INTRODUCTION TO TOPOLOGICAL CHIRALITY

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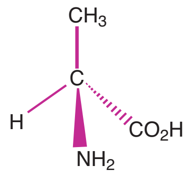
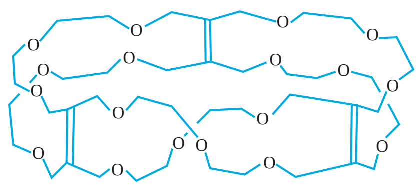
Molecular geometry and topology

The geometry of rigid molecules determines many of their properties.



For flexible molecules, their *topology* (i.e. deformations) determines their properties.

Example: Molecular Möbius ladder (Walba)



Recognizing a Möbius ladder:

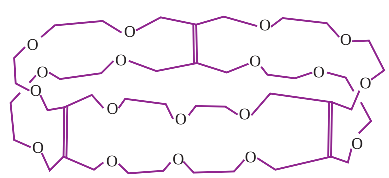
Walba's molecules were created by forcing the ends of ladder to join.

How did Walba know that some were joined with a half-twist, producing a Möbius ladder?

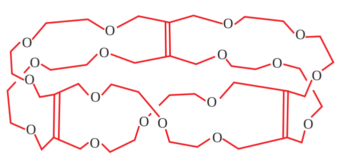
These molecules are too small to see in a microscope.

Some of Walba's molecules were chemically different from their mirror images.

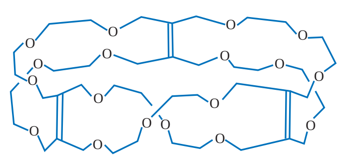
A circular ladder with no twists is the same as its mirror image.



Is a Möbius ladder chemically different from its mirror image?



Möbius ladder



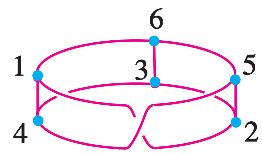
mirror image

A Möbius strip is different from its mirror image. But a Möbius ladder has deformations that a Möbius strip doesn't have.

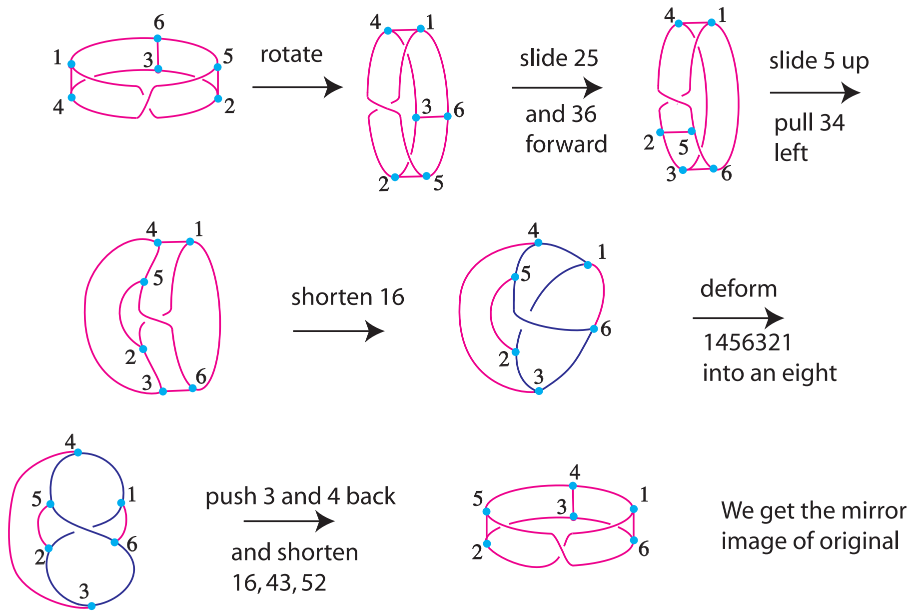
Here is a deformation from a Möbius ladder to its mirror image.

A deformation of a Möbius ladder to its mirror image

We represent the Möbius ladder as a graph without the atoms.

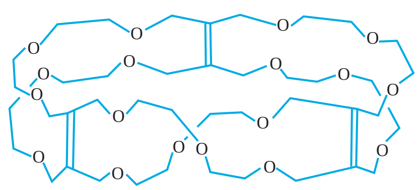


The numbers will help us keep track of the deformation



The deformation takes rungs $\overline{14}$ and $\overline{36}$ to sides of the ladder.

The molecular Möbius ladder is different from its mirror image



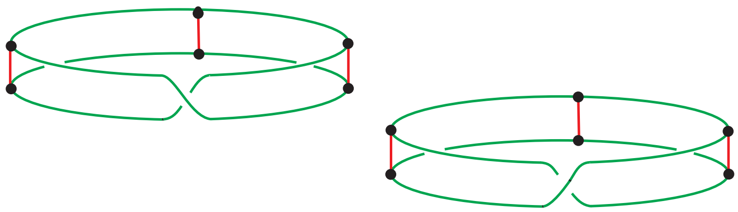
Rungs are carbon-carbon double bonds and sides are chains of carbons and oxygens.

Deforming rungs to sides makes no chemical sense. So our deformation is not chemically possible.

Jon Simon used topology to prove that a molecular Möbius ladder cannot chemically change into its mirror image.

Simon's Result

Simon represented a Möbius ladder and its mirror image as colored graphs in order to distinguish sides from rungs.



He proved one colored graph cannot be deformed to the other. (We will see a sketch of his proof later.) So a molecular Möbius ladder is chemically different from its mirror image.

Chirality

Knowing whether or not a molecule is different from its mirror image is chemically important.

DEFINITION: A molecule is said to be *chemically achiral* if it can change into its mirror image. Otherwise, it is *chemically chiral*

"Chiral" comes from the ancient Greek word for hand. Achiral means NOT like a hand.

Your right hand reacts differently to a right glove and a left glove.

Organisms have a preferred handedness

So they react differently to the two forms of a chiral molecule.

EXAMPLE: Carvone. One form smells like spearmint, other form smells like caraway.

Generally, one form of a medication is more effective and the mirror form has more side effects.

Sometimes the two forms have different uses:

EXAMPLE: These are mirror forms
Darvon— painkiller
Novrad— cough medicine

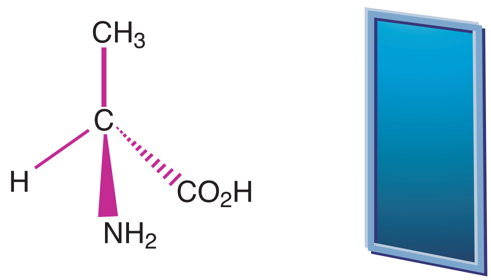
It is important to know if a potential medication is chiral, and perhaps manufacture only the prefered form.

Chirality of a molecular graph

It is useful to know whether a molecule will be chiral before it is synthesized.

Can we recognize chirality from a molecular graph?

LORD KELVIN (1884) "I call any geometrical figure or group of points *chiral*, and say it has *chirality*, if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself."



This molecule is chiral.

Geometric chirality

Modern organic textbook definition A *chiral* molecule is one which is not superposable on its mirror image.

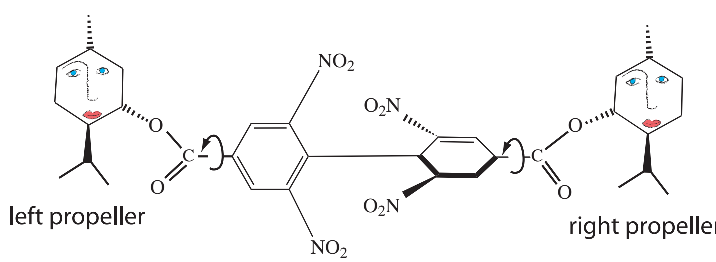
Mathematical restatement A molecule is *geometrically achiral* if, as a rigid object, it can be superimposed on its mirror image. Otherwise it is *geometrically chiral.*

Many chemists consider geometric chirality to be equivalent to chemical chirality.

But there are counterexamples.

A chemically achiral but geometrically chiral molecule

The following molecule was synthesized by Mislow in 1954.



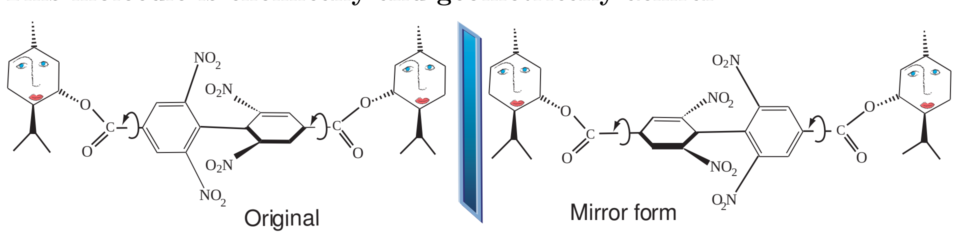
Left hexagon is vertical, right hexagon is horizontal.

Propellers turn simultaneously.

Left propeller has her left hand forward, right propeller has her right hand forward.

As rigid structures, a right propeller cannot become a left propeller.

This molecule is chemically and geometrically achiral



Mirror form is the same as original form, except vertical and horizontal hexagons are switched.

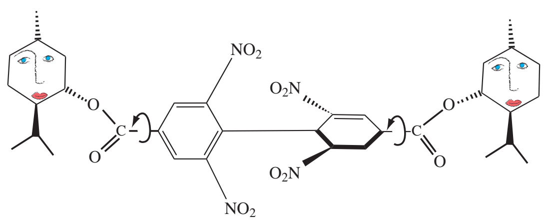
Proof of chemical achirality:

- Rotate original molecule by 90° about a horizontal axis
- Rotate propellers to vertical position to get mirror form

Proof of geometric chirality

- If molecule is rigid, then propellers don't rotate.
- In original form, left propeller is parallel to adjacent hexagon.
- In mirror form, left propeller is perpendicular to adjacent hexagon.
- A left propeller cannot be rigidly changed into a right propeller.
- As rigid objects, the original and mirror form are different.

This molecule is like a rubber glove



Recall, this molecule can change into its mirror image. But it cannot attain a position which can be rigidly superimposed on its mirror image.

Similarly, a rubber glove becomes its mirror image when it's turned inside out. But a rubber glove cannot attain a position which can be rigidly superimposed on its mirror image.

Definition: A molecule is said to be a *Euclidean rubber glove* if it is chemically achiral, but it cannot attain a position which can be rigidly superimposed on its mirror image.

The above molecule is a Euclidean rubber glove.

Why call it "Euclidean?"

If a rubber glove were completely flexible it could lie in the plane and be its own mirror image.

If our molecule were flexible, it could lie in the plane and be its own mirror image.

The word *Euclidean* indicates that geometric (i.e., physical) constraints are keeping the molecule from attaining a position which is its own mirror image.

Topological rubber gloves

If we remove all physical constraints, we can define

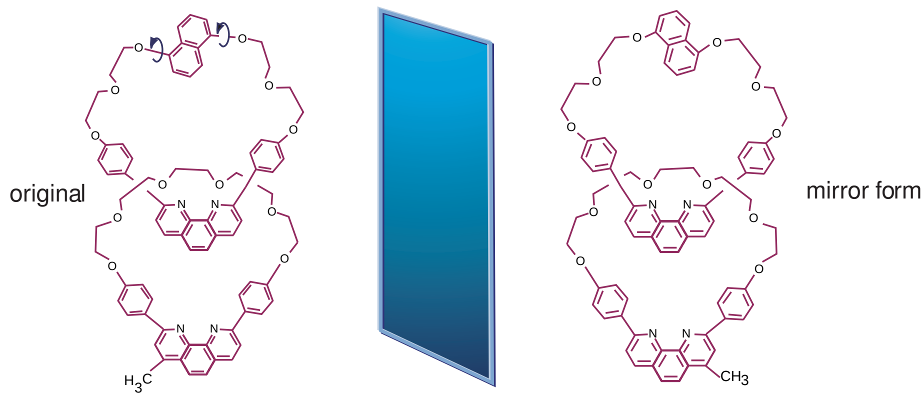
Definition: A molecule is said to be a *topological rubber glove* if it is chemically achiral, but (even if it is completely flexible) it cannot be deformed to a position which can be rigidly superimposed on its mirror image.

This molecule is not a topological rubber glove, because if it were completely flexible it could be deformed into the plane.

It seems like a topological rubber glove might be impossible.

A topological rubber glove

The first topological rubber glove was synthesized by Sauvage, Chambron, and Mislow.



The molecule is a pair of linked rings, where the pair of hexagons at the top can rotate.

Proof of chemical achirality.

- Turn over the bottom ring of original molecule.
- Rotate the pair of hexagons at top to get mirror image.

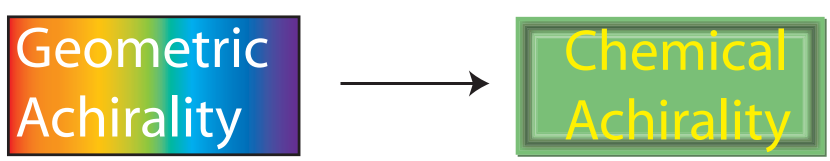
The CH_3 tail gives the bottom ring an orientation. If molecule is rigid, the hexagons at top give top ring an orientation.

This can be used to prove that the molecule cannot be deformed a position which can be rigidly superimposed on its mirror image.

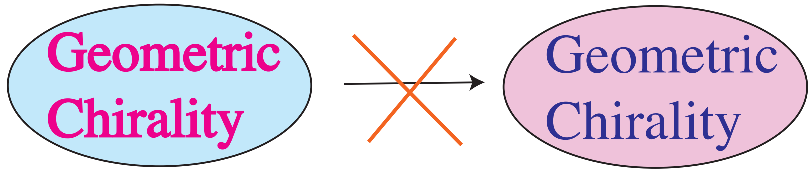
Hence the molecule is a topological rubber glove.

Summary: geometric vs. chemical chirality

If a structure can be rigidly superimposed on its mirror image, then it is physically the same as it's mirror image. Hence it must be chemically the same as its mirror image.



Rubber gloves are examples of molecules which are geometrically chiral but chemically achiral.



Topological chirality

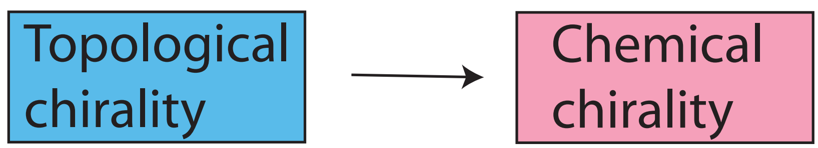
Not all molecules are completely rigid, and not all molecules are completely flexible.

In the definition of geometric chirality, we assumed complete rigidity. What if we assume complete flexibility?

Definition A molecule is said to be *topologically achiral* if, assuming complete flexibility, it can be deformed to its mirror image. Otherwise it is said to be *topologically chiral*.

If a molecule is topologically chiral, then there is no way to deform it to its mirror image.

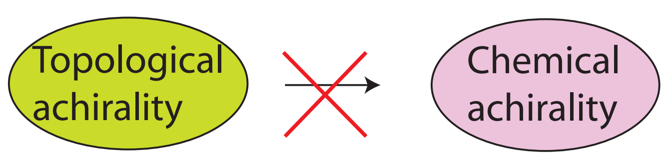
Hence there is no way for it to chemically change itself to its mirror image. So it is chemically chiral.



This molecule is chemically chiral.

If it is completely flexible we can interchange H and HO_2C to get the mirror image.

Hence it is topologically achiral.



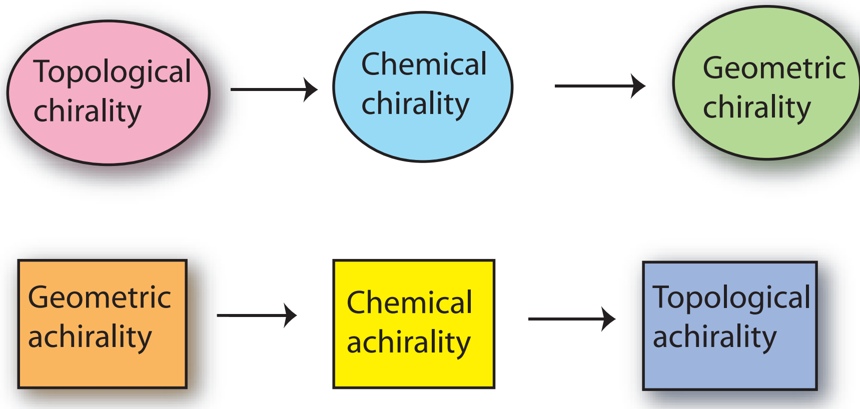
If we heat a geometrically chiral molecule enough, it will change to its mirror form.

Even if we heat a topologically chiral molecule, it will not change to its mirror form.

So topological chirality is more enduring then geometric chirality.

Thus topological chirality is a useful concept for chemists.

Summary

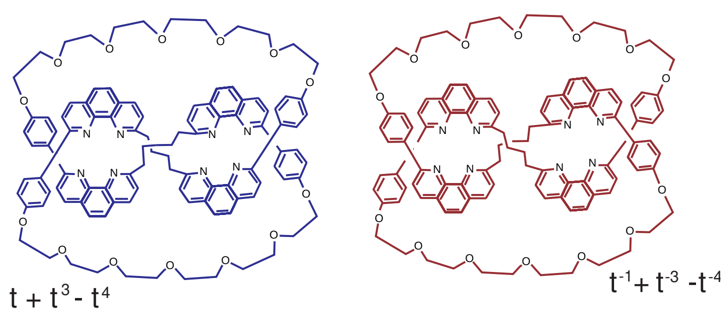


None of the reverse implications hold.

Techniques to prove topological chirality

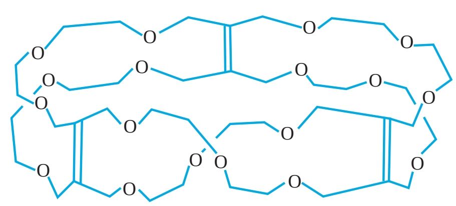
1. Use Knot Polynomials (Vaughan Jones)

IDEA: Every knot is assigned a (Laurent) polynomial. If one knot can be deformed to the other, then the knots have same polynomial.

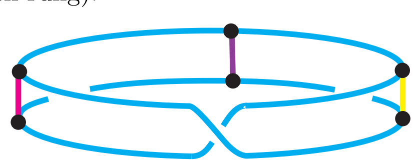


Polynomials are different, so molecule is topologically chiral.

2. Use 2-fold branched covers (Jon Simon)

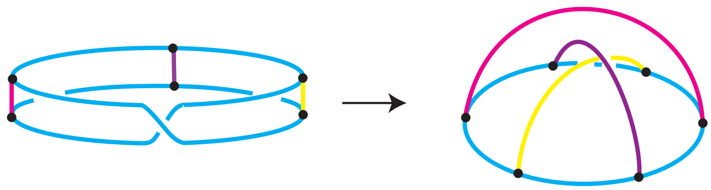


We represent the molecule as a colored graph (using different colors to keep track of what happens to each rung).

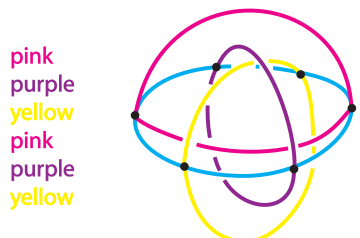


Sketch of branched cover argument

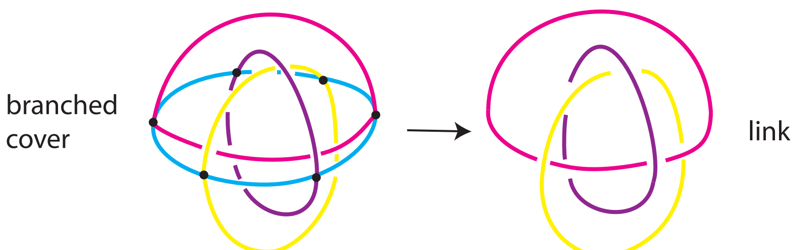
Assume complete flexibility, and deform sides of ladder to a planar circle.



To get the 2-fold cover branched over the blue circle, we glue two copies of the rungs together along the blue circle.

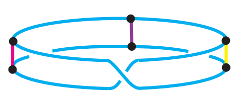


Remove the blue circle to obtain a link.



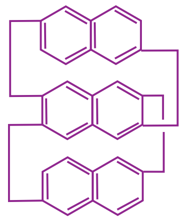
This link is topologically chiral (without colors).

So the branched cover was topologically chiral, distinguishing the link from the blue circle.



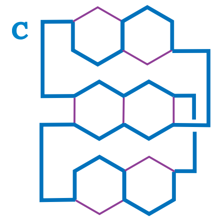
So the original graph was topologically chiral, distinguishing the rungs from the sides.

3. Use topological chirality of Möbius ladder to prove topological chirality of another graph. (Kurt Mislow)



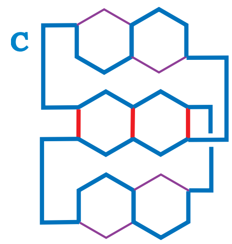
Triple layered
naphthalenophane
(TLN)

TLN contains a unique longest cycle C.

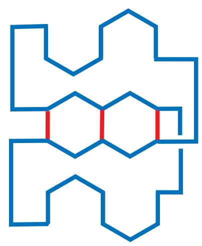


Any deformation of TLN will take C to the corresponding cycle.

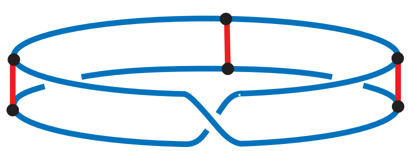
TLN has three unique edges with endpoints on C.



If TLN can be deformed to its mirror image, then so can this graph.



But this graph can be deformed to this graph:

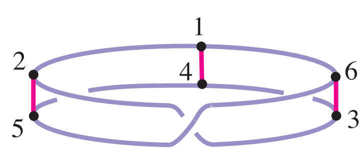


Since a Möbius ladder is topologically chiral, so is triple layered napthalenophane.

4. A combinatorial approach

Definition An *automorphism* of a graph is a permutation of the vertices which takes adjacent vertices to adjacent vertices.

Example



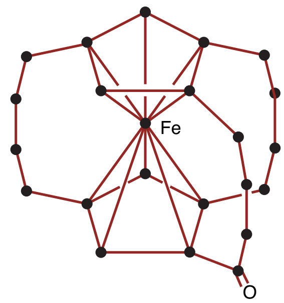
$2 \leftrightarrow 6$, $3 \leftrightarrow 5$ is an automorphism, $1 \leftrightarrow 2$ is not an automorphism.

Definition: The *order* of an automorphism is the number of times you have to perform the automorphism until every vertex is back to its original position.

The order of the above automorphism is 2.

Definition: The *valence* of a vertex is the number of edges that contain it.

ferrocenophane

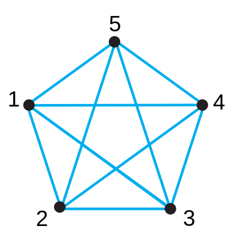


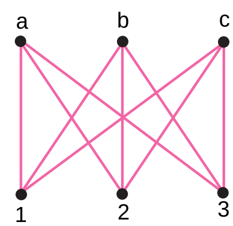
Properties of automorphisms of molecular graphs.

- valence is preserved.
- distance between vertices is preserved
- type of atom is preserved

Theorem: [Flapan] If a graph contains either K_5 or $K_{3,3}$ and has no order 2 automorphism, then any embedding of the graph is topologically chiral.

K_5





$K_{3,3}$

In K_5 every vertex is joined to every other vertex.

In $K_{3,3}$ every vertex in one set is joined to every vertex in other.

K_5 and $K_{3,3}$ are special because any graph containing either can't be embedded in a plane.

Theorem: [Flapan] If a graph contains either K_5 or $K_{3,3}$ and has no order 2 automorphism, then any embedding of the graph is topologically chiral.

This theorem translates a problem about the topology of how graphs are embedded in $\mathbb{R}^3$ into a problem about abstract graphs.

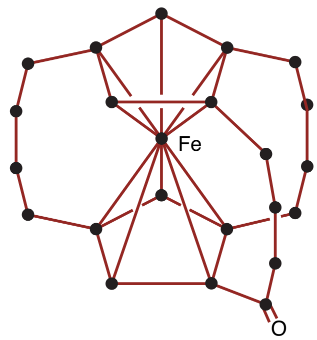
All of the topology is contained in the proof, which uses:

- Thurston's Hyperbolization Theorem
- Mostow's Rigidity Theorem
- Jaco-Shalen, Johannson Characteristic Submanifold Theorem

Application: ferrocenophane

We will use the theorem to prove that ferrocenophane is topologically chiral.

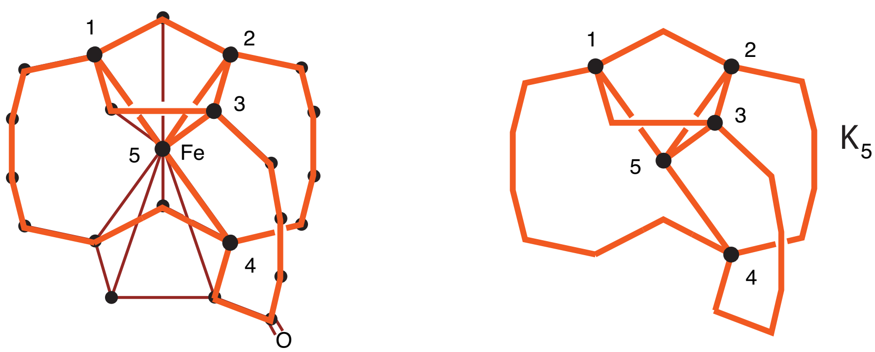
ferrocenophane



Any automorphism fixes the single oxygen. By using the valence of adjacent vertices, we progressively see that any automorphism fixes every atom.

So ferrocenophane has no non-trivial automorphisms.

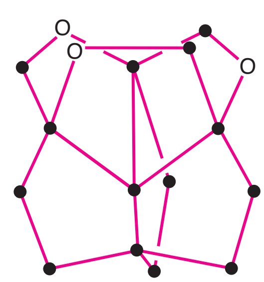
Ferrocenophane contains K_5.



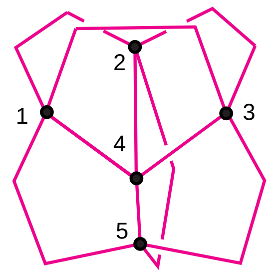
Thus by the theorem, ferrocenophane is topologically chiral.

Applicaiton: the Simmons-Paquette molecule

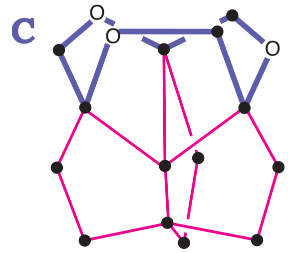
Simmons - Paquette
Molecule



The Simmons-Paquette molecule contains K_5.



The cycle C is the unique cycle containing all three oxygens.

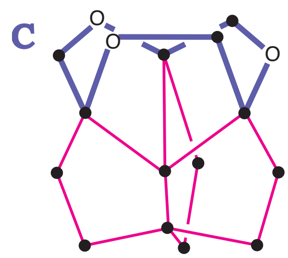


Assume the Simmons-Paquette molecule has an automorphism ϕ of order 2.

ϕ takes C to itself.

Since C has three oxygens and ϕ has order 2, one oxygen must be fixed by ϕ.

Since ϕ preserves valence, every vertex on C is fixed by ϕ.



Since ϕ preserves valence and fixes every vertex on C, ϕ fixes every vertex on the Simmons-Paquette molecule.

Thus the Simmons-Paquette molecule cannot have an automorphism of order 2.

It follows from the theorem that the Simmons-Paquette molecule is topologically chiral.

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