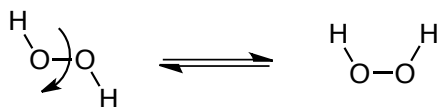# Chapter 3
Conformations of Alkanes and Cycloalkanes

Conformations of a molecule are different spatial arrangements of the atoms by simple rotation around carbon-carbon single bonds. For example, in hydrogen peroxide there are two conformations.

In this chapter we will learn how to draw molecules and we will study the relationship between the conformation and the energy.

Conformations of Ethane

Ethane has two conformations, the staggered conformation and the eclipsed conformations. As we will see, they are not the same in energy.

There are three ways of representing a molecule. For example, look at the staggered conformation of ethane. As we know, ethane is not a flat molecule and to study its shape in detail we need to be able to represent the three-dimensional structure on a flat surface. The drawing on the left is a flat picture but uses the convention of the bond that is the solid wedge as coming out of the surface and the dashed line as going back behind the surface.
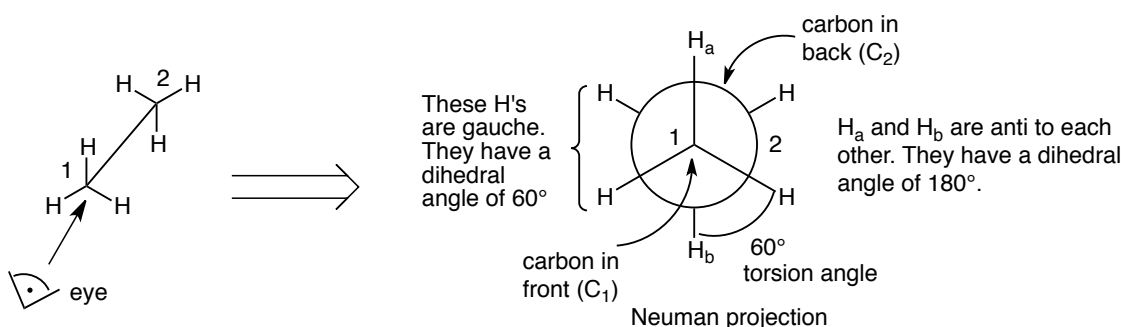
Another useful way to picture the three-dimensional structure is to use the sawhorse representation. (A sawhorse is a beam with four legs attached. Two of them are used as a support when sawing a piece of lumber.) The sawhorse drawing is an attempt at showing the actual shape in a perspective drawing. We do not need to be artists but we do need to be able to make accurate drawings that show the correct relationship between the substituents. Note that the carbon in front is labeled C1 and the carbon in back is C2. What is in front (coming at you) is indeed in front. At C1 one of the H's is pointing straight up and the other two are down. This is reversed at the back carbon. But we can simply rotate 60° at each carbon to put one of the H's down at C1 and the other two H's pointing up at C1. A similar rotation at C2 puts 2H's down and one H up.
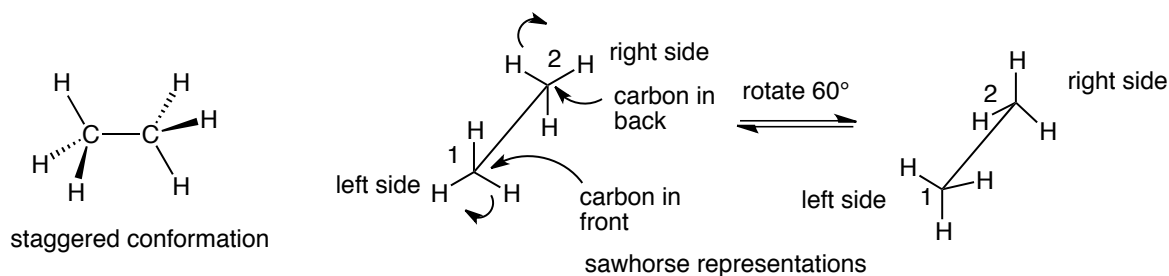
Another very useful representation is the Newman projection, devised by Professor Melvin H. Newman at Ohio State University. To make a Newman projection, sight down a carbon-carbon bond in a sawhorse representation. The bond disappears from view leaving the triangular arrangement of the three remaining substituents. The carbon that is in front is picture – by convention – as a dot and the carbon that is behind is pictured as a circle. It takes some practice to draw good Newman projections but it is a very valuable method for visualizing the actual angles between the substituents. This is called the torsion angle or dihedral angle.
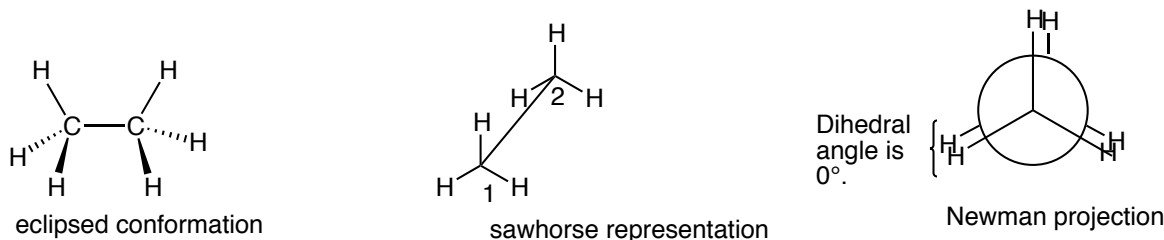
In the staggered conformation all of the dihedral angles (or torsion angles) are exactly 60°. This keeps the substituents as far away from each other as possible and it is the low energy conformation. The hydrogen atoms, with the two electrons in the C-H bonds want to be as far apart as possible. This minimizes electron-electron repulsion. When the angles are less than 60° the energy of the molecule is raised and we say there is torsional strain in the molecule.

When two substituents have a 60° relation between them, we say that they are in a gauche relationship. When they have a 180° relations between them we say they are anti.

These H's are gauche. They have a dihedral angle of 60°

H_a and H_b are anti to each other. They have a dihedral angle of 180°.

carbon in back (C_2)

carbon in front (C_1)

60° torsion angle

Neuman projection

Sight down C1 to C2. The C1-C2 bond disappears but the substituents remain. This is the Newman projection.

The eclipsed conformation can be reached from the staggered conformation by rotating 60° around one of the carbons, either the one in front or the one in back. Now the dihedral angles are all 0° and the hydrogens are all right on top of each other – they are "eclipsed" and there is electron-electron repulsion between the electrons in the two C-H bonds.

eclipsed conformation

sawhorse representation

Dihedral angle is 0°.

Newman projection

The eclipsed conformation is 12 KJ/mol (2.9 Kcal/mol) higher in energy than the staggered conformation.

If we plot energy versus the torsional angle between the hydrogens on C1 and C2 of ethane we get a cyclic pattern of energy minima (the staggered conformation) and energy maxima (the eclipsed conformation).
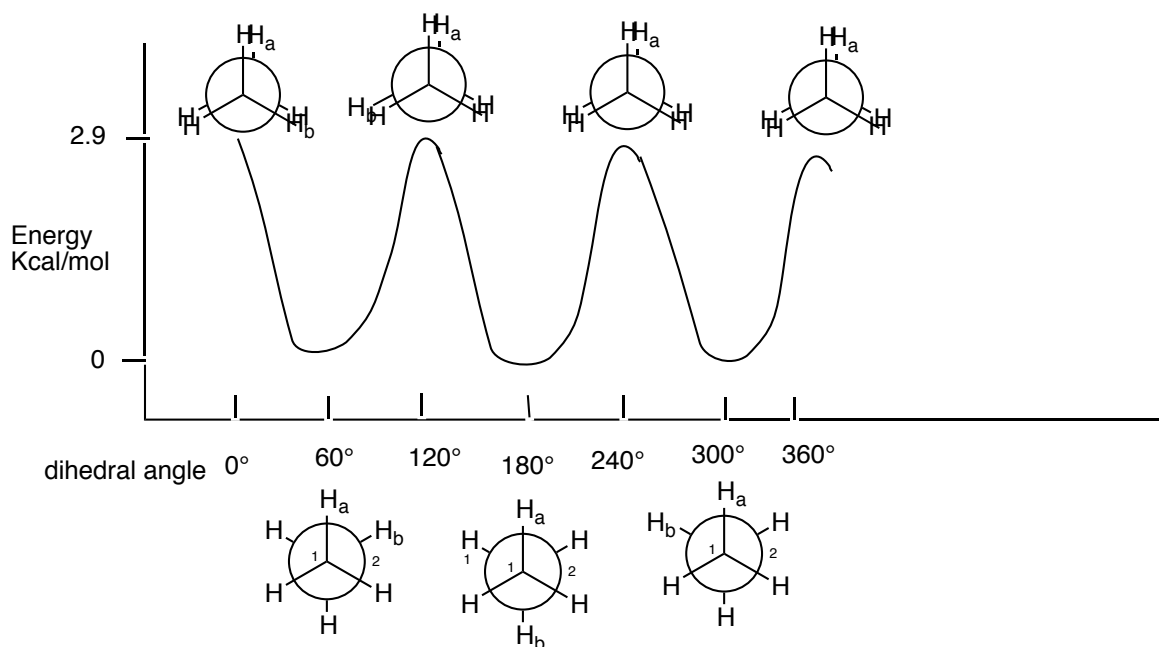
In order to go from one staggered conformation to another, the molecule must pass through an energy maximum. This is an activation energy (E_{ACT}). The point of maximum energy is called the transition state (TS).

As the temperature increases, more molecules will have the energy needed to cross over the transition state. In general a 10°C rise in temperature, causes a 2-3 fold increase in rate for a given process.
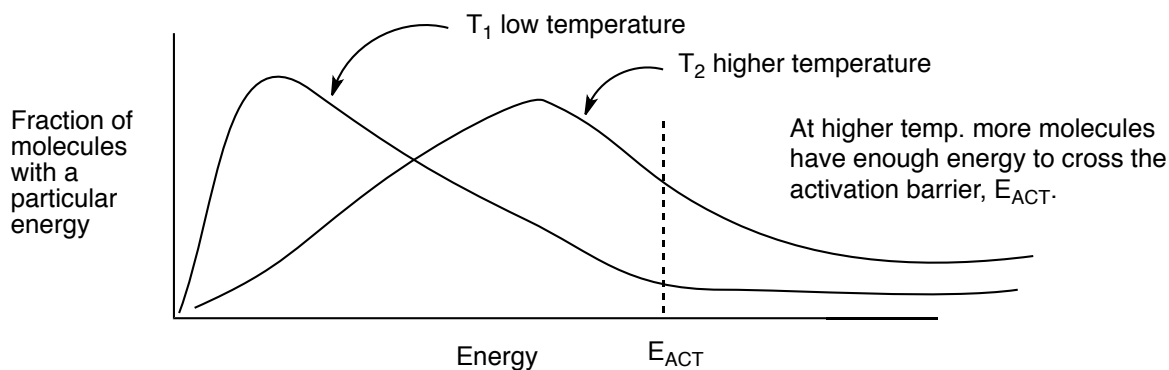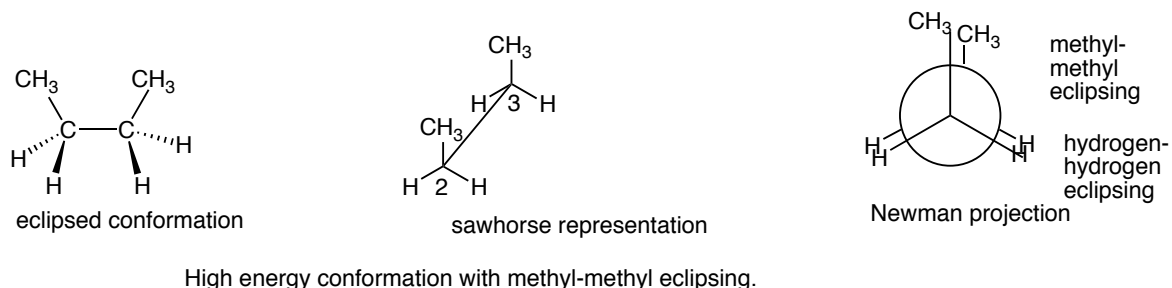
In the case of the transition between the staggered and eclipsed conformations, the rate of rotation is very fast. The time it takes for half the molecules to have rotated – the so-called half-life – is on the order of 10^{-6} seconds at 25°C.

Conformational Analysis of Butane

Butane is more complicated than ethane and has more conformations available. It is useful to think of butane as containing the central core of ethane but with a methyl group replacing a hydrogen on each carbon. For the sawhorse projection, look down the C2-C3 bond and do the same for the Newman projection. We see that the lowest energy conformation is the staggered conformation in which the methyl groups are as far apart as possible with a dihedral angle of 180°.

staggered conformation   sawhorse

Dihedral angle between the methyls is 180°.

Newman projection

Lowest energy conformation with the methyl groups as far apart as possible.
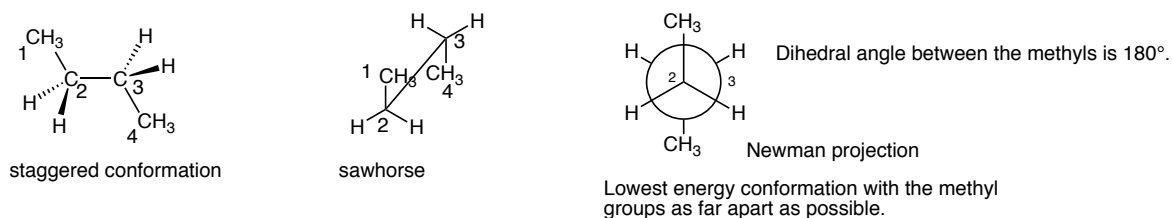
The highest energy conformation is the eclipsed conformation with the two methyl groups eclipsed. This conformation is about 25 KJ/mol (6.1 Kcal/mol) higher than the staggered conformation. The methyl groups are anti to each other.

eclipsed conformation

sawhorse representation

methyl-methyl eclipsing

hydrogen-hydrogen eclipsing

Newman projection

High energy conformation with methyl-methyl eclipsing.

The third conformation is where there is methyl-hydrogen eclipsing. This is not as high in energy as the conformation with methyl-methyl eclipsing. It is about 14 KJ/mol less stable than the fully staggered conformation.

eclipsed conformation   sawhorse representation   Newman projection
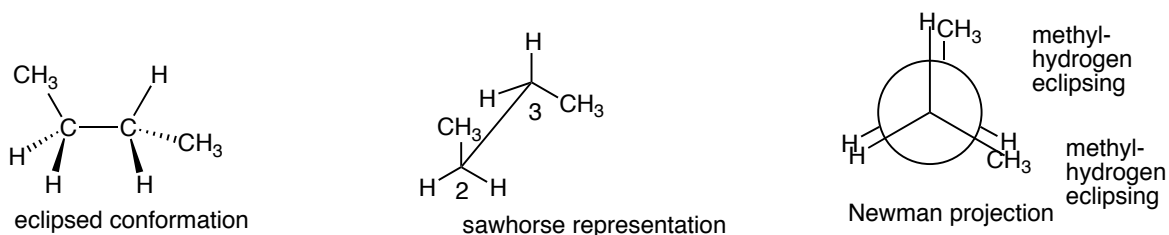
High energy conformation with methyl-methyl eclipsing.

The fourth conformation is when the two methyl groups are next to each other in a gauche relationship with dihedral angles of 60°. This is not nearly as high in energy as the eclipsed conformations but it is less favorable than the fully staggered. This is 3.3 KJ/mol higher in energy.

staggered conformation   sawhorse   Newman projection
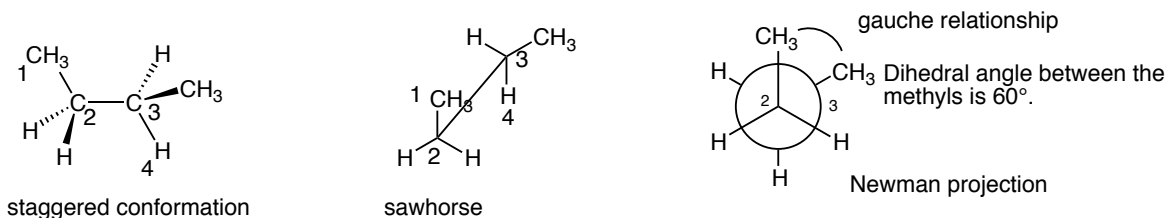
A plot of conformation versus energy will be more complicated than for the ethane case. We can have a CH_3-CH_3 eclipse. This is 25 KJ/mol higher in energy than the staggered conformation where the methyl groups are as far apart as possible. This will include two H-H eclipsing interactions as well. The methyl-methyl eclipsing will contribute much more to the total energy since the methyl groups are so much larger. We can also have methyl-hydrogen eclipsing. This conformation is 14 KJ/mol higher in energy than the staggered conformation. A third conformation is when the two methyl groups are right next to each other with a dihedral angle of 60°. This is called the gauche conformation. This is 3.3 KJ/mol higher in energy than the staggered. There is a small amount of steric hindrance between the two methyl groups.
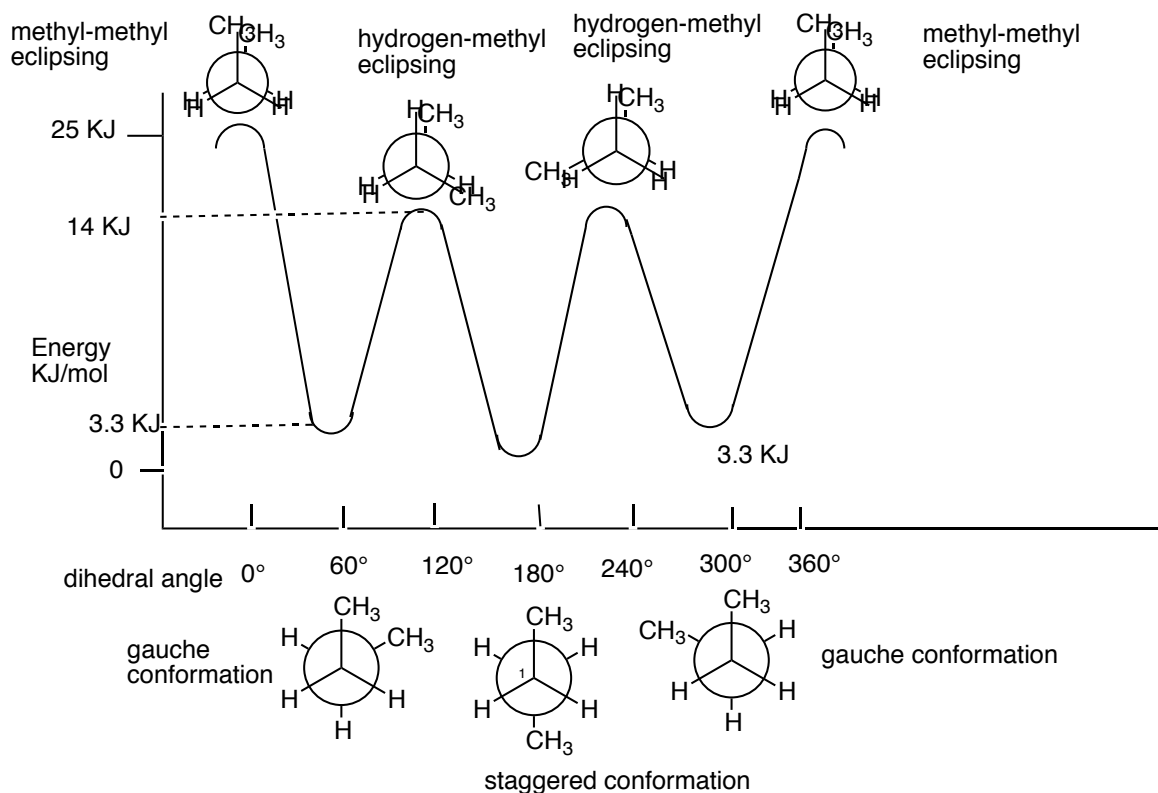
Cycloalkanes

A good way to compare the stability of the various cycloalkanes is to measure the heat of combustion per –CH₂ group. This is the total heat of combustion of one mole divided by the number of methylene units.

| Cycloalkane	heat of combustion	Strain due to ring
cyclopropane	697 KJ/mol	44 KJ/mol
cyclobutane	681	28
cyclopentane	658	5
cyclohexane	653	0
cycloheptane	657	4
cyclooctane	658	5

We see that for cyclohexane, the heat of combustion per methylene is the same as that found for open-chain alkanes. There is no increase in energy in the molecule due to the fact that it is constrained in a ring. There is a considerable increase in energy for the smaller ring sizes. We call this increase in energy ring strain. There are two sources of ring strain. One is due to torsional strain. This is the increase in energy due to eclipsing interactions of the substituents and gauche butane interactions as described above. The other is angle strain. This is due to the deviation of the angles from the ideal 109.5° of an sp³ carbon. When the angles are less the optimum 109.5°, the bonds are weakened because the overlap is not as efficient.

For **cyclopropane**, (1) there is considerable angle strain. The angles are 60° rather than 109.5 and normal sp^3-sp^3 bonds are not possible. The bonds cannot overlap end-to-end and are bent outward. This makes the bonds weaker.
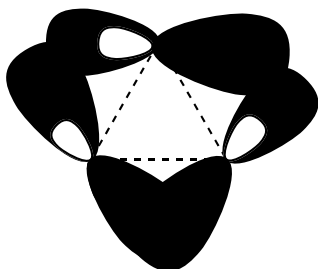

(2) Cyclopropane is necessarily planar. Therefore the three hydrogens facing up are eclipsed and the three hydrogens facing down are eclipsed.
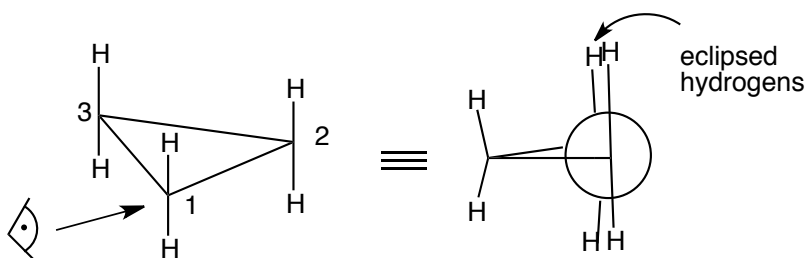
For **cyclobutane**, (1) there is still considerable angle strain, with angles of 90°C rather than 109.5 but it is less than in cyclopropane. (2) There is still some eclipsing of the hydrogens (torsional strain) but it is partially relieved by twisting around the C-C bonds so that the sigma framework is not planar and the hydrogens are no longer eclipsed. Cyclobutane adopts a bent conformation.
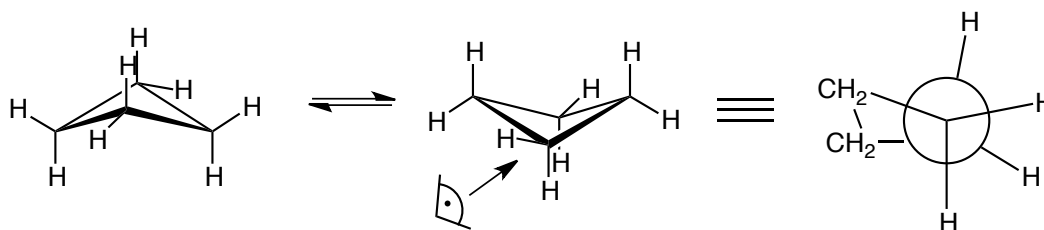

Cyclopentane has very little angle strain and has only a small amount of torsional strain. It also adopts a bent conformation. There are two conformations possible, the envelope and half-chair. In the envelope conformation, four atoms are in the same plane and one atom is raised above the plane. This causes twisting around the C-C bonds so that torsional strain is relieved.

envelope

half-chair
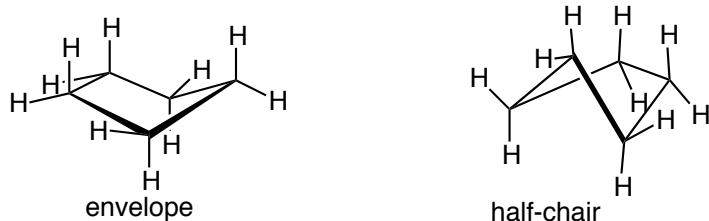
Cyclohexane is by far the most important of the cycloalkane derivatives. It is very stable and as such is a very common motif in both natural and synthetic molecules. There is very little angle strain and the dihedral angles are very close to the optimum values of 60° in which the substituent hydrogens are perfectly staggered.

The low energy conformation of cyclohexane is the chair conformation. We need to learn to make good chair drawings.

Start with (a) two parallel lines offset by about one-third. (b) Draw two more parallel lines from the first two. (c) Connect these two lines. Note that there are three sets of parallel lines.
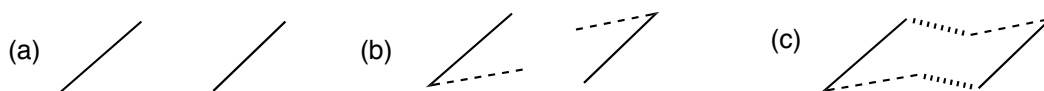
Notice that there is an alternating pattern of carbons in the cyclohexane structure. Recall the zigzag pattern of alkane chains where the carbon atoms are bonded in an up and down fashion. This is repeated in cyclohexane.
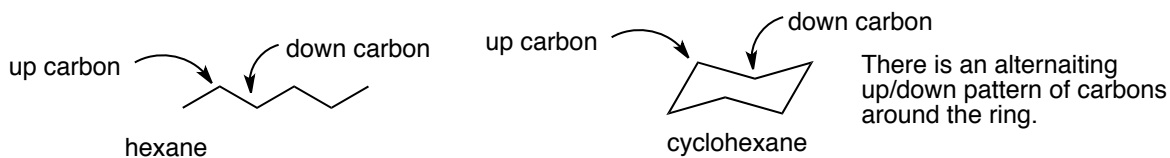

Now put in the substituents. We will start using only hydrogens. There are two types of substituents:
(1) Those pointing straight up. These are the axial substituents. There are six of these.
(2) Those pointing out to the side. These are the equatorial substituents. There are six of these.

There are two kinds of axial substituents and two kinds of equatorial: those pointing up and those pointing down.

Look at the axial hydrogens. Three of them are pointing up and three are pointing down and note that the up axial hydrogens are on every other carbon and the three down hydrogens are on the alternate carbons in between so that there is an alternating pattern of up down, up down all the way around the ring.

Note also that if a carbon itself is pointing up, then the axial substituent on this carbon will also be pointing up.

three "up" H's   three "down" H's
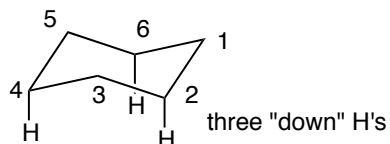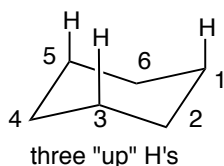
Note that in the absence of substituents other than hydrogen, the numbering of the ring is arbitary.

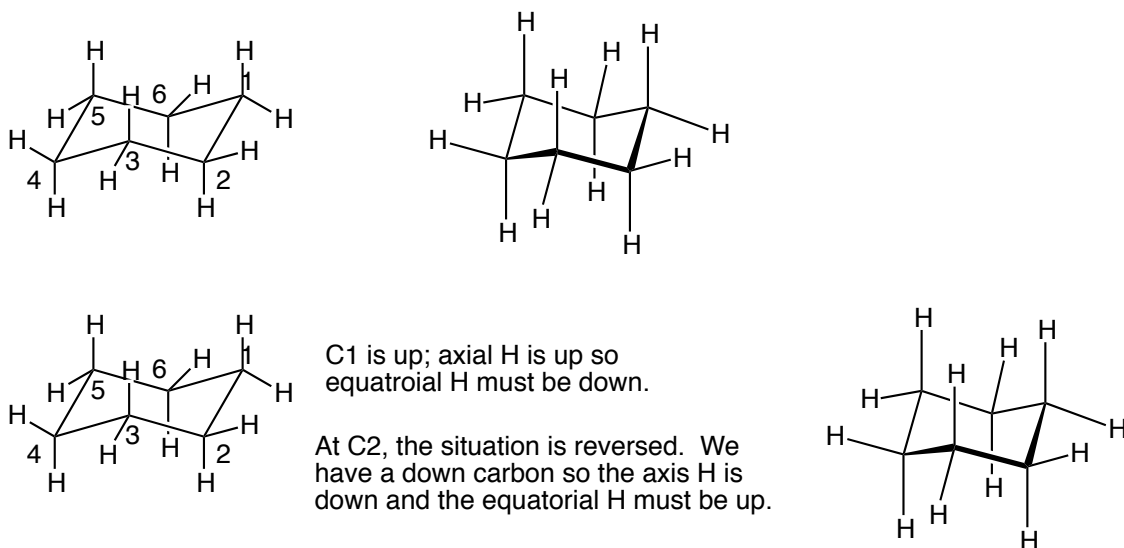Combine this into one drawing and we have our alternating up/down pattern.

Here are the six axial hydrogens in the alternating up/down pattern.
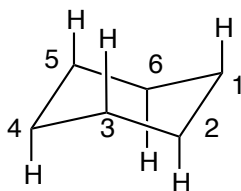
The equatorial substituents point out to the sides of the molecule ("the equator"). They are also in an alternating up/down pattern. An equatorial hydrogen on every other carbon is up and on the alternate carbons the equatorial hydrogens are down. The result is an up/down pattern all the way around the ring, similar to the axial hydrogens and to the carbon skeleton. If an equatorial hydrogen on C1 is down, the next equatorial hydrogen at C2 must be up.

three down equatorial H's   three up equatorial H's   all six equatorial H's
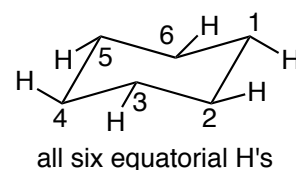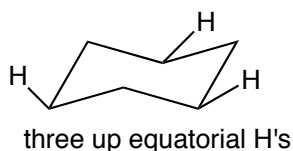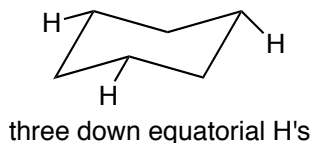
When both the axial and equatorial hydrogens are shown on the same molecule, we see a repeating pattern of an "up" carbon having an "up" axial hydrogen and then equatorial carbon at this position is "down".

C1 is up; axial H is up so equatroial H must be down.

At C2, the situation is reversed. We have a down carbon so the axis H is down and the equatorial H must be up.

Cyclohexane chairs undergo rapid chair-chair inter-conversion by means of rotation around the C-C bonds. We call this process a ring-flip, although the ring is not actually flipping over. It is changing from one chair conformation to another. This process is very fast and happens on the order of 10^6 times per second. When the ring-flip occurs, the three carbons that were pointing up, now point down and the three carbons that were pointing down, now are pointing up.


ring flip
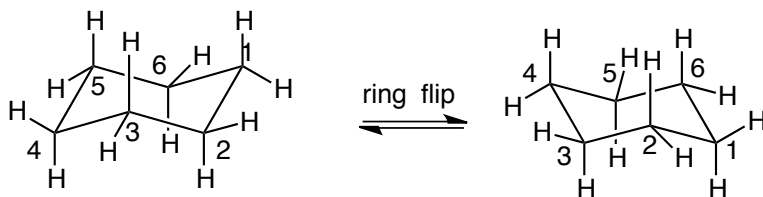
This process causes the substituents to shift from an equatorial position to an axial one and from an axial position to an equatorial one. All axial substituents become equatorial and all equatorial substituents become axial.

But note that a substituent that is pointing up in one conformation is still pointing up in the ring-flipped conformation. Look at the methyl group at C1 in the conformation on the left. It is axial and up and in the conformation on the right it is axial and still pointing up.


ring flip
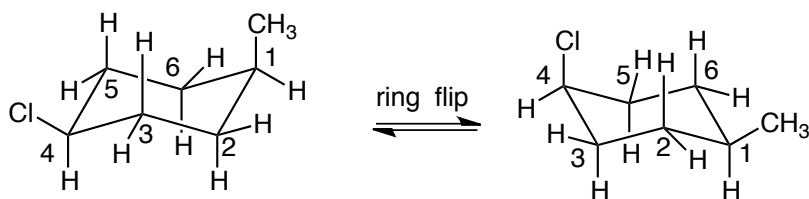
The conformation that puts the large substituent(s)s in the equatorial position is lower in energy than the conformation in which the large substituent(s) are axial. There is less steric hindrance in the equatorial position.
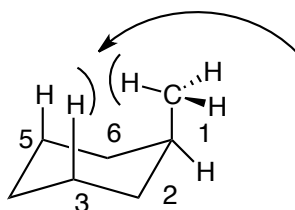
Bad steric interaction. the methyl group is too close to the axial hydrogens in a 1,3 relationship.

The axial substituent at C1 comes too close to the axial hydrogens at C3 and C5. Both of these hydrogens are in a 1,3-relationship with the axial substituent and so we call this a 1,3-diaxial repulsion. The axial methyl group is within 190-200 pm of the axial hydrogens and this is less than 240 pm, which is the sum of the van der Waals radii of two hydrogen atoms.

This is very similar to a gauche interaction in butane. This can be seen by making a Newman projection looking down the C2-C1 bond. It can be seen that the C3 methylene is in a gauche relationship with the C1 methyl when it is axial but it is perfectly staggered when the methyl is equatorial.
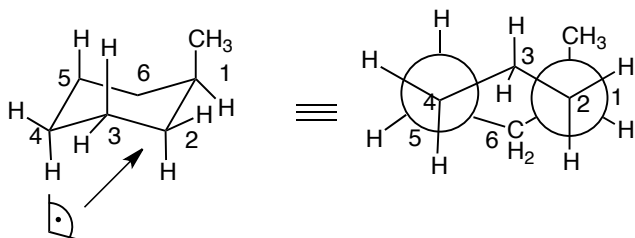
When the C1 methyl is axial, we see a bad gauche butane interaction between the methyl at C1 and the C3 methylene.

But when the methyl group is equatorial it is staggered with the C3 methylene group and also the C5 methylene.
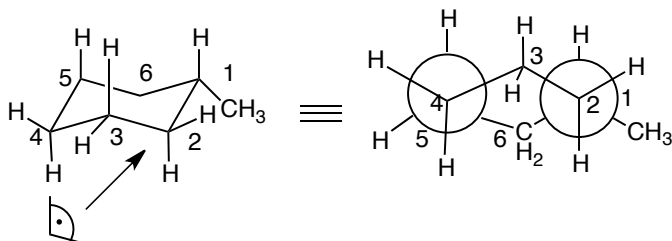

When the C1 methyl is equatorial, it is perfectly staggered with the C3 methylene.

The preference for the equatorial methyl substituent is about two times that of the gauche butane interaction. There are two axial hydrogens, one at C3 and one at C5, so 2 x 3.3 KJ/mol = 6.6 KJ/mol. The actual value is 7.4 KJ/mol.

11

The larger the substituent, the greater the preference for its being equatorial.

97%

3%

8.6 KJ/mol lower in energy
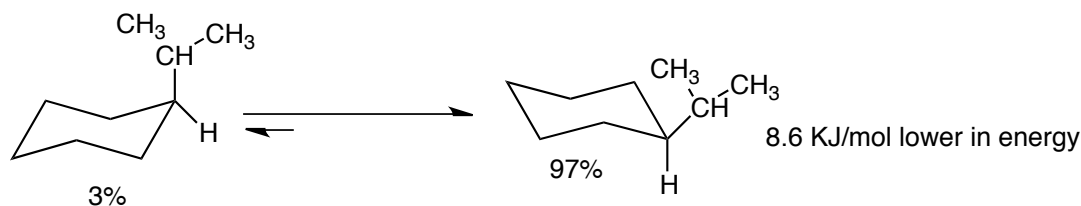
When there is a *tertiary*-butyl substituent it is virtually 100% in the equatorial position.

~0%

~100%

22.8 KJ/mol lower in energy
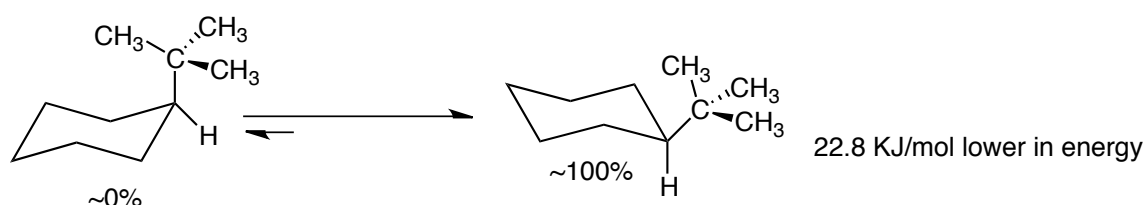
We can calculate the equilibrium constant from the difference in standard free energy between reactants and products:

$$\Delta G° = \Delta G°_{product} - \Delta G°_{reactant} = -RTlnK, \text{ where } \Delta G° = \Delta H° - T\Delta S°$$

Sustit. X	% axial	% equatorial	K_{eq}	$\Delta G°$ (KJ/mol)
-F	40	60	1.5	-1.0
$-CH_3$	5	95	19	-7.4
$-CH(CH_3)_2$	3	97	32.3	-8.6
$-C(CH_3)_3$	<0.01	~100	>10,000	-22.8

Disubstituted Cycloalkanes

We can have a new kind of isomers called stereoisomers. Stereoisomers are isomers in which the atoms are connected in the same way but have different arrangements of the atoms in space. If the two like substituents are on the same side of the ring, they are the *cis* isomer; if they are on opposite sides of the ring, they are the *trans* isomer. The *cis* and *trans* isomers are not inter-convertible by simple rotation.
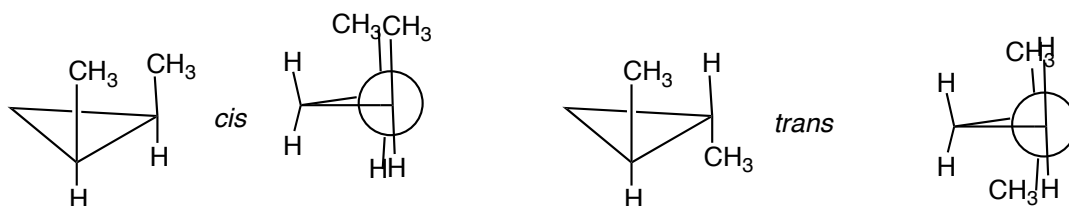
The *trans* isomer is more stable than the *cis* isomer due to steric hindrance. In the *trans* isomer the methyl groups are farther away and there is methyl-hydrogen eclipsing but in the *cis* isomer there is methyl-methyl eclipsing.
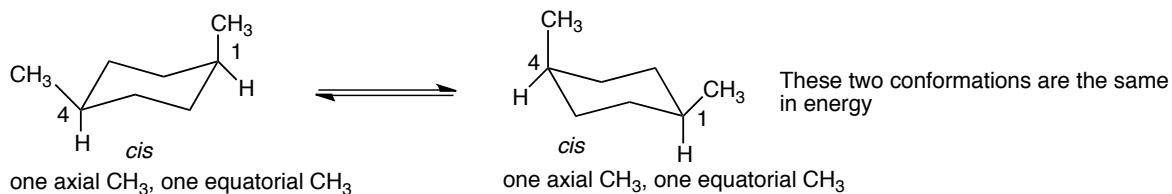
To measure the relative stability we can compare heats of combustion. We see that the *trans* isomer is 5 KJ/mol more stable than the *cis* isomer.
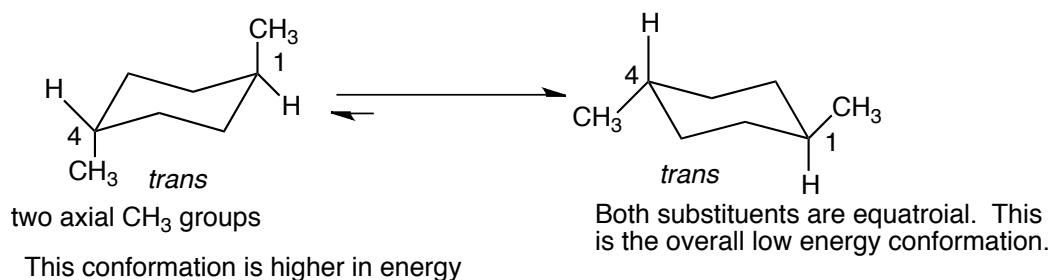
For *cis*, ΔH = 3371 KJ/mol

For *trans*, ΔH=3366 KJ/mol¬

Trans is more stable by 5 KJ/mol

cis

trans

3371 KJ/mol

3366 KJ/mol

$5\ CO_2 + 5H_2O$
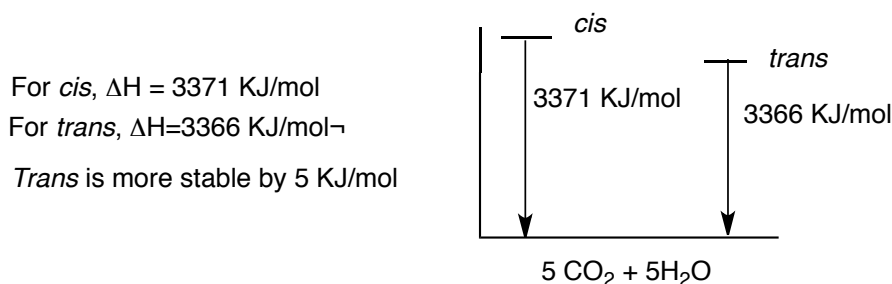
Disubstituted Cyclohexanes

Comparing the heats of combustion of *cis*-1,4-dimethylcyclohexane and *trans*-1,4-dimethylcyclohexane we see that the *trans* isomer is 7 KJ/mol more stable that the *cis*-isomer. The reason for this is that in the *cis*-isomer in both conformations one of the methyl groups must be in the axial position while in the *trans*-isomer, there is one conformation in which both methyl groups are in the equatorial position.

For the *cis* case:

one axial CH_3, one equatorial CH_3

These two conformations are the same in energy

one axial CH_3, one equatorial CH_3

For the *trans* case, there are again two conformations possible and they readily convert by means of a ring-flip. The *trans*-isomer in which both substituents are equatorial is the overall lowest energy conformation. Therefore, the *trans*-isomer is lower in energy than the *cis*-isomer because it has the di-equatorial conformation.

CH₃ trans
two axial CH₃ groups

This conformation is higher in energy

trans
Both substituents are equatroial. This
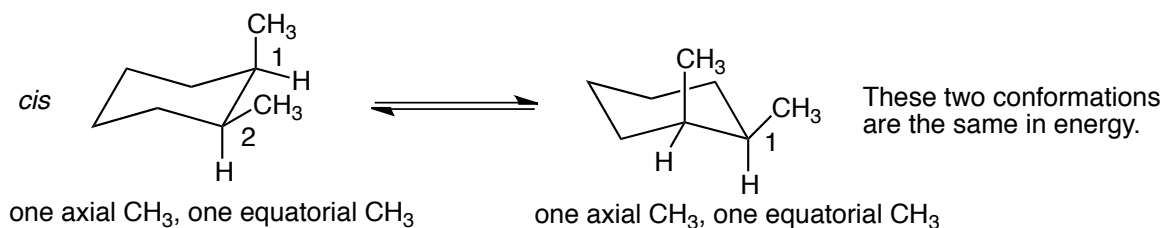is the overall low energy conformation.

Note that in the *cis*-isomer both substituents are pointing up, even though one substituent is axial and one substituent is equatorial and in the *trans* case, one substituent is pointing up and the other down. *Cis* isomerism does not mean both substituents are axial (or equatorial).

cis: both substituents are pointing up (or down)

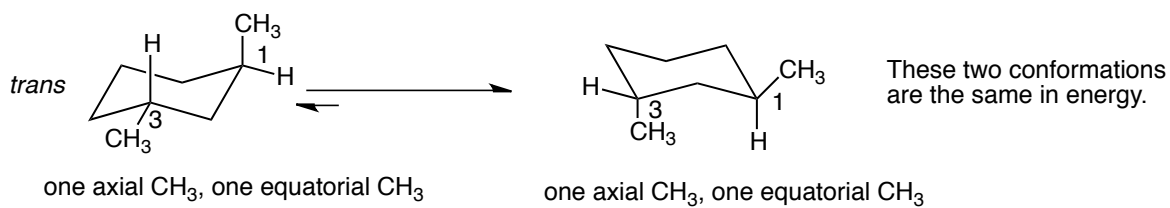*trans:* one substituent is pointing up, the other is pointing down.
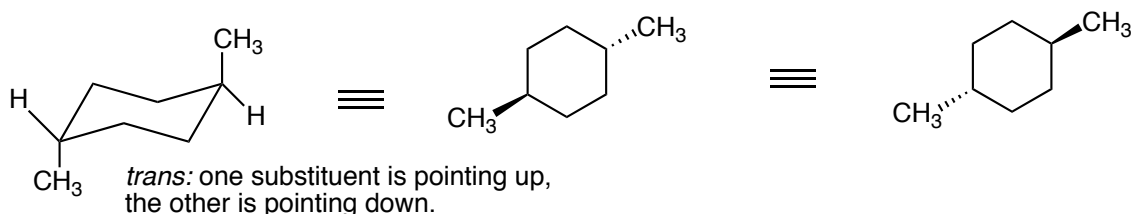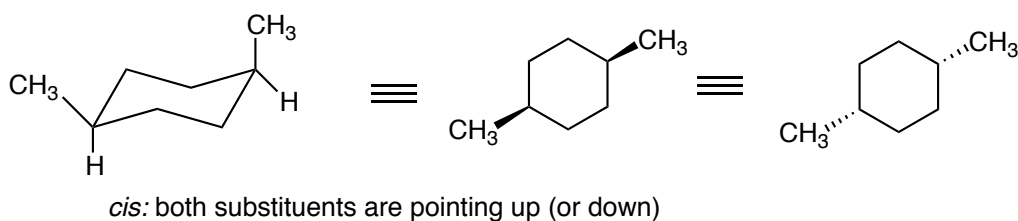
For 1,2-disubstituted cyclohexanes:
Here the *cis*-isomer has two conformations that are equal in energy, each having one equatorial substituent and one axial substituent.

cis

one axial CH₃, one equatorial CH₃

one axial CH₃, one equatorial CH₃

These two conformations
are the same in energy.

The *trans*-isomer has one conformation in which both substituents are equatorial. This conformation is the overall lowest in energy, making the *trans*-isomer more stable than the *cis*.

For 1,3-disubstituted cyclohexanes, the *cis*-isomer is lower in energy than the *trans*-isomer since there is one conformation in the *cis*-isomer in which both substituents are equatorial.

cis

both substituents are axial
higher energy conformation

both substituents are equatorial
lower energy conformation

The diequatorial substituent is overall lower in energy than either of the *cis*-conformations.

trans

one axial CH₃, one equatorial CH₃

one axial CH₃, one equatorial CH₃

These two conformations are the same in energy.
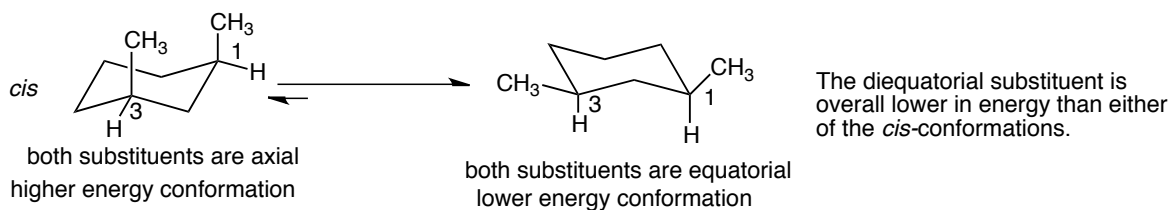
If there are two different substituents, the low energy conformation will be the one in which the larger substituent is in the equatorial position. The larger the difference in size between the two substituents, the greater the preference for the larger substituent to be equatorial. Therefore, if there is a *tertiary*-butyl group on the ring, there will still be rapid chair-chair inter-conversion but at any given instant most of the molecules will have the *t*-butyl group in the equatorial position.

~0%

~100%

The lower energy conformation has the large *t*-butyl group in the equatorial position.

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