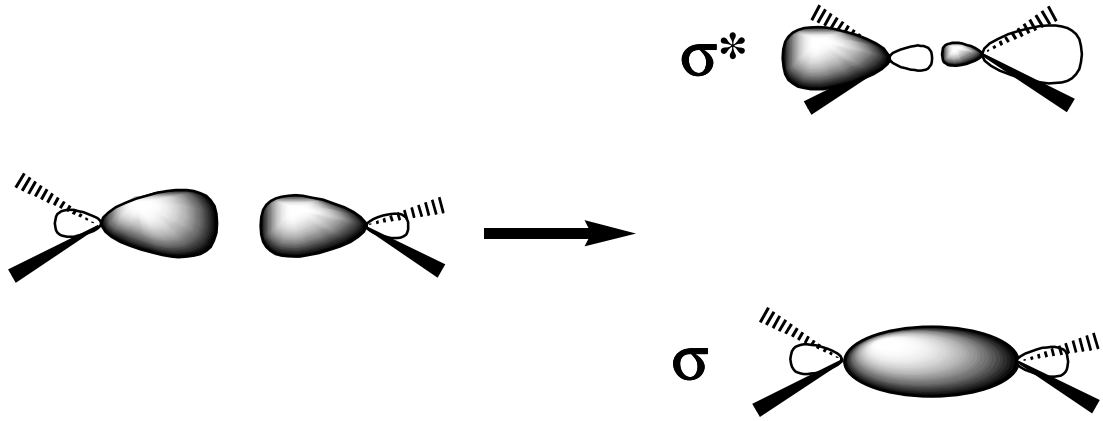
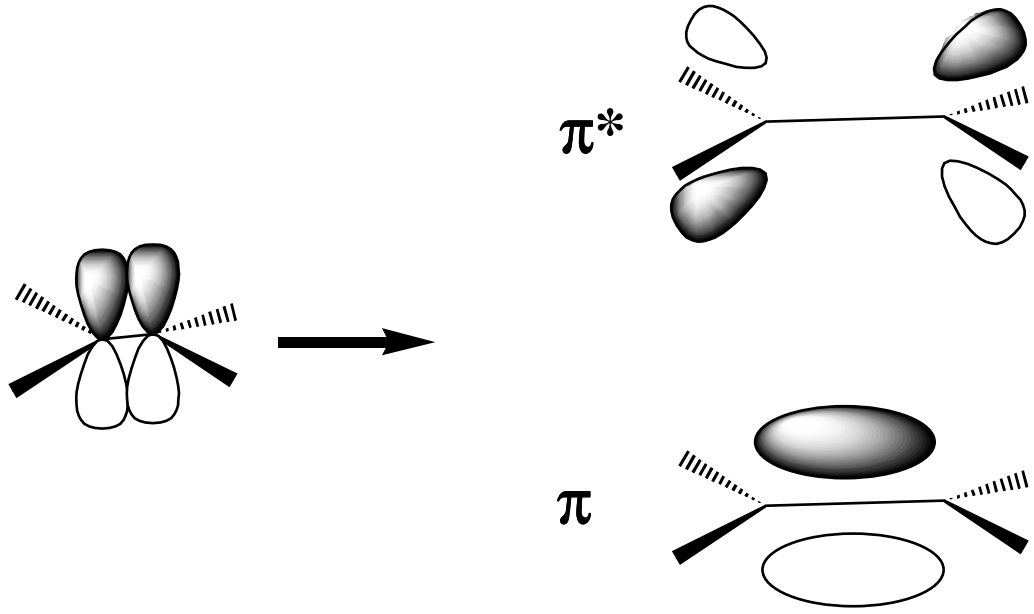
LECTURE 2

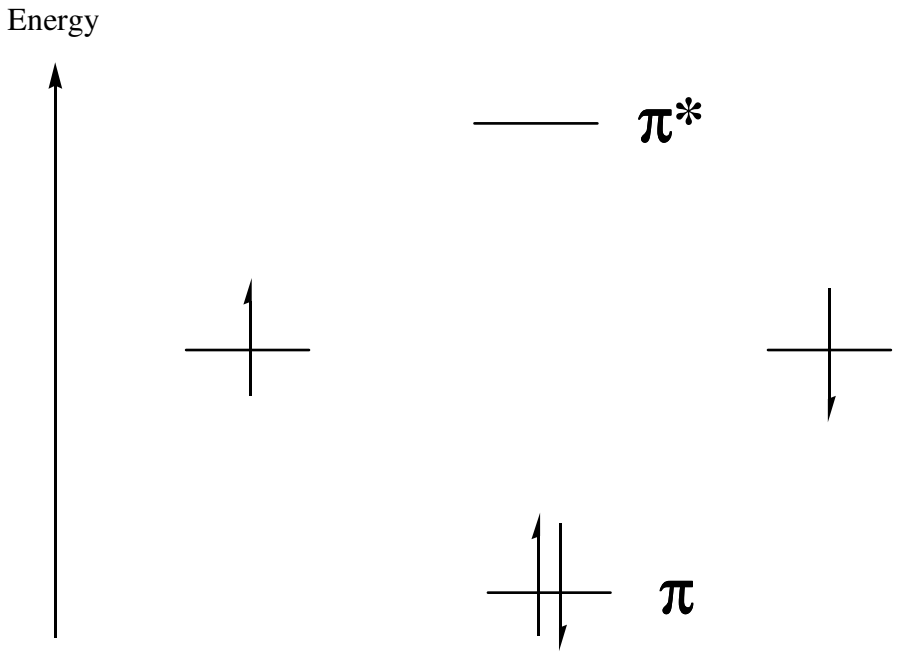
Alkenes: In alkenes we make the σ-bonds between carbon atoms by overlapping sp^2 hybrid orbitals which have been produced by the hybridisation of one s and only two p orbitals. These sp^2 hybrids have a very similar shape to the sp^3 hybrids but because there are only now three of them they point to the corners of a triangle in order to minimise the repulsion between the electrons in the bonds (the angle between the σ-bonds in alkenes is 120^o rather than the tetrahedral 109^o in alkanes). The sigma framework of alkenes is thus:



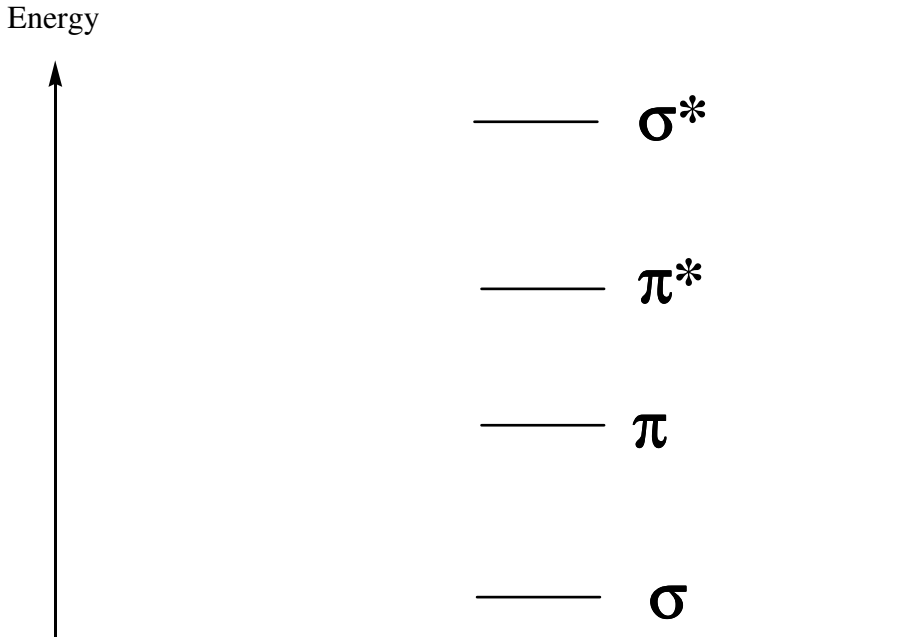
However, in alkenes we still have an atomic p orbital on each carbon which we have not yet used and which is at right angles to the plane of the sigma framework. These two orbitals can now overlap sideways to give a new type of bond, the π-bond, in which electron density is mainly above and below the internuclear axis. Again there is a corresponding empty, anti-bonding orbital (π*):



In energy terms, the π and π* orbitals show the same pattern as the corresponding σ and σ* orbitals i.e. the antibonding orbital is higher in energy:

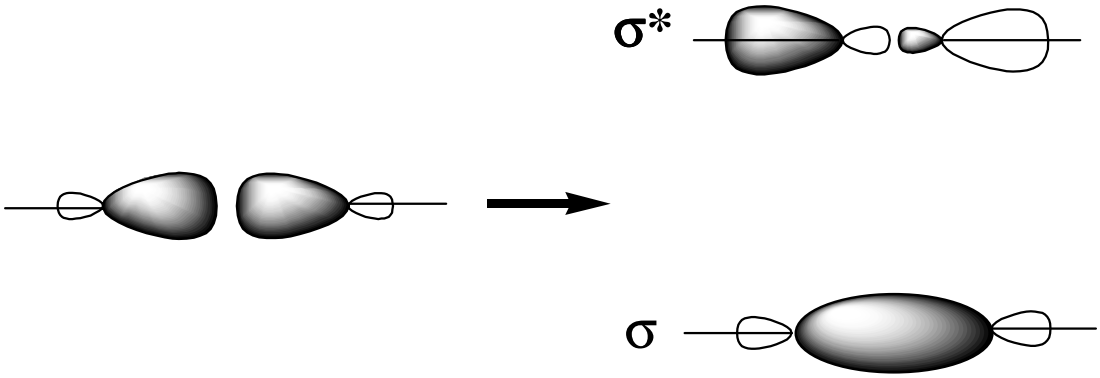


Thus a double bond actually consists of two types of bond, one π and one σ. However, because the sideways overlap to produce the π orbital is not as effective as the nose to nose overlap leading to the σ orbital, the former is somewhat weaker than the latter (C-C π bond = 270 kJ mole^{-1}; C-C σ bond = 350 kJ mole^{-1}). This leads to the following order of energies of the orbitals:

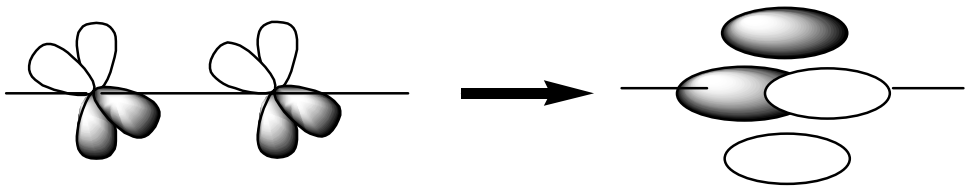


In contrast to the situation in alkanes, rotation about the central C-C bond in alkenes is now very difficult because to do so would break the 270 kJ mole^{-1} π-bond which lies above and below the plane of the molecule; this leads to the phenomenon of geometrical isomerism (see above).

Alkynes: In alkynes we make the σ-bonds between carbon atoms by overlapping sp hybrid orbitals which have been produced by the hybridisation of one s orbital and only one p orbital. These sp hybrids have a similar shape to sp^2 and sp^3 hybrids but because there are only now two of them they point along a straight line in order to minimise the repulsion between the electrons in the bonds (the angle between the σ-bonds in alkynes is 180^o). the sigma framework of alkynes is thus:



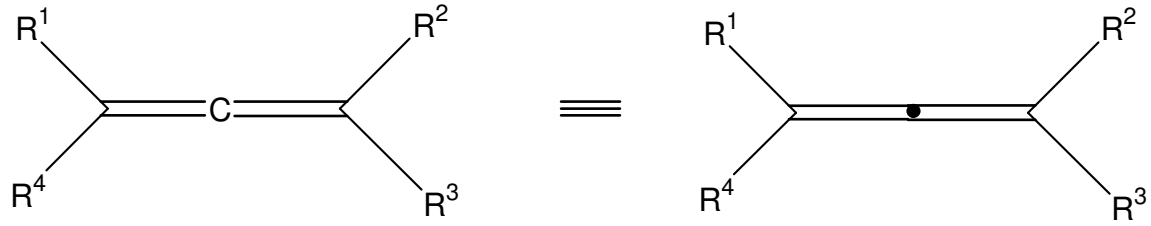
However, in alkynes we still have two atomic p orbitals on each carbon which we have not yet used and which are mutually at right angles and at right angles to the C-C sigma framework. These four orbitals can now overlap sideways in pairs to give two π-bonds. Again there are corresponding empty, anti-bonding π* orbitals:



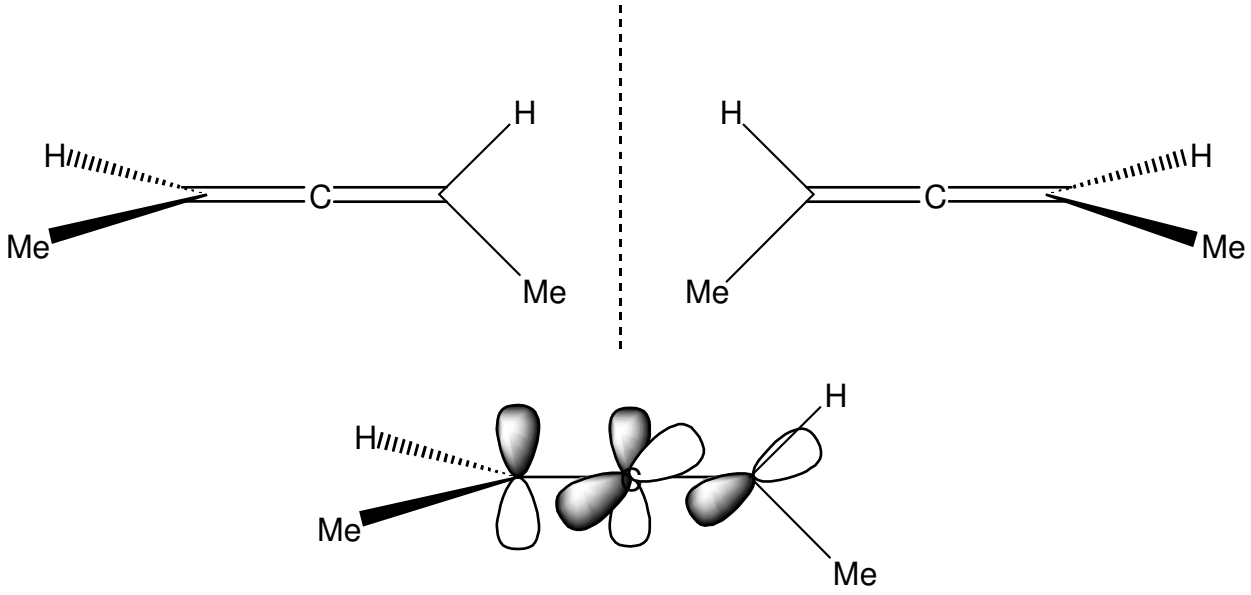
only two orbitals shown for clarity

Thus, a triple bond consists of one σ bond and two π bonds. Again rotation is impeded but there are no stereochemical implications because there is only one group on each carbon.

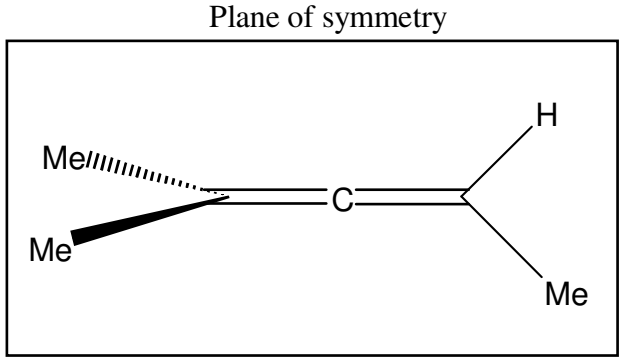
1,2-Dienes: 1,2-Dienes have two double bonds both joined to a central carbon which is often represented by a dot:



These molecules do not have a centre of asymmetry and yet some of them can exist as enantiomers. The reason for this is that the juxtaposition of the two double bonds causes the molecules to twist (essentially because the two π-systems are at right angles to one another):



Note that the necessary condition for enantiomers to exist is that the groups on either end of the double bonds must **not** be the same, otherwise a plane of symmetry bisects the molecule. For this reason the following compound cannot exist as enantiomers:

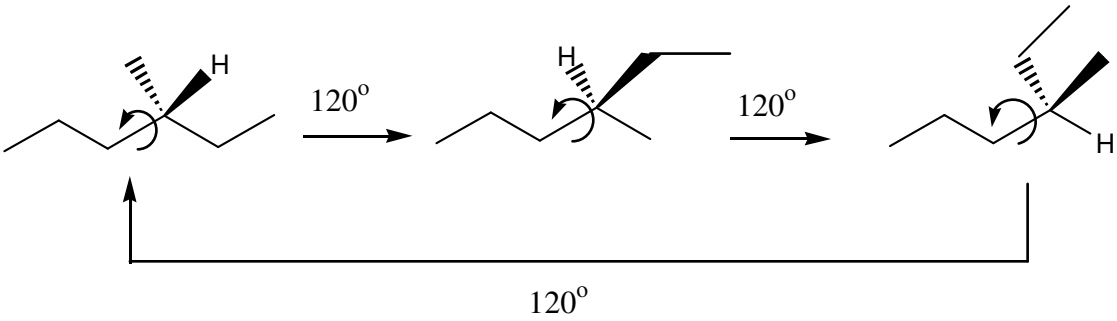


When molecules have planes of symmetry, one "enantiomer" can be superimposed upon the other after rotation in space i.e. they cannot enjoy independent existence.

Shape: Conformations and Configurations

Both the terms *conformation* and *configuration* refer to the shape of a molecule. A configuration is a shape which results from an arrangement of groups which cannot be changed by rotation. Geometrical isomers of alkenes and optical isomers are configurations. Shapes formed by rotation about C-C single bonds are conformations and thus another set of isomers called rotational isomers or rotamers or conformational isomers or conformers (any

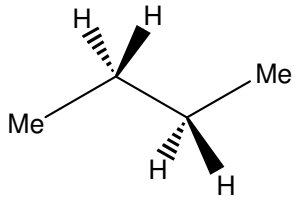
of these terms may be used) can result. Let us look at the 3-methylhexane and consider rotation about the central C-C bond to see what this means:



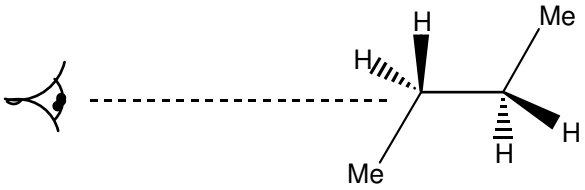
Of course, there are an infinite number of angles between 0^{o} and 360^{o} and hence an infinite number of conformations resulting from rotation about this bond. In addition all other single bonds have an infinite number of conformations. This leads to the following questions:

1. Can we separate and isolate all of these? In the vast majority of cases the answer is no because the energy required to rotate about C-C single bonds is so small that there is easily sufficient heat at room temperature to interconvert them all i.e. at room temperature all the single bonds are rotating rapidly.
2. Are conformations, therefore, unimportant? The answer to this is also no. You shall see later in your organic lectures that elimination of HX from alkyl halides will largely occur from one particular conformation. Similarly, in the second year you will learn that the analysis of conformations in cyclohexanes is fundamental to an understanding of the chemistry of such compounds.
3. Are conformations of equal energy? Again no! A molecule will tend to spend more time in the least energetic (most stable) conformation.

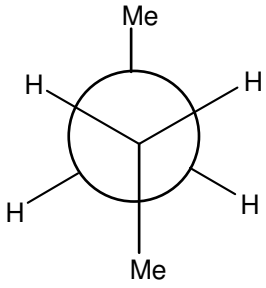
This last point can be explored qualitatively and quantitatively using a simpler molecule than the one above, namely, butane:



If this is tipped so that the central C-C bond is horizontal we get a view which is called the Sawhorse projection. Looking along the central bond as indicated in the Sawhorse projection then produces another projection, the Newman, in which groups attached to the first carbon under view project from the centre of the circle and groups on the back carbon project from the circumference:



Sawhorse projection



Newman projection

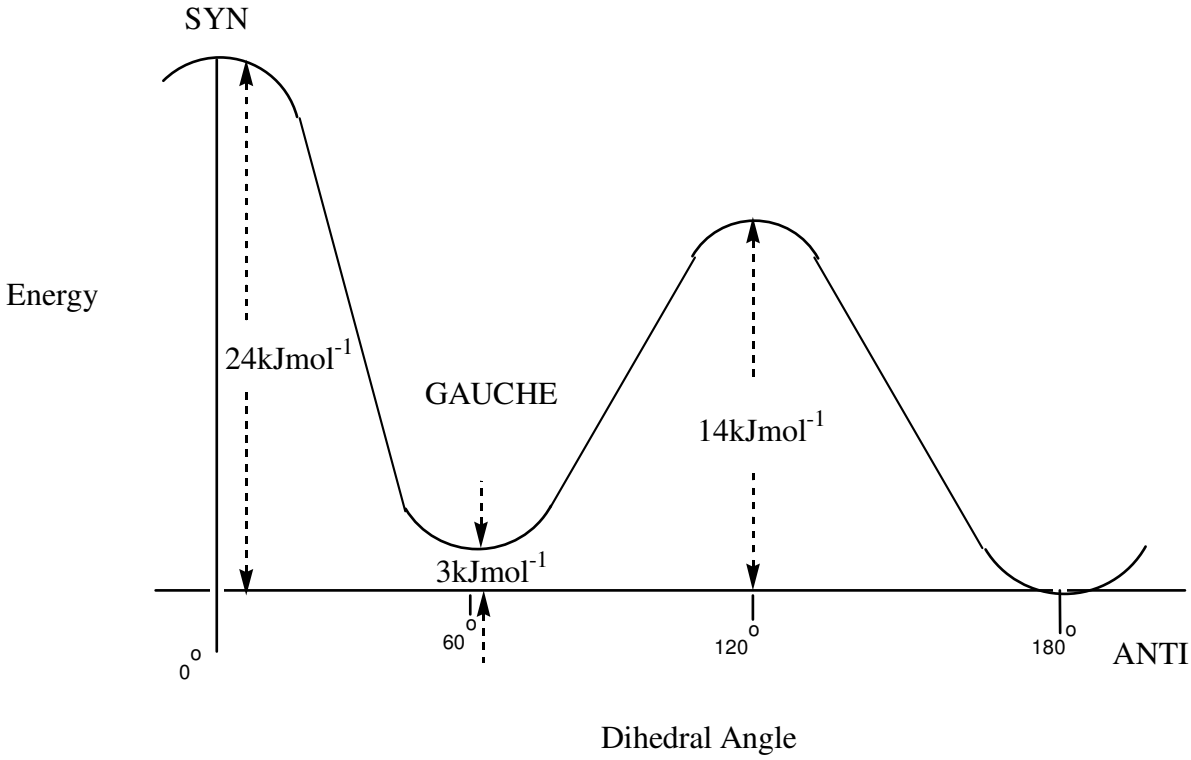
It is the Newman projection which will allow us to discuss the energies of the various conformations. There are six limiting conformations i.e. those which have a maximum or a minimum of energy:

See next page

First we see from these diagrams that there are two types of conformation – those in which the groups are spaced uniformly around a 360^{o} arc and those in which the groups appear to overlap. Those of the first type are called **staggered** conformations and those of the second, **eclipsed** conformations. For the eclipsed conformations there is strong electron-electron repulsion between the bonds overlapping and there is also nucleus-nucleus repulsion between the atoms at the ends of those bonds, although this is less important when the atom is hydrogen. Hence the eclipsed conformations are much higher in energy than the staggered ones. Because the nucleus-nucleus repulsion depends upon the size of the groups the eclipsed conformations in which hydrogen overlaps methyl are not so energetic as those in which methyl overlaps methyl. Finally, this effect of the size of the groups is also seen in the staggered conformations even though the groups are no longer overlapping. Hence, the order of stability of the conformations is:

ANTI > GAUCHE >> OTHER ECLIPSED > SYN

Quantitatively, we can plot the energy versus the dihedral angle (the angle between the two largest groups) and we obtain a graph as follows:



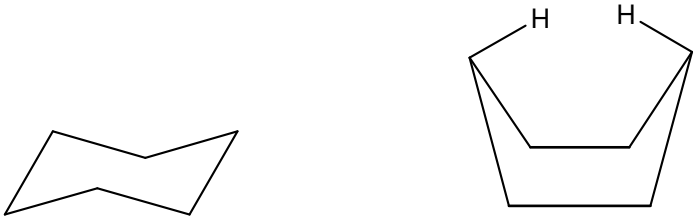
Given the values of these energies we can now work out the percentages of each rotamer in equilibrium at room temperature using the relationship:

$$\Delta G = -RT\ln K$$

and for butane we find that it exists in approximately 80% of the ANTI-conformation, approximately 20% of the GAUCHE-conformation with less than 1% of any eclipsed conformations.

Shape: Conformations of Cyclohexanes

Cyclohexane has two limiting conformations, the **chair** and the **boat**:

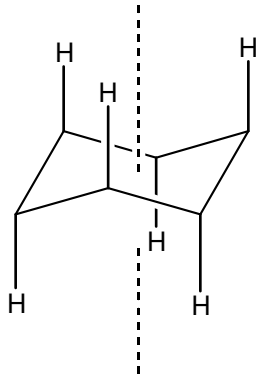


Chair Boat

The boat conformation is much less stable than the chair for two reasons. Firstly, Newman projections along either of the horizontal C-C bonds in the boat form show eclipsing and, secondly, the two hydrogens shown, the so-called bowsprit hydrogens, come within such a short distance of one another that a repulsive force is set up. Thus, we will concentrate upon the chair which constitutes > 99.9% of cyclohexane molecules.

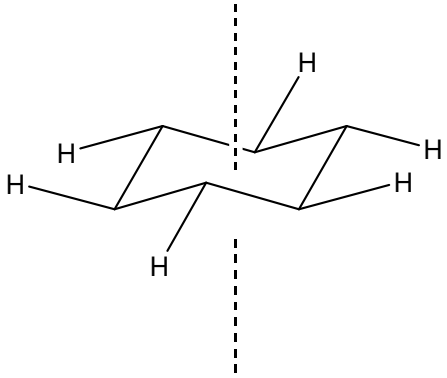
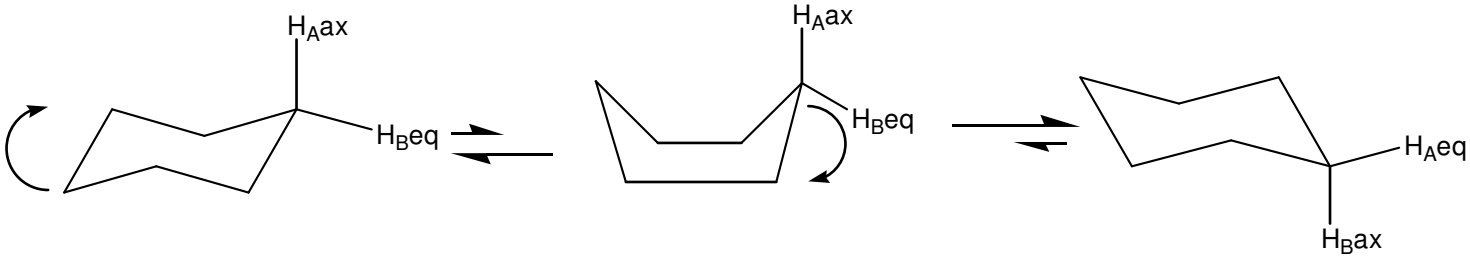
In the chair conformation there are two types of hydrogen. Six hydrogens are joined to their carbons by bonds which are parallel to an axis through the centre of the ring and are designated axial (ax) hydrogens:

Axial (ax)



The remaining six hydrogens project around the equator of the axis and are designated equatorial (eq) hydrogens:

Equatorial (eq)



The chair form can flip through the boat to give another chair in which the axial and equatorial hydrogens have exchanged places. This occurs very rapidly at room temperature and explains why the ^{1}H NMR spectrum of cyclohexane only contains one peak, the average value for H(ax) and H(eq):