional property that disappears when the third dimension disappears.

That pretend world can't exist, even in make-believe, for the topologic isomers synthesized by Walba and his colleagues and the ones made by Simmons, Paquette, and their colleagues. There's simply no way to squash the picture of that hexaquinane derivative in such a way that it can superimpose on its own mirror image. (At least, there's no way to do it and still represent that molecule.) Similarly, the molecular Möbius strip cannot be forced in this make-believe process to go through the looking glass, so to speak.

Not all of the interest in topology among chemists is vested in pure esthetics or in sleight-of-hand tricks in which pretend molecules are forced into flatland. Howard E. Simmons Jr., who is director of the central R&D department at Du Pont and who also is the father of Simmons III (the hexaquinane derivative synthesizer), has had a long-standing interest in applying the mathematics of topology to problems of chemical structure.

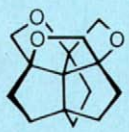
The elder Simmons, along with Richard E. Merrifield, has tried systematically to take a "rigorous" mathematical approach and apply it to particular chemical problems. For example, the behavior of π electrons lends itself to topologic description because π-bond distances are of relatively little importance, Simmons says. Also, the "wandering" quality of π electrons lends itself to description by this spatial branch of mathematics. Because topology addresses itself strictly to the "connectivity" of atoms, it offers one way of factoring out other properties, namely bond lengths and bond angles, when trying to measure their overall contributions to chemical behavior.

Thus, for instance, Simmons and Merrifield find that estimates of bond strengths, made using topology, correlate well with estimates made using molecular orbital theory. Besides bond strengths, other physical properties, including boiling points and heats of formation (especially among lower alkanes), correlate well with topologically assigned quantities. The Du Pont scientists speculate that certain chemical properties might be determined mainly by "molecular topology." But just how special spatial constraints and ordinary physics mesh gears to do something uniquely chemical is not known.

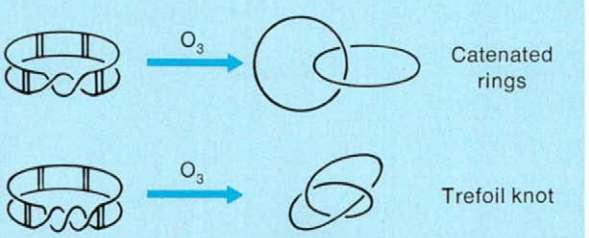
Besides these highly hypothetical matters, there are a number of very practical chemical problems with topological twists. These problems follow from an unofficial law of nature which states that practically any difficulty involving complex chemical synthesis probably already has been solved by individual living cells. This law is obeyed in topology by DNA molecules.

Many DNA molecules are found in nature as closed, double-stranded loops. Thus, on a much larger molecular scale, topologically contorted molecules had existed for a long while before Walba and his colleagues set out to make a chemical Möbius strip. Interestingly enough, Walba points

Other topologically interesting molecules



First topologically nonplanar molecule, made in 1981, must be depicted with intercepting edges and can't be interconverted with its mirror image



Larger and more twisted homologs (as yet unsynthesized) of Walba's Möbius strip molecule could give unusual structures, if cleaved by ozone

out, DNA does not twist its way into a Möbius strip. Although it is twisted, it always contains an even number of half twists, at least in nature.

Despite that limitation, DNA can get snarled into some very interesting—and undoubtedly vitally important—knots. DNA's contortions are aided by catalyts, of course, like everything else in biochemistry. A whole family of enzymes, known as topoisomerases (one such enzyme is called gyrase), helps to keep those knots and twists in proper order during stages when DNA molecules are replicated or when they are used as templates to specify RNA molecules of similar structure and sequence.

Recently, for example, Howard B. Gamper and John E. Hearst, both in the chemistry department at the University of California, Berkeley, proposed that an enzyme travels down DNA "like a nut on a bolt." That enzyme serves a topologic end; it unwinds and then rewinds the double helix as the base sequence of DNA is read and transcribed into an RNA molecule. Although the details of this nuts-and-bolts proposal still are being debated, they may prove important to the bigger problem of controlling gene activity.

DNA molecules thus can be formed into knots, including trefoil knots, and also into catenated (or linked) rings. Most of these biochemical magician's tricks are accomplished by enzymes. Eventually, however, Walba plans to duplicate such topologic tricks without enzymes, using synthetic chemistry methods and ingredients similar to (though larger than) those that went into making the tris(THYME) Möbius molecule. □

Josephson junctions may speed data processing

Researchers at Bell Laboratories have brought Josephson junction technology a step closer to practical application with the construction of the most complex circuit yet to be built with these devices. Ted A. Fulton and Larue N. Dunkleberger in the labs' interface electronics research department, Murray Hill, N.J., have constructed a working data processor that contains 548 Josephson junctions arranged in pairs to form logic "gates."

Bell Laboratories' photo

Dunkleberger, next to the helium Dewar, looks at the part of the apparatus that contains the multiplier chip

"For this experiment, we didn't aim for the fastest chip possible but rather at one that would be fairly easy to build," Fulton explains. "Yet we've built a chip fast enough for image processing, and we haven't begun to stretch the high-speed capabilities of Josephson junctions," he says.

The chip is designed specifically to be part of an experiment aimed at more efficient image processing for color television transmission, a field in which the Bell system is heavily involved. But the development also may have application in smaller, faster computers and in other fields where high-speed, densely packed integrated circuits would be useful.

Developing practical circuits using Josephson junctions has been a research goal in laboratories throughout the world since 1962 when Brian Josephson, then a graduate student at Cambridge University in England, first predicted the effect upon which these devices are based. Josephson, who later won a Nobel Prize for his work, suggested that if two superconducting plates are placed close to each other with an insulating substance between them, then, if the barrier between them is thin enough, electrons can be made to tunnel through it.

The beauty of Josephson junctions for microprocessing is that they are necessarily very small and they operate under superconducting conditions, where currents travel at the speed of light and the connections themselves offer no resistance. Thus they can turn on and off 10 times faster than the fastest conventional transistor switch. They also give off only a fraction of the heat produced by transistors, so they can be packed much closer together.

To use the junctions in data processing, they have to be connected with other circuitry so that the switching of the junction from current passing to not passing can be controlled. The entire unit that includes this control is called a logic gate, and several types of logic gates can be constructed, explain Fulton and Dunkleberger. The key to their data chip is the type of gate they have developed.

In Fulton and Dunkleberger's chip, the Josephson junctions are arranged in pairs to form a type of gate which the researchers have dubbed JAWS. The name, Fulton explains, is partly an acronym (for Josephson Atto-Weber Switch) and partly a reference to the way the switches look on an electrical circuit diagram. "The circuit diagram looks like a shark's face with two eyes—Josephson junctions—and a row of sharp teeth—a resistor," he says.

JAWS gates are controlled by varying the electric current in the gate circuit rather than by varying the applied magnetic field, as in most other Josephson junction switches. Because no magnetic field need be maintained the gates can be smaller and their fabrication is simpler than other types of gates.

In the Bell Labs system, the bottom layer of each junction is a lead-indium-gold alloy, the insulating layer is germanium and silicon oxide, and the upper superconducting layer is a lead-gold alloy. To form a gate, a pair of these junctions are connected in a loop with a small resistor.

When operating, the chip is placed on a small metal board in a container of liquid helium. The chip can multiply an eight-bit number by a 12-bit number within 30 nanoseconds using less than 1 mW of power. Actually, a complete cycle of the chip takes 75 nanoseconds, but the answer is returned within the first 30 nanoseconds.

The 75-nanosecond cycle time is important for the next step in the project to use Josephson junctions in television transmission, the researchers say. They plan to incorporate their chips in a video image transmission experiment that requires a no-more-than 75-nanosecond cycle time. □