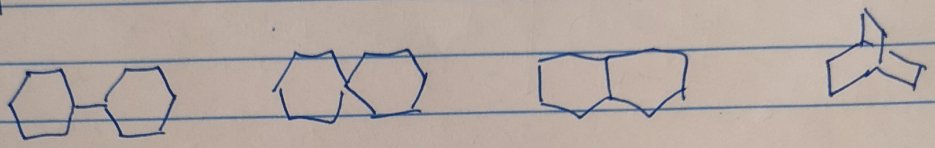
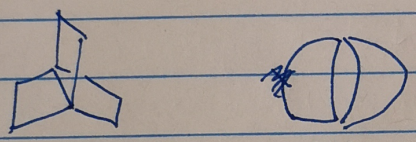
Lecture XXIII: Bridged & Fused, ~~and~~ Systems

03-27-2022

When you have multiple ring systems, they can have different relationships to each other:

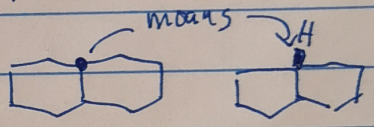


independent Spiro fused bridged

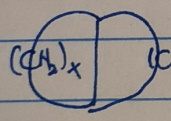


propellanes paddlane

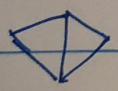
Notation



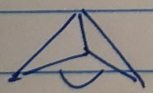
Fused rings



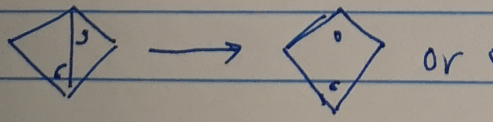
bicyclo[x.y.0]alkane



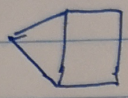
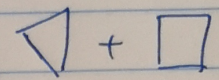
bicyclo[1.1.0]butane is the smallest and most strained 66.5 kcal mol^{-1}, more than 2x cyclopropane

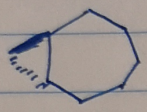


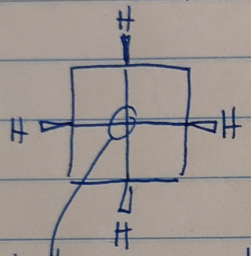
What's a maximum strain a compound can have? In theory, it is the strength of a C–C bond, if that relieves all the strain, you will get a stable bradical. But in this case that doesn't work.

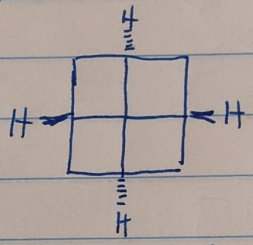


or still strained

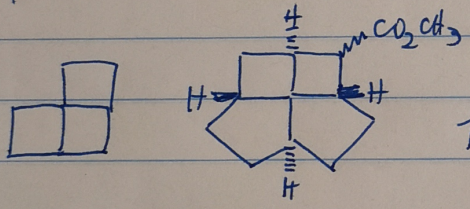
 bicyclo[2.1.0]pentane, strain approx. 

 Smallest trans-fused compound
trans-bicyclo[5.1.0]octane

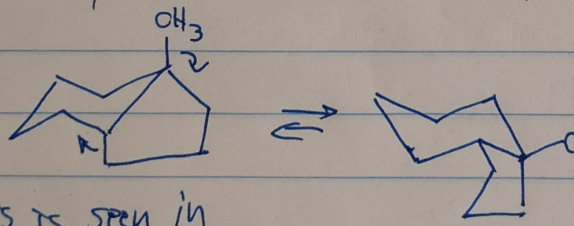
 cis-fenestrane

 trans-fenestrane

both were not made yet, but were studied to see if one can get a planar carbon atom.

 those were successfully made

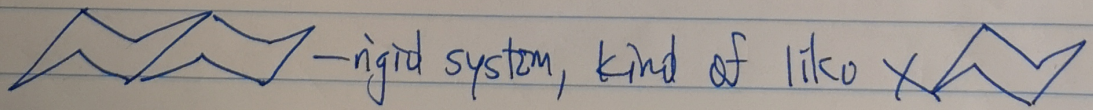
With larger rings, questions of angular strain are largely resolved, but they become conformationally flexible:

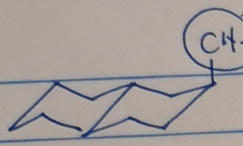


this is seen in C/D rings of steroids

cis-isomer is favored over trans

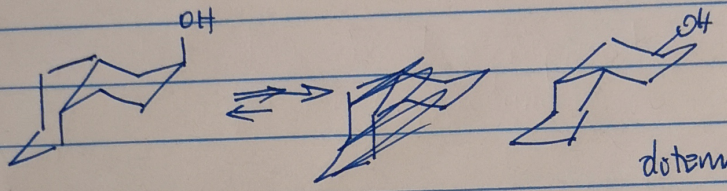
We've talked already about decalins:

 — rigid system, kind of like



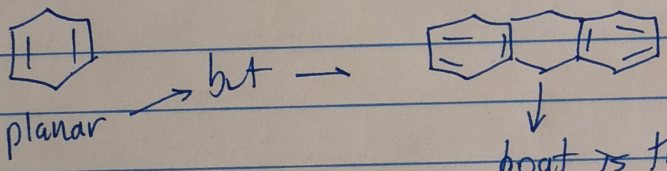
fixed in axial position

In cis-decalin, inversion of the chair can happen.

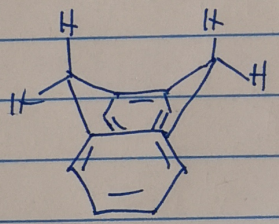


this equilibrium is determined by the substituent since the two chairs are enantiomeric

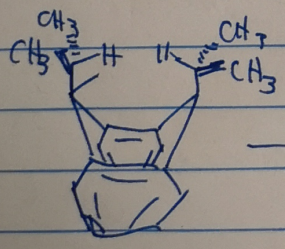
A very interesting six membered ring:



boat is the most stable

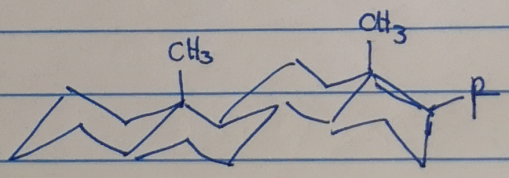


Furthermore, in this example, axial substituents are more stable! There is no 1,3-diaxial interaction anymore:

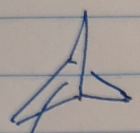


— defies anything we learned about six-membered rings!

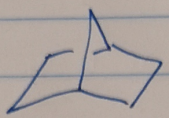
Steroids have multiple nice chairs:



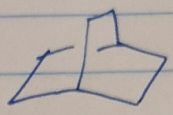
Bridged Rings



bicyclo[1.1.1]pentane

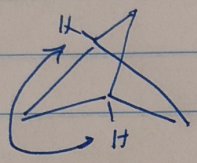


bicyclo[2.2.1]heptane
norbornane



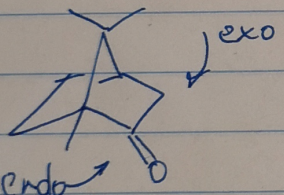
bicyclo[2.2.2]octane

Shortest nonbonded C–C distance 1.86 Å

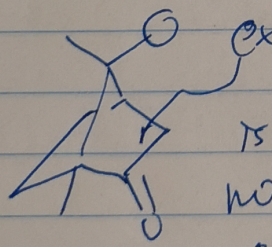


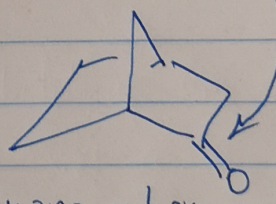
~60–68 kcal mol^{-1} of strain

^3J = 18 Hz!

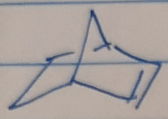


Camphor is a bridged system and also available in enantiopure forms

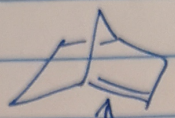




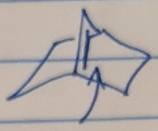
In unsaturated systems, double bond cannot be at the ring junction unless the ring is large enough:

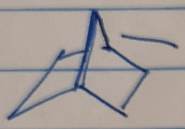

is stable

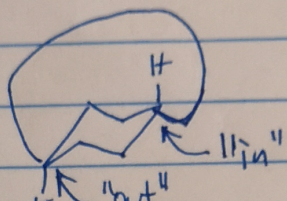
but

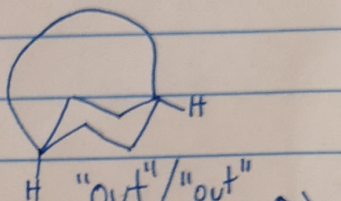

these would effectively be trans-bonds

or


are not

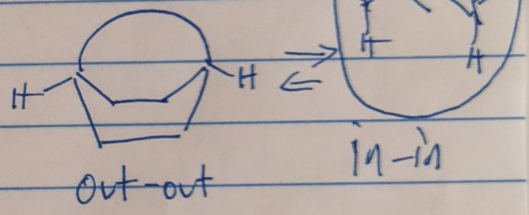

bridge is cis. Can it be trans?



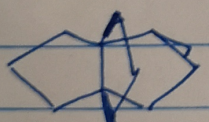


because H is out

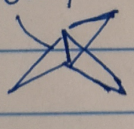
Three isomers instead of just two!

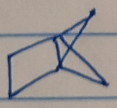


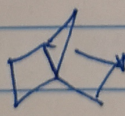
Paddlanes and Propellanes


[3.3.3.]propellane

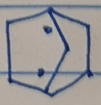
1.60Å, could be identified at rt


[1.1.1] propellane 103 kcal/mol of strain


[2.1.1] " 106 " " " "


[2.2.1] " 109 " " " "

↳ only this one can break the C-C bond productively into



Paddlanes do not exist until they are comparably large