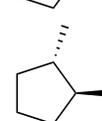
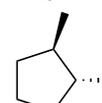
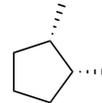
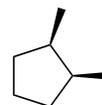
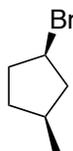
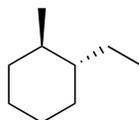


CHAPTER 4: CYCLOALKANES

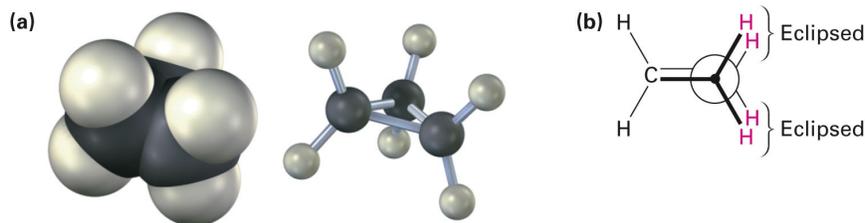
Naming. Write the complete IUPAC names for the following molecules

How many different molecules are drawn, below
(Hint: The answer is not 4)

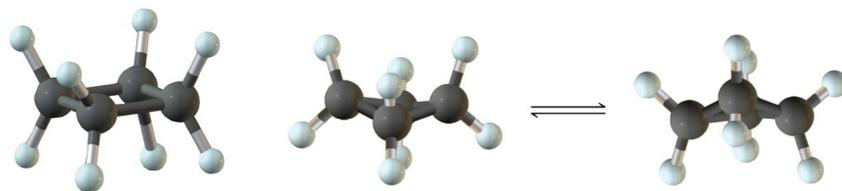
Don't forget to
use cis and
trans, when
necessary



Cyclopropane. Despite the fact that the carbons in cyclopropane are all _____ hybridized and the standard C-C-C angles for this hybridization is _____ degrees, the angles are actually about 60°. This deviation from tetrahedral creates A LOT of _____ strain. Since cyclopropane is mostly planar, there are also six fully eclipsed C-H sigma bonds, this adds _____ strain. All together, propane has 115 kJ/mol of strain energy - wow!



Cyclobutane. One might consider the C-C-C angles in cyclobutane to be 90°, however the molecule can alleviate some of its torsional strain by “puckering”, resulting in interior angles that are actually MORE strained (88°). Despite the *increase* in angle strain from the hypothetical planar conformation (90° angles), the total ring strain in cyclobutane is reduced to 110 kJ/mol. If *increasing* angle strain results in *lowering* the total strain, this must mean the resulting

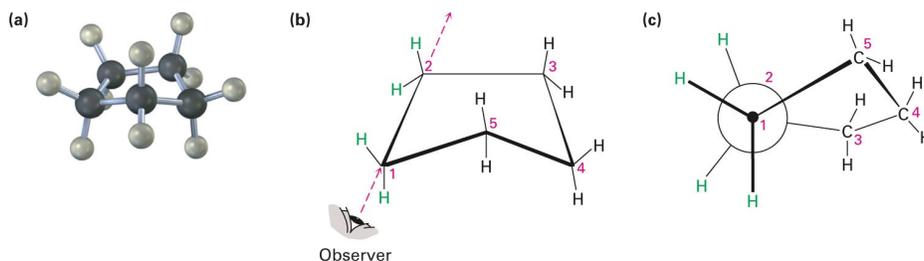


(a) Hypothetical planar conformation

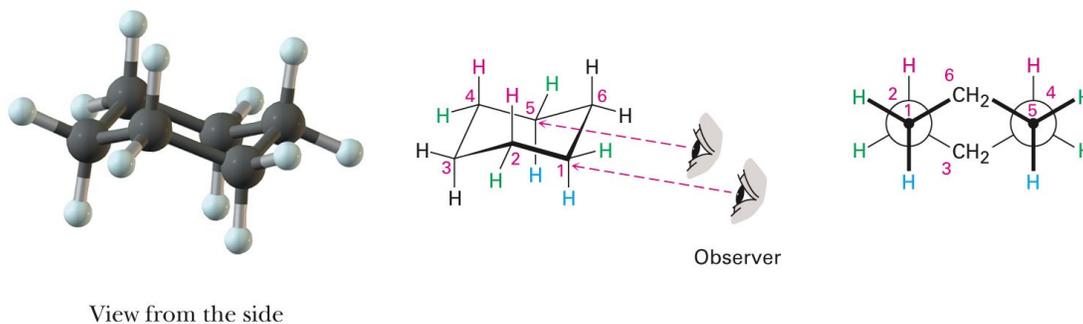
(b) Puckered (butterfly) conformations

reduction in _____ strain is significant! In fact, there are _____ eclipsing C-H interactions in cyclobutane.

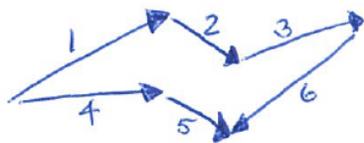
Cyclopentane. Cyclopentane also “puckers” since there are _____ eclipsing C-H interactions. Like cyclobutane, the relatively small increase in angle strain results in *lowering* the overall total ring strain to only 26 kJ/mol. Notice, in figure (c), the C-H bonds are not completely eclipsed!



Cyclohexane. The lowest energy conformation for a six membered ring is called a chair conformation, and despite there being 12 C-H bonds, there is NO torsional strain (check out the figure on the right). If that wasn't enough of a good thing, the bond angles in a chair mimic a nearly perfect tetrahedron. Relative to the three-, four- and five-membered rings, the six-membered ring has ZERO total ring strain!



Here's a tip on how to draw a chair - the numbers represent my pen/pencil strokes from 1 through 6. Notice 1 and 6, 2 and 5, and 3 and 4, are parallel to each other.



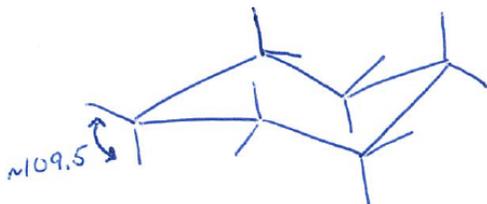
Now you practice (leave out the numbers and arrows):



Try tracing these chairs first, then draw your own

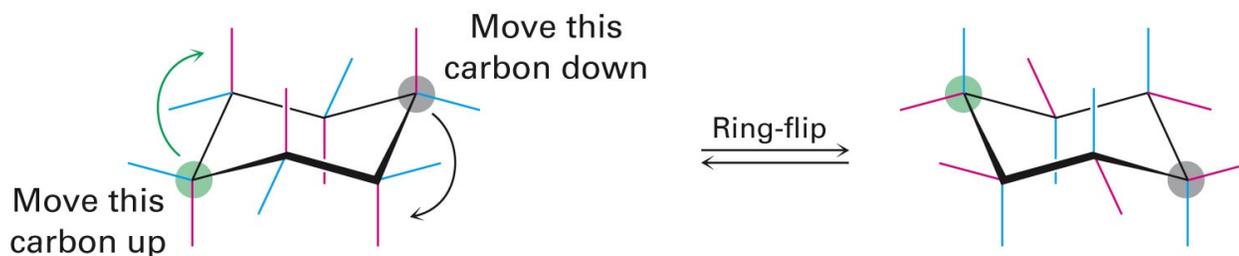
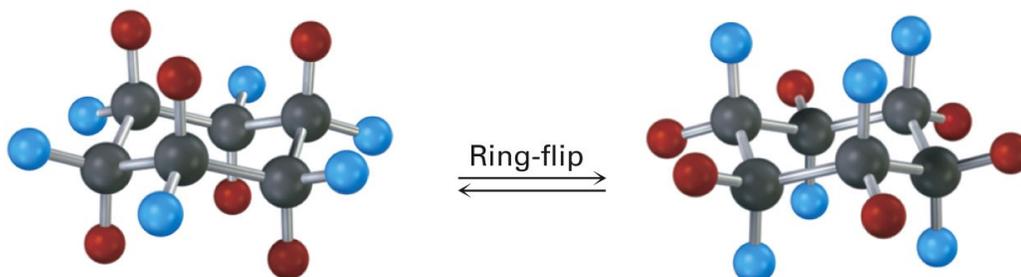
This time, draw a cyclohexane chair showing all axial and equatorial positions. Make sure your H-C-H angles are NOT 90°. Tip: Draw the six axial (three up, three down) positions first, then the equatorial ones (three up, three down - angles are near 109.5°).

Me:



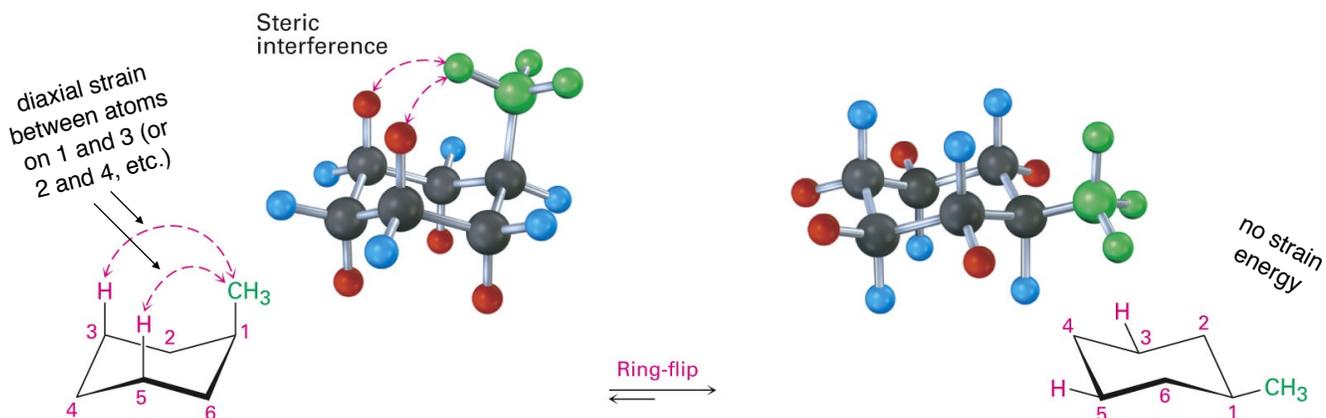
You:

At room temperature, chairs can ring flip. Notice all the vertical bonds to atoms on the left chair (called axial positions) after the ring flip are now located around the 'perimeter' of the chair (called equatorial positions). When a ring flips, all axial atoms become equatorial and all equatorial atoms become axial. Try this using your model kit.

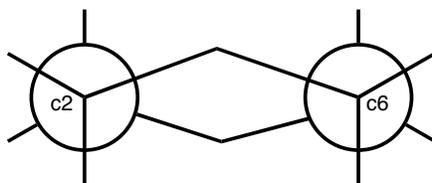


Now you try - can you draw the ring flip as shown above?

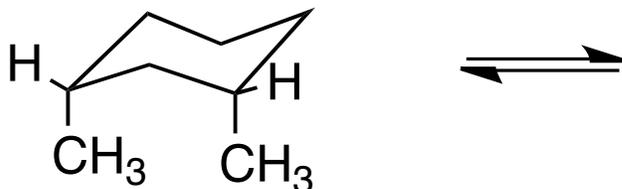
As a rule of thumb, when a cyclohexane ring has one or more substituents on it, the largest group will prefer to be equatorial (right structure) rather than axial (left structure). The two 1,3-diaxial interactions (steric) you see on the left structure each costs 3.8 kJ/mol - so what's the total diaxial strain of the structure on the left? _____



Here's a Newman projection of the above ring, sighting down the c2-c3 and c6-c5 bonds. Add hydrogens and the CH₃ group and show the 1,3-diaxial interactions:



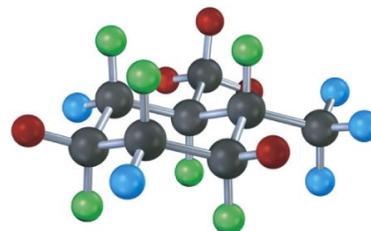
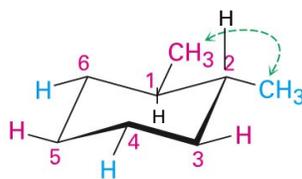
Can you identify the diaxial interactions on the structure of cis-1,3-dimethylcyclohexane? Try drawing a ring flip of this molecule.



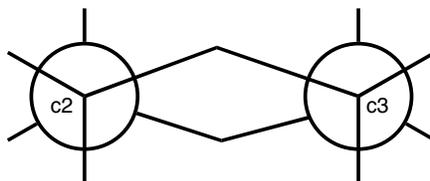
A *trans*-1,2-disubstituted cyclohexane can exist in two chair forms - when both groups are equatorial (below), notice the 60 degree dihedral angle between the two groups? This is a gauche interaction that creates 3.8 kJ/mol of strain energy.

***trans*-1,2-Dimethylcyclohexane**

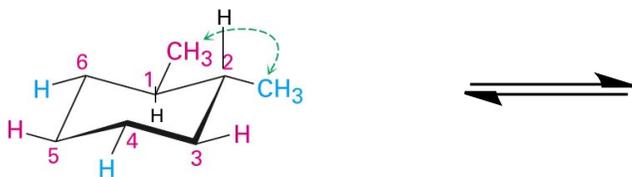
One gauche interaction (3.8 kJ/mol)



Like on the previous page, draw a Newman projection of this ring (shown again on the right) ring, sighting down the c2-c1 and c3-c4 bonds. Add hydrogens and the CH₃ groups and show the gauche interaction:

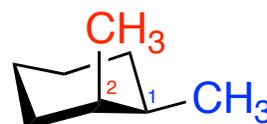
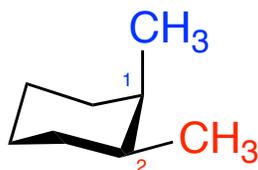


Here's the same ring again. Draw a ring flip of this molecule:



Strain Energy:

_____ kJ/mol

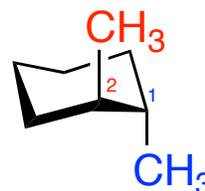
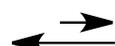
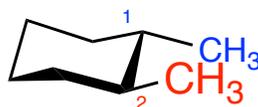


Strain Energy:

_____ kJ/mol

Strain Energy:

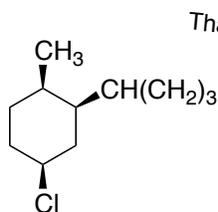
_____ kJ/mol



Strain Energy:

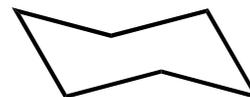
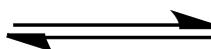
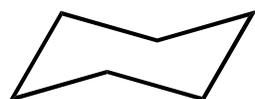
_____ kJ/mol

The top structure is *cis*-1,2-dimethylcyclohexane and the bottom structure is the *trans*-isomer. On the four structures, draw the hydrogens on carbons 1 and 2. Don't forget, these are tetrahedral carbons - do not draw 90° angles. Calculate the total strain energy for each molecule.

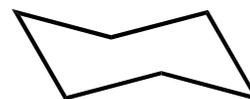
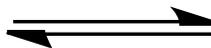
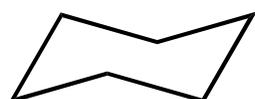


That's on the blank chairs drawn for you below (and on next page), draw the chair conformations for the *cis* and *trans* isomers of 1,3-dimethylcyclohexane and 1,4-dimethylcyclohexane. Then calculate the total strain energy for each conformation. As before, when you draw a methyl (or any other) substituent, please also draw the hydrogen that is attached to that carbon. This helps me out when I'm trying to decide if you've drawn something axial or equatorial.

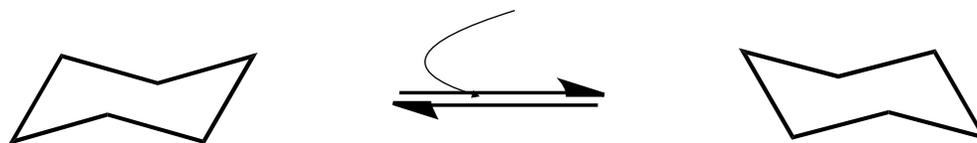
cis-1,3-dimethylcyclohexane



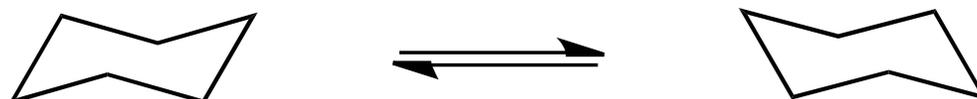
trans-1,3-dimethylcyclohexane



cis-1,4-dimethylcyclohexane



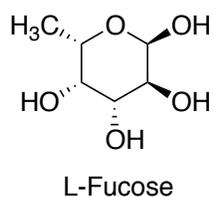
trans-1,4-dimethylcyclohexane



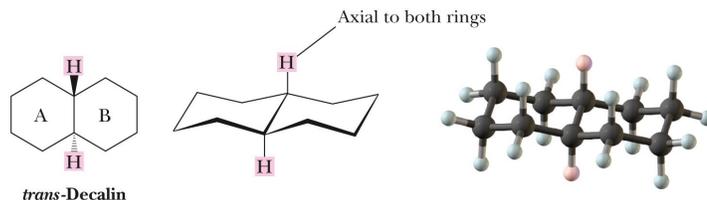
This symbol means, "same as".

Draw both chair forms of the structure below. Identify which is most stable:

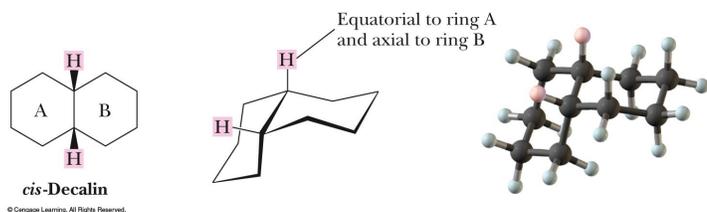
L-Fucose is a sugar component of the determinants of the A, B, O blood group typing. Draw the two chair conformations of L-Fucose and identify which is most stable:



Bicyclic Nomenclature. Bicyclic ring systems can have a *trans*- or *cis*-ring juncture. Decalin (10 carbons) is the common name given to two fused six-membered rings.



The IUPAC names, however, are *trans*- and *cis*-bicyclo[4,4,0]decane, where the first two numbers represent the number of carbons on each side of the ring juncture, and the last number is the number of carbon atoms between the two carbons at the ring juncture (the number of atoms in the bridge=0).



Likewise, the following molecule is named bicyclo[2,1,1]heptane:

In this case, the first two numbers represent the number of carbon atoms on either side of the 'bridge' (numbers are always written in descending order) and last is the number of carbons *in* the bridge (or between the two bridgehead carbons).

You try naming these:

