Stereochemical Topology.

Stereochemistry: study of 3-d structure of molecules.

Until 1960, all molecules could be deformed into a plane.

But since the 60's, chemists have discovered molecules in the form of knots or links.

Some of these were synthesized in the lab: synthetic chemists are trying to produce new molecules that may have interesting properties, and new techniques that may be used in synthesis.

With the development of better microscopy techniques it was discovered that knots and links can occur naturally in protein molecules or in DNA.

Topologically complex molecules.

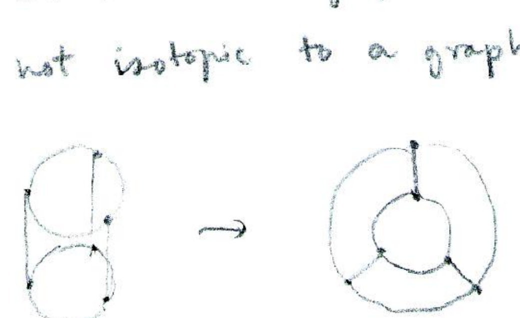
A molecular bond graph is a model of a molecule, which is represented by a graph embedded in $\mathbb{R}^3$.

The vertices represent atoms or collections of atoms

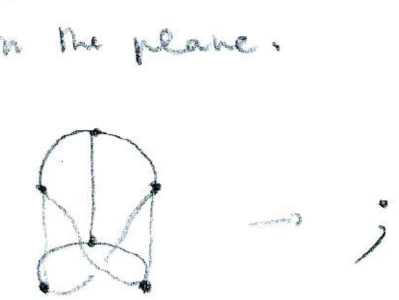
The edges represent bonds or chains of atoms.

The vertices and the edges may be labeled, with the different kinds of atoms for the vertices, and the different kinds of bonds for the edges.

A molecular bond graph is topologically complex if it is not isotopic to a graph on the plane.

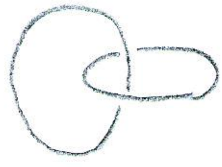


cylindrical



Möbius ladder

The first top. complex molecule to be synthesized was a <u>catenane</u>, (1961, Frisch & Wasserman)



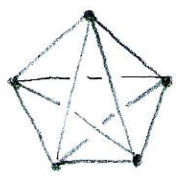
Two rings of hydrocarbons, with 34 atoms each, linked into a Hopf link.

The Hopf link cannot be deformed into the plane, but as an abstract graph it can be embedded in the plane  .

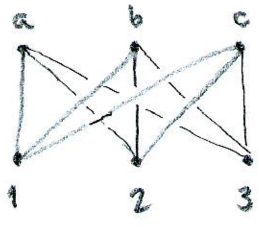
A <u>non-planar graph</u> is a graph that cannot be embedded in the plane. The Möbius ladder with 3 rungs ([illegible]) is such a graph.

<u>Theorem</u> (Kuratowski). A graph is non planar iff. it contains the complete graph on 5 vertices, K_5, or the bipartite graph on 3 vertices, $K_{3,3}$.

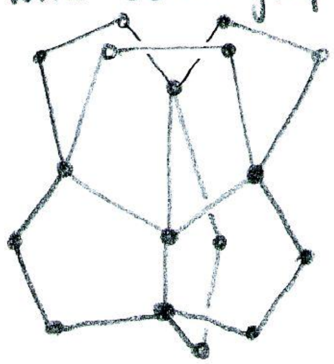
K_5 :



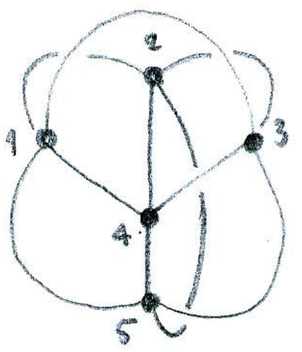
$K_{3,3}$:



In 1981, Simmons & Maggio and Paquette & Vazeux, synthesized a molecule with bond graph:



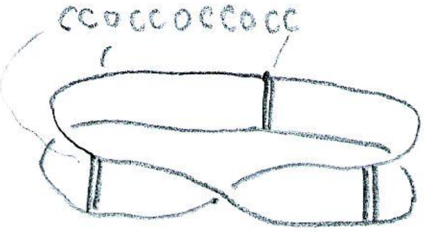
This bond graph contains a K_5, if we number 5 of the vertices

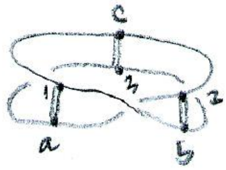


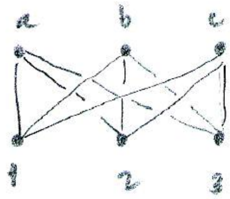
So the mol. bond graph of the S-P molecule cannot be embedded into a plane.

In 1982, Walba, Richards & Haltiwanger, synthesized a molecule whose mol bond graph contains a Möbius ladder with 3 rungs.

Fig 1.5.

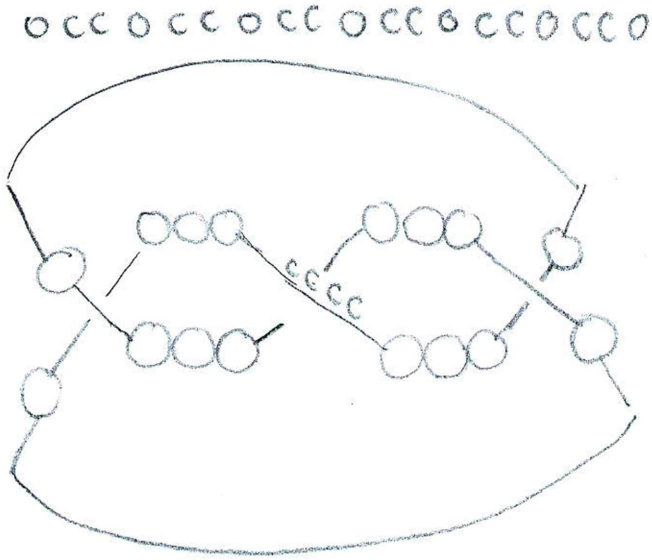




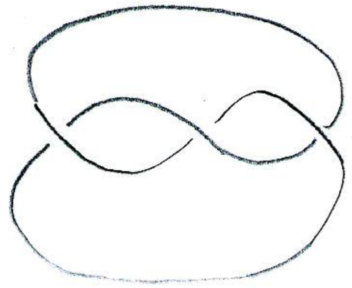


The Möbius ladder with 3 rungs contains a $K_{3,3}$, so it has no planar embedding.

In 1989, Dietrich-Buchecker & Sauvage, synthesized a



(right handed trefoil).



This embedding is not isotopic to an embedding of the graph in the plane, but in this case such an embedding exists: the unknot.

Besides the molecules synthesized in the lab, the development of microscopy methods has made possible the discovery of knotted or linked proteins and knotted or linked pieces of DNA.

Different kinds of isomers

1. Structural isomers: molecules with the same molecular formula but different bond graph.

e.g. butane

C_4H_{10}

isobutane

C_4H_{10}

2. Rigid stereoisomers Same abstract graph, but as embedded graphs one cannot be superimposed on the other.

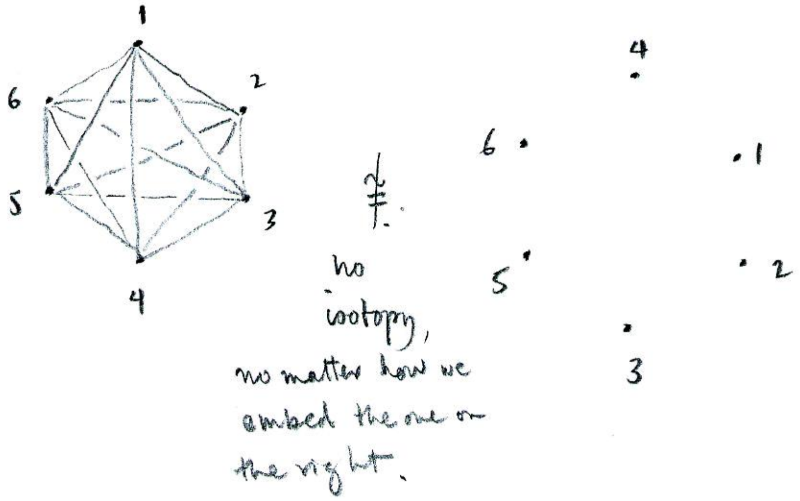
L-alanine mirror images D-alanine.
left-handed right-handed.

3. Topological stereoisomers Same abstract graph but not isotopic as embedded graphs (or as labelled embedded graphs).

eg. If the crossings change on the trefoil knot molecule, we get the reflected trefoil, which we know is not isotopic.

In general, whether an automorphism of a labelled graph can be obtained by an isotopy, depends on the particular embedding. But in some cases we can show that certain isomorphisms cannot be obtained by an isotopy, independently of the way they are embedded in $\mathbb{R}^3$.

Theorem (Flapan) Let K_6 be the complete graph on 6 vertices, labelled $1, 2, \ldots, 6$. It is not possible to embed K_6 in $\mathbb{R}^3$ in such a way that the automorphism $(1\,2\,3\,4)$ can be induced by an isotopy.



Chirality

A molecule is chiral if it is distinct from its mirror image.

But we can give different conditions for distinct.

Pasteur (1848) : mirror image crystals of tartaric acid rotate polarized light in different directions.

Most organisms have preferred orientation : snails, climbing plants.

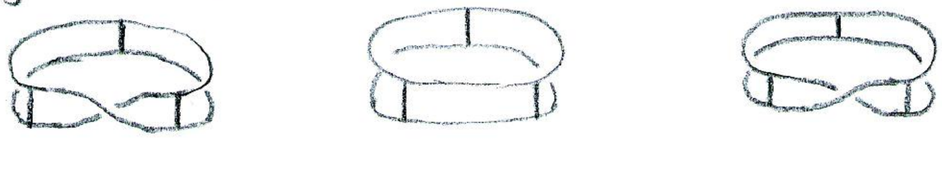
Most aminoacids in human proteins are chiral.

So chirality may be medically important. One enantiomer is medically active, the other may be inactive, or it may be harmful.

e.g. - Thalidomide : left-handed enantiomer used to treat morning sickness in pregnant women, but right-handed enantiomer caused birth defects.

- Limonine : one smells like lemon, the other like orange.

Walba and his colleagues had created molecular ladders, and joined the ends together. It was not possible to predict how they would join :

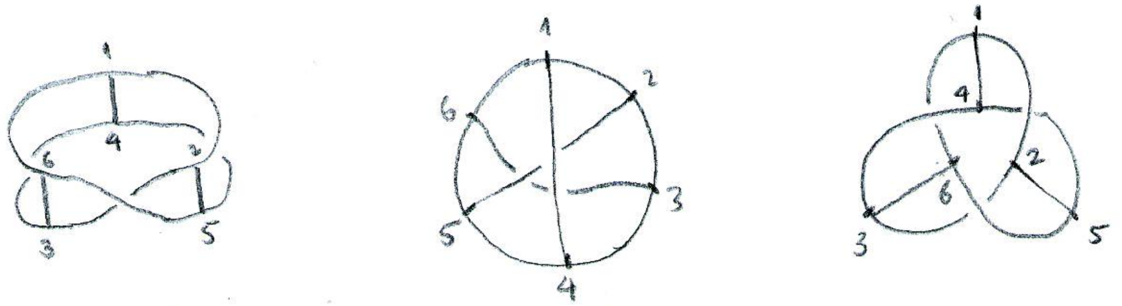


They used NMR to show that some of the synthesized molecules were chiral. Walba conjectured that it was impossible for a molecular Möbius ladder to deform to its mirror image. If this were true, the experimental evidence of chirality would support the assumption that some of the molecules were Möbius ladders.

Jon Simon proved the

<u>Theorem</u> The embedded graph of a molecular Möbius ladder with 3 or more rungs cannot be deformed into its mirror image in such a way that rungs go to rungs and sides go to sides.

An embedded (labelled) graph that cannot be deformed to its mirror image is <u>topologically chiral</u>. This is a property of the particular embedding. But maybe there exist other embeddings of the same graph which are not chiral.

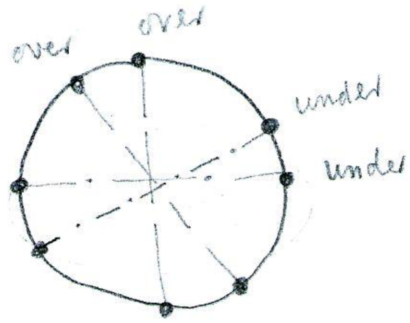


Different embedding of the 3-rung Möbius ladder graph.

<u>Theorem</u> No embedding of a Möbius ladder with an odd number of rungs greater than 1, can be deformed to its mirror image in such a way that rungs go to rungs and sides go to sides.

We say that the Möbius ladder with 3 rungs is <u>intrinsically chiral</u>.

In contrast, for the Möbius ladder with 4 rungs, there exists an embedding which is isotopic to its mirror image. In fact, much more than that, it can be rigidly rotated into its mirror image.



The same is true for any Möbius ladder with an even number of rungs.