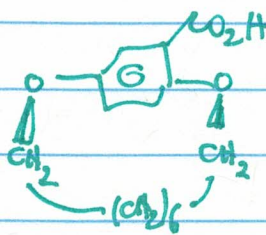
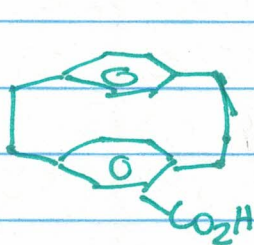


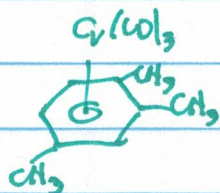
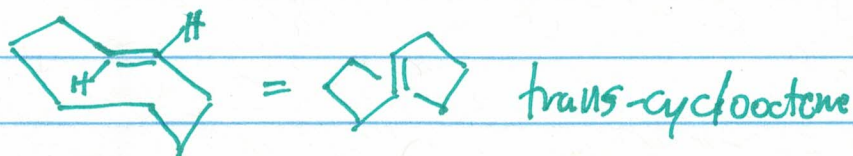
Lecture X: Planar Chirality

02-05-2020

In some molecules without a chiral center, axis is also absent, or is difficult to recognize. They are called compounds with planar chirality. The definition of this plane is tricky: it is a plane that contains most-but not all-of the atoms in the molecule. Examples:



CYCLOPHANES
restricted rotation of a benzene ring through the loop of the macrocycle

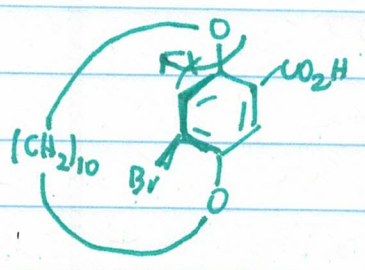


many complexes of unsymmetric benzenes

Some authors can classify these all as axially chiral, see for example: *Top. Stereochem.* 1970, 5, 31.

Cyclophanes are the most important class of planar chirality molecules. There are hundreds of relevant examples, as well as many pertinent reviews.

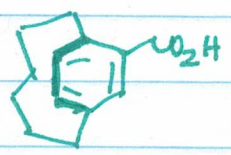
First resolved example:



1947 - the ring cannot swirl through
ansa-compounds (ansa = handle)
1,12-dioxo[12]paracyclophane

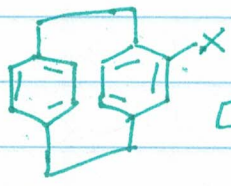
If Br → H, then isomerization can happen = atropisomerism. For small rings ($(CH_2)_8$) even H is big enough to allow resolution of enantiomers.

With even smaller rings, benzene starts bonding out of plane:



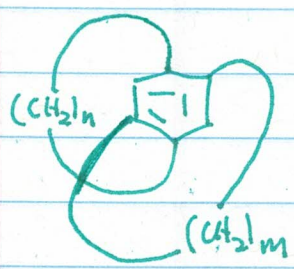
[6]paracyclophane
prepared by Tobe (JACS, 1983, 105, 1376)

Planar chirality influences the reactivity of these compounds - for example they are always reduced from the side opposite to the bridge.

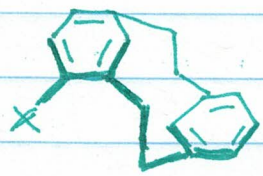


[2.2]paracyclophane, chiral if $X \neq H$

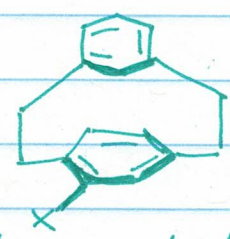
Many other geometries are out there:



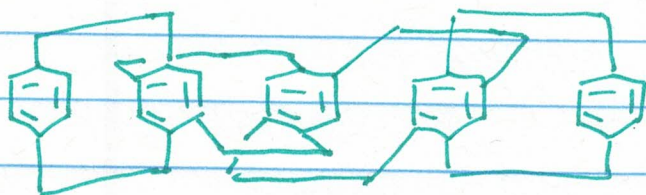
[m][n]paracyclophanes



metacyclophane



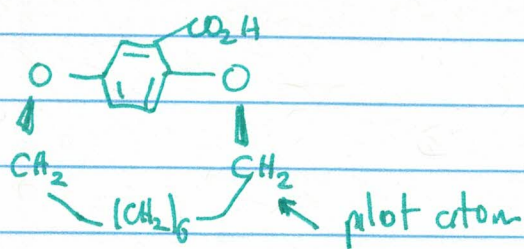
metaparacyclophane



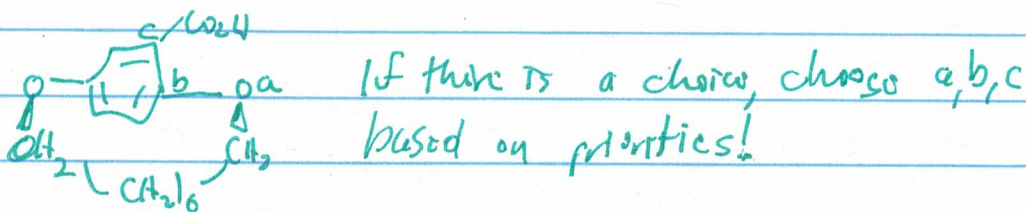
layered porphyrins
[n]catenanes

How do we name them?

- Choose an atom out-of-plane which will be our "pilot atom". It has to be the closest to the plane and of highest priority.



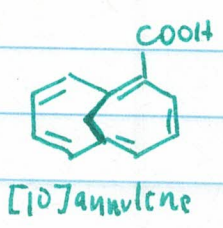
- Look at the three closest atoms in the plane from the view point of the pilot atom:



- If a → b → c is clockwise, viewed from the pilot atom ⇒ R otherwise: S. Occasionally pR and pS is used to distinguish this planar chirality from central atom-based one.

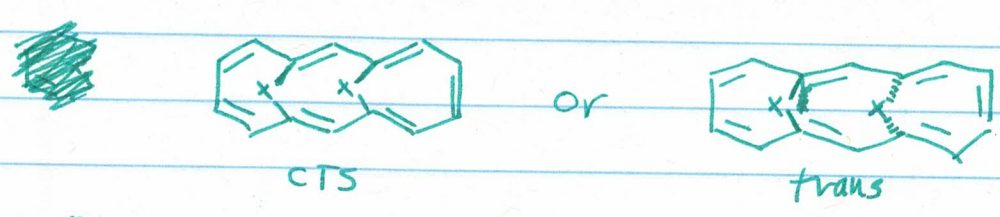
Annulenes

Fully conjugated cyclic molecules with alternating single and double bonds. If bridged, some of these apparently planar molecules can exhibit chirality.

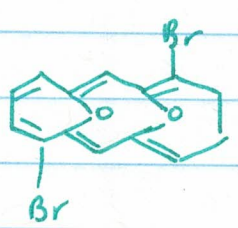


The bridge is always outside of the plane
(R) or (S)? Can be resolved

In larger annulenes, such as [14]annulene, the bridge can go through the ring:

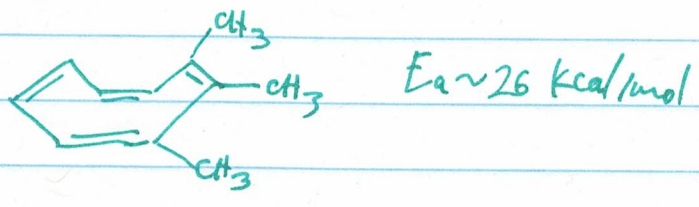


If $X = \text{C}=\text{O}$, conformationally stable. If $X = \text{O}$, flexible, and can go through the ring.



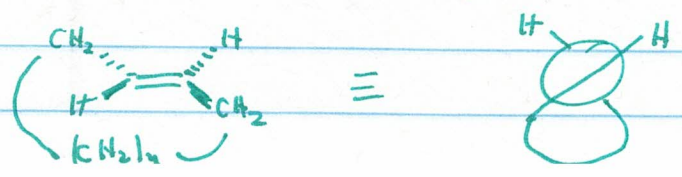
chiral, and racemizes @ 150°C, $E_a \sim 30$ kcal/mol

Even simple cyclooctatetraene, which is tub-shaped, can be forced into chirality with substitution:



Trans-cycloalkenes

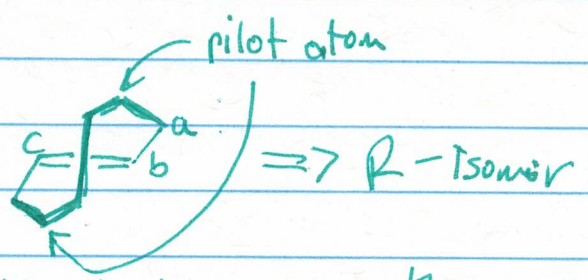
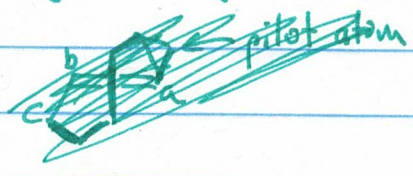
When the saturated part of a ^{trans-}cycloalkene is short enough, it will be forced out of planarity by the twist. Cyclooctene is the smallest stable trans-cycloalkene to show this effect:



However, only the small trans-cycloalkanes are conformationally stable. With larger ones, racemization barriers drop quickly:

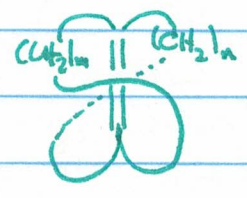
C8 35.6 kcal/mol C9 20 kcal/mol C10 10.7 kcal/mol

Let's assign configuration:



Putting Me groups onto the double bond increases the conformational stability.

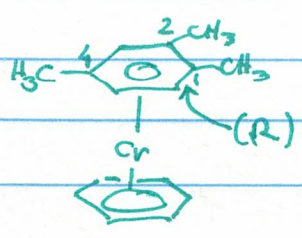
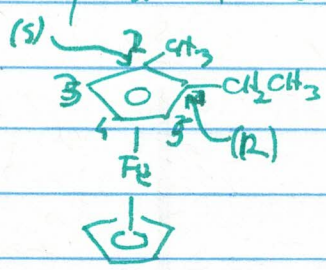
An exotic variant - bicyclics:



if $m=n=8$ or $m=n=10$, switching is not possible and chiral isomers can be isolated

Metalloenes

While these examples are very common, they are more asto-
marily viewed as having chiral centers:



not only do C1 and C2 become chiral centers, all upper carbons do! → specifying only 1S is generally enough as there is only one enantiomer pair