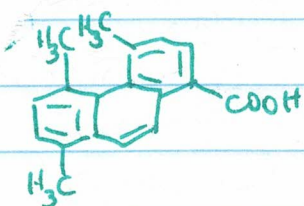


Lecture XI: Topological Chirality

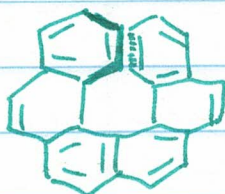
02-07-2020

Before we get into it, we will look at two examples of molecules which do not have a plane or axis, at least not a clearly distinguished one.

Helicenes



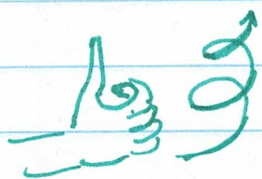
1947 - these three rings can no longer be coplanar



[6] helicene

JACS, 1956, 78, 4765

Since then, helicenes with as many as 14 rings have been made. They are named as P- or M- if they describe a right or left-handed helix respectively:

right-handed
(P-)left-handed
(M-)

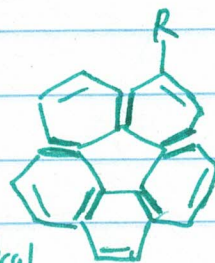
Helicenes are the closest to axially chiral compounds

Substituted corannulenes



bowl-shaped

single substituent makes it chiral

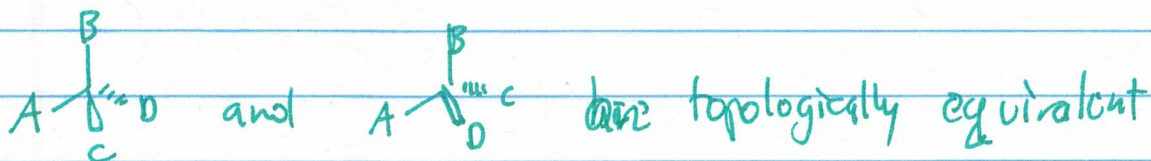


Topological Chirality

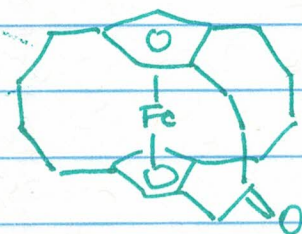
based mostly on Chem Soc Rev
2018, 47, 5266

What is molecule's topology?

It is simply its connectivity. Bonds and atoms can be stretched and turned but not made to cross each other.

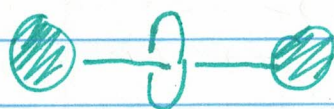


But some molecules are chiral as a consequence of their topology:



J. Organomet. Chem. 1977, 125, 79
remains chiral regardless of substitution

This type of chirality is quite common in mechanically interlocked molecules - rotaxanes and catenanes (MIMs)



[2]rotaxane



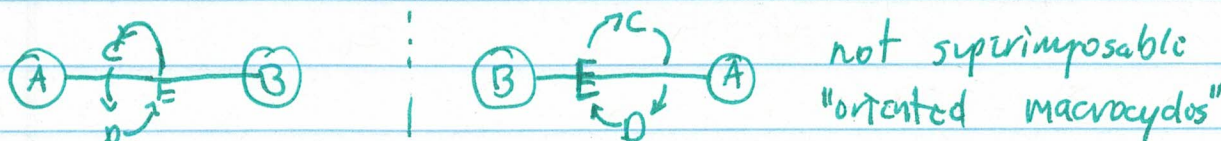
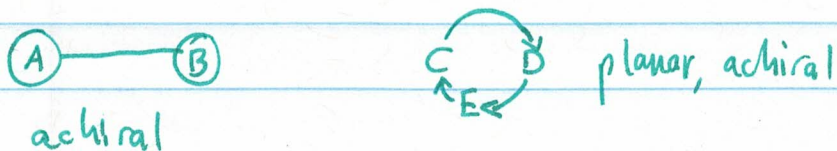
[2]catenane

two components which are not chemically connected but are still inseparable

they have a "mechanical bond"

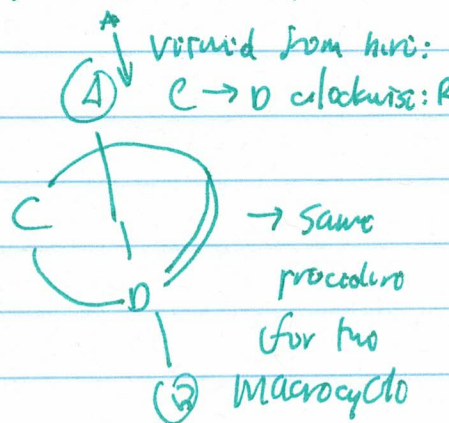
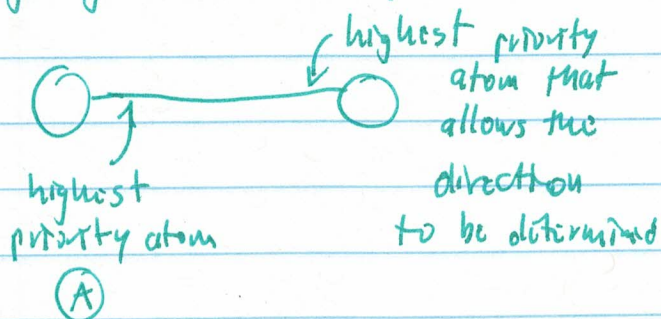
Rotaxanes composed of a C_{nh} -symmetric macrocycle and a C_{nv} -symmetric axle are going to be chiral - even though

neither one of their elements is chiral:

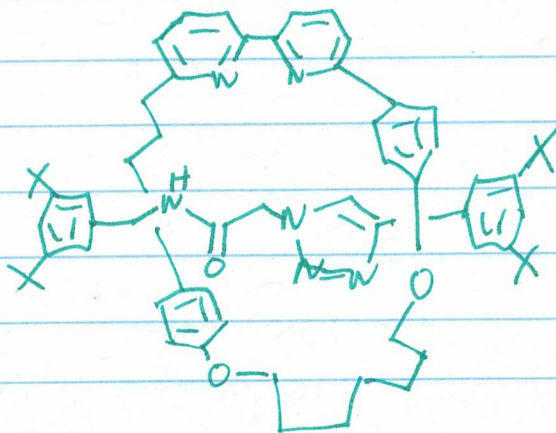
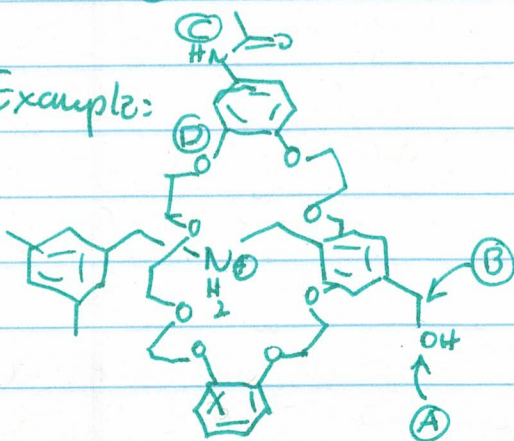


This can be viewed as a form of planar chirality. Macrocycle is the plane, which has been desymmetrized by the introduction of the axle.

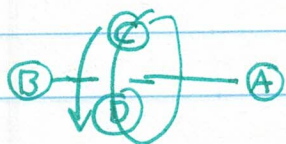
Assigning R/S configuration:



Example:



Goldup



(S)-configuration

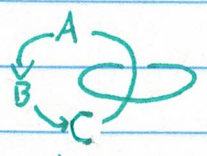
Topologically Chiral Catenanes

Both rings need to be oriented:

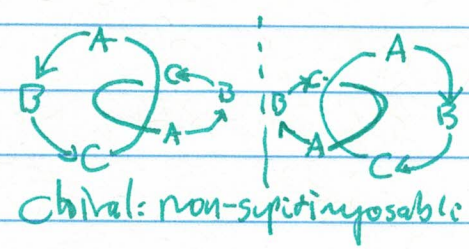
this is truly topological chirality!



achiral



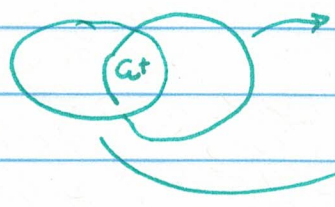
achiral



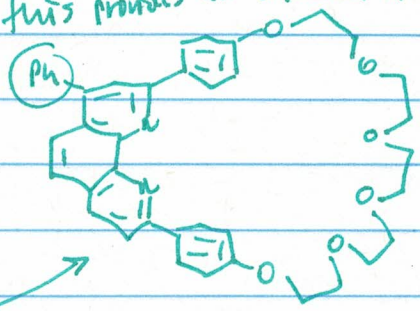
chiral: non-superimposable

Enantiomers have been separated, but their stereochemistry was not assigned.

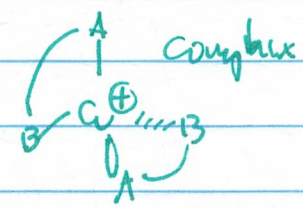
Example



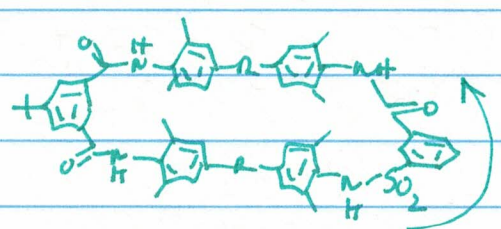
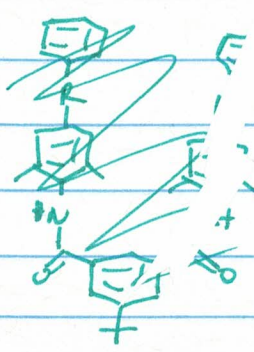
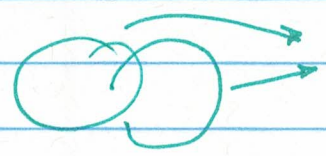
this provides an orientation



This can technically be viewed as a

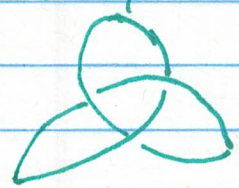


Examples without a metal center:



directionality introduced

Other, more complex mechanically interlocked molecules can also be chiral:

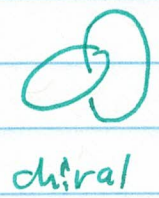
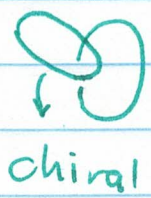


1

JACS, 2015, 137, 10437

trefoil knot - inherently chiral

In addition, MIMs show right co-conformational behavior, in which the two components change their relationship to each other:



JACS 2007, 129, 2236

depending on the system, this process can be fast or slow