Cyclohexane and the Chair Structure:

The chair structure of cyclohexane is considered to be the "perfect" conformation. The chair structure consists of a six-membered ring where every C-C bond exists in a staggered conformation. With no torsional strain (and no angle strain), cyclohexane is the most stable of all the small rings of the cycloalkanes.



There are twelve possible positions on a chair structure. Six of the positions exist in vertical positions (known as "axial" positions) and the other six point out and away from the center of the ring, in an outwards direction (away from the equator of the ring, "equatorial" positions). Three of the axial positions point upward and the other three point down. The same is the case for the equatorial substituents – three face upwards and the other three face downwards (although these are definitely subtler!)



Chair structures are considered to be conformationally mobile, meaning they are flexible (not as much so as a straight chain alkane but more so than any of the other smaller rings) and because of this flexibility, they "flip" from one possible chair to the other possible chair.



You will notice that as the chair "flips", the substituents in axial positions (such as A and D in the first chair) become equatorial in the second chair. Substituents in equatorial positions (such as B and C in the first chair) become axial. You should also take note that substituents that are pointing up (A, which is axial and C, which is equatorial) always stay facing up (A is up equatorial in the new chair and C is up axial). Up stays up, Down stays down but axials become equatorial and equatorials become axial.

Drawing Chair conformations:

At this point, you should be able to draw any molecule in two-dimensions. For example, you should be able to draw cis-1-bromo-3-methylcyclohexane and it should look like either of the figures shown at the top of the next page.



Let's translate this first drawing into a chair conformation (consider the first version, with both substituents drawn in the up position). Draw a chair, which consists of three sets of parallel lines, added in, one set at a time:



Now, pick a position 1, whichever carbon atom you want to call #1. You have six possibilities. Then determine where the next relative position occurs. In the example above, the bromine is on 1 and the methyl is on 3. Find position 3, relative to the carbon you called 1. In the example shown below, I chose the carbon on the right to be 1, so there are two possibilities for position 3. Both are correct. Use either one.



At this point, you need to attach your substituents – with the correct three-dimensional arrangement. The bromine is on carbon 1. If you want to put the bromine in an "up" position on carbon 1 (it's on a wedge in two dimensions), then you would place it in an axial position (on carbon 1, axial is up and equatorial is down). The methyl is also up in this <u>cis</u> molecule, so up on carbon 3 will be axial also. (Note – if you look at the chair, you will see a zig-zag around the ring, where three carbons are "up" and three carbons are "down". Those "up" and "down" positions are all the axial positions.)



What if I had chosen a different carbon to be the #1 position? Try this one again. In this case, I've chosen a different carbon #1:



Now, add the substituents, keeping the bromine and methyl group "up", on the chair. Since the new positions, 1 and 3, are on "down" carbons on the ring, the "up" position is equatorial this time.



Both of the chair conformations drawn are correct. There are many correct versions of the chair conformations for this type of problem, depending on what you determine to be position 1 and which chair conformation you start with.

Drawing the Chair Flipped Conformation:

To draw the chair flip conformation, you have to redraw the ring (as its mirror image). This will represent the new conformation, as it should look, if the ring flips:



Carbon #1, which was an "up" carbon, is now a "down" carbon. Carbon #4, which was "down" is now "up". Add in the substituents and remember that axials become equatorials and equatorials become axials.



Axial versus Equatorial Substituents:

The cyclohexane structure will continuously flip from one conformation to another. Cyclohexane (without any substituents) has two equivalent chair structures, both equal in energy and both exist in a 50:50 mixture. Once substituents begin to be added to the chair structure, the two forms may not be equal in energy. Axial substituents are always less stable (higher in energy) than equatorial substituents. Axial substituents (anything besides the H atom) have steric interactions with other



groups in axial positions (including H atoms). We call these $A_{1,3}$ interactions.

The larger X becomes, the greater the energy state of the system (more steric strain) and the more likely the molecule will want to flip into the other chair conformation, if that is lower in energy.



A_{1,3} Interactions

no steric interactions

Consider the following examples and determine which has the lower energy (and thus MORE FAVORED) conformation:

a. Trans – 1-bromo-4-methylcyclohexane (two axials versus two equatorials – no brainer!! Equatorials are always more stable.)



c. Cis – 1-tert-butyl-4-chlorocyclohexane (which is better – large group axial or equatorial?? The



larger the group, the less stable it will be in the axial position.)

You should be able to draw a cyclohexane in two-dimensions, then put it into a chair conformation, then draw its chair flipped conformation and evaluate which of the two possibilities is more stable.